ORGANIC COMPOUNDS CONTAINING HALOGENS [JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

JEE ADVANCED

Single Correct Answer Type

1. Chlorobenzene can be prepared by reacting aniline with:

a. hydrochloric acid
b. cuprous chloride
c. chlorine in the presence of anhydrous aluminium chloride
d. nitrous acid followed by heating with cuprous chloride

(IIT-JEE 1984)

2. The reaction of toluene with chlorine in the presence of ferric chloride gives predominantly:

a. benzoyl chloride
b. m-chlorotoluene
c. benzyl chloride
d. o- and p-chlorotoluene

(IIT-JEE 1986)

3. The reaction conditions leading to the best yields of C_2H_5Cl are:

a. $C_2H_6\text{ (excess)} + Cl_2 \xrightarrow{\text{UV light}}$

b. $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{dark}}$

c. $C_2H_6 + Cl_2\text{ (excess)} \xrightarrow{\text{UV light}}$

d. $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$ **(IIT-JEE 1986)**

4. *n*-Propyl bromide on treatment with ethanolic potassium hydroxide produces

a. Propane **b.** Propene

c. Propyne **d.** Propanol

(IIT-JEE 1987)

5. The number of structural and configurational isomers of a bromo compound, C_5H_9Br, formed by the addition of HBr to 2-pentyne respectively are

a. 1 and 2 **b.** 2 and 4

c. 4 and 2 **d.** 2 and 1 **(IIT-JEE 1988)**

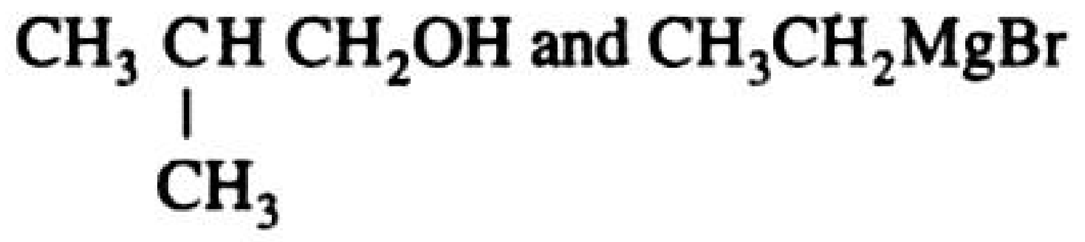
6. 1-Chlorobutane on reaction with alcoholic potash gives

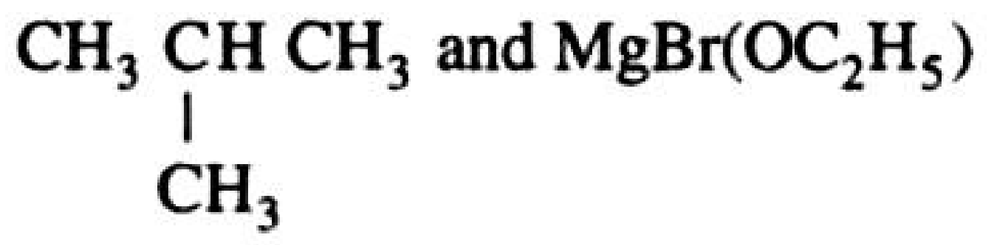
a. 1-butene **b.** t-butanol

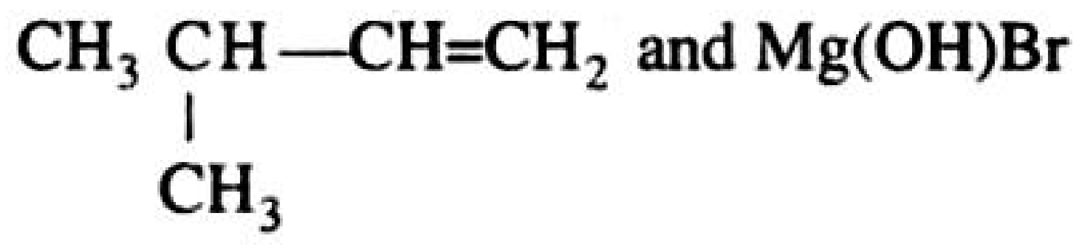
c. 2-butene **d.** 2-butanol

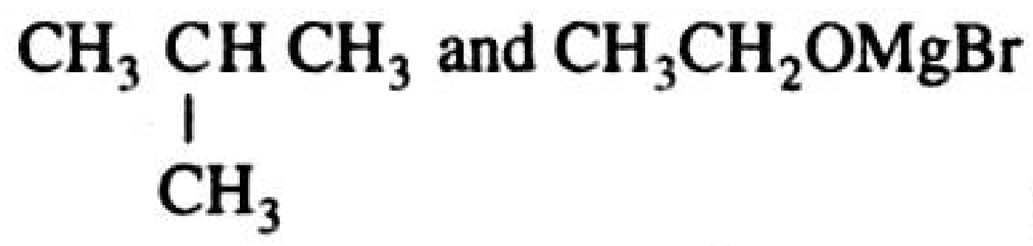
(IIT-JEE 1991)

7. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives:

a.

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\,CH_2OH$ and CH_3CH_2MgBr

b.

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\,CH_3$ and $MgBr(OC_2H_5)$

c.

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}CH{=}CH_2$ and $Mg(OH)Br$

d.

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H\,CH_3$ and CH_3CH_2OMgBr

(IIT-JEE 1995)

8. During debromination of meso-2, 3-dibromobutane, the major compound formed is

a. *n*-butane **b.** 1-butene

c. *cis*-2-butene **d.** *trans*-2-butene

(IIT-JEE 1997)

9. $(CH_3)_3CMgCl$ on reaction with D_2O produces:

a. $(CH_3)_3CD$ **b.** $(CH_3)_3OD$

c. $(CD_3)_3CD$ **d.** $(CD_3)_3OD$

(IIT-JEE 1997)

10. In the reaction of p-chlorotoluene with KNH_2 in liquid NH_3, the major product is

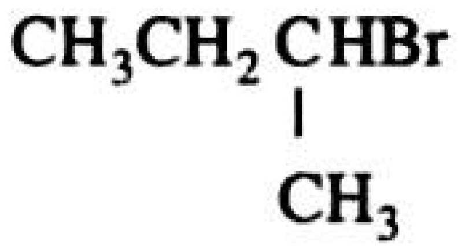
a. o-Toluidine **b.** m-Toluidine

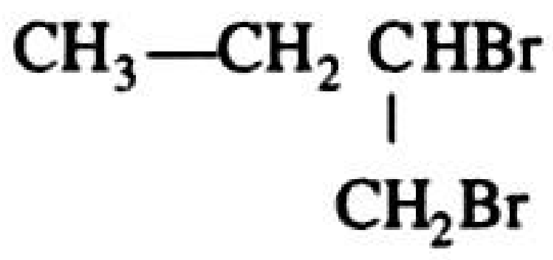
c. p-Toluidine **d.** p-Chloroaniline

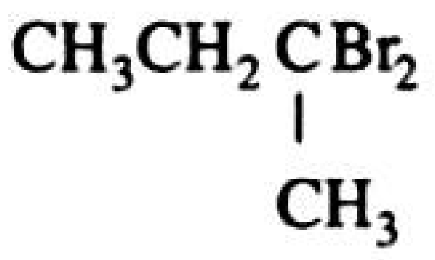
(IIT-JEE 1997)

11. The chief reaction product of reaction between *n*-butane and bromine at 130°C is:

a. $CH_3CH_2CH_2CH_2Br$

b.

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HBr$

c.

$CH_3{-}CH_2\underset{\displaystyle CH_2Br}{\underset{|}{C}}HBr$

d.

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}Br_2$

(IIT-JEE 1999)

12. A solution of (+) -2 chloro-2-phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of

a. carbanion **b.** carbene

c. free-radical **d.** carbocation

(IIT-JEE 1999)

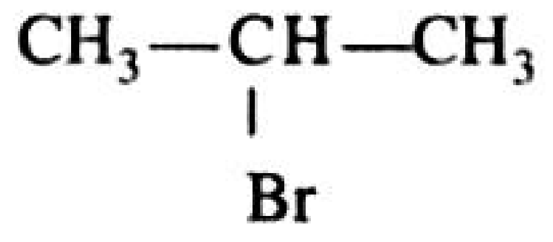
13. The order of reactivities of the following alkyl halides for an S_N2 reaction is

a. RF > RCI > RBr > RI **b.** FR > RBr > RCI > RI

c. RCI > RBr > RF > RI **d.** RI > RBr > RCI > RF

(IIT-JEE 2000)

14. Identify the set of reagent/reaction conditions 'X' and 'Y' in the following set of transformations

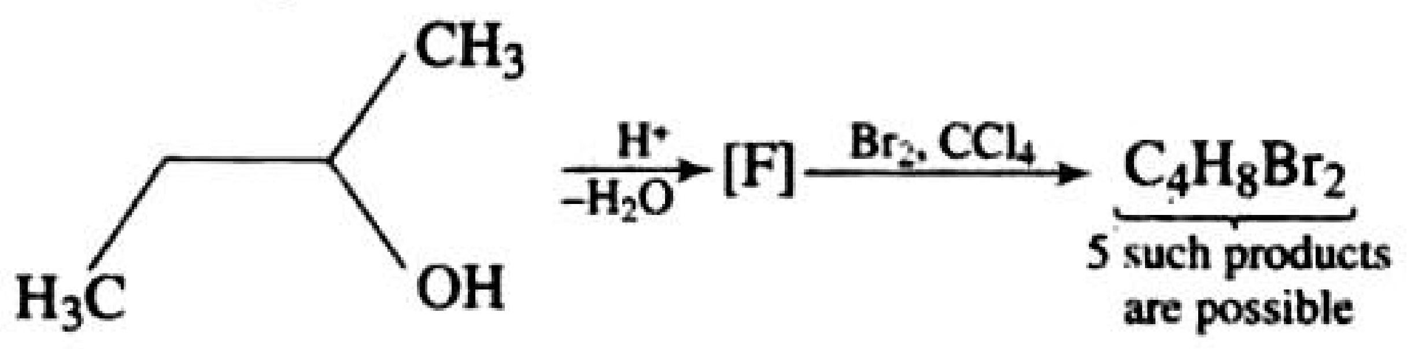
$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y}$

$CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}}H{-}CH_3$

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

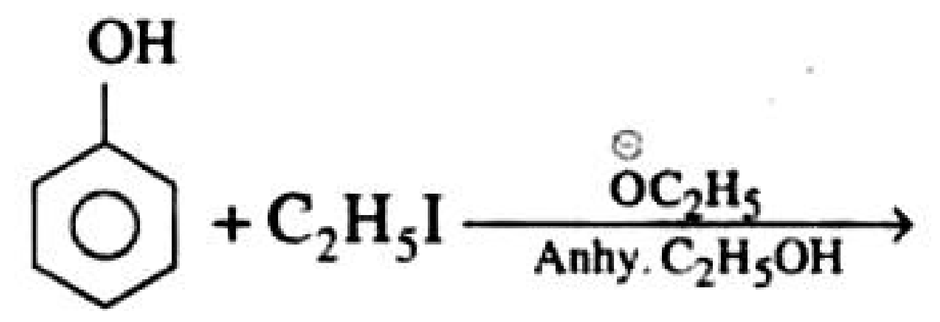
d. X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$ **(IIT-JEE 2002)**

15.


How many structures for F are possible?

a. 2 **b.** 5 **c.** 6 **d.** 3

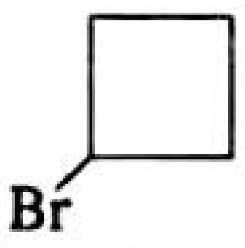
(IIT-JEE 2003)

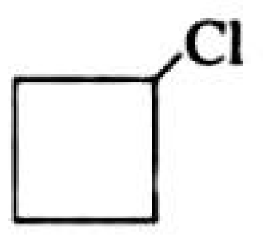
16.


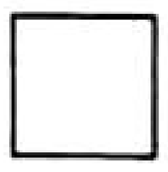
a. $C_6H_5OC_2H_5$ **b.** $C_2H_5OC_2H_5$

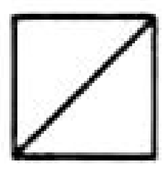
c. $C_6H_5OC_6H_5$ **d.** C_6H_5I **(IIT-JEE 2003)**

17. What would be the product formed when 1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether?

a.


b.


c.


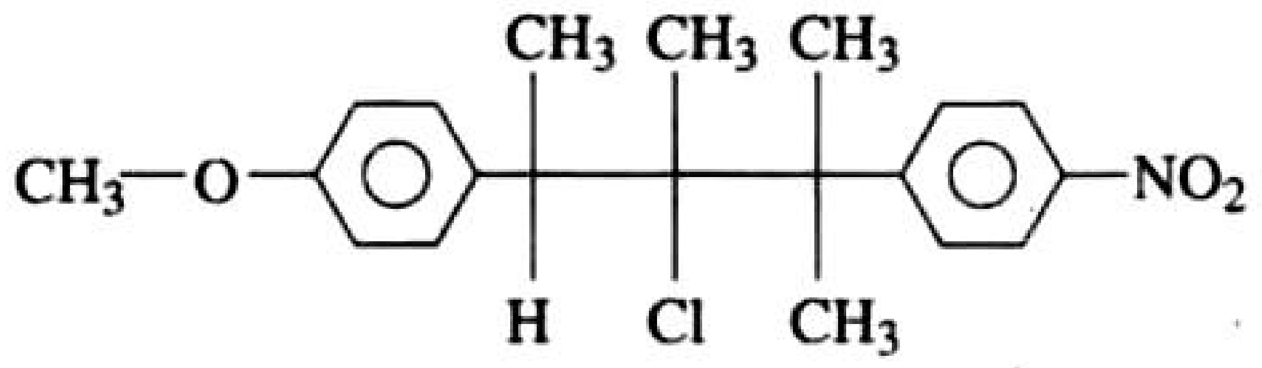
d.

(IIT-JEE 2005)

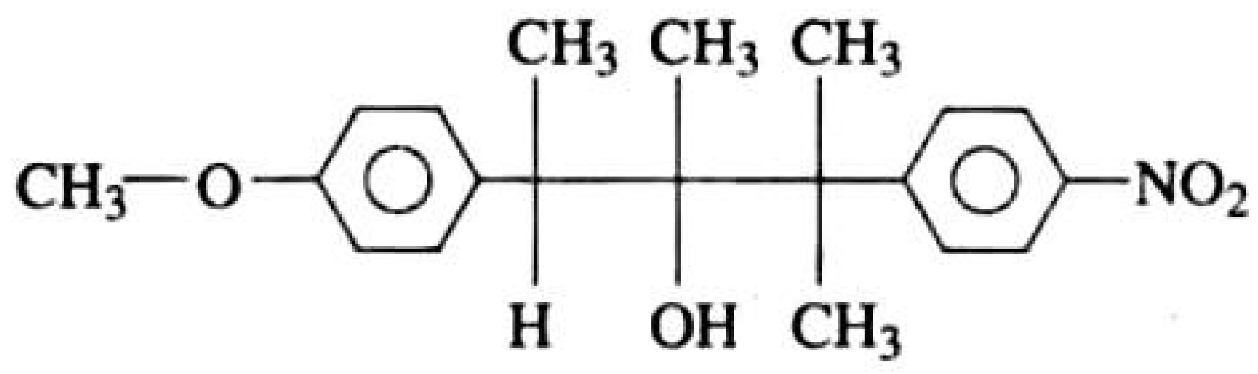
18. When phenyl magnesium bromide reacts with tert-butanol, the product would be

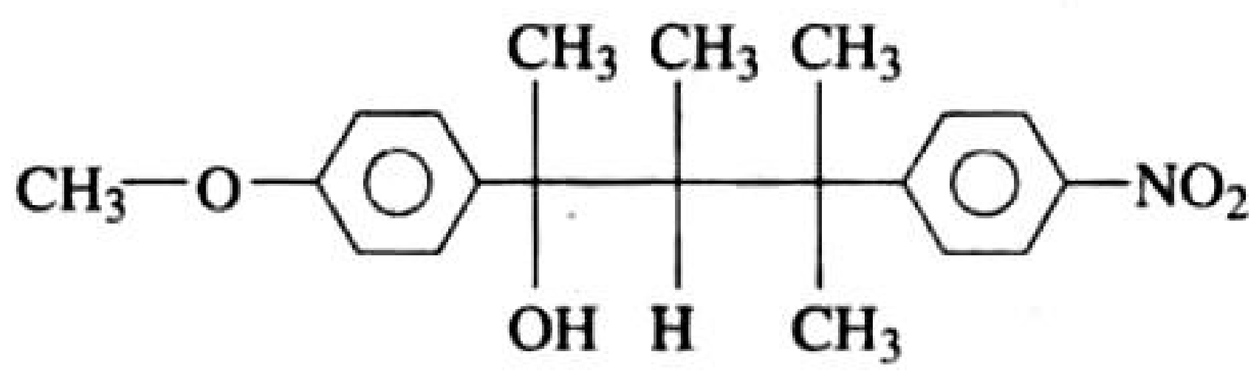
a. Benzene
b. Phenol
c. tert-butylbenzene
d. tert-butyl phenyl ether

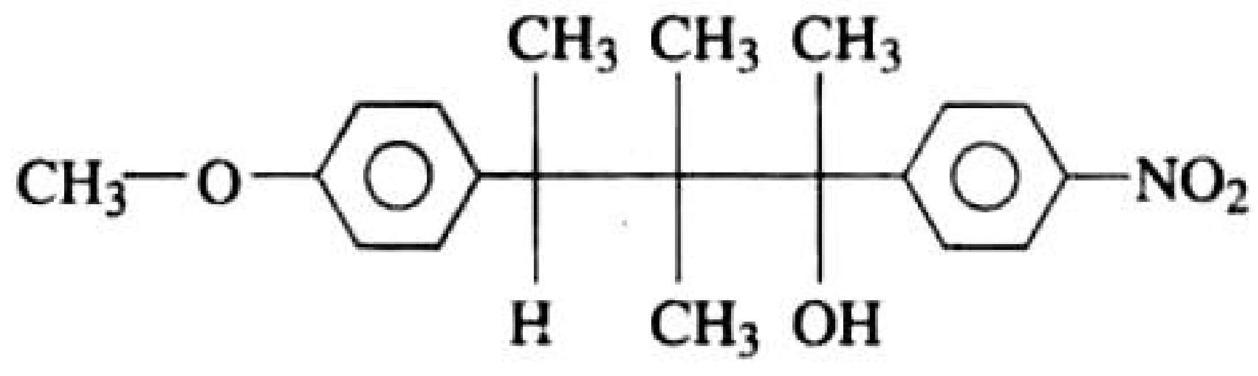
(IIT-JEE 2005)

