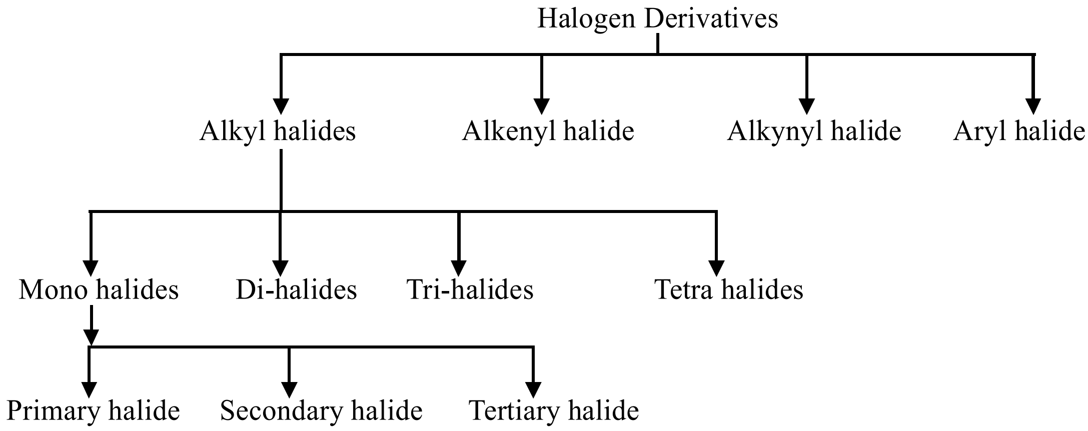
HALOGEN DERIVATIVES

INTRODUCTION

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding number of halogen atoms are known as halogen derivatives.

I. CLASSIFICATION

On the basis of nature of hydrocarbon from which they are obtained, helogen derivatives can be classified as :



(i) **Alkyl halides :** Halogen derivative of alkanes.

(ii) **Alkenyl halides :** Halogen derivative of alkenes.

(iii) **Alkynyl halides :** Halogen derivative of alkynes

(iv) **Aryl halides :** Halogen derivative of arenes (aromatic)

Alkyl halides can be further classified on the basis of number of halogen atoms introduced in alkane molecule.

(1) **Mono halides :** They are obtained by replacement of one hydrogen atom by one halogen atom in alkane.

General formula $C_nH_{2n+1}X$

Example : CH_3Cl Methyl chloride (Chloro methane)

CH_3CH_2Br Ethyl bromide (Bromo ethane)

(2) **Dihalides :** They are obtained by replacement of two hydrogen atom by two halogen atom in alkane molecule. The two halogen atoms may be on same cabon atom, known as geminal dihalides, if two halogen atoms are at adjacent carbon atoms they are known as vicinal dihalides.

General formula $C_nH_{2n}X_2$

Example : CH_2X_2 Methylene dihalide

CH_2X | CH_2X Ethylene dihalide or Vicinal dihalide

CH_3 | CHX_2 Ethylidene dihalide or geminal dihalide

(3) Trihalides : They are obtained by replacement of three hydrogen atom by three halogen atom in alkane.

General formula - $C_nH_{2n-1}X_3$.

Example : CHX_3 Trihalo methane or haloform

(4) Tetra halide and Perhalo compounds : They are obtained by replacement of four hydrogen atom by four halogen atom in alkane.

General formula $C_nH_{2n-2}X_4$ (tetra halide).

Example : $CH_4 \longrightarrow CX_4$ (Per halo methane)

$C_2H_6 \longrightarrow C_2X_6$ (Per halo ethane)

II. MONO HALIDES

These are classified on the basis of nature of C-atom carrying the halogen atom.

(1) Primary halide or 1^0 alkyl halides : Halogen atom attached with a primary or 1^0 C-atom.

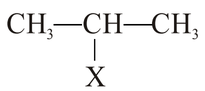
Example : CH_3—X Halo methane or methylhalide

CH_3—CH_2—X Halo ethane or ethyl halide

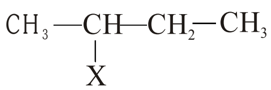
CH_3—CH_2—CH_2—X 1-Halo propane or n-propyl halide

(2) Secondary or 2^0 alkyl halides : Halogen atom linked with 2^0 C-atom.

Example :



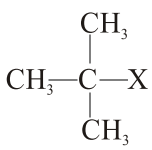
2-halo propane
or
Iso propyl halide



2-halo butane
or
Sec. butyl halide

(3) Tertiary halide or 3^0 alkyl halide : halogen atom linked with 3^0 C-atom.

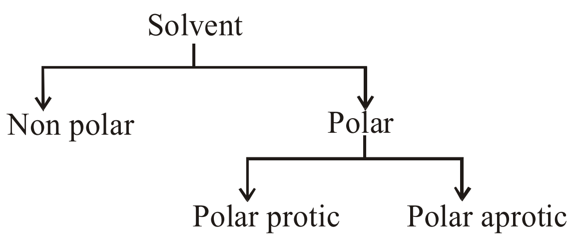
Example :



(tertiary butyl halide)

III. TYPES OF SOLVENT

Solvent can be classified as :-



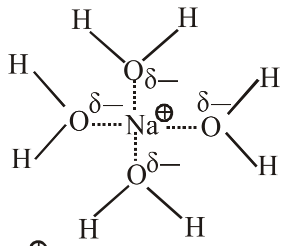
(i) **Polar Solvent :** Polar solvent has some overall dipole moment. They are of two types

(1) **Polar protic solvent** : Solvents in which H atom is directly attched with highly electronegative atom. Polar protic solvents are capable of forming intermolecular hydrogen bonding.

In polar protic solvents cation are solvated by ion dipole interaction while an anion is solvated by hydrogen bonding. Polar protic solvent can give H^+

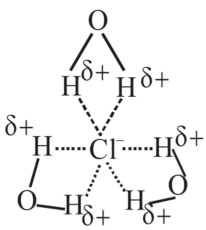
Example : H_2O, C_2H_5OH, CH_3COOH etc.,

Polar protic solvent can solvate both cation as well as anion. Cations are solvated by ion dipole interaction with H_2O while anions are solvated by hydrogen bonding with H_2O. Solvation of NaCl in H_2O can be explained as



$Na^{\oplus}$ is solvated by ion-dipole interaction with H_2O

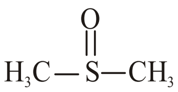
δ+



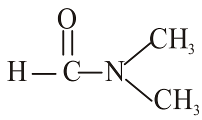
Cl^- is solvated by H-bonding with H_2O

(2) **Polar aprotic Solvents** : These are the solvents in which H is not attached with highly electro negative atom. These solvents can not give H^+

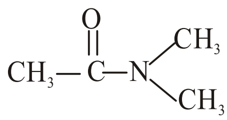
Examples :



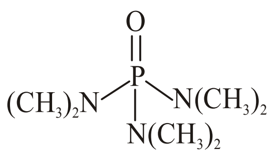
DMSO (Dimethyl sulphoxide)



DMF (Dimethyl formamide)

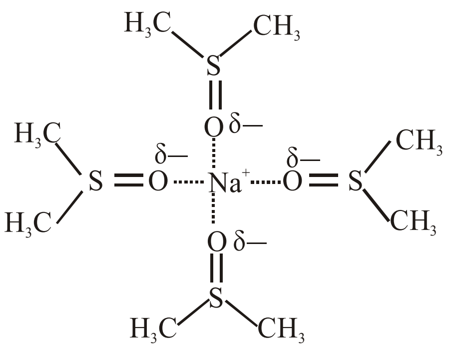


DMA (Dimethyl acetamide)

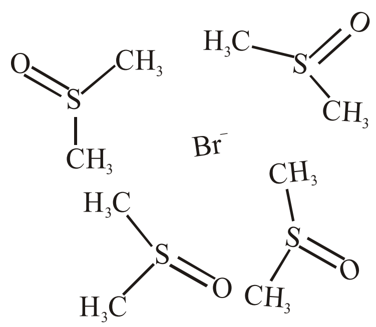


Hexamethylphosphoric triamide (HMPA)

Polar aprotic solvent can solvate cation very well, while anion is not solvated. When a salt is added then cation is trapped by ion dipole interaction, while Br^- is not well solvated



$Na^{\oplus}$ is solvated by ion dipole interaction with DMSO

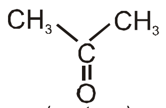
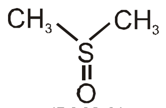
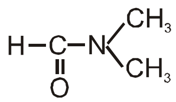
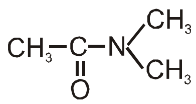


$Br^{\ominus}$ surrounded by solvent but not well solvated by DMSO

(ii) **Non Polar solvents :** These solvent has overall zero dipole moment.

Examples : CCl_4 , Benzene etc.,

Some Common examples of solvents :

SOLVENTS	POLAR PROTIC	POLAR APROTIC
1. H_2O	✓	–
2. CH_3CH_2OH	✓	–
3. H–COOH	✓	–
4. CH_3–COOH	✓	–
5. NH_3	✓	–
6.  (acetone)	×	✓
7.  (DMSO)	×	✓
8.  (DMF)	×	✓
9.  (DMA)	×	✓

IV. ELECTROPHILES & NUCLEOPHILES

(i) **Electrophile :** An electrophile is a positively charged species or neutral molecule with electron deficient center. Electrophiles can act as Lewis acids.

Electrophiles are of following type :

(1) Positively charged electrophiles

H^+, Br^+, Cl^+, I^+, NO_2^+, R_3C^+, NO^+ etc

(2) Neutral Electrophiles : In these electrophiles central atom has an incomplete octect and atleast one vacant orbital

SO_3, BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$, RCOCl, $(RCO)_2O$

(ii) **Nucleophiles :** It is an electron rich species which has atleast one lone pair of electrons. Nucleophile can be neutral or negativetely charged. Nucleophile is always a lewis base.

Example : CN^-, OH^-, Br^-, I^-, NH_3, H_2O

Nucleophile are of following types :

(1) Negatively charged nucleophiles :

Example **:** $\bar{H}$, $\bar{O}H$, $\bar{O}-R$, $\bar{C}H_3$, $\bar{X}$, $\bar{S}H$, $R-\bar{S}$, $\bar{N}O_2$, $R-\overset{O}{\overset{||}{C}}-\bar{O}$, etc

(2) Neutral nucleophiles : In these nucleophiles central atom has complete octet and atleast one lone pair of electron

Example : $R-\ddot{N}H_2$, $\ddot{N}H_3$, $\ddot{N}H_2-\ddot{N}H_2$, $H-\ddot{\underset{..}{O}}-H$ $R-\ddot{\underset{..}{O}}-H$, $R-\ddot{O}-R$,

$H-\ddot{\underset{..}{S}}-H$, $R-\ddot{\underset{..}{S}}-H$, $R-\ddot{\underset{..}{S}}-R$, $\ddot{P}H_3$,  ,

Organic compounds containing carbon-carbon double bonds can also behave as nucleophile.

$CH_2=CH_2$, , $CH_2=CH-CH=CH_2$, etc

(3) Ambident Nucleophile : Species having two nucleophilic sides, but only one can donate lone pair of electron at a time, known as ambident nucleophile.

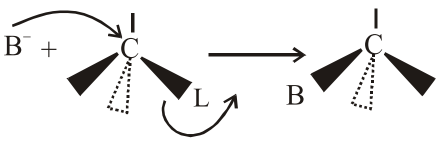
$\bar{C}\equiv\ddot{N}$, $\bar{O}-\ddot{N}=O$, etc

V. NUCLEOPHILICITY & BASICITY

Nucleophilitic̄y is defined as the tendency of any species to give electron pair to an electron deficient center, while basicity is the ability of the species to remove H^+ ion, from an acid

Example : Consider a species B^- ,

(i) It functions as a nucleophile is given as



(ii) It functions as base is indicated as

$$\bar{B}+H-A \rightleftharpoons B-H+A^-$$

The nucleophilicity is determined by the kinetics of the reaction, which is reflected by its rate constant (k) while basicity is determined by the equilibrium constant, which is reflected by its K_b.

Criteria for Nucleophilicity : The factors which increases electron density at donor atom increases nucleophilicity.

The more polarisable donar atom is a better nucleophile. Therefore, large size of donor atom increases nucleophilicity.

Effect of the solvent : In polar protic solvent large nucleophiles are good, and the nucleophilicity of halide ions follows the order as :

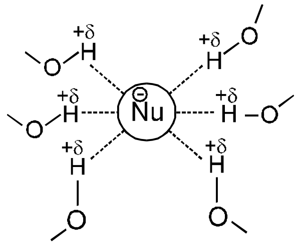
$$F^- < Cl^- < Br^- < I^-$$

In DMSO, the relative order of nucleophilicity of halide ions is given as

$$F^- > Cl^- > Br^- > I^-$$

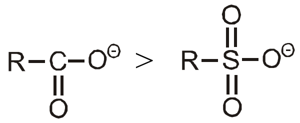
Also basic strength of halides follows the same order in DMSO but in polar protic solvent like H_2O they follow the reverse order of nucleophilicity.

This effect is related to the strength of the interaction between nucleophile and solvent molecules of polar protic solvent forms hydrogen bond to nucleophiles in the following manner :



Relative nucleophilicity in polar protic solvent

$SH^{\ominus} > I^{\ominus} > OH^{\ominus} > N_3^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus} > H_2O$

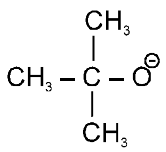


$HO^{-} > H_2O$

$NH_2^{-} > NH_3$

$CF_3SO_3^{-} < PhCOO^{-} < PhO^{-} < RO^{-}$

Steric effects on nucleophilicity



t-butoxide

(Stronger base, yet weaker nucleophile cannot approach the carbon atom so easily.)

$CH_3 - CH_2 - O^{\ominus}$ (Weaker base, yet stronger nucleophile)

ethoxide

Periodicity : Nucleophilicity decreases from left to right in a period and basicity also decreases.

$CH_3^- > NH_2^- > OH^- > F^-$

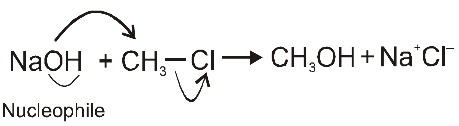
In a group, nucleophilicity increases from top to bottom due to increases in size of donor atom, but basicity decreases from top to bottom.

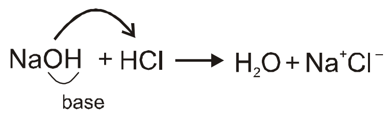
Acid strength : HI > HBr > HCl > HF

Basic strength : $F^- > Cl^- > Br^- > I^-$

Nucleophilicity : $F^- < Cl^- < Br^- < I^-$

It is the tendency to donate electron pair to $H^{\oplus}$ ion.

(a) 

(b) 

NUCLEOPHILICITY vs BASICITY			
Nucleophilicity		Basicity	Remarks
1.	$CH_3^- > NH_2^- > OH^- > F^-$	$CH_3^- > NH_2^- > OH^- > F^-$	If donor atoms belong to same period, nuclephilicity and basicity order is same
2.	$SiH_3^- > PH_2^- > SH^- > Cl^-$	$SiH_3^- > PH_2^- > SH^- > Cl^-$	—//—
3.	$F^- < Cl^- < Br^- < I^-$	$F^- > Cl^- > Br^- > I^-$	In a group nucleophilicity increases while basicity decreases. on moving top to bottom.
4.	$OH^- < SH^-$	$OH^- > SH^-$	—//—
5.	$RO^- < RS^-$	$RO^- > RS^-$	—//—

VI. LEAVING GROUP ABILITY / NUCLEOFUGALITY

Good leaving groups are those that become the most stable ion after they leave, because leaving group generally leave as a negative ion, so those leaving group are good, which stabilise negative charge most effectively and weak base do this best, so weaker is the base better is the leaving group.

– The leaving group should have lower bond energy with carbon.

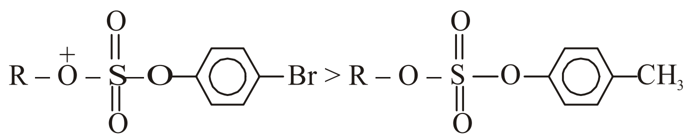
– Negative charge should be more stable either by dispersal or delocalization.

Strongly basic ions rarely act as leaving group →

$\overset{\ominus}{Br} + R - OH \not\rightarrow R - X + \overset{\ominus}{O}H$ (strong base / poor leaving group)

$\overset{\ominus}{Nu} + CH_3 - CH_3 \not\rightarrow CH_3 - Nu + \overset{\ominus}{C}H_3$ (It is not a leaving group)

Order of leaving ability of some groups

(1) 

(2) $R - O - SO_2 - C_6H_5 > R - SO_2 - CH_3 > RI > R - Br$

(3) $R - O - \overset{O}{\overset{\|}{C}} - CH_3 > R - O - H > R - O - R > R - H$

where group attached with R is a leaving group

(4) $CH_3^- < NH_2^- < OH^- < F^-$

(5) $R{-}COO^- > PhO^- > HO^- > RO^-$

(6) $^{-}SH > {}^{-}OH$

ILLUSTRATION :

(1) Ambident nucleophiles are ?

$$\underset{(a)}{NO_2^-}\ ,\ \underset{(b)}{NH_2-CH_2-\overset{\overset{\large O}{||}}{C}-O^-}\ ,\ \underset{(c)}{\bar{O}H}$$

Solution. (a), (b)

(2) Which among the following species is an ambident nucleophile :

(A) Ethene (B) Benzene

(C) Cyanide ion (D) Acetone

Solution. (C) Cyanide ion is an ambident nucleophile

(3) A nucleophile is :

(A) electron-rich species

(B) electron-deficient species

(C) a Lewis acid

(D) Positively charged species

Solution. (A) A nucleophile is electron-rich species

(4) Which is not a nucleophile –

(A) NH_3 (B) R—O—R (C) BF_3 (D) HOH

Solution. (C) BF_3

GOLDEN KEY POINT -1

(1) Nucleophilicity depends on the nature of solvent.

(2) Anions are better nucleophile than their neutral molecule.

(3) Nucleophilicity increases if adjacent atom of nucleophilic side has lone pair, because lone pairs repels each other. Example $\ddot{N}H_2–\ddot{N}H_2$.

CARBOCATION

Different reaction shown by carbocation

(i) Rearrangement

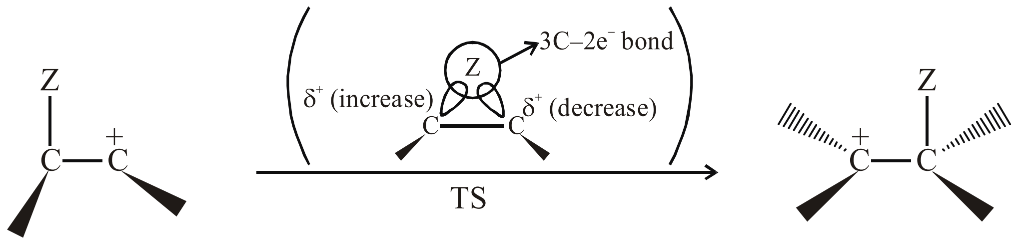
(ii) Combination

(iii) Elimination

REARRANGEMENT

(i) Less stable carbocation rearrange itself into more stable carbocation.
Stability must attain in each step.
Stability of T.S. (Transition state)

Ex.1



Note :

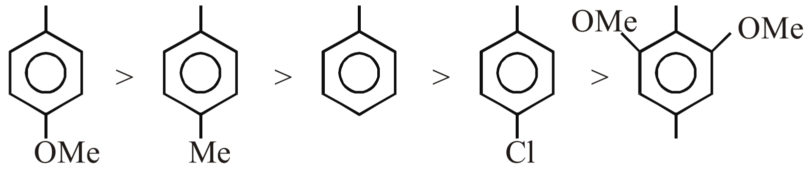
(i) Its a example of 1, 2 shift.

(ii) 3-MCTS (membered cyclic transition state) involve

(iii) Migrating order (when different atom / group attached to one carbon)

(a) –H > –Ar > – R

(b) –H > –D > –T

(c) 

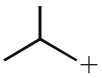
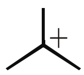
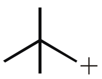
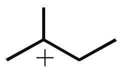
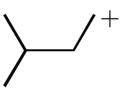
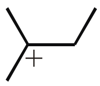
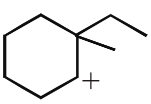
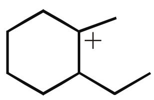
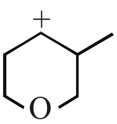
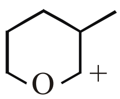
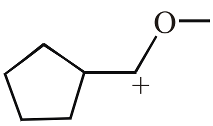
p-anisyl p-tolyl

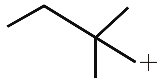
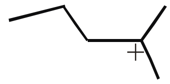
(d) –3° > –2°> –1° > Me

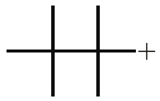
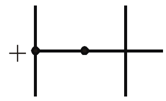
(e) $-CH_2CH_2CH_2CH_3 > -CH_2CH_2CH_3 > -CH_2CH_3 > -CH_3$

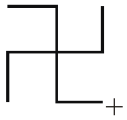
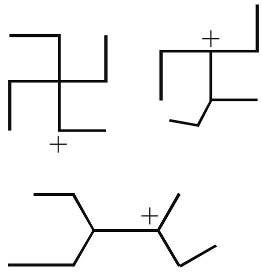
(iv) Bulkier group migrate first

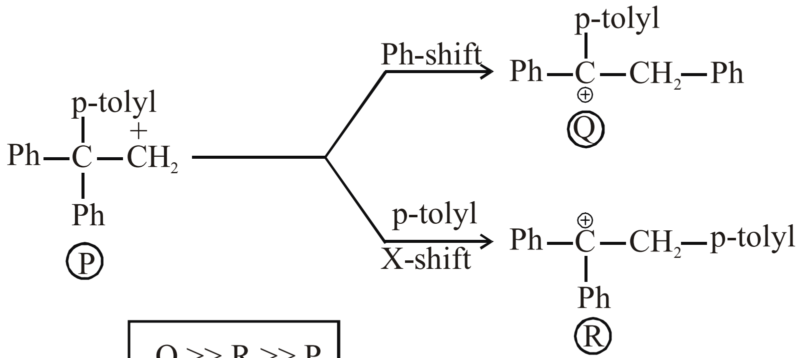
Q.

	Carbocation	No. of 1-2 shift	Most stable
1.		1(H)	
2.		1(Me)	
3.		2(H,H)	
4.		1(H)	
5.		1(Et)	
6.		2(H)	
7.		X	X

8.  1(Et) 

9.  1(Iso-p) 

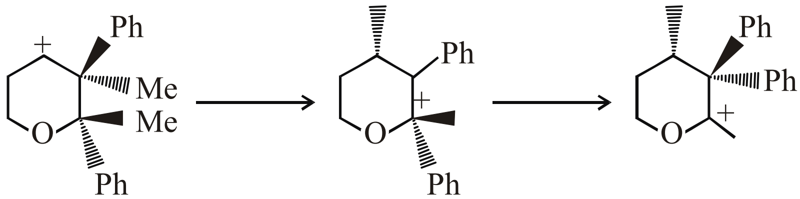
10.  3(H,Et, H) 

11. 

Q >> R >> P

* If after shift, carbocation stabilized by back bonding then migratory apptitude will be strictly followed.

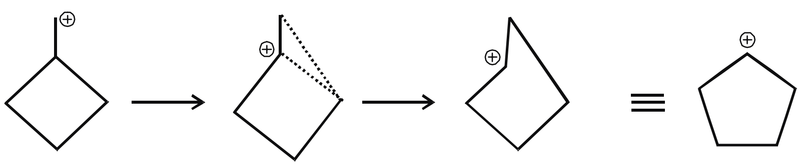
* If no such phenomena then form most stable carbocation

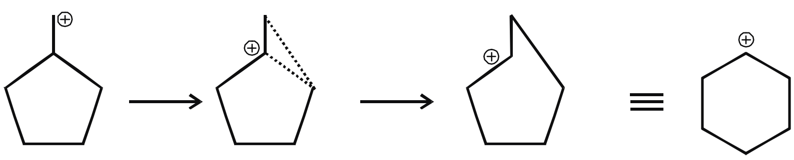
12. 

RING EXPANSION :

It is also an example of 1, 2 shift.

On ring expansion strain get released

1. 

2. 

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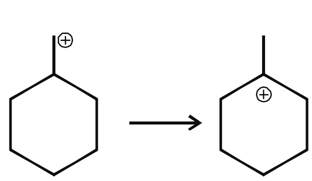
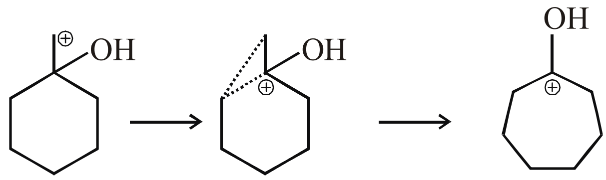


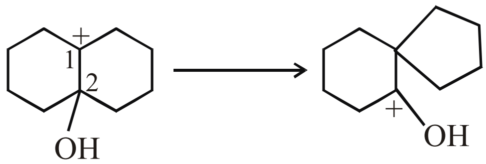
No Ring expansion takes place only 1, 2 $H^{\ominus}$ shift

4.

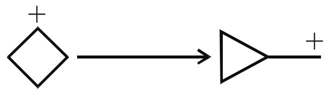


RING CONTRACTION :

1.



2.



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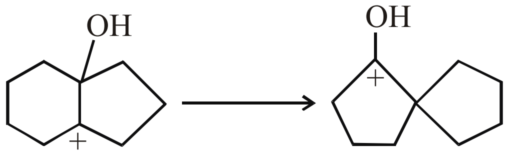
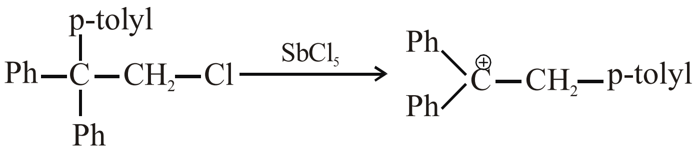
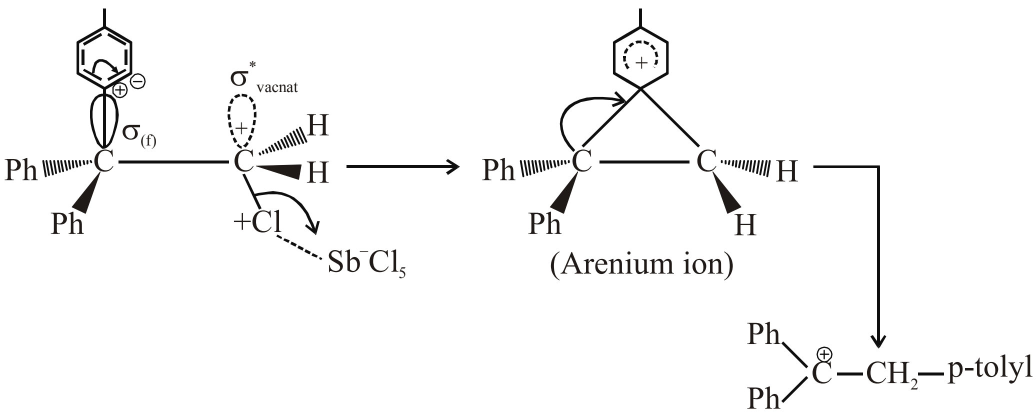


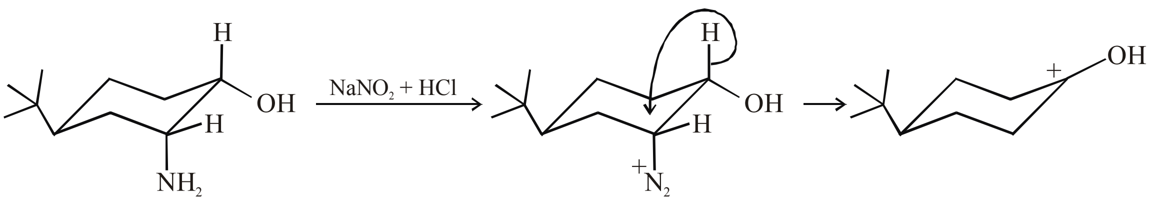
ANTI GROUP MIGRATION



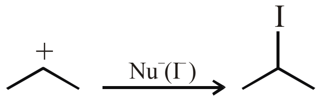
1.

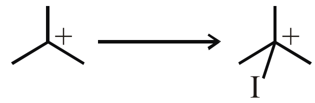


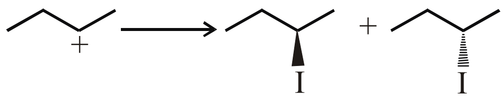
2.

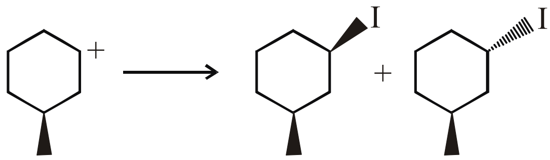


Carbocation involved in combination reaction (with I^- as nucleophile):

(a) 

(b) 

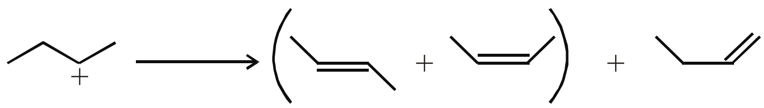
(c) 

(d) 

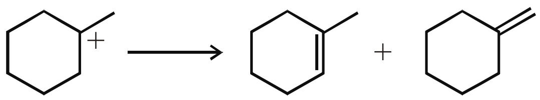
Carbocation involved in elimination reaction :

(a) 

(b) 

(c) 

Saytzeff alkene   Hoffman alkene

(d) 

Saytzeff   Hoffmann

Saytzeff product : The product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule.

Hoffmann product : Bulky bases can also accomplish dehydrohalogenations that do not follow the saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often that leads to formation of least substituted product, called the Hoffmann product.

REACTION INVOLVING CARBOCATION AS AN INTERMEDIATE

1. DIAZOTIZATION

$$R\text{–}NH_2 \xrightarrow[\text{or } HNO_2 \text{ or } NOCl]{NaNO_2/HCl} \left[R\text{–}\ddot{N}\text{=}\overset{+}{N} \longleftrightarrow R\text{–}\overset{\oplus}{N}\equiv N\right] \xrightarrow{-N_2} R^+ \xrightarrow{H_2O} R\text{–}OH$$

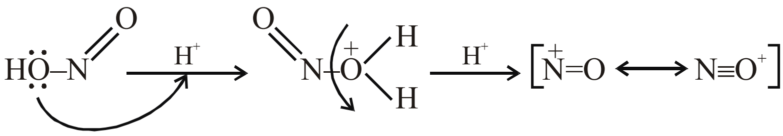
NOCl ⟶ Tilden reagent

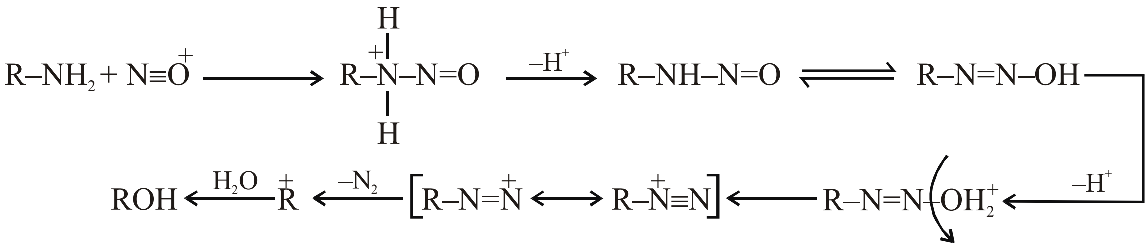
R–OH $\xrightarrow{\text{CAN (Cerric ammonium nitrate)}}$ Red colour

R^+ ⟶
- $\xrightarrow{H_2O}$ R–OH (Major when $NaNO_2$/HCl or HNO_2)
- $\xrightarrow{Cl^-}$ R–Cl (Major when NOCl is taken)
- $\xrightarrow{NO_2^-}$ R–NO_2
- $\xrightarrow{\overset{\ominus}{O}\text{–N=O}}$ R–ONO
- $\xrightarrow{\Delta}$ alkene

Mechanism :

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$



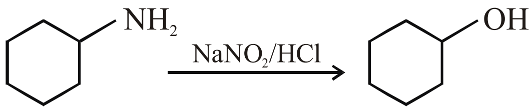


Note :(i) NO^+ is attacking electrophile

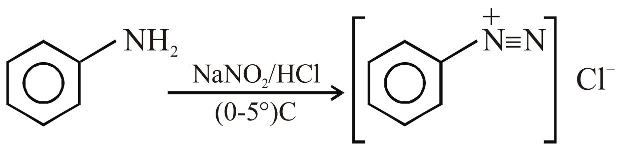
(ii) Carbocation involved during the reaction as an intermediate

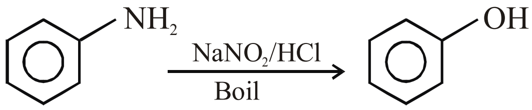
(iii) Rearrangement takes place if possible

(iv) Alkyl diazonium salt is highly unstable.

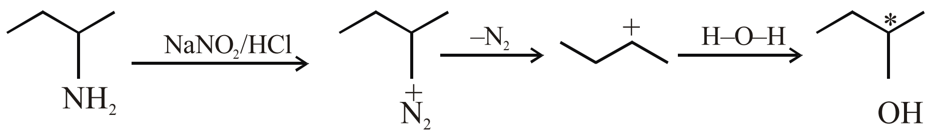
(1) 

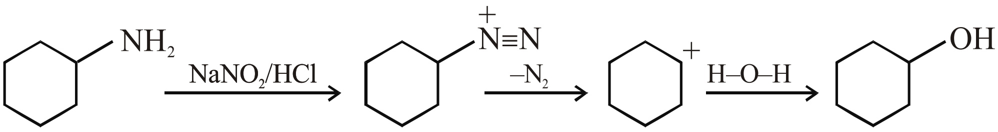
(v) Aryl diazolization salt is stable only at (0-5°)

(2) 

(3) 

(vi) In case of secondary amine yellow oily liquid (N-nitroso amine) is obtained.

(1) 

(2) 

DEHYDRATION OF ALCOHOL :

Alcohol on dehydration gives alkene as the major product.

$$CH_3{-}CH_2{-}OH \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2{=}CH_2$$

Mechanism:

$$CH_3{-}CH_2{-}OH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3{-}CH_2{-}\overset{+}{O}H_2 \overset{-HOH}{\rightleftharpoons} CH_3{-}\overset{+}{C}H_2 \overset{HSO_4^-}{\rightleftharpoons} CH_2{=}CH_2$$

Note:

1. Reaction involve E_1(unimolecular elimination) mechanism.

2. Endothermic Reaction

3. Carbocation involve as an intermediate

4. Rearrangement takes place if possible

5. Higher temperature is required for dehydration.

6. For dehydration following catalyst can be used

Ex.Conc. H_2SO_4, H_3PO_4, $KHSO_4$ etc.

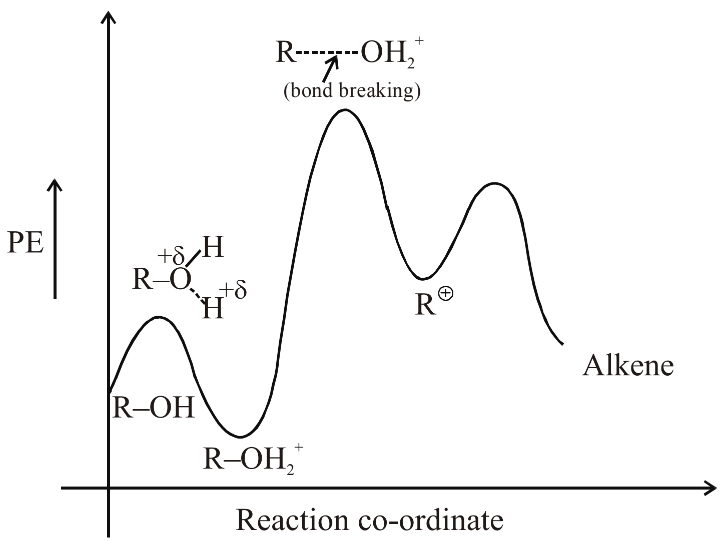
7. Two or more than two types of alkene can be obtained (Saytzeff and Hoffmann)

8. Usually Saytzeff alkene dominates over Hoffmann alkene.

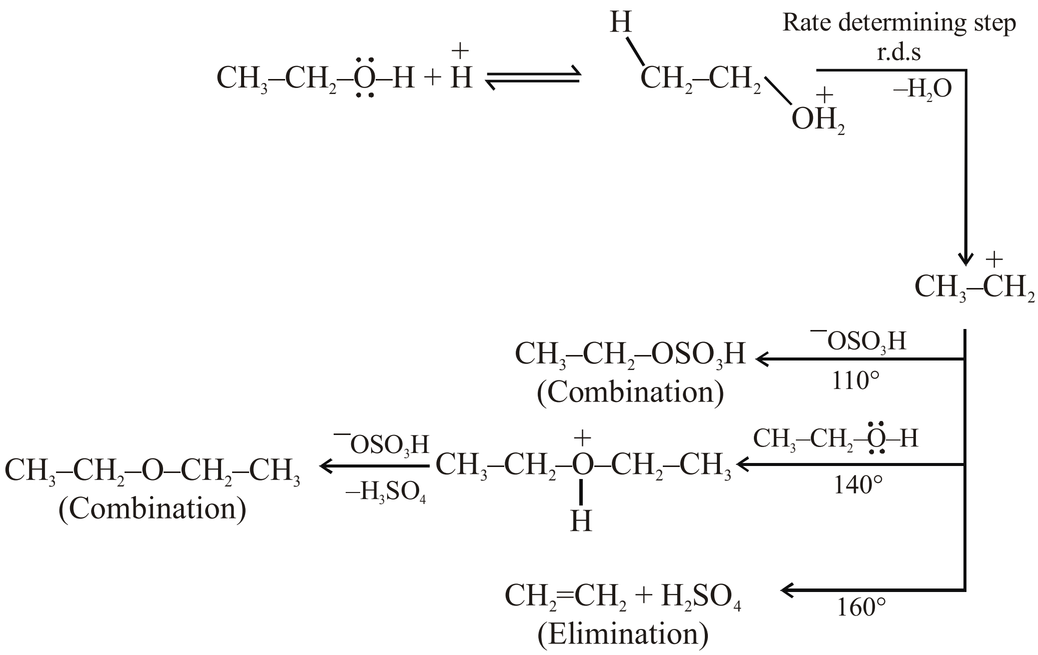
9. Rate : $r = k[R{-}OH_2^+]$

10. Unimolecular reaction.

ENERGY PROFILE DIAGRAM FOR DEHYDRATION OF ALCOHOL



Temperature variation for dehydration of $CH_3–CH_2–OH$

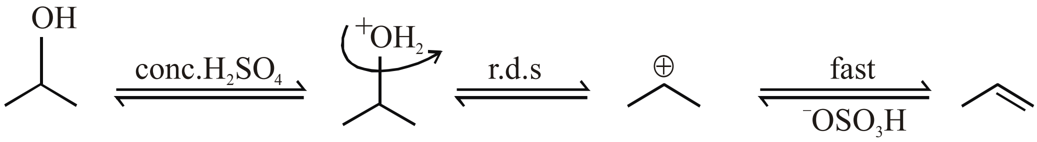


* In RDS, two different components are involved $\left(CH_3-CH_2-OH_2^+ \ \& \ O^-SO_3H\right)$

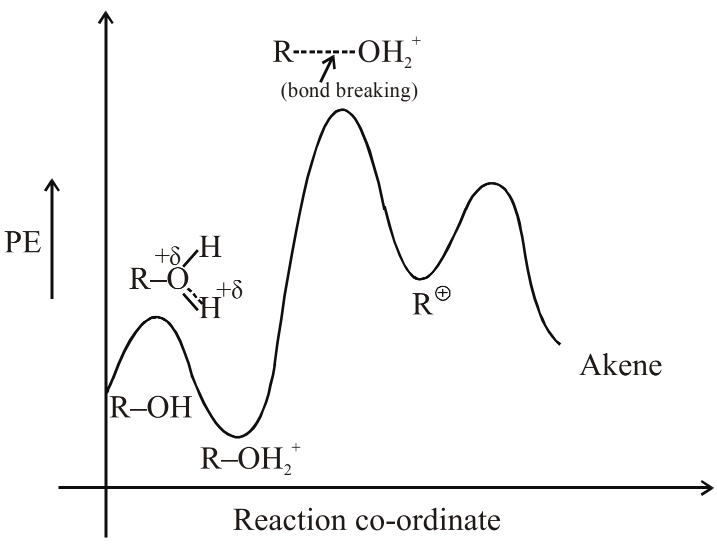
Complete the following reaction and draw and energy profile diagram

1.

Ans.

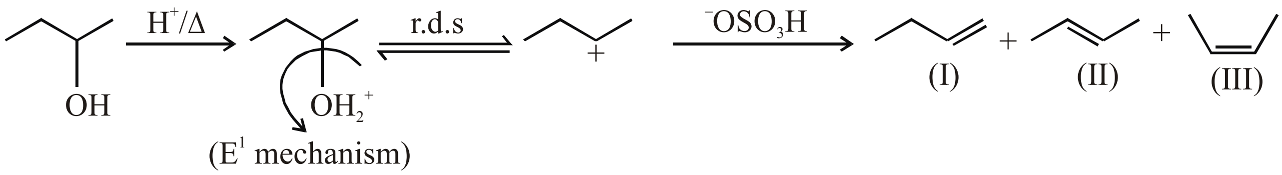


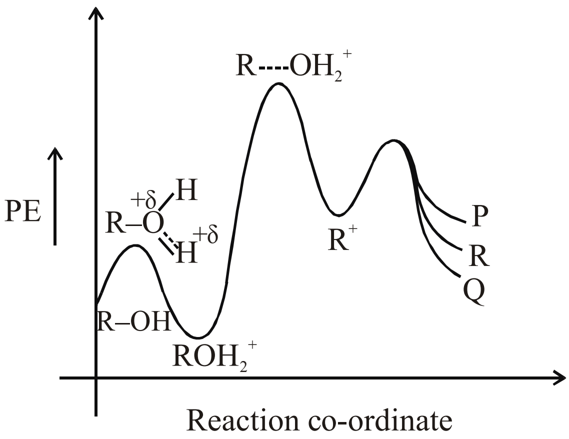
(E[1] mechanism)

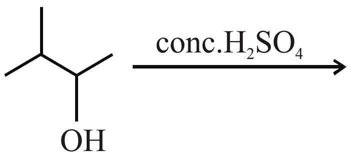


2. 
conc.H_2SO_4
OH

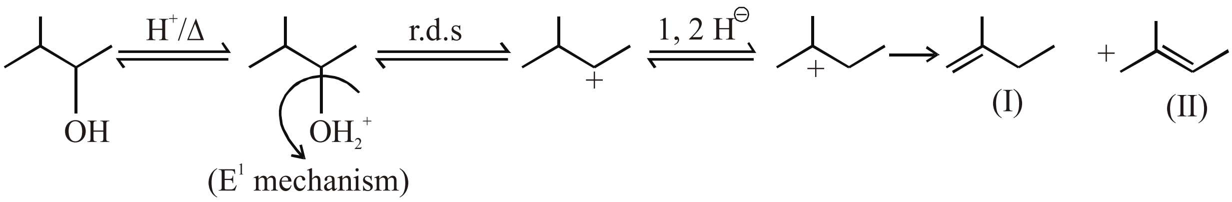
Ans.

