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CHEMISTRY

Target : JEE(Main)

REACTION MECHANISM (ALKYL HALIDES, ALCOHOLS & ETHERS)

REACTION MECHANISMS

(Alkyl Halides, Alcohols and Ethers)

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JEE (Main) Syllabus

Organic Compounds with functional groups Containing Halogens (x) :

Alkyl halides : Nature of C-X bond in haloalkanes, physical and chemical properties, mechanism of substitution reactions, elimination reactions and rearrangement reactions , reactivity of C-X bond in haloalkanes.

Some commercially important compounds : Dichloro, trichloro and tetrachloromethanes; freons, BHC, DDT, their uses and important reactions.

Organic compounds with functional groups containing oxygen

Alcohols & Ethers : Methods of preparation, physical and chemical properties;

Electronic structure, Structure of functional group, some commercially important compounds.

JEE (Advanced) Syllabus

Alkyl halides : Polarity and inductive effects in alkyl halides; rearrangement reactions of alkyl carbocation, Grignard reactions, nucleophilic substitution reactions; preparation of alkenes by elimination reactions.

Alcohols: Esterification, dehydration and oxidation, reaction with sodium, phosphorus halides, $ZnCl_2$ /concentrated HCl, conversion of alcohols into aldehydes and ketones;

Ethers : Preparation by Williamson's Synthesis.

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Alkyl Halides, Alcohols & Ethers

Introduction :

(A) Alkyl halides :

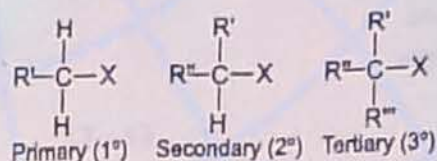
There are three major classes of organohalogen compounds ; the alkyl halides, the vinyl halides, and the aryl halides.

An alkyl halide simply has a halogen atoms bonded to one of the sp^3 hybrid carbon atoms of an alkyl group. (A vinyl halide or Aryl halide has a halogen atom bonded to one of the sp^2 hybrid carbon atoms of an aromatic ring. They are different from alkyl halides because their bonding and hybridization are different.)

Classification of halides :

(a) Alkyl halides or haloalkanes ($R-X$) Compounds Containing sp^3 C-X Bond :

They are classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



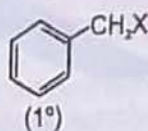
(b) Allylic halides :

These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to carbon-carbon double bond ($C=C$) i.e. to an allylic carbon.

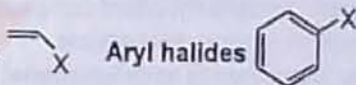


(c) Benzylic halides :

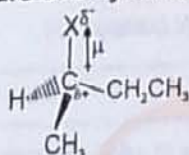
These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring.



(d) Compounds Containing sp^2 C-X Bond : Vinyllic halides



Structure of alkyl halide :



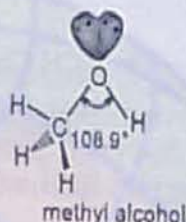
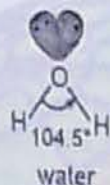
The carbon-halogen bond in an alkyl halide is **polar** because halogen atoms are more electronegative than carbon atoms. Most reactions of alkyl halides result from breaking this polarized bond. The carbon atom has a partial positive charge, making it somewhat **electrophilic**.



(B) Alcohols :

Alcohols have sp^3 hybridized oxygen atoms, but the C-O-H bond angle in methanol (108.9°) is considerably larger than the H-O-H bond angle in water (104.5°) because the methyl group is much larger than a hydrogen atom.

The bulky methyl group counteracts the bond angle compression caused by oxygen's nonbonding pairs of electrons. The O-H bond lengths are about the same in water and methanol (0.96 \AA), but the C-O bond is considerably longer (1.4 \AA), reflecting the larger covalent radius of carbon compared to hydrogen.



Classification of alcohols:

(a) Alcohols may be classified as mono-, di-, tri- or polyhydric alcohols depending on whether they contain one, two, three,hydroxy group.

