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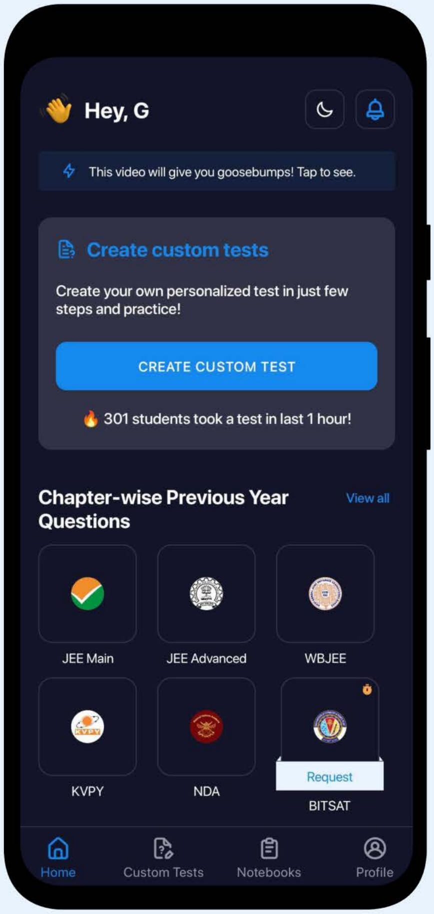

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ALKYL HALIDES

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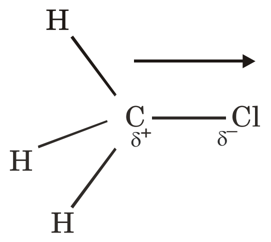
ALKYL HALIDES

Alkyl halides are a class of compound where a halogen atom or atoms are bound to an sp^3 orbital of an alklyl group.

$CHCl_3$ (Chloroform : organic solvent)
CF_2Cl_2 (Freon-12 : refrigerant CFC)
$CF_3CHClBr$ (Halothane : anesthetic)

Halogen atoms are more electronegative than carbon atoms, and so the C–X bond is polarized. Here X stands for halogens.



The C–X bond is polarized in such a way that there is partial positive charge on the carbon and partial negative charge on the halogen.

Electronegativity decreases in the order of :

$$F > Cl > Br > I$$

Carbon-halogen bond lengths increase in the order of :

$$C\text{-}F < C\text{-}Cl < C\text{-}Br < C\text{-}I$$

Bond Dipole Moments decrease in the order of :

	C-Cl	>	C-F	>	C-Br	>	C-I
μ =	1.56D		1.51D		1.48D		1.29D

Typically the chemistry of alkyl halides is dominated by this effect, and usually results in the C-X bond being broken (either in a substitution or elimination process).

This reactivity makes alkyl halides useful chemical reagents.

1. NOMENCLATURE

According to IUPAC, alkyl halides are treated as alkanes with a halogen substituent.

The halogen prefixes are Fluoro-, Chloro-, Bromo- and Iodo-.

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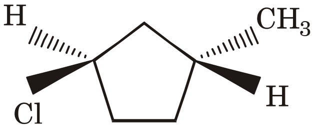
Examples :

$F–CH_2CH_3$

fluoroethane

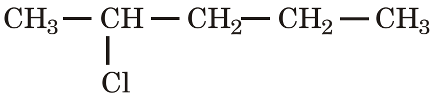


trans-1-chloro-3-methylcyclopentane

IUPAC nomenclature of alkyl halides with one halogen in haloakanes and with two similar halogens is halo alkanes. If the halogens present are different, they are prefixed in alphabetical order.

eg. $Cl—CH_2—CH_2—CH_2—CH_2—CH_3$,

1–Chloropentane



$CH_3—\underset{\displaystyle Cl}{\underset{|}{CH}}—CH_2—CH_2—CH_3$

2–Chloropentane

$ClCH_2\ CH_2\ CHClCH_3$

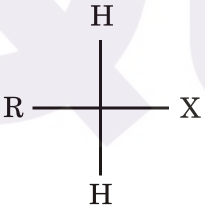
1, 3-dichlorobutane

Often compounds of CH_2X_2 type are called methylene halides (CH_2Cl_2 is methylene chloride).

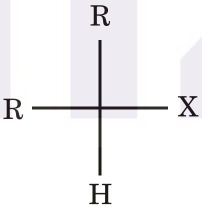
CHX_3 type compounds are called haloforms. (CHI_3 is iodoform).

CX_4 type compounds are called carbon tetrahalides. (CF_4 is carbon tetrafluoride).

Alkyl halides can be primary (1), secondary (2) or tertiary (3).



1



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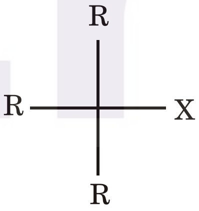
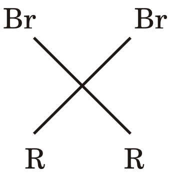


3

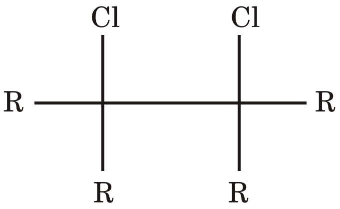
Other types :

A geminal (gem) dihalide has two halogens on the same carbon.

A vicinal dihalide has halogen on adjacent carbon atoms.



gem-dibromide



vicinal dichloride

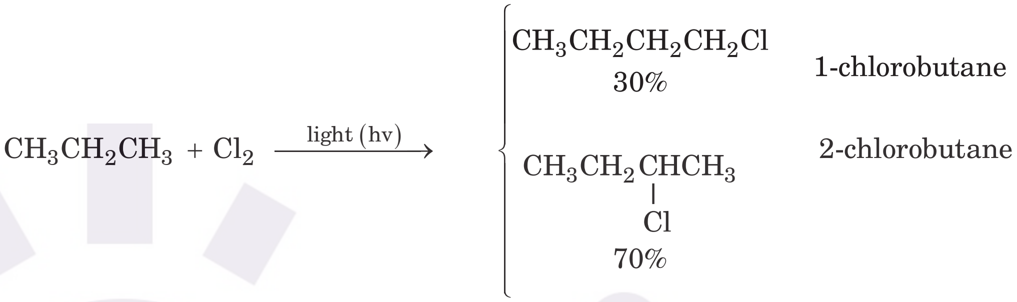
PREPARATION OF ALKYL HALIDES

Radical Halogenation of Alkanes

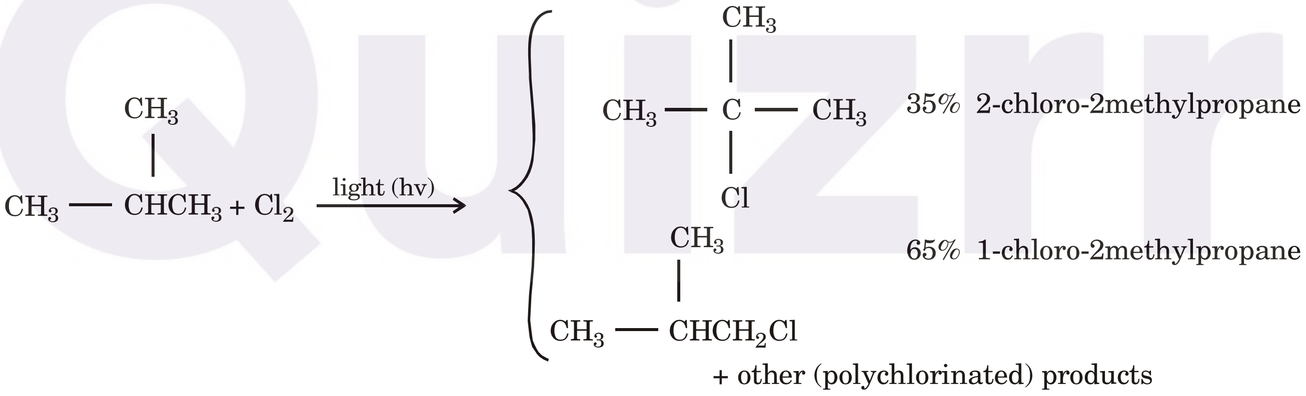
The one big limitation of this method (especially chlorination) is that it almost inevitably leads to a (often complex) mixture of products. Even chlorination of methane gives a mixture :

$$CH_4 + Cl_2 \xrightarrow{\text{light}} CH_3Cl, CH_2Cl_2, CHCl_3 \text{ and } CCl_4$$

The situation is even worse for the chlorination of alkanes that have more than one kinds of hydrogen:



$$CH_3CH_2CH_3 + Cl_2 \xrightarrow{\text{light (hv)}} \begin{cases} \underset{30\%}{CH_3CH_2CH_2CH_2Cl} & \text{1-chlorobutane} \\ \underset{70\%}{CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3} & \text{2-chlorobutane} \end{cases}$$



$$CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}}HCH_3 + Cl_2 \xrightarrow{\text{light (hv)}} \begin{cases} CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Cl}{\underset{|}{C}}}} - CH_3 & 35\% \text{ 2-chloro-2methylpropane} \\ CH_3 - \overset{\displaystyle CH_3}{\overset{|}{C}}HCH_2Cl & 65\% \text{ 1-chloro-2methylpropane} \end{cases}$$

+ other (polychlorinated) products

In the first example, 30% of primary halide means that each one of the six primary hydrogens (CH_3) is responsible for 30%/6 = 5% of product, whereas 70% of secondary alkyl halides means that each one of the four secondary hydrogens (CH_2) is responsible for 70%/4 = 17.5 of the product. Hence, chlorination at secondary carbon occurs about 3.5 times the rate of chlorination at primary carbon.

Similarly, in the second example, chlorination occurs at the single tertiary carbon (CH) at about 5 times the rate of chlorination at the primary carbons.

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The order of reactivity toward radical chlorination is

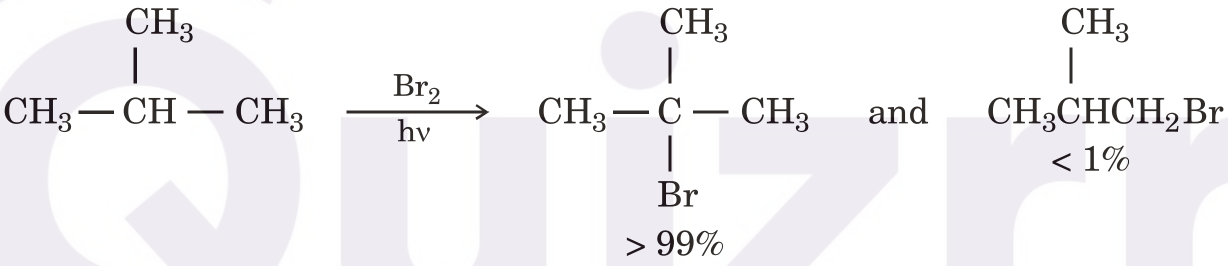
	$R\text{-}CH_3$	<	R_2CH_2	<	R_3CH
	1		**2**		**3**
relative rate	**1**		**3.5**		**5**

This order reflects the relative order of the C-H bond strengths : 3 < 2 < 1 . Since less energy is needed to break a tertiary C-H bond than either a 2 or a 1 C-H bond, the resulting tertiary radical is more stable than either a secondary or primary radical.

However, although the rates of chlorination at different carbon atoms are different, the difference is not great, so that in practice, some chlorination occurs at all sites.

Radical chlorination has poor selectivity

Bromination, on the other hand, is much more selective, mainly because of the lesser reactivity of the halogen species (in particular Br) :



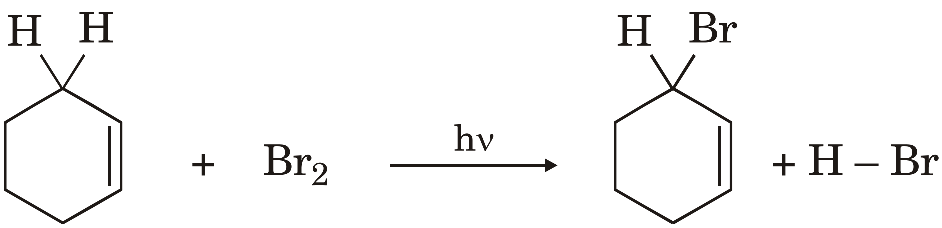
$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CH_3 \xrightarrow[h\nu]{Br_2} CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_3 \quad \text{and} \quad CH_3\overset{CH_3}{\overset{|}{C}}HCH_2Br$$

$> 99\%$ $< 1\%$

Allylic bromination and chlorination

(Allylic means adjacent to a C=C double bond)

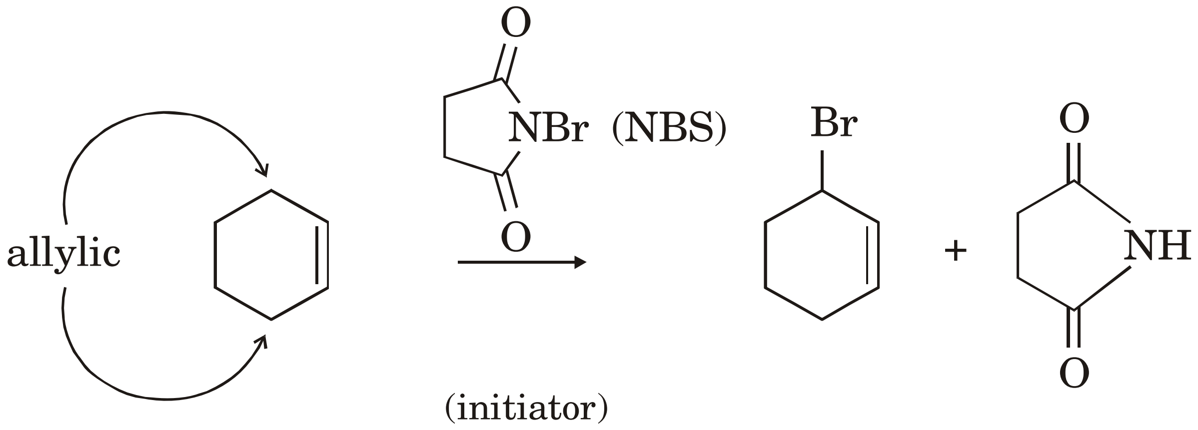
The bromination of cyclohexene produces a high yield of 3-bromocyclohexene.



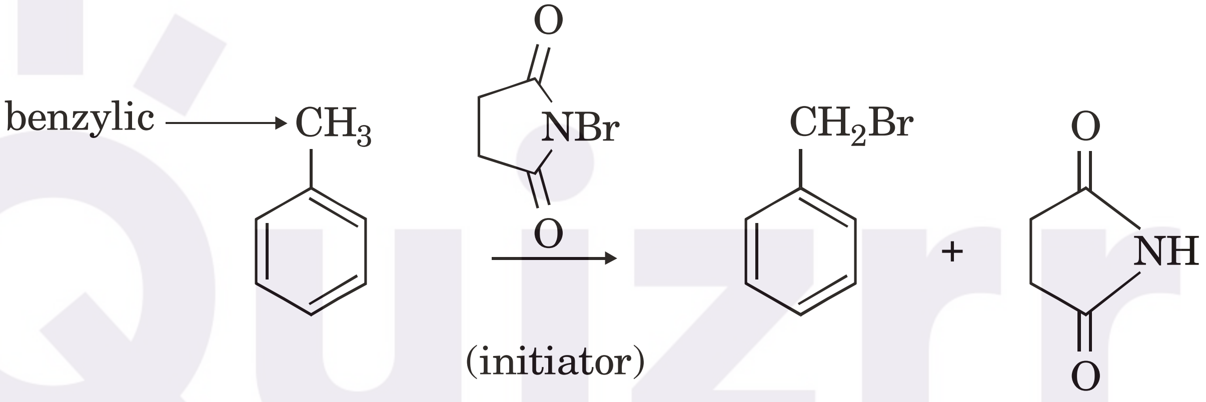
An allylic hydrogen has been substituted for a bromine.

- Compounds with allylic and benzylic hydrogen atoms can be brominated readily using the mild brominating agent N-bromosuccinimide (NBS) :

(a)



(b)



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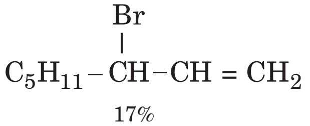
The reaction proceeds via radical substitution method.

One important synthetic consequence of the delocalized allyl radicals is that more than one bromination product is often obtained :

$$C_5H_{11}CH_2CH = CH_2 \xrightarrow[\text{initiator}]{\text{NBS}} C_5H_{11}\dot{C}H - CH = CH_2 \longleftrightarrow C_5H_{11}CH = CH - \dot{C}H_2$$

Br_2 thermodynamic control

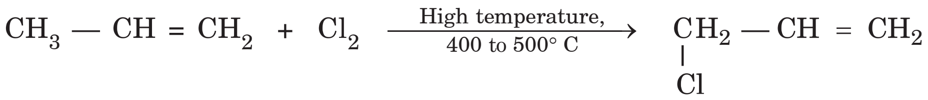


$$\underset{\substack{17\% \\ \text{3-bromo-1-octene}}}{C_5H_{11} - \overset{\overset{\text{Br}}{|}}{C}H - CH = CH_2} \quad + \quad \underset{\substack{83\% \\ \text{1-bromo-2-octene}}}{C_5H_{11}CH = CH - CH_2 - Br}$$

Note : F_2 is most reactive while I_2 is least reactive. Infact reaction with I_2 is reversible and is carried out in the presence of some oxidising agents like HIO_3, HNO_3 etc. to oxidise HI.

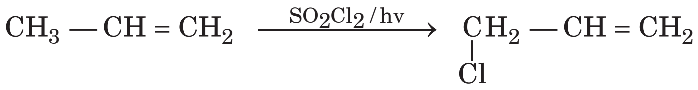
Some more reactions :

$$CH_3 - CH = CH_2 \xrightarrow{X^{\bullet}} X - CH_2 - CH = CH_2$$



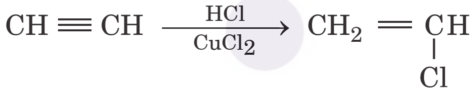
$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow[400 \text{ to } 500^\circ C]{\text{High temperature,}} \underset{\displaystyle Cl}{\underset{|}{CH_2}} - CH = CH_2$$

$$CH_3 - CH = CH_2 + Br_2 \xrightarrow[CCl_4]{\text{NBS in}} \underset{\displaystyle Br}{\underset{|}{CH_2}} - CH = CH_2$$



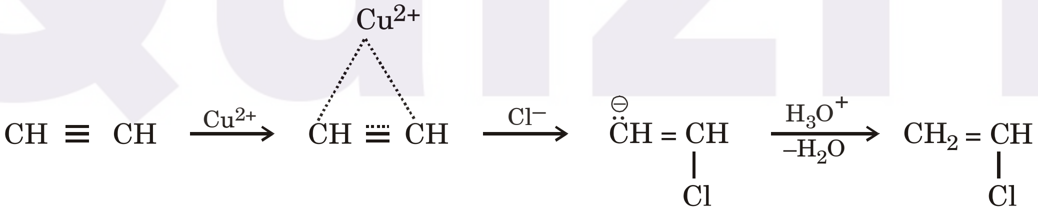
$$CH_3 - CH = CH_2 \xrightarrow{SO_2Cl_2/hv} \underset{\displaystyle Cl}{\underset{|}{CH_2}} - CH = CH_2$$

Preparation of Vinyl Halides



$$CH \equiv CH \xrightarrow[CuCl_2]{HCl} CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}}$$

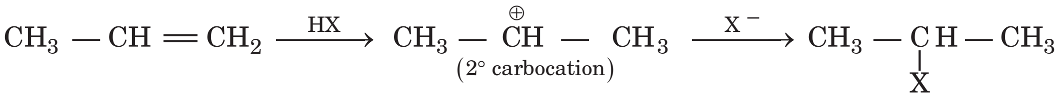
The above reaction proceeds via electrophilic addition as follows



$$CH \equiv CH \xrightarrow{Cu^{2+}} \overset{Cu^{2+}}{CH \equiv CH} \xrightarrow{Cl^-} \overset{\ominus}{\ddot{C}H} = \underset{\displaystyle Cl}{\underset{|}{CH}} \xrightarrow[-H_2O]{H_3O^+} CH_2 = \underset{\displaystyle Cl}{\underset{|}{CH}}$$

By Addition of H–X to Alkenes

Alkyl chlorides, bromides and iodides can be prepared by treating an alkene with corresponding hydrogen halide (HCl, HBr or HI). The addition of these compounds to alkene takes place according to Markownikov's rule. The reaction proceeds by electrophilic addition of H^+ to give more stable carbocation followed by attack of X^-. Anti-Markownikov addition of HBr can be achieved, if the reaction is carried out in presence of peroxides (H_2O_2 or benzoyl peroxide or di–tert–butyl peroxide). Addition of HBr to alkenes in the presence of peroxide follows free radical mechanism.



$$CH_3 - CH = CH_2 \xrightarrow{HX} CH_3 - \underset{(2^\circ \text{ carbocation})}{\overset{\oplus}{CH}} - CH_3 \xrightarrow{X^-} CH_3 - \underset{\displaystyle X}{\underset{|}{CH}} - CH_3$$

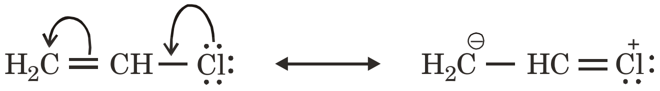
$$CH_3 - CH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} CH_3 - \underset{(2^\circ\ \text{radical})}{\dot{C}H} - CH_2 - Br \xrightarrow{\text{HBr}} CH_3 - CH_2 - CH_2Br + \dot{B}r$$

Example 1

The heterolytic bond dissociation energy of C–Cl bond in vinyl chloride is 207 kcal/mol as compared to 191 kcal/mol in the case of C–Cl bond in ethyl chloride. Give explanation for this observation.

Solution :

$H_2C \equiv CH - Cl$ (Vinyl chloride)



As we can see that C=Cl bond is formed in vinyl chloride; and hence its bond dissociation energy becomes 207 kcal/mol.

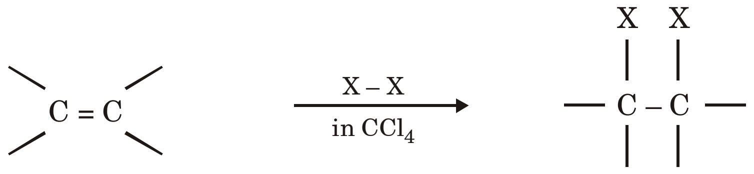
Example 2

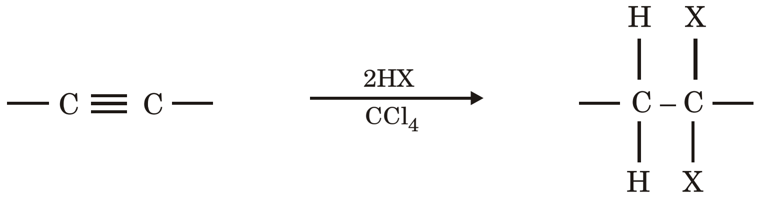
Haloarenes are insoluble in water and soluble in benzene.

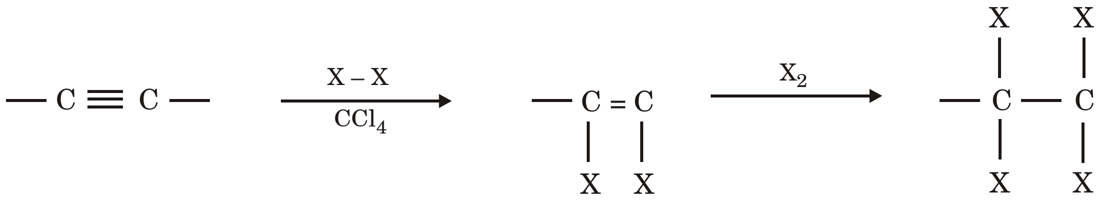
Solution :

Haloarenes are insoluble in water because neither can they form H-bonds with water nor can they break the H-bond already existing in water. However in accordance with general principle of solubility i.e. like dissolves like haloarenes due to presence of large hydrocarbon part (benzene ring) are soluble in hydrocarbon solvents such as benzene, petroleum, ether.

From alkenes and alkynes :







$$-C\equiv C- \xrightarrow[CCl_4]{X-X} \underset{X}{\underset{|}{-C}}=\underset{X}{\underset{|}{C}} \xrightarrow{X_2} -\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-$$

From alcohols

(1) Using hydrogen halides

$$R-OH \xrightarrow{H-X} R-X$$

Some Points :

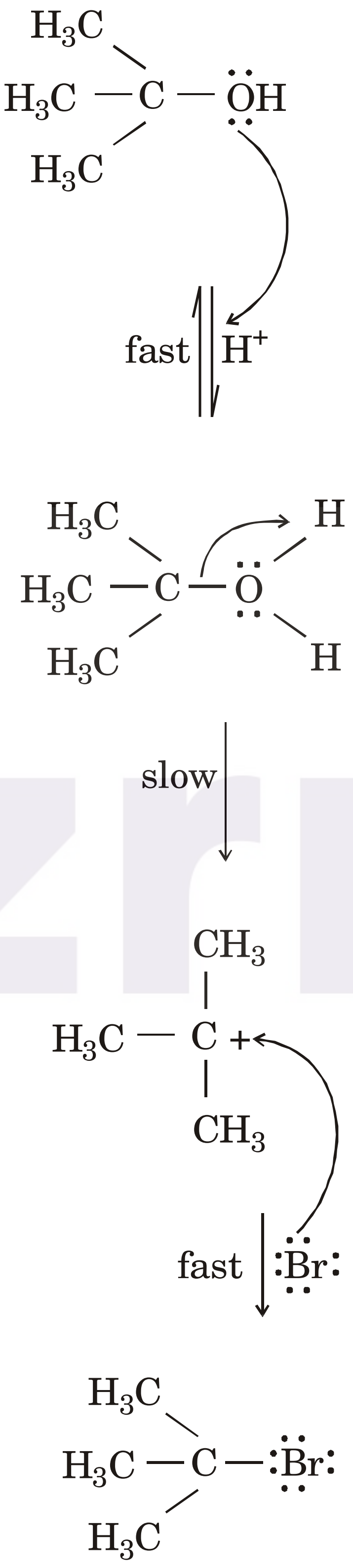
- When treated with HBr or HCl alcohols typically undergo a nucleophilic substitution reaction to generate an alkyl halide and water.
- Alcohol relative reactivity order : 3 > 2 > 1 > methyl
- Hydrogen halide reactivity order : HI > HBr > HCl > HF (paralleling acidity order).
- Reaction usually proceeds via an SN1 mechanism which proceeds via a carbocation intermediate, that can also undergo rearrangement.
- Methanol and primary alcohols will proceed via an SN2 mechanism since these have highly unfavourable carbocations.
- The reaction of alcohols with HCl in the presence of $ZnCl_2$ (catalyst) forms the basis of the Lucas test for alcohols.

