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	(SIR effect)		

IUPAC

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i) word root
ii) Prefix
iii) Suffix

Iupac name is made of three parts as above.

i) word root → It indicate no of carbon in main carbon chain.

No of carbon	
1	meth
2	Eth
3	Prop
4	But (a)
5	Pent
6	hen
7	Hept
8	oct
9	non
10	dec
11	undec
12	dodec
20	Icos
30	Tricont
40	Tetracont

2) Prefix :—

i) Primary or 1° Prefix ⇒ Cyclo (when com is cyclic

ii) Secondary or 2° Prefix ⇒ It indicate substit or side chains.

eg:- X → halo

Cl ⇒ chloro
I ⇒ Iodo
$-CH_3$ ⇒ methyl

$-OCH_3$ ⇒ methoxy
$-NO_2$ ⇒ Nitro

2) Suffix ⇒

1) Primary or 1° suffix ⇒ It indicate nature of principle carbon chain saturated or unsaturated.

If, saturated carbon chain — 1° suffix — ane — Alkane — C_nH_{2n+2}

If

Unsaturated carbon chain (=) ene — Alkene — C_nH_{2n}

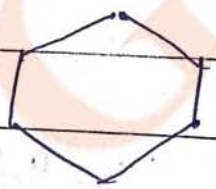
(≡) yne — Alkyne — C_nH_{2n-2}

Note! ⇒

= + ≡ → ene + yne → enyne

= + = → diene

eg ⇒ $CH_2=CH-CH=CH_2$ ⇒ Buta 1,3 diene



→ C_6H_{12} → Saturated

$CH_2=CH-CH=CH_2$ → C_4H_6 →

2) 2° suffix → Dt Indicate Principle function group

Functional Group	Prefix	Suffix
i) $-\overset{O}{\overset{\|}{C}}-O-H$ or COOH	- Carboxy	-ic acid
ii) $-SO_3H$ or $-\overset{O}{\overset{\|}{\underset{O}{\overset{\|}{S}}}}-O-H$	- Sulpho	- sulphonic acid
iii) $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ or $RCOOCOR$ or $(RCO)_2O$ Anhydride	—	oic anhydride
iv) $-\overset{O}{\overset{\|}{C}}-O-R$ or $-COOR$ ester	a) Alkanoyl oxy (connecting atom oxygen)	oate
	b) carbalkoxy or Alkoxy carbonyl (connecting atom carbon)	

v)	$-\underset{O}{\overset{\parallel}{C}}-X$ acyl Halide	Halo formyl	acyl halide
vi)	$-\underset{O}{\overset{\parallel}{C}}-NH_2$ Amide	a) Alkanoyl amino (Connecting atom "N") b) Amido Carbamoyl (Connecting atom C)	amide

Note
3, 4, 5, 6 are known as Carbonylic acid derivatives

VII)	$-CN$	-Cyano	Nitrile
VIII)	$-NC$	Isocyano	Isonitrile

IUPAC में "C" select नहीं करते जबकि Common में Consider करते हैं।

IX)	$-\underset{O}{\overset{\parallel}{C}}-H$	Formyl or oxo	Al
X)	$-\underset{O}{\overset{\parallel}{C}}-$	-oxo or keto	-one

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(xi)	$-OH$	-hydroxy	-ol
(xii)	$-SH$	-mercapto	-Thiol
(xiii)	$-NH_2$	-amino	-amine
(xiv)	$-OR$	-alkoxy	—

नोट:- किसी Compound में no of function group पता करने में consider किया जाता है। (जबकि Naming में function group कीतरह treat नहीं हो सकता)

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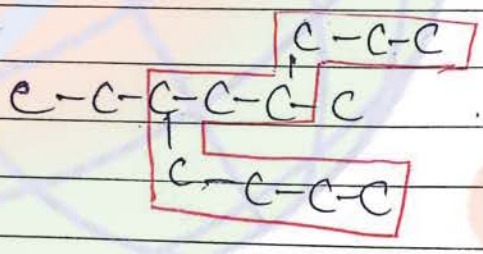
Iupac

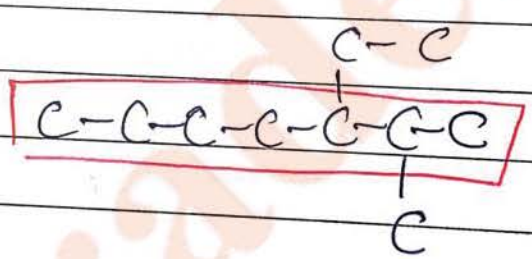
IUPAC Name ⇒ 2° prefix + 1° prefix + word root + 1° suffix + 2° suffix

Naming of saturated hydrocarbon

Rule 1 ⇒ selection of longest carbon chain



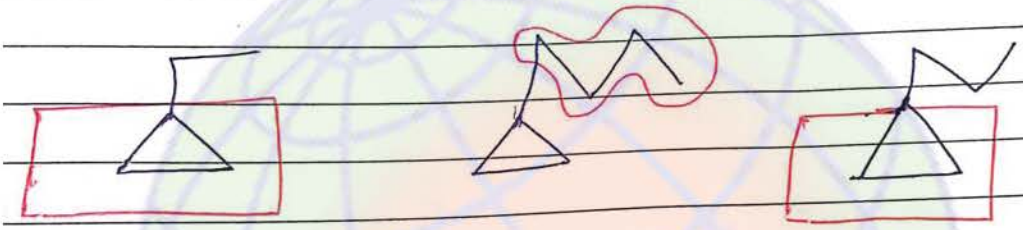
Rule 2 ⇒



more no. of sidechain.

we say that
if there are two carbon chain with equal no of carbon then Principal carbon chain contain more number of side chain.

→



case of substituted Alicyclic Compound
No. of carbon in ring ⩾ No. of carbon in open chain.
Then Ring is considered as Parent chain.

Other case open chain is considered as parent chain.

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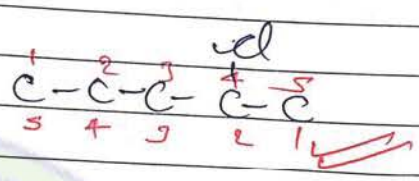
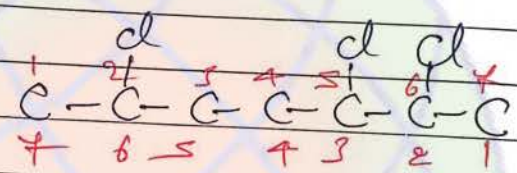
Rule no. 2 ⇒ Numbering of carbon chain

★ Lowest locant rule :-



★ Lowest set of locant :-

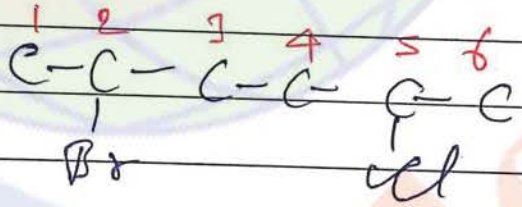


→ [2, 5, 6]

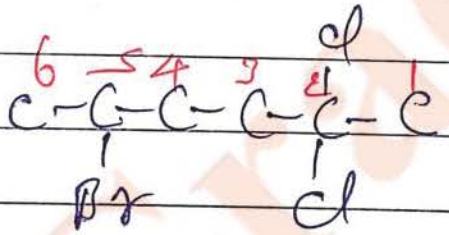
→ [2, 3, 6] ✓

Lowest set is decided by first point difference rule.

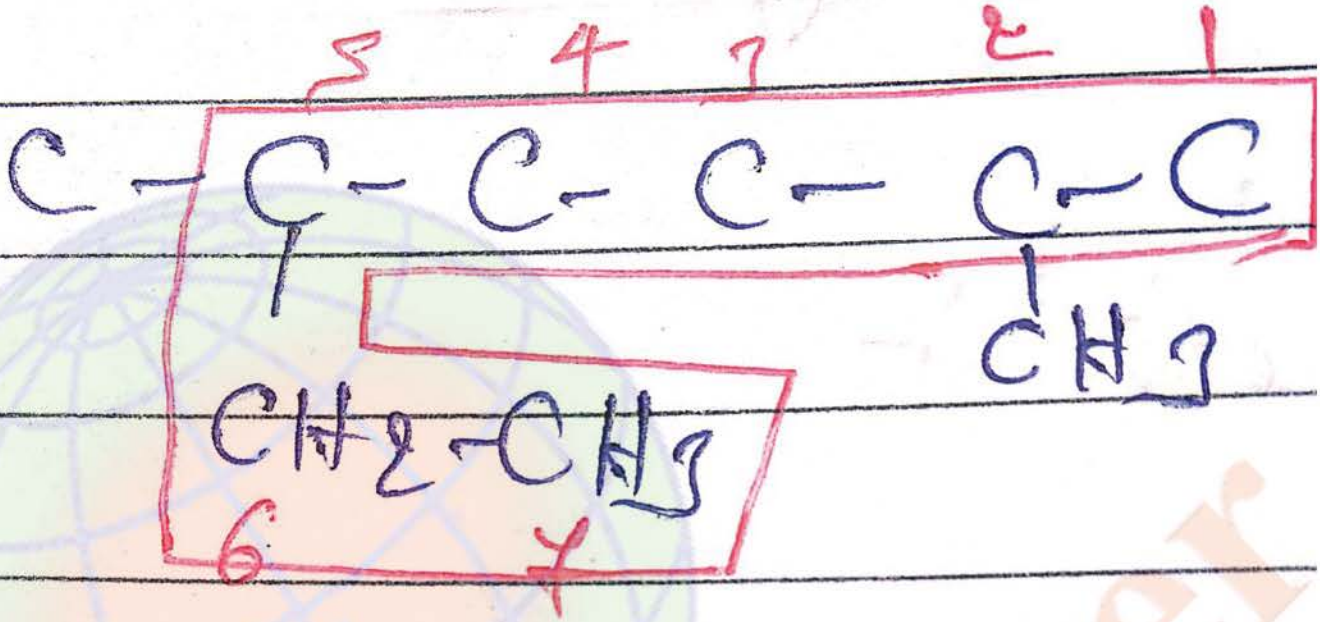
Note ⇒



→ (Alphabet का उपयोग अवश्यकता Rule fail होने पर)



If set of locant are similar then alphabetical order.


5 4 3 2 1
C-C-C-C-C-C
CH3
CH2-CH3
6 7

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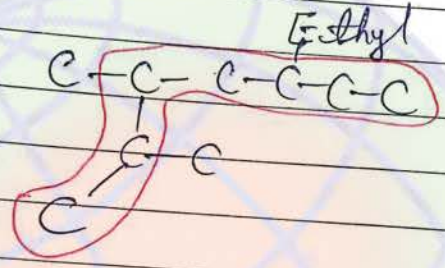
Rule 3 ⇒ Naming of Saturated Hydrocarbon ⇒

Name of substituents are written in alphabetical order.

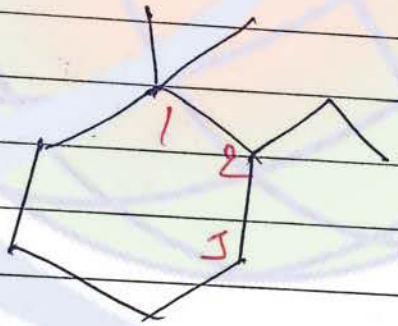
Di, Tri, Tetra are not considered for alphabetical comparison but Dio and neo are consider.

*



5 ethyl 2,3 dimethyl Heptane.

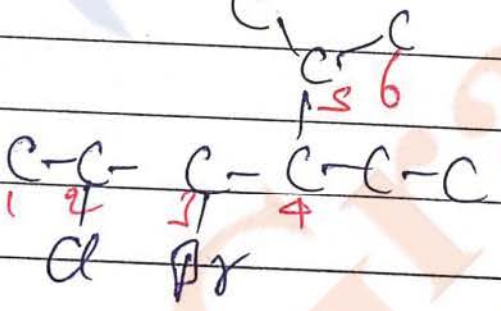
*



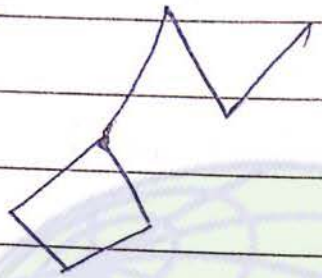
∵ 1, 1, 2 ↙
1, 2, 2

2 ethyl 1,1 dimethyl cyclo hexane.

*



3 Bromo 2 chloro 4 ethyl 5 methyl hexane



Propyl cyclo butane

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☆ Naming of hydrocarbon group →

C_nH_{2n+2} → C_nH_{2n+1}
(Alkane) Alkyl

CH_4

CH_3-CH_2

CH_3 – (methyl) (Me) shortcut

CH_3-CH_2 → (ethyl) (Et) shortform.

Ex. Possible hydrocarbon:–

C_3H_8 → $CH_3-CH_2-CH_3$ → $CH_3-CH_2-CH_2-$ (C_3H_7-)
Propane n-Propyl

$CH_3-\overset{1}{C}H-\overset{2}{C}H_3$
(1-methyl Ethyl) or Accepted common name (Iso propyl)

नोट ⇒ Radical केवल वो IUPAC naming में लिया जाता है जो "Alkyl" आखिरी में Alkane से H-atom को remove करते हैं Radical form करते हैं

जरूर Bracket बंद करें।

Note ⇒ Hydrocarbon में यदि free Radical होगा तो इस स्थिति में वहीं से Numbering शुरू की गई स्थिति नहीं है जो free Radical से प्रारंभ होती है।

Attention ⇒ In hydrocarbon group numbering always start free valency carbon atom and more toward longer carbon chain.

C_4H_{10}

$CH_3-CH_2-CH_2-CH_3$
n-butane

$CH_3-\underset{}{CH}(CH_3)-CH_3$
Iso-butane

$C-C-C-C-$ (C_4H_9-)
n-butyl

$C-C-C(-C)-$
1methyl Propyl
or
sec. butyl

$CH_3-CH(CH_3)-CH_2-$
(2methyl Propyl) or Iso butyl.

$CH_3-C(CH_3)(CH_3)-$
1,1 dimethyl ethyl
or
tertiary butyl
(t-But)

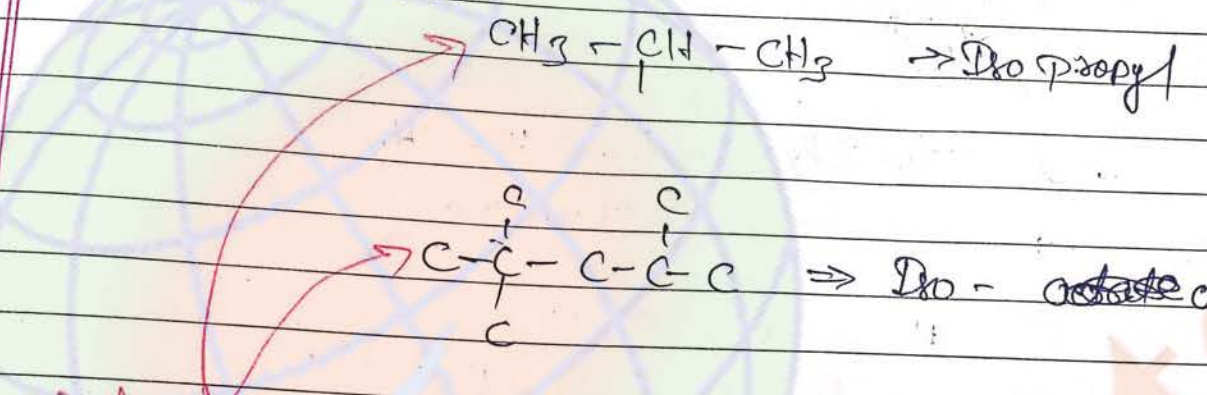
नोट :- इसी Number of carbon उसके electronic environment से पता चलता है, और इस प्रकार किसी compound में कितने प्रकार के Carbon atom है यह भी इसी पता चल जाएगी।

Note:-

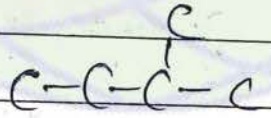
C_4H_9-[OH] → 4 Isomer Possible

Concepts of Iso, neo, Amyl are Active in Common naming →

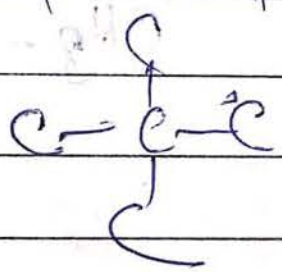
* Iso → This prefix is used when 2nd last carbon contain extra methyl substituent (or side chain)



Note → Iso-propyl and Iso-octane are exception to these Prefix.



* Neo → These prefix is used when 2nt last carbon contain two methyl substituent. इसके लिए Compound में minimum 5 carbon atom होना चाहिए



8. Active → This Prefix is used when hydrocarbon group contain chiral centre which is connected by four different group or valencies.

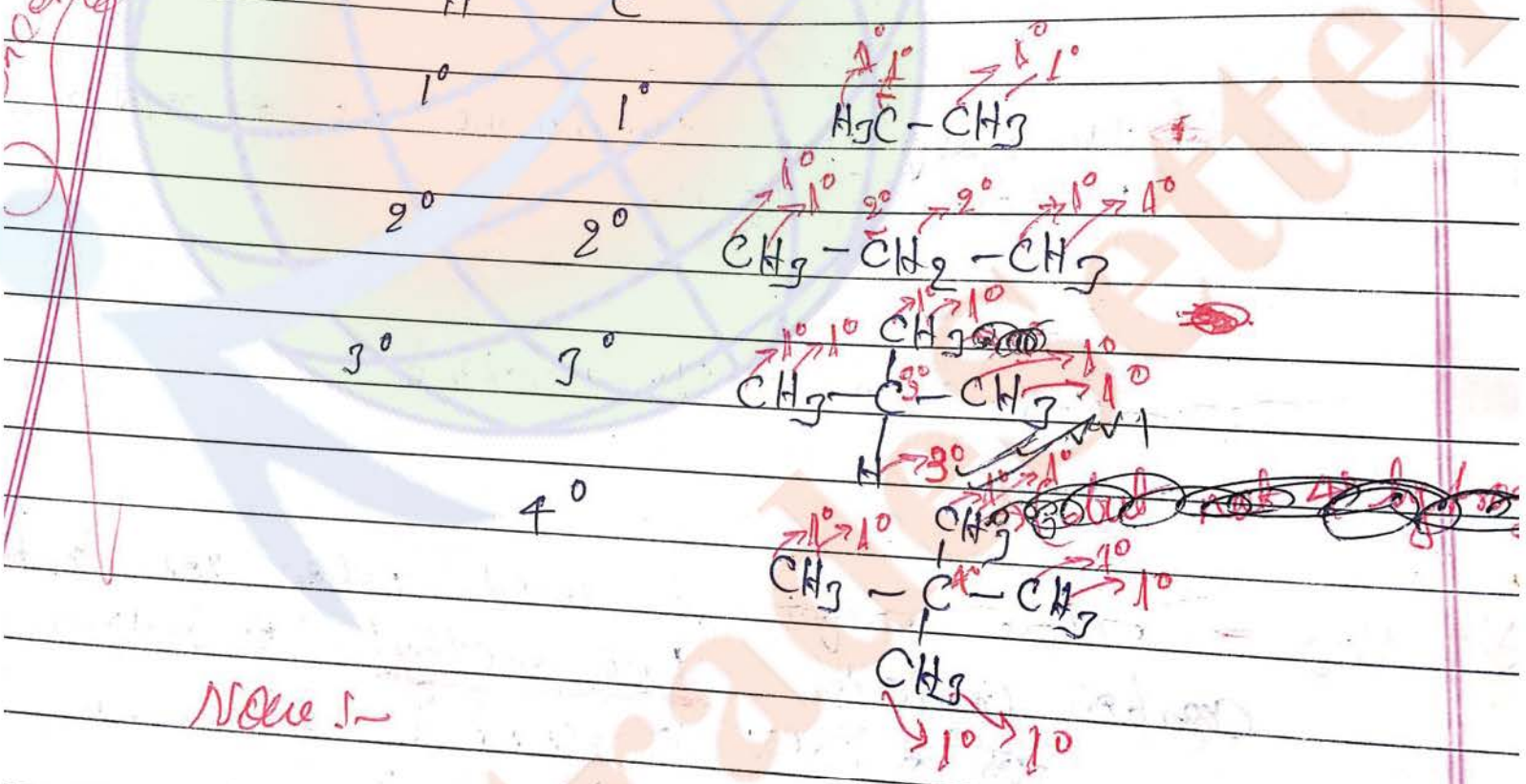
eg:-

C_5H_{12}

↓

$CH_3-CH_2-CH_2-CH_2-CH_3$

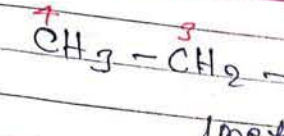
n-Pentane



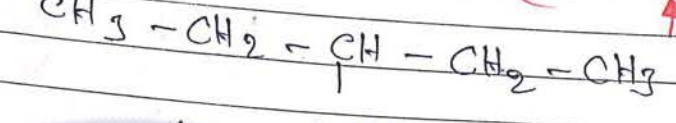
Note :-

$CH_3-CH_2-CH_2-CH_2-CH_2-$

Pentyl or n-Pentyl

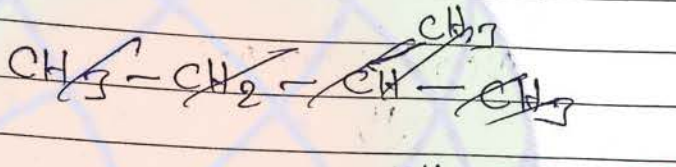


1 methyl Butyl or (~~2° Pentyl~~ 2° Active pentyl)



1 ethyl propyl (2° Pentyl)

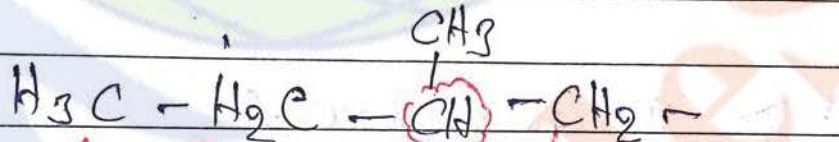
eg!>



these are same

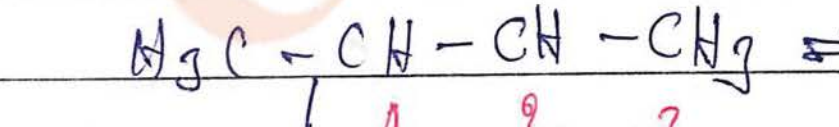
Iso-Pentane

(Here both type of Hydrogens are present.)

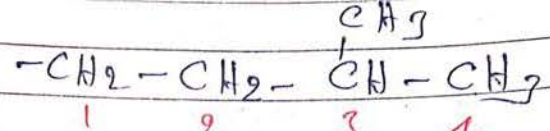


⇒ 2 methyl Butyl or 1° active Pentyl

⇒ 1,1 dimethyl Propyl or 3° Pentyl



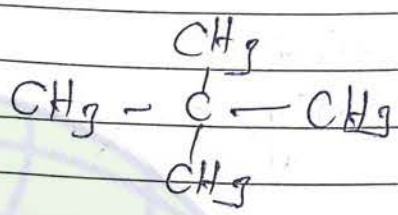
⇒ 1,2 dimethyl Prop or 2° Iso Pentyl



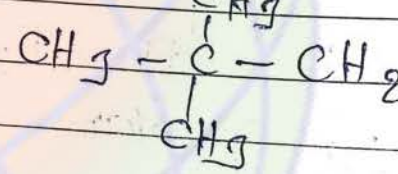
3-methyl Butyl

1° Iso Pentyl

eg)



Neo-Pentane



2-2 dimethyl Propyl
(Neo Pentyl)

Pentane C_5H_{12} → 3 arrangement

Pentyle C_5H_{11} → 8 arrangement

C_6H_4 → 5 "

C_6H_{13} → 17 "

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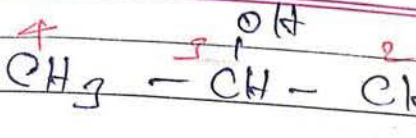
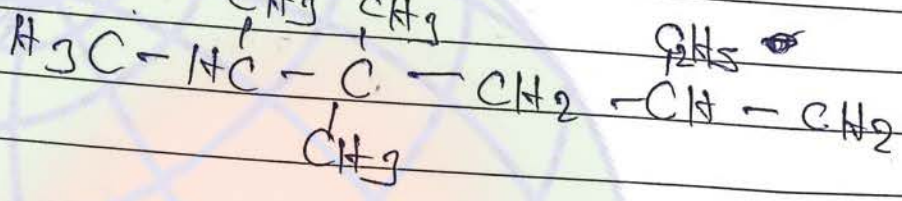


3-hydroxy 1 methyl Butyl



2-ethyl 4,4,5 trimethyl Hexy

1st Choice

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Note:- mono, di, tri etc का मेंशन → याद रखने :- mono, di, tri etc Complex कि Compound में Consider होता है। साधारण अर्थात simple Compound में mono, di, tri etc consider नहीं होता (alphabetical order में)

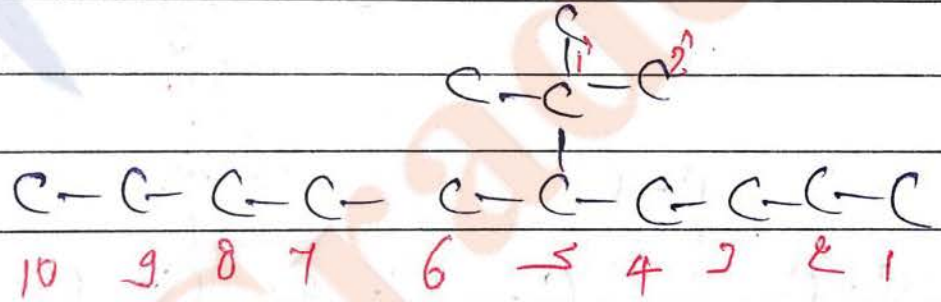
IUPAC naming of hydrocarbon Containing branched substituent →

Rule 1st ⇒ Name of branch substituent is written in bracket to avoid confusion.

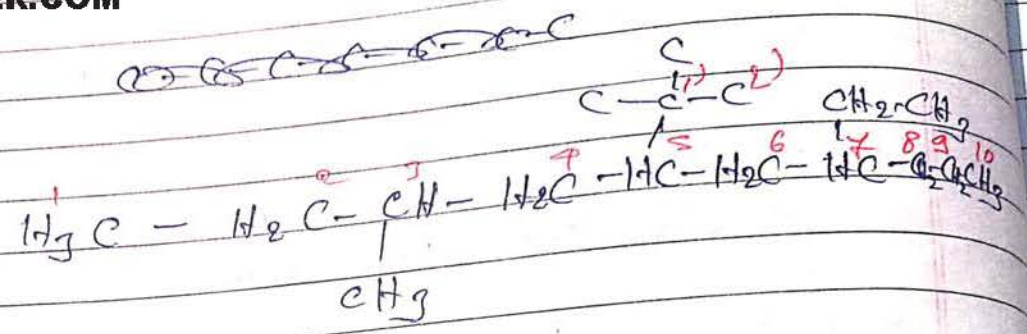
Rule 2nd = If more than one same branch substituent is present then their numbers are shown by

Bis → two
tris → three
tetrakis → four
Pentakis → five

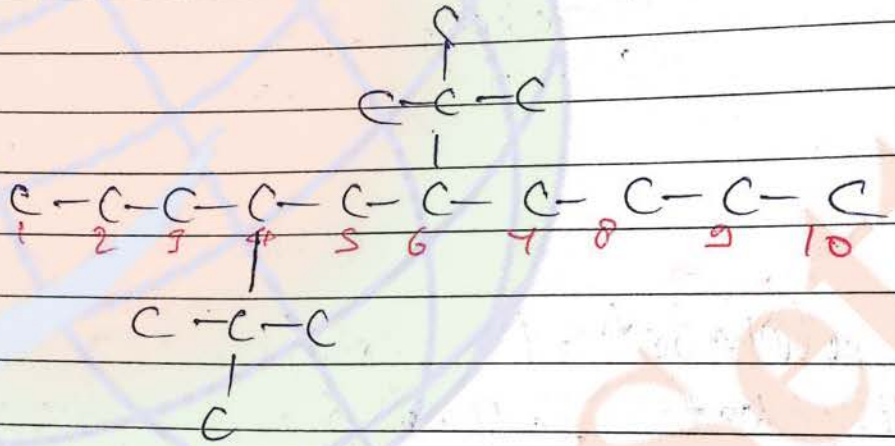
Rule 3rd ⇒
For alphabetical comparision 1st letter in the bracket is used for branched substituent whether it di, tri, tetra etc



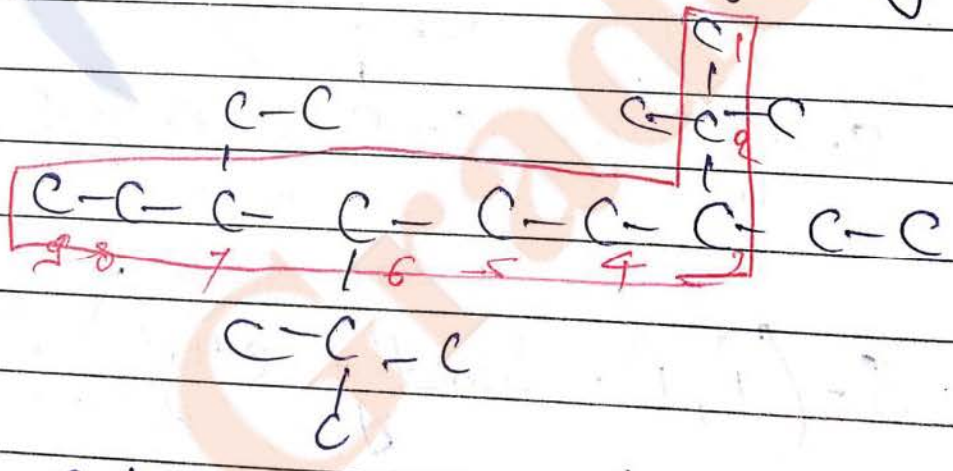
5-(1',1'-dimethyl ethyl) decane.



5-(1',1' dimethyl ethyl) 7-ethyl, 3-methyl decane



4,6 Bis(1',1' Dimethyl ethyl) Decane.



6(1',1' dimethyl ethyl) 3,7 ~~dimethyl~~ di-ethyl 2,2 dimethyl nonane

Date / /

Rules naming of unsaturated compound →

1) Selection of carbon chain →

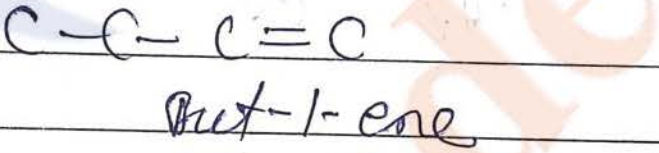
Longest possible C-chain is selected which contain maximum number of double bond (=) or triple (≡) bond it may not be longest.

2) Numbering of carbon chain →

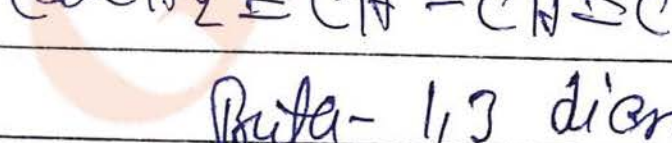
Numbering is done from the end so that unsaturation get's lowest number.

Note →

If double bond and triple bond are present at equal position then priority is given to double bond for numbering.

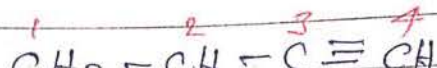


But-1-ene
or
1-butene

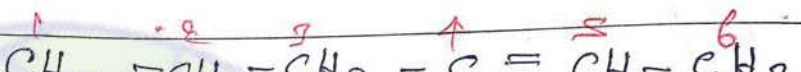


Buta-1,3 diene

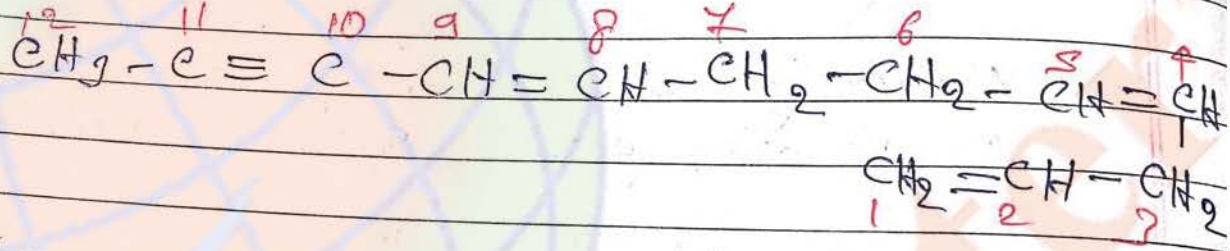
Hex - 3ene - 1yne



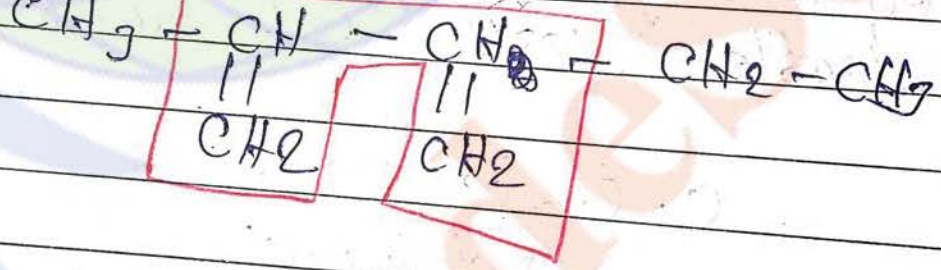
But - 1en - 3yne



Hex - 1en - 4yne

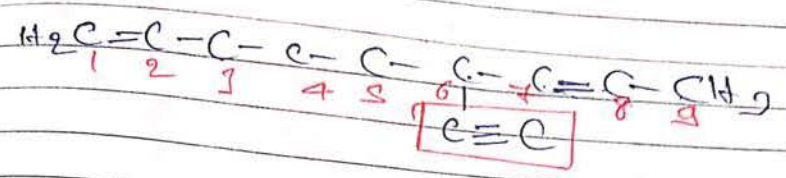


Dodec 1, 4, 8 trien - 10yne

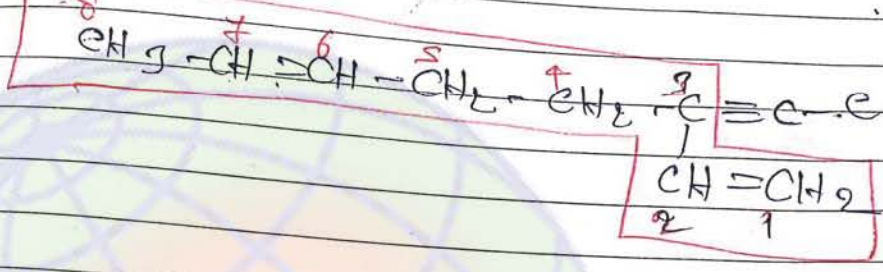


2 - ethyl, 3 - methyl

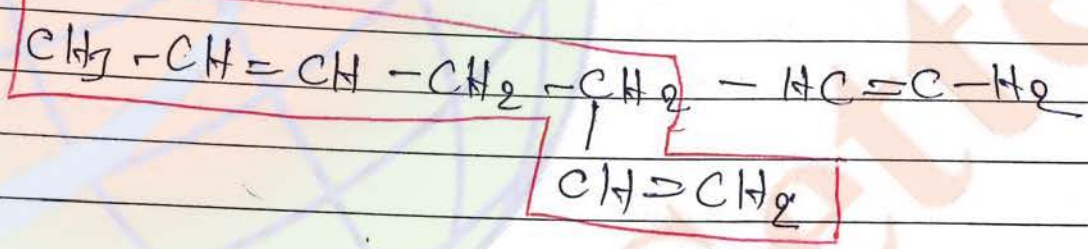
But 1, 3 diene.



6-ethynyl non 1,7 diene



3-ethynyl octa 1,6 diene



3 ethenyl Hepta-1,5 diene.

Note ⇒ common name is more important.

$CH_2=CH-$ → ethenyl or vinyl

$CH_2=\underset{2}{CH}-\underset{1}{CH_2}-$ → 2 Propenyl or Allyl

$CH\equiv C-CH_2-$ → 2 Propynyl or Propargyl

H.W → D.P.P.S → No

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* IUPAC naming of Compound's containing unifunctional group →

1) selection of Principle chain →

Principle functional group > unsaturation > No. of C > No. of substituent.

↓

Priority order for selection of Principle chain.

2) No. of Principal chain :-

In case of containing functional group number start from functional group carbon whereas in case of non-containing functional group number start from the end which is closer (near to functional group.

★ Note:

Naming of Anhydride :→

$$R-\underset{\underset{O}{\|}}{C}-O-H + H-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow[-H_2O]{\Delta}$$

$$R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R$$

Suffix:- oic Anhydride

Symmetrical anhydride

$R = R'$

word root = $\frac{\text{Total no of C}}{2}$

$CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{C} - CH_3$

IUPAC → ethanoic anhydride

common → acetic anhydride

Suffix:- oic Anhydride

Asymmetric anhydride

$R \neq R'$

word root (2)

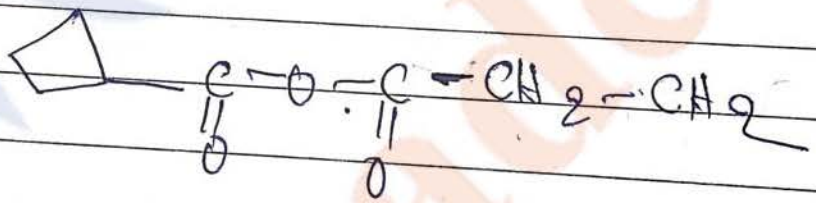
$CH_3 - \underset{\underset{O}{\|}}{C} - O - \underset{\underset{O}{\|}}{C} - CH_2 - CH_3$

ethanoic Propanoic anhydride

Acetic Propanoic anhydride

Form	1
Acet	2
Propion	3
Butyr	4
valer	5

eg:-



Cyclobutan carbonyle Propanoic anhydride

oice

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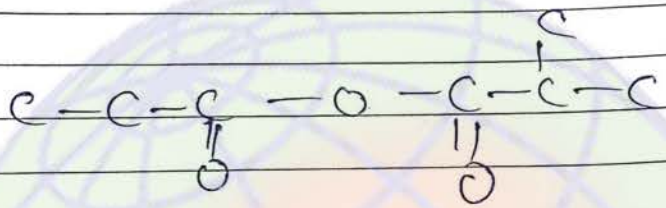
common naming Dearhydride is a suffix for anhydride.

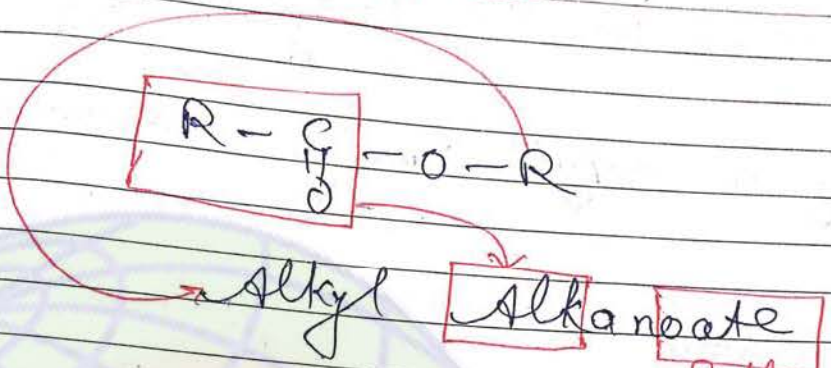


Dso-butanoic anhydride
Dso-butyric anhydride

mmon naming to show following are used:-

form → 1
Acet → 2
Propion → 3
Butyr → 4

Naming of ester →

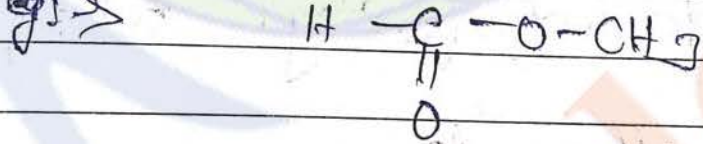


First of all name of alkyl group which is attached to oxygen is written and then word root is used for remaining carbon chain. followed by suffix oate.

Notes –

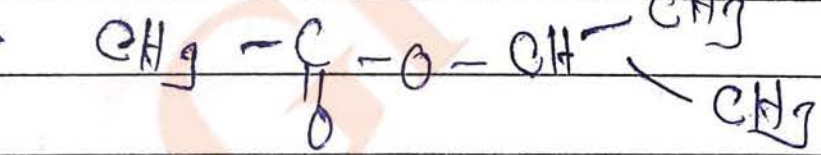
In common naming "ate" suffix is used for ester.

eg:→



IUPAC → methyl methanoate.
common → methyl formate.

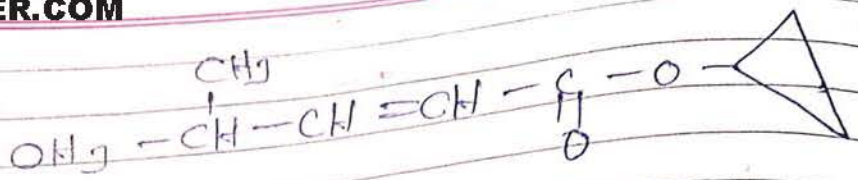
q ⇒



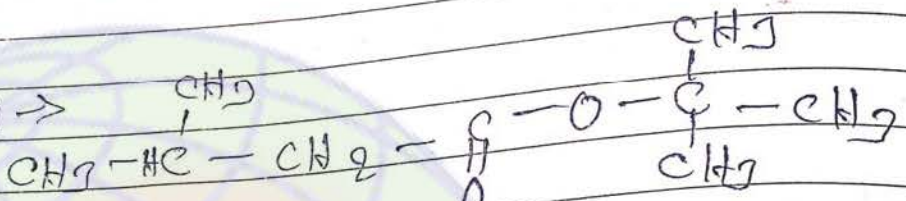
methyl ethyl ethanoate

or

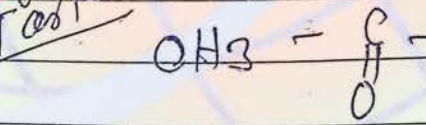
Iso propyl acetate

eg ⇒ 

Cyclo Propyl 4 methyl Pent-2-en oate

eg ⇒ 

1;1 dimethyl ethyl 3-methyl Butanoate

eg ⇒ 

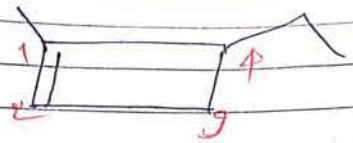
Ethyl Acetate (or ethyl ester)

IUPAC ⇒ ethyl ethanoate

eg ⇒

Keton, Amine, Alcohal are non-terminating ~~compound~~ position numbering must. 36

1st Choice

v) 

1-ethyl-1-methyl cyclo butene.

vi) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-CH_2-CH_3$

2-methyl Pentan-3-one

~~vii)~~ $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-CH_3$

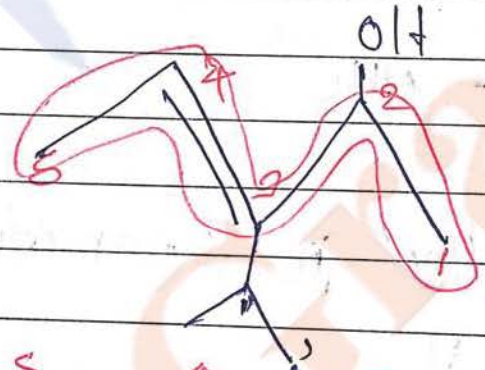
2-methoxy Propane

viii) $CH_3-CH_2-\underset{\underset{CH_2-CH_3}{|}}{CH}-NH_2$

Pentan-3-amine.

ix) $CH_3-CH_2-\underset{\underset{CH_2-CH_3}{|}}{\overset{NH-CH_3}{\overset{|}{C}}}-CH_3$

N,3, dimethyl Pentane-3-amine

x) 

3-(1'methylethyl) Pent-3-en-2-ol

xi) $CH_3-CH_2-CH=CH-CN$

↳ Pent-2-en-nitrile.

xii) CH_3-CH_2-NC

ethan Dimethyle or Propione Dinitrile

1st Choice

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Some more examples:

i) $CH_3-NH-\underset{\underset{O}{\|}}{C}-H$

→ N- methyl methanamide.

ii) $H-\underset{\underset{O}{\|}}{C}-NH-CH_3$

$-\underset{\underset{O}{\|}}{C}-NH_2$ → Methanoyl

iii) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{\underset{O}{\|}}{C}-N(CH_3)(C_2H_5)$

N ethyl, N, 2, dimethyl Propanamide.

1st Choice

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* IUPAC naming of compound containg Polying functional group →

I) Selection of Parent functional group →
It is selected according to priority Table.

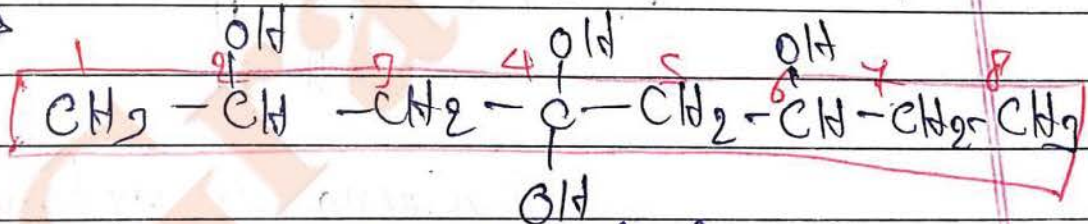
II) Selection of carbon chain :-
It is selected in the manner that they contain max no of Principal functing group.

old Recommendation
Once the Principal function group is selected other function group are treated as substituent

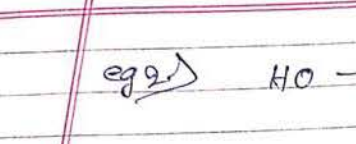
III) Numbering of carbon chain →

priority order
Principal functional group > Unsaturation > substituent

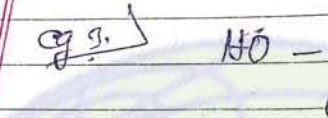
eg :-



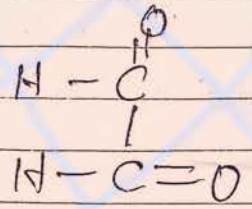
octan 2, 4A, 6 tetra ol

eg 2.) 

Prop 1, 3, dioic acid.

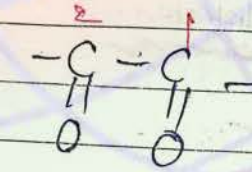
eg 3.) 

ethan 1, 1, dioic acid or oxalic acid

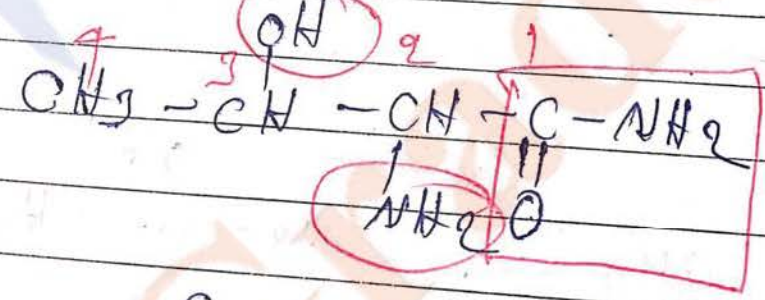
eg 4.) 

or Glyoxal

ethan 1, 2, dial

eg 5.) 

2-oxo-Propanal

eg 6.) 

2 amino 3-hydroxy Butanamide.

1st Choice

formyl → Aldehyde Carbon की शामिल नहीं किया है
oxo → C, O शामिल

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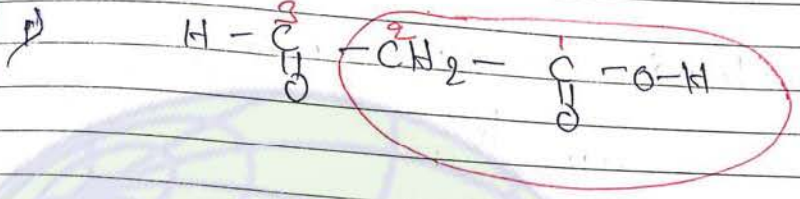
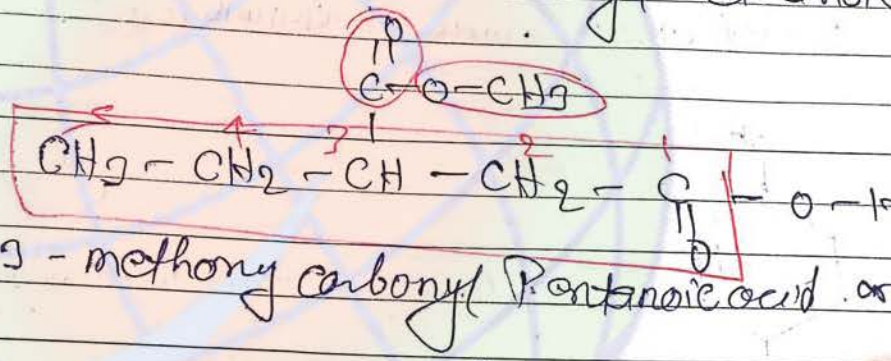
Date

(11)

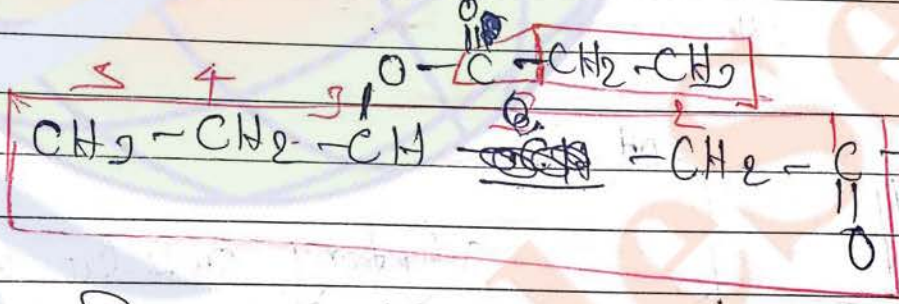
* Important examples

i) 

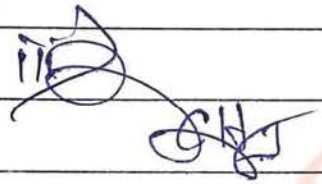
3-oxo propanoic acid
or
2-Formyl ethanoic acid.

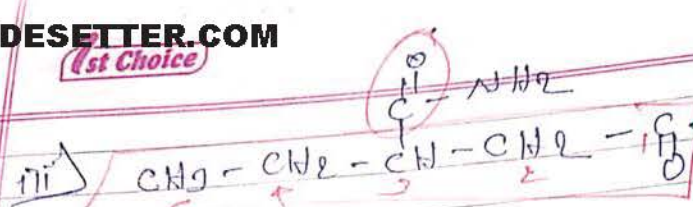
ii) 

3-methoxy carbonyl Pentanoic acid or 3 carbomethoxy Pentanoic acid

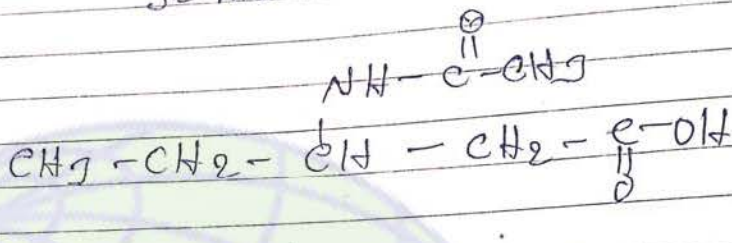


2-Propanoyl oxy pentanoic acid.

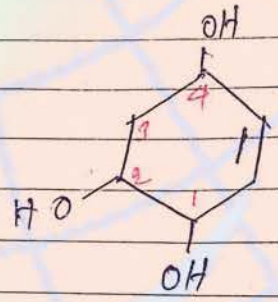
iii) 

iii) 

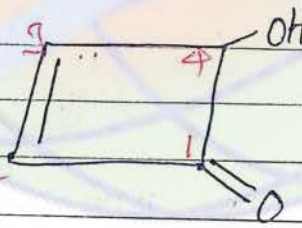
3-Amido Pentanoic acid.



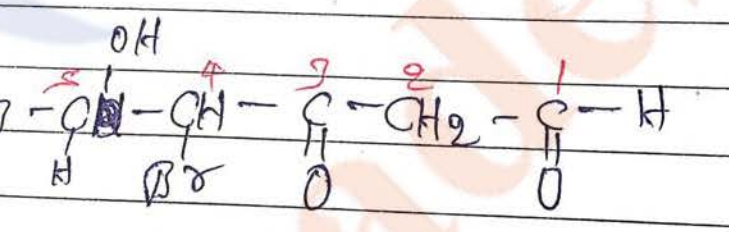
3-ethanoyl amino Pentanoic acid.

iv) 

cyclo hex-5en 1,2,4 triol

v) 

4-hydroxy cyclo but 2en 1one

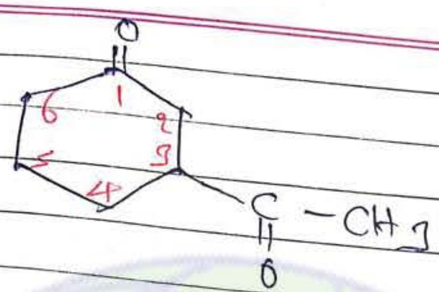
vi) 

4 Bromo 5-~~keto~~ hydroxy 3keto Hexanal

vii)

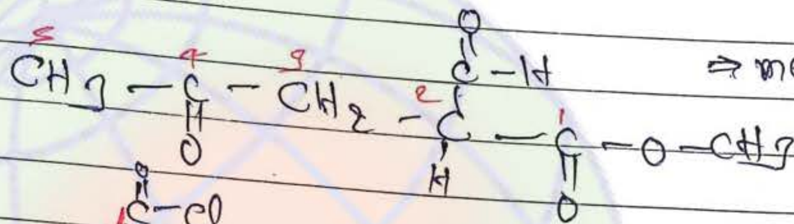
viii)

vii)



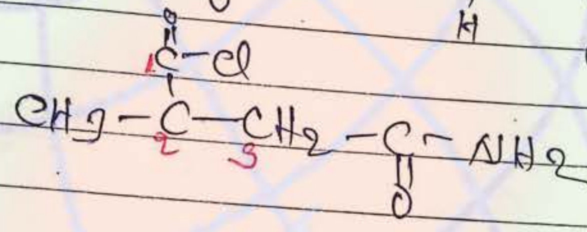
3-(1-oxo ethyl) cyclohexanone

viii)



⇒ methyl 2 formyl 4-oxo Pentanoate.

ix)



3-amino 2 methyl Propanoyl chloride.

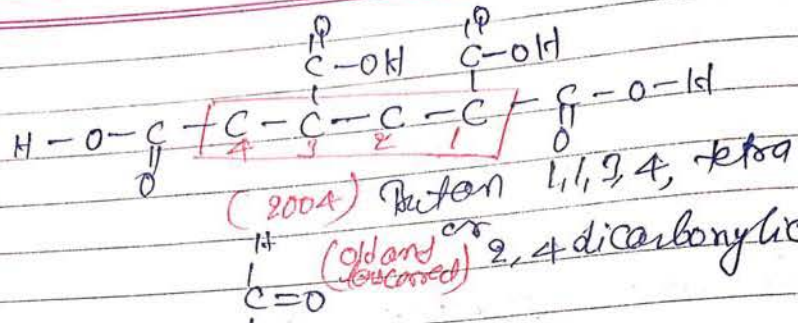
* IUPAC nomenclature of compound containing three or more same terminating functional group →

In such case Principle chain is selected in such a way that it do not include functional group carbon and

Special suffix are used for functional group →

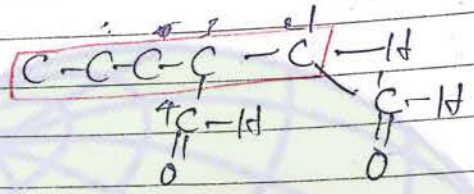
	Special suffix
$-COOH$	⇒ Carboxylic
$-CN$	⇒ Carbo nitrile
$-\overset{\overset{O}{\|}}{C}-H$	⇒ Carbaldehyde
$-\overset{\overset{O}{\|}}{C}-O-R$	⇒ Carboxylate
$-\overset{\overset{O}{\|}}{C}-X$	⇒ Carbonyl halide
$-\overset{\overset{O}{\|}}{C}-NH_2$	⇒ Carboxamide

eg)

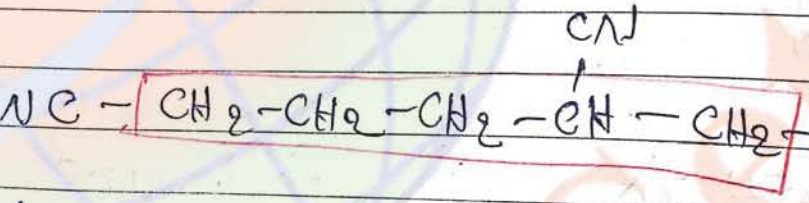


(2004) Buten 1,1,3,4, tetra carbonylic acid
(old any discussed) or 2,4 dicarbonylic Hexan 1,6 di

2.)



Pentan 1,1,2 tricarbaldehyde (2004 recommended)
or
2 formyl 3 Propyl Buten 1,4 diol (old)



Penton 1,2,5 tricarbonitrile (2004)
or
3 cyano Hepton 1,7 dinitrile (old.)

* This type of special suffix are used when three or more functional group are directly attached to carbon-chain in open chain
otherwise it is not usable

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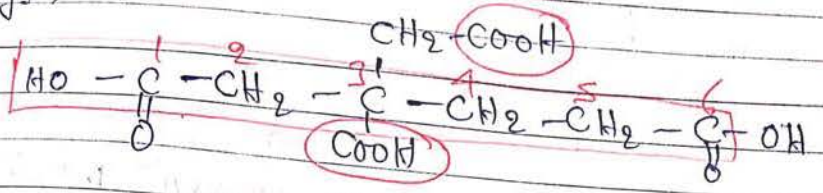
eg:-



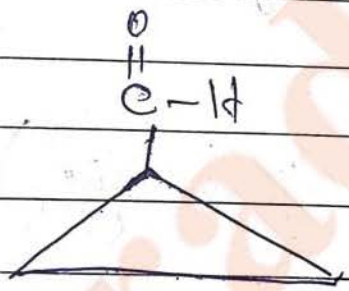
3 Carbony 3 Carbony methyl Hexan 1,6 dioic acid.

✳ Naming of Alicyclic compound:-

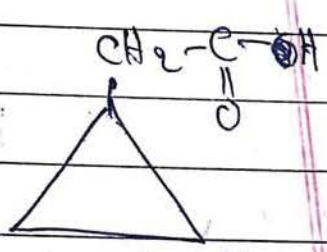
① If terminating functional group is directly attached to cyclic ring.

→ then special suffix are used for functional group and name is written in following way:-

Hydrocarbon + Suffix

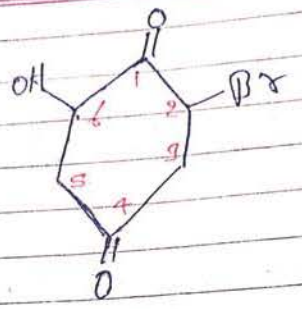


Cyclo Propan Carbaldehyde



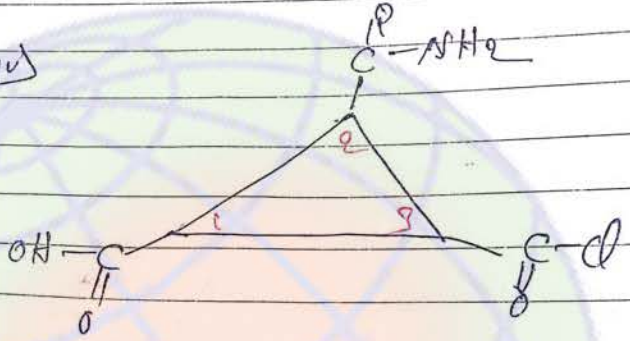
2 cyclo Propyl ethanol

iii)



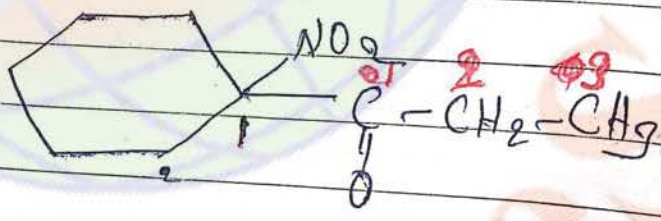
2-Bromo 6-hydroxy cyclo hexan 1,4-dione

iv)



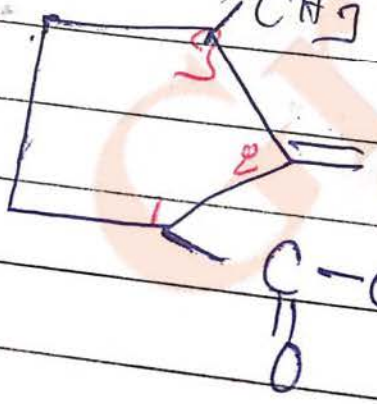
2 amido 3-chloro formyl cyclo Propan carboxylic acid

v)



1 (1 Nitro cyclohexyl) Propan-1-one

vi)



3-methyl 2-oxo cyclo Penten carboxylate

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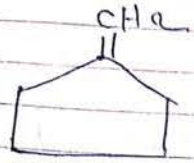
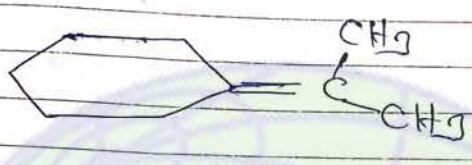
VII) 

methylene cyclo Pentane

VIII) 

Iso Propylidene cyclohexane

Note:-

$CH_2 <$	$CH_3-C <$	CH_2-CH_2
methylene	Alkylidene	Alkylene
methylene	Ethylidene	Ethylene

(exception)

*

If two valencies are free from one carbon then hydrocarbon group is name as Alkylidene and

If two valencies are ~~from~~ free from adjacent two different then hydrocarbon group is termed as alkylene.

Here

methylene is an exception

1st Choice

9)

CH_3-CHCl_2 ⇒ Ethylidene chloride

⇒ Vicinal dihalide

↓

(chloride)

CH_3-CHCl_2 ⇒ Geminal dihalide

↓

(chloride)

⇒ Ethylene chloride

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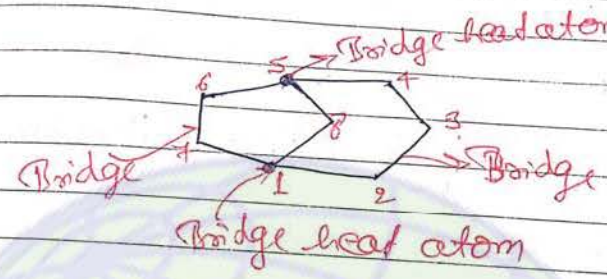
IUPAC naming of Bicyclo (bicycle) compound →

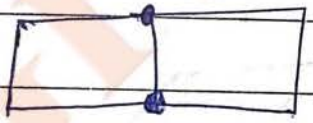


Bycle [3.2.1] octane

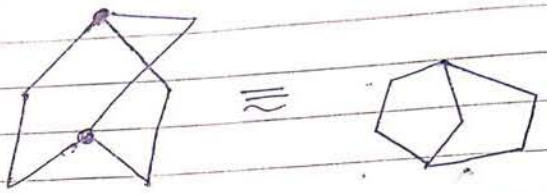
- Those compound in which two cycle ring's are attached by two common carbon
  In this compound bicyclo prefix is followed by a square Bracket in which number of carbon present in bridge are expressed in descending order.

- Numbering in bi-cycle compound start from one bridge head atom and move toward's another bridge head atom by longest bridge and then process continued.

Bicyclo [1,1,0] butane.

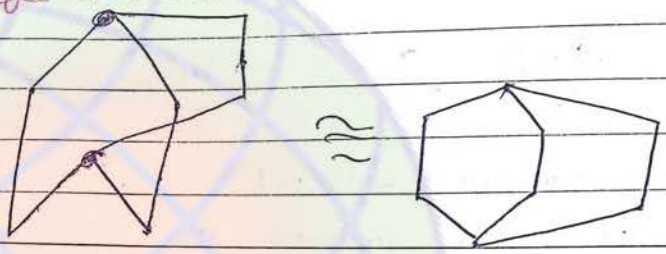


Bicyclo [2,2,0] Hexane

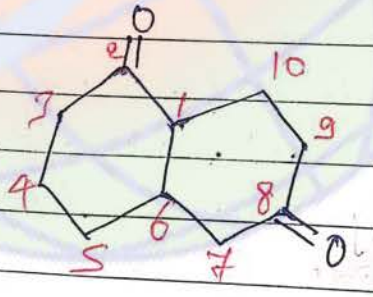


Bycle [2.2.1] Heptane

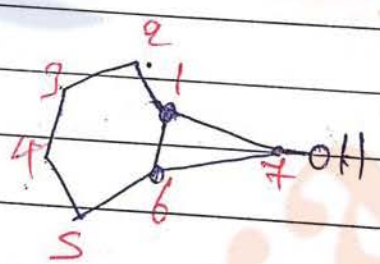
Bridge head की संख्या [2] है
Simple structure बनता है



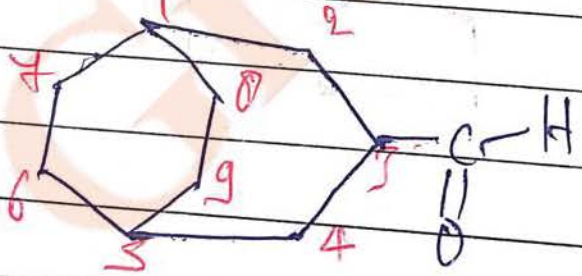
Bycle [2.2.2] octane.



Bicyclo [4.4.0] decan 2,8 dione



Bycle [4.1.0] Heptan 7-ol



Bi-cyclo [3.2.2] nonan 3-carbaldehyde

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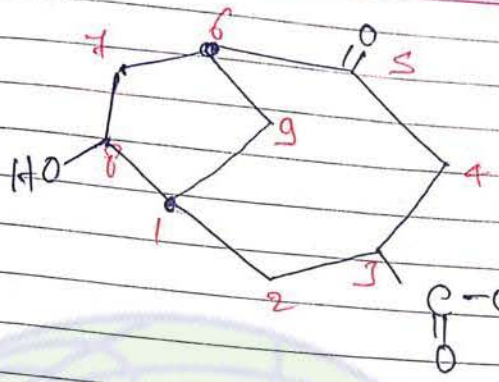
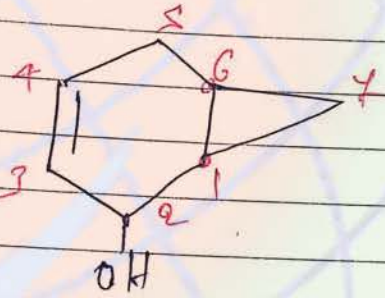
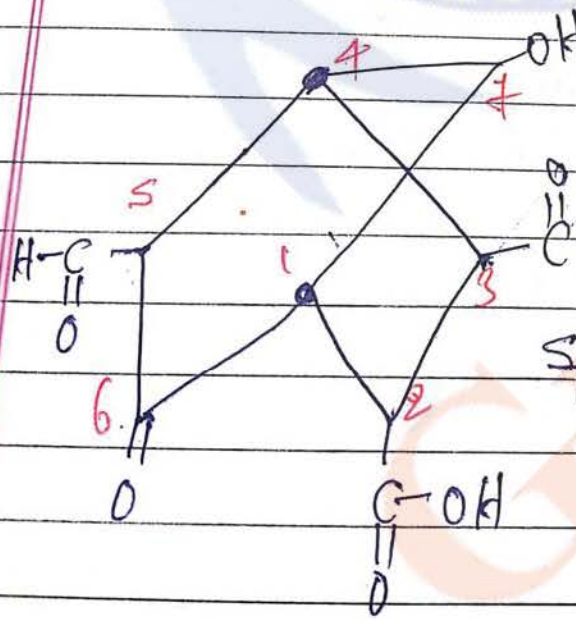


5-hydroxy 5-oxo Bicyclo [4.2.0] nonan-3-carboxylic acid.

(Substituent का नाम पहले लिखें)



Bicyclo [4.1.0] Hept-3-en-2-ol



5formyl, 4-hydroxy ~~5formyl~~ 6-oxo Bicyclo [2.2.1] hepton 2,3-di-~~carboxyl~~ carboxylic acid.

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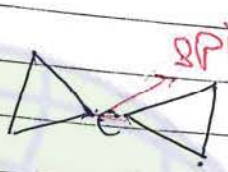
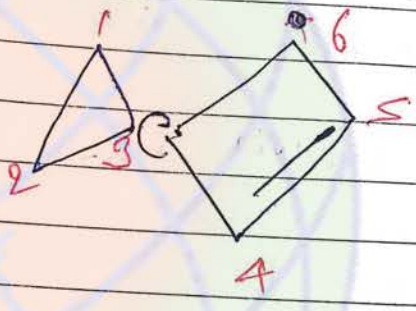
Nomenclature of Spiro-Compound →

Two cyclic ring are attached by (single) one quaternary carbon



2° Prefix + Spiro [ ]

Spiro [2.2] Pentane



Spiro [2,3] Hex-4-ene

i) Numbering start in smaller ring next to spiro carbon.

ii) Spiro prefix is followed by square bracket in which no of C-present in the ring are enclosed in ascending order.

2° Prefix + Spiro [ ]

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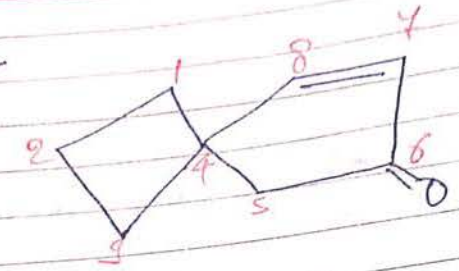
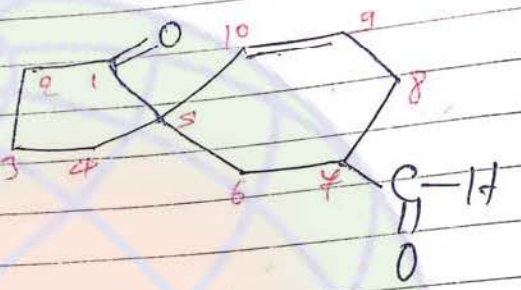
Eg:-



Spiro [3.4] oct-7-en-6-one



1-oxo Spiro [4.5] dec 9-en-7-carbaldehyde

1st Choice

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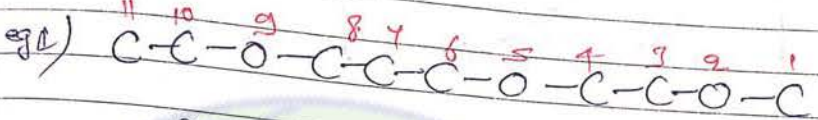
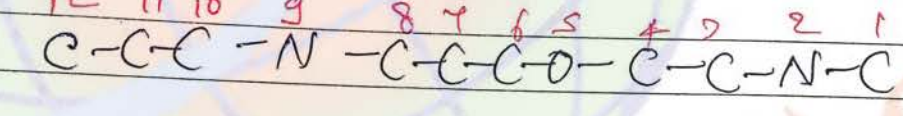
Replacement nomenclature →

eg1) 

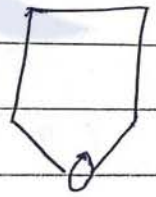
2,5,9 Tri oxa undecane

- O ⇒ oxa
- N ⇒ Aza
- S ⇒ Thia

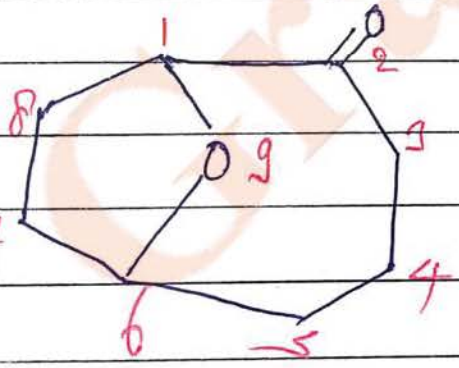
- In this nomenclature Hetero atom which are part of chain are considered as carbon and their position is mentioned by using special prefixes

eg2) 

2-N di aza-, 5 oxa dodecane

eg3.) 

oxa-cyclo Pentane

eg4.) 

9-oxa Bicyclo [4.2.1] nonal-2-ene

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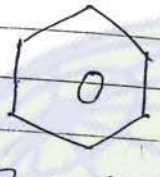
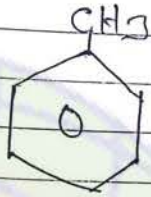
Nomenclature of aromatic compound's

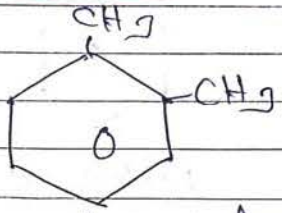
A) Aromatic - hydrocarbon (Arenes)



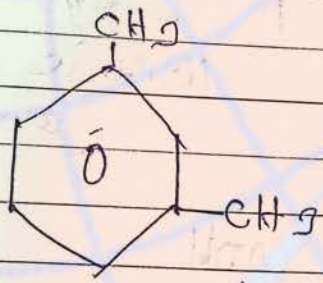
Benzene



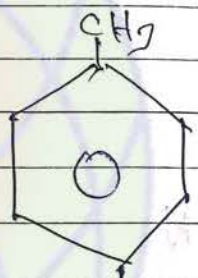
Toluene



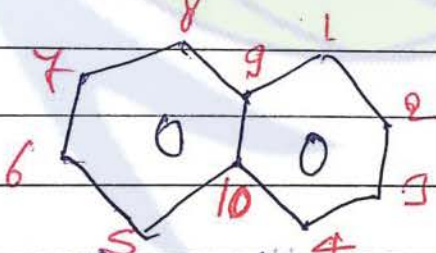
ortho xylene



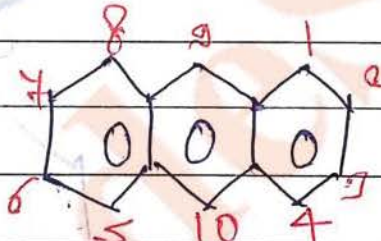
meta xylene



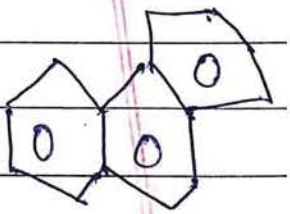
para xylene.



Naphthlene



anthracene



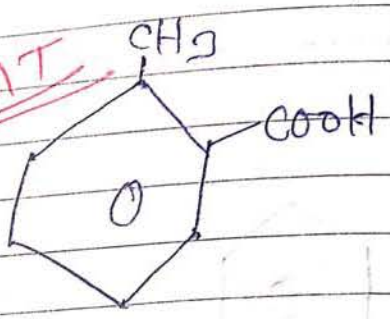
Phenan threne

Numbering also Important

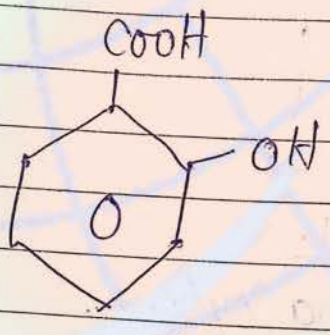
(B) Carboxylic acid and it's derivative

Benzoic acid
or Benzene carboxylic acid

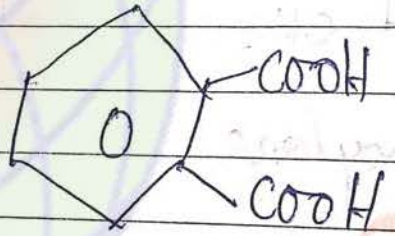
IIT



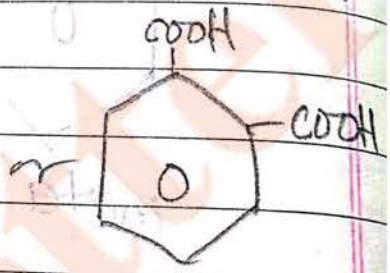
o-toluic acid
or
2 methyl Benzene carboxylic acid

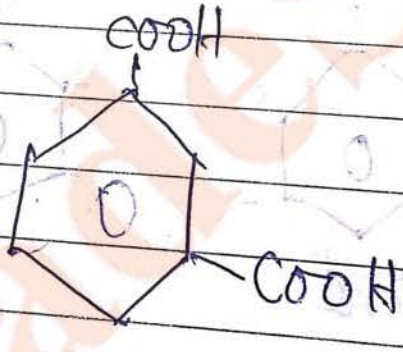


Salicylic acid

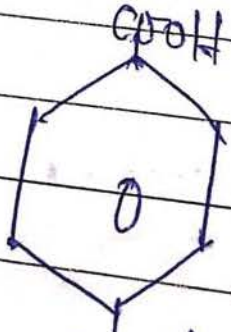


Pthallic acid



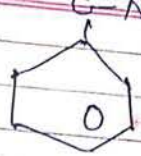


Iso Pthallic acid

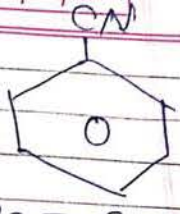


Ter Pthallic acid

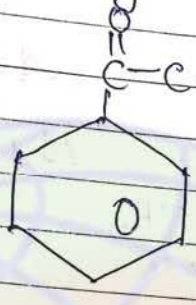
Benzoyl chloride
or
Benzen carbonyl chloride



Benzamide

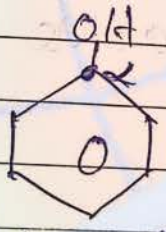


Benzene Carbonitrile
or
Benzonitrile

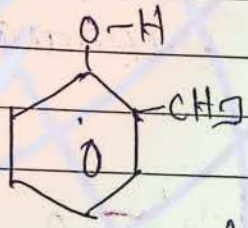


methyl Benzene Carboxylate
or
methyl Benzoate

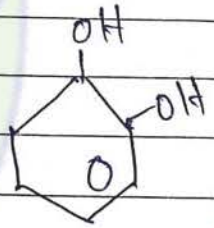
(c) Phenols →



Phenol

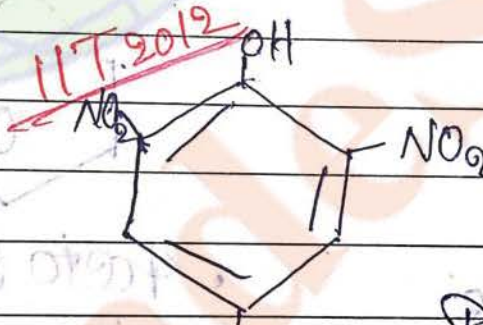


O-cresol



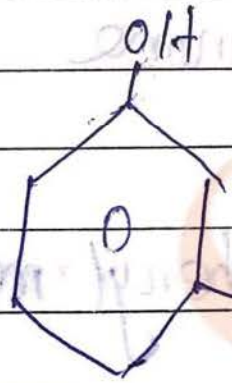
catechol

quinol



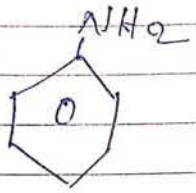
IIT 2012

Picric acid

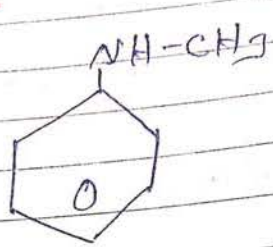


Resorcinol

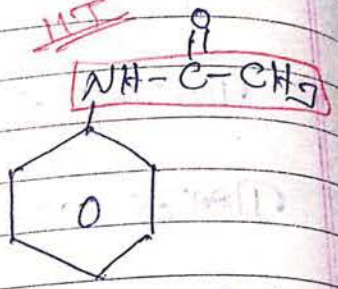
(D) Amines →



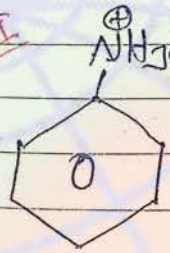
Aniline



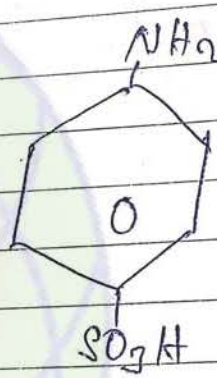
N-methyl aniline



Acetanilide or N phenyl Ethanamide

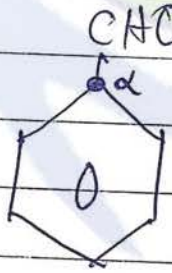


Anilinium chloride

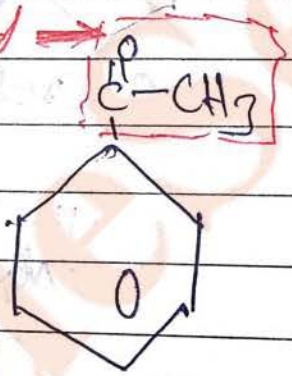


Sulphanalic acide

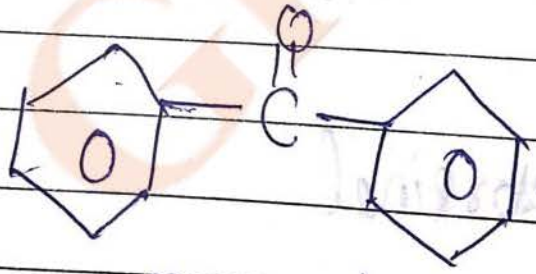
(E) Carbonyl compound →



Benzaldehyde



Aceto phenone
Phenyl ethanone



Benzophenone

Diphenyl methanone

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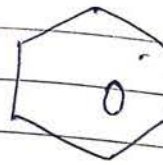
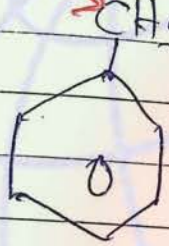
Aromatic Hydrocarbon group →



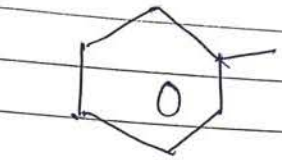
C_6H_5-

Benzen ring Directly attached Carbon

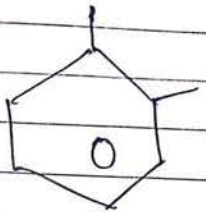
Benzyl carbon



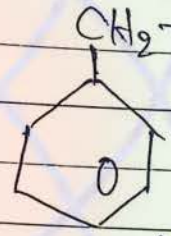
CH_3



Phenyl

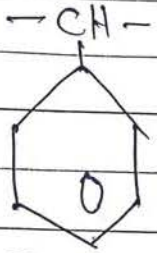


o-Phenylene



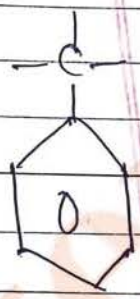
CH_2-

Benzyl



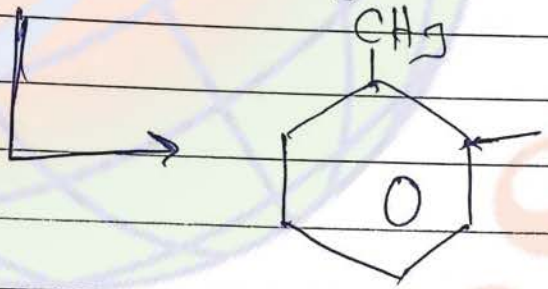
-CH-

Benzal



-C-

Benzo

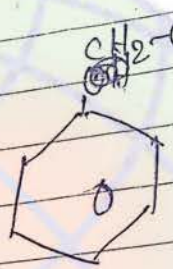


CH_3

o-Tolyl

$CH_3-CH_2-NH_2$
$CH_3-NH-CH_3$

q1. $CH_2=CH-\{-CH_2-CH=CH_2$ Allyl vinyl ke

q2. 