Monohydric : Contains one -OH group $(C_2H_5OH ; CH_3-CH_2-CH_2-OH)$

Dihydric : Contains two -OH group $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$ (Glycol)

Trihydric (Polyhydric): Contains three or more than three -OH groups $\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$ (Glycerol)

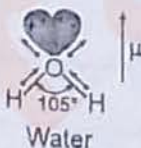
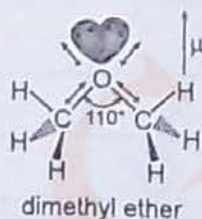
(b) **Allylic alcohols :** $CH_2=CH-CH_2-OH ; CH_2=CH-\underset{\substack{| \\ CH_3}}{C}-OH ; CH_2=CH-\overset{\substack{| \\ CH_3}}{C}-OH$

(c) **Vinyl Alcohol:** $CH_2=CH-OH$ (unstable at room temperature)

(d) **Benzylic alcohols:** Primary Secondary Tertiary

(C) Ethers :

Like water, ethers have a bent structure, with an sp^3 hybrid oxygen atom giving a nearly tetrahedral bond angle.



Bonding in ethers is readily understood by comparing ethers with water and alcohol. Van der Waals strain involving alkyl groups causes the bond angle at oxygen to be larger in ethers than in alcohol, and larger in alcohols than in water. An extreme example is di-tert-butyl ether, where steric hindrance between the tert-butyl groups is responsible for a dramatic increase in the C-O-C bond angle.

Reaction Mechanism

1.3 Bases and their basicity :

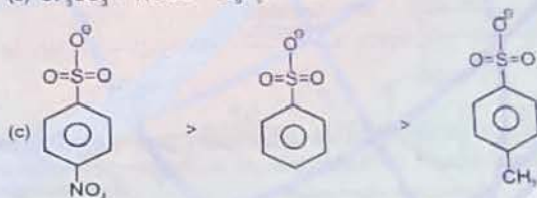
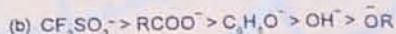
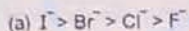
Bases are the species which accept the proton or which donates l.p. of electron to proton.

- Basicity decreases down the group while nucleophilicity increases
F⁻ > Cl⁻ > Br⁻ > I⁻
- Nucleophilicity and basicity order will be same across the period
- For the same donor atom nucleophilicity and basicity order will be same

1.4 Leaving group ability :

- Weaker base is better leaving group.
- More resonance stabilised ion will be better leaving group
- Weaker the carbon-leaving group bond (C-X) better will be the leaving group
- If activation energy of a reaction is low then reaction will be fast and leaving group will be better.

Ex.



Note : More stable anions are weak bases & hence better leaving group.

2. Types of solvents :

S.N.	Solvent	Polar	Nonpolar	Protic	Aprotic
1.	CH ₃ COOH	✓	×	✓	×
2.		✓	×	×	✓
3.	H ₂ O	✓	×	✓	×
4.	ROH	✓	×	✓	×
5.		✓	×	×	✓
6.		✓	×	×	✓
7.	R-O-R	✓	×	×	✓
8.		×	✓	×	✓
9.	DMF	✓	×	×	✓
10.	DMA	✓	×	×	✓

Note : If H atom is attached to oxygen, nitrogen or sulphur then it is said to be protic solvent.

3. Nucleophilic substitution reactions of alkyl halides :

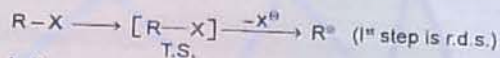
Alkyl halide undergoes nucleophilic substitution reaction.



Nucleophilic substitution reactions are of two types :

3.1 Unimolecular nucleophilic substitution reaction (S_N1) :

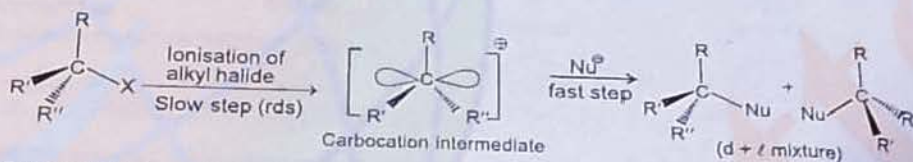
- It is a two step process.
- First step is the heterolytic cleavage of carbon halogen bond (>C-X) to give carbocation intermediate.