19. The following compound on hydrolysis in aqueous acetone will give:



(K) 

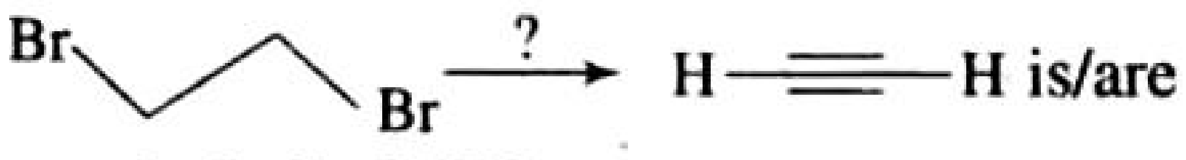
(L) 

(M) 

a. Mixture of (K) and (L)
b. Mixture of (K) and (M)
c. Only (M)
d. Only (K)

(IIT-JEE 2005)

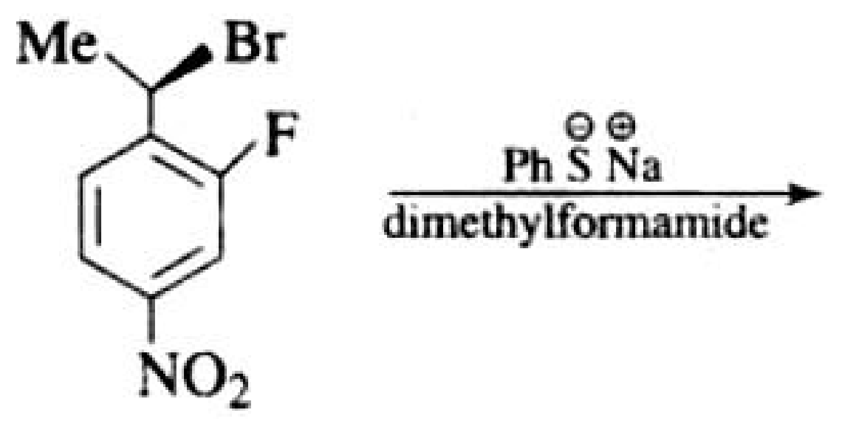
20. The reagent(s) for the following conversion.

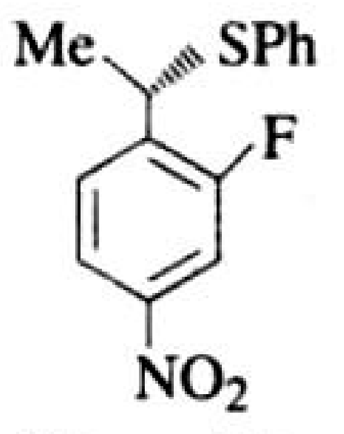


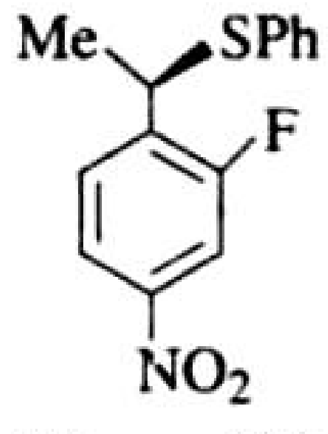
a. alcoholic KOH
b. alcoholic KOH followed by $NaNH_2$
c. aqueous KOH followed by $NaNH_2$
d. Zn/CH_3OH

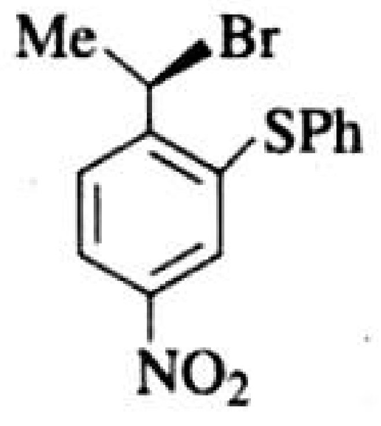
(IIT-JEE 2007)

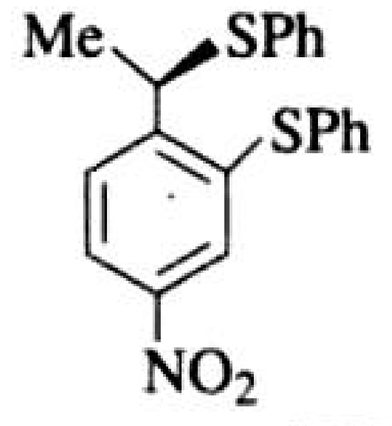
21. The major product of the following reaction is—



a. 

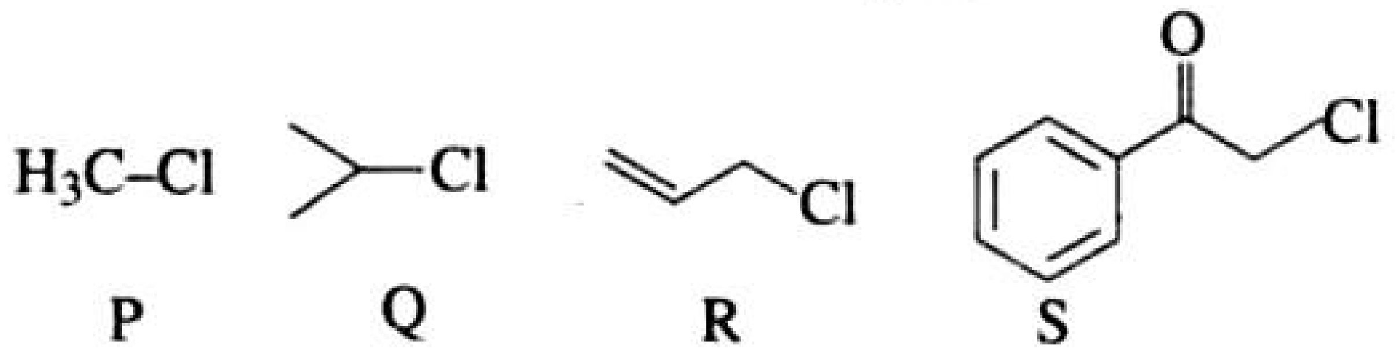
b. 

c. 

d. 

(IIT-JEE 2008)

22. KI in acetone undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as



P Q R S

a. $P > Q > R > S$
b. $S > P > R > Q$
c. $P > R > Q > S$
d. $R > P > S > Q$

(JEE Advanced 2013)

Multiple Correct Answers Type

1. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to:

a. The formation of less stable carbonium ion
b. Resonance stabilization
c. Longer carbon-halogen bond
d. The inductive effect
e. sp^2 hybridized carbon attached to the halogen.

(IIT-JEE 1990)

2. The compounds used as refrigerant are

a. NH_3
b. CCl_4
c. CF_4
d. CF_2Cl_2
e. CH_2F_2

(IIT-JEE 1990)

3. The products of reaction of alcoholic silver nitrite with ethyl bromide are:

a. Ethane
b. Ethene
c. Nitroethane
d. Ethyl alcohol
e. Ethyl nitrite

(IIT-JEE 1991)

4. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with

a. SO_2Cl_2
b. $SOCl_2$
c. Cl_2
d. NaOCl

(IIT-JEE 1998)

Integer Answer Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is

(IIT-JEE 2011)

Assertion-Reasoning Type

Read the following statement and explanation and answer as per the options given below:

a. Statement 1 is true, Statement 2 is true; Statement 2 is the correct explanation for Statement 1.
b. Statement 1 is true, Statement 2 is true; Statement 2 is NOT a correct explanation for Statement 1
c. Statement 1 is true, Statement 2 is false
d. Statement 1 is false, Statement 2 is true

1. Statement 1: Aryl halides undergo nucleophilic substitution with ease.

Statement 2: The carbon-halogen bond in aryl halides has partial double bond character **(IIT-JEE 1991)**

2. Statement 1: Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.

Statement 2: Cyanide $(\overset{\ominus}{C}N)$ is a strong nucleophile.

(IIT-JEE 1998)

3. **Statement 1:** Bromobenzene upon reaction with Br_2/Fe gives 1, 4-dibromobenzene as the major product.
Statement 2: In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile. **(IIT-JEE 2008)**

Fill in the Blanks Type

1. The halogen which is most reactive in the halogenation of alkanes under sunlight is _______. (chlorine, bromine, iodine) **(IIT-JEE 1981)**
2. The compound prepared by the action of magnesium on dry ether bromide in ether is known as ______ reagent. **(IIT-JEE 1982)**
3. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with ______ **(IIT-JEE 1983)**
4. Formation of phenol from chlorobenzene is an example of ______ aromatic substitution **(IIT-JEE 1989)**
5. The interaction of elemental sulphur with Grignard reagent gives ______. **(IIT-JEE 1991)**
6. Vinyl chloride on reaction with dimethyl copper gives ______. **(IIT-JEE 1997)**
7. The structure of the intermediate product formed by the oxidation of toluene with CrO_3 and acetic anhydride whose hydrolysis gives benzaldehyde, is ______ **(IIT-JEE 1992)**

True/False Type

1. Carbon tetrachloride burns in air when lighted to give phosgene. **(IIT-JEE 1983)**
2. The yield of ketone when a secondary alcohol oxidised is more than the yield of aldehyde when a primary alcohol is oxidised. **(IIT-JEE 1983)**
3. Carbon tetrachloride is inflammable. **(IIT-JEE 1985)**
4. m-Chlorobromobenzene is an isomer of m-bromochlorobenzene. **(IIT-JEE 1985)**
5. Sodium ethoxide is prepared by reacting ethanol with aqueous sodium hydroxide. **(IIT-JEE 1986)**
6. In benzene carbon uses all the three *p*-orbitals for hybridisation. **(IIT-JEE 1987)**
7. An electron-donating substituent in benzene orients the incoming electrophilic group to the *meta*-position. **(IIT-JEE 1987)**
8. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule. **(IIT-JEE 1989)**
9. Photobromination of 2-methyl propane gives a mixture of 1-bromo-2-methyl propane and 2-bromo-2-methyl propane in the ratio 9 : 1. **(IIT-JEE 1993)**

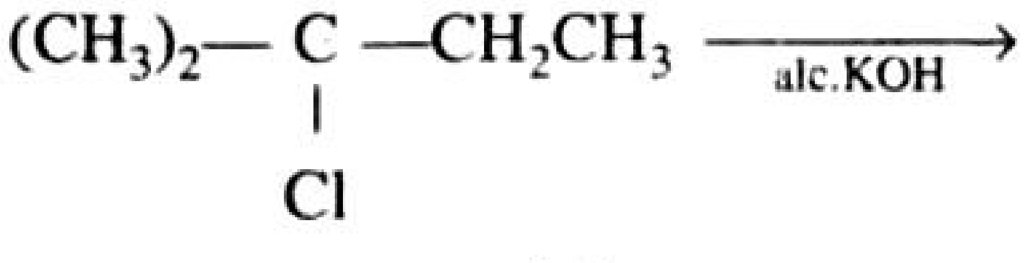
Subjective Type

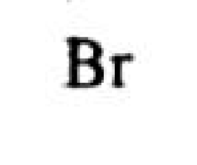
1. **a.** Show by chemical equations only, how you would prepare the following from the indicated starting materials. Specify the reagents in each step of the synthesis.
   - **i.** Hexachlorethane, C_2Cl_6, from calcium carbide.
   - **ii.** Chloroform from carbon disulphide.

   b. Give one chemical test which would distinguish between C_2H_5OH and $CHCl_3$. **(IIT-JEE 1979)**
2. Explain the following in not more than two sentences Chloroform is stored in dark coloured bottles. **(IIT-JEE 1980)**
3. State the conditions under which the following preparation are carried out. Give the necessary equations which need not be balanced:
   - **i.** Lead tetraethyl from sodium-lead alloy
   - **ii.** Methyl chloride from aluminium carbide

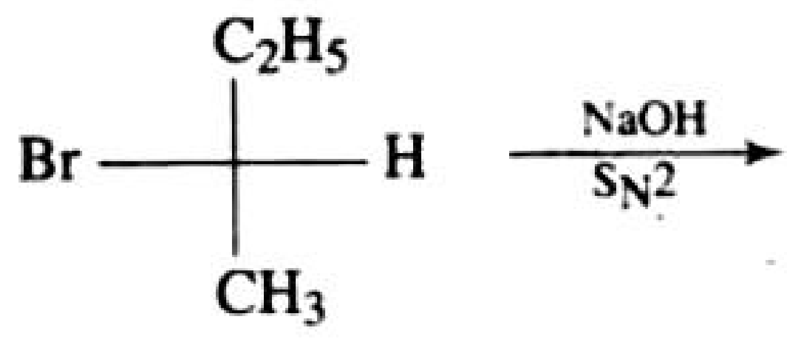
   (IIT-JEE 1983)
4. State with balanced equations, what happens when chloral is heated with aqueous sodium hydroxide. **(IIT-JEE 1984)**
5. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment? **(IIT-JEE 1985)**
6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? **(IIT-JEE 1987)**
7. What effect should the following resonance of vinyl chloride have on its dipole moment? **(IIT-JEE 1987)**

   $$CH_2 = CH - Cl \leftrightarrow CH_2^- - CH_2 = Cl^+$$
8. An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures Y and Z. Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z. **(IIT-JEE 1989)**
9. Arrange the following in the order of their:
   - **i.** Increasing basicity: H_2O, $\overset{\ominus}{O}H$, CH_3OH, CH_3O^-
   - **ii.** Increasing reactivity in nucleophilic substitution reactions: CH_3F, CH_3I, CH_3Br, CH_3Cl

   (IIT-JEE 1992)
10. Write the structural formula of the major product in each of the following cases: **(IIT-JEE 1992)**
    - **i.** chloroform reacts with aniline in the presence of excess alkali.
    - **ii.** 
      $(CH_3)_2\text{—}\underset{\substack{|\\ Cl}}{C}\text{—}CH_2CH_3 \xrightarrow[\text{alc.KOH}]{}$
    - **iii.** $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}}$
11. What will be the major product? **(IIT-JEE 1993)**


$$C_6H_5\text{—}CH_2\text{—}\underset{\substack{|\\ Br}}{CH}\text{—}CH_3 \xrightarrow[\text{KOH},\Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$$

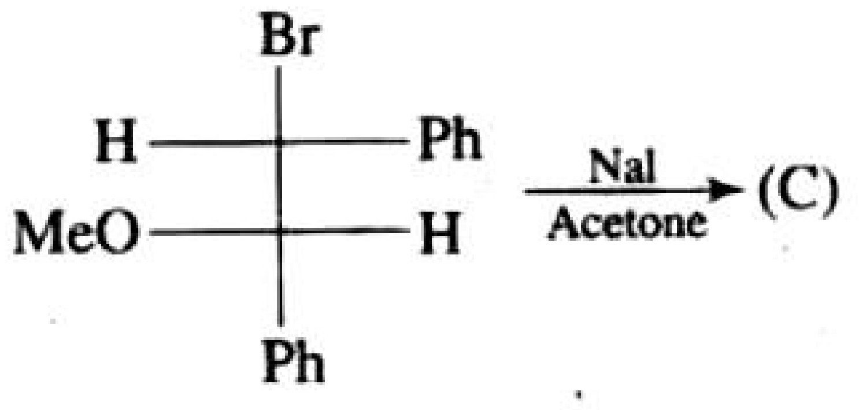
12. Draw the stereochemical structures of the products in the following reaction: **(IIT-JEE 1994)**



13. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. **(IIT-JEE 1995)**

14. Toluene reacts with bromine in the presence of light of give benzyl bromide, while in the presence of $FeBr_3$, it give *p*-bromotoluene. Give explanation for the above observations. **(IIT-JEE 1996)**

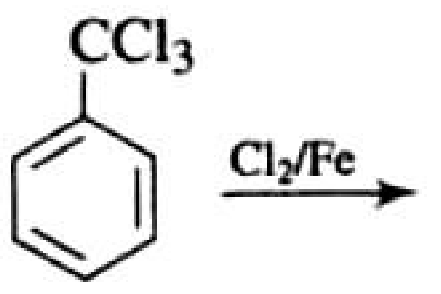
15. Predict the structure of the product in the following reaction: **(IIT-JEE 1996)**



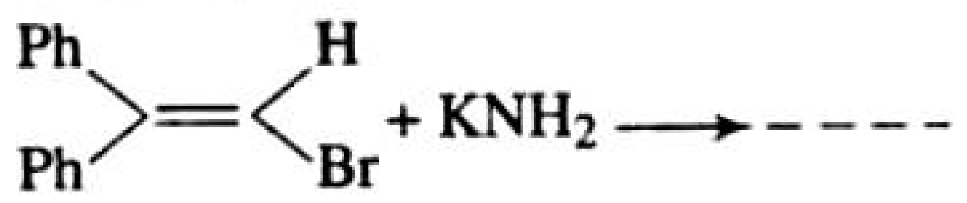
16. An alkyl halide, X, of formula $C_6H_{13}Cl$ on treatment with potassium tertiary butoxide gives two isomeric alkenes Y and Z (C_6H_{12}). Both alkenes on hydrogenation give 2, 3-dimethylbutane. Predict the structures of X, Y and Z. **(IIT-JEE 1996)**

