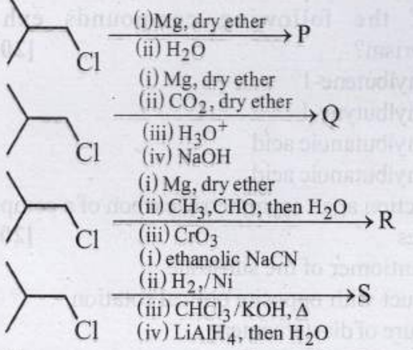
Chapter
Haloalkanes & Haloarenes

Topic-1: Preparation and Properties of Haloalkanes

1 MCQs with One Correct Answer

1. In the following reactions, P, Q, R, and S are the major products. **[Adv. 2023]**



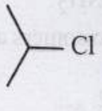
The correct statement about P, Q, R, and S is

(a) P is a primary alcohol with four carbons.
(b) Q undergoes Kolbe's electrolysis to give an eight-carbon product.
(c) R has six carbons and it undergoes Cannizzaro reaction.
(d) S is a primary amine with six carbons.

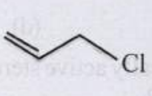
2. KI in acetone, undergoes S_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as **[Adv. 2013]**

H_3C-Cl

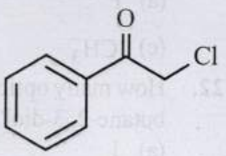
P



Q



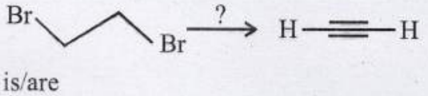
R



S

(a) P > Q > R > S
(b) S > P > R > Q
(c) P > R > Q > S
(d) R > P > S > Q

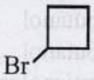
3. The reagent(s) for the following conversion,

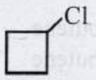


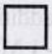
is/are **[2007]**

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

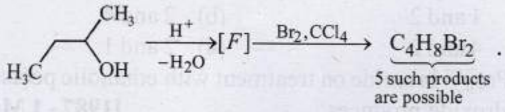
4. What would be the product formed when 1–bromo–3–chlorocyclobutane reacts with two equivalents of metallic sodium in ether? **[2005S]**

(a) 

(b) 

(c) 

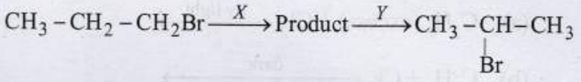
(d) 

5. 

How many structures for F are possible? **[2003S]**

(a) 2 (b) 5 (c) 6 (d) 3

6. Identify the set of reagent / reaction conditions '*X*' and '*Y*' in the following set of transformations **[2002S]**



$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\substack{| \\ Br}}{CH}-CH_3$$

(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

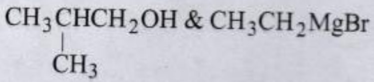
7. A solution of (+) –2–chloro–2–phenylethane in toluene racemises slowly in the presence of small amount of $SbCl_5$, due to the formation of **[1999 - 2 Marks]**

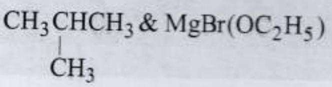
(a) carbanion
(b) carbene
(c) free-radical
(d) carbocation

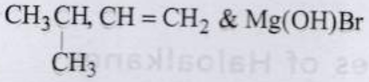
8. $(CH_3)_3CMgCl$ on reaction with D_2O produces : **[1997 - 1 Mark]**

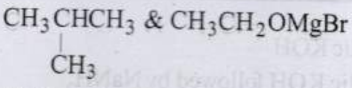
(a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
(c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$

9. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives : **[1995S]**

(a) 
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2OH$ & CH_3CH_2MgBr

(b) 
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_3$ & $MgBr(OC_2H_5)$

(c) 
$CH_3\underset{\underset{CH_3}{|}}{CH}\,CH = CH_2$ & $Mg(OH)Br$

(d) 
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_3$ & CH_3CH_2OMgBr

10. The chief reaction product of reaction between *n*-butane and bromine at 130°C is : **[1995S]**

(a) $CH_3CH_2CH_2CH_2Br$ (b) $CH_3CH_2CH(Br)CH_3$
(c) $CH_3-CH_2CH(Br)CH_2Br$ (d) $CH_3CH_2C(Br_2)CH_3$

11. 1-Chlorobutane on reaction with alcoholic potash gives **[1991 - 1 Mark]**

(a) 1-butene (b) 1-butanol
(c) 2-butene (d) 2-butanol

12. 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 **[1988 - 1 Mark]**

(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

13. n-Propyl bromide on treatment with ethanolic potassium hydroxide produces **[1987 - 1 Mark]**

(a) Propane (b) Propene
(c) Propyne (d) Propanol

14. The reaction conditions leading to the best yields of C_2H_5Cl are : **[1986 - 1 Mark]**

(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) $C_2H_6 + Cl_2 \text{ (excess)} \xrightarrow{\text{uv light}}$

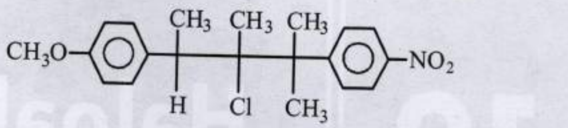
(d) $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$

15. Among the following compounds, the most acidic is **[2011]**

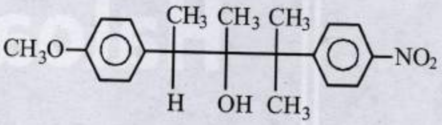
(a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid

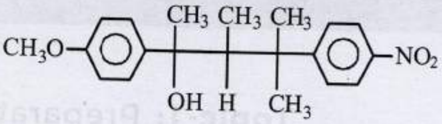
16. The number of stereoisomers obtained by bromination of *trans-2-butene* is **[2007]**

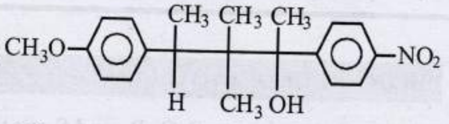
(a) 1 (b) 2
(c) 3 (d) 4

17. 

compound on hydrolysis in aqueous acetone will give **[2005S]**

(i) 

(ii) 

(iii) 

(a) Mixture of (i) and (ii) (b) Mixture of (i) and (iii)
(c) Only (iii) (d) Only (i)

18. Which of the following compounds exhibits stereoisomerism? **[2002S]**

(a) 2-methylbutene-1
(b) 3-methylbutyne-1
(c) 3-methylbutanoic acid
(d) 2-methylbutanoic acid

19. An S_N2 reaction at an asymmetric carbon of a compound always gives **[2001S]**

(a) an enantiomer of the substrate
(b) a product with opposite optical rotation
(c) a mixture of diastereomers
(d) a single stereoisomer

20. The order of reactivity of the following alkyl halides for a S_N2 reaction is **[2000S]**

(a) RF > RCl > RBr > RI
(b) RF > RBr > RCl > RI
(c) RCl > RBr > RF > RI
(d) RI > RBr > RCl > RF

21. Which of the following has the highest nucleophilicity? **[2000S]**

(a) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

22. How many optically active stereoisomers are possible for butane-2, 3-diol? **[1997]**

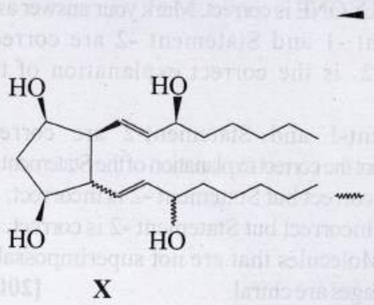
(a) 1 (b) 2
(c) 3 (d) 4

23. The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about **[1988]**

(a) 120° and 109.5° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

2 Integer Value Answer

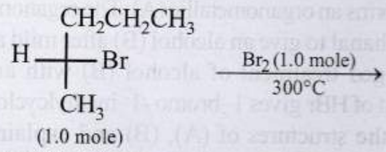
24. For the given compound **X**, the total number of optically active stereoisomers is ____ **[Adv. 2018]**



◄ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed

This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is **NOT** fixed

25. In the following monobromination reaction, the number of possible chiral products is **[Adv. 2016]**



(1.0 mole)
(enantiomerically pure)

26. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is **[2011]**

4 Fill in the Blanks

27. Vinyl chloride on reaction with dimethyl copper gives .... **[1997 - 1 Mark]**

28. The interaction of elemental sulphur with Grignard reagent gives .... **[1991 - 1 Mark]**

29. Isomers which are .... mirror images are known as .... **[1988]**
(superimposable, non-superimposable, enantiomers, diastereomers, epimers)

30. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as .... reagent. **[1982 - 1 Mark]**

31. The halogen which is most reactive in the halogenation of alkanes under sunlight is ....
(chlorine, bromine, iodine) **[1981 - 1 Mark]**