- In the second step nucleophile attacks from either side of carbocation to generate product (racemic mixture).



Mechanism :

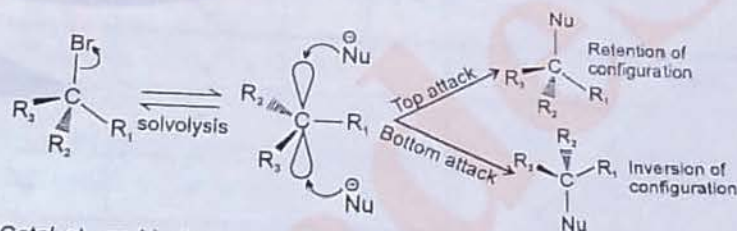


- Carbocation intermediate is formed so rearrangement is possible in S_N1 reaction.

Kinetics :

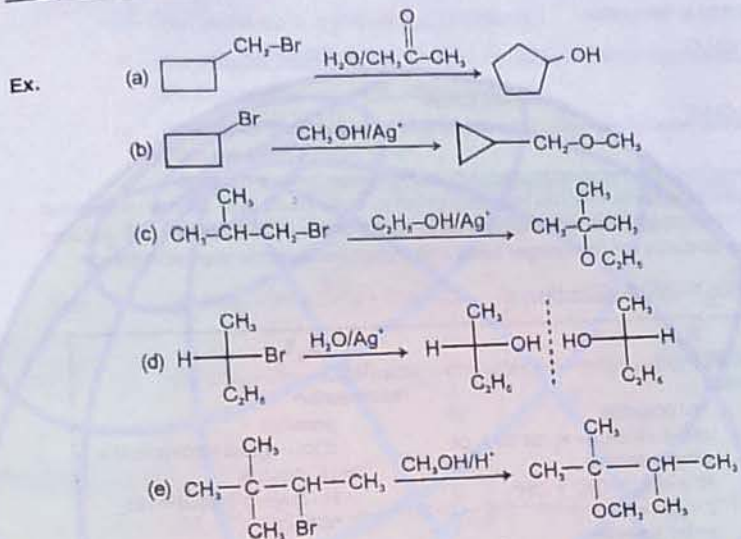
- Rate \propto [Alkyl halide]
- It is unimolecular and first order reaction.
- Rate of S_N1 reaction is independent of the concentration and reactivity of nucleophile.

Stereochemistry :



- Catalyst used is Ag^+ .
- More polar protic solvent is more favourable for S_N1 .
 $H_2O > ROH > NH_3$ (order of polar protic solvent).
- In S_N1 reaction carbocation is formed along with anion and to solvate these ions, polar protic solvent is used.
- Decreasing order of reactivity of alkyl halides. ; $R-I > R-Br > R-Cl > R-F$

Reaction Mechanism

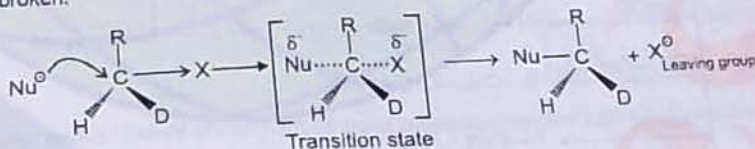


3.2 Bimolecular nucleophilic substitution reaction (S_N2) :

It is a single step reaction as the rate of reaction depends upon concentration of substrate as well as nucleophile.

Mechanism :

- In this reaction nucleophile attack from back side on the carbon atom bearing leaving group. It is a concerted reaction where bond breaking and bond formation takes place simultaneously to achieve a transition state (trigonal bipyramidal shape) where half bond has been formed and half bond has been broken.

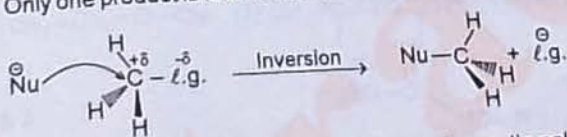


Kinetics :

- rate \propto [alkyl halide] [nucleophile]
- It is a bimolecular, one step **concerted** process.
- It is a second order reaction because in the r.d.s. both species are involved.