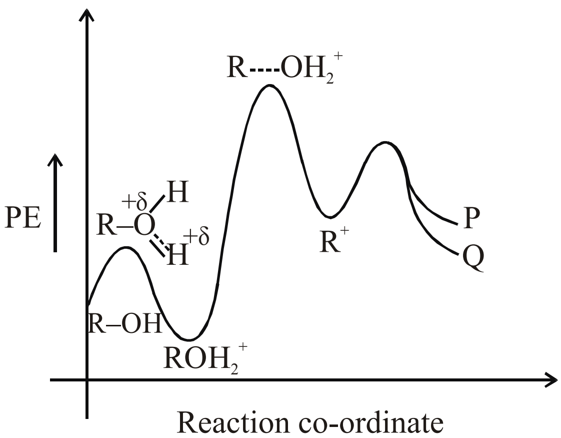

H+/Δ
OH
r.d.s
OH2+
(E1 mechanism)
−OSO3H
(I)
(II)
(III)

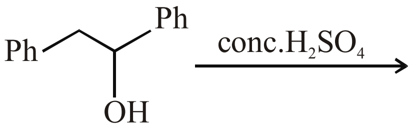

R----OH2+
PE
+δ H
R–O
+δ
H
R+
P
R
Q
R–OH
ROH2+
Reaction co-ordinate

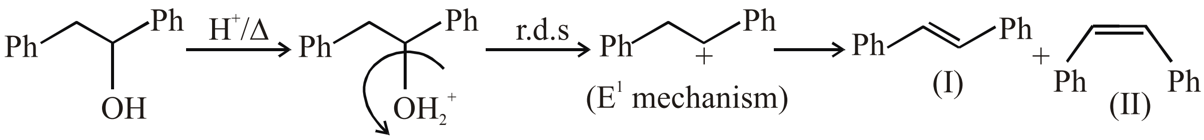
3. 
conc.H_2SO_4
OH

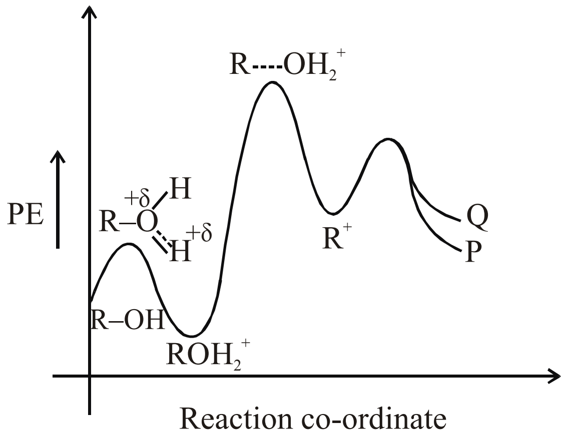
Ans.

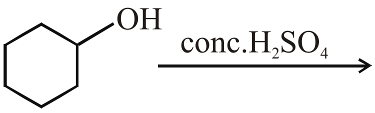

H+/Δ
OH
r.d.s
OH2+
(E1 mechanism)
1, 2 H⊖
(I)
(II)

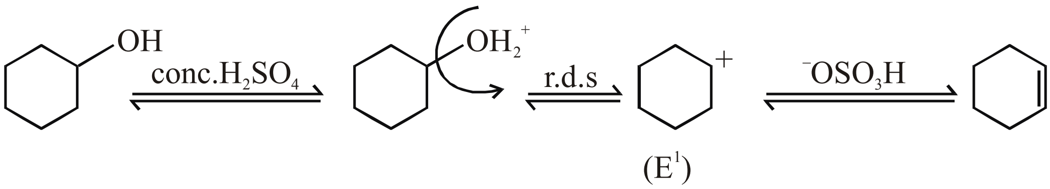

R----OH2+
PE
+δ H
R–O
+δ
H
R+
P
Q
R–OH
ROH2+
Reaction co-ordinate

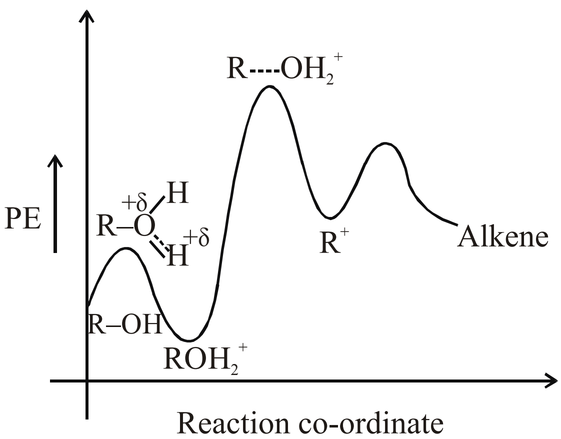
4. 

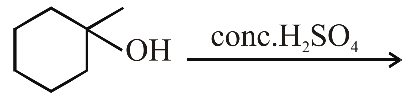
Ans. 
H⁺/Δ
r.d.s
(E¹ mechanism)
(I)
(II)

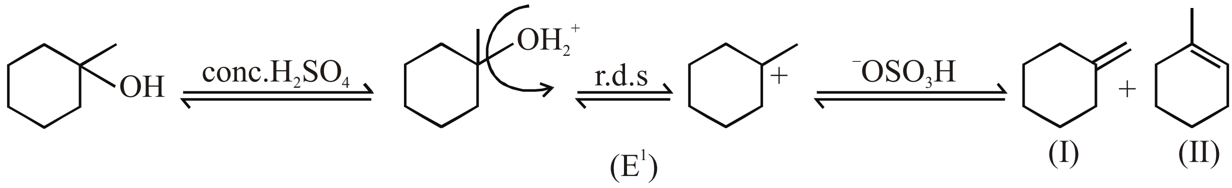

R----OH₂⁺
PE
R–O–H
+δ
+δ
R⁺
Q
P
R–OH
ROH₂⁺
Reaction co-ordinate

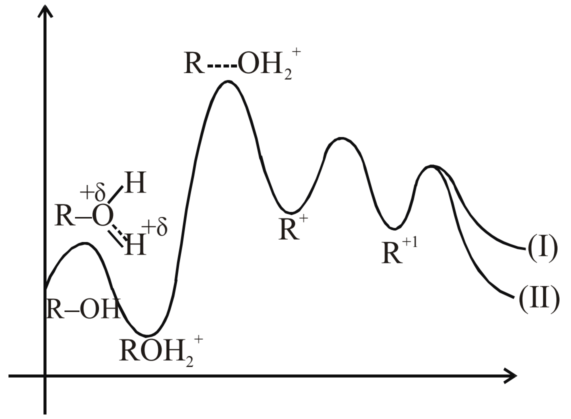
5. 

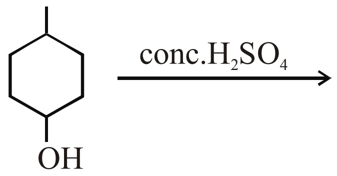
Ans. 
conc.H₂SO₄
r.d.s
⁻OSO₃H
(E¹)

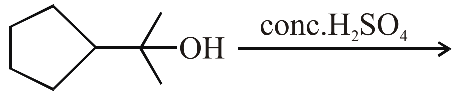

R----OH₂⁺
PE
R–O–H
+δ
+δ
R⁺
Alkene
R–OH
ROH₂⁺
Reaction co-ordinate

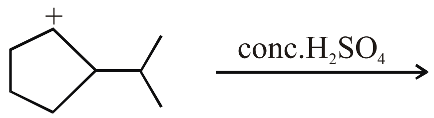
6. 

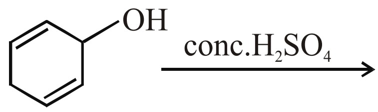
Ans. 

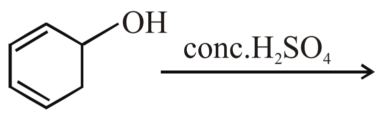


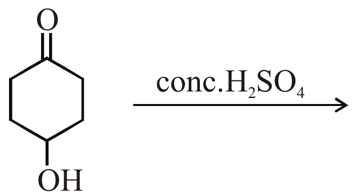
7. 

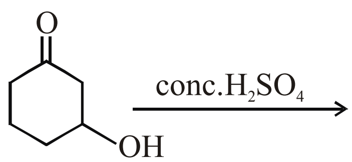
8. 

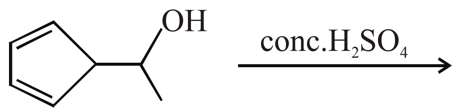
9. 

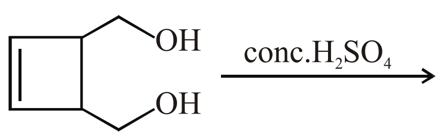
10. 

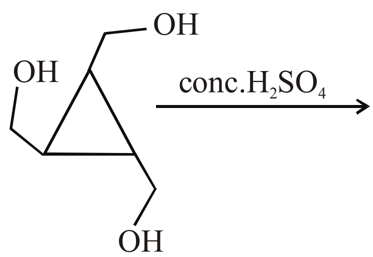
11. 

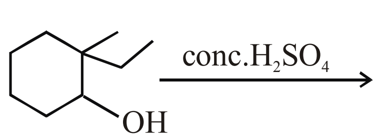
12. 

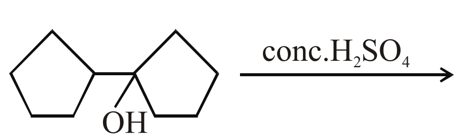
13. 

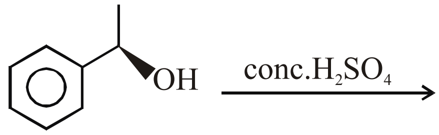
14. 

15. 

16. 

17. 

18. 

19. 

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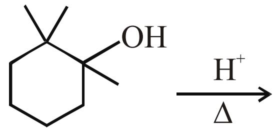
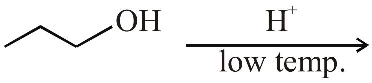
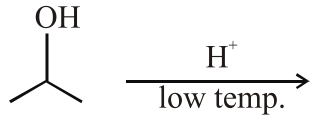
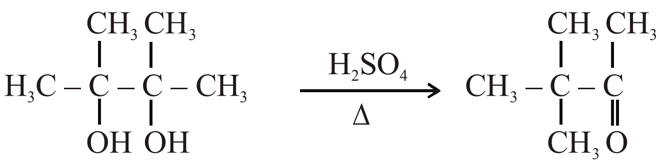
22. 

23. 

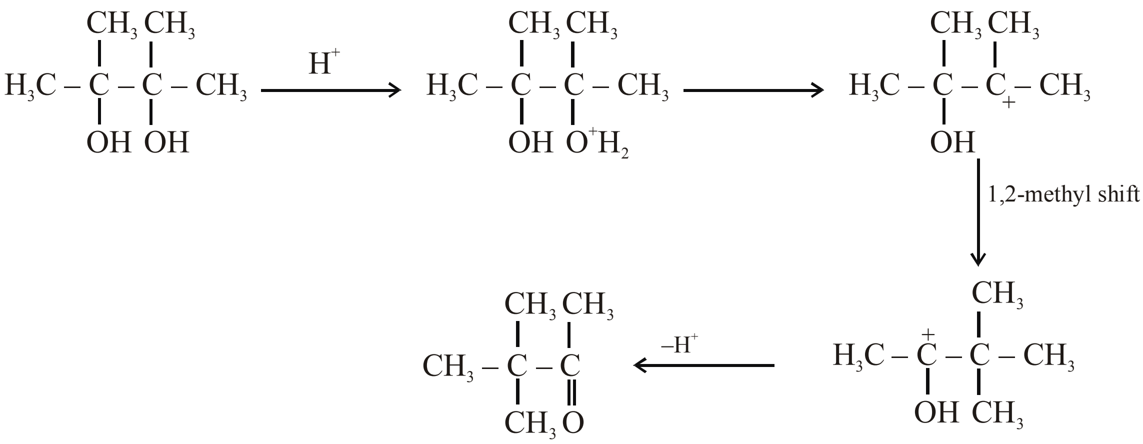
24. 

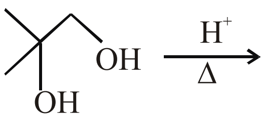
PINACOLE-Pinacolone

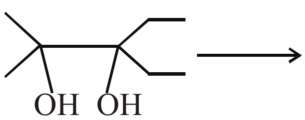
Rearrangement

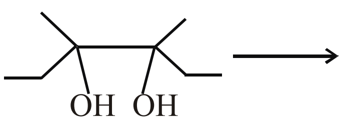


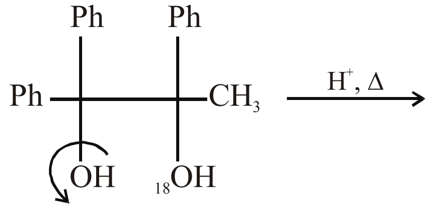
Mechanism

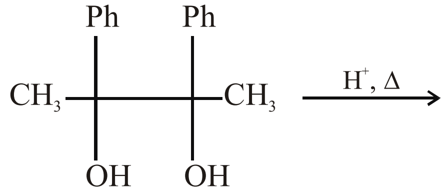


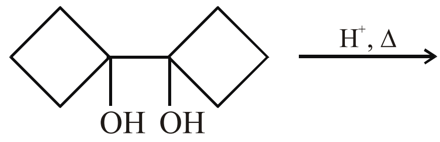
1. 

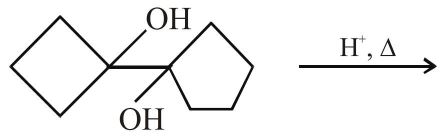
2. 

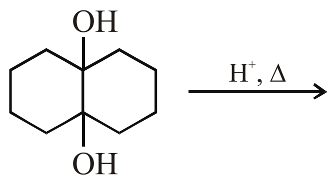
3. 

4. 

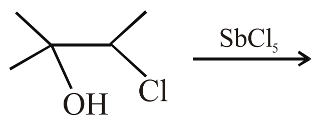
5. 

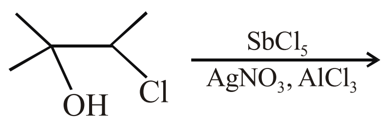
6. 

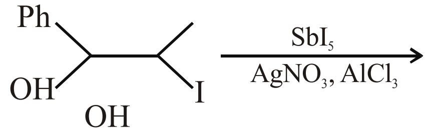
7. 

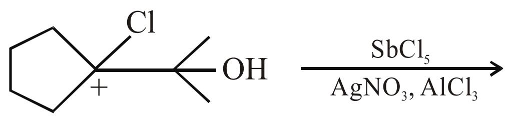
8. 

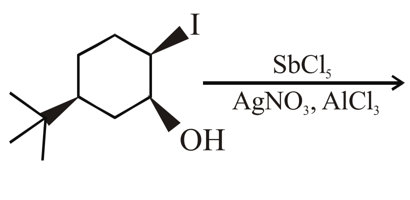
Semi-pinacole rearrangement (Damjanov's Reaction)

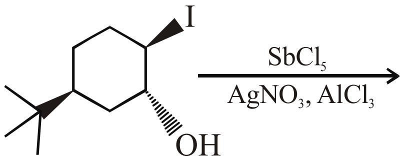
1. 

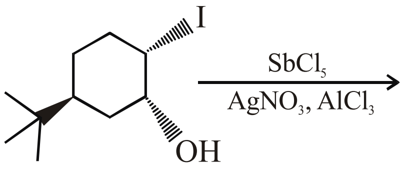
2. 

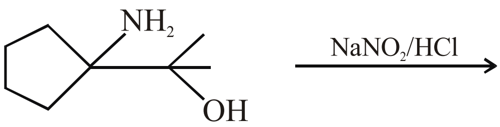
3. 

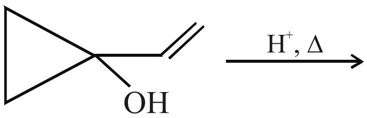
4. 

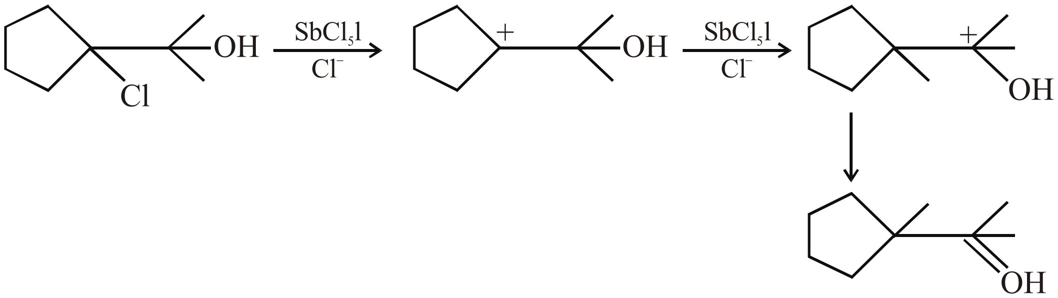
5. 

6. 

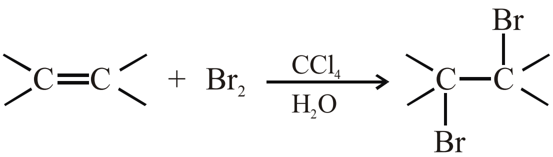
7. 

8. 

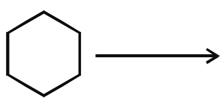
9. 

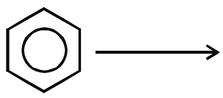
10. 

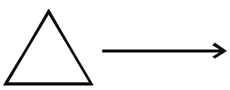
TEST OF UNSATURATION

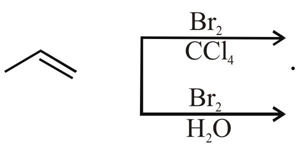


(Reddish brown) (Colourless)

*  (–) Br$_2$/H$_2$O test

 (–) Br$_2$/H$_2$O test

 (+) Br$_2$/H$_2$O test

1. 

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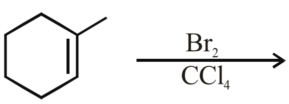
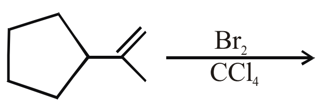
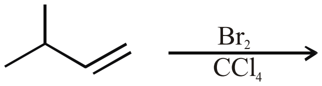
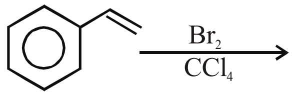
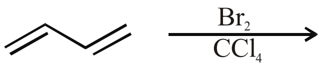
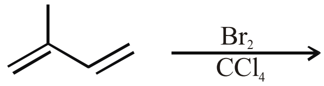
3. 

4. 

5. 

6. 

7. 

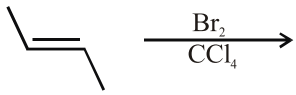
8. 

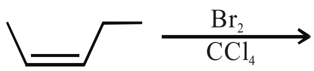
9. $HC \equiv CH \xrightarrow[\text{excess}]{Br_2}$

10. $CH_3{-}C{\equiv}CH \xrightarrow[\text{excess}]{Br_2}$

*** Stereochemistry Involved During Addition of X_2**

1. 

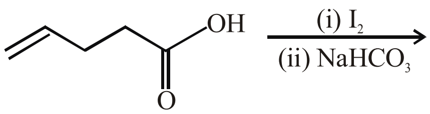
2. 

3. 

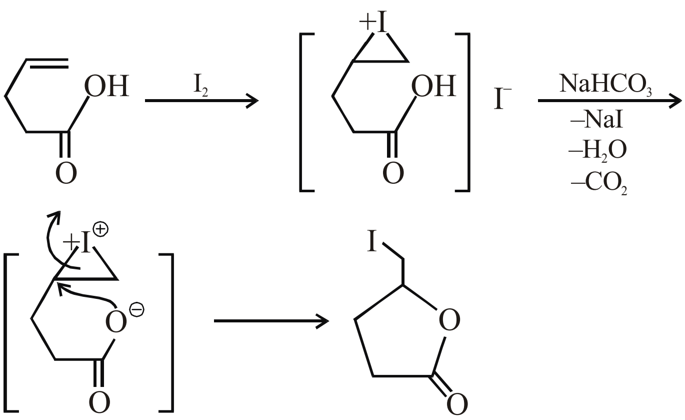
4. 

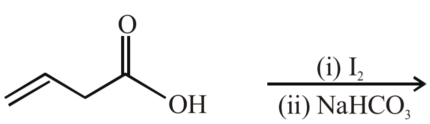
IODOLACTONIZATION

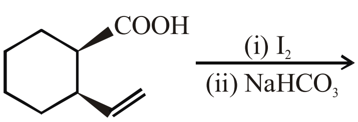
Note: Formation of five membered ring can be considered as norm for iodolactonization

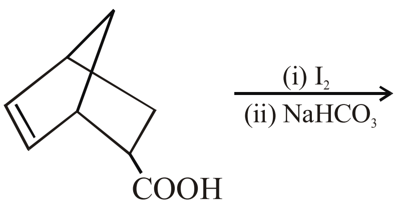
1. 

Mechanism:

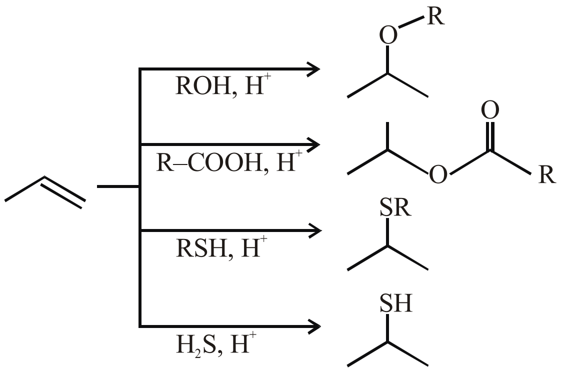


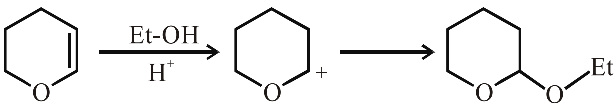
2. 

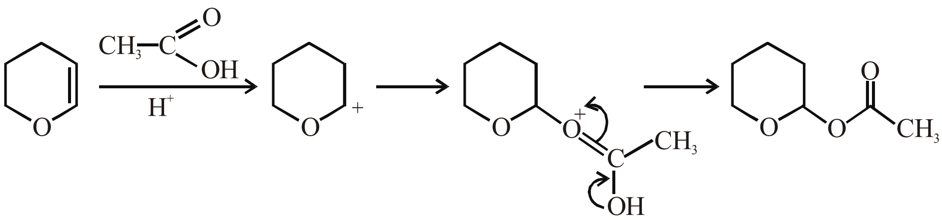
3. 

4. 

Addition of R–OH/R–COOH/R–SH/H_2S

1. 

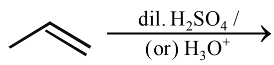
2. 

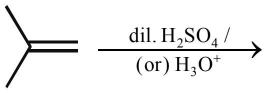
3. 

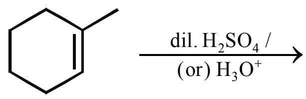
REACTION WITH DIL. H_2SO_4

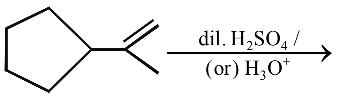
Reverse of dehydration of alcohol.

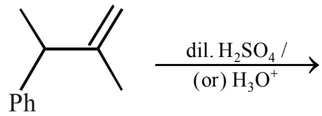
1. $CH_2=CH_2 \xrightarrow[\text{(or) } H_3O^+]{\text{dil. } H_2SO_4 /}$

2. 

3. 

4. 

5. 

6. 

7. $CH_2=C=CH_2 \xrightarrow[\text{(or) } H_3O^+]{\text{dil. } H_2SO_4 /} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

HYDRATION OF ALKYNE (KUCHEROOV'S REACTION)

Alkyne are hydrolyced in presence of Hg^{+2} salt (sulphate and acetate) as a catalyst.

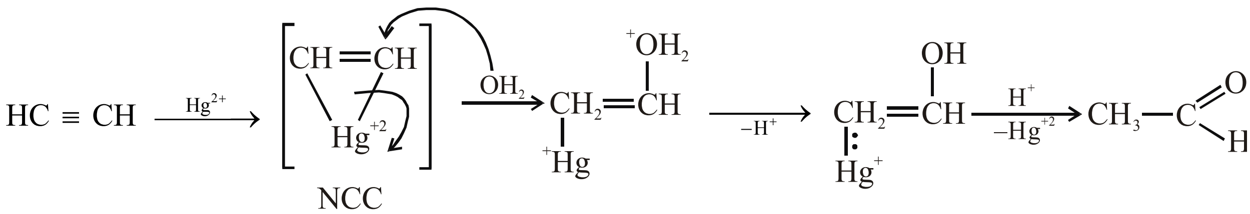
$HC \equiv CH \longrightarrow$ Aldehyde

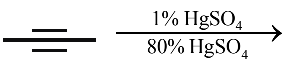
$RC \equiv CH \longrightarrow$ ketone

$RC \equiv CR' \longrightarrow$ Both ketones are possible

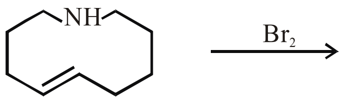
1. $HC \equiv CH \xrightarrow[80\% \, HgSO_4]{1\% \, HgSO_4}$

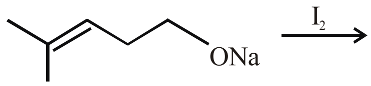
Mechanism:

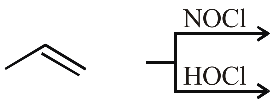


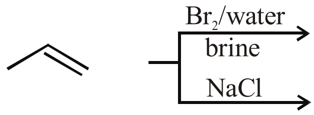
2. 

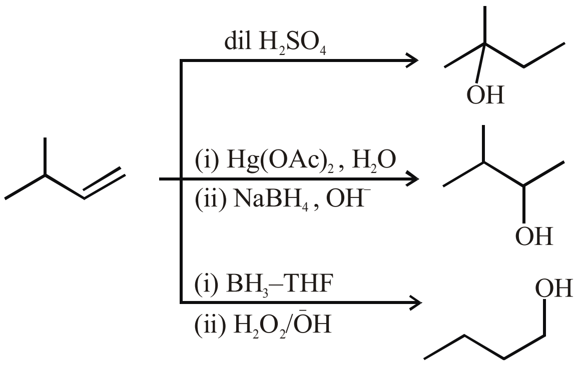
Attack by intramolecular Nu⁻ site:

1. 

2. 

3. 

4. 

5. 

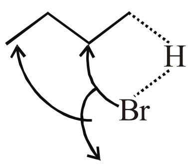
KCP V TCP:

(i) KCP ⇒ Kinetically controlled product
⇒ Product which is quickly formed
⇒ Product formed by lowest activation energy

(ii) TCP ⇒ Thermodynamically controlled product
⇒ Most stable

(iii) KCP and TCP may be same.

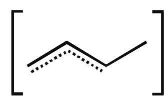
(v) 1, 2 product is always KCP because of proximity factor (closeness)

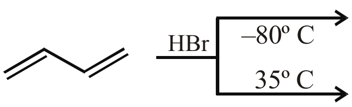


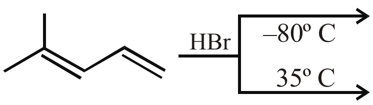
Closer, proximity is high

(vi) At low temp. (–80ºC), KCP is major as the energy barrier is low

(vii) At high temp.(35ºC), TCP is major because at high temp, reaction are reversible. 1-2 product has less energy barrier so quickly reverts but while going back (R→product), the reverssibility of reaction is still high, so it prefers the high energy barrier where reversibility factor is low. So, TCP forms

1-2 product ⇌  ⇌ 1, 4 product





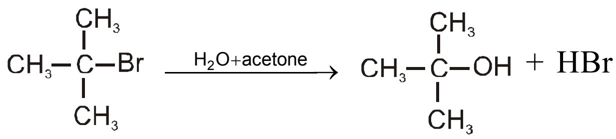
D) The nature of the leaving group :

Weaker bases are good leaving groups. A good leaving group always stabilise the transition state and lowers its free energy of activation and there by increases the rate of the reaction. Order of leaving ability of halide ion $F^- < Cl^- < Br^- < I^-$

Better is the leaving group, more will be rate of S_N2 reacton

(ii). Unimolecular nucleophilic substitution reaction (S_N1) :

Mechanism : S_N1 in alkyl halides



(3° alkyl halide)

Nucleophilic substitution involves two step process

First step : Slow step involves ionisation to form carbocation. It is a rate determining step

$$R - L \longrightarrow R^+ + L^- \text{ (Slow)}$$

Ionisation is always assisted by the solvent since energy necessary to break the bond is largely recovered by solvantion of R^+ and L^-

Second step : Attack of nucleophile on carbocation to result into product, it is a fast step

$$R^+ + Nu^- \longrightarrow R\text{–}Nu \text{ (fast)}$$

(1) Characteristics of S_N1 reactions :

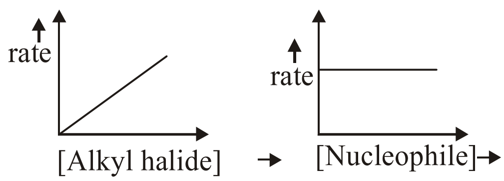
(A) It is unimolecular, two step process.

(B) Carbocation intermediate is formed so rearrangement is possible in S_N1 reaction.

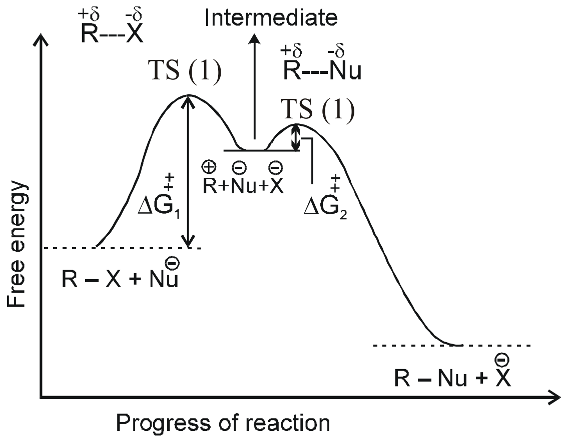
$$\text{Rate} \propto [\text{Alkyl halide}]^1$$

$$\text{Rate} = K\ [\text{Alkyl halide}]^1$$

Rate of S_N1 reaction is independent of concentration and reactivity of nucleophile, i.e., It is first order reaction

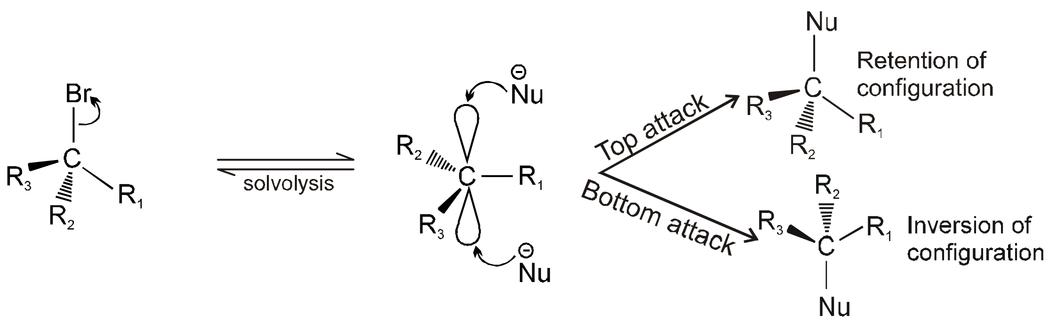


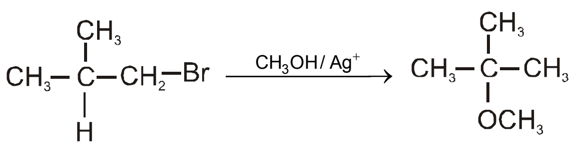
(2). Energetics of the S_N1



(3). Stereochemistry of S_N1 reactions → In the S_N1 mechanism, the carbocation intermediate is sp^2 hybridized and planar, A nucleophile can attack on the carbocation from either face, if reactant is chiral than after attack of nucleophile, from both faces, both enantiomers are fomed as the product, which is called racemisation.

Mechanism of racemisation (S_N1) →

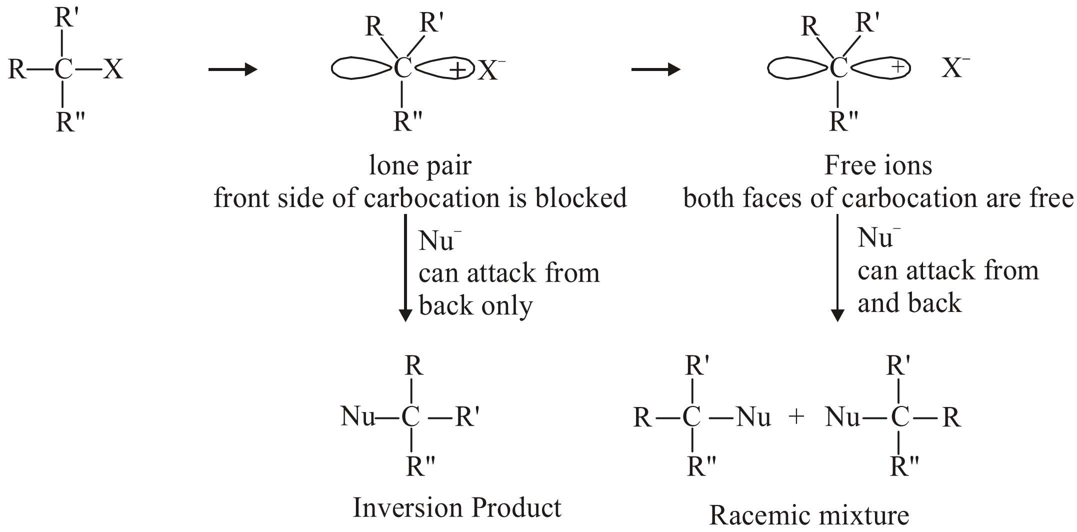




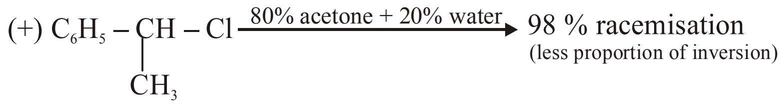
(carbocation rearrangement)

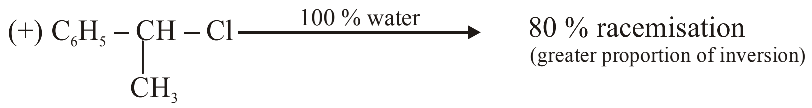
If enantiomers are formed in equal amounts then reaction is said to proceed with complete racemisation. In the case of complete racemisation no optical acivity is detected in the mixture. However, in practice the expected complete racemisation is rarely observed. The products usually consists of more inversion product than retention product.

In most of the case the product has usually of 5-20 % inverted product and 80-95% racemised species. Thus reaction proceed with partial racemisation and some inversion. This may be explained by considering that the attack by a nucleophile occurs before the leaving groups has completely departed from the neighbourhood of the carbocation, thus, to a certain extent the leaving group sheilds the front side of the carbocation from attack. Consequently, the backside attack is preferred to some extent resulting in the inversion of configuration.



The more stable is the carbocation, the greater is the proportion of racemisation. This is because in such cases the leaving group gets time to leave neighbourhood of the carbocation before the attack by a nucleophile occurs, thus, there is almost equal facility for attack from either side of the carbocation plane leading to a greater degree of racemisation. In solvolysis reaction, more nucleophilic is solvent, greater is the proportion of inversion. For example

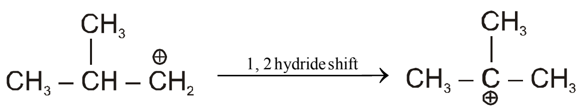


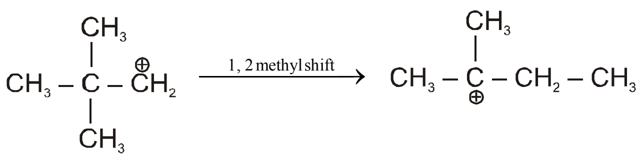


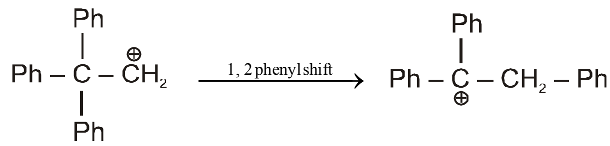
(5) Formation of rearranged products : Since formation of carbocation takes place in S_N1 reaction hence rearrangement of carbocation is possible to form more stable product.

The driving force responsible for carbocation rearrangement is formation of more stable carbocation.

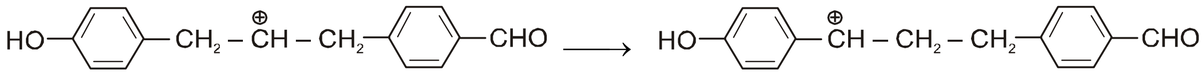
(A) **Carbocation rearrangement by (1, 2) Shifting of H, alkyl, aryl, bond**







$$CH_2 = CH - CH_2 - \overset{\oplus}{C}H_2 \longrightarrow CH_2 = CH - \overset{\oplus}{C}H - CH_3$$

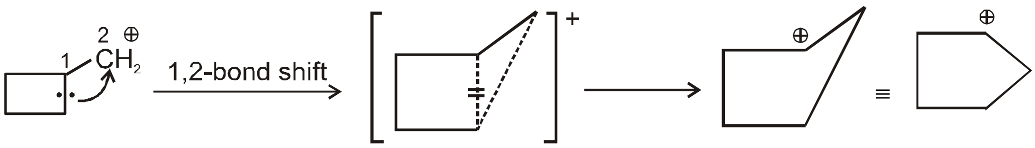


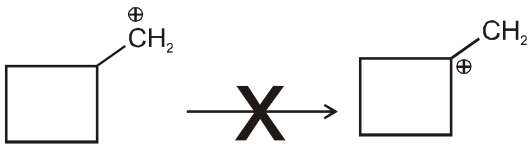
(B) Carbocation rearrangement by Ring expansion

(1) Ring expansion or contraction release angle strain in the ring. Hence it can be observe in following manner :

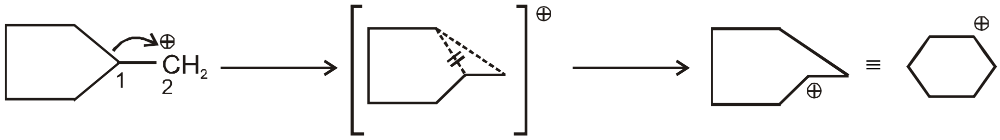
(a) $C_4 \rightarrow C_5$ (b) $C_5 \rightarrow C_6$ (c) $C_7 \rightarrow C_6$

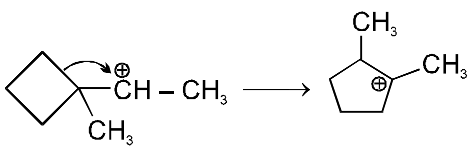
(2)  (Stability order)

(3) (i) 

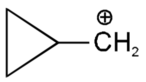


(Angle strain)

(ii) 

(iii) 

One very stable carbocation reported is cyclopropylmethyl carbocation. This unique stabilisation is seen in this case of three member ring only.

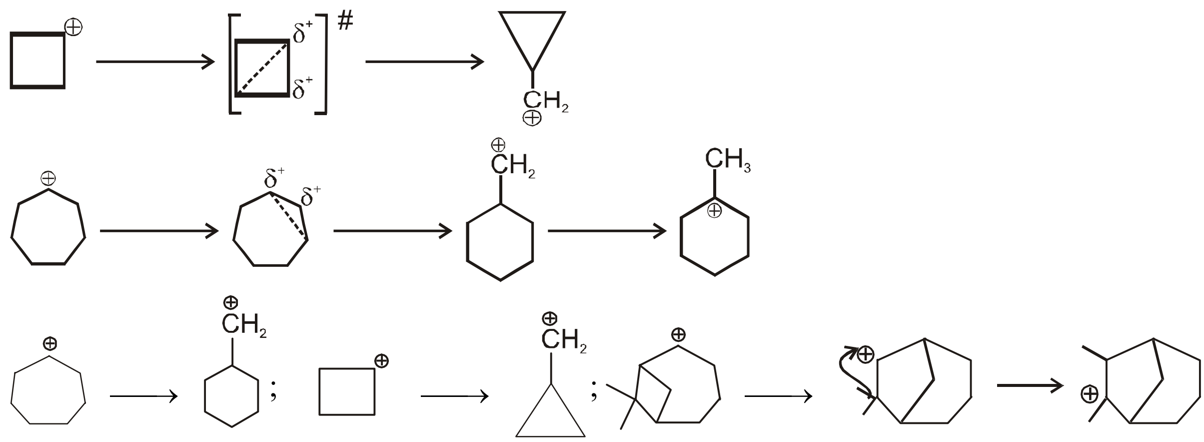


(more stable than Benzyl)

cyclopropyl methyl carbocation

(C) Carbocation rearrangement by Ring contraction

Whenever strained ring such as 4 membered or 7 membered has +ve charge on ring atom contraction may take place.



(6) Factors affecting reactivity in S_N1 reactions :

(A) Effect of substrate structure : Since rds involves formation of carbocation hence all the factors which affect stability of carbocation, will also affect rate of S_N1 reactions.

Decreasing order of reactivity of some substrates in S_N1 reactions

$Ar_3CX > Ar_2CHX > R_3CX > ArCH_2X > CH_2 = CH - CH_2 - X > R_2CHX > RCH_2X$

(a) Unsaturation at the α-carbon: In such cases S_N1 reactions are highly unfavoured because unsaturation at α carbon creates partial double bond character in C–X bond. That's why vinyl halides and aryl halides do not give S_N1 reactions.