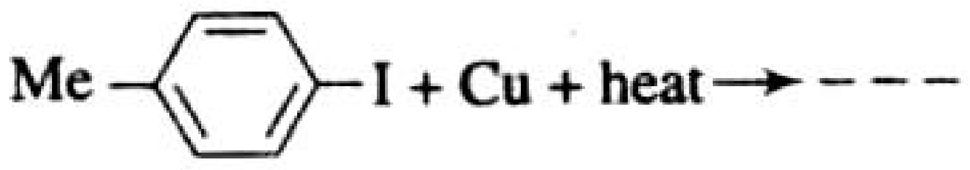
17. How will you prepare m-bromoiodobenzene from benzene (in not more than 5–7 steps)? **(IIT-JEE 1996)**

18. Write the structural formula of the major product in each of the following cases:

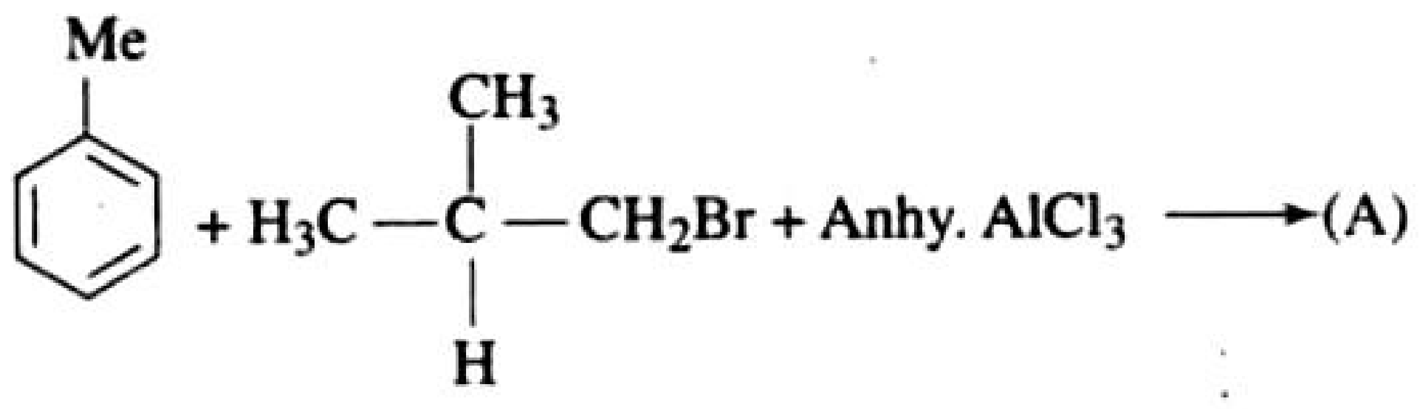
i. 

ii. $CH_3CH_2Br \xrightarrow{AgCN}$

iii. 

iv.  **(IIT-JEE 1997)**

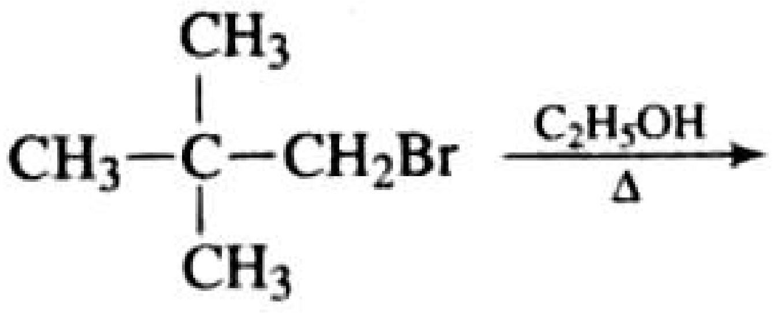
19. Complete the following giving structure of the principal organic products. **(IIT-JEE 1997)**



20. Arrange the following in the increasing order of reactivity towards sulphonation with fuming sulpuric acid. Benzene, toluene, methoxybenzene, chlorobenzene. **(IIT-JEE 1998)**

21. What will be the major product?

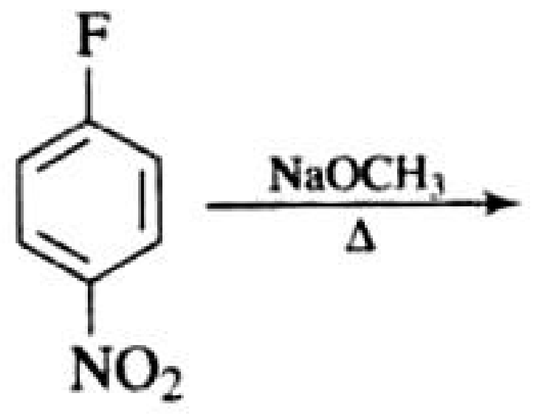
i. $C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{alcoholic KOH}}$ 2 Products

ii. 

$$CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$$

(IIT-JEE 2000)

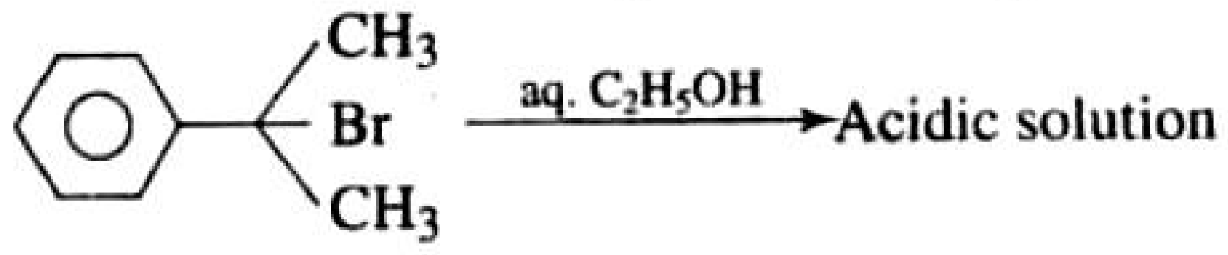
22. What would be the major product in each of the following reactions **(IIT-JEE 2000)**

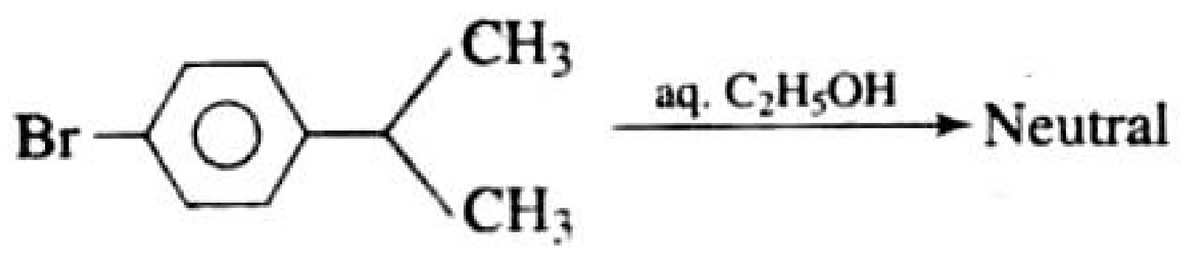


23. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1-bromo-1-methylcyclopentane (C). Write the structures of (A), (B) and explain how (C) is obtained from (B). **(IIT-JEE 2001)**

24. Give reasons for the following:

i. 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in the presence of Ag^+ ion. Explain.

ii. 



(IIT-JEE 2004)

Answer Key

JEE Advanced

Single Correct Answer Type

1. d. 2. d. 3. a. 4. b. 5. b.
6. c. 7. b. 8. d. 9. a. 10. b.
11. b. 12. d. 13. d. 14. b. 15. d.
16. b. 17. d. 18. a. 19. a. 20. b.
21. a. 22. b

Multiple Correct Answers Type

1. b., d., d., e.
2. a., d.
3. c., e.
4. a., c

Integer Answer Type

1. (5)

Assertion–Reasoning Type

1. d.
2. d.
3. c

Fill in the Blanks Type

1. Chlorine
2. Grignard (RMgX)
3. Acetylene
4. Nucleophile
5. Thioalcohol
6. polyvinyl chloride
7. $C_6H_5CH(OCOCH_3)_2$ benzal diacetate

True/False Type

1. False
2. True
3. False
4. False
5. False
6. False
7. False
8. False
9. False

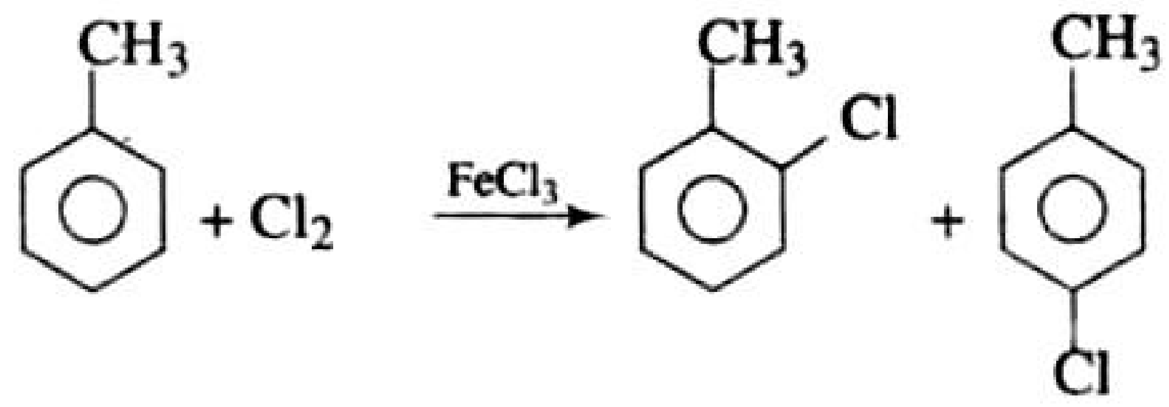
Hints and Solutions

JEE ADVANCED

Single Correct Answer Type

1. d. $C_6H_5NH_2 \xrightarrow[HCl]{HONO} C_6H_5N_2Cl \xrightarrow{CuCl} C_6H_5Cl$

2. d. The given reaction is an example of electrophilic substitution as it is taking place in the presence of Lewis acid. Further, CH_3 group in toluene is o, p-directing.



3. a. Chlorination beyond monochlorination during the preparation of alkyl halides in the presence of UV light can be suppressed by taking *alkane in excess*. As it will happen in case of (c) and (d).
In (b) free radical substitution can't take place in dark.

4. b. $\underset{n\text{-Propyl bromide}}{CH_3{-}CH_2{-}CH_2Br} \xrightarrow[-HBr]{\text{ethanolic KOH}} \underset{\text{Propene}}{CH_3{-}CH{=}CH_2}$

Further dehydrohalogenation of $CH_3CH = CH_2$ can be done only by strong base like $NaNH_2$.

5. b. Addition of HBr of 2-pentyne gives two structural isomers (I) and (II)

$CH_3 - C \equiv C - CH_2CH_3 \xrightarrow{HBr}$

$\underset{(I)}{CH_3C(Br) = CHCH_2CH_3} + \underset{(II)}{CH_3CH = C(Br)CH_2CH_3}$

Each one of these will exist as a pair of geometrical isomers. Thus, there are two structural and four configurational isomers.

6. c. $H_3C - H_2C - H_2C - CH_2Cl \xrightarrow{\text{alc. KOH}}$

$\underset{\text{1-butene}}{CH_3{-}CH_2CH{=}CH_2} + \underset{\substack{\text{2-Butene}\\ \text{(Major)}}}{CH_3{-}CH{=}CH{-}CH_3}$

Alkyl halides give alcohols with aq. KOH, which is a substitution reaction, with aq. KOH it undergoes elimination that proceeds via carbocation.

$CH_3{-}CH_2{-}CH_2{-}CH_2Cl \longrightarrow \underset{\substack{1^\circ\ \text{carbocation}\\ (A)}}{CH_3{-}CH_2{-}CH_2{-}\underset{\oplus}{C}H_2}$

$\xrightarrow{\text{1,2-Hydride}} \underset{\substack{2^\circ\ \text{carbocation}\\ (B)}}{CH_3{-}CH_2{-}\underset{\oplus}{C}H{-}CH_3}$

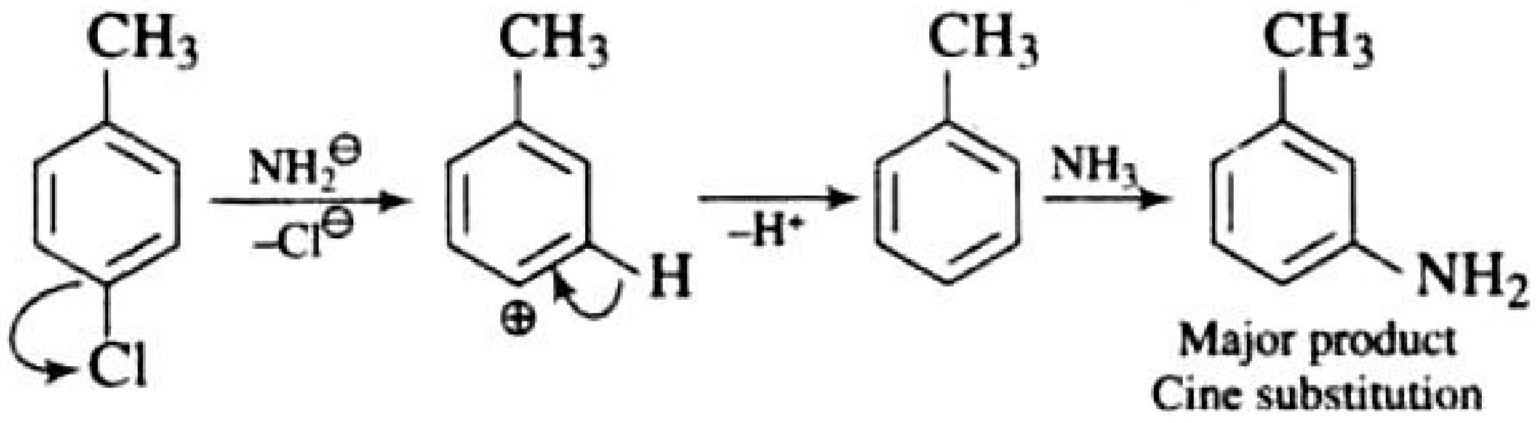
'A' will give 1-butene and 'B' will but-2-ene which is major.

7. b. $(CH_3)_2\ CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2\ CHCH_3 + C_2H_5O$ MgBr as R of Grignard's reagent will take proton and form alkane.

8. d. Debromination is a *trans*-elimination reaction.
meso-2, 3-Dibromobutane on debromination gives *trans*-2-butene.

9. a. $(CH_3)_3C - MgCl + D_2O \longrightarrow (CH_3)_3\ C - D + Mg(OD)Cl$
as R of Grignard's reagent will take proton and form alkane.

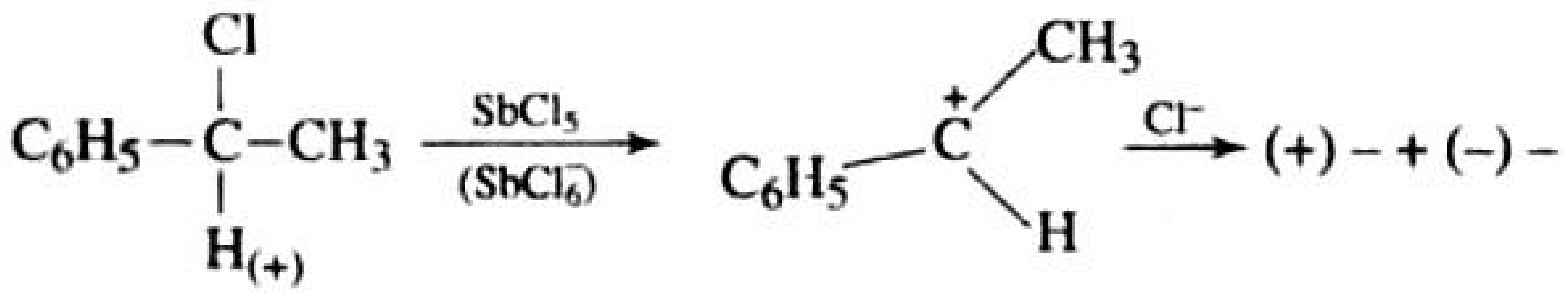
10. b.



Major product
Cine substitution

11. b. The reaction proceeds via free radical mechanism and rate of abstraction of 2° hydrogen is faster. As 2° free radical is more stable than 1°, so $CH_3CH_2CH(Br)CH_3$ would be formed.

12. d. Occurrence of racemization points towards the formation of carbocation as intermediate, which being planar can be attacked from either side and leads to formation of racemic mixture.