Benzyl alcohol

q3. $CH_2=CH-CH_2-OH$
Allyl Alcohol

q4. $CH_2=CH-OH$
vinyl Alcohol

q5. $CH_2=CH-\underset{CH_3}{N}-CH_2-CH=CH_2$
Allyl methyl vinyl amine

q6. $CH_3-CH_2-\underset{Br}{CH}-CH_3$
sec-butyl Bromide

1st Choice

D with terminating functional group →

Prefix + Suffix
No. of carbon (Functional group)

1.) → Form
2.) → Acet
3.) → Propion
4.) → Butyr
5.) → valer

$-COOH$	Dc acid
$-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$	Dc anhydride
$-\overset{O}{\overset{\|}{C}}-NH_2$	Amide
$-\overset{O}{\overset{\|}{C}}-Cl$	yl chloride
$-\overset{O}{\overset{\|}{C}}-O-R$	ate
$-CN$	dA Nitrile
$-NC$	o-Dc Nitrile
$-\overset{O}{\overset{\|}{C}}-H$	Aldehyde

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eg1.) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CN$

Iso valero nitrile

eg2.) CH_3-CH_2-NC

Propiono Isonitrile

eg3.) $CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{\underset{O}{\|}}{C}-H$

Iso butyraldehyde

eg4.) $HCOOH$

Formic acid

eg5.) CH_3COOH

Acetic acid

eg6.) $NH_2-\underset{\underset{O}{\|}}{C}-H$

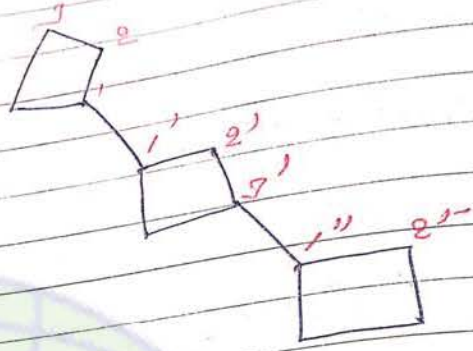
Formamide

eg7.) or $CH_3-\underset{\underset{O}{\|}}{C}-Cl$

Acetyl chloride

eg8.) $H-\underset{\underset{O}{\|}}{C}-H$

gg.)

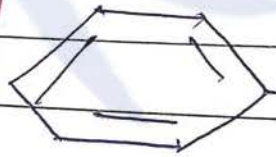


1, 1', 3', 1'' ter cyclobutane

(8) Some Important General name of the given Compound ⇒

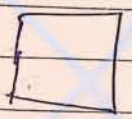
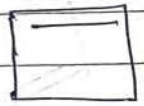
1) Acrolein ⇒ $CH_2=CH-\overset{O}{\overset{\|}{C}}-H$

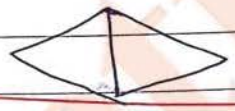
2)



$-CH_2-\ddot{N}H_2$ ⇒ Benzyl amine

Degree of (DU) unsaturation or double bond equivalent (DBE)

Alkane	Alkene	Alkyne
C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}
C_4H_8	D.U ⇒ 1	D.U ⇒ 2
	C-C=C-C	C-C≡C-C
	 cyclo Alkane	C=C-C=C
		



degree of unsaturation (D.U) → one double bond

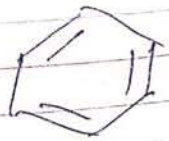
1 D.U = 1 D.B = 1 ring

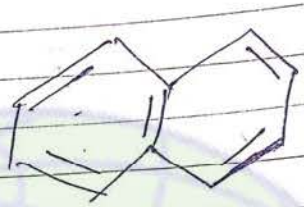
मतलब अगर कोई compound में एक double bond है या एक cyclic Ring है तो उसका degree of unsaturation एक होगा।

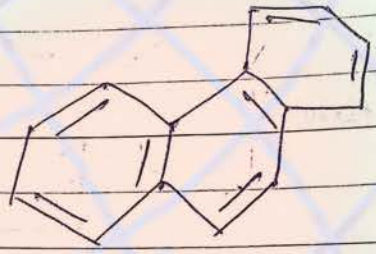
2 D.U = 1 triple bond = 2 D.B = 1 D.B + 1 ring or = 2 ring

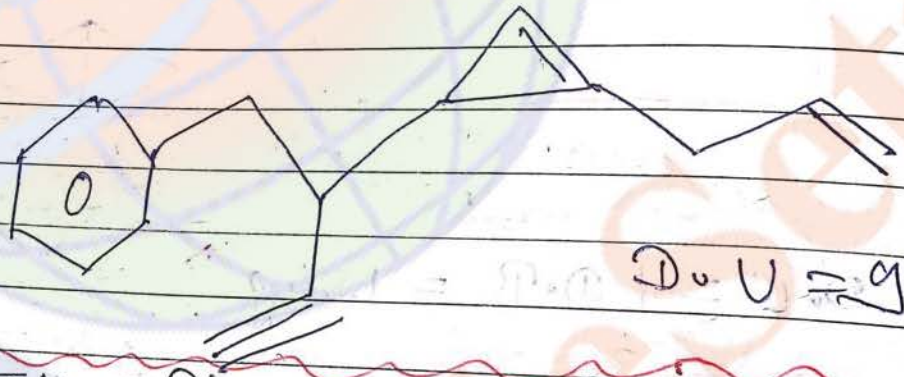
मतलब किसी compound में अगर एक triple bond है या दो double bond, या एक double bond + एक ring या दो Ring है तो D.U 2

☆ No. of H-(molecule) required to con. any compound into saturated chain (या degree of unsaturation)

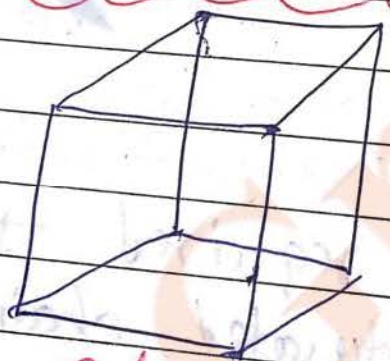
eg1.)  D.U ⇒ 4

eg2.)  D.U ⇒ 7

eg3.)  D.U = 10

eg4.)  D.U = 9

नोट:- अगर 3-D compound हो तो उस compound में जितना face हो उसमें से एक घटा दें बची D.U



Cubane

C_8H_8

D.U = 5

Prism

C_6H_6

D.U = 4

1st Choice के अद्" universal formula
→ गा है किसी भी compound में यदि ये सभी element का संयोजन हो तो उसका D.U
ज्ञात कर सकते हैं।

For compound "$C_aH_bN_cO_d$" degree of unsaturation can be determined by :—

$$D.U = a + 1 - \frac{(b-c)}{2}$$

(*) Treat halogen as hydrogen

must याद रखें

eg 1 → $C_{20}H_{24}N_2O_2$

$\Rightarrow 20 + 1 - \frac{(24-2)}{2}$

$\Rightarrow 10.$

eg 2. → CH_2Cl_2

D.U ⇒ 0

eg 3. → C_6H_5Br

D.U = 2

[∵ Treat halogen as hydrog]

eg 5. → $C_{10}H_8$

D.U = 7 or $10 + 1 - \frac{(8)}{2} = 7$

Date / /

Determination of Hybridisation and it's application

4) No. of hybrid orbital = (No. of σ bond) σ.P + l.P

4 = sp^3 ⇒ 25% s + 75% p
3 = sp^2 ⇒ 33.33 s + 6666 p
2 = sp ⇒ 50% s + 50% p

eg 1) $\overset{\oplus}{C}H_2 - CH_2 - CH_3$

eg 2) $\overset{\oplus}{C}H_2 - CH = CH_2$

3) $\overset{sp^2}{\overset{\oplus}{C}}H_2 - \overset{sp^2}{C}H = \overset{sp^2}{C}H_2$

write type of Hybridisation for underlined atom:-

1) $CH_3 - \underset{sp}{C} \equiv \underset{sp}{N}$:

2) $\underset{sp^3}{CH_3} - \underset{sp^2}{CH} = \underset{sp}{C} = CH_2$

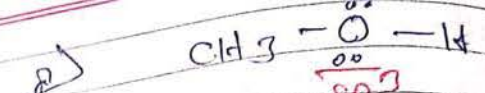
3) $CH_3 - \underset{sp^2}{CH} = \underset{sp^2}{NH}$

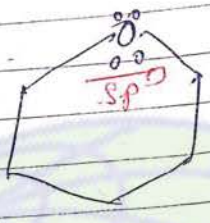
4) $CH_3 - \underset{sp^2}{C} = O$

5) $CH_3 - \underset{sp^2}{CH} = \underset{sp}{C} = O$

6) $HO - \underset{\underset{O}{\underset{\|}{O}} \rightarrow sp^3}{\overset{\overset{O}{\|}}{S}} - O - H$

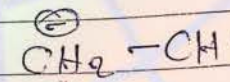
7.) 

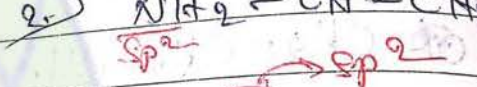
8.) 

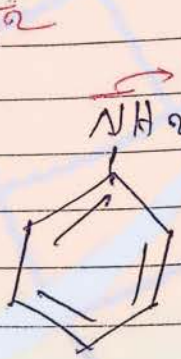
9.) 

10.)

Important conceptual example —

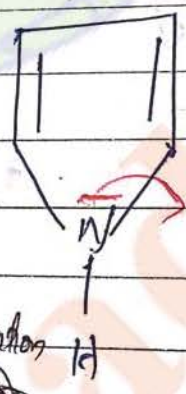
1.) 

2.) 

3.) 

4.) 

Conjugation में हैं पता कैसे चलेगा?

5.) 

Ans:- यदि किसी compound में lone pair हो और उसके बाद कोई single bond हो और फिर उसके बाद double bond हो तो वह compound में lone pair और (double bond) conjugation में आने के कारण Resonance होने के कारण उस molecule का hybridisation sp^3 की जगह sp^2 हो जाता है।

नोट :→ ये सभी compound "—" "—" "—" होने पर conjugation possible होता है।

इसलिए किसी भी Copound का hybridisation यदि sp^3 आता है तो यह जान लें कि वहाँ वह Conjugation में है नहीं है।

1st Choice

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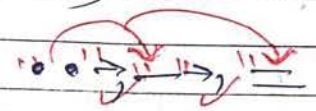
Note :->

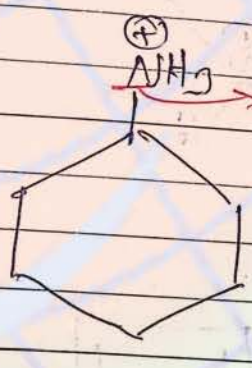
- When a lone pair containing atom or -ve charge is in conjugation with double bond or benzene ring then it's hybridisation is sp^2

and it's lone pair is in unhybrid orbital

(If other bond's are 6)

(Conjugation :⇒ 

(a)



(b)

$\ddot{N}H_2$
sp^3

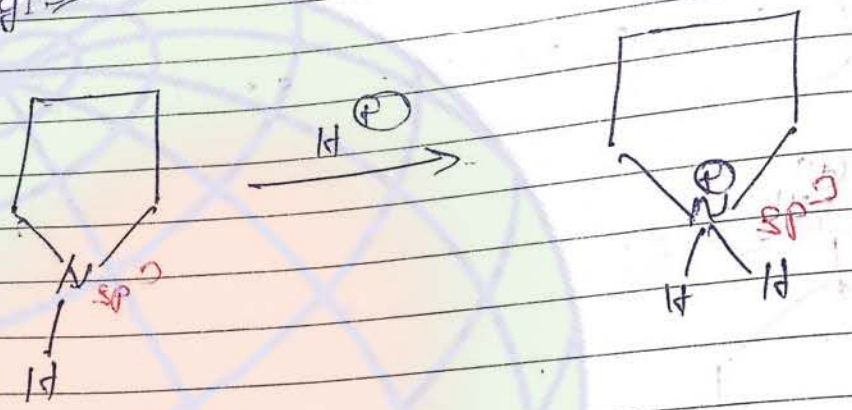
BF_3
sp^2

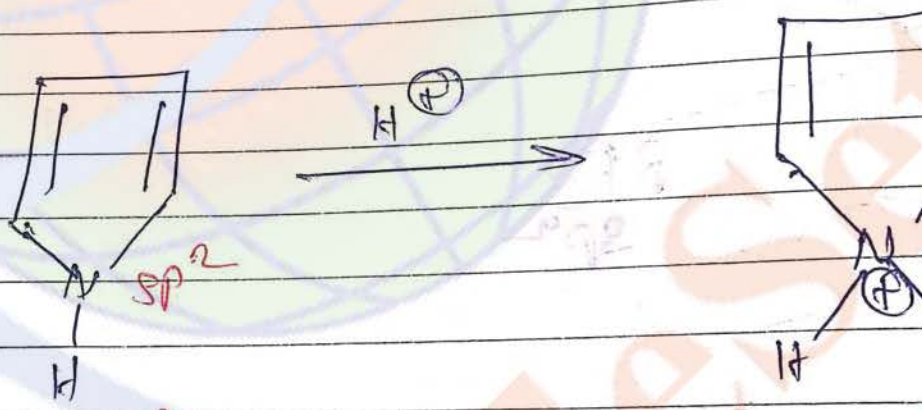
$H_2N \rightarrow BF_3$
sp^3 sp^3

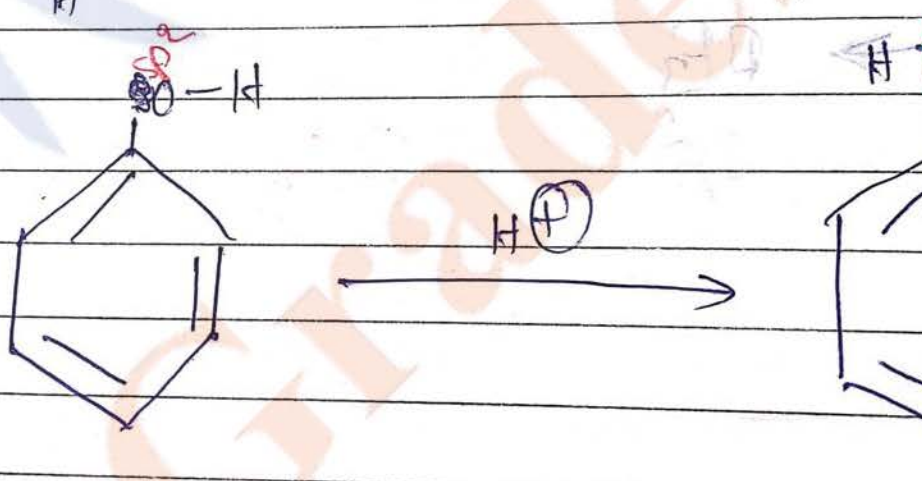
Important Point

If a lone pair containing atom which is in conjugation, form's a co-ordinate bond then it's hybridisation changes

eg1 →

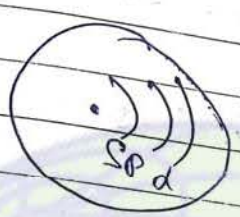






Application of Hybridisation →

1) Bond length और Bond energy →



s-character बढ़ने से bond energy बढ़ती है
bond angle बढ़ता है
bond length कम होती है

Acidic character ∝ s-character ∝ $\frac{1}{\text{Bond length}}$ ∝ Bond energy ∝ bond angle

∝ Reactivity

eg. $CH_3 - \overset{sp^3}{CH_2} - \overset{(a)}{H}$

$CH_2 = \overset{sp^2}{CH} - \overset{(b)}{H}$

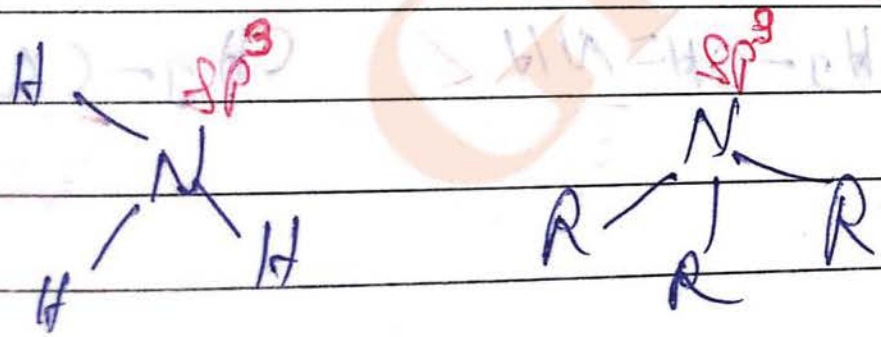
$CH \equiv \overset{sp}{C} - \overset{(c)}{H}$

Bond length :- c < b < a

Bond energy :- a < b < c

Note :→

s-character ↑ Bond angle ↑



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2.) S-character and E.N

S-character ↑ ⟹ E.N ↑

(S-orbital)

E.N ⇒ P < SP^3 < SP^2 < SP < S

(*) Note ⟹ Extent of overlaping ∝ P-character

P > SP^3 > SP^2 > SP

Note ⟹ C_{SP} > N_{SP^3}

F > O > N_{SP} > N_{SP^2} > C_{SP} > N_{SP^3} > $C.SP^2$ > C_{SP^3}

C_{SP^3} 2.5 | C_{SP^2} 2.7 | C_{SP} 3.1

E.N of SP hybrid carbon is greater than Nitrogen (SP^3)

eg ⟹ order of Electron Negativity ⟹

CH_3-NH_2 < $CH_3-CH=NH$ < CH_3-CN

SP^3 | SP^2 | SP

eg2.

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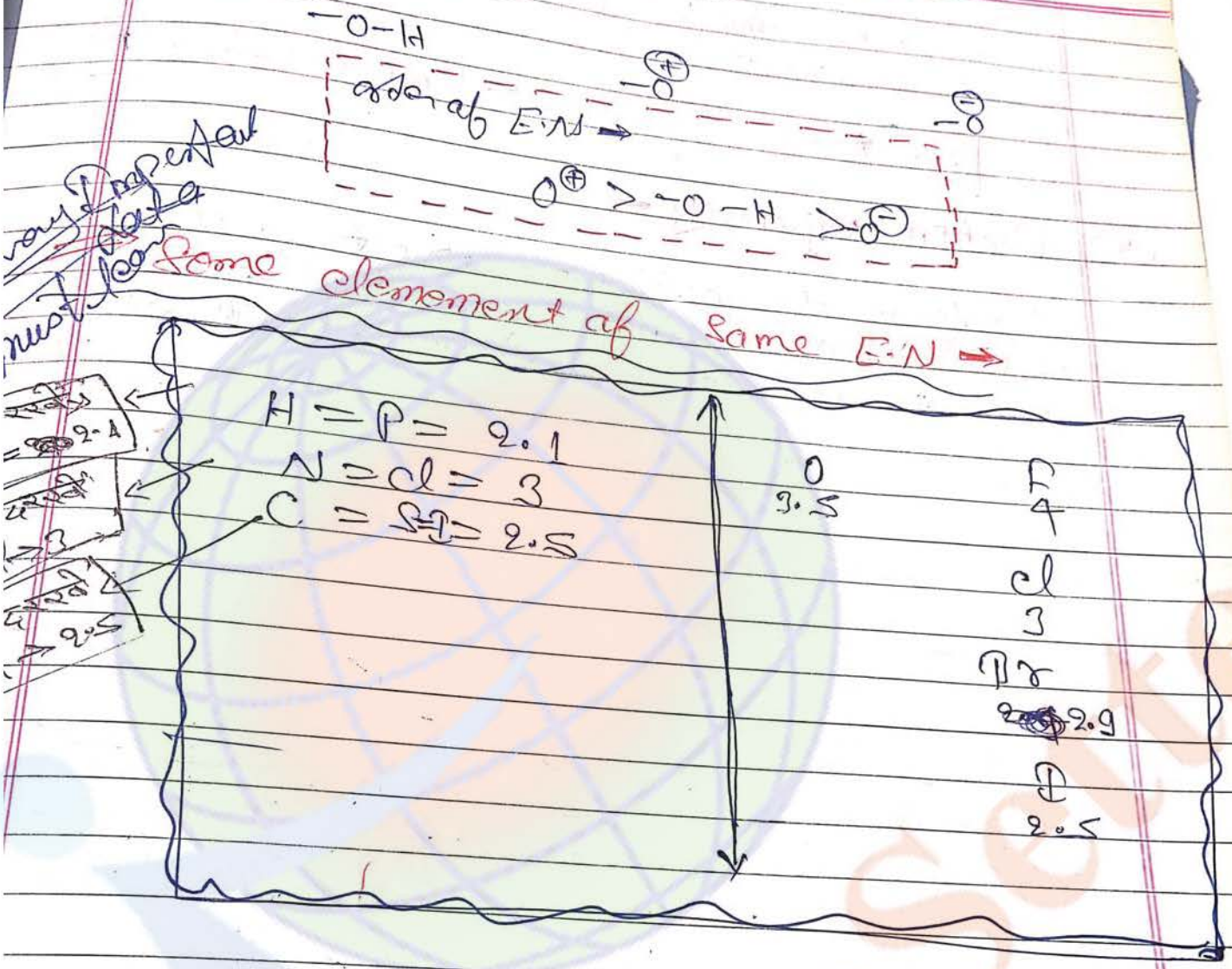

Note → Ionisation energy → The minimum energy required to remove "e⁻" from an "Isolated gaseous atom" in it's "ground state" is known as Ionisation energy of that element atom(element)

Electron affinity → change in enthalpy when an Isolated gaseous atom accepts an electron(e⁻). This is called as electron gain enthalpy ~~electron affinity~~

So, we say that:
Electron affinity gives the tendency to gain electron (e^-)

[E.A ↑ Tendency to gain electron ↑]

(5) Electron negativity →

Tendency to withdraw or attract bonded pair of "e^-" towards itself by an atom in a molecule is known as electron negativity (E.N)

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Type of Reagent → (Read :- Dr. R.K. Gupta Page :- 152, 157) table → 5.2 of 153

1) Electrophile → e⁻ deficient → e⁻ loving → e⁻ accept.
(Lewis acid) → also called this
(H⁺ ion के अलावा)

(i) cations → H^+, Cl^+, Br^+, $^+CH_3$ etc

Note → Alkali metal and Alkali earth metal cations do not act as electrophile

(ii) Free radical's and carbene

$CH_3^\bullet$ → 7e⁻ → एक हाइड्रोजन हटाने में एक e⁻ लेना पड़ेगा

$:CH_2$ → 6e⁻ → एक C हटाने में दो e⁻ लेना पड़ेगा

c) Incomplete octates →

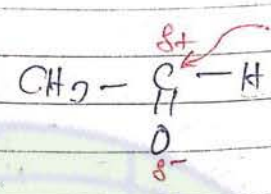
BeF_2, BF_3, $AlCl_3$ etc.

d) molecules with vacant d-orbital →

PCl_5, $FeCl_3$, $SnCl_4$ etc.

→ third period element के पास vacant d-orbital होता है।

e) multiple bonded atom which are attached with more E.N atom →



2.) Nucleophile → e⁻ rich → e⁻ repelling
→ Nucleus loving
↳ (Also called lewis base)

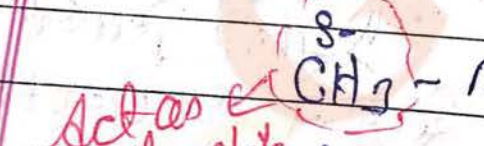
i) Anions →
$Cl^{\ominus}$, $Br^{\ominus}$, $OH^{\ominus}$

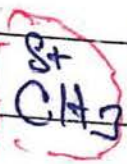
ii) ~~Nucleophile~~ neutral molecule containing lone pair →

$R-\ddot{O}-H$, $H_2\ddot{O}$, $R-\ddot{N}H_2$, $\ddot{N}H_3$ etc

iii) π-bonded unsaturated Alkene, Alkyne, Aromatic Compound

iv) organometallic compound →





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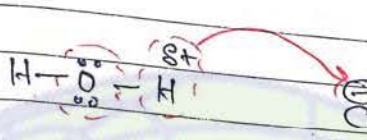
3) Ambiphile (behave like both electrophile as well as nucleophile.)
↳ (Amphoteric)



1% → electrophile
99% → Nucleophile

So, eg:- → $R\ddot{O}H$, $H\ddot{O}H$, $R\ddot{P}H_2$, $H_3O^{\oplus}$

Type of bond cleavage:-

Homolytical cleavage

1) $A\ddot{-}A \longrightarrow A^{\cdot} + A^{\cdot}$

(equal breaking of bond)

2) Free radical obtained as intermediate
(Paramagnetic
↳ (unpaired electrons))

3) Non-Polar

Same electron negativity
or
less EN difference.

Heterolytical cleavage

E·N ⇒ B > A

1) $A\ddot{-}B \longrightarrow A^{+} + B^{\ominus}$

(unequal breaking)

2) Ions

3) Polar solvent.

4) more ⊛ EN difference

Ionic bond is stronger than co-valent bond but is dissolve easily in Pola

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1st Choice

v) At higher temp or in light.

Examples- which of the following bond undergo hydrolysis fusion easily

C-O , O-H , C-N , C-H

Sol^n

2.5 3.5 3.5 2.1 2.5 3 2.5 2.1

C-O , O-H , C-N, C-H

1st Choice

Similar करता गया है Like dissolves like

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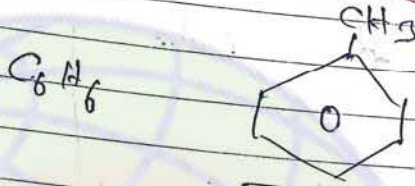
Type of Solvent →

1) Non-Polar solvent ⇒ $\mu = 0$ (गणित में → Non-Polar में $\mu = 0$ होता है)

eg:-



C_6H_6 , CCl_4, CS_2 etc.

Ethers

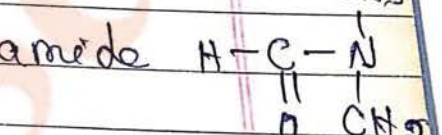
2) Polar solvent ⇒ ($\mu \neq 0$)

a) Polar (Protic) solvent.

H_2O, HCl , NH_3 , H_2SO_4 , CH_3COOH etc.
, HF , R-OH , R-COOH

b) Polar AProtic solvent

i) DMF → Dimethyl Formamide



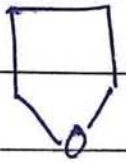
ii) DMSO → Dimethyl Sulphoxide

iii) ether iv) THF v) HMPT

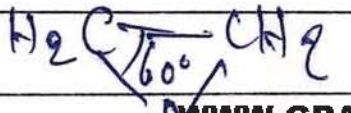
c) Ether :-

(a) open chain ether ⇒ R-O-R

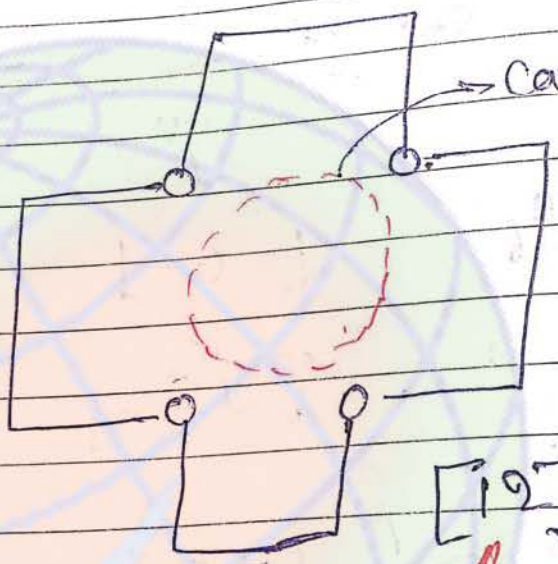
(b) Cyclic ether → THF



Tetra hydro furan.



c) Crown ether:-



[12] crown [4]

↑ total no. of atom in ring

↑ No. of oxygen atom

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General comparison of acidic and basic strength

Acidic strength →

Acid →
- H^+ donor in H_2O (Arrhenius)
- H^+ donor (or Proton donor) (Bronsted lowry theory)
- e⁻ pair acceptor (e⁻ deficient) (electrophile) } (lewis acid)

$$HA \rightleftharpoons H^+ + A^-$$
(Conjugate base)

$$K_a = \frac{[H^+][A^-]}{[HA]}, \quad pK_a = -\log K_a$$

Acidic strength or K_a or degree of dissociation (α) $\propto$ Stability of "Conjugate" Anion (A^-) $\propto \frac{1}{\text{Basic strength of } A^-}$

understand carefully.

$$\propto \frac{1}{pK_a}$$

1st Choice

Power of effect
N > H > I

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Note:- If acid is Strong then it's conjugate base is weak.

⊛ Stability of "Anion" is decided by following three factor →

Understand carefully otherwise you may take more time.

A) Size of Anion
B) EN of atom carying -ve charge
C) S-character.

नोट → याद रखो :- किसी भी Compound का Acidic strength और उसके द्वारा बनने वाले anion का stability एक ही होता है।

A) Size of Anion →

↳ In one group size is dominating factor.

Stability of anion ∝ Size of anion	"In one group".

eg 1.→

Acidic Strength- HF < HCl < HBr < HI

Stability- $F^\ominus$ < $Cl^\ominus$ < $Br^\ominus$ < $I^\ominus$

eg 2 →

NH_3 (a) AsH_3 (b) PH_3 (c)

b > c > a

Anion Stability $AsH_2^\ominus > PH_2^\ominus > NH_2^\ominus$

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eg:-

Acidic strength → $CH_4 < SiH_4 < GeH_4$

$H_2O < H_2S < H_2Se$

(2) E.N of atom carrying "-ve charge" → In a period E.N is dominating factor.

Stability of anion ∝ E.N

In a Period :

eg.1)

Acidic strength: $CH_4 < NH_3 < H_2O < HF$

Stability of anion: $CH_3^- < NH_2^- < OH^- < F^-$

eg.2)

Acidic strength: $PH_3 < H_2S < HCl$

Stability: $PH_2^- < HS^- < Cl^-$

encircled order

eg. Acidic strength: NH_3 (sp^3) $< CH \equiv CH$ (sp)

Stability order: $NH_2^- < CH \equiv C^-$

Ra

(Most acidic proton) — Terminal carbon ⇒ $C-C-C \overset{sp}{\equiv} C-H$

(Not 1st choice / Less acidic) — Non-terminal carbon ⇒ $C-C \equiv C-C$

E.N ⇒

$F > O > N_{sp} > N_{sp^2} > C_{sp} > N_{sp^3} > C_{sp^2} > C_{sp^3}$

c) s-character ⇒ Acidity is compared b/w same atom ⇒

Acidic strength: $CH_3-CH_3 < CH_2=CH_2 < CH \equiv CH$

Stability: $CH_3-\overset{\ominus}{C}H_2$ (sp^3) $\quad CH_2=\overset{\ominus}{C}H$ (sp^2) $\quad CH \equiv \overset{\ominus}{C}$ (sp)

Notes: Among's hydrocarbon only terminal Alkyne shows acidic behave. ⇒ that means it release H gas with metal.

eg's ⇒

$C-C-C \equiv C-H$

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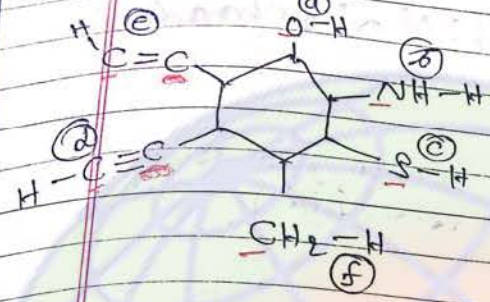
Eg) Among following in order of their Pka.



Pka order.

Soln

Acidic strength :-

c > a > d > b > e > f

size

Pka

c < a < d < b < e < f

Eg) Acidic strength order.

HF (a) HCl (b) HBr (c) CH_3COOH (d)

H_2O (e) NH_3 (f) HI (g)

Soln

g > c > b > a > d > e > f

N H_2O CH_3COOH F Cl Br I

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(*) इसलिए Acidic character पता करने के लिए निम्न तरह से याद रखेंगे :-

Acidic strength ∝ Acidic character ∝ SIZE ∝ E.N ∝ S-character
↓ Across group ↓ Across period ↓ In same atom

और इस प्रकार अम्लीय और क्षारीय के basic character निकाल लेंगे।

इसमें इसी तरह याद रखना होगा। उल्टा प्रयोग करने पर गलत भी हो सकता है।

1st Choice

जैसे जैसे Acidic Strength बढ़ती है वैसे वैसे Basic Strength कम होती है।

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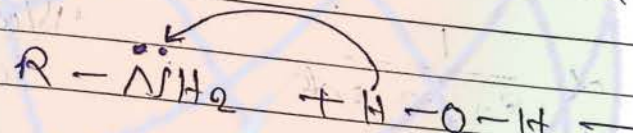
B) Basic Strength Comparison:

I)

→ OH^- donor (Arrhenius)
→ H^+ acceptor (Proton acceptor) (Bronsted lowry)
→ lone pair donor (lewis base) (e⁻rich) (e⁻ repelling) (nucleophile)

II)

Base → Anion or neutral molecule with lone pair



$$R-\ddot{N}H_2 + H-O-H \rightleftharpoons RNH_3^{\oplus} + OH^{\ominus}$$

$$K_b = \frac{[RNH_3^+](OH^-)}{[RNH_2]}, \quad pK_b = -\log K_b$$

or

$$A^{\ominus} + H^{\oplus} \rightleftharpoons HA$$

(Conjugate Acid)

III)

Basic Strength or K_b ∝ Tendency to donate e⁻ ∝ Tendency to accept H^+ ∝ $\frac{1}{\text{Stability of anion}}$

iv) Basic strength depends on three factor →

a) Basic strength $\propto \frac{1}{size}$ — In a group

b) Basic strength $\propto \frac{1}{E.N}$ — In a Period

c) Basic strength $\propto \frac{1}{s\text{-character}}$ — B/w same atom

Examples- Arrange following in basic strength order →

i) In a period due to E.N

$CH_3^{\ominus}$ (a) $> NH_2^{\ominus}$ (b) $> OH^{\ominus}$ (c) $> F^{\ominus}$ (d)

ii) → not act as base.

CH_4 (a) $\quad \ddot{N}H_3$ (b) $\quad H_2\ddot{O}$ (c) $\quad H\ddot{F}$ (d)

b) c > d > a

↳ do not have lone pair of electron

1st Choice

"Li" thires is best reducing agent

Next one group P.Q discuss

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iii) $CH_3-\overset{\ominus}{C}H_2$ > $CH_2=\overset{\ominus}{C}H$ > $CH\equiv C^{\ominus}$

sp^3 sp^2 sp

same atom & 1 & 2-charge

iv) $F^{\ominus}$ > $Cl^{\ominus}$ > $Br^{\ominus}$ > $I^{\ominus}$ (In a group)

v) $NaOH$ < $NaNH_2$ < CH_3Li

vi) (a) CH_3MgBr (b) CH_3Li (c) $(CH_3)_2Cd$

b > a > c

Some basic strength factor according to importance

1. SIP/SIR
2. ± M
3. ± H
4. ± D

1st Choice

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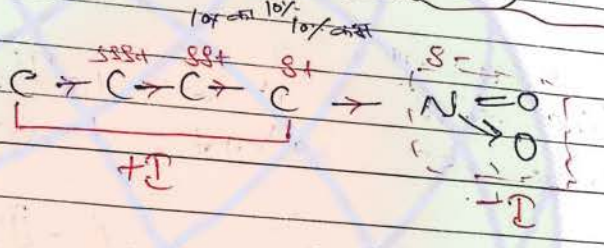
Different effects in organic chemistry

A) Inductive effect
B) mesomeric effect or Resonance } Permanent effect
C) Hyper conjugation.
D) Electromeric effect. } Temporary effect

1) Inductive effect (or I effect) or Transmission effect →



Here σ bond is polarised

1) Polarisation of a sigma bond due to adjacent polar bond is known as "Inductive effect"

2) This effect arise due to electronegativity difference.

3) It is Permanent effect but weak effect

4) It is chain effect and it moves in carbon chain but it decreases significantly on Increasing carbon.

after three (3) carbon it is almost Insignificant.

5) In this effect electron (e⁻) partially shifts but do not chang their atomic orbital.

In Inductive effect H- ko yakon as a reference atom and it's Inductive effect ko considered zero.

★ Type of I-effect →

+I-effect

1) e⁻ donating effect (e⁻ repealing)
2) It Increase e⁻ density
3) order of +I effect

$-O^{\ominus} > -\underset{\underset{O}{\|}}{C}-O^{\ominus} > -\overset{CH_3}{\overset{|}{C}}-CH_3 > -\overset{CH_3}{\overset{|}{CH}}-CH_3 > CH_3-CH_2-CH_2- > CH_3-CH_2- > -CH_3 > T > D > H$

-I-effect

1) e⁻ withdrawing effect (electrophile / lewis acid)
2) It decrease e⁻ density
3) order of -I effect

$-\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I > -O\text{-}Me > O-H > C\equiv CH > Ph > CH_2=CH- > R-H$

In one group →

(ध्यान में रखें)

C < Si < Ge

1st Choice

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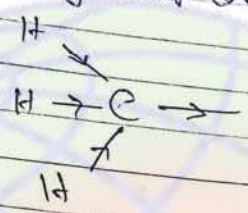
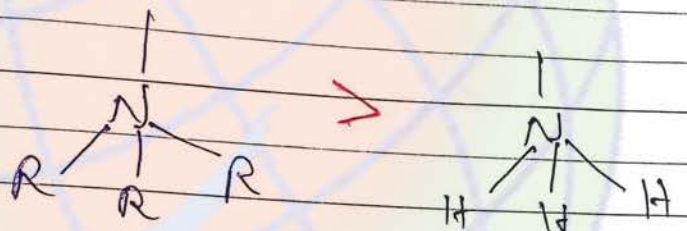
Imp. Point →

1) Hydrocarbon groups are E.D by +I effect

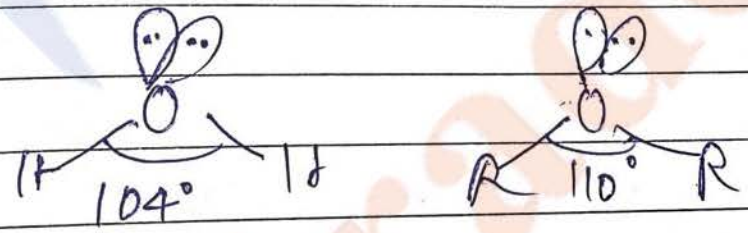


2) -I effect :→



Create bond angle
Create s-character
So,
-I effect is more

eg! →



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2.) Application of Inductive effect:-

A) Acidic strength → (of carboxylic acid and alcohol)

(i) $R-\underset{\underset{O}{\|}}{C}-O-H \rightleftharpoons R-\underset{\underset{O}{\|}}{C}-O^{\ominus} + H^{\oplus}$

carboxylate

$R-C(=O)-O^{\ominus} \longleftrightarrow R-C(-O^{\ominus})=O$

Acidic strength of carboxylic acid $\propto$ stability of carboxylate ion $\propto$ $-I$ effect $\propto \frac{1}{+I\text{ eff}}$

(ii) $R-O-H \rightleftharpoons R-O^{\ominus} + H^{\oplus}$

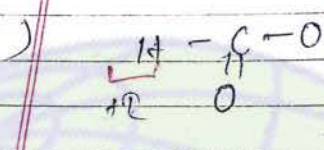
Alkoxide

Acidic strength of Alcohol $\propto$ Stability of Alkoxide Ion. $\propto -I\text{ eff} \propto \frac{1}{+I\text{ eff}}$

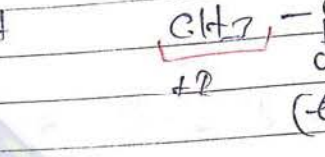
1st Choice

Q:- Compare the Acidic Strength of following carboxylic acid-

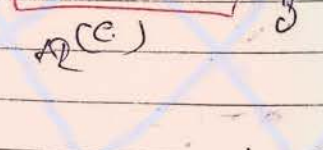
(i)



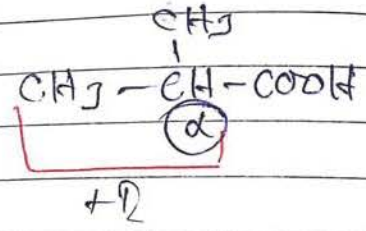
(a)



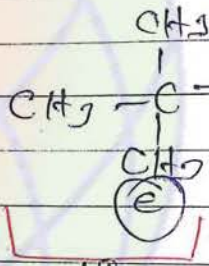
(b)



(c)



(d)

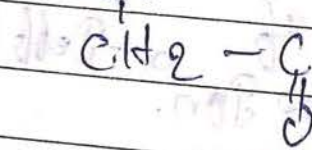


(e)

a > b > c > d > e

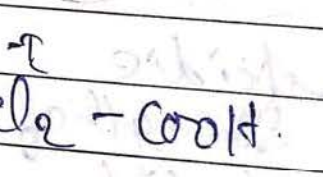
Acidic strength $\propto$ -I effect $\propto \frac{1}{+I \text{ effect}}$

(ii)



(a)

(b)



(c)

Number

c > b > a

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eg:- $CH_3-\underset{Br}{\overset{-I}{CH}}-CH_2-COOH$ (a)

$CH_2-CH_2-CH_2-COOH$ (b) — Br : $-I$

$CH_3-CH_2-\underset{Br}{\overset{-I}{CH}}-COOH$ (c)

Distance

$c > a > b$ (According to distance)

eg:-

$CH_3-\underset{K}{\overset{-I}{CH}}-COOH$ (a)

$CH_3-\underset{CH_3}{\overset{+I}{CH}}-COOH$ (b)

$CH_3-\underset{NO_2}{\overset{-I}{CH}}-COOH$ (c)

$CH_3-\underset{\overset{\oplus}{N}Me_3}{CH}-COOH$ (d)

Power

$d > c > a > b$

Note :- $d > N > P$

Distance 1st see, 2nd see Number, 3rd see Power.

eg 4:) a) $CH_3 - \underset{F}{CH} - CH_2 - COOH$

b) $CH_3 - \underset{Cl}{CH} - CH_2 - COOH$

c) $CH_3 - CH_2 - \underset{F}{CH} - COOH$

d) $CH_3 - CH_2 - \underset{Cl}{\overset{Cl}{C}} - COOH$

e) $CH_3 - \underset{Cl}{CH} - CH_2 - COOH$

f) $CH_3 - \underset{Cl}{CH} - \underset{Cl}{CH} - COOH$

$$d > f > e > a > b$$

* Concept:- ~~दो weake group मिले~~

I Two weake group at the same position is more powerful

II In Inductive effect distance is very important factor that is why a weaker group which is closed is more powerful than a stronger group which is at more distance (eg:- see above question "d and e" option)

III Two weak group at the same position are more powerful than one stronger group at the same position. (eg:- see above question "d and d")

-ve charge always empart +I effect

1st Choice

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eg:- $CH_2-CH_2-CH_2-COOH$ < CH_3-CH_2-O-H
CH_2-COOH → -I-effect effect, max. तीन carbon तक ही देखा जाता है।

eg:- Arrange following in order of Pka ?

$CH_2-CH_2-CH_2-COOH$
$CH-COOH$
(Adipic acid) (6 carbon)
(a) → आदत खराब - Adipi 6

CH_3-CH_2-O-H
(b)

CH_2-COOH
$COOH$
(c)
(malonic acid)

$COOH$
$COOH$
(d)
(oxalic acid)

Acidic strength :- d > c > b > a

Pka order :- d < c < b < a

1st Choice

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नोट :⇒ एक General बात याद रखें कि यदि किसी compound में "-ve" charge है तो वह nucleophile or lewis base का +I effect show कर सकता है।

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(B) Arrange following alcohol in order of their acidic strength

eg:

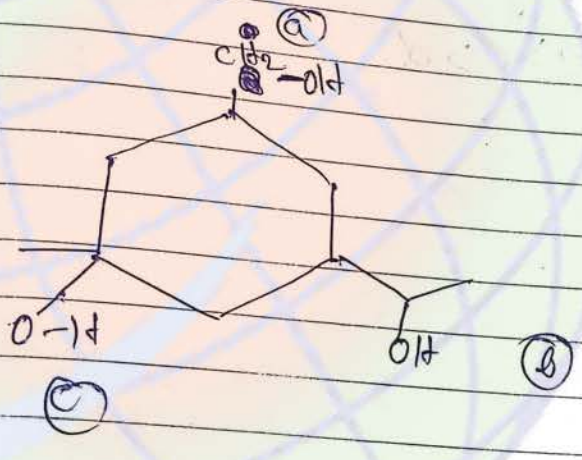
CH_3-CH_2-OH (+I) — 1° alcohol

$CH_3-CH(CH_3)-OH$ (+I) — 2° alcohol

$CH_3-C(CH_3)_2-OH$ (+I) — 3° alcohol

$1° > 2° > 3°$

eg 2:



a > b > c

eg:

CH_3-CH_2-O-H < $H-O-H$

$CH_3-CH_2-O^{\ominus}$ < $OH^{\ominus}$

+I

imet.

	pKa
H_2O	15.76
CH_3-O-H	15.72

Acidic strength $\propto \frac{1}{pKa}$

1st Choice

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(exception (experimentally found))

Note ⇒

All alcohol are less acidic than water except methanol

eg:- a) $CH_3-\underset{\underset{NO_2}{\uparrow}}{CH}-O-H$ (-I)

b) $CH_3-\underset{\underset{\overset{+}{N}Me_3}{\uparrow}}{CH}-OH$ (-I)

c) $CH_3-\underset{\underset{F}{\uparrow}}{CH}-OH$ (-I)

d) $CH_3-\underset{\underset{CH_3}{\uparrow}}{CH}-OH$ (+I)

Acidic strength:-

b > a > c > d

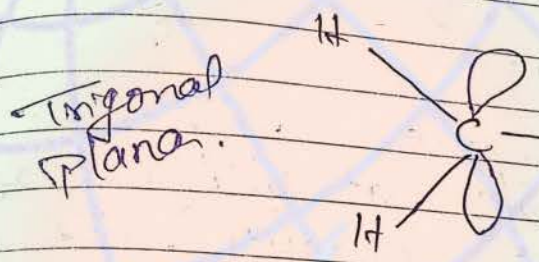
All oxide

3) Type of Reaction Intermediate and their stability comparision

Reactant → Intermediate → Product
exist for small period of time

(A) Carbocation or Carbonium Ion or

1) Intermediate in which carbon carried +ve charge
2) 6e⁻ in outermost cell so electrophile or lewis acid
3)



Trigonal Planar.

CH_3^+, sp^2 (In general)

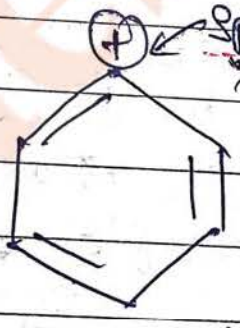
Their general hybridisation is sp^2 and geometry is trigonal planar

but in some rare case sp hybridisation also observed.

$CH_2=\overset{\oplus}{C}H$

sp

(vinyl carbocation)



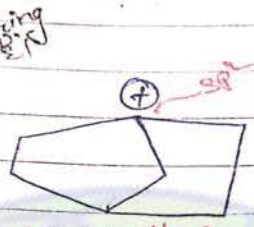
hybridisation and +ve charge on carbon

Phenyl carbocation.

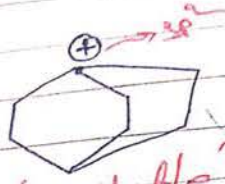
4) Bredt's Rule →

4) Bredt's Rule → (Applicable for carbocation and Alkene)

"Nine" membered ring तक stable carbon होता है



(unstable)



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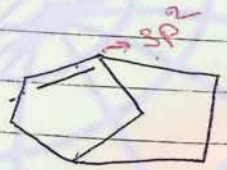

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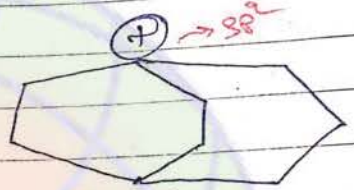
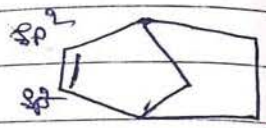


stable



(Stable)
(Bridge head carbon)

According to this rule sp^2 hybrid carbon is not stable at bridge head carbon before nine member ring

This is applicable to carbocation and alken's

नोट :→ Bredt's ने experimentally यह बताया कि sp^2 hybridized carbon जो एक bridge Head पर तब stable होता है जब उस compound में No. of carbon atom Nine या nine से अधिक हो इससे कम पर sp^2 hybridized carbon stable नहीं होता है।

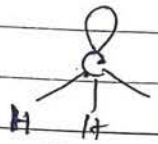
लेकिन यह भी याद रखें :→ यह केवल carbocation और Alken's के लिए ही Applicable है।

Stability ↑

(B) Carbanion or $-\overset{\ominus}{C}-$

1) Intermediate in which carbon carrying "-ve" charge
2) $-8e^-$ in outermost shell with lone pair ; lewis base and nucleophile.
3) Carbanion can have all type of hybridisation.

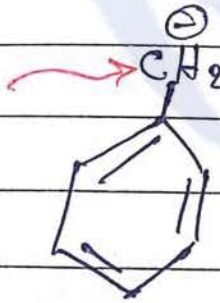
$\overset{\ominus}{C}H_3$ $\quad 3\sigma + 1\,l.p$ $\quad sp^3$ $\quad$ Pyramidal



$CH_2=\overset{\ominus}{C}H$ $\quad 2\sigma + 1\,l.p$ $\quad sp^2$ $\quad$ V shape or Bent

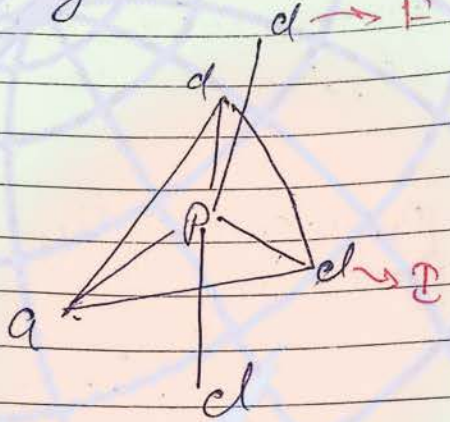
$CH\equiv\overset{\ominus}{C}$ $\quad 1\sigma + 1\,l.p$ $\quad sp$ $\quad$ Line

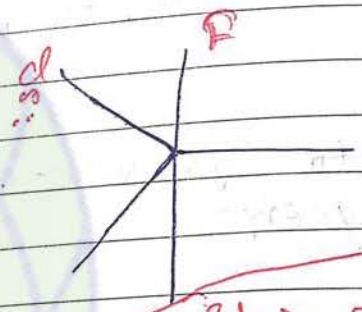
$CH_2-CH=\overset{\ominus}{C}H_2$ $\quad sp^2$, sp^2 $\quad$ double bond Conjugation π



5) It is electrophile in nature.
It's hybridization is sp^2 if surround atom is less electronegativity.

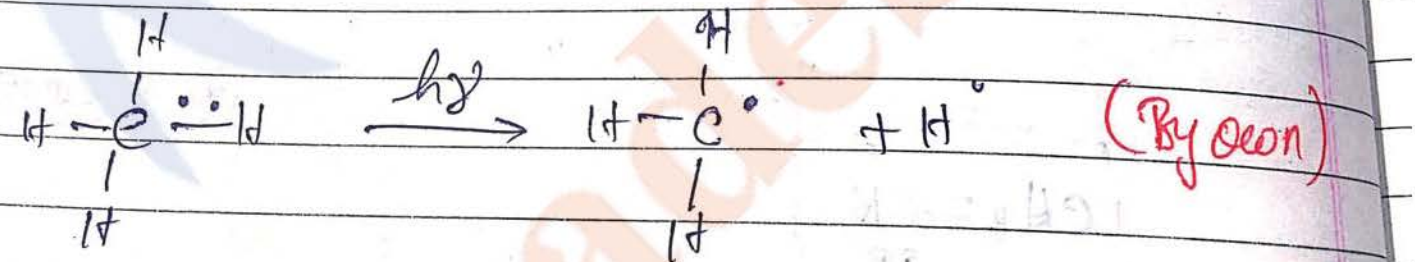
but if surrounding atom's more electronegative then 3-character of central atom decrease. and it's hybridization is sp^3. (Also see point 3)

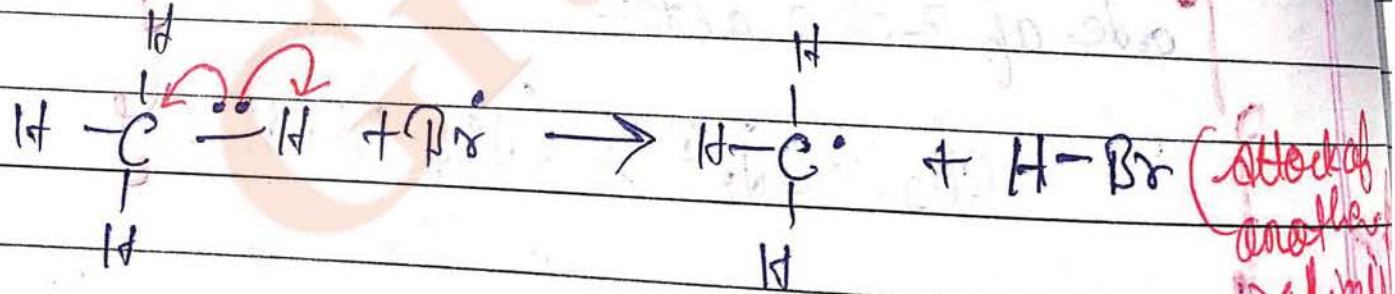




$sp^3d \Rightarrow sp^2 + Pd$

6) Free radical are found by homolytical cleavage either "one" or by attack of "another free radical".





homolytically homolytical cleavage से टूटते हैं

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$Br_2 \xrightarrow{h\nu} Br + Br$

(2) Carbene or $:CH_2$ or $H-\overset{H}{\underset{|}{C}}:$

इसके पास भी 6e⁻ है लेकिन यह दूसरा e⁻ देना चाहता है so it behaves like electrophile.

I) Reactive neutral Intermediate in which carbon contain two "unused e⁻"

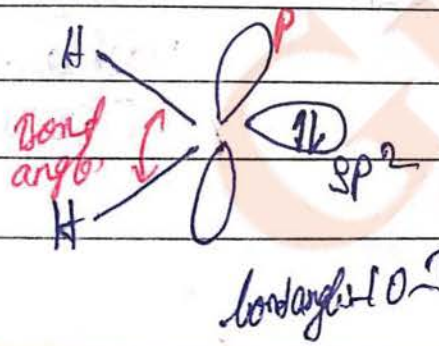
II) 6e⁻ in outermost cell that is why it is electrophile and lewis acid.

III) Carbene is of two type:—

Singlet carbene

$\uparrow\downarrow CH_2$

→ both e⁻ paired (Paired spin)

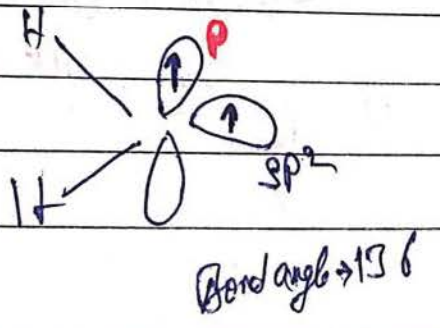


bond angle 102

Triplet carbene

$\uparrow \cdot CH_2$

→ Both e⁻ unpaired (Parallel spin)



Bond angle → 136

1st Choice

→ Relatively less Stable	→ Relatively more Stable
→ $2S+1 = 1$ (multiplicity)	→ $2S+1 = 3$ (multiplicity)
(S)	(1)
→ Bond angle :→ 100 – 110	→ Bond angle → 130 – 150

Note →

$2S+1$

$S = \frac{n}{2}$ → No. of unpaired e⁻

↓ total spin

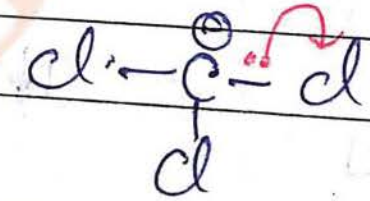
iv) on inert environment or on standing Singlet carbene can convert into Triplet Carbene →

eg :→ Inert gas :→ Nitrogen, Neon की उपस्थिती में

v) Carbenes are prepared by following methods →

a) From chloroform or Base (Halo form)

$CHCl_3 + OH^{\ominus}$ (Alk. KOH) $\longrightarrow$ $\overset{\ominus}{C}Cl_3 \xrightarrow{-Cl^{\ominus}} CCl_2$ Dichlorocarbene (DCC)



b) From decomposition of;
- Diazomethane (CH_2N_2)
- Ketene $CH_2=C=O$
- Diiodomethane CH_2I_2

$$CH_2=\overset{\oplus}{N}=\overset{\ominus}{N} \xrightarrow{\Delta} 2CH_2 + N_2$$

$$CH_2=C=O \xrightarrow{\Delta} :CH_2 + CO$$

$$CH_2I_2 \xrightarrow{Zn-Cu} CH_2(ZnI_2) \longrightarrow :CH_2 + ZnI_2$$

(carbenoid)

v) Stability comparision of Intermediates →

Electrophile { stability of carbocation or free radical or carbene or Basic strength (K_b) }

$\propto +\mathcal{I} \propto \frac{1}{-\mathcal{I}} \propto \frac{1}{\text{s-character}}$

$\propto +M, +H$ (not in meta)

Nucleophile { Stability of carbanion or Acidic strength (K_a) }

$\propto -\mathcal{I} \propto \frac{1}{+\mathcal{I}} \propto$ s-character

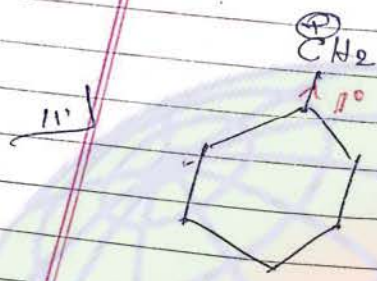
$\propto -M, -H$

5] Arrange following in stability order →

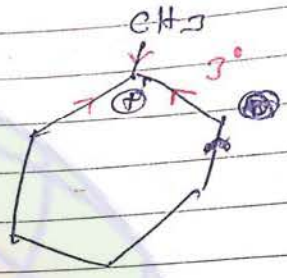
I) $CH_3^{\oplus}$ < $CH_3-CH_2^{\oplus}$ < $CH_3-CH^{\oplus}-CH_3$ < $CH_3-C^{\oplus}(CH_3)_2$

methyl ethyl or 1° Dropropyl 2° t-butyl 3°

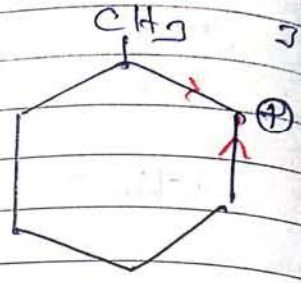
II)



(a)



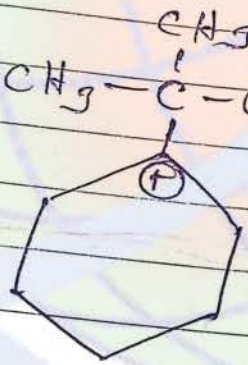
(b)

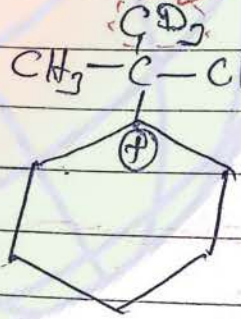


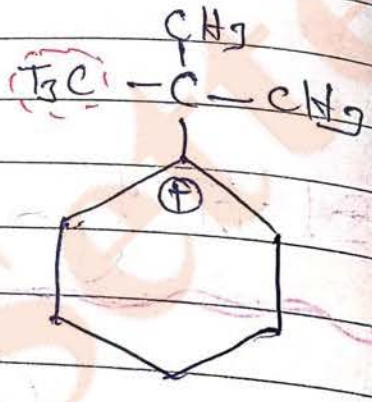
(c)

b > c > a

III)

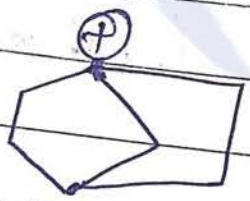




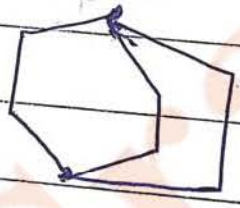


c > b > a

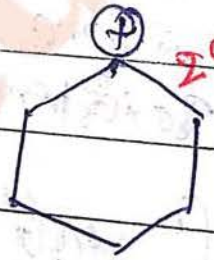
IV)



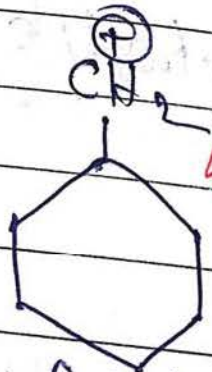
(a)



(b)



(c)



(d)

Bredt's rule.

c > d > b > a

1st Choice

Stability or Basic Strength ∝ e⁻ density
e⁻ deficient or Acidic Strength
(Acid का मतलब e⁻ कम)

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nent-
D.P.P.2

v) $CH_3-\overset{\oplus}{C}H_2$ (sp^2) > $CH_2=\overset{\oplus}{C}H$ (sp) > $CH\equiv\overset{\oplus}{C}$

vi) $CCl_3-CH_2-\overset{\oplus}{C}H_2$ (a) — $-I$

$HCCl_2-CH_2-\overset{\oplus}{C}H_2$ (b) — $-I$

$F_3C-CH_2-\overset{\oplus}{C}H_2$ (c) — $-I$

$CH_3-CH_2-\overset{\oplus}{C}H_2$ (d) — $+I$

$$d > b > a > c$$

vii) $CH_3-\underset{NMe_3}{\overset{\oplus}{CH}}-CH_2$ (a) — $+I$

$CH_2-\underset{CH_3}{\overset{\oplus}{CH}}-CH_2$ (b) — $+I$

$CH_3-\underset{CN}{\overset{\oplus}{CH}}-CH_2$ (c) — $-I$

$CH_3-\underset{O^{\ominus}}{\overset{\oplus}{CH}}-CH_2$ — $+I$

$$d > b > c > a$$

1st Choice

viii) a) $CH \equiv C - CH_2 - \overset{\oplus}{C}H_2$

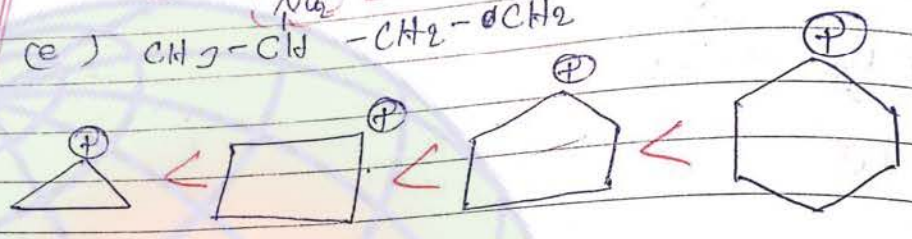
b) $Ph - CH_2 - \overset{\oplus}{C}H_2$

c) $CH_2 = CH - CH_2 - \overset{\oplus}{C}H_2$

d) $CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2$

e) $CH_3 - \underset{Na_2}{CH} - CH_2 - \overset{\oplus}{C}H_2$

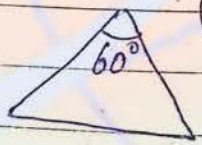
ix)



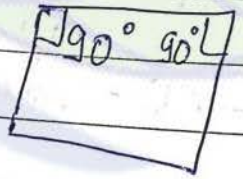
3 < 4 < 5 < 6

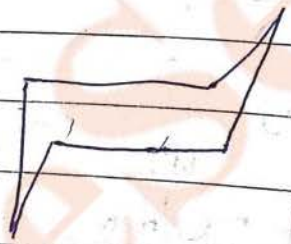
Size of ring

Explanation:-

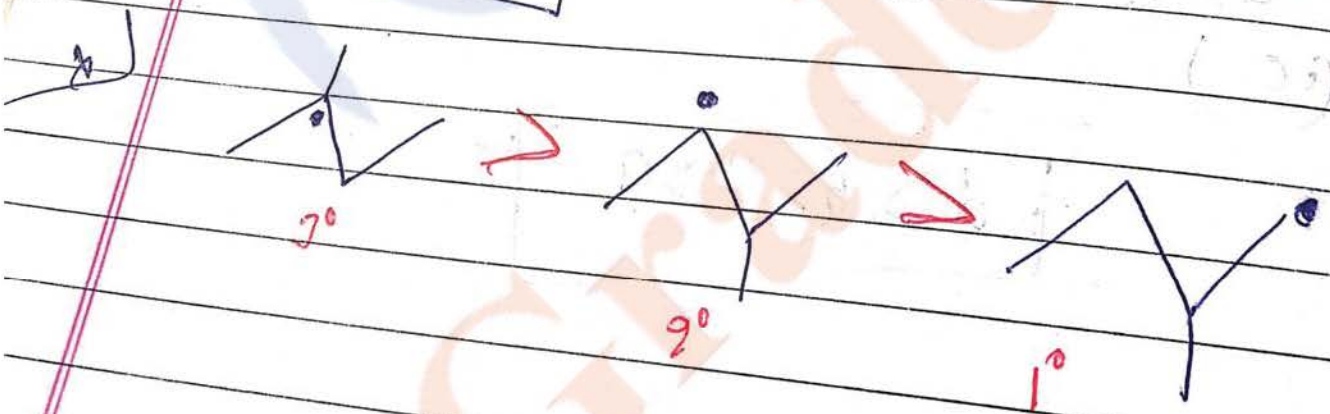


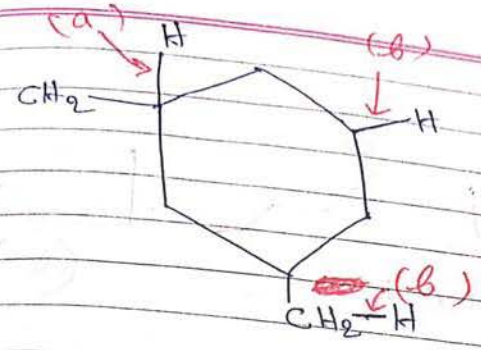
(sp^3 except 109°)





x)





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Arrange following carbon Hydrogen bond in order of bond energy.

Sol^n

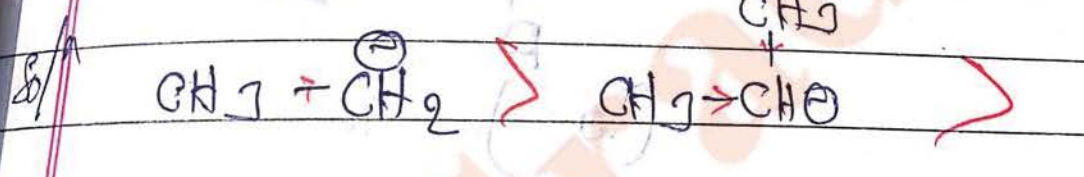
B.E of C-H $\propto$ $\frac{1}{\text{Stability of free radical}}$

$R-H \longrightarrow R^{\bullet}$

$a < b < c$

2) Arrange following carbonion in order of their stability.

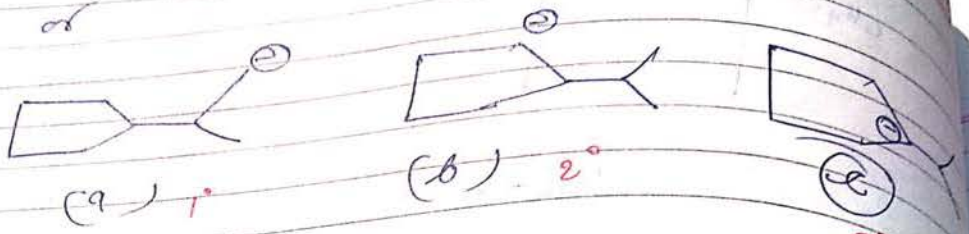
Sol^n



1^0 2^0 3^0

$1^0 > 2^0 > 3^0$

or



(a) 1° (b) 2° (c) 3°

a > b > c

Ex 3.

$CH_3-\overset{\ominus}{C}H_2$ (a) sp^3 $\quad CH_2=\overset{\ominus}{C}H_2$ (b) sp^2 $\quad CH\equiv\overset{\ominus}{C}$ sp (c)

$\overset{\ominus}{N}H_2$ (a)

c > d > b > a

Ex 4.

$CH_3-\underset{NO_2}{CH}-\overset{\ominus}{C}H_2$ (a)

$CH_3-\underset{F}{\underset{F}{C}}-\overset{\ominus}{C}H_2$ (b)

$CH_2-CH-\overset{\ominus}{C}H_2$ (with F, F)

b > a > c

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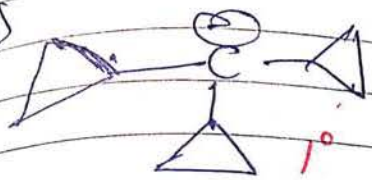
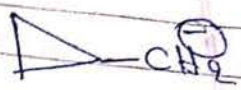
(Q6.)





$c > b > a$

1st Choice

4) Induction effect and dipole moment →

dipole moment is mainly related with charge seperation & and greate Inductive effect cause greate dipole moment.

$$\mu = q \times d$$

dipole moment

(Q1) a) $CH_3 - CH_2 - \overset{+}{N}Me_3$

b) $CH_3 - CH_2 - NO_2$

c) $CH_3 - CH_2 - CN$

dominating factor charge seperate

a > b > c

Q2) $CH_3I > CH_3Br > CH_3-I$

Q3) Exception:-

$CH_3 - F \; < \; CH_3 - Cl$ → dominating factor length.

1st Choice

Note:-

Eg:- $CH_3 \rightarrow C^{sp^2} \equiv N^{sp}$

Resultant →

$CH_3 \rightarrow N \equiv C$

↳ Due to co-ordinate bond.

Note:-

$C \equiv O$

Resultant
(∵ due to co-ordinate bond)

Note In Alkyl cyanide resultant dipole moment is from carbon to Nitrogen whereas in Diso cyanide direction is from Nitrogen to carbon.

(Direct Co-ordinate bond की direction ; final dipole moment जाएगा)

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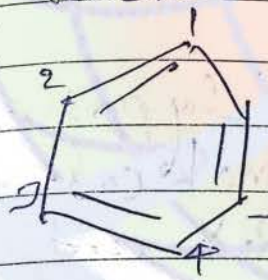
Resonance →

1) De-localisation of π-electron is known as Resonance.

2) Due to de-localisation of π-electron all properties of some compound can not be explain by one lewis structure that is why more than one lewis structures are written. These structures are known as Resonating structure or canonical structure, and this phenomena is known as resonance

eg:—

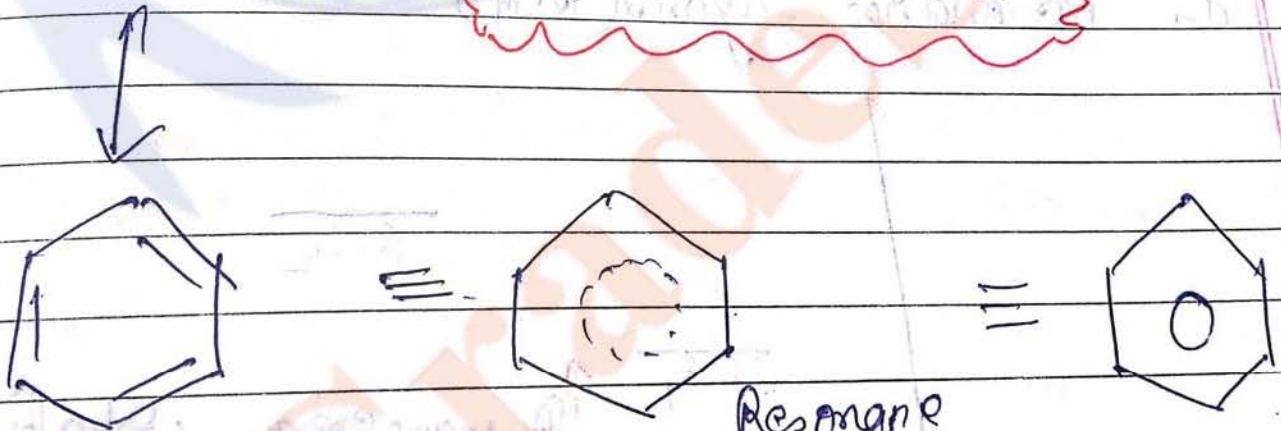
3) Equal bond length in benzene, carbonate ion, ozone can not be explain by only one structure



C=C ⇒ 1.34 A°

C–C ⇒ 1.54 A°

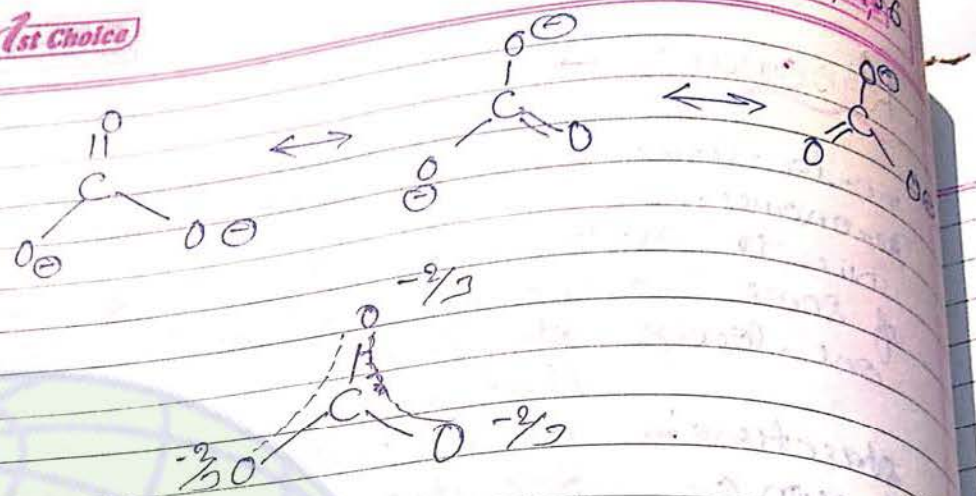
Benzene → 1.39 A°



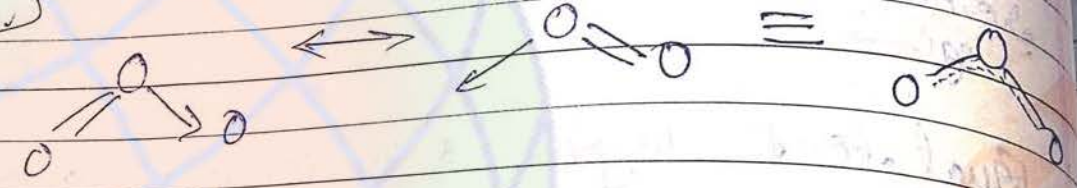
Resonance hybrid

1st Choice

eg:-

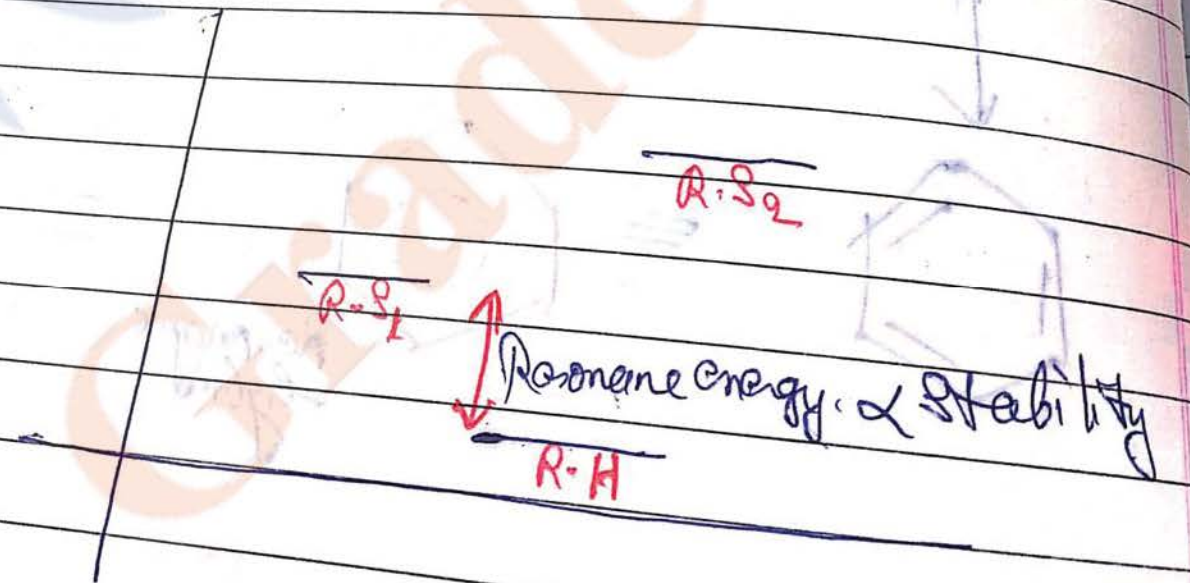


eg:-



4) All resonating structure are hypothetical and actual structure of molecule is average of all all R.S and known as Resonance hybrid (R.H)

5)



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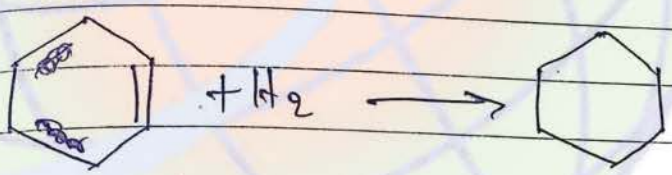
- Resonance hybrid is more stable than any resonating structure. and less energy resonating structure contribute more in resonance hybrid.

ii) Energy difference b/co (most stable) resonating structure and Resonance hybrid is known as Resonance energy and this is determined by:—

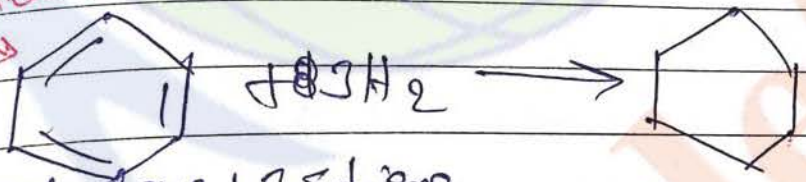
Resonance energy	=	Theritical value − Exp. value

example:—



$\Delta H_{HOH} = -28.6$ kJ/mole
(Theoritical)

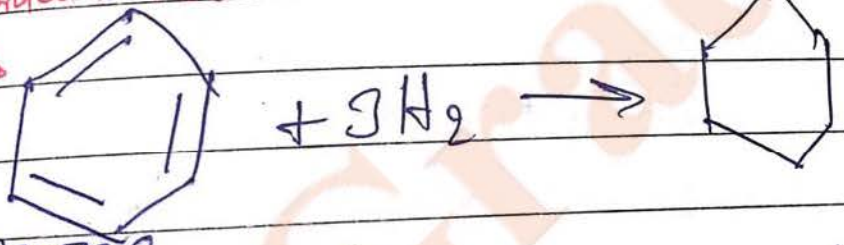
Theoritical molecule



cyclo-hexa 1,3,5-triene

$\Delta H_{HOH} = -28.6 \times 3$ kJ/mole
(theoritical)

experimental molecule:



Benzene

$\Delta H_{HOH} = -49.8$ kJ/
(experimental)

So, R.E = 36 kJ/mole

1st Choice

Heat of Hydrogination (HoH) →

It is the energy released when one mole of unsaturated compound is hydrogenated.

R.E ↑ ∝ Stability of ↑ molecule

Resonance energy

Resonance in which Identical R.S are found is more effective than Unequivalent R.S

1st Choice

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Ques

Conditions for Resonance:-

1) molecule should be planar (sp^2 hybridisation)
(Pure "P" orbital → sp^2) → 99%
In some cases → sp } → 1%

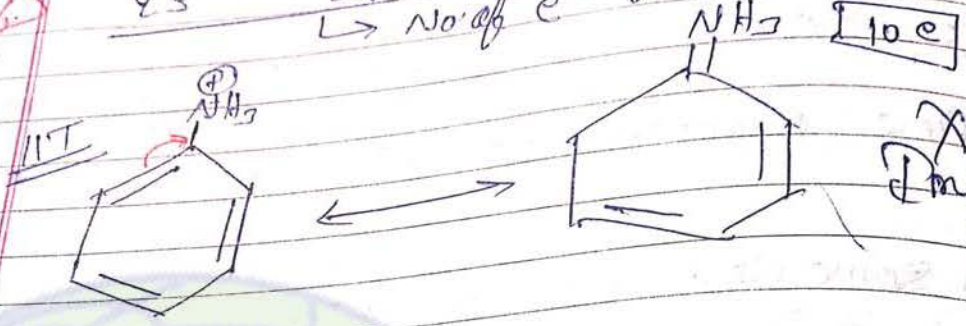
2) Resonating structure should not differ by high energy.

3) Total charge must be same in all Resonating Structure (R.S)

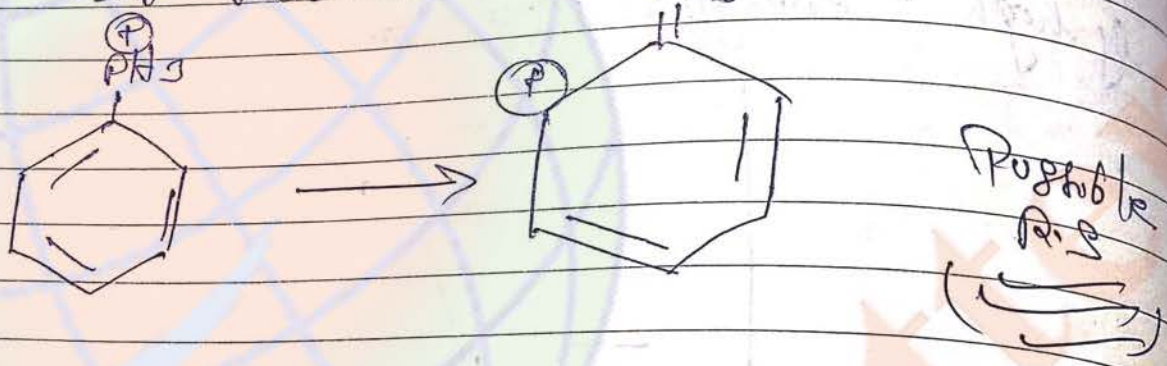
4) Total no. of unpaired e^- must be same in all R.S

5) Total no. of bond pair + lone pair must be same although a bond pair can convert into lone pair and vice versa

2S 2P → No. of e⁻ "8"



Expension of octate is impossible in 2nd period element



Ex. 1

In following two condition octate of oxygen and NH is complete otherwise if the charge is present on 2nd period element then it's octate is Incomplete

1st Choice

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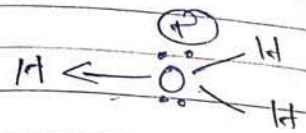
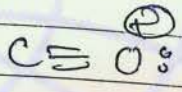
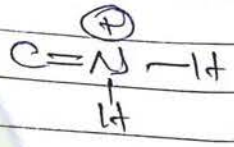


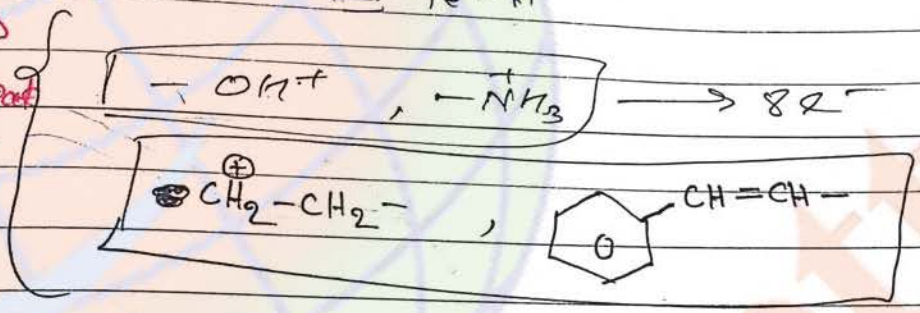
3 bond + 1 l.p

4 bond





(There group's don't participate in resonance with other suitable group.)