5 True / False

32. 2, 3, 4-Trichloropentane has three asymmetric carbon atoms. **[1990]**

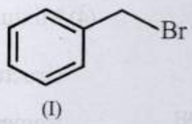
33. During S_N1 reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule. **[1990]**

34. The reaction of vinyl chloride with hydrogen iodide to give 1-chloro-1-iodoethane is an example of anti-Markovnikov's rule. **[1989 - 2 Marks]**

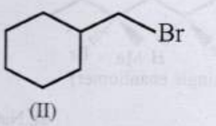
35. Iodide is a better nucleophile than bromide. **[1985 - ½ Mark]**

6 MCQs with One or More than One Correct Answer

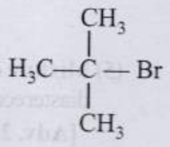
36. For the following compounds, the correct statement(s) with respect to nucleophilic substitution reaction is(are) **[Adv. 2017]**



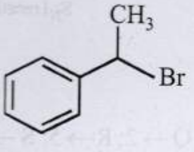
(I)



(II)



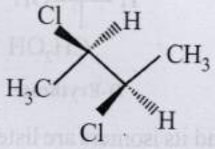
(III)



(IV)

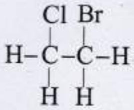
(a) I and III follow S_N1 mechanism
(b) I and II follow S_N2 mechanism
(c) Compound IV undergoes inversion of configuration
(d) The order of reactivity for I, III and IV is : IV > I > III

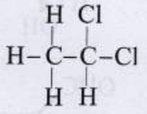
37. The correct statement(s) about the compound given below is (are) **[2008]**

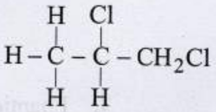


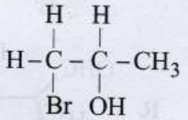
(a) The compound is optically active
(b) The compound possesses centre of symmetry
(c) The compound possesses plane of symmetry
(d) The compound possesses axis of symmetry

38. Which of the following have asymmetric carbon atom? **[1989]**

(a)

$H-\overset{Cl}{\underset{H}{C}}-\overset{Br}{\underset{H}{C}}-H$

(b)

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

(c)

$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}-CH_2Cl$

(d)

$H-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{OH}{C}}-CH_3$

7 Match the Following

39. Match the reactions in List–I with the features of their products in List–II and choose the correct option.

List–I	List–II
(P) (−) – 1 – Bromo – 2 – ethylpentane (single enantiomer) $\xrightarrow[S_N2\text{ reaction}]{\text{aq.NaOH}}$	(1) Inversion of configuration
(Q) (−) – 2 – Bromopentane (single enantiomer) $\xrightarrow[S_N2\text{ reaction}]{\text{aq.NaOH}}$	(2) Retention of configuration

(R) (–) – 3 – Bromo – 3 – methylhexane (single enantiomer) $\xrightarrow[\text{S}_N\text{1 reaction}]{\text{aq.NaOH}}$ (3) Mixture of enantiomers

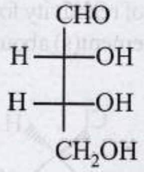
(S)

(single enantiomer) $\xrightarrow[\text{S}_N\text{1 reaction}]{\text{aq.NaOH}}$ (4) Mixture of structural isomers

(5) Mixture of diastereomers

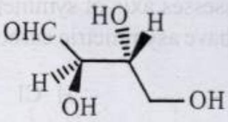
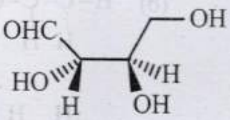
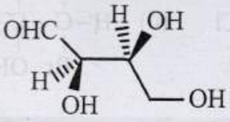
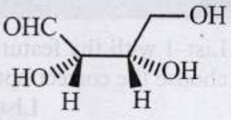
(a) P → 1; Q → 2; R → 5; S → 3 **[Adv. 2023]**
(b) P → 2; Q → 1; R → 3; S → 5
(c) P → 1; Q → 2; R → 5; S → 4
(d) P → 2; Q → 4; R → 3; S → 5

40. The Fischer projection of D-erythrose is shown below.



D-Erythrose

D-Erythrose and its isomers are listed as **P**, **Q**, **R**, and **S** in **Column-I**. Choose the correct relationship of **P**, **Q**, **R**, and **S** with D-erythrose from **Column II**. **[Adv. 2020]**

Column-I	Column-II
P. 	**1.** Diastereomer
Q. 	**2.** Identical
R. 	**3.** Enantiomer
S. 	

(a) **P** → 2, **Q** → 3, **R** → 2, **S** → 2
(b) **P** → 3, **Q** → 1, **R** → 1, **S** → 2
(c) **P** → 2, **Q** → 1, **R** → 1, **S** → 3
(d) **P** → 2, **Q** → 3, **R** → 3, **S** → 1

9 Assertion and Reason Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement-1 and Statement-2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

41. **Statement - 1 :** Molecules that are not superimpossable on their mirror images are chiral. **[2007]**

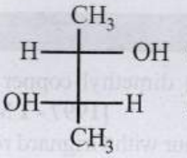
Statement - 2 : All chiral molecules have chiral centres.

10 Subjective Problems

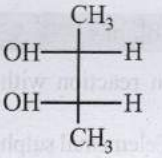
42. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic (A). The organometallic reacts with ethanal to give an alcohol (B) after mild acidification. Prolonged treatment of alcohol (B) with an equivalent amount of HBr gives 1–bromo–1–methylcyclopentane (C). Write the structures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

[2001 - 5 Marks]

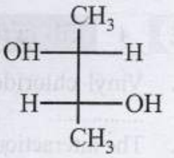
43. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III **[2000]**



I



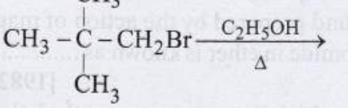
II



III

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

(*i*)



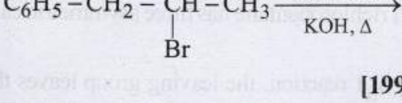
$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Br \xrightarrow[\Delta]{C_2H_5OH}$$

[2000 - 1 Mark]

(*ii*) $C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{alcoholic KOH}}$ 2 Products

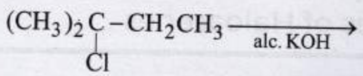
[1998 - 2 Marks]

(*iii*)



$$C_6H_5-CH_2-\underset{Br}{\underset{|}{C}H}-CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$$

[1993 - 1 Mark]

(*iv*) $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}}$ **[1992 - 1 Mark]** (*v*)  [1992 - 1 Mark]

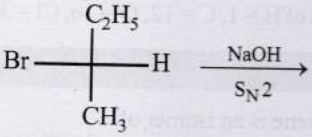
$(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2CH_3 \xrightarrow[\text{alc. KOH}]{}$

(*vi*) bromoethane reacts with one-half of the molar quantity of silver carbonate. [1981 - ½ Mark] [1992 - 1 Mark]

(*vii*) chloroform reacts with aniline in the presence of excess alkali [1981 - ½ Mark]

45. 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*. [1996 - 3 Marks]

46. Draw the stereochemical structures of the products in the following reaction : [1994 - 4 Marks]



47. Arrange the following in :
Increasing reactivity in nucleophilic substitution reactions
CH_3F, CH_3I, CH_3Br, CH_3Cl [1992]

48. 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*. [1989 - 4 Marks]

49. What effect should the following resonance of vinyl chloride have on its dipole moment? [1987 - 1 Mark]

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

50. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment? [1985 - 2 Marks]

51. 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 [1983 - 1 Mark]

(*ii*) Methyl chloride from aluminium carbide [1983 - 1 Mark]

52. (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.

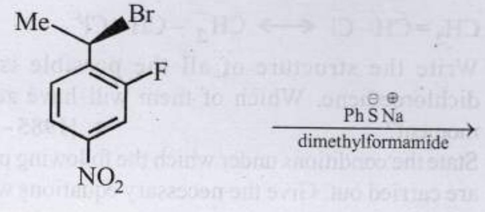
(ii) Chloroform from carbon disulphide.