SN1 mechanism for reaction of Alcohols with HBr

Step 1 : An acid/base reaction, Protonation of the alcoholic oxygen to make a better leaving group. This step is very fast and reversible. The lone pairs on the oxygen make it a Lewis base.

Step 2 : Cleavage of the C-O bond allows the loss of the good leaving group, intermediate. This is the rate determining step (bond breaking is endothermic)

Step 3 : Attack of the nucleophilic bromide ion on the electrophilic carbocation creates the alkyl bromide.



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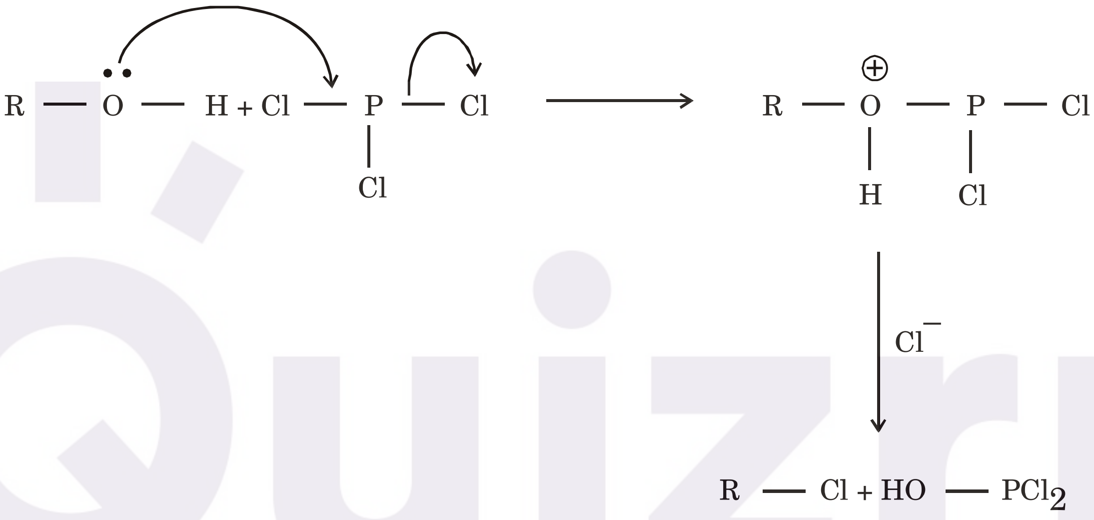
Reaction of alcohols with sulfur and phosphorous halides

Alcohols can be converted to alkyl halides by reaction with thionyl chloride, $SOCl_2$; phosphorous trichloride, PCl_3, phosphorous pentachloride, PCl_5; or phosphorous tribromide, PBr_3. For example, ethyl chloride or ethyl bromide can be prepared from ethyl alcohol via reactions with sulfur and phosphorous halides.

Reaction of Alcohol with PCl_3

$$3ROH + PCl_3 \longrightarrow RCl + H_3PO_3$$

Mechanism :



$HOPCl_2$ reacts further to give H_3PO_3 and 2 RCl molecules.

- This method is the method because the product formed is gaseous in nature.

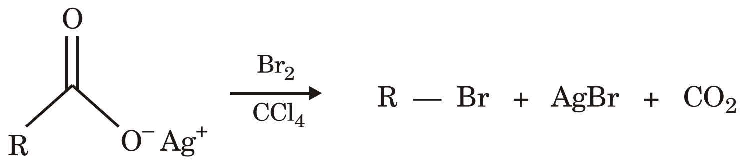
$$CH_3CH_2OH + SOCl_2 \xrightarrow{\Delta} CH_3CH_2Cl + SO_2 + HCl$$

$$CH_3CH_2OH + PCl_3 \xrightarrow{\Delta} CH_3CH_2Cl + P(OH)_3 + HCl$$

$$CH_3CH_2OH + PCl_5 \xrightarrow{\Delta} CH_3CH_2Cl + POCl_3 + HCl$$

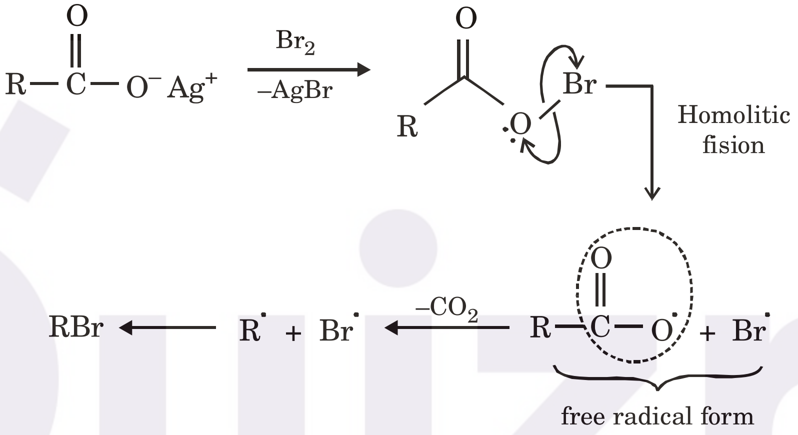
$$CH_3CH_2OH + PBr_3 \xrightarrow{\Delta} CH_3CH_2Br + P(OH)_3{}^{+} HBr$$

HUNSDIECKER REACTION



The silver(I) salts of carboxylic acids reacts with halogens to give unstable intermediates which readily decarboxylate thermally to yield alkyl halides. The reaction is believed to involve homolysis of the C-C bond and a radical chain mechanism.

Mechanism :



FINKELSTEIN REACTION

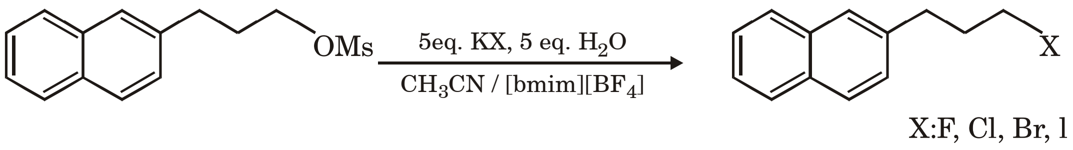
$$R-CH_2-X \underset{MX}{\overset{MX'}{\rightleftharpoons}} R-CH_2-X'$$

Treatment of a primary alkyl halide or pseudohalide with an alkali metal halide (e.g. KF, KI) leads to replacement of the halogen via an S_N2 Reaction.

The classic case of finkelstein reaction includes the conversion of alkyl chloride or bromide to alkyl iodide in presence of sodium iodide in acetone.

$$CH_3CH_2Br \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3CH_2I + NaBr$$

The equilibrium position of the reaction depends on the nucleophilicity of the anion, whether a good leaving group is present, and whether one anion is better stabilized than the other in a given solvent. For example, reactions with KF will thus lead cleanly to fluoroalkanes, because fluoride is such a poor leaving group due to the stability of the C-F bond.



In general, the reaction is run with an excess of the metal halide. The use of metal salts that have a high lattice energy require the addition of a crown ether.

The equilibrium position of the reaction also depends on the solubility of the metal salt in the solvent used. Thus, the substitution of bromo-and chloroalkanes with KI in acetone leads cleanly to the desired iodoalkane products, since KCl and KBr are insoluble in acetone and are consequently removed from the equilibrium :

$$R - CH_2 - Cl \xrightarrow[\text{Acetone}]{\text{KI}} R - CH_2 - I$$

Exception :

$$R{-}F + NaI \longrightarrow \times$$

The reaction does not occur because the bond energy of R-F is too high.

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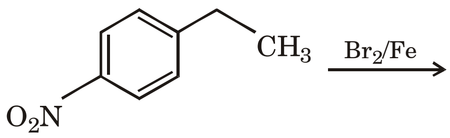
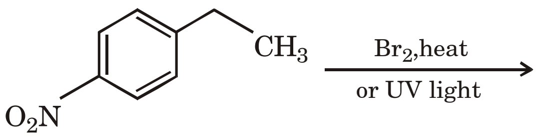
Example 3

Draw the structures of the major monohalo product in each of the following reactions :

(a)

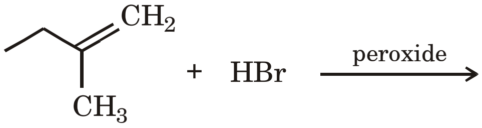


(b)



(c) $CH_3CH_2C \equiv CH + HCl\ (1\ \text{equiv}) \longrightarrow$

(d)



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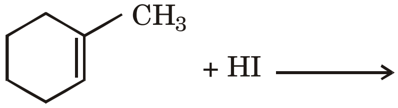

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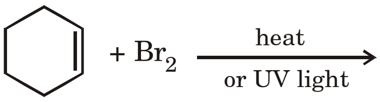
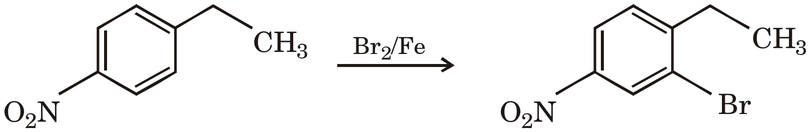
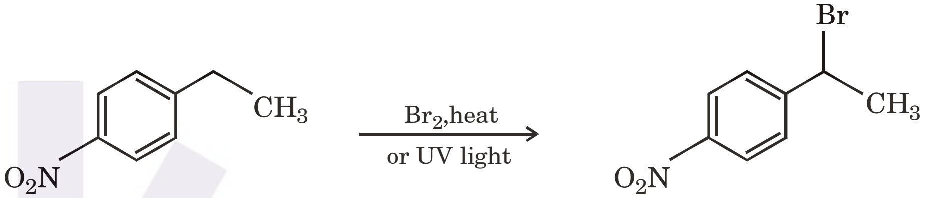


Solution :

(a) In presence of halogen carrier and absence of light, electrophilic substitution occurs at position ortho (since the p-position is already occupied) to the electron-donating CH_2CH_3 group.



(b) In presence of light, side chain (free radical) halogenation occurs at the benzylic hydrogen.



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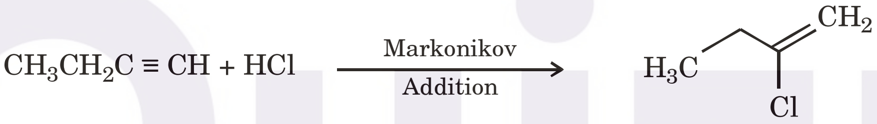

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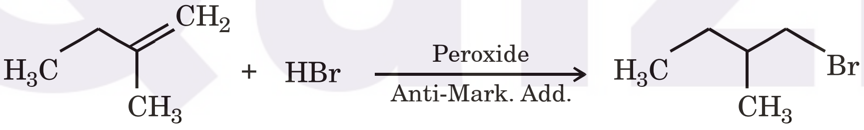

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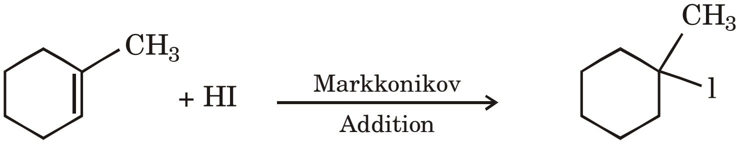

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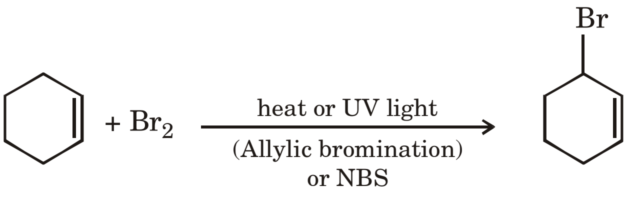

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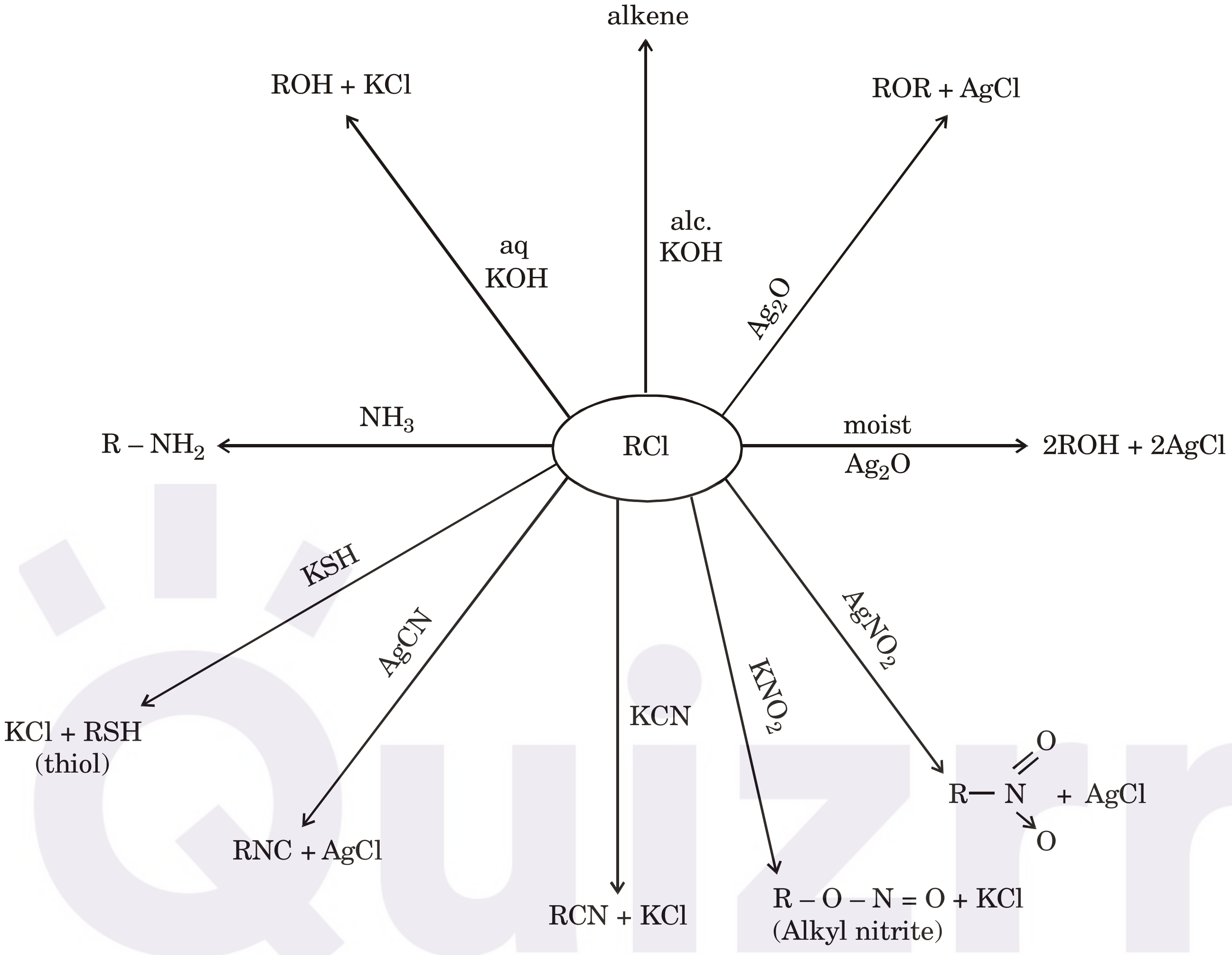
Reactions of Alkyl Halides



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$$RNH_2 \xrightarrow[-\,HCl]{RCl\ excess} R_2NH \xrightarrow{RCl} R_3N \xrightarrow[RCl]{excess} R_4N^+Cl^-$$

Some Basic Terms

(1) The halogen atom may leave with its bonding pair of electrons to give a halide ion which is stable – a halide is called a **good leaving group.**

(2) If an atom replaces the halide the overall reaction is substitution.

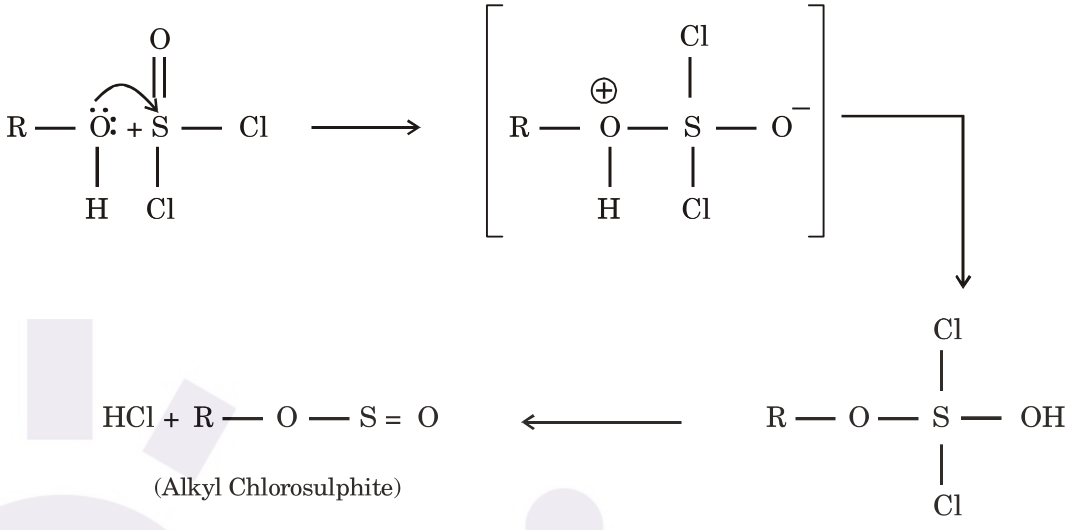
If the halide loss is accompanied by the loss of another atom, the overall reaction is called an **elimination.**

(3) Very often the other atom lost is a hydrogen (as H$^+$). The elimination of H-X is common, and is called a **dehydrohalogenation.**

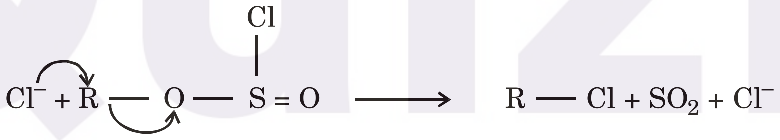
Note : Often substitution and elimination reactions will occur in competition with each other.

Mechanism 1

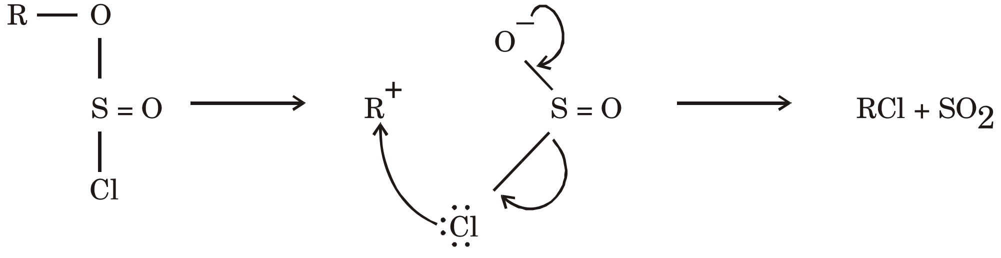
Alcohol first reacts with $SOCl_2$ to form an intermediate chlorosulphate ester, which gives alkyl chlorosulphite and HCl. In presence of pyridine, HCl reacts with it to give pyridinium (PyH^+) ion and chloride (Cl^-) ion. The Cl^- displaces the leaving group $ClSO_2^-$ and chloro sulphite ester decomposes to SO_2, Cl^- and R-Cl with inversion of configuration.



$$Py + HCl \longrightarrow PyH^+ + Cl^-$$



In the absence of a base and polar solvent, the chlorosulphite ester dissociates into an intimate ion-pair. The Cl^- of the anion of ion-pair attacks from the front side of R^+ to give retention of configuration. The retention is observed because Cl cannot reach the rear of the R^+ group but is close to its front side.



intimate ion-pair

This is referred as S_Ni (substitution nucleophilic internal) mechanism because a part of the leaving group detaches itself from the rest of the leaving group during the process and attacks the substrate.

HSAB Theory (Hard Soft Acid Base theory)

Hard acid : Which has less tendency to accept the lone pair of electrons. For example H^+, Li^+, Mg^{2+}, 3 carbocation.

Soft acid : More tendency to accept pair of electrons. For example Ag^+, Au^+, Hg_2^{2+}, Cu^{2+}

Hard base : Which has less tendency to donate lone pair of electrons.

$$\underbrace{O^{2-}, -O^-, N^{\odot}}_{\left(N^- \text{ is a soft base w.r.t. } -O^-\right)}, F^-$$

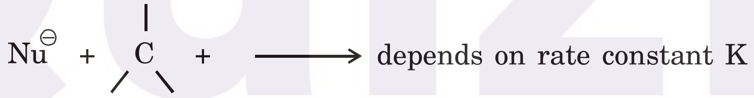
{Tip : More electronegative the element, higher is hard base character}.

Soft base : Which has more tendency to donate lone pair of electrons. $-S^-$, S^{2-}, $-\underset{1}{P}^{\odot}$

Generally, hard acids react with hard base and soft acids reacts with soft base.

Nucleophilicity and Basicity

Nucleophilicity : It is the tendency to attack on electron deficient atom.



Higher the K, higher the nucleophilicity.

Basicity : It is the tendency to abstract a proton

$$B^- + H_2O \rightleftharpoons BH + OH^-$$

In comparing molecules with the same attacking atom, there is generally a direct relationship between basicity and Nucleophilicity. **Stronger bases are better nucleophiles.**

Trends in Nucleophilicity

(1) Species with a negative charge are stronger nucleophiles than analogous species without a negative charge. (Bases are always stronger nucleophiles than their conjugate acids).

$$^-OH > H_2O \qquad ^-SH > H_2S \qquad ^-NH_2 > NH_3$$

(2) Nucleophilicity decreases from left to right across the periodic table. (The more electronegative elements hold on more tightly to their non-bonding electrons).

$^{-}OH > F^{-}$ $:NH_3 > H_2\ddot{O}:$ $(CH_3CH_2)_3P > (CH_3CH_2)_2S$

(3) Nucleophilicity increases down the periodic table. (Increase in polarizability and size).

$I^{-} > Br^{-} > Cl^{-} > F^{-}$ $HSe^{-} > HS^{-} > HO^{-}$

$(CH_3CH_2)_3P > (CH_3CH_2)_3N$

whereas basicity decreases down the group.

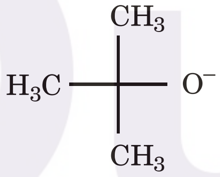
∴ $I^{-}, Br^{-}, Cl^{-}, F^{-}$

← increasing mucleophiticity

← decreasing basicity

Steric Effects :

In general, the steric bulk has a detrimental effect on nucleophilicity.



t-butoxide
weak nucleophile
strong base

$CH_3CH_2 - O^{-}$

t-butoxide
weak nucleophile
strong base

Since nucleophilicity involves the attack of the nucleophile at a carbon center, large groups tend to hinder this process.

Example 5

In non-polar solvents, which of the following represents correct order of decreasing nucleophilicity ?

(a) $OH^{-} > MeO^{-} > CH_3CO_2^{-}$ **(b)** $OH^{-} > HS^{-}$

(c) $F^{-} > Cl^{-} > Br^{-}$ **(d)** $CH_3^{-} > NH_2^{-} > OH^{-} > F^{-}$

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Solution :

In non-polar solvents, the salts of nucleophile are present as ion-pairs in which nearby cations diminish the reactivity of the anion. The order in which largest nucleophile appears first, will be the right order. Ion-pairing in NaOH is stronger than NaOMe or NaHS. In NaF, ion-pairing is stronger than NaCl and NaCl has stronger pairing than NaBr.

∴ (d)

Example 6

Explain why I^- is better nucleophile than F^- ?

Solution :

As the size of an atom increases, its outer electrons get further from the attractive force of nucleus. The electrons are held less tightly and are said to be more polarizable – they are more able to move toward a positive charge.

More polarizable atoms can form bonds at greater distances, which gives rise to stronger bonding in the T.S.

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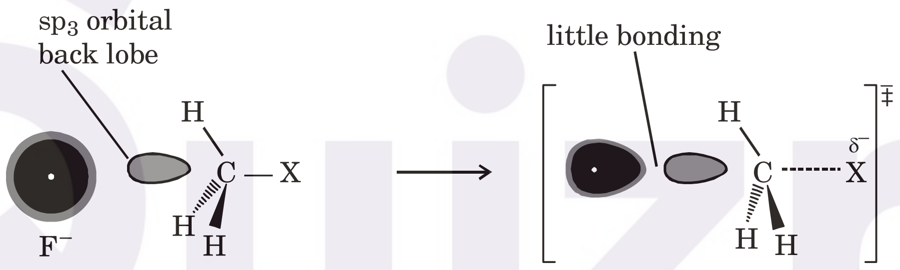
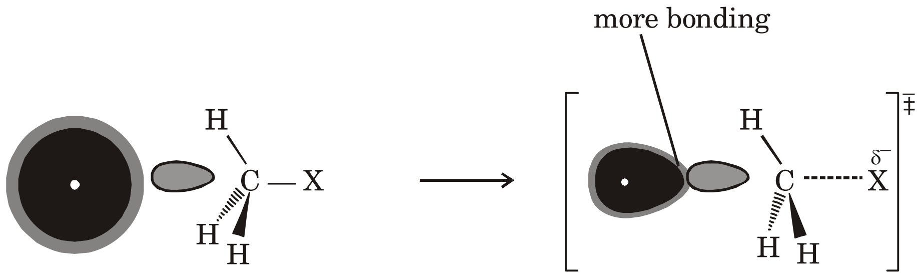


"hard," small valence shell transition state



"soft," large valence shell transition state

Fluoride is a "hard" or low polarizability nucleophile, with its electrons held close to the nucleus, and it must approach the carbon nucleus closely before orbital overlap can occur.