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★ Stability Comparision for Resonating Structure

↳ किसी भी compound के Resonating Structure के बीच में पता रहता है।

1) R.S with more number of covalent bond is more stable.

2) (charge और neutral में neutral more stable है)
Non-polar → (uncharge) Structure is more stable than Polar Structure (charge)

3) A R.S with complete octate of all atoms is more stable than Incomplete octet Resonating Structure

4) In case of polar R.S the charge is stable on less E.N atom and -ve charge is stable on more E.N atom.

(But first check condition of octeate)

5) In polar Structure similar charges should be at more distance and opposite charges should be closer or nearer.

It is Impossible to form a R.S in which 2nd period element contain more than eight electron.

1st Choice

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★ Conjugated system

1) Conjugation b/w double bonds →

eg:-

$CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2$

1,3 butadien

(1st)

(2nd)

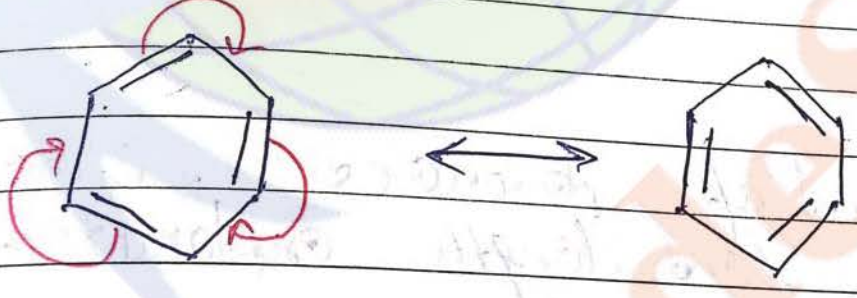
1st is more stable than 2nd and 3rd

I > II = III

$\overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2$

(3rd)

eg:-

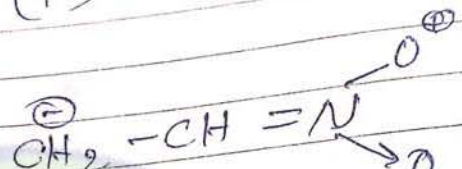


(I) (II)

I = II

eg.)

(I) (II)



(III)

Stability

$$I > II >>> III$$

(V) If multiple bond is b/w different EN atom's then π-e^- towards more electronegativity.

(VI) CH_2

Their kind of resonance is mainly used in bond length explanation.

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2) Conjugation b/w double bond and "+ve" charge (vacant orbital)

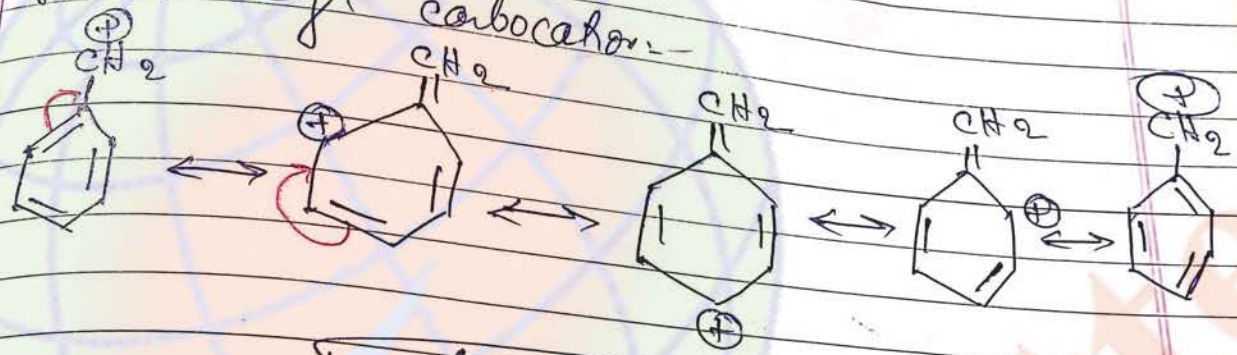
eg 1.)

$CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-C=CH_2$

Allyl carbocation

Stability :- same

eg 2.) Benzyl carbocation :-



Stability I = II

eg 3.)

$CH_2=CH-\overset{\oplus}{N}H_2$ (Resonance not possible)

(No of e^- is decrease by one vacant)

eg 4.) $CH_2=CH-\overset{\oplus}{N}H_2 \longleftrightarrow CH_2-CH=\overset{\oplus}{N}H_2$

(I) (II)

Stability :- II > I

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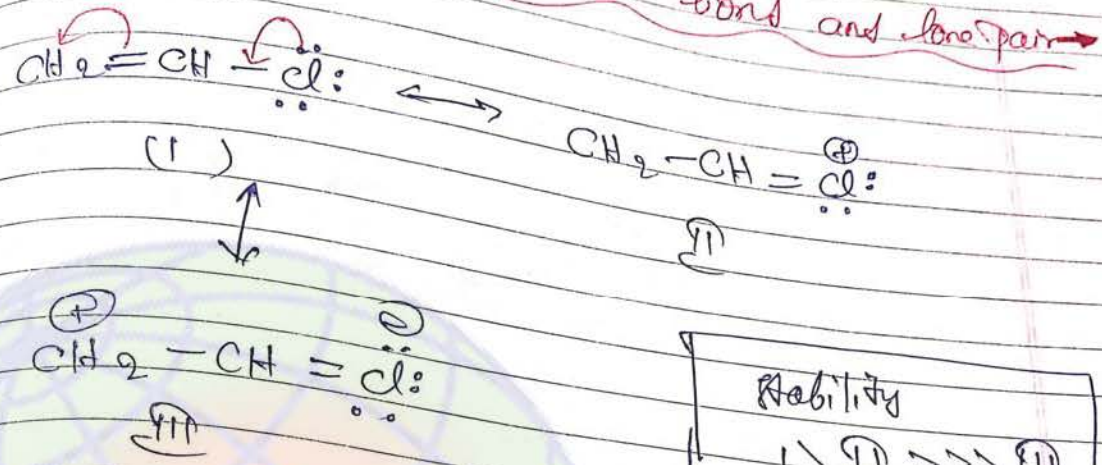
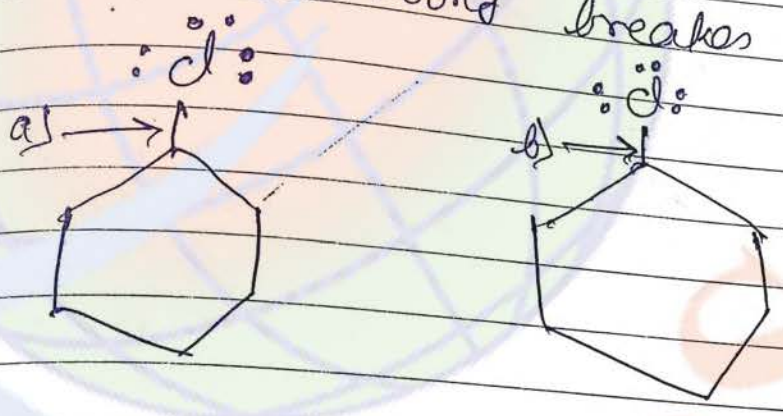
3) Conjugation b/w double bond and lone pair →



Stability
I > II >>> III

Q) which C-Cl bond breaks easily :-



~~a is more stable than~~

"a" is breaks easily

1st Choice

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1) Conjugation π/co double bond bond ⊕ and free radical →

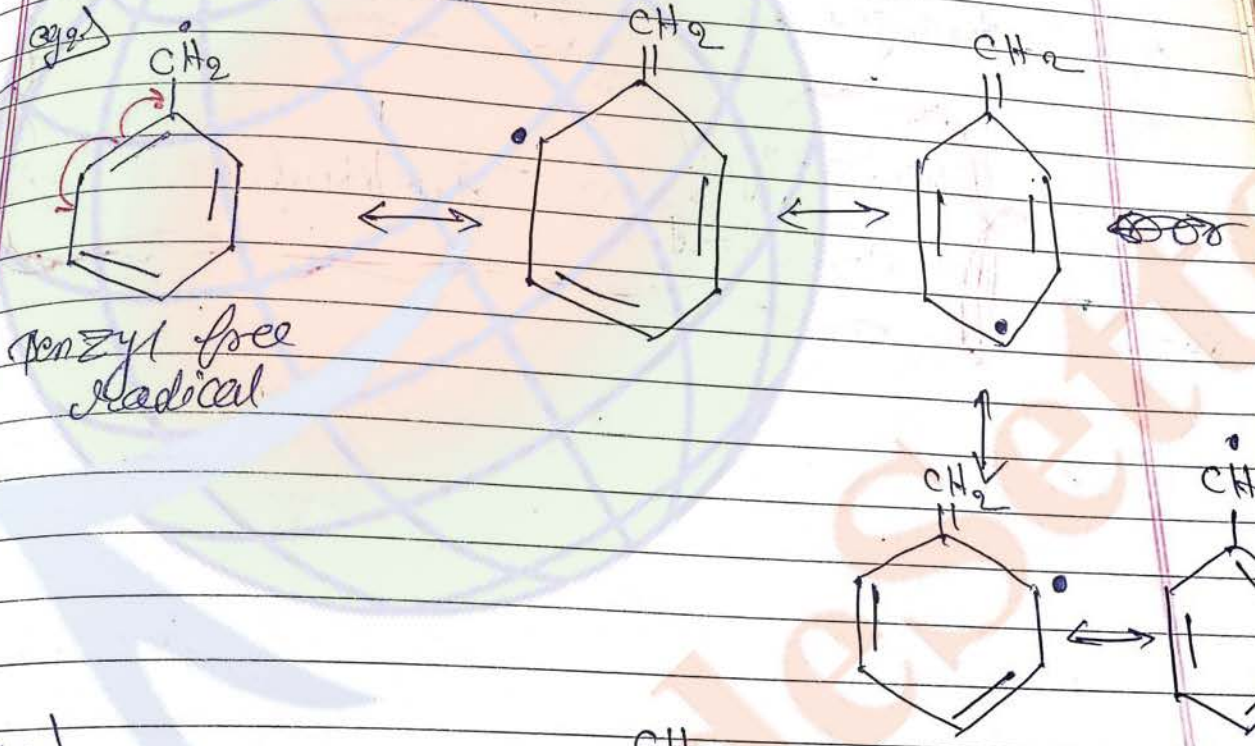
eg)

$CH_2 - CH = CH_2 \longleftrightarrow CH_2 = CH - \dot{C}H_2$

Allyl free radical

Stability same

eg)



Benzyl free radical

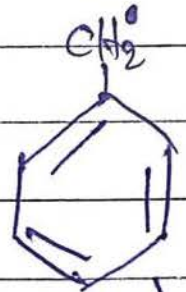
eg 1.

(a) $CH_3 - \dot{C}H_2$ 1°

(b) $CH_3 - \underset{|}{\overset{\cdot}{C}}H - CH_3$ 2°

(c) $CH_3 - \underset{CH_3}{\overset{\cdot}{\underset{|}{C}}} - CH_2 - CH_3$ 3°

(d)



(e) $Ph - \dot{C}H - Ph$

(f) $Ph_3\dot{C}$

(g) $CH_2 = CH - \dot{C}H_2$

1st Choice

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Introduction

$f > e > d > g > c > b > a$

Stability of free radical $\propto$ ~~delocalisation~~ delocalisation

Q-) Arrange in bond energy :-

Bond energy of C-H bond $\propto \frac{1}{\text{Stability of free radical}}$

Ra →

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> Conjugation b/w the charge in lone pair.

eg 1)

$CH_3 - \overset{\oplus}{C}H - \ddot{N}H_2 \longleftrightarrow CH_3 - CH = \overset{\oplus}{N}H_2$

(I) (II)

Stability ⇒ II > I

eg 2)

$CH_3 - \overset{\oplus}{C} = \ddot{O}: \longleftrightarrow CH_3 - C \equiv \overset{\oplus}{O}:$

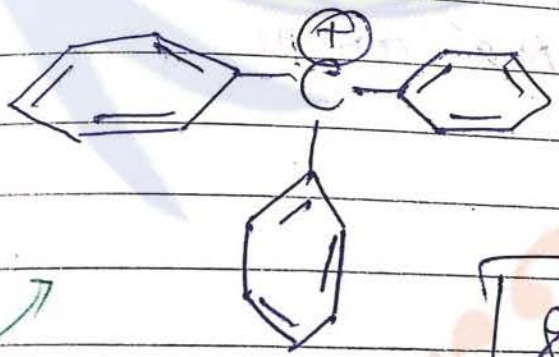
(I) (II)

Stability ⇒ II > I

(V) Imp ⇒ octet condition

Important

eg 1)



$< CH_3 - \overset{\oplus}{C} = \ddot{O}:$

Stability

Rg

1st Choice

If hetroatom containing lone pair is present adjacent to carbocation then this kind of Resonance stabilise carbocation very strongly.

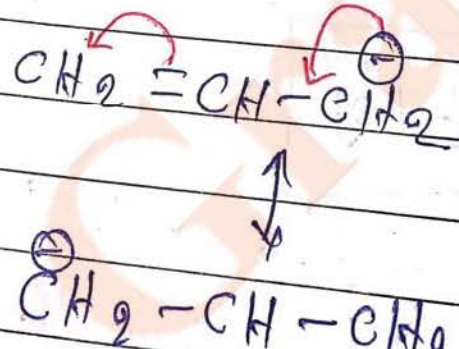
Imp 6.) Conjugation w/o -ve charge and double bond ⇒

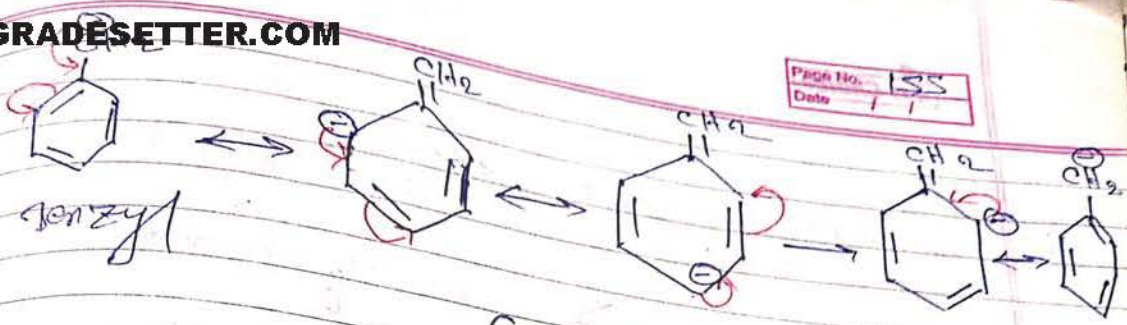
1) This conjugation or Resonance is useful to explain stability of anion or acidic strength.

Stability of anion or Acidic strength ∝ De-localisation of "-ve".

2) "-ve" charge is more stable on more electronegative atom.

Eg:-

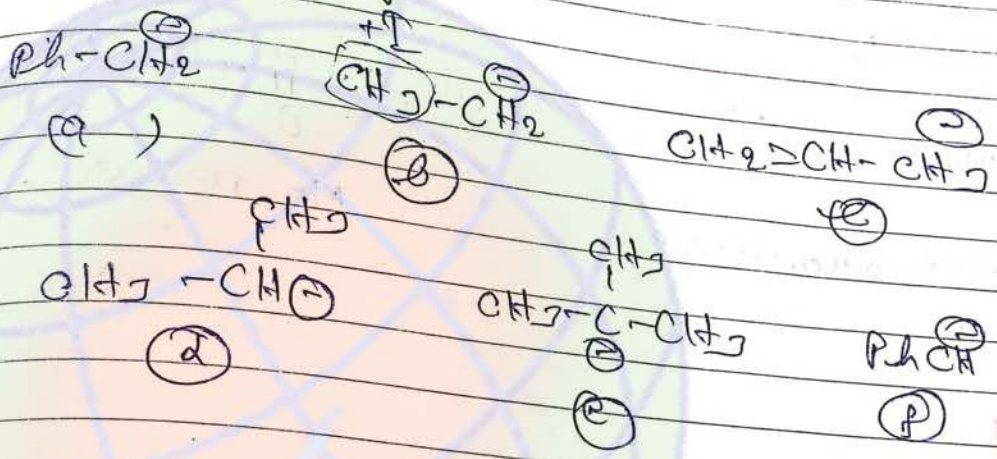




Benzyl

(Benzyl is more stable)

a) Arrang in stability order.—



(a) (b) (c) (d) (e)

(f) (g) (h)

In "h" ring's are connected that is why it is completely planar. whereas in case of "g" rotation is possible ✱ so all the ring's are not in the same plane.

h > g > f > a > c > b > d > e

Resonance | +I effect

Ex.) Acidic strength

$CH_3-\overset{O}{\overset{\|}{C}}-O-H$ > $CH_3-\overset{O}{\overset{\|}{C}}-O-O-H$

Acetic acid — Peroxy acetic acid

$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus}$ — $CH_3-\overset{O}{\overset{\|}{C}}-\ddot{O}:-\ominus$

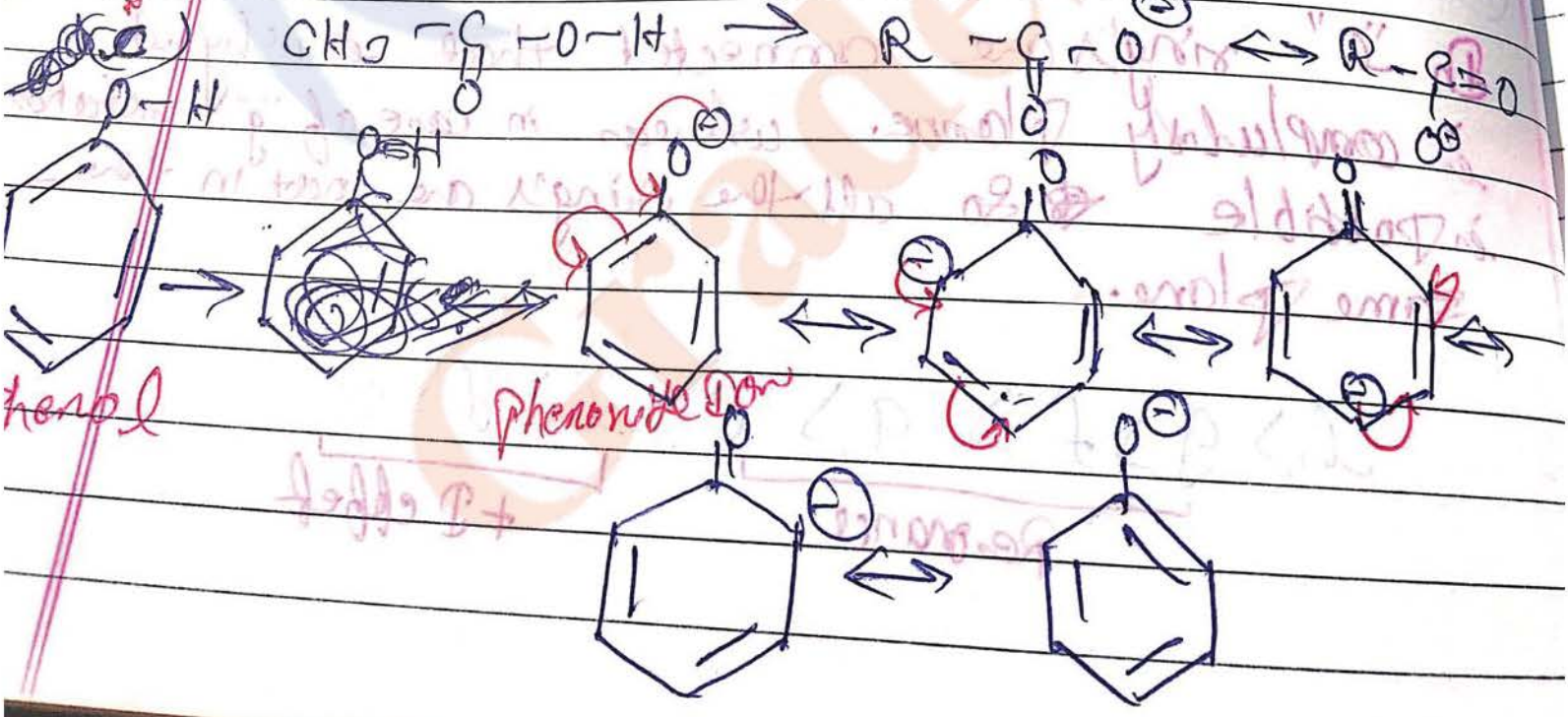
-ve delocalize — No resonance.

Ex.2) Acidic strength.

a) $CH_3-\overset{O}{\overset{\|}{\underset{O}{\underset{|}{S}}}}-O-H$ > $R-\overset{O}{\overset{\|}{\underset{O}{\underset{|}{S}}}}-O \leftrightarrow CH_3-\overset{O}{\overset{\|}{C}}=O$

Sulphonic acid — Sulphonate ion

$CH_3-\overset{O}{\overset{\|}{C}}-O-H$ > $R-\overset{O}{\overset{\|}{C}}-O \leftrightarrow R-\overset{O}{\overset{\|}{C}}=O$



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b) $CH_3-\overset{O}{\overset{\|}{C}}-O-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} \longleftrightarrow CH_3-C=O$
carbonyle acid

d) $CH_2=CH-O-H \Rightarrow CH_2=CH-O^{\ominus} \longleftrightarrow {}^{\ominus}CH_2-CH=O$
(vinyl alcohol)

e) $H_2O \longrightarrow OH^{\ominus}$

f) $CH_3-CH_2-OH \longrightarrow CH_3-CH_2-O^{\ominus}$

-ve on more E.N

a > b > c > d > e > f

-ve charge on 3-oxygen atom

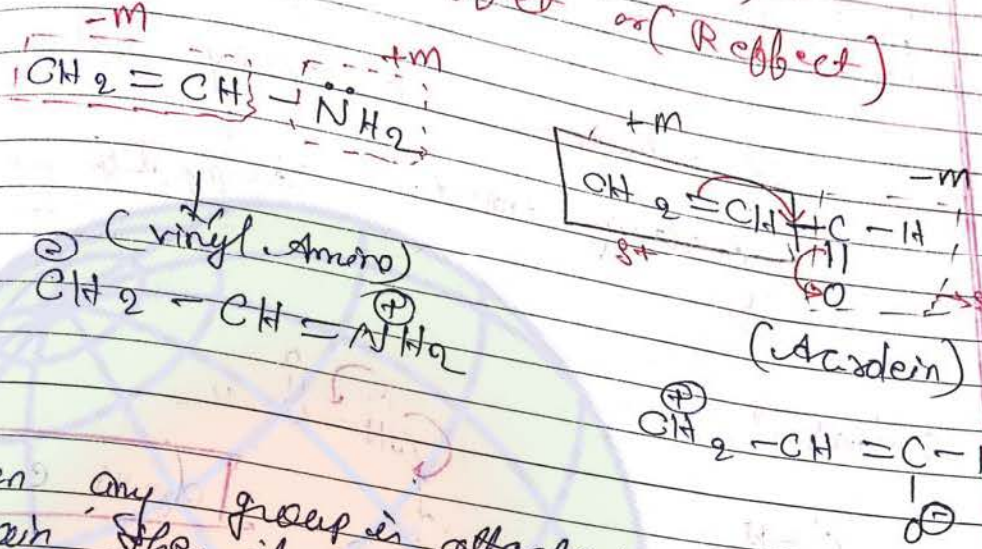
-ve charge on two oxygen atom

-ve charge on oxygen and carbon

↳ No. of R.S

$CH_3-\overset{O}{\overset{\|}{C}}=O$
$O^{\ominus}$

Mesomeric effect (m effect) or Resonance effect (R effect)



When any group is attached with unsaturated chain then it can increase or decrease e⁻ density by conjugation. This effect is known "mesomeric effect"

Types of mesomeric effect :-

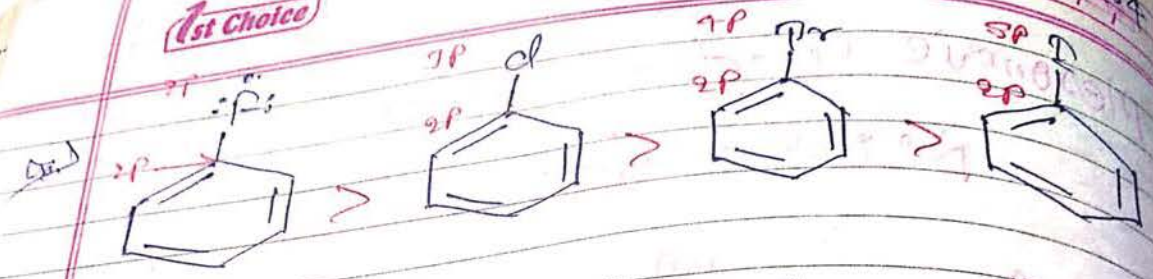
1) +m effect ⇒ a) e⁻ donating group
b) This effect is shown by the group which is attached by a σ bond and contain a lone pair on directly attached atom

order of "+m" → (Benzene के द्वारा तुलना किया जाता है)

$$O^- > \ddot{N}R_2 > \ddot{N}HR > \ddot{N}H_2 > \ddot{O}-H \geq \ddot{O}-R >$$

$$-\ddot{N}H-\overset{O}{\overset{\|}{C}}-R > -O-\overset{O}{\overset{\|}{C}}-R > -Ph > CH=CH_2 > F > Cl > Br$$

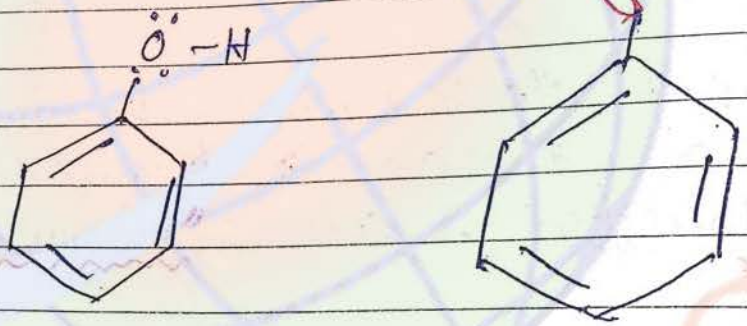
1st Choice



It is based on overlapping extent

overlaping extent $\propto \frac{1}{\text{energy diff bet orbitals}}$

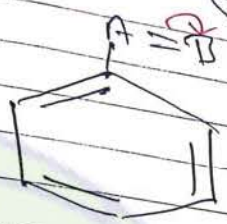
eg:- Explanation



does conjugation

* -m -effect →

a) e⁻ withdrawing effect.



E.N ⇒ B > A

b) This effect is shown by the group which multiple bond b/w diff. E. Negativity one more E.N atom is away.

(*) order of -m order

$-NO_2 > -CN- > -SO_3H > \overset{O}{\overset{\|}{C}}-\underset{*}{Cl} > -\overset{O}{\overset{\|}{C}}-\underset{*}{H}$

$> -\overset{O}{\overset{\|}{C}}-\underset{*}{R} > -\overset{O}{\overset{\|}{C}}-\ddot{O}-\overset{O}{\overset{\|}{C}}-R > -\overset{O}{\overset{\|}{C}}-\ddot{O}-H$

$> -\overset{O}{\overset{\|}{C}}-O-R > \overset{O}{\overset{\|}{C}}-NH_2$

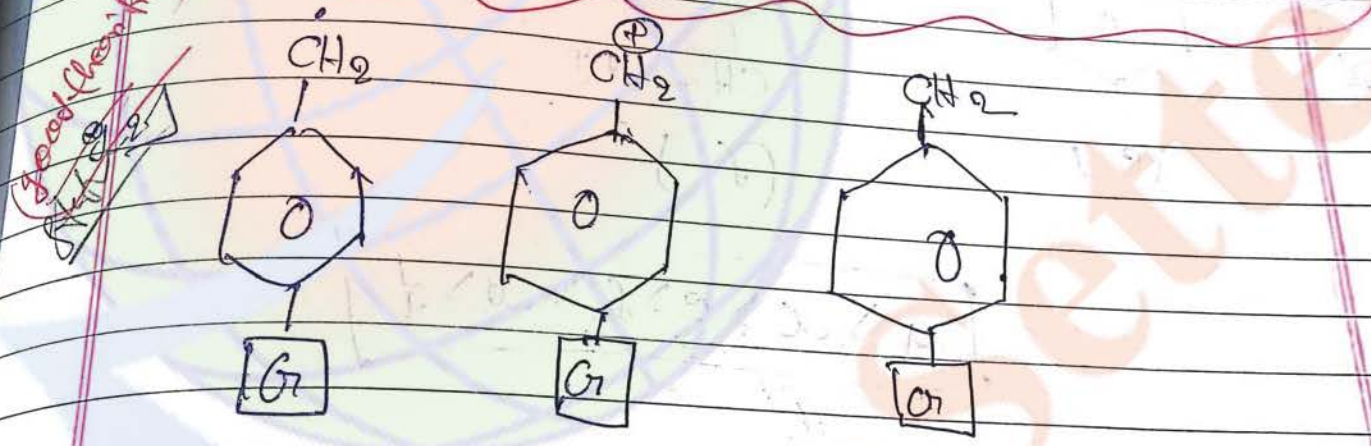
Application of mesomeric effect →

(i) Stability of Intermediate →

Eg.)

$Ph_3\dot{C} > Ph_2\dot{C}H > PhC\dot{H}_2 > CH_2=CH-\dot{C}H_2$

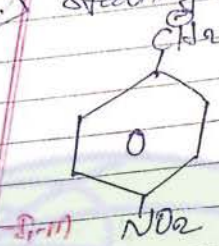
Stability of carbocation or free radical $\propto +I, +M \propto \frac{1}{-M}, \frac{1}{-I}$



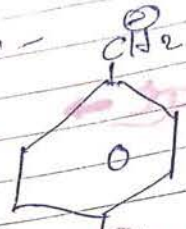
+I, +M	Stable	Stable	Unstable
-I, -M	Unstable	Unstable	Stable

1st Choice

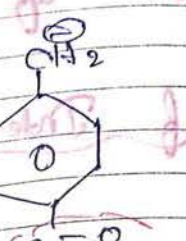
Q.) Stability order:-



(a)

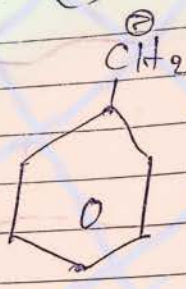


(b)

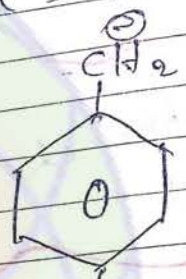


(c)

(d)



(e)

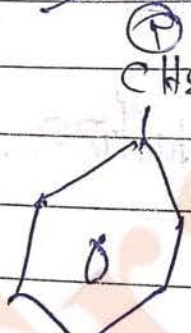


(f)

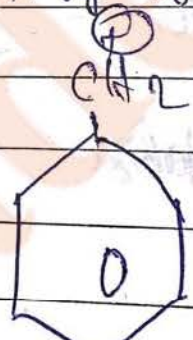
$$a > c > e > f > b > d$$

eg:- Arrange in stability order:

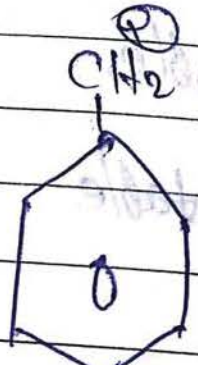
(a)



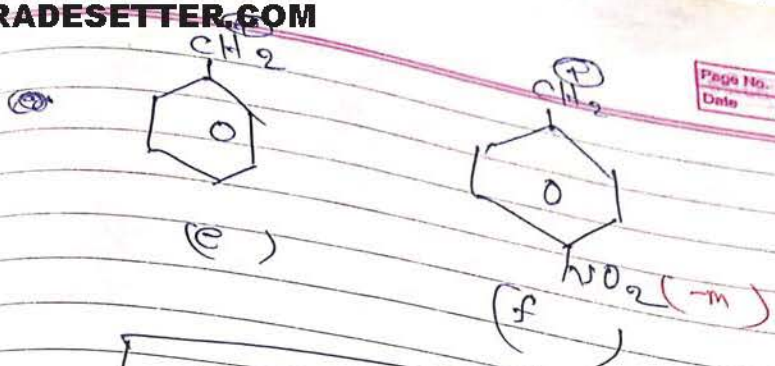
(b)



(c)

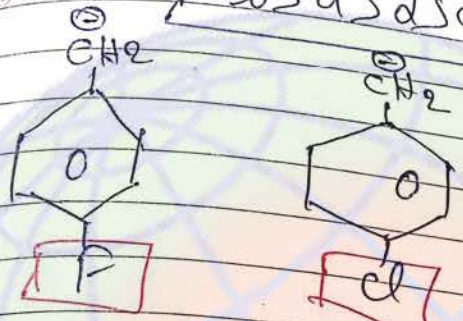


(d)



(e) (f) NO_2 (−M)

b > a > d > e > c > f



vacant d-orbital

b > a

Note ⇒

+m and −I of Florine (F) are greater than chlorine (cl) but chlorine is more e⁻ withdrawing than F because in case of F"

For

F	+m ≃ −I
Cl	+m < −I

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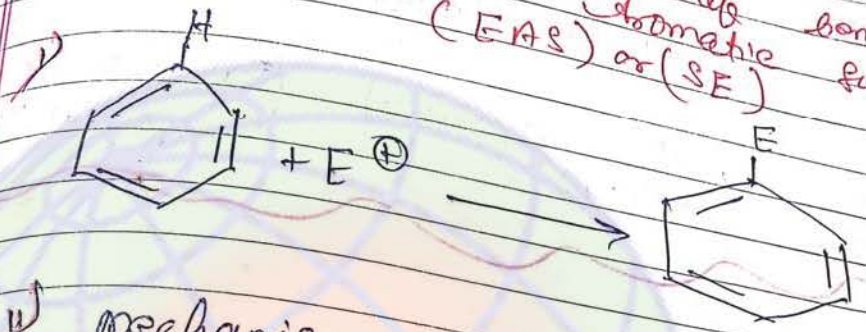
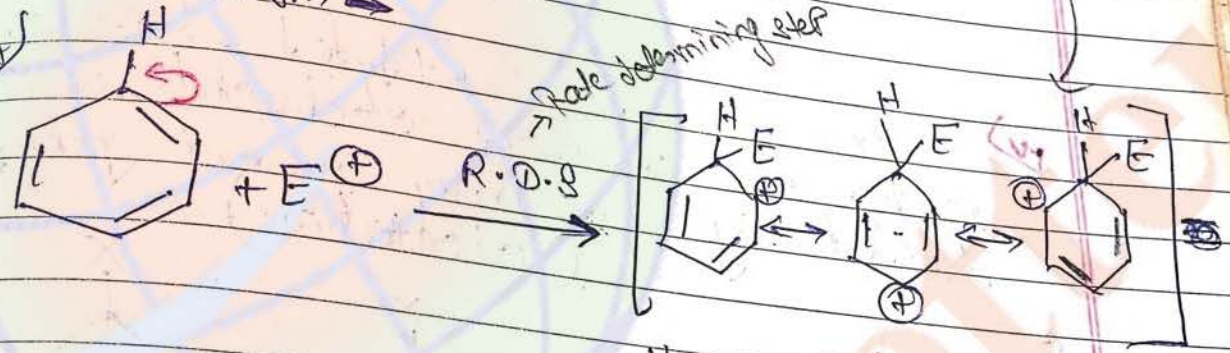
Reactivity & And orientation In monosubstituted benzene ring →

A) characteristics Reaction of benzene ring is electrophilic aromatic substitution (EAS) or (SE)



I) mechanism →

A)

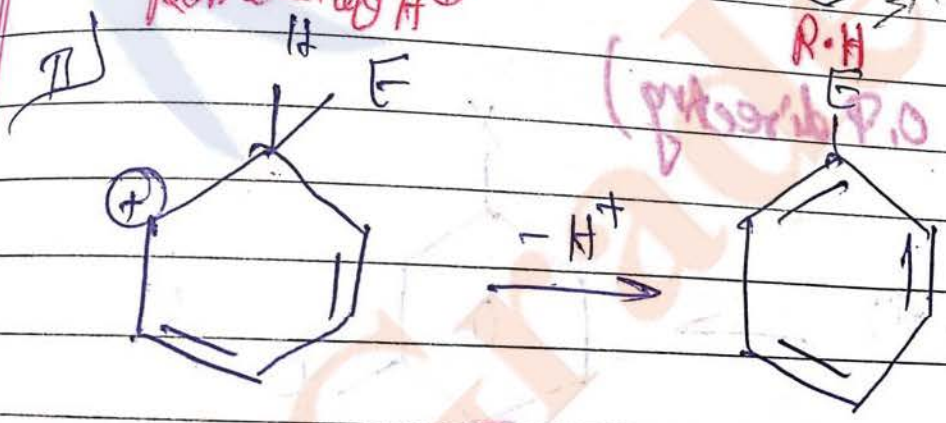


Carbocation Intermediate

≡

Resonance hybrid

Removal of H^+



(substitution product)

1st Choice

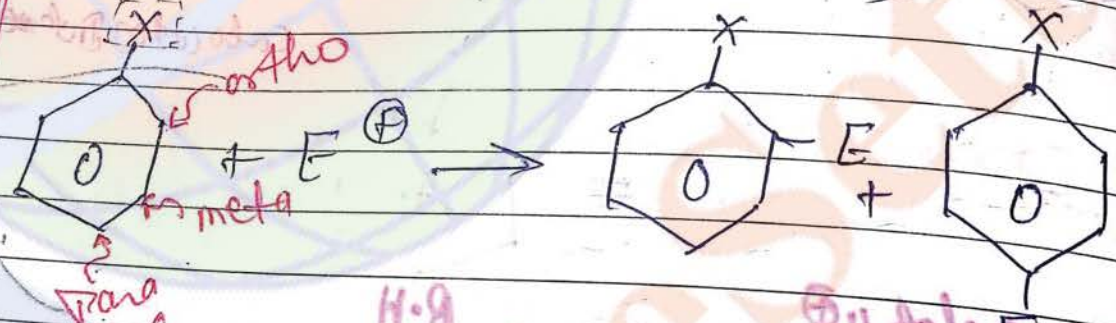
iii) Rate of E.A.S Reaction $\propto$ Stability of carbocation

$\propto$ e⁻ density in benzene ring

$\propto +I, +M$ (EDG) (Activating group)

$\propto \frac{1}{-I, -M}$ (E.W.G) (De-activating group)

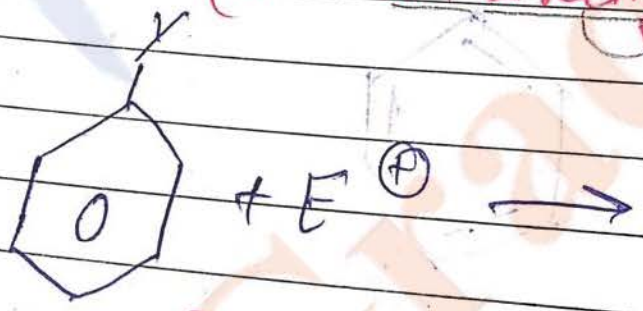
iv) In case of mono substituted benzene ring position of incoming electrophile is decided by already present group. (orientation)



H·G

(X = O, P directing)

यदि X, O, P directing है तो electrophile (E⊕) attack Para position पर attack कर रहा है।



(Y = meta directing)

यदि Y है तो Electrophile (E⊕) meta position पर attack कर रहा है।

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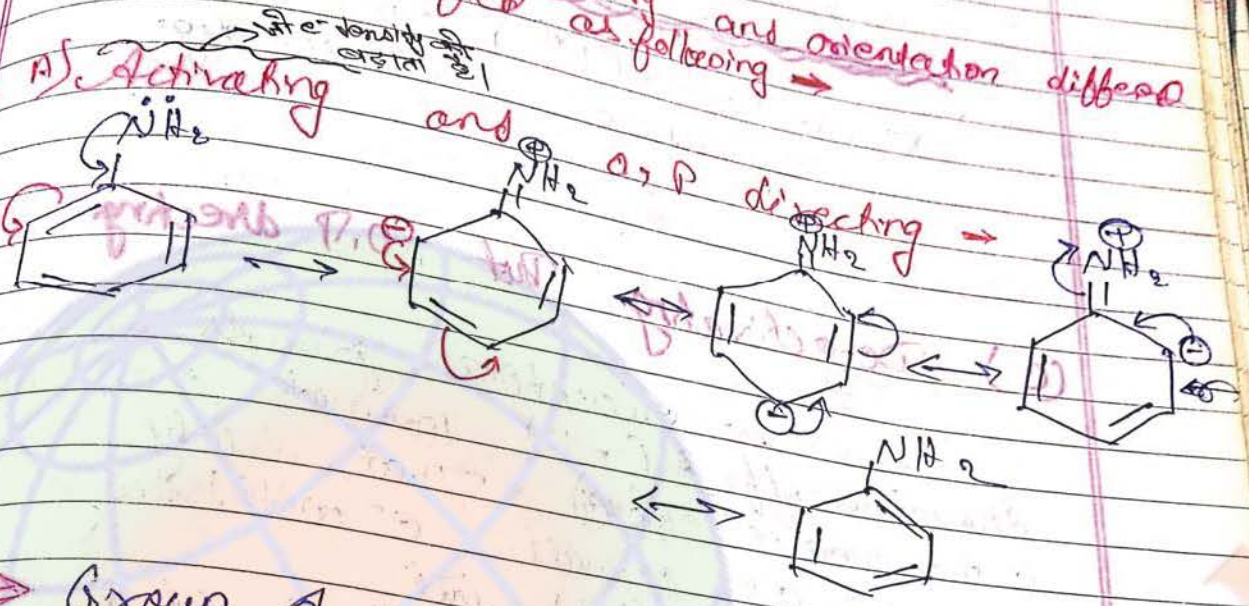
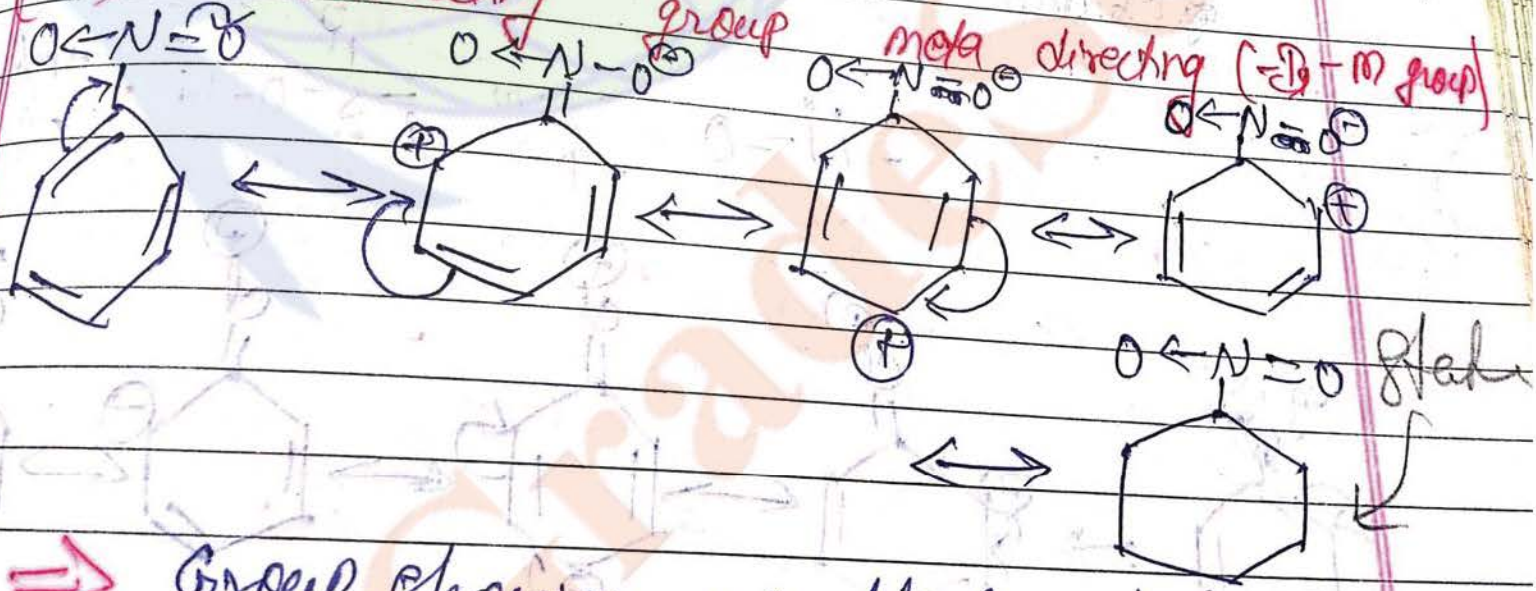
We the basical reactivity and orientation differed groups are classified as following →

A) Activating and o, p directing →



⇒ Group showing +m effect Increase e⁻ density so "activating" Group Increase e⁻ density at o, p so o, p directive (+m group Increase e⁻ density on ortho and Para position (i.e. ortho and Para becomes -ve charged)).

(B) Deactivating group meta directing (-I, -M group)



⇒ Group showing -m effect decrease e⁻ density so "de-activating" group decrease

"m" group decreases e⁻ density on ortho and para (i.e. ortho and para become +ve charge) relatively meta पर e⁻ density ज्यादा होगी।

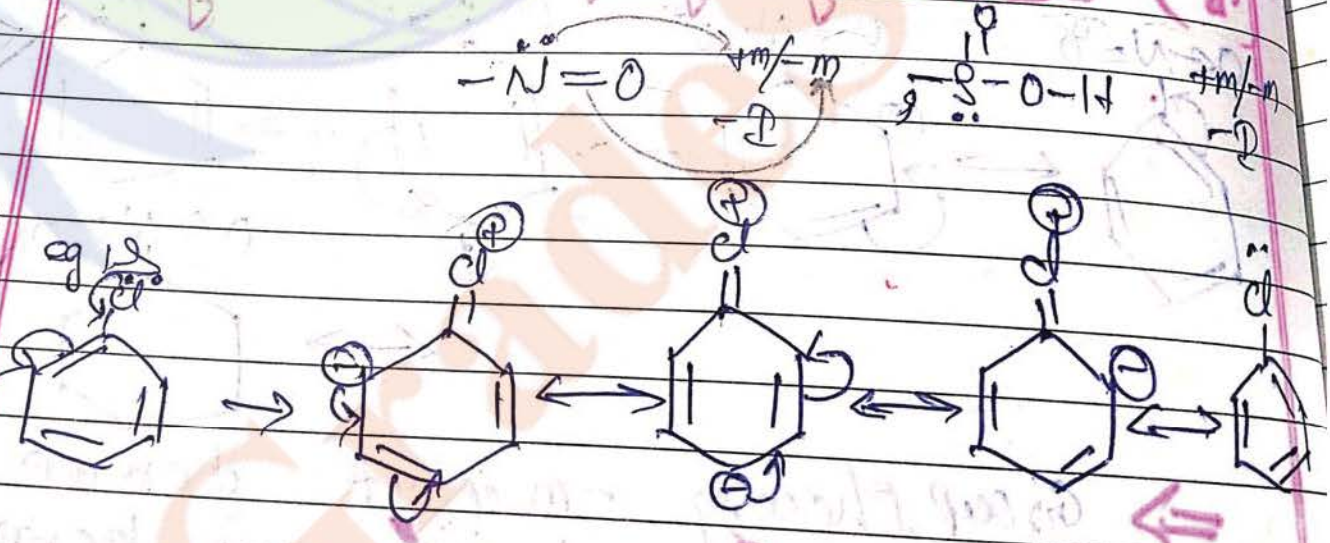
e⁻ density mainly at o, p. so Relative e⁻ density is higher at meta.

so electrophile (E⊕) comes at meta so these groups are meta directing.

(C) De-activating But o,p directing

There are exceptional groups in which Inductive effect (-I) dominate over +m (mesomeric effect). That is why these group's are overall e⁻ withdrawing (De-activating) but due to "+m" effect Relative e⁻ density is higher at o, p, so these group's are o, p directing.

Example → F, Cl, Br, I,



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Topic Point Conclusion:-

1) mesomeric effect dominate over Inductive but halogens and Nitroso (N=O) groups are exception

2) mesomeric effect do not depend upon distance but it is applicable in o, p position only. (not meta) (but I-effect also works on meta position)
(Extent of I-effect ortho > meta > para)
(depends on distance)

Q) Arrang following in order of rate of E.A.S

(a) O-H (+m)

(b) NH2 (+m)

(c) NH-C-CH3 (+m)

(d) C-NH2 (-m)

(e)

(f) CH3 +I

(g) Cl
-I > +m
Poor deactive

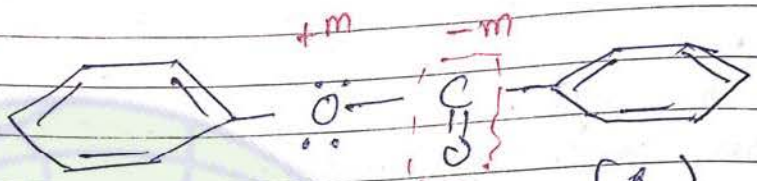
(h) O⊖

(i) NO2

(h) > b > a > c > f > e > g > d > I

(IIT) Q) In which ring electrophile attack more easily

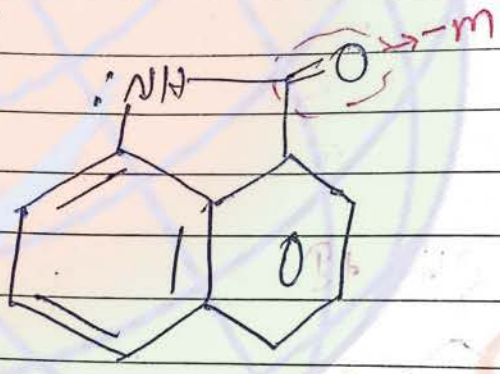
i)



(a) (b)

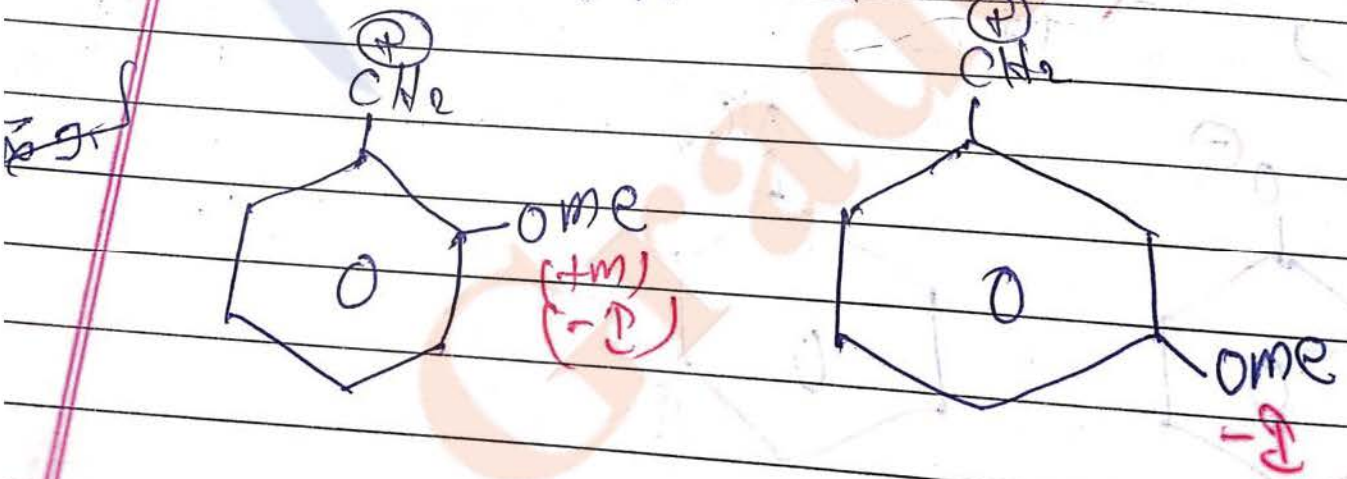
Ans → "a"

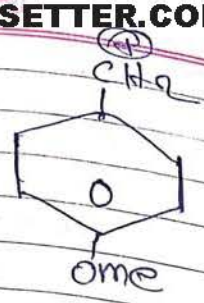
ii)



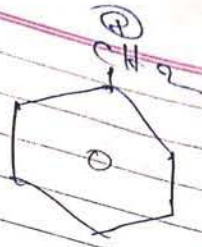
(a) (b)

Ans "a"





(+m)
(-I)



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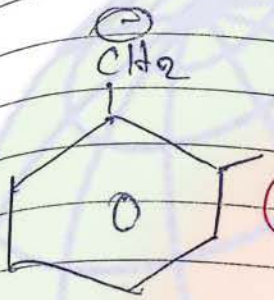
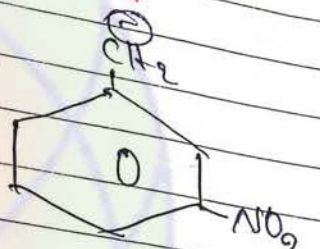
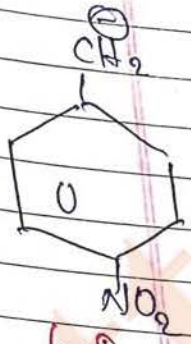
c > a > d > b

-I > -I distance

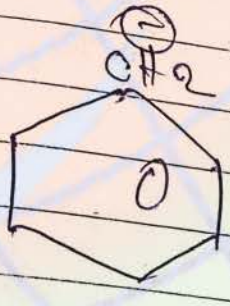


(+I, -m)

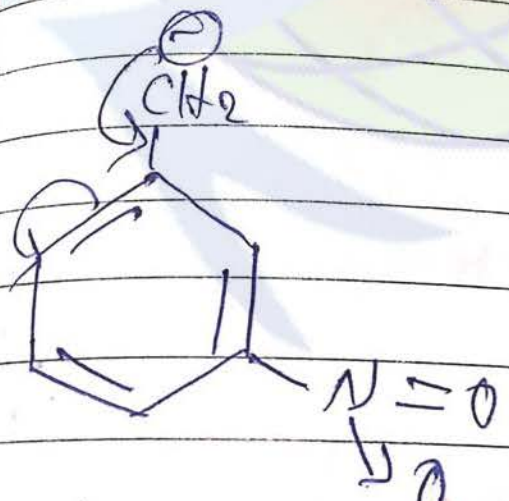


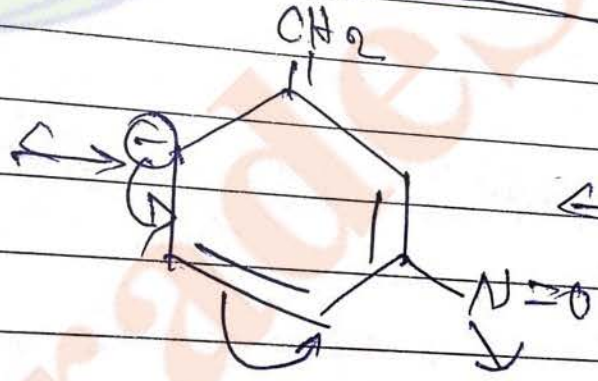


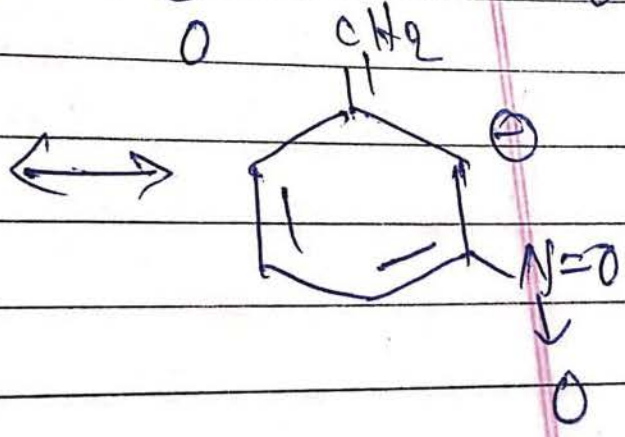
(-I, -m)



a > c > b > d







EN > No of zeros

New topic

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4) Effect of Resonance on Acidic strength →

i) Acidic strength ∝ stability of Anion

ii) Stability of anion ∝ size of anion ✓ (same group)
∝ E.N of anion ✓ (same Period)
∝ -M, -I (same atom carrying -ve charge)

iii) order of acidic strength:- (∝ compare ∝ Ka)

eg 1) HI > HBr > HCl > HF (atom directly bonded)

eg 2) $H-\overset{\ominus}{O}-\underset{-I}{I}$ < $H-\overset{\ominus}{O}-\underset{-I}{Br}$ < $H-\overset{\ominus}{O}-\underset{-I}{Cl}$ < $H-\overset{\ominus}{O}-\underset{-I}{F}$

(i.e. atom directly bonded)

eg 3)

HClO < $HClO_2$ < $HClO_3$ < $HClO_4$

$Cl-O^{\ominus}$ $O=Cl-O^{\ominus}$ $O=Cl(=O)-O^{\ominus}$ $O=Cl(=O)_2-O^{\ominus}$

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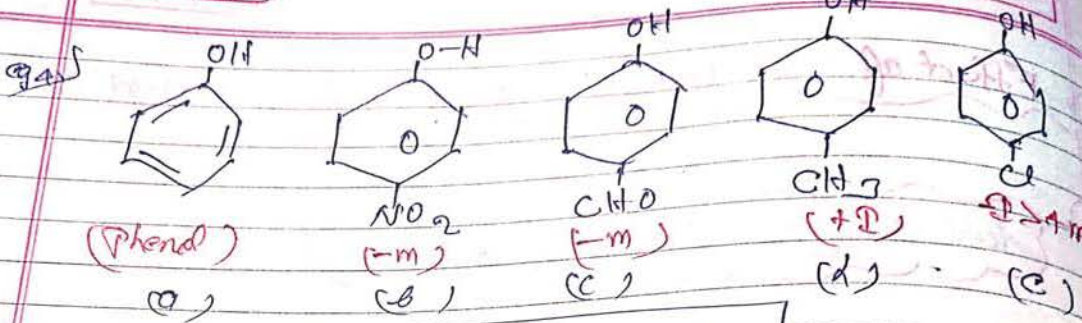
Q.47 Sol

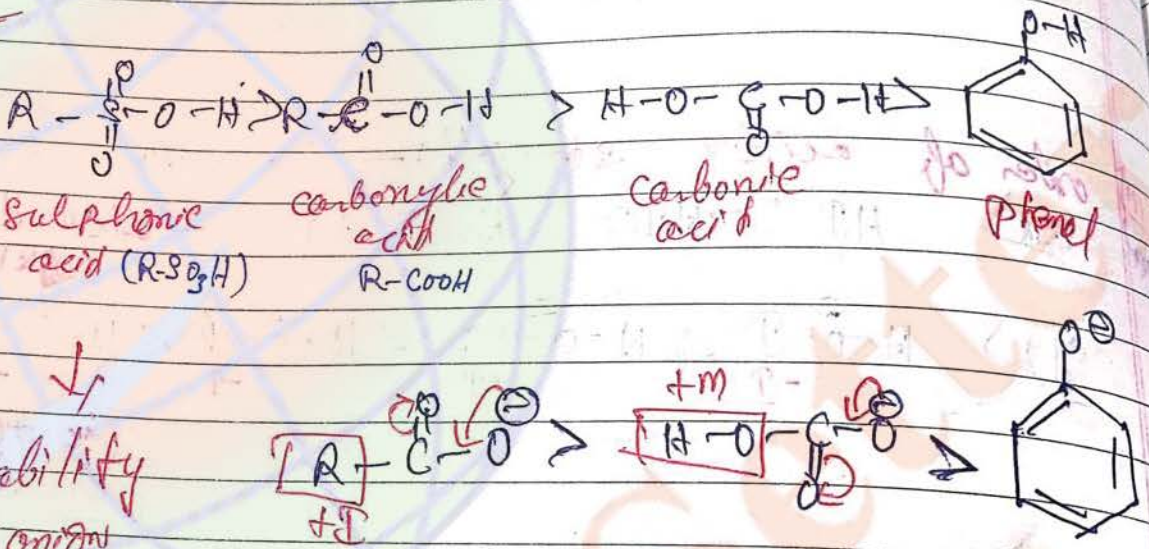


(Phenol) (-m) (-m) (+I) -I > +m

(a) (b) (c) (d) (e)

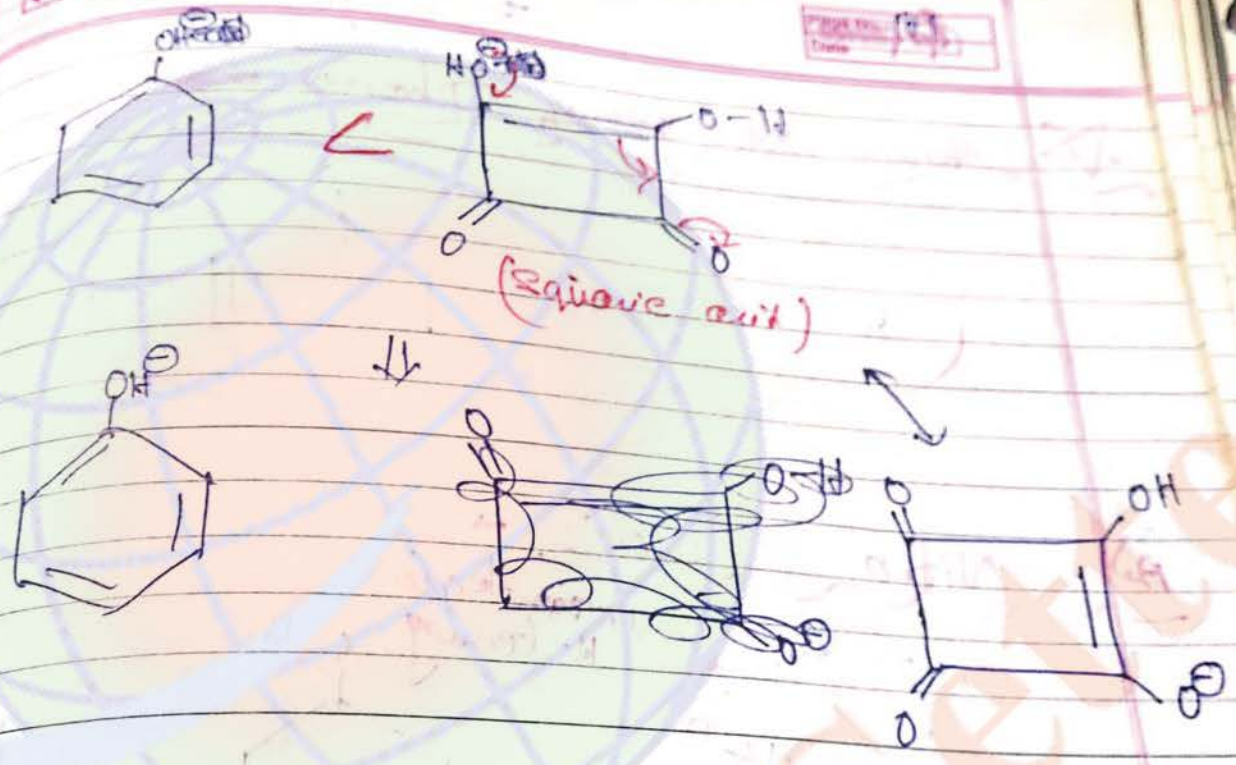
b > c > e > a > d

Q.48 Sol



Note ⇒

Carboxylic acid ei stronger acid than carbonic acid because +m of carbonic OH decrease acidic strength but carboxylic acid is stronger acid than phenol



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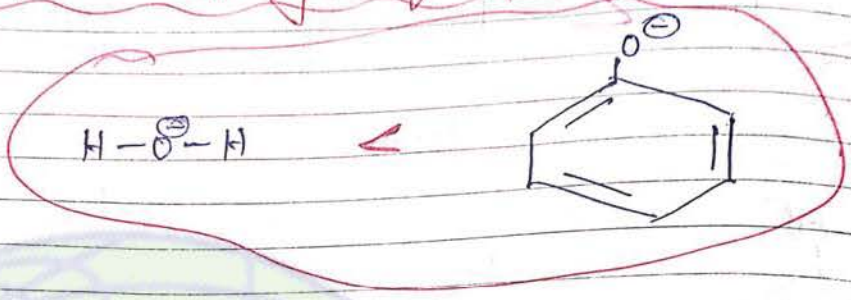
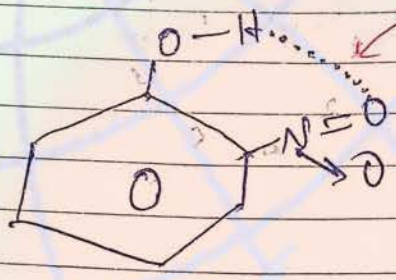
☆ Acidic Strength of Phenol ⟹

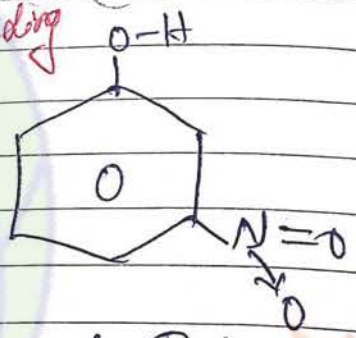


IIT asked

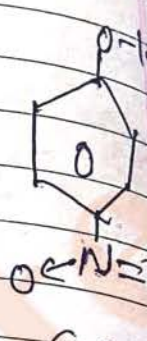
Nitro Phenol's →



(-M, -I)



(-I)



(-I, -M)

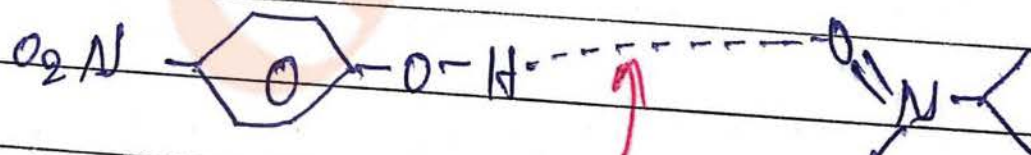
Intra molecular H-bonding

Acidic Strength →

Para Nitro Phenol > ortho Nitro Phenol > meta Nitro phenol > Phenol

Note:⇒

Due to Intramolecular H-bonding Acidic strength of ortho is less than Para.



Inter molecular (याद रखें ⇒ जिसकी चर्चा हो गई)

Important.

ortho Nitro Phenol

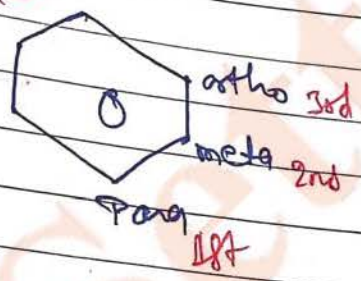
1) Intra H-bond
2) less acidic
3) less Boiling-Point
4) less soluble in water
5) Steam volatile (Boiling point ↓)

para Nitro Phenol

Inter H-bond
more acidic
High Boiling point.
more soluble in water

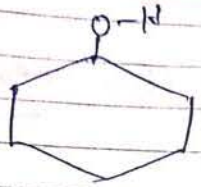
Solubility / Boiling Point

P > M > O

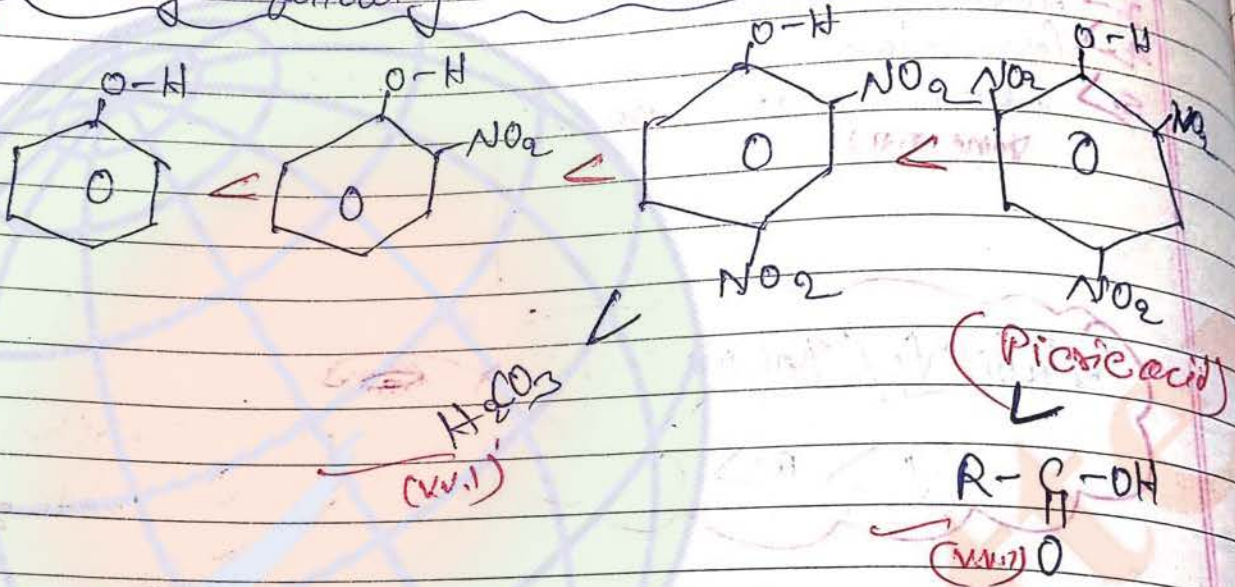


Note → molecule in which Intra molecular H-bonding is present are known as Steam volatile substance. and they have very little tendency to form Inter molecular H-bonding.

Boiling Point order:-
$H_2O > HF > NH_3$ due to H-bond



Q.) Arrange following in acidic strength



On Increasing Number of NO_2 group acidic strength of phenol Increases.

and 2, 4, di Nitro Phenol becomes more acidic than carbonic acid (H_2CO_3) and Infact Picric acid is more acidic than carboxylic acid (RCOO

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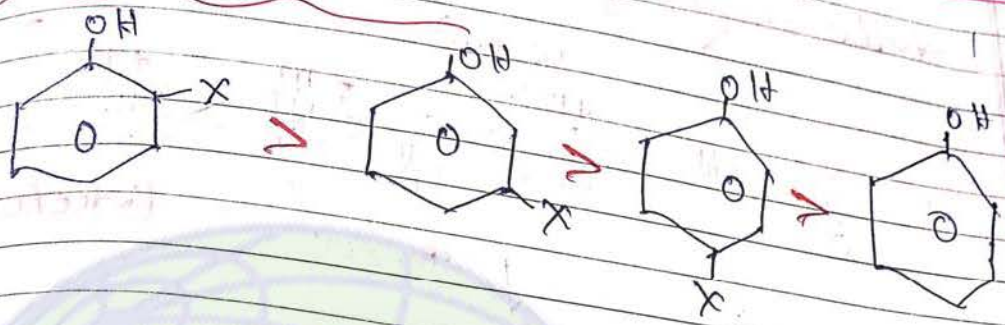
B) Halo Phenol →



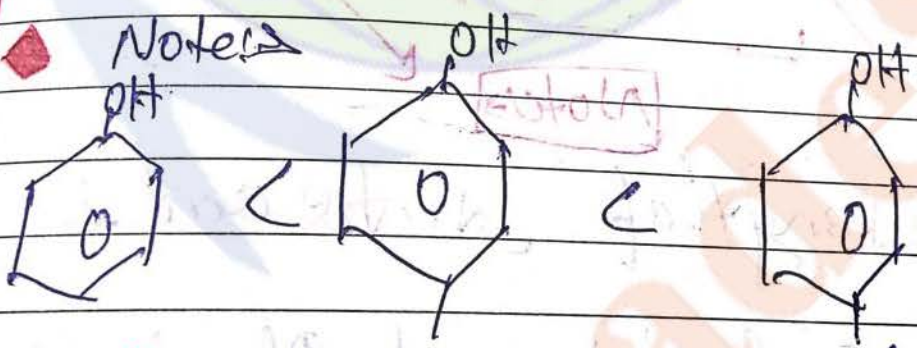
(X ⇒ same halogen)

Note:⇒ Here "Effect" dominate in case of halogen.

O > m > P

when "same halogen" is compare than order strength only decided by only Inductive Effect.

- Note:⇒



F Cl

Note

Overall e⁻ withdrawing power of chlorine is greater than fluorine

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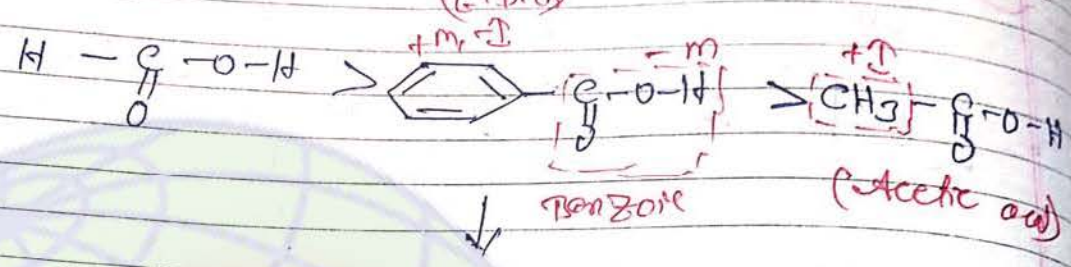
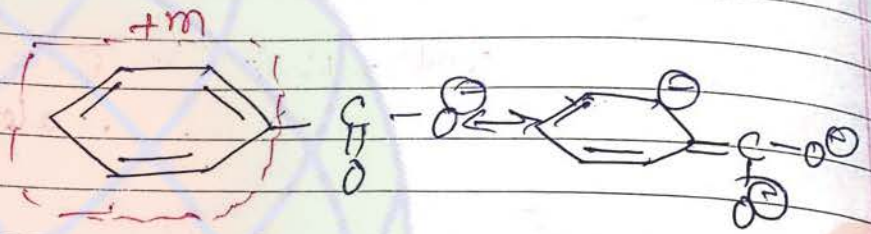
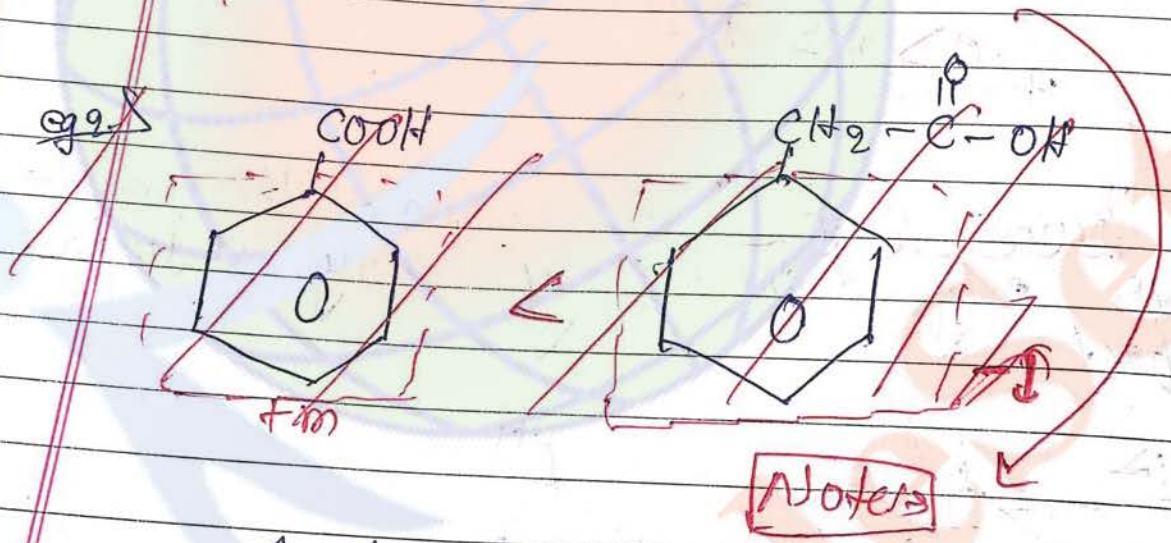
Acidic strength Benzoic acid =

(G.D.G)



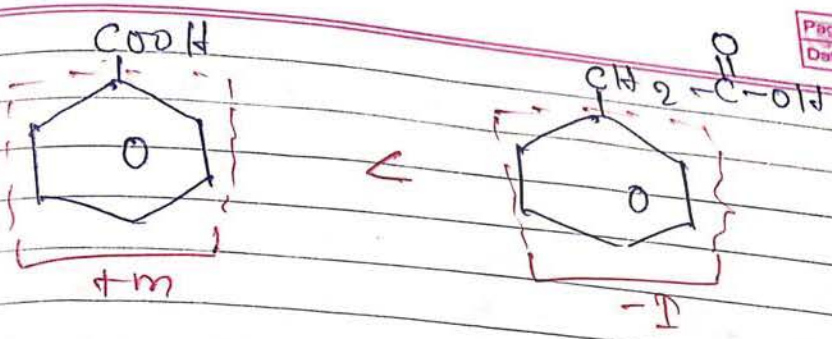


Q2.

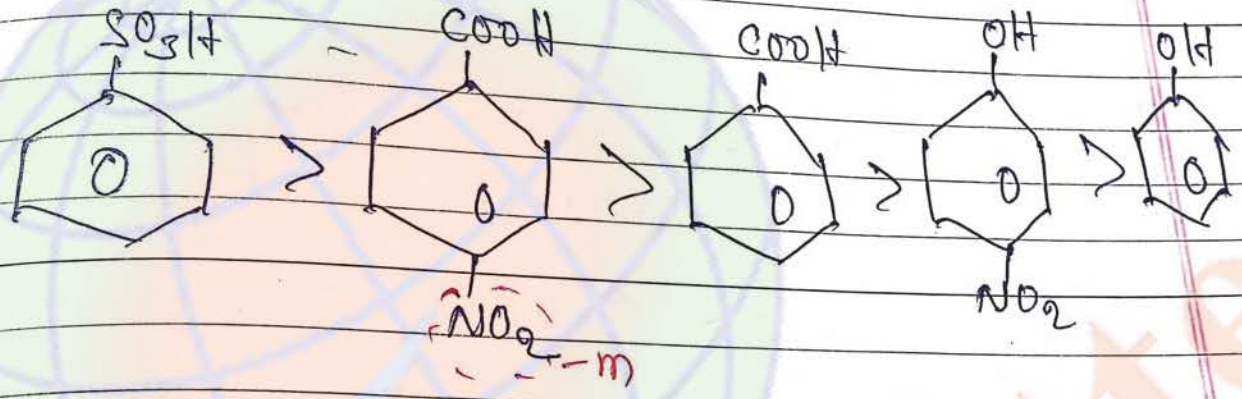


Acidic strength Acetic acid is lesser than benzoic acid Bcoz overall e⁻ donating power of "CH_3" is greater than Phenyl (In this case.)

Q#



Q#



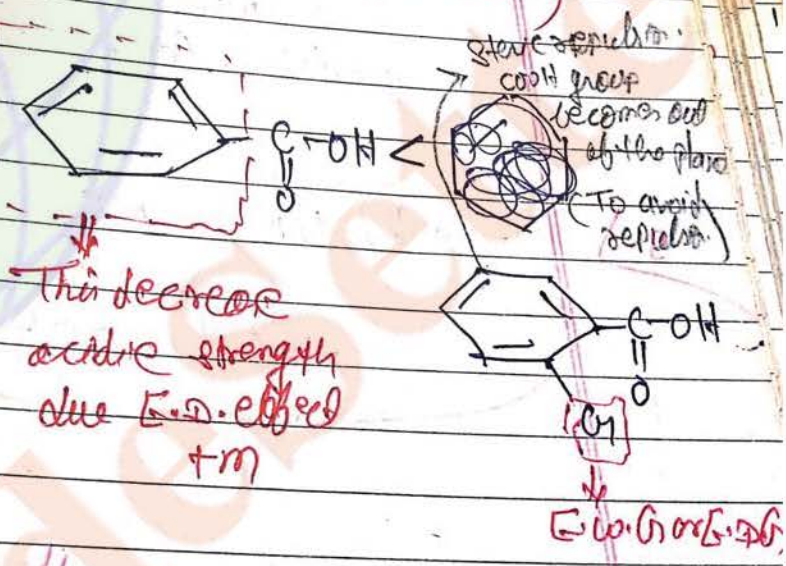
Ortho effect in Benzoic acid →

1) It is observed that ortho substituted benzoic acid are stronger acid than benzoic acid and in comparision to their meta and para isomer.

Ortho group is whatever present at ortho position (e⁻ withdrawing or e⁻ donating)

2) ortho effect in benzoic acid is caused by following two factor :-

1) SIR effect (Steric Inhibition of Resonance)

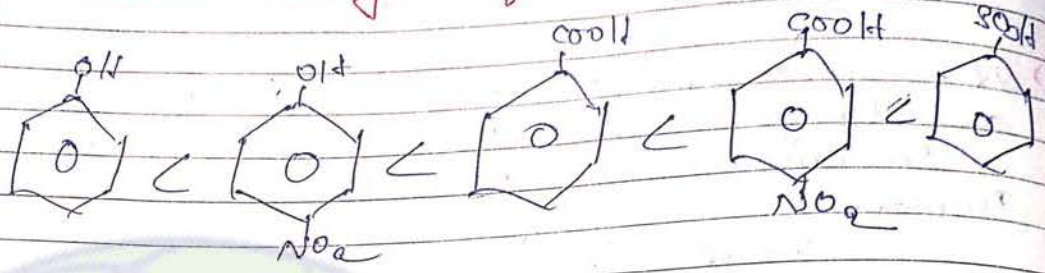


This decrease acidic strength due +I effect +M

when ortho group is present than due to steric repulsion "COOH" group becomes out of the plane to avoid repulsion.

So benzene ring can not donate e⁻ to COOH group. that is why

acidic strength of COOH group Increases.



2.) Per resonance, it is essential that groups should be co-planar if Planarity is disturbed by steric hinderance than extent of resonance it decreases which can change. This is called as SIR effect. This can change acidic, basic properties, bond length.