Stereochemistry :

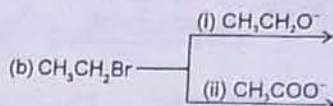
Only one product is formed where inversion of configuration takes place.



- Polar aprotic solvent is favourable not polar protic solvent. Because in case of polar protic solvent nucleophilicity of anion is decreased due to solvation and such solvation is not possible in case of polar aprotic solvent.
- Electron withdrawing group increases the rate of s_N2 reaction.
O=CH-CH₂-Br > CH₃-O-CH₂-Br > H-CH₂-Br > CH₃-CH₂-Br

Reaction Mechanism

Que. Which one in the given reaction is favourable

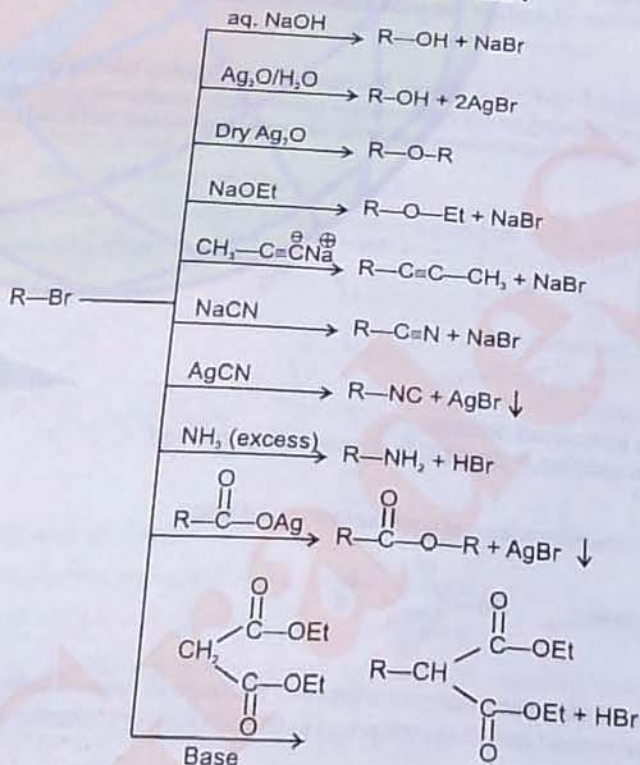


Ans. (a) In case of (i) rate is slower than (ii) because nucleophilicity increases down the group.
 (b) In case of (i) rate of reaction is faster than (ii) because (i) ion is more basic than (ii) it is known that for the same donor atom nucleophilicity and basicity have same order. Acetic acid is stronger acid than ethyl alcohol hence ethoxide ion is stronger base and better nucleophile than acetate ion.

Comparison between $\text{S}_\text{N}1$ / $\text{S}_\text{N}2$ reaction :

Characteristics	$\text{S}_\text{N}2$ $r \propto [\text{RX}][\text{Nu}]$	$\text{S}_\text{N}1$ $r \propto [\text{RX}]$
1. Kinetics	$r \propto [\text{RX}][\text{Nu}]$	$r \propto [\text{RX}]$
2. Stereochemistry	Inversion	racemisation
3. Rearrangement	not possible	possible
4. Nature of R-X	$\text{CH}_3\text{-X} > \text{RCH}_2\text{-X} > \text{R}_2\text{CH-X} > \text{R}_3\text{CX}$	$\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{-X} > \text{CH}_3\text{X}$
5. Nucleophile	strong anionic $\text{R}^- > \text{NH}_2^- > \text{OR}^- > \text{OH}^-$ $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$	weak neutral $\text{H}_2\text{O} > \text{MeOH} > \text{EtOH} > \text{NH}_3$ (same)
6. Leaving group		
7. Solvent	polar aprotic	polar protic

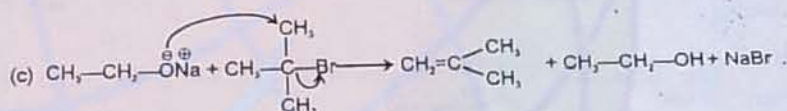
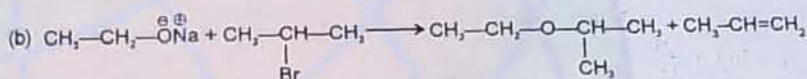
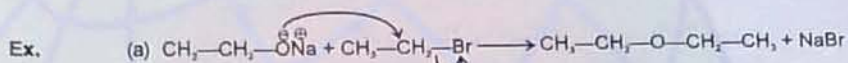
Examples of $\text{S}_\text{N}2$ reaction of alkyl halides :