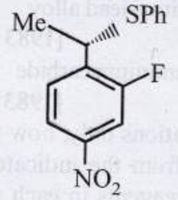
(b) Give one chemical test which would distinguish between C_2H_5OH from $CHCl_3$. [1979]

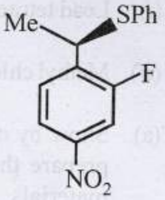
Topic-2: Preparation and Properties of Haloarenes

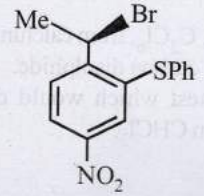
1 MCQs with One Correct Answer

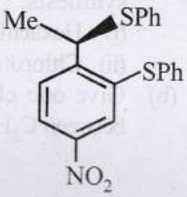
1. The major product of the following reaction is – **[2008]**



(a)


(b)


(c)


(d)


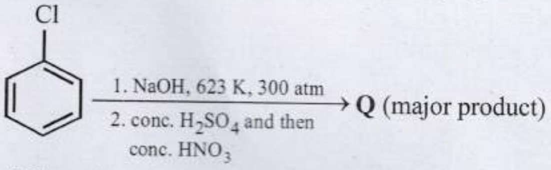
2. When phenyl magnesium bromide reacts with *tert* – butanol, the product would be **[2005S]**
   - (a) Benzene
   - (b) Phenol
   - (c) *ter*–butylbenzene
   - (d) *ter*–butyl phenyl ether

3. The reaction of toluene with chlorine in presence of ferric chloride gives predominantly : **[1986 - 1 Mark]**
   - (a) benzoyl chloride
   - (b) *m*-chlorotoluene
   - (c) benzyl chloride
   - (d) *o*- and *p*-chlorotoluene

4. Chlorobenzene can be prepared by reacting aniline with : **[1984 - 1 Mark]**
   - (a) hydrochloric acid
   - (b) cuprous chloride
   - (c) chlorine in presence of anhydrous aluminium chloride
   - (d) nitrous acid followed by heating with cuprous chloride

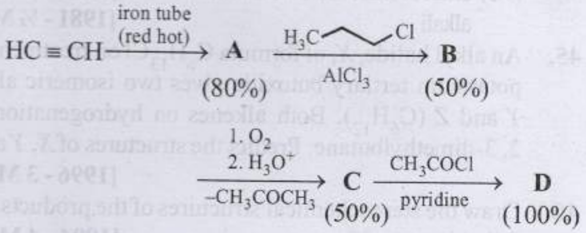
3 Numeric / New Stem Based Questions

5. The weight percentage of hydrogen in **Q**, formed in the following reaction sequence, is ________. **[Adv. 2022]**



[Given: Atomic mass of H = 1, C = 12, N = 14, O = 16, S = 32, Cl = 35]

6. If the reaction sequence given below is carried out with 15 moles of acetylene, the amount of the product **D** formed (in g) is ________. **[Adv. 2022]**



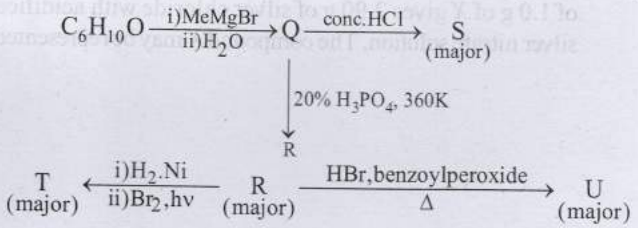
The yields of **A**, **B**, **C** and **D** are given in parentheses.
[Given: Atomic mass of H = 1, C = 12, O = 16, Cl = 35]

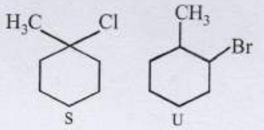
5 True / False

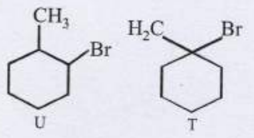
7. *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene. **[1985 - ½ Mark]**

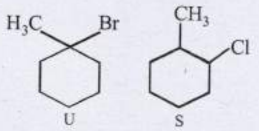
6 MCQs with One or More than One Correct Answer

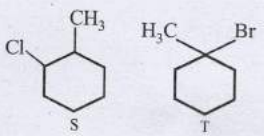
8. Choose the correct option(s) for the following set of reactions **[Adv. 2019]**



(a)


(b)


(c)


(d)


9. Benzyl chloride ($C_6H_5CH_2Cl$) can be prepared from toluene by chlorination with **[1998 - 2 Marks]**
   - (a) SO_2Cl_2
   - (b) $SOCl_2$
   - (c) Cl_2
   - (d) NaOCl

10. Aryl halides are less reactive towards nucleophilic substitution reaction as compared to alkyl halides due to: **[1990 - 1 Mark]**

(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.

7 Match the Following

11. Given below are certain matching type questions, where two columns (each having 4 items) are given. Immediately after the columns the matching grid is given, where each item of **Column I** has to be matched with the items of **Column II**, by encircling the correct match(es). Note that an item of **Column I** can match with more than one item of **Column II**. All the items of **Column II** must be matched.

Match the following : **[2006 - 6M]**

Column I	**Column II**
(A) $C_6H_5CH_2CD_2Br$ on reaction with $C_2H_5O^-$ gives $C_6H_5–CH=CD_2$	(p) E1 reaction
(B) $PhCHBrCH_3$ and $PhCHBrCD_3$, both react with the same rate	(q) E2 reaction
(C) $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ and C_2H_5OD gives $C_6H_5CD=CH_2$	(r) E1cB reaction
(D) $C_6H_5CH_2CH_2Br$ reacts faster than $C_6H_5CD_2CH_2Br$ on reaction with $C_2H_5O^-$ in ethanol	(s) First order reaction

9 Assertion and Reason Type Questions

Each question contains **STATEMENT-1 (Assertion)** and **STATEMENT-2 (Reason)**. Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
(b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
(c) If Statement -1 is correct but Statement -2 is incorrect.
(d) If Statement -1 is incorrect but Statement -2 is correct.

12. Read the following Statement-1 (Assertion) and Statement -2 (Reason) and answer as per the options given below :

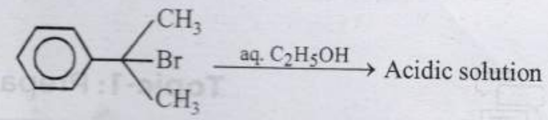
Statement-1 : Bromobenzene upon reaction with Br_2/Fe gives 1,4-dibromobenzene as the major product. **[2008S]**

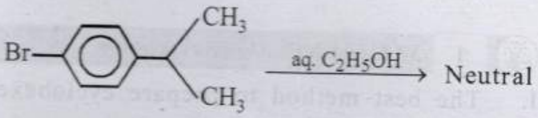
Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

10 Subjective Problems

13. Give reasons for the following :

(*i*)

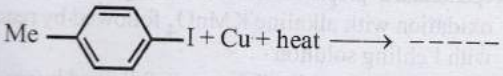




solution. Explain. **[2005 - 1 Mark]**

(*ii*) 7-Bromo-1, 3, 5-cycloheptatriene exists as ionic compound, while 5-bromo-1, 3-cyclopentadiene does not ionise even in presence of Ag^+ ion. Explain. **[2004 - 2 Marks]**

14. Write the structural formula of the major product in the following case :



[1997 - 1 Mark]

15. How will you prepare *m*-bromoiodobenzene from benzene (in not more than 5-7 steps)? **[1996 - 2 Marks]**

16. Give reasons for the following :
Aryl halides are less reactive than alkyl halides towards nucleophilic reagents **[1994]**

17. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? **[1987 - 1 Mark]**

AnswerKey

Topic-1 : Preparation and Properties of Haloalkanes

1. (b) **2.** (b) **3.** (b) **4.** (d) **5.** (d) **6.** (b) **7.** (d) **8.** (a) **9.** (b) **10.** (b)
11. (a) **12.** (b) **13.** (b) **14.** (a) **15.** (c) **16.** (a) **17.** (a) **18.** (d) **19.** (d) **20.** (d)
21. (c) **22.** (c) **23.** (a) **24.** (7) **25.** (5) **26.** (5) **28.** (Thioalcohol)
29. (non-superimposable, enantiomers) **30.** (Grignard (RMgX)) **31.** (Chlorine) **32.** (False)
33. (True) **34.** (False) **35.** (True) **36.** (a,b,c) **37.** (a,d) **38.** (c,d) **39.** (b) **40.** (c) **41.** (c)

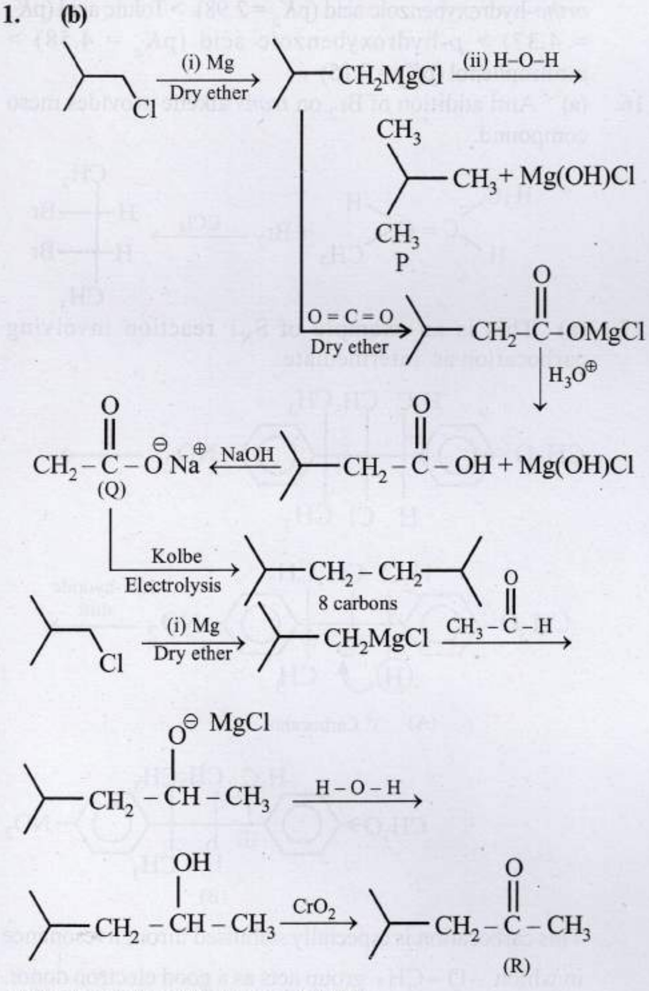
Topic-2 : Preparation and Properties of Haloarenes