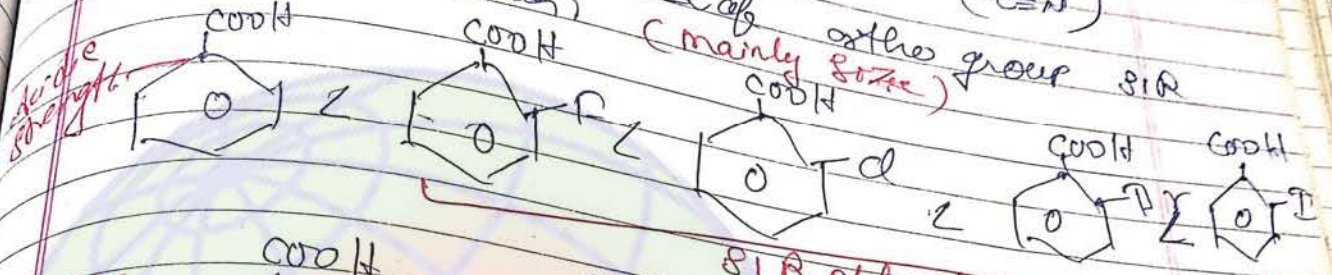
3.) $-COOH$, NR_2, NSO_2, I, Br, $-C(CH_3)_3$

$\rightarrow NH_2$, $-OH$, $-C\equiv N$

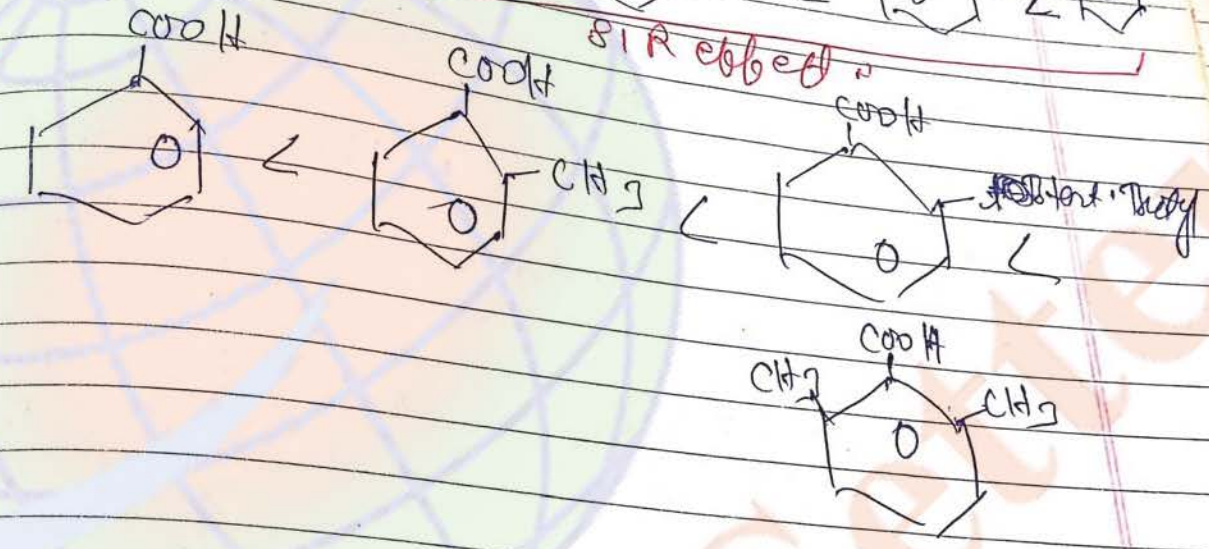
In SIR effect "Bulkey groups" like $COOH$, NO_2, NR_2, I, Br, $-HC(CH_3)_2$ can be out of the plane.

Note: SIR effect is not applicable on smaller groups like NH_2, OH, cyanide etc. ($-C\equiv N$)

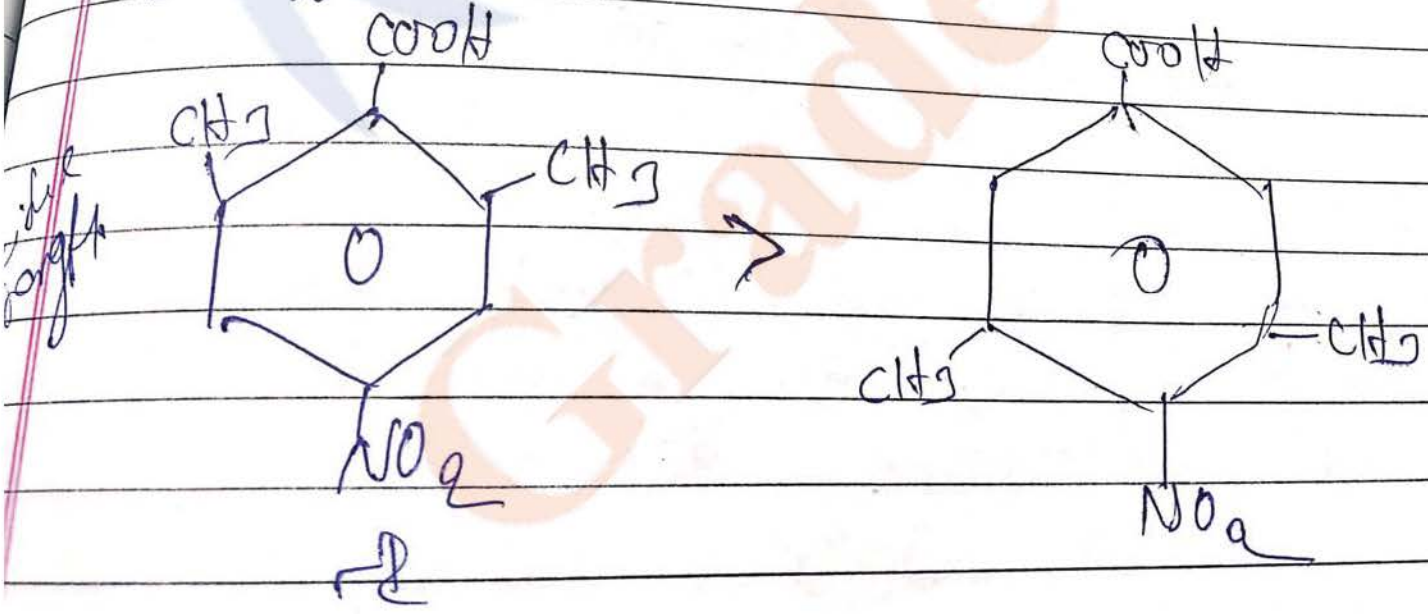
1) On Increasing size of ortho group SIR effect Increases (mainly Steric)



SIR effect:



5) (d) Two smaller groups at ortho cause more SIR effect



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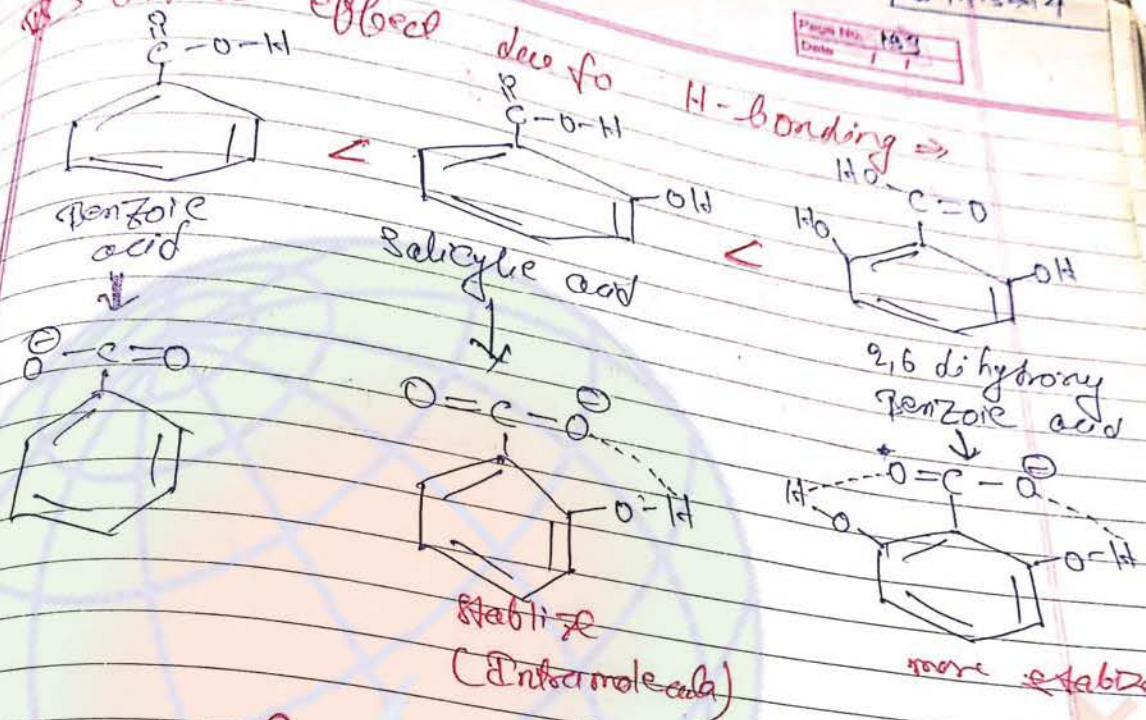
(1) ortho effect due to H-bonding ⇒



* Note :- (Data based) ⇒

$$CH_3-\overset{O}{\overset{\|}{C}}-OH > CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 > H_2O > CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$CH_3-\overset{O}{\overset{\|}{C}}-O^{\ominus} \qquad CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-\overset{O}{\overset{\|}{C}}-CH_3 \qquad OH^- \qquad \overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H$$

If -ve charge is present on same number of electro negative atom than it becomes important that H is attached to more E.N atom to becomes more acidic

1st Choice

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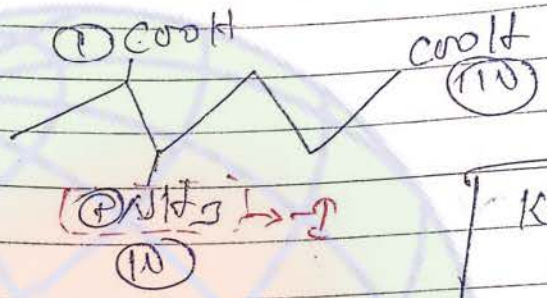
11)

$$R-\overset{\overset{O}{\|}}{C}-O-H > R-\overset{\oplus}{N}H_3 > R-O-H > NH_3$$

eg 1 →



Ka order ⇒

I > II > III

Basic Strength Comparison →

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$R-\ddot{N}H_2 + H_2O \rightleftharpoons R-\overset{\oplus}{N}H_3 + OH^-$

(Amphoteric)

Basic Strength ∝ tendency to donate e^- ∝ Stability of Cation ∝ +I, +m ∝ $\frac{1}{-I, -m}$ e- cloud (E-D-G) — [E-D-G]

Basic Strength order :-

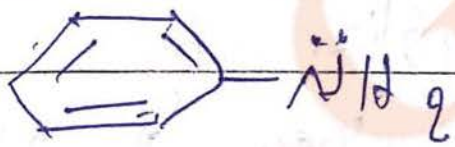
eg 1. $\underbrace{CH_3}_{+I} - CH_2 - \ddot{N}H_2 > \underbrace{CCl_3}_{-I} - CH_2 - \ddot{N}H_2 > \underbrace{CF_3}_{-I} - CH_2 - \ddot{N}H_2$

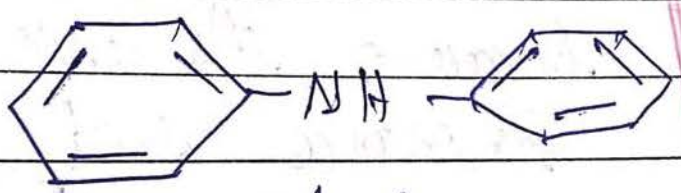
eg 2. $CH_3 - CH_2 - \underset{sp^3}{\ddot{N}H_2} > CH_3 - CH = \underset{sp^2}{\ddot{N}H} > CH_3 - C \equiv \underset{sp}{N:}$

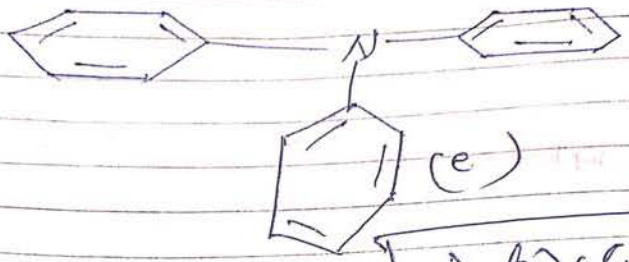
Note → (Concept of lone pair) →
when lone pair present on Nitrogen atom participate in resonance and more delocalised than basic strength ~~increase~~ decrease;

a) $CH_3 - \ddot{N}H_2$

b) $CH_2 = CH - \ddot{N}H_2$

c) 

d) 



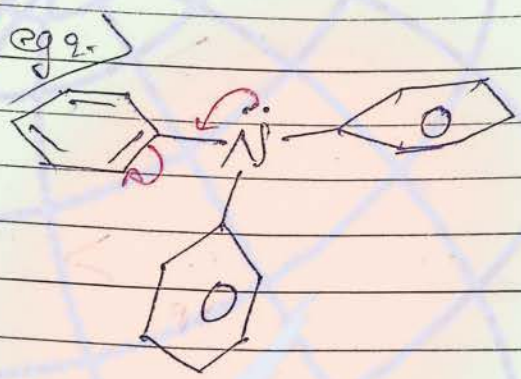
(e)

a > b > c > d > e

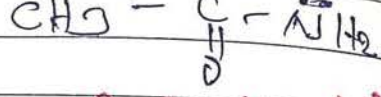
Note →

Generally Aliphatic Amines are more basic than aromatic

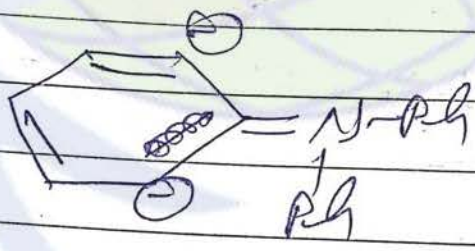
eg 2.

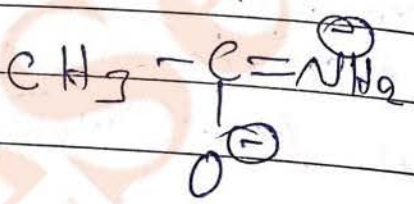


Basic strength



(Acetamide)





Amides behave as amphoteric substance because it's anion is stablize by resonance that is why they behave as weak acid.

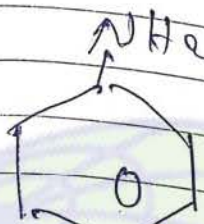
Q 7.)

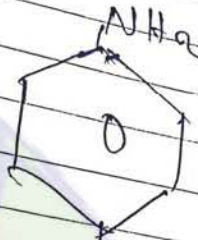

(a)

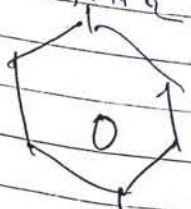

(b) OH (+m)


(c) CH_3 (+I)


(d) Cl -I > +m


(e) CHO (-m)


(f) NO_2 (-m)


(g) CN (-m)

$$b > c > a > d > e > g > f$$

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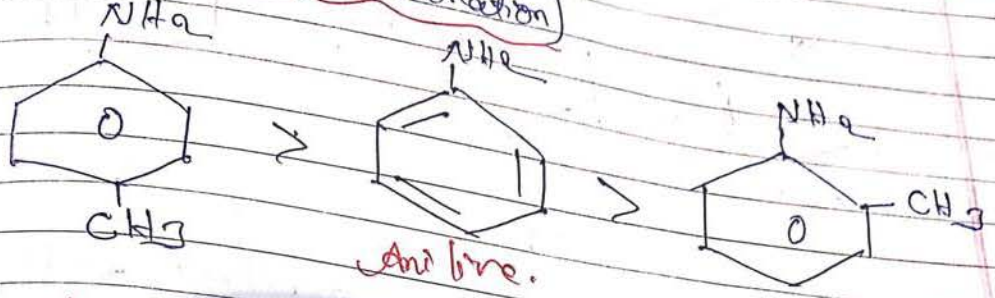
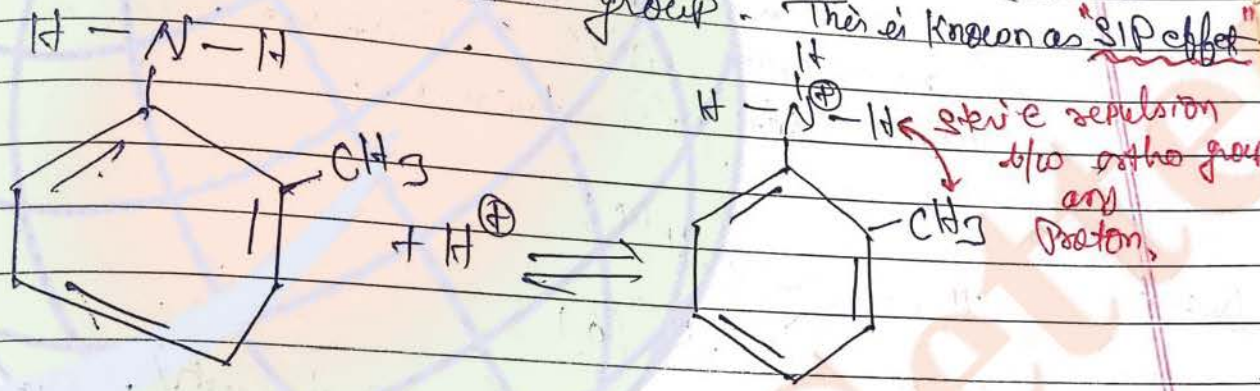
Aniline →

Steric Inhibition of Protonation

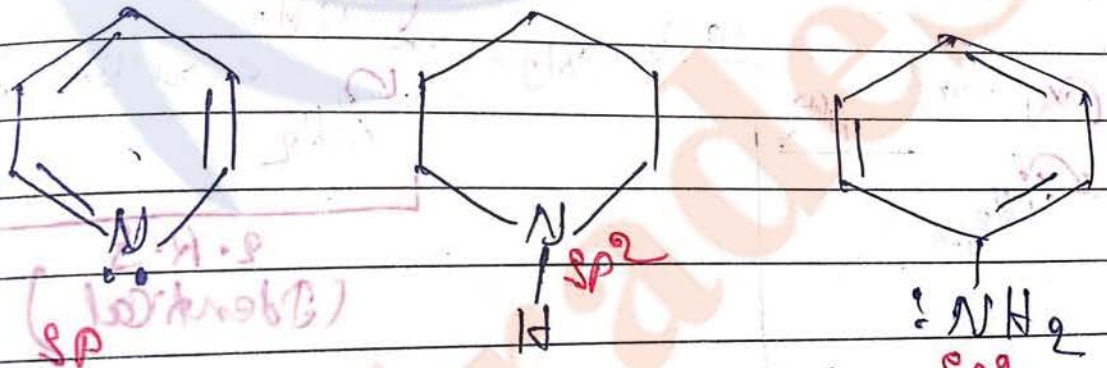


Definition →

It is observed that basic strength of o-substituted aniline is less than aniline it is because incoming proton shows repulsion (steric hindrance) with ortho group. This is known as "SIP effect"



Ref.



basic effect

$$a < a < b$$

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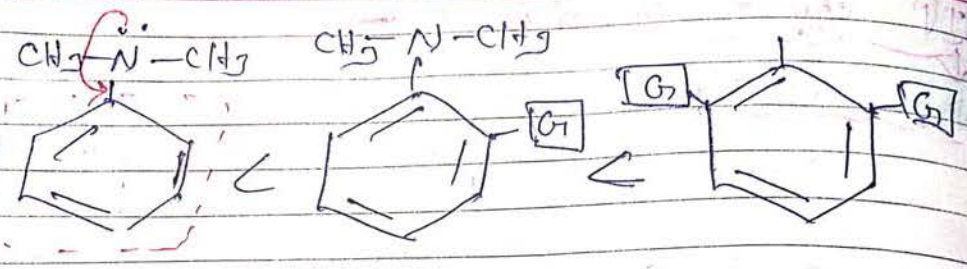
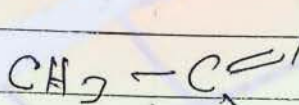
Ex 6.)



This is explain on the base of SIR effect due to presence of ortho group (NR_2) (bulky group) becomes out of the plane.

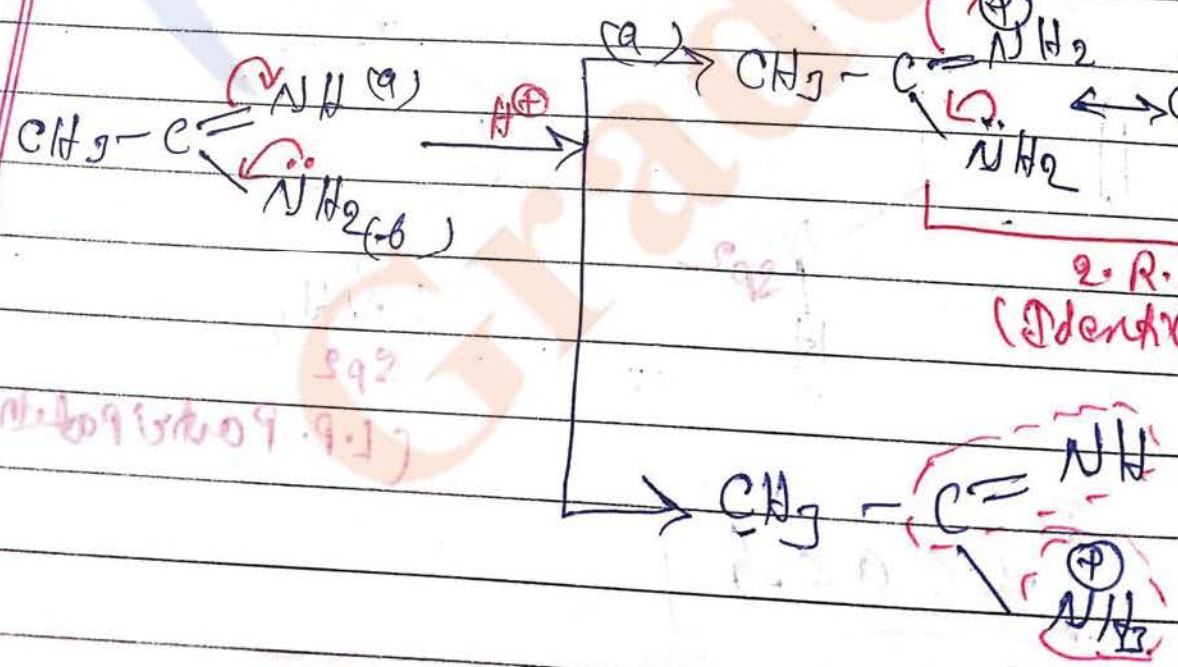
due to this lone pair present on N-atom can not participate in resonance with benzene ring so basic strength Increase.

Ex 7.)



which Nitrogen get protonated easily,

So/4



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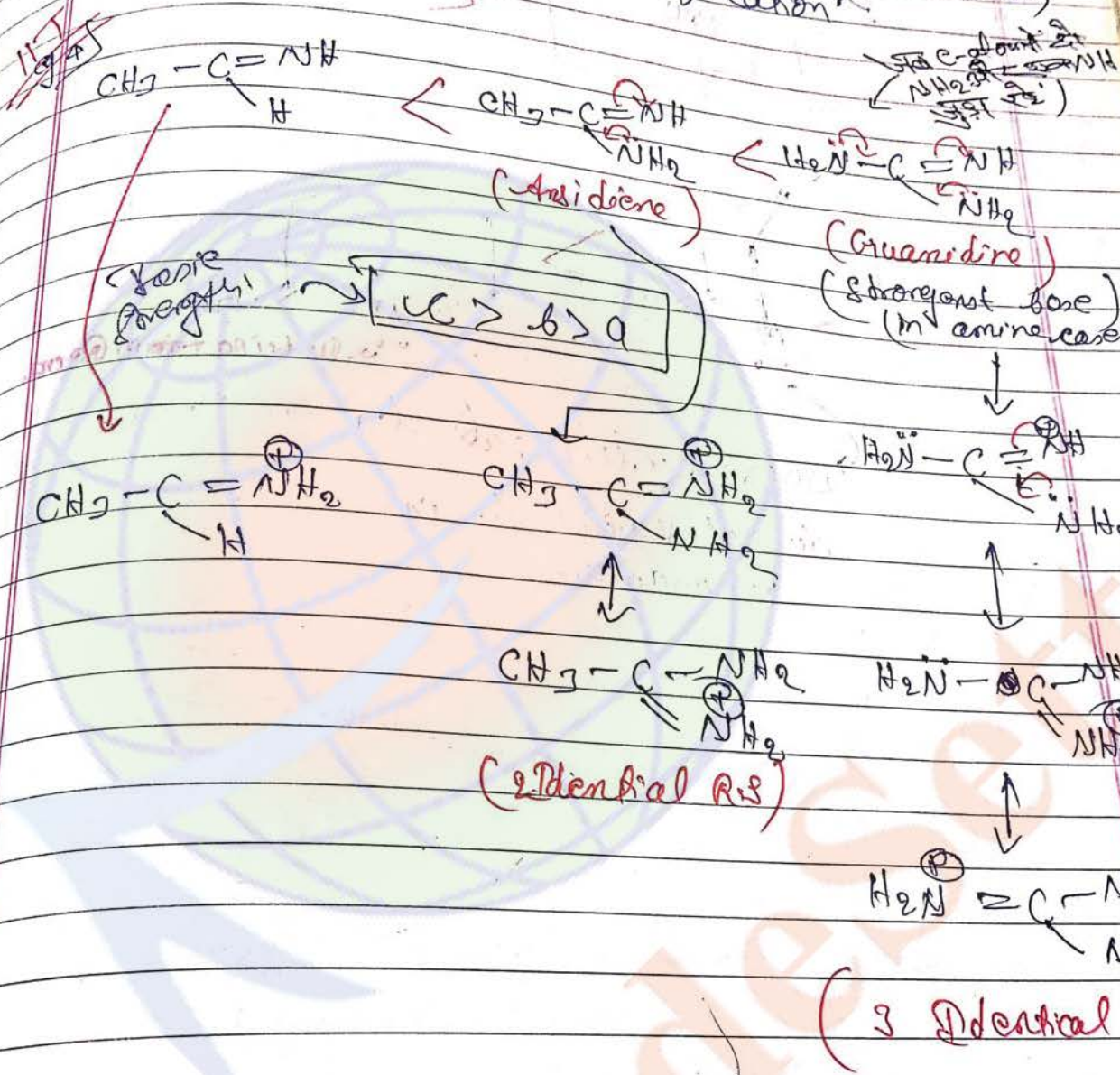
for "a" more base strength
easily protonated due to resonance, stabilisation of cation.



(lone pair पास आने पर basic strength बढ़ता है)

* Guanidine is one of the most strongest organic basic among's amines.

1st Choice

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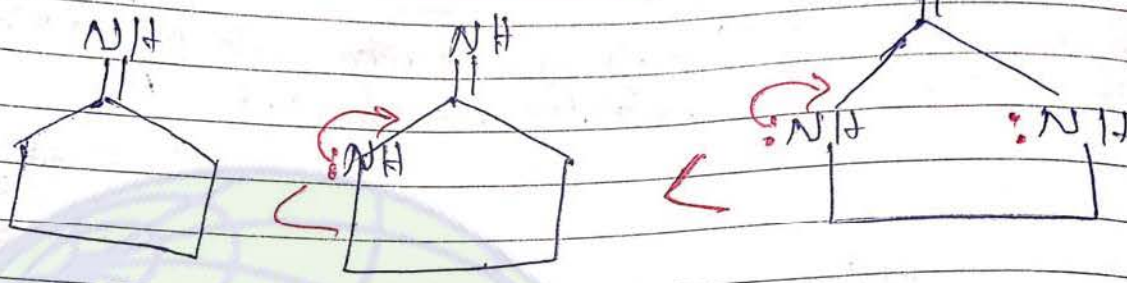
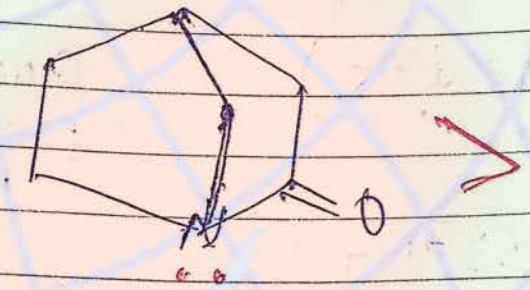
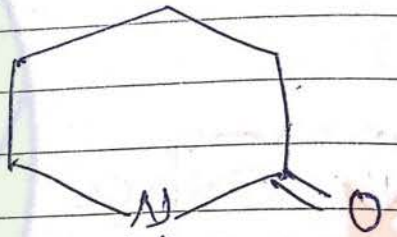
Q5)



base strength

Q6)





→ Participation in Resonance.

→ Due to Br's sole l.p on N-atom do not participate in resonance

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amine ~~gas~~ Comparision of Aliphatic

NH_3 < CH_3-NH_2

1) In case of gaseous ~~state~~ phase or in ~~non~~ aprotic solvent basic strength is decided by only Inductive effect.

$NH_3 < CH_3-NH_2 < CH_3-NH-CH_3 < CH_3-N(CH_3)-CH_3$

↓ aprotic solvent

2) In case of protic solvent three opposite factor decided basic strength :-

a) Inductive effect →

$3^\circ > 2^\circ > 1^\circ > NH_3$

b) Steric hindrance. → On increasing size of group on Nitrogen atom (N-atom) approach of proton become's difficult due to more hindrance.

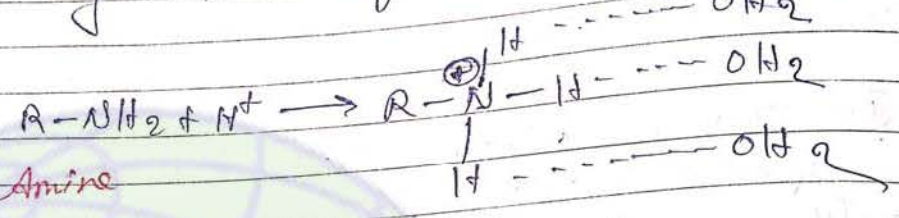
$NH_3 > 1^\circ > 2^\circ > 3^\circ$

c) Stabilisation of Protonated cation by H-bonding →

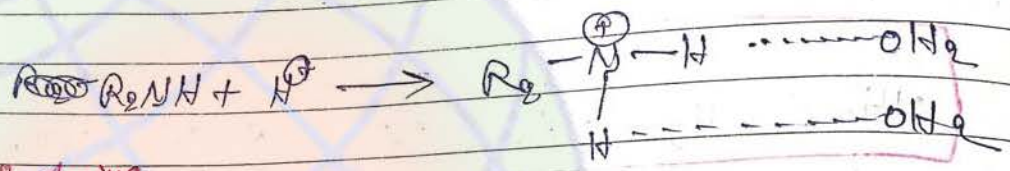
After protonation cation's are stabilise

1st Choice

by H-bonding in protic solvent and cation of 1° amine stabise maximum by H-bonding.



1° Amine



2° Amine

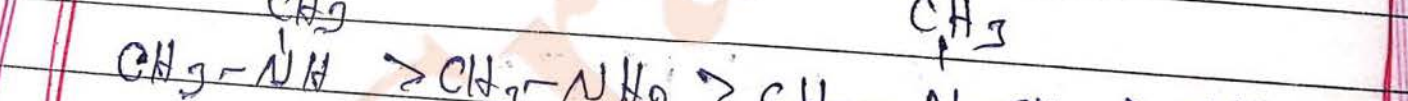
3° Amine.

Conclusion ⇒

overall conclusion is that 2° Amine becomes most basic among aliphatic amine.

(8) Data based order ⇒ (Acid strength order में) 213

In case of methyl ⇒



$2^0 > 1^0 > 3^0 > NH_3$

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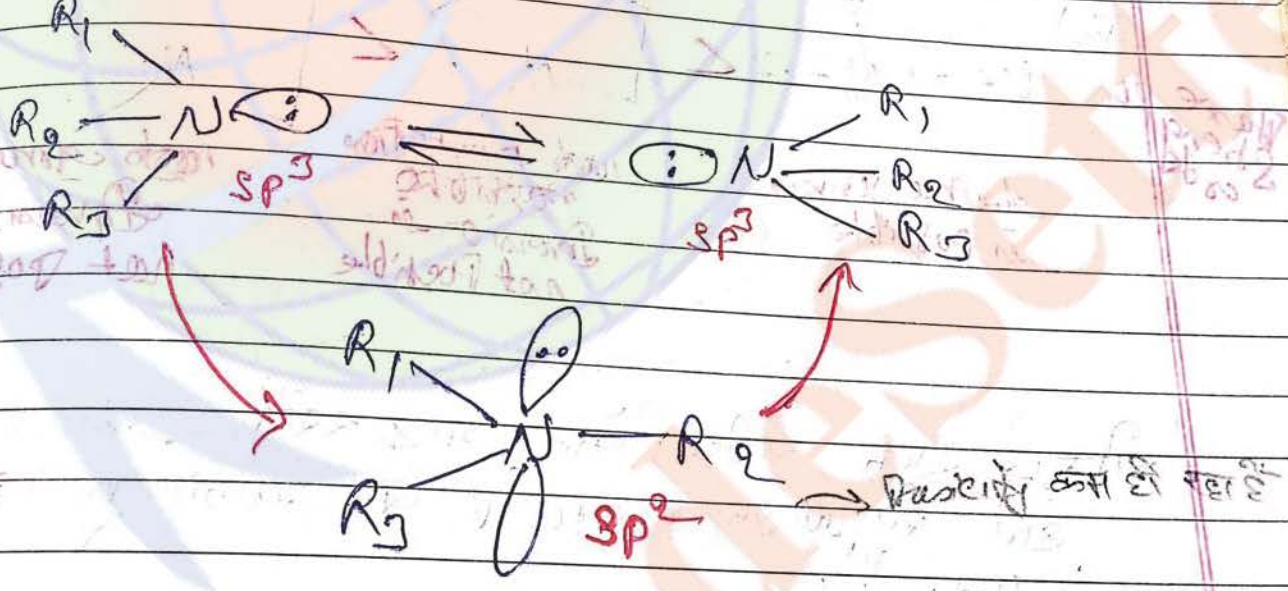
In case of ethyl →

$2^{\circ} > 3^{\circ} > 1^{\circ} > NH_3$

$CH_3-CH_2-NH \xrightarrow{CH_2-CH_3} CH_3-CH_2-\underset{CH_3}{\overset{CH_2-CH_3}{N}} > CH_3-CH_2-NH_2 > NH_3$

(Steric-D.P.P.S - 15) (0-A.S.O -> 16)

✡ Amine Inversion →



Basicity कम हो गई है

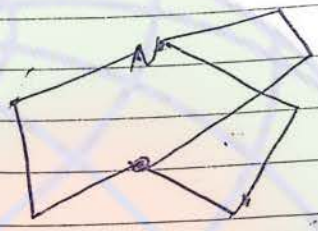
Transition state

(Amine Inversion is possible)

S-character ↓ Acid

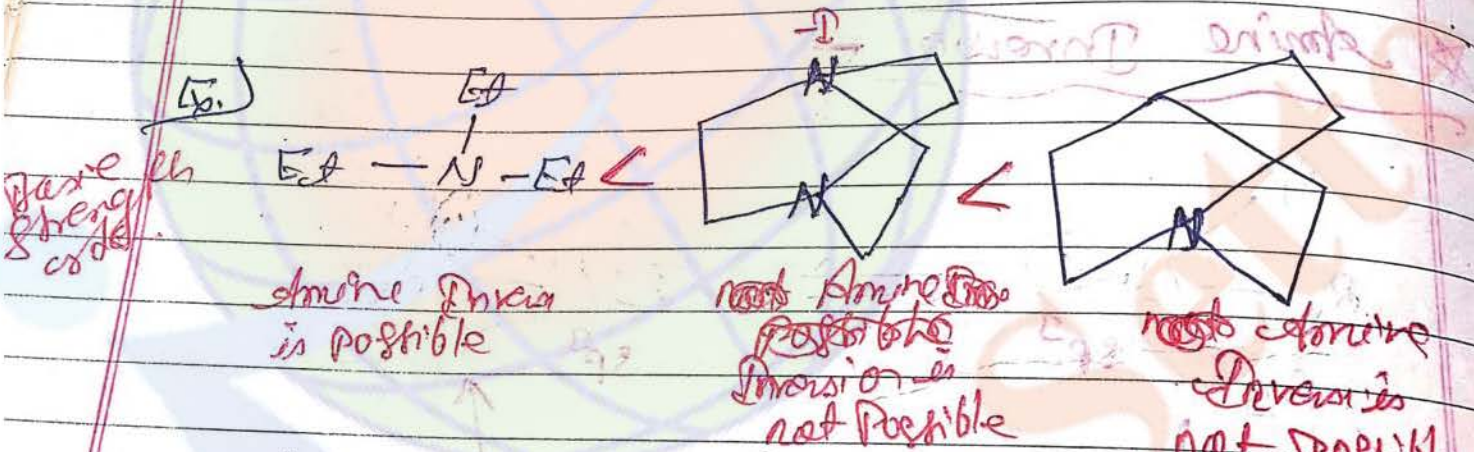
Open chain Nitrogen exist in a rapid equilibria with it's mirror Image. This is known as Amine Inversion

In this process Nitrogen changes its hybridisation in transition state and due to this its basic strength is less compare to the Amines where Amine Inversion is not possible (Where Nitrogen is part of ring.)



Amine Inversion is not possible

(5.)



(problem is in D.P.P.S-15, Q.No.-11)

नोट:- एक सीधा केदा याद रखें:- Amine Inversion होने से उस Compound की basicity कम हो जाता है।

इस तरह (Cycle 3-D के कारण) N-atom वाला अधिक basic हो गया।

जबकि (generally) अधिक NH_2 वाला अधिक basic होता है।

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Huckle observed that some unsaturated compound's which have cyclic de-localisation of (4n+2) π e⁻ (Huckle number) are more stable that expected and they do not show normal reactions of unsaturated compound. These compounds are known as aromatic compound. and this properties is known as aromaticity.

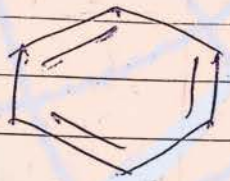
Aromatic Compound	Anti-aromatic compound	Non-Aromatic Comp
1) 4n+2 π e⁻ n = 0, 1, 2, 3, 4 —— π e = 2, 6, 10, 14, 18 ——	4n π e⁻ n = 1, 2, 3, —— π e = 4, 8, 12, 16 ——	If molecule is non-planar and one of the atom in the ring is sp^3 hybrid.
2) cyclic planar [sp^2 / sp]	cyclic planar [sp^2 / sp]	
(Atleast one unhybrid p-orbital থাকতে হবে)		
Continuous cyclic conjugation.	Continuous cyclic conjugation	
Cyclic delocalisation.	(Cyclic delocalised)	

Note =>

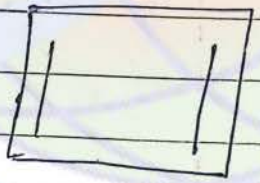
i) If ring atom contain a lone pair or -ve charge it's hybridisation is sp^2 and it can consider as "$2\pi e^-$" (if it is conjugation with double bond)

ii) If free radical is present in compound then it is non-aromatic.

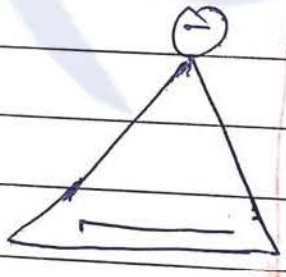
(8) Some Stodard examples -

1) 

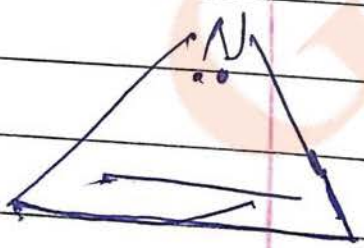
cyclic plana ($6\pi e^-$)
(Aromatic)

2) 

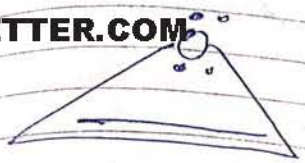
Anti-aromatic
(cyclic plana
($4\pi e^-$)

3) 

Anti aromatic
4πe^-

4) 

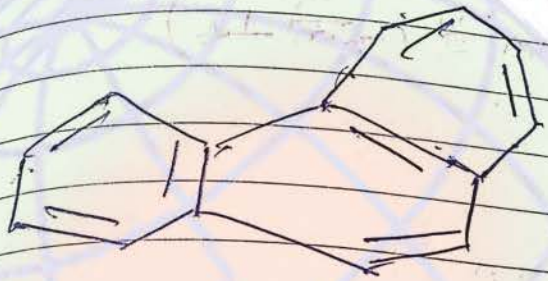
4πe^-
Anti-aromatic



4πe⁻
(Anti aromatic)

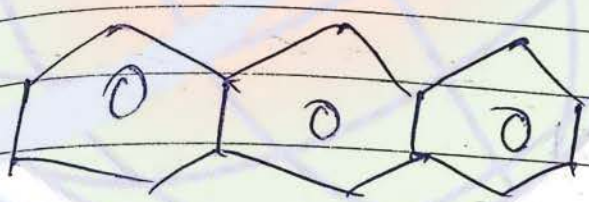
Napthalene

12πe⁻
sp2
(Aromatic)

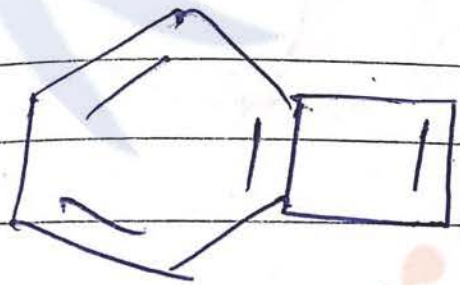


phenathren

14πe⁻
Aromatic)



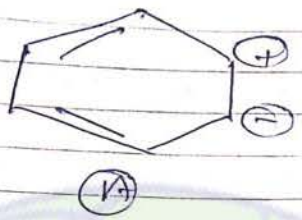
14πe⁻
Aro.



8πe⁻
(AA)

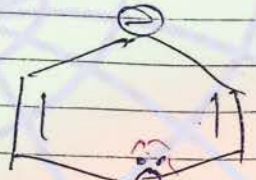
"≡" bond को 2A एक ही π-bond मान कर लिये क्योंकि triple bond में दोनों π-bond ~~1a~~ होने के कारण Participate ये मानते

9)



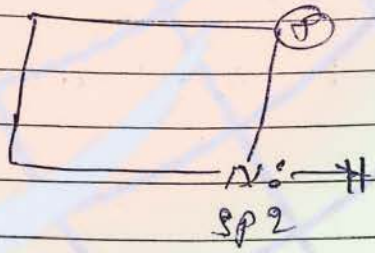
Atom
6π e⁻

10)



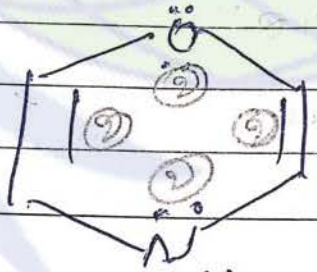
8π e⁻
(Anti-Aron)
→ एक ही count होता है (पूरी ring)

11)



AA
4π e⁻

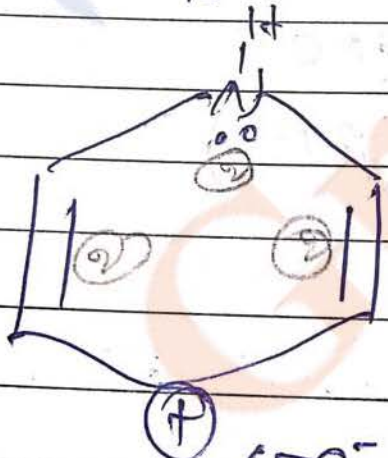
12)



(AA)
8π e⁻

"2 π-e को Indian कर रहा है कि कौन-कौन से π-e- consider करें ?

13)



6π e⁻
Aron

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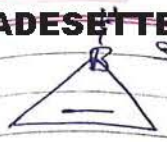
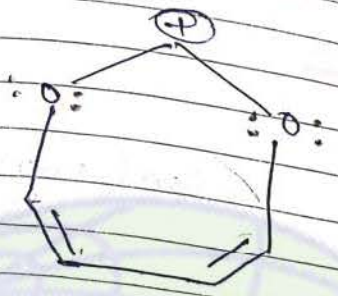


vacant orbital

2πe⁻

(Aromatic)

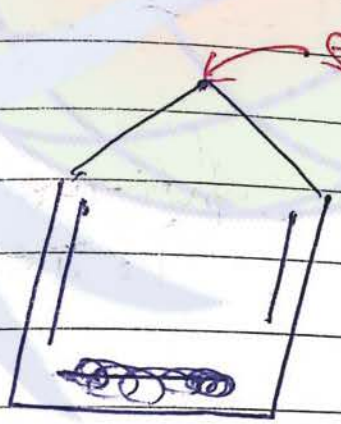


8πe⁻

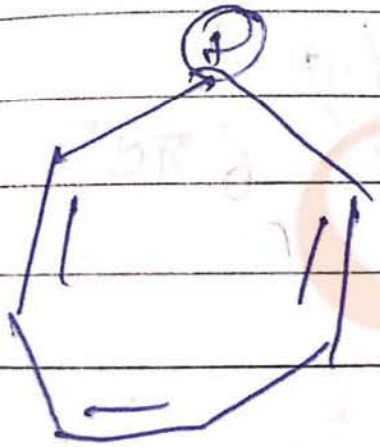
(AA)

6πe⁻

Aromatic)



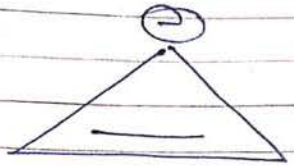
(Non-Aromatic)



Aromatic (6πe⁻)

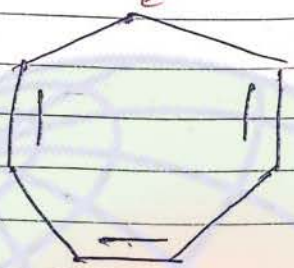
(A)

18)



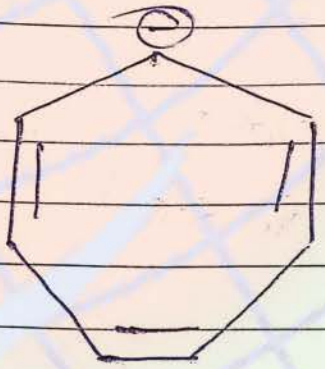
4 πe^- (AA)

19)



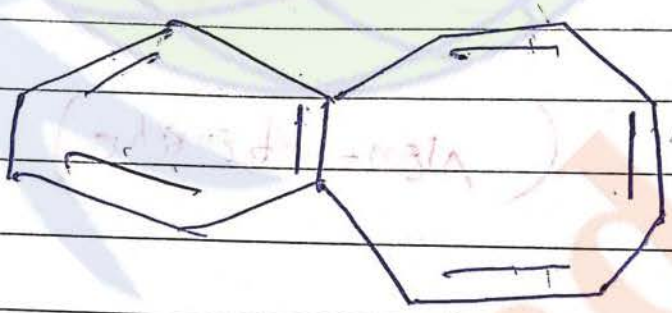
Non-aromatic

20)

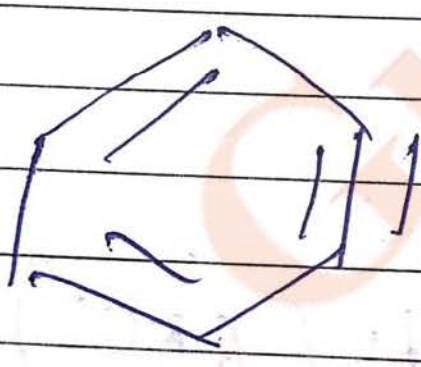


(AA)

21)



Anti-aromatic
12 πe^-



Aromatic
6 πe^-

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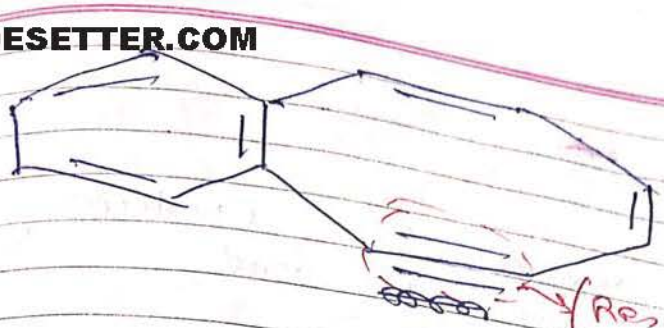
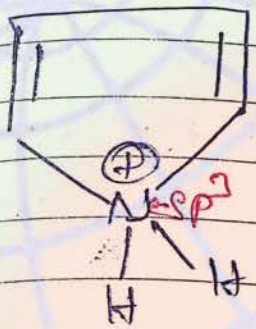
2.)



(Resonance only π-e consider होगा)

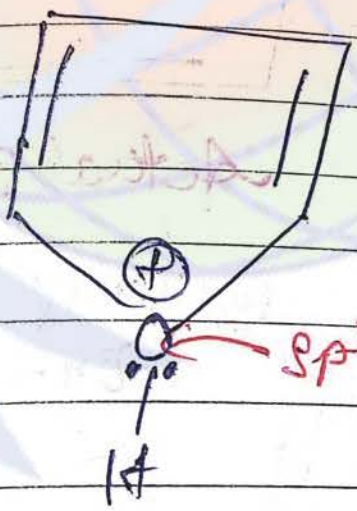
Anti aromatic ($12\pi e^-$)

2.)



(Non-aromatic)

3.)



Non-aromatic

(Aromatic > Non-aromatic > Antiaro.)

1st Choice

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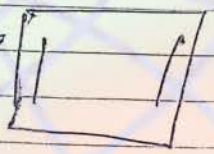
Annulenes →

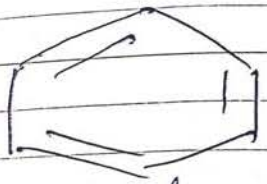
monocyclic compound's containing alternate double bond and single bond

i)

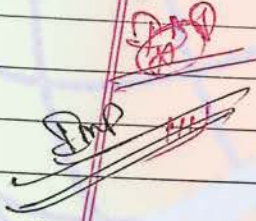


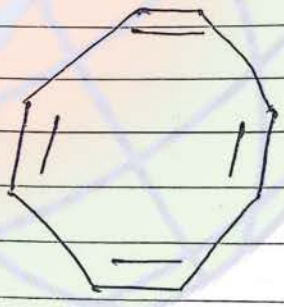
Annulene [4]
Anti-aron.

ii)



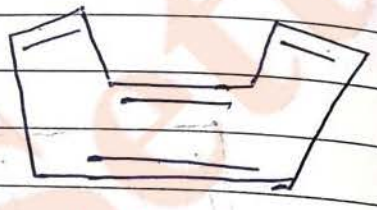
Annulene [6]
Aromatic



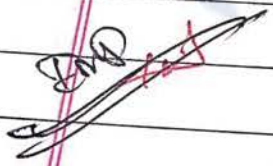


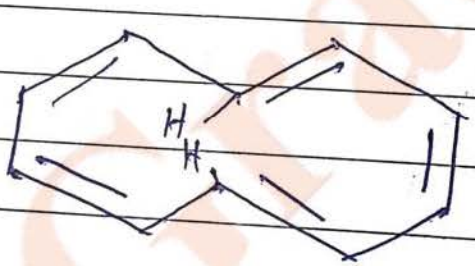
cyclooctatetraene
or
Annulene [8]

≡



Actual shape
(Non-Planar)
Non-Aromatic





Non-Planar
(Non-Aromatic)

Annulene [10]

Due to Internal Hydrogen Repulsion Annulens can become non-aromatic.

1st Choice

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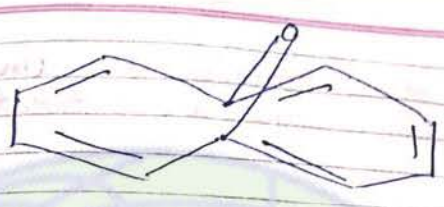
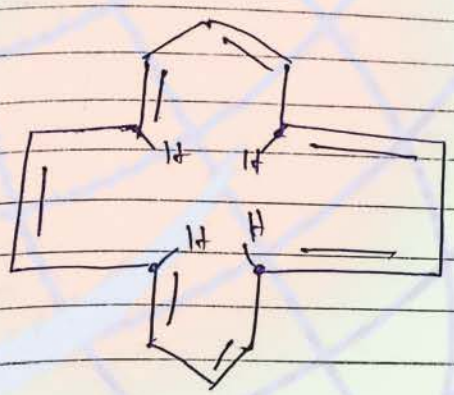


(Aromatic)

If these H-are removed as a bridge then compound becomes aromatic.



Annulen [14]
(Aromatic)

(Due to Increase in size repulsion b/w Internal Hydrogen is less.)

(लेकिन [14] H के समान पर [18] समान पर वह वह Non-aromatic property show करती लगेगा चूंकि more repulsion में take place)

1st Choice

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★ Anti aromatic compound's are unstable due to presence of unpaired electron

1st Choice

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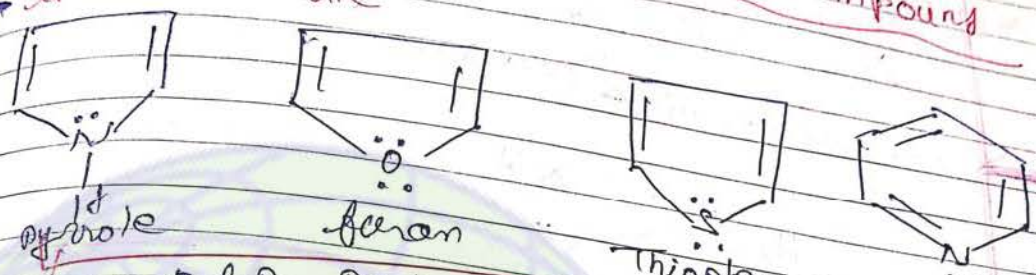
Aromaticity in Heterocyclic Compound

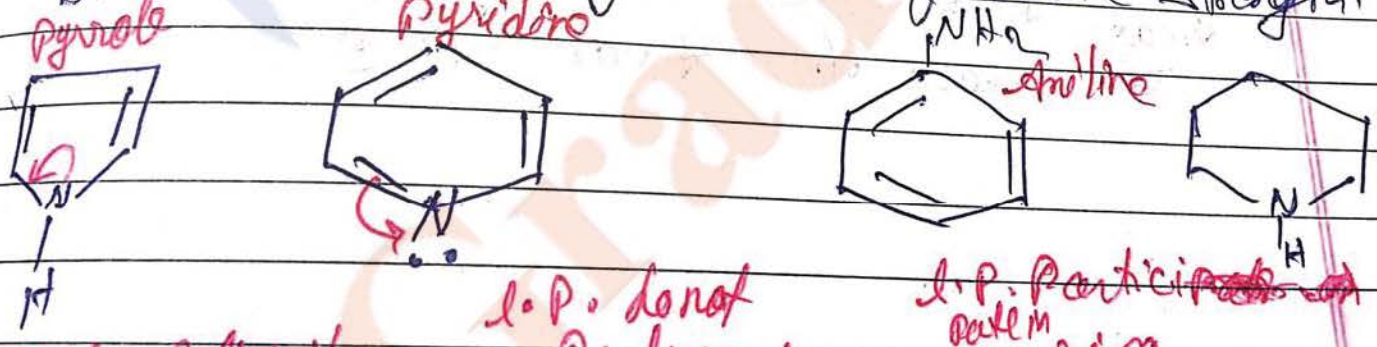
Q: All are aromatic



i) In Pyrole, furan and thiophene lone pair present on hetero atom (comparatively) participate in ring resonance (cyclic delocalisation) to comple condition for aromaticity (6πe⁻)

ii) In Pyridine lone pair present on Nitrogen atom do not participate in the ring and it is aromatic due to presence of 6πe⁻

Ex: Arrange following in order of basic strength.



(l.P. compulsorily participate in ring)

l.P. donot Participate in ring

l.P. Participate in ring.

d > b > c > a

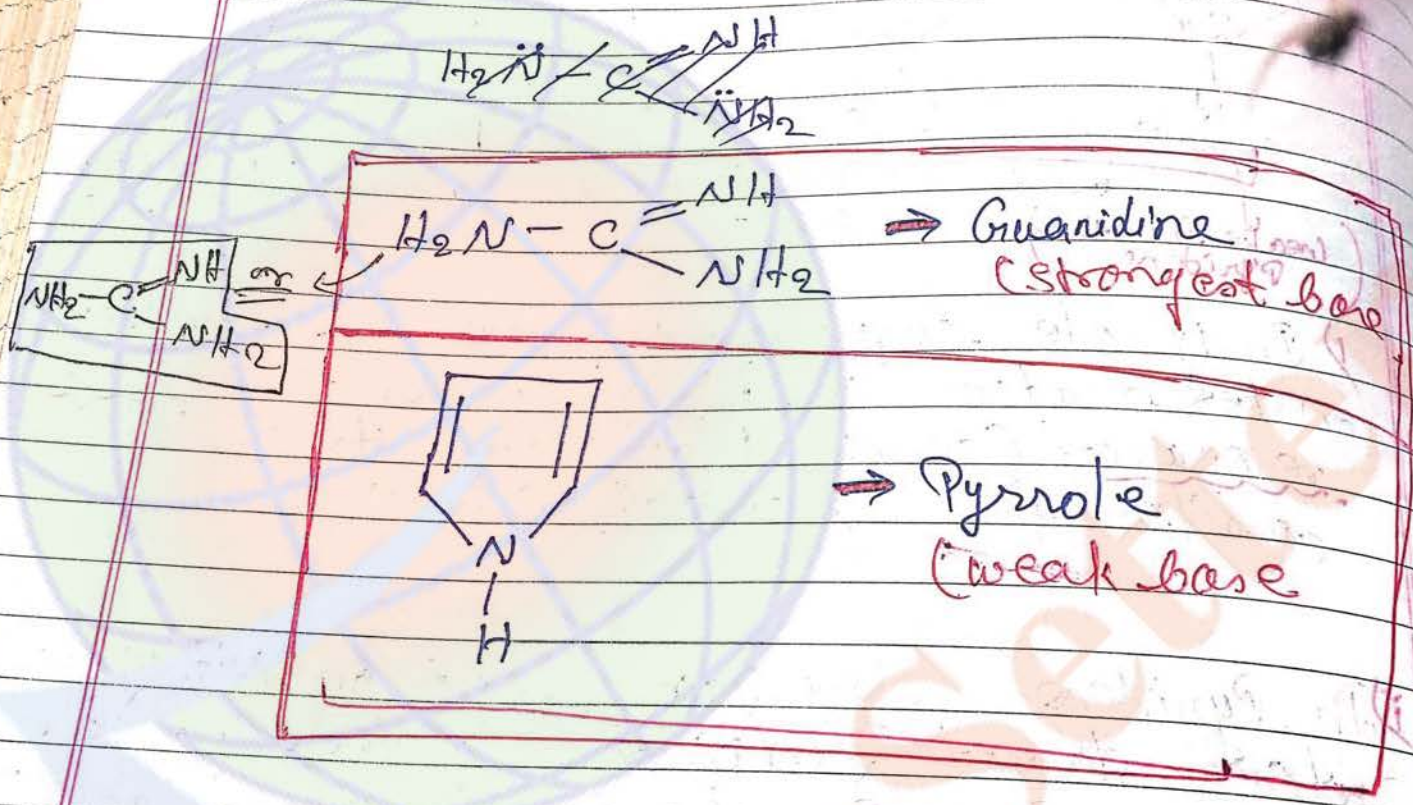
S-chaock

1st Choice

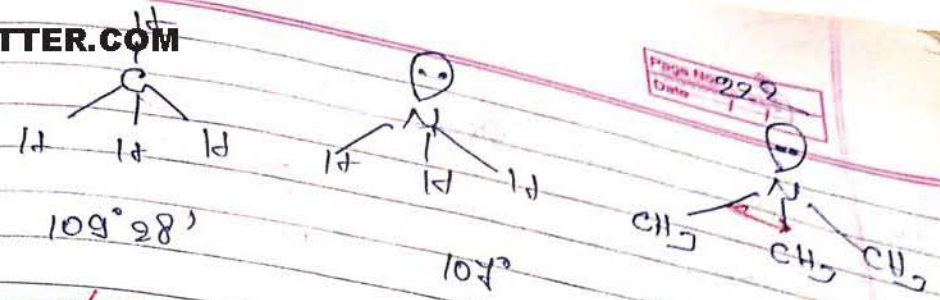
Gr-1 ⇒ 22 to 45
Gr-2 ⇒ 22, 24, 25, 27, 28, 31, 33, 35 to 40, 42, 43, 5 to 6, 6 to 7

Note—
Pyrole can also act as weak acid, Pyrole is the one of the least base among Nitrogenous base.

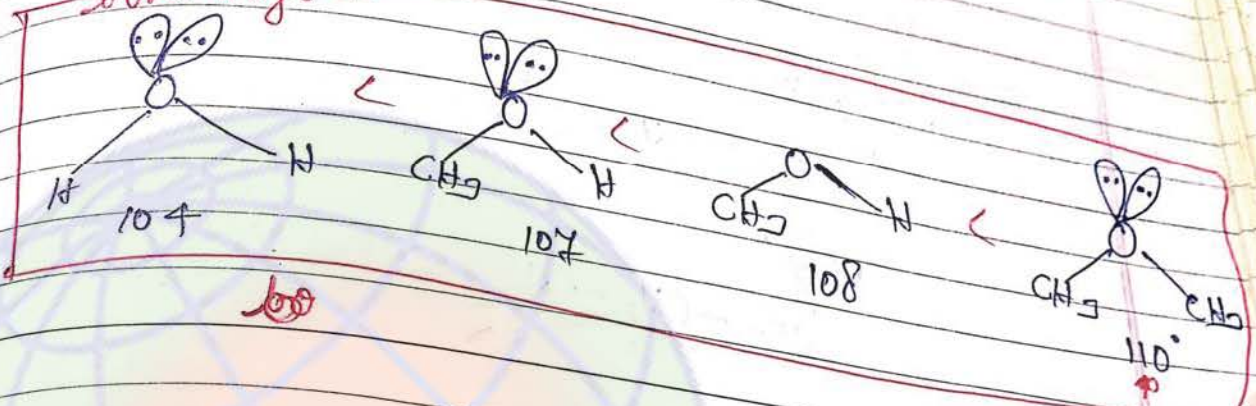
⇒ General point ⇒ (अधिकतर जगह इसी से)



⊛ Greater one में यदि basic comparison में Guanidine आ जाए तो इसे Strongest base treat करेंगे और यदि Pyrole आ जाएगी इसे weak base treat करेंगे।



bond angle →



Lactic acid ⇒ $CH_3-\underset{OH}{\underset{|}{CH}}-COOH$

$\overset{\oplus}{CH_3}-COOH$ (+I)

CH_2-CH_2-COOH (+I)

CH_2-CH_2-COOH (+I)

more +I effect

(See sheet solute

Exp 2
Q.No 63

CH_3-O-CH_3 (X)

CH_3-CH_2-O-H ——— p-Cresol

Q.64

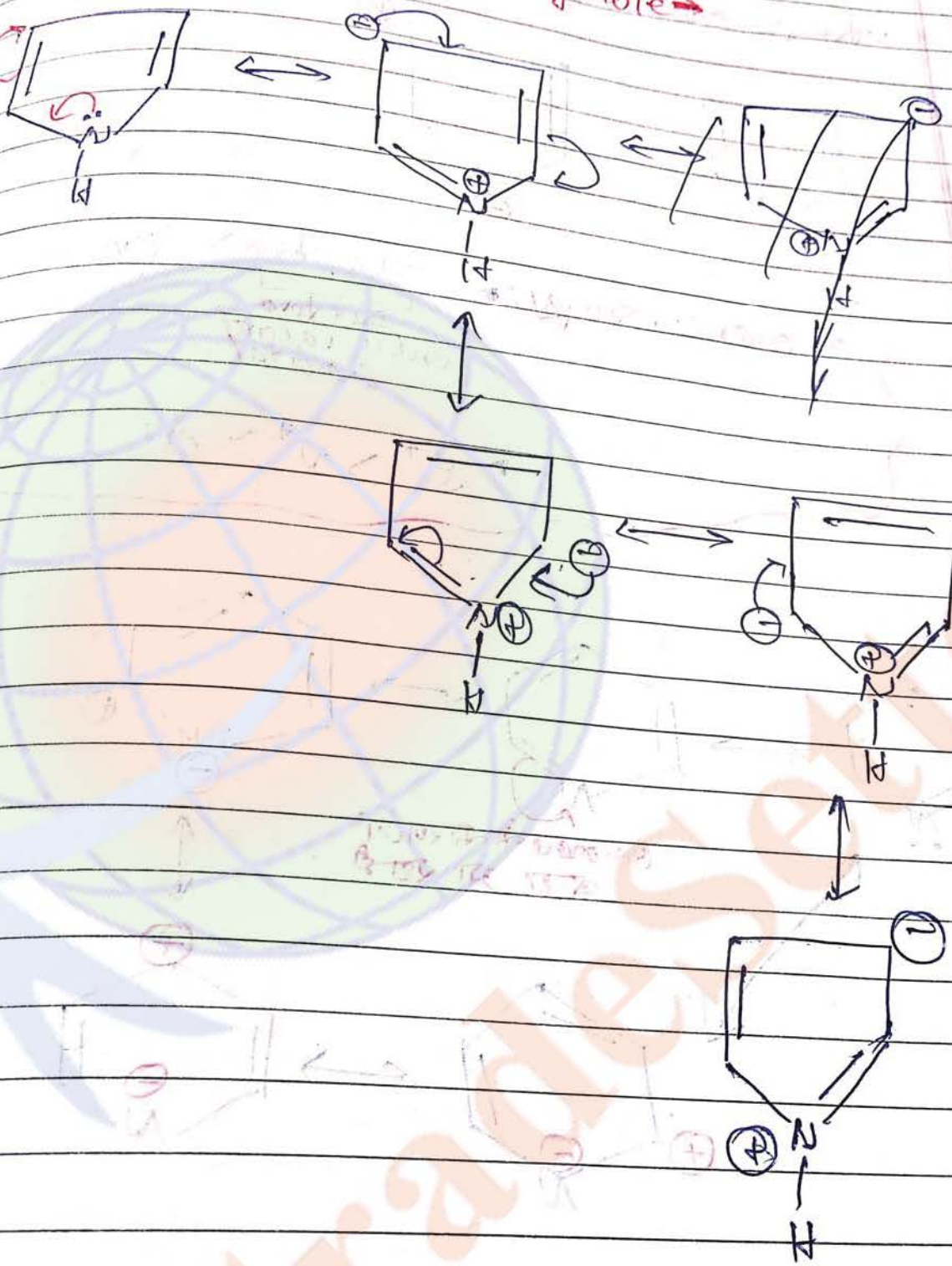
Allyl:

$CH_2=CH-\overset{+}{C}H_2$

vinyl

CH_3-CH_2-CH

Resonating Structures of Pyrrole →



1st Choice

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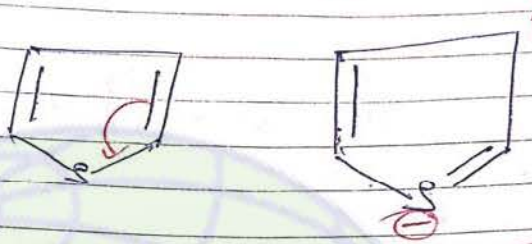
कम ⊕ E. N वाला पर्त chare more stable

(8) Extra Resonance of Thiophene →

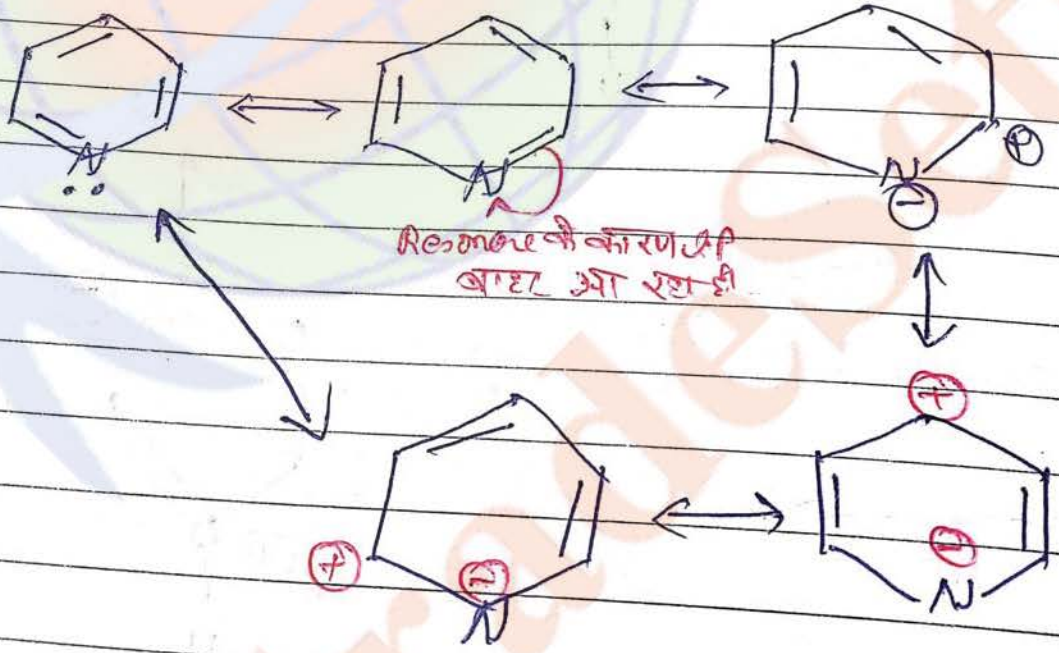


Resonance energy :- Thiophene > Pyrrole > Furan

Due to extra vacant d-orbital

$S^+ > N^+ > O^+$

(X)



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(viii) Arrange these molecules in order of E.A.S reaction.
Pyrrole Benzene Pyridine

Sol: Pyrrole > Benzene > Pyridine
+m of N -m of N

1st Choice

H.W
Q. P. P. 2 → 16

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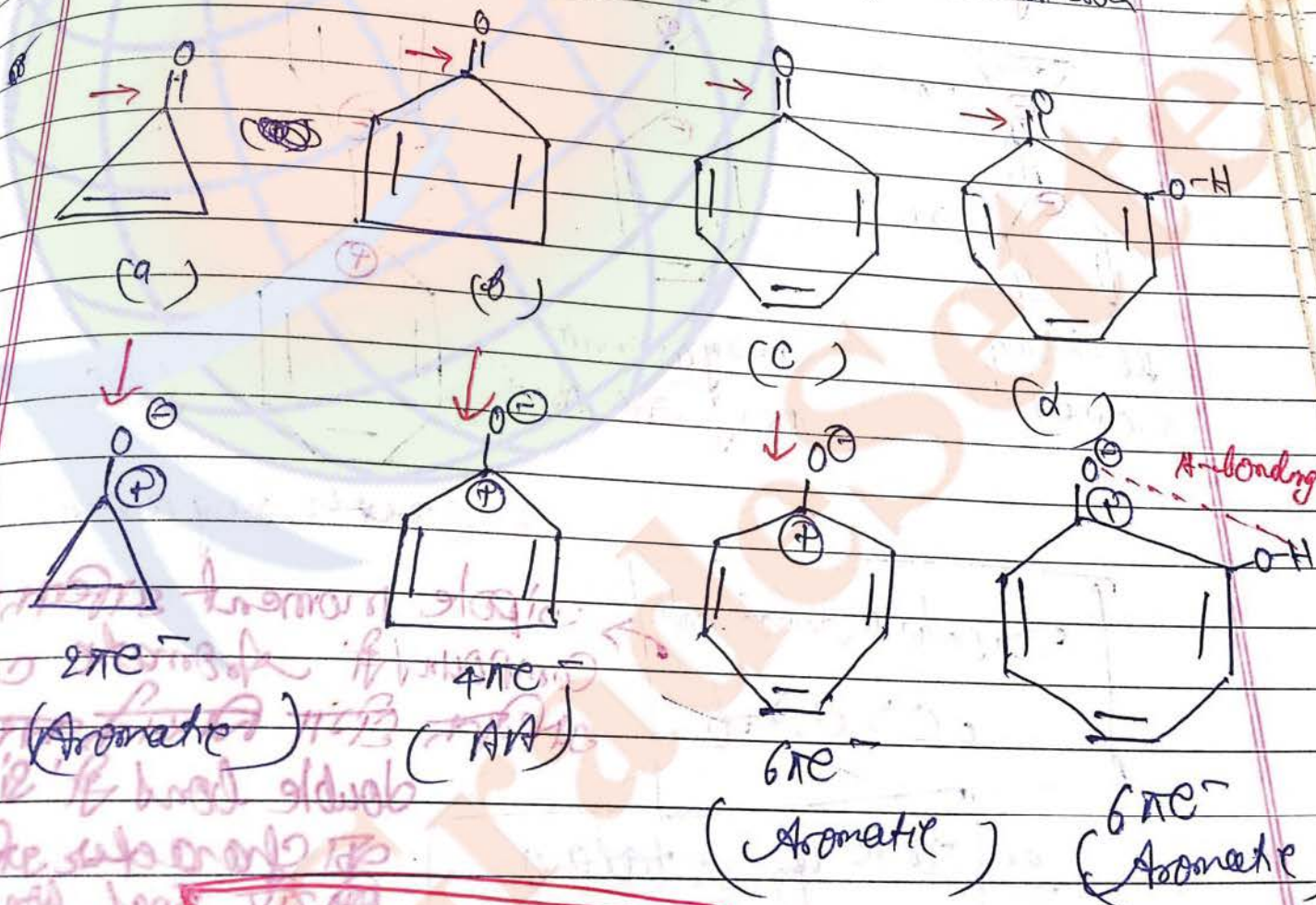
Aromaticity and Dipole moment ⇒

If polarisation of bond create aromatic Ions that is it occurs easily and dipole moment is high. iii) If rotate easily.
If Polarisation create Anti-aromatic Ion then it occurs very less.
Polarisation creat aromatic Ions & occurs easily & dipole moment is high & rotate easily

Ex: Arrange these compony/ compound in order or dipole moment.



Dipole moment :-

d > c > a > b

A-A

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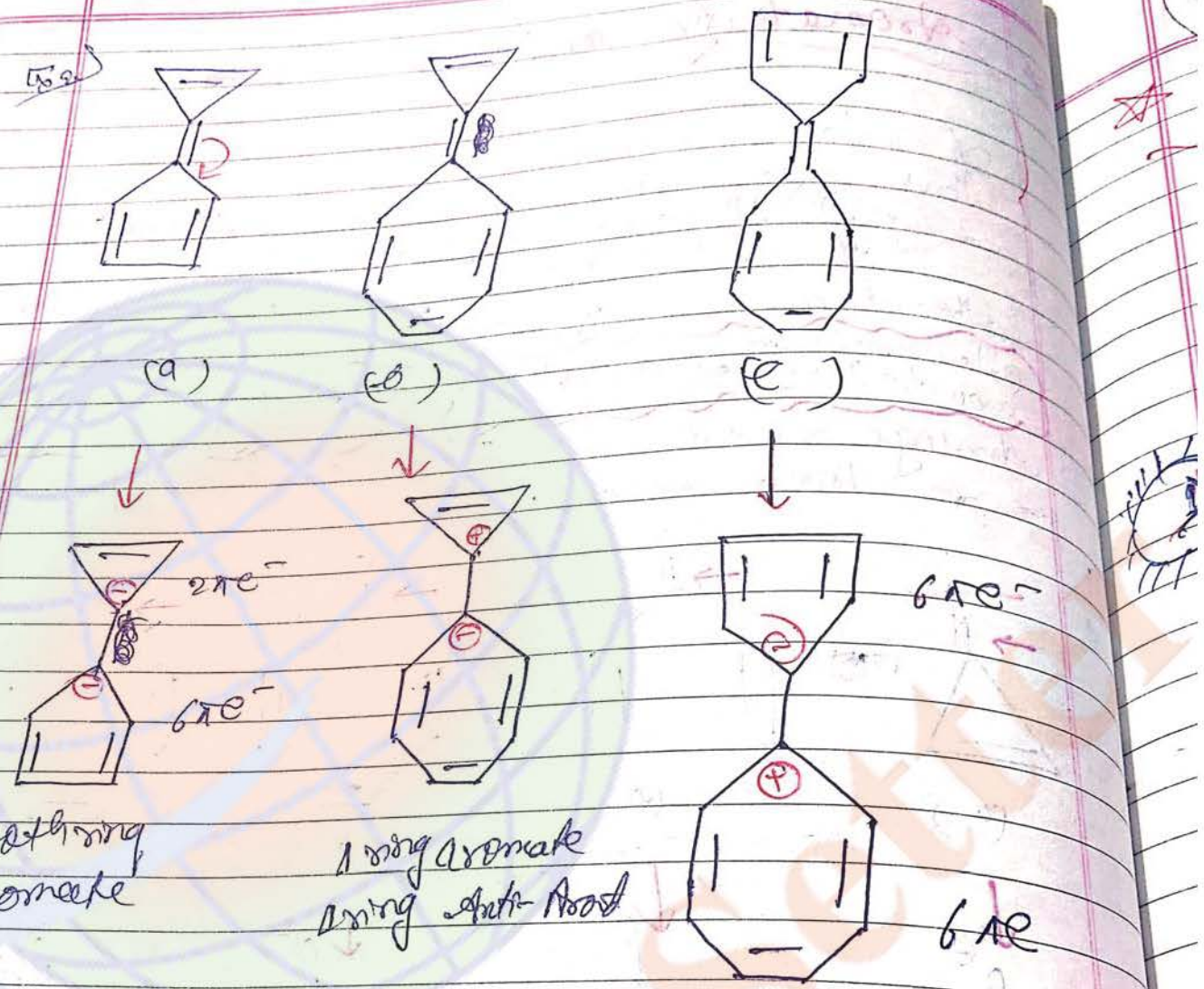


Dipole moment order
c > a > b

= or case of rotation
c > a > b

Dipole moment अधिकतर ही compound में Aromatic character अधिक होगा जिसके कारण double bond में single bond का character अधिक होगा और single bond character अधिक होने से rotation कम

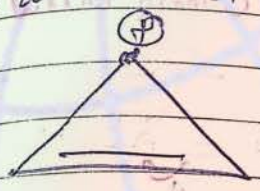
General Instruction → double bond को तोड़ कर लिखकर ले जाने से compound aromatic बन जाएँ।

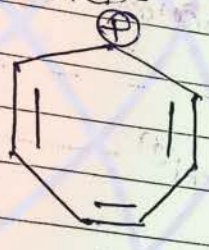
Compounds having partial aromatic character (due to one R-3 bi aromatic in nature)
1st Choice Quasi aromatic compound are subclass of aromatic compounds.

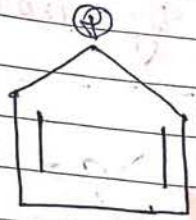
Aromatic Ion's (Quasi aromatic) →

↳ Stable
↳ High R.E
↳ High dipole moment
↳ more solubility in water
↳ show charge seperation always

Aromatic cations → (formation of aromatic cation's)
(Q) → which is more stable?