The outer shell of the "soft" iodide has losely held electrons, and these can easily shift and overlap with the carbon atom at a relatively far distance.

Solubility and Role of Solvent

Rule of thumb : **Like Dissolves Like**

This means that reactants dissolve in solvents of similar polarity i.e., non polar or weakly polar dissolve in weakly polar solvents only.

That is the reason why hydrocarbons and alklyl halides do not dissolve in water, whose molecules are high polar and held together by strong hydrogen bonding.

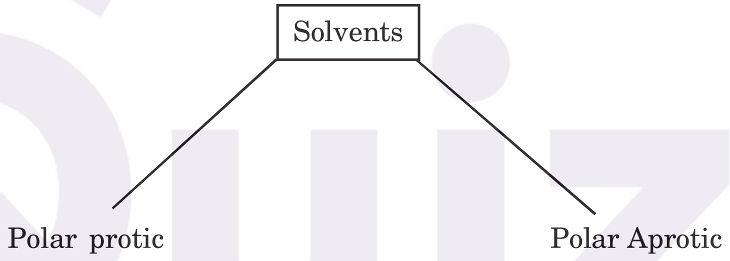
Some terms :

- Hydrophilic (water loving) i.e. soluble in water
- Hydrophobic/lilophilic (water hating) i.e. very less soluble in water as compared to solubility in non polar solvents

Note : As the number of carbon increases, the solubility decreases.

$$CH_3OH > CH_3CH_2OH > (CH_3)\ CH_2CH_2OH > .... > CH_3(CH_2)_n - CH_2OH$$

Nature of Solvents



- Though there can be two more categories, i.e., weakly polar aprotic and non polar solvents but we will constraint our explanation to the above 2 categories only.

1. Polor Protic Solvents

These are solvents containing hydrogen that is attached to oxygen or nitrogen and hence acidic enough to form hydrogen bonds. In short, protic solvents are ones which have acidic hydrogen like H_2O, methanol etc.

How they work :

Substrate contains both cations and anions. Here in protic solvents, Cations are attracted to negative pole of polar solvent. In H_2O, negative part is the oxygen atom, as it is most electronegative and also has unshared lone pair.

To add to this, O is attached with tiny hydrogen atoms which makes oxygen well exposed without crowding it.

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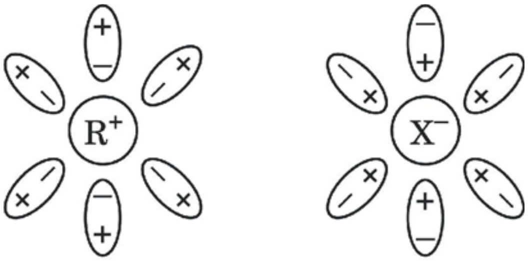
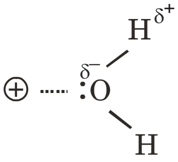
Whereas,

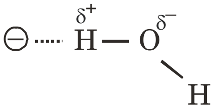
Anions are attracted to positive pole of polar solvent which is hydrogen in case of H_2O, thus forming hydrogen bonds.



Solvated cation & anion

Case of H_2O

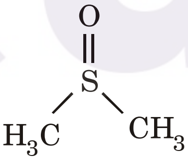




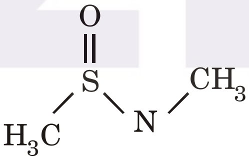
2. Polar Aprotic Solvents

These are solvents which do not have acidic hydrogen i.e. hydrogen is not attached to electronegative O or N.

Common example of such solvents :



DMSO

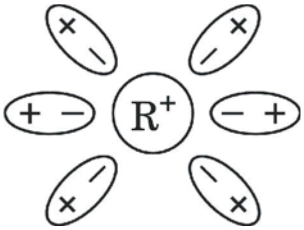


DMF

How they work :

They also dissolve ionic compounds but their action is completely different from protic solvent. Since they do not have acidic hydrogen they are not able to Solvate anions. Though they do solute cations by their electro-negative part.

So only this effect takes place.



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Key to success

- For ionic/polar substrate, the more solvated the cations and anions, faster is the reaction.

⇒ Polar protic solvents will favour ionic reactants

i.e., SN1 mechanism (as carbocations are formed in the process)

- Solvation differs from ion to ion, for ex in gaseous state, reactivity/basicity of halides is $F^- > Cl^- > Br^- > I^-$

  but when we talk of protic solvents, the order reverses i.e. $I^- > Br^- > Cl^- > F^-$

Why ? :

Since F is a small atom, hence the Charge is concentrated in a small space & hence it is able to form hydrogen bonding at a very large scale as compared to that of I^- which has charge over a large area & hence weak hydrogen bonding.

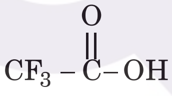
Same reasoning can be given for, Li^+ & Na^+. Again, in Aprotic solvents, since here is no formation of hydrogen bonding, hence order remains the same i.e $F^- > Cl^- > Br^- > I^-$

So

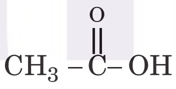
$F^- \xrightarrow{H_2O}$ a weak nucleophile

$F^- \xrightarrow[DMSO]{}$ a strong nucleophile

Tip : Common polar protic solvents



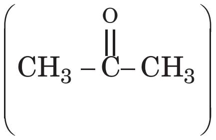
$CF_3-\overset{\overset{O}{\|}}{C}-OH$ H_2O CH_3OH



$CH_3-\overset{\overset{O}{\|}}{C}-OH$ CH_3CH_2OH

Common polar Aprotioc solvents

DMSO DMF Acetone



$\left(CH_3-\overset{\overset{O}{\|}}{C}-CH_3\right)$

Summing up the halogen series

	↓ size increases	↑ Basicity increase	↑ nucleophilicity increase in polar aprotic solvents	↓ nucleophilicity in polar protic solvents
F^-				
Cl^-				
Br^-				
I^-				

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Nucleophilic Substitution (S_N)

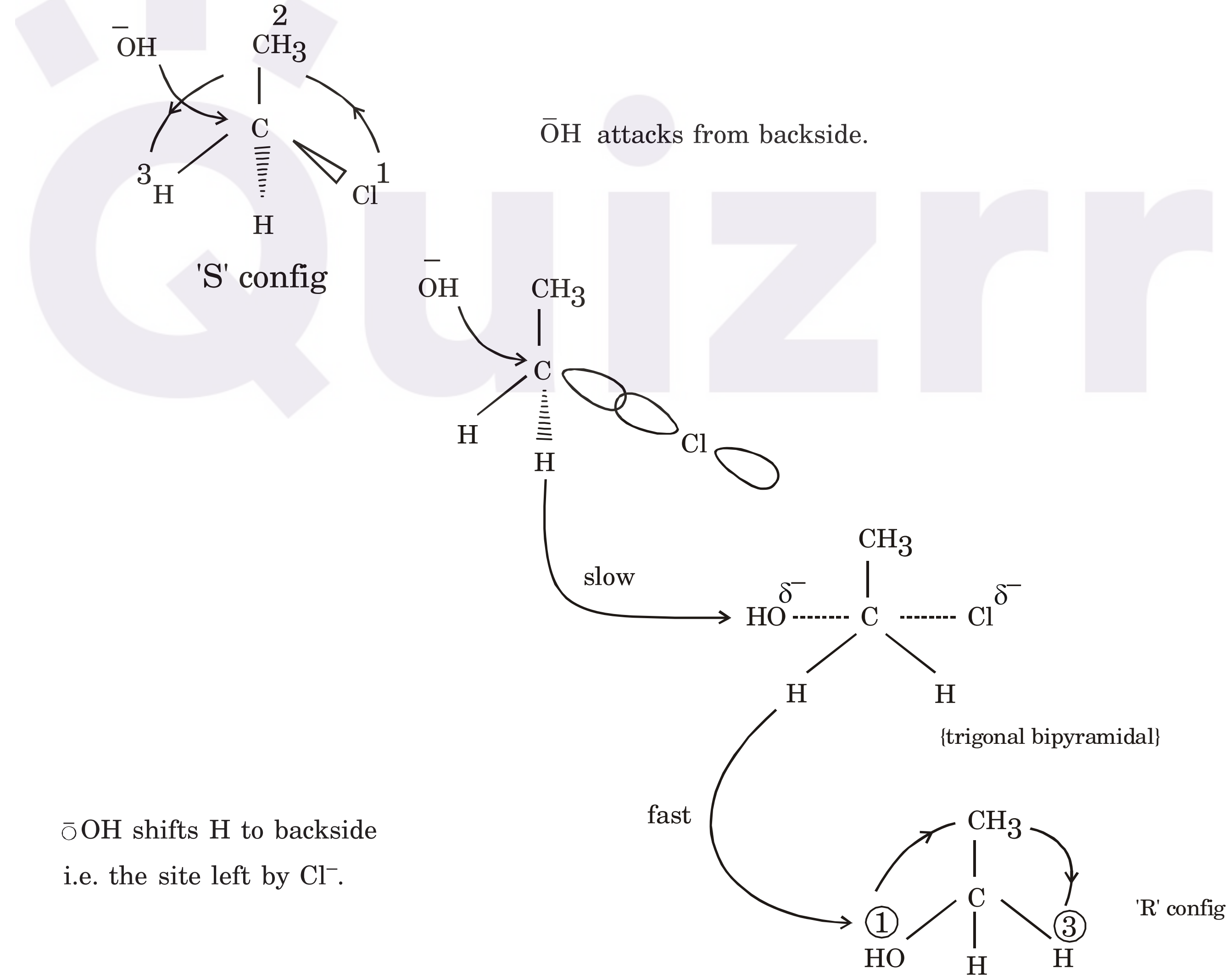
$$\underset{\text{(Substrate)}}{R-X} + \underset{\text{(Reagent)}}{Nu^-} \longrightarrow \underset{\text{(Product)}}{R-Nu} + \underset{\left(\begin{array}{c}\text{leaving}\\ \text{group}\end{array}\right)}{X^-}$$

SN_1	SN_2
(Unimolecular nucleophilic substitution)	(bimolecular nucleophilic substitution)
{occurs only for those species capable of forming a stable carbocation}	{Only by those which do not form stable carbocation}

Second Order / Bimolecular nucleophilic Substitution (SN_2)

$$CH_3CH_2Cl + {}^-OH \longrightarrow CH_3CH_2OH + Cl^-$$

Mechanism :



$\bar{O}H$ attacks from backside.

$\bar{o}$OH shifts H to backside i.e. the site left by Cl^-.

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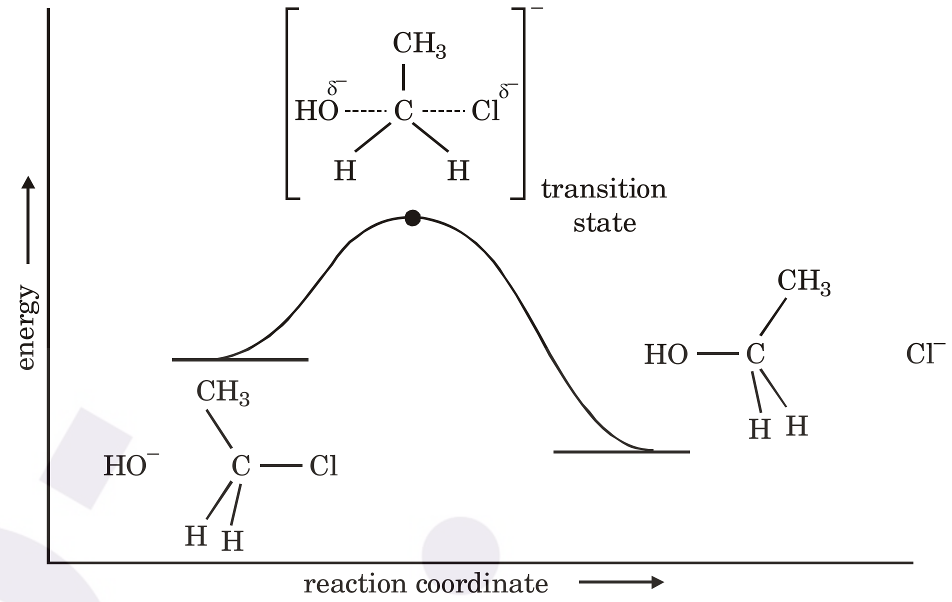
Hence, SN_2 leads to **inversion of configuration,** but only when the same priority group is replaced.

Note : It does not lead to change in d-l configuration.

Energy profile of the Reaction

The transition state is a point of highest energy (not an intermediate).



Kinetic information tells us that the rate is doubled when the CH_3CH_2Cl also doubled when the $[HO^-]$ is doubled.

The rate is first order w.r.t. both reactants and is therefore 2nd order overall.

$$\boxed{\text{Rate} = K_r\,[CH_3CH_2Cl]\,[HO^-]}$$

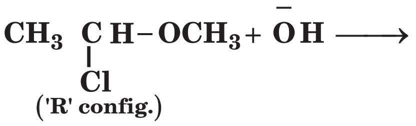
The rate and mechanism are consistent since the mechanism requires a collision between the hydroxide ion and methyl iodide. Both species are present in the transition state, and the frequency of collisions is proportional to the concentrations of the reactants.

S_N2 = substitution, nucleophilic, bimolecular

Bimolecular means that the transition state of the RDS involves the collision of two molecules (Bimolecular reactions generally have 2nd order overall rate equations).

Example 7

If the given compound is an 'R' isomer, what configuration will the product have, if it follows S_N2 mechanism.



$$CH_3\underset{\underset{Cl}{|}}{C}H-OCH_3 + \overset{-}{O}H \longrightarrow \quad \text{'R' config}$$

('R' config.)

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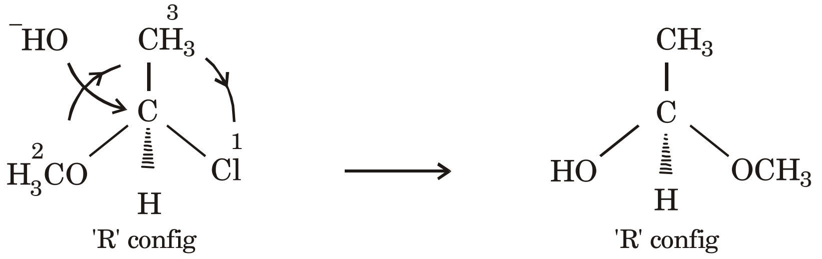
Solution :



Here, no inversion takes place because priority of attacking group is not same as the leaving group.

Example 8

The following reaction proceeds by an S_N2 pathway.

$$C_6H_5CH_2Br + NaN_3 \longrightarrow C_6H_5N_3 + NaBr$$

(a) Write an equation for the expected rate constant.

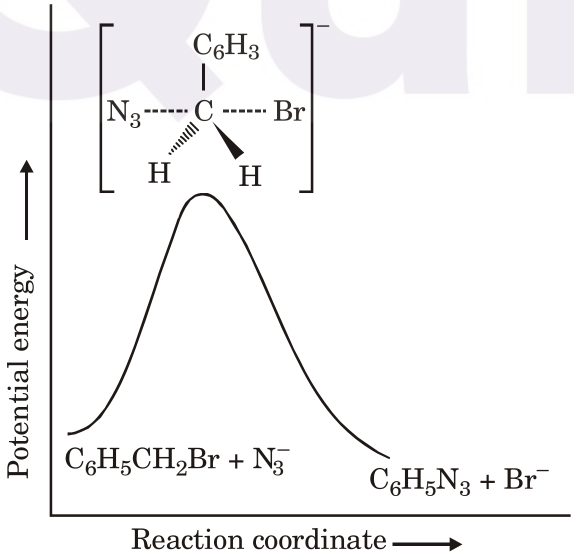
(b) Draw a potential energy diagram for the reaction.

(c) How would the rate of the reaction change if concentration of sodium azide is doubled?

Solution :

(a) Rate = k $[C_6H_5CH_2Br]\,[NaN_3]$

(b)



(c) The rate will be doubled.

Versality of the S_N2 mechanism

The S_N2 mechanism is a common reaction mechanism and can cover a variety of functional group transformation of alkyl halides.

All of the type $\quad Nu: + R\text{-}X \rightarrow Nu\text{-}R + X^-$

		Nucleophile		Product	Class
R-X	+	I^-	$\longrightarrow$	R-I	alkyl halide
R-X	+	HO^-	$\longrightarrow$	R-OH	alcohol
R-X	+	$R'O^-$	$\longrightarrow$	R-O-R'	ether
R-X	+	HS^-	$\longrightarrow$	R-SH	thiol
R–X	+	$:NH_3$	$\longrightarrow$	$R–NH_2$	amine
R–X	+	N_3^-	$\longrightarrow$	$R–N_3$	azide
R–X	+	$^-C{\equiv}C–R'$	$\longrightarrow$	$R–C{\equiv}C–R'$	alkyne
R–X	+	–CN	$\longrightarrow$	$R–C{\equiv}N$	nitrile
R–X	+	$R'CO_2^-$	$\longrightarrow$	$R–CO_2R'$	ester
R–X	+	$:P(Ph)_3$	$\longrightarrow$	$(R–PPh_3)^+ X^-$	phosphonium salt
R-X	+	$R'S^-$	$\longrightarrow$	R-S-R'	thioether

Note : Halogen exchange reactions are normally used to prepare either iodo-or fluoro-compounds from other alkyl halides since direct iodination is too slow and direct fluorination is too violent.

$$H_2C{=}CH\text{-}CH_2Cl + NaF \longrightarrow H_2C{=}CH\text{-}CH_2F + NaCl$$

$$H_3C–CH_2Cl + KF \xrightarrow{18\text{–crown–}6} H_3C–CH_2F + KCl$$

Nucleophile Strength

The rate of the S_N2 reaction strongly depends on the nature of the nucleophile – a good nucleophile gives faster rates than a worse nucleophile.

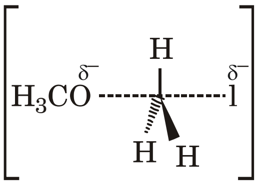
Consider methanol (CH_3OH) and methoxide (CH_3O^-) reacting with CH_3I. It is found that methoxide reacts about a million times faster in S_N2 reactions than methanol.

Generally negatively charged species are much better nucleophiles than analogous neutral species.

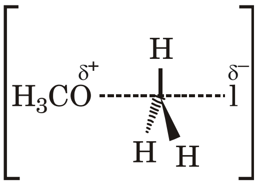
The two transition states are different energetically.

The T.S. with methoxide has the negative charge shared over the oxygen atom and the leaving halide.

methoxide
lower E_a



methoxide
higher E_a



In the methanol case, there is no negative charge. The halide has a partial negative charge and the oxygen has a partial positive charge. This is of higher energy.

Substrate Effects

–Leaving group effects
–steric effects

(1) Leaving group effects

A good leaving group has the following features :

(1) Electron withdrawing (to polarize the C-X bond, making the C electrophilic).

(2) Stable once it has left (not a strong base).

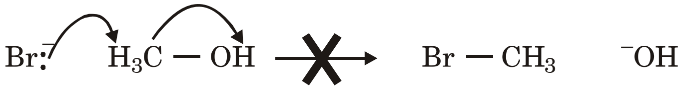
(3) Polarizable (to stabilize the T.S. – like I^- previously)

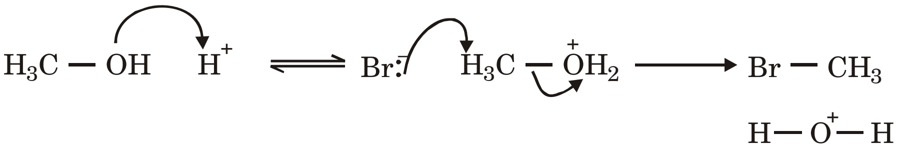
Common leaving groups :

(ions) Cl^-; Br^-, I^-, RSO_3^- (sulfonate), RSO_4^- (sulfate), RPO_4^- (phosphate)

(neutral) H_2O, R-OH, R_3N, R_3P

Hydroxide ions are not good leaving groups (strong bases), but in acidic media, the





O gets protonated, and now H_2O can serve as a good leaving group.

Quizrr

Neutral molecules can be good leaving groups from positively charged electrophiles. But the need to protonate the electrophile first limits the choice of nucleophiles to those that are not strong bases, since the nucleophile would simply get protonated.

(2) Steric Effects of the Substrate

Large groups on the electrophile hinder the approach of the nucleophile.

Rel. rates for S_N2 : $CH_3X > 1 > 2 > 3$ alkyl halides

For an S_N2 reaction, the nucleophile must approach the small backside lobe of the C-X sp^3 orbital.

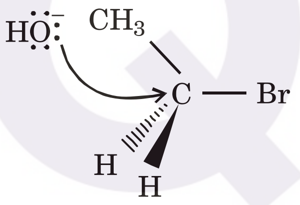
Generally, one alkyl group slows the reaction, two alkyl groups make it difficult three alkyl close to impossible.

Thus decreasing reactivity by S_N2

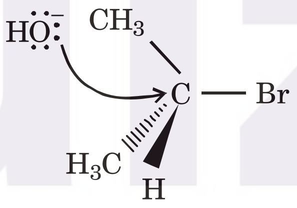
$$\xrightarrow[\text{decreasing reactivity by } S_N2]{CH_3X > CH_3CH_2X > (CH_3)_2CHCH_2X > (CH_3)_3CX}$$

$$\xrightarrow[\text{decreasing reactivity by } S_N2]{CH_3CH_2X > CH_3CH_2CH_2X > (CH_3)_2CHCH_2X > (CH_3)_3CCH_2X}$$

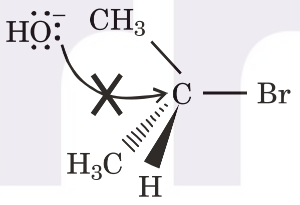
Quizrr



ethyl bromide (1)
attack is easy

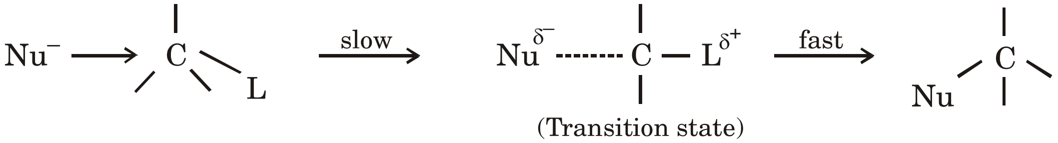


isopropyl bromide(2)
attack is possible



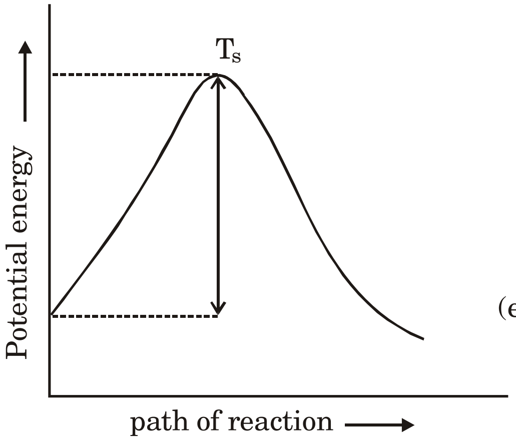
t-butyl bromide (3)
attack is impossible

Effect of Solvent on S_N2



Energy Profile

{Here Ts is the transition state, and GS is the initial state}



(exothermic reaction)

Rate of reaction increases only when

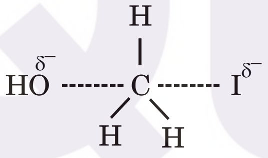
(1) If H_{TS} decreases (this is because less energy would be required to reach the transition state)

(2) If H_{GS} increases

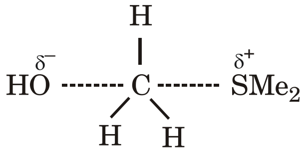
(3) If both of the above occur simultaneously.

Some applications

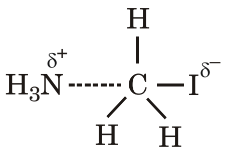
(a) $MeI + {}^{-}OH \longrightarrow MeOH + I^{-}$



(b) $Me^{-}\ S^{+}\ Me_2 + {}^{-}OH \longrightarrow MeOH + S\ Me_2$



(c) $MeI + NH_3 \longrightarrow Me^{+}\ NH_2 + I^{-}$



Quizrr

In case of (a) and (b), reacting mixture has full charges whereas transition state has partial negative charges.

∴ Reacting species will be more solvated. Hence H_{Gs} will decrease more than H_{Ts} with the introduction of protic solvent.

Whereas in (c) reacting mixture is charge free and in transition state some partial charge has developed. Therefore, Ts will be more solvated. Thus H_{Ts} decreases more than H_{Gs} in this case.