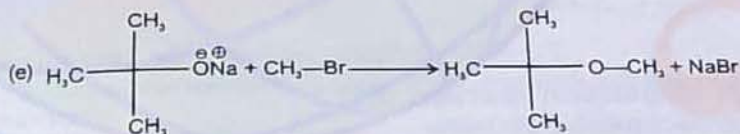
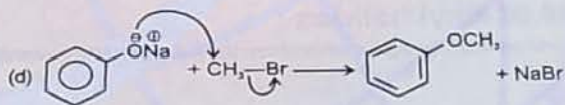
Reaction Mechanism

(i) Williamson's synthesis of ethers :

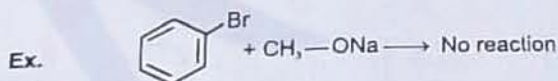
- It is used for the preparation of symmetrical as well as unsymmetrical ether.
- $R-Br + NaOEt \longrightarrow R-OEt + NaBr$
- Williamson's synthesis involve attack of an alkoxide on alkyl halide to give ethers. In place of alkoxide, phenoxide can also be used.
- This is an S_N2 reaction because alkoxide is a strong nucleophile.
- On using 2° & 3° alkylhalide we get alkene not ether as a product.



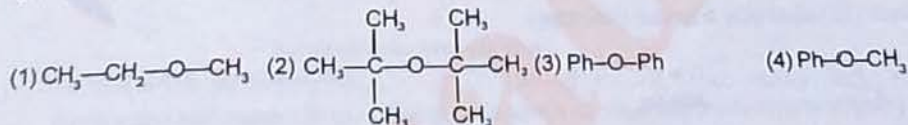
(Elimination reaction)



Note: Vinyl or Aryl halide should not be used because they don't give S_N2 reaction.

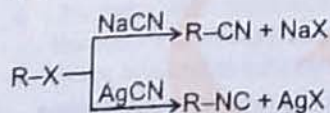


Que. Which of the following ethers cannot be prepared by Williamson's synthesis reaction :



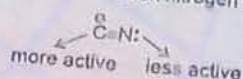
Ans. 2 & 3

(ii) Reaction with AgCN and NaCN :



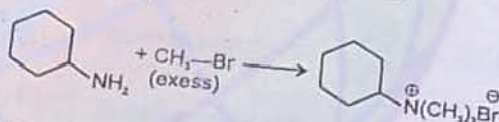
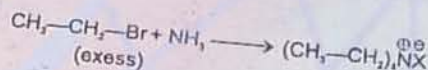
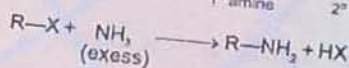
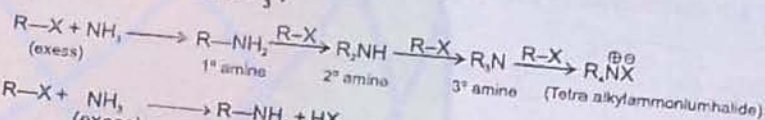
Reaction Mechanism

- NaCN is a more ionic hence ionized to give free $\overset{\ominus}{\text{C}}\text{N}$ (an ambident nucleophile) where carbon side is more active than nitrogen side. That is why with NaCN, RCN is formed.



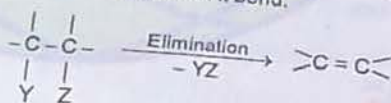
- On the other hand AgCN is more covalent so it is not ionized therefore only nitrogen side is free to act as a nucleophile and give isocyanide (R-NC)

(iii) Reaction with NH_3 :



4. Elimination reactions of alkyl halides :

In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of π bond.