(b) Unsaturation at the β-carbon: In such cases S_N1 reactions are highly favoured because formed carbocation is resonance stabilised

(c) Presence of heteroatom at α-carbon: If heteroatom is present at α position then it can stabilize formed carbocation by direct lone pair donation

$CH_3-CH_2-\ddot{\underset{..}{O}}-\overset{\alpha}{C}H_2-X \rightarrow CH_3-CH_2-\ddot{\underset{..}{O}}-\overset{+}{C}H_2+\overline{X}$

(Excellent substrate)

$\updownarrow$

$CH_3-CH_2-\overset{+}{\underset{..}{O}}=CH_2$

Highly stable because all atoms has its complete octet

$CH_3-CH_2-\ddot{N}H-CH_2-X \rightarrow CH_3-CH_2-\ddot{N}H-\overset{+}{C}H_2+X^-$

(Excellent substrate)

$\updownarrow$

$CH_3-CH_2-\overset{+}{N}H=CH_2$

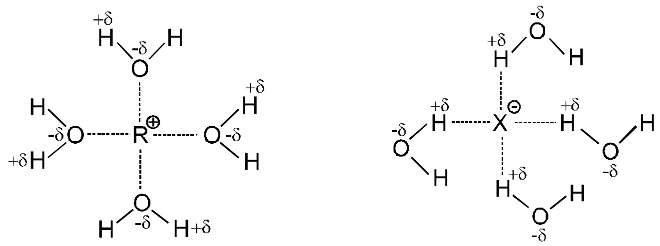
Highly stable because all atoms has its complete octet

(d) Presence of carbonyl group on β-carbon : carbonyl group at β carbon destabilizes carbocation, that's why in such cases S_N1 is not possible.

(e) Substitution effect : Greater is the number of alkyl group at C^+ , more will be stability of formed carbocation. Hence rate of reaction will be faster

(B) Effect of Solvent : Greater is the ionising ability of the solvent more will be rate of S_N1. Because to solvate cations and anions so effectively the use of a polar protic solvent will greatly increase the rate of ionisation of an alkyl halide in any S_N1 reaction. It does this because solvation stabilises the transition state leading to the intermediate carbocation and halide ion more than it does the reactant, thus the energy of activation is lower.

$$R - X \rightleftharpoons \overset{\oplus}{R} + \overset{\ominus}{X} \quad \text{(Solvolysis)}$$



Solvated ions

Table - : Dielectric constants (∈) and ionisation rates of t-Butylchloride in common solvents

Solvent	∈	**Relative rate**
H_2O	80	8000
CH_3OH	33	1000
C_2H_5OH	24	200
$(CH_3)_2CO$	21	1
CH_3CO_2H	6	–

(C) Effect of leaving group ; In the S_N1 reaction the leaving group begins to acquire a negative charge as the transition state is reached. Stabilisation of this developing negative charge at the leaving group stabilises the transition state and this lowers the free energy of activation and there by increases the rate of reaction. Leaving ability of halogen is $F^- < Cl^- < Br^- < I^-$

Hence greater is the leaving power of leaving group, more will be reactivity of substrate towards S_N1.

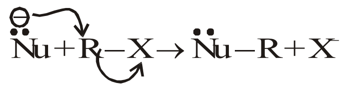
(D) Effect of the attacking nucleophile : RDS does not involve nucleophile or its nucleophilicity. Hence rate of S_N1 reactions are unaffected by the concentration and nature of the nucleophile. Hence neither nucleophile nor its nucleophilicity has any effect on rate of S_N1.

Weak, neutral, mostly solvents (protic) itself functions as nucleophiles in S_N1 reaction. So S_N1 reaction are termed as solvolysis reaction.

water → hydrolysis ; C_2H_5OH → ethanolysis

CH_3COOH → acetolysis ; NH_3 → ammonolysis

Some S_N reactions of alkyl halide →



KEY POINT

(1) When base is weak but strongly nucleophilic toward carbon, then $E2/S_N2$ ratio is low but in the presence of strong base the $E2/S_N2$ ratio increases.

(2) Rate of reaction increases as temperature increases. Thus the $E2/S_N2$ ratio will increase with the increasing temperature.

EXAMPLES

1. The elimination of HX from an alkyl halide forms an alkene. The order of the elimination reaction is -

(A) 3º halide > 2º halides > 1º halides

(B) 1º halide > 2º halides >3º halides

(C) 1º halide = 2º halides > 3º halides

(D) 2º halide > 1º halides > 3º halides

2. A strong solution of alcoholic alkali will preferentially promote alkyl halide into an alkene by-

(A) Addition (B) Elimination

(C) Polymerisation (D) Substitution

3. In the following reaction

$CH_3CH_2CHBrCH_3 + (CH_3)_3COK \longrightarrow$ the major product is-

(A) $CH_3CH_2CH(OC(CH_3)_3)CH_3$ (B) $CH_3CH_2CH(OH)CH_3$

(C) $CH_3CH_2CH{=}CH_2$ (D) $CH_3CH{=}CHCH_3$

4. The ease of dehydrohalogenation with alcoholic KOH in case of chloroethane (I), 2-chloropropane(II), 2-chloro- 2-methylpropane (III) is of the order -

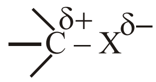
(A) III > II > I (B) I > II > III

(C) II > I > III (D) I > III > II

VIII. NUCLEOPHILIC SUBSTITUTION REACTION (S_N)

Nature of C – X bond

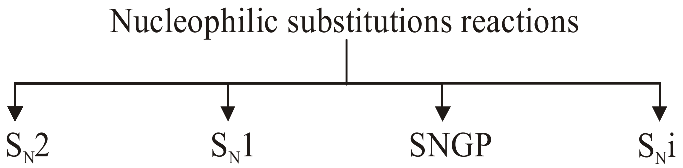
Since halogen atoms are more electronagtive than carbon, the carbon halogen bond or alkyl halide is polarised, the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge.



Replacement (displacement) of an atom or group by an other atom or group in molecule is known as substitution reaction. If substitution reaction is brought about by a nucleophile then it is known as nucleophilic substitution reaction. Generally substitution takes place at sp^3 carbon.

$$R–L + Nu^- \longrightarrow R – Nu + L^- \qquad (L – \text{leaving group})$$

Nucleophilic substitution reactions can be classified as following :



(i). Bimolecular nucleophilic substitution reaction (S_N2)

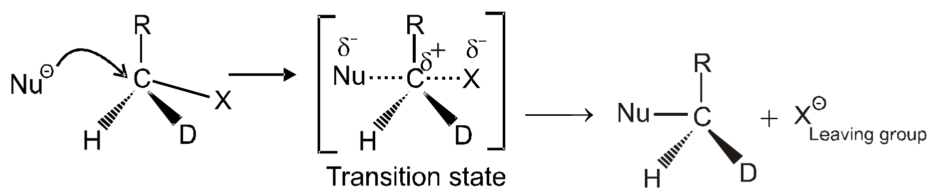
Nucleophilic substitution in which incoming group replaces leaving group in one step only.

Reaction does not involve formation of any intermediate.

S_N2 Reaction of Alkyl halide :

$$R – X + Nu^- \rightarrow R – Nu + X^-$$

Mechanism :



(1) Characteristics of S_N2 reactions

(A). Nucleophile attacks on the substrate from just opposite side to the leaving group.

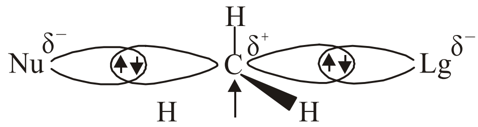
(B) Hybridisation of the cation at which substitution occurs changes from sp^3 to sp^2 in the transition state

(C) It is bimolecular, one step concerted process

$$\text{rate} \propto [\text{alkyl halide}]\ [\text{nucleophile}]$$

$$\text{rate} = k[\text{alkyl halide}]\ [\text{nucleophile}]$$

(D) Transition state has following structure



(Pentacordinated carbon
in sp2 hybridised state)

Bond with nucleophile and leaving group are relatively long and weak in transition state

(2) Energetics of the reaction :

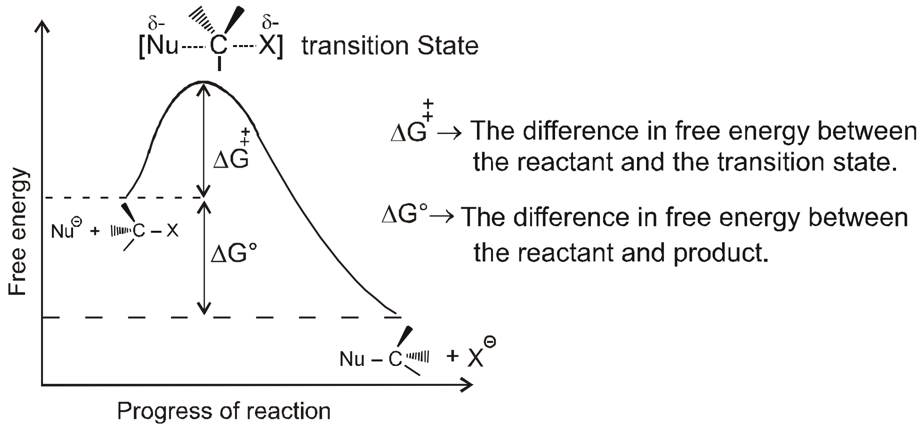
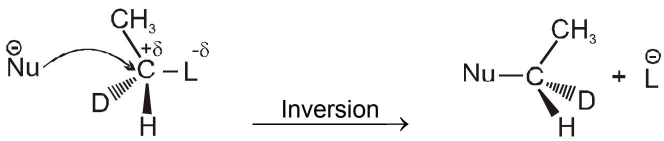


Figure : A free energy diagrams for S_N2 reaction

No intermediates are formed in S_N2 reaction, the reaction proceeds through the formation of an unstable arrangment of atoms or group called transition state.

(3). The stereochemistry of S_N2 reactions → In S_N2 mechanism the nucleophile attacks from the back side, that is from the side directly opposite to the leaving group. This mode of attack causes an inversion of configuration at the carbon atom that is the target of nucleophilic attack. This inversion is also known as **Walden inversion**.



It is always not necessary that absolute configuration will change. Absolute configuration will invert when both incoming nucleophile and leaving group have same priority according to C.I.P rule

(4) Factor's affecting the rate of S_N2 reaction

Number of factors affect the relative rate of S_N2 reaction, the most important factors are

(A) Effect of substrate structure

(a) Alkyl groups at the α and β carbons : Since S_N2 reaction are very sensitive to steric hinderance, hence if alkyl groups are present at α and β carbon, then they will increase steric crowding that leads to decrement in rate of reaction.

Reactivity order towards S_N2 reaction

$CH_3 - X$ > 1° alkyl halide > 2° alkyl halide >> 3° alkyl halide (unreactive)

The important reason behind this order of reactivity is a steric effect. Very large and bulky groups can often hinder the formation of the required transition state and crowding raises the energy of the transition state and slows down reaction.

Relative rate of reactions of alkyl halide in S_N2 reaction.

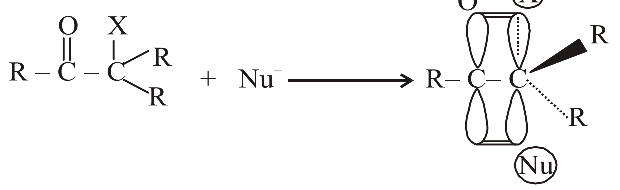
Substituent	Compound	Relative rate
Methyl	CH_3X	30
1°	CH_3CH_2X	1
2°	$(CH_3)_2CHX$	0.02
Neopentyl	$(CH_3)_3CCH_2X$	0.00001
3°	$(CH_3)_3CX$	~ 0

(b) Presence of unsaturation on β carbons : Presence of unsaturation on β carbon in primary alkyl halide increases rate of S_N2 , that's why allyl halide and benzyl halides are good substrate for S_N2

(c) Presence of hetero atom on α carbon : Lone pair present on hetero atom stabilizes transition state by delocalization. Hence rate of reaction increases.

(d) Presence of carbonyl group at β carbon : Presence of carbonyl group at α -carbon makes a substrate favourable for S_N2 reactions it is due to p-orbitals on carbonyl group are parallel to the p-orbital in S_N2 transition state. In such cases reaction will be exceptionally faster A comparison of rate of relations towards S_N2

Substrate	$CH_3 - X$	$CH_2 = CH - CH_2 - X$	$C_6H_5 - CH_2 - X$	$CH_3 - O - CH_2 - X$	$C_6H_5 - C(=O) - CH_2X$
Relative rate	200	79	200	920	10^5



[Transition state]
Stabilisation of the transition state by p-orbital of the CO group

(B) Concentration and reactivity of the nucleophile

(i) Since nucleophile is involved in expression of rate of S_N2. Hence on increasing concentration of nucleophile, rate of S_N2 increases.

(ii) As nucleophilicity of nucleophile increases rate of S_N2 reaction increases.

(iii) Anionic nucleophiles mostly give S_N2 reaction

some common nucleophiles listed in decreasing order of nucleophilicity in hydroxylic solvent	
Strong nucleophiles :	Moderate nucleophile :
$(CH_3CH_2)_3\ddot{P}$	$Br^{\ominus}$
$-:\ddot{S}H^{\ominus}$	$\ddot{N}H_3$
$I^{\ominus}$	$(CH_3)_2\ddot{S}$
$(CH_3-CH_2)_2\ddot{N}H$	$Cl^{\ominus}$
$-CN^{\ominus}$	$AcO^{\ominus}$
$(CH_3CH_2)_3\ddot{N}$	Weak nucleophile :
$HO^{\ominus}$	$F^{\ominus}$
$CH_3O^{\ominus}$	H_2O
	CH_3OH

(C) The effect of the solvent : Polar aprotic solvent have crowded positive centre, so they do not solvate the anion appreciably therefore the rate of S_N2 reactions increased when they are carried out in polar aprotic solvent.

Solvent	Dielectric Constant	Relative Rate
CH_3OH	32.6	1
DMSO	48.9	1300
N, N -Dimethyl -formamide	37.5	2800
Acetonitrile	36.7	5000

X. PREPARATION OF ALKYL HALIDE

(i). By direct halogenation of alkanes :

$$R-H \xrightarrow{X_2/hv} R-X+HX$$

Reactivity of above reaction with respect to type of hydrogen to be replaced follows given order

Tertiary hydrogen > Secondary hydrogen > Primary hydrogen

As far as the reactivity of halogen is concerned, 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 into I_2.

(ii). By the addition of H—X on alkenes :

Alkyl chlorides, bromides and iodides can be prepared by treating an alkene with corresponding halogen acid (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^-.

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

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.

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

(iii). By Alcohols :

(a) By the action of hydrogen halides :

Example : $R—CH_2—OH \xrightarrow[ZnCl_2]{H-X} RCH_2—X$

Mechanism :

$$R—CH_2—\ddot{O}H \underset{(H—X)}{\overset{H^+}{\rightleftharpoons}} \underset{\text{(unstable)}}{R—CH_2—\underset{\underset{H}{|}}{\overset{\oplus}{O}}—H} \xrightarrow{-H_2O} R—\overset{\oplus}{C}H_2 \xrightarrow{X^{\ominus}} \underset{\text{(Product)}}{R—CH_2—X}$$

In this reaction intermidiate carbocation is formed so rearrangement (H^- shifting or CH_3^- shifting) can take place.

$ZnCl_2$ act as dehydrating agent and absorbs H_2O from the reaction so good yield of halide is obtained. Also it generates H^+ from HCl.

$$HCl + ZnCl_2 \longrightarrow ZnCl_3^{\ominus} + H^{\oplus}$$

Reactivity order for alcohol :

| Reactivity ∝ stability of intermediate carbocation | , so reactivity order : **Tert. alc. > Sec. alc. > Pri. alc.**

Reactivity order of H—X is : **HI > HBr > HCl**

HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.

$$R—OH + HI \longrightarrow R—I + H_2O$$

HCl and also 1° alcohol are less reactive so $ZnCl_2$ or some amount of H_2SO_4 is needed to increase the reactivity.

Example : $CH_3—CH_2—OH + HCl \xrightarrow{ZnCl_2} CH_3—CH_2—Cl$

At normal condition :

$$CH_3—CH_2—OH + HCl \longrightarrow \times \text{ (no reaction)}$$

Note : $HCl + ZnCl_2$ is called as **lucas reagent,** alchol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to give turbidity	in 30 min.	in 5-10 min.	Immediate

(b) By the action of phosphorus halides :

$$R-OH+PCl_5 \longrightarrow R-Cl+POCl_3+HCl$$

$$3R-OH+PCl_3 \longrightarrow 3R-Cl+H_3PO_3$$

$$3R-OH+PBr_3 \longrightarrow 3R-Br+H_3PO_3$$

$$3R-OH+PI_3 \longrightarrow 3R-I+H_3PO_3$$

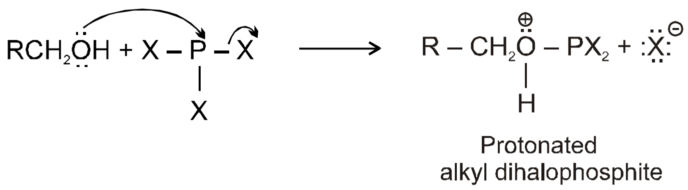
Phosphorous halides are prepared by treating red phosphorous and halogen. The advantage of using phosphorous halides is that the reaction does not involve carbocation intermediate so, it is free from rearrangement.

PBr_3 and PI_3 are less stable, thus for bromides and Iodides, $(P + Br_2)$ Or $(P + I_2)$ mixture is used.

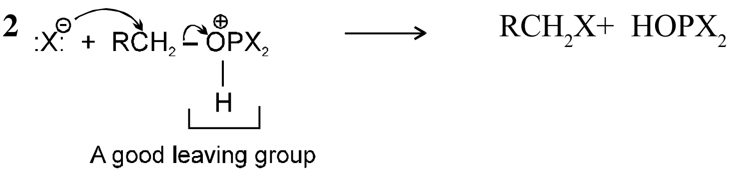
Mechanism for Reaction with phosphorus trihalides

$$3R-OH + PX_3 \xrightarrow{(PX_3 = PCl_3,\ PBr_3,\ PI_3)} 3R-X + H_3PO_3$$

Step : 1



Step : 2



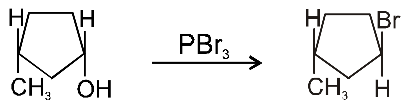
The mechanism for the reaction involves attack of the alcohol group on the phosphorus atom, displacing a halide ion and forming a protonated alkyl dihalophosphite

In second step a halide ion acts as nucleophile to displace $HOPX_2$, a good leaving group due to the electronegative atoms bonded to the phosphorus.

Example
$$\underset{2-\text{Methyl}-1-\text{butanol}}{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-OH} \xrightarrow{PBr_3} \underset{2-\text{Methyl}-1-\text{bromobutane}}{CH_3-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-Br}$$

Example
$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{P + I_2} \underset{\text{Ethyl iodide}}{CH_3CH_2I}$$

Example



(c) By reaction with thionyl chloride - (Darzen's reaction) :

$$R-OH+SOCl_2 \xrightarrow{\text{Pyridine}} R-Cl+SO_2\uparrow +HCl\uparrow$$

The usefulness of this method is that there is not side product, which has to be separated. The side products are gaseous, which escape from the reaction mixture and HCl, which forms a salt with the base (pyridine), named pyridinium chloride ($C_5H_5N^+Cl^-$). The product alkyl chloride has a configuration inverted with respect to the reactant alcohol (if it is chiral) in the presence of pyridine base. In absence of a base and polar solvent, the chiral alcohol gives alkyl chloride with **retention of configuration.**

Williamson Ether Synthesis:

Formation of ether by reaction between alkoxide (R–OX) with substrate.

Alkyl Halide Reaction

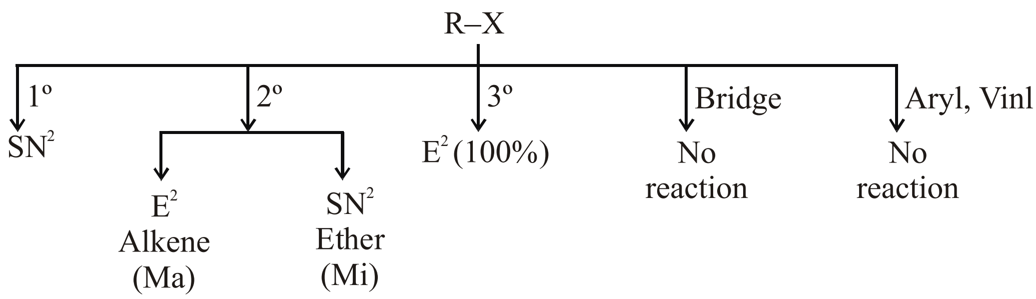
$$RONa+RX \xrightarrow{(SN^2\ \text{mechanism})} R-O-R$$

$RONa + R'–X$ and $R'ONa + R–X$ $\longrightarrow$ R–O–R'

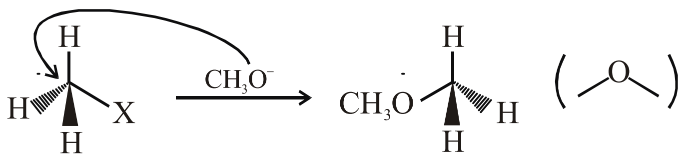
$ArONa + R–X$ and $R–ONa + Ar–X$ $\longrightarrow$ Ar–O–R

Note: (i) It follows SN^2 mechanism

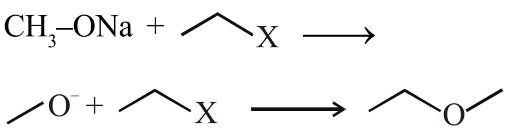
(ii) For Williamson ether synthesis reaction

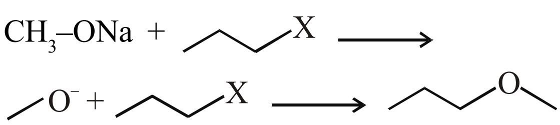


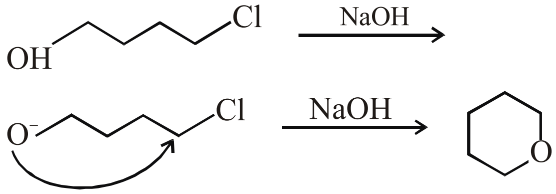
1. $CH_3ONa+CH_3X \longrightarrow$

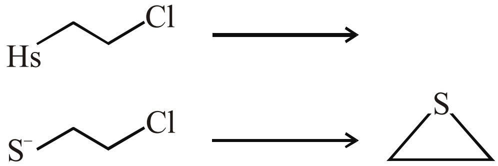


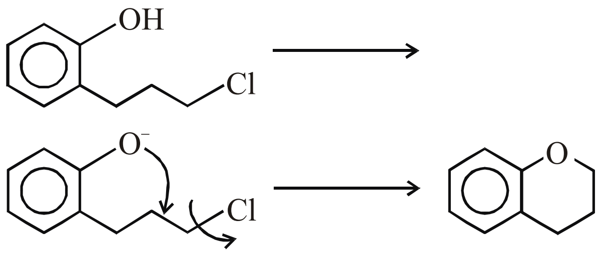
2.

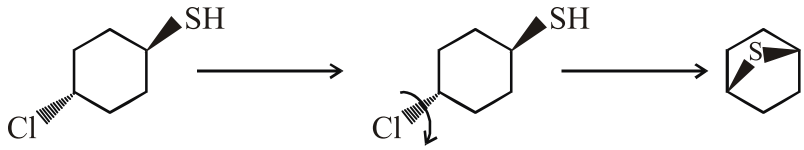


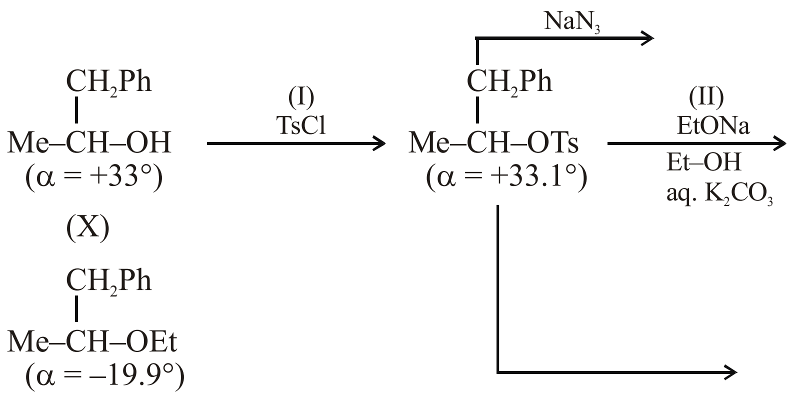
3. 

4. 

5. 

6. 

7. 



$$\underset{(\alpha = +33^\circ)}{\text{Me–}\overset{\overset{\text{CH}_2\text{Ph}}{|}}{\text{CH}}\text{–OH}} \xrightarrow[\text{Na Metal}]{\text{(III)}} \text{Me–}\overset{\overset{\text{PhCH}_2}{|}}{\text{CH}}\text{–ONa} \xrightarrow[\text{CH}_3\text{CH}_2\text{Br}]{\text{(IV)}} \text{Me–}\overset{\overset{\text{CH}_2\text{Ph}}{|}}{\text{CH}}\text{–OEt}$$

This reaction process SN^2 reaction involves bond inversion. In the first step SN^{AE} ($\alpha = +23.5^\circ$) where TsCl makes OH as a leaving group and chiral centre is not disturbed. Similarly in III, chiral centre is not touched as well as in IV and (X) behaves as a nucleophile. Only in II, SN^2 mechanisam takes places which causes bond inversion and thus the product of II which is the inantious of the product of reaction IV has opp signs of angles of rotation.

CLEAVAGE OF ETHER

Reaction of ROR with HI :

(i) $R-O-R \xrightarrow{NaOH}$ No reaction.

Hence ethers are stable in basic medium

(ii) R–O–R + conc. HI $\longrightarrow$ R–OH + RI

or

cold HI

(iii) R–O–R + conc. HI (excess) $\longrightarrow$ 2RI + H_2O

or

Hot HI

(iv) R–O–R + conc. $\longrightarrow$ RI + R'I + H_2O

or

Hot HI

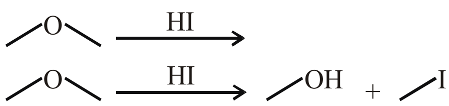
(v) Ar–O–R $\xrightarrow{\text{Cold HI or conc. HI}}$ Ar–OH + RI

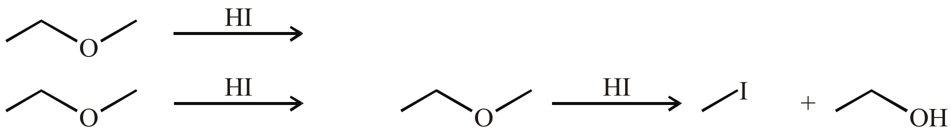
Ar–O–R $\xrightarrow{\text{Hot HI or conc. HI (excess)}}$ Ar–OH + RI

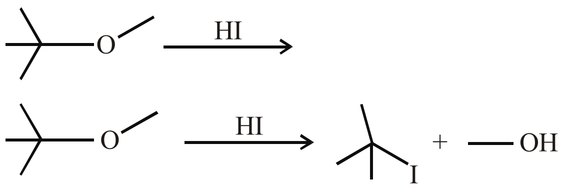
as Ar–X can't be forms by SN^1 and SN^2 on Ar–O

(vi) R–O–R + conc. HI $\longrightarrow$ R–I + R'OH

R–O–R + conc. HI $\longrightarrow$ R'I + R'OH

1. 

2. 

3. 

4. Ph–O–$CH_3 \xrightarrow{HI}$

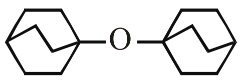
Ph–O–$CH_3 \xrightarrow{HI}$ Ph–OH–CH_3I

5. Ph–O–Ph $\xrightarrow{HI}$ No reaction

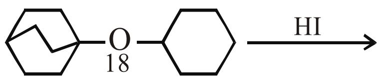
SN^1/SN^2 can't take place in –Ph group.

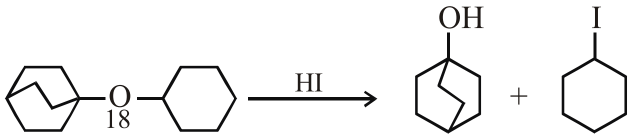
6. Ph–O–  $\xrightarrow{HI}$ No reaction

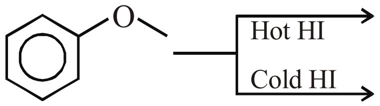
SN^1/SN^2 can't occur at smaller bridgehead.

7.  $\xrightarrow{HI}$ No reaction

SN^1/SN^2 can't occur at smaller bridgehead.

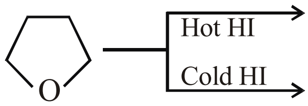
8. 

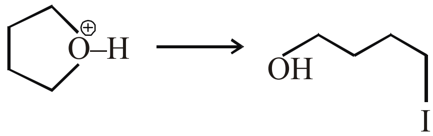


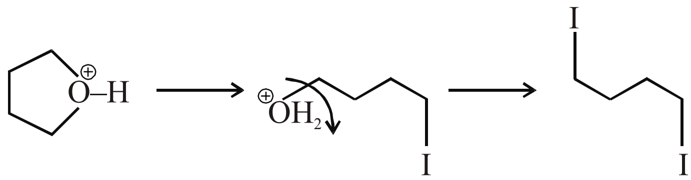
9. 

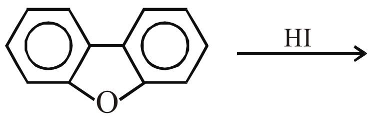
(i) $Ph-O-CH_3 \xrightarrow{\text{cold HI}} Ph-OH+CH_3I$

(ii) $Ph-O-CH_3 \xrightarrow{\text{hot HI}} Ph-OH+CH_3I$

10. 

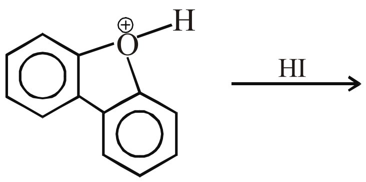
(i) 

(ii) 

11. 

No reaction

SN[1]/SN[2] can't take place at Ph.



No reaction

HYDROLYSIS OF ETHER

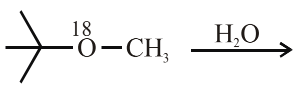
1. $R-O-R \xrightarrow{NaOH/H_2O}$ No reaction.

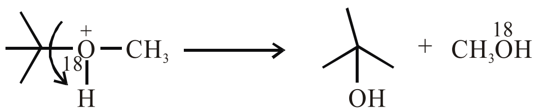
2. $R-O-R \xrightarrow[\text{(or) dil.}H_2SO_4]{H^+/H_2O} 2ROH$

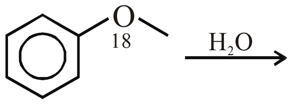
$H_2O+H^+ \longrightarrow OH^- + H_2$

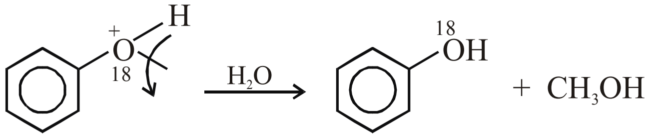
3. $R-O-R \xrightarrow[\text{(or) dil.}H_2SO_4]{H^+/H_2O} R-OH+R'OH$

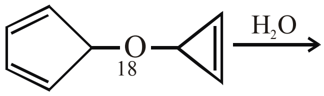
Note : (i) SN[1] mechanism.

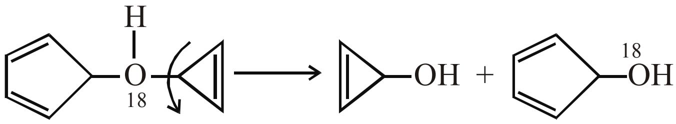
4. 

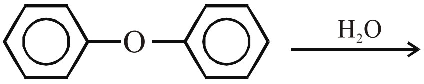


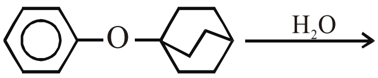
5. 

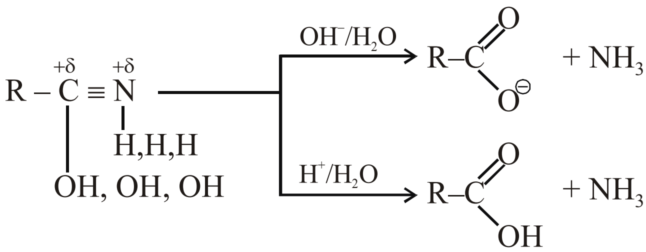


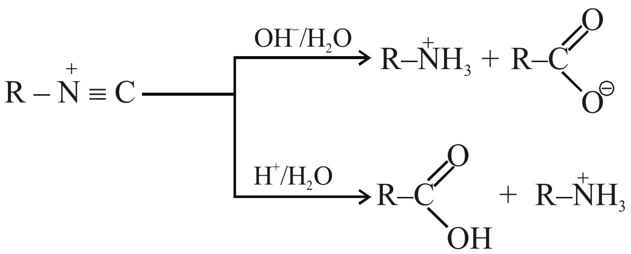
6. 



7.  No reaction as can't appear on benzen or bridgehead.

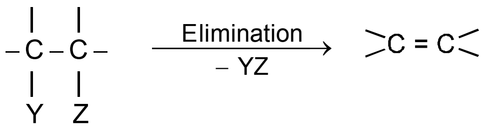
8.  No reaction

9. (a) 

(b) 

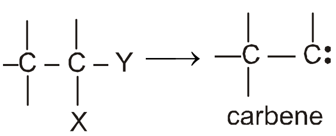
VII. ELIMINATION REACTIONS

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

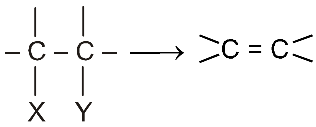


Elimination can be of following types :

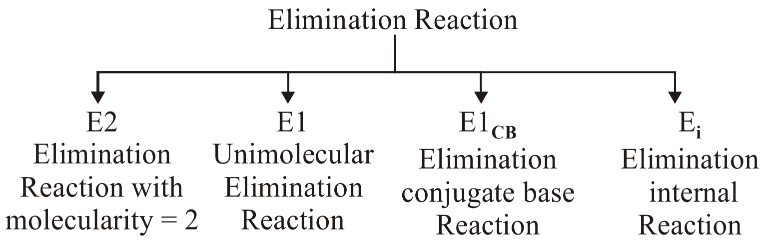
(1) α**-elimination :** When two groups or atoms are lost from the same carbon it is known as α elmination. It gives a carbene (or nitrene). This is also called 1–1 elimination.



(2) β-Elimination : When two groups or atoms are lost from adjacent atoms so that a new π bond is formed. This is also called 1–2 elimination.



Based on mechanism, elimination Reactions can be classified as following :



(i). Bimolecular elimination reaction (E2) :

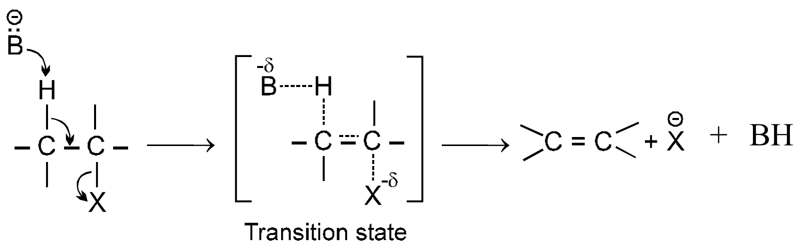
Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene.

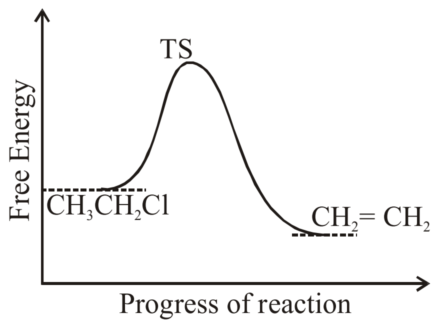
Example : $CH_3CH_2Cl \xrightarrow{\text{Alc.KOH}} CH_2 = CH_2$

Reagent Used :

(i) alcoholic solution of KOH or $EtO^-/EtOH$ (ii) $NaNH_2$ (iii) $t\text{-}BuO^-K^+$ in t-BuOH

Mechanism :





(1) Characteristics of E2 reaction :

(i) This is a single step, bimolecular reaction and follows a concerted mechanism.

(ii) It is a second order reaction and the kinetics of the reaction can be given as

Rate $\propto$ [R – X] [Base] ; Rate = k [R – X] $[\overset{\ominus}{B}]$

(iii) Rearrangment is not possible, since carbocation is not formed.

(iv) The orientation of proton & leaving group should be antiperiplanar, i.e., they should be anti to each other or at the angle of 180 to each other.

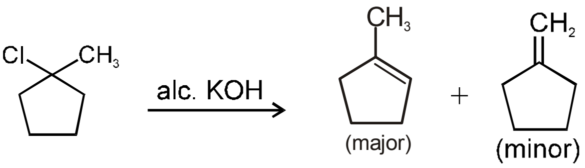
(v) Reactivity order for alkyl halide towards E2 reaction is given as

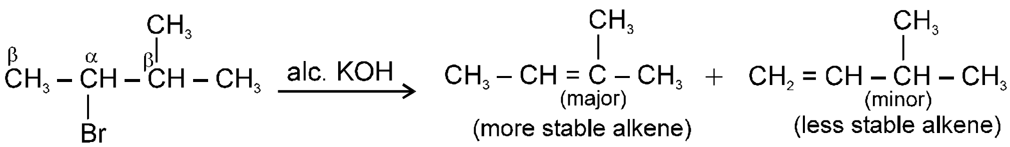
R – I > R – Br > R – Cl > R – F

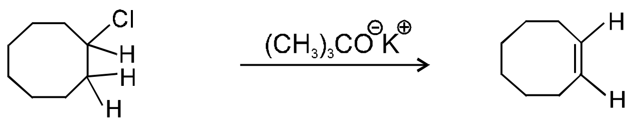
(vi) Positional orientation of elimination → In most E2 eliminations where there are two or more possible elimination products.

(2) Formation of saytzeff product : The product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule.

Example :

(i) 

(ii) 

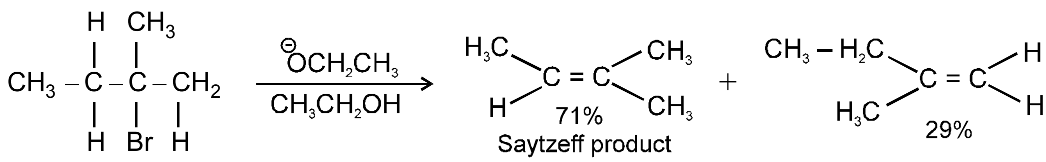
(iii) 

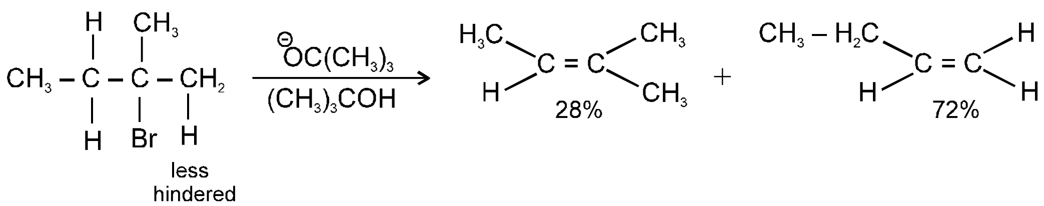
Chlorocyclooctane

Cyclooctene

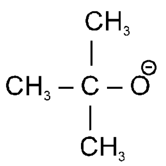
(3) Formation of the Hoffmann product

Bulky bases can also accomplish dehydrohalogenations that do not follow the saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often that leads to formation of least substituted product, called the Hoffmann product.

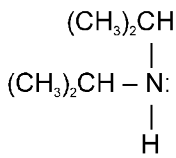




Bulky base :



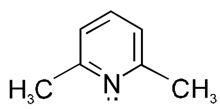
t-Butoxide



Di-isopropylamine

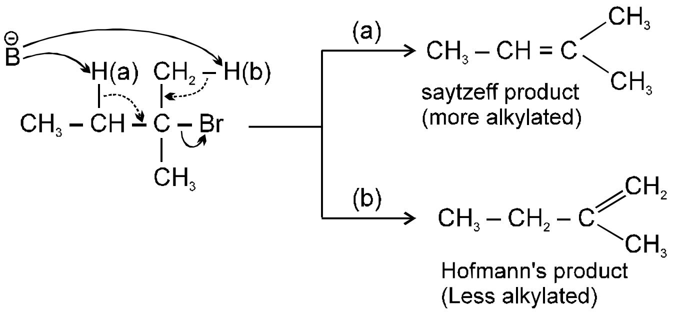
$(CH_3CH_2)_3N:$

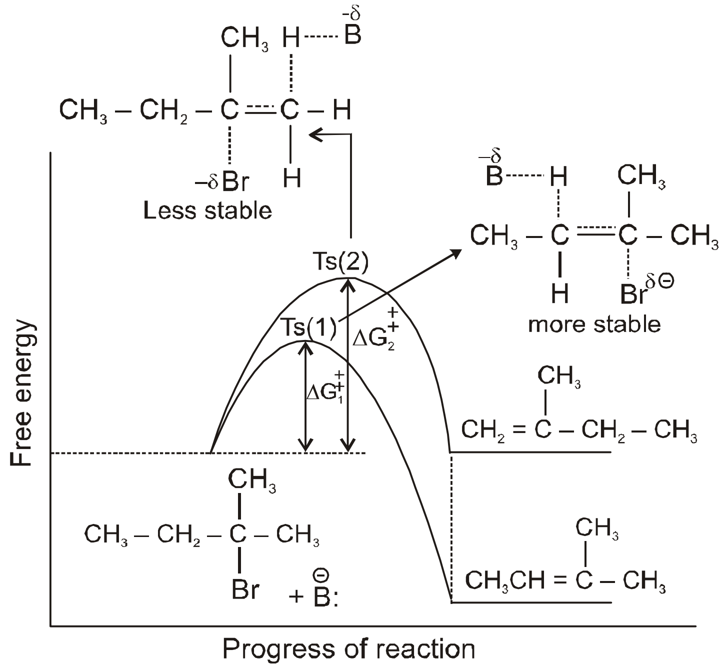
Triethylamine



2, 6-dimethyl pyridine

Example : Dehydrohalogenation of 2-bromo-2-methylbutane can yield two products.



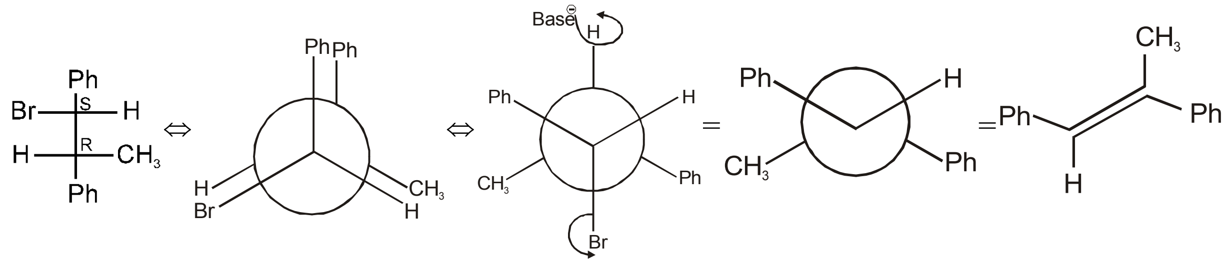


(4) Stereo Chemistry of E2 reactions :

E2 reaction is an example of anti-elimination in which both H and leaving group are antiperiplanar to each other.