Example

An optically active 3–bromo–3–methyl hexane on hydrolysis gives

- **(a) 3–methyl–3–hexanol with retention of configuration.**
- **(b) 3–methyl–3–hexanol with inversion of configuration.**
- **(c) a partially racemic mixture of 3–methyl–3–hexanol.**
- **(d) optically inactive 3–methyl–3–hexanol.**

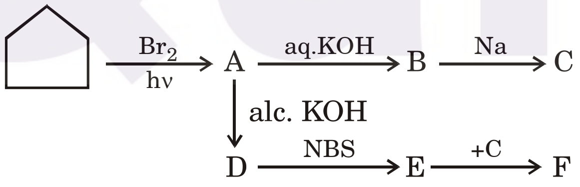
Solution :

3–bromo–3–methyl hexane, on ionization gives a 3 carbocation, which can be attacked by nucleophile (H_2O) to give both dextro and levo in unequal amounts of 3–methyl–hexanol.

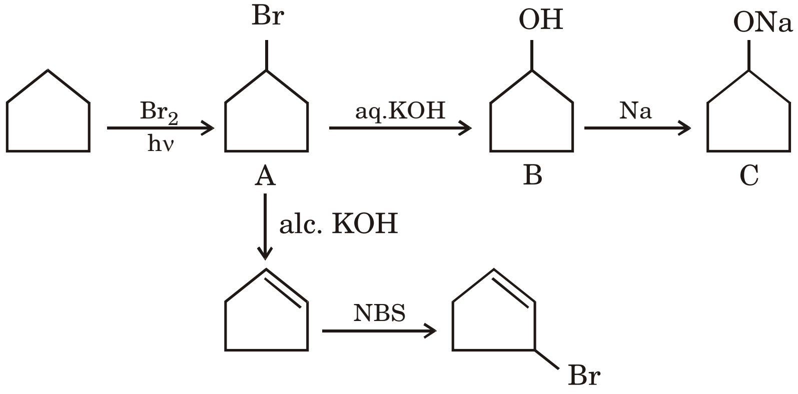
∴ (c)

Example

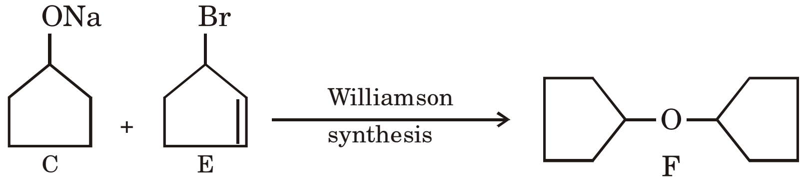
Identify A, B, C, D, E and F in the following series of reaction.



Solution :



Quizrr



Example

Arrange following compounds in the decreasing order of their reactivity towards S_N2 reaction.

$PhCH_2(Cl)$	**$PhCH(Cl)Me$**	**$PhC(Cl)Me_2$**
(A)	**(B)**	**(C)**

(a) **(C) > (B) > (A)**
(b) **(A) > (B) > (C)**
(c) **(B) > (A) > (C)**
(d) **(B) > (C) > (A)**

Solution :

The rate of S_N2 reaction depends on steric crowding in the transition state. More is the steric crowding, less stable the transition state is, less will be the rate of S_N2 reaction. Thus, the reactivity order of S_N2 reaction would be (A) > (B) > (C).

$\therefore$ (b)

First order Nucleophilic Substitution (S_N1)

There is also an S_N1 reaction. (Substitution, nucleophilic, unimolecular)

Consider the reaction of t-butylbromide and methanol :

$$(CH_3)_3C\text{-}Br + CH_3\text{-}OH \rightarrow (CH_3)_3C\text{-}O\text{-}CH_3 + H\text{-}Br$$

The rate was found to depend only on the concentration of t-butylbromide.

$$\text{Rate} = k_r\,[(CH_3)_3C\text{-}Br]$$

The rate is first order overall – unimolecular

It appears that the nucleophile is not present in the R.D.S. (rate determining step), but must react somewhere after the R.D.S. has occured.

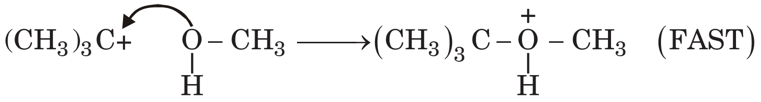
Mechanism :

Step 1 : Formation of carbocation (R.D.S.)

$$(H_3C)_3C\overset{\curvearrowright}{-Br} \longrightarrow (CH_3)_3\,C^+ + Br^- \quad (\text{SLOW})$$

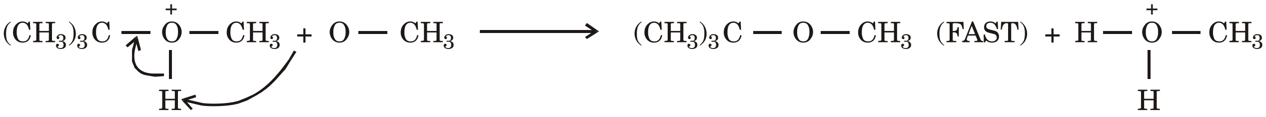
Quizrr

Step 2a : Nucleophilic Attack



$$(CH_3)_3C^+ \quad \underset{H}{O}-CH_3 \longrightarrow (CH_3)_3C-\overset{+}{\underset{H}{O}}-CH_3 \quad \text{(FAST)}$$

Step 2 (b) : Loss of a proton



$$(CH_3)_3C-\overset{+}{\underset{H}{O}}-CH_3 + O-CH_3 \longrightarrow (CH_3)_3C-O-CH_3 \quad \text{(FAST)} + H-\overset{+}{\underset{H}{O}}-CH_3$$

The S_N1 reaction is a two step process, with the first being a slow ionization reaction generating a carbocation.

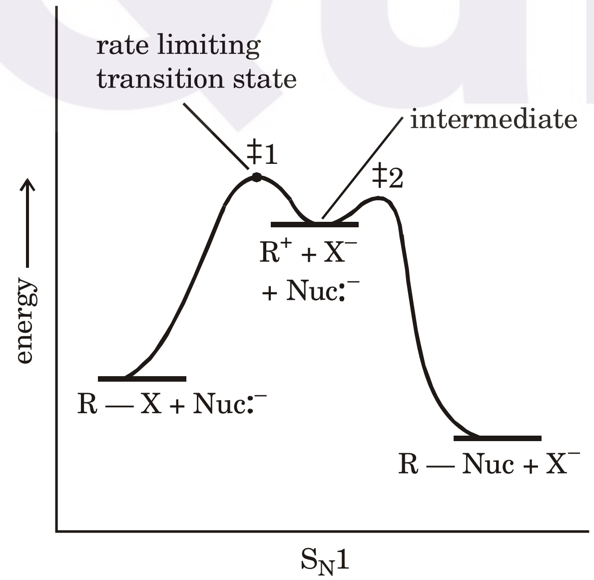
The second is the quick nucleophilic attack by the nucleophile on the carbocation. (In some case, like when water or alcohol is the nucleophile, a quick loss of a proton gives the final product).

⇒ Solvation assists the ionization process, since the energy of activation required for breaking of the bond is largely recovered for solvation of ions produced.

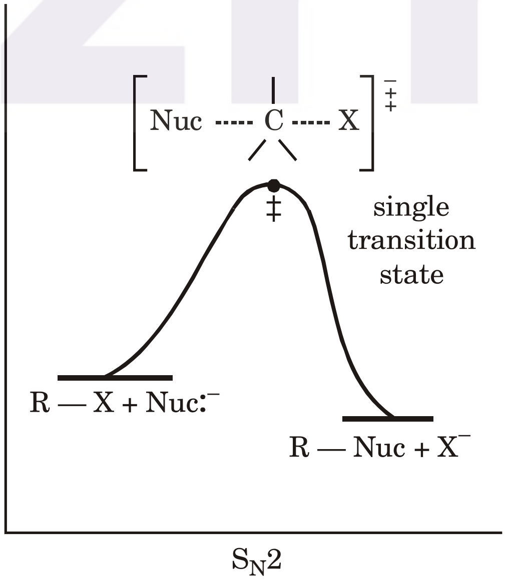
In general :

$$R\text{-}X \rightarrow R^+ + X^- \quad \text{(R.D.S., slow)}$$

$$R^+ + Nuc^- \rightarrow R\text{-}Nuc \quad \text{(fast)}$$



S_N1



S_N2

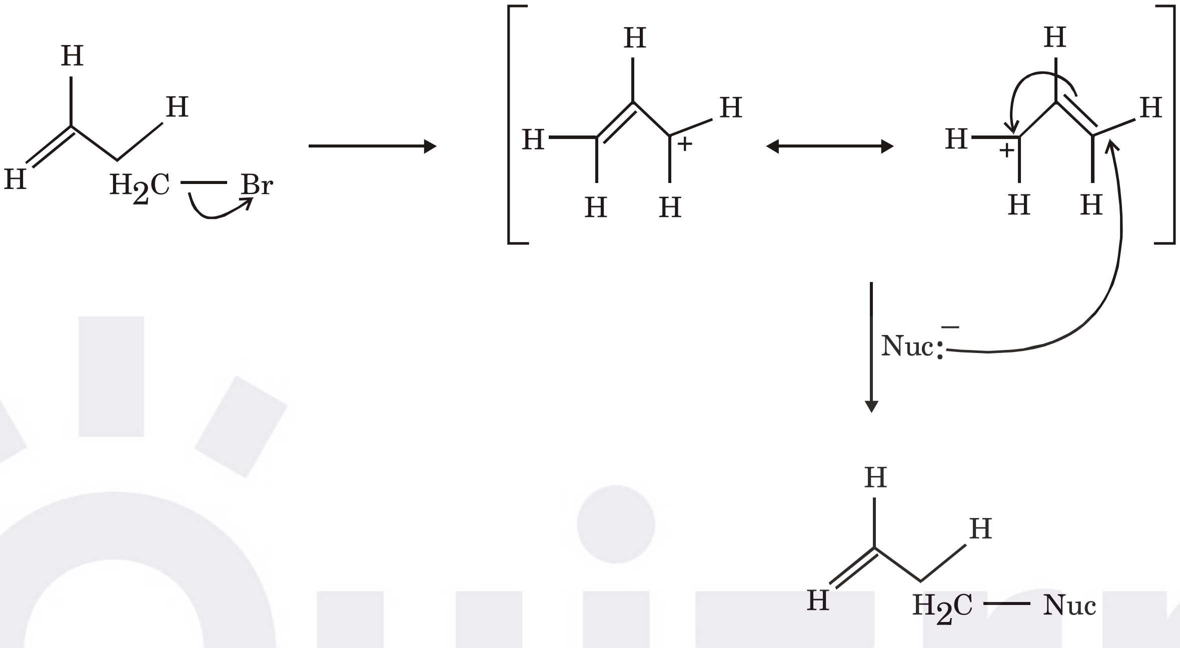
The S_N1 reaction has two transition states, whereas the S_N2 only has one transition state. Consequently, S_N1 rates depend on carbocation stability.

Quizrr

Since alkyl groups are known to stabilize carbocations (inductive effects and hyperconjugation), S_N1 reactivities decrease in the order of :

$$3 > 2 > 1 > \text{methyl cation}$$

(This is the opposite for S_N2 reactivity).



Resonance stabilized cation are also important for S_N1 reactivity, for example, allyl bromide is much more reactive than other primary halides in S_N1 reactions.

Leaving Group Effects

In the R.D.S. for an S_N1 reaction, the bond to the leaving group is breaking therefore a highly polarizable leaving group helps stabilize the T.S. through partial bonding as it leaves (like for S_N2 case).

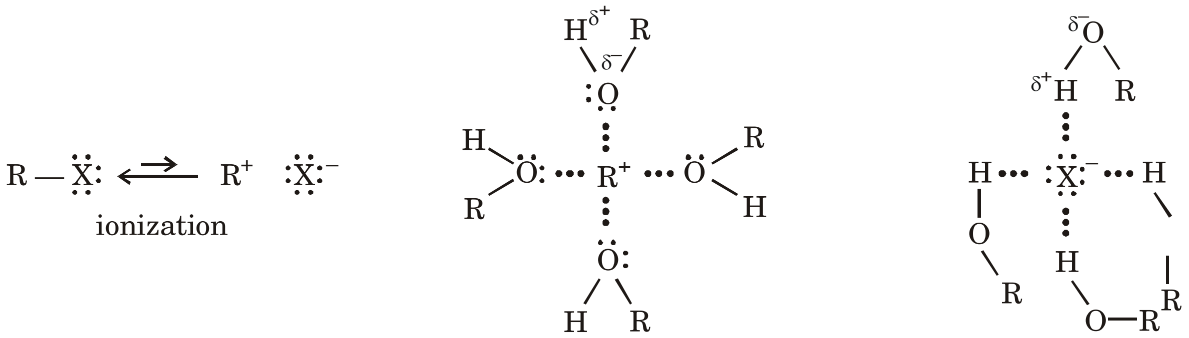
The leaving group should be stable after it has left with the bonding electrons, and also be a weak base.

The leaving group starts to take on partial negative charge as the cation starts to form. Good leaving groups are essential for both S_N1 and S_N2 reactions.

Solvent Effects

The R.D.S. of an S_N1 reaction involves the formation of 2 ions, therefore polar solvents (which stabilize ions) enhance S_N1 reactivities.

Protic solvents are especially useful since the hydrogen bonding stabilizes the anionic leaving group after ionization.



solvated ions

Stereochemistry of the S_N1 Reaction

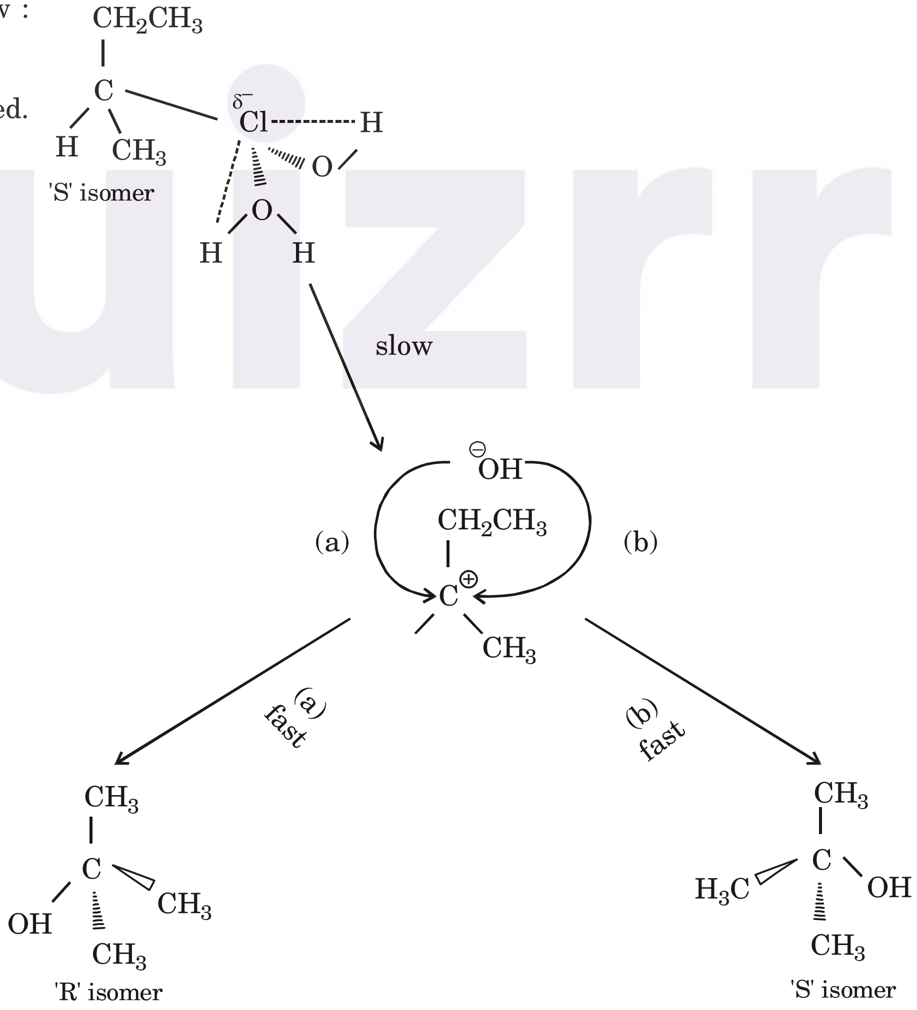
(Recall that the S_N2 reaction is stereospecific, always proceeding with inversion).

The S_N1 reaction is not stereospecific.

Consider the reaction below :

The carbocation produced

is planar and sp^2 hybridized.



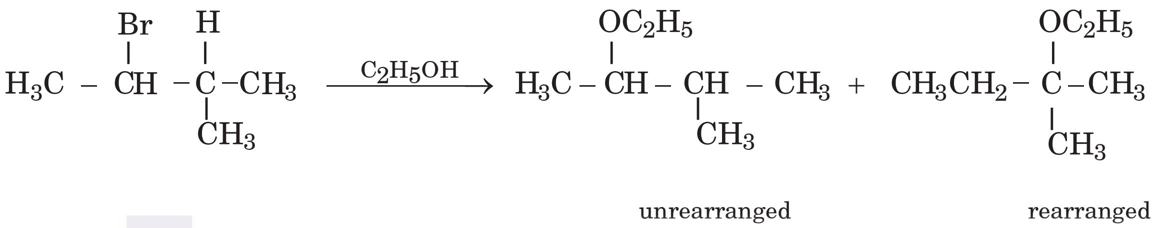
Quizrr

If the nucleophile attacks from the side that the leaving group is attached, the product displays retention of configuration. So, S_N1 leads to reacemization.

Rearrangements in S_N1 Reactions

Carbocations will often undergo **rearrangements,** producing more stable ions.

For example the products of the S_N1 reaction of 2-bromo-3-methylbutane and ethanol are a mixture of structural isomers – the expected product and a rearranged product.

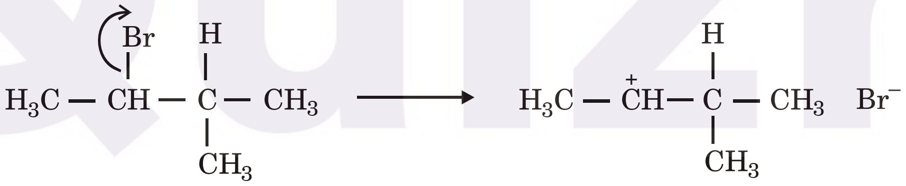


$$H_3C-\underset{}{\overset{Br}{CH}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \xrightarrow{C_2H_5OH} H_3C-\overset{OC_2H_5}{CH}-\underset{CH_3}{CH}-CH_3 + CH_3CH_2-\underset{CH_3}{\overset{OC_2H_5}{C}}-CH_3$$

The two products arise from the same carbocation. In one case the cation is trapped by the nucleophile before it can rearrange, whereas the second product arises by quenching of the **rearranged** cation by the nucleophile.

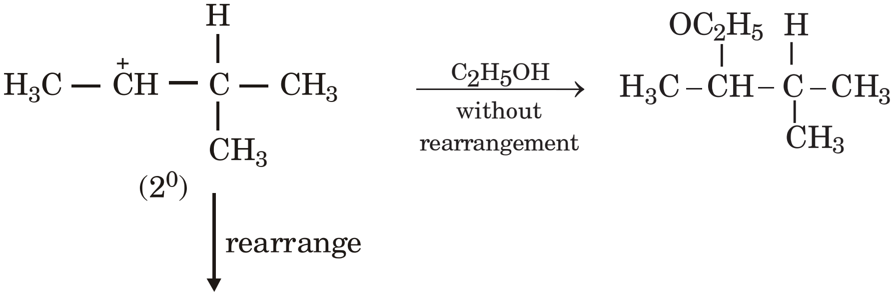
Mechanism :

Step 1 : Formation of carbocation :



$$H_3C-\overset{Br}{CH}-\underset{CH_3}{\overset{H}{C}}-CH_3 \longrightarrow H_3C-\overset{+}{C}H-\underset{CH_3}{\overset{H}{C}}-CH_3 \quad Br^-$$

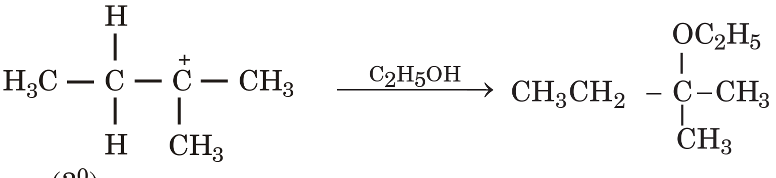
Step 2 : Attack of solvent before and after rearrangement.



$$\underset{(2^0)}{H_3C-\overset{+}{C}H-\underset{CH_3}{\overset{H}{C}}-CH_3} \xrightarrow[\text{without rearrangement}]{C_2H_5OH} H_3C-\overset{OC_2H_5}{CH}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

$$\Big\downarrow \text{rearrange}$$

Quizrr



$$H_3C-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{+}{C}}-CH_3 \xrightarrow{C_2H_5OH} CH_3CH_2-\underset{CH_3}{\overset{OC_2H_5}{C}}-CH_3$$

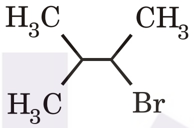
(3^0)

(Rearrangements do not occur in S_N2 reactions since carbocations are not intermediates).

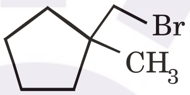
Example

Given the major product (with proper explanation) when following halogen compounds are treated with sodium exthoxide.

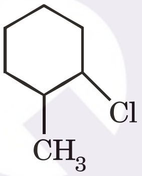
(a)



(b)



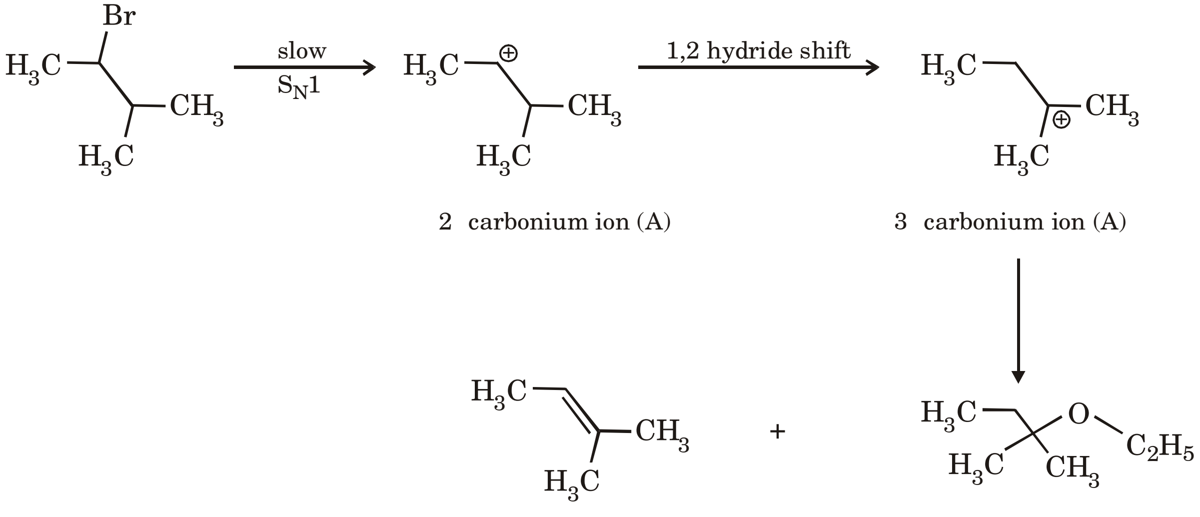
(c)



Quizrr

Solution :

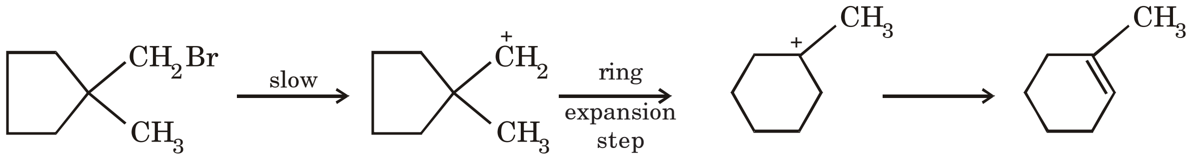
(a)



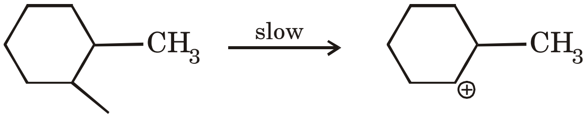
major

minor

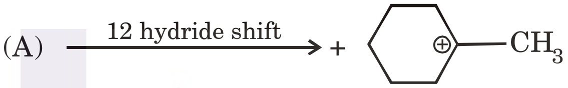
(b)



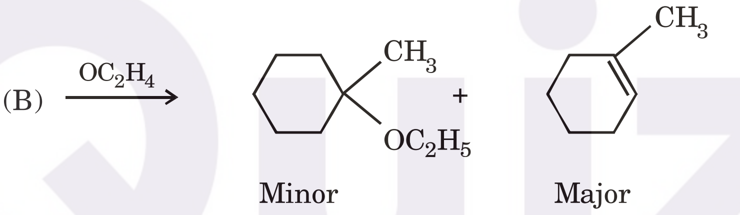
(c)



2^+ carbonium ion (A)



3^+ carbonium ion (B)

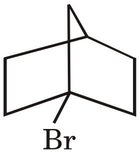


Quizrr

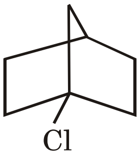
Example

Rank the following halides in order of increasing rates of S_N1 solvolysis. Explain your answer.

(a)

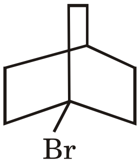


(b)



(c) **$(CH_3CH_2CH_2)_3CBr$**

(d)



Solution :

(c > d > a > b), because

(c) Forms a stable carbocation.

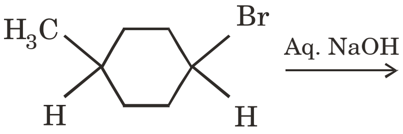
(d) Flexible structure, thus can support a carbocation.

(a) (b) being alkyl bromide are more reactive than an alkyl chloride.