1. (a) **2.** (a) **3.** (d) **4.** (d) **5.** (1.31) **6.** (136) **7.** (False) **8.** (a,b) **9.** (c) **10.** (b,e)
11. (A) - q; (B) - p, s; (C) - r, s; (D) - q **12.** (c)

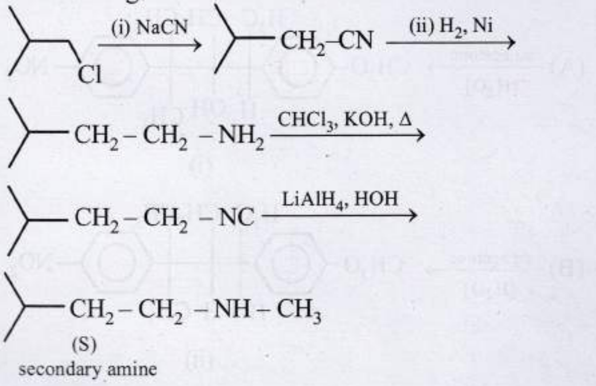
Hints & Solutions

Topic-1: Preparation and Properties of Haloalkanes

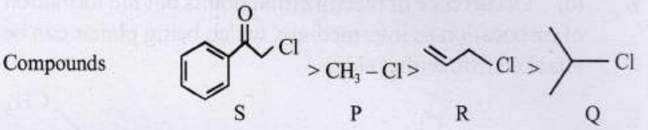
1. **(b)**



It does not give Cannizaro reaction.



2. **(b)**



Relative reactivities towards S_N2 reaction 1,00,000 ; 200 ; 79 ; 0.02

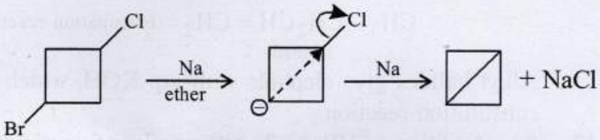
The electron withdrawing groups (–I effect) stabilise the transition state formed in the rate determining step of S_N2 reaction. Hence, the benzoylic, allylic system increases the reaction rate to more than 1° carbon system. But reactivity is higher for $—CH_3$ than that for allylic ($CH_2=CH–$) system.

3. **(b)** $BrCH_2 - CH_2Br \xrightarrow{\text{Alc.KOH}} CH_2 = CHBr$

$\xrightarrow{NaNH_2} CH \equiv CH$

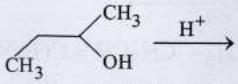
Elimination of HBr from $CH_2= CHBr$ requires a stronger base because here, C – Br acquires partial double bond character due to resonance.

4. **(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.

5. **(d)**

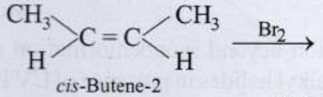


$$\underbrace{\underset{\text{Butene-1}}{CH_3CH_2CH = CH_2} + \underset{\substack{\text{Butene-2}\\(\textit{cis-} \text{ and } \textit{trans})}}{CH_3CH = CHCH_3}}_{F}$$

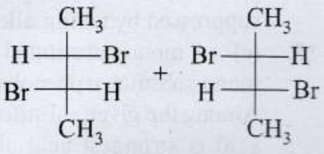
$$\underset{\text{Butene-1}}{CH_3CH_2CH = CH_2} \xrightarrow{Br_2} CH_3\,CH_2\,\overset{*}{C}HCH_2Br$$

Br

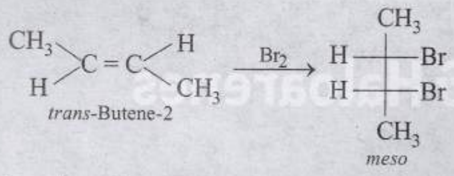
(+) – and (–) enantiomer



cis-Butene-2



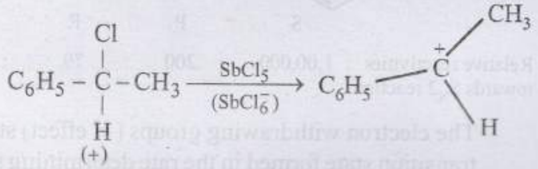
Enantiomers



So F can have three possible structures.

6. (b) Dehydrobromination by strong base (alc. NaOH) followed by Markownikoff addition of HBr.

7. (d) Occurrence of racemization points out the formation of carbocation as intermediate, which being planar can be attacked from either side.



(+)

$$\xrightarrow{Cl^-} (+)(-)(+)(-)$$

8. (a) $(CH_3)_3C-MgCl + D_2O \longrightarrow$

$$(CH_3)_3C-D + Mg(OD)Cl$$

9. (b) $(CH_3)_2CHCH_2MgBr \xrightarrow{C_2H_5OH} (CH_3)_2\,CHCH_3$

10. (b) The reaction proceeds via free radical mechanism. As 2° free radical is more stable than 1°, so $CH_3CH_2CH(Br)CH_3$ would be formed.

11. (a) $H_3C-H_2C-H_2C-CH_2Cl \xrightarrow{\text{alc. KOH}}$

$$\underset{\text{1-butene}}{CH_3-CH_2CH=CH_2} \quad \text{(Elimination reaction)}$$

Alkyl halides give alcohols with **aq.** KOH, which is a substitution reaction.

12. (b) Addition of HBr to 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 (I and II) and four configurational isomers *cis*-and *trans*-of I and II.

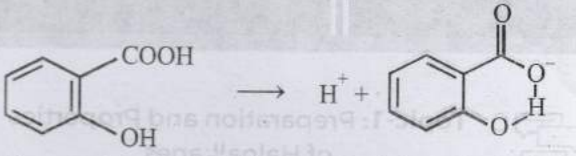
13. (b) $\underset{n\text{-Propyl bromide}}{CH_3-CH_2-CH_2Br} \xrightarrow[-HBr]{\text{ethanolic KOH}}$

$$\underset{\text{Propene}}{CH_3-CH=CH_2}$$

14. (a) Chlorination beyond monochlorination during the preparation of alkyl halides in presence of UV light can be suppressed by taking **alkane in excess**.

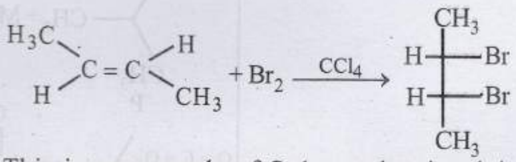
15. (c) A mono-substituted benzoic acid is stronger than a mono-substituted phenol as former being a carboxylic acid. Among the given substituted benzoic acid, *ortho*-hydroxy acid is strongest acid although —OH causes electron donation by resonance effect which tends to decrease acid strength.

It is due to a very high stabilisation of congugate base by intramolecular H-bond which outweigh the electron donating resonance effect of —OH.

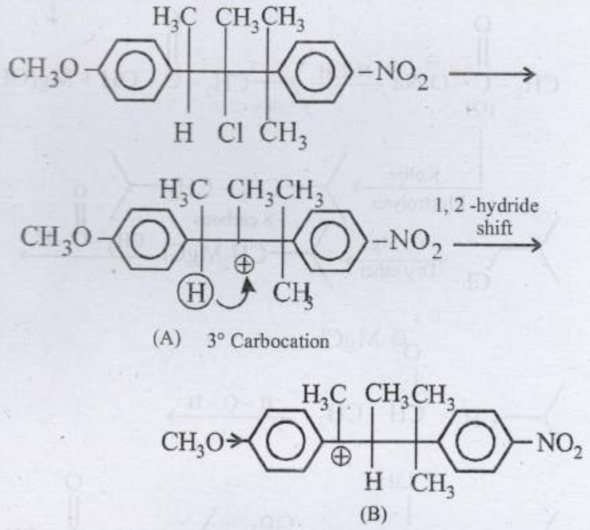


The overall order of acid-strength of given four acids is *ortho*-hydroxybenzoic acid ($pK_a = 2.98$). > Toluic acid ($pK_a = 4.37$) > *p*-hydroxybenzoic acid ($pK_a = 4.58$) > *p*-nitrophenol ($pK_a = 7.15$)

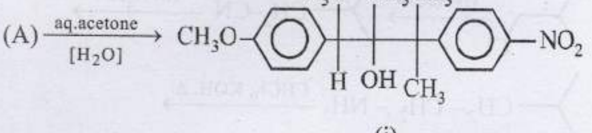
16. (a) Anti addition of Br_2 on *trans* alkene provides meso compound.