The E2 is stereospecific because it normally goes through an anti periplanar transition state. The sterio specific products are alkene. Formation of product in E2 can be explained as following :

Example :



(5) Factors affecting E2 reactions :

(A) Structure of substrate : Branching at α and β carbon increase rate of E2 reaction. As number of substituents increase stability of transition state increases. Hence order of reactivity of alkyl halides towards E2 reaction is 3° > 2° > 1°

(B) Nature of leaving group : Better is the leaving group higher is the rate of E2 reaction

(C) Strength of the base : Since RDS involves base hence increase in basic strength of increase rate of E2.

(D) Nature of solvent : The yield of the product formation in E2 reaction increases with decrease in solvent polarity.

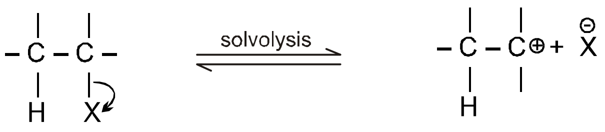
(ii). Unimolecular Elimination Reaction (E1) : Proton and leaving group depart in two different step.

First step : - Slow step involves ionisation to form carbocation

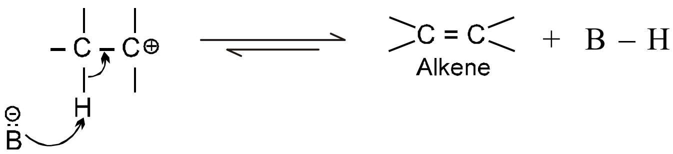
Second step : Abstraction of proton

Mechanism :

Step 1 :



Step 2 :



(1) Characteristics of E1 reaction :

(A) It is unimolecular, two step process.

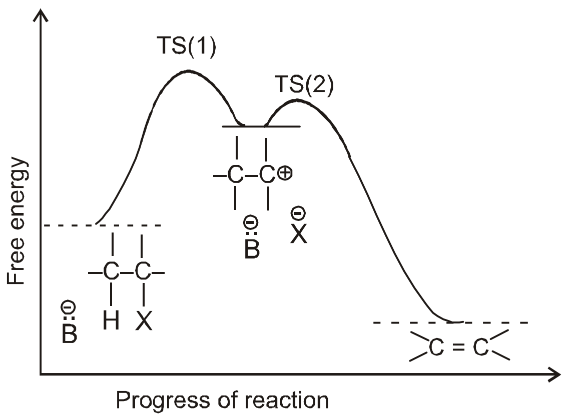
(B) It is a first order reaction.

$$\text{Rate} \propto [\text{Alkylhalide}]^1$$
$$\text{Rate} = k\,[\text{Alkylhalide}]^1$$

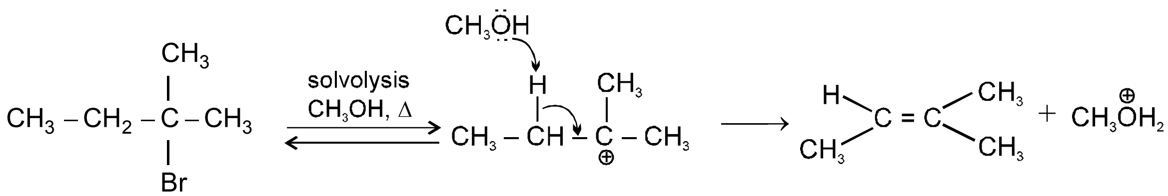
(C) Reaction intermediate is carbocation, so rearrangment is possible

(D) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

(2) Energetics of E1 reaction :



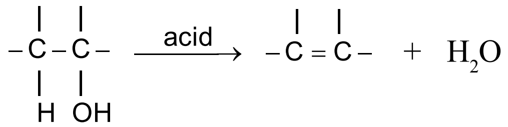
Example :



E1 Reaction of Alcohol :

Dehydration requires an acidic catalyst to protonate the hydroxyl group of the alcohol and convert it to a good leaving group. Loss of water, followed by loss of proton, gives the alkene. An equilibrium is established between reactants and products. For E1 mechanism reagents are

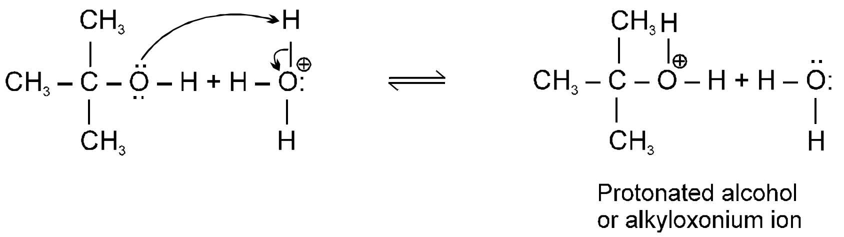
(i) H_3PO_4/Δ (ii) H_2SO_4 / 160º



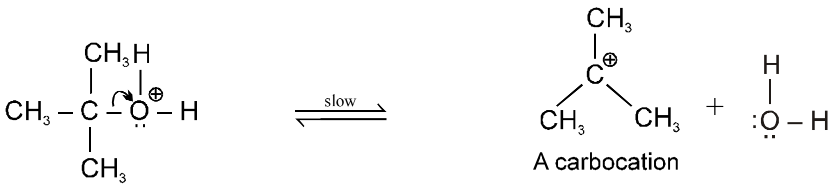
(Rearrangement may occur)

Mechanism :

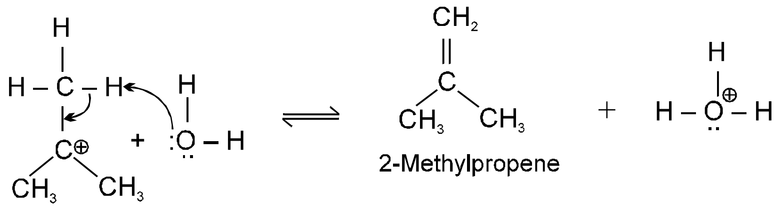
Step 1 :



Step 2 :



Step 3



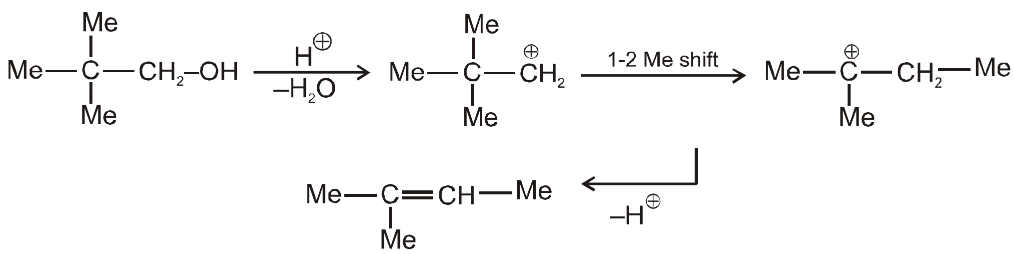
In first step, an acid-base reaction occurs, as a proton rapidly transferred from the acid to one of the unshared electon pairs of oxygen atom of the alcohol.

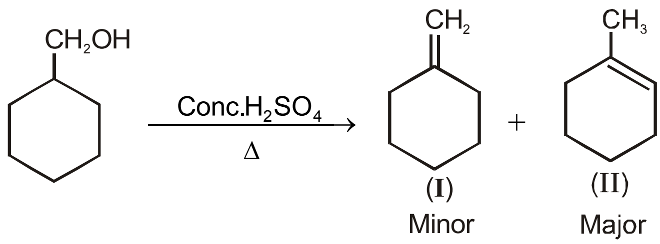
In second step the carbon oxygen bond breaks. The leaving group is molecule of water :

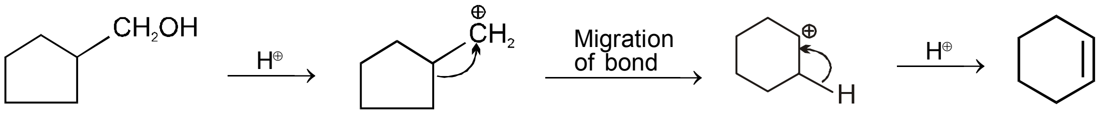
Finally,in third step the carbocation transfers a proton to a molecule of water. The results in the formation of a hydronium ion and an alkene.

Reactivity order of ROH : 3° alcohol > 2° alcohol > 1° alcohol

Example



Example 

Example 

(4) Factors Affecting E1 Elimination Reactions :

(A) Structure of Substrate : Since rate determining step involves formation of carbocation hence order of reactivity will be 3º > 2º > 1º alkyl halide. Alkyl and aryl substitutions on α and β -carbons with respect to the leaving group increase the rate of E1 reactions. As the strain increases the yield of the E1 product increases.

(B) Strength and concentration of the base : Since E1 reactions do not usually required any base in rds on increasing the strength and concentration of the base have nothing to do with rate of reaction

(C) Nature of the leaving group : Better is the leaving group more easier will be formation of carbocation.

(D) Nature of solvent : Greater is the polarity of solvent, more will be rate of E1

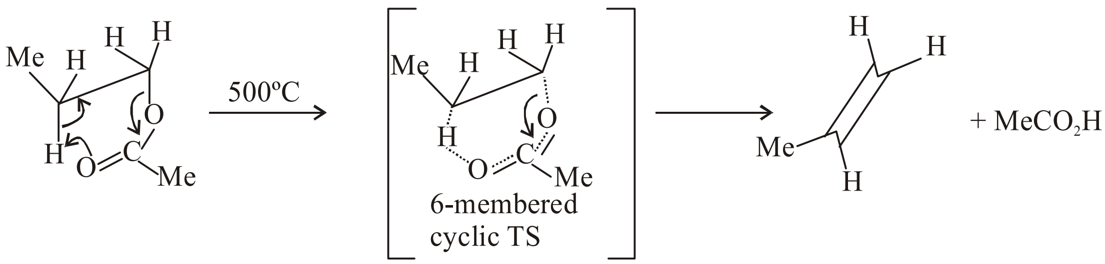
(E) Temperature : With rise in temperature E1/S_N1 ratio rises, as in the elimination process.

(iii). Elimination Internal (Ei) or Pyrolytic Syn-Elimination

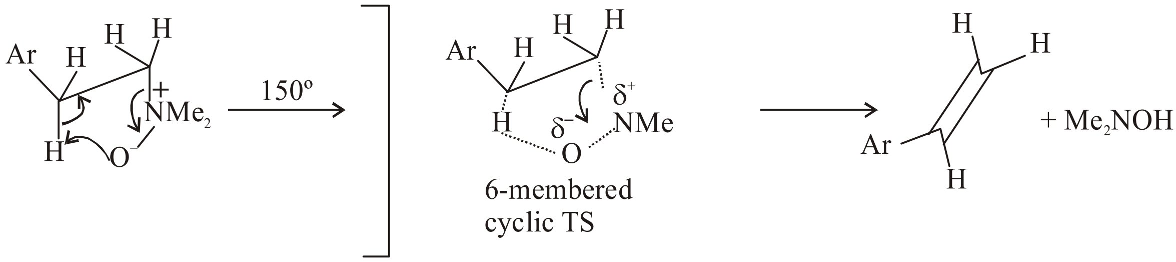
These elimination reaction occur through formation of cyclic transition state involving only one molecule of substrate. These elimination reactions occur within a small family of compounds. Like acetates, amine oxides sulphoxides, xanthates etc.

Example :

(1) Pyrolysis of esters



(2) Cope's reaction :

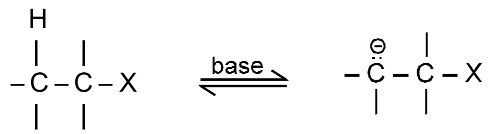


Both of the above reactions take place through formation of 5/6 membered cyclic TS and rate is found to be Rate = k[Substrate]. The reactions are possible because the leaving groups are lying in the same plane and on the same side.The elimination process have synthetic utility in producing terminal unrearranged alkene. The above elimination is thus steroselective.

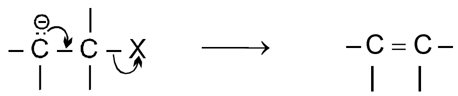
(iv). Unimolecular conjugate base reaction (E1 cB Reaction) :

In the E1 cB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism :

Step 1 : 

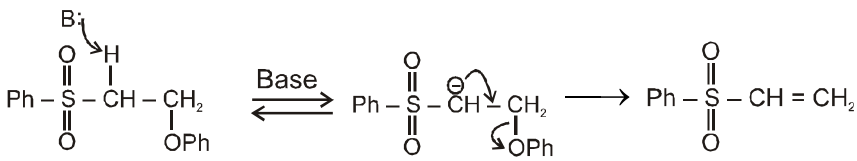
(conjugate base)

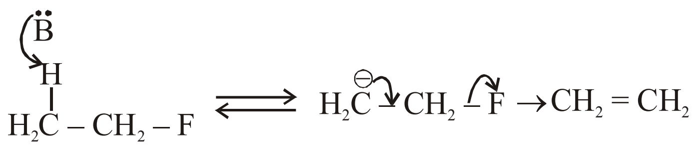
Step 2 : 

First step consists of the removal of a proton, $\overset{\oplus}{H}$, by a base generating a carbanion

In second step carbanion looses a leaving group to form alkene

Condition : For E1 cB, (i) substrate must be containing acidic hydrogens and (ii) poor leaving groups.

(i) 

(ii) 

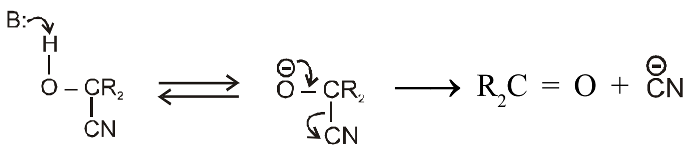
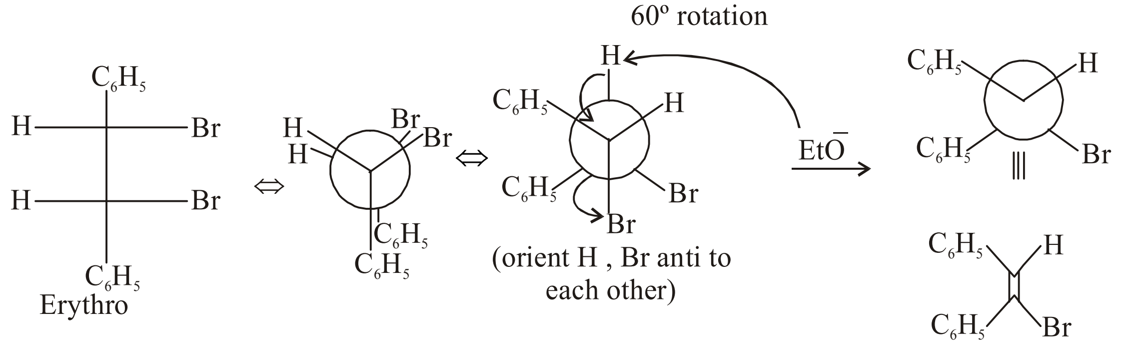
(iii) 

ILLUSTRATION :

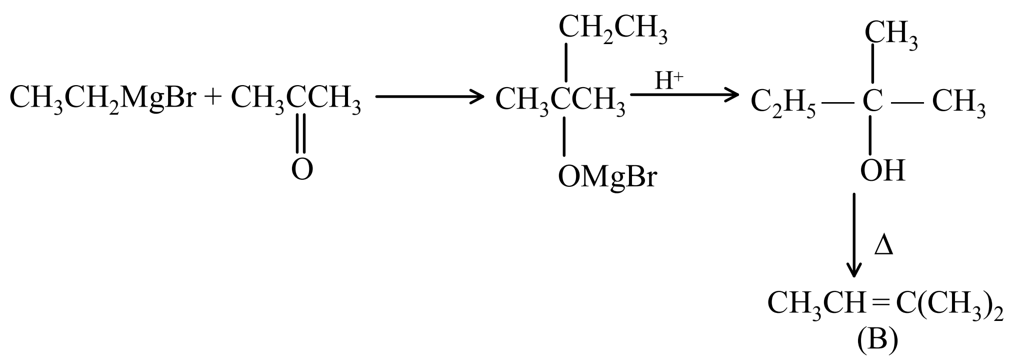
(5)



(6) (A) $\xrightarrow[250°]{Al_2O_3}$. (B) $\xrightarrow[\text{(ii) AgOH}]{\text{(i) HI}}$ (C) $\xrightarrow[150°C]{Al_2O_3}$ (B) $\xrightarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } B_2H_6}$ (A)

(A) and (C) are isomers. (B) has a formula of C_5H_{10} which can also be obtained from the product of reactions of CH_3CH_2MgBr and acetone. Identify (A), (B), and (C).

Solution : (B) [M.F = C_5H_{10}] can be obtained as



Since (B) is formed by heating (A) with Al_2O_3, (A) must be an alcohol. Moreover, (A) and (C) are isomers. Hence

(A) is $CH_3CH(CH_3) - CH(OH)CH_3$; (B) is $CH_3CH = C(CH_3) - CH_3$; (C) is $CH_3 - C(CH_3)(OH) - CH_2CH_3$

FREE RADICALS :

(i) Trivalent

(ii) Incomplete octed

(iii) Odd electron species

(iv) Highly unstable

(v) Highly reactive

(vi) B.P. = 3

(vii) U.P. = 1

(viii) L.P. = 0

(ix) Paramagnetic

(x) sp^2 hybrid, (sp^3 when surrounded by E.N. atom)

(xi) Formes by hommolytic fission

(xii) Formed in gas phase/non-polar solvent

(xiii) Trigonal planar

(xiv) Can be approached from both side. (***)

* Halogen radical are responsible for ozone layer depletion

Stability :

$Ph_3\dot{C} > Ph_2\dot{C}H_2 > Ph\dot{C}H_2 > \dot{C}H_2\text{–}CH\text{=}CH_2 > \dot{3}° > 2° > 1°$

$\dot{C}H_3 > \dot{C}H_2\text{=}CH_2 >$ 

REACTION SHOWN BY RADICAL :

(i) Combination / dimerization

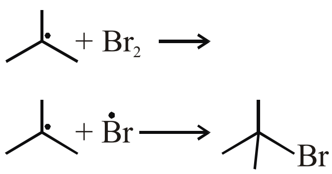
(ii) Elimination / disproportion

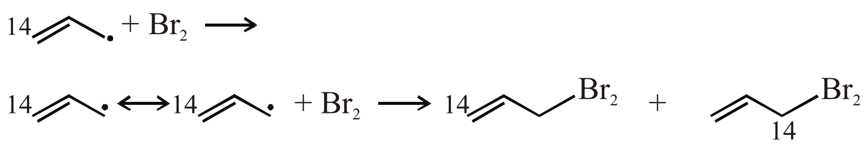
(iii) Rearrangement

1. COMBINATION :

$$\text{rate of combination} \propto \frac{1}{\text{Steric crowding}}$$

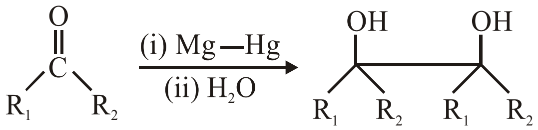
1. $\dot{R} + \dot{C}l \longrightarrow R\text{–}Cl$ or $\dot{R} + Cl_2 \longrightarrow R\text{–}Cl + \dot{C}l$

2. 

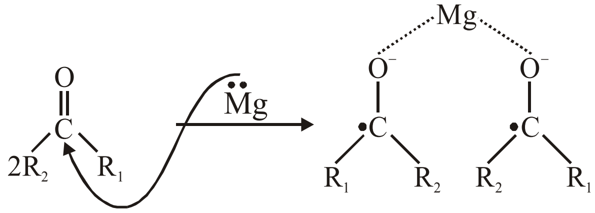
3. 

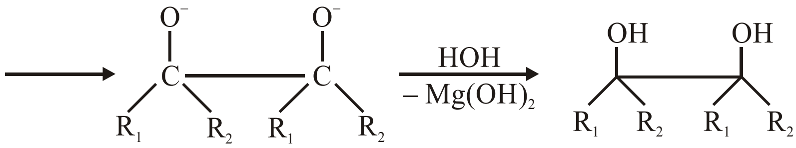
PINACOLE FORMATION :

When Carbonyl are treated with amalgamated magnessium, vicinal diols are obtained as a product followed by hydrolysis.



Mech^n :

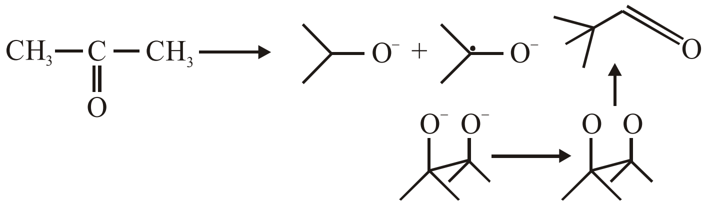




	No. of Pinacole
If $R_1 = R_2$,	1
$R_1 \neq R_2$,	3

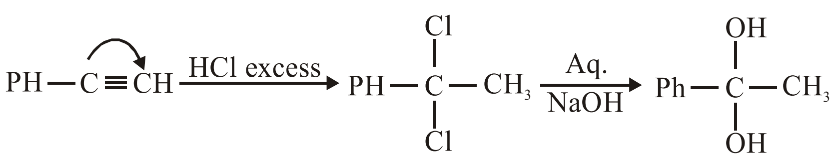
1. $CH_3-C\equiv CH$

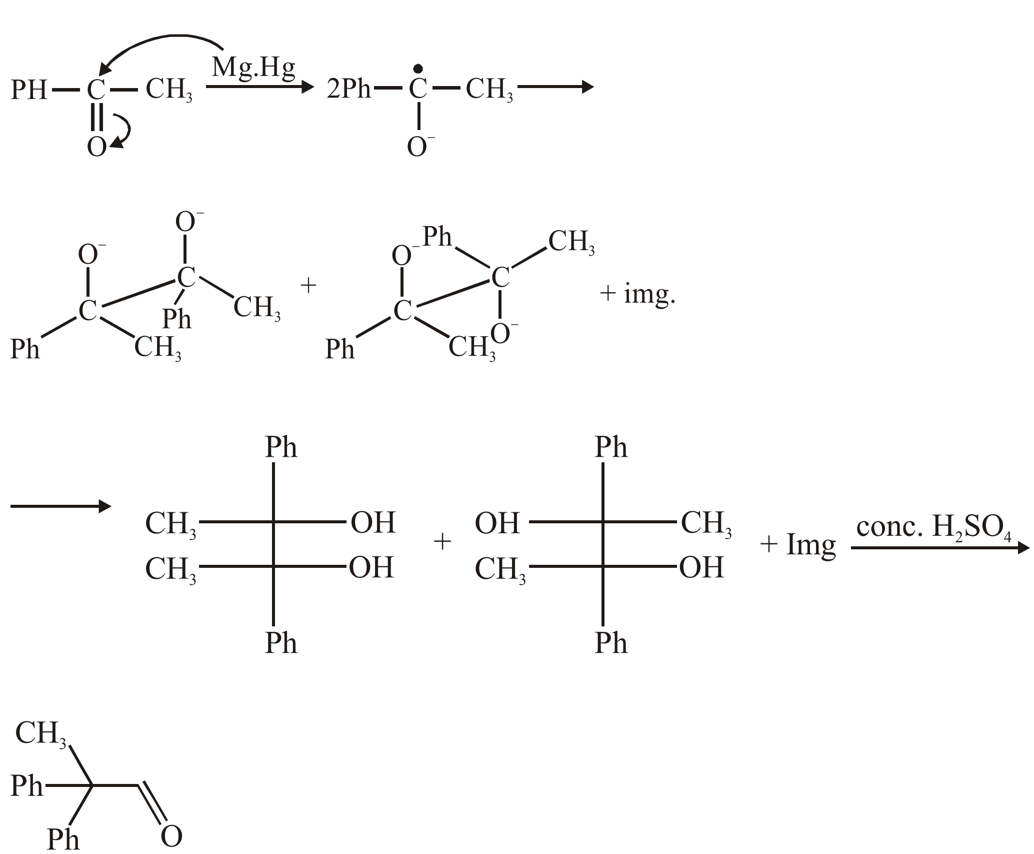
(i) $HgSO_4/H_2SO_4$
(ii) Mg – Hg
(iii) H_2O
(iv) H^+/Δ



2. $PH-C\equiv CH$

(i) HCl (excess)
(ii) Aq. NaOH
(iii) Mg – Hg
(iv) H_2O
(v) Conc. H_2SO_4





WURTZ REACTION :

In this reaction, alkyl halide is treated with sodium metal in dry ether condition so that hydrocarbon alkane is obtained as product.

Mechanisam : $R-Cl \xrightarrow[Et_2O]{Na} R-R$

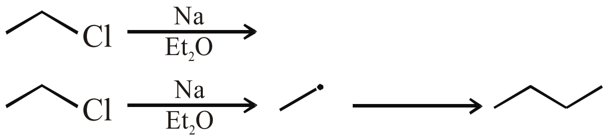
Free radical : $2Na + 2RCl \xrightarrow{r.d.s.} 2\dot{R} + 2NaCl \longrightarrow R–R$

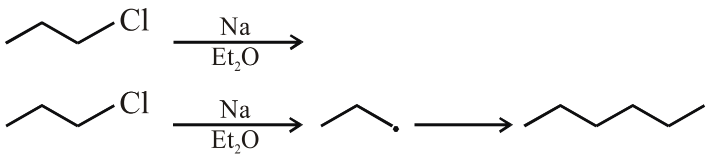
Ionic mechanism : $2Na + R-Cl \xrightarrow{r.d.s.} \overset{\ominus}{R}\,\overset{\oplus}{Na} + NaCl \longrightarrow \overset{\ominus}{R}\,\overset{\oplus}{Na}$

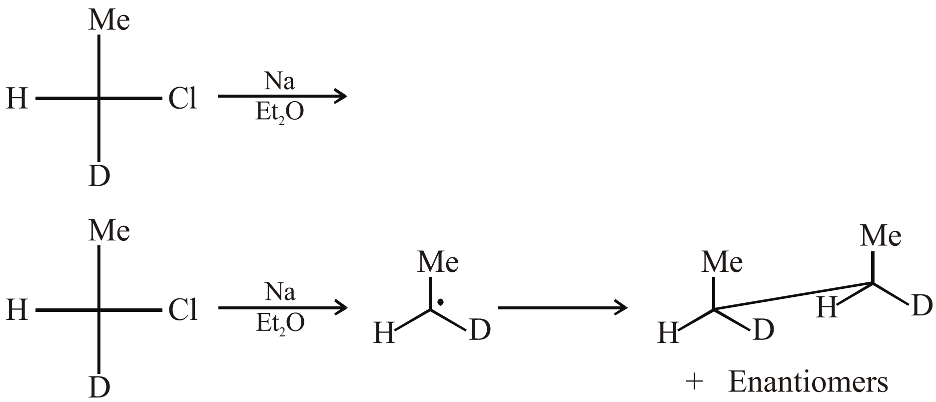
$\overset{\ominus}{R}\,\overset{\oplus}{Na} + R-Cl \xrightarrow{r.d.s.} R–R$

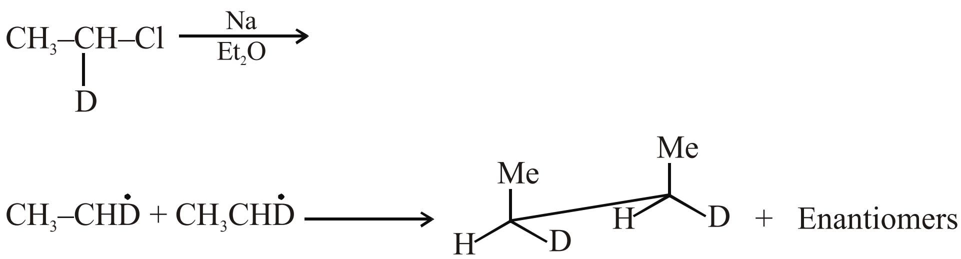
Note :
(i) Free radical and carbanion both are intermediate.
(ii) Order of rate of reaction : RI > RBr > RCl
(iii) CH_4 can't be obtained
(iv) Odd 'C' alkanes not obtained (poor yield)
(v) Dry ether condition required or else Na can take H^+ from OH in water, alcohol.

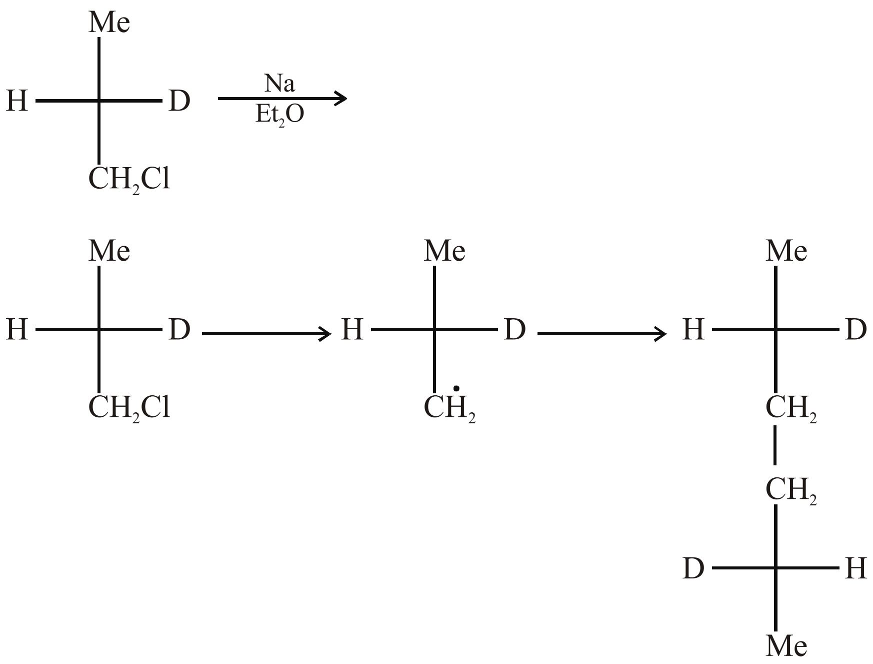
1. $CH_3-Cl \xrightarrow[Et_2O]{Na} CH_3-Cl \longrightarrow \dot{C}H_3 \longrightarrow CH_3-CH_3$

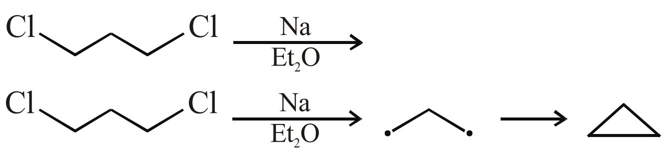
2. 

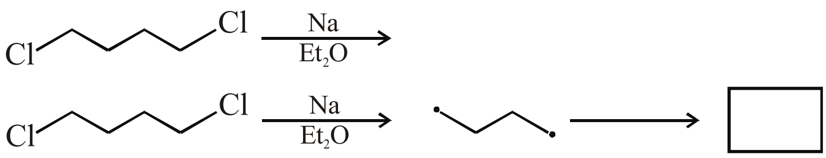
3. 
Cl
Na
Et2O

4. 
Me
H
Cl
D
Na
Et2O
+ Enantiomers

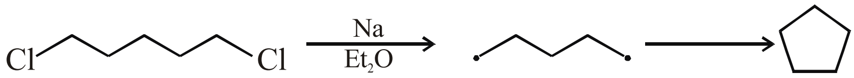
5. 
Na
Et2O
+ Enantiomers

6. 
Na
Et2O

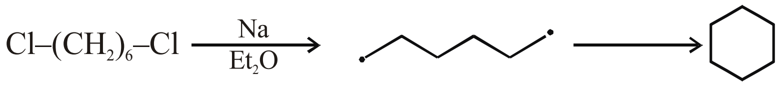
7. 
Cl
Cl
Na
Et2O

8. 
Cl
Cl
Na
Et2O

9. $Cl-(CH_2)_5-Cl \xrightarrow[Et_2O]{Na}$



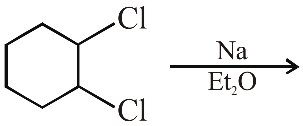
10. $Cl-(CH_2)_6-Cl \xrightarrow[Et_2O]{Na}$

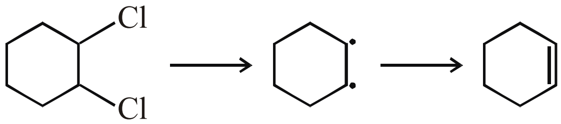


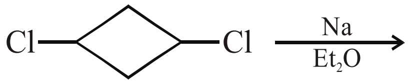
11. $Cl-(CH_2)_7-Cl \xrightarrow[Et_2O]{Na}$

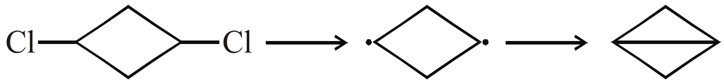
$Cl-(CH_2)_7-Cl \longrightarrow -(CH_2)_n-$ (polymerization)

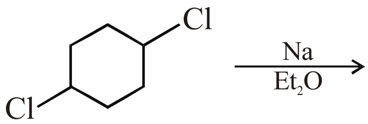
It undergoes polymarization as after seven carbon the terminals are for & ring is unstable.

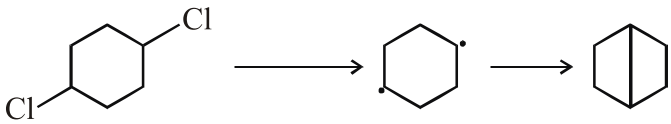
12. 

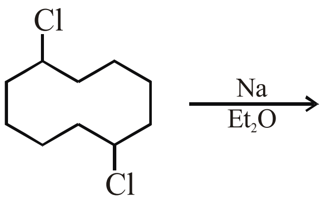


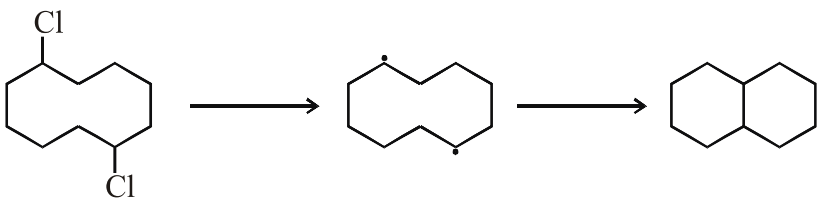
13. 

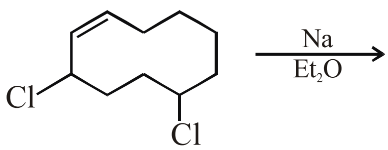


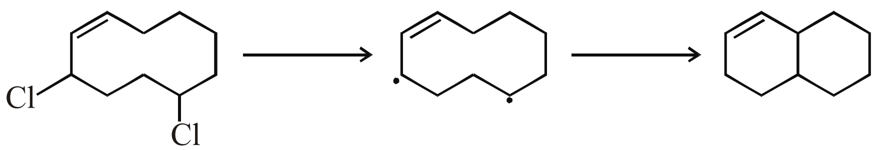
14. 

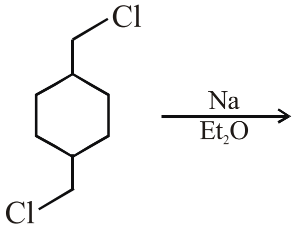


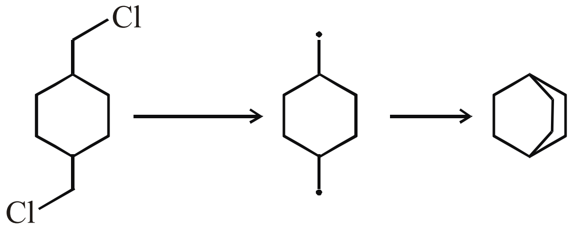
15. 

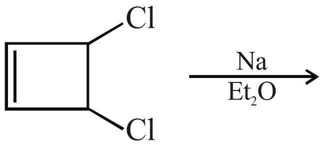


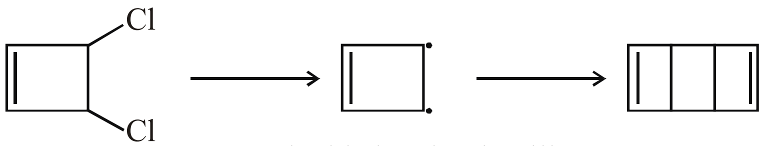
16. 



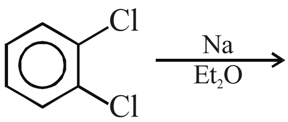
17. 

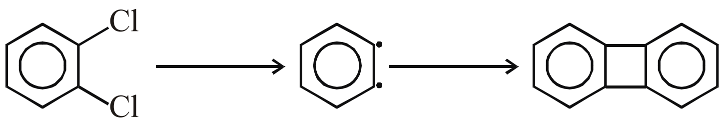


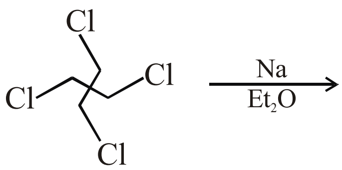
18. 

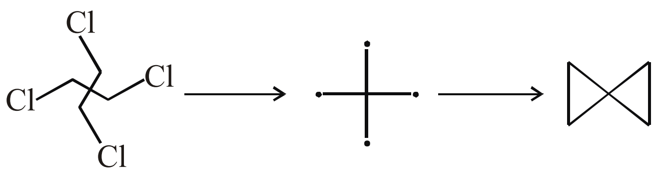


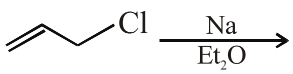
no double bond as it will
become antiaromatic

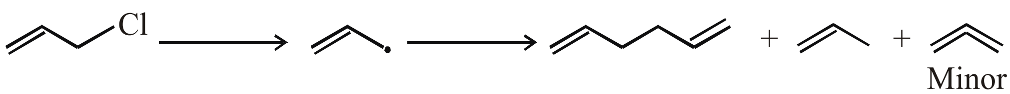
19. 



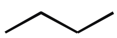
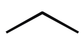
20. 



21. 



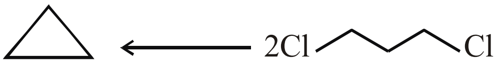
22. $CH_3–Cl + CH_3–CH_2–Cl \xrightarrow[Et_2O]{Na}$

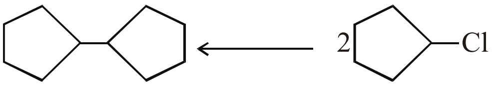
$\dot{C}H_3 + CH_3\dot{C}H_2 \xrightarrow[Et_2O]{Na} CH_4 + CH_3–CH_2 +$  + 

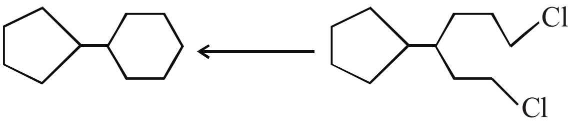
23. Which compound can be obtained in good yield with single reactant in Wurtz reaction ?

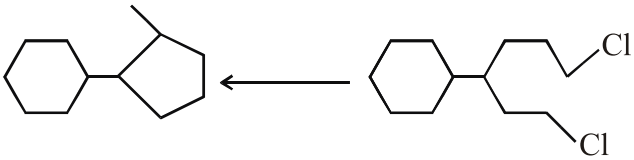
(i) CH_4 – XX

(ii)  – XX

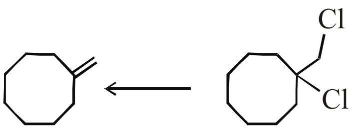
(iii) 

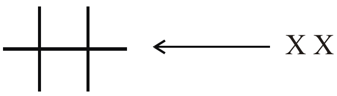
(iv) 

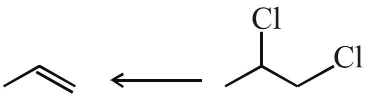
(v) 

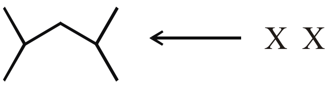
(vi) 

(vii) 

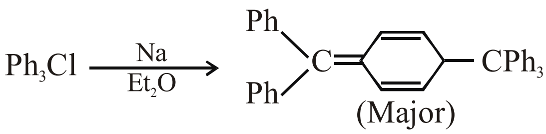
(viii) 

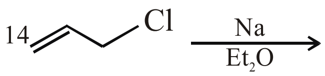
(ix) 

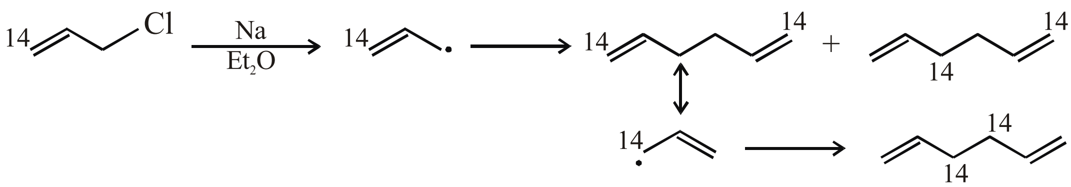
(x) 

(xi) 

24. $Ph_3Cl \xrightarrow[Et_2O]{Na}$



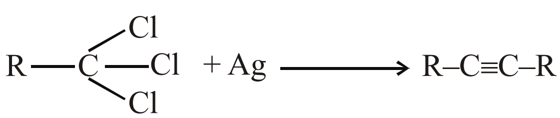
25. 



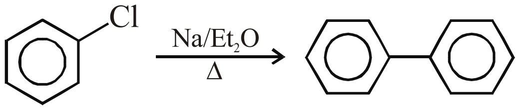
26. $2CHCl_3 + 6Ag \longrightarrow HC\equiv CH + 6AgCl$

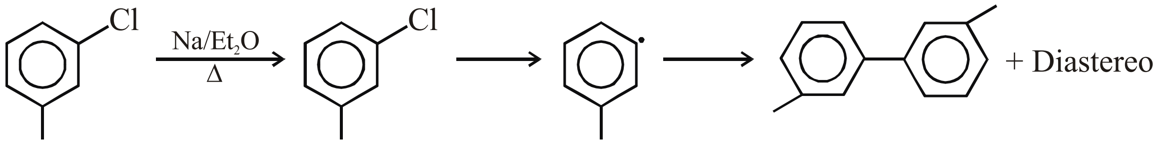
Remove Cl, from radical, form bond

27. $R–CCl_3 + Ag \longrightarrow$

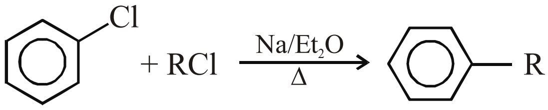


Fitting Reaction (Aryl Halide) :

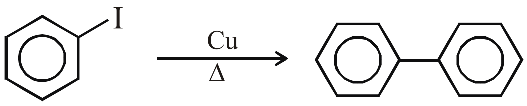
28. 