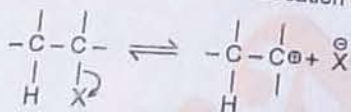


4.1 Unimolecular elimination reaction (E1) :

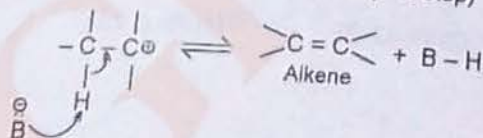
Proton and leaving group depart in two different step.

Mechanism :

Step 1 : Formation of the carbocation (r.d.s.)



Step 2 : Base (B^{\ominus}) abstracts a proton (fast step)



- Reaction intermediate is carbocation, so rearrangement is possible

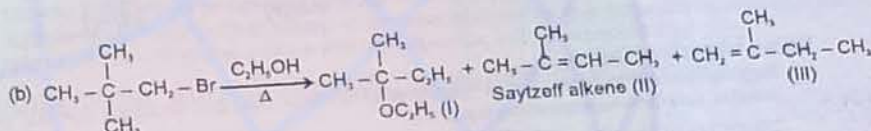
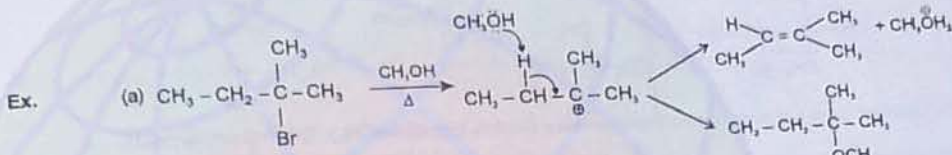
Kinetics :

- Rate \propto [Alkylhalide]
- It is a unimolecular and first order reaction.
- Reactivity order is similar to $\text{S}_{\text{N}}1$ because Carbocation Intermediate is formed in the first step.

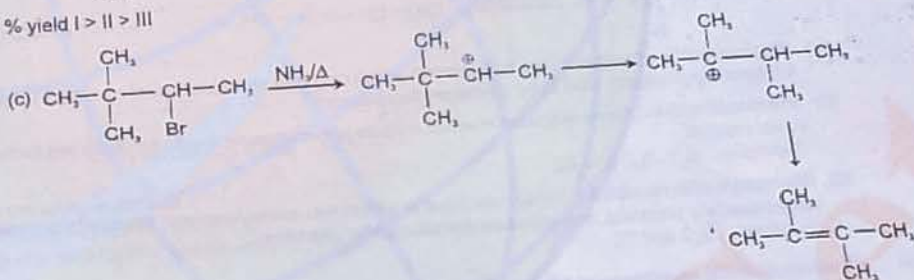
Reaction Mechanism

S_N1 v/s E1 :

- In case of alkyl halides S_N1 product is generally more than E1 product



% yield I > II > III

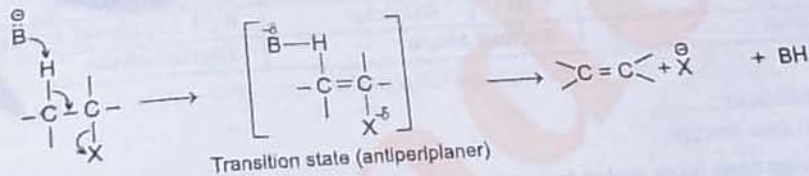


4.2 Bimolecular elimination reaction (E2) :

- It is a second order reaction because rate of reaction depends upon conc. of substrate as well as base.

Mechanism :

- Orientation of eliminated proton and leaving group are antiparallel or antiperiplanar to each other because in anti conformation the transition state is more stable due to minimum electronic repulsion.

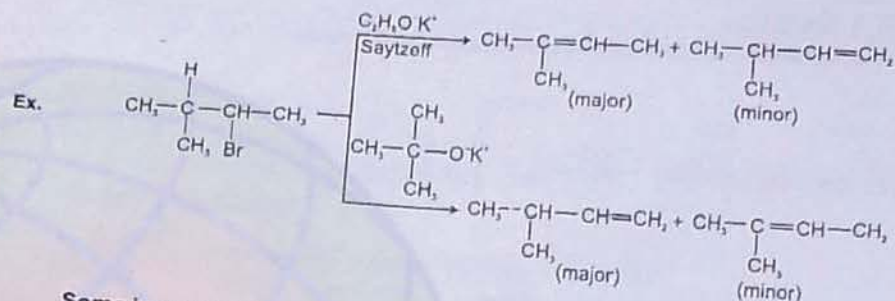


- E2 reaction is stereospecific.
- E2 reaction also depends upon size of base which decides major or minor product.