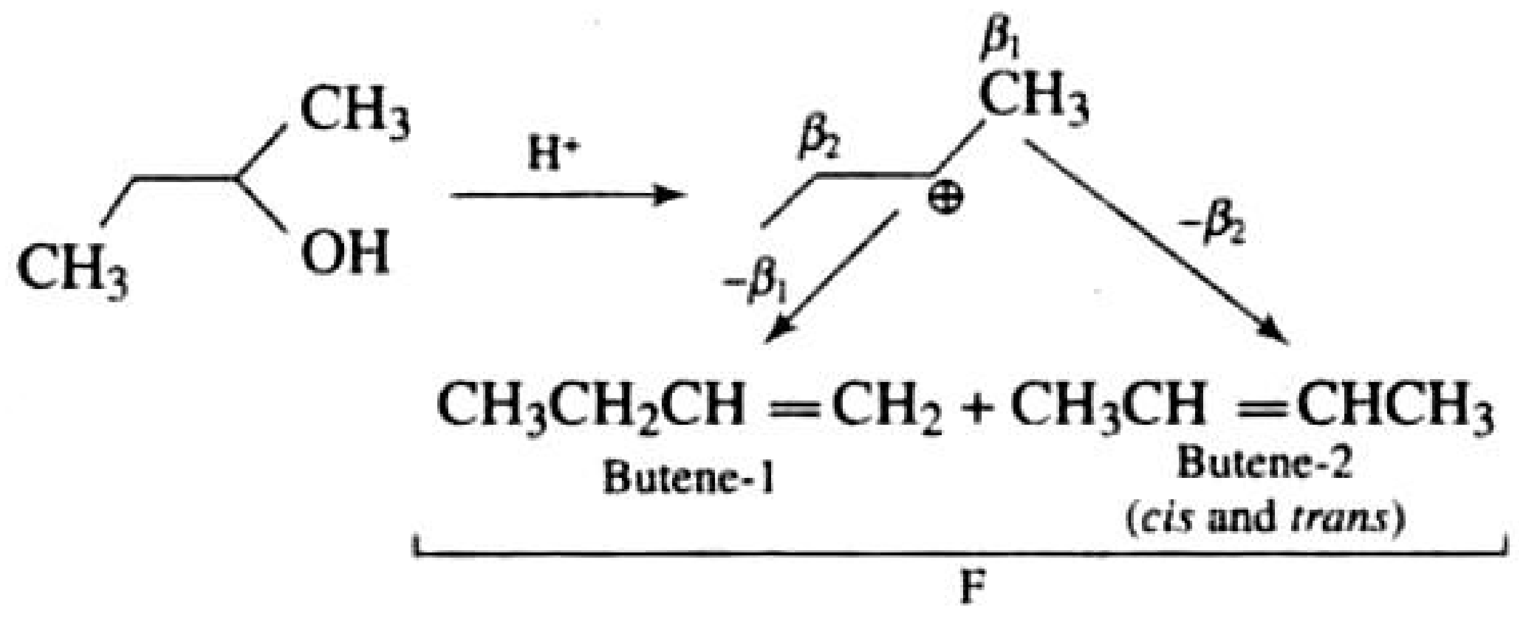
13. d. The order of reactivity of alkyl halides in S_N1 or S_N2 reactions is:

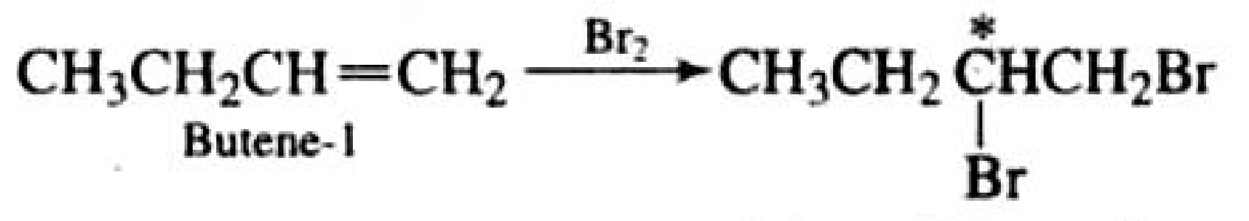
$(R - I) > (R - Br) > (R - Cl) > (R - F)$

I^- is a better nucleophile and a better leaving group. Leaving group order: $I^- > Br^- > Cl^- > F^-$

14. b. Dehydrobromination by strong base (alc. NaOH) followed by Markownikoff addition of HBr.
Dil. base carries out substitution. Strong base at high temperature favours elimination.

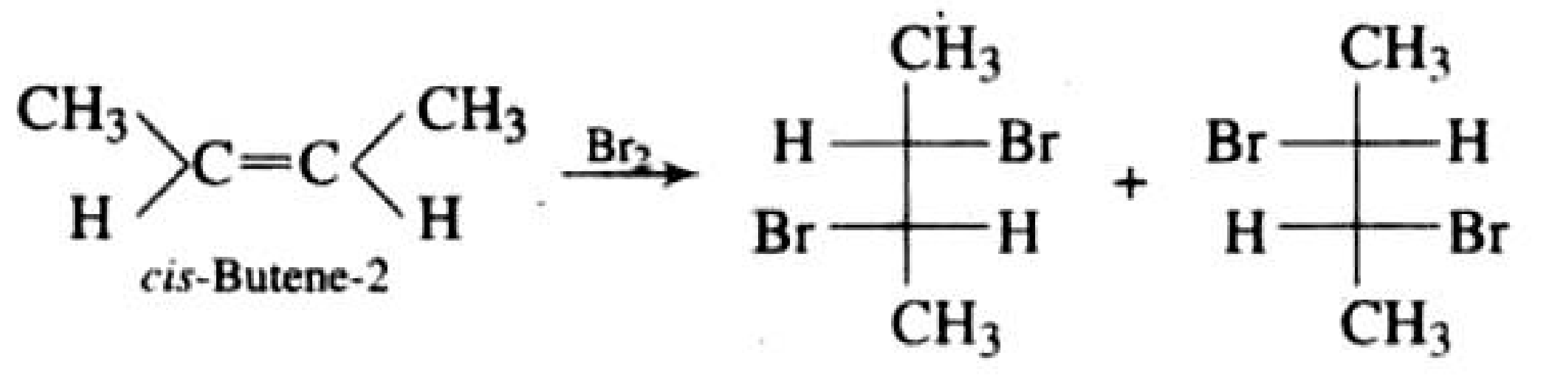
15. d.



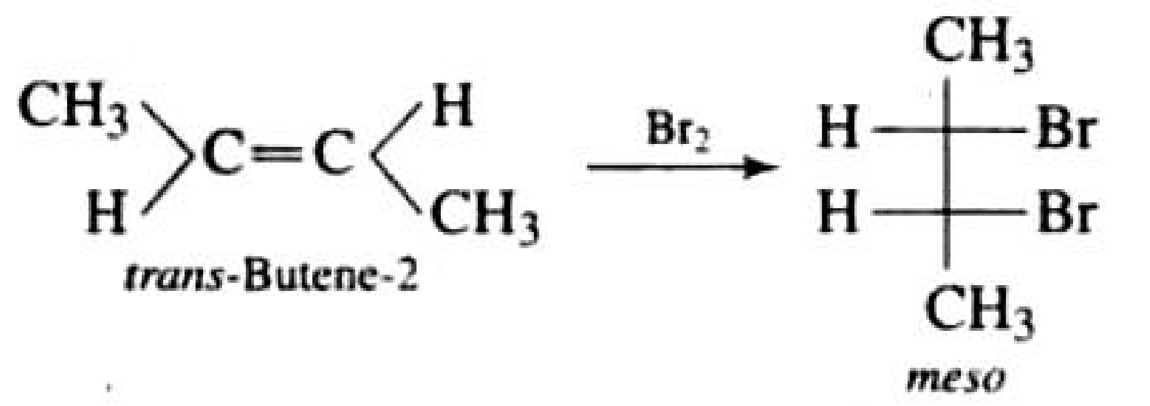


$\underset{\text{Butene-1}}{CH_3CH_2CH{=}CH_2} \xrightarrow{Br_2} CH_3CH_2\underset{Br}{\overset{*}{C}}HCH_2Br$

(+) – and (–) enantiomer



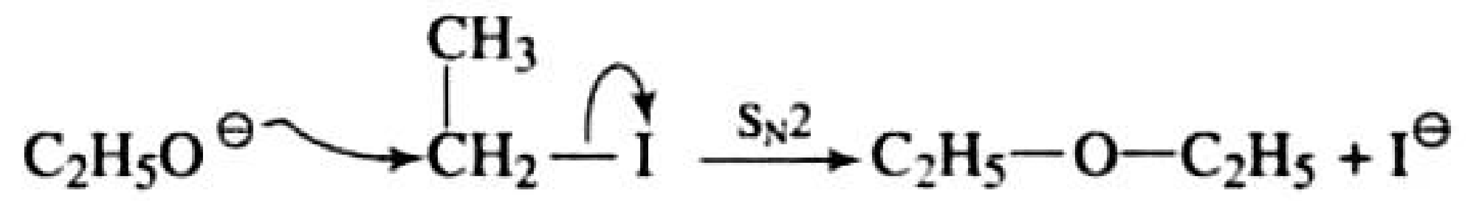
Enantiomers



meso

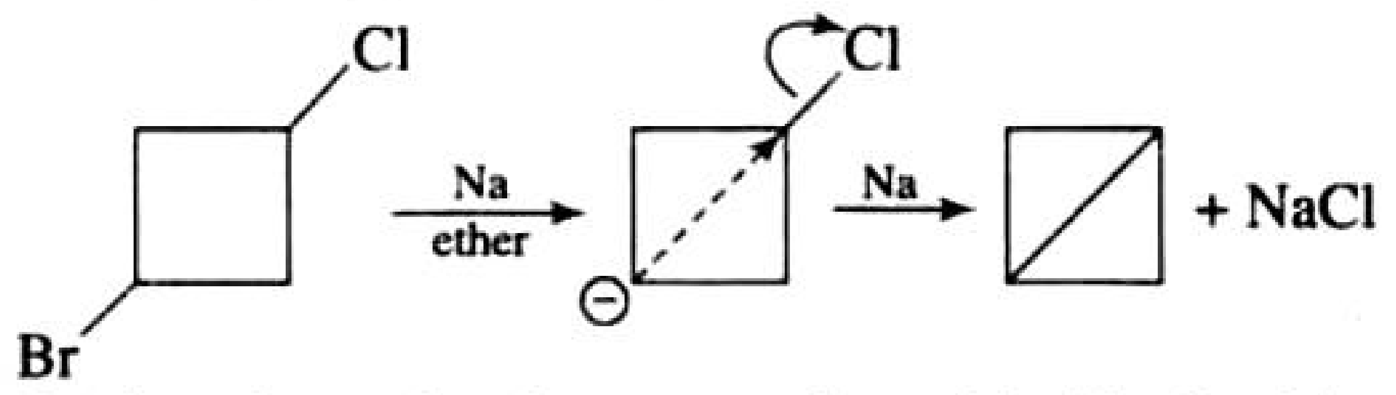
So F can have three possible structures.

16. b. $C_2H_5O^\ominus$ will attract the proton from phenol converting it into phenoxide ion. This would then make nucleophilic attack on the methylene carbon of alkyl iodide. But $C_2H_5O^\ominus$ is in excess. $C_2H_5O^\ominus$ is a better nucleophilic than $C_2H_5O^-$ (phenoxide) ion since in the former, the negative charge is localized over oxygen and in the latter, it is delocalized in the ring. So it is $C_2H_5O^-$ ion that would make nucleophilic attack at ethyl iodide to give diethyl ether (Williamson's synthesis).



$$C_2H_5O^{\ominus} + \overset{CH_3}{\overset{|}{C}}H_2-I \xrightarrow{S_N2} C_2H_5-O-C_2H_5 + I^{\ominus}$$

17. d. It is an example of intramolecular Wurtz reaction.

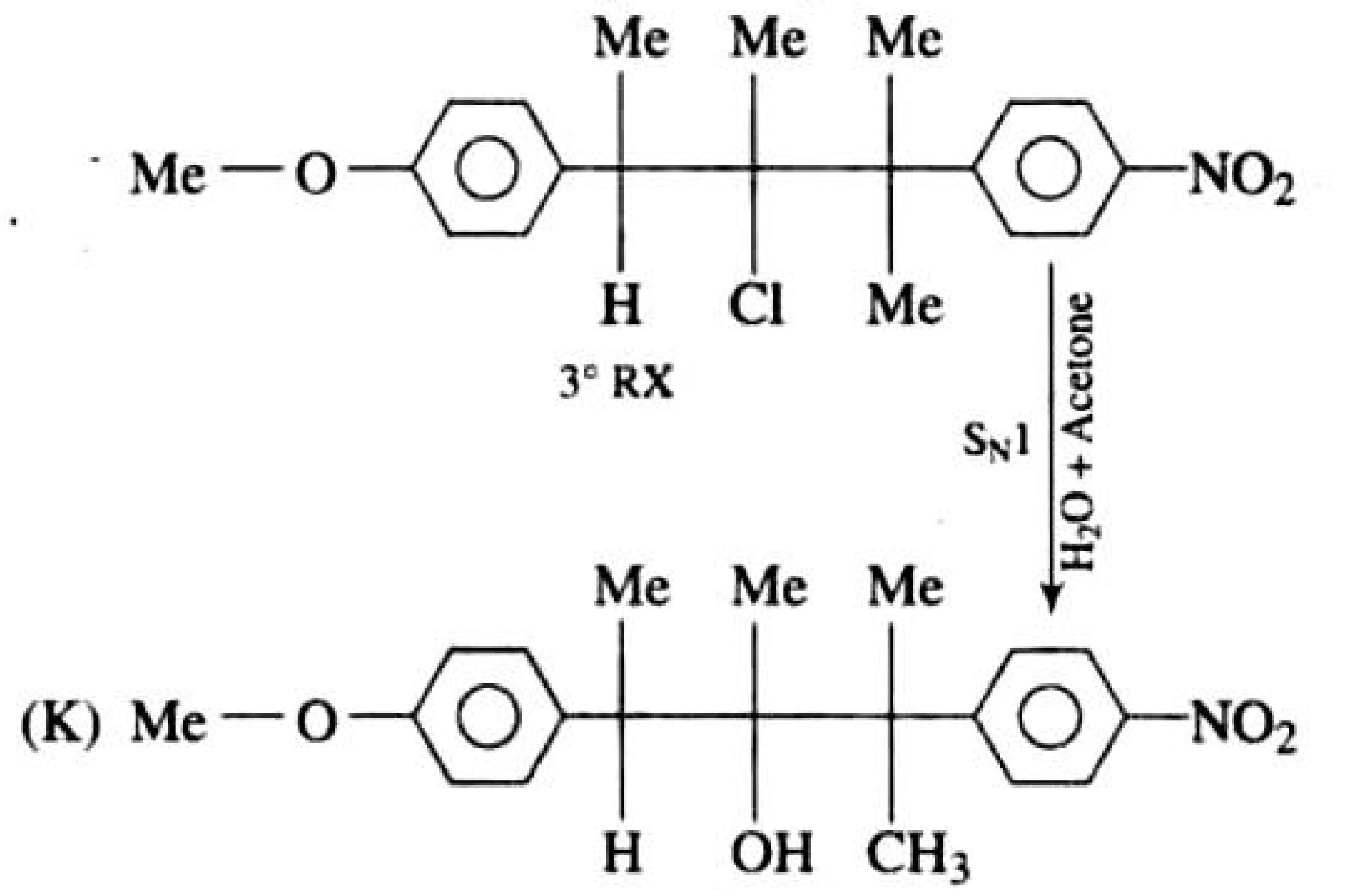


Br^- is a better leaving group than chloride. In this reaction alkali metal (Na) is electron donor.

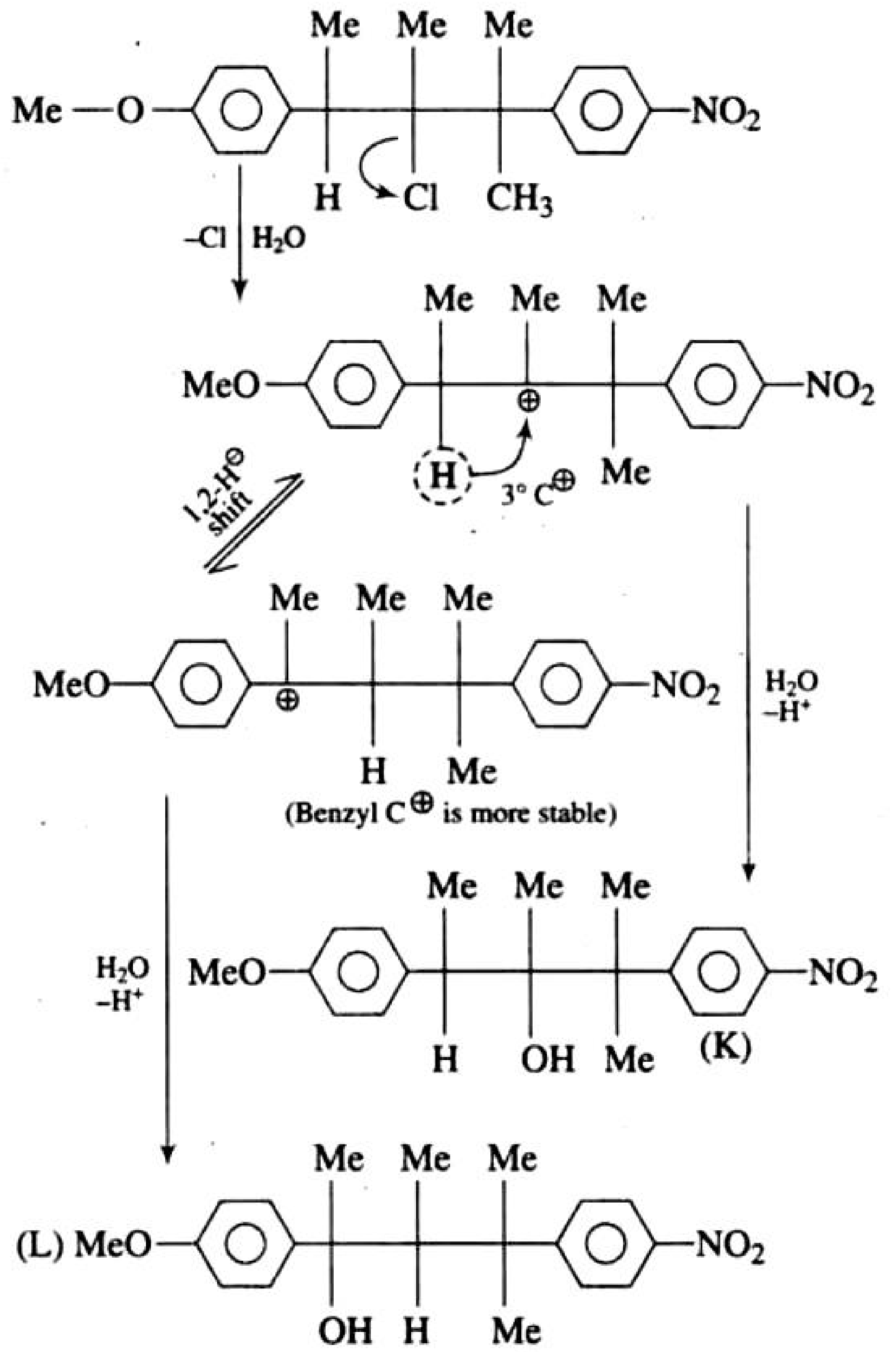
18. a. Grignard reagents react with compounds containing active hydrogen to form hydrocarbons corresponding to alkyl (or aryl) part of the Grignard's reagent.

$$C_6H_5MgBr + Me_3COH \longrightarrow C_6H_6 + Me_3COMgBr$$

19. a. The product (K) is formed through simple nucleophilic substitution while the major product (L) is formed through 1,2 – $H^{\ominus}$ shift *via* S_N1 reaction and the methoxy group stabilizes the carbocation intermediate of product (L).