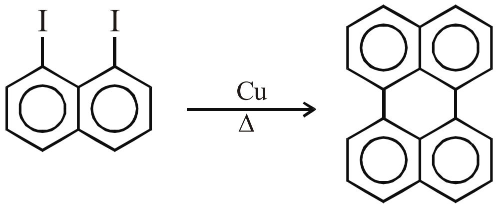
29. 

Wurtz-Fitting Reaction (Alkyl-Aryl) :

30. 

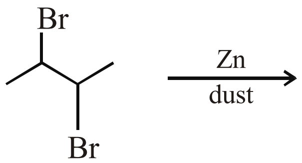
Ullmann Reaction :

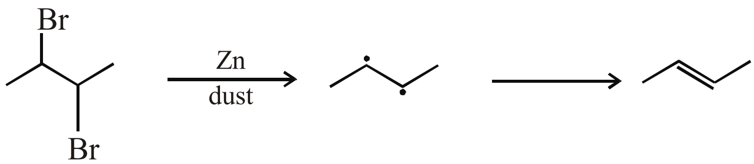
31. 

32. 

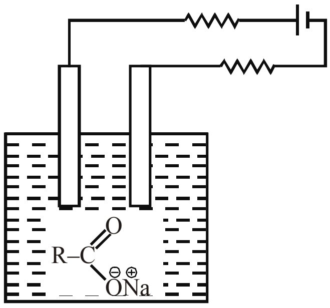
Frankland Reaction :

33. $CH_3-Br \xrightarrow[\text{Dust}]{\text{Zn}} CH_3-CH_3$

34. 



KOLBE'S ELECTROLYSIS :



$$2RCOONa \longrightarrow R\text{–}R + 2CO_2 + 2NaOH + H_2$$

Mechanism :

$$2R-C(=O)-O^{\ominus} \longrightarrow 2R-C(=O)-\dot{O} + 2e^{-}$$

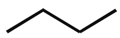
Anode : $$2R-C(=O)-\dot{O} \longrightarrow 2\dot{R} + 2CO_2$$

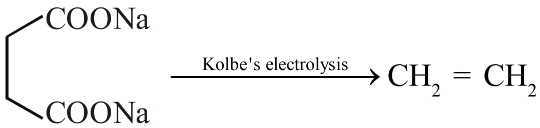
$$\dot{R} + \dot{R} \longrightarrow R-R$$

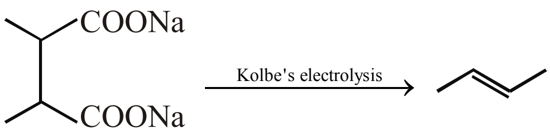
Cathode : $$2HOH + e^{-} \longrightarrow H_2 + 2\overset{\ominus}{O}H$$

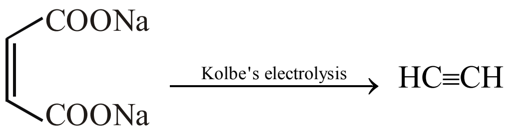
* pH increases as reaction proceeds because NaOH is formed.

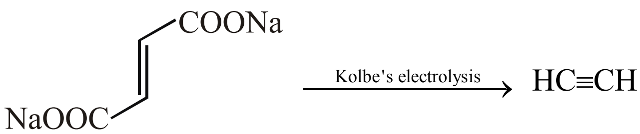
1. aq. $CH_3-COONa \xrightarrow{\text{Kolbe's electrolysis}} CH_3-CH_3$

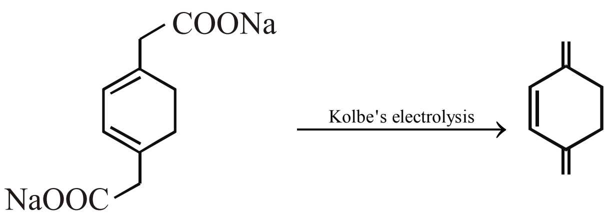
2. aq. $CH_3-CH_2-COONa \xrightarrow{\text{Kolbe's electrolysis}}$ 

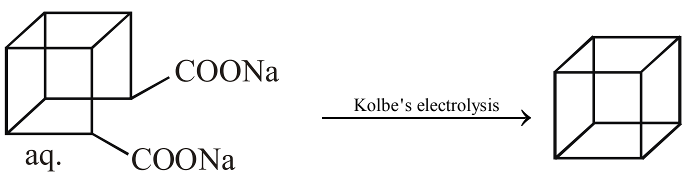
3. aq. 

4. aq. 

5. aq. 

6. aq. 

7. aq. 

8. 

9. $$\begin{array}{l} CH_2-COONa \\ | \\ CH_2-SO_3Na \end{array} \xrightarrow{\text{Kolbe's electrolysis}} CH_2{=}CH_2 + CO_2 + SO_3$$
(aq.) at anode

10. DCOONa (aq.) 1 eq. $\xrightarrow{\text{Kolbe's electrolysis}}$ No. of moles of gases at anode & cathode

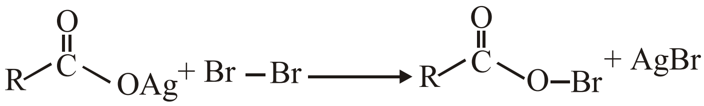
Hint : $2D-\overset{\overset{\large O}{||}}{C}-\overset{\ominus}{O}\overset{\oplus}{Na} \xrightarrow{\text{K.E.}} D_2 + CO_2 + H_2$

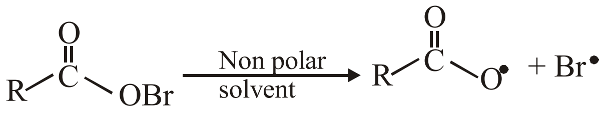
Anode	Cathode
1/2 D_2	1/2 H_2
CO_2	

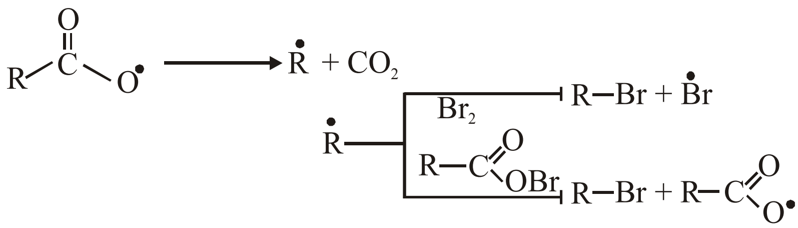
1. **Borodine hunsdiecker reaction.**

Overall reaction

$$R-\overset{\overset{O}{||}}{C}-OAg + Br_2 \xrightarrow{CCl_4} R\text{-}Br + CO_2 + AgBr$$

Mechanisam : 



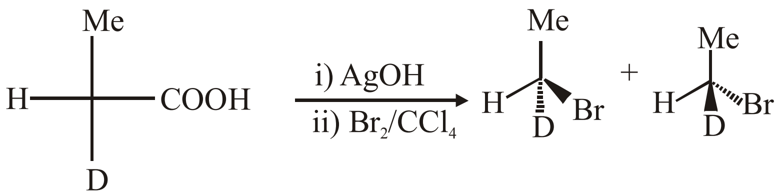


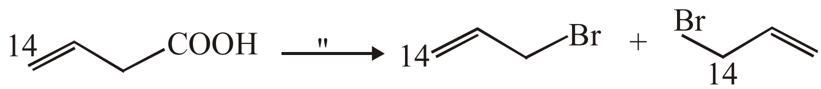
(i) Radical intermediate is involved

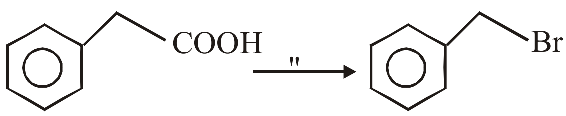
(ii) Degradation (Carbon length reduces) reaction.

(iii) Reaction is BIRNBORN SIMONINI Reaction. If I_2 is taken instead of Br_2, ester is formed.

1. $CH_3-C(=O)-OAg \xrightarrow[CCl_4]{Br_2} CH_3Br$

2. 

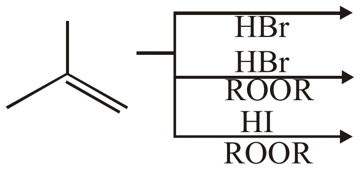
3. 

4. 

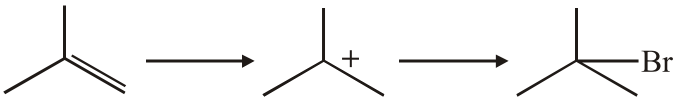
5. $CH_3-\overset{\overset{O}{||}}{C}-OAg \xrightarrow[\text{(ii) } I_2/CCl_4]{\text{(i) AgOH}} CH_3-\overset{\overset{O}{||}}{C}-OCH_3$

Complete the following reaction

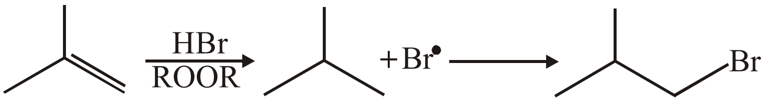
1.



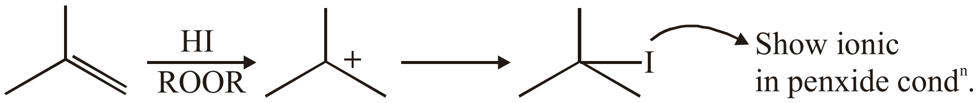
(i)



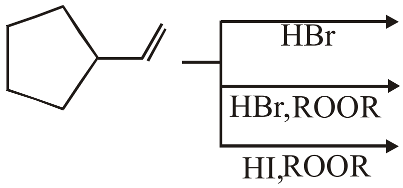
(ii)



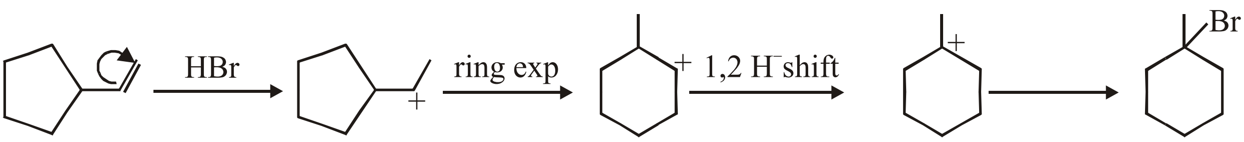
(iii)



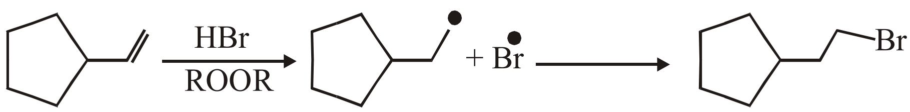
2.



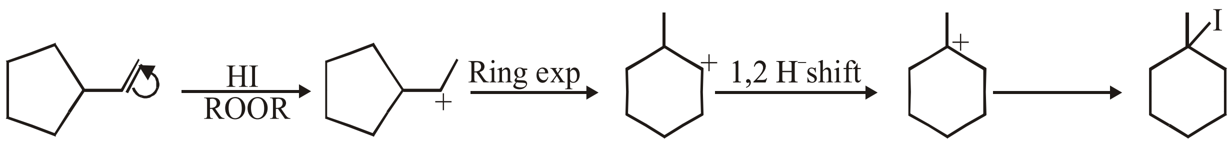
(i)



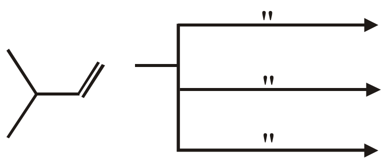
(ii)



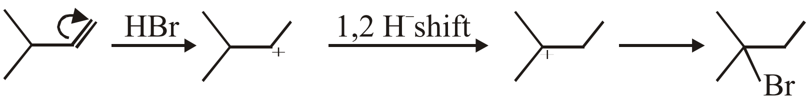
(iii)



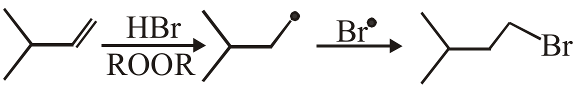
3.



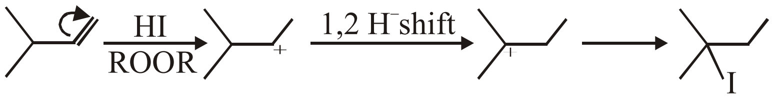
(i)

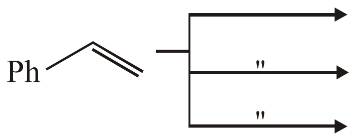


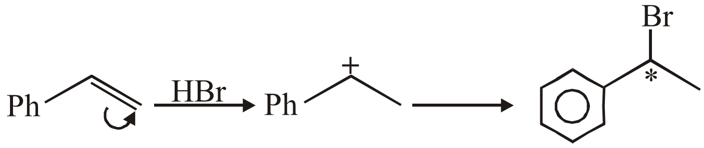
(ii)

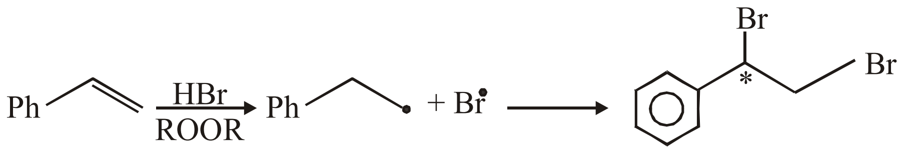


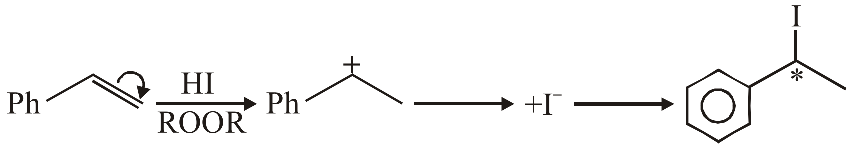
(iii)

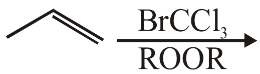


4. 

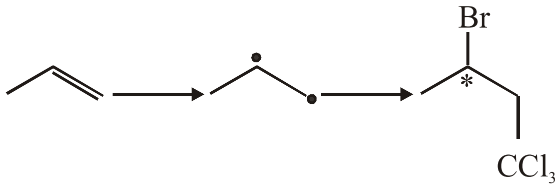
(i) 

(ii) 

(iii) 

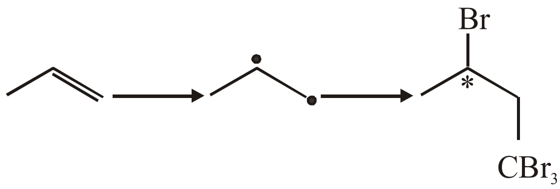
5. 

$BrCCl_3 \longrightarrow Br^{\bullet} + \underset{\text{More stale}}{CCl_3^{\bullet}}$



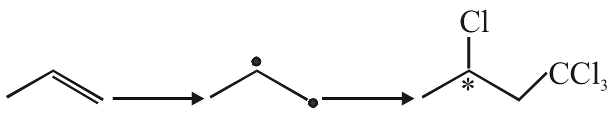
6. 

$ICBr_3 \longrightarrow I^{\bullet} + CBr_3^{\bullet}$



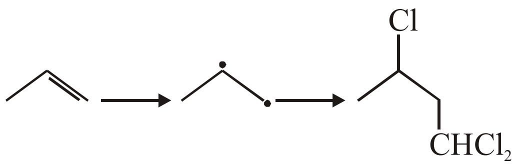
7. 

$CCl_4 \longrightarrow Cl^{\bullet} + CCl_3^{\bullet}$

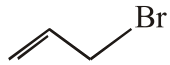


8. 

$CHCl_3 \longrightarrow \dot{H} + \dot{C}Cl_3$



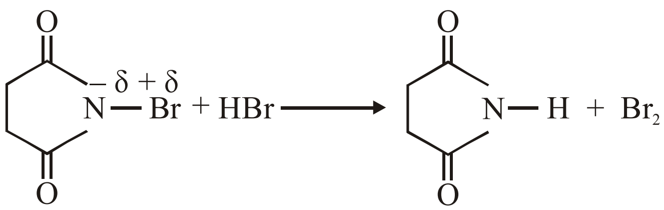
check the answer***

1. $CH_3-CH=CH_2 + NBS \longrightarrow$ 

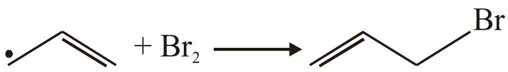
Mech^n : Let us consider Br_2 as impurity.

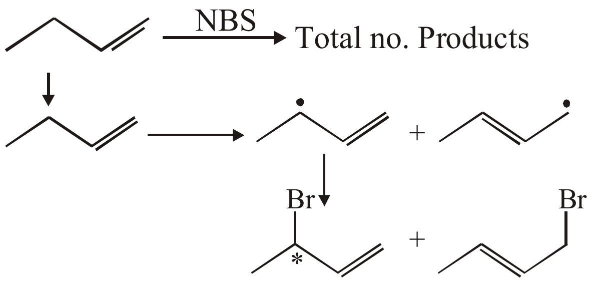
(i) $Br_2 \xrightarrow{hv} 2Br^{\bullet}$

(ii) 

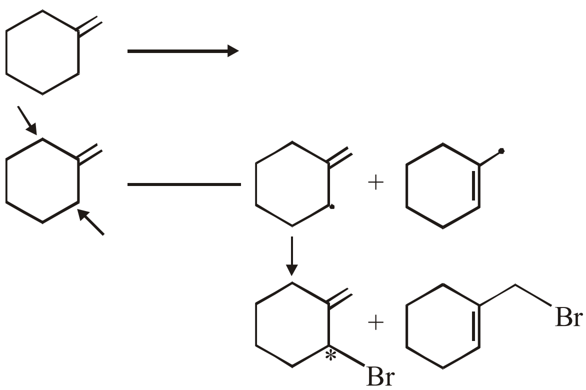
(iii) 

Acid base type Reaction

(iv) 

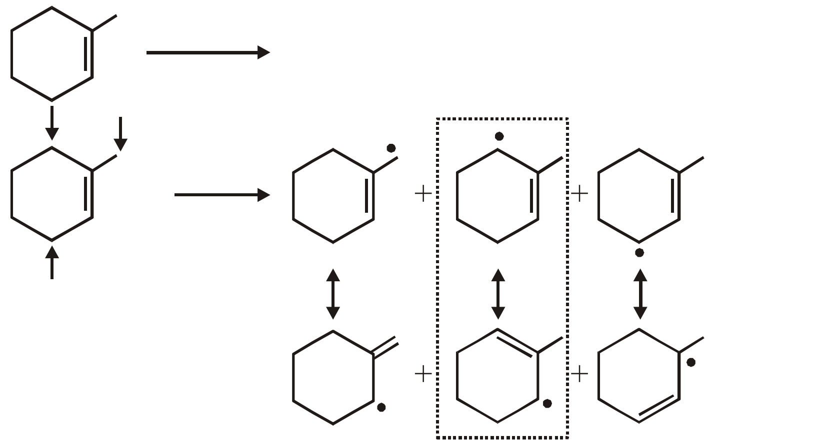
2. 

(4)

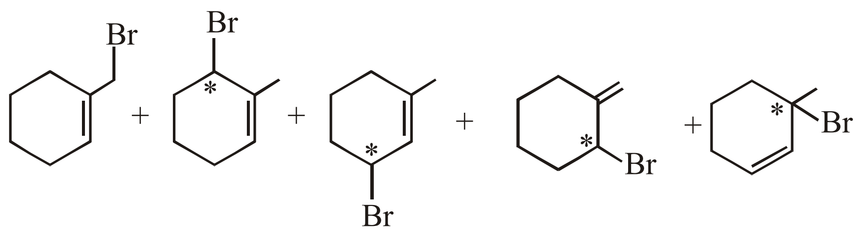
3. 

(3)

4.

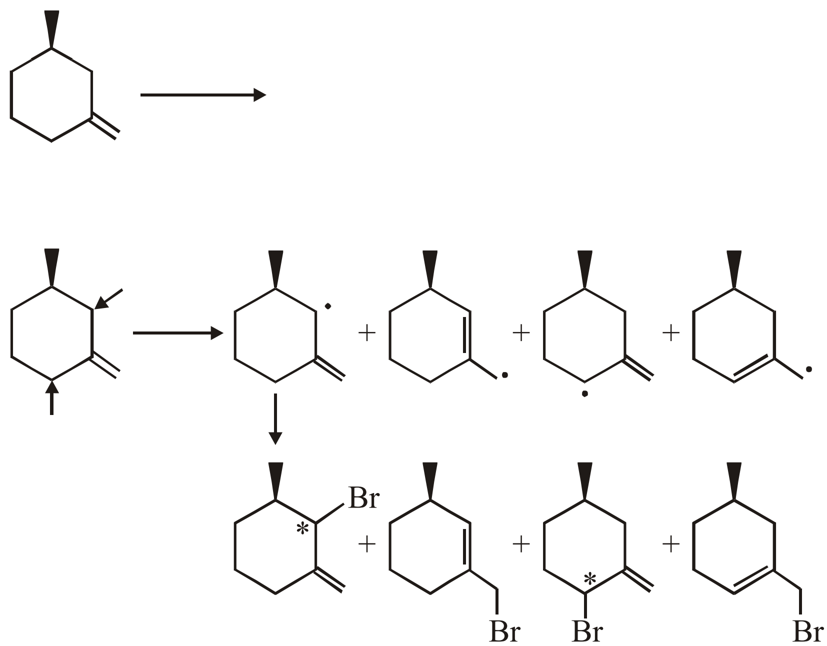


same structure take anyone out of two



(9)

5.



(6)

1. PHOTOHALOGENATION

The reaction of halogen with an alkane in the presence of ultraviolet (UV) light/sunlight hν or heat leads to the formation of a haloalkane (akyl halide). For example **Flourination, Chlorination, Bromination, Iodination**

Free radical mechanism is involved during the reaction.

Different steps involve in free radical mechanism are :

(a) Free radical initiation

(b) Free radical propagation

(c) Free radical termination

Overall reaction

$$\boxed{R-H+X_2 \longrightarrow R-X+HX}$$

Mechanism:

(i) Initiation :

$$X_2 \xrightarrow{h\nu} 2X^{\bullet}$$

(ii) Propagation :

$$X^{\circ} + RH \xrightarrow{r.d.s} R^{\bullet} + HX$$

$$R^{\bullet} + X_2 \longrightarrow RX + X^{\bullet}$$

(iii) Termination : $R^{\bullet} + R^{\bullet} \longrightarrow R_2$

$$X^{\bullet} + X^{\bullet} \longrightarrow X_2$$

Note :

(i) Reaction involve free radical as an intermediate

(ii) Order of rate of reaction of RH (alkane)

$$\boxed{3^{\bullet} > 2^{\bullet} > 1^{\bullet}}$$

(iii) Order of rate of reaction for X_2 :

$F_2 >>>> Cl_2 > Br_2 >> I_2$

(iv) Kinetic isotopic effect is present

(v) Involve free radical substitution

(vi) Chain reaction occur

(vii) Reaction can be slow down by adding S_2, O_2 etc. known as free raoical SCAVENGER.

$$\boxed{R^{\bullet} + O_2 \longrightarrow R-O-O^{\bullet}}$$

(A) Flourination :

Highly explosive and highly exothermic

$CH_4 + 2F_2 \longrightarrow C_{(black)} + 4HE$

(B) Chlorination :

(i) Highly explosive and exothermic like flourination and $C_{(black)}$ is obtained in bright sunlight

$CH_4 + 2Cl_2 \xrightarrow{B.S.L} C_{black} + 4HCl$

(ii) Chlorination can be carried out in diffused sunlight.

$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$

Mechanism :

$Cl_2 \longrightarrow 2Cl^{\bullet}$

$Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$

$CCl_3^{\bullet} + Cl_2 \longrightarrow CH_3Cl + Cl^{\bullet}$

$Cl^{\bullet} + CH_3Cl \longrightarrow \dot{C}H_2Cl + HCl$

$\dot{C}H_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$

$Cl^{\bullet} + CH_2Cl_2 \longrightarrow \dot{C}H_2Cl + HCl$

$\dot{C}HCl + Cl_2 \longrightarrow CHCl_3 + Cl^{\bullet}$

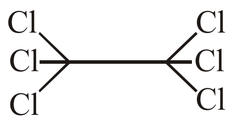
$Cl^{\bullet} + CHCl_3 \longrightarrow \dot{C}Cl_3 + HCl$

$\dot{C}Cl_3 + Cl_2 \longrightarrow CCl_4 + Cl^{\bullet}$

(ix) Monohalogenation can be carried out in presence of excess R – H

(a) $\underset{(excess)}{CH_4} + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$

(b) $CH4 + \underset{(excess)}{Cl_2} \xrightarrow{hv} CCl_4 + HCl$

(c) $C_2H_6 + \underset{(excess)}{Cl_2} \xrightarrow{hv}$  $+ 6HCl$

(x) Chlorination is highly reaction & less selective

(C) Bromination :

(i) It is less reactive & more selective then clorination

(ii) Bromination is slighlty reversible

(iii) Reducing tendency order of HX.

HI > HBr > HCl > HF

Bromination Reaction :

$CH_4 + Br_2 \rightleftharpoons CH_3Br + HBr$

(D) Iodination :

It is highly reversible and it can be carried out only is presence of oxidizing agent like HNO_3, HIO_3 etc.

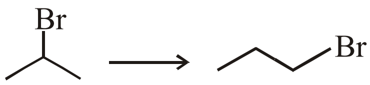
Iodination Reaction :

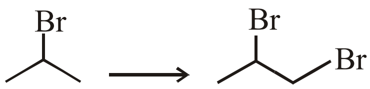
$CH_4 + I_2 \longrightarrow CH_3I + HI$

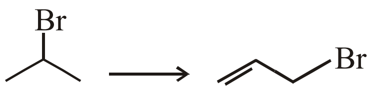
$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$

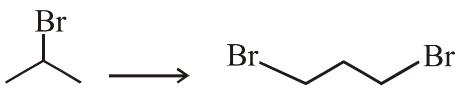
(i) Conversion :

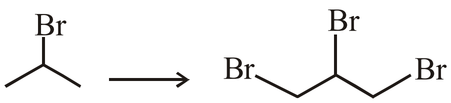
1. 

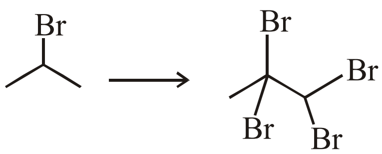
2. 

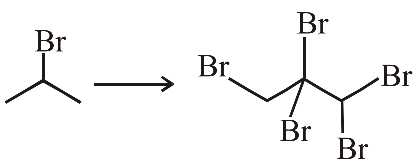
3. 

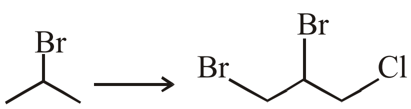
4. 

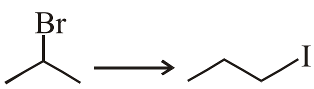
5. 

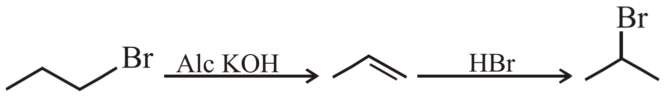
6. 

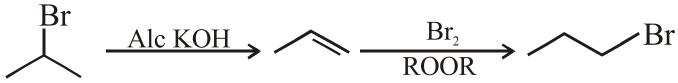
7. 

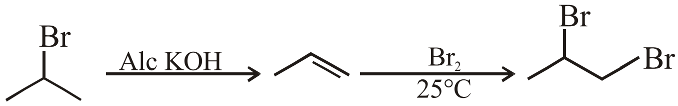
8. 

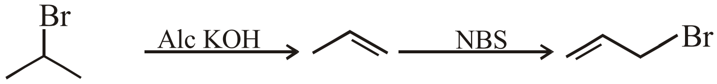
9. 

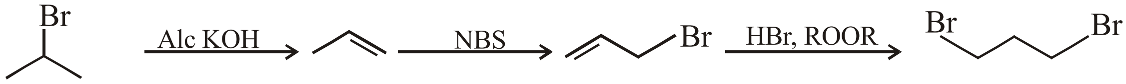
10. 

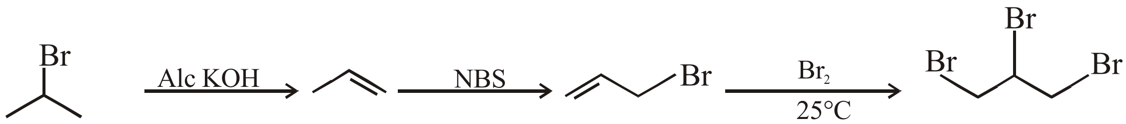
1. 

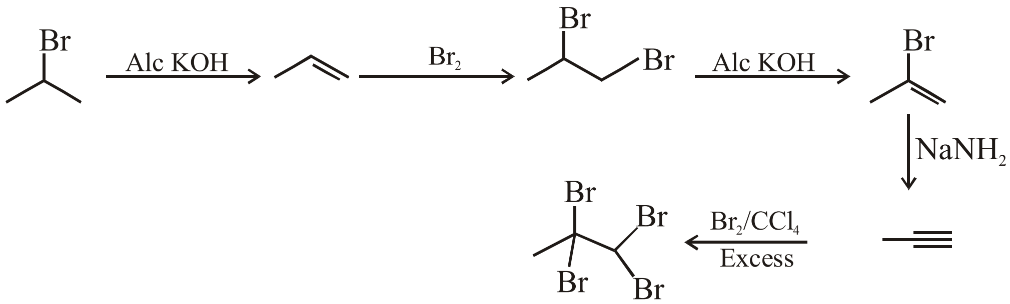
2. 

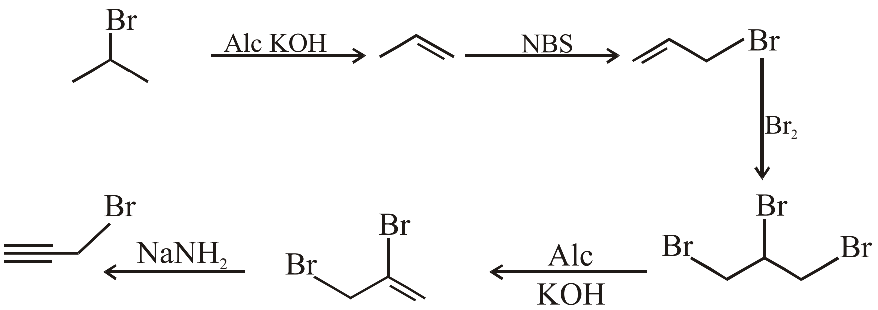
3. 

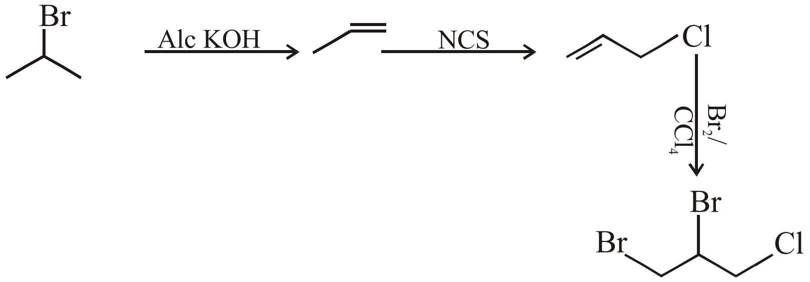
4. 

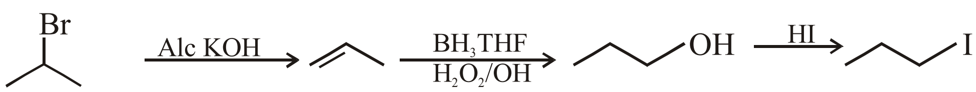
5. 

6. 

7. 

8. 

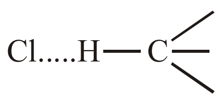
9. 

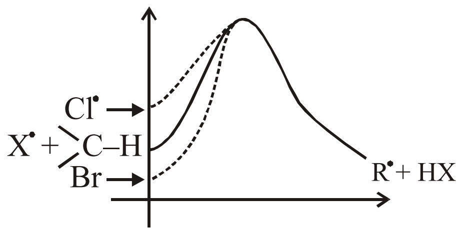
10. 

Reactivity $\propto \dfrac{1}{\text{Stability}} \propto \dfrac{1}{\text{Selectivity}}$

* Relative yield = Rel reactivity × Probability factor
* Rel reactivity of chlorinan^n towards 1°, 2° , 3° H :
  H → 1°: 2° : 3° = 1 : 3.8 : 4.5
* For Brominal^n 1° : 2° : 3° = 1 : 80 : 1600 at 100°C
* Selectivity towards chlorination & bromination

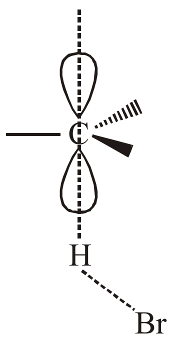
For Chlorination





Tetraheral T.S

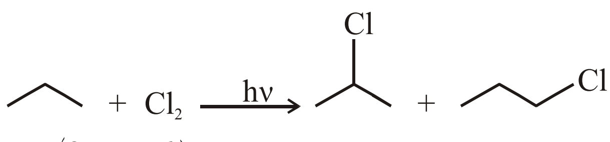
For bromination



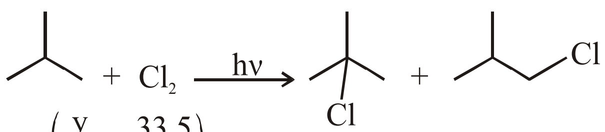
Br_2 is more stable hence less reactive & more selective as compared to $Cl^{\bullet}$. So, the T.S. of

$Br^{\bullet}$ + >C—H ⟶ $R^{\bullet}$ + HX is planar whereas it is tetrahedral in case of Cl. (By Hammond's postulates)

At any temp T. The following observations are made

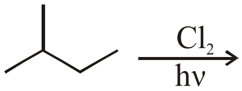


$\left(\dfrac{2x}{6} = \dfrac{56}{44}\right)$ (56%) (44%)

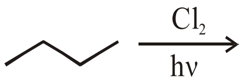


$\left(\dfrac{y}{9} = \dfrac{33.5}{66.5}\right)$ (33.5%) (66.5%)

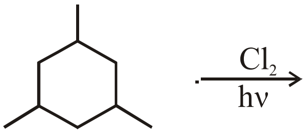
Que. Now calculate% yield of products of mono chlorination at same temp T

(i) 

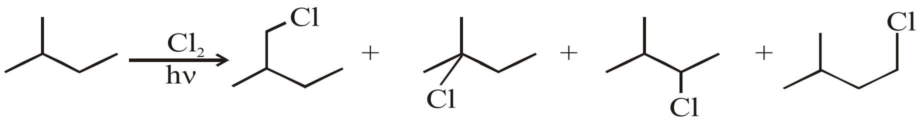
Assuming relative reactivity be
1 : x : y

(ii) 

From above reaction
x = 3.8
y = 4.5

(iii) 

* Assuming relativity reactivity be 1 : x : y
* Above reactions x = 3.8 and y = 4.5

(i) 

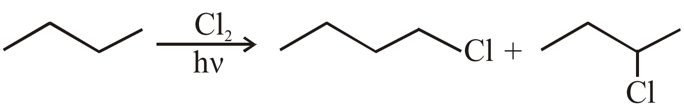
a b c d

Let total H Be H., n = 12

$a = \frac{6}{n}\cdot 1$, $b = \frac{1}{n}\cdot y$, $c = \frac{2}{n}\cdot x$, $d = \frac{3}{n}\cdot 1$

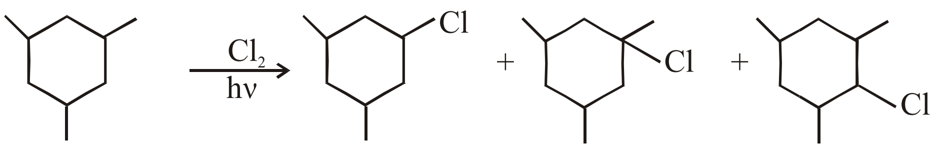
$a = \frac{6}{n}$, b = $b = \frac{3.8}{n}$, $c = \frac{9}{n}$, $d = \frac{3}{n}$

% a = 27.2% c = 40.5%
b = 18.8% d = 13.5%

(ii) 

$a = \frac{6}{n}\cdot 1$ $b = \frac{4}{n}\cdot x = \frac{15.2}{n}$

% yield of the products : a ≈ 29% , b ≈ 71%

(iii) 

$a = \frac{9}{n}\cdot 1$ $b = \frac{3}{n}\cdot 4.5$ $c = \frac{6}{n}\cdot 3.8$

$= \frac{9}{n}$ $= \frac{13.5}{n}$ $= \frac{22.8}{n}$

% yield of the products : a ≈ 20.5% , b ≈ 29% , c ≈ 51.5%

EXERCISE # O-I (MAINS ORIENTED)

1. Identify set of electrophiles :

(A) CO_2, $\overset{\oplus}{C}H_3$, $:\overset{\square}{C}H_2$, Br_2

(B) HOH, SO_3, $:\overset{\square}{C}Cl_2$, $Cl^{\oplus}$

(C) SO_2, $CH_3-\ddot{\underset{\cdot\cdot}{O}}H$, $\overset{\oplus}{N}O_2$, $:\overset{\square}{C}(Cl)(F)$

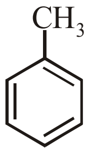
(D) $H-\overset{\oplus}{C}=O, \overset{\oplus}{N}=O, Ph-\overset{\oplus}{C}H_2, \ddot{N}H_3$ **HD0001**

2. Identify set of nucleophiles :

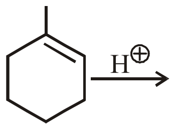
(A) $\overset{\ominus}{Cl}, \overset{\ominus}{O}H, \overset{\ominus}{R}, :\overset{\square}{C}H_2$

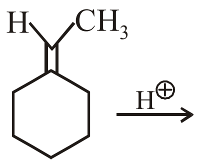
(B) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}$, $\overset{\ominus}{N}_3$, $H_3O^{\oplus}$, $\overset{\ominus}{S}H$

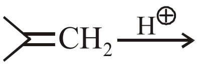
(C) $CH_2=CH_2$, $CH_3-\ddot{N}H_2$, $CH_3-CH_2-\ddot{O}H$, 

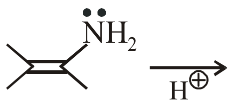
(D) $\ddot{H}^{\ominus}$, $:\overset{\ominus}{C}N$, CS_2,  **HD0002**

3. Which of the following will form 2° carbocation?

(A) 

(B) 

(C) 

(D)  **HD0003**

4. Incorrect statement about carbocation is :

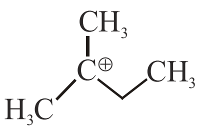
(A) It is lewis acid

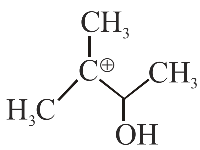
(B) It has 6 electrons in valency shell

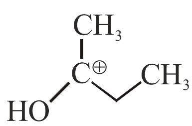
(C) It is electrophile

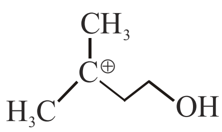
(D) It is always trigonal planer **HD0004**

5. Which of the following carbocation is most stable ?

(A) 

(B) 

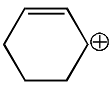
(C) 

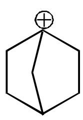
(D) 

HD0005

6. Which carbocation is least likely to be formed as an intermediate ?

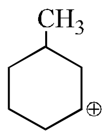
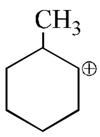
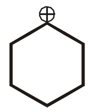
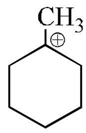
(A) $(C_6H_5)_3\overset{\oplus}{C}$

(B) 

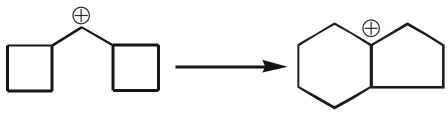
(C) 

(D) $CH_3-\overset{\oplus}{C}H_2$ **HD0006**

7. Which one of the following carbocation would you expect to rearrange :

(A)  (B)  (C)  (D)  **HD0007**

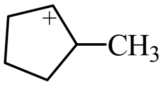
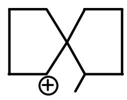
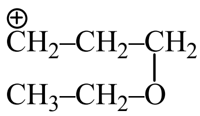
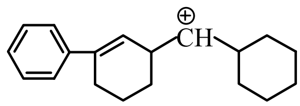
8. How many 1,2-shifts are involved during the course of following reaction :



(A) 1 (B) 2 (C) 3 (D) 4 **HD0008**

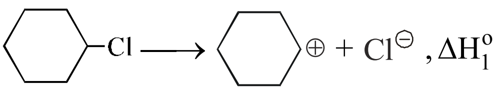
9. How many following carbocation undergo re-arrangement -

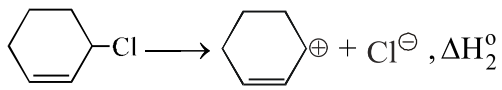
(a) $CH_3CH_2\overset{+}{C}H_2$ (b) $(CH_3)_2CH\overset{+}{C}HCH_3$ (c) $(CH_3)_3C\overset{+}{C}HCH_3$ (d) $(CH_3CH_2)_3C\overset{+}{C}H_2$

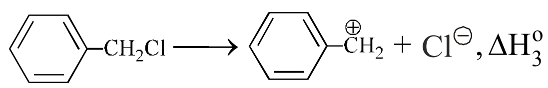
(e)  (f)  (g)  (h) 

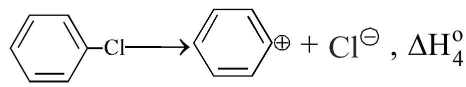
(A) 5 (B) 8 (C) 6 (D) 7 **HD0009**

10. For the reactions

(I) 

(II) 

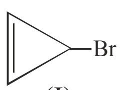
(III) 

(IV) 

The correct decreasing order of enthalpies of reaction for producing carbocation is :

(A) $\Delta H_1^o > \Delta H_2^o > \Delta H_3^o > \Delta H_4^o$ (B) $\Delta H_4^o > \Delta H_1^o > \Delta H_2^o > \Delta H_3^o$

(C) $\Delta H_3^o > \Delta H_2^o > \Delta H_1^o > \Delta H_4^o$ (D) $\Delta H_2^o > \Delta H_1^o > \Delta H_4^o > \Delta H_3^o$ **HD0010**

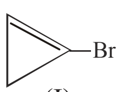
11.  , which is not the correct statement :

(I)

(A) I is more soluble in water than bromocyclopropane

(B) I gives pale yellow ppt. on addition with aq. $AgNO_3$

(C) I is having lower dipole moment than bromocyclopropane

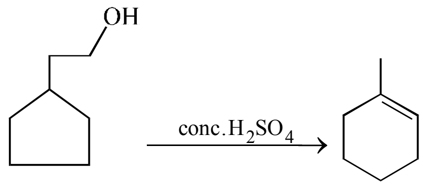
(D) I is more ionic than  **HD0011**

(I)

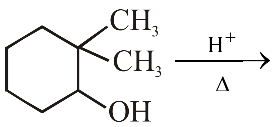
12. A solution of (–) –1–chloro–1–phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of :-

(A) carbanion (B) Carbene (C) carbocation (D) free radical **HD0012**

13. How many 1,2-Shifts of carbocation intermediate are involved during the course of following reaction :

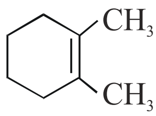


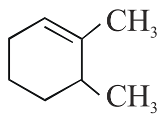
(A) 1 (B) 2 (C) 3 (D) 4 **HD0013**

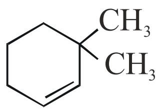
14. 