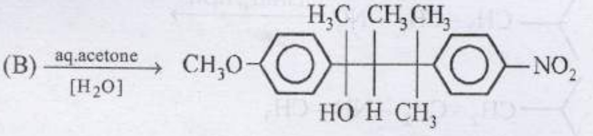
17. (a) This is an example of S_N1 reaction involving carbocation as intermediate.



This carbocation is especially stabilised through resonance in which $-\ddot{O}-CH_3$ group acts as a good electron donor.

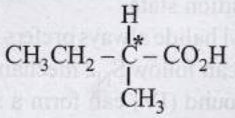


(i)



(ii)

18. **(d)** 2-Methylbutanoic acid contains one asymmetric centre



$$CH_3CH_2-\overset{H}{\underset{CH_3}{C^*}}-CO_2H$$

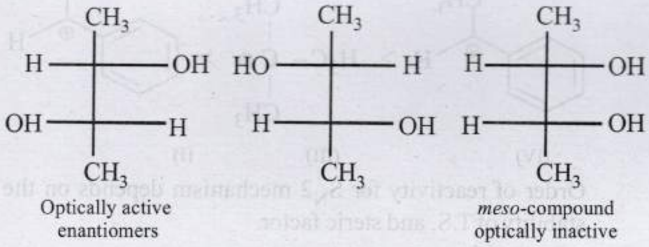
19. **(d)** S_N2 reaction at asymmetric carbon occur with inversion of configuration and a single steroisomer is formed because the reactant and product are not enantiomer. Therefore the sign of optical rotation may or may not change.

20. **(d)** Rate of reaction will be R – I > R – Br > R – Cl > R – F. because I^- is the best, while F^- is the poorest leaving group among halide ions.

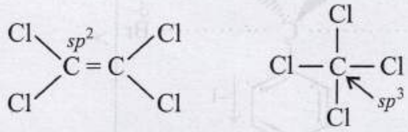
21. **(c)** CH_3^- is the best nucleophile because carbon is least electronegative among the given options. The order is

$$H_3\bar{C} > \bar{N}H_2 > \bar{O}H > F^-$$

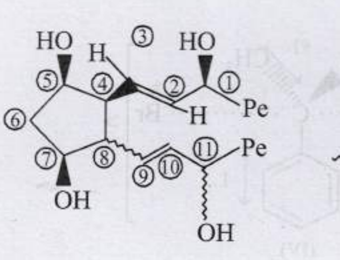
22. **(c)** The stereoisomers of butane -2,3-diol are



23. **(a)** The bond angle in sp^3, sp^2 and sp hybridisad carbon atoms is respectively 109.28', 120° and 180°.



24. **(7)** The given compound **X** is :



◄ Position in space and geometry (*cis-trans* configuration) is fixed.

~~~~ Position in space and geometry is not fixed.

Pe : *n*-pentane

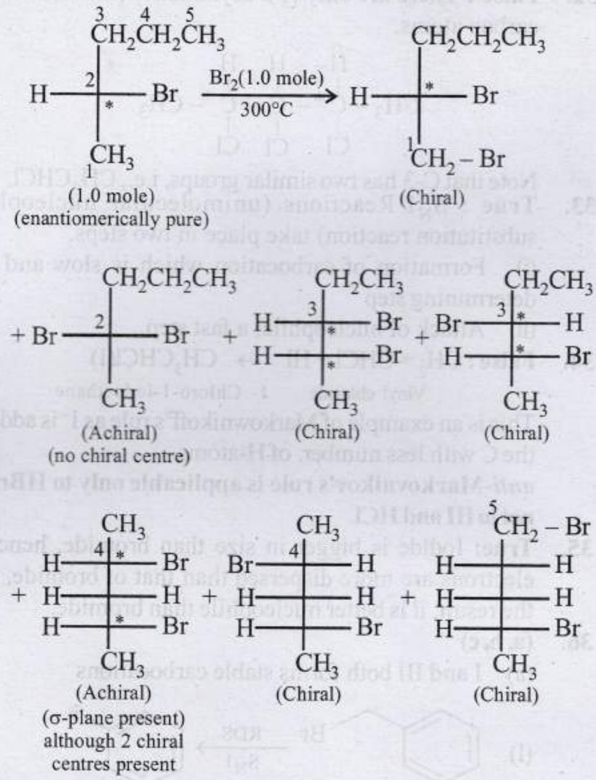
Trick : If the bottom double bond C⑨ = C⑩ is in *trans* position then there can be distinct possibilities with the C⑧ – C⑨ and C⑪ – OH. Similarly, there will be additional 4 distinct possibilities when the double bond C⑨ = C⑩ is in *cis* configuration. Now, out of these 8 distinct possibilities, only one configuration has a plane of symmetry. This makes it an optically inactive compound. We can also solve this problem by considering the two chiral centers at C⑧ and C⑪.

Number of stereoisomers : : = $2^2 = 4$

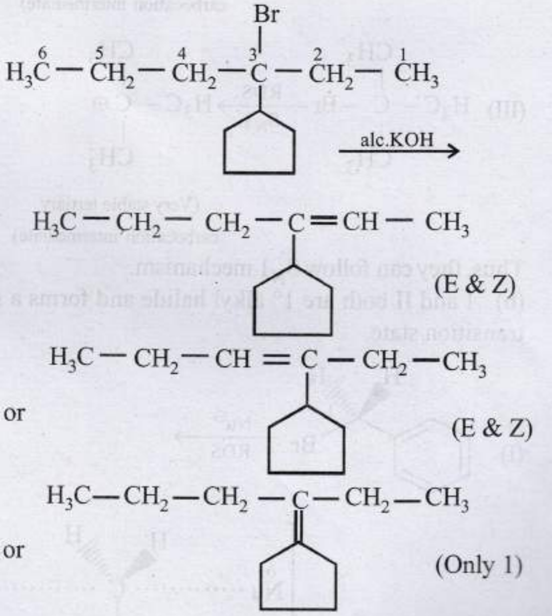
Now, each of these 4 stereoisomers can be in *cis* or *trans* configuration about C⑨ = C⑩ bond. This makes the total number of stereoisomers = 4 × 2 = 8

Total number of optically active stereoisomers = 8 – 1 = 7

25. **(5)**



26. **(5)** Total no. of alkenes will be = 5



27. $(CH_3)_2Cu + CH_2 = CHCl \rightarrow \underset{\text{Propene}}{CH_3CH = CH_2}$

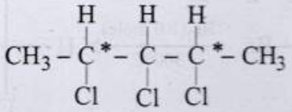
28. **Thioalcohol**
~~~~

29. **non-superimposable, enantiomers;**

30. **Grignard (RMgX)**

31. **Chlorine;** because rate of formation of $^{\bullet}CH_3$ (one of the propagating steps) is high when $X^{\bullet}$ is Cl.
$CH_4 + X^{\bullet} \longrightarrow {}^{\bullet}CH_3 + H-X$

32. **False :** There are only two asymmetric (marked with *) carbon atoms.



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

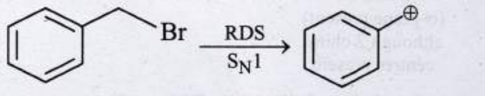
Note that C-3 has two similar groups, i.e., CH_3CHCl^-

33. **True :** S_N1 Reactions (unimolecular nucleophilic substitution reaction) take place in two steps.
(i) Formation of carbocation which is slow and rate determining step
(ii) Attack of nucleophile, a fast step.

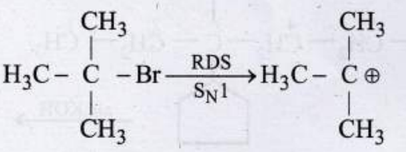
34. **False :** $\underset{\text{Vinyl chloride}}{CH_2=CHCl} + HI \rightarrow \underset{\text{1- Chloro-1-iodoethane}}{CH_3CHCl(I)}$
This is an example of Markownikoff's rule as I^- is added at the C with less number. of H-atoms.
***anti*-Markovnikov's rule is applicable only to HBr, but not to HI and HCl.**

35. **True:** Iodide is bigger in size than bromide, hence its electrons are more dispersed than that of bromide, with the result, it is better nucleophile than bromide.