(a)


(b)

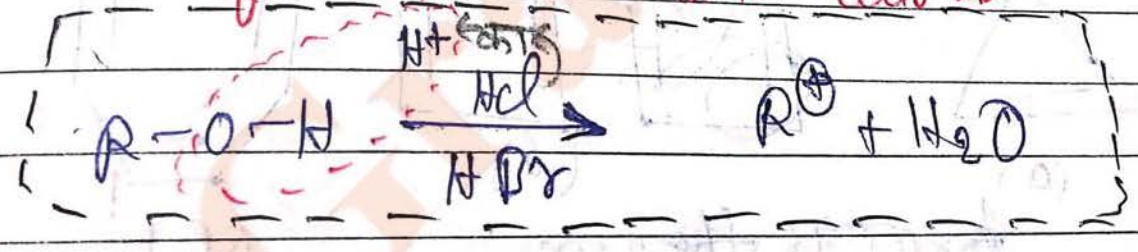

(c)

b > a > c
size

→ Anti aromatic

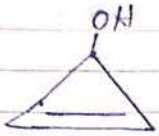
⇒ cation's are formed in following reaction →

A) Reaction of Alcohol with acid →

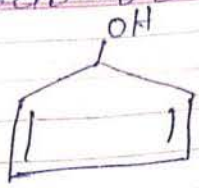


Rate of reaction of Alcohol with acid

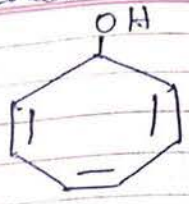
A) Rate of Reaction of Alcohol with acid →



(a)



(b)



(c)

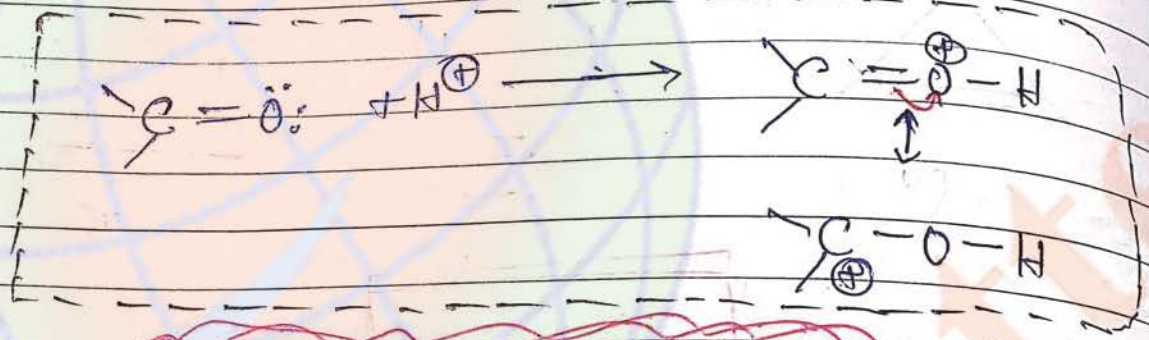
$CH_2=CH-CH_2$

(d)

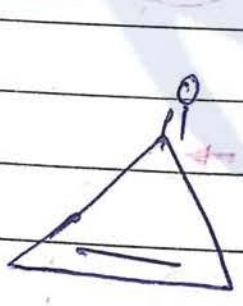
c > a > d > b

एक simple केस में यह
अच्छे Antiaromatic
सबसे या द में भी होता है

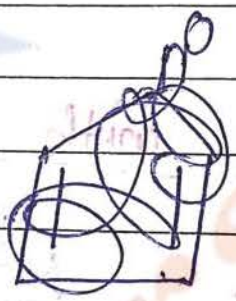
B) By protonation of carbonyl compound →



Rate of protonation ∝ Stability of carbocation



(a)



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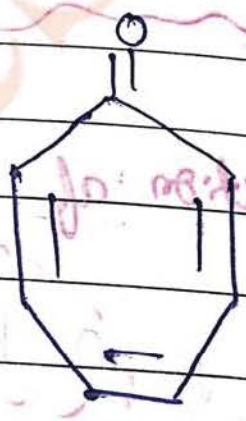
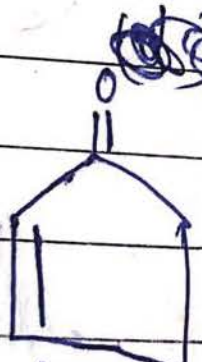


(c)

(d)

Aromaticity theorem



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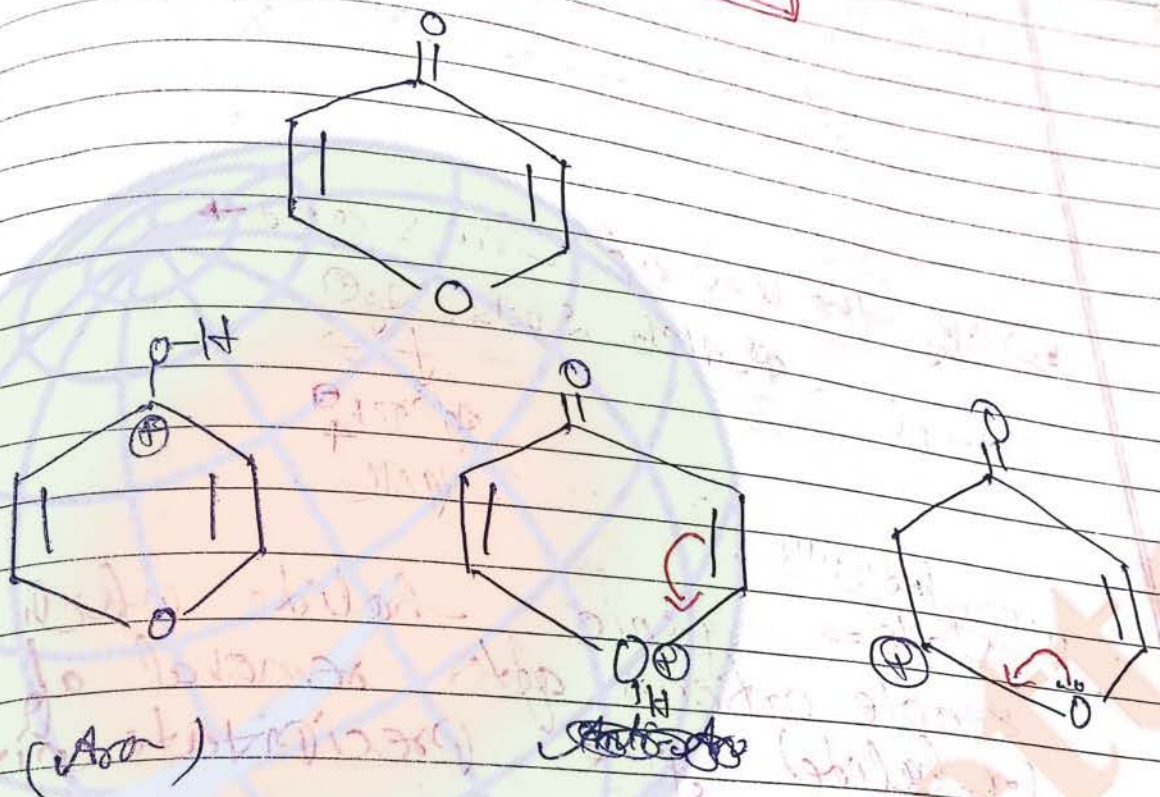
Ans/ Aromatic shape on rate of protonation

c > a > e > d > b



Note ⇒
Protonation occurs at the side which gives more stable cation.

c) By Ionisation of Alkyl Halide →

1) Self Ionisation →

$$R^{\delta+}-X^{\delta-} \longrightarrow R^{\oplus} + X^{\ominus}$$

2) By the use of lewis acid →

$$R-Cl \xrightarrow{AlCl_3,\ SbCl_5,\ Ag^{\oplus}} R^{\oplus} + AlCl_4^{\ominus}$$

$Ag^{\oplus}, BF_4^{\ominus}$
$AgNO_3$

IIT asked 2012

Note ⇒ organic halide which form's stable cation's after removal of halogen (or halide) give precipitate with $AgNO_3$

$$R-X + AgNO_3 \longrightarrow R^{+} + AgX$$

- AgF → soluble in water
- AgCl → white P.P.t
- AgBr → yellowish white P.P.t / white yellowish P.P.t
- AgI → yellow P.P.t

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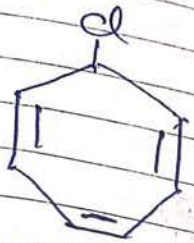
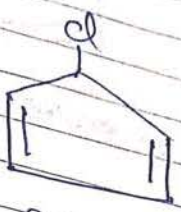
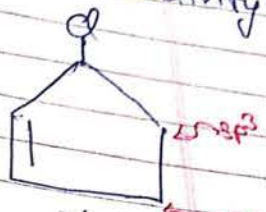
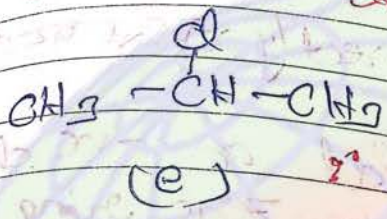
towards $AgNO_3$ halide in order of their reactivity

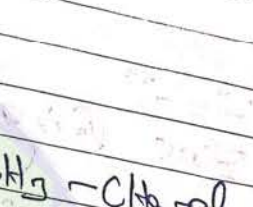

(a)
Acetal


(b)
Acetal


(c)

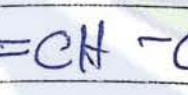

(d)


(e) 2°

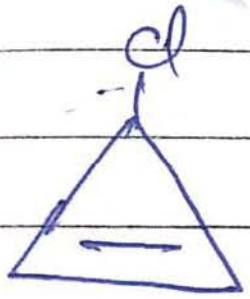

(f) 1°

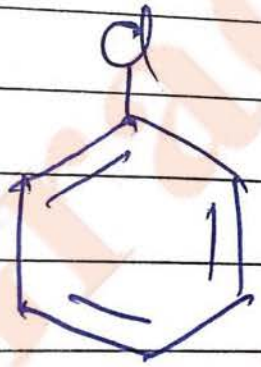
b > a > d > e > f > c

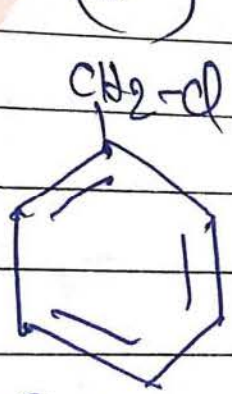
(Q3) which of the following halide is white PPt with $AgNO_3$

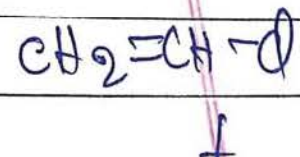

(a)


(b)


(c)

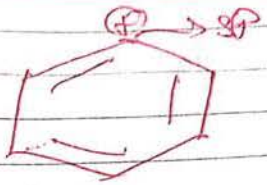

(d)


(e)


f

a, b, d, e

Reason –



Resonance

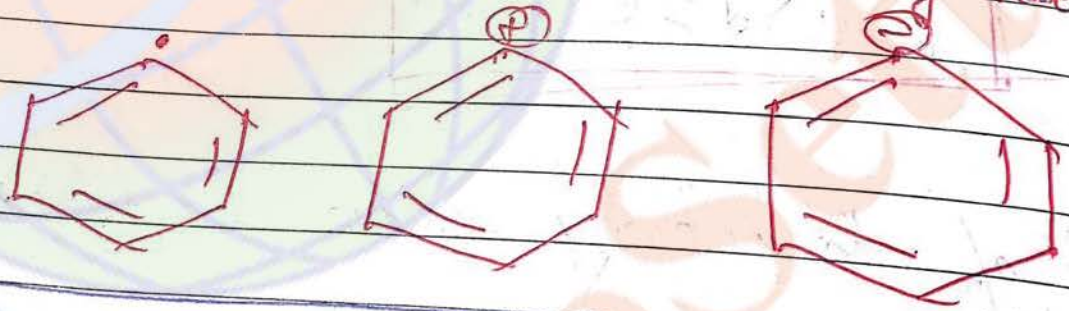
$CH_2 = \overset{\oplus}{C}H$

Concept by S. S. Sir

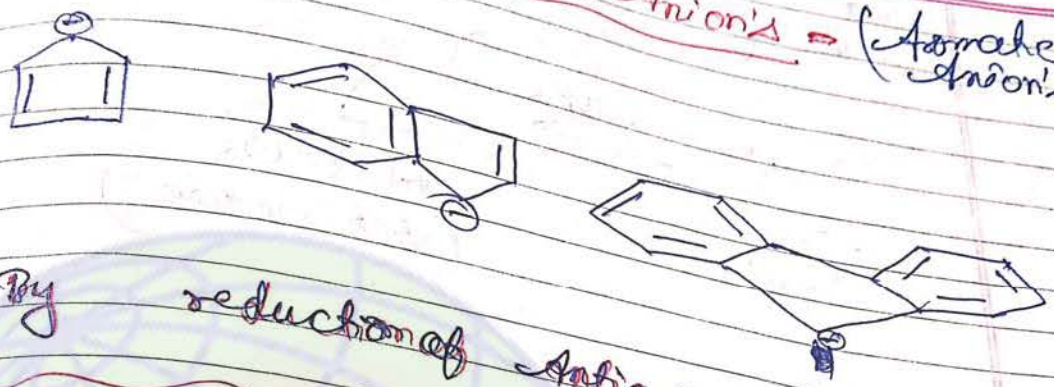
Benzene Ring पर directly जुड़ने पर

Note:-

If the charge free radical or -ve charge is directly present on benzene ring then it is not stablise by resonance.

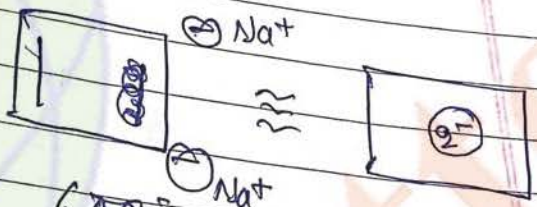


Formation of Aromatic Anion's ⇒ (Aromatic Anion's)

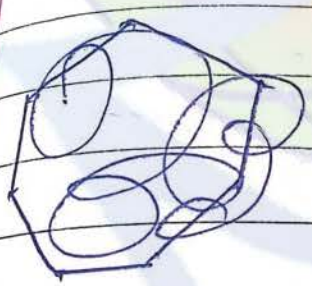


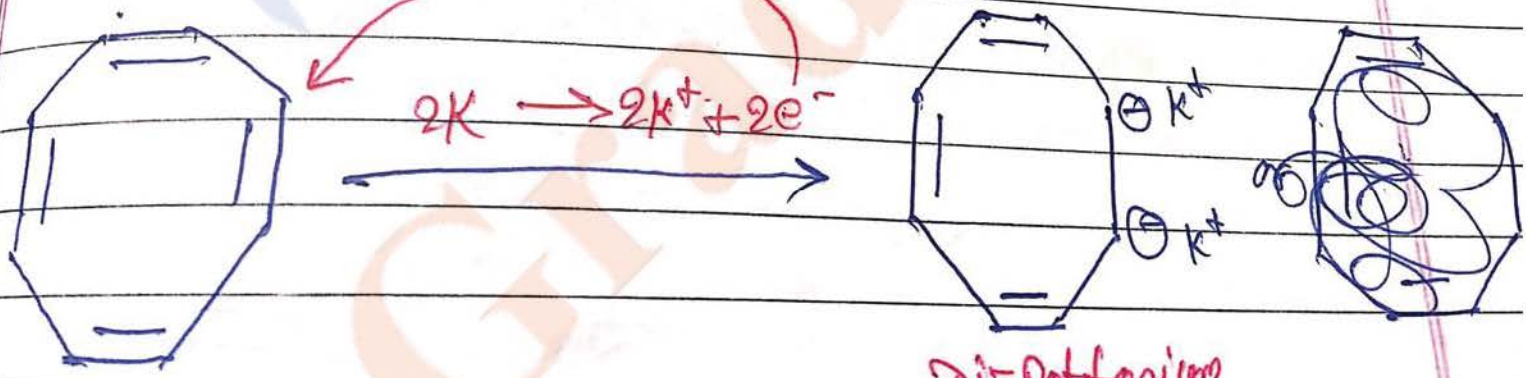
1) By reduction of Antiaromatic and Non-Aromatic Compound ⇒

Cyclo Octa di'one
(Anti-aromatic)



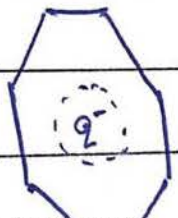
6 π e⁻
(Aromatic)
(Di sodium salt)





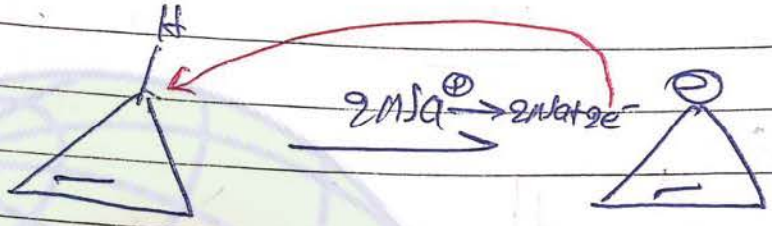
Di-Potassium salt

or



Note →

Reducing is not Possible



(Approach)

Not Possible

(Anti-approach)

1st Choice

$H^+ + e^- \rightarrow \frac{1}{2} H_2$

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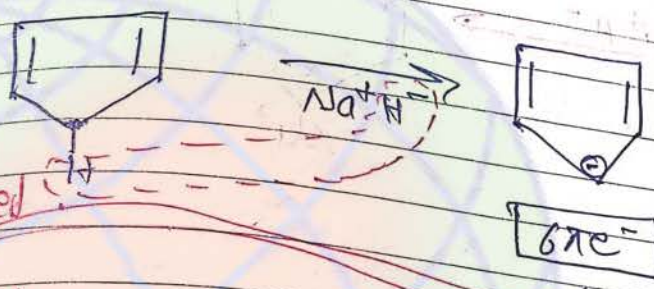
1) Removal of Acidic Hydrogen →

2) Cyclopentadienyl anion is Aromatic and stable that is why cyclopentadiene shows Acidic nature slaughtly weak acid.

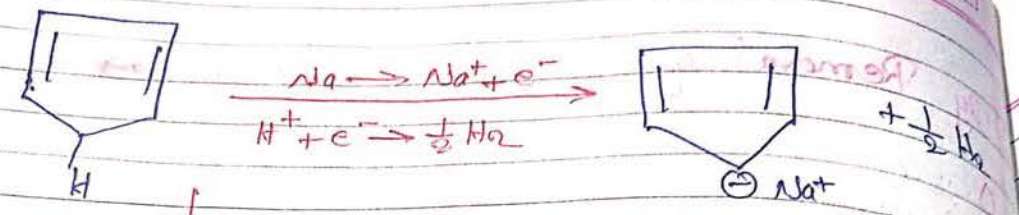


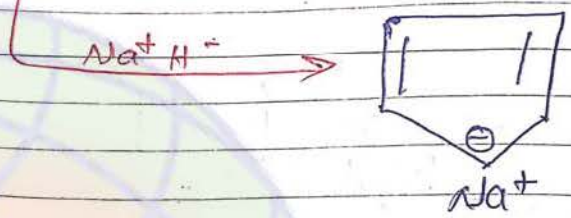
3) Acidic strength order

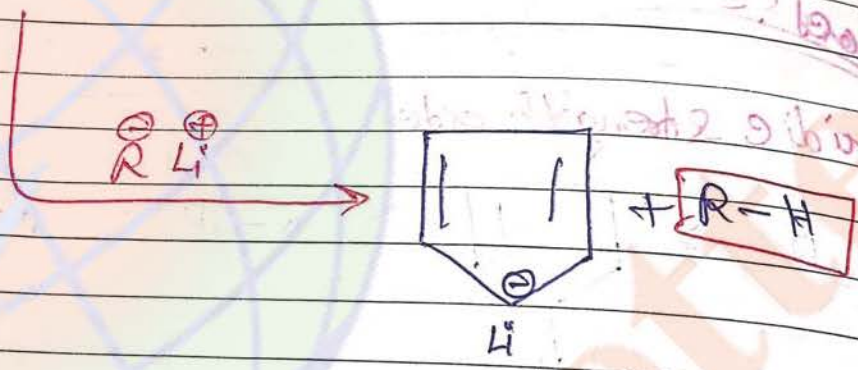
$H_2O > \text{(cyclopentadiene)} > R\text{-}OH > CH \equiv CH > NH_3$

Pkas 15.76 16 16

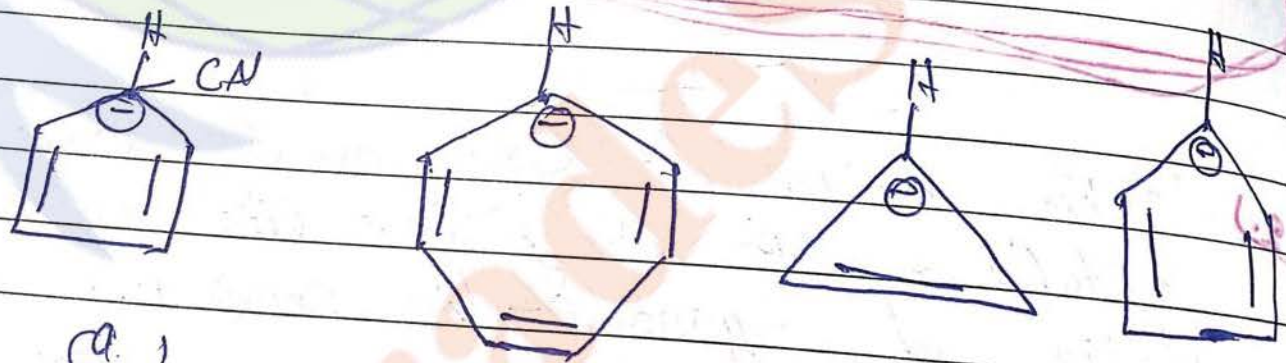
2) This acidic hydrogen can be removed by metal's or with strong bases like metal hydrides of organometallic compound.







Order Acidic H-order:



Size

a > d > b > c

1st choice

bond ~~are~~ are compare on the basis of size
3 member ring are highly unstable due to strain
(except Aromatic)

Comparision of Resonance Energy →

i) R.E

Aromatic > Non-Aromatic > Anti aromatic

ii) Resonance energy →

$CH_2=CH-CH=CH-CH=CH_2$ > $CH_2=CH-\underset{\underset{CH_2}{\|}}{C}-CH=CH_2$

Extended (same direction conjugate)
(एक तरफ के "i" bond हो)
alternate चलता जाए)

(Cross conjugation)
(Different direction conjugate)

$CH_2=CH-CH=CH_2$
(less conjugation)

Extended Conjugation is more effective than cross conjugation. when "number of conjugation is same.

Example → ~~Stability order~~ while when number of conjugation is less comparable to number of extended or cross conjugation is known as less conjugation.

1st Choice

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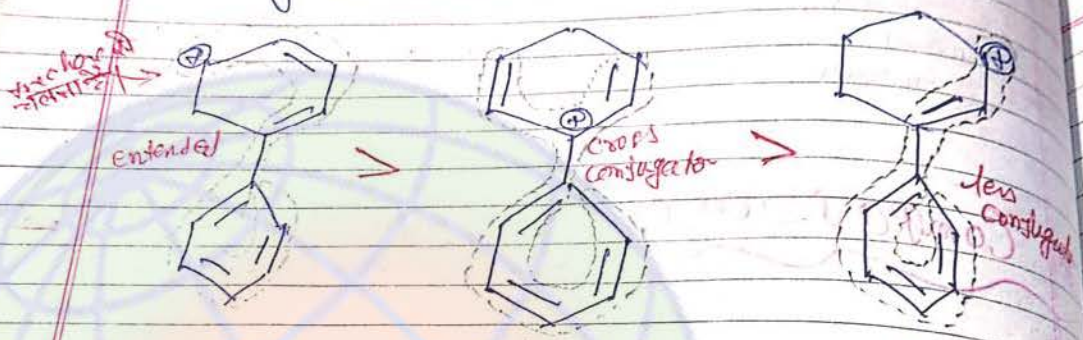
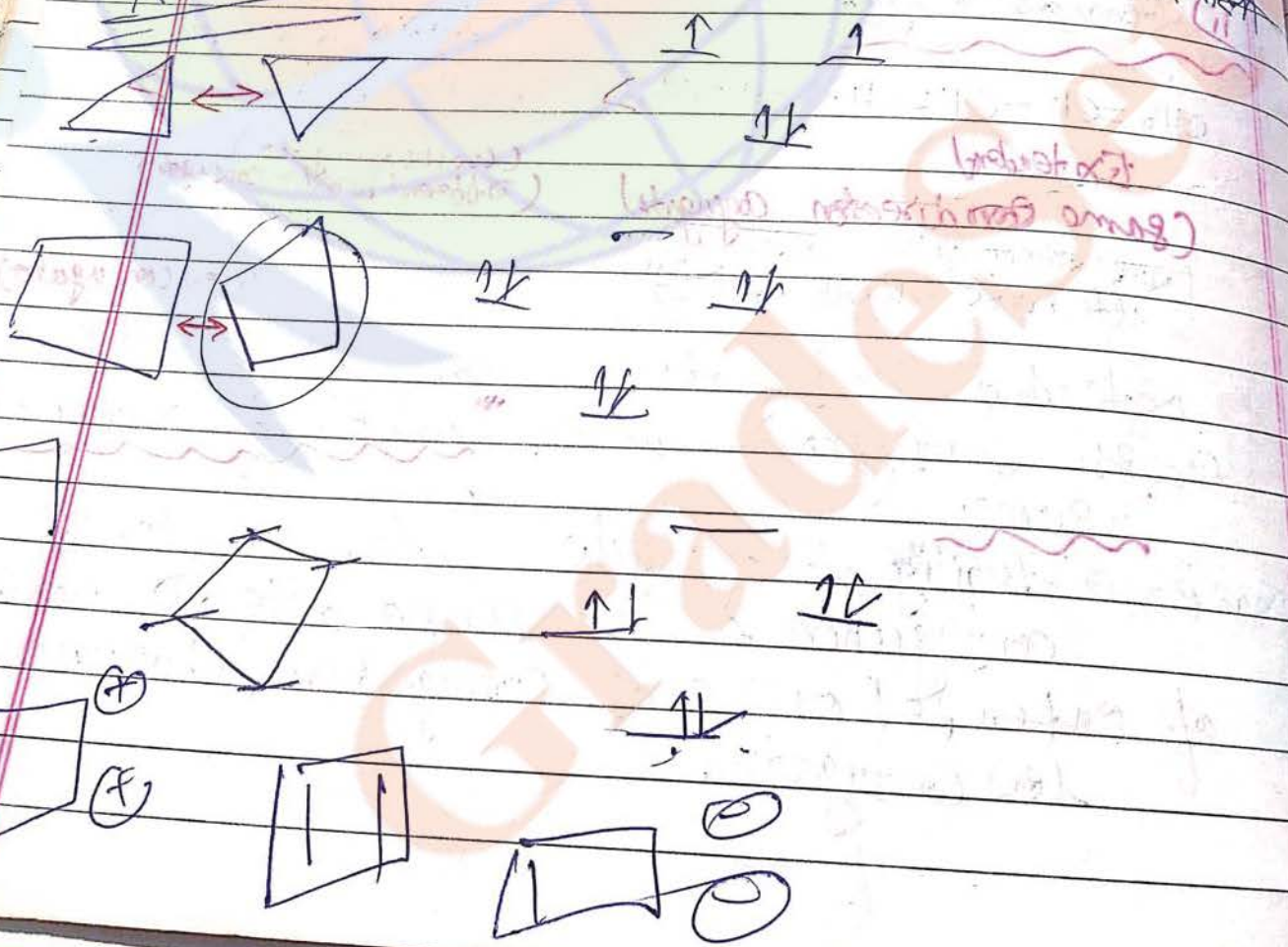
Examples
Stability order



Note:-

|| Aromatic || Anti aromat ⇒ Anti aromatic
| Aromatic | Non-aromatic ⇒ Aromatic

Acc. to Resonance energy



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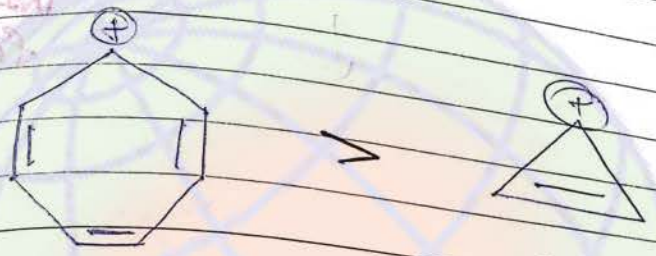
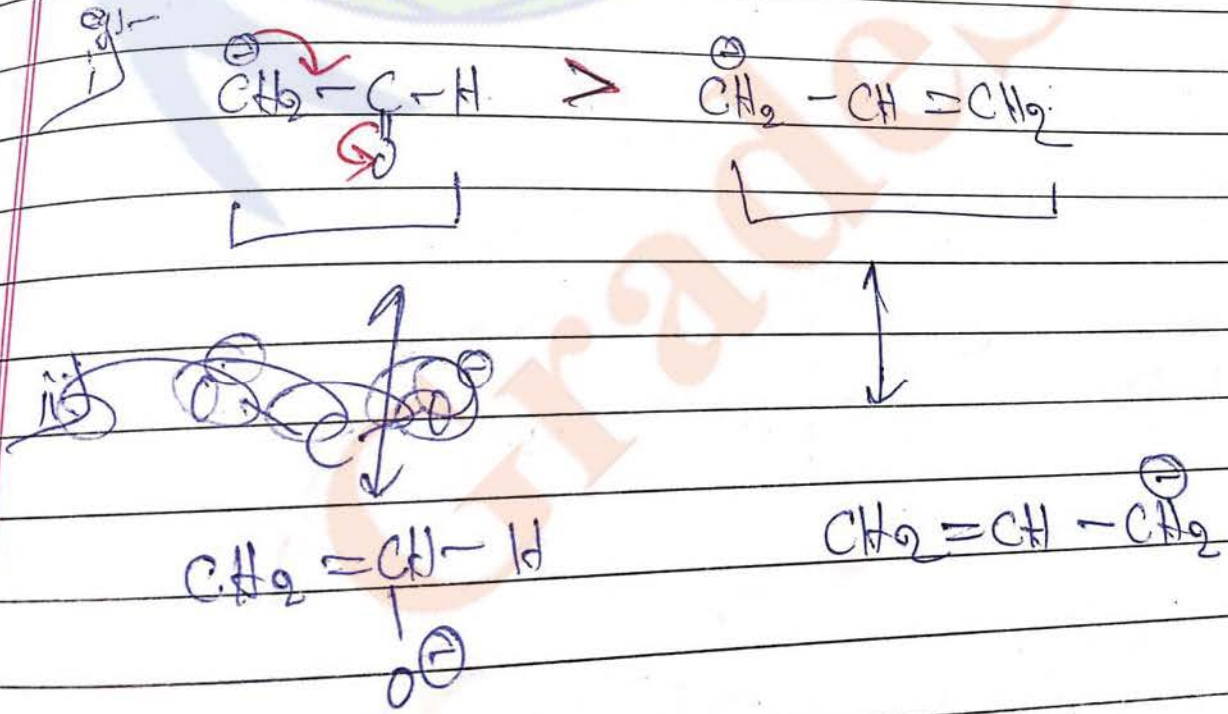
3) If resonating structures are similar than more conjugation means more R.E (means more stability)



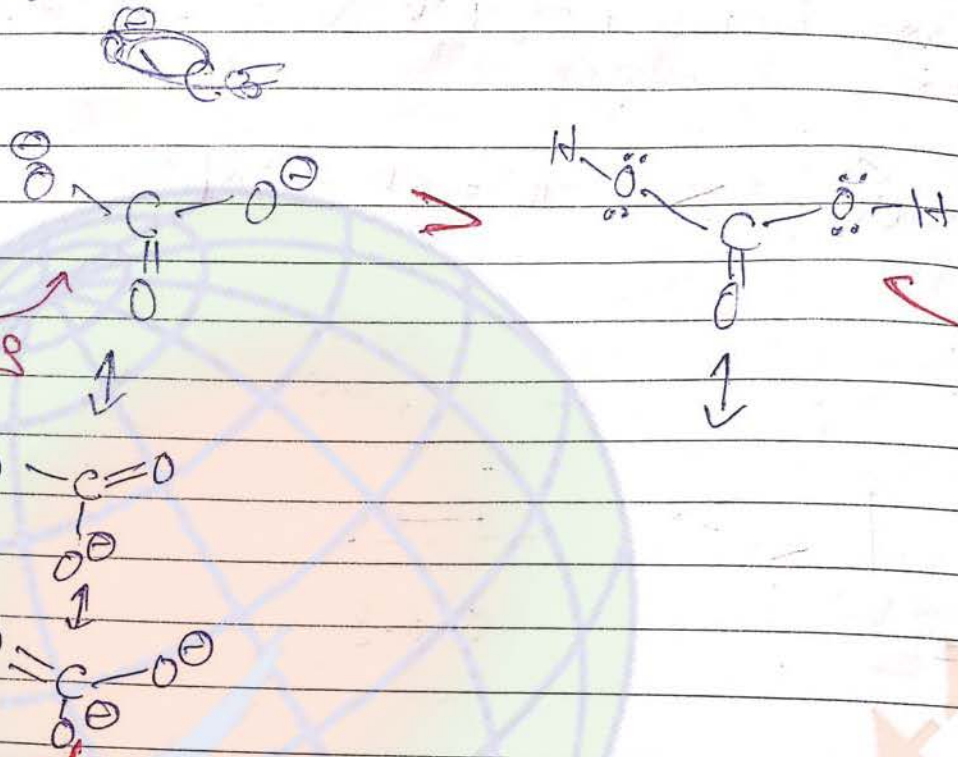
7-R.S

3-R.S

4) If resonating structure are not similar than more effective resonating structure will have more resonance energy.



eg.



Concept →

R.E in case of Identical R.S is greater than non-Identical Resonating Structure.

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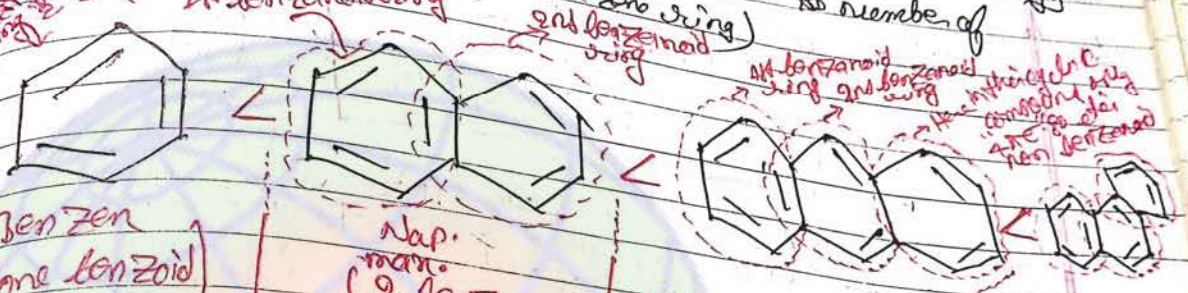
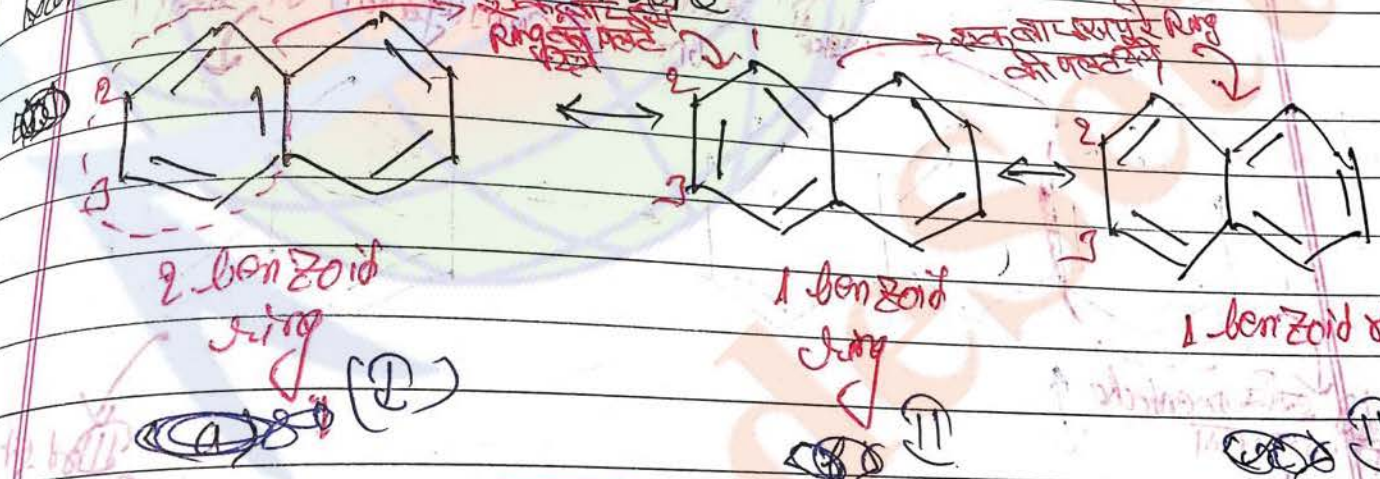
vii) Fries Rule →

In case of Poly cycle ring Increase with Increase in benzoid ring (6π e⁻ in benzo ring)



No. of R.S	1	2	3	4	5

Example → R.S of Naphthalene



(I) (II) (III)

stability order ⇒

(I) > (II) = (III)

Here we see that in Naphthalene 3 R.S are possible

नोट → यहाँ R.S Resonance के आधार पर बन रहा है। इस आधार पर सरल ज्ञान

1st Choice

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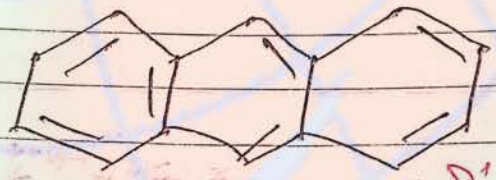
Note ⇒ (In above example)
In naphthalene C_1-C_2 bond occupy greater double bond character than C_2-C_3 bond.
that is why

bond length
$C_2-C_3 > C_1-C_2$

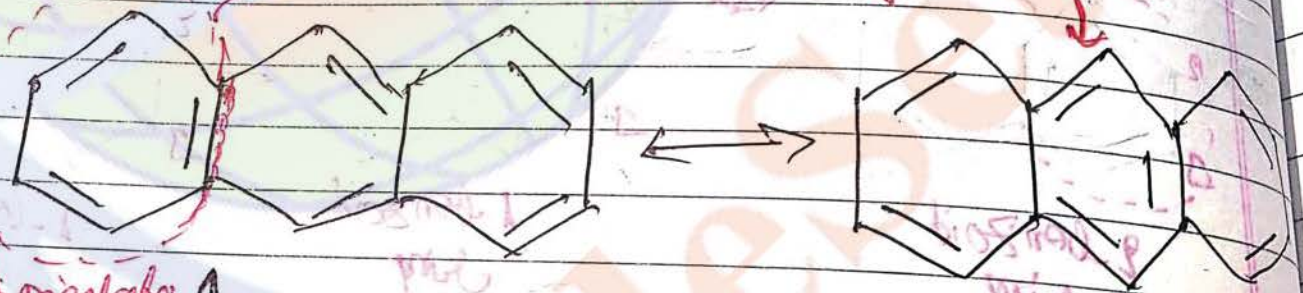
नोट ⇒ इस उदाहरण में हम देखते हैं कि जिस पर ये double bond है उसकी bond length इस पर उसकी तुलना में double bond है bonds -

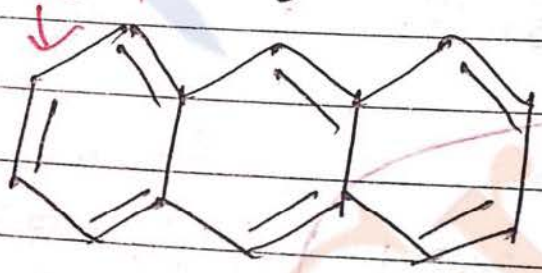
→ यदि Initial में double bond था तो Resonance होने पर terminal में single bond का ~~double~~ character आ जाता है और यदि Initial में single bond था तो bond double का ~~double~~ character आ जाता है अर्थात vice versa.

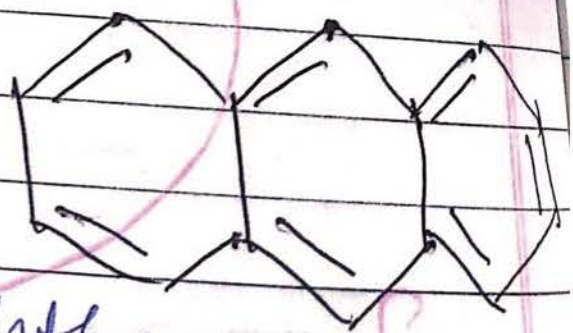
Ex-5) R.S of Anthracene



80/-







Note ⇒ Here we see that in Anthracene 4 R.S are possible.

1st Choice

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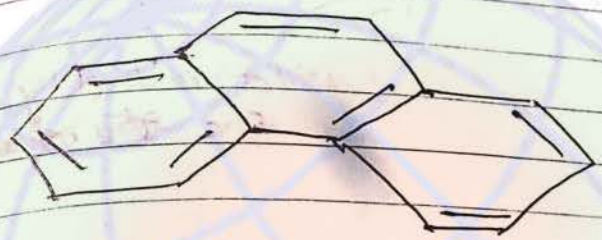
Date

(Q.7) R.S of Phenanthrene



1st Choice

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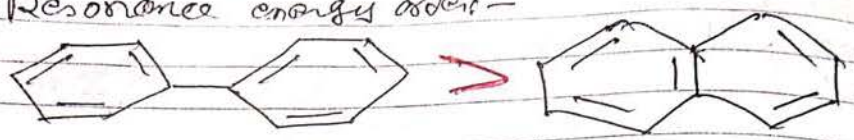
Resonance energy order:-



2 benzenoid ring in all R.S

2 benzenoid ring in one R.S

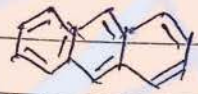
Note ⇒

1. ⟹ (n+1) Rule

According to this in case of polycyclic fused ring (linearly).

Number of R.S is (n+1) where "n" is the number of fused rings.

eg:-

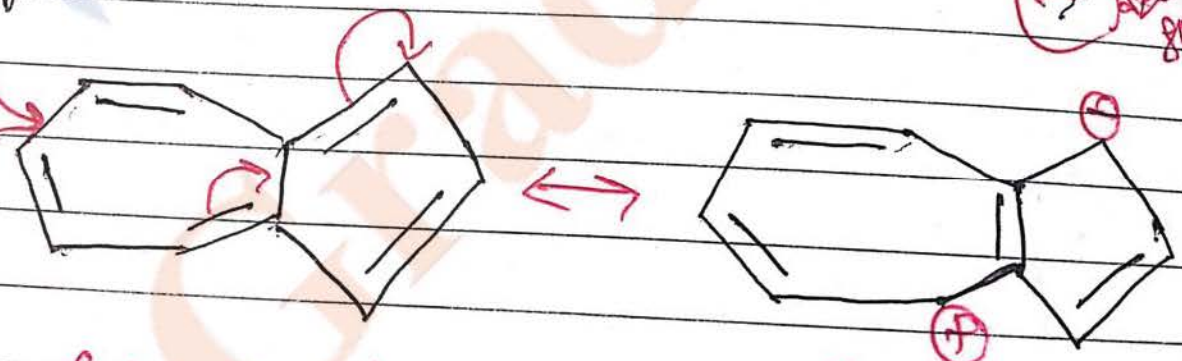


Here we see that polycyclic fused ring are linearly connected so, Here we use this formula (n+1) i.e.

2. ⟹ Polar nature of Azule can also be explained on the basic of Hückel's rule because it's polar structure contain two benzoid ring.

Hence it is very stable.

eg:-



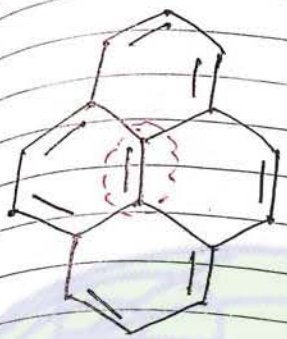
(Azulene)
(1 benzoid ring)

(2 benzoid ring)
(polar structure)

Note: Azulene is some molecule formula with 10 carbon atom but Naphthalene is not

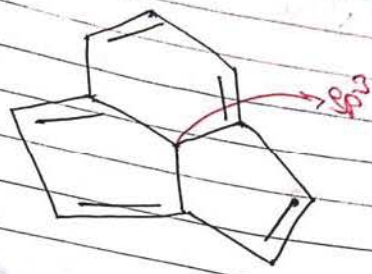
इसमें सीधा सात C का cyclic ring है।

Examples where Hucked Rule is Not Applicable



Pyrene

(Total 16 πe^-), Aromatic



(Total 10 πe^-), Aromatic

In case of pyrene Although 16 πe^- is present but it is Aromatic. which can be explain by suggesting non-participation of central double bond in de-localisation. so only 14 πe^- participate in cyclic de-localisation. Hence it is "Aromatic"

In case of polycyclic fused ring $(4n+2)\pi e^-$ should delocalised at the periphery

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Conceptual point about Fleming's left hand rule

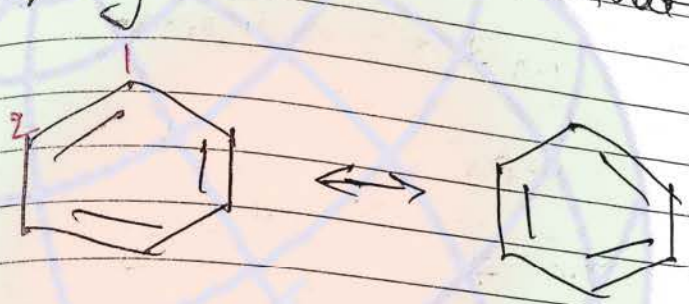
1) Fleming's left hand rule is:

Effect of Resonance on Bond length and Bond length →

Bond order = Total no. of bonds b/w two atom in all R.S / Total no. of R.S (Total no of atom in R.S)

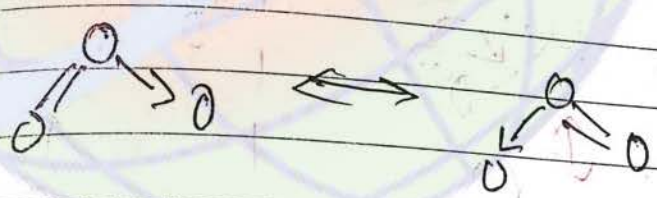
Attention → This formula is applicable when all R.S are identical because in that case they contribute equally

eg 1)



B.O = 3/2 = 1.5

eg 2)

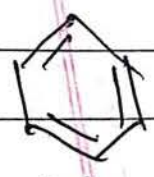


B.O = 3/2 = 1.5

Q2) Arrange in C-C bond length

IIT i)

$CH_3 - CH_3$ (a) $CH_2 = CH_2$ (b) $CH \equiv CH$ (c)


(d)

a) d) b) c
1 1.5 2 3

1st Choice

H_2O_2 O_2 O_3

H–O–O–H O=O

a > c > b

Q4) write bond order of

CO_3^{2-} $NO_3^{\ominus}$ PO_4^{3-}

C–O N–O P–O

B.O → 4/3 B.O → 4/3 B.O → 5/4

2 2 2.1

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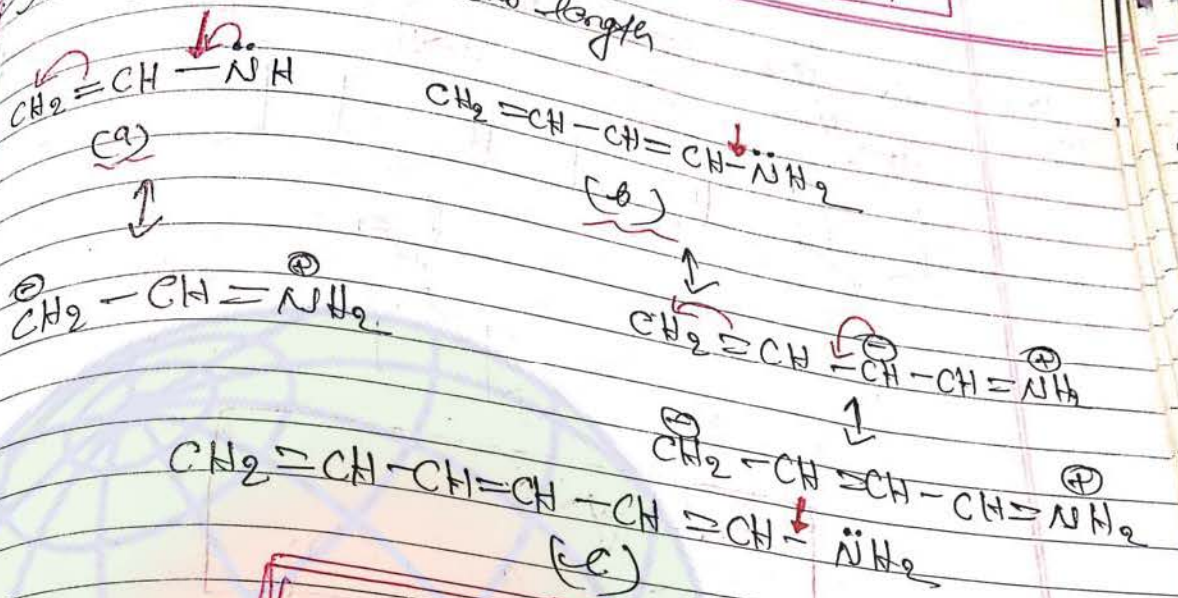
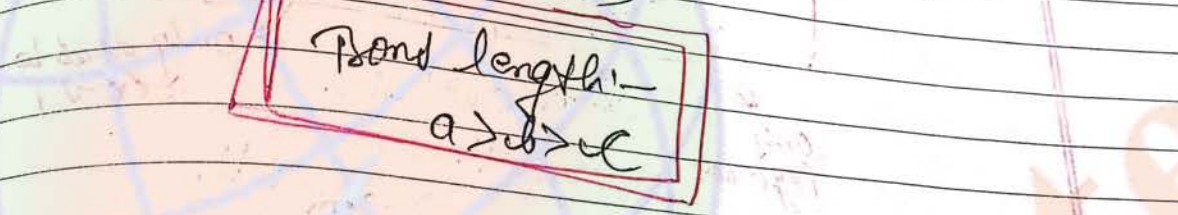
(iii) Arrange in C–N bond length

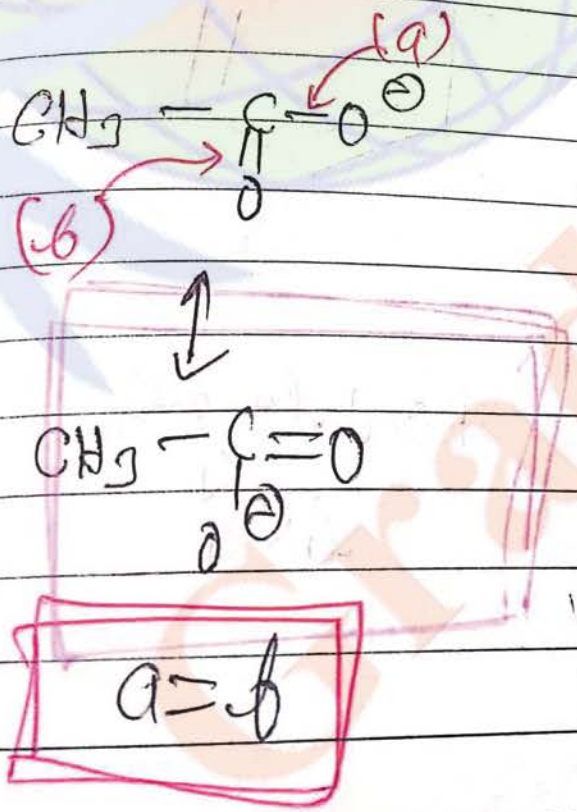


(c) < (a) < (b)

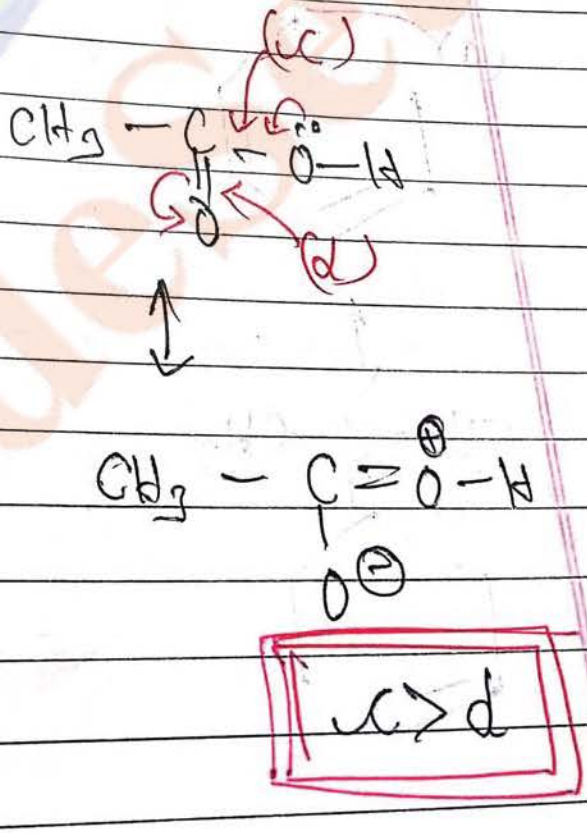


Bond length:-
a > b > c

(iv) Compare bond length :-

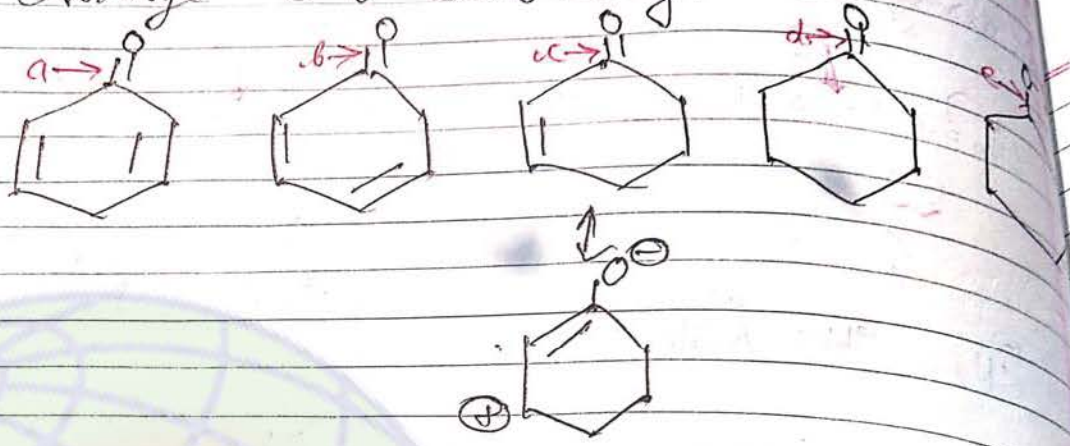


a = b



c > d

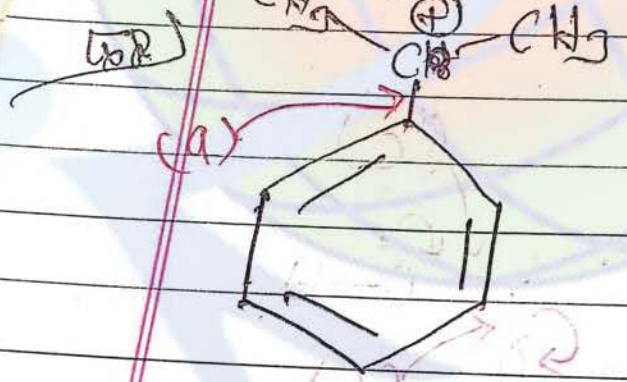
Q#) Arrange C–O bond length

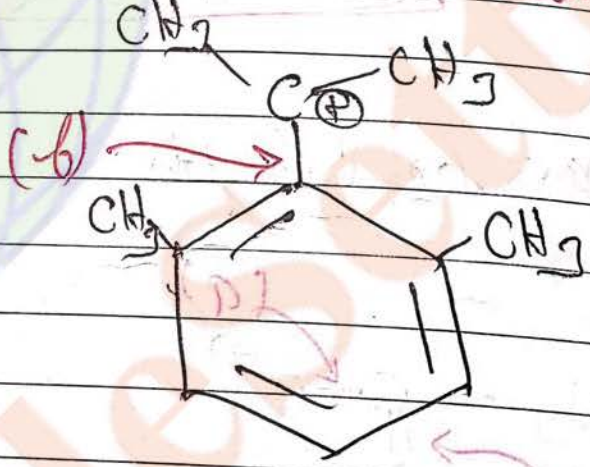


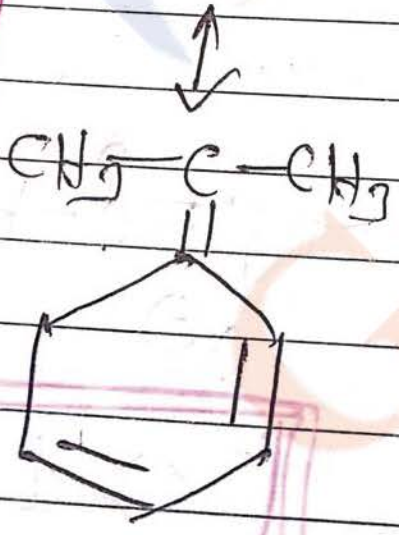
bond length =>

c > b > a > e > d

c → only hyperconj
b → extended cross conj.
a → cross conj.
e → only double bond
d → no conj.







Bond length

b > a

1st Choice

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Bronsted Acid base concept →

Reaction is possible
Strong → weak

1) $HA + B \rightleftharpoons A^{\ominus} + BH^{\oplus}$

HA: Acid-1, B: Conjugate base-2, $A^{\ominus}$: Conjugate base-1, $BH^{\oplus}$: Acid-2

Stronger acid → weaker acid

Acidity: $HA > BH^{+}$

forward reaction

2) Bronsted acid-base reaction order is decided by strength of acid or base:
Reaction always more from strong acid to weak acid direction.

3) If there is very less diff" b/w acidic strength of two acid than reaction occurs reversibly. In such case opposite reaction can be possible by taking excess amount of base.

W.A — S.A

$R-O-H + NaOH \rightleftharpoons R-O^{\ominus}Na^{\oplus} + H_2O$

Alcohol — W.A — S.B — $P_{ka} = 15.75$

P_{ka}

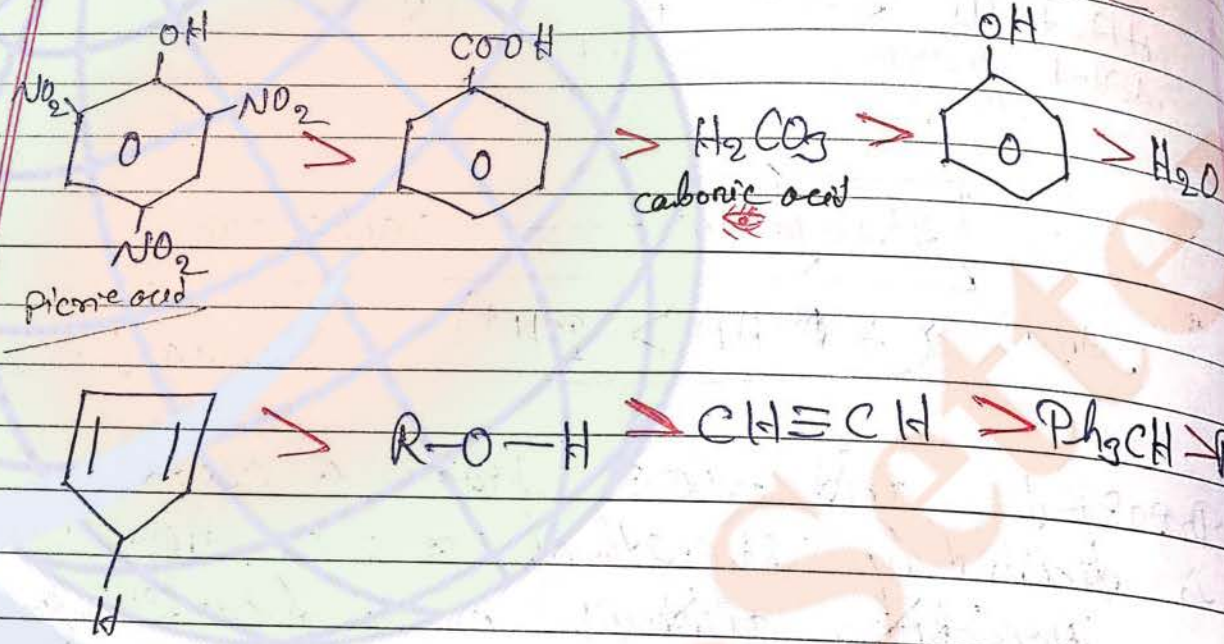
backward reaction is possible

Supe. acids $HSbF_6$

1st Choice

Although this reaction is in backward direction but by taking excess amount of NaOH forward direction is possible upto some extent.

Overall order of acidic strength



$> R-O-H > CH \equiv CH > Ph_3CH > Ph_2CH_2$

$H_2 > NH_3 > Ph-CH_3 > Ph > CH_2 = CH_2 > CH_4$

1st Choice

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3) mineral acid like HCl, HF are more acidic than H_2CO_3

$HA + Na \longrightarrow NaA + \frac{1}{2}H_2$

$HA + Na^{\oplus}H^{\ominus} \longrightarrow NaA + H_2$

$HA + NaNH_2 \longrightarrow NaA + NH_3$

$HA + NaOH \longrightarrow NaA + H_2O$

$HA + NaHCO_3 \longrightarrow NaA + H_2CO_3$

$H_2CO_3 \rightleftharpoons H_2O + CO_2(g)$

effervescence

Important → Those acid which are stronger than carbonic acid (H_2CO_3) gives effervescence of CO_2 with sodium bicarbonate. or dissolves in sodium bi-carbonate. or decomposes sodium bicarbonate ($NaHCO_3$).

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Hyper Conjugation → σ-P resonance / σ-π resonance / no-bond resonance

i) It is a special type of resonance, in which σe⁻ of C-H (mainly) delocalise with P-orbital of π-orbital.

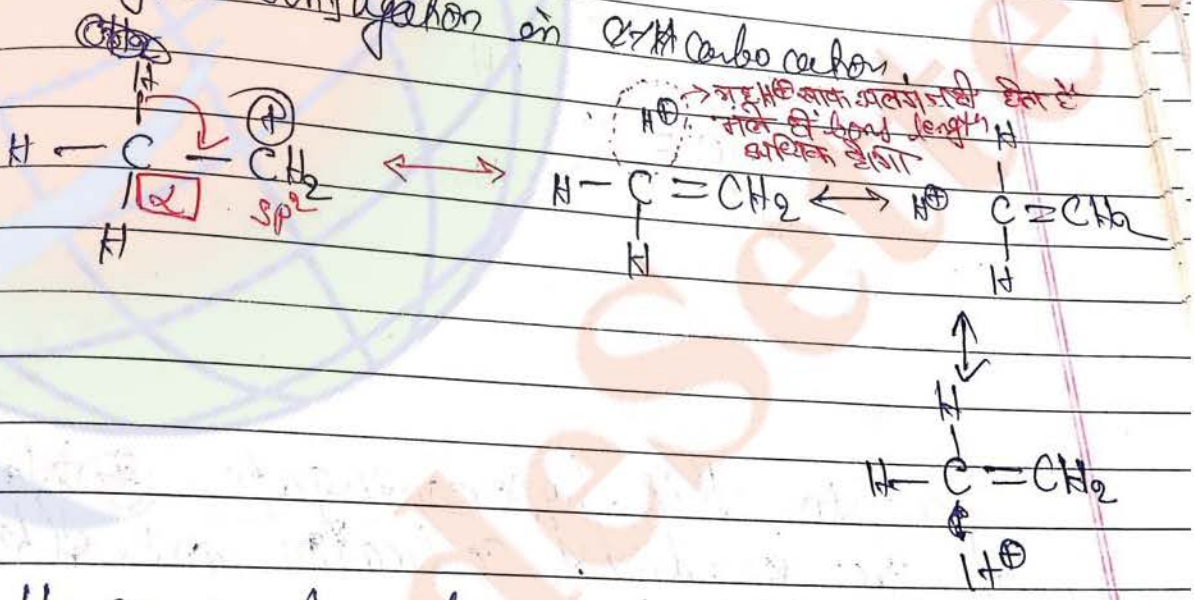
ii) It is also known as σ-P or σ-π resonance

iii) Baker-Nathan effect

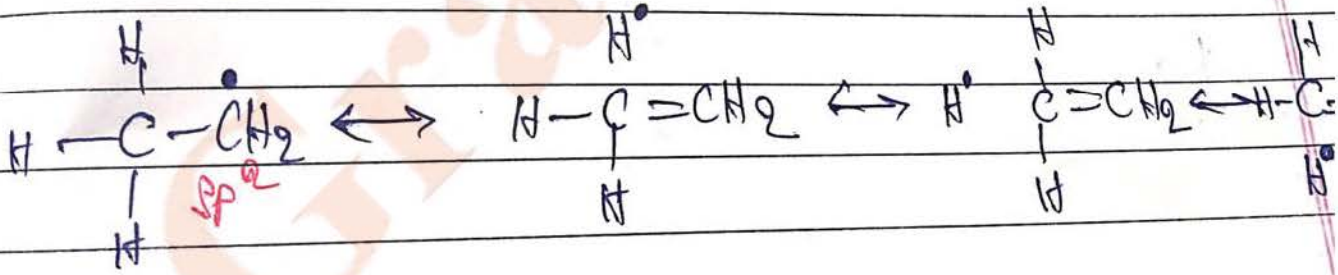
iv) This effect is used to explain stability of free radical, Alkene, carbocation

(i) (ii) (iii)

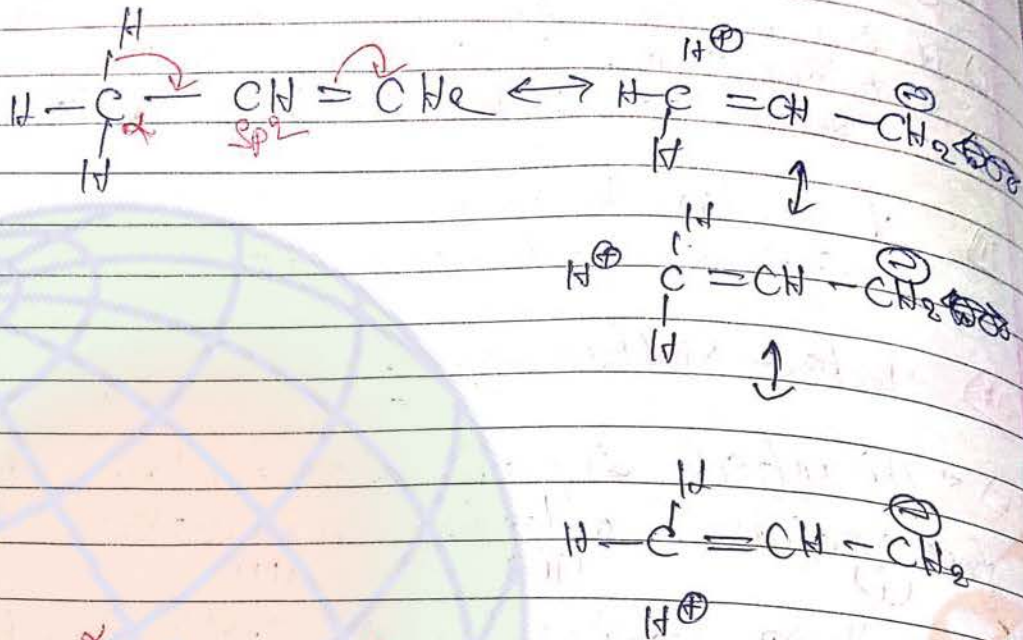
v) Hyper conjugation in C+ carbocation

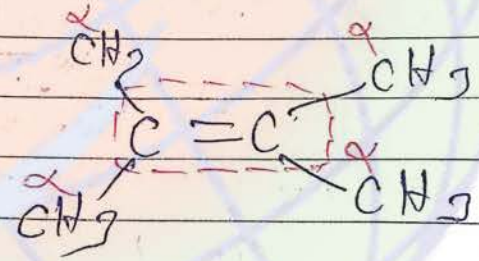


vi) Hyper conjugation in free radical →



VII) Hyperconjugation in alkene. -





VIII) Due to this hyperconjugate stability of free radical, carbocation and alkene increase

Per

1st Choice

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i) For hyperconjugation at least one α-H is necessary and number of hyperconjugative structure is equal to No. of α-hydrogen.

sp²-hybrid carbon के next sp³ hybrid carbon को α-carbon कहलाता है।

ii) In hyperconjugation α-carbon should be sp^3 hybrid and directly attach to sp^2 hybrid carbon. (+T)

iii) This hyperconjugation is also known as No bond resonance.

iv) In hyperconjugation C-H bond act as e⁻ donating group and hyperconjugation power of different Isotope

+H	H > D > T	B.E → C-H < C-D < C-T
+I	T > D > H	

Q1 >

Stability order.

+H ∫ $\overset{\alpha}{C}D_3-\overset{\oplus}{C}H_2 < \overset{\alpha}{C}H_3-\overset{\oplus}{C}H_2$

+I ∫ $\overset{\oplus}{C}D_3 > \overset{\oplus}{C}H_3$

(+H is not applicable because α-H is not present)

DP-P-S → 17, 18
Pg. No. 264
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Application of Hyperconjugation effect →

1) Stability of Alkene →

Stability of Alkene & Hyperconjugation & No. of α-H

(The number of α-H are same than stability of Compare on the basis of stability of Hyperconjugation Structure.) (Diabetes and heart disease)

eg: →

(i) $CH_2=CH_2$ < $CH_3-CH=CH_2$ < $CH_3-CH=CH-CH_3$

(a) αH = 0 (b) αH = 3 (c) αH = 6

(d) αH = 9

(e) αH = 12

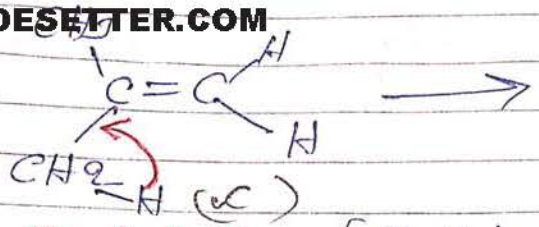
(ii)

αH = 6

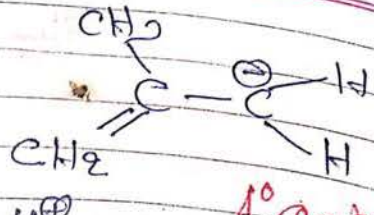
(a) CH3-but-2ene (6α-H)

Trans-but-one (6α-H)

2° Anion (less stable)



Diabutene (2-H)

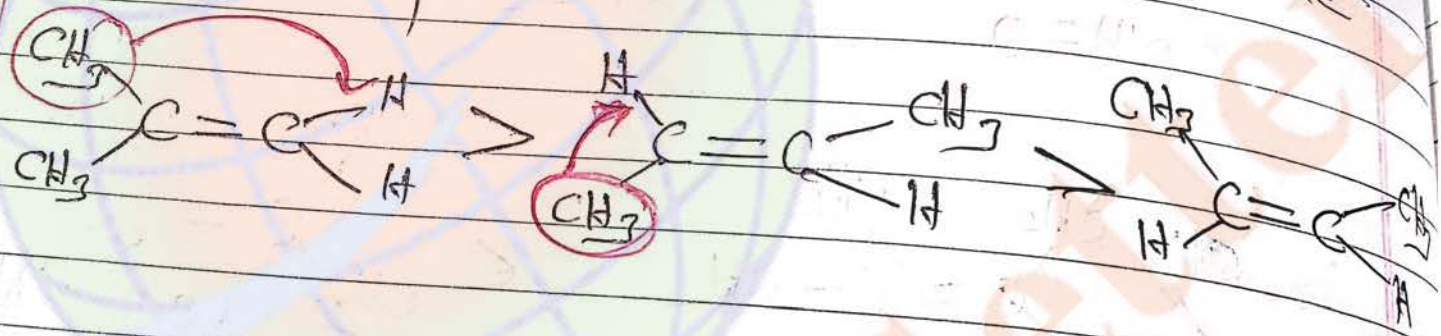


1° anion. (not stable)

So, Stability order —

Diabutene > Trans but-2-ene > Cis-But-2-ene

Note → इस रीजन Point को फिट के तरह
याद रखें।



1st Choice

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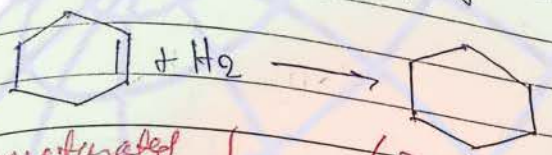
Stability of Alkene can be compare on the basis of two parameter.

1) Heat of Hydrogenation (enthalpy of hydrogenation) (H·O·H)

1) when one more unsaturated compound is hydrogenated then energy release is known as enthalpy of hydrogenation.



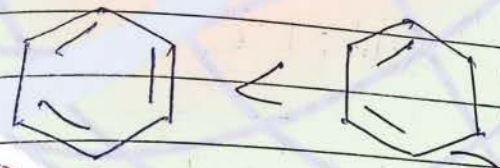
(unsaturated) (saturated)

$-\Delta H = H{\cdot}O{\cdot}H$

(always enothermic)

2) on Increasing number of π-bond H·O·H also Increase, but ⇒

exception



→ यूनी सह Anti-aromatic हैं।

2) If numb of π-bonds are same then stability of Alkene (reactant) can be compare on the basis of H·O·H.

$$H{\cdot}O{\cdot}H \propto \frac{1}{\text{Stability}}$$

when No. of π-bond are same.

$$H{\cdot}O{\cdot}H \propto \text{No. of } \pi\text{-bond}$$

" " " different

पहले सह हैं!

1st Choice

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Date

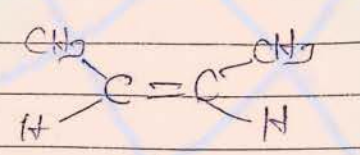
Stability of Alkene $\propto \frac{1}{\text{H.O.H Per } \pi\text{-bond}}$ (when more π-bonds are present)

Q: Compare Stability and H.O.H of following molecules

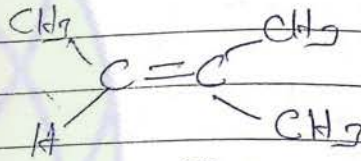
$CH_2=CH_2$ (a) $\propto H = 0$

$CH_3-CH=CH_2$ (b) $\propto H = 3$

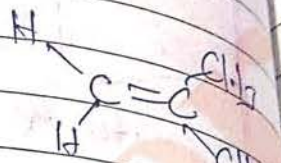
$CH_3-CH=CH-CH_3$ (Trans) (c) $\propto H = 6$



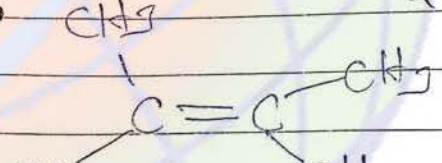
(d) $\propto H = 6$



(e) $\propto H = 9$



(f) $\propto H = 6$



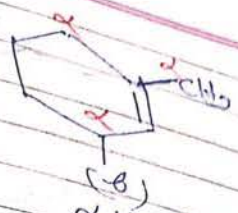
(g) $\propto H = 12$

Stability :- $g > e > f > c > d > b > a$

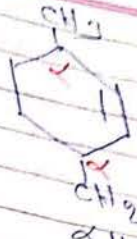
H.O.H $\rightarrow$ $g < e < f < c < d < b < a$

Conclusion:-
Generally on ↑ Increasing Substituent Stability ↓ double bond Increase.

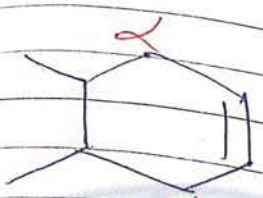
(a) $\alpha H = 10$



(b) $\alpha H = 6$



$\alpha H = 2$



$\alpha H = 4$

H.O.H order

$c > d > b > a$

Note → Three member cyclic ring is highly strained and External double bond make it more unstable.

Relatively Stable. (a)

Unstable (b)

H.O.H order

$a < b$

(b) Arrange these in H.O.H order.

a) $CH_2 = CH - CH_2 - CH = CH_2$

$\alpha H = 2$

(b) $CH_2 = C = CH - CH_3$ (Cumulated double

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Conjugated

(c) $CH_2=CH-CH=CH-CH_2$

(d) $CH_2=CH-CH_2-CH=CH-CH_2$

$b > a > d > c$

Note:-
Stability →

Conjugated > Isolated > Cumulated

Alternate double bond.

दोहरे Regular way नहीं है।

दोहरे आसपास

Resonance →

1) Heat of hydrogination (H.O.H) No. of C-H

सिद्धान्त केवल यह मात्र रखें कि H.O.H और यह stability के Inversely Proportional होता है।

लेकिन किसी -M Compound में सबसे पहले यह देखें कि कौन π-bond कितना है चूंकि π-bond के बढ़ने से H.O.H बढ़ता है।

H.O.C में -M एक कुल H.O.H के तरह ही है लेकिन H.O.C में π-bond कि जगह No. of Carbond atom देखते हैं।

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Heat of Combustion (Hoc)

i) It is the enthalpy change when one mole of compound is completely combusted (carbon in CO_2 and Hydrogen in H_2O)

ii) Generally combustion is exothermic process but few exceptions are present like combustion of Flourine (F_2) and N_2 are endothermic process.

iii)

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

1 mole $\quad x + \frac{y}{4}$ mole

1 vol $\quad x + \frac{y}{4}$ vol.

Calculate volume of air required for combustion of 10 litre of ethane.

C_2H_6 (g)

In air 20% oxygen

$$C_2H_6 + \frac{7}{2} O_2 \longrightarrow 2CO_2 + 3H_2O$$

10 L $\quad$ 35 L

20 L of O_2 $\longrightarrow$ 100 air

1 $\longrightarrow \frac{100}{20}$

$(100 \times 35 = 175 L)$

ii) H·O·C Increases with Increase in no. of carbon atom in case of Isomers. H·O·C ∝ Stability of molecule.

$$H.O.C \propto \text{No. of } C\text{-}H_\alpha$$

$$\propto \frac{1}{\text{Stability of molecule}} \quad \left(\text{No. of carbon same or Isomers}\right)$$

Ex-1) Arrange following in order of H·O·C ?

$CH_3-CH=CH_2$ $\propto H=3$ (a)

$CH_3-C(CH_3)=CH_2$ $\propto H=6$ (b)

$CH_3-C(CH_3)=C(CH_3)_2$ (c) $\propto H=6$

$CH_3-C(H)=C(H)-CH_3$ (d) $\propto H=6$

Order of H·O·C

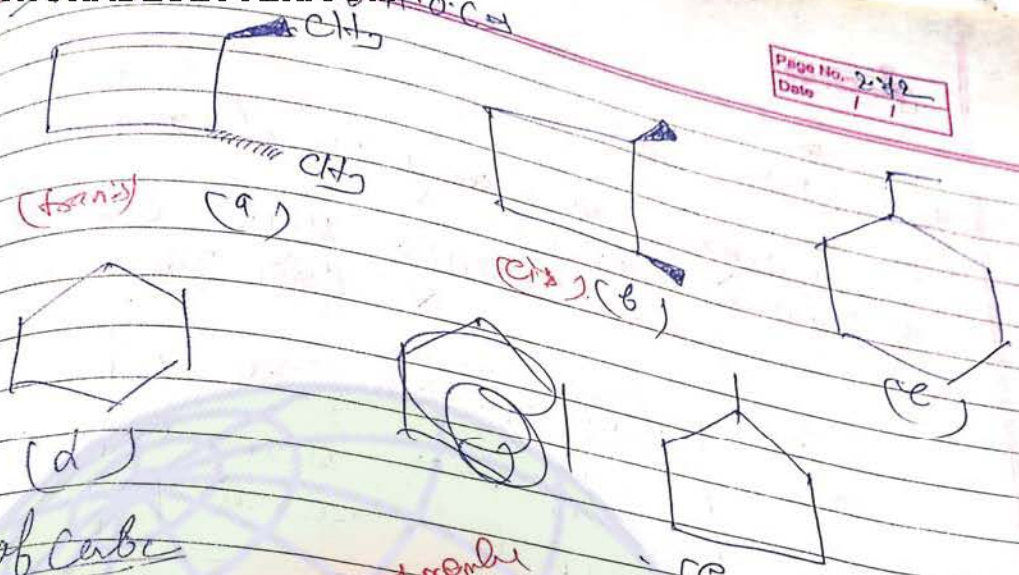
$c > d > b > a$

Stability ∝ 1/H·O·C ; No. of Carbon

i) No. of carbon same है तो Stability

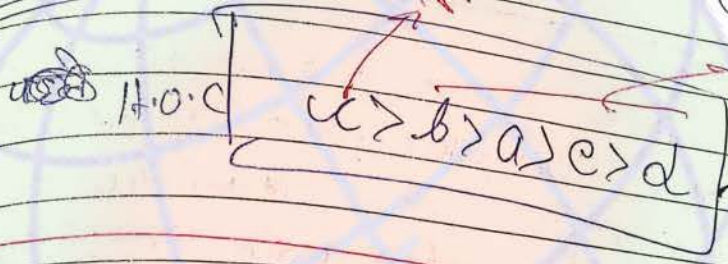
ii) अगर Stability भी same है तो Diversity Prop. से देखो पता करो

Stability of Compound ∝ No. of α-H



(a) (b) (c) (d) (e)

no of carbon

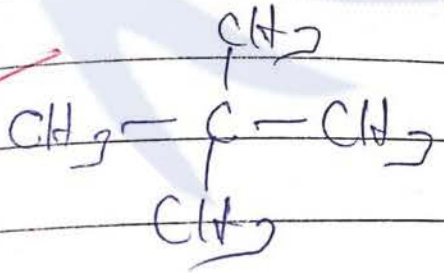


Number of carbon बढ़ने से H.O.C बढ़ता है।

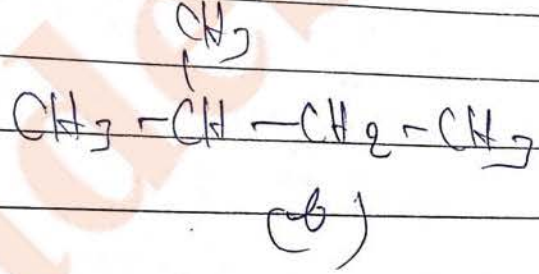
Note:-
Stability due to long size

c > b > a > e > d

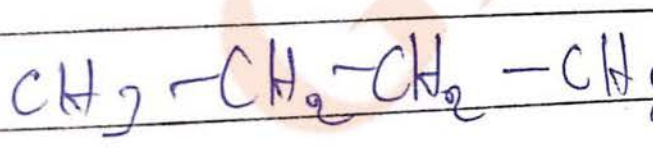
CH_4



neo-Pentane



n-Pentane



n-Pentane

H.O.C कम है।

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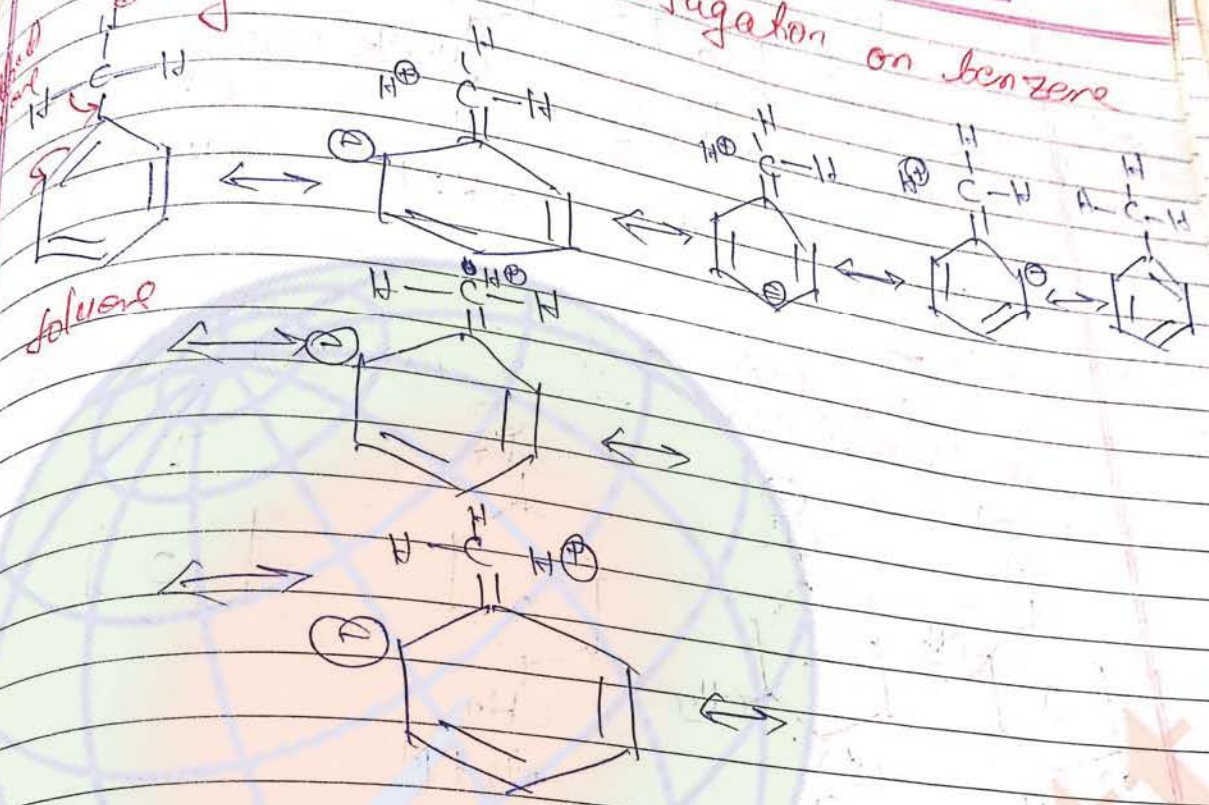
Note →
Important point

On Increasing branching in alkane Stability of alkane Increase
That is why H.O.C decrease (for Isomers.)