Kinetics :

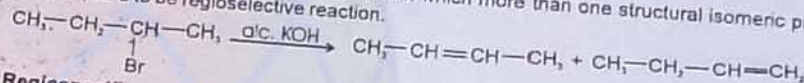
- Rate $\propto [R-X][Base]$
- This is a single step, bimolecular reaction
- No carbocation intermediate is formed hence there is no rearrangement but a transition state is achieved because it is a single step reaction.
- More favourable substrate is tertiary alkyl halide because it will give more stable alkene according to saytzeff rule.

Reaction Mechanism



Some important terms :

(a) **Regioselective reaction** : Those reaction in which more than one structural isomeric products are possible, said to be regioselective reaction.



(b) **Regiospecific reaction** : Those reaction in which only one structural isomer product is formed out of the possible products, said to be regiospecific reaction.

(c) **Stereoselective** : Those reactions in which mixture of two stereoisomeric products are formed with one major product.
Examples : S_N1 , S_N2 and E2

(d) **Stereospecific reaction** : Those reactions in which two stereoisomeric reactants give two different stereoisomeric products, are called as stereospecific reactions.
Examples : S_N2 and E2

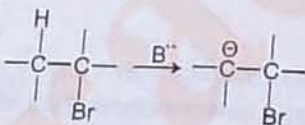
Note : All stereospecific reactions are stereo selective.

Comparison between E1 and E2 reactions :

	E1	E2
Base	Weak base	Strong base required
Substrate	$3^\circ > 2^\circ > 1^\circ$	$3^\circ > 2^\circ > 1^\circ$
Leaving group	Better one required	Better one required
Kinetics	$k[R-X]$, first order	$k[R-X][\text{Base}]$ second order
Orientation	Saytzeff alkene	Saytzeff alkene

4.3 E1cB Reaction :

- It is two step reaction.
- In first step base takes proton from adjacent carbon atom of halogen bearing carbon and generate **carbanion intermediate**.

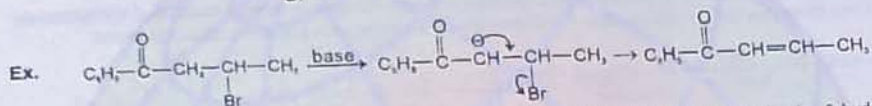
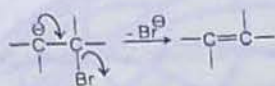


- In second step there is loss of leaving group by carbanion to get alkene :



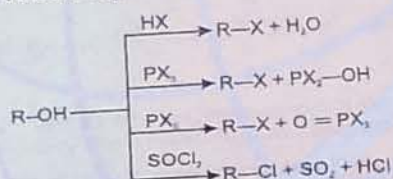
Corporate Office: CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.)-324005
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Reaction Mechanism

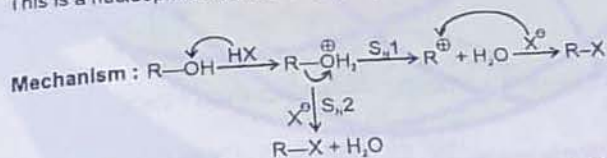
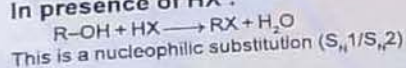


- β -hydrogen atom should be more acidic which is possible only if carbon atom having β -hydrogen atom should be link to with electron withdrawing group (-m, -I group).
- Leaving group should be more electronegative because it also increases acidity of β -hydrogen atom.
- Experimentally it is found that 1st step i.e. formation of carbanion intermediate is fast step and second step i.e. removal of leaving group is slow step thus r.d.s. in E1cB is second step.