The mechanism of this reaction is represented as follows.



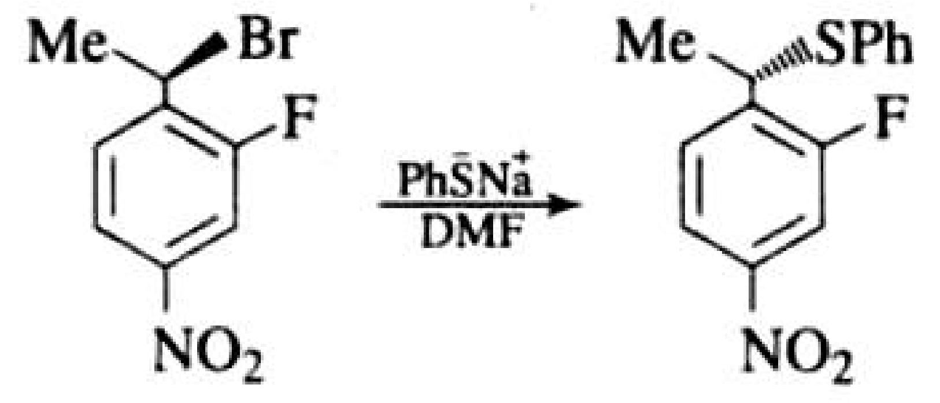
20. b. $BrCH_2-CH_2Br \xrightarrow{\text{Alc. KOH}} CH_2=CHBr \xrightarrow{NaNH_2} CH\equiv CH$

Elimination of HBr from $CH_2=CHBr$ requires a stronger base because here Br acquires partial double bond character due to resonance.

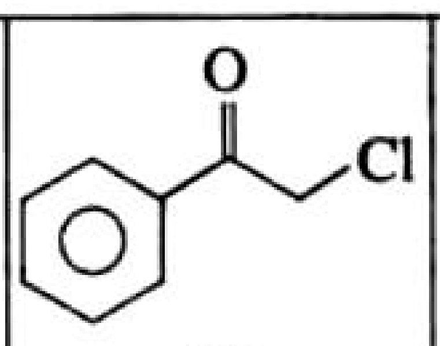
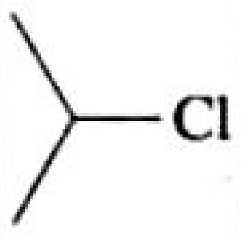
21. a. The product (a) will be formed.

Nucleophilic substitution of an alkyl halide is easier as compared to that of an aryl halide.

PhS^- is a strong nucleophile and dimethyl formamide $\left(H\overset{\overset{O}{\|}}{C}NMe_2\right)$ is a highly polar aprotic solvent. These reagent favour S_N2 reaction, the major product formed is inversion product.



22. b. Relative reactivity for S_N2 reaction in the given structures is

Substrate		CH_3Cl	$H_2C=CH-CH_2Cl$	
	(S)	(P)	(R)	(Q)
Relative Rates Towards S_N2	100000	200	79	0.02

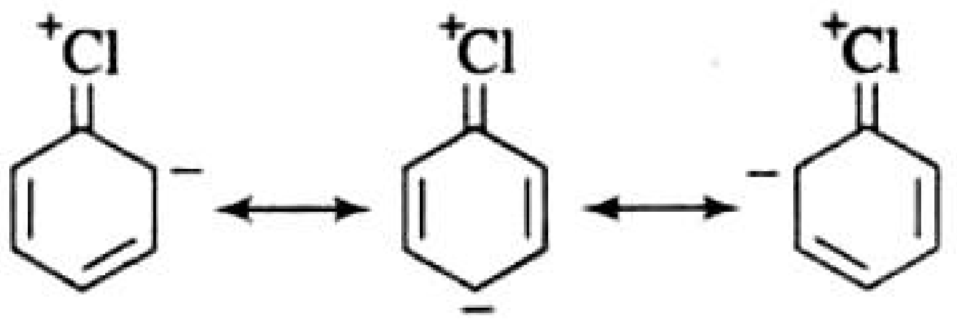
Multiple Correct Answers Type

1. **a., b., d., e.**

Aryl halides are stable due to resonance stabilization.

Phenyl carbocation if formed is highly unstable due to –I effect of phenyl group.

The resonating structures

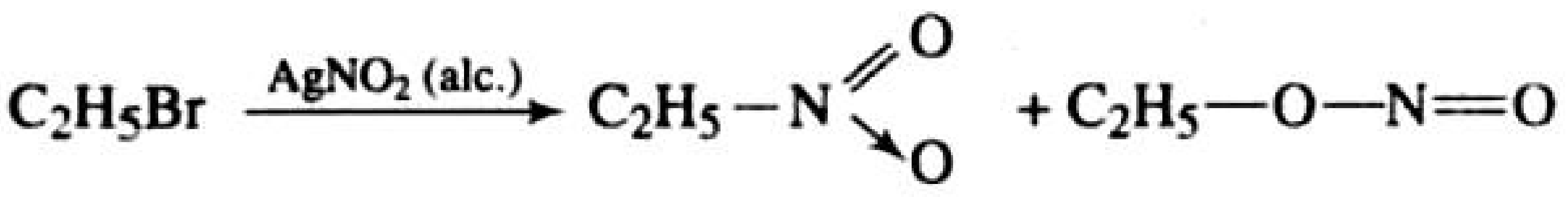


Stabilise the aryl halide. These structures include a double bond between C and Cl which is shorter and thus stronger than the usual C – Cl single bond. The sp^2 hybridised carbon, being electronegative, makes the C – Cl bond shorter and stronger.

2. **a., d.**

NH_3 and dichlorodifluoromethane are used as refrigerants.

3. **c., e.**



$$C_2H_5Br \xrightarrow{AgNO_2\,(alc.)} C_2H_5-N\overset{\nearrow O}{\underset{\searrow O}{}} + C_2H_5-O-N=O$$

Nitroethane (Main product)

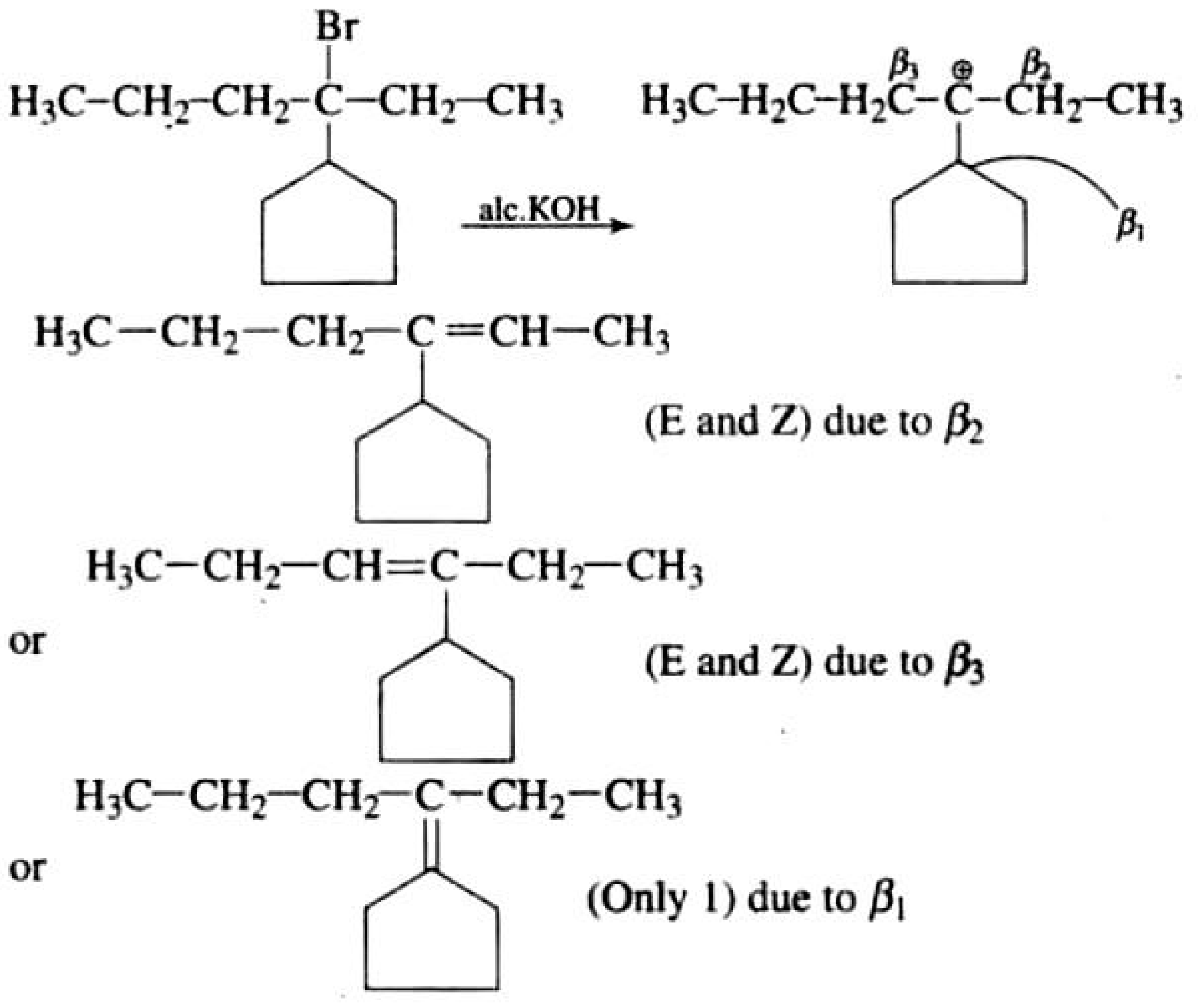
Ethyl nitrite

The main product of this reaction is nitroethane but ethyl nitrite is also formed as a product along with silver bromide.

4. a., c.
Chlorination of toluene to form benzyl chloride is a free radical substitution reaction; only Cl_2 can give Cl in the presence of light.
(a) SO_2Cl_2 as it is allylic halogenation.

Integer Answer Type

1. (5) Total no. of alkenes will be = 5

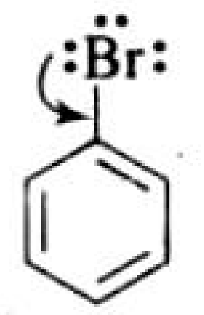


Assertion-Reasoning Type

1. d. Aryl halides do not undergo nucleophilic substitution reaction under ordinary conditions. Thus, statement 1 is incorrect. In aryl halides, the carbon-halogen bond has a partial double bond character, so it becomes shorter and stronger and cannot be easily replaced by a nucleophile. Statement 1 is false but statement 2 is true.

2. d. Aryl halides do not undergo nucleophilic substitution reaction under ordinary conditions, thus benzonitrile is not prepared by the reaction of chlorobenzene with KCN.
Cyanide (CN^-) is a strong nucleophile.
Hence, statement 1 is incorrect, but statement 2 is correct.

3. c. When halogen is present directly on the benzene nucleus it produces two opposing effects namely + M (activating effect) and –I (deactivating)



(–I effect, + M effect)

However, +M > –I hence halogens are said to be o, p-directing (due to + M effect) but deactivating group (due to –I effect) groups giving mainly p-substituted product.

Fill in the Blanks Type

1. Chlorine; because rate of formation of $^{\bullet}CH_3$ (one of the propagating steps) is high when X is Cl.

$$CH_4 + X^{\bullet} \longrightarrow {}^{\bullet}CH_3 + H - X$$

2. Grignard (RMgX)
3. $HC \equiv CH + HCl \longrightarrow CH_2 = CHCl$

$$\underset{\text{Acetylene}}{HC \equiv CH} + HCl \longrightarrow \underset{\text{Vinyl chloride}}{CH_2 = CHCl}$$

4. Nucleophile
5. Thioalcohol
6. polyvinyl chloride.
7. $C_6H_5CH(OCOCH_3)_2$ (benzal diacetate or benzylidene acetate).

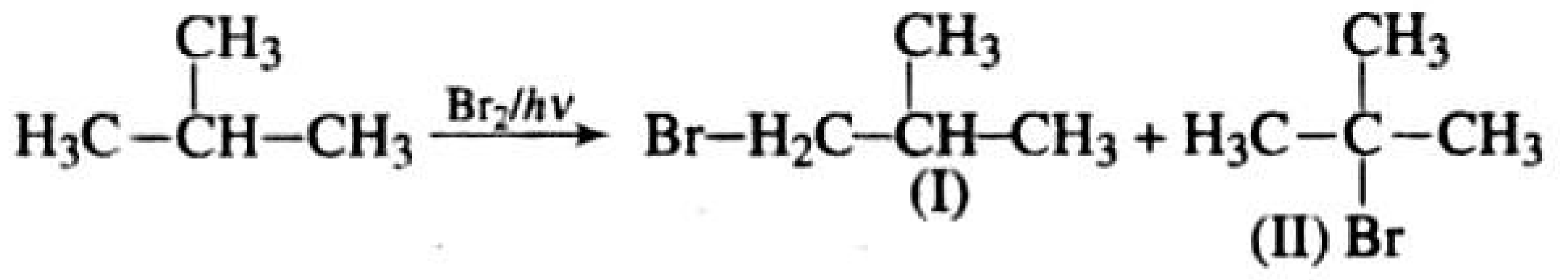
True/False Type

1. **False:**
2. **True:**
3. **False:**
4. **False:**
m-Chlorobrompobenzene and m-bromochlorobenzene is one and the same compound.
5. **False:**
Ethanol is not so much acidic.
6. **False:**
In benzene, each carbon atom is sp^2-hybridised; hence, carbon uses only two p-orbitals for hybridisation.
7. **False:**
An electron-donating substituent in benzene orients the incoming electrophile to the *ortho*- and *para*-positions.
8. **False:**

$$\underset{\text{vinyl chloride}}{CH_2 = CHCl} + HI \longrightarrow \underset{\text{1-Chloro-1-iodoethane}}{CH_3CHCl(I)}$$

This is an example of Markownikoff's rule as I^- is added at the C with less number of H-atoms.
Anti-Markownikoff's rule is applicable only to HBr, but not to HI and HCl.

9. **False:**
Br radical, being less reactive is less influenced by the probability factor. The bromination primarily depends on the reactivity of H atom which is 3° > 2° > 1°. Relative rate bromination of 3°, 2°, 1° is 1600 : 82 : 1, respectively.



$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3 \xrightarrow{Br_2/h\nu} \underset{\text{(I)}}{Br-H_2C-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3} + H_3C-\underset{\underset{\text{(II) } Br}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

1° H = 9, 3° H = 1, ratio of (II) and (I):

$$\frac{(II)}{(I)} = \frac{\text{No. of } 3^\circ \text{ H}}{\text{No. of } 1^\circ \text{ H}} \times \frac{\text{Reactivity of } 3^\circ \text{ H}}{\text{Reactivity of } 1^\circ \text{ H}} = \frac{1 \times 1600}{9 \times 1} = \frac{1600}{9}$$

$$\text{Percentage of (II)} = \frac{1600}{1600 + 9} \times 100 = 99.4\%$$

So it is clear in case of bromination percentage of 3° RX (II) will always predominate.

Subjective Type

1. a. i. $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

$$C_2H_2 \xrightarrow{H_2/Ni} C_2H_6 \xrightarrow[UV]{Cl_2\text{(excess)}} CCl_3 - CCl_3$$

ii. $CS_2 + 3Cl \longrightarrow CCl_4 + S_2Cl_2$

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$$

$$CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

b. Carbylamine test.

$CHCl_3$ + aq KOH + aniline (i.e. primary amine) $\longrightarrow$ foul smelling isocyanide

$CHCl_3 + \text{aq } KOH + C_2H_5OH \longrightarrow$ No reaction

This test is given by primary amines only on reaction with $CHCl_3$

2. Chloroform forms poisonous phosgene gas ($COCl_2$) when in contact with sunlight and air. To avoid this, $CHCl_3$ is stored in dark coloured bottles.

1% ethanol is added to bottles, which act as negative catalyst.

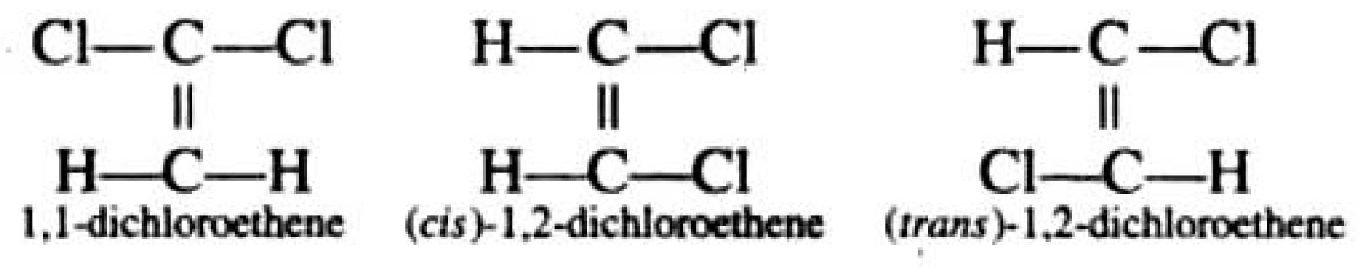
$$2CHCl_3 + O_2 \xrightarrow{\text{Sunlight}} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

3. i. $4C_2H_5Br + 4(Na\text{–}Pb) \xrightarrow{\text{dry ether}} Pb(C_2H_5)_4 + 4NaBr + 3Pb$

ii. $Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[\text{sunlight}]{Cl_2} CH_3Cl$

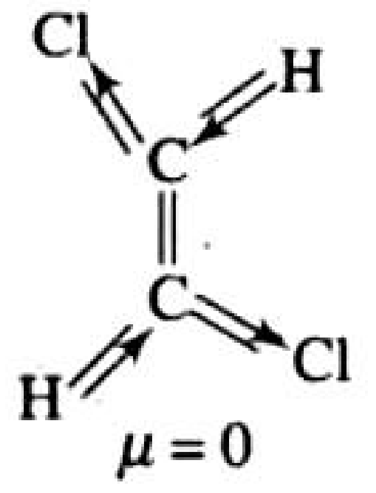
4. $\underset{\text{Chloral}}{CCl_3CHO} \xrightarrow{NaOH} CHCl_3 + HCOONa$

5. Dichloroethene exists in three isomeric forms.



1,1-dichloroethene (*cis*)-1,2-dichloroethene (*trans*)-1,2-dichloroethene

Trans- 1, 2-Dichloroethene has zero dipole moment.