H.O.C order ⇒	c > b > a
Stability order ⇒	a > b > c
Boiling point	c > b > a

Note →
On Increasing branching surface area decrease. Hence Intermolecular vanderwaal attraction force also decrease. Due to this reason boiling point decreases on branching in case of Isomer.
अगर अधिक branching होती है तो molecule compact होगा।

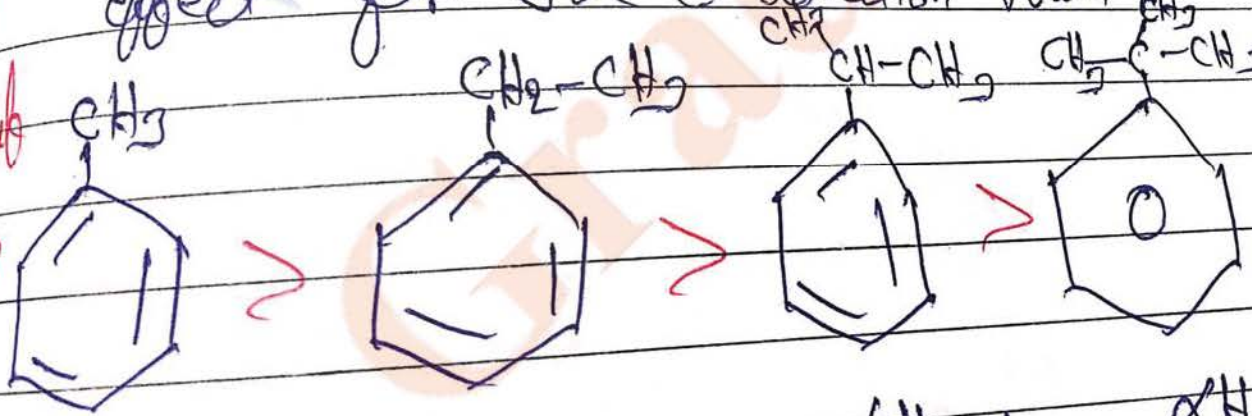
Effect of Hyperconjugation on benzene ring



Toluene

i) Alkyl group attached to benzene ring increase e⁻ density by hyperconjugation that is why activating and o-P directing.

ii) Hyper conjugation dominate over Inductive effect for the e⁻ donation power



Activating power

$\alpha H = 3$ $\alpha H = 2$ $\alpha H = 1$ $\alpha H = 0$

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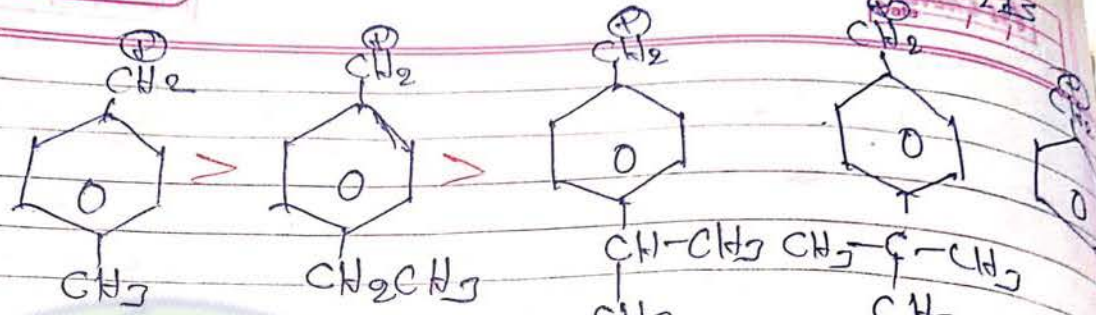
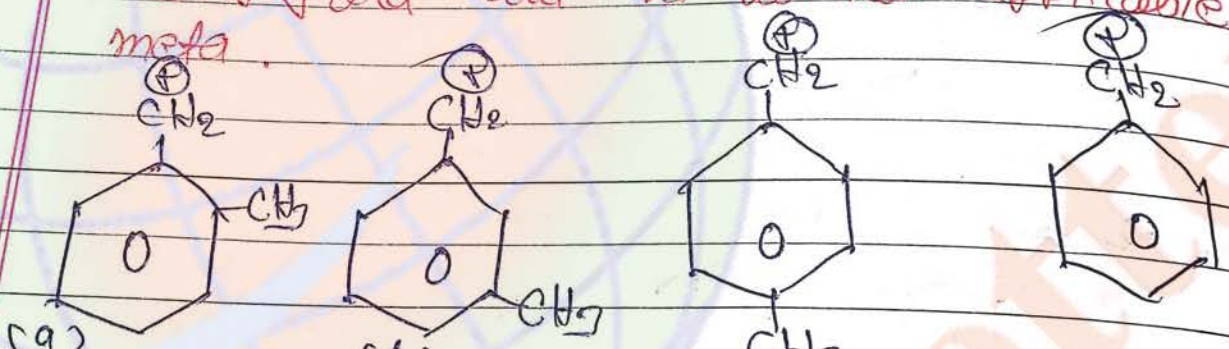
Stability of benzyl carbocation



$\alpha H = 3$ $\alpha H = 2$ $\alpha H = 1$ $\alpha H = 0$

(a) Note → Hyperconjugate effect is same at ortho and para but it do not applicable on meta.



(a) $+I, +H$ (b) $+I$ $+I, +H$

$a > c > b > d$

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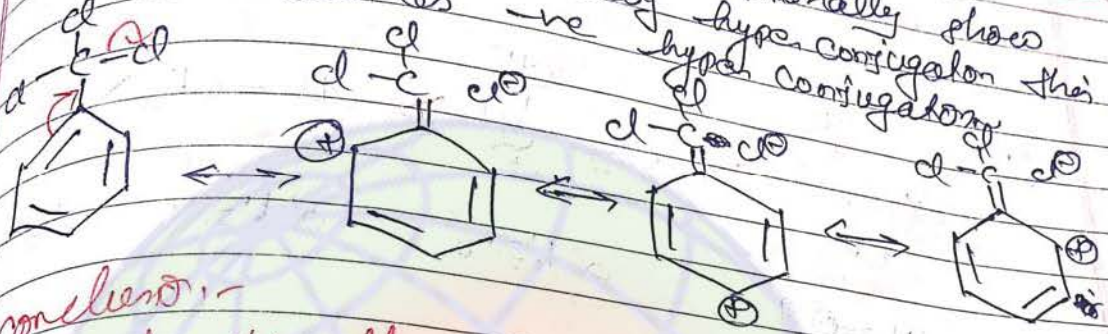
-ve Hyper Conjugation of "$-CX_3$" → (α_6-H effect)

Carbon halogen bond exceptionally shows e^- withdrawing power by hyper conjugation this is known as -ve hyper conjugation



conclusion:-
Due to this effect $-CX_3$ is deactivating and meta directing with resp. to E.A.S reaction of benzene

Stability of Intermediate:-

Stability of carbocation and free radical $\propto$ +H, +I, +M

Stability of carbanion $\propto$ -I, -H, -M

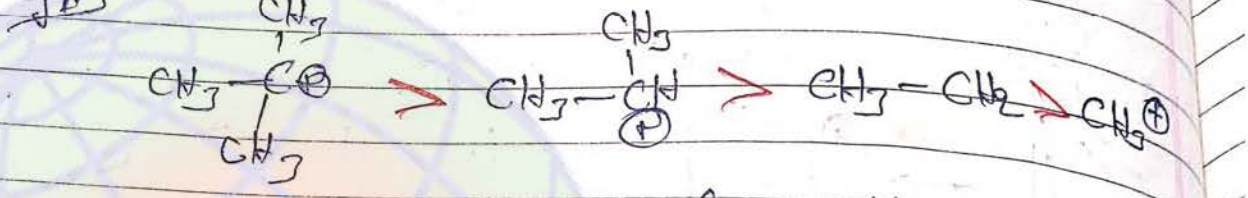
Note:-

not

Note →

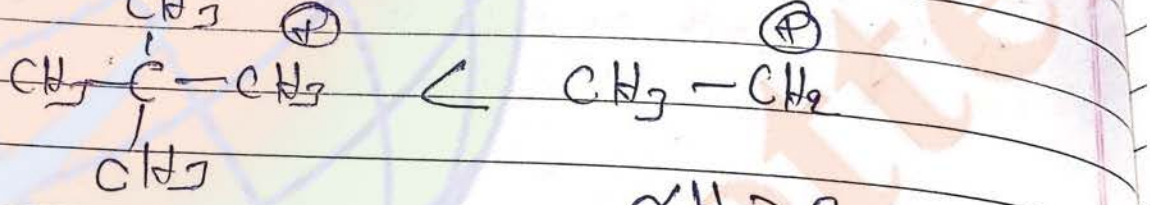
+H effect C-H bond is not applicable in case of open chain carbanion

eg 1)



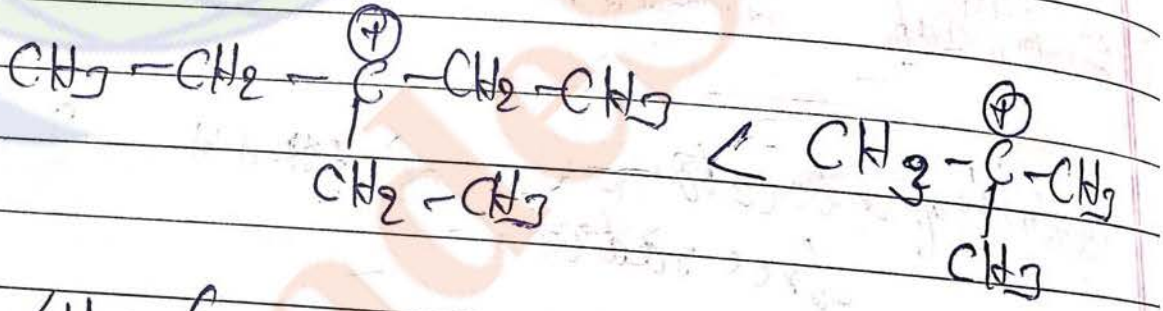
$\alpha H = 9$ $\alpha H = 6$ $\alpha H = 3$ $\alpha H = 0$

eg 2)



$\alpha H = 0$ $\alpha H = 3$

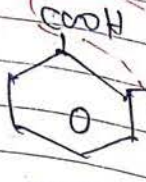
eg 3)

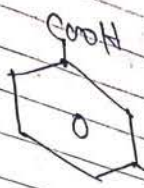


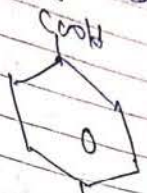
$\alpha H = 6$ $\alpha H = 9$.

Arrange bracket this according to properties given in


(a)

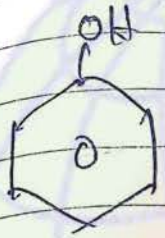

(b)

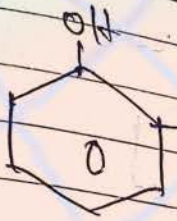


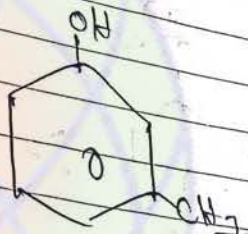


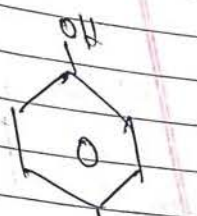
(Acidic strength)

Acidic strength:-
b > a > c > d

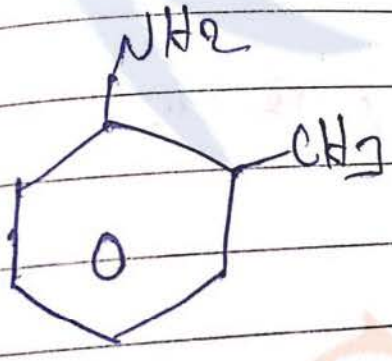

a)

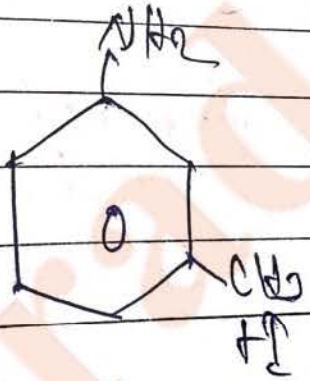

(b)

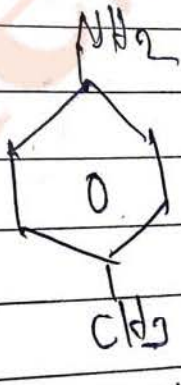

(c)

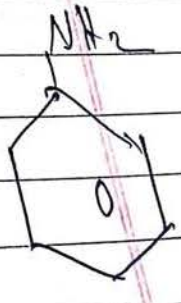

(d)

Acidic strength
a > c > d > b


(a)


(b)


(c)


d

Base strength
c > b > d > a

1st Choice

due to SIR-basic strength increase.

(COOH और NR_2 के case में -SIR effect की strength ज्यादा होती है।)

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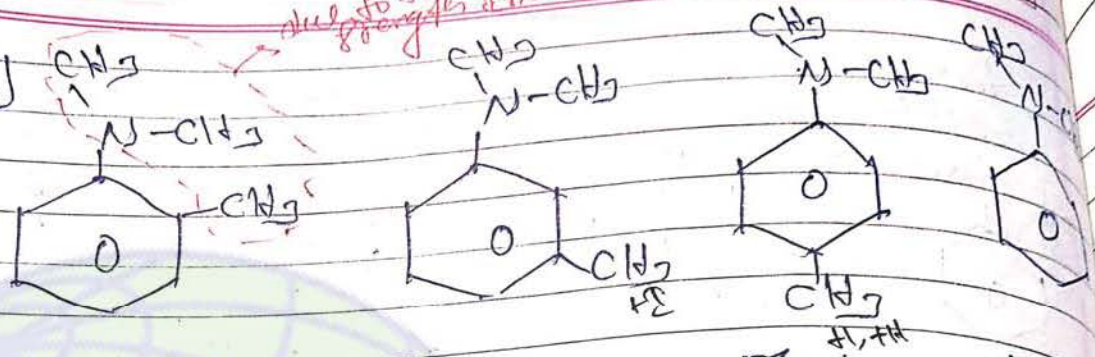
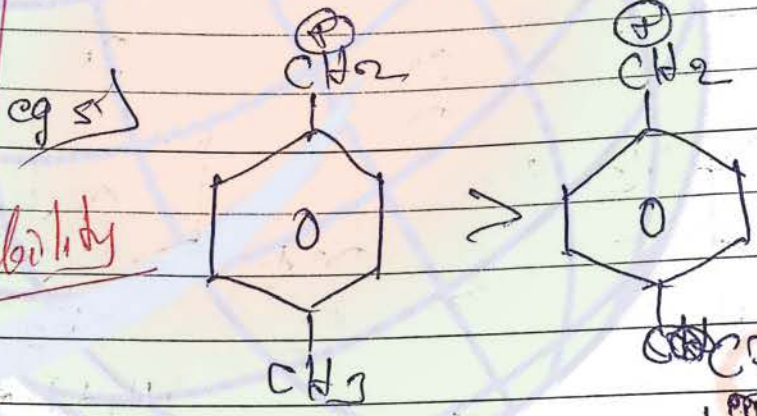
eg 4]



(a) (b) (c) (d)

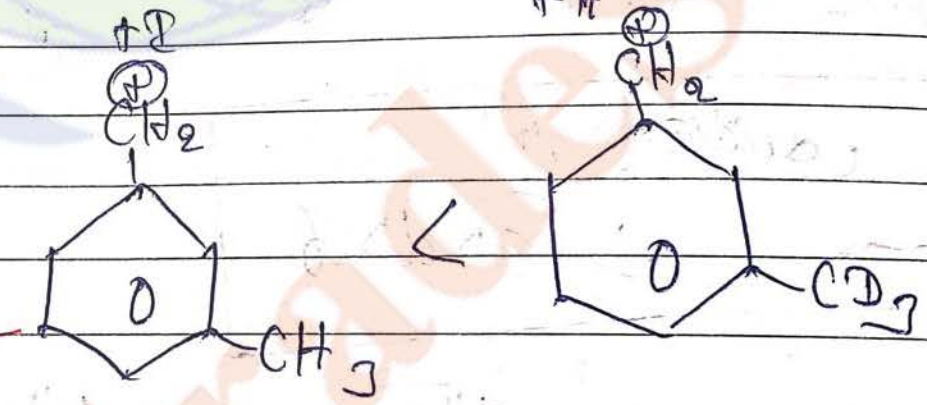
Basic strength
a > c > b > d

eg 5]



Reactivity

eg 6]



Stability

(H effect not applicable in meta.)

1st choice

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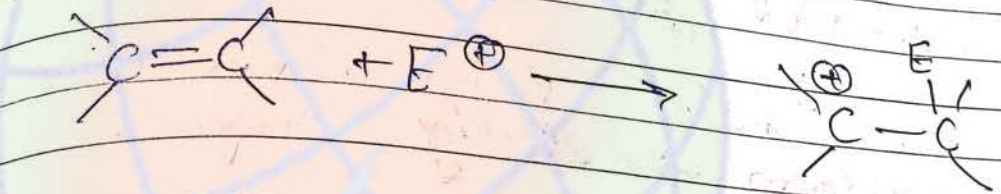
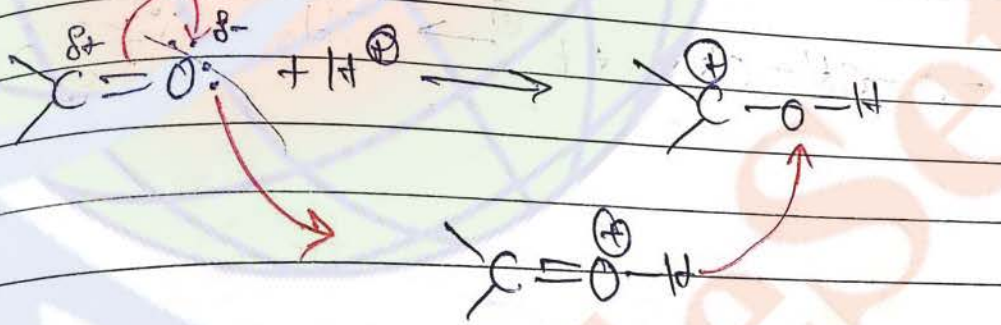
Electromeric effect (E effect) →

This is temporary effect which is observed only in presence of attacking reagent.

a) +E effect

This effect is observed in presence of electrophile and π-e⁻ move toward the atom where the electrophile attached.



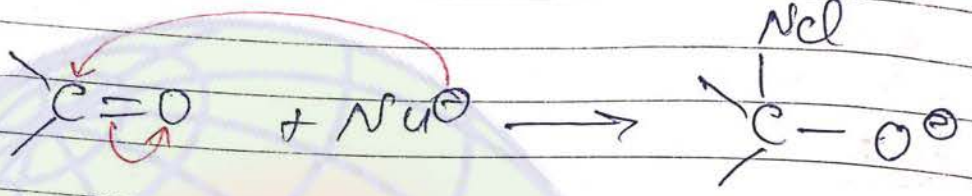


Note →

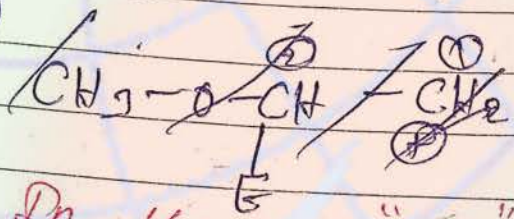
(*) Protonation of carbonyl group Increase electrophilicity of carbonyl carbon.

2) -E effect

— This is in the presence of of Nucleophile ($Nu^{\ominus}$)



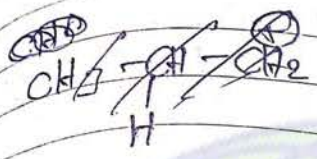
(a)



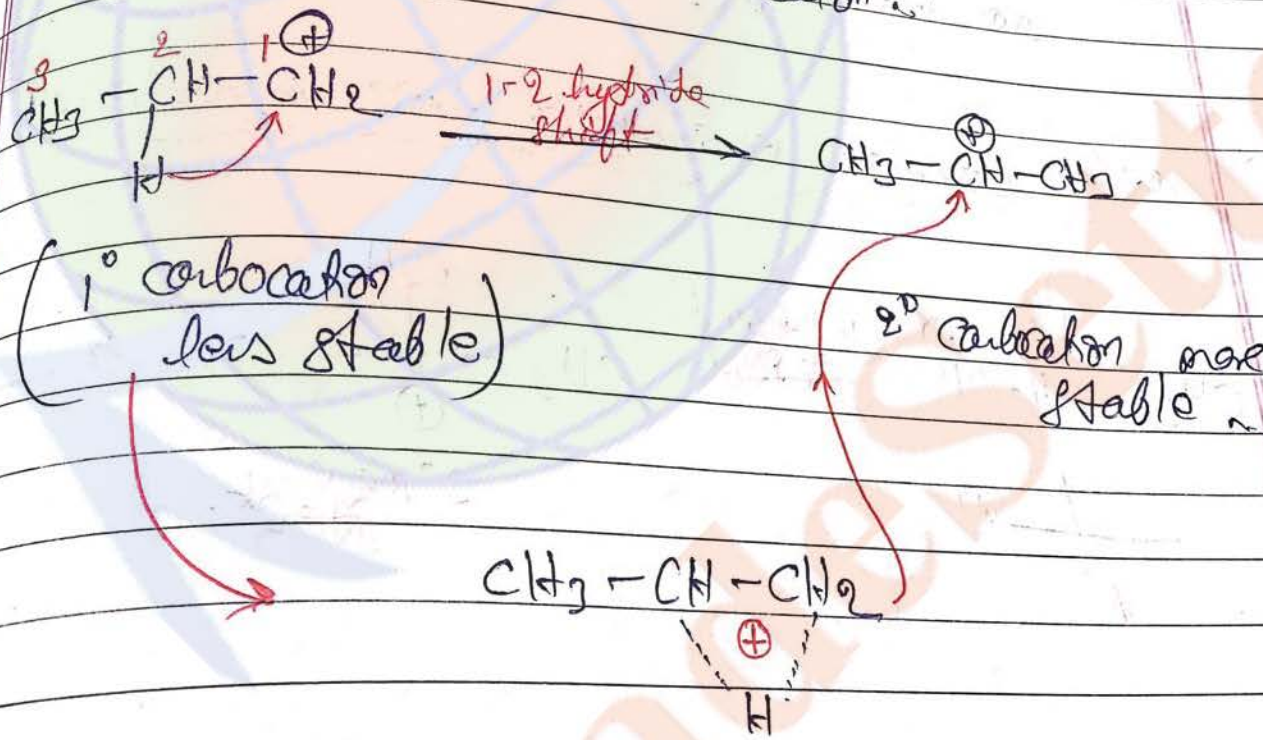
In this case "e⁻" transfered to the opp. direction to the attacking reagent.

(b) $CH_3-O-CH-CH_2 + E^{\oplus} \longrightarrow CH_3-\ddot{O}-CH-CH_2$ ($\oplus$ on CH, E on CH_2)

Re-arrangement of carbocation →



1) If transfer of ~~carbocation~~ a group from adjacent carbon makes more stable carbocation than this process is known as Re-arrangement of carbocation.



Three member cyclic transition state (TMCTS)

2) This is spontaneous and exothermic process

3) This occurs by formation of three membered cyclic transition state that is why re-arrangement is always 1,2-shift.

4) Re-arrangement can occur in any number but each time new carbocation should be more stable and each time 1-2 shift only.

Imp

Other common examples of rearrangements

1) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\oplus}{CH}}-CH$ —(1-2 hydride shift)→ $CH_3-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_3$ or

$\overset{\oplus}{|}$

2° → 3° more stable.

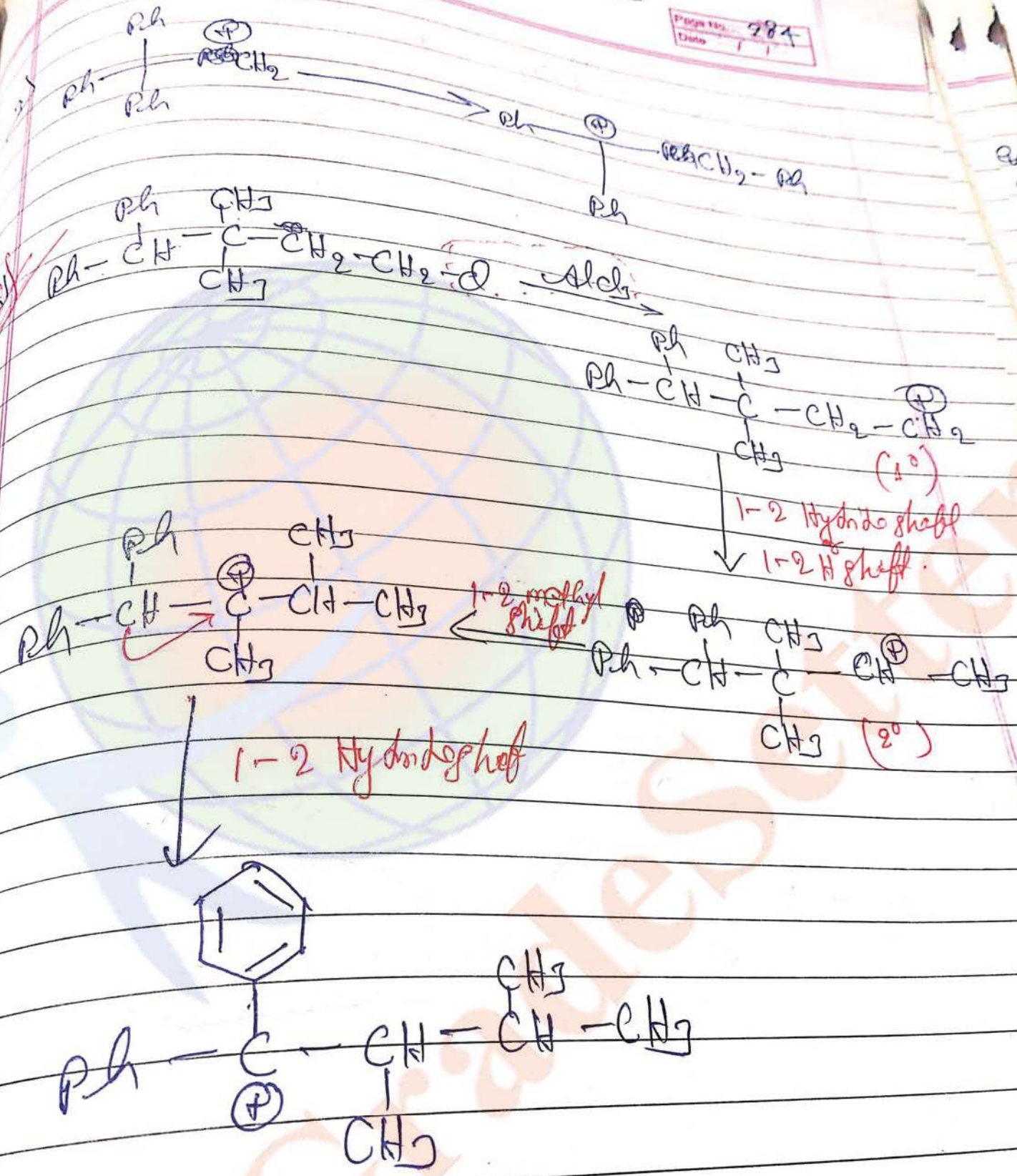
2) $\overset{\oplus}{|}$ or $CH_3-\overset{\overset{CH_3}{|}}{\underset{CH_3}{C}}-\overset{\oplus}{CH_2}$ —(1-2 methyl shift)→ $CH_3-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_2-CH_3$

1° → 3° or

neo-Pentyl carbocation.

$\overset{\oplus}{|}$

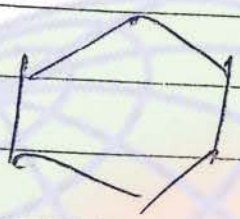
tertiary Pentyl



1st Choice

Pa
Da

of which of the following can rearrange



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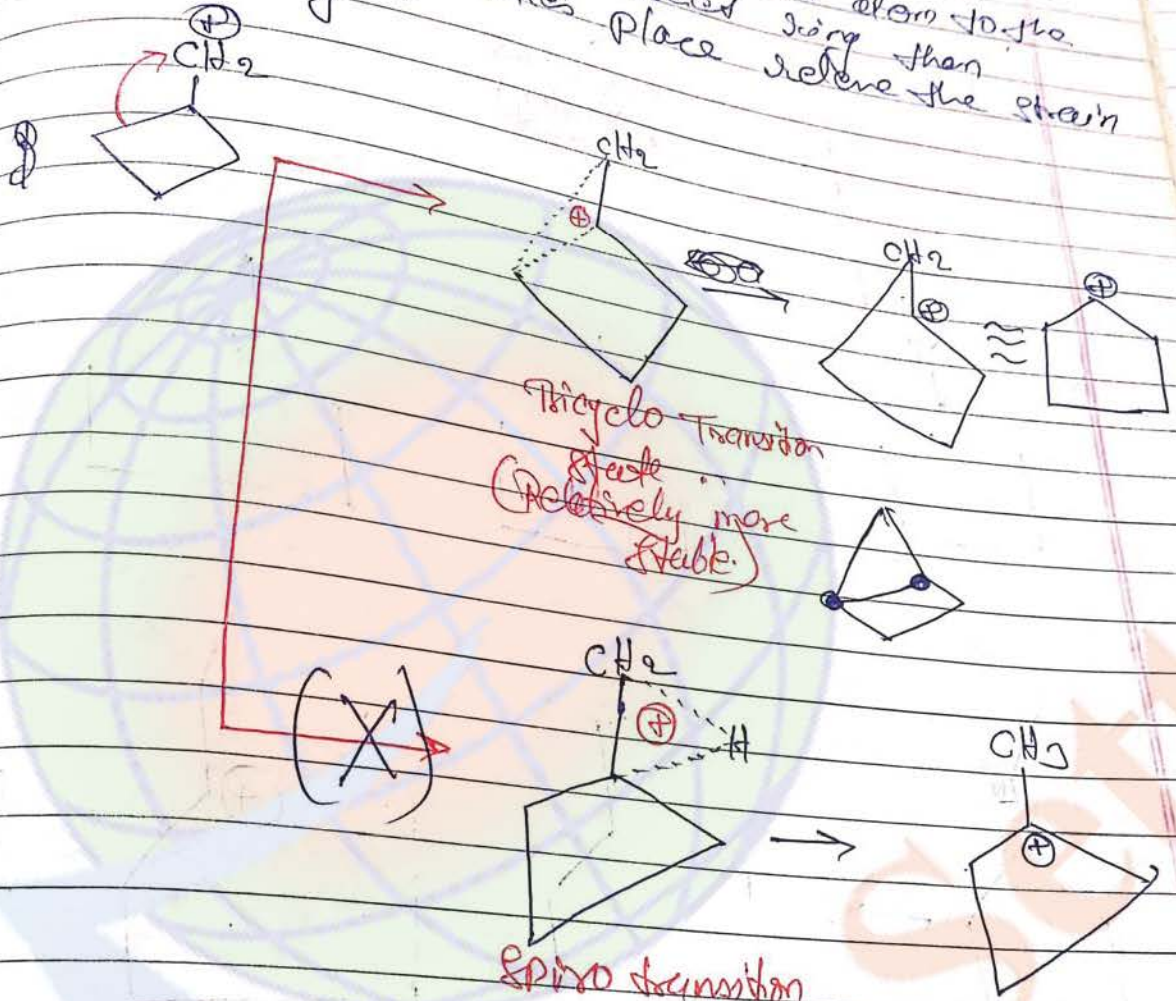
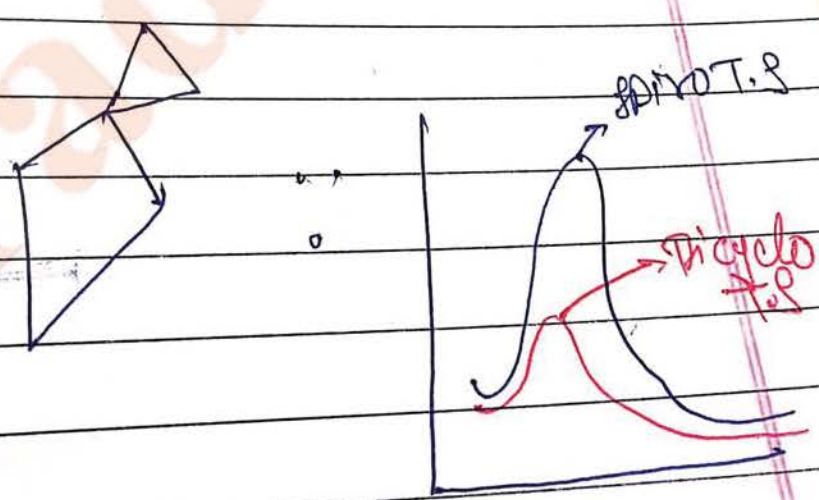
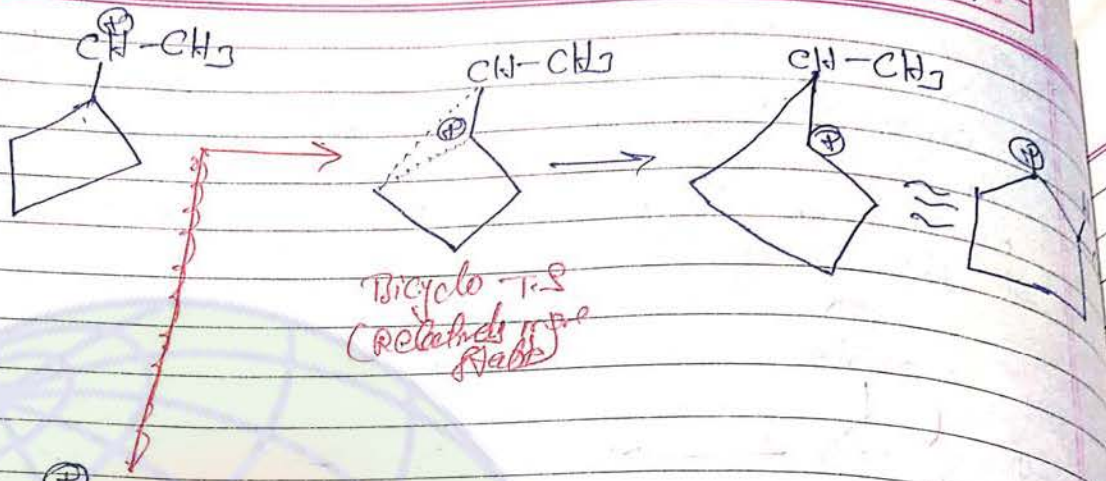
Ring Enlargement of Rearrangement

If carbocation is present at adjacent atom to the five membered ring then extension of ring takes place relieve the strain in the ring.



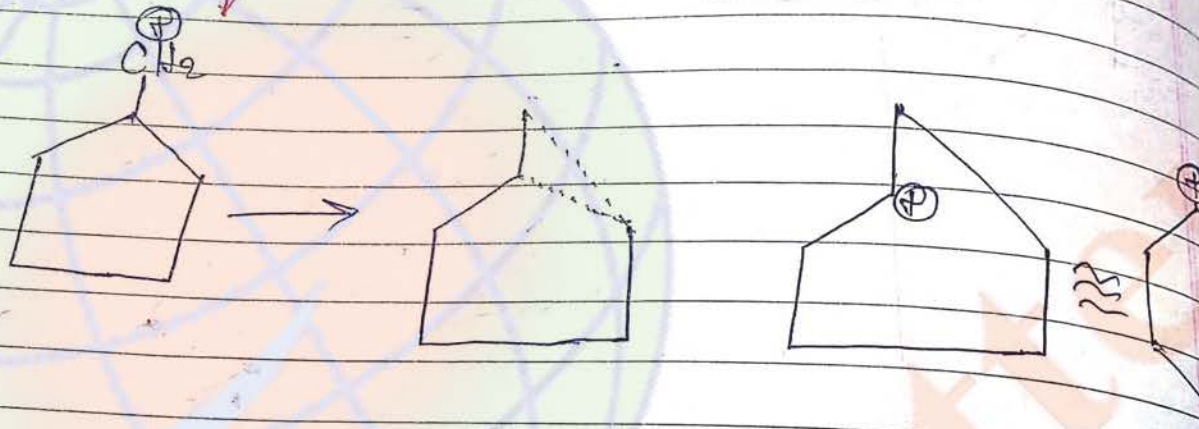


eg 1.

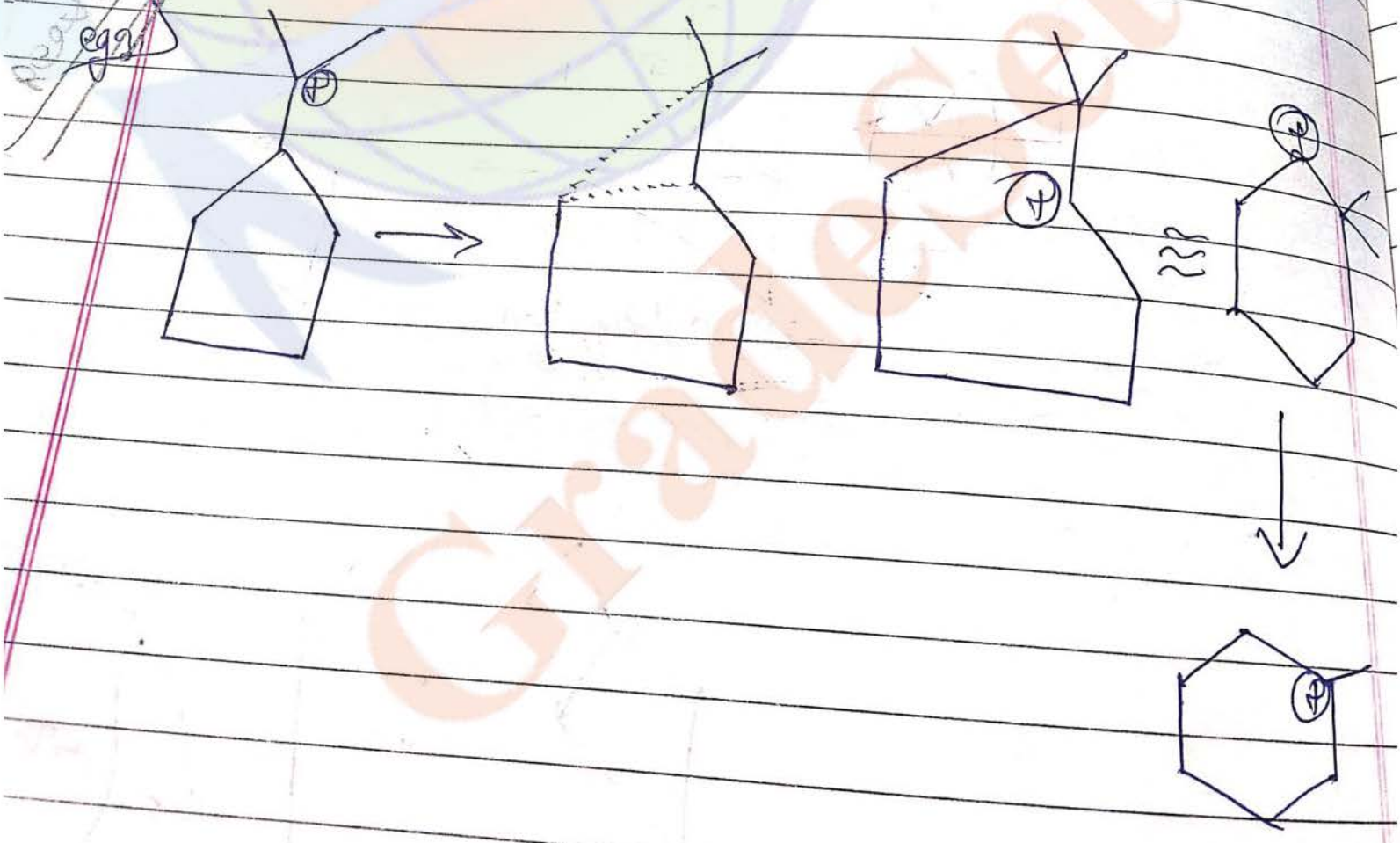


Bicyclo 1.2
(Reactivity type
Rabi)

eg 2



eg 3



1st Choice

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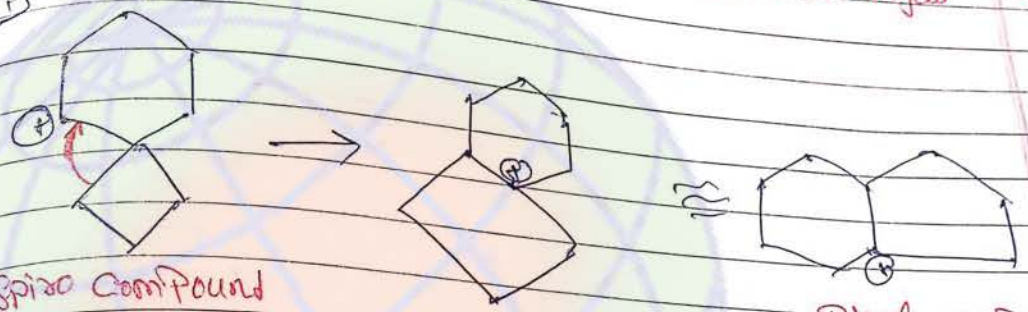
Other examples

If the charge is present outside a spiro ring then expansion in the case leads to bicyclo carbocation

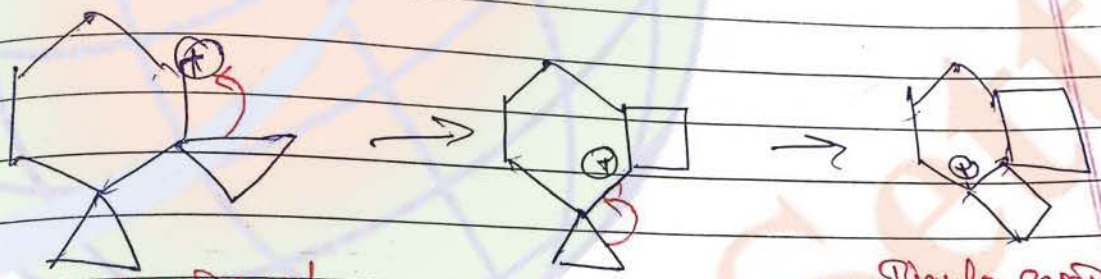
Eg.1)



Spiro Compound

Bicyclo Compound

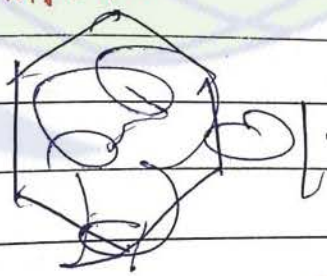
Eg.2)



Spiro Compound

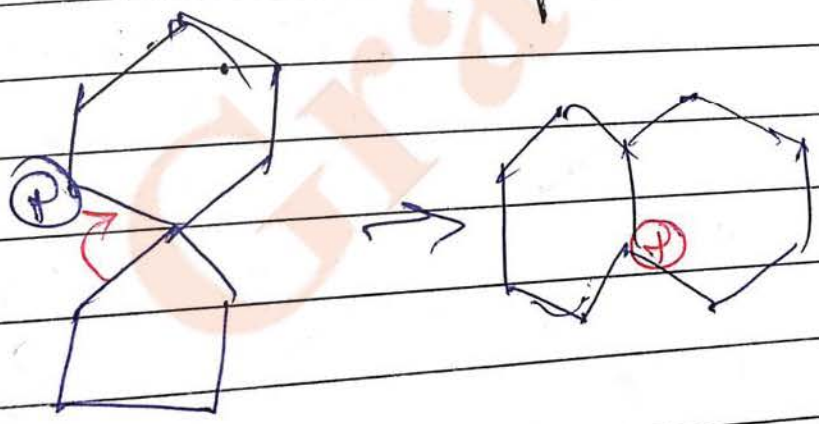
Bicyclo Compound

Eg.3)

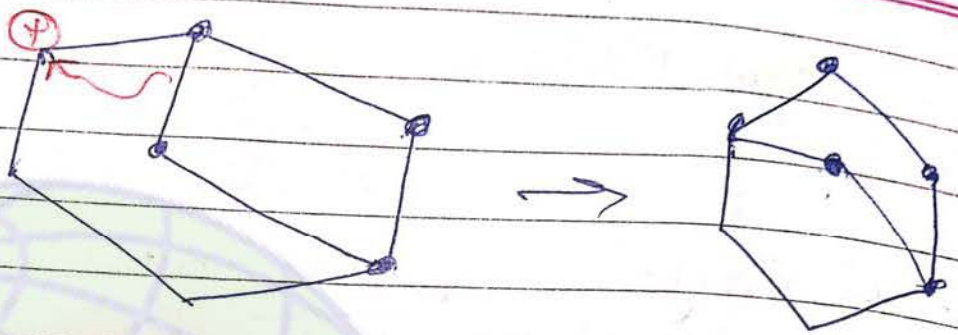


नोट:- यदि spiro point (nearest) पर finally the charge आता है और उसके कारण Compound का एक bonded ring का the charge के पास से जाकर मिल जाता है।

Eg.4)



Eg 1)



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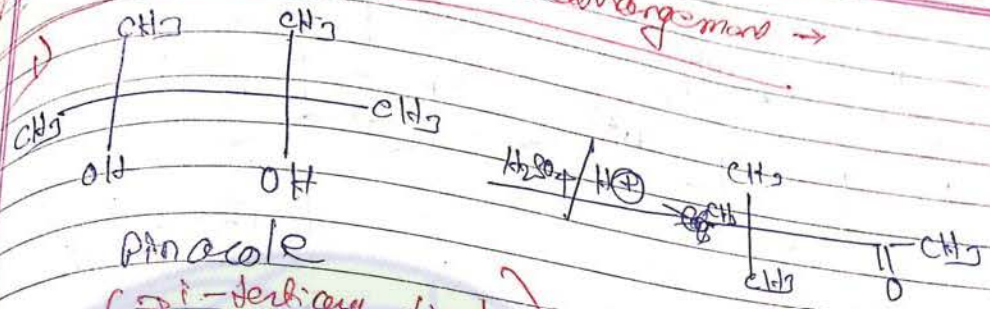
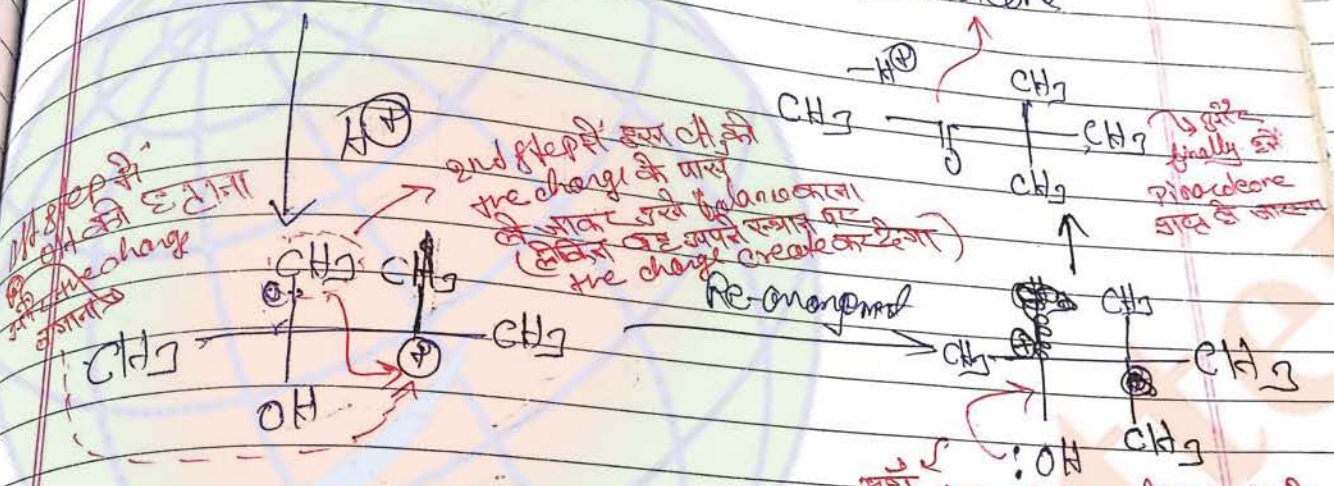
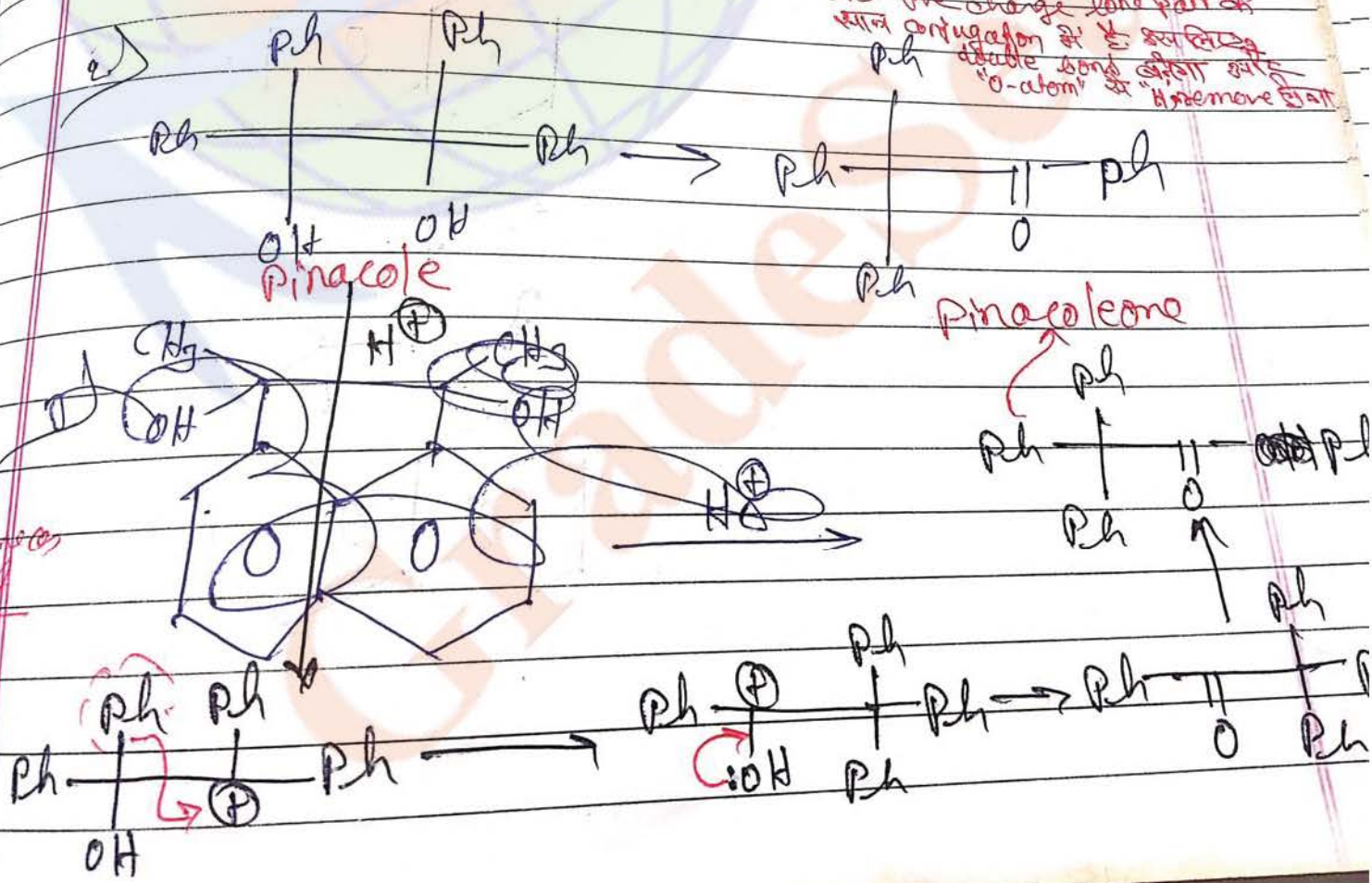
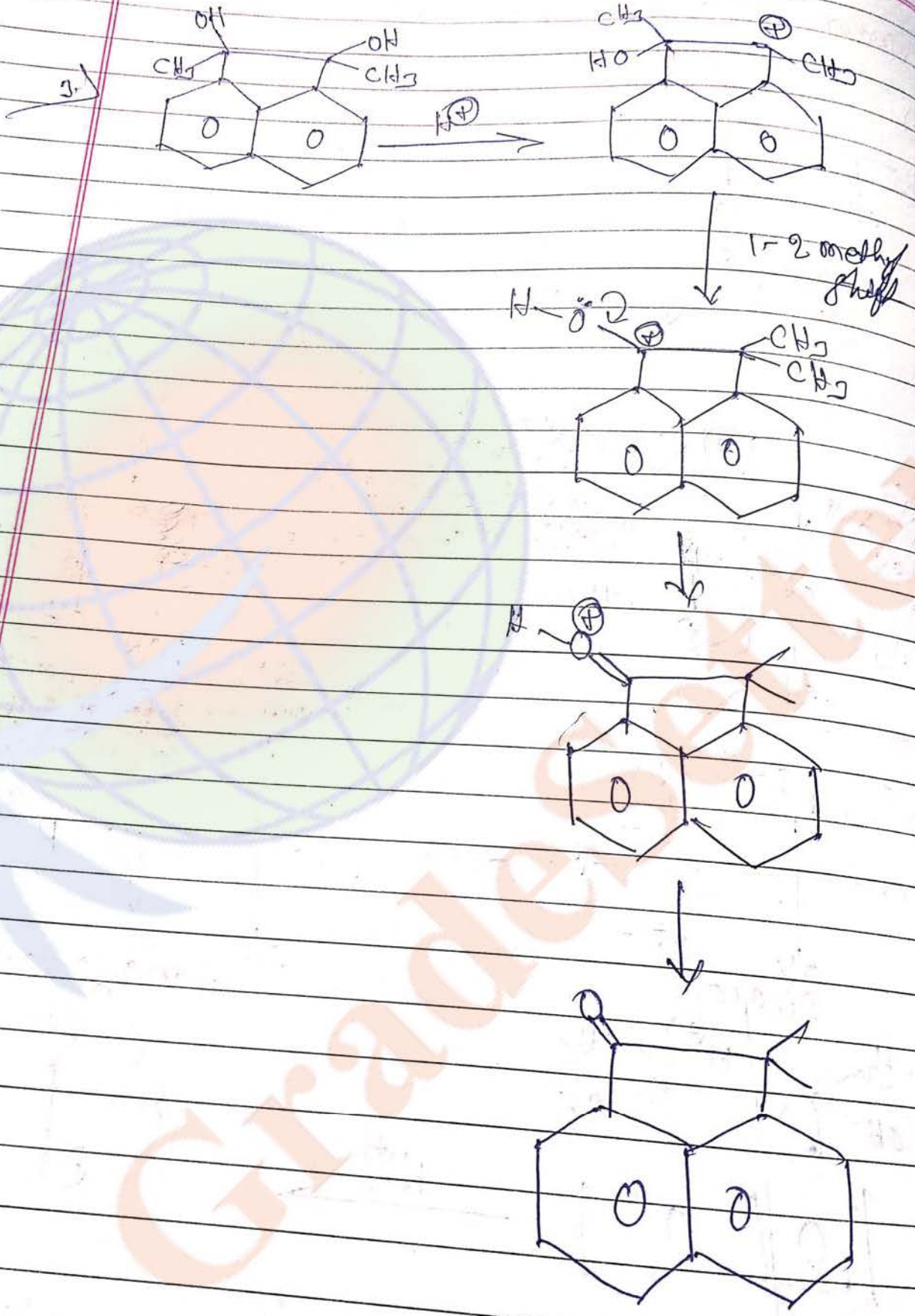
Pinacol - Pinacole Rearrangement →





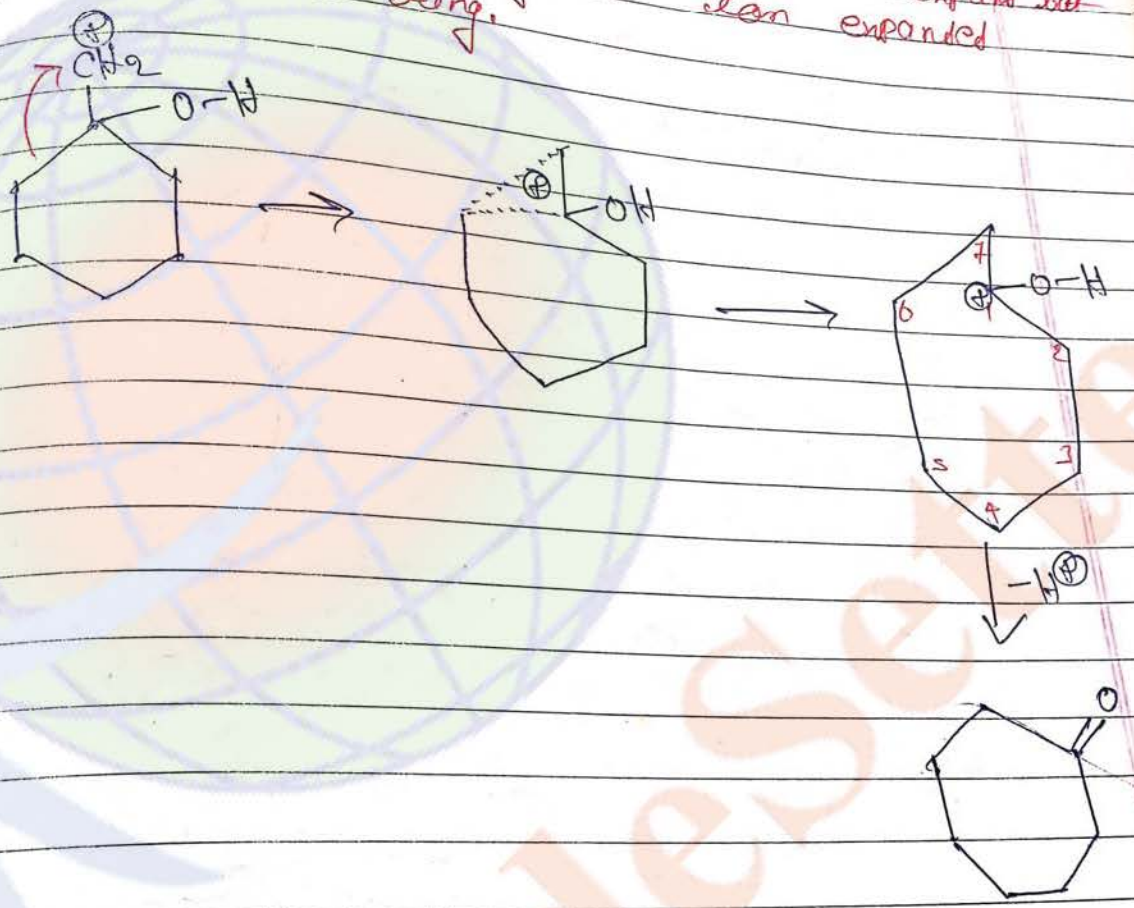




Note:

1) Whenever the charge is present on to carbon which is attached to OH then finally OH group convert into carbonyl group.

2) Generally "6" member ring do not expand but this type of de-arrangement can expanded six-membered ring.



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migratory group Aptitude (शिफ्ट की tendency) →

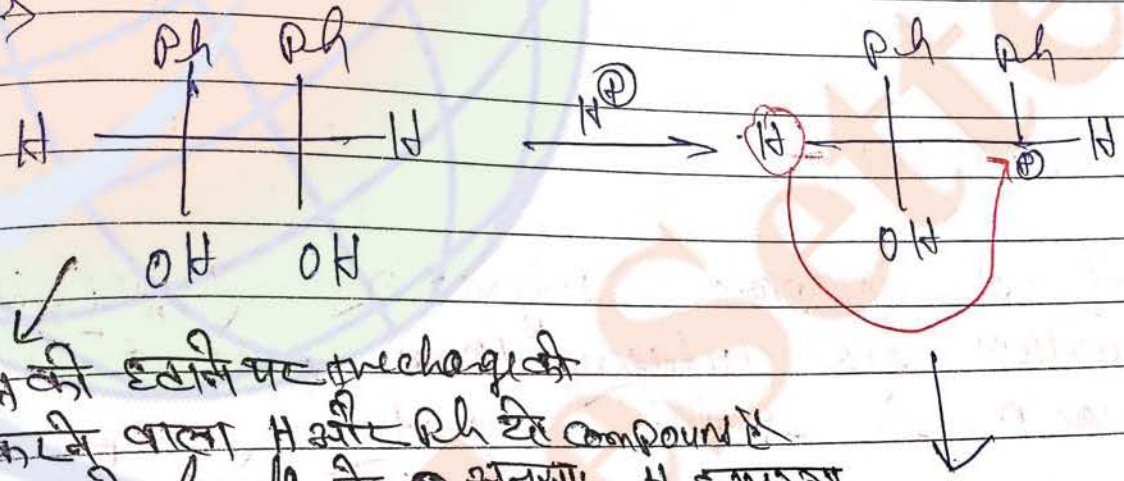
In case of Heteroatom resonance transfering group ei decide by tendency to leave. (Not on the basic of neo carbocation.

⇒ migratory group aptitude

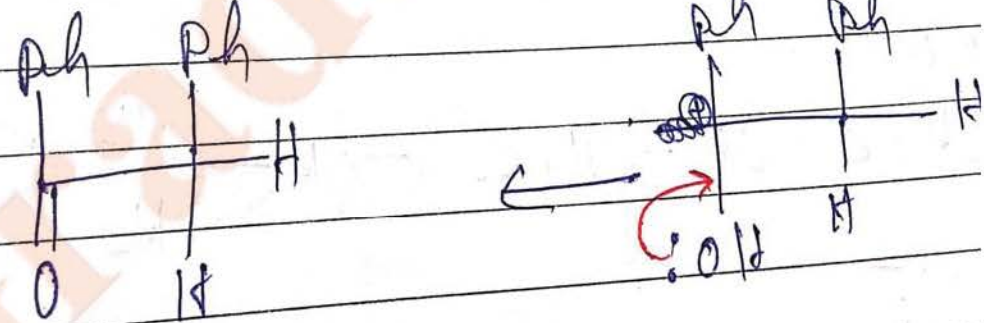
$H^{\ominus} > Ar > -R > -Ph$

(Ar → Aromatic, R → Alkyl, Ph → phenyl)

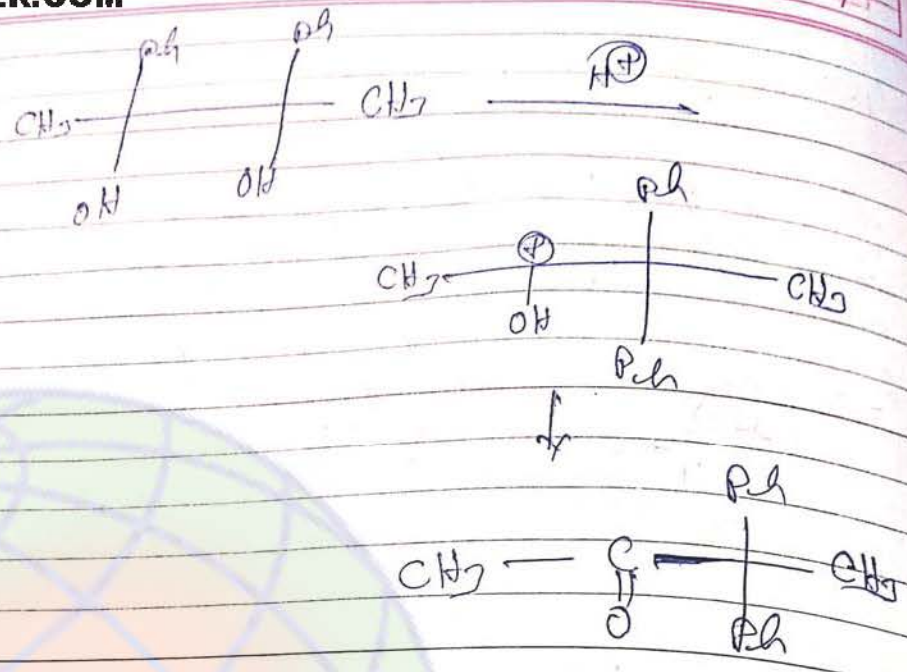
eg:-



यहाँ OH की इलेक्ट्रॉन पर charge को balance करने वाला H और Ph ये compound में लेकिन ऊपर वाले formula के अनुसार H इलेक्ट्रॉन



eg:-



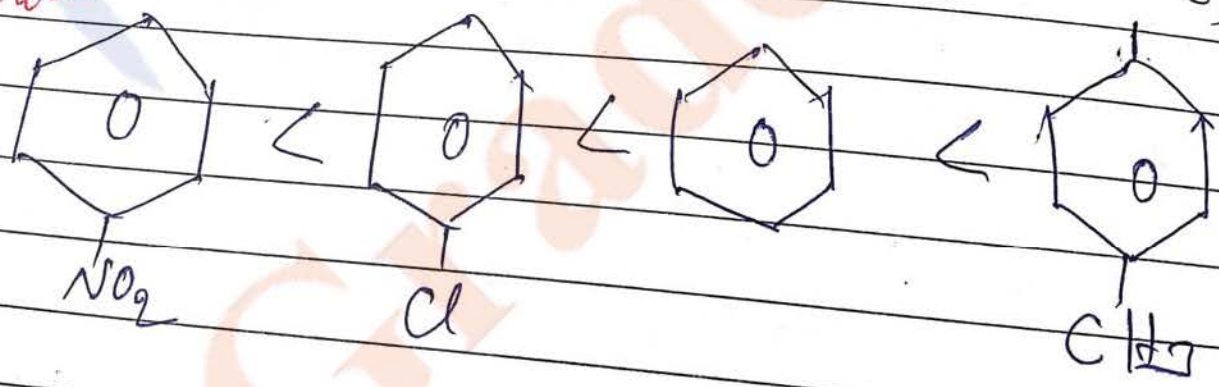
Imp. Point ⇒

If we compare migratory group, aptitude within one category than more e⁻ releasing group is better migratory group.

Alkyl group:-

$-CH_3 < -CH_2-CH_3 < -CH(CH_3)_2 < -C(CH_3)_3$

Aryl group:-



migrator group aptitude

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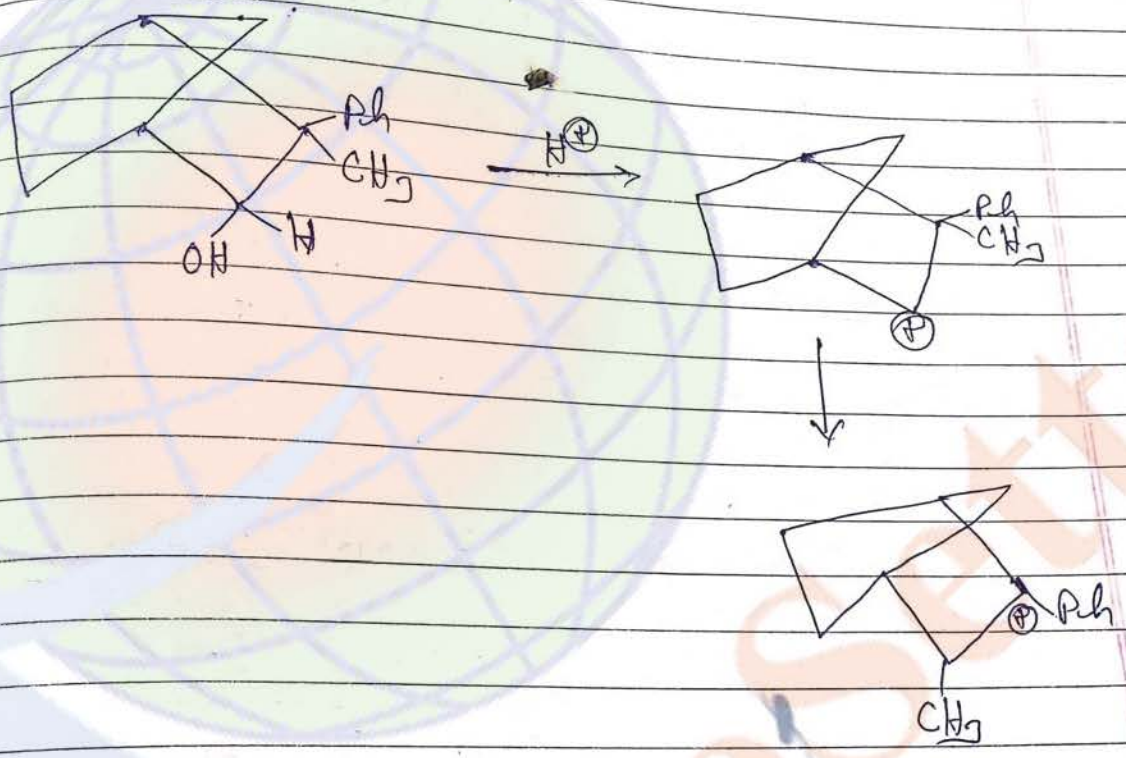
Note →

migratory group aptitude should be checked in case of heteroatom resonance otherwise formation of more stable carbocation is preferred.



Note

migrator group ↓

$H^- > Ph^- > 3^\circ R^- > 2^\circ R^- > 1^\circ R^- > Me^-$

1st Choice

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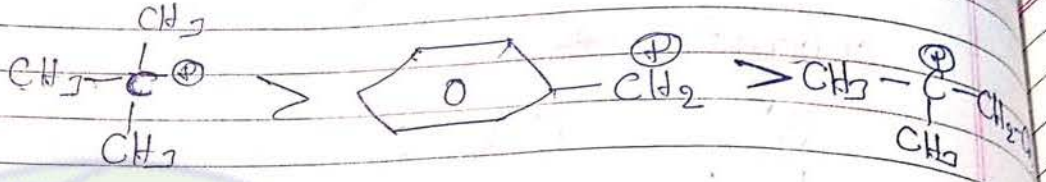
Exceptional Note:-



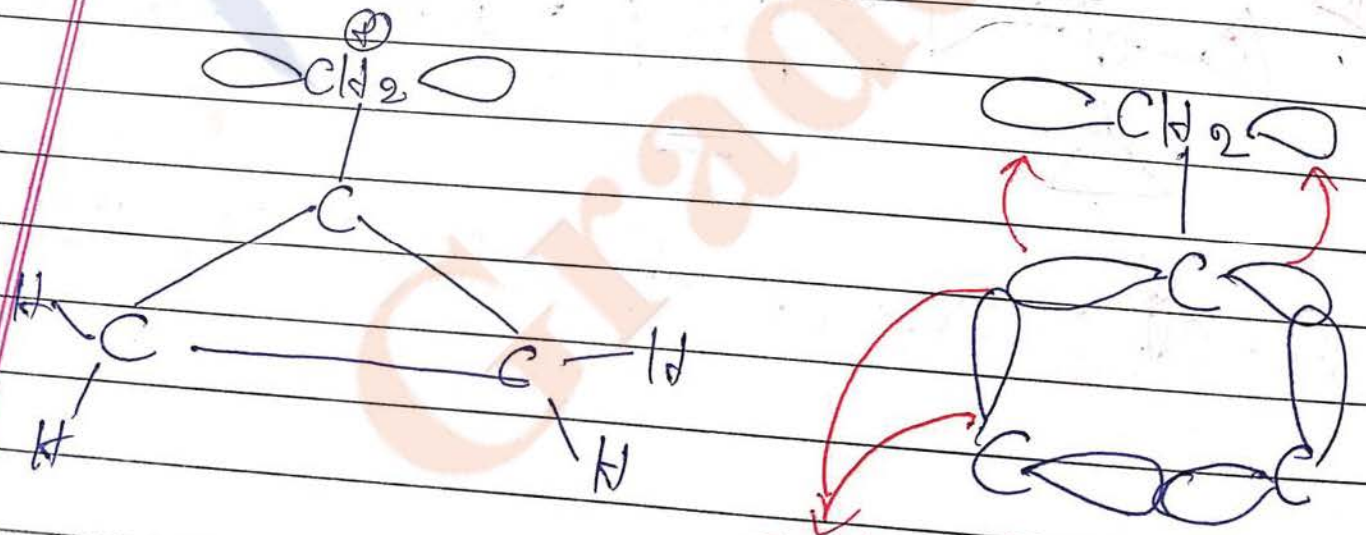
Greater than

3° H

Tertiary butyl carbocation in gaseous phase is more stable than benzyl carbocation

Exceptional stability of cyclopropyl carbocation is due to "dancing orbital" resonance which is present b/w vacant orbital of carbocation and sp^2 hybrid orbital carbon atom present in the ring.

overlaping b/w C-C in the ring is bent overlaping (less overlaping)



Bent overlaping

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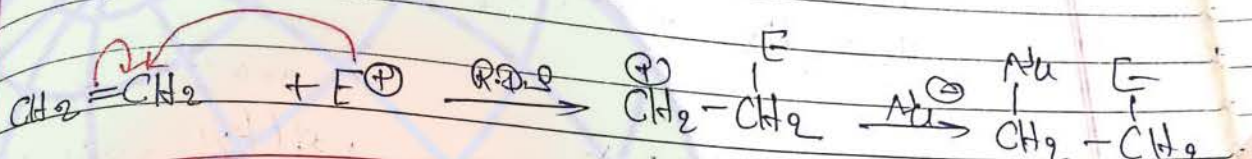
Type of Chemical reactions :-

1. Addition Reaction →

These reaction's in which one π-bond break's to form two new "σ-bonds".
eg :-

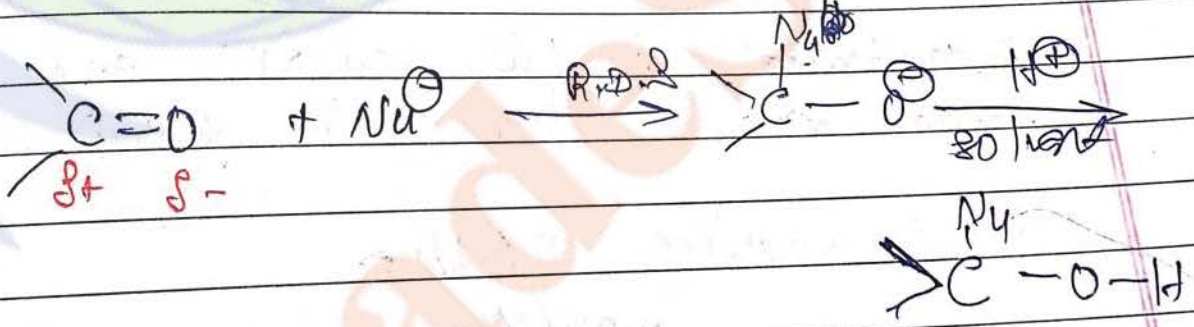
A) Electrophilic addition reaction -



* Rate of reaction ∝ Stability of carbocation
1° < 2° < 3°

It is main reaction of Alkene & Alkyne.

B) Nucleophilic addition :-

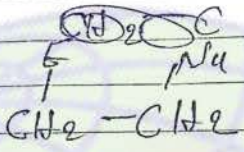


It is Nucleophilic addition ∝ -I, -M, -H
It is main reaction of carbonyl compound

2) Elimination

In this two σ-bond breaks to form 1 new π bond. This endothermic reaction.

Dehydrohalogenation



$CH_2-CH_2 \longrightarrow CH_2=CH_2 + E-Nu$

Reactant I

E = H Nu = X Alkyl halide

E = H Nu = OH Alcohol

E = X Nu = X Dihalide

3) Substitution reaction:

In this reaction one group replace other group

A) Electrophilic substitution

(See page (one copy) ⇒ 71)

Nucleophilic Substitution Reaction :-

$$R-G + Nu^{\ominus} \longrightarrow R-Nu + G^{\ominus}$$

(leaving group)

$G \Rightarrow -X, -OH$

Rate of reaction ∝ Nucleophile Strength of $Nu^{\ominus}$
∝ Ability of leaving group
∝ Stability of anion
∝ $\frac{1}{\text{Basicity}}$

Carboxylic acid derivative :-

$$R-\overset{\overset{O}{\|}}{C}-G + Nu^{\ominus} \longrightarrow R-\overset{\overset{O}{\|}}{C}-Nu + G^{\ominus}$$

Re-arrangement reaction :-

Nucleophilicity ∝ tendency to donate e^- ∝ $\frac{1}{\text{Stability of Anion}}$

leaving group ∝ Stability of anion

leaving group ability :- $F^{\ominus} < Cl^{\ominus} < Br^{\ominus} < I^{\ominus}$

$CH_3SO_3^{\ominus} < CF_3SO_3^{\ominus}$

1st Choice

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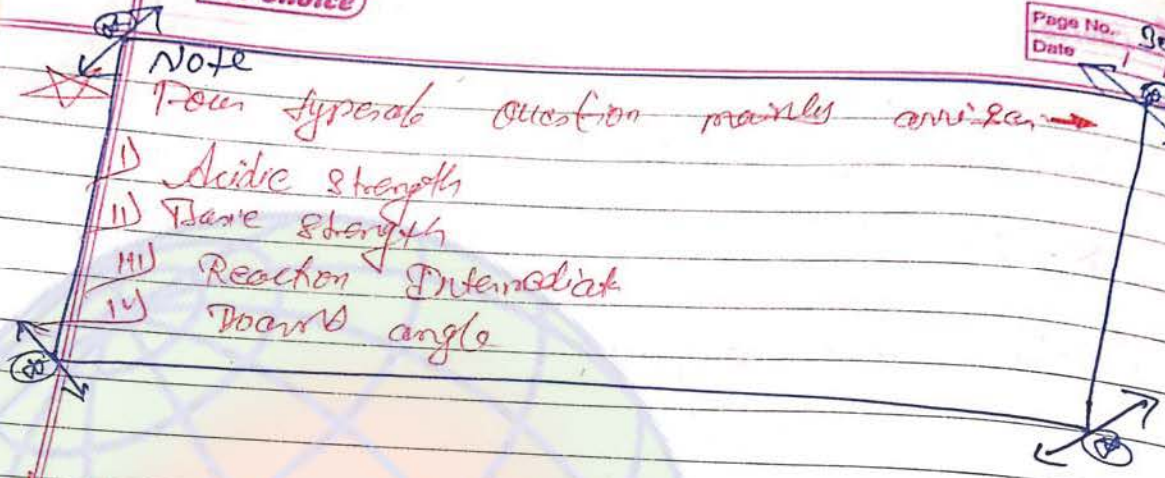
Note
Four typical question mainly arise →

i) Acidic strength
ii) Basic strength
iii) Reaction Intermediate
iv) Bond angle



4) Re-arrangement reaction →

In these reaction atom's change their position and Isomer is formed.

1st Choice

Isomerism (TFmCP)

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Those compounds which have same molecular formula but have either different connectivity of atoms (Structural Isomers) or different spatial arrangement (stereo Isomers)

Type of Isomerism

- Structural Isomers or Constitutional
  - chain Isomers
  - Position Isomers
  - Ring chain Isomers
  - Functional group Isomers
  - metamerism
  - Tautomerism
- Stereo Isomers
  - Conformational Isomers
    - optical Isomers
  - Configurational Isomers
    - optical Isomers
    - Geometrical Isomers

(*) Structural Isomerism →

1) chain Isomerism →

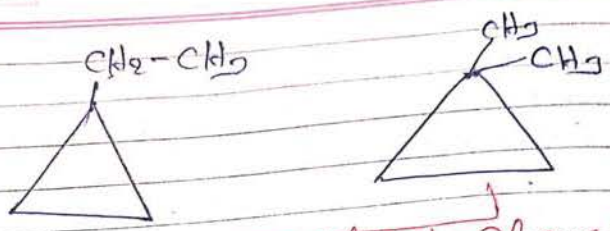
Those Isomers in which number of carbon is different in either :-

i) Parent chain or
ii) Side chain

$CH_3-CH_2-CH_2-CH_3$
(Butane)

$CH_3-CH(CH_3)-CH_3$
Iso-butane

Diff Parent chain so chain Isomer



Diff side chain in chain Isomer.

2.) Position Isomerism →

Those Isomers in which position of side chain (substituent) or functional group or unsaturation

Note:→

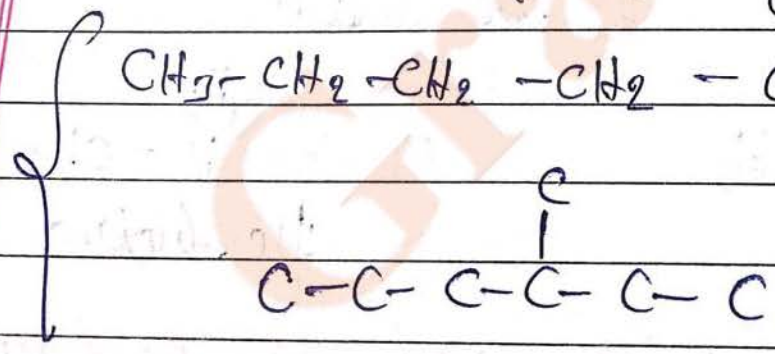
(i) check they should not be position

Notes:→ (i) It check they should not be chain Isomer.

(ii) Diff position of terminating function group & different then Isomers is known as ~~position Isomer~~ chain Isomer's.

position

P.I



1st Choice

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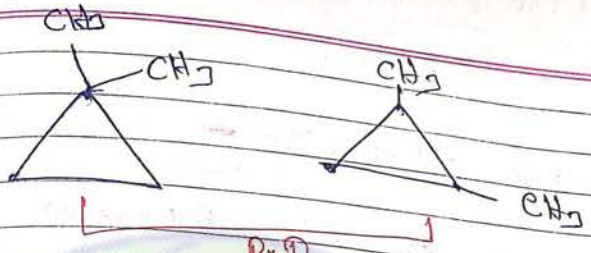
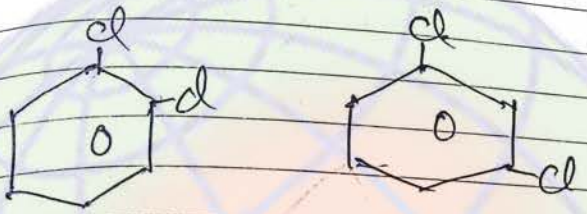
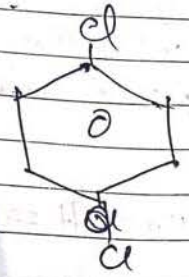


P.I



P.II



P.III

P.II

$CH_3-CH_2-CH=CH_2$
1 butene

$CH_3-CH=CH-CH_3$
2 butene

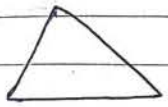
P.I

$CH_3-CH_2-CH_2-CH_2OH$
1 butanol

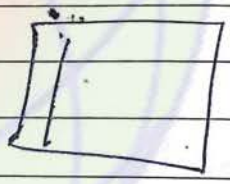
$CH_3-CH_2-\underset{OH}{CH}-CH_3$
2 butanol.

3) Ring chain Isomerism →

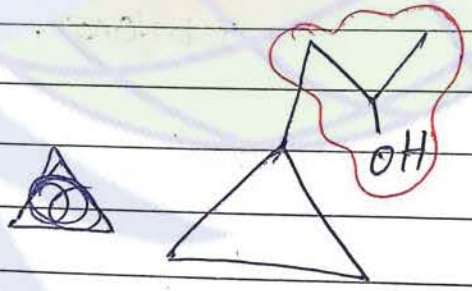
~~Those Isomers~~ In this Isomerism one Isomer have open chain as a parent chain and other Isomers have cyclic ring as parent chain.

$CH_3-CH=CH_2$  → R.C. Isomer.

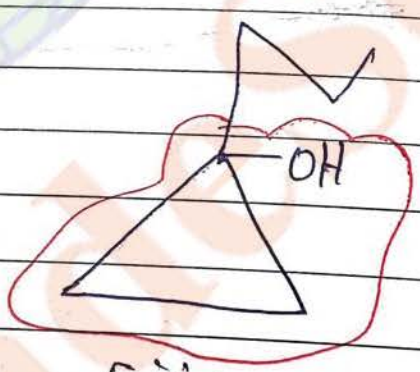
$CH_3-CH=CH-CH_3$  → R.C.I

$CH_3-C\equiv C-CH_3$  → R.C.I

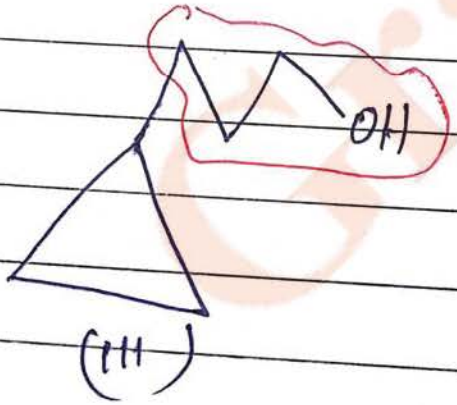
Ex 4)



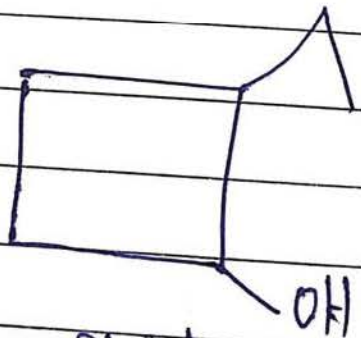
(I)



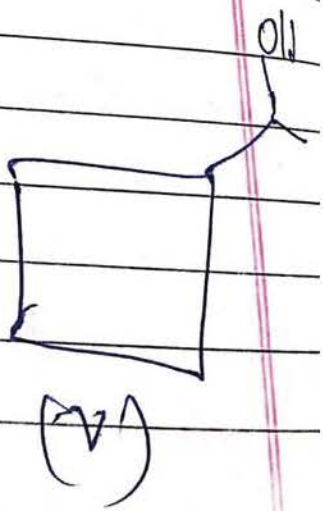
(II)



(III)



(IV)



(V)

1st Choice

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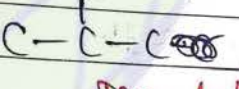
I and II → R.C.I	I and III → P.I
II and III → R.C.I	II and IV → C.I
III and IV → R.C.I	III and IV → C.I
IV and V → R.C.I	I and IV → R.C.I
	I and V → C.I
	I and V → R.C.I

Q) Find out total number of Isomers in following example.