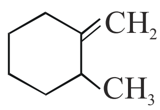
(X) (Major product)

Major product (X) is :

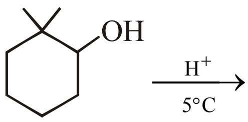
(A) 

(B) 

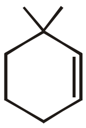
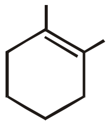
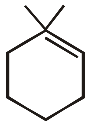
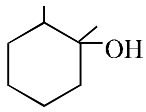
(C) 

(D) 

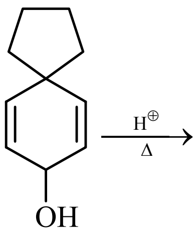
HD0014

15. 

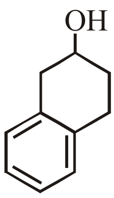
P. The product P is :

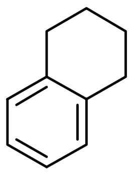
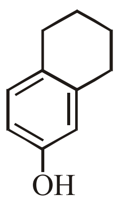
(A)  (B)  (C)  (D) 

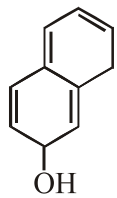
HD0015

16. 

Product ; Product is :

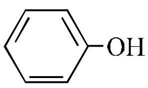
(A) 

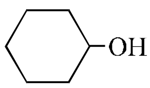
(B) 
(C) 

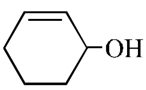
(D) 

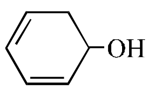
HD0016

17. Among the given compounds, the correct order of rate of dehydration is :

(I) 

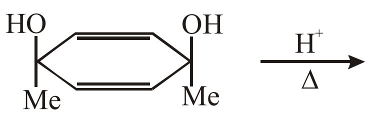
(II) 

(III) 

(IV) 

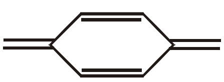
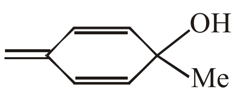
(A) I < II < III < IV (B) II < III < IV < I (C) I < III < IV < II (D) I < II < III = IV

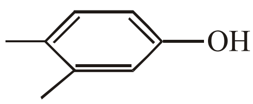
HD0017

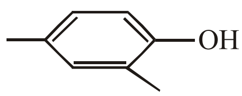
18. 

Major product -

Major product is :

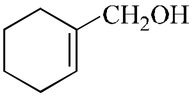
(A) 
(B) 

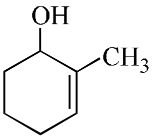
(C) 

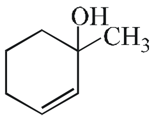
(D) 

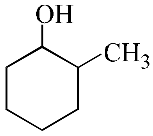
HD0018

19. Identify the correct order of rate of dehydration when given compounds are treated with conc. H_2SO_4 :

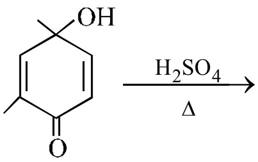
(P) 

(Q) 

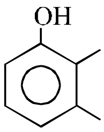
(R) 

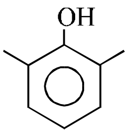
(S) 

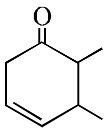
(A) P > Q > R > S (B) Q > P > R > S (C) R > Q > P > S (D) R > Q > S > P **HD0019**

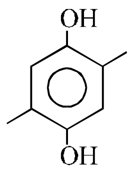
20. 

X ; X is :

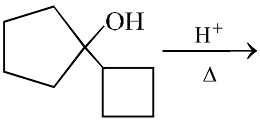
(A) 

(B) 

(C) 

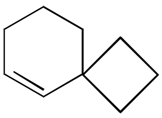
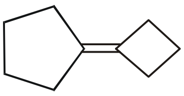
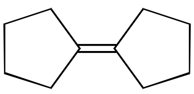
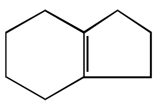
(D) 

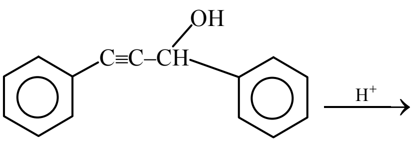
HD0020

21. 

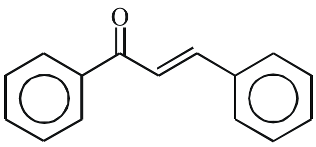
Products

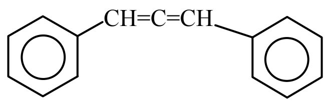
Major products is :

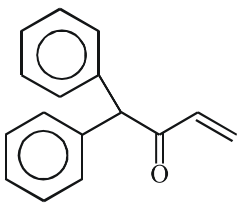
(A) 
(B) 
(C) 
(D) 
HD0021

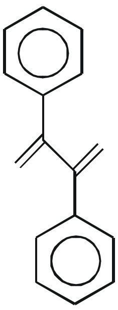
22. 

Product is :

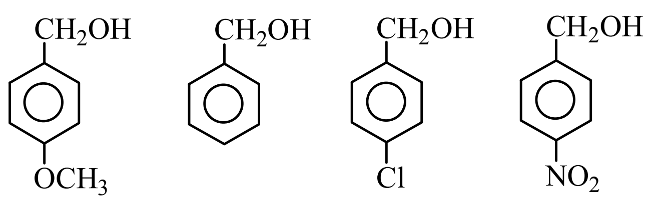
(A) 

(B) 

(C) 

(D) 
HD0022

23. What is the decreasing order of rate of reaction with HBr for the following benzyl alcohol and its derivative :



(A) (B) (C) (D)

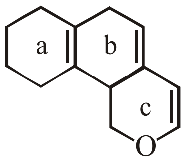
(A) A > C > D > B (B) A > B > D > C (C) D > C > B > A (D) A > B > C > D

HD0023

24. Which will dehydrate at fastest rate by H_3PO_4 :

(A) 2-methyl butan-2-ol (B) 3-methyl butan-2-ol

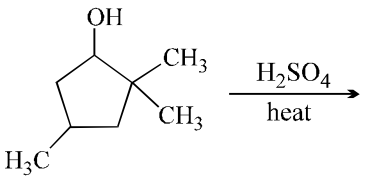
(C) Butan-1-ol (D) 2-methyl butan-1-ol **HD0024**

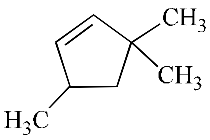
25. 

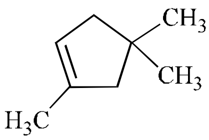
The double bond which is most reactive towards attack of electrophile :

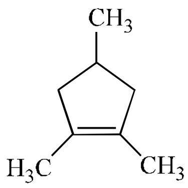
(A) a (B) b (C) c (D) None **HD0025**

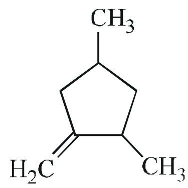
26. The major product formed in the following reaction is :



(A) 

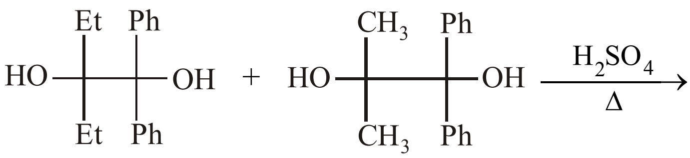
(B) 

(C) 

(D) 

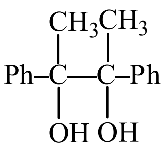
HD0026

27. How many products are obtained in the given reaction :

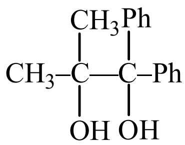


(A) 1 (B) 2 (C) 3 (D) 4 **HD0027**

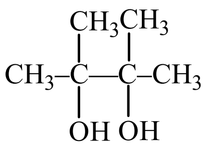
28. Compare rate of reaction towards pinacol pinacolone rearrangement.



(I)

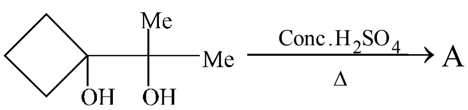


(II)

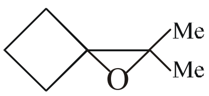


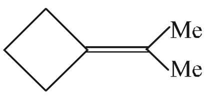
(III)

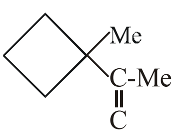
(A) II > III > I (B) III > II > I (C) II > I > III (D) I > II > III **HD0028**

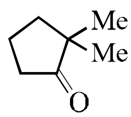
29. 

Product A is :

(A) 

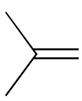
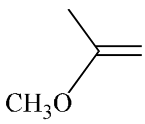
(B) 

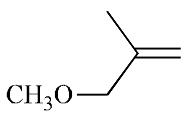
(C) 

(D) 

HD0029

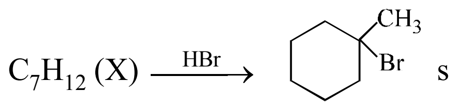
30. What is the order of reactivity with HBr :

(x) 
(y) 

(z) 

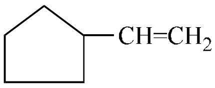
(A) x > y > z (B) y > x > z (C) z > y > x (D) y > z > x **HD0030**

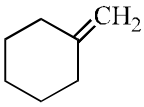
31. In the given reaction

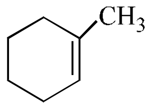


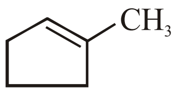
as major product

(X) can not be :

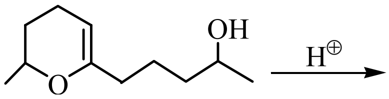
(A) 

(B) 

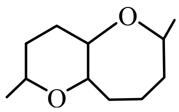
(C) 

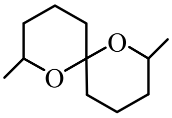
(D) 

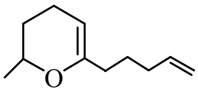
HD0031

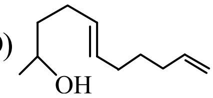
32. 

'P' (Major Product)

(A) 

(B) 

(C) 

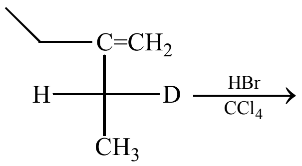
(D) 

HD0032

33. Arrange the following compounds in decreasing order of electrophilic addition :

'P' 'Q' 'R'

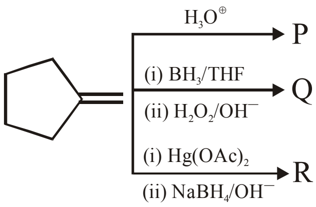
(A) P > Q > R (B) P > R > Q (C) R > P > Q (D) R > Q > P **HD0033**

34. 

Product (without rearrangement of carbocation)

What is stereochemistry of product :

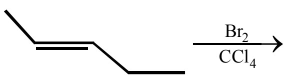
(A) Racemic mixture
(B) Optically inactive
(C) Mixture of diastereomers
(D) Meso product **HD0034**

35. 

Correct statement regarding products P, Q & R

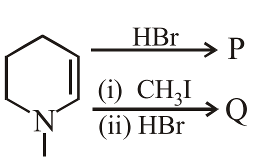
(A) Product P & R are same
(B) Product Q & R are same
(C) P & Q are functional isomers
(D) Product P, Q & R all are different **HD0035**

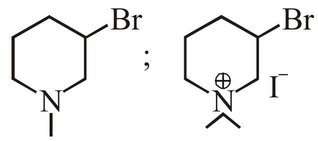
36. Select the incorrect statement about the product mixture in the following reaction :

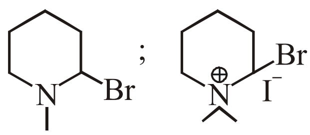


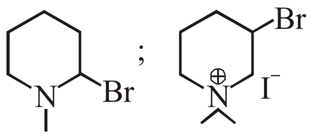
Products

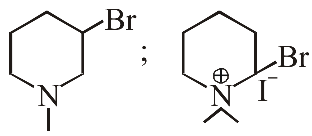
(A) It is optically active
(B) It is racemic mixture
(C) It is a resolvable mixture
(D) It is a mixture of erythro compounds **HD0036**

37.  If P & Q are the major products then P & Q are respectively :

(A) 

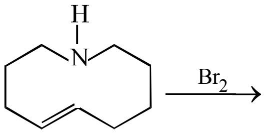
(B) 

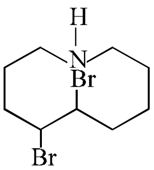
(C) 

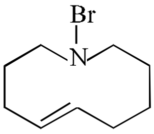
(D) 

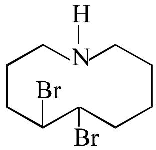
HD0037

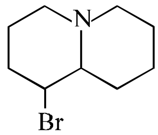
38. In the given reaction :

 [X] , [X] is :

(A) 

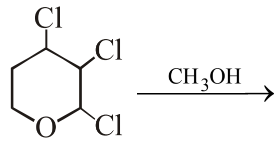
(B) 

(C) 

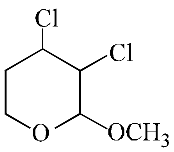
(D) 

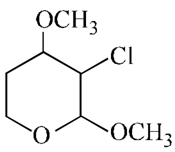
HD0038

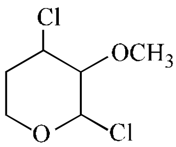
39. In the given reaction:

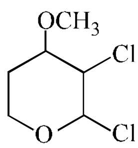
 [X] is :

(Excess)

(A) 

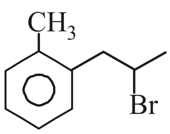
(B) 

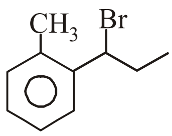
(C) 

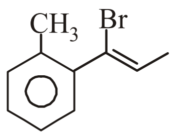
(D) 

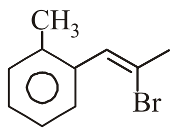
HD0039

40. Which compound undergoes hydrolysis by the S_N1 mechanism at the fastest rate?

(A) 

(B) 

(C) 

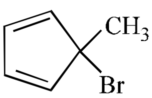
(D) 

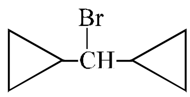
HD0040

41. Arrange the following compounds in decreasing order of their reactivity for hydrolysis reaction

(I) $C_6H_5-CH_2-Br$

(II) $C_6H_5-\underset{\displaystyle Br}{\underset{|}{CH}}-C_2H_5$

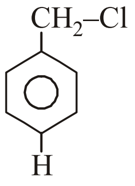
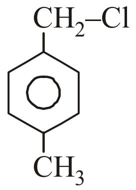
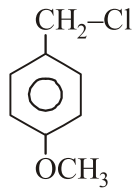
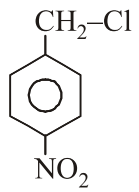
(III) 

(IV) 

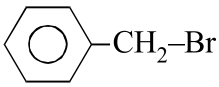
(A) I > II > III > IV (B) IV > II > I > III (C) III > IV > II > I (D) IV > III > II > I

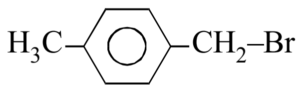
HD0041

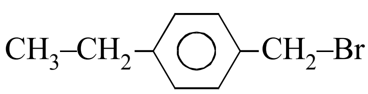
42. Which of the following is most reactive toward S_N1 reaction.

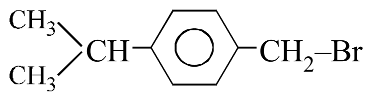
(A)  (B)  (C)  (D)  **HD0042**

43. Arrange the following compounds in order of decreasing rate of hydrolysis for S_N1 reaction:

(I) 

(II) 

(III) 

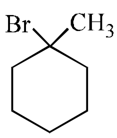
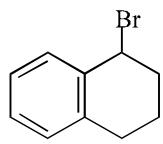
(IV) 

(A) II > III > IV > I (B) IV > III > II > I (C) III > IV > II > I (D) I > II > III > I **HD0043**

44. Which one of the following compounds will give enantiomeric pair on treatment with HOH?

(A) $C_6H_5-C(C_2H_5)(C_2H_5)-I$ (B) $CH_3-C(CH_3)(C_2H_5)-Br$ (C) $C_6H_5-C(H)(D)-Br$ (D) $C_2H_5-C(C_2H_5)(CH_3)-Br$ **HD0044**

45. Consider the S_N1 solvolysis of the following halides in aqueous formic acid:

(I) $(CH_3)_2CH-CH(Br)-CH_3$ (II)  (III) $C_6H_5-CH(Br)-C_6H_5$ (IV) 

Decide decreasing order of reactivity of above alkyl halide?

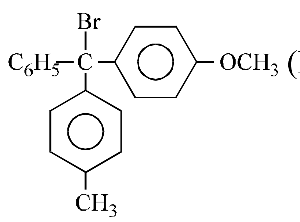
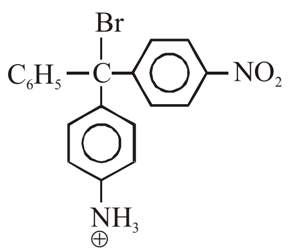
(A) III > IV > II > I (B) II > IV > I > III (C) I > II > III > IV (D) III > I > II > IV

HD0045

46. For the given reaction

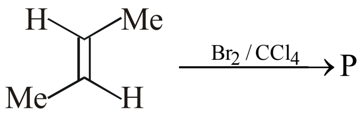
$$R-C(R_1)(R_2)-X \xrightarrow{HOH} R-C(R_1)(R_2)-OH$$

Which substrate will give maximum racemisation?

(A) $C_6H_5-C(CH_3)(C_2H_5)-Br$ (B) $CH_2=CH-C(CH_3)(C_2H_5)-Br$ (C)  (D) 

HD0046

47. Select incorrect statements about the product (P) of the reaction :



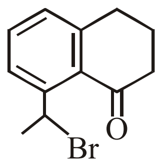
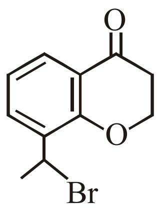
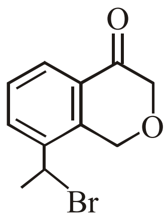
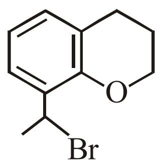
(A) P is optically inactive due to internal compensation

(B) P is optically inactive due to the presence of plane of symmetry in the molecule

(C) The structure of P can have three optical isomers possible.

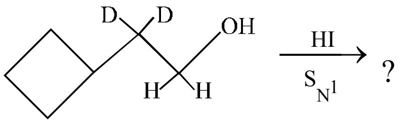
(D) P can have four possible optical isomers. **HD0047**

48. Consider the following molecules :

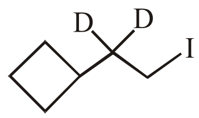
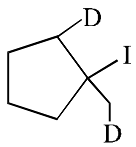
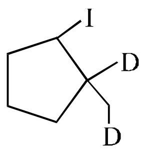
(I)  (II)  (III)  (IV) 

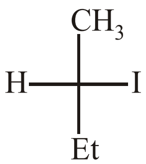
The correct decreasing ease of hydrolysis of alkyl halide is :

(A) II > III > IV > I (B) II > IV > III > I (C) II > I > III > IV (D) IV > II > III > I **HD0048**

49. 

Major product is:

(A)  (B)  (C)  (D) None of these **HD0049**

50.  $\xrightarrow{HOH}$ Products. (If 96% racemisation takes place)

Find out the correct statement about the reaction.

(A) Among the products 48% S and 48% R configuration containing molecules are present

(B) Among the products 50% S and 50% R configuration containing molecules are present

(C) Among the products 48% S and 52% R configuration containing molecules are present

(D) Among the products 52% S and 48% R configuration containing molecules are present **HD0050**

51. In the given reaction the product [P] can be :

$CH_3–CH=CH–CH_2–OH \xrightarrow[S_N1']{HBr} [P]$

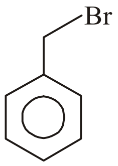
(A) $CH_3–CH=CH–CH_2–Br$

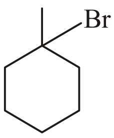
(B) $CH_3-\underset{}{\overset{Br}{\overset{|}{C}}}H-CH=CH_2$

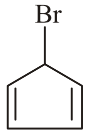
(C) $CH_2=CH–CH=CH_2$

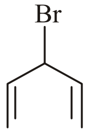
(D) $CH_3-\overset{Br}{\overset{|}{C}}H-CH_2-CH_2-OH$ **HD0051**

52. Which of the following can not give S_N1 reaction easily?

(A) 

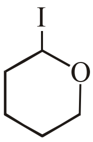
(B) 

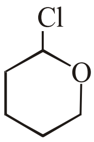
(C) 

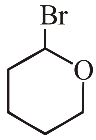
(D) 

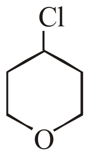
HD0052

53. Which one of the following compounds will be most reactive for S_N1 reactions ?

(A) 

(B) 

(C) 

(D) 

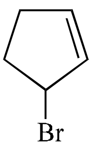
HD0053

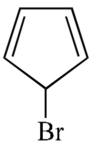
54. Which of the following compounds is most rapidly hydrolysed by S_N1 mechanism ?

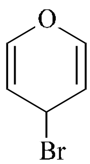
(A) C_6H_5Cl (B) $Cl–CH_2–CH=CH_2$

(C) $(C_6H_5)_3CCl$ (D) $C_6H_5CH_2Cl$ HD0054

55. Among the bromides I–III given below, the order of reactivity in S_N1 reaction is:

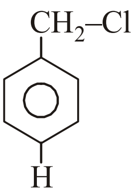
(I) 

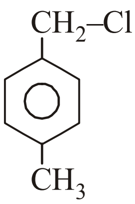
(II) 

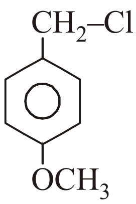
(III) 

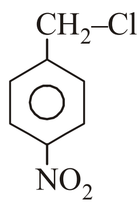
(A) III > I > II (B) III > II > I (C) II > III > I (D) II > I > III HD0055

56. Which of the following is most reactive toward S_N2.

(A) 

(B) 

(C) 

(D) 

HD0056

57. For reaction $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$

the rate of reaction is given by the expression :

(A) Rate = k $[CH_3Br]$ (B) Rate = k $[OH^-]$

(C) Rate = k $[CH_3Br][OH^-]$ (D) Rate = k $[CH_3Br]^o [OH^-]^o$ HD0057

58. Select suitable reason for non-occurence of the following reaction.

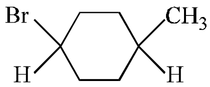
$$Br^- + CH_3OH \longrightarrow BrCH_3 + OH^-$$

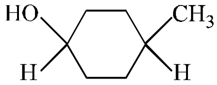
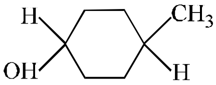
(A) Attacking nucleophile is stronger one

(B) Leaving group is a stronger base than nucleophile

(C) Alcohols are not good substrate for S_N reaction

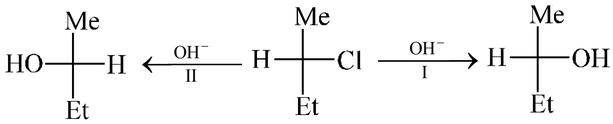
(D) Hydroxide ions are weak bases HD0058

59.  $+ OH^- \xrightarrow{S_N2} A$; A is :

(A)  (B)  (C) Both (D) None **HD0059**

60. The reactivity of 2-bromo-2-methylbutane (I), 1-bromopentane (II) and 2-bromopentane (III) towards S_N2 displacement is such that :

(A) I > II > III (B) I > III > II (C) II > III > I (D) II > I > III **HD0060**

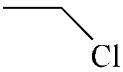
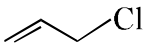
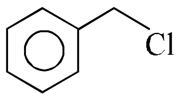
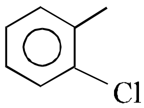
61. 

B A

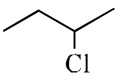
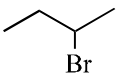
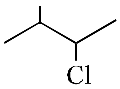
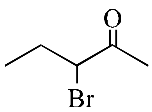
Mechanism involved :

(A) I can't be S_N1 (B) II can't be S_N2 (C) I S_N1 & II S_N2 (D) I S_N2 & II S_N1 **HD0061**

62. In which of the following replacement of Cl^- is most difficult ?

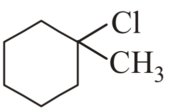
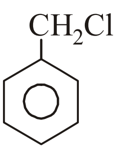
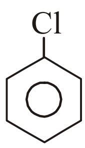
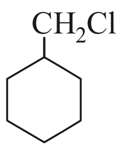
(A)  (B)  (C)  (D)  **HD0062**

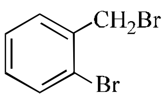
63. Arrange these compounds in order of increasing S_N2 reaction rate :

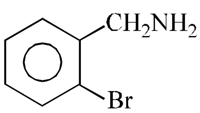
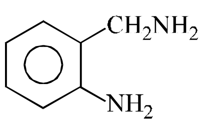
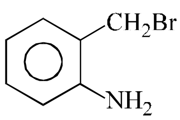
 (I)  (II)  (III)  (IV)

(A) III < I < II < IV (B) III < II < I < IV (C) IV < III < I < II (D) III < IV < I < II **HD0063**

64. Which reaction proceeds faster with NaI in DMSO ?

(A)  (B)  (C)  (D)  **HD0064**

65. The major product in the given reaction:  $+ NH_3 \longrightarrow$

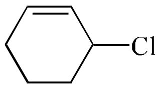
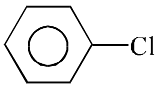
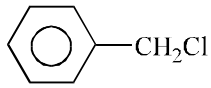
(A)  (B)  (C)  (D) All of these **HD0065**

66. The given compound $CH_3–O–CH_2–Br$ gives which one of the following reactions:

(A) Only S_N1 (B) Only S_N2

(C) S_N1 as well as S_N2 (D) E_1 only **HD0066**

67. Which will give white ppt. with $AgNO_3$?

(A) 
(B) 
(C) 
(D) Both A & C **HD0067**

68. Consider the following groups :

(I) –OAc (II) –OMe (III) $-OSO_2Me$ (IV) $-OSO_2CF_3$

The order of leaving group nature is:

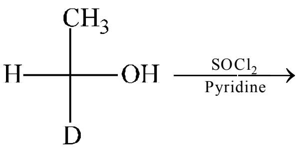
(A) I > II > III > IV (B) IV > III > I > II (C) III > II > I > IV (D) II > III > IV > I **HD0068**

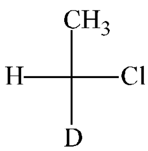
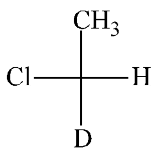
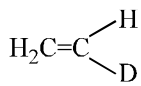
69. When ethyl bromide is treated with moist Ag_2O, the main product is:

(A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these **HD0069**

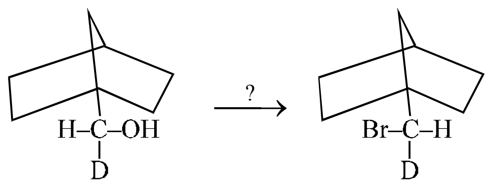
70. When ethyl bromide is treated with dry Ag_2O, the main product is:

(A) Ethyl ether (B) Ethanol (C) Ethoxy ethane (D) All of these **HD0070**

71.  (A). The product A will be :

(A) 
(B) 
(C) $H_2C = CH_2$
(D)  **HD0071**

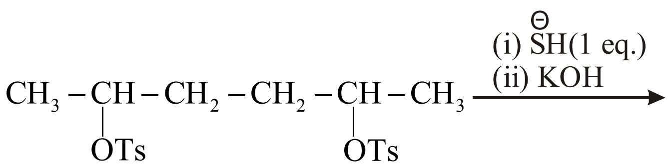
72. Which reaction conditions (reagents) is suitable for the following reaction:

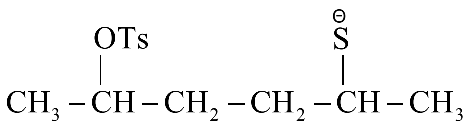
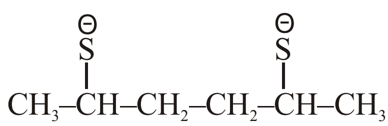


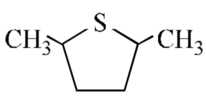
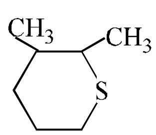
(A) Br_2 / CCl_4 (B) $SOBr_2$ (C) PBr_3 (D) HBr / conc H_2SO_4

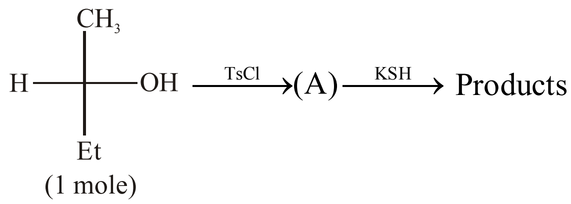
HD0072

73. In the given reaction


(X), X will be :

(A) 
(B) 

(C) 
(D)  **HD0073**

74. 

(Assuming all the substrate convert into substitution products containing 0.05 mole of S-configuration)Calculate the percentage of S_N2 mechansim.

(A) 90%   (B) 80%   (C) 70%   (D) 95%   **HD0074**

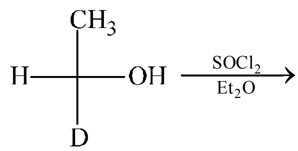
75. The reaction of $SOCl_2$ on alkanols to form alkyl chlorides gives good yields because

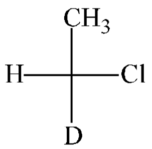
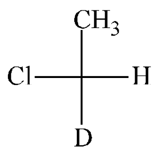
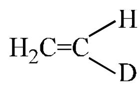
(A) Alkyl chlorides are immiscible with $SOCl_2$

(B) The other products of the reaction are gaseous and escape out

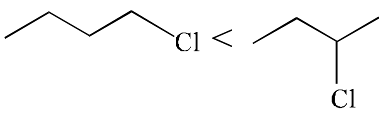
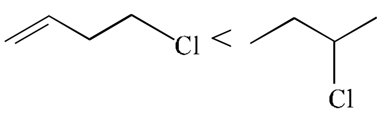
(C) Alcohol and $SOCl_2$ are soluble in water

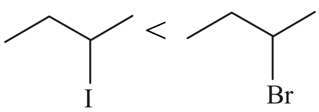
(D) The reaction does not occurs via intermediate formation of an alkyl chloro sulphite\   **HD0075**

76.  (A). The product A will be :

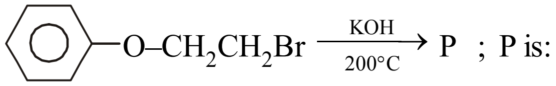
(A)    (B)    (C) $H_2C = CH_2$ (D)    **HD0076**

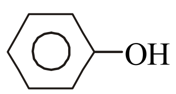
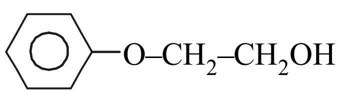
77. In the given pairs, which pair represent correct order of rate dehydrohalogenation reaction.

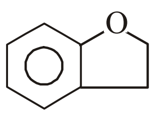
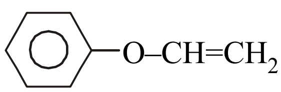
(A)    (B) 

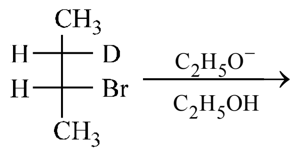
(C)    (D) $CH_3 - CH_2 - Cl < CD_3 - CD_2 - Cl$ **HD0077**

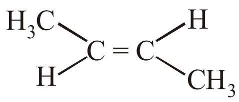
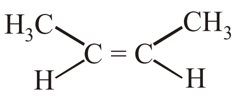
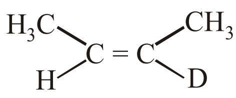
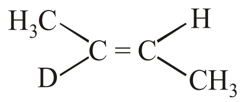
78. The product of the reaction



(A)    (B) 

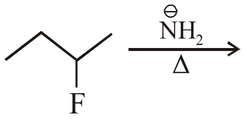
(C)    (D)    **HD0078**

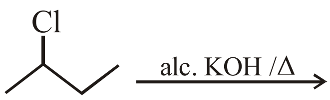
79.  ? Major product is:

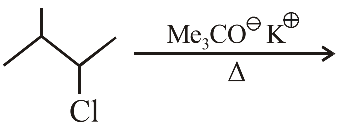
(A)  (B)  (C)  (D) 

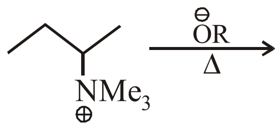
HD0079

80. Which of following reaction(s) produce Saytzeff product as a major product :

(A) 

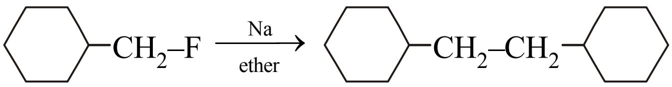
(B) 

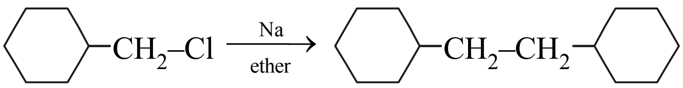
(C) 

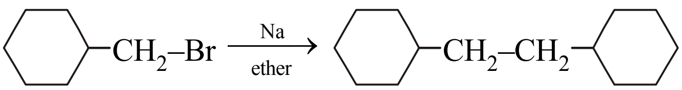
(D) 

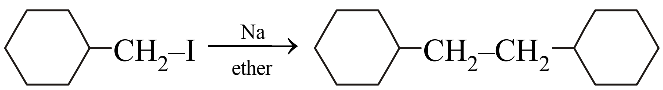
HD0080

81. The correct order of rate of following Wurtz recations :

(I) 

(II) 

(III) 

(IV) 

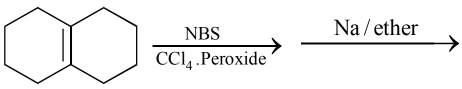
(A) I > II > III > IV

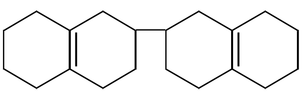
(B) II > I > III > IV

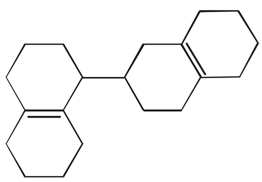
(C) IV > III > II > I

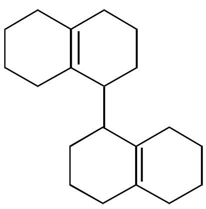
(D) In all rate of Wurtz reaction is same

HD0081

82.  (X) ; X is

(A) 

(B) 

(C) 

(D) None of these

HD0082

83. Find out the correct order of rate of reaction towards free radical allylic substitution :

(I) $CH_3–CH=CH_2$ (II) $CH_3–CH_2–CH=CH_2$ (III) $CH_3–\underset{}{\overset{CH_3}{\overset{|}{C}}}H–CH=CH_2$

(A) I > II > III (B) II > I > III (C) III > II > I (D) III > I > II **HD0083**

84. What will be the major product, when 2-methyl butane undergoes bromination in presence of light ?

(A) 1-Bromo-2-methyl butane (B) 2-Bromo-2-methyl butane

(C) 2-Bromo-3-methyl butane (D) 1-Bromo-3-methyl butane **HD0084**

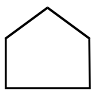
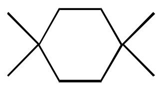
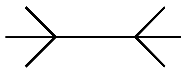
85. Which can not be the possible product of the given reaction ?

$$CH_3-CH_2-\underset{\underset{O}{||}}{C}-OAg \xrightarrow[CCl_4,\Delta]{Br_2} \text{product(s)}$$

(A) CH_3-CH_2-Br (B) $CH_3-CH_2-\underset{\underset{O}{||}}{C}-O-CH_2-CH_3$

(C) $CH_3-CH_2-CH_2-CH_3$ (D) $CH_3-CH_2-CH_3$ **HD0085**

86. Choose that alkane which cannot give only one monochloro derivative upon reaction with chlorine in sun light :

(A)  (B)  (C)  (D)  **HD0086**

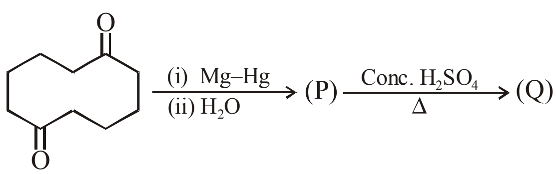
87. 2-chloropentane on halogenation with chlorine gives 2,3, dichloropentane. What will be the structure of free radical species formed in the reaction ?

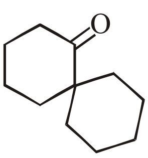
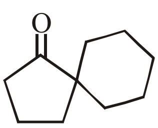
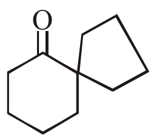
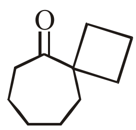
(A) Tetrahedral (B) Trigonal planar (C) Square planar (D) Pyramidal **HD0087**

88. On mixing a certain alkane with chlorine and irradiating it with ultraviolet light, it forms only one monochloroalkane. This alkane could be -

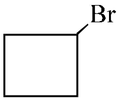
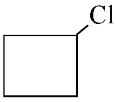
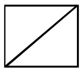
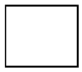
(A) neopentane (B) propane (C) pentane (D) isopentane **HD0088**

89. Major product (Q) of following reaction is :



(A)  (B)  (C)  (D)  **HD0089**

90. 1-Bromo-3-chloro cyclobutane on reaction with 2-equivalent of sodium in ether gives

(A)  (B)  (C)  (D)  **HD0090**

91. Correct order of rate of photochlorination for following compounds is :

(I) $CH_3–CH_3$

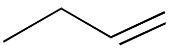
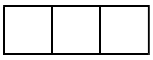
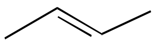
(II) $CD_3–CD_3$

(III) $CH_3-C(CH_3)_2-CH_3$ (central C bearing CH_3 above and CH_3 below)

(A) II < I < III (B) I < II < III (C) III < I < II (D) II < III < I **HD0091**

92. $\begin{matrix} CH_3-CH-CO_2K \\ | \\ CH_3-CH-CO_2K \end{matrix} \xrightarrow{\text{electrolysis}}$ (A) (Major)

Major product (A) of above reaction :

(A)  (B)  (C)  (D)  **HD0092**

93. During the preparation of ethane by Kolbe's electrolytic method using inert electrode the pH of the electerolyte

(A) Decreases progressively as the reaction proceeds

(B) Increaes progressively as the reaction procces

(C) Remains constant throughout the reaction

(D) May decrease if concentration of the electrolytes is not very high **HD0093**

94. When isobutane is chlorinated in the presence of diffused sunlight, then the product formed is :

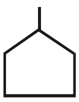
(A) Tertiary butyl chloride in major amount

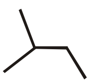
(B) Isobutyl chloride in major amount

(C) Both 50 % each

(D) n-Butyl chloride, isobutyl chloride and sec-butyl chloride are formed **HD0094**

95. Consider the following reactions :

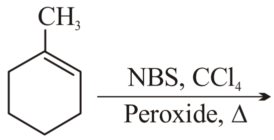
 $\xrightarrow{Cl_2 / h\nu}$ Total number of monochlorinated product = X (Excluding stereoisomers)

 $\xrightarrow{Cl_2 / h\nu}$ Total number of monochlorinated product = Y (Excluding stereoisomers)

Identify value of X + Y.

(A) 8 (B) 9 (C) 11 (D) 10 **HD0095**

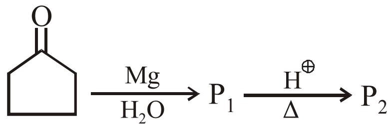
96. Find out the total no. of products (including stereo) in the given reaction :



Products.

(A) 8 (B) 9 (C) 10 (D) 11 **HD0096**

97. Which of the following is not correct about P_2 :



(A) It is a spiro compound (B) It is a Ketone

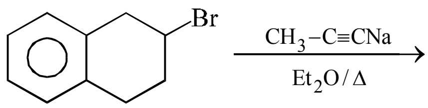
(C) It can show tautomerism (D) Its double bond equivalent is 4 **HD0097**

98. On heating glycerol with excess amount to HI, the product formed is–

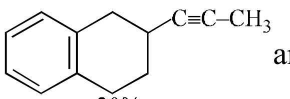
(A) Allyl iodide (B) Isopropyl iodide

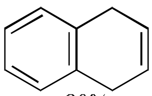
(C) Propylene (D) 1,2,3–tri-iodopropane **HD0098**

99. In the given reaction:



the products are:

(A) 

20%
and 
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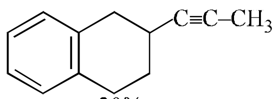
(B) 

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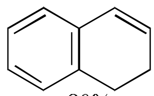
\+ 
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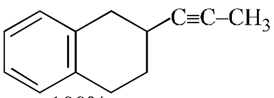
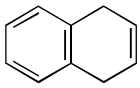
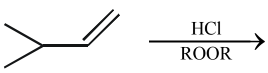
(C) 

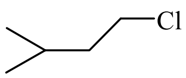
100%

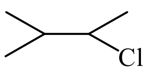
(D) 
100%

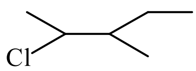
HD0099

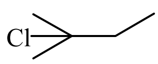
100. Major product of the reaction -



(A) 

(B) 

(C) 

(D) 

HD0100

EXERCISE # O-II

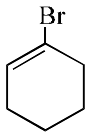
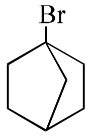
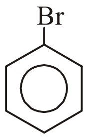
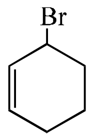
(*Choose the correct option. One or more than one are correct*)

1. Rate of S_N2 depends on :

(A) Conc of Nucleophile (B) Conc of substrate

(C) Nature of leaving group (D) Nature of solvent **HD0101**

2. S_N2 reaction will be negligible in

(A)  (B)  (C)  (D)  **HD0102**

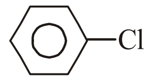
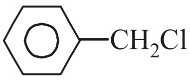
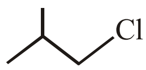
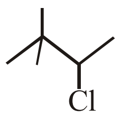
3. $Br{-}\underset{CH_3}{\underset{|}{C}H}{-}\overset{14}{C}H{=}CH_2 \xrightarrow{HI}$

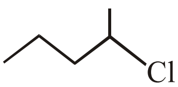
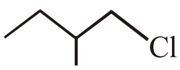
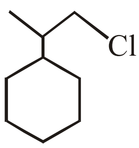
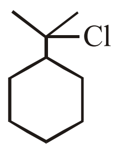
Products which can be obtained during the reaction in good yield :

(A) $Br{-}\underset{CH_3}{\underset{|}{C}H}{-}\underset{CH_3}{\underset{|}{\overset{14}{C}H}}{-}I$ (B) $I{-}\underset{CH_3}{\underset{|}{C}H}{-}\underset{CH_3}{\underset{|}{\overset{14}{C}H}}{-}Br$ (C) $Br{-}\underset{CH_3}{\underset{|}{C}H}{-}\overset{14}{C}H_2{-}CH_2{-}I$ (D) $I{-}\underset{CH_3}{\underset{|}{C}H}{-}CH_2{-}\overset{14}{C}H_2{-}Br$

HD0103

4. In the given pair in which pair the first compound is more reactive than second towards S_N2 reaction.

(A)   (B)  

(C)   (D)   **HD0104**

5. Consider the given reaction

$$H{-}\underset{C_2H_5}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{-}OTs\ (S) \xrightarrow[(DMF)]{NaCN} CH_3CH_2\underset{CH_3}{\underset{|}{C}H}{-}CN$$

which of following statements is/are correct for the above reaction.