$\mu = 0$

6. $C_6H_5CH_3 \xrightarrow[\text{UV Light}]{Cl_2} C_6H_5CH_2Cl \xrightarrow{Cl_2} C_6H_5CHCl_2$

$\xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$

This follows free radical mechanism. So it is a chain reaction.

7. Resonance decreases the dipole moment of vinyl chloride ($CH_2 = CHCl$).

The positive charge on Cl and a negative charge on C (developed by resonance) oppose each other hence diminish the electronegativity of Cl and thus polarity (and dipole moment) of the bond. The dipole moments of vinyl chloride and chlorobenzene are 1.4 D and 1.7 D respectively, while the dipole moment of alkyl halides is 2 – 2.2 D.

8. $\underset{\substack{(108+35.5)\\ 2.9}}{AgCl} \equiv \underset{\substack{35.5\\ ?}}{Cl}$

$$\Rightarrow \quad \% \, Cl = \frac{35.5}{143.5} \times \frac{2.9}{\text{wt.}} \times 100 \text{ of sample}$$

$$\% \text{ of Cl in X} = \frac{35.5 \times 2.9}{143.5} \times 100 = 71.72\%$$

Empirical formula of (X)

Element	%	Relative no. of atoms	Simplest ratio
C	24.24	24.24/12 = 2.02	2.02/2.02 = 1
H	4.04	4.04/1 = 4.04	4.04/2.02 = 2
Cl	71.72	71.72/35.5 = 2.02	2.02/2.02 = 1

∴ Empirical formula of (X) is **CH_2Cl**

Since X has two isomers Y and Z; both react with $KOH_{(aq.)}$

$Y \xrightarrow{KOH_{(aq)}}$ dihydroxy compound, i.e., 2Cl atoms on adjacent carbon

$Z \xrightarrow{KOH_{(aq)}} CH_3CHO$, i.e., Z should have 2Cl atoms on one C atom, i.e., gem dihalide.

Thus Z should be CH_3CHCl_2 (1, 1-dichlorethane) and Y should CH_2ClCH_2Cl (1, 2-dichloroethane)

Reactions:

$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow{KOH_{(aq)}} CH_3CH(OH)_2 \longrightarrow \underset{\text{(ethanal)}}{CH_3CHO}$$

$$\underset{(Y)}{CH_2ClCH_2Cl} \xrightarrow{KOH_{(aq)}} \underset{\text{(ethane-1,2-diol)}}{CH_2OHCH_2OH}$$

9. i. Basic character: Stronger the acid, weaker is its conjugate base.

$CH_3OH < H_2O < CH_3O^- < \overset{\ominus}{O}H$

ii. Reactivity of RX towards S_N2 reaction:

Stronger the leaving group, faster is S_N2 or/and S_N1

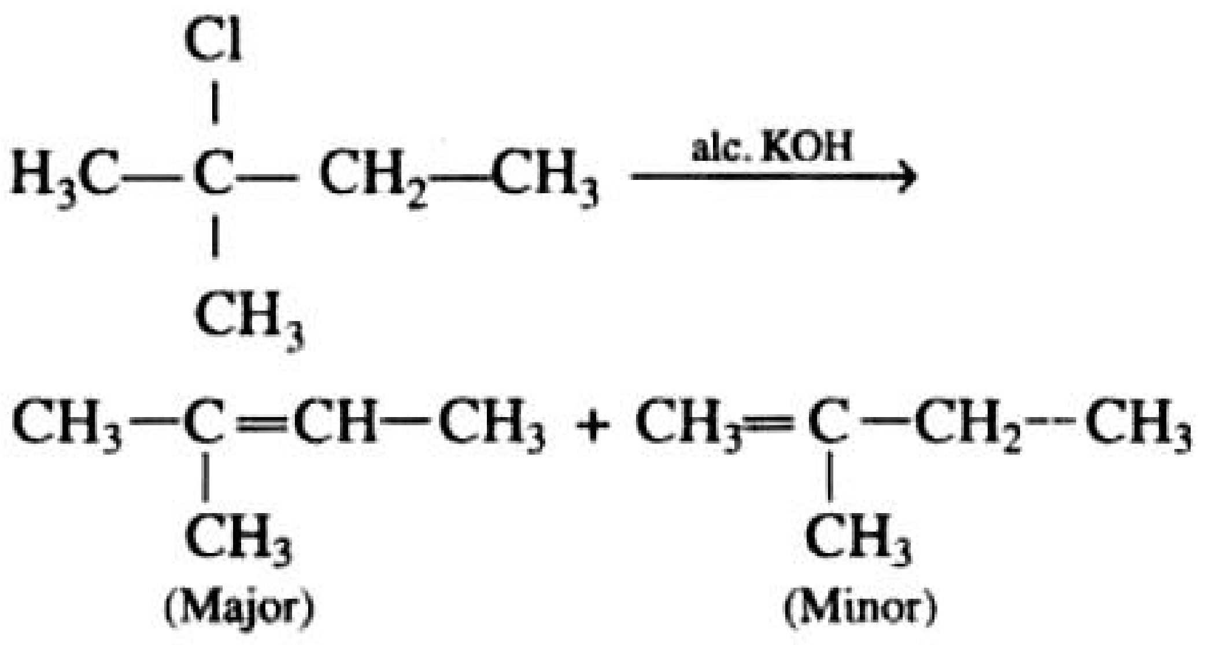
Leaving group order: $F^- < Cl^- < Br^- < I^-$

S_N2 reactivity: $CH_3F < CH_3Cl < CH_3Br < CH_3I$.

10. i. $C_6H_5NH_2 + CHCl_3 \xrightarrow[\text{KOH}]{\text{alkali}} \underset{\text{Phenyl isocyanide}}{C_6H_5\text{-}N \overset{\rightarrow}{=} C}$

(carbylamine reaction)

ii.



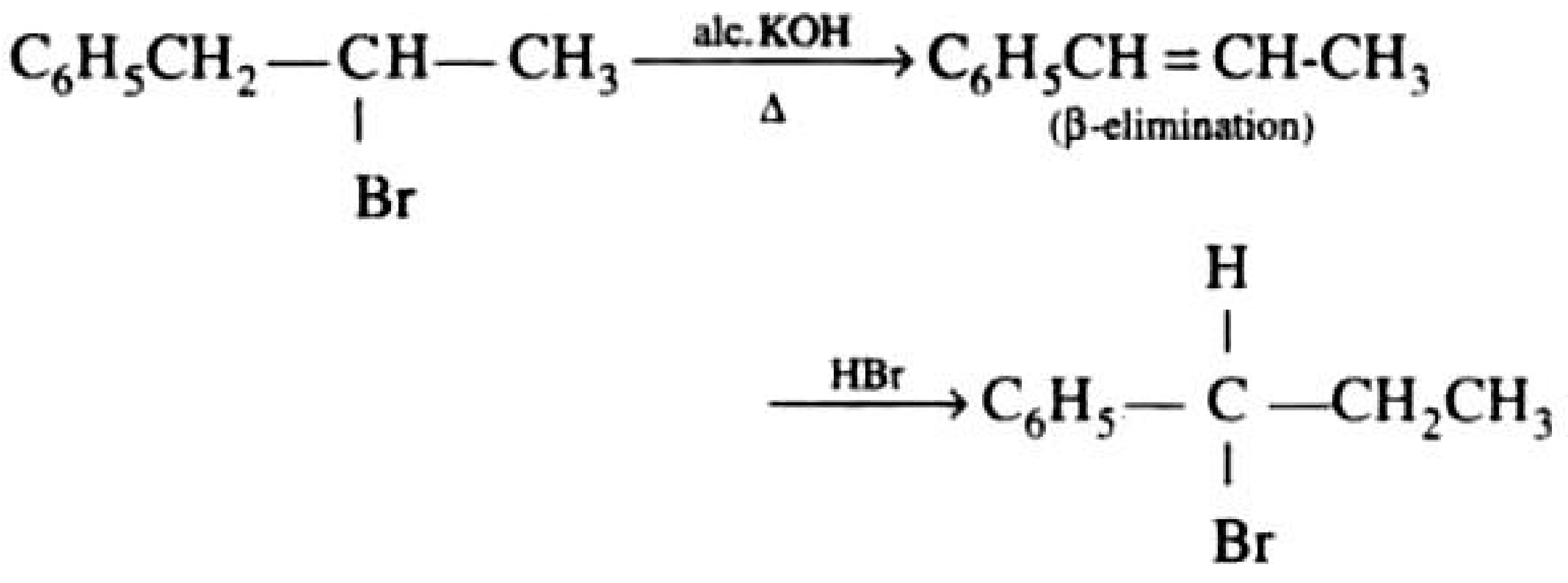
$$H_3C—\overset{\overset{\large Cl}{|}}{\underset{\underset{\large CH_3}{|}}{C}}— CH_2—CH_3 \xrightarrow{\text{alc. KOH}}$$

$$\underset{\text{(Major)}}{CH_3—\underset{\underset{CH_3}{|}}{C}=CH—CH_3} + \underset{\text{(Minor)}}{CH_3=\underset{\underset{CH_3}{|}}{C}—CH_2\text{--}CH_3}$$

iii. $\underset{\text{Gem dihalide}}{CH_3CH_2CHCl_2} \xrightarrow[\text{alkali}]{\text{boil}} CH_3CH_2CH(OH)_2$

$\xrightarrow[(-H_2O)]{} CH_3CH_2CHO$

11.

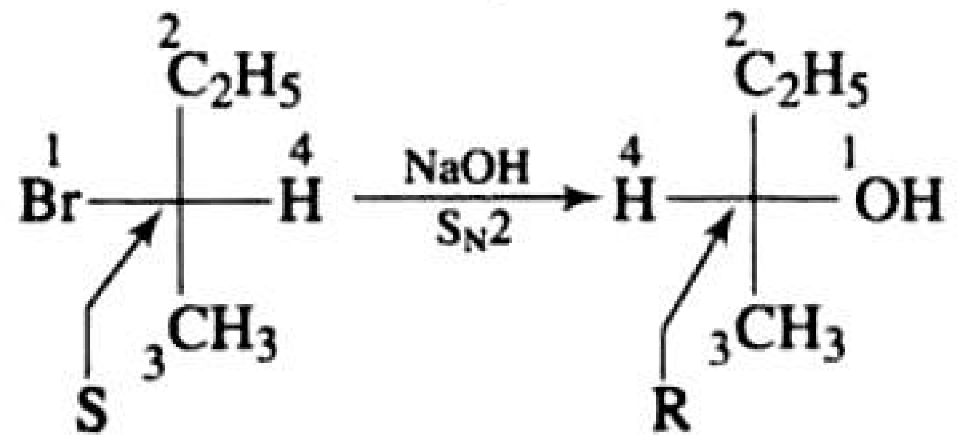


$$C_6H_5CH_2—\underset{\underset{Br}{|}}{CH}— CH_3 \xrightarrow[\Delta]{\text{alc.KOH}} \underset{\text{(β-elimination)}}{C_6H_5CH = CH\text{-}CH_3}$$

$$\xrightarrow{HBr} C_6H_5— \overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}} —CH_2CH_3$$

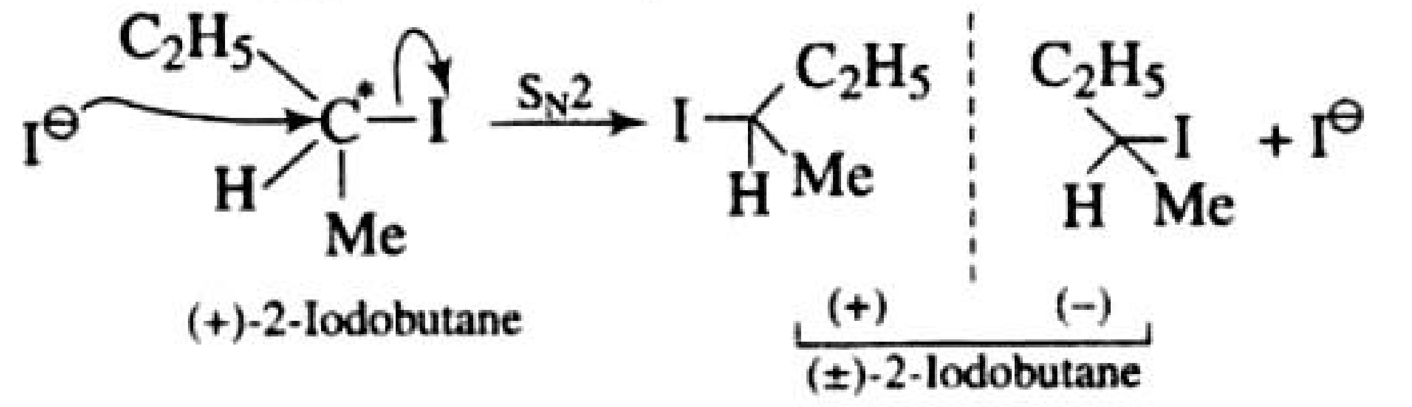
$C_6H_5CH_2\overset{+}{C}HCH_3$ and $C_6H_5\overset{+}{C}HCH_2CH_3$ carbocations are formed on addition of HBr on $C_6H_5CH = CHCH_3$, the latter being benzylic carbocation is stabilised due to resonance and hence Br^- adds on it forming $C_6H_5CHBr \cdot CH_2CH_3$ as the final product.

12. S_N2 reaction leads to inversion in configuration.



Using Cahn–Ingold rules on priority of groups and using golden rule that if 4th priority group is horizontal then configuration is opposite to that obtained in rotation.

13.

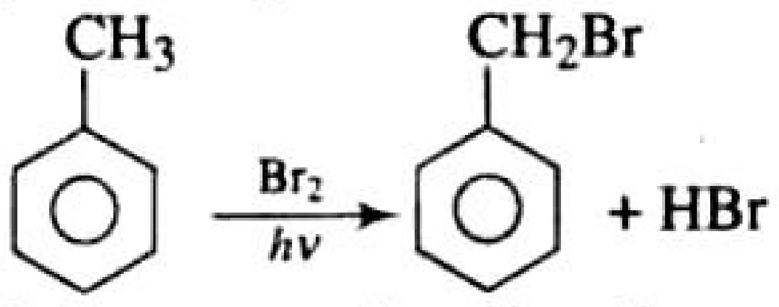


It is an experimental proof for S_N2 reaction. Hughes and Ingold show that inversion takes place in S_N2 reaction. When optically active, 2-iodobutane was treated with NaI in dry acetone; the compound losses optical activity, i.e., (±)-2-iodobutane was obtained.

Suppose there are n molecules of optically active, 2-iodobutane, when $n/2$ molecules have been exchanged with I^- and in doing so have been inverted, leaving behind $n/2$ untreated molecules with retention in configuration. Racemisation is complete, although exchange has taken place with only half of the total molecules. Thus, this observation leads to the assumption that inversion always occurs in S_N2 mechanism, and it was also found that the rate of racemisation was twice the rate of inversion.

Therefore, a general rule can be formulated that whenever the nucleophile and leaving groups are same, racemisation takes place in S_N2 reaction.

14.

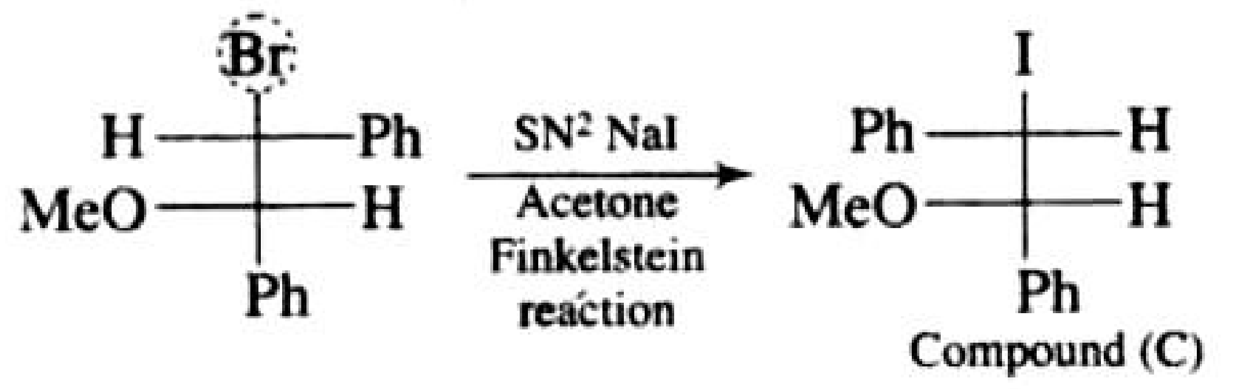


Toluene Benzyl bromide

This reaction is based on the free radical substitution concept, i.e., it is completed in the form of free radical mechanism.

So, in the presence of sunlight, the substitution takes place from the side chain while in the presence of $FeBr_3$, the substitution takes place from the benzene nucleus.