(A) C_4H_{10} (Butane)

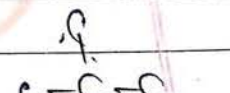
C-C-C-C
(n-butane)


Iso-butane

(B) C_5H_{12} (Pentane)

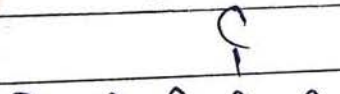
C-C-C-C-C
n-Pentan


Iso-Pentan


Neopentan

(C) C_6H_{14} →

C-C-C-C-C-C



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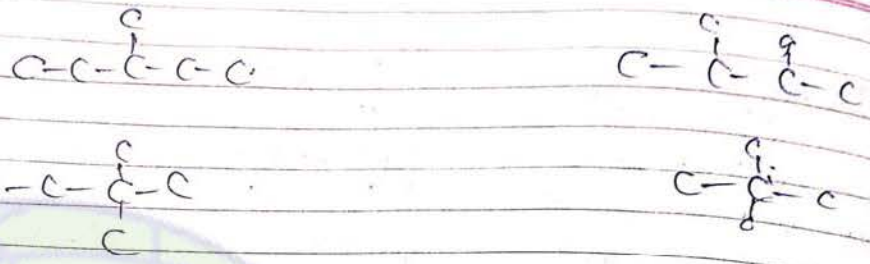
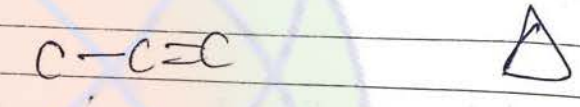
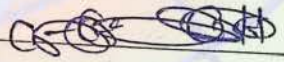
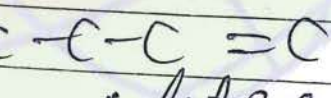


c) C_3H_6 (Propene)

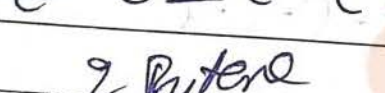


d) C_4H_8 (Butene)





1 butene



2 Butene

2 butene

C_5H_{10} (pentene)

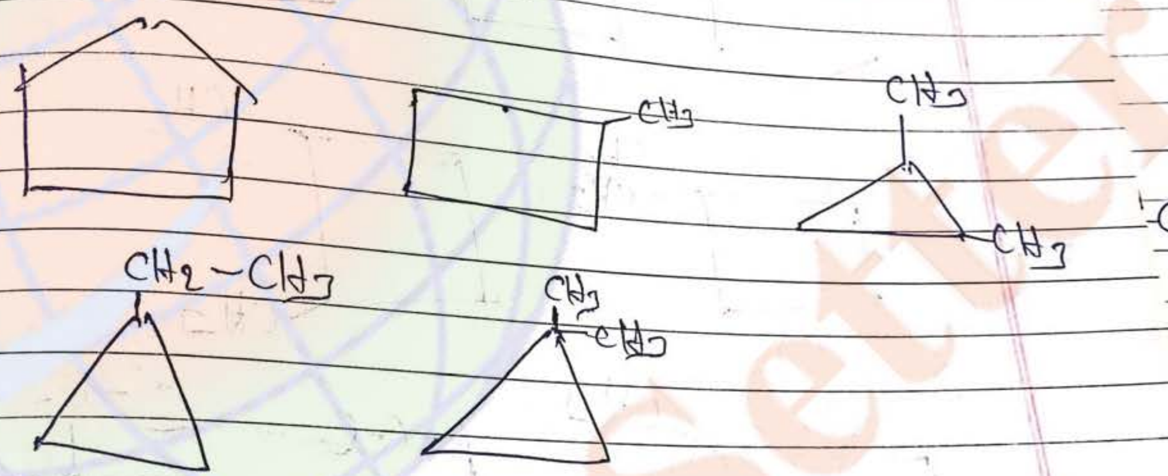
C–C–C–C=C

C–C(C)–C=C , C–C–C=C–C

C–C=C(C)–C

C–C(C)–C–C

C=C–C(C)–C



Compound

C_3H_8	1
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_3H_6	2

Hybrid Hydrocarbon group

C_3H_7 = 2

C_4H_9 = 4

C_5H_{11} = 8

Important to Rea

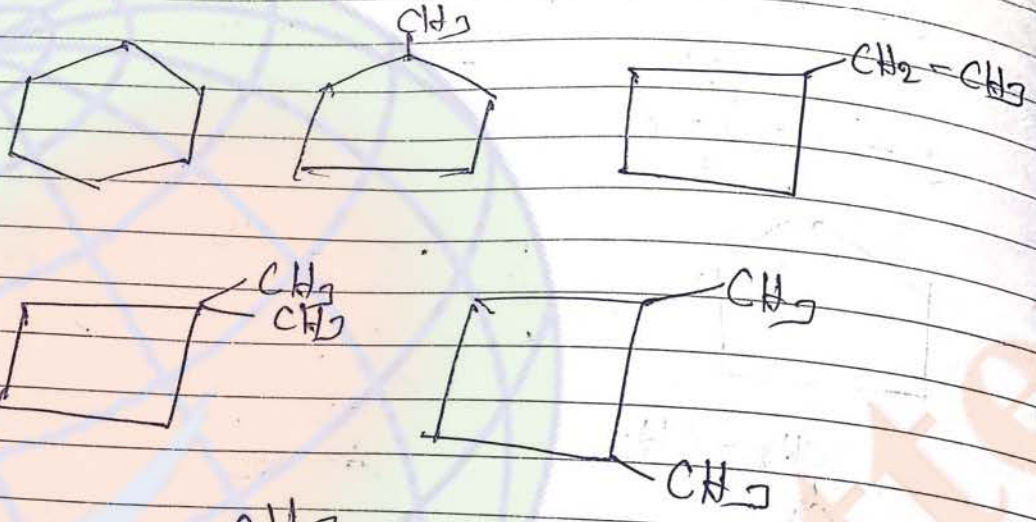
C_4H_8 : $5(3+2)$

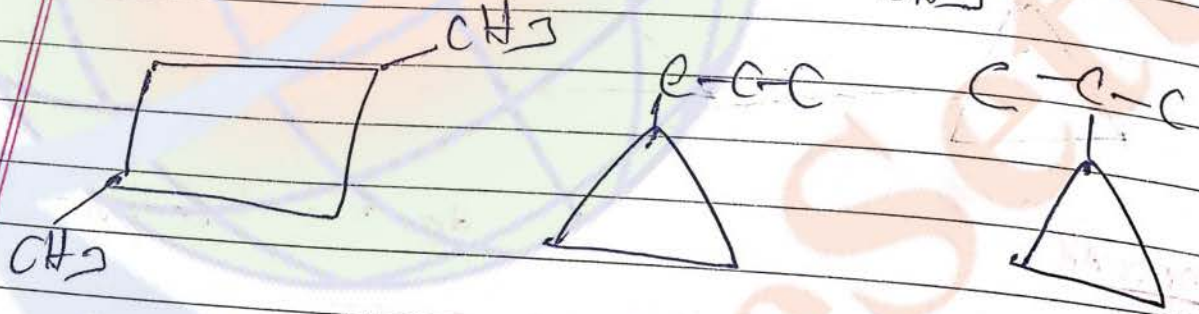
C_5H_{10} $10(5+5)$.

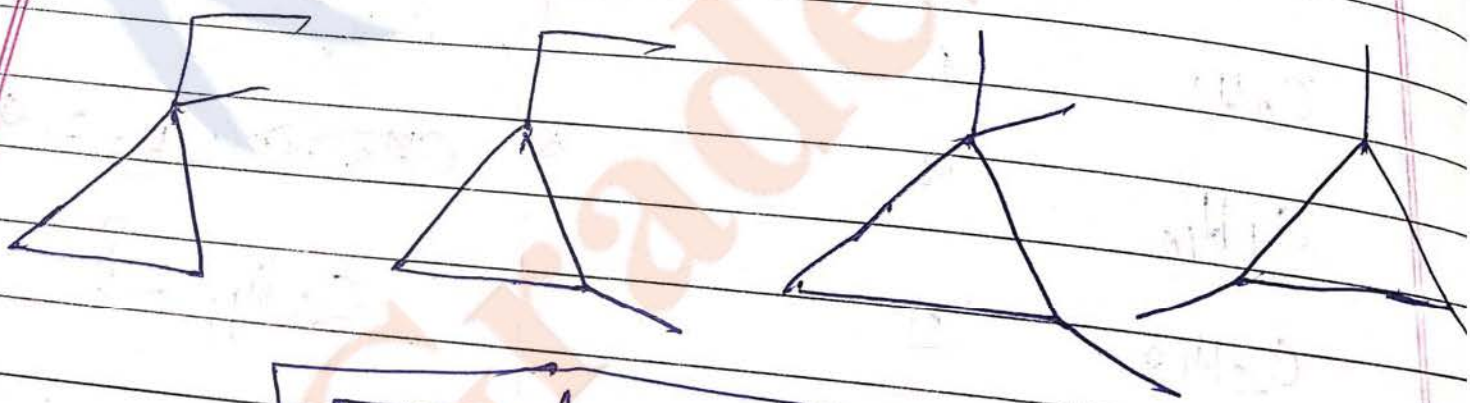
Q) Cyclic Isomers Drawn

C_6H_{12}

So/







Total Cyclic ⇒ 12

1st Choice

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Q.1) Find out minimum number of carbon required to show Position Isomerism in following :

a) Alkane
b) Alkene
c) Alkyne
d) Alcohol
e) Aldehyde
f) mono substituted alkane.
g) Di-substituted alkane.

Ans)

a) 6.

b) 4 , $C-C-C\equiv C$ $C-C=C-C$

c) 4 $C-C-C\equiv C$ $C-C\equiv C-C$

d) 3 $C-C-\overset{O}{\overset{\|}{C}}-H$, $C-\overset{O}{\overset{\|}{C}}-H$

e) 5 $C-C-\overset{C}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-H$, $C-\overset{C}{\overset{|}{C}}-C-\overset{O}{\overset{\|}{C}}-H$

f) "3" H हटाकर कोई group जोड़ दिया जाये ,

$C-C-C-Cl$ $C-\overset{Cl}{\overset{|}{C}}-C$

g) 2 $C-\overset{Cl}{\overset{|}{C}}-Cl$ $Cl-\overset{Cl}{\overset{|}{C}}-C$

1st Choice

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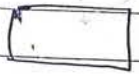
1) Functional group Isomerism →

I) These Isomers which have different functional group or different group deciding chemical properties.

II) Ring chain Isomer can also be functional group Isomers.
eg:⇒ Butene and cyclo butane.
C=C-C-C



किस direction में सीखना है:—

(I) C_nH_{2n+2} ⇒ only alkane

II) C_nH_{2n} → Alkene, cyclo Alkane
(D.U ⇒ 1)

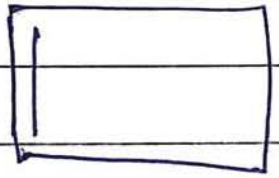
III) C_nH_{2n-2} → Alkyne, Alkadiene, cycloalkene, Tricyclo (min 4C), Spiro (min 5C)

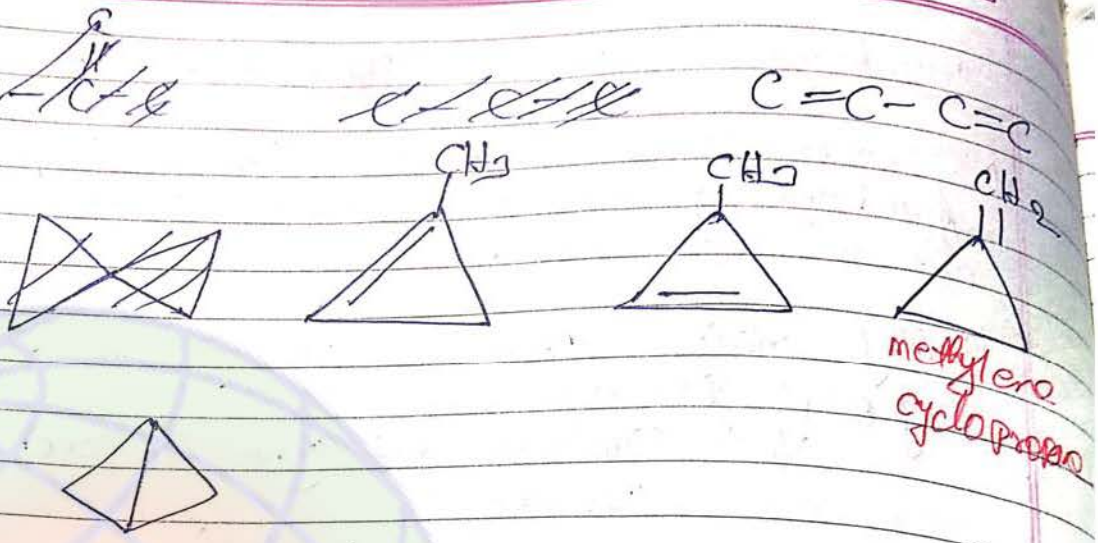
Ex) C_4H_6

↳ C_nH_{2n-2}

C-C≡C-C , C-C-C≡C

C-C=C=C ,

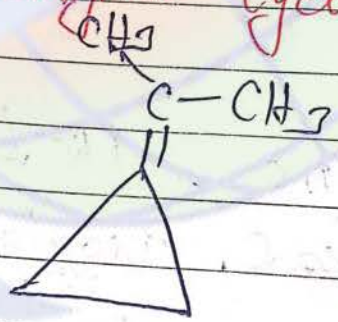




methylcyclopropane

Note ⇒

Iso Propene cyclopropane



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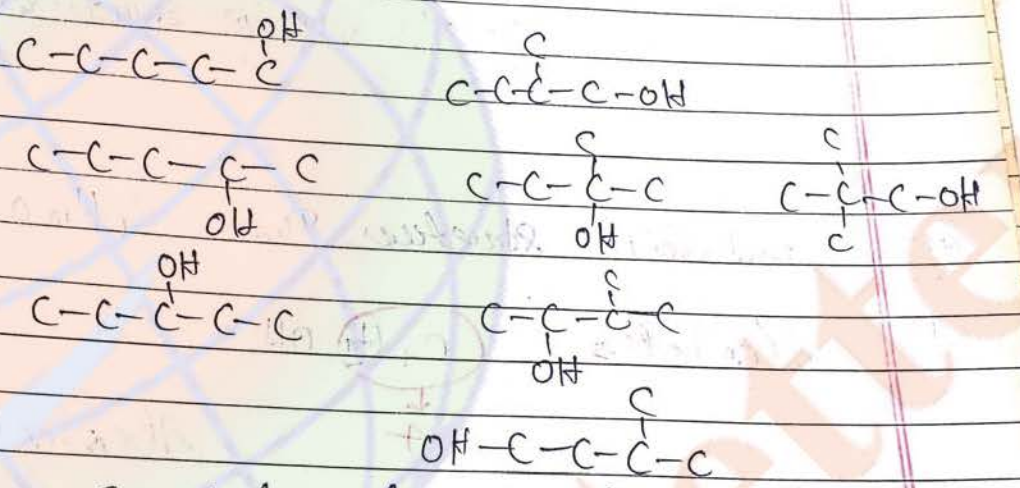
iv) $C_nH_{2n+2}O$ → Alcohol and ether.

~~$C_5H_{12}O$~~ ⇏ ~~$C_5H_{11}OH$~~

Q:→ find out total number of Isomer of $C_5H_{12}O$

* Alcohol = min $-OH$

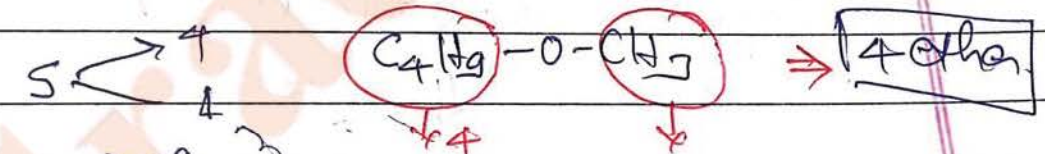
8 ways ← $C_5H_{11}-OH$



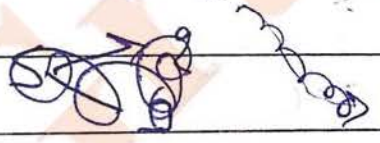
(~~total no. of alcohol~~ = 8)

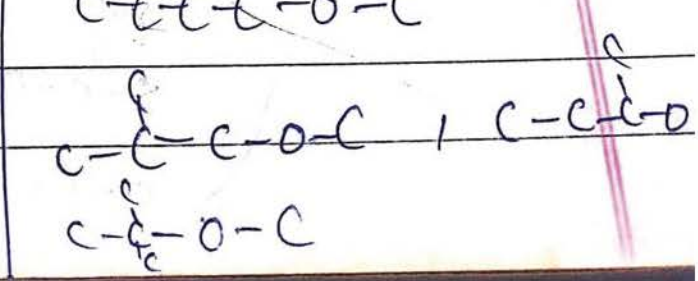
Note:→ 2° Alcohol ⇒ 3
1° Alohel ⇒ 4
3° Alcohol = 4

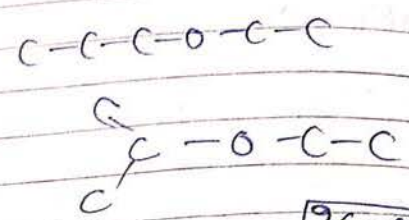
* In Ether = min $-O-$



⇒ 4 ether







ether

So, total possible structural Isomer are 14

eg) Find total structure Isomer $C_4H_{10}O$

Sol^n Alcohol ⇒ C_4H_9OH

C_4H_9 ⇒ 4

, Alcohol ⇒ 4

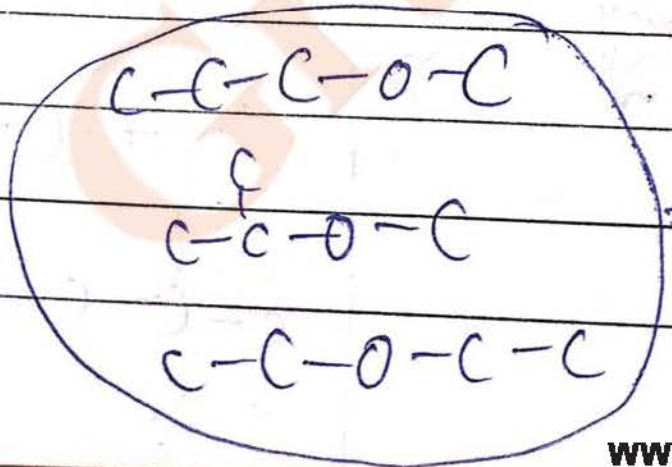
ether ⇒

C_3H_7-O-C

C_3H_7 ⇒ 2

ether ⇒ 3

total ⇒ 7



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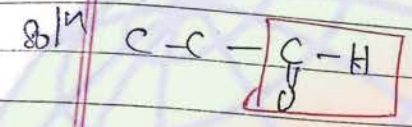
5) $C_nH_{2n}O$ (D.U = 1) → Aldehyde, ketone
→ unsaturated Alcohol or ether
→ cyclic Alcohol or Ether.

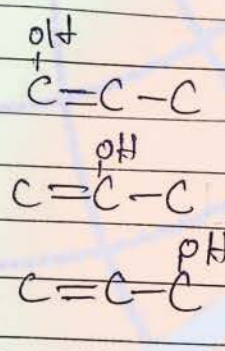
Sol: Total number of structural Formula Present for C_3H_6O

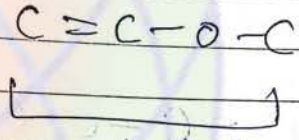
8/14



→ Aldehyde, ketone

⇒ 2

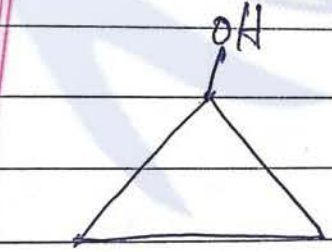




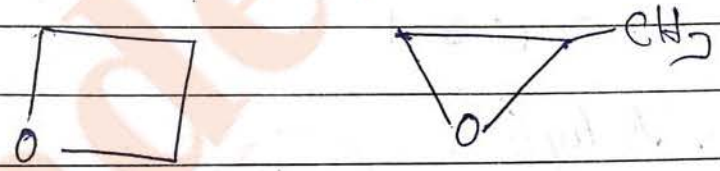
unsaturated ether

⇒ 4

~~Unsaturated~~ Alcohol



cyclic Alcoh



cyclic ether

⇒ 3

Total Isomers ⇒ 9

Q.9) find out total number of carbonyl compound in following.

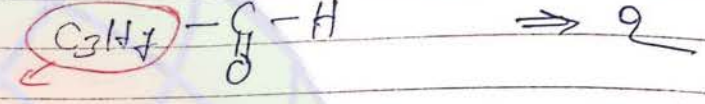
a) C_4H_8O

b) $C_5H_{10}O$

Sol) a) C_4H_8O

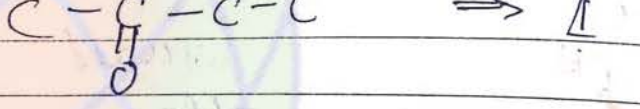
D.U $\Rightarrow$ 1

Aldehyde:



$\Rightarrow$ 2

Ketone:



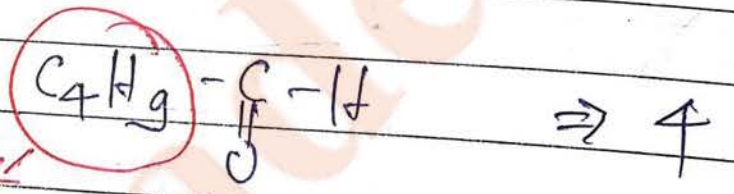
$\Rightarrow$ 1

So, total carbonyl compound $\Rightarrow$ 3

b) $C_5H_{10}O$

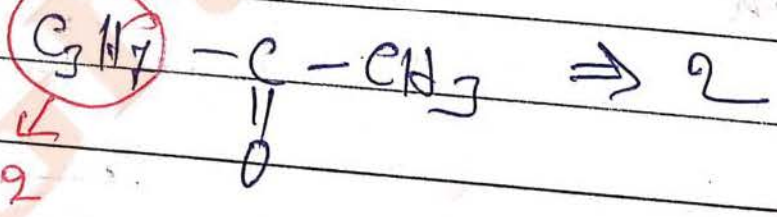
D.U = 1

Aldehyde:



$\Rightarrow$ 1

Ketone:



$\Rightarrow$ 2

1st Choice

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C-C-C(=O)-C-C ⇒ 1

So, total carbonyl compound = 7

6) $C_n H_{2n} O_2$ ⇒ carboxylic acid, and ester

D.U ⇒ 1

- Unsaturated Diol or di ether or ether + Alcohol
  - C(=O)-O-H
- Cyclic diol or di ether or ether + Alcohol

Ex) Find out Structural Isomers of carboxylic acid and ester. $C_5H_{10}O_2$?

Sol) carboxylic acid ⇒

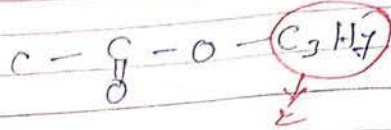
C_4H_9 – C(=O)–O–H ⇒ 4

(C_4H_9 ⇒ 4)

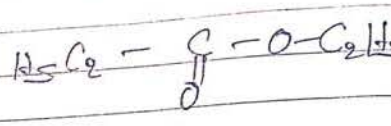
ester ⇒

H – C(=O) – O – C_4H_9 ⇒ 4

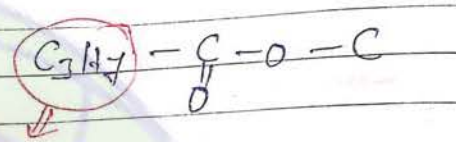
(C_4H_9 ⇒ 4)



$\Rightarrow 2$



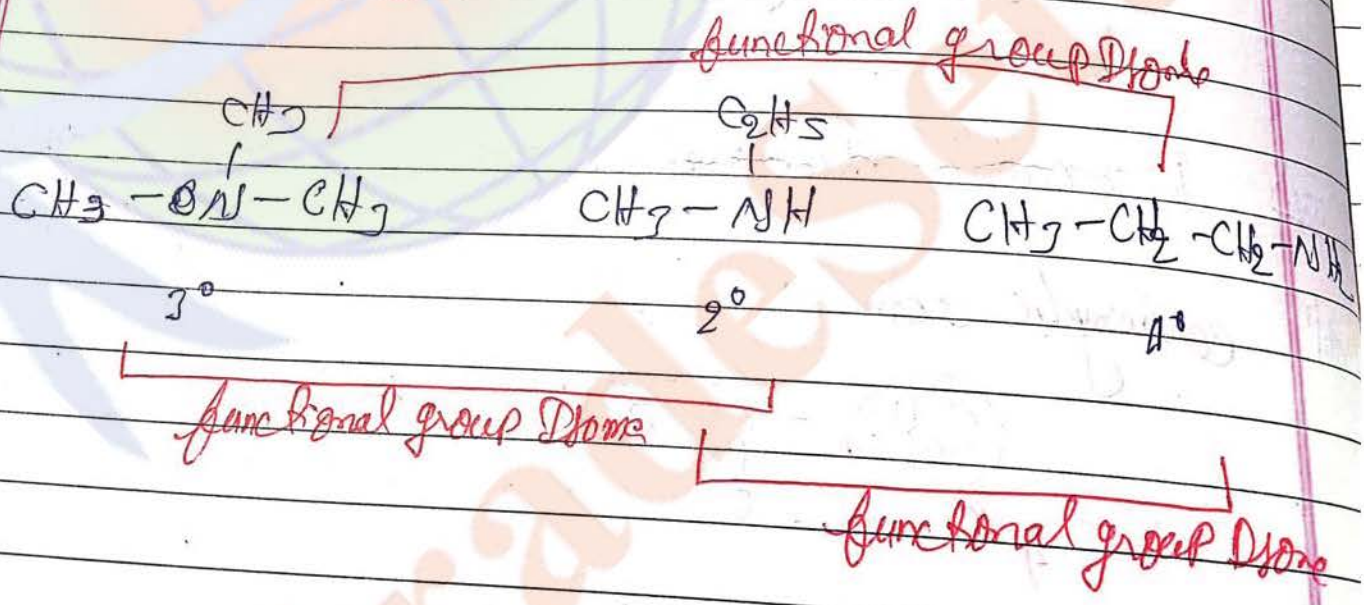
$\Rightarrow 1$



$\Rightarrow 2$

total Isomers $\Rightarrow \Rightarrow 5$

Q7) 1°, 2°, 3° Amine



Sol) How many 1°, 2° and 3° Amines are possible with the molecular formula $C_5H_{13}N$?

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8/11 1° ⇒ $C_5H_{11}-NH_2$ ⇒ 8

2° ⇒ 4:4:1 ⇒ $C_4H_9-NH-CH_3$ ⇒ 4

3:2:1 ⇒ $C_3H_7-NH-C-C$ ⇒ 2

3° ⇒ 1:1:1 ⇒ $C_3H_7-\overset{C}{N}-C$ ⇒ 2

2:2:1 ⇒ $\overset{C-C}{C-N-C-C}$ ⇒ 1

total Ques ⇒ 17

Q2) Find how many 1°, 2° and 3° Amines are possible with the molecular formula $C_4H_{11}N$?

$C_4H_{11}N$

1° → $C_4H_9-NH_2$ ⇒ 4

2° ⇒ $C_3H_7-NH-CH_3$ ⇒ 2

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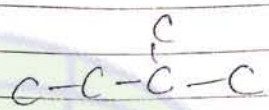
$C-C-NH-C-C \Rightarrow 1$

$3^\circ \Rightarrow$



$\Rightarrow 1$

total $\Rightarrow 8$

$1^\circ \Rightarrow 4$
$2^\circ \Rightarrow 3$
$3^\circ \Rightarrow 1$

1st Choice

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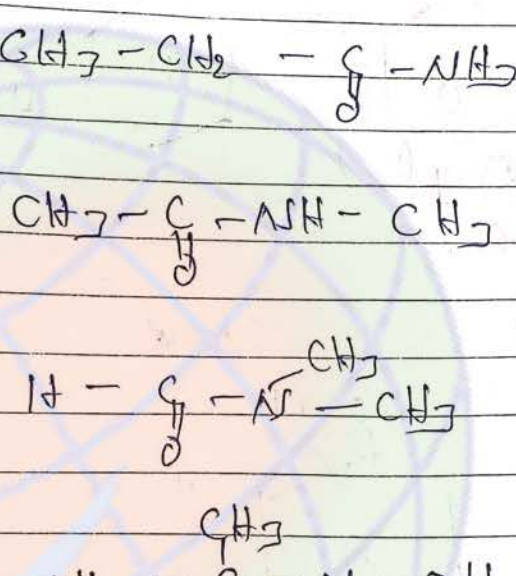
8.) 1°, 2°, 3° Amide and oxime :

सभी प्रकार के functional group के लिए



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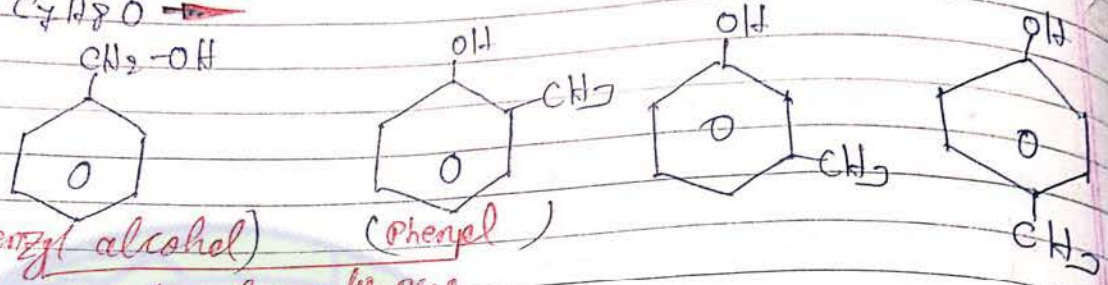
9.) Aromatic alcohol, Phenol, Aromatic ether.

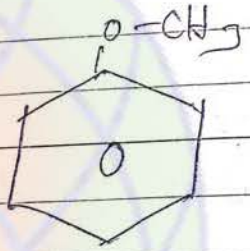
eg:) C_7H_8O →



(Benzyl alcohol) (Phenol) (Phenol)

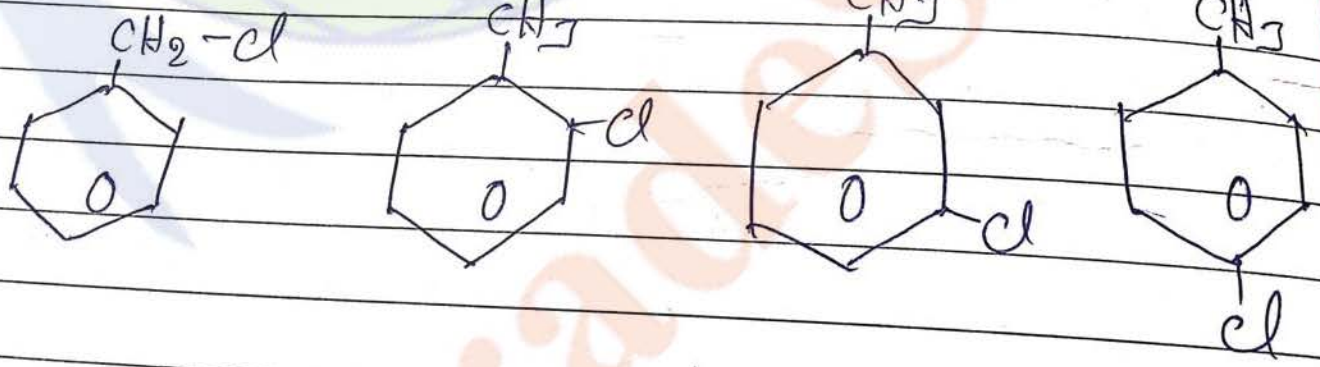
functional group isomers.

Aromatic ether:



⇒ total Isomers = 5

eg2) C_7H_7Cl ; Total benzoid Isomers.



⇒ total benzoid Isomers = 4

1st Choice

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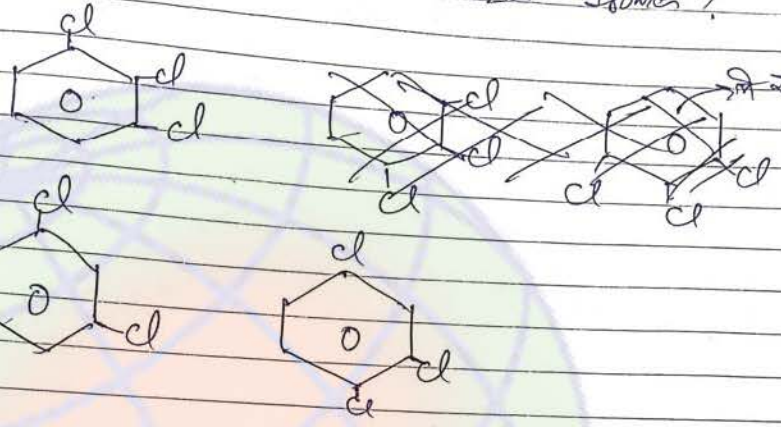
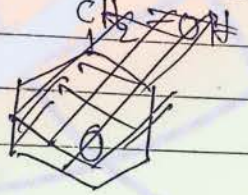
eg 3.) $C_6H_3Cl_3$, total benzoid Isomers ?

Sol^n

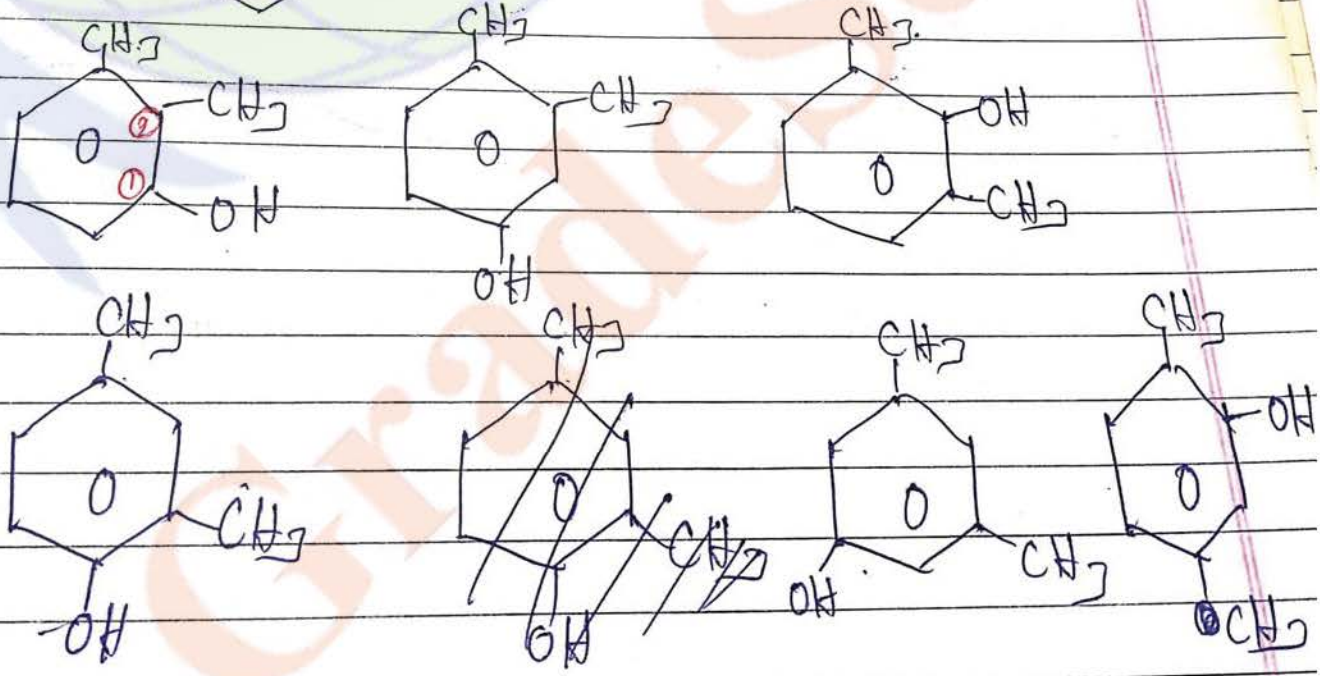


total benzoid Isomers ⇒ 3

eg 4) Find total number of Isomers of di-methyl phenol



Sol^n



⇒ total Isomers ⇒

Note ⇒ Summary for functional group Bsc

1) C_nH_{2n+2} → Alkane

2) C_nH_{2n} → Alkene, cyclo alkane

3) C_nH_{2n-2} → Alkyne, cyclo alkene, Bicycle, diene,

4) $C_nH_{2n+2}O$ → Alcohol, ether

5) $C_nH_{2n}O$ → Carbonyl compound

6) $C_nH_{2n}O_2$ → Carboxylic acid and ester.

7) 1°, 2°, 3° Amine

8) 1°, 2°, 3° Amide, Oxime

9) Phenol, Aromatic alcohol, ether

10) Nitrile and Nitroalkane

11) Cyanide and Isocyanide

CAREER POINT

Fresher Course for IIT JEE – 2013

Phase - 1

DAILY PRACTICE PROBLEM SHEET

Course : Fresher (Eng.)	Subject : C_2	DPPS No. : 21	Discussion on : 15 June 2012

Q.1 How many alcohols (neglecting stereoisomers) are possible with the molecular formula $C_5H_{12}O$?
(A) 5 (B) 6 (C) 7 (D) 8

Q.2 The total number of benzene derivatives having the molecular formula C_7H_7Cl is –
(A) 2 (B) 3 (C) 4 (D) 5

Q.3 The total number of amines (neglecting stereoisomers) possible with the molecular formula C_3H_9N is –
(A) 2 (B) 3 (C) 4 (D) 5

Q.4 The total number of secondary amines (neglecting stereoisomers) possible with the molecular formula $C_4H_{11}N$ is –
(A) 2 (B) 3 (C) 4 (D) 5

Q.5 How many alkenes are possible with the molecular formula C_4H_8 ?
(A) 2 (B) 3 (C) 4 (D) 6

Q.6 The total number of carboxylic acids and esters with the molecular formula $C_4H_8O_2$ is –
(A) 3 (B) 4 (C) 5 (D) 6

Q.7 The total number of benzene derivatives with the molecular formula $C_6H_3Cl_3$ is –
(A) 2 (B) 3 (C) 4 (D) 5

Q.8 The total number of dimethylphenols having the molecular formula $C_8H_{10}O$ is –
(A) 3 (B) 4 (C) 6 (D) 8

Q.9 The total number of isomers having the molecular formula $C_2BrClFI$ is
(A) 3 (B) 4 (C) 5 (D) 6

Q.10 The total number of benzene derivatives having the molecular formula C_7H_8O is -
(A) 3 (B) 4 (C) 5 (D) 6

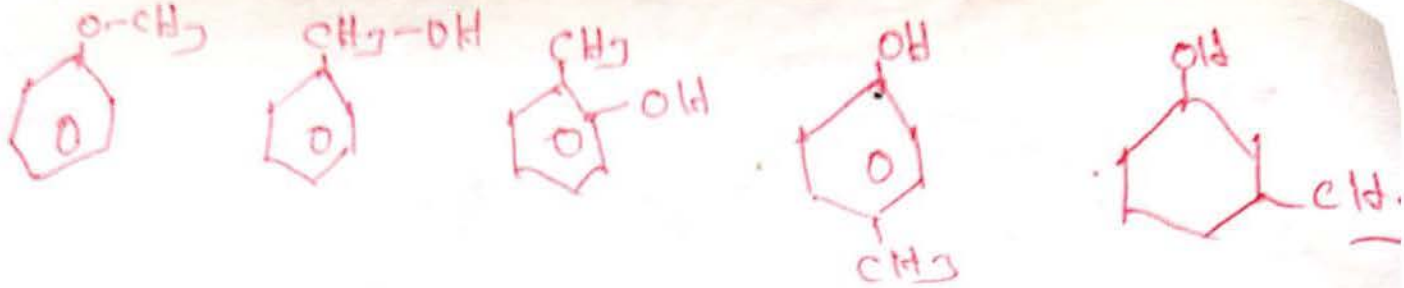
Q.11 Calculate the molecular weight of the lowest hydrocarbon which contains sp & sp^2 hybridised carbon atoms only.

Q.12 Identify the molecular weight of the compound 'X' containing carbon and hydrogen atoms only with 3σ and 2π bonds in one molecule.

Answer key

1. (D) **2.** (C) **3.** (C) **4.** (B) **5.** (C)
6. (D) **7.** (B) **8.** (C) **9.** (D) **10.** (C)
11. $H_2C = C = CH_2$; M.W. = 40 **12.** H – C ≡ C – H, Mol. wt. = 26

(a)

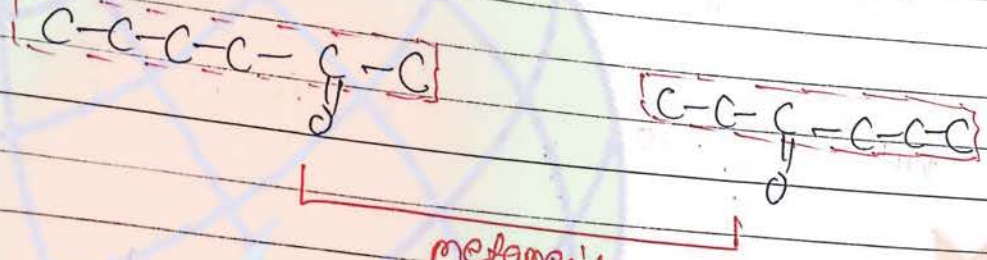


5) Metamerism → co-existant position and chain

i) Those Isomers which have different carbon chain around polyvalent functional group.

ii) metamerism co-exist with chain or position Isomerism

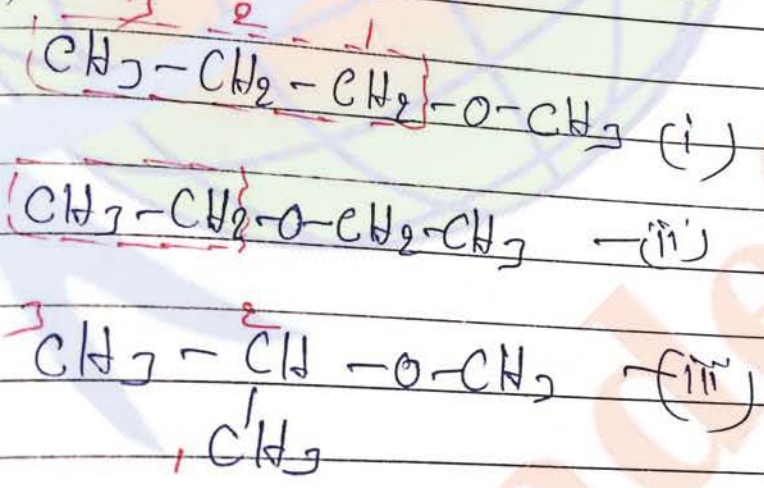
iii) Example. →



metamers

(and also position Isomers)

eg2)



(i)

(ii)

(iii)

so/n:) (i) only (ii) → metamers and C.I

(ii) and (iii) → metamers and C.I

(i) and (iii) → only Position Isom

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iv) following groups can show intermolecular

(Ans) i) $-O-$ (ether)

ii) $-S-$ (thio ether)

iii) $-\overset{O}{\overset{\|}{C}}-$ (ketone)

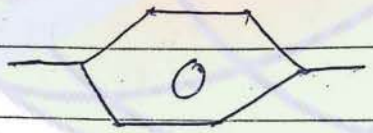
iv) $-NH-$ (2° Amine)

v) $-\overset{|}{N}-$ (3° Amine)

vi) $-\overset{O}{\overset{\|}{C}}-O-$ (ester)

vii) $-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$ (Anhydride)

viii)



(Benzene ring)

CAREER POINT

Fresher Course for IIT JEE – 2013

Phase - 1

DAILY PRACTICE PROBLEM SHEET

Course : Fresher (Eng.) | Subject : C_2 | DPPS No. : 20 | Discussion on : 14 June 2012

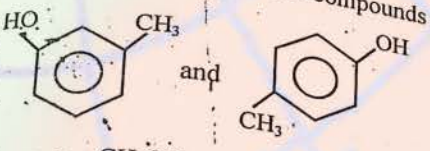
Q.1 The hybridization states of the carbon atom (1) and carbon atom (2) in the compound $\overset{3}{C}H_2 = \overset{2}{C}H - \overset{1}{C} \equiv N$ are respectively

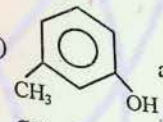
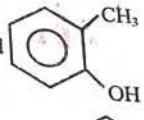
(A) sp^2 & sp (B) sp^3 & sp (C) sp & sp^2 (D) sp & sp

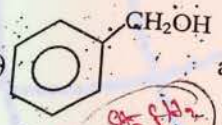
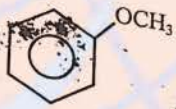
Q.2 Ethylcyclopropane and 1, 1-dimethylcyclopropane are

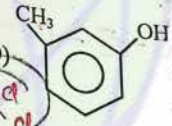
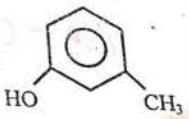
(A) position isomers (B) ring-chain isomers (C) chain isomers (D) tautomers

Q.3 Which of the following pairs of compounds are not isomers ?

(A)  and

(B)  and 

(C)  and 

(D)  and 

Q.4 Ethylene dichloride and ethylidene dichloride are

(A) geometrical isomers (B) chain isomers (C) position isomers (D) not isomers

Q.5 How many structural isomers are possible with molecular formula C_3H_6O ?

Q.6 How many structures of dibromo derivatives are formed from isopentane ?

Q.7 How many cyclic structural isomers are possible with molecular formula C_4H_7Cl ?

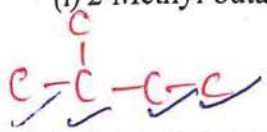
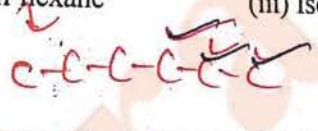
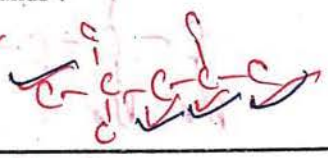
Q.8 In which compounds all types of hybridization states are present ?

(A) $CH_3 - CH = C = CH - CH_3$ (B) $CH_3 - C \equiv C - CH_3$

(C) $CH_3 - CH = CH - CH_2 - C \equiv C - CH_3$ (D) $CH_3 - CH = C = CH - CH_2 - CH = CH_2$

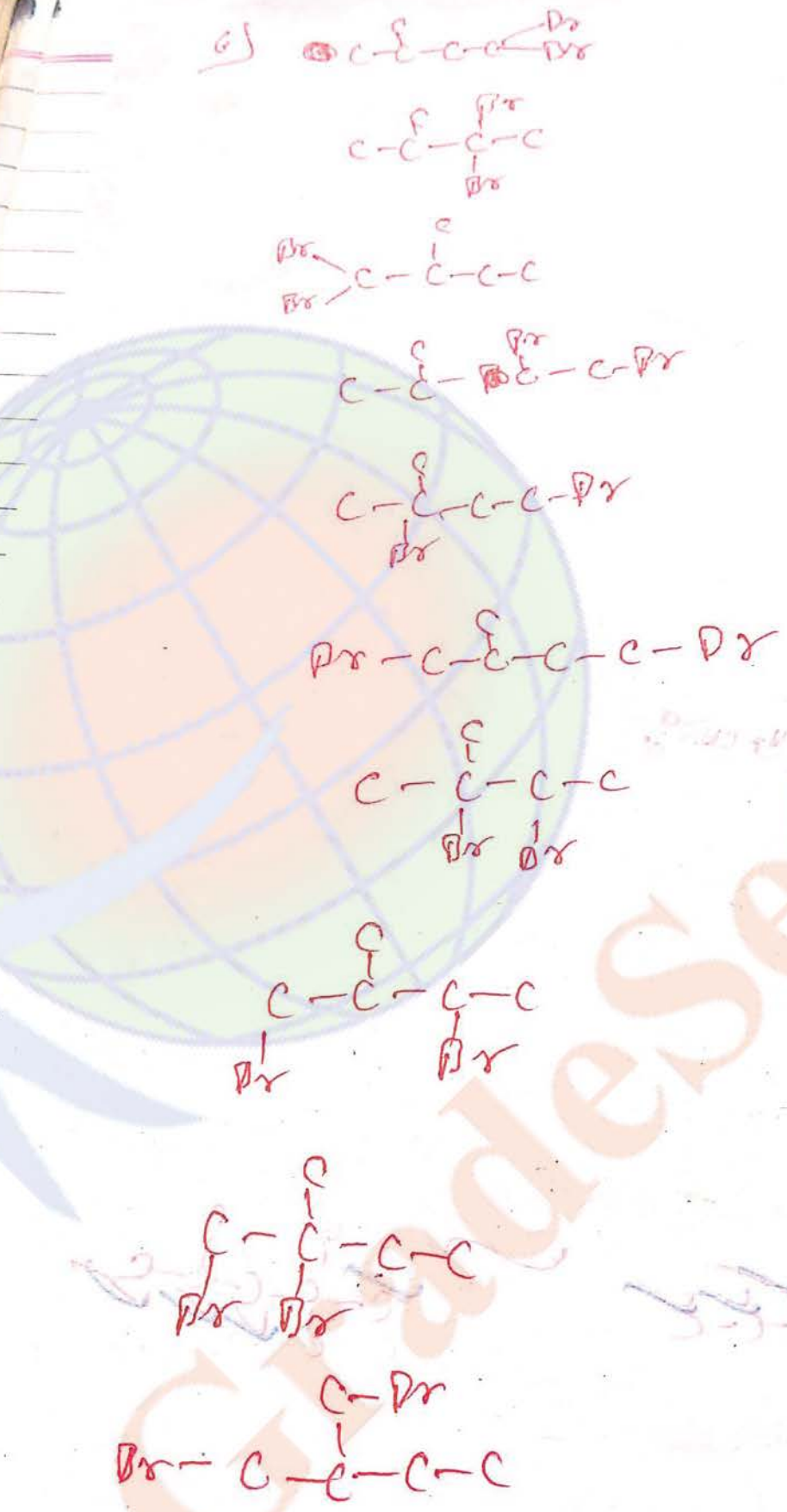
Q.9 How many different types of hydrogens are present in following compounds ?

(i) 2-Methyl butane (ii) n-hexane (iii) Isooctane

Answer key

2. (C) 3. (D) 4. (C) 5. 9 6. 10
7. 4



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6) Tautomerism or allelotropism or dynamic Isomerism

i) In this Isomerism two Isomers exist in dynamic equilibrium due to transfer of acidic hydrogen b/w two polyvalent atom. (or proton)

ii) Tautomers are also functional group's Isomers.

iii) This is also known as "Desmotropism"
(movement of Hydrogen, phenomena)

iv) Type of tautomerism :-

a) Dial system - when transfer of Hydrogen in '1-2' transfer.

$$H-\underset{1}{C}\equiv\underset{2}{N} \rightleftharpoons :C\equiv N-H$$
(sp)

(Hydrocyanic acid) (Diocyanic acid (more acidic))

$$K = \frac{P}{R}$$ (P → Product, R → Reactant)

for

$$K = \frac{P}{R} < 1$$

जब Reactant का Concentration, Product के Concentration से अधिक (greater than one) होता है तो Reaction stable

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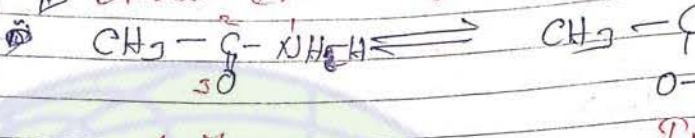
b) Triad System → when transfer of Hydrogen is 1,3

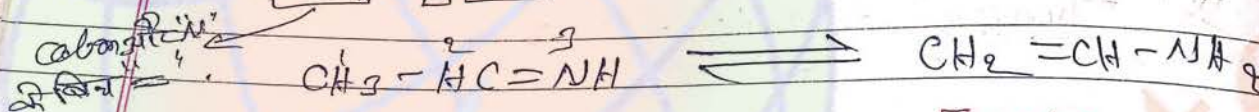
i) Amide - Imidol tautomerism.



Amide — Imidol

$K_{eq} = \frac{P}{R} < 1$

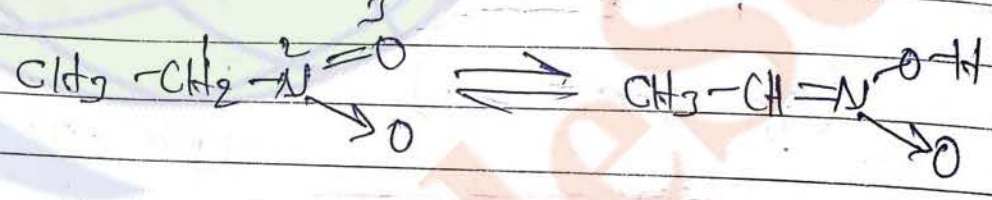
ii) Imine - Enamine tautomerism.



Imine — Enamine

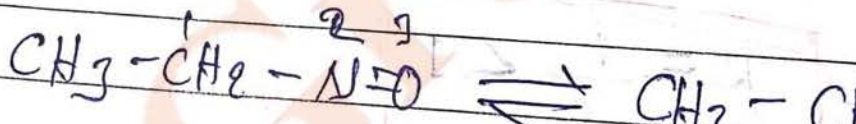
$K < 1$

iii) Nitro - aci Nitro - tautomerism.



(Stable) $K < 1$

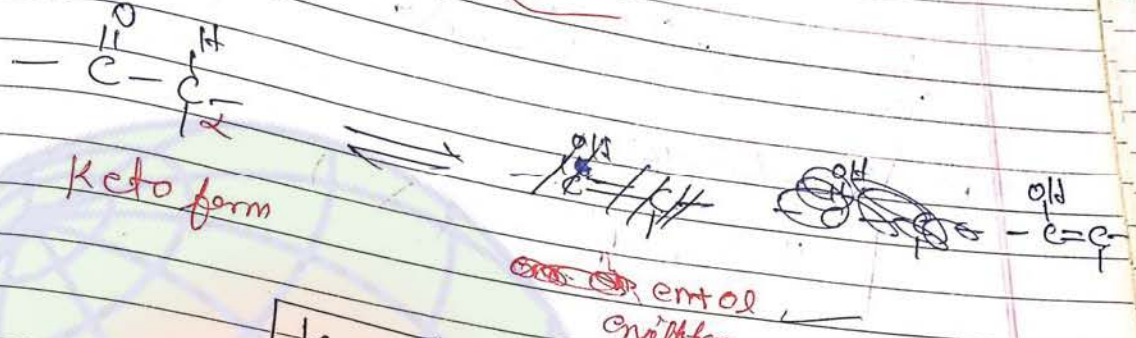
iv) Nitroso - oxime tautomerism →



Nitroso — oxime

$K > 1$ because oxime is much more stable than Nitroso.

Keto-enol tautomerism



Keto form ⇌ enol form

$K < 1$

10^{-5} %

Generally keto form is more stable than enol form because 'C' bond is very stable.

Essential condition for tautomerism →

1) Keto form should contain atleast one α-H which is acidic.
(α-C should be sp^3 hybrid.

2) In enol form OH should be attached to doubly bonded carbon (=C)
↳ Rambe Bredt's rule.

OH जिस carbon से attach होता है उसके adjacent carbon से double bond होना चाहिए।

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Q. Which of the following compound can show keto-enol tautomerism

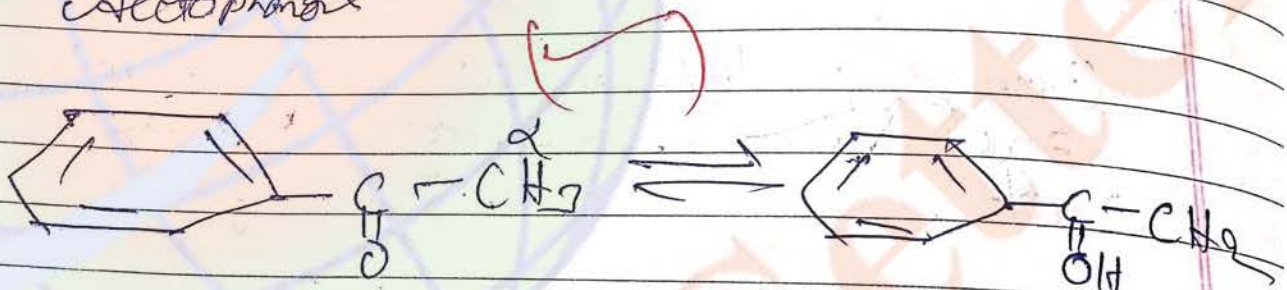
i) Formaldehyde

$H-\underset{\underset{O}{\|}}{C}-H$ (X)

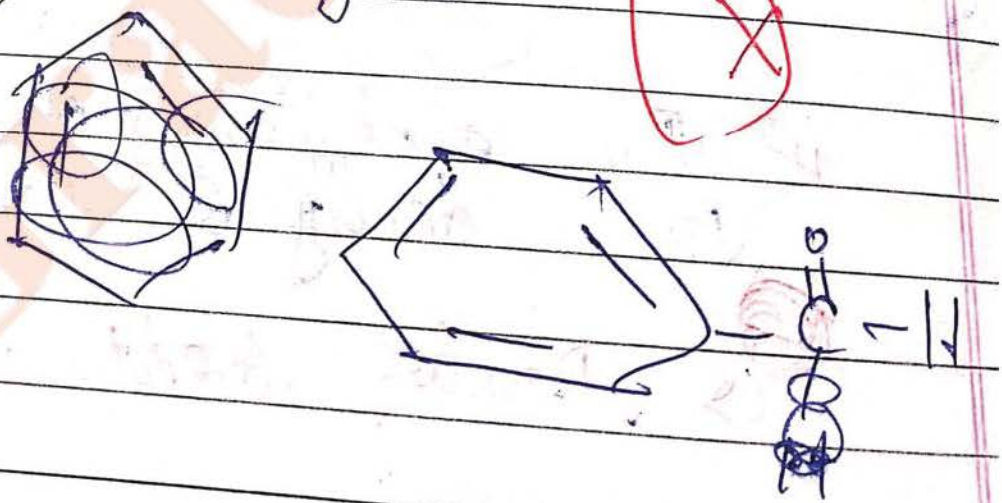
ii) Acetone

$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2$ (✓)

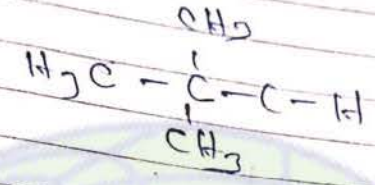
iii) Acetophenone



iv) ~~Benzoic~~ Benzaldehyde

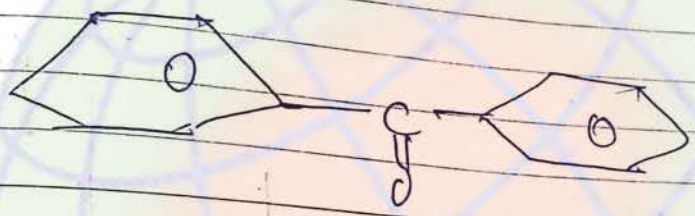


v) 2-2- dimethyl propanal

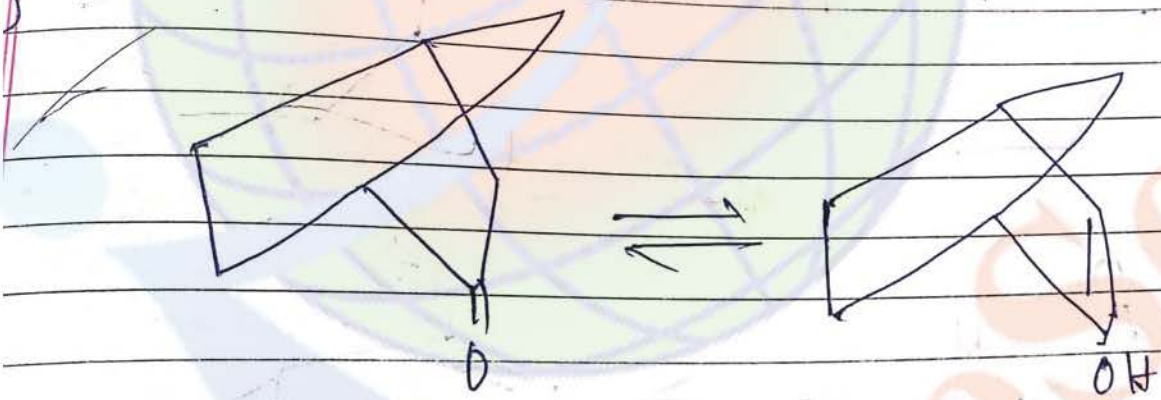


(✓)

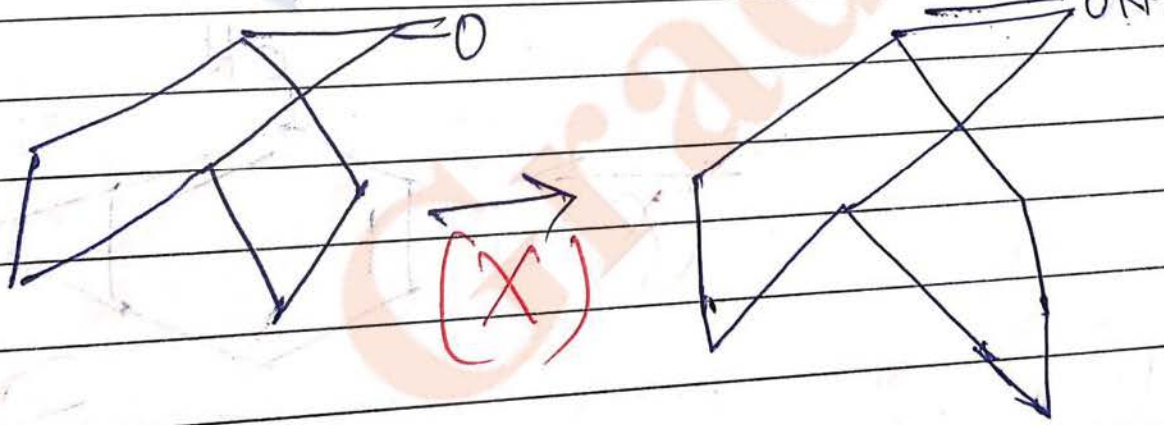
vi) Benzophenone



(X)

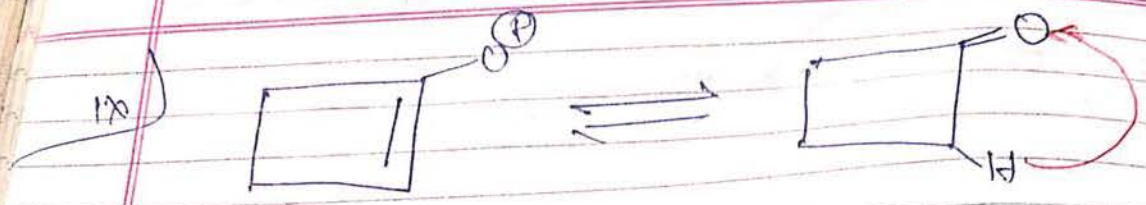


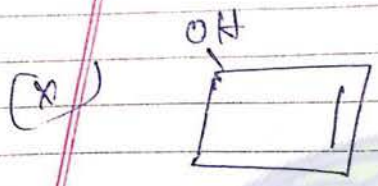
(✓)

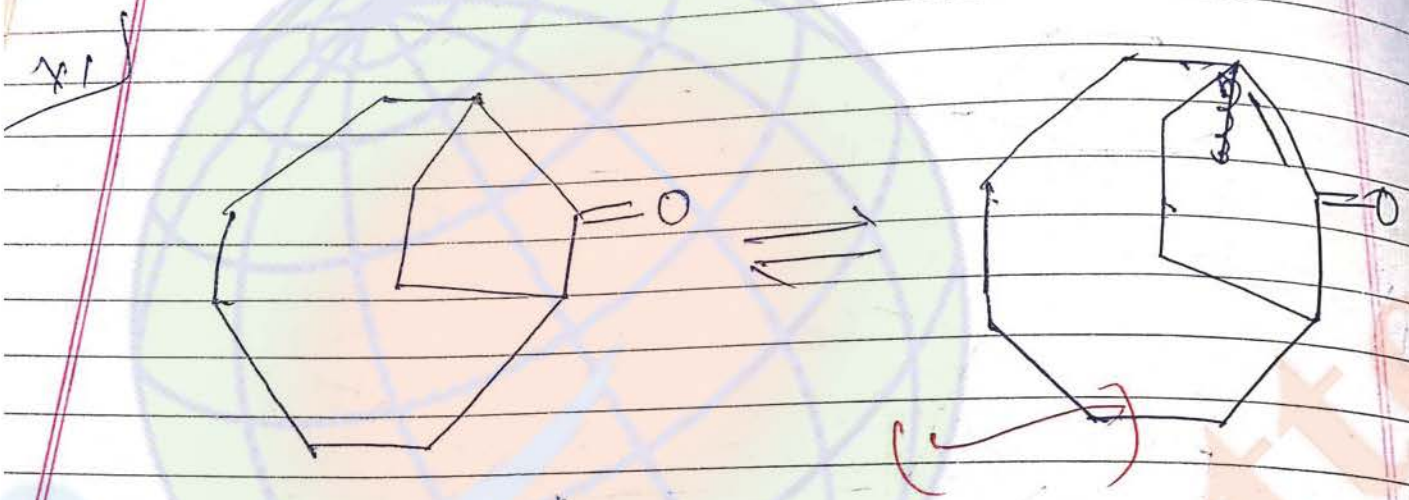


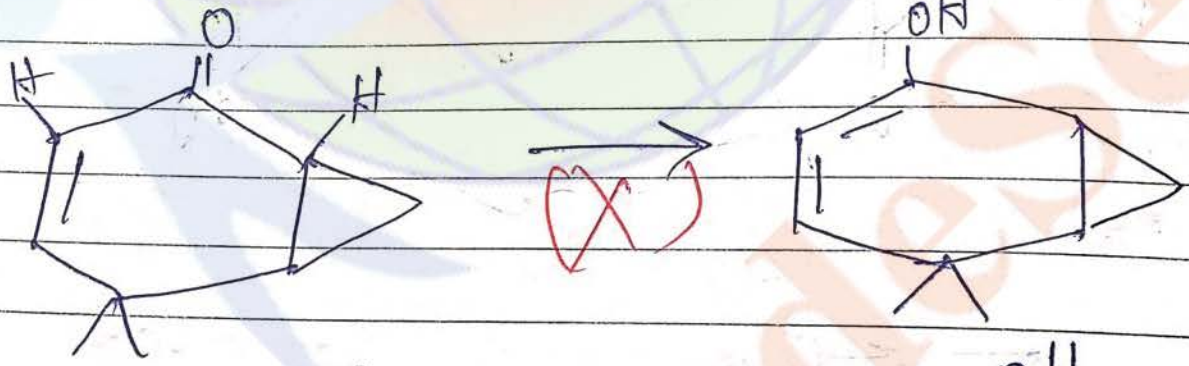
(X)

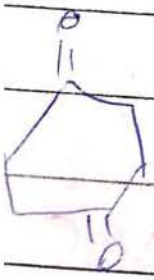
Bad ks sub











Mechanism of Tautomerism →

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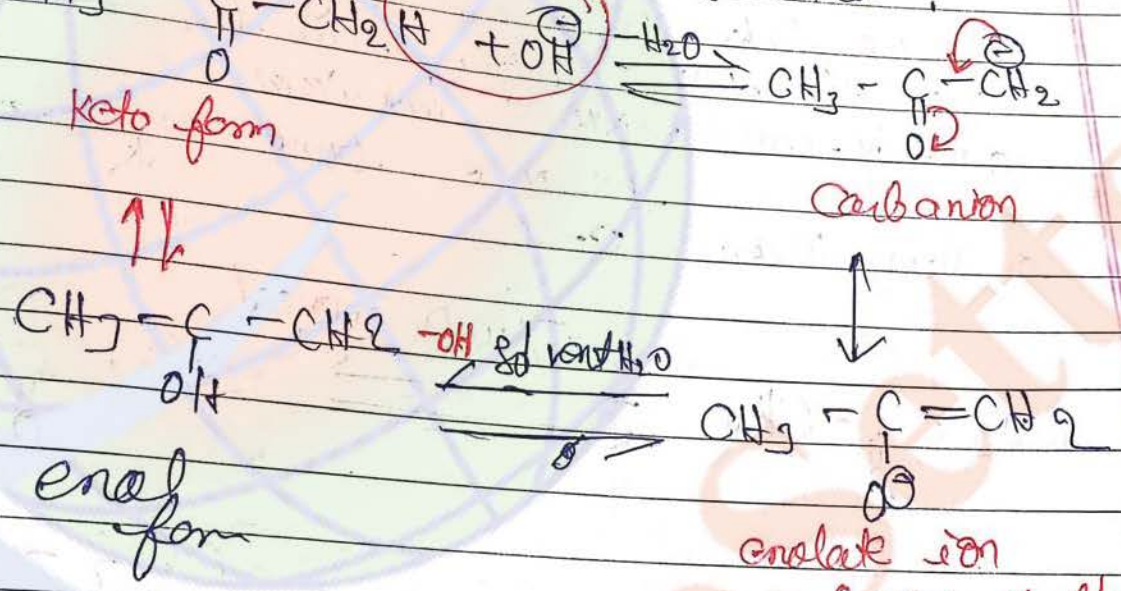
1) Base catalysed tautomerism (most common) →

2) In this case ~~H~~ of all base abstract (हटाना) a "α-H" and form carbanion. which is resonance stabilized.



2) The proton which is attached to oxygen comes from solvent

The proof for this mechanism is if we take D_2O as the solvent then deuterium is transfer to oxygen (enolate ion) finally deuterium is transfe to "α-C".

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$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \underset{}{\overset{OH^{\ominus}/D_2O \text{ or } NaOD}{\rightleftharpoons}} CH_3-\overset{\overset{O-D}{|}}{C}=CH_2 \rightleftharpoons CH_3-\overset{\overset{O}{\|}}{C}-CH_2D$$

(more stable) Keto in case of less strong base.

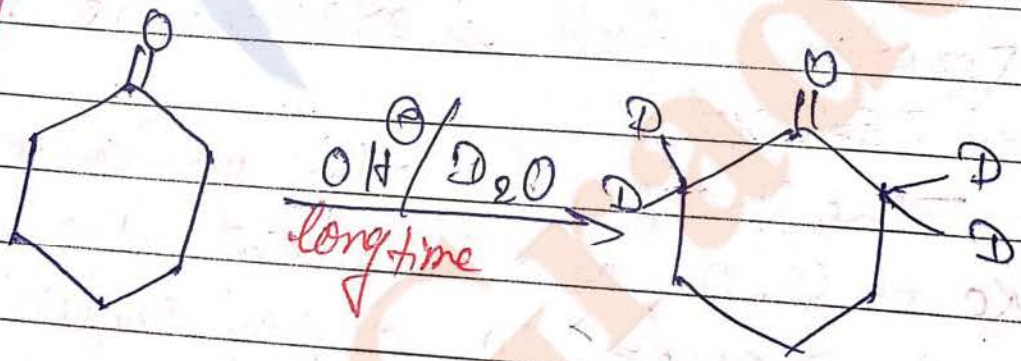
3) **B.E. C-H < C-D**

If we take D_2O for long time as solvent then all α-H hydrogen can be removed one-by-one with deuterium because bond energy of C-H is less than C-D

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2 \underset{}{\overset{OH^{-}/D_2O \text{ Prolonged time}}{\rightleftharpoons}} CD_3-\overset{\overset{O}{\|}}{C}-CD_3$$

or

$$CD_3-\overset{\overset{O-D}{|}}{C}=CD_2$$



1st Choice

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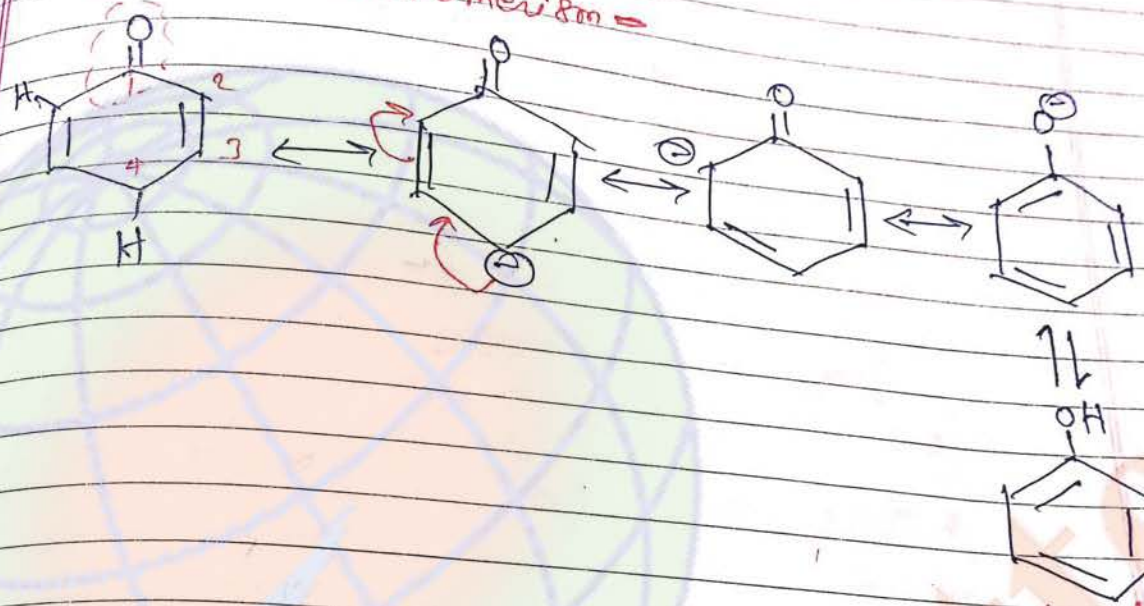
Note ⇒ (special example)

Para Tautomerism ⇒



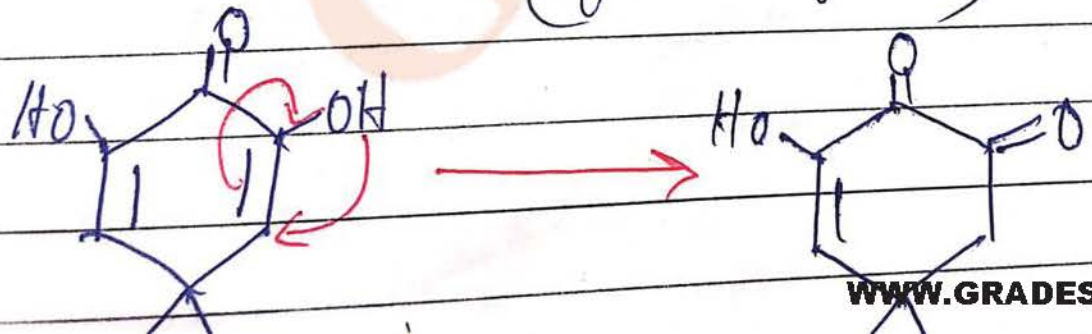
Aromatic 100%

Generally tautomerism involve loss of α-H ~~by base~~ due to base but cyclohex 2,5 dienetone is a special example in which para-hydrogen (P-H) is removed it is because carbanion stability and finaly enol form is aromatic.

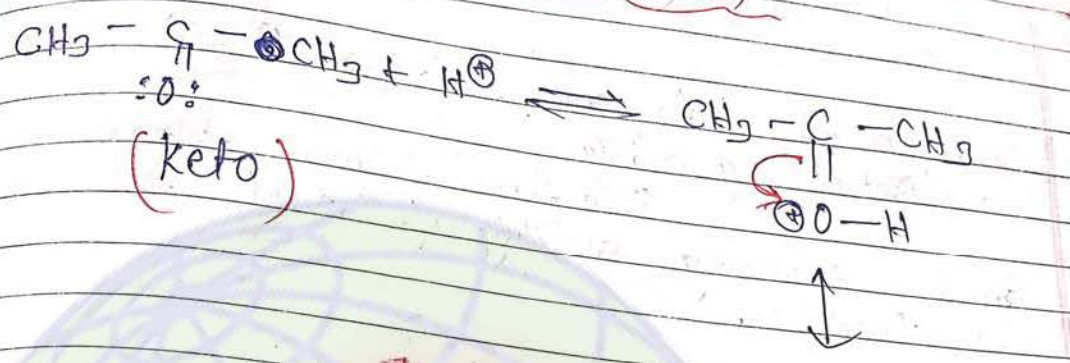
Following example can show ⇒

a) Tautomerism

b) Enolisation
(formation of enol)



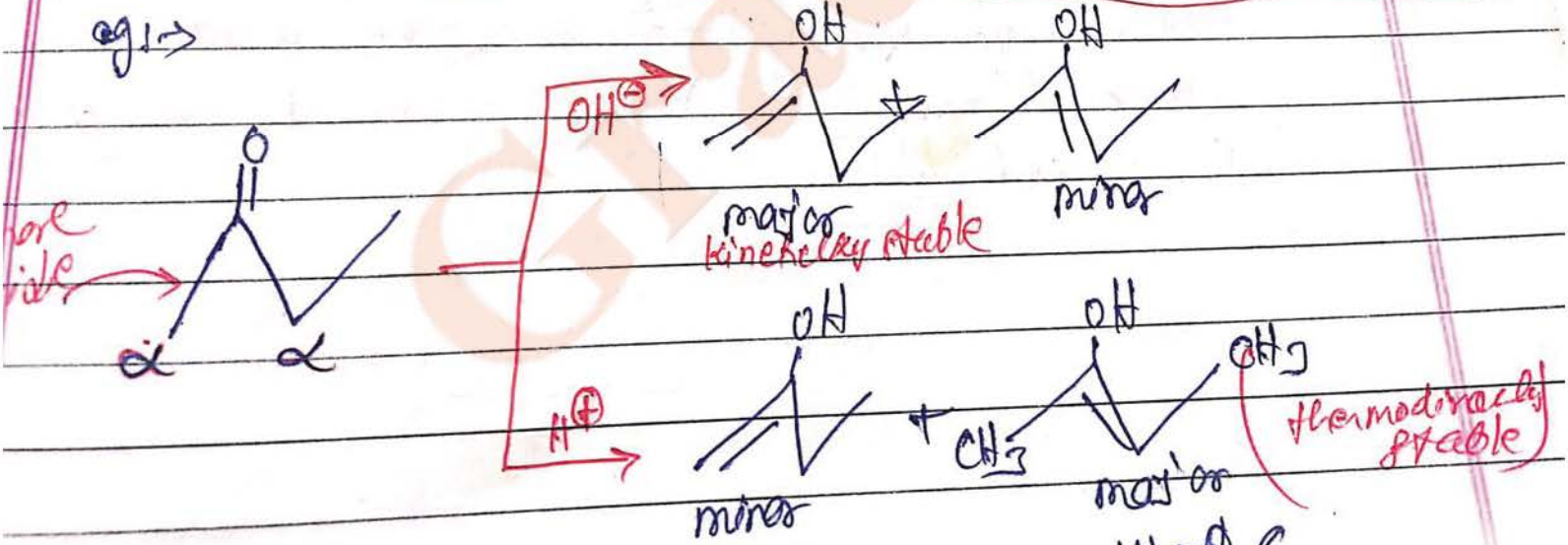
2) Acid catalyzed tautomerism →



- In case of "basic medium" formation of enol involve removal of most acidic hydrogen
- In acidic medium formation of enol depend upon stability of double bond in enol form (No. of αH)

(In acidic medium less acidic hydrogen is removed.)

eg:→



Factor affecting enolization →

Conversion of keto form into enol is known as enolisation, generally keto form is more stable but on Decreasing stability of enol it's amount also Decrease.

Acidic strength of α-H →

Enolisation ∝ Acidic strength of α-H

α-D, -M, -H, Schroeder

Q. Arrange following compound in order of their enol content?

Sol^n

$CH_3-\underset{\underset{O}{\|}}{C}-\overset{\alpha}{CH_3}$ < $CH_3-\underset{\underset{O}{\|}}{C}-\overset{\alpha}{\underset{\underset{O}{\|}}{C}}-CH_3$ <

monoketon

α-diketone

$CH_3-\underset{\underset{O}{\|}}{C}-\overset{\alpha\ominus}{CH_2}-\underset{\underset{O}{\|}}{C}-CH_3$

β-diketon

In case of β-diketone or more acidic α-H (attached to carbon) enol content is greater than keto form.

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eg2.) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (a) $CF_3-\overset{O}{\overset{\|}{C}}-CH_3$ (b)

$CHF_2-\overset{O}{\overset{\|}{C}}-CF_3$ (c) $CF_3-\overset{O}{\overset{\|}{C}}-CF_3$ (d)

c > b > a > d

↓ Nucleophilicity

eg3.) a) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$ (+I)

α-diketone

b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (+I)

10^-5 %

c) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$ (−m, −m)

β-keto ester

d) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (−m, −m)

β-diketone

e) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ (−m)

β-keto aldehyde

e > d > c > a > b

1st Choice

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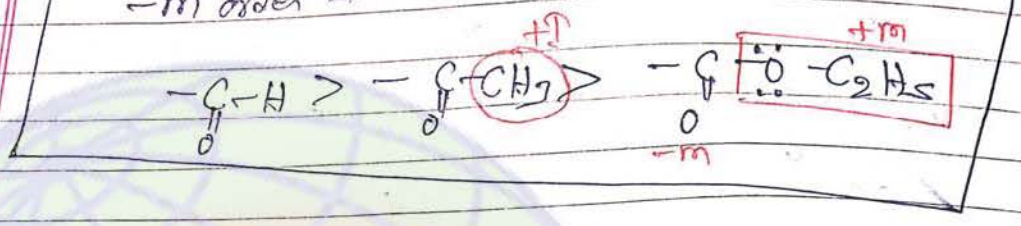
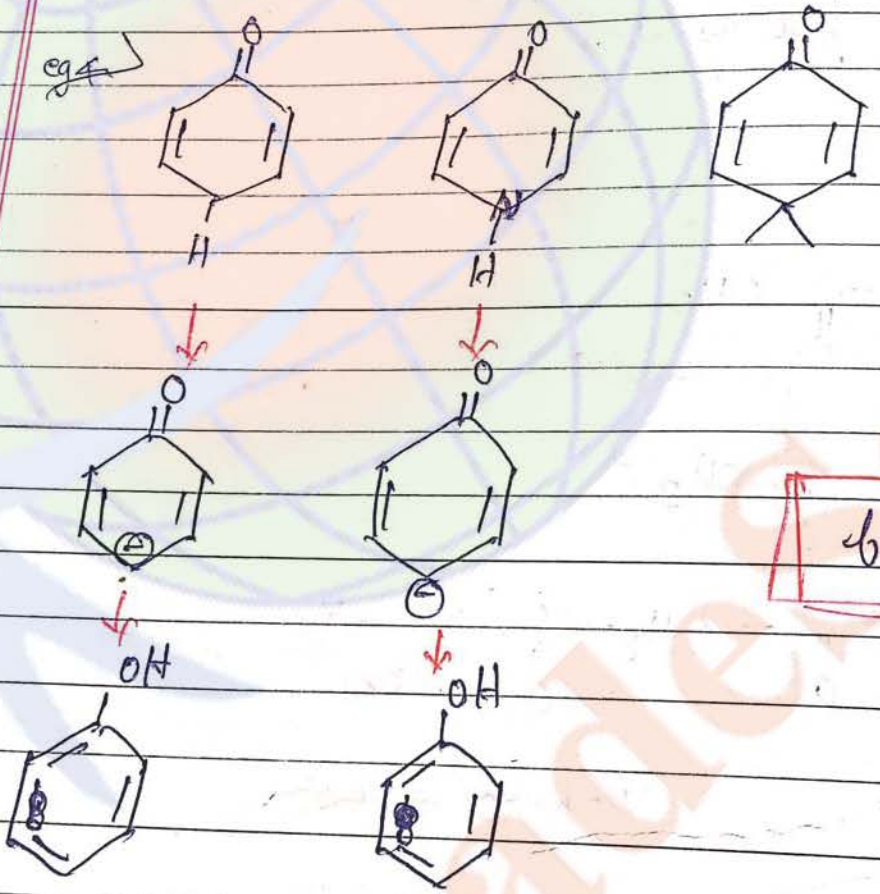
Note:-
-m order →



eg:-



b > a > c

1st Choice

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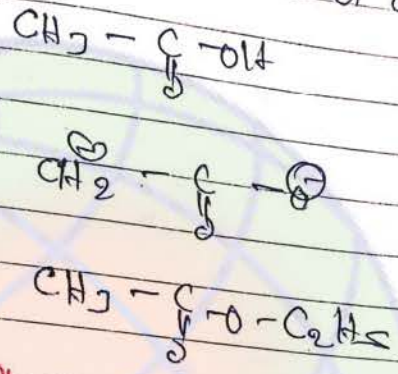
Note:—

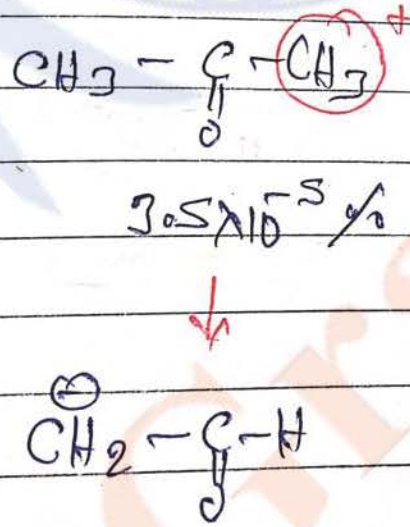
1) carboxylic acid do not show tautomerism because acidic Hydrogen is not attached with carbon it is attached with oxygen.