(A) Product formation takes place due to the breaking of O–Ts

(B) The reaction is S_N2

(C) The reaction is S_N1

(D) Configuration of product is (R) **HD0105**

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Halogenderivatives\Eng\03_Ex.-O-II.p65

6. Which of the following statements is / are true?

(A) $CH_3–CH_2–CH_2–I$ will react more readily than $(CH_3)_2$ CHI for S_N2 reactions.

(B) $CH_3–CH_2–CH_2–Cl$ will react more readily than $CH_3–CH_2–CH_2–Br$ for S_N2 reaction.

(C) $CH_3–CH_2–CH_2–CH_2–Br$ will react more readily than $(CH_3)_3C–CH_2–Br$ for S_N2 reactions

(D) $CH_3–O–C_6H_4–CH_2Br$ will react more readily than $NO_2–C_6H_5–CH_2Br$ for S_N2 reaction **HD0106**

7. Incorrect statement about alkyl halides is / are:

(A) Tertiary alkyl halides undergo S_N2 substitutions

(B) Alkyl iodides on exposure to sunlight gradually darken

(C) Photo iodination is irreversible in presence of HIO_3

(D) A nucleophilic substitution is most difficult in alkyl iodides **HD0107**

8. S_N1 & S_N2 is not favourable in

(A) $H_2C = CH–Cl$ (B) $Ph–CH_2–Cl$ (C) $Ph–Cl$ (D) $H_2C=CH–CH_2–Cl$

HD0108

9. Correct statement(s) for the product(s) of following reaction.

$$CH_2 = CH - CH_2 - Ph \xrightarrow[Cl_2/500°C]{}$$

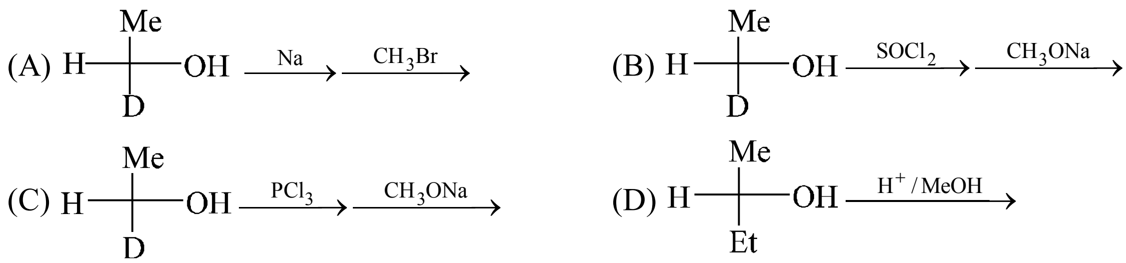
(A) Four different products are formed

(B) Two optically active products are formed

(C) The optically active compound formed here can also be made by the reaction of HCl

(D) The reaction path is free radical substitution. **HD0109**

10. In which of the following reaction configuration about chiral C is retained in the final product



HD0110

11. A gem dichloride is formed in the reaction :

(A) CH_3CHO and PCl_5 (B) CH_3COCH_3 and PCl_5

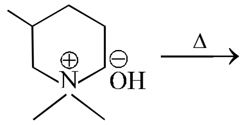
(C) $CH_2 = CH_2$ and Cl_2 (D) $CH_2 = CHCl$ and HCl **HD0111**

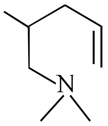
12. In which product formation takes place according to Hoffmann's rule

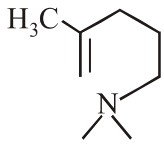
(A) $CH_3CH_2-CH(Br)-CH_3 \xrightarrow[\Delta]{t-Bu\overset{\ominus}{O}\overset{\oplus}{K}}$ (B) $CH_3CH_2-CH(Br)-CH_3 \xrightarrow[\Delta]{CH_3CH_2\overset{\ominus}{O}\overset{\oplus}{K}}$

(C) $CH_3CH_2–CH(CH_3)–\overset{\oplus}{N}(CH_3)_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H}$ (D) $CH_3CH_2CH(\overset{\oplus}{S}(CH_3)_2)-CH_3 \xrightarrow[\Delta]{\overset{\ominus}{O}H}$ **HD0112**

13. Which of following are correct for given reaction



(A) Major product of reaction is 

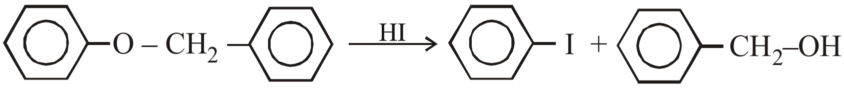
(B) Major product is 

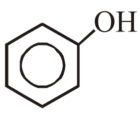
(C) The reaction is thermal elimination reaction (D) The reaction is E_2 reaction **HD0113**

14. In which case incorrect products are formed :

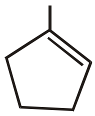
(A) $Me_3C–O–CH_3 \xrightarrow{HI} Me_3C–OH + CH_3I$

(B) $H_3C–O–CH_2–CH_3 \xrightarrow{HI} CH_3OH + ICH_2CH_3$

(C) 

(D)Anisole $\xrightarrow{HI}$ 

$+ CH_3I$ **HD0114**

15. In the given reaction :  $\xrightarrow{NBS}$

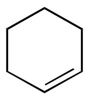
Find out the correct statement

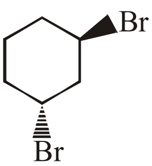
(A) It gives total 9 allylic brominated products

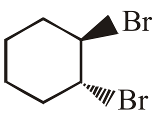
(B) 6 fractions are obtained on fractional distillation of product mixture

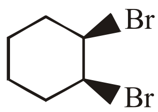
(C) Subtrate has 7 allylic hydrogens

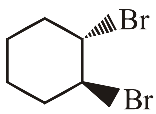
(D) NBS is a brominating agent for allylic positions **HD0115**

16.  $\xrightarrow[CCl_4 / h\nu]{NBS} \xrightarrow{HBr}$ (X) + (Y) enantiomeric pair :

(A) 

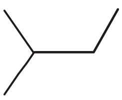
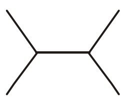
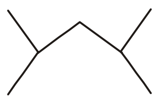
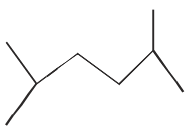
(B) 

(C) 

(D) 

HD0116

17. Which of the following can be produced by Wurtz reaction in good yield :

(A) 
(B) 
(C) 
(D) 

HD0117

node06\B0B0-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Halogenderivatives\Eng\03_Ex.-O-II.p65

18. Products formed when HCl adds to 2,4-hexadiene is :

(A) 4-chloro-2-hexene (B) 2-chloro-3-hexene

(C) 2-chloro-4-hexene (D) 1-chloro-2-hexene **HD0118**

19. Correct statement among the following is/are :

(A) The rate of hydrolysis of tertiary butyl bromide increases by addition of Ag_2O

(B) Aqueous Ag_2O produces nucleophilic OH^-

(C) The addition of a small amount of oxygen slows down the photochemical chlorination of methane. **HD0119**

(D) CH_3CH_2Cl is more reactive than $PhCH_2Cl$ for bimolecular nucleophilic substitution reaction

20. Incorrect statement among the following is/are :

(A) R—OH with NaI in the presence of phosphoric acid gives R—I, but not in the absence of phosphoric acid

(B) 2-methyl propane on chlorination (Cl_2, hν) gives 1-chloro-2-methyl propane while bromination (Br_2, hν) gives 2-bromo-2-methyl propane

(C) Usually higher temperature prefers substitution over elimination

(D) Triphenyl chloromethane cannot be hydrolysed **HD0120**

21. Correct statements among the following is/are :

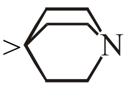
(A) Dihaloalkanes having the same type of halogen atoms on same atom are named as alkylidene dihalides

(B) Dihaloalkanes having the same type of halogen atoms on adjacent atoms are named as alkylene dihalides

(C) In common name system gem-dihalides are named as alkylidene halide

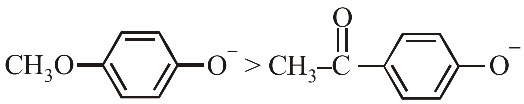
(D) In common name system vic-dihalides are named as alkylene halide **HD0121**

22. Which of the following is correct order of nucleophilicity ?

(A) $(CH_3CH_2)_3N$ > 

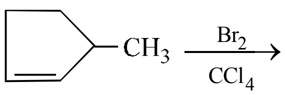
(B) HOO– > HO– in DMSO

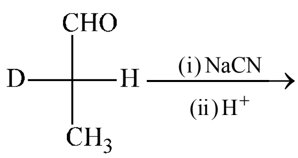
(C) $H_2S > H_2O$

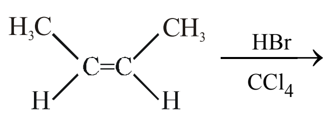
(D) 

HD0122

23. Which of following reaction products are diastereomer of each other :

(A) 

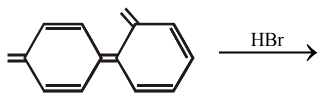
(B) 

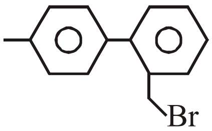
(C) 

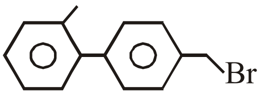
(D) $CH_3-\underset{\displaystyle Et}{\underset{|}{CH}}-CH=CH-Ph \xrightarrow[\text{peroxide}]{HCl}$
(Optically pure)

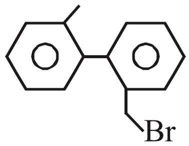
HD0123

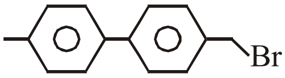
24. Product obtained in given reaction in good yield are :



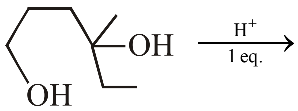
(A) 

(B) 

(C) 

(D) 

HD0124

25. 

Correct statements for given reaction :

(A) Product mixture is resolvable

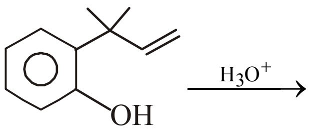
(B) Product can be separated by fractional distillation of mixture

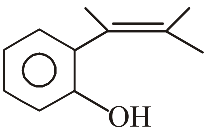
(C) Two products possible & both are optically active

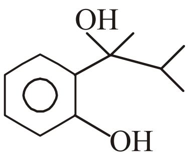
(D) Products are diastereomer

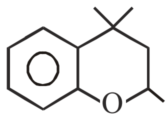
HD0125

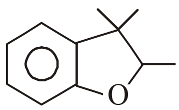
26. Which of the following can be formed during this reaction ?



(A) 

(B) 

(C) 

(D) 

HD0126

27. Select **true** statement(s) :

(A) Cyclopropane decolorizes bromine water

(B) In general, bromination is more selective than chlorination.

(C) The 2,4,6-tri-tert, butylphenoxy radical is resistant to dimerization.

(D) The radical-catalysed chlorination, $ArCH_3 \rightarrow ArCH_2Cl$, occurs faster when Ar = phenyl than when Ar = p-nitrophenyl.

HD0127

28. From left to right, correct statements are :

$CH_3-CH(CH_3)-Cl$ $\quad$ $CH_3-CH(CH_3)-Br$ $\quad$ $CH_3-CH(CH_3)-I$

(A) Rate of S_N1 mechanism increases in polar protic solvent

(B) Rate of S_N2 mechanism increases in DMSO

(C) Rate of E_2 mechanism increases

(D) Rate of E_1 mechanism increases

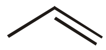
HD0128

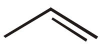
29. Number of following reactions which produces hydrocarbon as major product ?

(i) $CH_3-CH_2-Cl \xrightarrow[Et_2O]{Na}$

(ii) $CH_3-\overset{O}{\overset{||}{C}}-OK \xrightarrow{Electrolysis}$

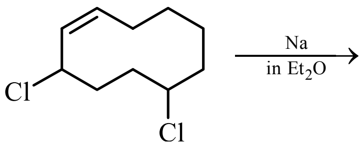
(iii) $\underset{Cl}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}} \xrightarrow[dust]{Zn}$

(iv)  $\xrightarrow[(ii)\ NaBH_4]{(i)\ Hg(OAc)_2 / H_2O}$

(v)  $\xrightarrow[CCl_4]{Br_2}$

(vi) $CH_3-CH_2-CH=CH_2 \xrightarrow[(ii)\ CH_3COOH / H_2O]{(i)\ B_2H_6\text{ - THF}}$

(A) 2 (B) 4 (C) 5 (D) 6 **HD0129**

30. 

Product

Correct statement is/are :

(A) odd no. of double bond equivalent in product

(B) product is bicyclic compound

(C) product can show geometrical isomerism

(D) reaction involve carbocation as intermediate **HD0130**

31. $Ph—CH = CH_2 + BrCCl_3 \xrightarrow{Peroxide}$ Product is :

(A) $Ph-\underset{Br}{\overset{H}{C}}-CH_2CCl_3$ (B) $Ph-\underset{CCl_3}{\overset{H}{C}}-CH_2Br$ (C) $Ph-\underset{H}{\overset{Br}{C}}-CH_2CCl_3$ (D) $Ph-\underset{H}{\overset{CCl_3}{C}}-CH_2Br$

HD0131

EXERCISE # S-I

Comprehension Type :

Paragraph for Q.No. 01 to 02

Groups like CN & $[-O-\ddot{N}=O]$ possess two nucleophilic centre and are called ambident nucleophiles. Actually cyanide group is hybride of two contributing structures and therefore can act as nucleophile in two different ways $[\overset{\ominus}{C}\equiv N \longleftrightarrow :C=N^{\ominus}]$. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage $[O-\ddot{N}=O]$.

1. Correct option among the following :

(A) $\underset{\text{Haloalkane}}{R-X} \xrightarrow{KCN} \underset{\text{Major product}}{RNC}$

(B) $R-X \xrightarrow{AgCN} \underset{\text{Major}}{R–CN}$

(C) $R-X \xrightarrow{KNO_2} \underset{\text{Major}}{R-O-N=O}$

(D) $R-X \xrightarrow{AgNO_2} \underset{\text{Major product}}{R-O-N=O}$ **HD0132**

2. Incorrect statement

$$R-X \begin{array}{c}\xrightarrow{KCN} \\ \xrightarrow{AgCN}\end{array}$$

(A) KCN is predominentely ionic in nature

(B) AgCN is mainly covalent in nature

(C) In AgCN, carbon is the donor atom

(D) In AgCN nitrogen is the donor atom **HD0133**

3. **Statement-1 :** HBr shows antimarkownikoff 's addition on propene but not HCl.

Statement-2 : H-Br is stronger acid than H–Cl.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true. **HD0134**

4. Match the List I with List II and select the correct answer using the codes given below the Lists.

List I	List II
(A) $CF_3–CHCl_2 \xrightarrow{alc.KOH/\Delta} CF_2=CCl_2$	(P) Elimination Reaction
(B) $CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH \xrightarrow{H^{\oplus}} CH_3-\underset{\displaystyle CH_3}{C}=CH_2$	(Q) Carbocation
(C) $CH_3–CH_2–Br \xrightarrow[\Delta]{alc.KOH} CH_2=CH_2$	(R) Carbanion
(D) $CH_3-\overset{\displaystyle Br}{\underset{\displaystyle CH_3}{C}}-CH_3 \xrightarrow[\Delta]{EtOH} CH_3-\underset{\displaystyle CH_3}{C}=CH_2$	(S) Free radical

HD0135

5. Match List I with List II and select the correct answer from the codes given below:

List I (Reactions)	**List II (Products)**
(A) $CH_3{-}O{-}SO_2CH_3 + C_2H_5\overset{\ominus}{O}$	(P) $CH_3{-}CH_2{-}PH_2$
(B) $CH_3{-}CH_2{-}I + PH_3$	(Q) $CH_3{-}O{-}C_2H_5$
(C) $HC \equiv \overset{\ominus}{C}\overset{\oplus}{Na} + CH_3{-}CH_2{-}Br$	(R) $CH_3{-}O{-}CH_3$
(D) $CH_3{-}Cl + CH_3{-}\overset{\ominus}{O}$	(S) $CH{\equiv}C{-}CH_2{-}CH_3$

HD0136

6. Match List-I with List-II for given S_N2 reaction & select the correct answer from the codes given below

$$Z{-}CH_2Br + CH_3O^{\ominus} \longrightarrow Z{-}CH_2{-}OCH_3 + Br^{\ominus}$$

List-I (Z–)	**List-II (relative reactivity)**
(A) H–	(P) 0.1
(B) CH_3–	(Q) 3
(C) C_2H_5–	(R) 1
(D) $(CH_3)_2CH{-}$	(S) 100

HD0137

7. Match the List I with List II and select the correct answer using the codes given below the Lists.

List I	**List II**
(A) E_{1CB}	(P) $CH_3CH_2CH_2\overset{\oplus}{N}(CH_3)_2{-}O^{\ominus}$
(B) Saytzeff alkene as major product	(Q) $CH_3CH_2CH_2-O-\underset{\underset{S}{\parallel}}{C}-S-CH_3$
(C) E_2	(R) $CH_3-CH_2-\overset{\overset{Cl}{\vert}}{C}H-CH_3$
(D) E_i	(S) $C_6H_5-CH_2-\underset{\underset{F}{\vert}}{C}H-CH_3$

HD0138

8.

Column - I (Reactions)	**Column - II (Characteristics)**
(A) $CH_3CH_2CH = CH_2 \xrightarrow{HBr}$	(P) Bimolecular
(B) $CH_3CH_2CH = CH_2 \xrightarrow{HBr,\ Peroxide}$	(Q) Carbocation intermediate
(C) $PhCH(CH_3)OH \xrightarrow{SOCl_2}$	(R) Regioselective
(D) $PhCH(CH_3)OH \xrightarrow{HBr}$	(S) Racemic modification
	(T) Stereospecific reaction

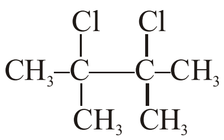
HD0139

9. **Column - I** **(Statements)** | **Column - II** **(Consistent path of reaction)**

Column - I (Statements)	**Column - II (Consistent path of reaction)**
(A) Reactions are concerted	(P) S_N1
(B) CH_3X cannot react	(Q) S_N2
(C) 3º R–X > 2º R–X > 1º R–X	(R) E1
(D) R–I reacts faster than R–Cl	(S) E2

HD0140

10. Each of the compounds in column A is subjected to further chlorination. **Match the following** for them :

Column – A	**Column – B**
(A) $CHCl_2–CH_2–CH_3$	(P) Optically active original compound
(B) $CH_2Cl–CHCl–CH_3$	(Q) Only one trichloro product
(C) $CH_2Cl–CH_2–CH_2–Cl$	(R) Three trichloro product.
(D) $CH_3–CCl_2–CH_3$	(S) Four trichloro product
(E) 	(T) Atleast one of the trichloro product is optically active
	(U) Two trichloro products.

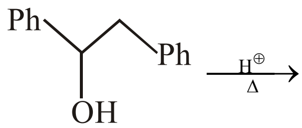
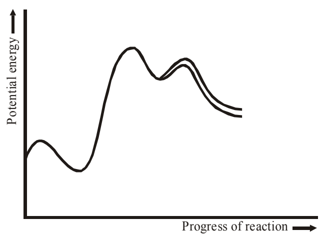
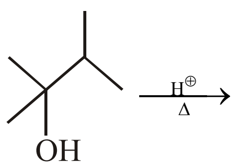
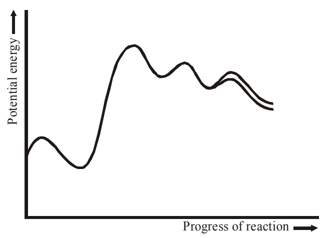
HD0141

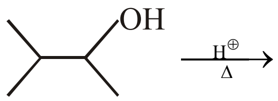
11.

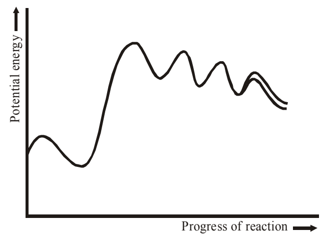
Column - I (Intermediate)	**Column - II**
(A) Carbocation	(P) Kolbey Electrolysis
(B) Carbanion	(Q) Wurtz reaction
(C) Free radical	(R) Dehydration of alcohol
(D) Octet complete in one of the intermediate	(S) Monocarboxylic acid with sodalime

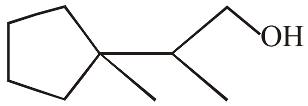
HD0142

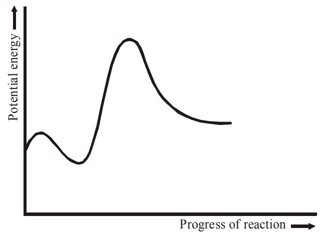
12. Match the column

Column–I (Reaction)	**Column–II (Potential energy curve)**
(A) 	(P) 
(B) 	(Q) 

(C) 

(R) 

(D) 

(S) 

HD0143

Subjective Type :

13. RCl is treated with Li in ether to form R – Li, R – Li reacts with water to form isopentane. R – Cl also reacts with sodium to form 2, 7–dimethyloctane. What is the structure of R – Cl. **HD0144**

14. A chloroderivative 'X' on reduction gave a hydrocarbon with five carbon atoms in the molecule. When X is dissolved in ether and treated with sodium, 2, 2, 5, 5-tetramethyl hexane is obtained. What is compound X. **HD0145**

15. C (Resolvable) $\xleftarrow{\text{HBr, peroxide}}$ A ($C_6H_{11}Br$) $\xrightarrow{\text{HBr}}$ B (Non-resolvable) $\xrightarrow{\text{Zn, Heat}}$ D (C_6H_{12}) Symmetrical Alkene

A: Decolourise Br_2 water and cannot be resolved

A $\xrightarrow{\text{Alc. KOH}}$ E (a single possible product)

Identify A, C & E in the sequence of reaction. **HD0146**

16. With the help of following data show HBr exhibits the peroxide effect.

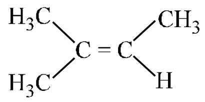
	ΔH_1^0/kJ mol^{-1}	ΔH_2^0/kJ mol^{-1}
H–X	$\dot{X} + CH_2 = CH_2 \rightarrow XCH_2 - \dot{C}H_2$ ↓	$XCH_2-\dot{C}H_2 + H-X \rightarrow XCH_2CH_3 + \dot{X}$
HCl	–67	+ 12.6
HBr	–25.1	– 50.2
HI	+46	–117.1

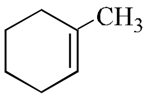
HD0147

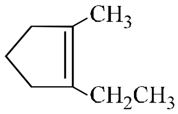
17. Write all the monochlorinated products (including stereo) of isohexane. **HD0148**

18. What are the products of the following reactions ?

(a) $PhCH = CHCH_3 + HBr \longrightarrow A$

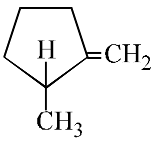
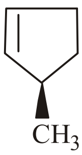
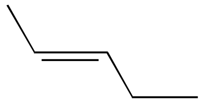
(b)  $+ HI \longrightarrow B$

(c)  $+ HBr \xrightarrow{\text{Peroxide}} C$

(d)  $+ HCl \longrightarrow D$ **HD0149**

19. It required 0.7 g of a hydrocarbon (A) to react completely with Br_2 (2.0 g) and form a non resolvable product. On treatment of (A) with HBr it yielded monobromo alkane (B). The same compound (B) was obtained when (A) was treated with HBr in presence of peroxide. Write down the structure formula of (A) and (B) and explain the reactions involved. **HD0150**

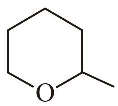
20. Complete following reaction :

(a)  $\xrightarrow{HCl}$ (b)  $\xrightarrow[CCl_4]{Br_2}$ (c)  $\xrightarrow[CS_2]{Cl_2}$ **HD0151**

21. $CH_3–CH_2I$ reacts more rapidly with strong base in comparison to CD_3CH_2I. **HD0152**

22. $CH≡C–CH_2–CH=CH_2$, adds up HBr to give $CH≡C–CH_2–CHBr–CH_3$ while $CH≡C–CH=CH_2$ adds up HBr to give $CH_2 = C(Br) – CH = CH_2$ **HD0153**

23. Predict the product(s) and write the mechanism of the given reaction :

 $\xrightarrow[\Delta]{\text{excess HI}}$ **HD0154**

24. What are the products of the following reactions?

(a) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + \bar{O}CH_3 \longrightarrow$ (b) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^- + CH_3 - X \longrightarrow$ **HD0155**

25. A primary alkyl bromide (A), C_4H_9Br, reacted with alcoholic KOH to give compound (B). Compound (B) reacted with HBr to give an isomer of (A). When (A) was reacted with sodium metal it gave compound (D), C_8H_{18}, which was different from the compound produced when n-butyl bromide was reacted with sodium. Draw the structure of (A) and write equations for all the reactions. **HD0156**

26. In study of chlorination of propane four products (A,B,C,D) of molecular formula $C_3H_6Cl_2$ were obtained. On further chlorination of the above products A gave one trichloro product, B gave two whereas C and D gave three each. When optically active C was chlorinated one of trichloro propanes was optically active and remaining two were optically inactive. Identify the structures of A,BC and D, and explain formation of products. **HD0157**

EXERCISE # (J-MAINS)

1. Following reaction :

$$(CH_3)_3C\text{–}Br + H_2O \longrightarrow (CH_3)_3C\text{–}OH + HBr$$

is an example of- **[AIEEE-2002]**

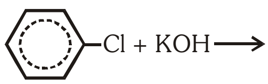
(1) Elimination reaction (2) Free radical substitution

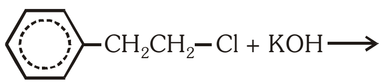
(3) Nucleophilic substitution (4) Electrophilic substitution **HD0158**

2. SN^1 reaction is feasible in- **[AIEEE-2002]**

(1) 

(2) 

(3) 

(4) 

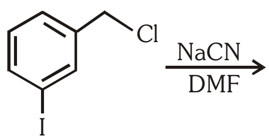
HD0159

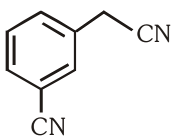
3. Bottles containing C_6H_5I and $C_6H_5\text{–}CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in a test tube and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment. **[AIEEE-2003]**

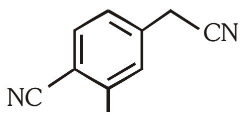
(1) A was C_6H_5I (2) A was $C_6H_5CH_2I$

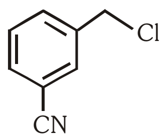
(3) B was C_6H_5I (4) Addition of HNO_3 was unnecessary **HD0160**

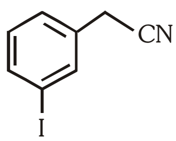
4. The structure of the major product formed in the following reaction is : **[AIEEE-2006]**



(1) 

(2) 

(3) 

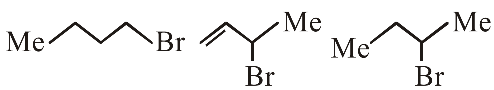
(4) 

HD0161

5. Which of the following on heating with aqueous KOH, produces acetaldehyde ? **[AIEEE-2009]**

(1) CH_2ClCH_2Cl (2) CH_3CHCl_2 (3) CH_3COCl (4) CH_3CH_2Cl **HD0162**

6. Consider the following bromides :- **[AIEEE-2010]**



(A) (B) (C)

The correct order of $S_N{}^1$ reactivity is

(1) A > B > C (2) B > C > A (3) B > A > C (4) C > B > A **HD0163**

7. In S_N2 reactions, the correct order of reactivity for the following compounds : **[JEE(Main)-2014]**

CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is :

(1) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$

(2) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

(3) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$

(4) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$ **HD0164**

8. In a nucleophilic substitution reaction : **[JEE(Main)-On-Line-2014]**

$R - Br + Cl^- \xrightarrow{DMF} R - Cl + Br^-$,

which one of the following undergoes complete inversion of configuration?

(1) $C_6H_5CCH_3C_6H_5Br$ (2) $C_6H_5CHCH_3Br$

(3) $C_6H_5CHC_6H_5Br$ (4) $C_6H_5CH_2Br$ **HD0165**

9. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

(1) 2-bromo-2-methylbutane **[JEE(Main)-On-Line-2014]**

(2) 2-bromo-3-methylbutane

(3) l-bromo-2-methylbutane

(4) l-bromo-3-methylbutane **HD0166**

10. In the presence of peroxide, $HC\ell$ and HI do not give anti-Markownikoff s addition to alkenes because :- **[JEE(Main)-On-Line-2014]**

(1) All the steps are exothermic in HCl and HI

(2) One of the steps is endothermic in HCl and HI

(3) HCl is oxidizing and the HI is reducing

(4) Both HCl and HI are strong acids **HD0167**

11. The major product formed when 1,1,1 - trichloro - propane is treated with aqueous potassium hydroxide is : **[JEE(Main)-On-Line-2014]**

(1) 2 - Propanol (2) Propionic acid (3) Propyne (4) 1 - Propanol **HD0168**

12. The synthesis of alkyl fluoride is best accomplished by : **[JEE(Main)-2015]**

(1) Finkelstein reaction (2) Swarts reaction

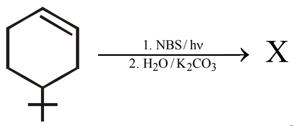
(3) Free radical fluorination (4) Sandmeyer's reaction **HD0169**

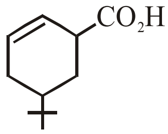
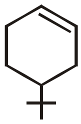
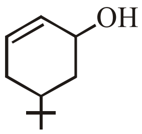
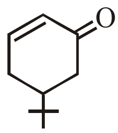
13. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields :

(1) $C_2H_5CH_2C(CH_3)_2-OCH_3$ (2) $C_2H_5CH_2C(CH_3)=CH_2$ (3) $C_2H_5CH_2=C(CH_3)-CH_3$ **[JEE-MAIN-2016]**

(1) (1) and (2) (2) All of these (3) (1) and (3) (4) (3) only **HD0170**

14. The product of the reaction given below is : **[JEE-MAIN-2016]**



(1)  (2)  (3)  (4)  **HD0171**

15. The reaction of propene with HOCl (Cl_2 + H_2O) proceeds through the intermediate : **[JEE-MAIN-2016]**

(1) $CH_3–CHCl–CH_2^+$ (2) $CH_3–CH^+–CH_2–OH$

(3) $CH_3–CH^+–CH_2–Cl$ (4) $CH_3–CH(OH)–CH_2^+$ **HD0172**

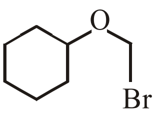
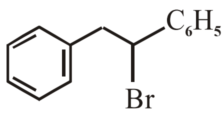
16. The increasing order of the reactivity of the following halides for the S_N1 reaction is : **[JEE-MAIN-2017]**

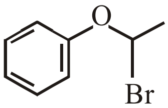
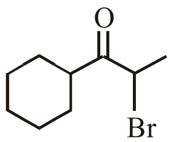
$CH_3CH(Cl)CH_2CH_3$ (I) $CH_3CH_2CH_2Cl$ (II) $p-H_3CO–C_6H_4–CH_2Cl$ (III)

(1) (III) < (II) < (I) (2) (II) < (I) < (III) (3) (I) < (III) < (II) (4) (II) < (III) < (I)

HD0173

17. Which of the following , upon treatment with tert-BuONa followed by addition of bromine water, fails to decolourize the colour of bromine ? **[JEE-MAIN-2017]**

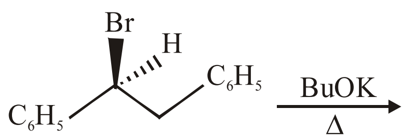
(1)  (2) 

(3)  (4)  **HD0174**

18. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : **[JEE-MAIN-2017]**

(1) Six (2) Zero (3) Two (4) Four **HD0175**

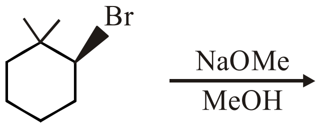
19. The major product obtained in the following reaction is : **[JEE-MAIN-2017]**

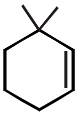
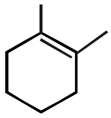
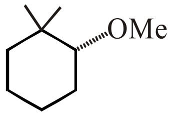
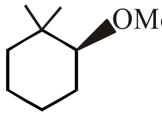


(1) $(\pm)C_6H_5CH(O^tBu)CH_2CH_6H_5$ (2) $C_6H_5CH=CHC_6H_5$

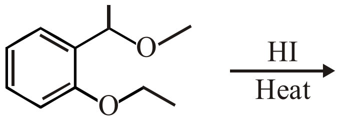
(3) $(+)C_6H_5CH(O^tBu)CH_2H_5$ (4) $(-)C_6H_5CH(O^tBu)CH_2C_6H_5$ **HD0176**

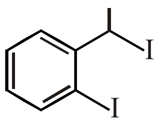
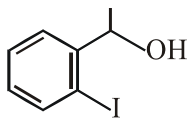
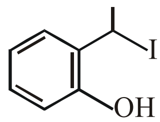
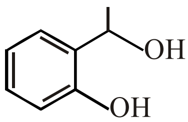
20. The major product of the following reaction is : **[JEE-MAIN-2018]**



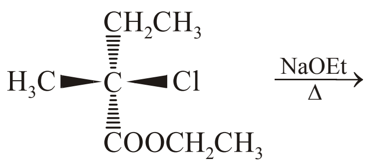
(1)  (2)  (3)  (4)  **HD0177**

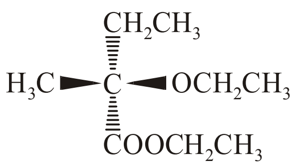
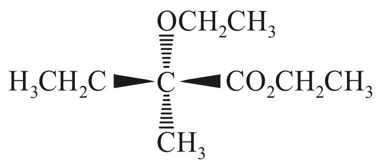
21. The major product formed in the following reaction is : **[JEE-MAIN-2018]**

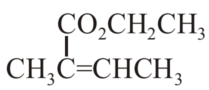
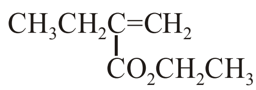


(1)  (2)  (3)  (4)  **HD0178**

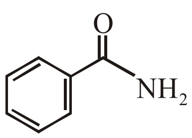
22. The major product of the following reaction is: **[JEE-MAIN-(January) -2019]**

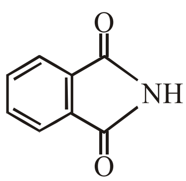


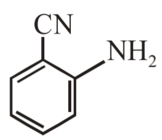
(1)  (2) 

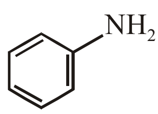
(3)  (4)  **HD0179**

23. The increasing order of reactivity of the following compounds towards reaction with alkyl halides directly is : **[JEE-MAIN-(January) -2019]**


(A)


(B)


(C)


(D)

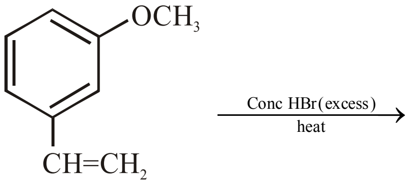
(1) (B) < (A) < (D) < (C)

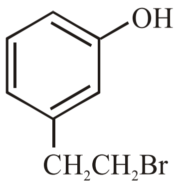
(2) (B) < (A) < (C) < (D)

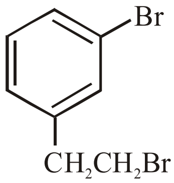
(3) (A) < (C) < (D) < (B)

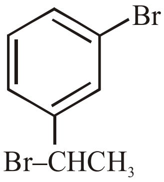
(4) (A) < (B) < (C) < (D) **HD0180**

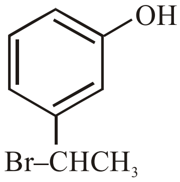
24. The major product of the following reactions: **[JEE-MAIN-(April) -2019]**



(1) 

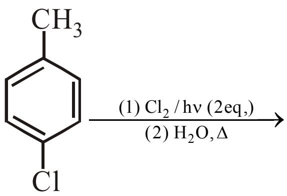
(2) 

(3) 

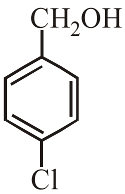
(4) 

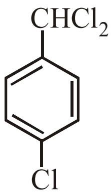
HD0181

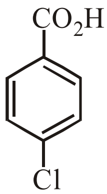
25. The major product of the following reaction is:

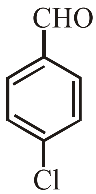


[JEE-MAIN-(April) -2019]

(1) 

(2) 

(3) 

(4) 

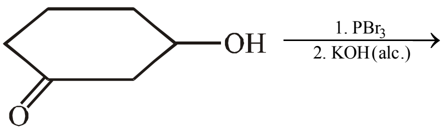
HD0182

26. Which one of the following alkenes when treated with HCl yields majorly an anti Markovnikov product? **[JEE-MAIN-(April) -2019]**

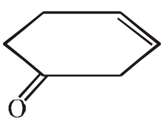
(1) $F_3C - CH = CH_2$ (2) $Cl - CH = CH_2$

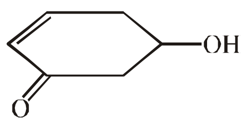
(3) $CH_3O - CH = CH_2$ (4) $H_2N - CH = CH_2$ **HD0183**

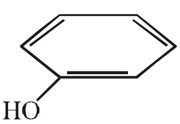
27. The mojor product of the following reaction is :

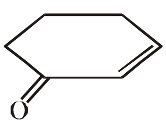


[JEE-MAIN-(April) -2019]

(1) 

(2) 

(3) 

(4) 

HD0184

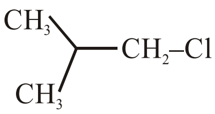
28. The major product of the following reaction is :

$$CH_3C\equiv CH \xrightarrow[\text{(ii) DI}]{\text{(i) DCl (1 equiv.)}}$$ **[JEE-MAIN-(April) -2019]**

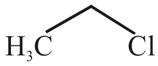
(1) $CH_3CD(Cl)CHD(I)$ (2) $CH_3CD_2CH(Cl)(I)$

(3) $CH_3CD(I)CHD(Cl)$ (4) $CH_3C(I)(Cl)CHD_2$ **HD0185**

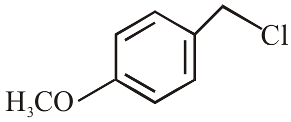
29. Increasing order of reactivity of the following compounds for S_N1 substitution is:
[JEE-MAIN-(April) -2019]



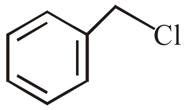
(A)



(B)



(C)

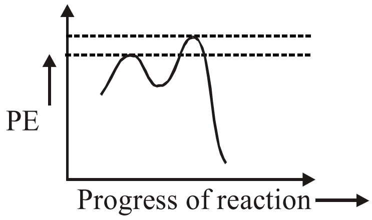


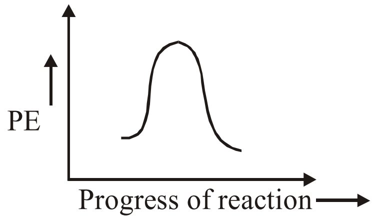
(D)

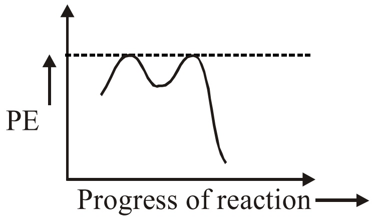
(1) (B) < (C) < (D) < (A) (2) (A) < (B) < (D) < (C)

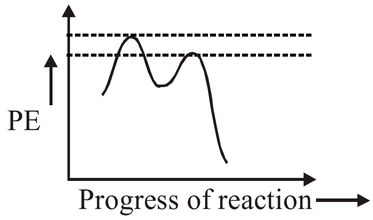
(3) (B) < (A) < (D) < (C) (4) (B) < (C) < (A) < (D) **HD0186**

30. Which of the following potential energy (PE) diagrams represents the S_N1 reaction?
[JEE-MAIN-(April) -2019]

(1)


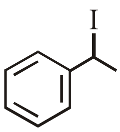
(2)


(3)


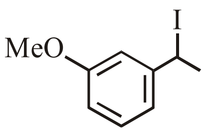
(4)


HD0187

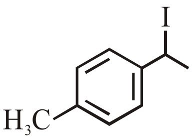
31. Increasing rate of S_N1 reaction in the following compounds is :



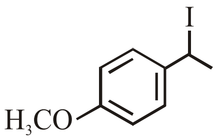
(A)



(B)



(C)



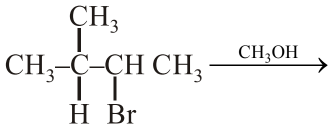
(D)

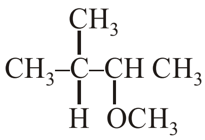
[JEE-MAIN-(April) -2019]

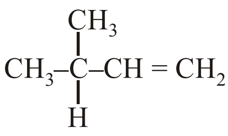
(1) (A) < (B) < (C) < (D) (2) (B) < (A) < (D) < (C)

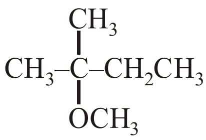
(3) (B) < (A) < (C) < (D) (4) (A) < (B) < (D) < (C) **HD0188**

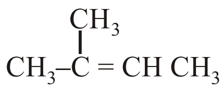
32. The major product of the following reaction is :- **[JEE-MAIN-(April) -2019]**



(1) 

(2) 

(3) 

(4) 