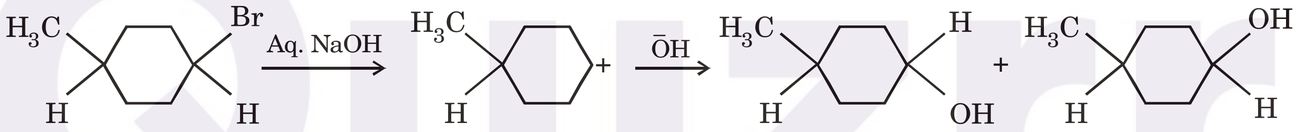
(a) and (b) are less reactive because the three carbon atoms attached to the electron deficient carbon are tied back units the bicyclic ring structure. They cannot become coplanar without introducing a great deal of strain into the molecule.

Example

Write the structure of the products that would be obtained in an S_N1 reaction of cis-1-bromo-4-methylcyclohexane with dilute aqueous NaOH.



Solution :



This is an example of syn-elimination where the two leaving groups cannot attain an anti-periplanar conformation. The products are held in eclipsed conformation.

Example

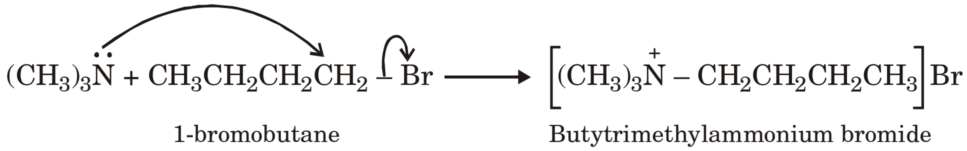
Give the structure of major substitution product from reaction 1-bromobutane with

(a) $(CH_3)_3N$ **(b) $(CH_3)_2S$**

(c) CH_3COOAg

Solution :

(a)



$$(CH_3)_3\ddot{N} + CH_3CH_2CH_2CH_2-Br \longrightarrow \left[(CH_3)_3\overset{+}{N}-CH_2CH_2CH_2CH_3\right]Br$$

1-bromobutane

Butytrimethylammonium bromide

(b) $(CH_3)_2\ddot{S}: + CH_3CH_2CH_2CH_2 - Br \longrightarrow \left[(CH_3)_2\overset{+}{S} - CH_2CH_2CH_2CH_3\right]Br$

Butytrimethylammonium bromide

(c) $CH_3COOAg + CH_3CH_2CH_2CH_2 - Br \longrightarrow CH_3COOCH_2CH_2CH_2CH_3 + Br$

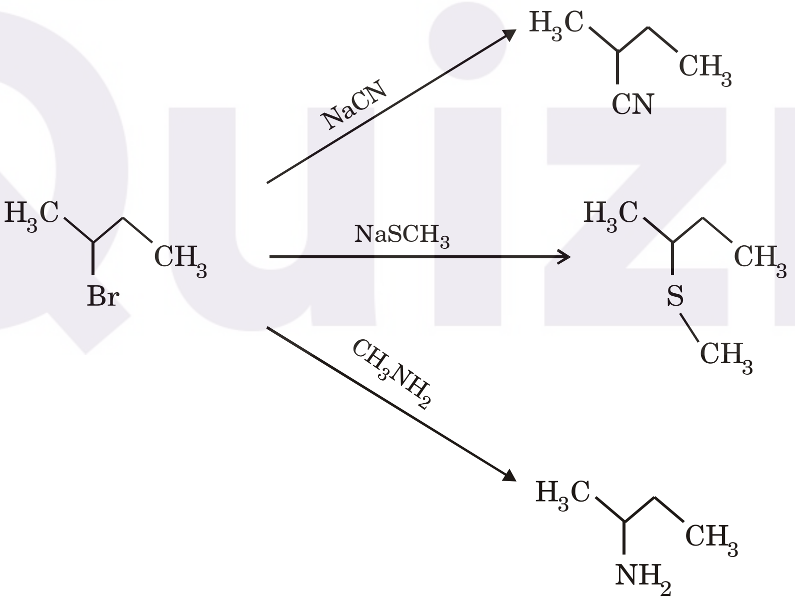
butyl ethanoate

Example

Give the structure of the major organic product obtained from the reaction of 2-butyl bromide with the following reagents :

- **(a)** **NaCN**
- **(b)** **$NaSCH_3$**
- **(c)** **CH_3NH_2**

Solution :



S_N1 vs S_N2

Which mechanism the reaction will follow is decided upon the following 4 factors i.e.

1. Nature of substrate
2. Strength of Nucleophile
3. Nature of leaving group
4. Role of solvent

We will now see the affect of each of these factors.

1. Nature of Substrate

RX

1

$\Rightarrow \left\{ \begin{array}{l} \text{will never go for } S_N1 \\ \text{will show } S_N2 \text{ only} \end{array} \right\}$

3

$\left\{ \begin{array}{c} \text{will always show } S_N1 \\ \text{because of 3 stable carbocation} \end{array} \right\}$

For 2 RX we will have to see for more factors

2. Strength of Nucleophile

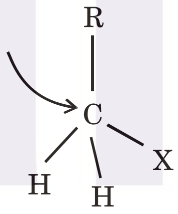
<u>"for S_N2, key to success is the attack of nucleophile".</u>

So, generally,

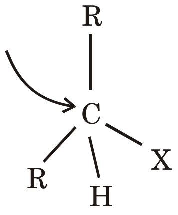
weak Nu^- : S_N1
strong Nu^- : S_N2

Here in S_N2, the effect of steric hindrance also has to be taken in count.

- In case, there is not much hindrance, nucleophile can attack easily.



Now it has 2 alkyl groups present which shows some hindrance. Hence nucleophile has to be a strong one so as to attack the carbon & go for S_N2 attack.



Nucleophilicity vs Basicity

In general Nu^- & basic character run in parallel but their order is reversed in the same group of periodic table.

$$I^-,\ Br^-,\ Cl^-,\ F^-$$

$$\xleftarrow{\text{nuelceophilicity}}$$

$$\xrightarrow{\text{basicity}}$$

Nucleophilicity is a function of polarizability. And bigger the size, greater is polarizability.

And a better nucleophile favours substitution, whereas base favours elimination, which we will deal later.

Note : Nu^+ does not play an important role in S_N1 because it does not play any role in rate determining step.

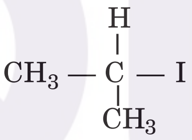
3. Nature of Leaving group

For substitution, either S_N1 or S_N2 the presence of a good leaving facilitates the reaction.

A good leaving group → a stable ion
→ a weak base

eg. I^- is a good leaving group because its a weak base. It is a weak base because its a conjugate base of a strong acid HI.

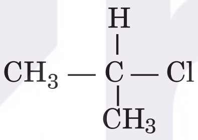
∴



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-I$

(a)

vs



$CH_3-\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}-Cl$

(b)

(a) will more readily go for substitution as compared to (b) as I^- is a better leaving group than Cl^-.

⇒ $$RI > RBr > RCl > RF$$

$$\xrightarrow[\text{order of substitution}]{\text{decreasing}}$$

4. Role of Solvent

Remember the rule of thumb "like dissolves like" as done earlier.

⇒ Ionising solvents solvate ionic compounds.

Quizrr

Solvent

Protic solvent

- (ionising solvents)

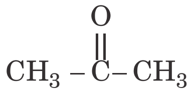
  $\boxed{S_N1 \text{ is preferred}}$

- examples of protic solvents
  - H_2O (aq)
  - EtOH

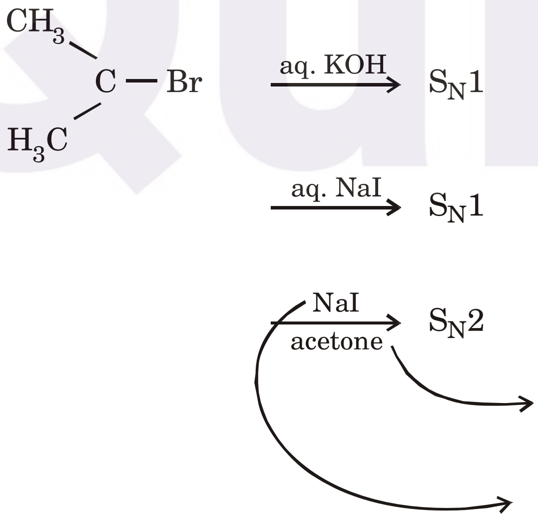
Aprotic solvent

-

  $\boxed{S_N2 \text{ is preferred}}$

- examples
  - DMSO
  - 
    $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$
    (acetone)

For eg.



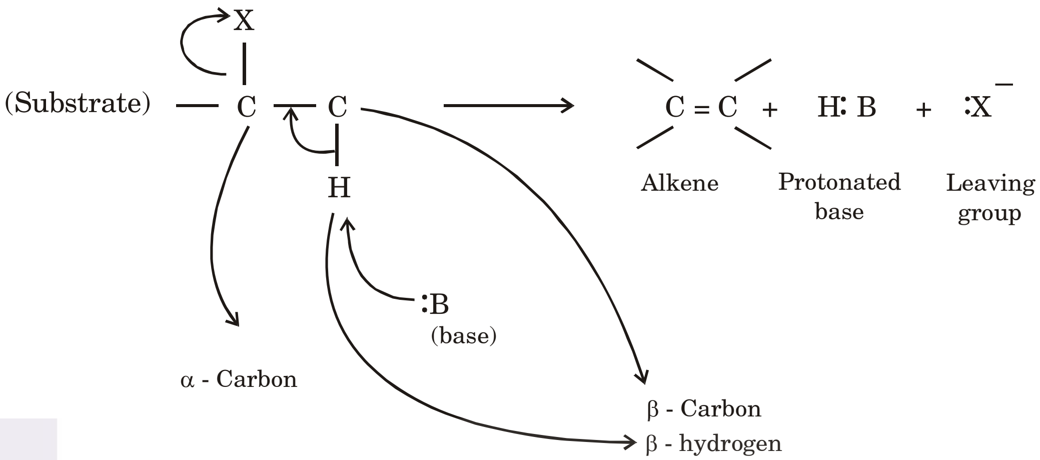
aq medium present, giving acidic Hydrogen for S_N1.

non polarising solvent so no posibility of S_N1

also I is a strong nucleophile favouring S_N2.

ELIMINATION/DEHYDROHALOGENATION

Also known as 1-2 elimination. This mechanism involves the elimination of the halogen atom and hydrogen atom from carbon adjacent to the one losing the halogen to form alkene.



Elimination → loss of β-hydrogen

α – carbon → where halogen is attached

β – carbon → carbon adjacent to α-carbon

β – hydrogen → hydrogen attached to β-carbon

Note : Reaction is brought about by action of base only.

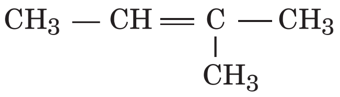
Before we go into details of 2 mechanisms governing eliminations i.e. E_1, & E_2, first do a rule known as 'SAYTZEFF RULE' for alkenes.

Saytzeff Rule

It says that in alkenes, the alkene with greater number of alkyl groups attached to the doubly bonded carbon atom is more stable and hence will be major product for example.

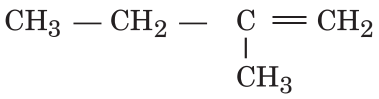
$CH_3 — CH = CH — CH_3$
(major), more stable

$CH_3 — CH_2 — CH = CH_2$
(minor)



$$CH_3 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3$$

major, more stable



$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$$

(minor)

Ease of formation of alkenes

$$R_2C = CR_2 > R_2C = CHR > RCH = CHR > R_2CH = CH_2 > RCH = CH_2 > CH_2 = CH_2$$

In dehydrohalogenation, the more stable the alkene the faster it is formed.

Elimination Mechanism

Elimination can follow two mechanisms

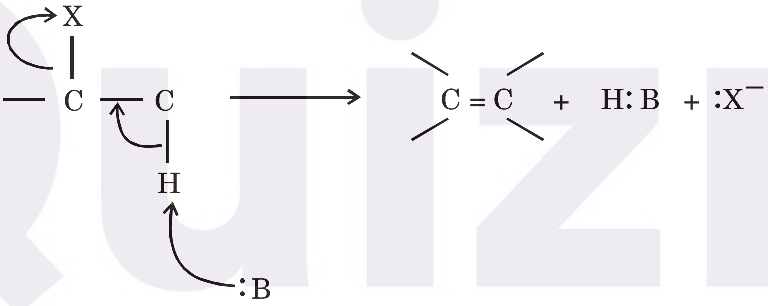
- E1 mechanism
- E2 mechanism

Let us do them in detail separately.

E2 Mechanism

As the name suggest, E2 follows second order kinetics. This means that the rate is dependent upon the concentration of 2 substances :

1. Alkyl Hallide
2. Base

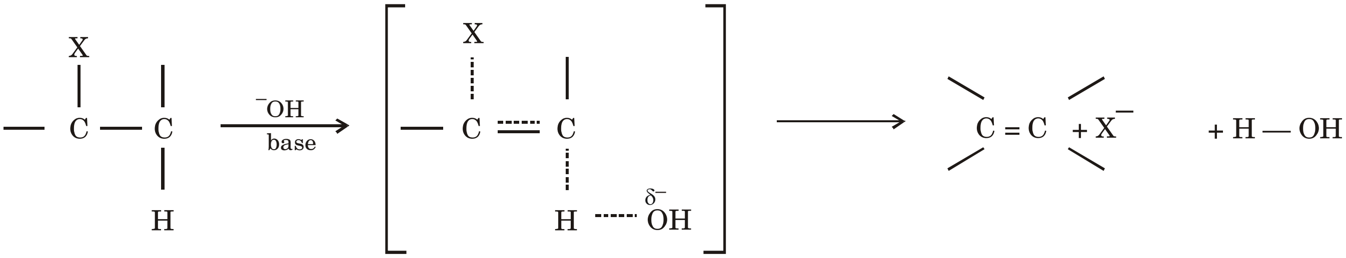


rate = k [RX] [: B]

Hence is it also known as Bimolecular elimination.

How it occurs ?

E2 like S_N2 is a single step reaction.



T.S. (Transition State)

Bonds to hydrogen and the leaving groups are partly broken bond. Double bond is partly formed in transition state. All these things are taking place simultaneously.

Factors that stabilize the alkene, also stabalizes the transition state as it is already partly alkene.

There are 2 factors that we look while talking about the stability of alkenes.

1. Saytzeff rule
2. Hoffman rule

We have already discussed Saytzeff rule, & we will discuss Hoffman rule a bit later (Hoffman rule is opposite of Saytzeff Rule)

Since the transition state depends upon the stability of alkene, hence substituted alkenes are more stable and hence the order of dehydrohalogenation becomes

3 > 2 > 1

E1 Mechanism

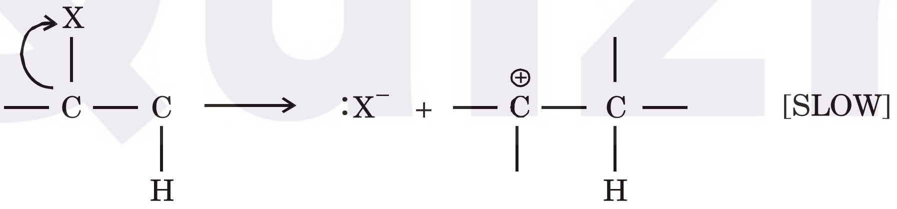
As the name suggest it is first order kinetics and analogous to S_N1.

here bond breaking & bond formation are same as in E2, however it happens in two steps rather than just one step as in E1.

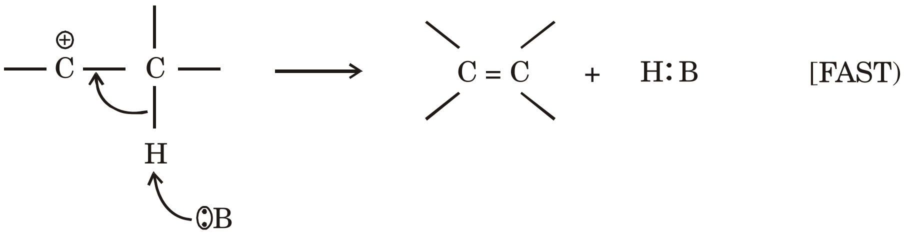
E1

(Unimolecular elimination)

Step 1 :



Step 2 :



Here step 1 is identical to as in S_N^1, where the formation of carbocation takes place

& in step 2, carbocation reacts with base to yield elimination product, whereas in S_N^1 carbocation reacted with nucleophile to yield substituted product.

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Here again the first step is the rate determining step.

∴ $r = \text{rate} = k\,[RX]$

i.e. rate is dependent only on the concentration of substrate and independent of base concentration.

You can see that there are so many similarities between E1 & S_N^1 mechanisms

Carbocations formed

- **may combine with nucleophile, to show S_N^1 mechanism**
- **rearrange to a more stable carbocation**
- **eliminate a proton to form an alkene Thus showing E1 mechanism**

∴ Wherever E1 can occur there will be a possibility of S_N^1 also. We will discuss how to eliminate this confusion later.

Reactivity in E1 : $3 > 2 > 1$

because you have to check for stabality of carbocation in E1.

Orientation in E1 : Again here saytzeff rule comes into play. Later on we will also see how Hoffman rule affects the orientation.

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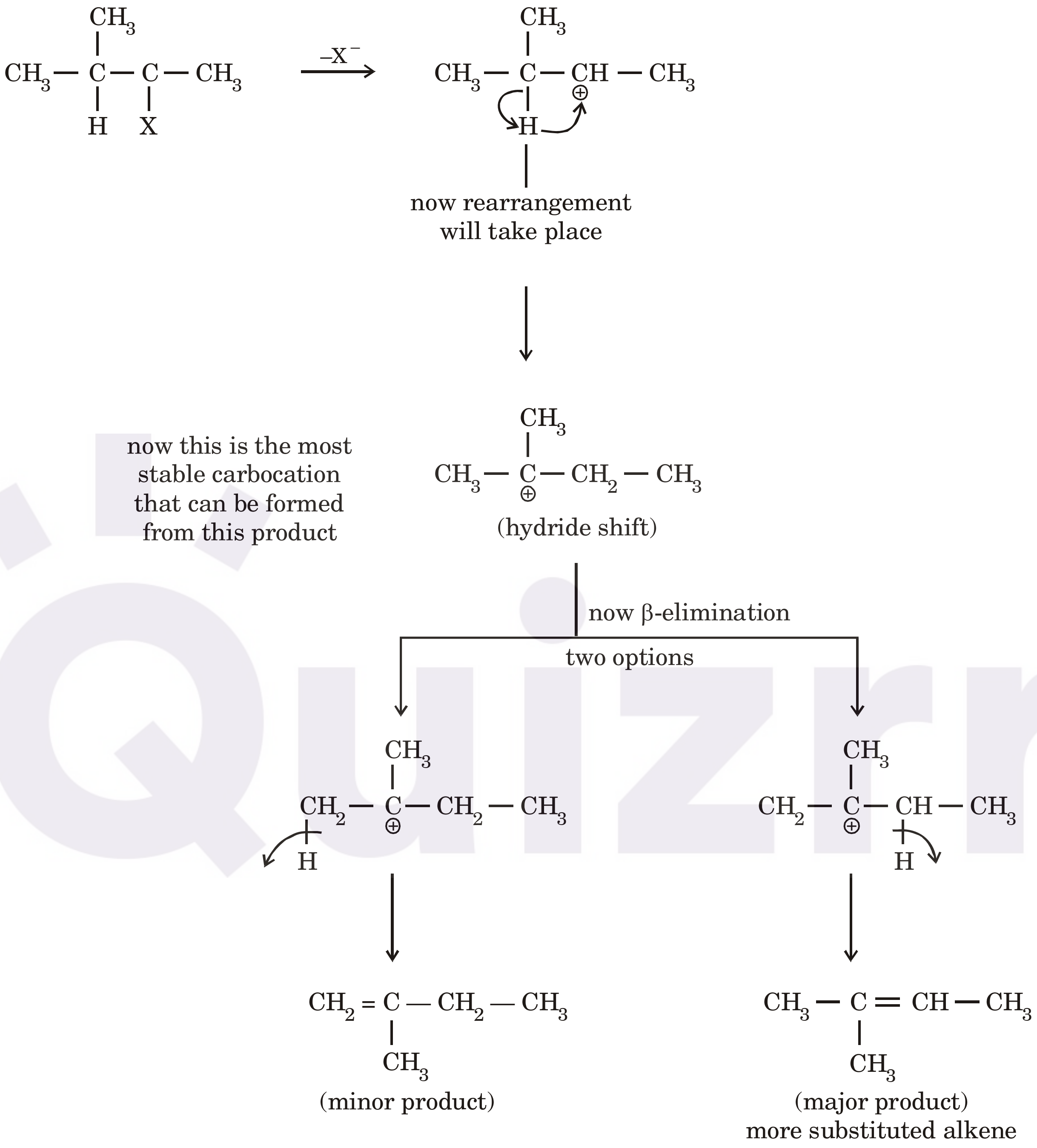
Let us take an example to understand the mechanism.



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{X}{C}-CH_3 \xrightarrow{-X^-} CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H-CH_3$$

now rearrangement will take place

$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3$$

(hydride shift)

now this is the most stable carbocation that can be formed from this product

now β-elimination

two options

$$\underset{H}{CH_2}-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-CH_3 \qquad CH_2-\underset{\oplus}{\overset{CH_3}{C}}-\underset{H}{CH}-CH_3$$

$$CH_2=\underset{CH_3}{C}-CH_2-CH_3 \qquad CH_3-\underset{CH_3}{C}=CH-CH_3$$

(minor product)

(major product)
more substituted alkene

Quizrr

E2 vs E1

How to figure out which elimination mechanism is favourable when the order of both mechanisms is

3 > 2 > 1

- The stronger the base, the more E2 is favoured over E1.

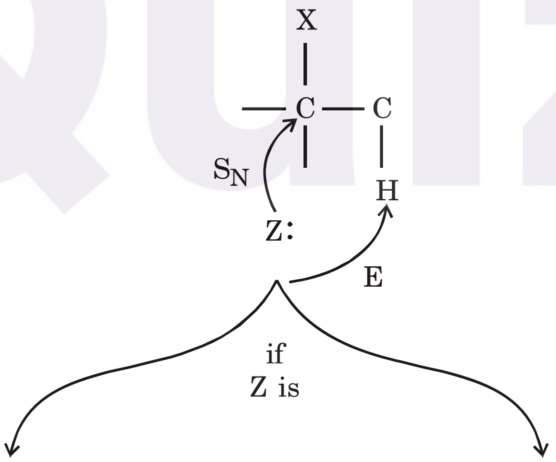
  Why

  → Because E1 mechanism is independent of base and E2 mechanism depends on the concentration of base.
- Polar medium favours E1, whereas Non polar medium favours E2 This is analogous to S_N^1 and S_N^2. Though this effect is not that affective
- Bulky base favours E2.

  {TIP : alc. KOH is classical reagent for elimination}
- E1 mechanism is encountered only with secondary and tertiary substractes or where base is of low concentration or weak or where base is the solvent i.e. <u>SOLVOLYSIS</u>

ELIMINATION VS. SUBSTITUTION

This is the most common confusion point among the students. We will try and help you to the best possible extent ☺

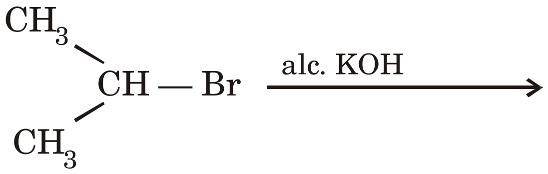


Nucleophile	Base
↓	↓
Substitution	Elimination
↓	↓
Favourable conditions	favourable conditions
→ better nucleophiles, weak base	→ good base
→ lower temperature	→ Higher temperature
→ More polar solvent	→ Less polar solvent

Illustration

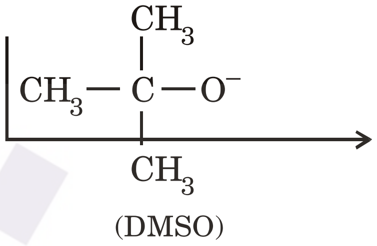
Dehydrohalogenation of isopropyl bromide, which takes hours with alc. KOH, is brought about in less than a minute at room temperature by t **–** $\mathbf{BuO^-K^+}$ **in DMSO. Suggest a possible explanation.**

Solution :



$(CH_3)_2CH-Br \xrightarrow{\text{alc. KOH}}$

weakly polar reagent suggesting elimination



$\xrightarrow[\text{(DMSO)}]{(CH_3)_3C-O^-}$

A very strong base and presence of polar Aprotic solvent i.e. ideal condition for elimination hence a very fast reaction.