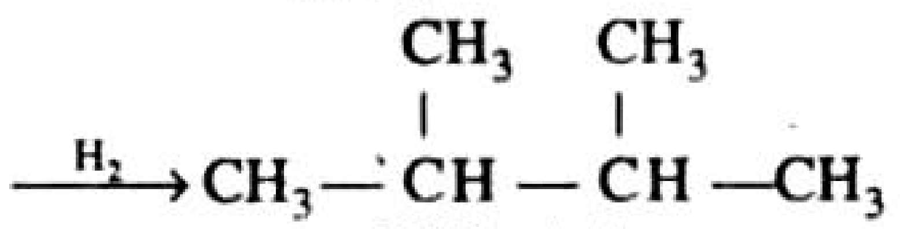
15. Br is replaced with I in acetone followed by S_N2 reaction mechanism. Due to S_N2 reaction mechanism, Walden inversion takes place.



Compound (C)

16. Given:

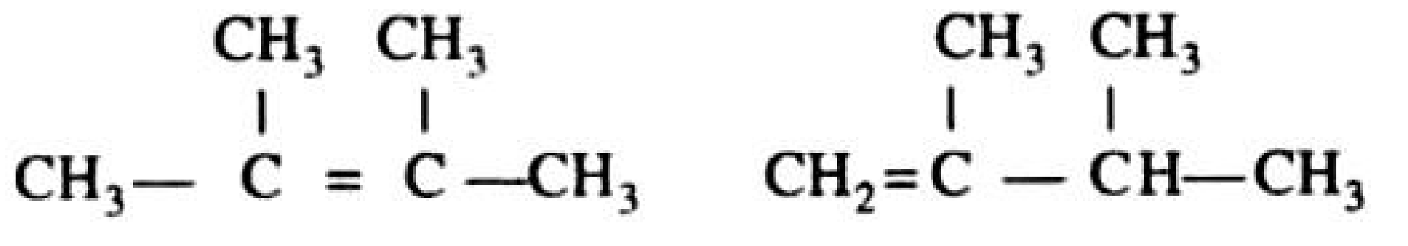
$$\underset{X}{C_6H_{13}Cl} \xrightarrow{(CH_3)_3COK} \underset{Y \text{ and } Z}{\text{Two isomeric alkenes}}$$



$$\xrightarrow{H_2} CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

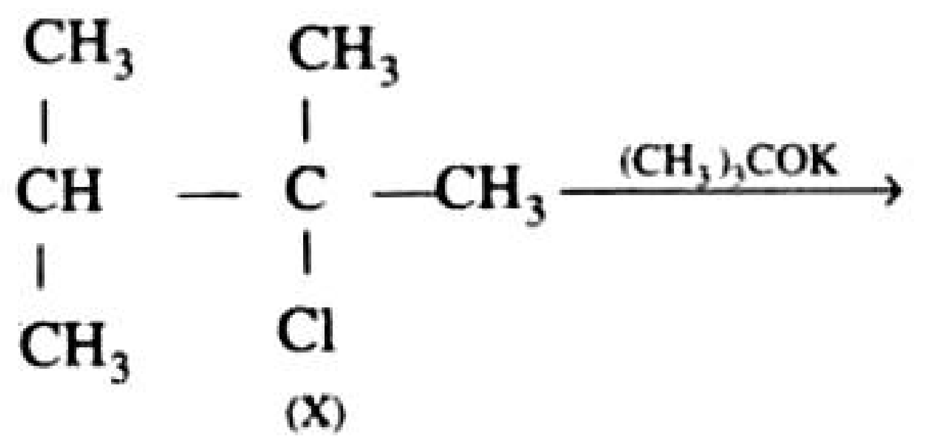
2,3-Dimethylbutane

The two isomeric precursors (Y and Z) of 2, 3-dimethylbutane are



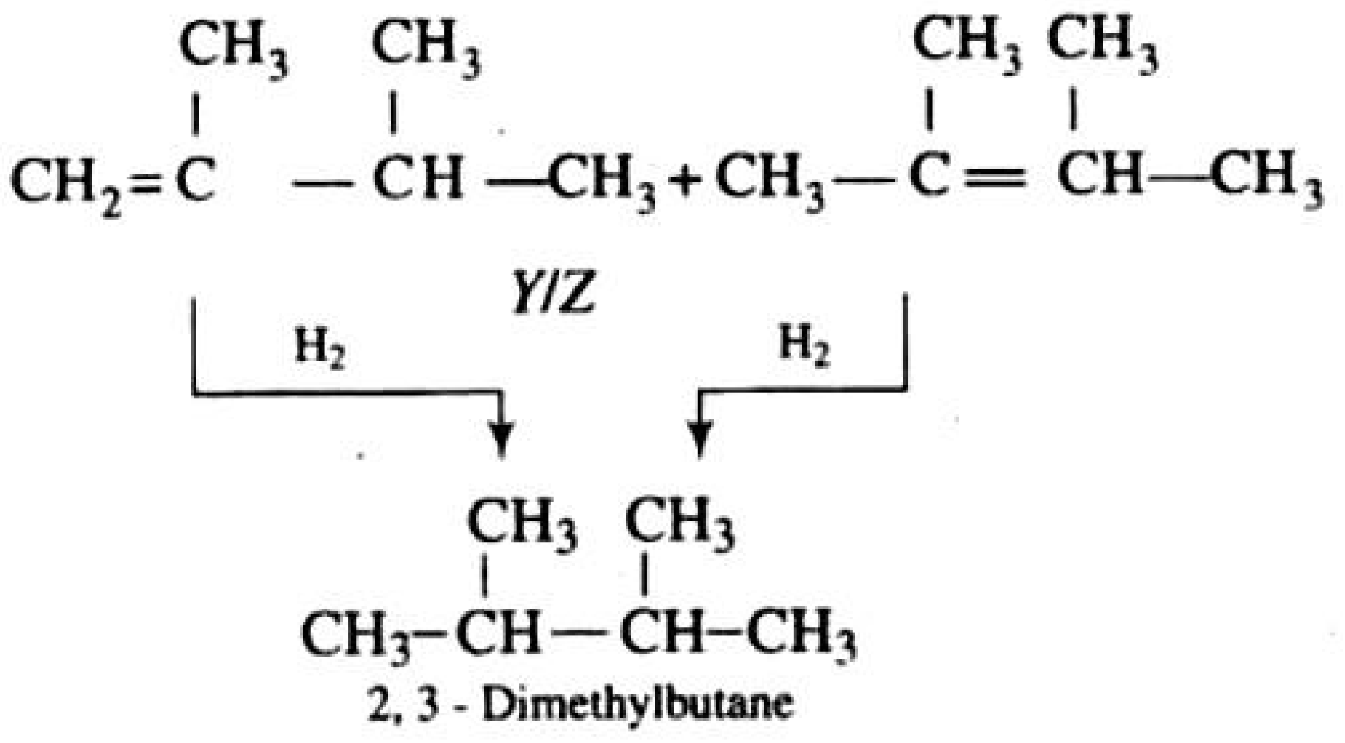
$$CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3 \qquad CH_2=\overset{CH_3}{\overset{|}{C}}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

Hence the precursors of Y and Z should have following structure which explains all the given facts



$$CH_3-\underset{CH_3}{\underset{|}{\overset{|}{C}H}}-\underset{Cl}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3 \xrightarrow{(CH_3)_3COK}$$

(X)



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

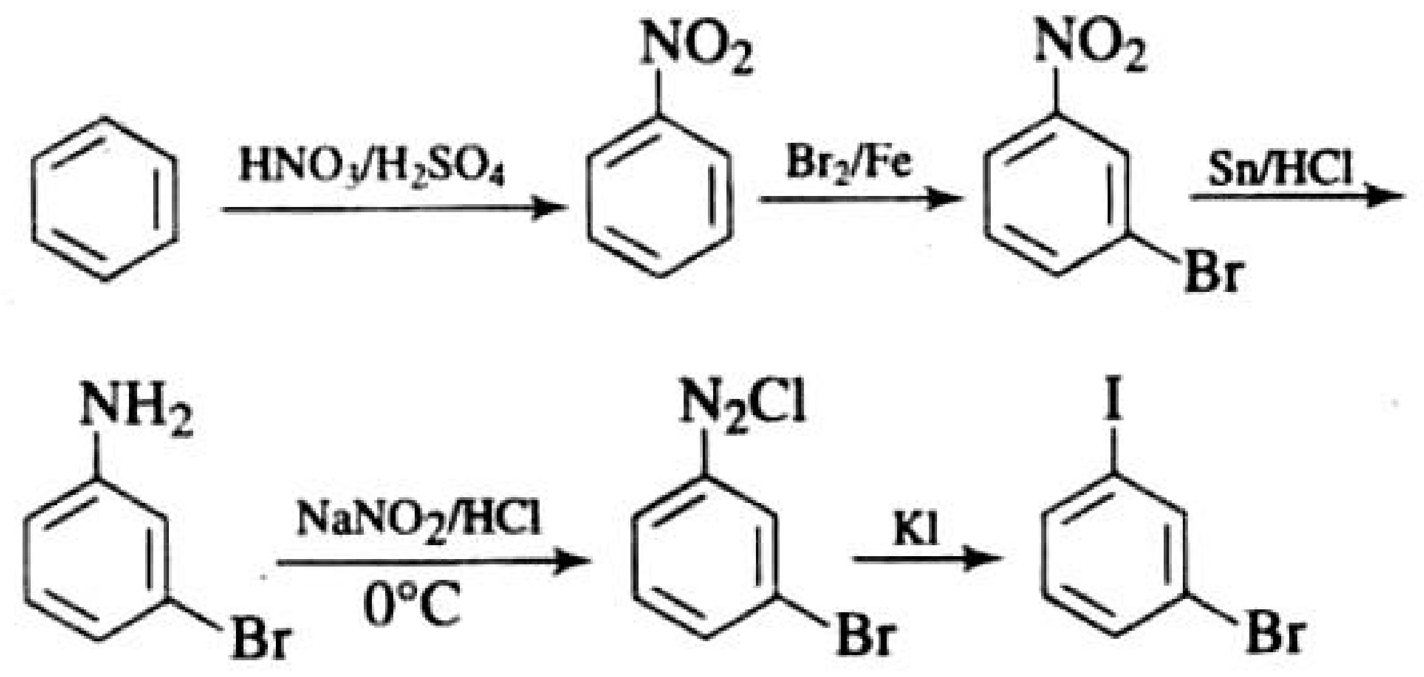
Y/Z

H_2 H_2

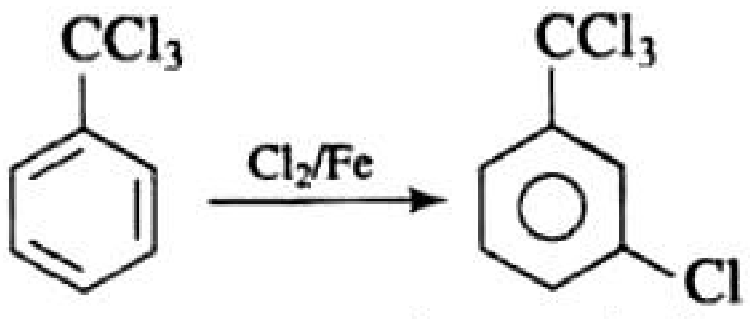
$$CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{CH_3}{\overset{|}{C}H}-CH_3$$

2, 3 - Dimethylbutane

17.



18. i.



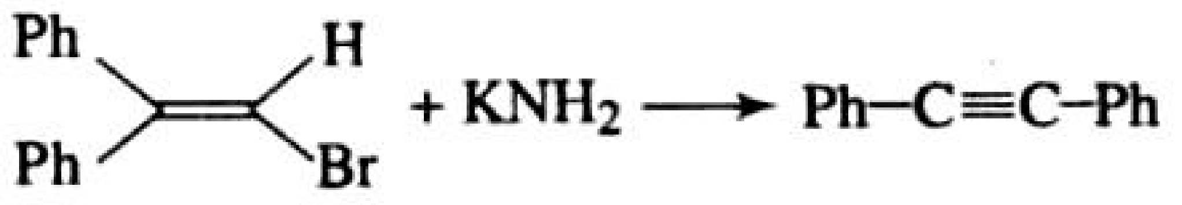
(meta product)

as $-CCl_3$, group becomes meta director due to three electron withdrawing –Cl group which develops positive charge at ortho and para positions.

ii. $CH_3CH_2Br \xrightarrow{AgCN} \underset{\text{Isocyanide}}{CH_3CH_2-N\equiv C}$

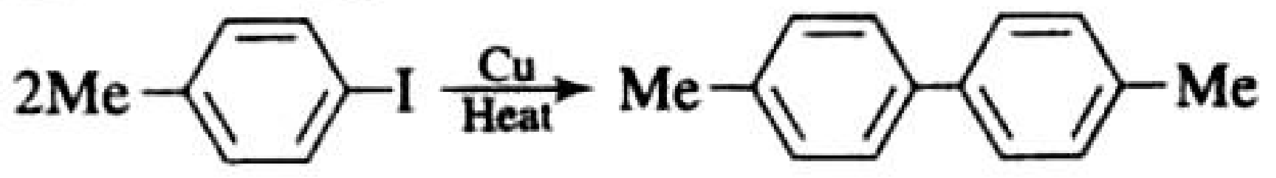
AgCN being covalent compound, N end is available through its lone pair.

iii.



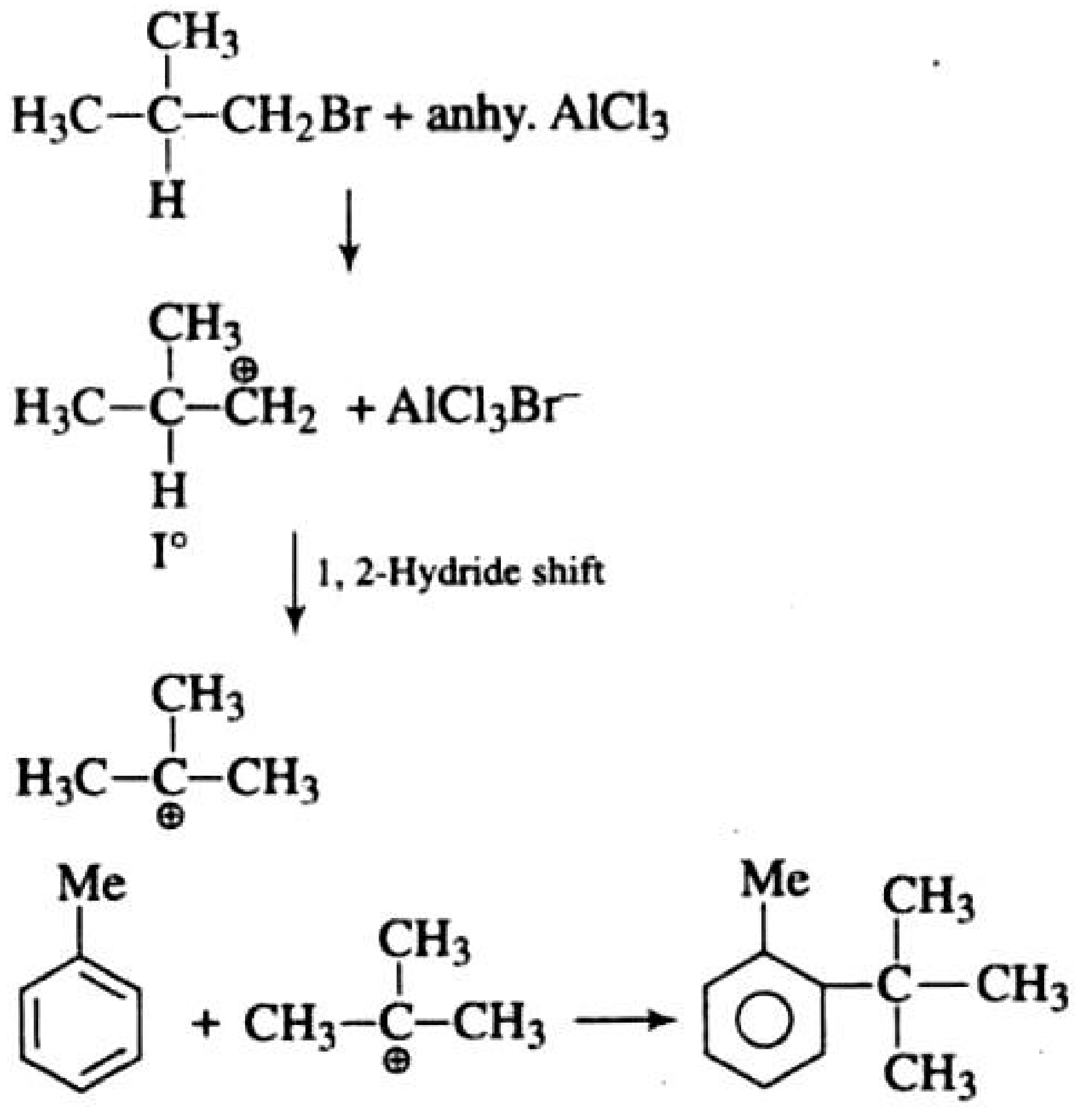
$+ KNH_2 \longrightarrow Ph-C\equiv C-Ph$

iv.