36. **(a, b, c)**
(a) I and III both forms stable carbocations

(I) 

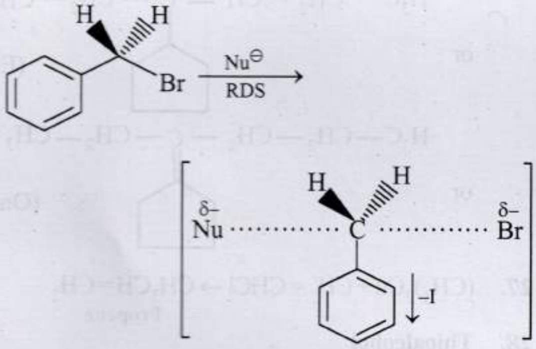
(Resonance stabilised very stable carbocation intermediate)

(III) 

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[S_N1]{RDS} H_3C-\underset{CH_3}{\overset{CH_3}{C}}\oplus$$

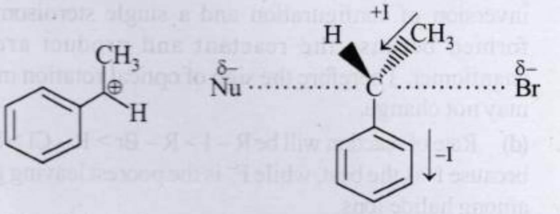
(Very stable tertiary carbocation intermediate)

Thus, they can follow S_N1 mechanism.
(b) I and II both are 1° alkyl halide and forms a stable transition state.

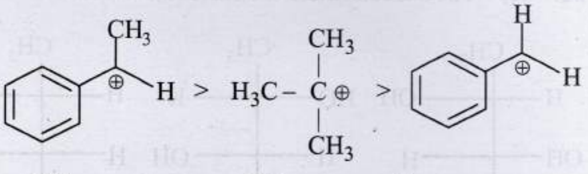
(I) 

transition state

Due to an electron withdrawing group, it forms a very stable transition state.
(II) 1° alkyl halide always prefers S_N2 mechanism. Thus, they can follow S_N2 mechanism.
(c) Compound (IV) can form a stable carbocation and also a stable transition state as :

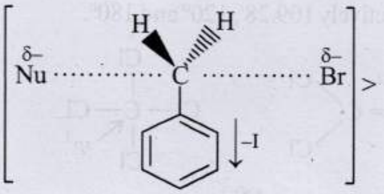


(d) Order of reactivity for S_N1 reaction depends on the stability of intermediate carbocation formed in the rate determining step:
Stability order of carbocations :

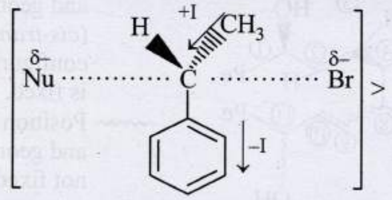


(IV) (III) (I)

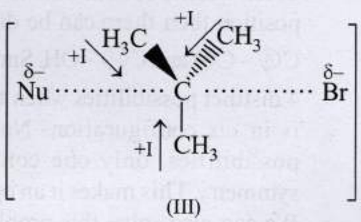
Order of reactivity for S_N2 mechanism depends on the stability of T.S. and steric factor.
Stability order of transition states :



(I)



(IV)

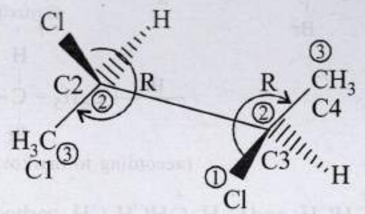


(III)

Hence, option (d) is wrong.

37. **(a, d)**

(a)

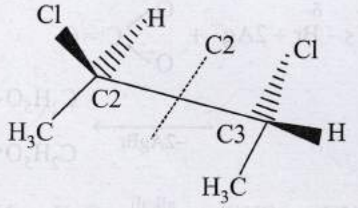


In both C2 and C3 carbons, the lowest priority group/atom (*i.e.* H) is in wedge position. Thus, we can directly assign the R–S configuration to the given compound.

The R–S configuration of the compound is (2R, 3R). Hence, the compound is opticaly active.

Option (b) and (c) can not be correct as the molecule is optically active.

(d) If we make a conformer of the given compound by taking the C2 – C3 axis and rotating the groups on C3 carbon by 180°, then the compound can be represented as:



A C_n axis of symmetry is an axis about which the molecule can be rotated by $360°/n$ to produce a molecule indistinguishable from the original molecule. If we rotate the molecule by 180° along the axis which is perpendicular to C2 – C3 bond, then we will get the exactly same molecule. Hence, this molecule has C2 axis of symmetry.

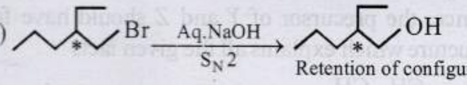
Any optically active compound may or may not possess axis of symmetry but it cannot possess alternate axis of symmetry.

38. **(c, d)**

An asymmetric carbon atom is one which is attached with 4 different groups. Hence, (c) & (d) are correct.

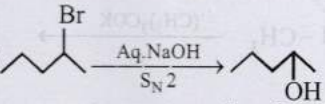
39. **(b)** $P \rightarrow 2, Q \rightarrow 1, R \rightarrow 3, S \rightarrow 5$

(P)



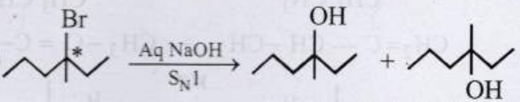
Retention of configuration

(Q)



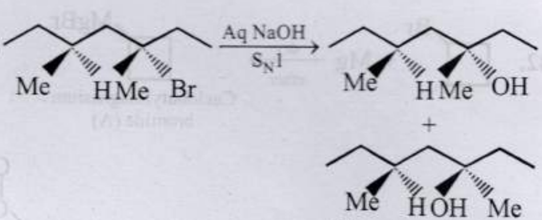
Inversion of configuration

(R)



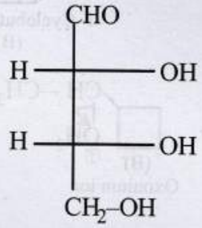
Mixture of enantiomers

(S)



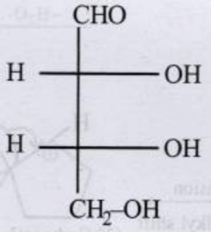
Diastereomeric mixture

40. **(c)**



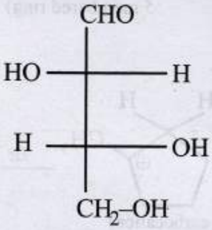
D-Erythrose

Compound P



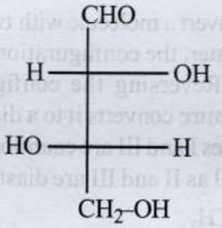
identical

Compound Q



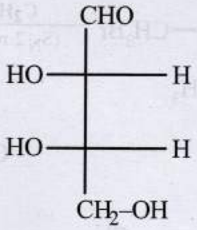
diastereomer

Compound R



diastereomer

Compound S

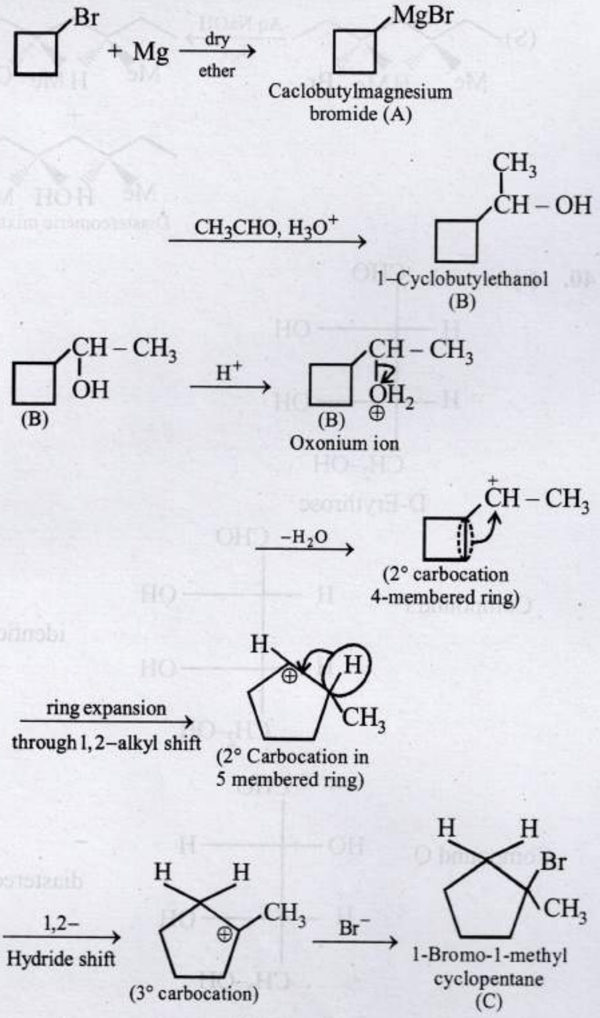


enantiomer

P-2, Q-1, R-1, S-3

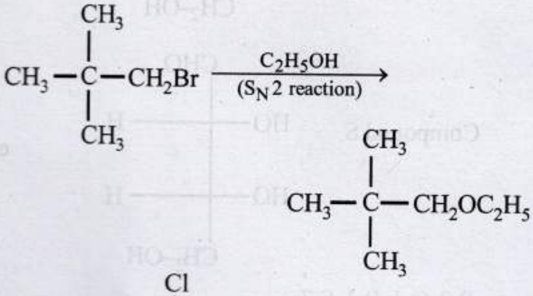
41. **(c)** Statement-1 is correct. Statement-2 is incorrect because compound can be chiral even in the absence of chiral atoms.