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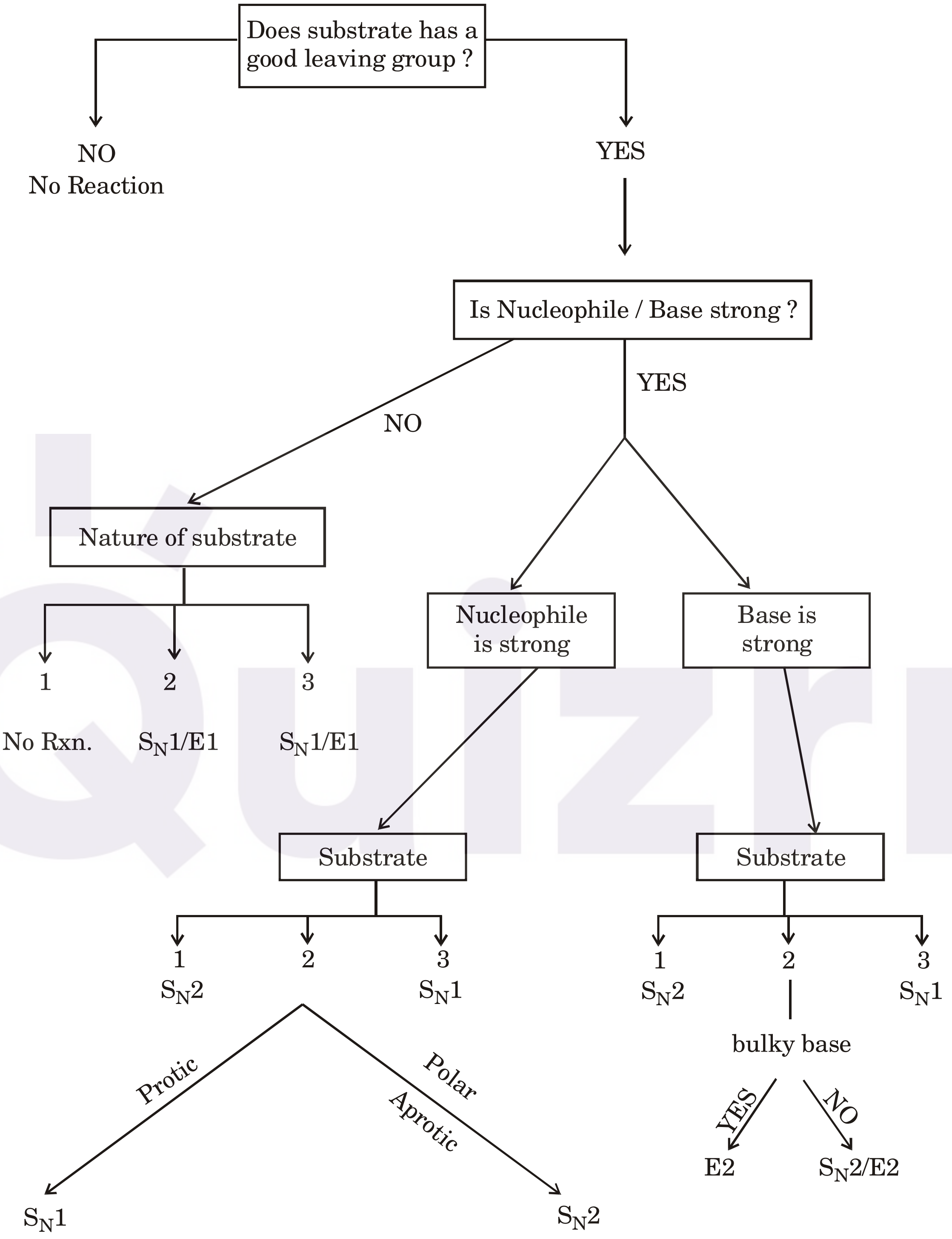
The following chart says everything about elimination vs substitution.



Quizrr

TIP : In 3 Alkyl, generally elimination is the major product over substitution.

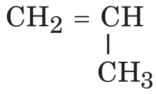
Taking some examples to understand the concept

1. $CH_3CH_2Br \xrightarrow{EtO^-}$ 90% S_N2 (major) + 10% E2 (minor)

CH_3CH_2OEt $\qquad$ $CH_2 = CH_2$

{as EtO^- is a good base and nucleophile}

2. $(CH_3)_2CHBr \xrightarrow{EtO^-}$ 79% E2 (major) + 21% S_N2 (minor)



$CH_2 = \underset{\displaystyle CH_3}{\underset{|}{CH}}$ $\qquad$ $(CH_3)_2CHOEt$

{ a little hindered 'C' atom, elimination preferrable}

3. $(CH_3)_3 - C - Br \xrightarrow[25]{EtO^-}$ 90% E2 + 10% SN1

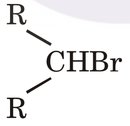
{good base + 3 RX → favour E2}

$\xrightarrow{55 \; - 66 \; C}$ 100%. (E1 + E2)

{high temperature favours elimination}

Here no point of $S_N{}^2$ as α-Carbon is sterically hindered.

4.



$\xrightarrow{CH_3COO^-}$ S_N2

a weak base, aprotic polar solvent, hence S_N2

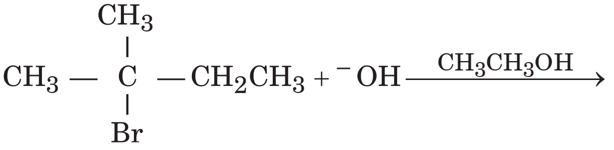
$\xrightarrow{CH_3COOH}$ S_N1

Protic polar solvent.

5. $CH_3CH_2CH_2 - Cl + CH_3O^- \xrightarrow[CH_3OH]{}$ CH_3O^- is a strong base and nucleophile

So possibilities of S_N2 & E2, but S_N2 is major product, $CH_3CH_2CH_2OCH_3$

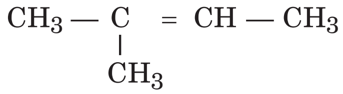
Quizrr

6. 

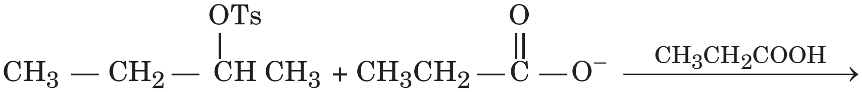
$$CH_3-\underset{Br}{\overset{CH_3}{C}}-CH_2CH_3 + {}^{-}OH \xrightarrow{CH_3CH_3OH}$$ –OH is a strong base

- a 3 RX, hence possibilities of S_N2 / E2.
- Hindered carbon for S_N2

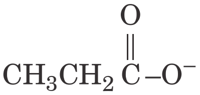
  ⇒ E2 favoured

∴ 

$$CH_3-\underset{CH_3}{C}=CH-CH_3$$

7. 

$$CH_3-CH_2-\overset{OTs}{CH}\,CH_3 + CH_3CH_2-\overset{O}{\overset{\|}{C}}-O^- \xrightarrow{CH_3CH_2COOH}$$

here  $CH_3CH_2\overset{O}{\overset{\|}{C}}-O^-$ is a weak base

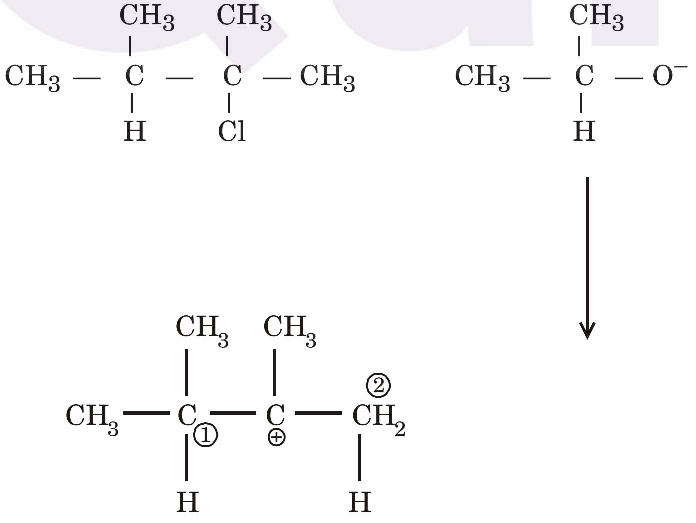
---

What happens when the base is bulky or the substrate is sterically hindered ?

Let us take the case when substrate is sterically hindered

In these cases **"HOFFMAN RULE"** is followed, which is anti-saytzeff rule. i.e. less substituted alkene is the main product.

Take for example



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{Cl}{\overset{CH_3}{C}}-CH_3 \qquad CH_3-\underset{H}{\overset{CH_3}{C}}-O^-$$

$$CH_3-\underset{H}{\overset{CH_3}{C}}_{①}-\overset{CH_3}{\underset{\oplus}{C}}-\underset{H}{\overset{②}{CH_2}}$$

since the base is bulky there is scope for a SN attack and also the substrate is little bulky so complete NO to S_N.

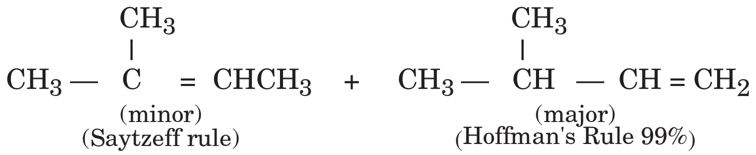
Only elimination, but since base is strong E_2 will be major product.

Now there are 2 positions to attack, i.e. 2 β-hydrogens at position (1) & (2).

According to Saytzeff Rule β-hydrogen at position (1) should be eliminated.

But is is not so, elimination of β-hydrogen at position 2 takes place i.e. Hoffman's Elimination But WHY ?

Position (1) is sterically hindered for such a big base, where β-hydrogen at position 2 is free. Alkyl groups at position (1) makes the attack difficult. Hence elimination occurs at position (2).

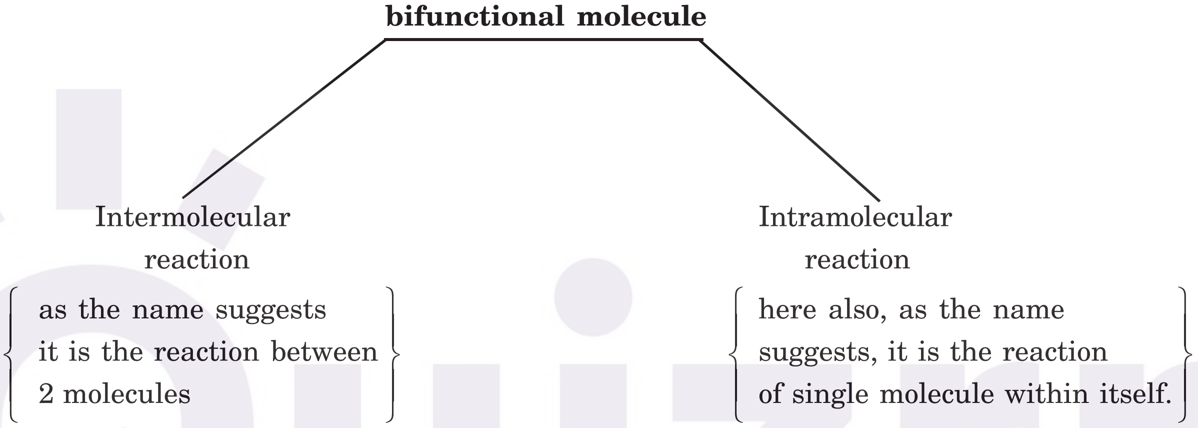


$$CH_3-\overset{\overset{CH_3}{|}}{C}=CHCH_3 + CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2$$

(minor) (Saytzeff rule) (major) (Hoffman's Rule 99%)

INTERMOLECULAR AND INTRAMOLECULAR REACTIONS :

When a molecule has 2 functional group, also known as bifunctional molecule, two kind of reactions are possible.



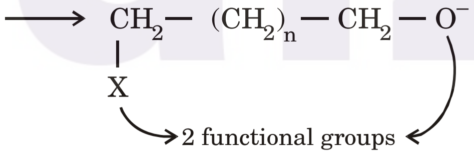
as the name suggests it is the reaction between 2 molecules

here also, as the name suggests, it is the reaction of single molecule within itself.

Quizrr

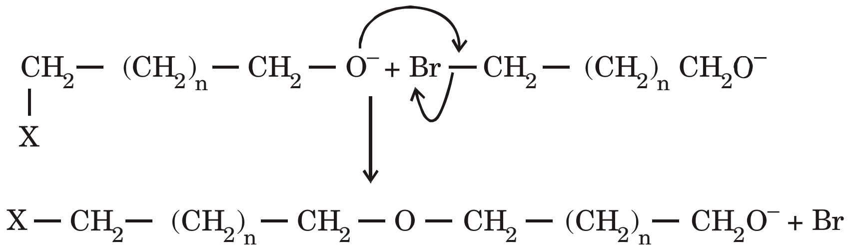
Let us take an example to understand these 2 mechanisms.

Bifunctional molecule →



$$\underset{\underset{X}{|}}{CH_2}-(CH_2)_n-CH_2-O^-$$

Intermolecular reaction :



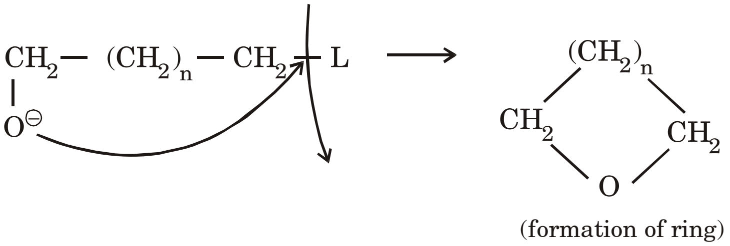
$$\underset{\underset{X}{|}}{CH_2}-(CH_2)_n-CH_2-O^- + Br-CH_2-(CH_2)_n\,CH_2O^-$$

$$\downarrow$$

$$X-CH_2-(CH_2)_n-CH_2-O-CH_2-(CH_2)_n-CH_2O^- + Br$$

Here molecules of the same compound combine together to give inter molecular reaction.

Intramolecular Reaction :



(formation of ring)

Inter vs Intra-molecular reactions :

- Intra molecular reactions are prefered when Rings formed are stable
- 5-6 member rings are stable and hence favour intra mechanism.
- EXCEPTION : 3 membered rings are also stable and hence show intra mechanism.

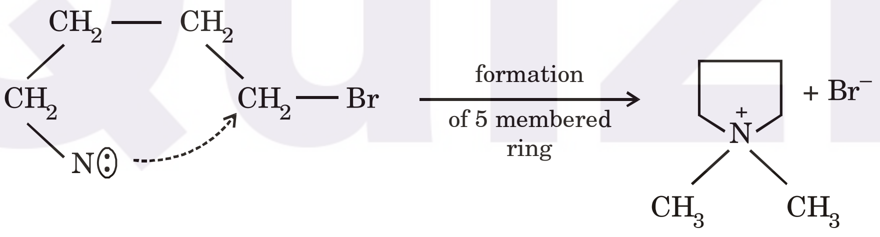
For intermolecular

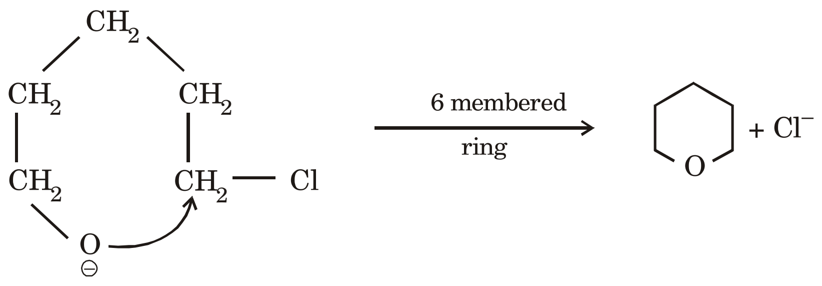
⇒ If ring formation occurs in the form of 4 membered ring or greater than 6 membered rings, then ring formation is discarded & inter molecular reaction takes place.

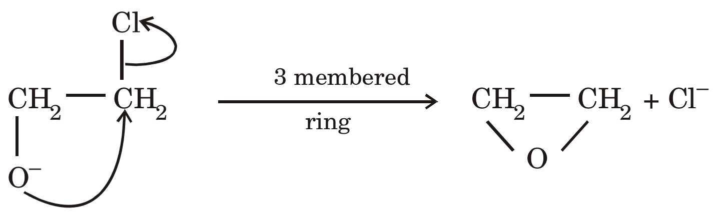
Note :

6 membered ring is more stable than 5 or 3 membered ring. So given the option 6 membered ring will be the major product in reaction.

Some examples of intramolecular reactions







AMBIDENT NUCLEOPHILES

Some nucleophiles have lone pair of electrons on more than one atom and can attack through more than one site. Such nucleophiles are called ambident nucleophiles. In such cases, different products are possible due to attack through different sites. Attack by a specific site can be promoted under special conditions. Two well-known examples are discussed in detail.

Attack by CN– nucleophile (: $^{-}C \equiv N$:)

$$R - N \xrightarrow{CN^-} \underset{\text{nitriles}}{R-CN} + \underset{\text{isonitriles}}{R-NC} + X^-$$

In CN⁻, carbon (negatively charged) will be a soft base as compared to nitrogen. So, if the reaction proceeds via S_N1 mechanism, which produces a free carbocation (a hard acid), then attack through nitrogen (hard base) will take place. But if the reaction proceeds via S_N2 mechanism (small positively charged carbon is soft acid) then attack through carbon (soft base) will take place. So, if we want to increase relative yield of nitriles, we can use NaCN or KCN etc. in a less polar solvent, which facilitates S_N2 substitution. Similarly, if we want to increase the yield of isonitriles, we can use AgCN. Ag^+ has very strong affinity for X^-, so it favours the formation of R^+ and the reaction proceeds via S_N1 mechanism. This will result in attack by hard base given R–NC. Further if we compare primary, secondary and tertiary alkyl halides, formation of R–NC should be favoured due to more favourable S_N1 substituion in tertiary alkyl halide. But the exception is that tertiary alkyl halides undergo elimination and the yield decreases. This is because CN^- is a strong base, which can also cause elimination reaction.

Attack by NO_2^- nucleophile ($^{-}O–N = O$)

$$R - X \xrightarrow{NO_2^-} \underset{\text{alkane nitrite}}{R-O-N=O} + \underset{\text{nitro alkane}}{R-NO_2} + X^-$$

In NO_2^-, oxygen (negatively charged) will be a hard base as compared to nitrogen. So, if the reaction proceeds via S_N1 mechanism, then attack through oxygen (hard base) will take place to produce alkane nitrite. But if the reaction takes place via S_N2 mechanism then attack through nitrogen (soft base) takes place to give nitro alkane.

If we want to increase the yield of nitro alkane, the reaction should proceed via S_N2 mechanism, i.e. we can use $NaNO_2$, KNO_2 etc. Moreover, the yield will be best if we use primary alkyl halide and less polar solvent. Formation of nitrite will dominate, if we use tertiary alkyl halide, more polar solvent and $AgNO_2$ because Ag^+ has strong affinity for X^- and can form a carbocation to force the reaction to proceed via S_N1 mechanism. Primary alkyl halide with $AgNO_2$ chiefly gives nitro alkane but if secondary and tertiary alkyl halides are used then $AgNO_2$ will yield nitrite as the major product.

Quizrr

Example 15

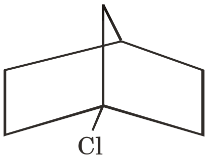
Provide the products of the reactions of the following substrates with $NaNO_2$ in EtOH : (i) n–BuCl and (ii) $ClCH_2OCH_2CH_3$.

Solution :

(i) n-Bu-NO_2 and (ii) $ONO–CH_2OCH_2CH_3$ + $EtO–CH_2OCH_2CH_3$.

The less the positive charge on the attacked carbon, the more likely it will bond to the less electronegative nucleophilic site of the ambident ion (N). This happens in the S_N2 reaction in (i), where a C–N bond forms. The greater the positive charge on the attacked carbon, the more likely it will bond to the more electronegative nucleophilic site of the ambident ion (O). This happens in the S_N1 reaction in (ii), where a C–O bond forms. Since the R^+ in (ii) is so stable, it has a long enough half-life to react with any added nucleophile as well as nucleophillic solvent.

Example 16

For the given compound  **, the nucleophilic substitution does not occur regardless of the conditions under which the reaction is run explain.**

Solution :

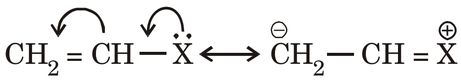
In the given compound, S_N2 reaction does not occur due to impossibility of attack of nucleophile from rear side while SN1 reaction is also not possible because the carbocation formed after ionization is not stable as the bridge head carbon having one carbon bridge cannot be sp^2 hybridized.

Example 17

What kind of substitution does vinyl halides undergo ?

Solution :

In general, vinyl halides are inert towards displacement reactions. This is because of resonance in vinyl halides,



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

Now, during S_N1 reaction, they ionize to give vinyl cations, which are very unstable because the carbon bearing positive charge is sp hybridized. More the S-character in carbocation, the less stable it would be.

During S_N2 attack, backside attack of nucleophile is difficult because it would approach in the plane of molecule where it would be repelled by p electron density. Thus, vinyl haldies have little or no tendency to undergo S_N1 and S_N2.

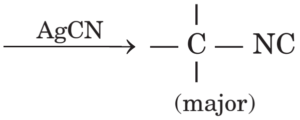
Quizrr

Important Concept

Behaviour of Silver Ion

- Silver ion has got high affinity for halides
- Due to this affinity, Ag+ reacts with alkyl halides through S_N1 mechanism {They have an eagerness, carbocation is formed}

1 alkyl halide
2 alkyl halide
3 alkyl halide



$$\left.\begin{matrix}1 \text{ alkyl halide}\\ 2 \text{ alkyl halide}\\ 3 \text{ alkyl halide}\end{matrix}\right\} \xrightarrow{AgCN} -\overset{|}{\underset{|}{C}}-NC$$

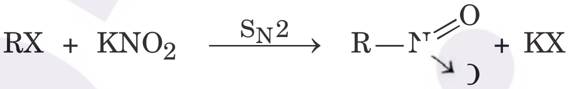
(major)

But with KCN

$$R-X + KCN \longrightarrow R-CN + KX$$

Similarly

$$RX + AgNO_2 \xrightarrow{S_N1} RONO + AgX$$



$$RX + KNO_2 \xrightarrow{S_N2} R-N(=O)\rightarrow O + KX$$

Reactions of Alkyl Halide

Wurtz reaction

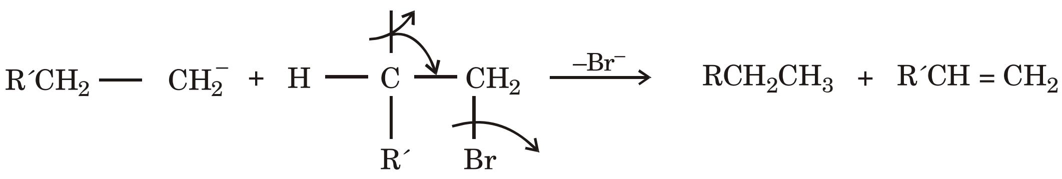
It is a coupling reaction whereby two alkyl halides are reacted with sodium to form a new carbon-carbon bond :

$$2R-X + 2Na \longrightarrow R-R + 2Na^+X^-$$

The related reaction dealing with aryl halides is called the Wurtz-Fitting reaction.

Limitations

The Wurtz reaction is limited to the synthesis of symmetric alkanes. If two dissimilar alkyl halides are taken as reactants, then the product is a mixture of alkanes that is, often, difficult to separate. Since the reaction involves free radical species, a side reaction also occurs to produce an alkene. This side-reaction becomes more significant when the alkyl halides are bulky at the halogen-attached carbon. This is because the activation energy required for the S_N2 reaction in the second step becomes significantly high, so the alternate elimination mechanism is favored.



Mechanism

This reaction involves the radical species R•.

One electron from sodium is transferred to the halogen to produce a sodium halide and an alkyl radical.

$$R-X + Na \longrightarrow R\bullet + Na^+X^-$$

The alkyl radical then accepts an electron from another sodium atom to form an alkyl anion and the sodium becomes cationic.

$$R\bullet + Na \longrightarrow R^-Na^+$$

The alkyl anion then displaces the halide in an S_N2 reaction, forming a new carbon-carbon covalent bond.

$$R-Na^+ + R-X \longrightarrow R-R + Na^+X^-$$

Example 16

$$\underset{\text{Methyl Iodide}}{\mathbf{2CH_3I}} + \underset{\text{Sodium}}{\mathbf{2Na}} \xrightarrow[\text{ether}]{\text{anhydrous}} \underset{\text{ethane}}{\mathbf{CH_3CH_3}} + \mathbf{2NaI}$$

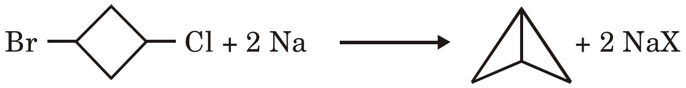
$$\mathbf{2CH_3CH_2Cl} + \underset{\text{Sodium}}{\mathbf{2Na}} \xrightarrow[\text{ether}]{\text{anhydrous}} \underset{\text{n-butane}}{\mathbf{CH_3CH_2CH_2CH_3}} + \underset{\text{Sodium Chloride}}{\mathbf{2NaCl}}$$

Solution :

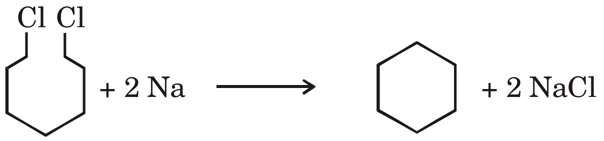
Here methyl iodide and ethyl chloride are reacted with powdered sodium metal in anhydrous ether. Alkanes containing double the number of carbon atoms are formed, i.e. methyl iodide give ethane, and ethyl chloride gives n-butane.