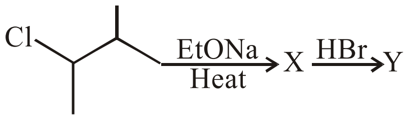
HD0189

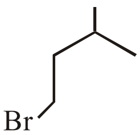
33. The increasing order of nucleophilicity of the following nucleophiles is : **[JEE-MAIN-(April) -2019]**

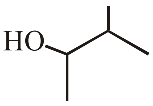
(a) $CH_3CO_2^{\ominus}$ (b) H_2O (c) $CH_3SO_3^{\ominus}$ (d) $\overset{\ominus}{O}H$

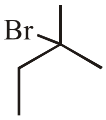
(1) (b) < (c) < (a) < (d)
(2) (a) < (d) < (c) < (b)
(3) (d) < (a) < (c) < (b)
(4) (b) < (c) < (d) < (a) **HD0190**

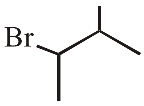
34. The major product 'Y' in the following reaction is: **[JEE-MAIN-(April) -2019]**



(1) 

(2) 

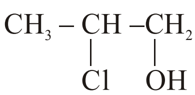
(3) 

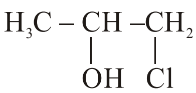
(4) 

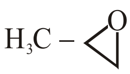
HD0191

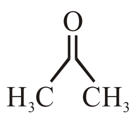
35. The major product of the following addition reaction is : **[JEE-MAIN-(April) -2019]**

$$H_3C - CH = CH_2 \xrightarrow{Cl_2/H_2O}$$

(1) 

(2) 

(3) 

(4) 

HD0192

36. An ' Assertion' and a 'Reason' are given below. Choose the correct answer from the following options.
Assertion (A) : Vinyl halides do not undergo nucleophilic substitution easily.
Reason (R) : Even though the intermediate carbocation is stabilized by loosely held π-electrons, the cleavage is difficult becuase of strong bonding.
[JEE-MAIN-(April) -2019]

(1) Both (A) and (R) are wrong statements
(2) Both (A) and (R) are correct statements and (R) is the correct explanation of (A)
(3) Both (A) and (R) are correct statements but (R) is not the correct explanation of (A)
(4) (A) is a correct statement but (R) is a wrong statement. **HD0193**

37. The reaction of 2, 4-hexadiene with one equivalent of bromine at 0ºC gives a mixture of two compounds 'X' and 'Y'. If 'X' is 4, 5 - dibromohex-2-ene, 'Y' is - **[NSE -2019]**

(1) 2,5-dibromohex-2-ene (2) 2,5-dibromohex-3-ene

(3) 2,3-dibromohex-3-ene (4) 3,4-dibromohex-3-ene **HD0194**

38. Consider the following reactions : **[JEE-MAIN-2020]**

(a) $(CH_3)_3CCH(OH)CH_3 \xrightarrow{\text{conc.}H_2SO_4}$

(b) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow{\text{alc.KOH}}$

(c) $(CH_3)_2CHCH(Br)CH_3 \xrightarrow[\text{It should be }(CH_3)_3CO^{\ominus}K^{\oplus}]{\text{given by NTA }(CH_3)_3O^{\ominus}K^{\oplus}}$

(d) $(CH_3)_2C(OH)–CH_2–CHO \xrightarrow{\Delta}$

Which of these reaction(s) will not produce Saytzeff product ? **[JEE-MAIN-2020]**

(1) (c) only (2) (a), (c) and (d)

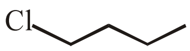
(3) (d) only (4) (b) and (d) **HD0195**

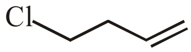
39. Arrange the following bonds according to their average bond energies in descending order : C–Cl, C–Br, C–F, C–I **[JEE-MAIN-2020]**

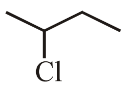
(1) C–I > C–Br > C–Cl > C–F (2) C–Br > C–I > C–Cl > C–F

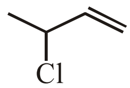
(3) C–F > C–Cl > C–Br > C–I (4) C–Cl > C–Br > C–I > C–F **HD0196**

40. The decreasing order of reactivity towards dehydrohalogenation (E_1) reaction of the following compounds is : **[JEE-MAIN-2020]**

(A) 

(B) 

(C) 

(D) 

(1) B > D > A > C (2) B > D > C > A

(3) D > B > C > A (4) B > A > D > C **HD0197**

EXERCISE # (J-ADVANCE OBJECTIVE)

1. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives : **[IIT 1990]**
(A) o-cresol (B) p-cresol
(C) 2,4-dihydroxytoluene (D) Benzoic acid **HD0198**

2. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to **[IIT 1990]**
(A) The formation of less stable carbonium ion (B) Resonance stabilization
(C) The inductive effect (D) sp^2 hybridised carbon attached to the halogen **HD0199**

3. 1-Chlorobutane on reaction with alcoholic potash gives : **[ITT 1991]**
(A) 1-butene (B) 1-butanol (C) 2-butene (D) 2-butanol **HD0200**

4. The products of reaction of alcoholic $AgNO_2$ with ethyl bromide are **[IIT 1991]**
(A) Ethane (B) Ethyl nitrite (C) Nitroethane (D) Ethyl alcohol **HD0201**

5. Arrange the following compounds in order of increasing dipole moment **[IIT 1996]**
Toluene (I), m-dichlorobenzene (II), o-dichlorobenzene (III), p-dichlorobenzene (IV)
(A) I < IV < II < III (B) IV < I < II < III (C) IV < I < III < II (D) IV < II < I < III **HD0202**

6. $(CH_3)_3CMgCl$ reaction with D_2O produces: **[IIT 1997]**
(A) $(CH_3)_3CD$ (B) $(CH_3)_3OD$ (C) $(CD_3)_3CD$ (D) $(CH_3)_3OD$ **HD0203**

7. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with: **[IIT 1998]**
(A) SO_2Cl_2 (B) $SOCl_2$ (C) $Cl_2,(h\nu)$ (D) NaOCl **HD0204**

8. The order of reactivity of the following alkyl halides for a S_N2 reaction is: **[IIT 2000]**
(A) RF > RC > R–Br > R–I (B) R–F > R–Br > R–Cl > R–I
(C) R–Cl > R–Br > RF > RI (D) R–I > RBr > R–Cl > R–F **HD0205**

9. Which of the following has the highest nucleophilicity? **[IIT 2000]**
(A) F^- (B) OH^- (C) CH_3^- (D) NH_2^- **HD0206**

10. An S_N2 reaction at an asymmetric carbon of a compound always gives. **[IIT 2001]**
(A) an enantiomer of the substance (B) a product with opposite optical rotation
(C) a mixture of diasteremoers (D) a single stereoisomer **HD0207**

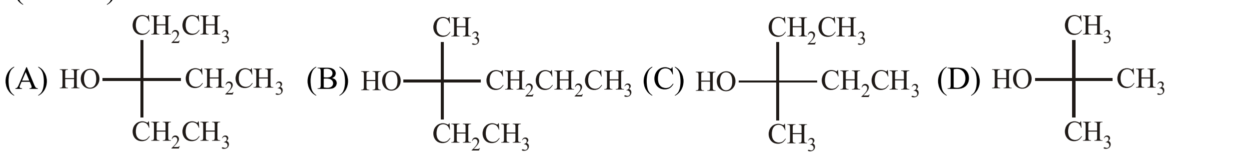
11. The compound that will react most readily with NaOH to form methanol is **[IIT 2001]**
(A) $(CH_3)_4N^+I^-$ (B) CH_3OCH_3 (C) $(CH_3)_3S^+I^-$ (D) $(CH_3)_3CCl$ **HD0208**

12. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformation: **[IIT 2002]**

$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

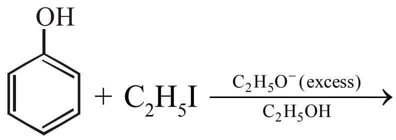
(A) X = dilute aqueous NaOH, 20°C; Y = HBr / acetic acid, 20°C
(B) X = concentrated alcoholic NaOH, 80°C; Y = HBr/ acetic acid 20°C
(C) X = dilute aqueous NaOH, 20°C; Y = Br_2 / $CHCl_3$, 0°C
(D) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C **HD0209**

13. CH_3MgBr + Ethyl ester → which can be formed as product. **[IIT 2003]**
(excess)



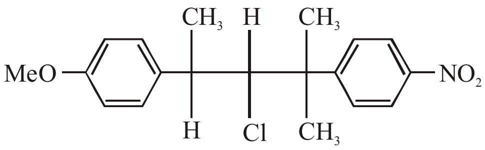
HD0210

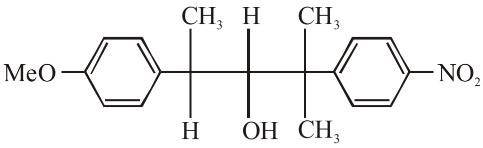
14. The product of following reaction is **[IIT 2003]**

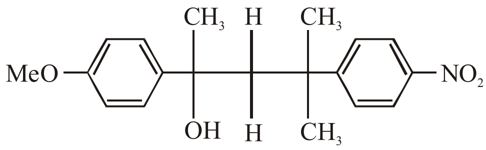


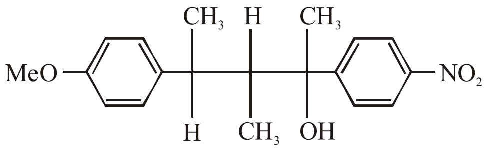
(A) $C_6H_5OC_2H_5$ (B) $C_2H_5OC_2H_5$ (C) $C_6H_5OC_6H_5$ (D) C_6H_5I **HD0211**

15. The following compound on hydrolysis in aqueous acetone will give: **[IIT 2005]**



(K) 

(L) 

(M) 

It mainly gives

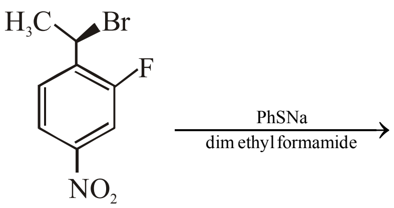
(A) K and L (B) Only K (C)L and M (D) Only M **HD0212**

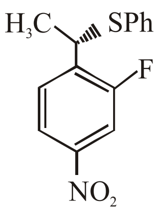
16 Match the following: **[IIT 2006]**

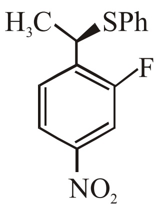
Column I	Column II
(A) CH_3–CHBr–CD_3 on treatment with alc. KOH gives CH_2=CH-CD_3 as a major product.	(P) E1 reaction
(B) Ph – CHBr - CH_3 reacts faster than Ph-CHBr-CD_3.	(Q) E2 reaction
(C) Ph-CD_2-CH_2Br on treatment with $C_2H_5OD/C_2H_5O^-$ gives Ph-CD=CH_2 as the major product.	(R) E1cb reaction
(D) $PhCH_2CH_2Br$ and $PhCD_2CH_2Br$ react with same rate.	(S) First order reaction

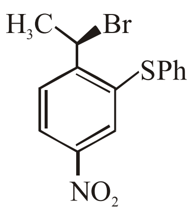
HD0213

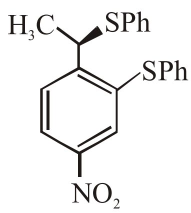
17 The major product of the following reaction is **[IIT 2008]**



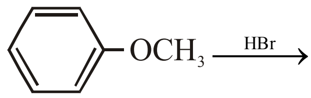
(A) 

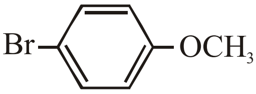
(B) 

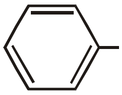
(C) 

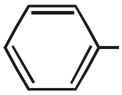
(D) 

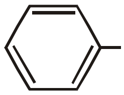
HD0214

18 In the reaction  the products are **[IIT 2010]**

(A)  and H_2

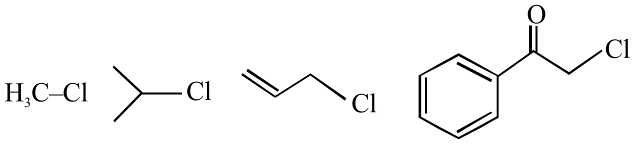
(B)  and CH_3Br

(C)  and CH_3OH

(D)  and CH_3Br

HD0215

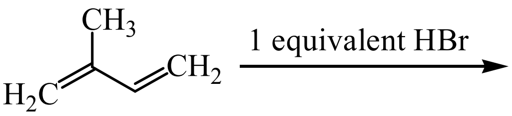
19. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as - **[IIT 2013]**

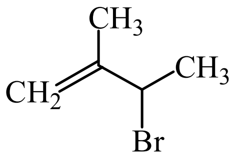
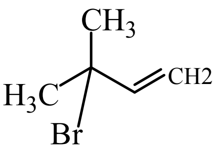
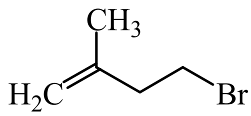
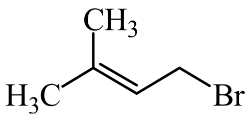


P **Q** **R** **S**

(A) P > Q > R > S (B) S > P > R > Q (C) P > R > Q > S (D) R > P > S > Q **HD0216**

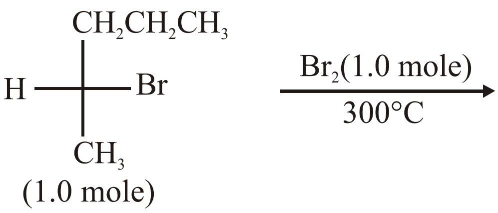
20. In the following reaction, the major product is - **[IIT 2015]**



(A)  (B)  (C)  (D) 

HD0217

21. In the following monobromination reaction, the number of possible chiral products is **[IIT 2016]**

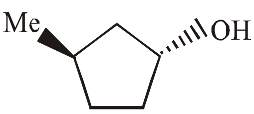
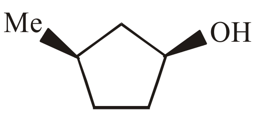
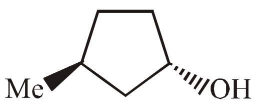
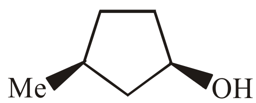


(enantiomerically pure)

HD0218

22. In the following reaction sequence, the correct structure(s) of X is (are) **[IIT-2018]**

enantiomerically pure

(A)  (B)  (C)  (D) 

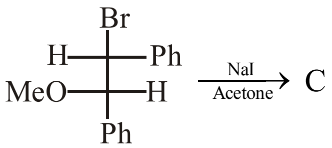
HD0219

EXERCISE # (J-ADVANCE SUBJECTIVE)

1. An alkyl halide X of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2,3–dimethylbutane. Predict the structures of X, Y and Z. **[IIT 1996]**

HD0220

2. Predict the structure of the intermediates/products in the following reaction sequence –**[IIT 1996]**



HD0221

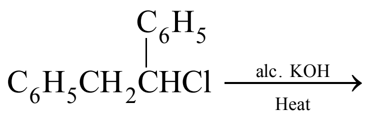
3. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

$(CH_3)_3$ CBr + NaOMe $\longrightarrow$ or CH_3Br + NaO-t-Bu $\longrightarrow$ **[IIT 1997]**

HD0222

4. Write the structures of the products: **[IIT 1998]**

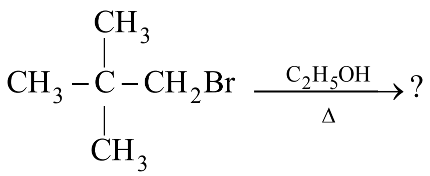
$C_6H_5CH_2CHClC_6H_5 \xrightarrow{\text{Alc.KOH}}$ **HD0223**

5. (a)  A + B Write structures of (A) and (B). **HD0224**

(b) $(CH_3)_2CHOCH_3 \xrightarrow[\text{Heat}]{\text{HI(excess)}}$ A + B Write structures of A and B. **[IIT 1998]**

HD0224

6. What would be major product? **[IIT 2000]**

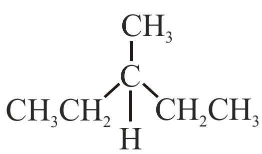


HD0225

7. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **[IIT 2011]**

HD0226

8. The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compounds, is **[IIT 2011]**



HD0227

ANSWER KEY

EXERCISE # O-I

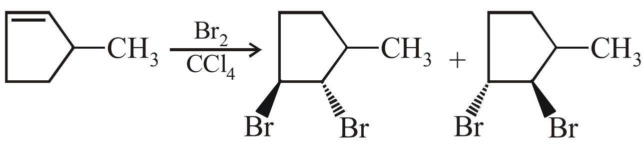
1.	**Ans. (A)**	**2.**	**Ans. (C)**	**3.**	**Ans. (D)**	**4.**	**Ans. (D)**	**5.**	**Ans. (C)**
6.	**Ans. (C)**	**7.**	**Ans. (B)**	**8.**	**Ans. (D)**	**9.**	**Ans. (B)**	**10.**	**Ans. (B)**
11.	**Ans. (C)**	**12.**	**Ans. (C)**	**13.**	**Ans. (C)**	**14.**	**Ans. (A)**	**15.**	**Ans. (D)**
16.	**Ans. (B)**	**17.**	**Ans. (A)**	**18.**	**Ans. (D)**	**19**	**Ans. (C)**	**20.**	**Ans. (D)**
21	**Ans. (D)**	**22.**	**Ans. (A)**	**23.**	**Ans. (D)**	**24.**	**Ans. (A)**	**25.**	**Ans. (B)**
26.	**Ans. (C)**	**27.**	**Ans. (B)**	**28.**	**Ans. (C)**	**29.**	**Ans. (D)**	**30.**	**Ans. (B)**
31.	**Ans. (D)**	**32**	**Ans. (B)**	**33.**	**Ans. (B)**	**34**	**Ans. (C)**	**35.**	**Ans. (A)**
36.	**Ans. (A)**	**37.**	**Ans. (C)**	**38.**	**Ans. (D)**	**39.**	**Ans. (A)**	**40**	**Ans.(B)**
41.	**Ans. (B)**	**42.**	**Ans. (C)**	**43.**	**Ans. (A)**	**44.**	**Ans. (C)**	**45.**	**Ans. (A)**
46.	**Ans. (C)**	**47.**	**Ans. (D)**	**48.**	**Ans.(D)**	**49.**	**Ans. (B)**	**50**	**Ans. (C)**
51	**Ans. (B)**	**52**	**Ans. (C)**	**53.**	**Ans. (A)**	**54.**	**Ans. (C)**	**55.**	**Ans. (A)**
56.	**Ans. (D)**	**57.**	**Ans. (C)**	**58.**	**Ans. (B)**	**59.**	**Ans. (B)**	**60.**	**Ans. (C)**
61.	**Ans. (C)**	**62.**	**Ans. (D)**	**63.**	**Ans. (A)**	**64.**	**Ans. (B)**	**65.**	**Ans. (A)**
66.	**Ans. (C)**	**67.**	**Ans. (D)**	**68.**	**Ans.(B)**	**69.**	**Ans. (B)**	**70.**	**Ans. (C)**
71.	**Ans. (B)**	**72.**	**Ans. (C)**	**73.**	**Ans. (C)**	**74.**	**Ans. (A)**	**75.**	**Ans. (B)**
76.	**Ans. (A)**	**77**	**Ans. (A)**	**78.**	**Ans. (D)**	**79.**	**Ans.(C)**	**80.**	**Ans. (B)**
81.	**Ans. (C)**	**82.**	**Ans. (C)**	**83**	**Ans. (C)**	**84**	**Ans. (B)**	**85**	**Ans. (D)**
86.	**Ans. (C)**	**87.**	**Ans.(B)**	**88.**	**Ans. (A)**	**89.**	**Ans. (C)**	**90.**	**Ans. (C)**
91.	**Ans. (A)**	**92.**	**Ans. (C)**	**93.**	**Ans. (B)**	**94.**	**Ans. (B)**	**95.**	**Ans. (A)**
96.	**Ans. (B)**	**97.**	**Ans. (D)**	**98.**	**Ans.(B)**	**99.**	**Ans. (B)**	**100.**	**Ans. (D)**

EXERCISE #O-II

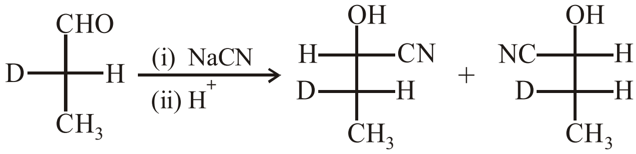
1.	**Ans. (A,B,C,D)**	**2.**	**Ans. (A,B,C)**	**3.**	**Ans. (A,B)**	**4.**	**Ans. (B,D)**
5.	**Ans. (B,D)**	**6.**	**Ans. (A,C)**	**7.**	**Ans. (A,C,D)**	**8.**	**Ans. (A,C)**
9.	**Ans. (A,B,D)**	**10.**	**Ans. (A,C)**	**11.**	**Ans. (A,B,D)**	**12.**	**Ans. (A,C,D)**
13.	**Ans. (A,CD)**	**14.**	**Ans. (A,B,C)**	**15.**	**Ans. (A,C,D)**	**16.**	**Ans. (B, D)**
17.	**Ans. (B,D)**	**18.**	**Ans. (A,B)**	**19.**	**Ans. (A,B,C)**	**20.**	**Ans. (C,D)**
21.	**Ans. (B,C)**	**22.**	**Ans. (B,C,D)**				

23. **Ans.**

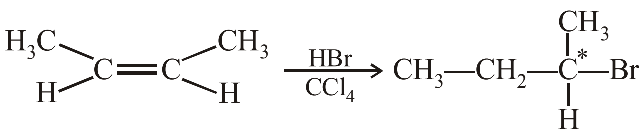
(A)



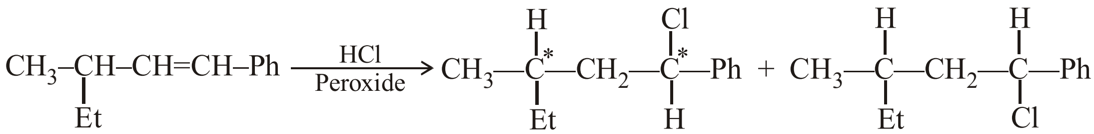
(B)



(c)



(d)



24. **Ans. (A,B)** **25.** **Ans. (A,C)** **26.** **Ans. (A,B,D)** **27.** **Ans. (A,B,C,D)**
28. **Ans. (A,B,C,D)** **29.** **Ans. (B)** **30.** **Ans. (A,B,C)** **31.** **Ans. (A,C)**

EXERCISE # S-I

1. **Ans. (C)** **2.** **Ans. (C)** **3.** **Ans. (B)**

4. **Ans. (A) → P, R ; (B) → P, Q ; (C) → P ; (D) → P, Q**

5. **Ans. (A)→Q ; (B)→P ; (C)→S ; (D)→R**

6. **Ans. (A) → S ; (B) → Q ; (C) → R ; (D) → P**

7. **Ans. (A) → S ; (B) → R, S ; (C) → R ; (D) → P, Q**

8. **Ans. (A) → P, Q, R, S ; (B) → P, R ; (C) → P, T ; (D) → Q, S**

9. **Ans. (A) → Q, S ; (B) → P, R, S ; (C) → P, R, S ; (D) → P, Q, R, S**

10. **Ans. (A) → S, T ; (B) → P , S, T ; (C) → U ; (D) → Q ; (E) → T, U**

11. **Ans. (A) → R ; (B) → Q, S ; (C) → P, Q ; (D) → Q, S**

12. **Ans. (A) → P ; (B) → P ; (C) → Q ; (D) → R**

13. **Ans.**

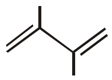
C–I bond being less stable than C–Cl bond and thus on heating heterolytic cleavage of C–I form I^- which gives yellow precipitate with $AgNO_3$.

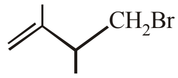
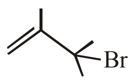
14. **Ans.** X is $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-Cl$

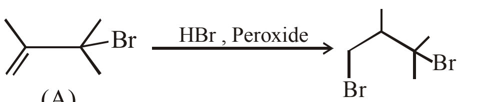
15. **Ans.** Molecule A, $C_6H_{11}Br$ has 1 unsaturation

$$\Big\downarrow \text{Alc. KOH}$$

A single possible product , it suggests a symmetrical arrangement

So, E = 

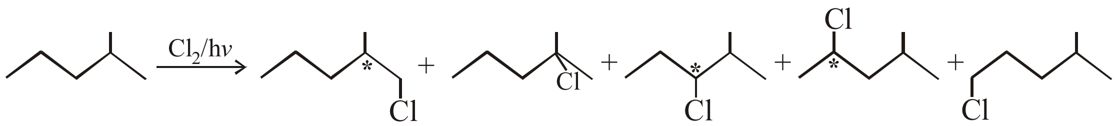
There are only two possibilities of A  (I) or  (II) structure I can be resolved while structure II cannot be resolved so 'A' :



(A) resolvable product (C)

16. **Ans.** Both step is exothermic with HBr

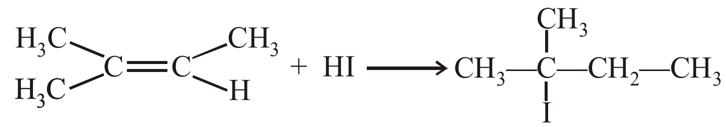
17. **Ans.**

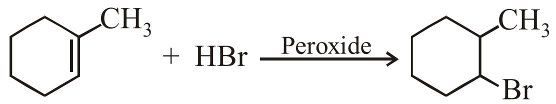


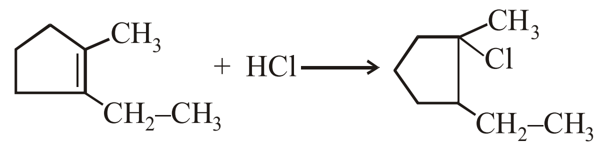
2 2 2

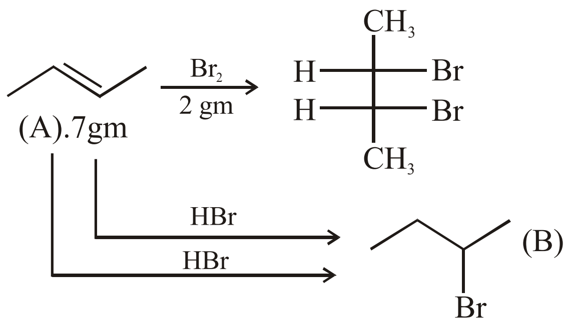
18. Ans.

(a) $Ph—CH = CHCH_3 + HBr \longrightarrow Ph—\underset{\displaystyle Br}{CH}—CH_2—CH_3$

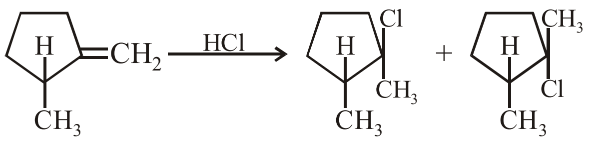
(b) 

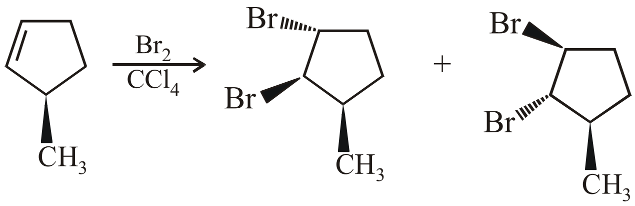
(c) 

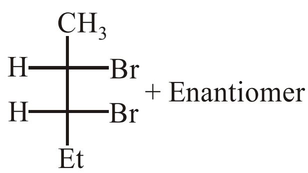
(d) 

19. Ans. 

20. Ans.

(a) 

(b) 

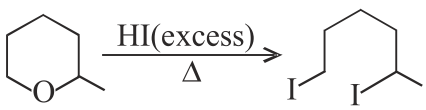
(c) 

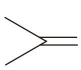
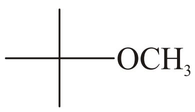
21. Ans.

The elimination of HI (or DI) in presence of strong base shows E2 elimination. The rate determining step involves breaking up of C – H (or C–D) bond. The C–D bond being stronger than C–H and thus elimination is faster in case of $CH_3 - CH_2I$.

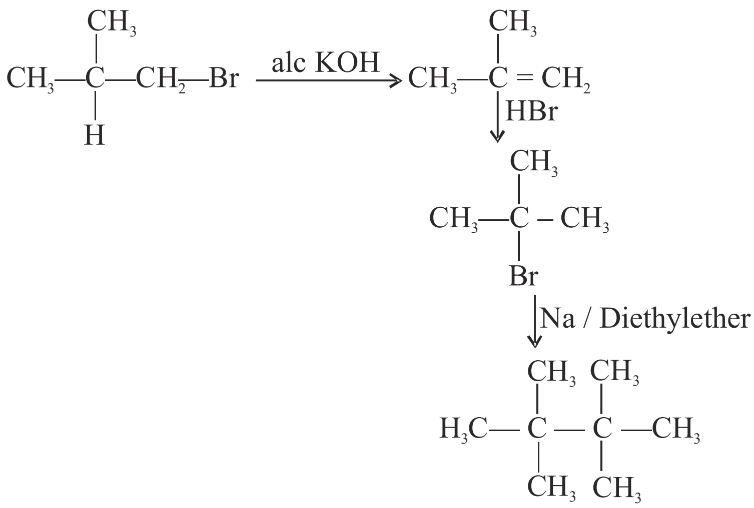
22. Ans.

In second compound π bonds are conjugated so due to resonance given product is formed as major product.

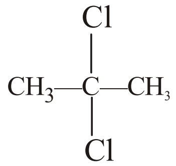
23. Ans. 

24. Ans. (a)  **(b)** 

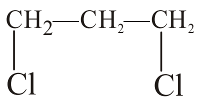
25. Ans.



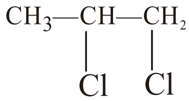
26. Ans. **(A)**



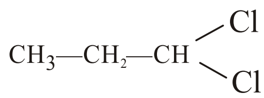
(B)



(C)



(D)



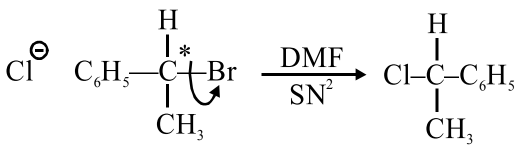
EXERCISE # (J-MAINS)

1. Ans. (3) **2. Ans. (1)** **3. Ans. (1)** **4. Ans. (4)**

5. Ans. (2) **6. Ans. (2)** **7. Ans. (4)**

8. Ans. (2)

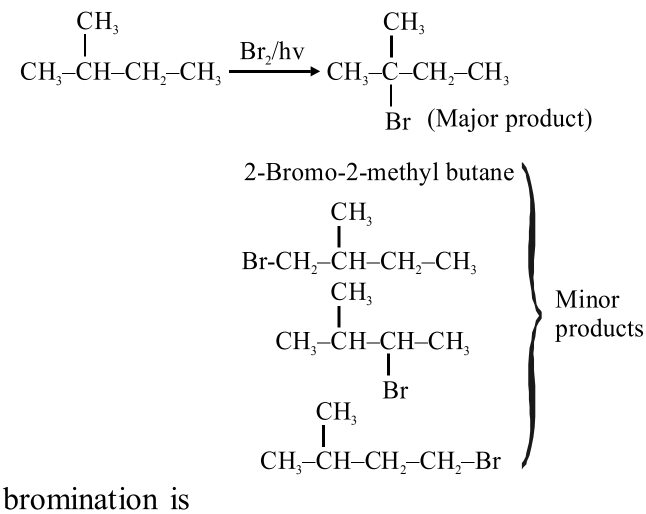
Sol.



inverted product

9. Ans. (1)

Sol.



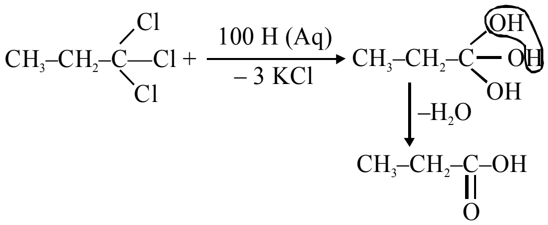
relectivity ratio for bromination is

1° : 2° : 3° : : 1 : 82 : 1600

Hence 3° product will be major product.

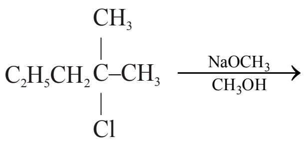
10. Ans. (2)

11. Ans. (2)

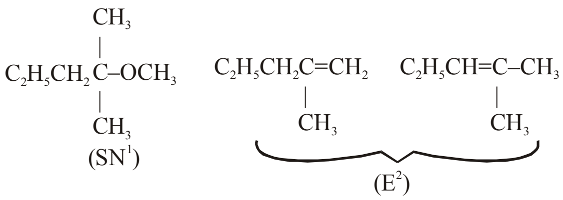
Sol. 

12. Ans. (2)

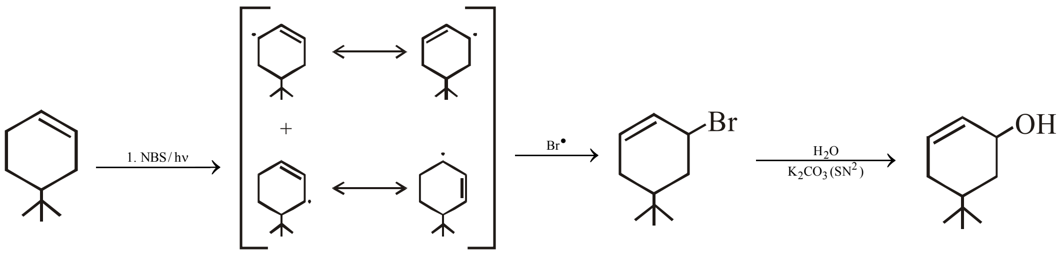
13. Ans. (2)

Sol. 

possible mechanism which takes place is E^2 & SN^1 mechanism. Hence possible products are.

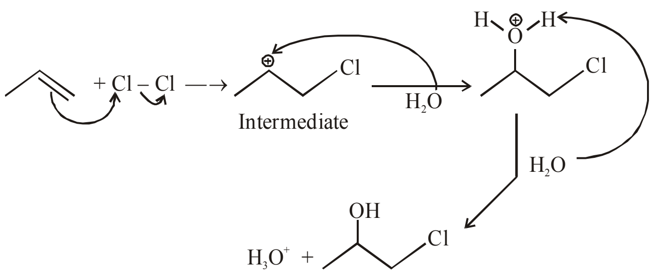


14. Ans. (3)

Sol. 

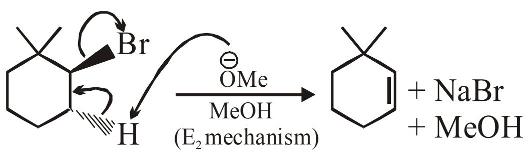
15. Ans. (3)

Sol.



16. Ans. (2) **17. Ans. (1)** **18. Ans. (4)** **19. Ans. (2)**

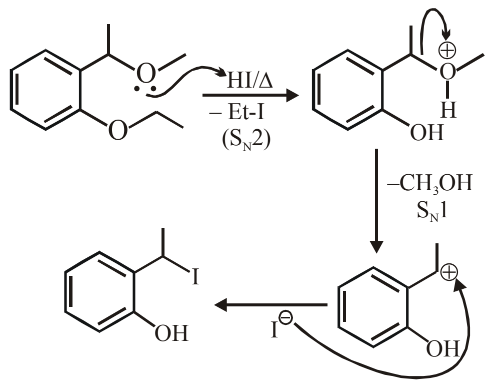
20. Ans. (1)

Sol. 

Reaction is dehydrohalogenation E^2-elimination reaction. Elimination takes place in single step and proceed by formation of transition state from anti position.

21. Ans. (3)

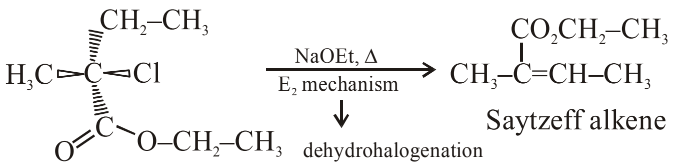
Sol.



It is nucleophilic substitution reaction.

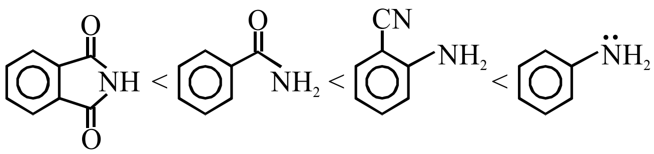
22. Ans. (3)

Sol.



23. Ans. (2)

Sol. Nucleophilicity order



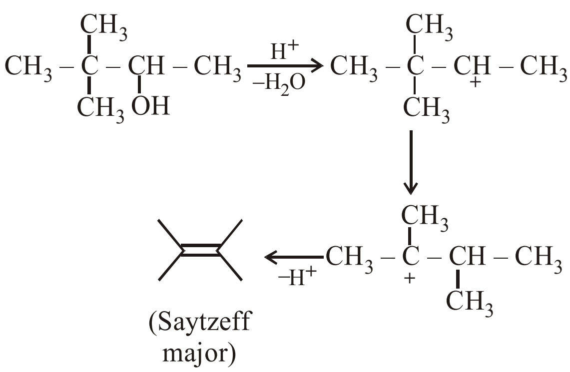
B A C D

24. Ans.(4)	**25. Ans.(4)**	**26. Ans.(1)**	**27. Ans.(4)**
28. Ans.(4)	**29. Ans.(3)**	**30. Ans.(4)**	**31. Ans.(3)**
32. Ans.(3)	**33. Ans.(1)**	**34. Ans.(3)**	**35. Ans.(2)**
36. Ans.(4)	**37. Ans.(2)**		

38. Ans.(1)

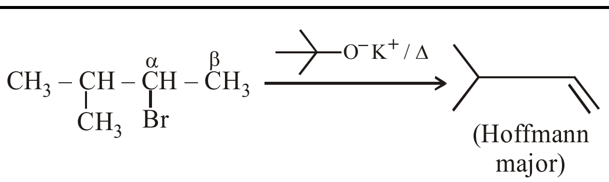
Sol.

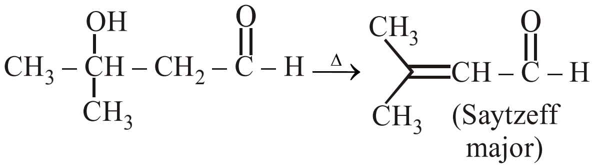
(a)



(b) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3 \xrightarrow[\Delta]{alc.KOH} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_3$

(Saytzeff major)

(c) 

(d) 

$(CH_3)_3O^-K^+$ is incorrect representation of potassium tert-butoxide $[(CH_3)_3CO^-K^+]$.
So it is possible that it can be given as Bonus

39. Ans. (3)

Sol. Bond length order in carbon halogen bonds are in the order of C – F < C – Cl < C – Br < C – I
Hence, Bond energy order
C – F > C – Cl > C – Br > C – I

40. Ans. (3)

Sol. Reactivity D > B > C > A
Carbocation formed from D is most stable
Carbocation formed from A is least stable

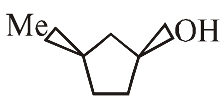
EXERCISE # (J-ADVANCE OBJECTIVE)

1. Ans. (D)	**2. Ans. (B,D)**	**3. Ans. (A)**	**4. Ans. (C)**	**5. Ans. (B)**
6. Ans. (A)	**7. Ans. (A,C)**	**8. Ans. (D)**	**9. Ans. (C)**	**10. Ans. (D)**
11. Ans. (A)	**12. Ans. (B)**	**13. Ans. (D)**	**14. Ans. (B)**	**15. Ans. (A)**

16. Ans. (A) → Q ; (B) → Q ; (C) → R, S ; (D) → P, S

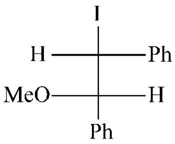
17. Ans. (A)	**18. Ans. (D)**	**19. Ans. (B)**	**20. Ans. (D)**	**21. Ans. (5)**
22. Ans. (B)				

Sol. X $\xrightarrow[\text{(2)NaI, Me}_2\text{C=O} \quad \text{(3)NaN}_3\text{, HCONMe}_2]{\text{(1)PBr}_3\text{Et}_2\text{O}}$ 

all the three reaction are S_{N^2} so X is 

EXERCISE # (J-ADVANCE SUBJECTIVE)

1. Ans. (X) : $CH_3-\underset{Cl}{\overset{CH_3}{C}}-\overset{CH_3}{CH}-CH_3$ **; (Y) :** $CH_2=\overset{CH_3}{C}-\overset{CH_3}{CH}-CH_3$ **; (Z) :** $CH_3-\underset{CH_3}{C}-\underset{CH_3}{CH}-CH_3$

2. Ans.  (NGP due to MeO, so retention of configuration)

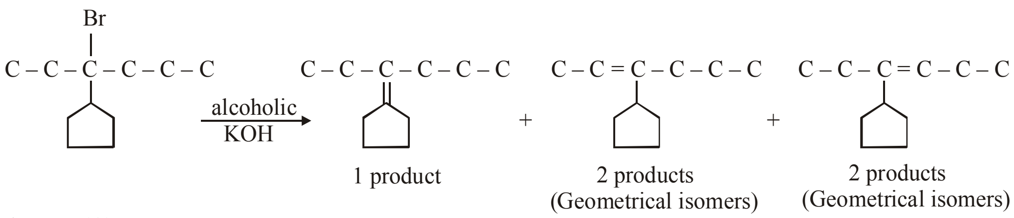
3. Ans. $CH_3-C(CH_3)_2-Br + CH_3O^- \xrightarrow{E2} CH_2=C(CH_3)_2$; $CH_3-C(CH_3)_2-O^- + CH_3Br \xrightarrow{S_N2} CH_3-C(CH_3)_2-OCH_3$

4. Ans. $C_6H_5-CH_2-CH(Cl)-C_6H_5 \xrightarrow[E2]{Alc.KOH} C_6H_5-CH=CH-C_6H_5$

5. Ans. (a) Cis and trans forms of stibene $C_6H_5CH=CHC_6H_5$; (b) $(CH_3)_2CHI + CH_3I$

6. Ans. $CH_3-C(CH_3)=CHCH_3$

7. Ans. (5)



8. Ans. (8)

$CH_3-CH_2-CH(CH_3)-CH_2CH_3 \xrightarrow[h\nu]{\text{monochlorination } Cl_2} CH_3CH_2-\overset{*}{C}H(CH_3)-CH_2CH_2Cl$ (2 isomers)

$+\ CH_3-CH_2-\overset{*}{C}H(CH_3)-\overset{*}{C}H(Cl)-CH_3$ (4 isomers)

$+\ CH_3-CH_2-C(Cl)(CH_3)-CH_2-CH_3$

$+\ CH_3-CH_2-C(CH_2Cl)(CH_3)-CH_2CH_3$

Important Notes