42.



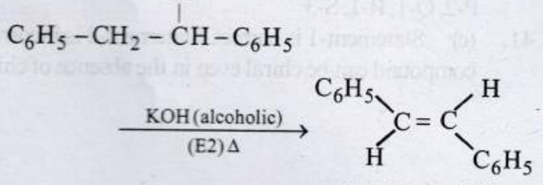
43. In order to convert a molecule with two stereogenic centres to its enantiomer, the configuration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a distereomeric structure. Thus, structures I and III are enantiomers; while structures I and II as well as II and III are diastereomers.

44. (*i*)



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

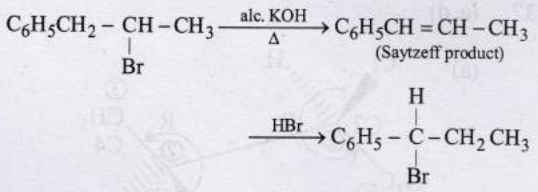
(*ii*)



$$C_6H_5-CH_2-\overset{Cl}{CH}-C_6H_5 \xrightarrow[(E2)\,\Delta]{\text{KOH (alcoholic)}}$$

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

(*iii*)



$$C_6H_5CH_2-\underset{Br}{CH}-CH_3 \xrightarrow[\Delta]{\text{alc. KOH}} C_6H_5CH=CH-CH_3$$

(Saytzeff product)

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

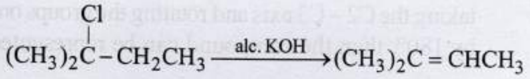
(according to markovnikov rule)

[$C_6H_5CH_2\overset{+}{C}HCH_3$ 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 $C_6H_5CHBr.CH_2CH_3$ as the final product.]

(*iv*) $CH_3CH_2CHCl_2 \xrightarrow[\text{alkali}]{\text{boil}} CH_3CH_2CH(OH)_2$

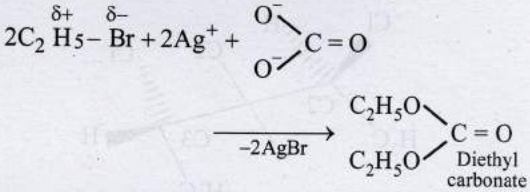
$$\xrightarrow{(-H_2O)} CH_3CH_2CHO$$

(*v*)



$$(CH_3)_2\overset{Cl}{C}-CH_2CH_3 \xrightarrow{\text{alc. KOH}} (CH_3)_2C=CHCH_3$$

(*vi*)



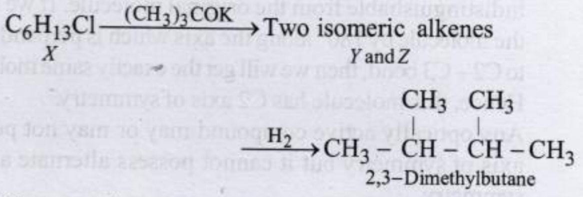
$$2C_2\overset{\delta+}{H_5}-\overset{\delta-}{Br}+2Ag^+ + \;{}^-O(O^-)C=O \xrightarrow{-2AgBr} (C_2H_5O)_2C=O$$

Diethyl carbonate

(*vii*) $C_6H_5NH_2+CHCl_3 \xrightarrow[\text{KOH}]{\text{alkali}} C_6H_5-N\overset{\rightarrow}{=}C$

Phenyl isocyanide

45. Summary of the given facts

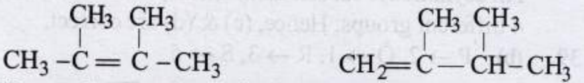


$$\underset{X}{C_6H_{13}Cl} \xrightarrow{(CH_3)_3COK} \underset{Y\text{ and }Z}{\text{Two isomeric alkenes}}$$

$$\xrightarrow{H_2} CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$$

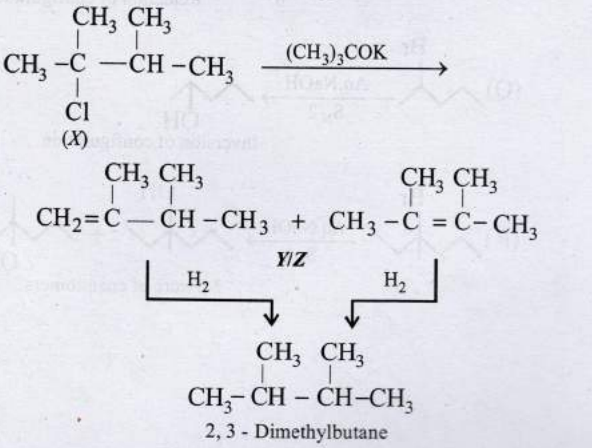
2,3–Dimethylbutane

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



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

Hence, the precursor of *Y* and *Z* should have following structure which explains all the given facts



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

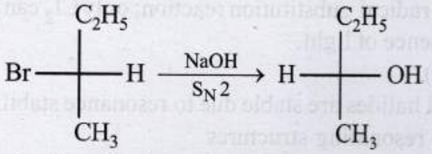
(*X*)

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

$$CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-CH_3$$

2, 3 - Dimethylbutane

46. S_N2 reaction leads to inversion in configuration.



47. A weaker base is a better leaving group.
Thus, rate of reaction will be $R-I > R-Br > R-Cl > R-F$. because I^- is the best, while F^- is the poorest leaving groups among halide ions.

48. $\%$ 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	2.02	1
H	4.04 4.04	2	
Cl	71.72	2.02	1

∴ Empirical formula of (*X*) is $\mathbf{CH_2Cl}$

Since, *X* has two isomers *Y* and *Z*; both react with KOH(aq).

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

$Z \xrightarrow{\text{KOH(aq.)}} CH_3CHO$ *i.e.* *Z* should have 2Cl atoms on one C atom

Thus *Z* should be $\mathbf{CH_3CHCl_2}$ (1, 1-dichlorethane) and *Y* should be $\mathbf{CH_2ClCH_2Cl}$ (1, 2-dichloroethane)

Reactions :

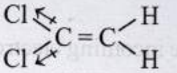
$$\underset{(Z)}{CH_3CHCl_2} \xrightarrow{\text{KOH(aq.)}} CH_3CH(OH)_2 \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3CHO}$$

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

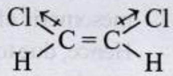
49. Resonance decreases the dipole moment of vinyl chloride ($CH_2 = CHCl$).

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

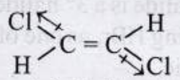
50. Dichloroethene exists in three isomeric forms.



1,1–Dichloroethene



cis–1, 2–Dichloroethene



trans–1, 2–Dichloroethene

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

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

(*ii*) $Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[\text{sun light}]{Cl_2} CH_3Cl$

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

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

(ii) $CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$

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

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

(b) Carbylamine test.

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

C_2H_5OH + aq KOH + aniline $\longrightarrow$ No reaction

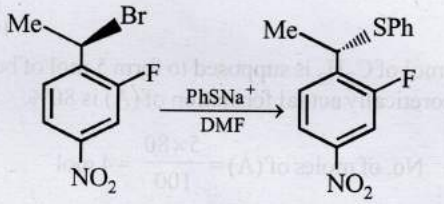
Topic-2: Preparation and Properties of Haloarenes

1. **(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 $HCONMe_2$ is a highly polar aprotic solvent. These reagents favour S_N2 reactions at 2° benzylic carbon.

In a S_N2 reaction, the major product formed is inversion product.