The Wurtz Coupling is one of the oldest organic reactions, and produces the simple dimer derived from two equivalents of alkyl halide. The intramolecular version of the reaction has also found application in the preparation of strained ring compounds :

(1)



(2)



Quizrr

CHEMISTRY OF GRIGNARD REAGENT

Victor Grignard discovered that a dry alkyl halide will react with dry magnesium metal in a dry ether solvent to produce an organometallic compound which behaves as if it has the structure R-Mg-X It is now called an alkylmagnesium halide or Grignard reagent :

$$R - X + Mg \xrightarrow{\text{dry ether}} R - Mg - X$$

R = alkyl (all types) or vinyl or alkynyl or aryl X = I, Br, Cl

Grignard Reagent can act both as a base and as a nucleophile. It happens due to the polar nature of grignard reagent

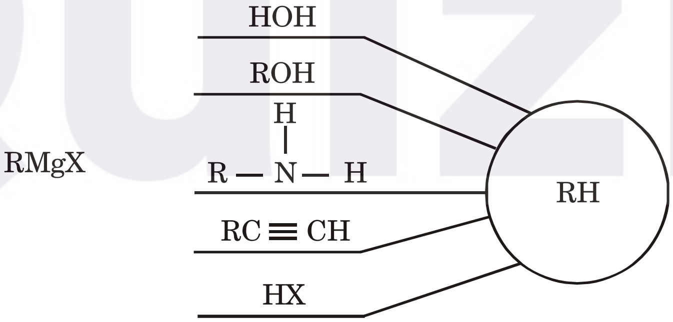
$$R^{\delta-} - Mg^{\delta+} X$$

Also in the preparation of grignard reagent, the reactivity of halides is as follows

$$I > Br > Cl > F \quad \text{(though F is very less reactive)}$$

Grignard Reagent as Base

As a base it will try to abstract hydrogen from other compounds like H_2O, alcohols, amines terminal alkynes etc. to form alkanes

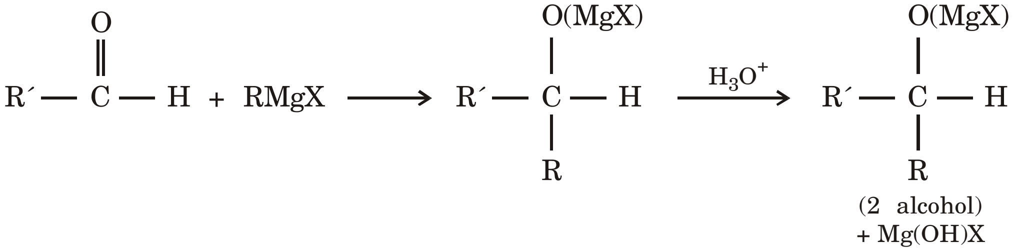


Gridnard Reagent as Nucleophile

As a nucleophile it will attack electrophiles. Let us take its reaction with compounds like aldehydes & ketones, esters, acid halides etc to understand it. Also we take into consideration that which reaction is step up (i.e increase in no. of carbon) or step down (i.e. decrease in no. of carbon)

1. With aldehydes :

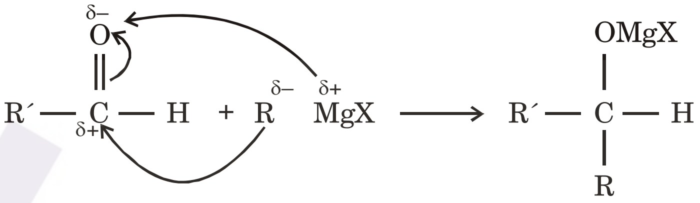
With aldehydes. RMgX gives alcohols and its a **Step up** reaction



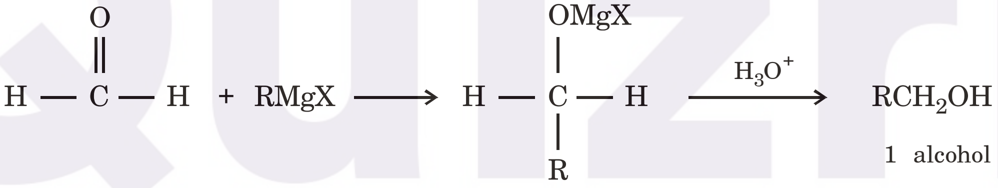
$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-H + RMgX \longrightarrow R'-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O(MgX)}{|}}{C}}-H \xrightarrow{H_3O^+} R'-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle O(MgX)}{|}}{C}}-H$$

(2 alcohol)
+ Mg(OH)X

me chanism is simple



1 alcohol are only given by formaldehyde



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-H + RMgX \longrightarrow H-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-H \xrightarrow{H_3O^+} RCH_2OH$$

1 alcohol

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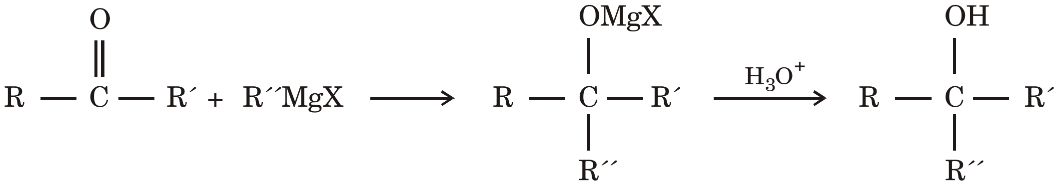
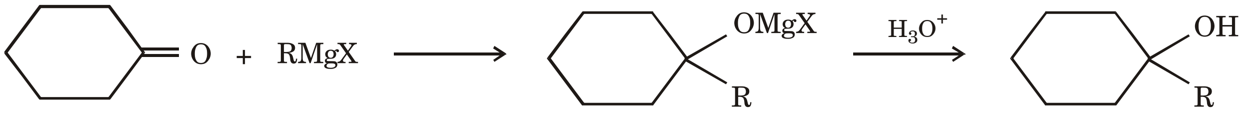
2. With Ketones

We have 1 & 2 alcohol as product from aldehydes, so for 3 alcohols Ketones are used. Ketones on reaction with grignard reagent gives 3 alcohol.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' + R''MgX \longrightarrow R-\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle OMgX}{|}}{C}}-R' \xrightarrow{H_3O^+} R-\underset{\underset{\displaystyle R''}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-R'$$

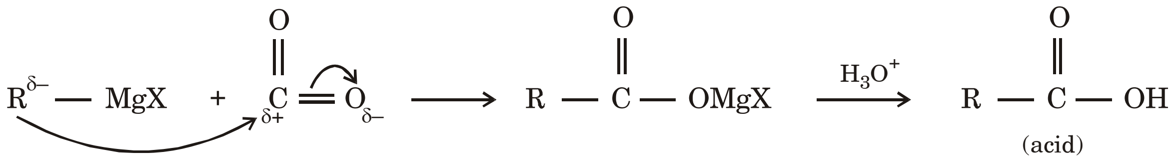


(3 alcohol)

This is also a STEP UP reaction

3. With CO_2

This is also a STEP UP reaction & used in formation of acids.



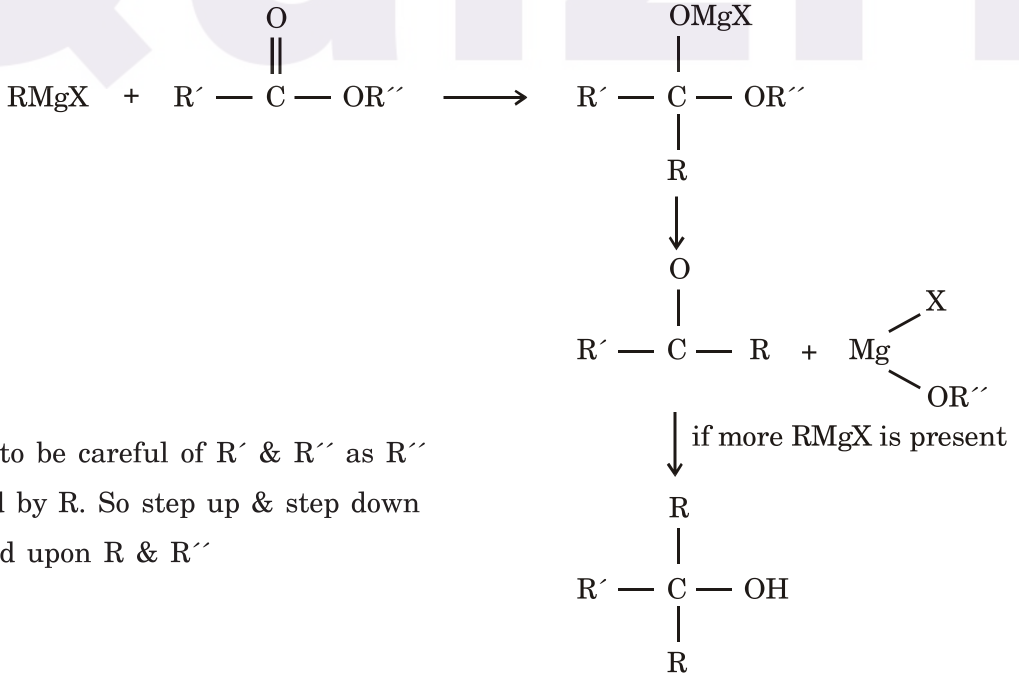
(acid)

So for

$$\begin{tikzcd} RX \arrow[r] \arrow[d, "Mg"] & RCOOH \\ RMgX \arrow[ur, "CO_2"', "H_3O^+"] & \end{tikzcd}$$

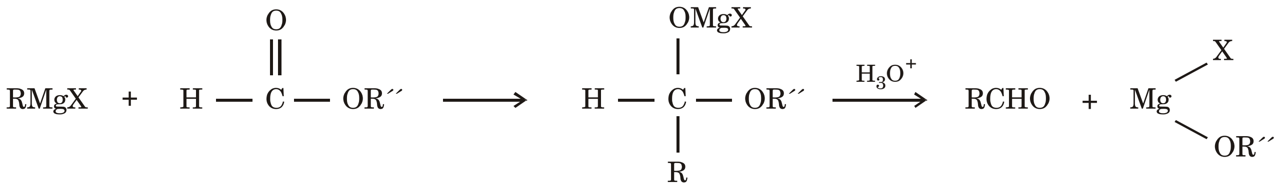
4. With esters

It leads to formation of ketones & further to 3 alcohol



You have to be careful of R´ & R´´ as R´´ is replaced by R. So step up & step down will depend upon R & R´´

For aldehydes HCOOR´ is used.



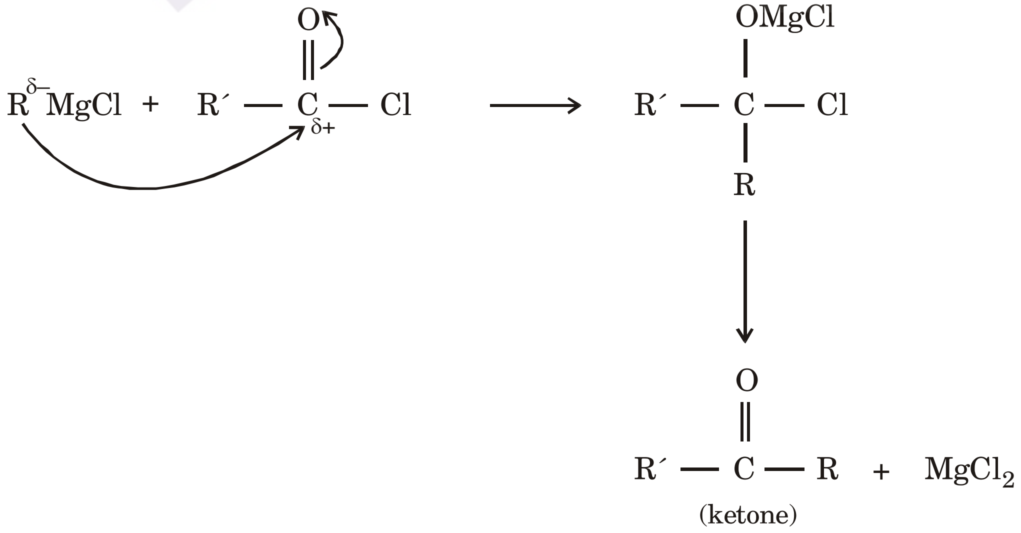
$$RMgX + H-\overset{O}{\overset{\|}{C}}-OR'' \longrightarrow H-\underset{R}{\overset{OMgX}{C}}-OR'' \xrightarrow{H_3O^+} RCHO + Mg\begin{smallmatrix}X\\ OR''\end{smallmatrix}$$

Note : OR´´ of ester does not appear in aldehyde or ketone

Example :

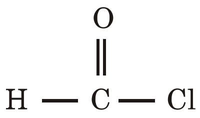
$$\begin{tikzcd}
C_2H_5X \arrow[r] \arrow[d, "Mg"] & phCOC_2H_5 \\
C_2H_5MgX \arrow[d, "CO_2"] & \\
C_2H_5COOH \arrow[r] & C_2H_5COOCH_3 \arrow[uu, "1.\ phMgBr \quad 2.\ H_3O^+"']
\end{tikzcd}$$

5. <u>With Acid Halides</u>



$$\overset{\delta-}{R}MgCl + R'-\underset{\delta+}{\overset{O}{\overset{\|}{C}}}-Cl \longrightarrow R'-\underset{R}{\overset{OMgCl}{C}}-Cl \longrightarrow \underset{(ketone)}{R'-\overset{O}{\overset{\|}{C}}-R} + MgCl_2$$

Quizrr

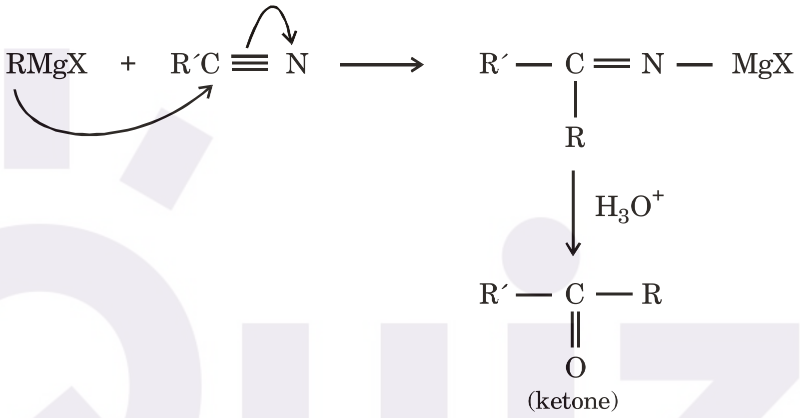
Here  $H-\overset{\overset{\large O}{\|}}{C}-Cl$ does not react as it is not a stable compound

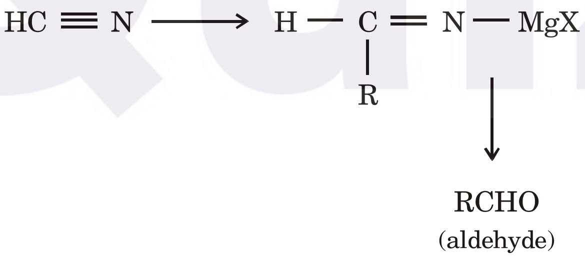
$$\therefore \text{ acid halide} \xrightarrow{RMgX} \text{Ketone} \xrightarrow{RMgX} 3^\circ \text{ alcohol}$$

Note :

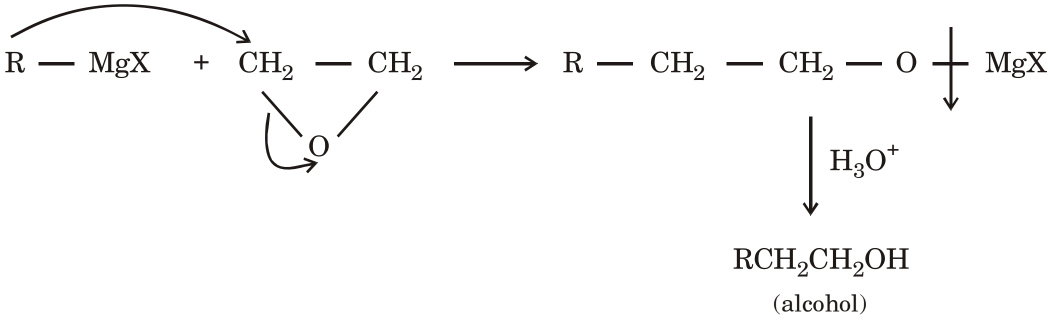
$$\left.\begin{array}{l} RMgX \ + RCONH_2 \\ \qquad\quad\ + RCOOH \end{array}\right\} \longrightarrow \text{No RXN}$$

6. With Cynides



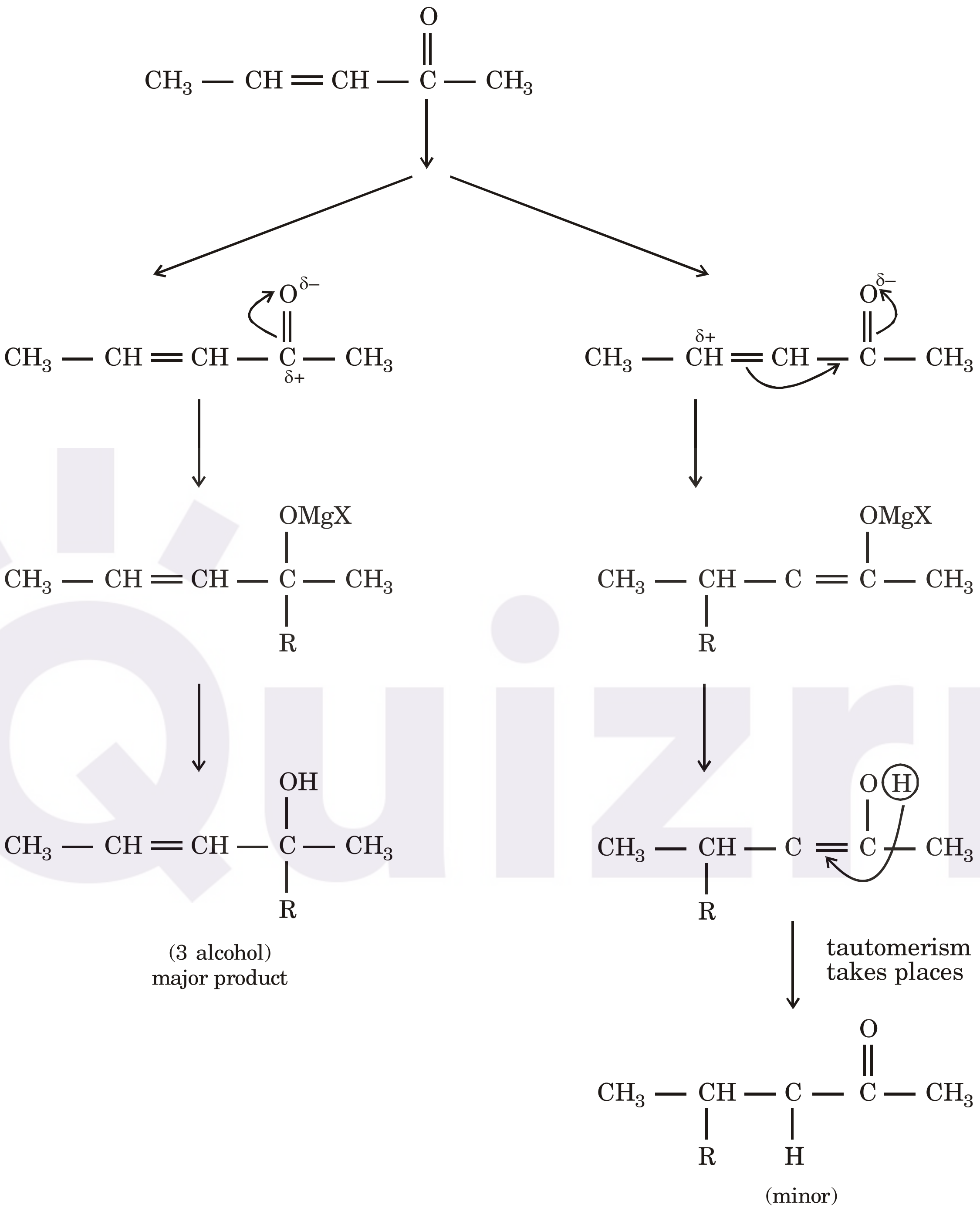
with 

7. With Oxiranes



Quizrr

Special Case

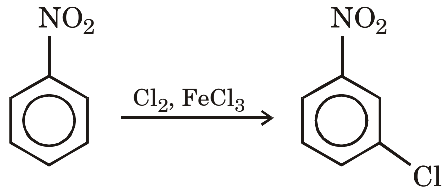


Quizrr

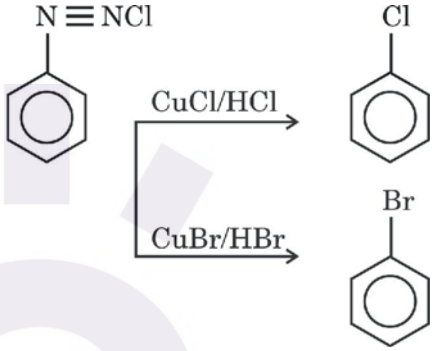
ARYL HALIDE

Preparation

(1) Halogenation of Arenes



(2) Sandmeyer's Reaction



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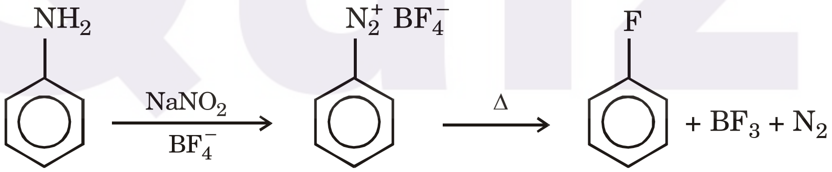
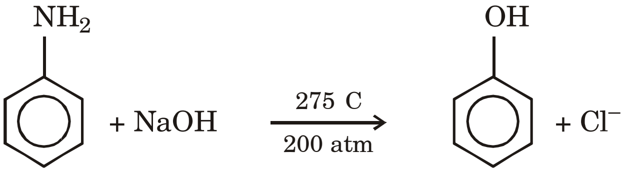
(3) Balz Schiemann Reaction



Nucleophilic Aromatic Substitution

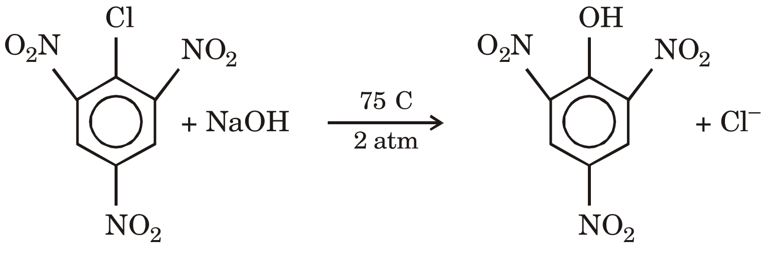
(1) S$_N$Ar mechanism

When strong electron withdrawing groups are attached at ortho and/or para position to the halogen atom, The reaction involves formation of carbanion as intermediate.

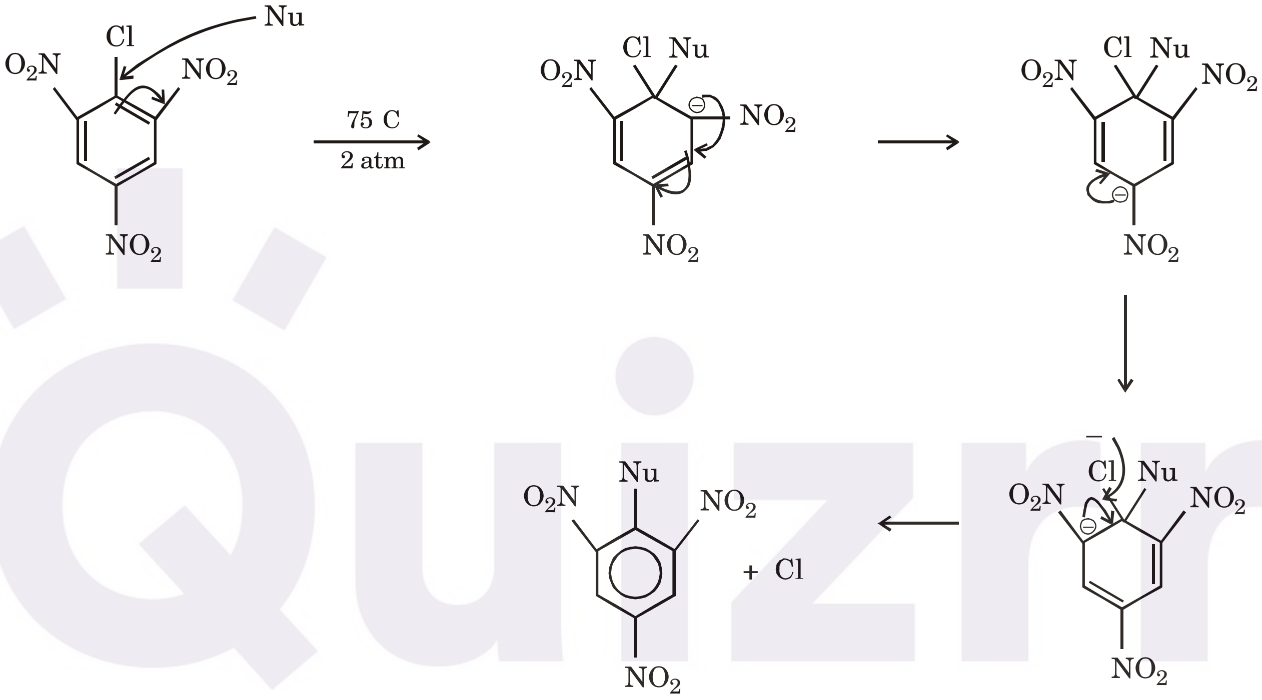


(Dows process)

Note : Drastic conditions are required for the reaction to take place.



{easily carried out} {picric acid}



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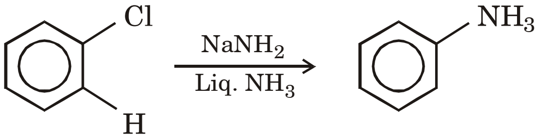
Here in the above case, the negative charge is stabilized by electron withdrawing group on the ring.