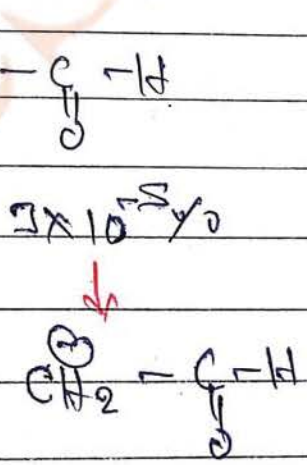


2) "-m effect" of ester is very less that is why along ester do not show tautomerism.

Exceptions

1. Although acidic Hydrogen of acetone is less acidic than acetaldehyde but enol content of acetone is high than acetaldehyde it is due to greater number of α-H





D.P.P.S based on tautomerism

CAREER POINT

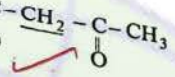
Fresher Course for IIT JEE - 2013

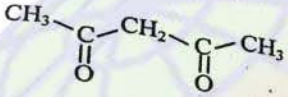
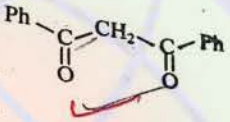
Phase - 1

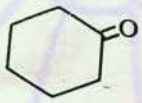
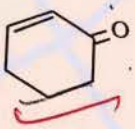
DAILY PRACTICE PROBLEM SHEET

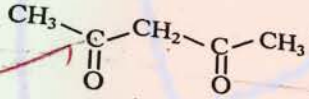
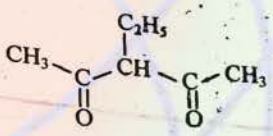
Course : IIT Fresher (Engg.)	Subject : C_2	DPPS No. : 33	Discussion on : 13 July 2012

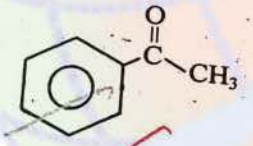
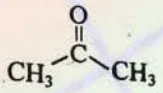
Q.1 Which has higher enolic content ?

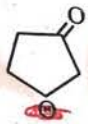
(A)  and 

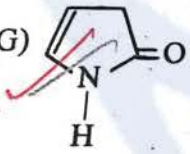
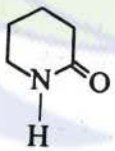
(B)  and 

(C)  and 

(D)  and 

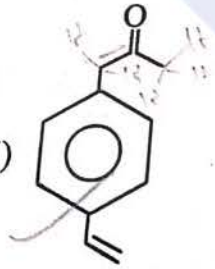
(E)  and 

(F)  and 

(G)  and 

(H)  and 

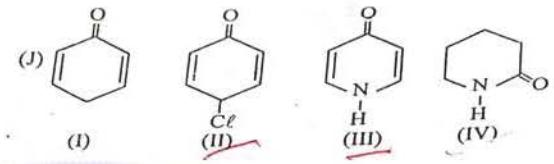
Reason :→ In six membered cyclo monoketone enol content is higher than Acetone (Data Bed

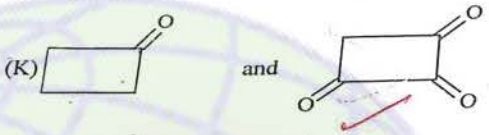
(I) 

(I) (II) (III)

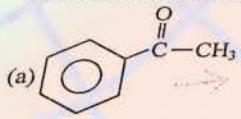
NO₂

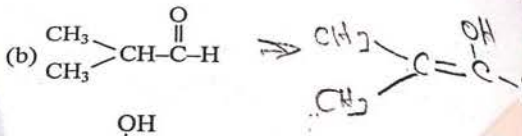
II > I > III

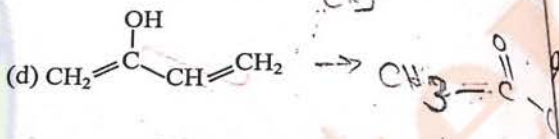


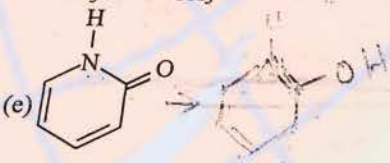


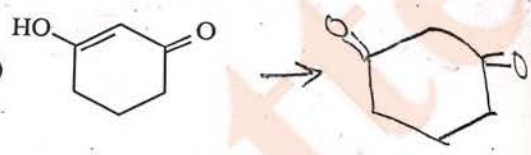
Q.2 Write down tautomeric structure of the following compounds







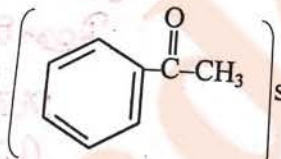




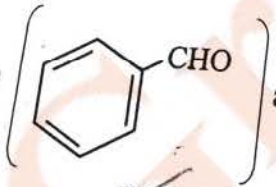
Passage based question (Q.3 to Q.7)

Tautomerism arises due to 1, 3-migration of a proton form one polyvalent atom to the other within the molecule. Two isomers thus obtained exist in dynamic equilibrium with each other are called tautomer the phenomenon is called tautomerism or allelotropism or dynamic isomerism.

For an aldehyde or ketone to exhibit keto-enol tautomerism, it is essential that it must have at least one α-hydrogen atom. In simple aldehydes and ketones the 'enolic' form is negligibly small. This is due to stability of the 'keto' form with respect to 'enol' form. Strength of (C = O) bond in keto form has greate energy than (C = C) bond in enol form.

Q.3 The compound acetophenone  shows the 'keto' - 'enol' tautomerism.

(a) True (b) False

Q.4 Benzaldehyde  and benzophenone  both possess tautom

(a) True (b) False

Phenol is more stable than 2, 4-cycloheaxediene-1-one

(a) True (b) False

Acetylacetone is more stable than α-methyl acetyl acetone.

(a) True (b) False

'Enol' form of acetoacetic ester is more stable than 'keto' form.

(a) True (b) False

(A) Which of the following compounds will not show enolisation ?

(i) (ii) (iii) (iv) (v)

(B) Draw the enol tautomers for each of the following compounds, for those which have more than one enol, indicate which is more stable.

(i) (ii) (iii) (iv) (v)

Which of the following compounds shows tautormerism ?

(A) NH_2-C-NH_2 (B) NH_2-C-NH_2 (C) HO– –N=O (D) CH_3-C-CH_3

Which of the following compounds can not show tautomerism ?

(A) $HO-CH=CH_2$ (B) (C) (D)

eg:-

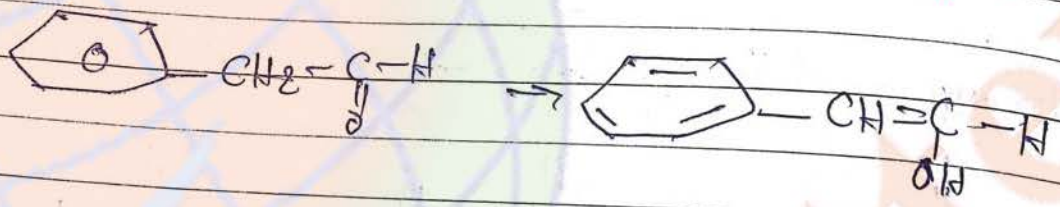
a) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftharpoons CH_3-\overset{OH}{\overset{|}{C}}=CH_2$

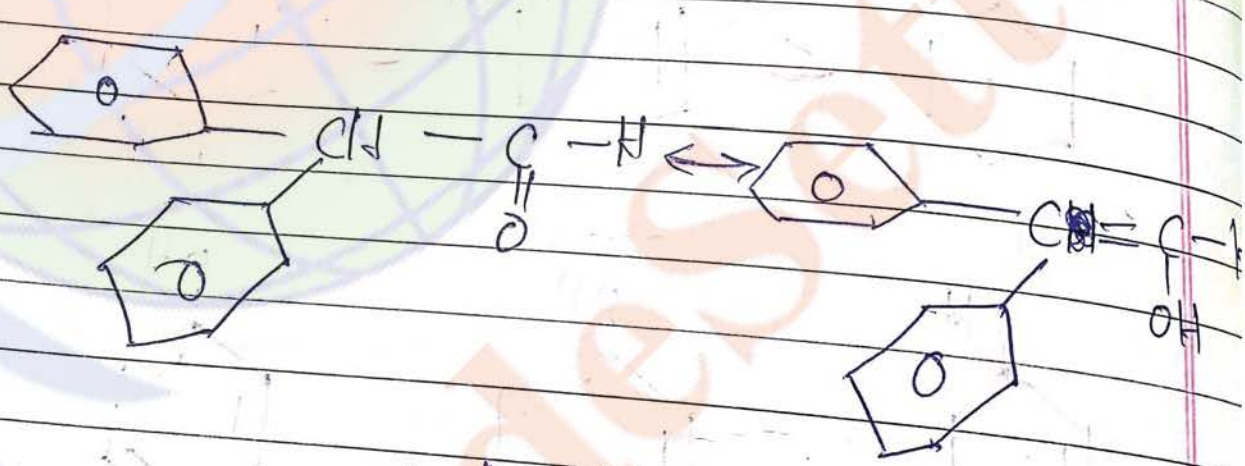
b) $CH_2=\underset{sp^2}{CH}-\overset{O}{\overset{\|}{C}}-H \rightarrow CH_2=C=\overset{OH}{\overset{|}{C}}-H$

Conjugated

c) $CH_2-CH-CH_2-\overset{O}{\overset{\|}{C}}-H \rightarrow CH_2=CH-CH=\overset{OH}{\overset{|}{C}}-H$

Conjugated

d) 

e) 

c > d > e > a > b

1st Choice

3. Hydrogen bonding →

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If enol form have extra molecular H-bonding than it's extent Increase.

(i) $CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{OH}{|}}{C}=CH_2$ (less than 1%)

dimer H-bond

$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-O-C_2H_5 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}=CH-\underset{\underset{O}{\|}}{C}-O-C_2H_5$

dimer oxide hydrogen

Aceto acetic acid (AAE) or ethyl aceto Acetate (β. keto ester)

↑ Hydrogen bonding

8%

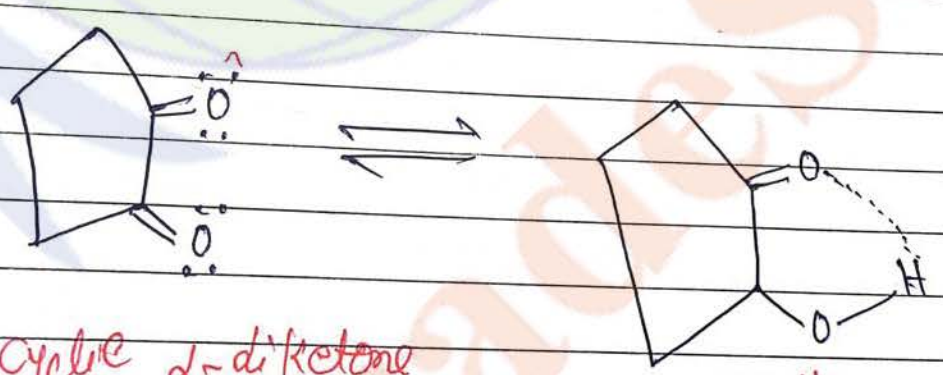
$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{O}{\|}}{C}=CH-\underset{\underset{O}{\|}}{C}-CH_3$

Acetal Acetone (β Diketone)

H-bonding

46%

(ii)



Cyclic α-diketone
Highly unstable

Stable
Almost 100%

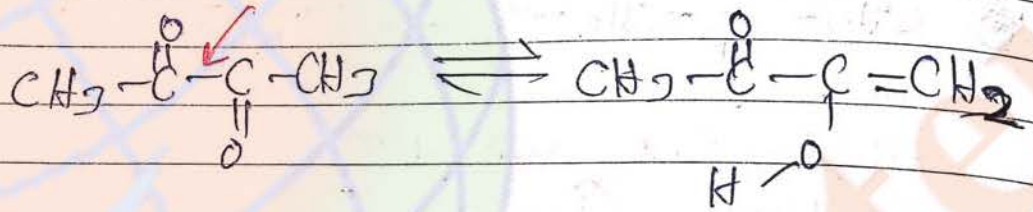
Note ➡

1) Cyclic α-diketone is highly unstable due to repulsion b/w two $\sqrt{-C=O}$ group that is why it easily convert into

enol form where it's hydrogen bonding stabilize molecule (Almost 100%)

(1) This kind of repulsion is not present in open chain β-diketone so in this case keto is more dominating.

both C=O groups are in opposite direction



$K < 1$

1st Choice

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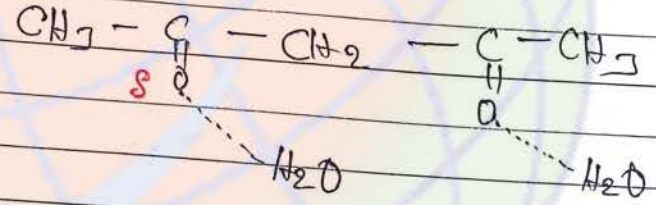
4⇒ Solvent effect:→

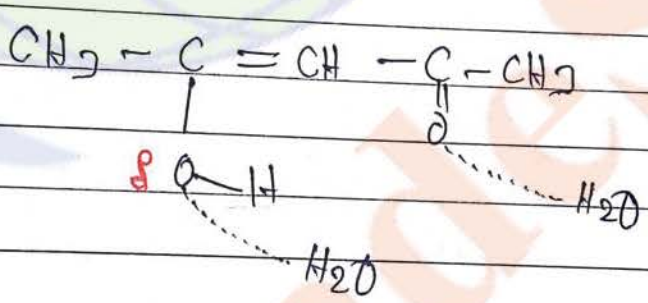
It is observed that in case of Protic solvent keto form is more dominating than enol form it is because Protic solvent stablize keto form more by H-bonding compare to enol form

Acetyl Acetone→ % enol :⇒ Gas phase = 92%
liquid phase = 76%
Protic solvent = 15%



more powerful H-bonding

keto form



less powerful H-bonding

Summary ⇒⇒⇒⇒
Generally keto form is more dominating but in case of Aromatic enol
II] β-diketone (or higher order than β-diketone)
and
III] cyclic α-diketone
enol form is more dominating than keto form

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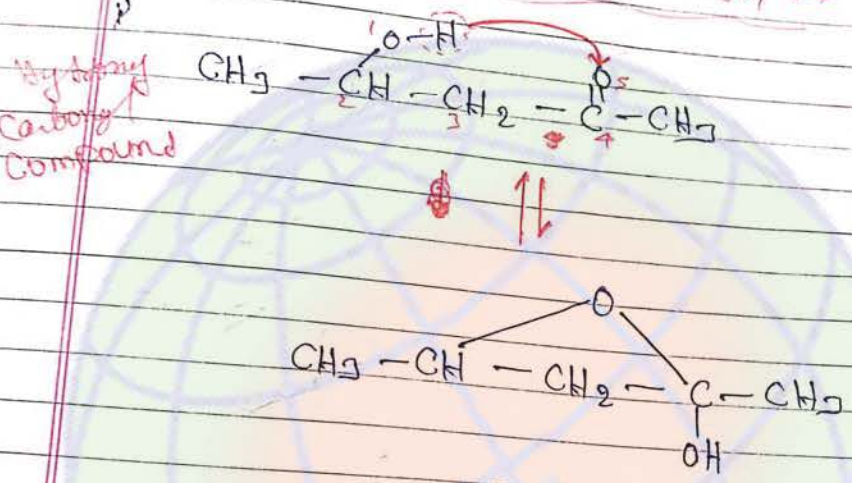
Ring chain tautomerism →



ii) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

Acetyl acetone

form di

Draw di-enol form of Acetyl acetone

Sol^n ⇒

$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

$CH_3-\underset{OH}{C}-CH=\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\underset{OH}{C}=C=\underset{OH}{C}-CH_3$

Cumulated is unstable

(X)

$CH_3-\underset{OH}{C}=CH-\underset{OH}{C}=CH_2$

Conjugated

1st Choice

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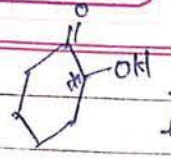
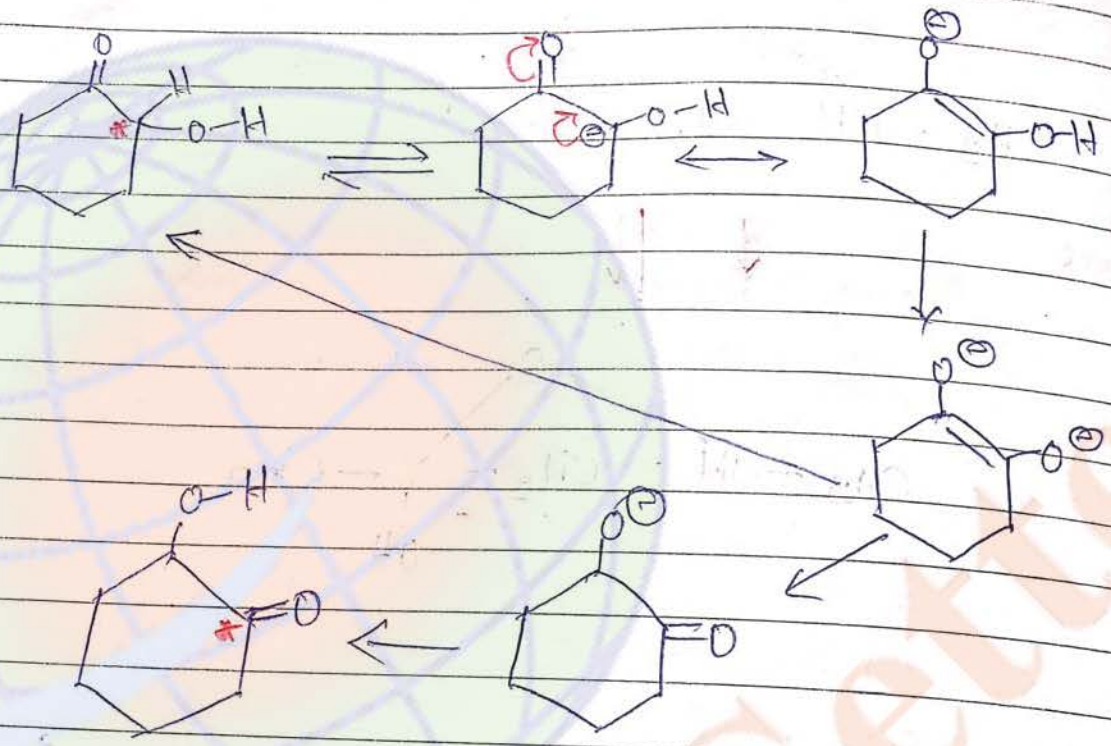
Exp 2
@NO >= 14



$\xrightleftharpoons{base}$ (A), unknown compound A is ? who #C = 14

8/4



Stat

1st Choice

Stereo Isomerism

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Those Isomers which have same connectivity of atoms but have diff" orientation of of atoms.

1) Conformational Isomerism ⇒

i) ← Those Isomers which are Interconvertible by rotation of single bond (C-C) are known conformers or Rotomers.

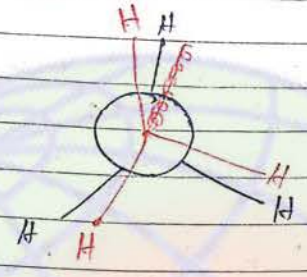
ii) For any molcule Infinite number of conformers (single bond rotation) are possible

iii) Conformers are Interconvertible at room temperature because ther energy difference b/w them is very less and it is available at room temperature.

At room temperature most stable conformers is higher in amount but on Increasing temperature amount of less stable conformer Increase.

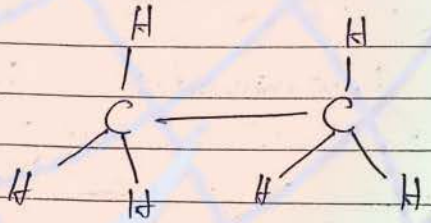
☆ Neoman formula and sawhorse formula →

CH_3-CH_3 → (conformers of ethane)



(Neoman formula)

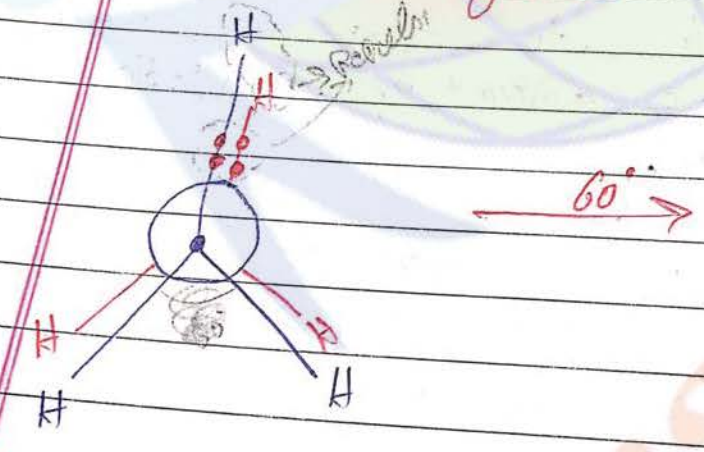
$\theta = 0°$, where θ = dihedral angle



(Sawhorse formula)

⇒ Conformers of ethane; $\theta = 60°$

→ Neoman formula

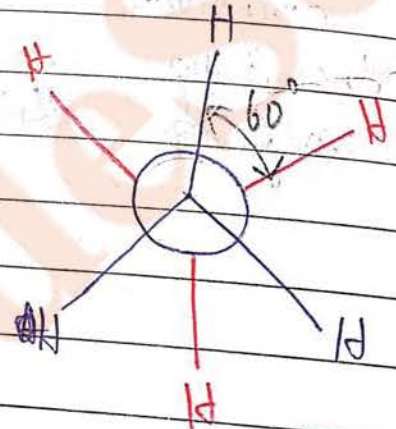


Eclipsed

Dihedral angle ⇒ $\theta = 0°$

→ less stable

→ more energy



Staggered

$\theta = 60°$

→ more stable

→ less energy

Gauche conformation (गौश कन्फॉर्मेशन)

1st Choice

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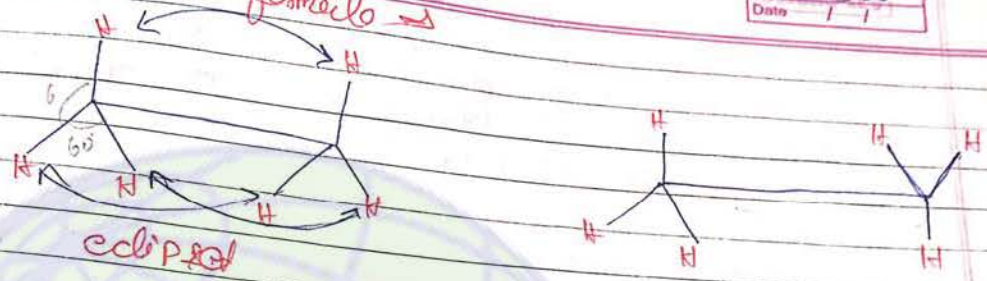
→ Spectacle formula →



eclipsed
$\theta = 0°$

Staggered
$\theta = 60°$

There are two Important conforme of ethane →

1) Eclipsed one
2) Staggered.

Note ⇒

1) In Eclipsed conforme ⇒ C-H bond of one carbon is in overlaping condition, with another C-H bond.
So their is repulsion b/w bond-pair one bond-pair and due to this repulsion energy of eclipsed is higher and stability is lower compare to Staggered conforme.

2) Along with bond pair – bond pair repulsion, Repulsion b/w H – H is also present where is Steric repulsion or vandaeall repulsion or Strain
(repulsion = Strain)

3) In eclipsed formed dihedral angle is 0°

4) In Staggered form C-H bond of one carbon is in b/w two C-H bond of another carbon. That is why repulsion in staged form is very less ✓

1st Choice Pg 1

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5) The energy difference b/w eclipsed and staggered form is known as Torsional energy.
Torsional strain.

6) Torsional strain is absent in staggered form.

7) Dihedral angle for eclipsed form is 0° and for staggered form it is 60°

H – C_f – C_b — Plane – 1

H – C_b – C_f — Plane – 2

8) Stability of staggered > Stability of eclipsed.

9) when temperature is Increased % of eclipsed form Increase.

Note ① No. of conformers of ethane are Infinity

② At room temp the eclipsed and the staggered form of ethane be isolated because they Interconvert rapidly.

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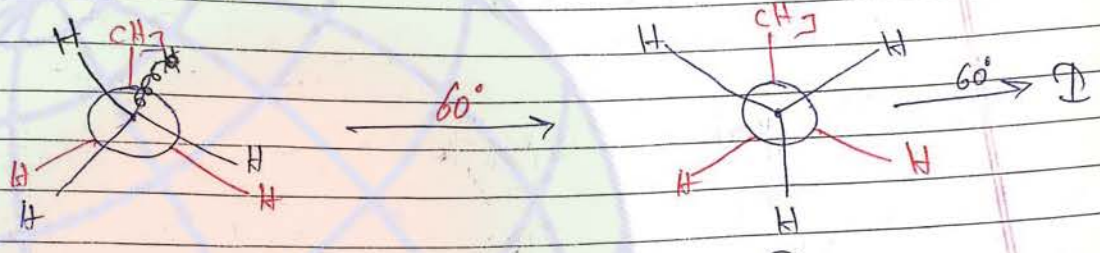
☆ Conformers of Propane ($CH_3-CH_2-CH_3$) →



I
eclipsed
✓

II
staggered
✓

☆ Conformers of Butane

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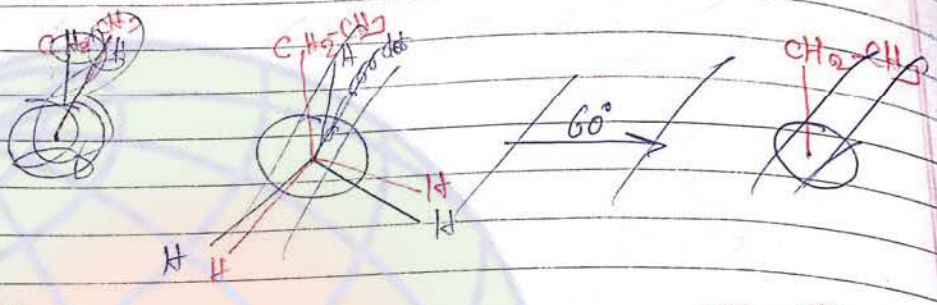
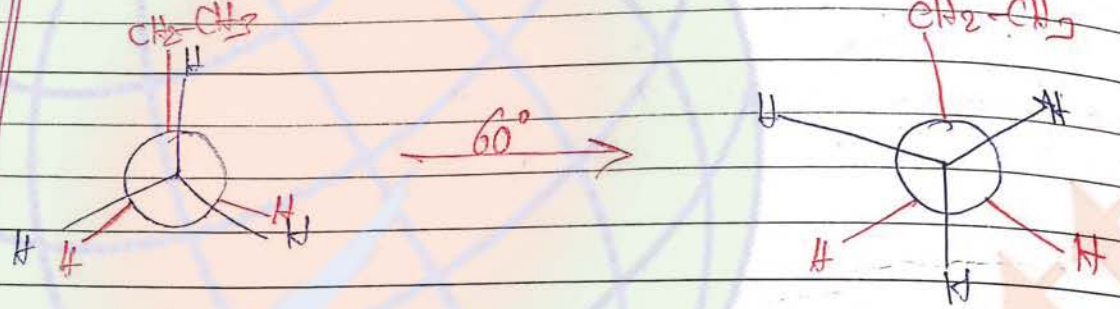
☆ Conformers of Butane

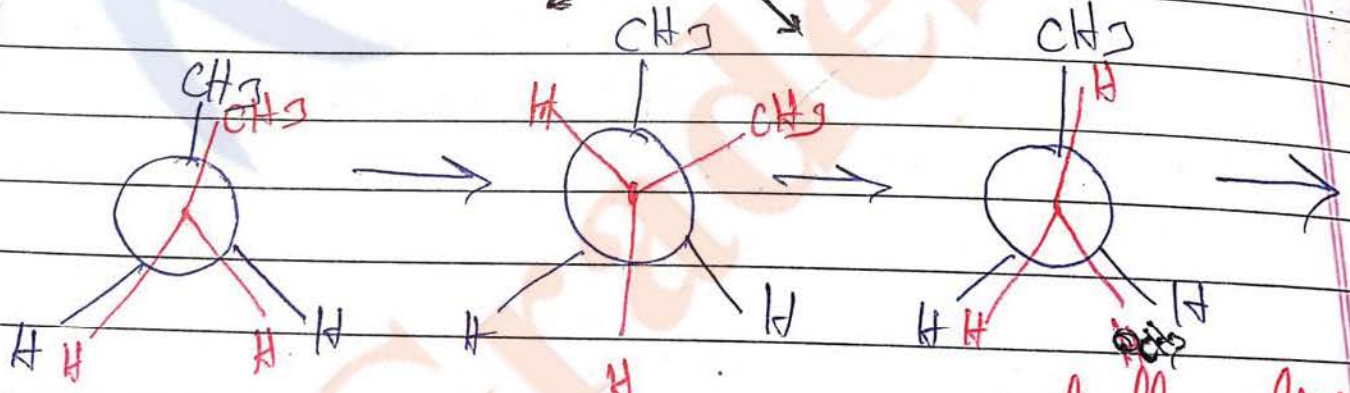
A) $CH_3 - CH_2 - CH_2 - CH_3$ along $C_1 - C_2$





B) Along $C_2 - C_3$

(Same atom का 60° स्थानान्तरण)



Eclipsed
$\theta = 0°$
(I)
दो same atom पास-पास

Gauche or skew
$\theta = 60°$
(II)

partially eclipsed
$\theta > 120°$
(III)
दो other atom पास-पास

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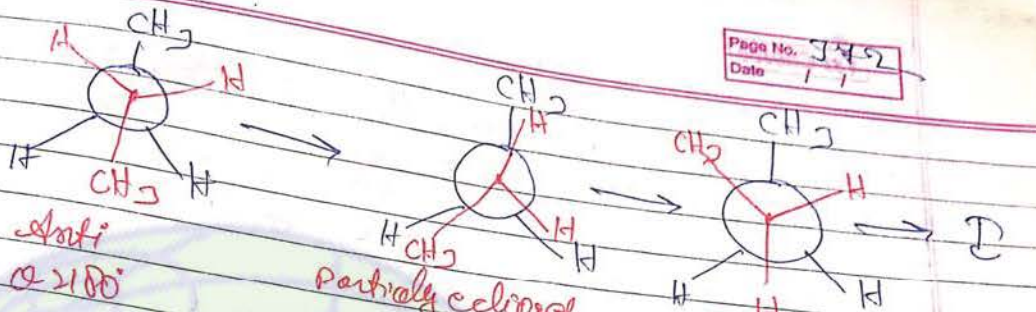

1) Four significant conformer possible for butane along $C_2 - C_3$ bond the stability order is

anti > Gauche > Partially > eclipsed
(IV) or skew eclipse
(II) = (VI) (III) = (V)

hidden ~~of~~ stability A.G.P.E

2) Anti is generally more stable because large group are at maximum distance. If large group's are close than repulsion is high and stability is less.

Amount wise mainly present at room temperature

Anti > Gauche
or skew

Amount wise two conformers are important and they mainly exist at room temperature Anti or Gauche.

Anti or Gauche.

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@ So equilibrium is present mainly b/w anti and Gauche

Gauche ⇌ Anti

$\Delta G^\circ = -2.303\ RT \log K$

$$\Delta G^\circ = -2.303\ RT \log \frac{\text{anti}}{\text{Gauche}}$$

3) Dipole moment of complete molecule is also depend upon conformers

$$\mu_R = \sum \mu_i X_i$$

(Resultant dipole moment)

where

μ_i ⇒ D.M (Dipole moment) of ith conforme.

X_i ⇒ mole fraction of ith conforme.

$$\mu_R = \sum \mu_{anti} X_{anti} + \mu_g X_g$$

Assume :⇒

$$X_{anti} + X_{gauche} \simeq 1$$

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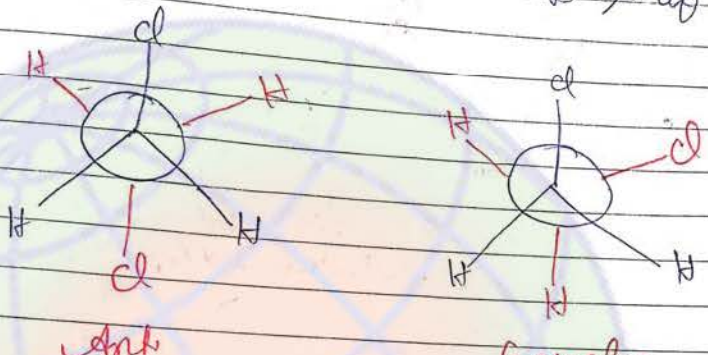
Example If resultant dipole moment of 1-2 dichloro ethane is 1.8 debai and the dipole moment of gauche form is 5 then calculate % of Anti form present.

Solution



$\mu_{anti} = 0$ (क्योंकि दोनों dipole एक दूसरे को काट देंगे)

$1.8 = 0 \times x_{anti} + 5 \times x_g$

$x_g = \frac{1.8}{5} = 0.36$

$x_g \simeq 0.6$ $\quad (\because x_{anti} + x_{gauche} = 1)$

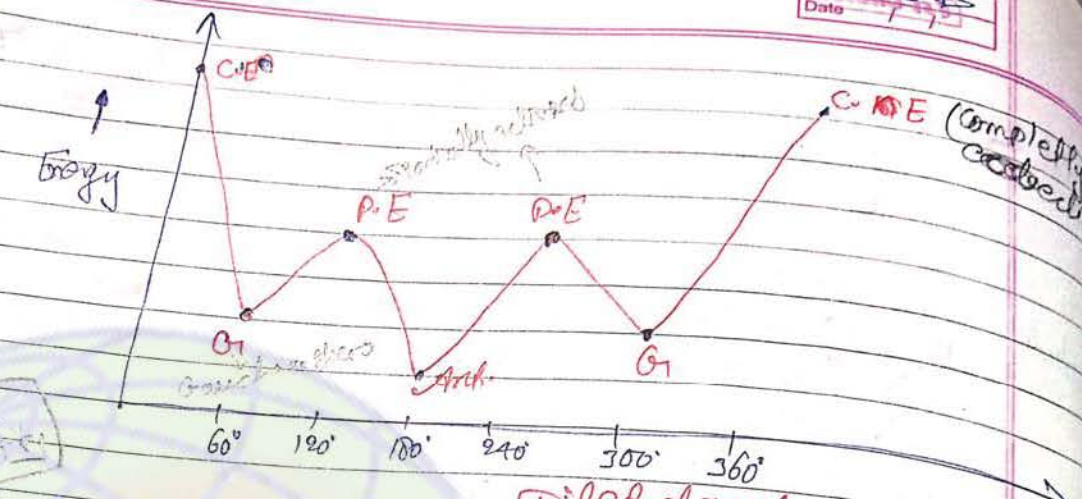
So,

% Anti = 64 %

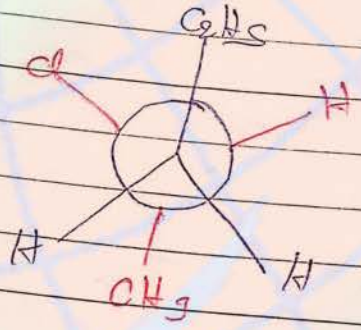
On Increase in temperature dipole moment of this molecule is Increases.

Ex 2.) Draw energy profile diagram for butane along $C_2 - C_3$

So)



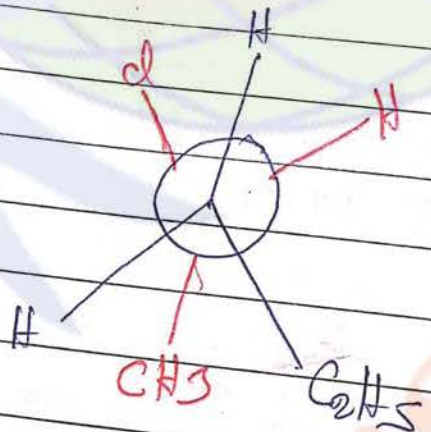
Ans:



→ front carbon

If C_2 is rotated by 120° then which conformer is form by clockwise rotation,

Sol:



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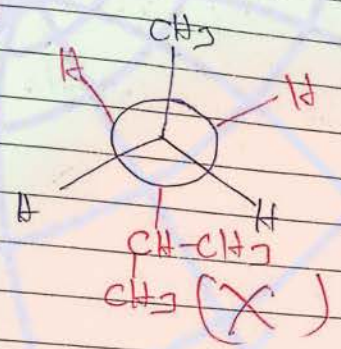
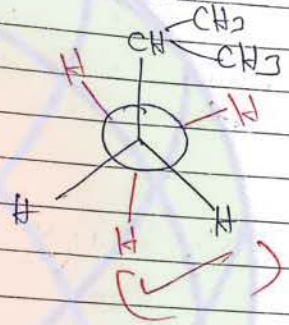
Eg:- which of the following conformer is possible for Dispentane →

$CH_3-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

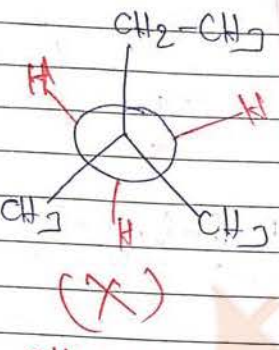
Sol^n



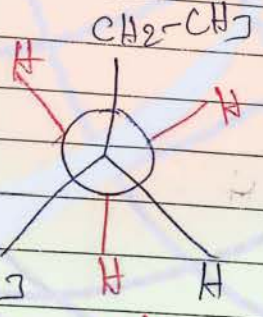
(X)



(✓)



(X)



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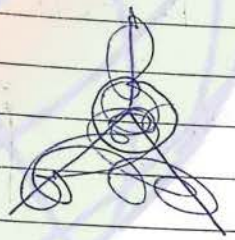
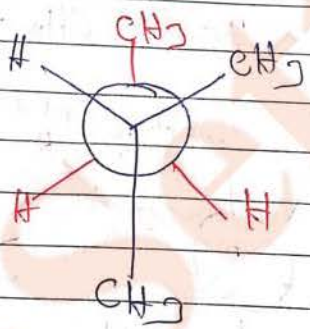
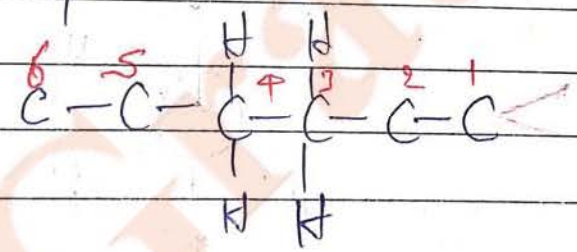




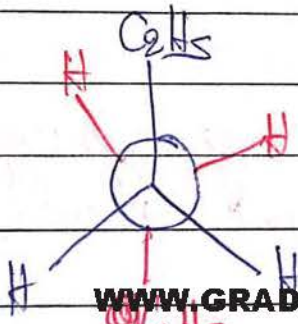
(✓)

Question :- Draw most stable conformer in hexane along C_3-C_4

Solution



most stable conformer →



1st Choice

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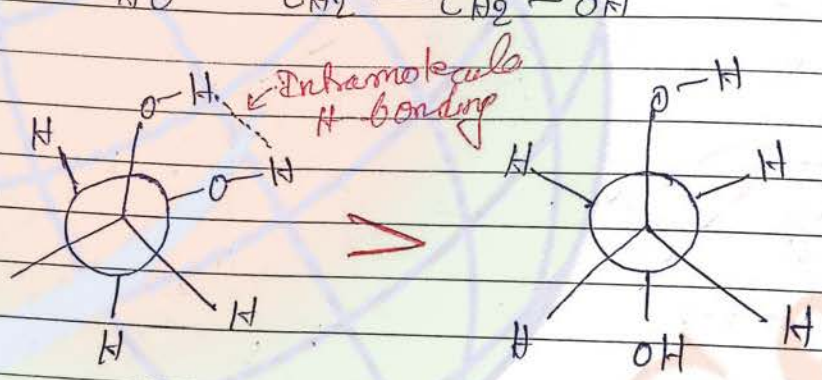
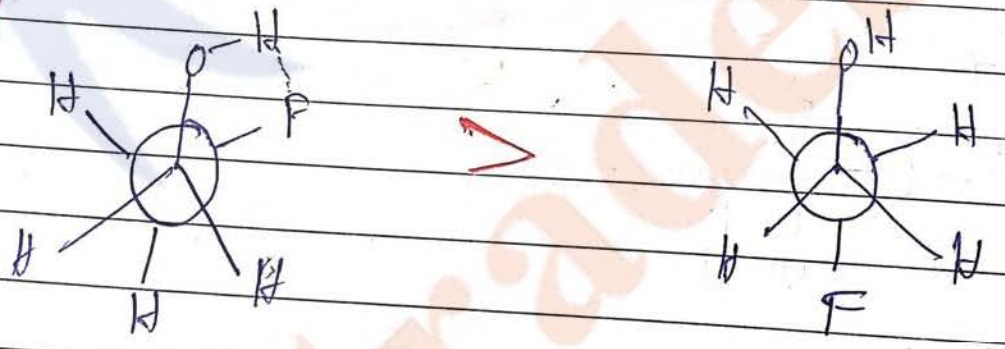
Examples where gauche form is more stable →

when there is repulsion b/w large groups then anti form is more stable than gauche
but if there is some attraction force then gauche form can be more stable.

1) Intramolecular H-bonding



more stable



For following type of molecule, gauche form is more stable than anti

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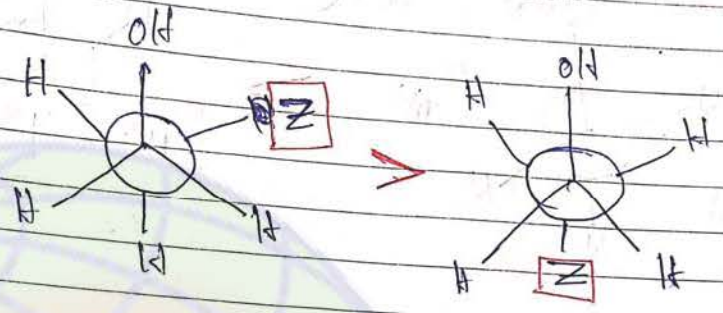
$Z - CH_2 - CH_2 - O-H$



Ans: $Z \Rightarrow -OH$, $-F, -Cl, -NH_2$, $-NHR$, $-\overset{O}{\overset{\|}{C}}-H$, $-\overset{O}{\overset{\|}{C}}-O-H$, $-\overset{O}{\overset{\|}{C}}-NH_2$

Q.11) Draw most stable conformer of succonic acid of PH=2 and PH=12

$HOOC - CH_2 - CH_2 - COOH$

PH=2 (Acid) → Undissociated

PH=12 (Base) → dissociated

Undissociated:

$CH_2 - COOH$
|
$CH_2 - COOH$

(Gauche form is more stable due to H-bonding)

dissociated:

$CH_2 - COO^{\ominus}$
|
$CH_2 - COO^{\ominus}$

(Antiform is more stable

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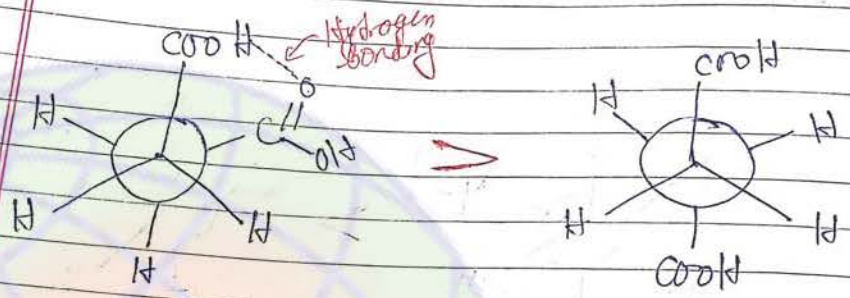
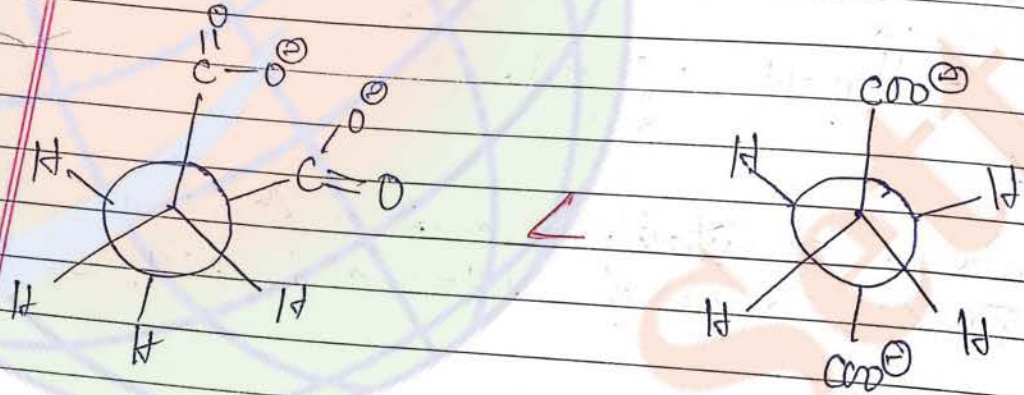
So, At $P_H = 2$ →



At $P_H = 12$ →



Example→ which form of this molecule is more stable anti or gauche

Ans Gauche due to electrostatic attraction.

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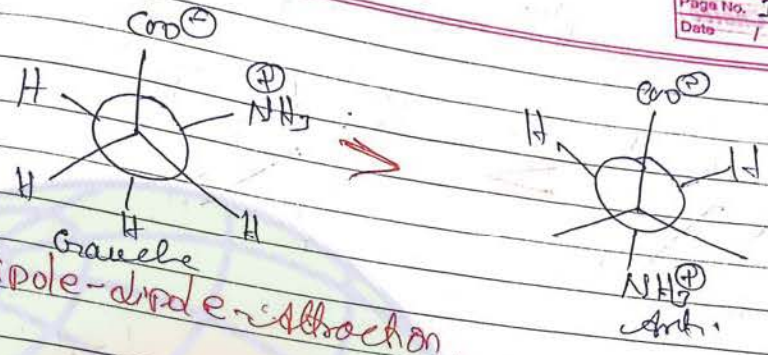
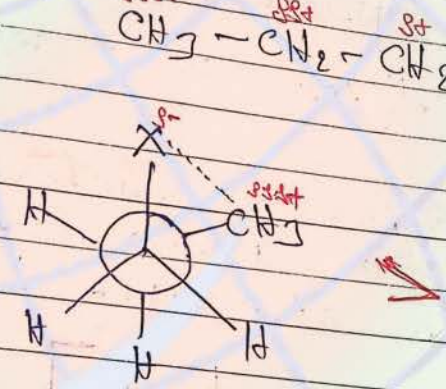
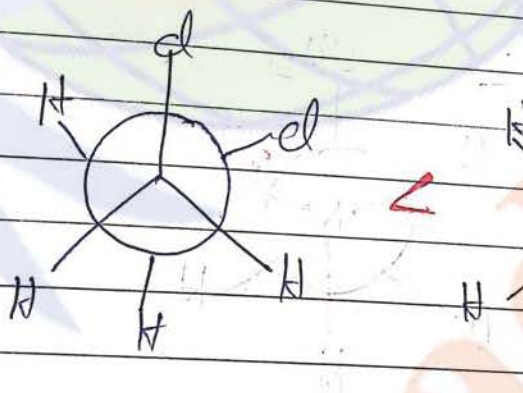
Ans



2.) Dipole-dipole attraction.





In case of 1-2 dihalo ethane Anti form is more stable than gauche but 1-2 difluoro ethane is an exception where gauche form is more stable than Anti.

Ans

1st Choice

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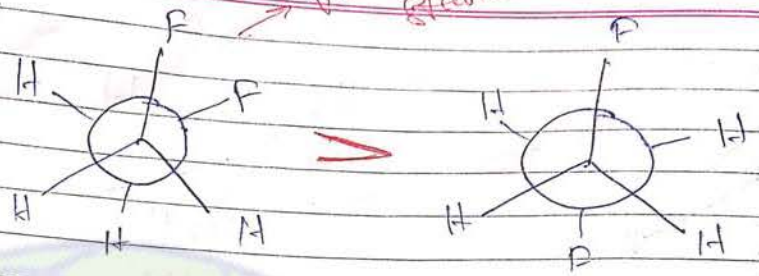
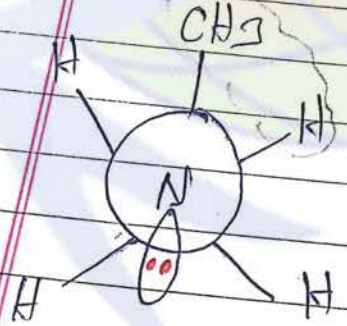
Above Staggered से more stable होता है



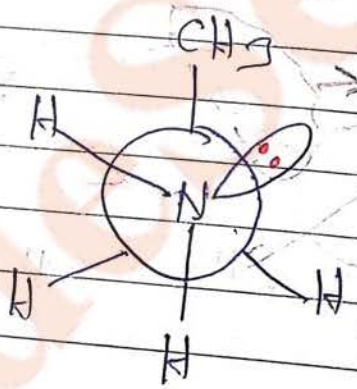
Note → Steric Repulsion is caused by a lone pair is less than Hydrogen (H-atom) atom
(L.P का Repulsion, Hydrogen atom से कम है)

In ethyl amine conformer in which lone pair is on gauche position to the large group is more stable than other conformer.

[ethyl Amine → $CH_3-CH_2-NH_2$]



(यहाँ Repulsion अधिक है)



→ यहाँ कम Repulsion है

1st Choice

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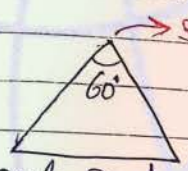
Conformation of Alicyclic Compounds

Ring stability →
C3 > C5 ≈ C7 > C8 > C4 > C3

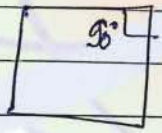
सबसे ज्यादा stable C3 होता है।

1) Open chain compounds are generally more stable than cyclic specially in case of smaller ring.

2)



cyclo Propane



cyclo butane

→ sp^3

expected bond angle $109°28'$

Deviation from Ideal bond angle.

planar.

Smaller size ring's are unstable due to deviation from Ideal bond angle.

3) It is observed that ring's size membered greater than 6 membered are completly non-planer and have bond angle $109°28'$

So,
Angular Strain is not present

Angular Strain → Deviation of bond angle from Ideal bond angle.

Ideal bond Angle = $109°28'$
(जिसमें more stable होता है)

1st Choice

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Conformation of cyclo Hexane →

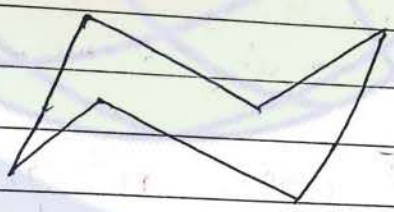
Cyclohexane is completly non-planar (Puckered) structure and it have four Important Conforms

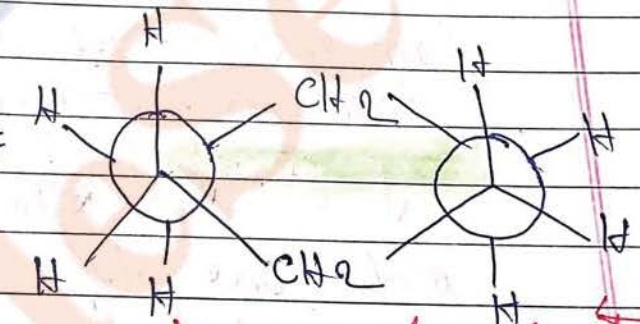
i) chair form (resistance 99% so more stable)
ii) Boat form
iii) Twist boat form
iv) Half chair form.

{ नाव जैसा →
कुर्सी जैसा दिखाई देता

i) chair form →

i)

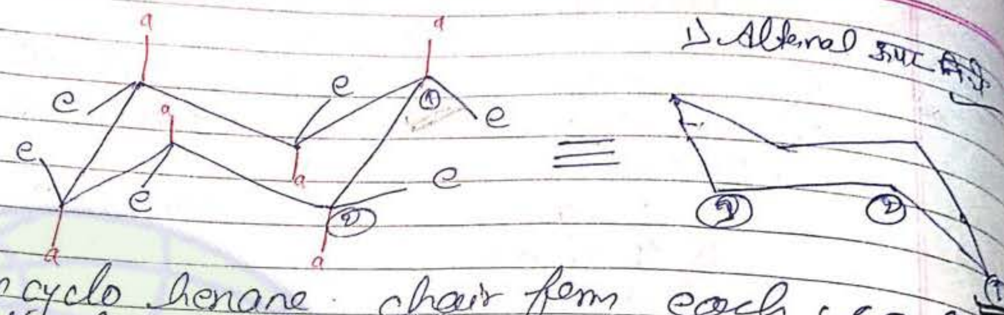




Newman formula of chair form.

It is the most stable conform of cyclo hexane and because it is free from Angular strain and free from torsional strain (all C-H are in staggered condition w.r.t. each other.

2.)



In cyclo hexane chair form each carbon is attached with two type of bond's in

a) Axial

These bond's are ⊥r to the Average plane and vertically upand down alternatively

b) Equitorial

These bond's are in average plane and Parallel to next C-C bond.

chair form exist in equillibrium with another chair form. This phenomena is known as ring fliping. and In this case all axial bond of one chair form convert into equitorial & vice-versa.

1st Choice

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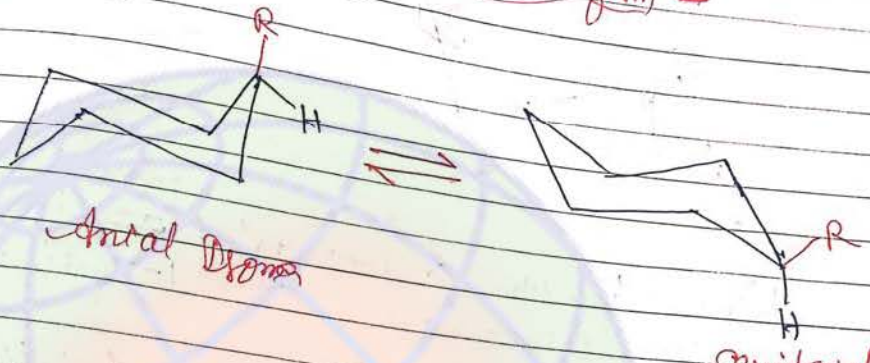
mono-substituted chair form →



Axial Form ⇌ Equitorial Form

$$K = \frac{[P]}{[R]}$$

$R = H$	$K = 1$
$R = CH_3$	$K = 8$
$R = CH_2-CH_3$	$K = 21$
$R = CH(CH_3)_2$	$K = 38$
$R = -C(CH_3)_3$	$K = 3800$

In monosubstituted cyclohexane substituent prefer to remain in equitorial position and if substituent is larger than relative stability of equitorial Form also Increase

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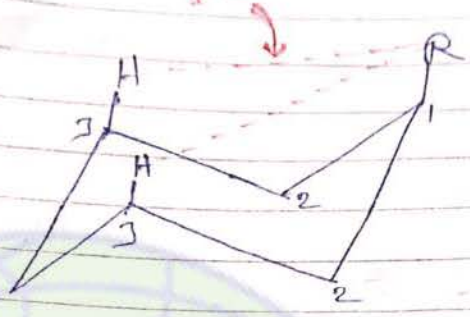
2.)



Axial Dome is less stable because in axial position there is 1-3 diaxial repulsion.

because axial bond at H and axial carbon are in the same direction (crowded)

1st Choice

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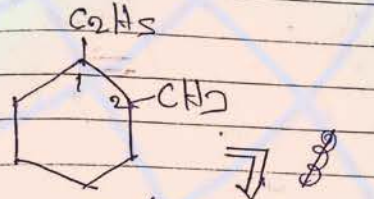
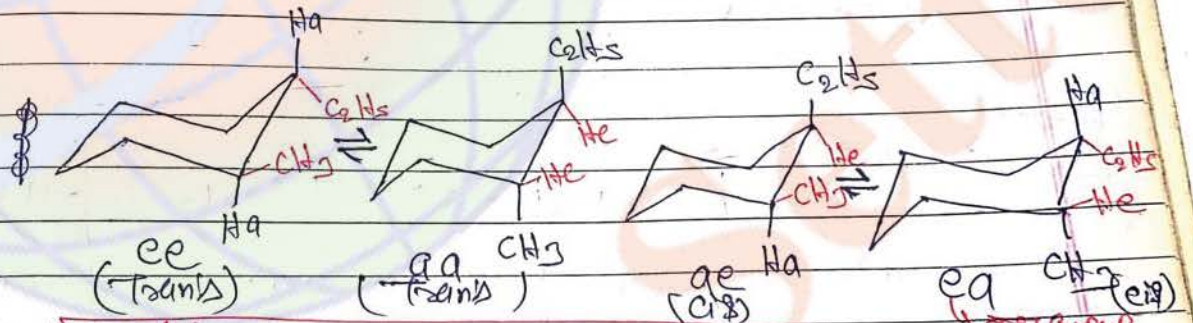
Disubstituted cyclo Hexane →

Substituent are more stable at equitorial position mainly at larger group.



1-2 disubstituted



Stability → ee > ea > ae > aa

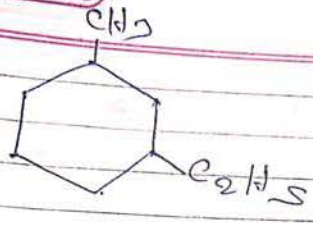
ee, aa → Trans

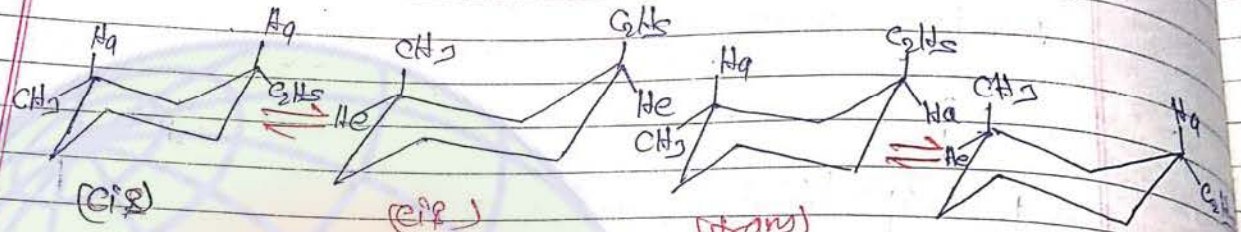
ea, ae → Cis

ea → 1 बड़ा group है,

Stability equitorial के आधार पर देखते है

1st Choice





(cis) ee

(cis) aa

(trans) ae

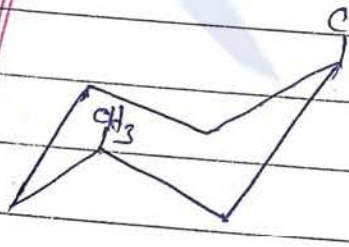
(trans) ea

Stability ⇒ ee > ea > ae > aa
cis trans trans cis

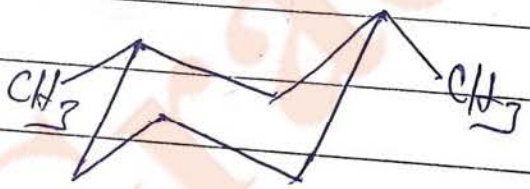
Summary ⇒

	aa → ee		ea → ae	
1, 2	Trans	Trans	cis	cis
1, 3	cis	cis	trans	trans
1, 4	Trans	trans	cis	cis

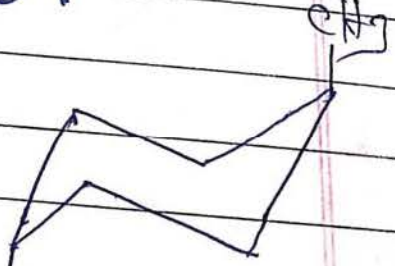
Interconvertible

Ex. 

सिर्फ मद मद करके पता मार्क रख सकते हैं (TGT



(a)



(b)

(c)

a and b conforme
b and c

Stability → chair > twist

1st Choice

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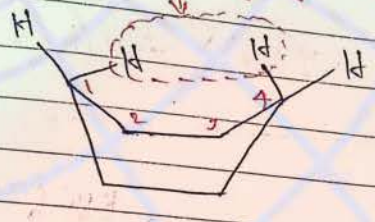
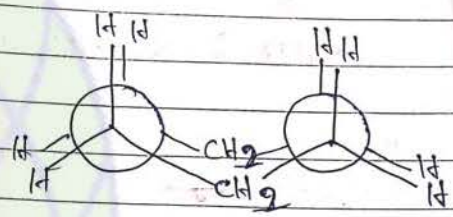
2) Boat formation →

- This is less stable than chair form due to two diff^n type of repulsion. A torsional strain (all carbon are in eclipsed condition)

torsional str.

1-4 flagpole hydrogen repulsion

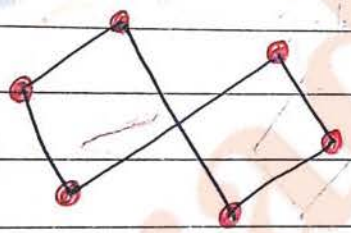




Newman formula

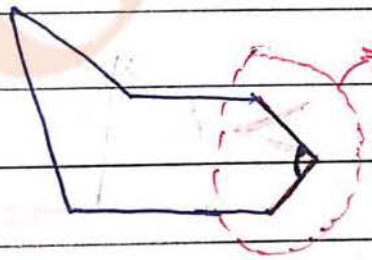
3) Twist boat conformation →

In twist boat form some torsional strain is decrease due to twisting that is why it is more stable than boat form.



→ This is chiral form of carbons

4) Half chair form →



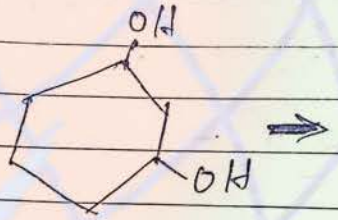
It is the most unstable conform of cyclohexane because some part of the ring's become planar and Angular strain is present.

Note:
Overall Stability order

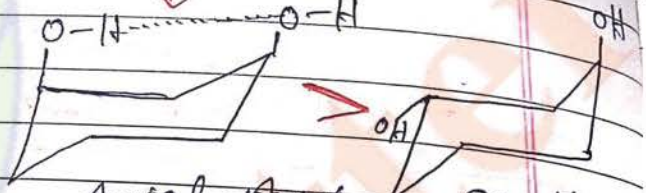
chair > twist boat > boat > half chairs

⭐ Exception ⇒

i) ~~Generally~~



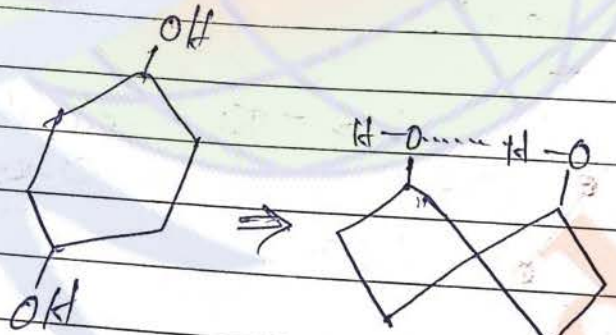
Due to Hydrogen bond



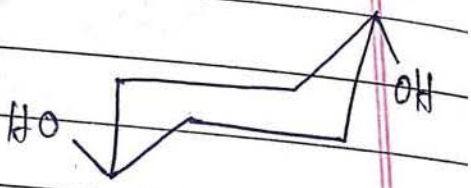
Axial-Axial is more stable due to H-bonding

equitorial

ii)

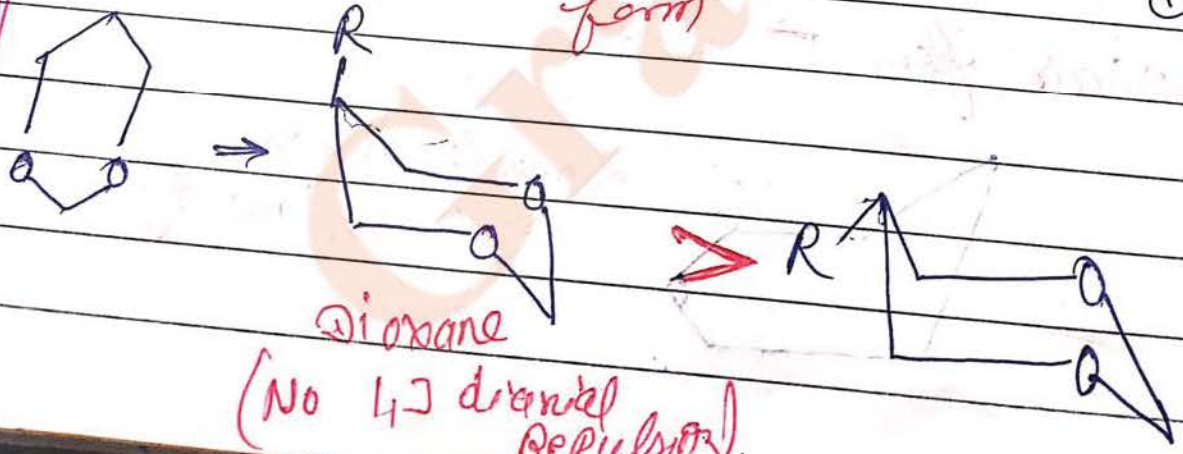


Twist boat form



chair form.

iii)



Dioxane

(No 1,3 diaxial Repulsion).

1st Choice

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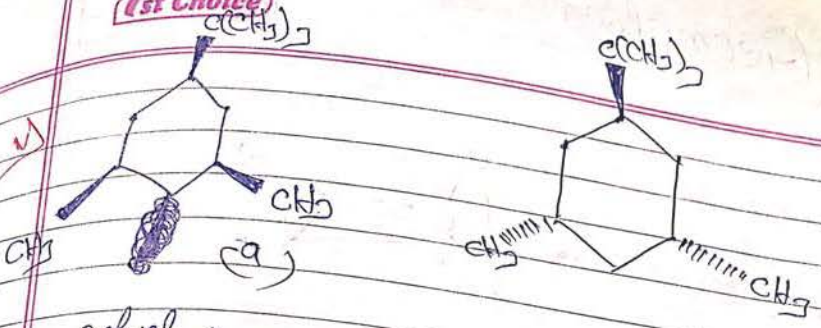
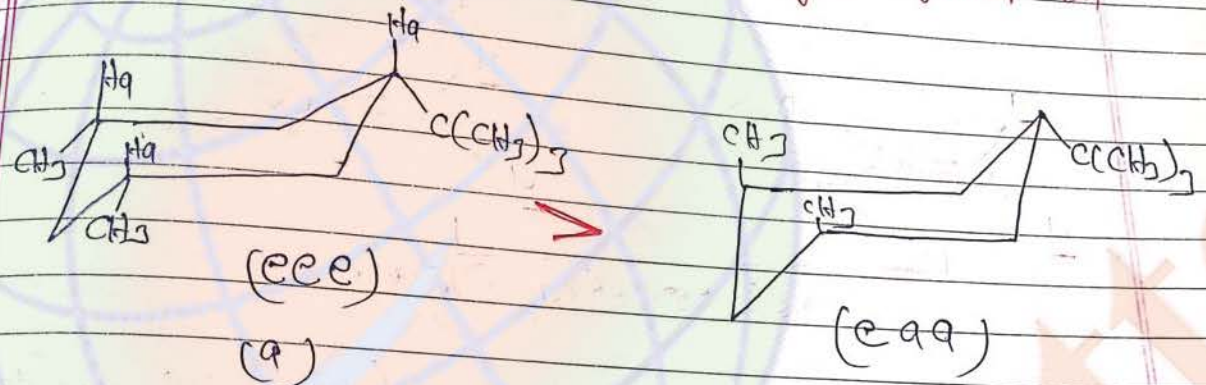
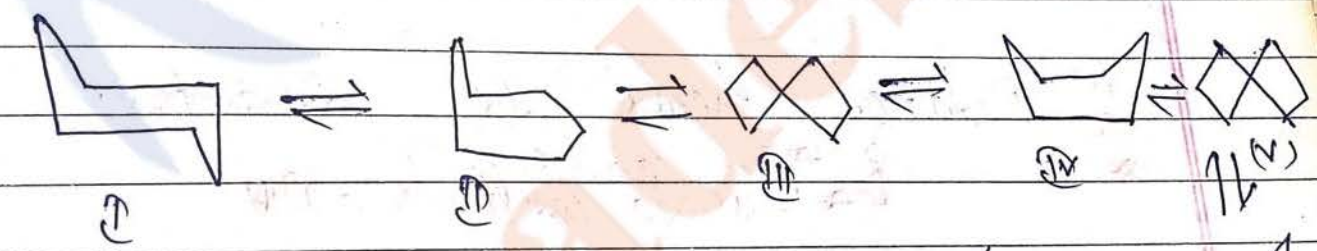


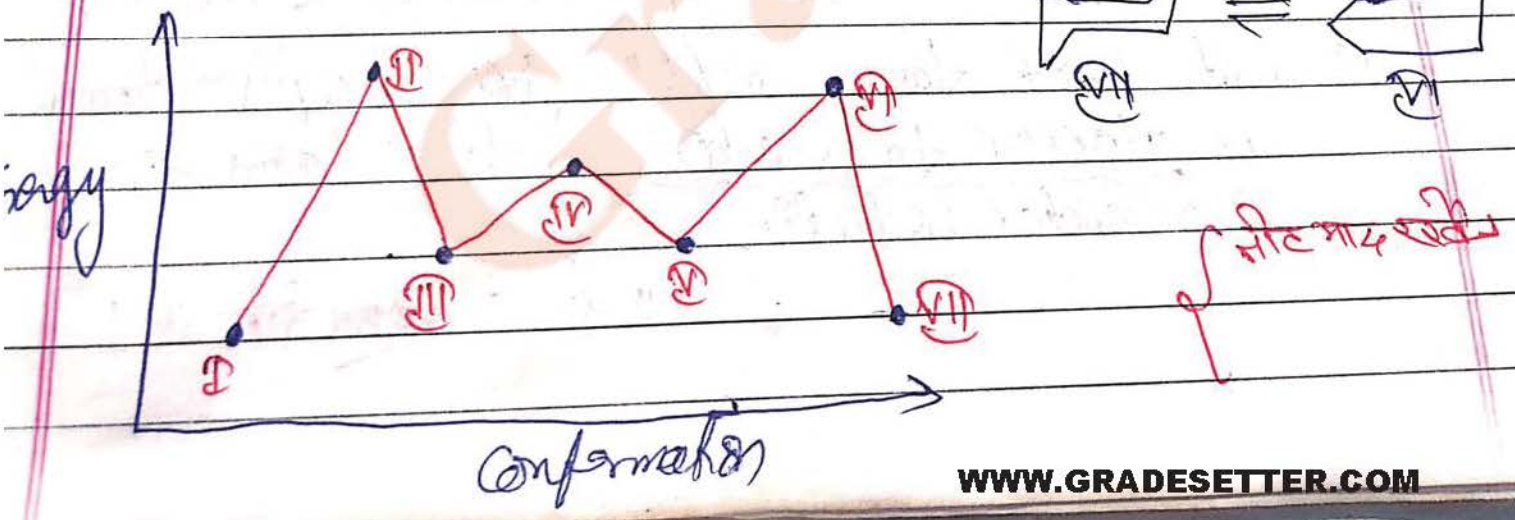
which is more stable "a" or "b"

Sol[n] Step-1 → In such case H⁺ place largest group on equitorial position



(b) Draw energy profile diagram for cyclohexane





1st Choice

Geometrical Isomerism

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cis

trans's

Geometrical Isomers.

Not Geometrical Isomers.

→ Those stereo isomers which are found due to different relative arrangement of atom around restricted Rotation.

Conditions of G.I →

i) Rotation should be Restricted.
↳ It can be Due to multiple bond
C=C, C≡C, Due to ring

ii) At least two diff" groups should be attached to carbon which is attached by restricted rotation.
but it can vary

1st Choice

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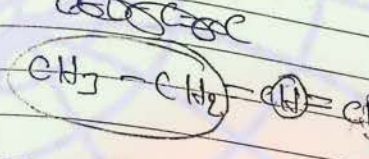
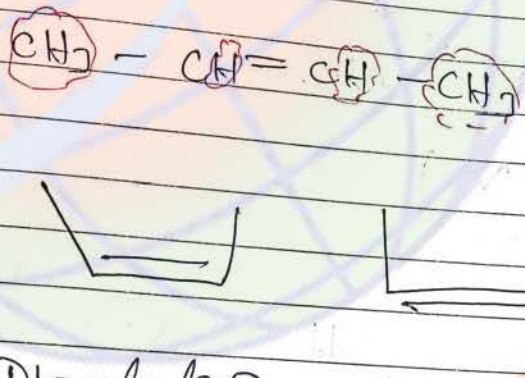
Q) Which of the following molecule can show G.I.
i) 1-Butene ii) 2-Butene



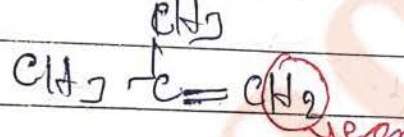
If same group so Not show G.I (X)

ii) 2-Butene



(✓)

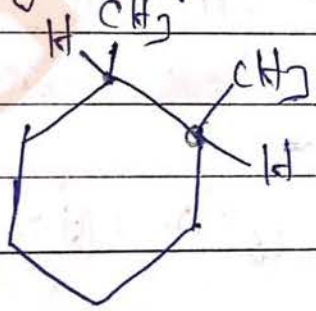
iii) Iso-butene



(X)

same, so Not show G.I

1- 2 dimethyl cyclohexane



(✓)

1st Choice

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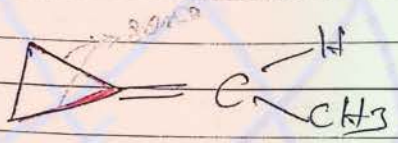
v) $CH_3 - CH = \overset{\cdot\cdot}{N} - OH$

concept ⇒ L.P is considered as one G.N. it's atomic no. is zero

(✓)

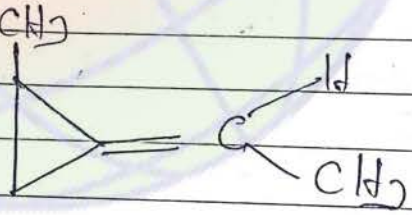
vi) $Ph - \overset{\cdot\cdot}{N} = \overset{\cdot\cdot}{N} - Ph$ (✓)

vii)



(X)

viii)



(✓)

ix) styrene

$C_6H_5 - CH = CH_2$

same (X)

x) cinnamic acid ⇒

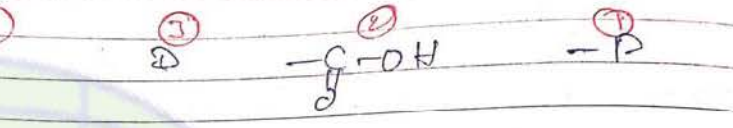
$C_6H_5 - CH = CH - COOH$

(✓)

1st Choice

eg1.

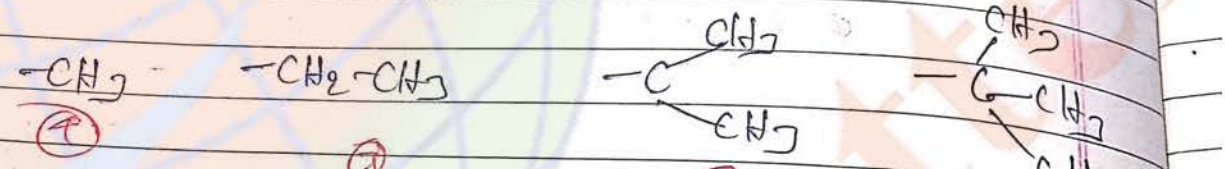
eg2.



2.) when priority is not decided by 1st atom (directly attach) then it is decided by 2nd atom

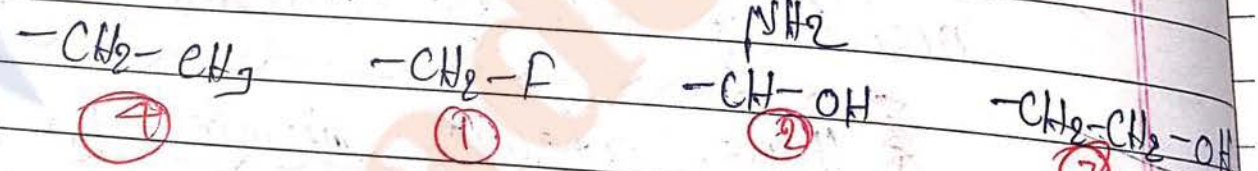
and if not decided by 2nd atom then we move to third atom.

eg1



1st atom	C	C	C	C
2nd atom	H, H, H	C, H, H	C, C, H	C, C, C

eg2



1st atom	C	C	C	C
2nd atom	C, H, H	F, H, H	O, N, H	C, H, H
3rd atom	H, H, H	—	H, H, H	O, H, H

1st Choice

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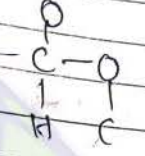
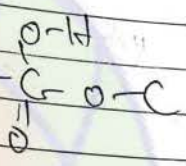
7.) i) $-C=CH_2$ ≡

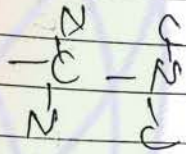
ii) $-\overset{\overset{O}{\|}}{C}-H$ ≡



iii) $-\overset{\overset{O}{\|}}{C}-O-H$ ≡



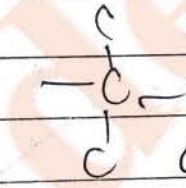
iv) $-C\equiv N$ ≡



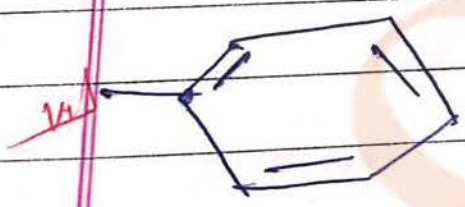
Note ⇒

If multiple bonded groups are present then they are open in such a manner that each atom is considered to be attached by same number of atom as many bond is forms with other atoms

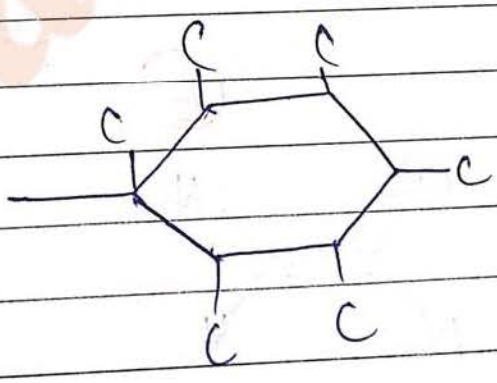
v) $-C\equiv C-H$ ≡



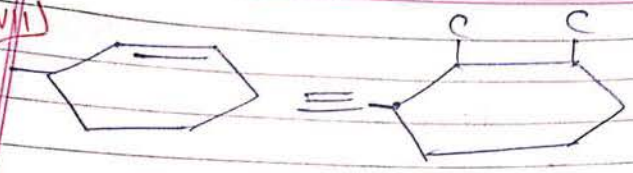
vi)



≡



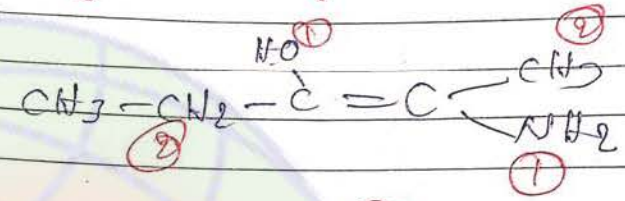
vii)



viii)

Priority deciding →

i)



E

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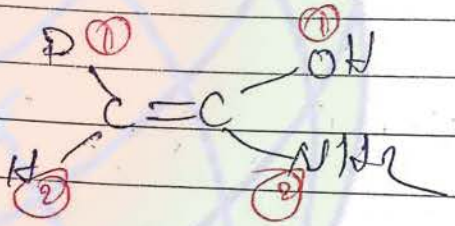
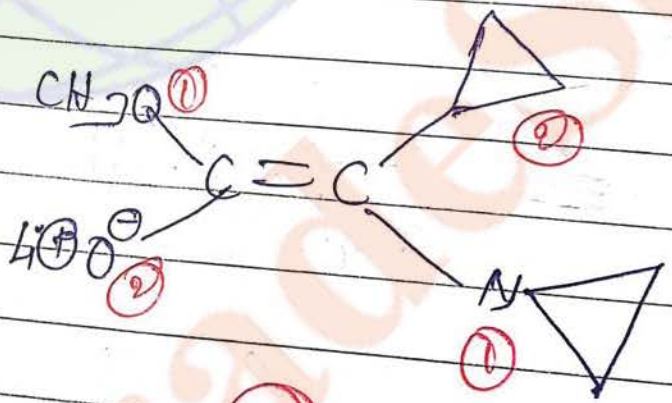


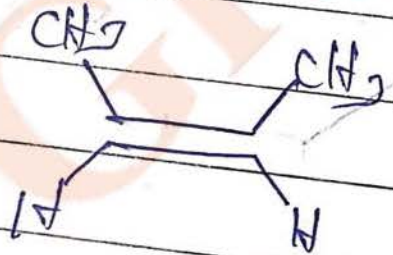
Z

iii)

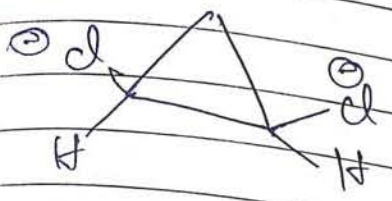


R

iv)



cis / Z



(2)