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

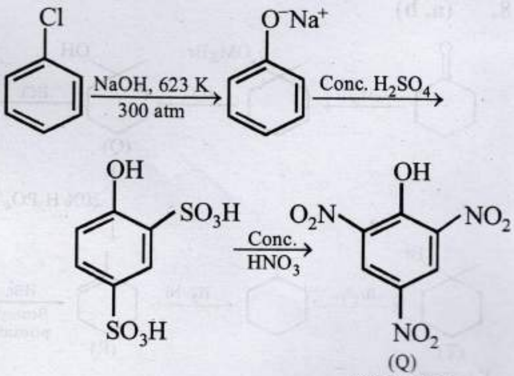
$C_6H_5MgBr + Me_3COH \longrightarrow C_6H_6 + Me_3COMgBr$

3. **(d)** The given reaction is an example of electrophilic substitution. Further, CH_3 group in toluene is *o*, *p*-directing

4. **(d)**

$C_6H_5NH_2 \xrightarrow[\text{HCl}]{\text{HONO}} C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{\text{CuCl}} C_6H_5Cl$

5. **(1.31)**



(Q)
(Picric acid)

Picric acid = $C_6H_3N_3O_7$

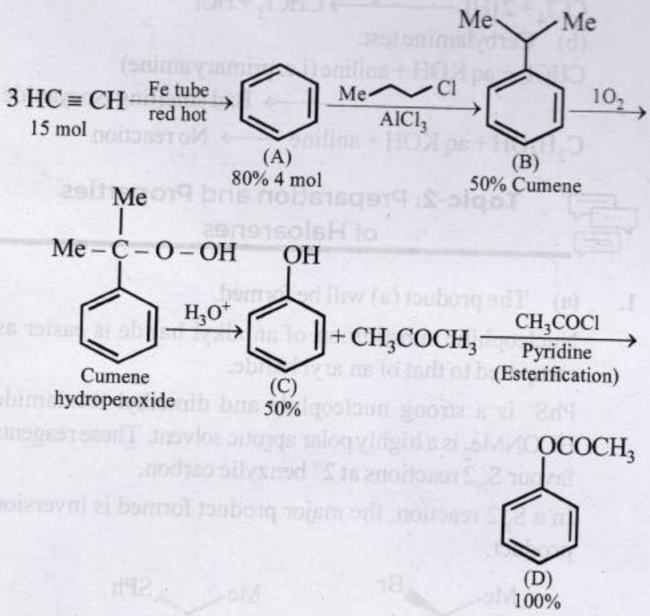
$\therefore$ M.W. of picric acid

$= 6 \times 12 + 3 \times 1 + 3 \times 14 + 7 \times 16 = 229$

1 mol of picric acid contains 3-H atoms

$\therefore$ The wt.(%) of 'H' in (Q) $= \dfrac{3 \times 100}{229} = 1.31$

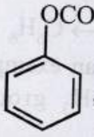
6. **(136)**



15 mol of C_2H_2 is supposed to form 5 mol of benzene (A) theoretically actual formation of (A) is 80%.

$\therefore$ No. of moles of (A) $= \dfrac{5 \times 80}{100} = 4$ mol

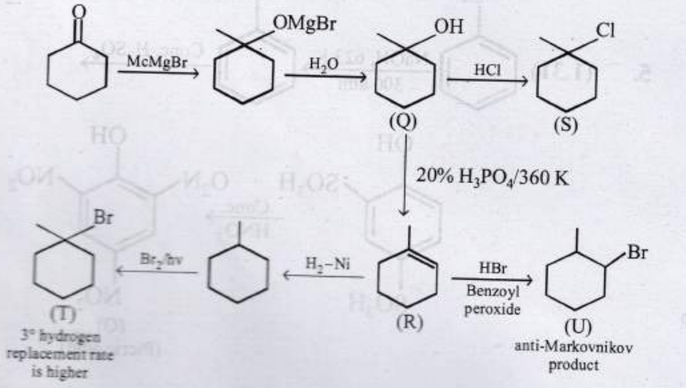
4 moles of (A) produces 50% of (B) = 2 moles of (B).
Further, 2 moles of (B) produces 50% of (C) = 1 mol of (C)
$\therefore$ 1 mole of (C) produces 100% of (D) = 1 mol of (D).

M.W. of (D),  , acetophenone = 136

$\therefore$ The amount of the product D formed is 136 g.

7. **False :** *m*-Chlorobromobenzene and *m*-bromochlorobenzene is one and the identical compound.

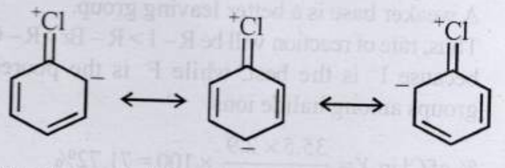
8. **(a, b)**



9. **(c)** Chlorination of toluene to form benzyl chloride is a free radical substitution reaction; only Cl_2 can give $\dot{C}l$ in presence of light.

10. **(b, e)**

Aryl halides are stable due to resonance stabilization. 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.

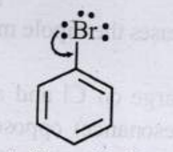
11. **(A) - q; (B) - p, s; (C) - r, s; (D) - q**

E1 mechanism is encountered only with tertiary or secondary substrates and in presence of either a weak base or a base in low concentration. So, primary substrates will follow E2 mechanism, *i.e.* (A) → E2 and (D) → E2.

Further, E1 mechanism (similar to S_N1) proceeds by first order kinetics and is determined by the slower (first) step of the formation of carbanion. Hence, (B)→E1 and first order reaction.

Reaction of $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ in presence of C_2H_5OD gives $C_6H_5CD{=}CH_2$. This reaction follows $E1_CB$ (Elimination unimolecular conjugate base) mechanism.

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



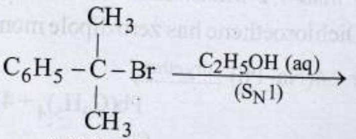
(–I effect, + M effect)

The inductive effect (–I) of bromo group is more than the mesomeric effect (+M).

This is the reason why bromo group deactivates the ring. But the directing influence with always governed by the mesomeric effect.

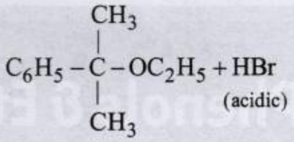
Hence, due to +M effect of –Br, the incoming electrophile attacks at *ortho* and *para* positions.

13. (i) The former halide is a 3° halide, hence it undergoes S_N1 reaction forming HBr, as one of the products, which make solution acidic.

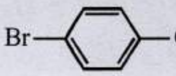


$$C_6H_5-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \xrightarrow[(S_N1)]{C_2H_5OH\,(aq)}$$

A 3° bromide

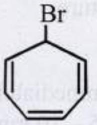


$$C_6H_5-\underset{CH_3}{\overset{CH_3}{C}}-OC_2H_5+HBr \quad \text{(acidic)}$$



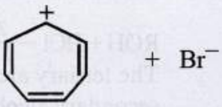
Br–C₆H₄–CH(CH₃)₂ is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence, the solution will remain neutral.

(ii) 7-Bromo-1,3,5-cycloheptatriene is aromatic whereas 5-Bromo-1,3-cycloheptadiene is non aromatic.



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

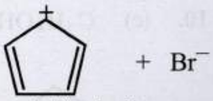
Its corresponding cation is



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

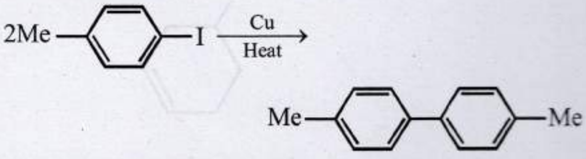
5-Bromo-1,3-cyclopentadiene

Its corresponding cation is



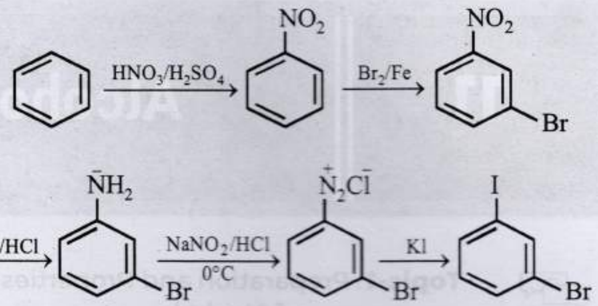
Cyclopentadienyl cation (It has 4 π electrons, hence not aromatic, thus **not easily formed**)

14.

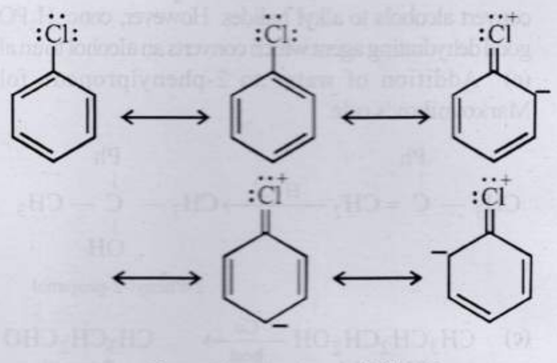


This is ullmann reaction

15.



16. The low reactivity of halogen atom in aryl and vinyl halides towards nucleophiles is due to resonance.



Resonating structures of chlorobenzene

Due to resonance, carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.

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

$$\xrightarrow{Cl_2} C_6H_5CHCl_2 \xrightarrow{Cl_2} \underset{\text{Benzotrichloride}}{C_6H_5CCl_3}$$

[This follows free radical mechanism.]