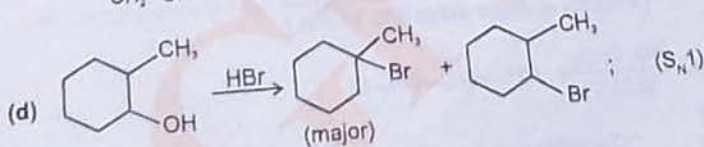
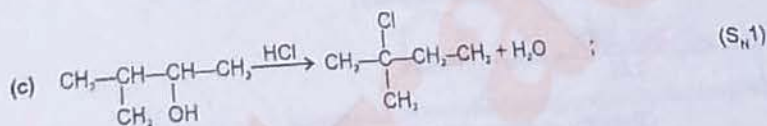
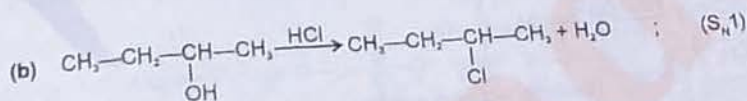
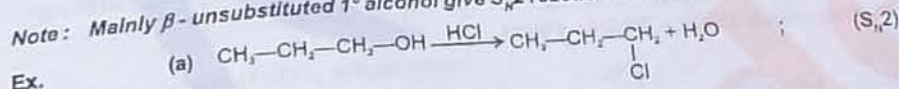
5. Nucleophilic substitution (S_N) reaction of alcohols :



5.1 In presence of HX :



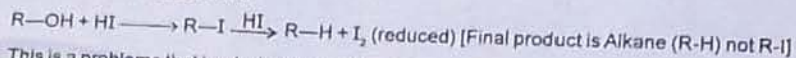
Note : Mainly β -unsubstituted 1° alcohol give S_N2 reaction with HX.



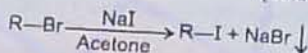
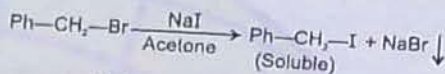
- Reactivity of HX is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

Reaction Mechanism

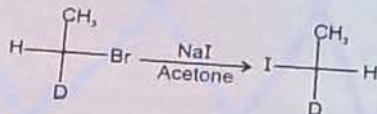
5.2 Finkelstein reaction :



This is a problem that is why iodides are best prepared through halogen exchange reaction. It is also known as Finkelstein reaction. In this reaction R-Cl and R-Br is treated with sodium iodide in acetone.

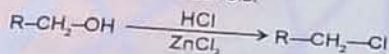


- NaI is soluble in acetone. In this reaction acetone is used because sodium iodide is soluble in acetone but NaBr and NaCl are insoluble so precipitated out. This eliminates any possibility of reverse reaction.
- It is an S_N2 reaction therefore only 1°RX and 2°RX is used.

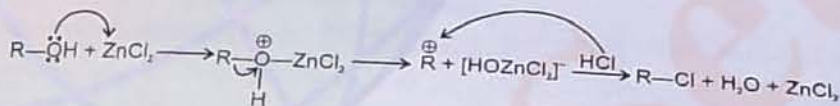


5.3 Lucas reagent :

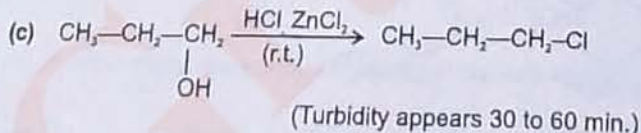
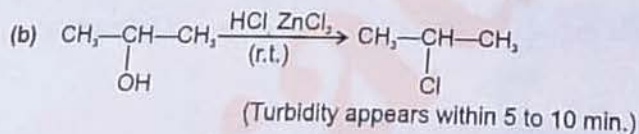
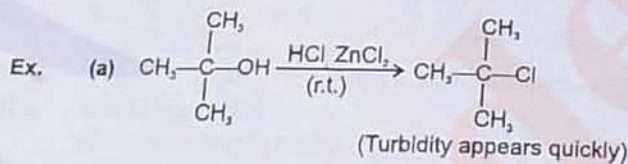
The 1 : 1 mixture of anhydrous ZnCl₂ : HCl (conc.) is called Lucas reagent which is used to distinguish between 1°, 2° and 3° alcohols.



Mechanism :



- ZnCl₂ increases the rate of reaction by making -OH group into a much better leaving group just through complexation.
- Reactivity of alcohols is 3°ROH > 2°ROH > 1°ROH



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