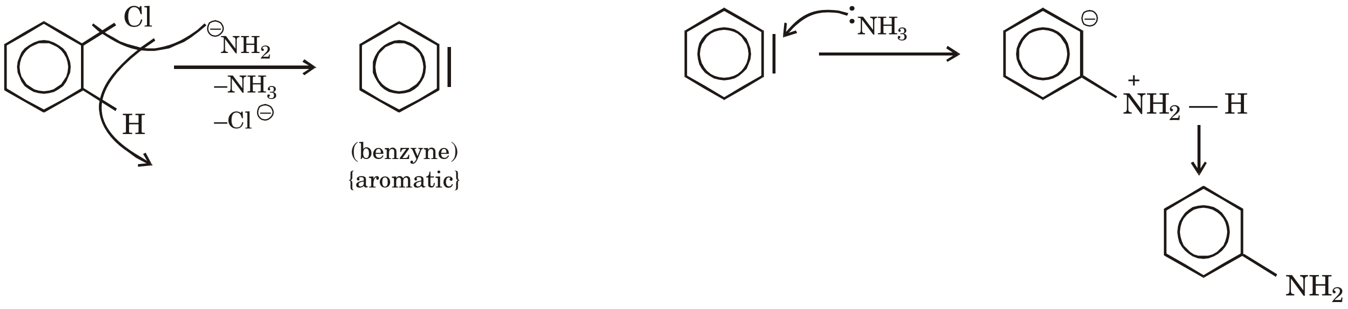
Note : If NO_2 is attached at meta position, then the carbanion again is not stabilized. Hence, again we will require drastic conditions.

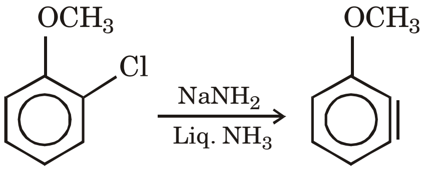
(2) Benzyne Mechanism

The rings which are not activated towards bimolecular displacement, undergo substitution by benzyne mechanism



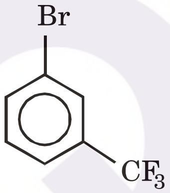
Mechanism :

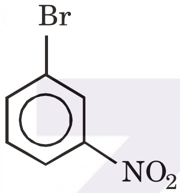


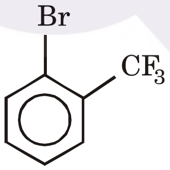


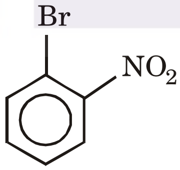
Example :

Which of the following aryl halide undergo nucleophilic substitution by benzyne mechanism ?

(a) 

(b) 

(c) 

(d) 

Solution :

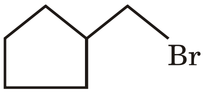
Unsubstituted aryl halide and those containing electron releasing groups or electron withdrawing groups at meta position undergo nucelophilic substitution reactions by benzyne mechanism.

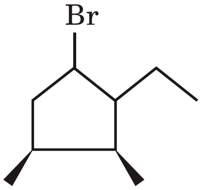
Hence only (a) contain electron withdrawing groups at meta position.

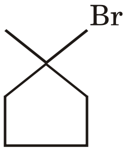
Example :

Heating many alkyl chlorides or bromides in water affects their conversion into alcohol through S_N1 reaction. Order each of the following sets of compounds with respect to solvolytic reactivity.

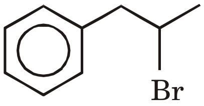
(a)

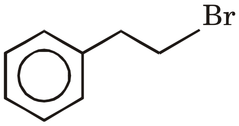

I

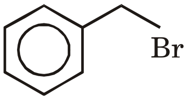

II


III

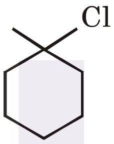
(b)

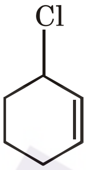

I

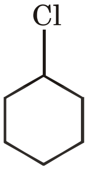

II


III

(c)


I


II


III

Quizrr

Solution :

Since they follow S_N1 mechanism, hence their reactivity will be governed by the stability of carbocation formed.

(a) I < II < III

since, III will form 3 carbocation

(b) II < I < III

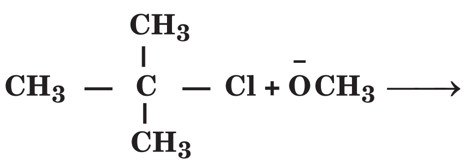
III is benzylic carbocation

(c) III < I < II

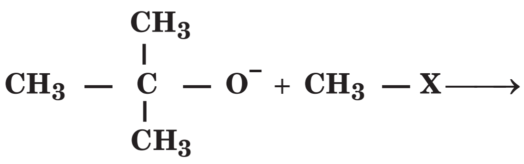
II is allylic carbocation

Example :

What are the products of the following reactions ?

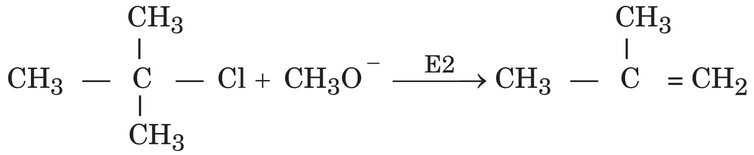
(a) 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl+\bar{O}CH_3\longrightarrow$$

(b) 

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O^-+CH_3-X\longrightarrow$$

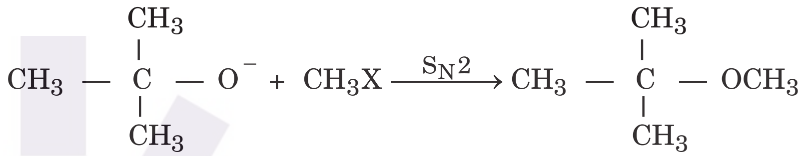
Solution :

(a) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl+CH_3O^- \xrightarrow{E2} CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$$

$^{\ominus}OCH_3$ (nucleophile) cannot attack 3 carbon, as this carbon has high-electron density. Hence nucleophilic substitution is ruled out.

Now this CH_3O^- attacks to give elimination product.

(b) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O^-+CH_3X \xrightarrow{S_N2} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OCH_3$$

Methyl halides can only undergo S_N2 mechanism. Here, $(CH_3)_3\,CO^-$ acts as a nucleophile.

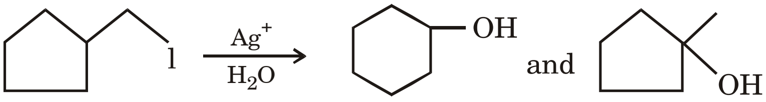
Doubt : Why would the new nucleophile replace X^- from methyl ?

Answer : Because X^- is more stable than $(CH_3)_3\,CO^-$

Quizrr

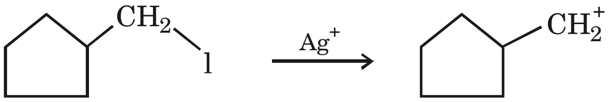
Example :

When alkyl halides are treated with aqueous $AgNO_3$, silver halide precipitates and an alcohol is formed. From what you know about the S_N1 reaction, propose a mechanism for the following conversion.



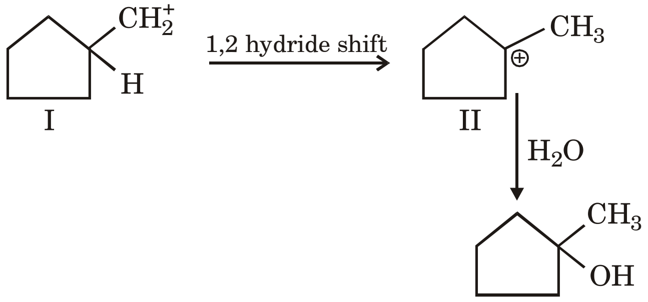
Solution :

Step I :



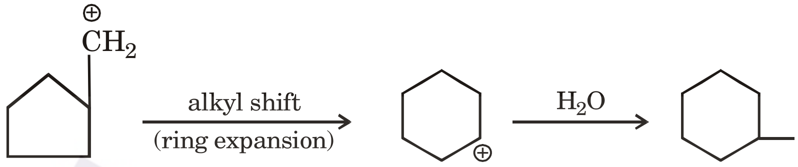
1^+ carbonium ion

Step II :



OR

Step II :

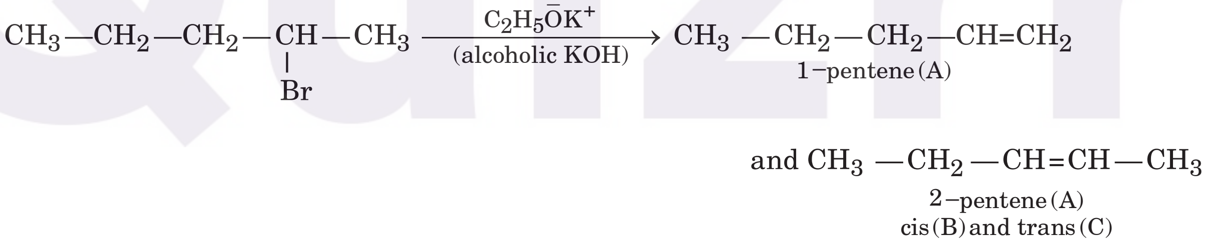


Example :

2-Bromopentane, when treated with alcoholic KOH yields a mixture of three alkenes A, B and C. Identify A, B and C. Which is predominant ?

(Assume reaction proceeds through E2 mechanism)

Solution :



$$CH_3—CH_2—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3 \xrightarrow[\text{(alcoholic KOH)}]{C_2H_5\bar{O}K^+} \underset{\text{1−pentene (A)}}{CH_3—CH_2—CH_2—CH{=}CH_2}$$

$$\text{and } \underset{\substack{\text{2−pentene (A)}\\ \text{cis (B) and trans (C)}}}{CH_3—CH_2—CH{=}CH—CH_3}$$

By Saytzeff rule, substituted alkenes are more stable, hence B or C is predominant than A. Out of cis and trans, trans is more stable. Hence C is predominant.

Example :

When CH_3—CH = CH – CH_2Cl reacts with alcoholic KCN**, a mixture of isomeric products is obtained. Explain.**

Solution :

It can undergo S_N1 and S_N2 reaction. By S_N2 reaction only one product is formed. But by S_N1 reaction, intermediate is carbonium ion.

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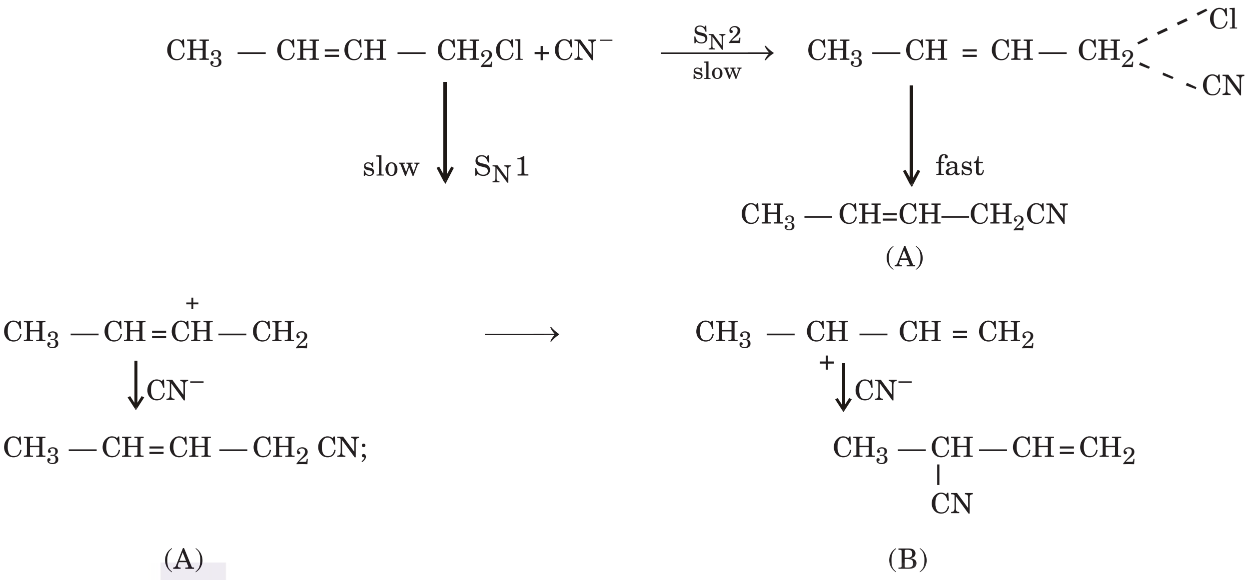

$$CH_3-CH=CH-CH_2Cl+CN^- \xrightarrow[\text{slow}]{S_N2} CH_3-CH=CH-CH_2\overset{\cdots Cl}{\underset{\cdots CN}{}} \xrightarrow{\text{fast}} \underset{(A)}{CH_3-CH=CH-CH_2CN}$$

$$CH_3-CH=CH-CH_2Cl+CN^- \xrightarrow[\text{slow}]{S_N1} CH_3-CH=\overset{+}{C}H-CH_2 \longrightarrow CH_3-\overset{+}{C}H-CH=CH_2$$

$$CH_3-CH=\overset{+}{C}H-CH_2 \xrightarrow{CN^-} \underset{(A)}{CH_3-CH=CH-CH_2CN;}$$

$$CH_3-\overset{+}{C}H-CH=CH_2 \xrightarrow{CN^-} \underset{(B)}{CH_3-\underset{CN}{\underset{|}{C}H}-CH=CH_2}$$

Thus we get two isomeric products by S_N1 reaction.

Example :

Identify A to I in the given sequence of reactions and also give the reactions involved. [Ignore geometrical isomers].

$\xrightarrow{Br_2}$ **A + B + C**
(major) (minor)

$$\text{Now, } A \xrightarrow{\text{alc KOH}} \underset{(\text{major})}{E} + \underset{(\text{minor})}{D}$$

$$B \xrightarrow{\text{alc KOH}} E$$

$$C \xrightarrow{\text{alc KOH}} D$$

$$D \xrightarrow{\text{NBS}} F \xrightarrow{\text{alc KOH}} G$$

$$E \xrightarrow{\text{NBS}} \underset{(\text{major})}{H} + \underset{(\text{minor})}{H}$$

$$H \xrightarrow{\text{alc KOH}} G$$

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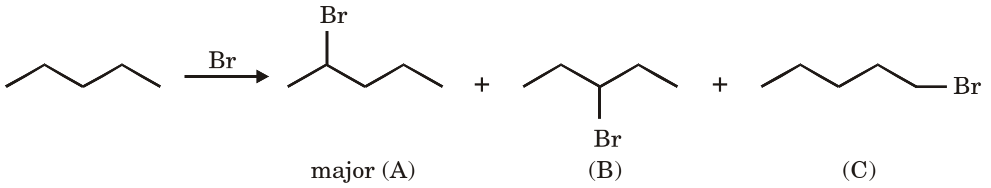
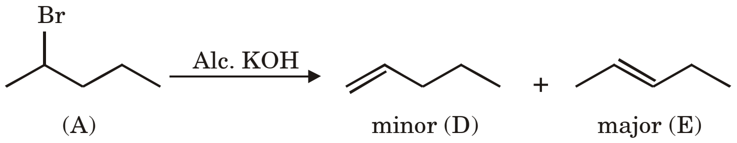
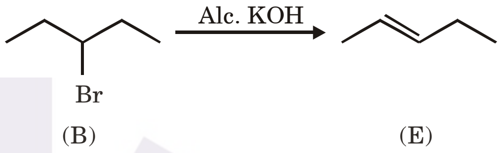
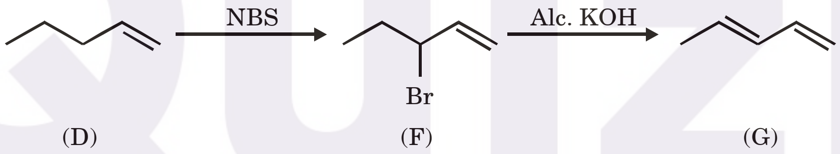
Solution :

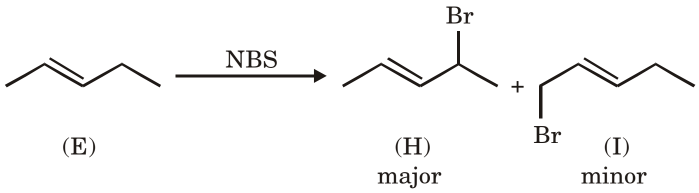


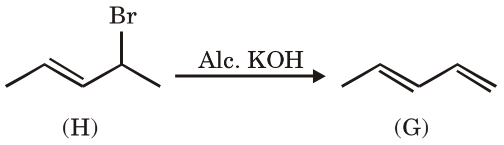
Now











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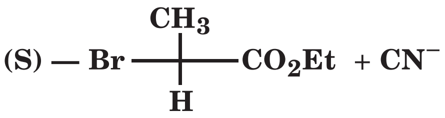
Example :

Give the products of the following displacement reactions.

(a) **(R) — $CH_3CHBrCH_2CH_3$ + MeO^-** **(b)** **(S) — $CH_3CHBrCH_2CH_3$ + EtO^-**

(c) **cis—4—iodoethylcyclohexane + OH^-** **(d)**



$$(S) - Br - \underset{H}{\overset{CH_3}{C}} - CO_2Et + CN^-$$

Solution :

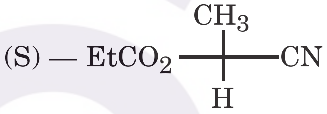
These are S_N2 reactions involving inversion of configuration. Change in configuration from (R) to (S) or (S) to (R) is observed only when the nucleophile and leaving group have same priorities. Thus, reaction (a), (b) and (c) show inversion of configuration whereas reaction (d) shows retention of configuration.

(a) (S) – CH_3CH (OMe) CH_2CH_3

(b) (R) – CH_3CH (OEt) CH_2CH_3

(c) trans – 4 – ethylcyclohexanol

(d)



$$(S) - EtCO_2 - \underset{H}{\overset{CH_3}{C}} - CN$$

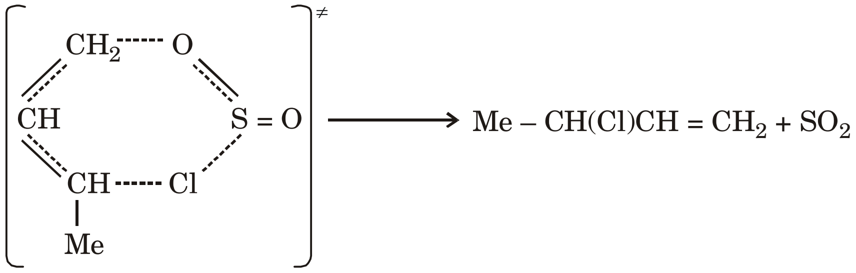
Example :

Give plausible mechanism of the following reaction.

$$\mathbf{MeCH = CHCH_2OH \xrightarrow{SOCl_2} MeCH(Cl)CH = CH_2\ (100\%)}$$

Solution :

(a) $MeCH = CHCH_2OH \xrightarrow{SOCl_2} MeCH = CHCH_2OSOCl \longrightarrow$



$\longrightarrow Me - CH(Cl)CH = CH_2 + SO_2$

Transition state

The intermediate $MeCH = CHCH_2OSOCl$ dissociates to an intimate ion pair whose $ClSO_2^-$ loses SO_2 and Cl^- attacks at C_3 with movement of pi–e's to give a double bond between C_1 and C_2.

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Example 11 :

Explain the fact that a small amount of NaI catalyzes the general reaction :

$$\mathbf{R - Cl + R'O:^- Na^+ \longrightarrow R - OR' + NaCl}$$

Solution :

With I^- ion, the overall reaction occurs in two steps, each of which is faster than the uncatalyzed reaction.

Step 1. $R - Cl + I^- \longrightarrow R–I + Cl^-$. This step is faster because I^-, a soft base has more nucleophilicity than OR^-, a hard base.

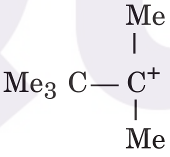
Step 2. $R - I + R'O: \longrightarrow R–OR' + I^-$. This step is faster because I^-, a soft base has more nucleophilicity than OR^-, a hard base.

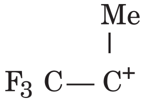
Example 12 :

Account for the following observations : (a) t–BuF is solvolyzed only in very acidic solutions. (b) t–BuCl is solvolyzed more slowly than 2-chloro–2, 3, 3–trimethylbutane (A). (c) t–BuCl is solvolyzed much faster than 2–chloro–1, 1, 1–trifluoro–2–methylpropane (B). (d) t-BuCl is solvolyzed more slowly in 90% D_2O–10% dioxane than in 90% H_2O– 10% dioxane solution.

Solution :

(a) F– is a poor leaving group but H-bonding with a strong acid encourages its departure. This is an example of electrophilic catalysis.

(b) Formation of  $Me_3\,C - \overset{Me}{\underset{Me}{C^+}}$ alleviates some of the steric crowding in (A) induced by the two Me's and the t–Bu on the α-carbon. This is an example of steric acceleration.

(c)  $F_3\,C - \overset{Me}{C^+}$ is destabilized by the strongly electron-withdrawing $–CF_3$ group, making the solvolysis of (B) slower.

(d) D-bonds are not as stabilizing as H-bonds.

Example 13 :

Compare the rates of S_N1 and S_N2 reactions of (a) cyclopropyl and cyclopentyl chloride and (b) 1–chlorobicyclo[2.2.2] octane and 9–chlorodecalin (A).

Solution :

(a) Cyclopropyl chloride is much less reactive than cyclopenytyl chloride in each type of reaction because the sp^2 hybridised carbon (120 bond angle) created in each transition state augments the ring strain.

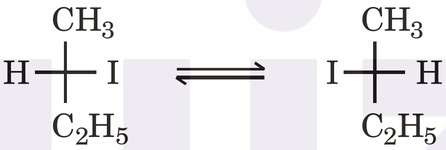
(b) The bridgehead halide is inert by both reaction types. A flat R^+ cannot be formed at the bridgehead carbon, making S_N1 reaction impossible and the three bridges prevent the backside attack necessary for S_N2 reaction. Furthermore, inversion is impossible. (A) is a typical 3 halide and reacts rapidly via S_N1 reaction, but poorly via S_N2 reaction.

Example 14

Optically active 2-iodobutane on treatment with NaI in acetone gives a product, which does not show optical activity. Explain why ?

Solution :

In this reaction C–I bond is broken and reformed to give a recemic mixture of 2-iodobutane and thus remains optically inactive. The presence of I^- provides opportunity for the remaking of the C–I bond.



Example 15

Dehydrobromination of compounds (A) and (B) yield the same alkene (C). Alkene (C) can regenerate (A) and (B) by the addition of HBr in the presence and absence of peroxide respectively. Hydrolysis of (A) and (B) give isomeric products, (D) and (E) respectively. 1, 1-diphenyl ethane is obtained on reaction of (C) with benzene in the presence of H^+. Give structures of (A) to (E) with reasons.

Solution :

The given reactions suggest that

(i) (B) is $C_6H_5CH(Br)CH_3 \xrightarrow[-\ HBr]{\text{alc. KOH}} \underset{(C)}{C_6H_5CH{=}CH_2} \xrightarrow{HBr} \underset{(B)}{C_6H_5CH(Br)CH_3}$

$\xrightarrow{HOH} C_6H_5CH(OH)CH_3$

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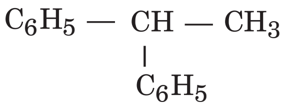
and (A) is $\underset{(E)}{C_6H_5CH_2CH_2Br} \xrightarrow[-HBr]{\text{alc. KOH}} C_6H_5CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr}$

$$\underset{(A)}{C_6H_5CH_2CH_2Br} \xrightarrow{HOH} \underset{(D)}{C_6H_5CH_2CH_2OH}$$

(ii) (D) and (E) are isomeric alcohols.

(iii) $C_6H_5CH = CH_2 + C_6H_6 \xrightarrow{H^+}$



$$C_6H_5 - \underset{\underset{C_6H_5}{|}}{CH} - CH_3$$

1, 1-diphenyl ethane

Example 16

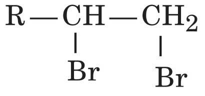
The alkyl halide C_4H_9Br (A) reacts with alcoholic KOH and gives an alkene (B), which reacts with bromine to give dibromide (C). (C) is transformed with sodamide to a gas (D) which forms a precipitate when passed through an ammonical silver nitrate solution. Give the structural formulae of the compounds (A), (B), (C) and (D) and explain the reactions involved.

Solution :

(1) (D) is a terminal alkyne since it forms precipitate with ammonica

(2) $$\underset{(A)}{C_4H_9Br} \xrightarrow[-HBR]{\text{alc. KOH}} \underset{\substack{(B)\\ \text{Alkene}}}{C_4H_8} \xrightarrow{Br_2} \underset{\substack{(C)\\ \text{Dibromide}}}{C_4H_8Br_2} \xrightarrow[2HBr]{NaNH_2} \underset{(D)}{C_4H_6}$$

(3) Thus, if (D) is R–C $\equiv$ CH, then (C) should be $R - \underset{\underset{Br}{|}}{CH} - \underset{\underset{Br}{|}}{CH_2}$ because it is formed by the action of Br_2 on (B). Thus, (B) should be R–CH=CH_2.



(4) Since (B) is obtained by dehydrobromination of (A) and thus, (A) should be R–CH_2CH_2Br. (A) is of 4 carbon atoms and therefore, (A) is $CH_3CH_2CH_2CH_2Br$.

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Reactions and answers :

$$\underset{\substack{\text{1–bromobutane}\\ \text{(A)}}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[-\,HBr]{\text{alc. KOH}} \underset{\text{(B)}}{CH_3CH_2CH{=}CH_2}$$

$$\underset{\substack{\text{But–1–ene}\\ \text{(B)}}}{CH_3CH_2CH{=}CH_2} \xrightarrow{Br_2} \underset{\text{(C)}}{CH_3CH_2CH(Br)CH_2Br}$$

$$\underset{\substack{\text{1–2–bromobutane}\\ \text{(C)}}}{CH_3CH_2CH(Br)CH_2Br} \xrightarrow[-2HBr]{NaNH_2} \underset{\text{(D)}}{CH_3CH_2C \equiv CH}$$

$$\underset{\text{But–1–yne}}{CH_3CH_2C \equiv CH} + \underset{\substack{\text{Tollen's}\\ \text{reagent}}}{Ag_2O} \longrightarrow \underset{\text{While ppt.}}{CH_3CH_2C \equiv Ag}$$

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