$2Me-C_6H_4-I \xrightarrow[\text{Heat}]{Cu} Me-C_6H_4-C_6H_4-Me$

19.



$$H_3C-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2Br + \text{anhy. } AlCl_3$$

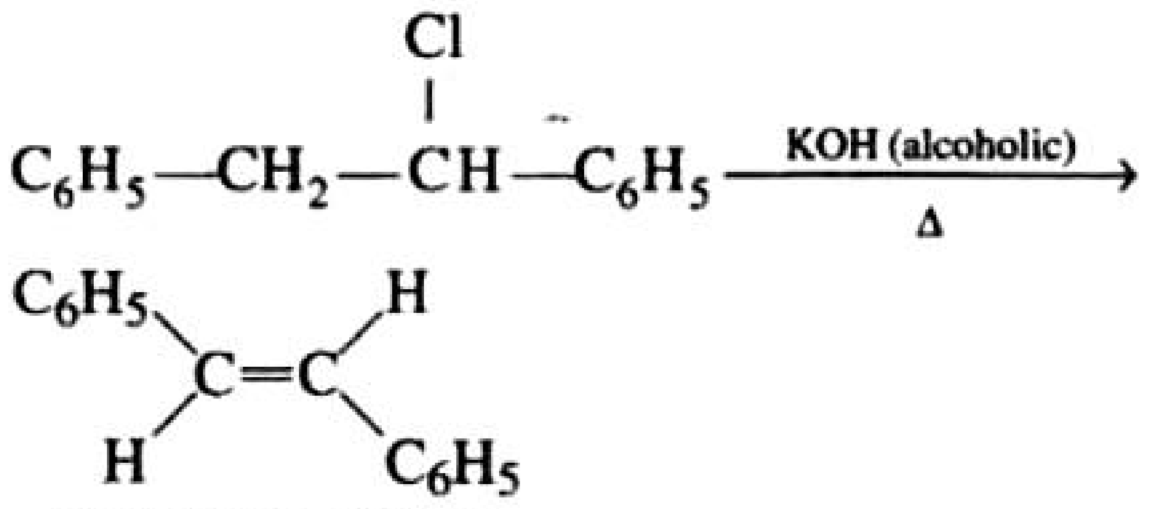
$$H_3C-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\overset{\oplus}{C}H_2 + AlCl_3Br^-$$

I°

1, 2-Hydride shift

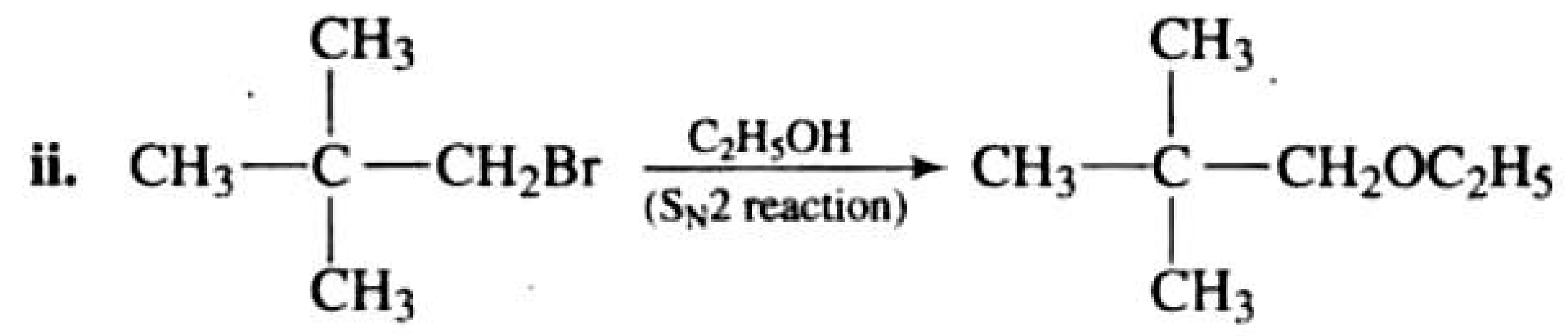
$$H_3C-\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}-CH_3$$

20. Chlorobenzene < Benzene < Toluene < Methoxy benzene.

21. i. 

$$C_6H_5-CH_2-\overset{\displaystyle Cl}{\overset{|}{C}H}-C_6H_5 \xrightarrow[\Delta]{\text{KOH (alcoholic)}}$$

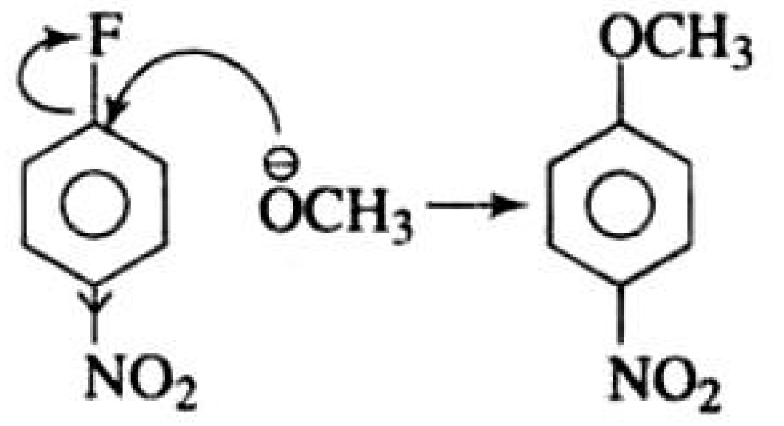
cis and *trans*- stilbene
(*trans* is major)

ii. 

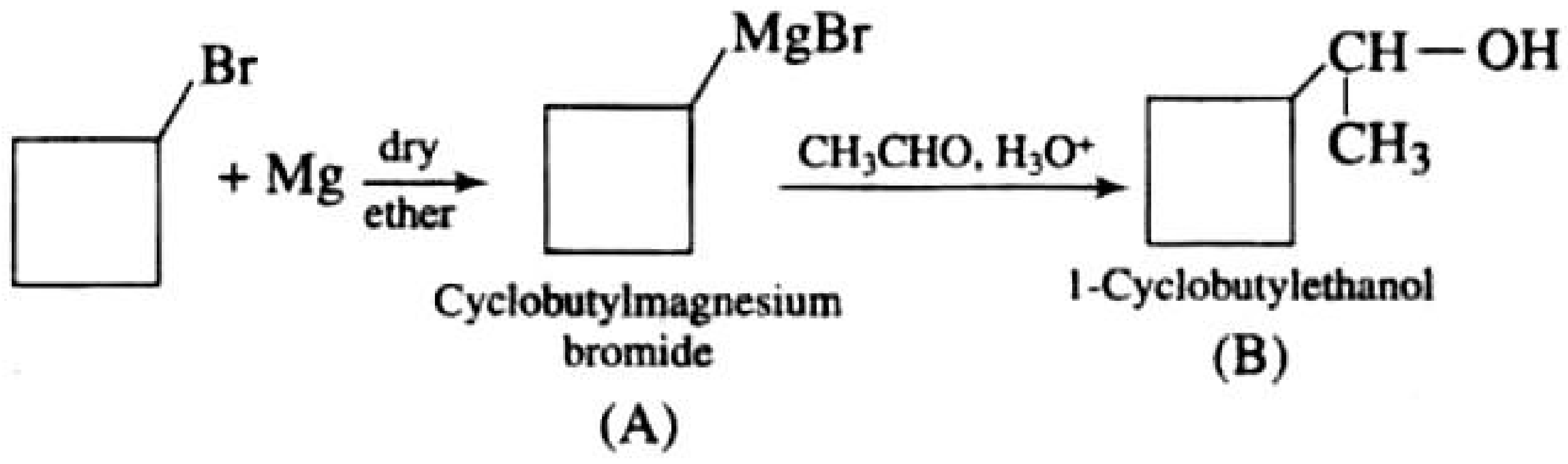
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2Br \xrightarrow[(S_N2\text{ reaction})]{C_2H_5OH} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2OC_2H_5$$

as reaction is 1° so S_N2.

22. Due to the presence of strong EWG [(–NO_2) group], $F^{\ominus}$ is expelled by nucleophilic ($\overset{\ominus}{O}CH_3$). It is ArSN (addition–elimination reaction).

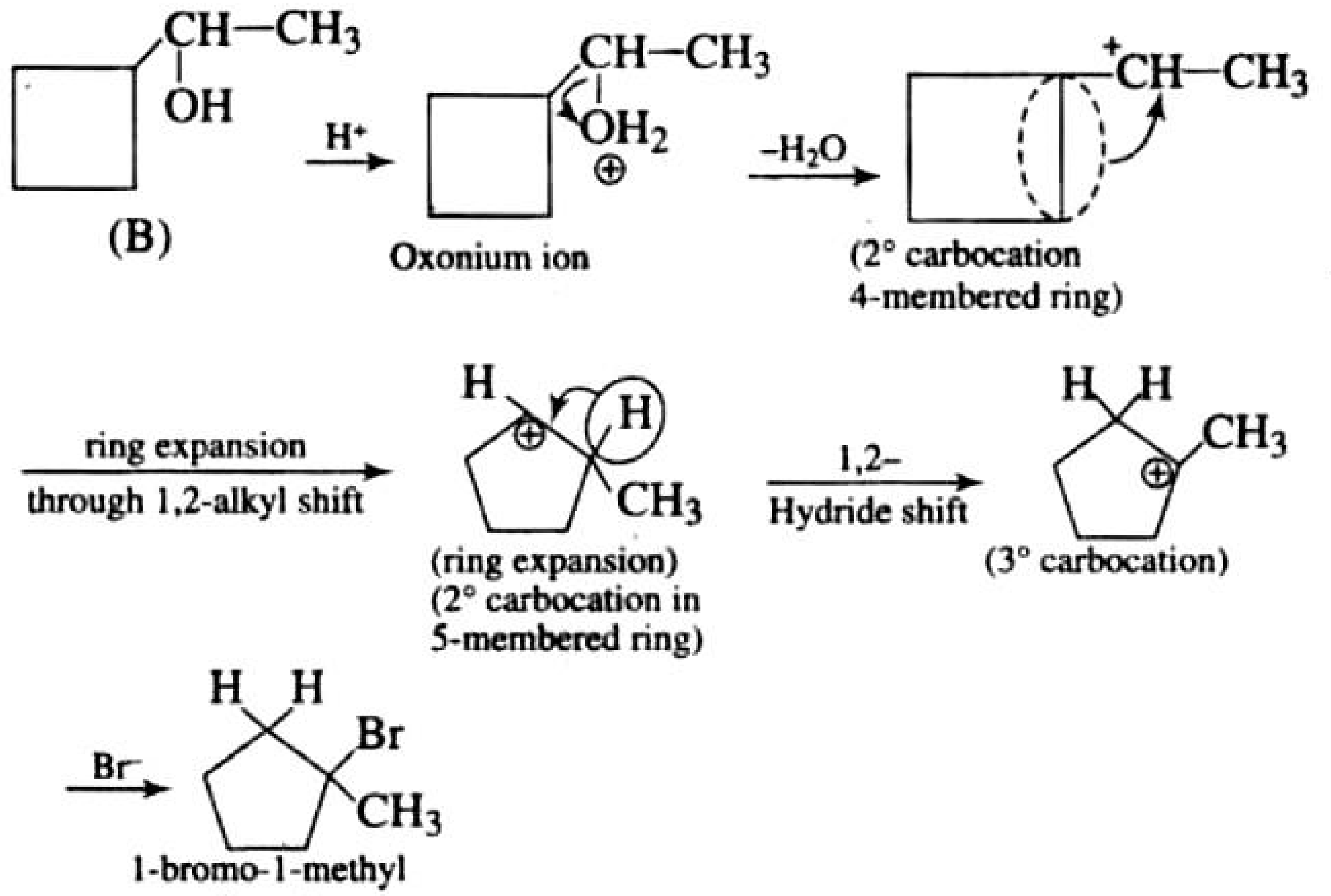


23.



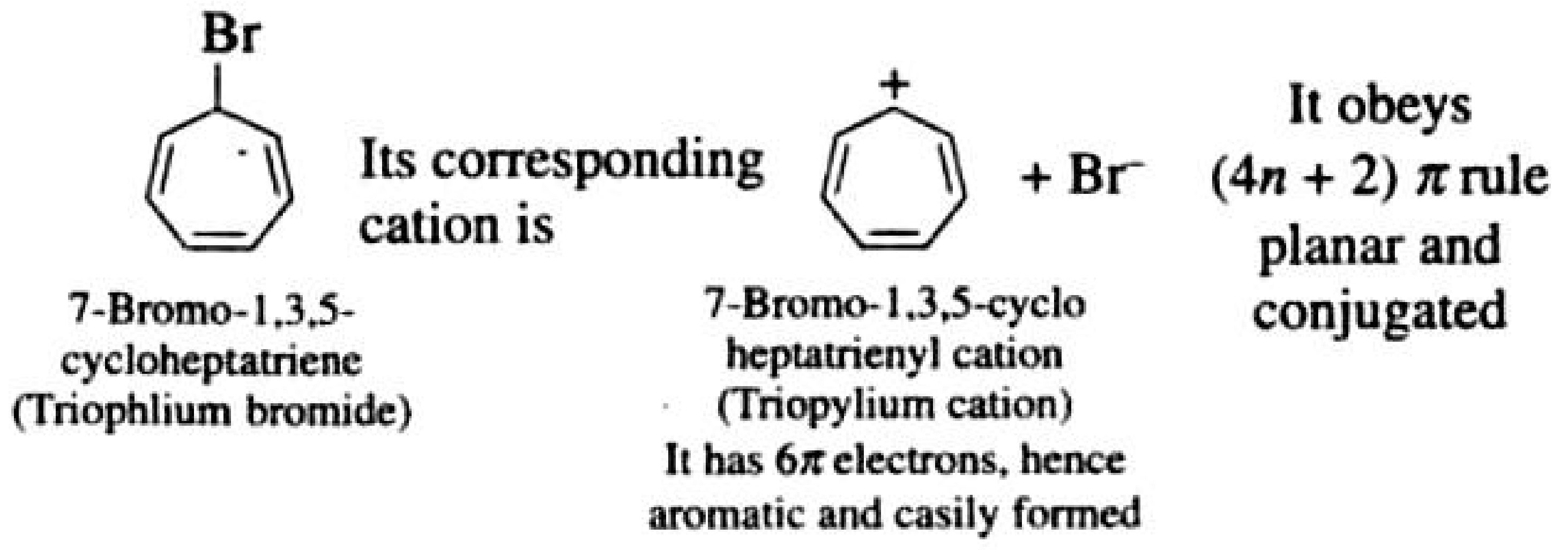
Cyclobutylmagnesium bromide
(A)

1-Cyclobutylethanol
(B)



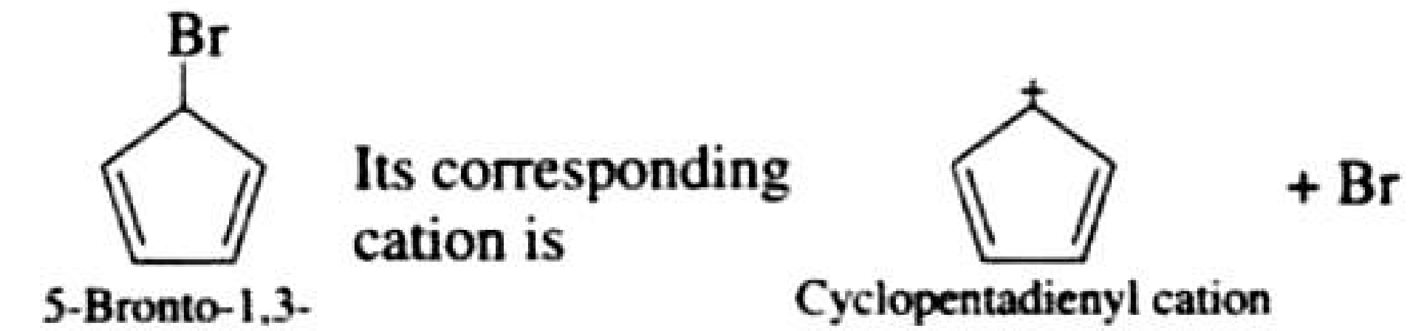
1-bromo-1-methyl cyclopentane

24. i. Cation corresponding to 7-Bromo-1, 3, 5-cycloheptatriene is aromatic whereas that corresponding to 5-Bromo-1, 3-Cycloheptadiene is nonaromatic.



7-Bromo-1,3,5-cycloheptatriene (Triophlium bromide)

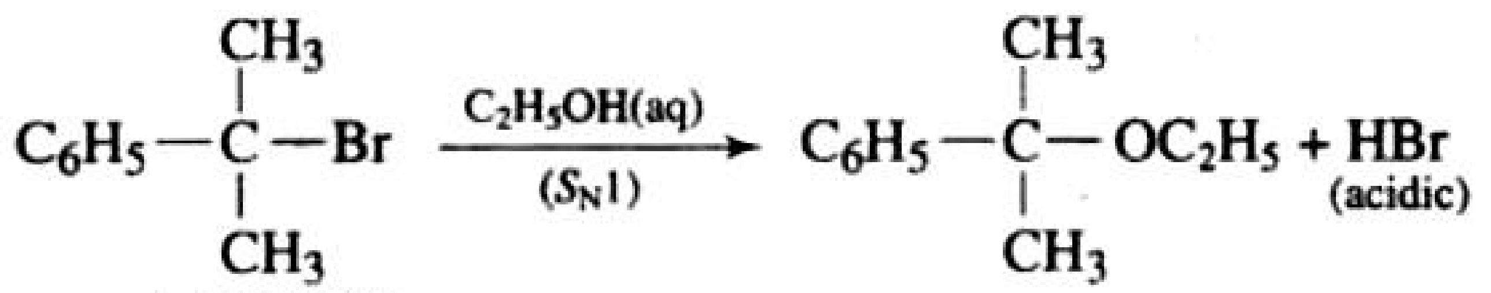
7-Bromo-1,3,5-cyclo heptatrienyl cation (Triopylium cation) It has 6π electrons, hence aromatic and easily formed



5-Bronto-1,3-cyclopentadiene

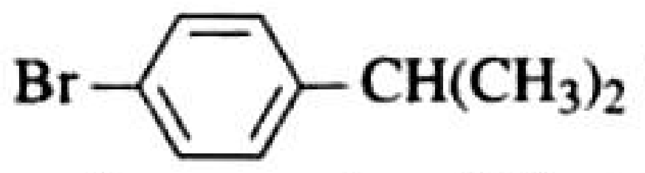
Cyclopentadienyl cation (It has 4 π electrons, hence not aromatic thus not easily formed)

ii. The former halide is a 3° halide, hence it undergoes S_N1 reaction forming HBr, as one of the product, which make solution acidic.



$$C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-Br \xrightarrow[(S_N1)]{C_2H_5OH(aq)} C_6H_5-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OC_2H_5 + \underset{\text{(acidic)}}{HBr}$$

A 3° bromide

 is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence the solution will remain neutral.