CHAPTER 18

Haloalkanes and Haloarenes

Section-A JEE Advanced/ IIT-JEE

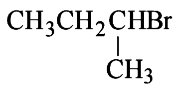
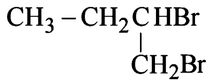
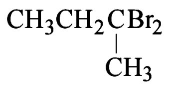
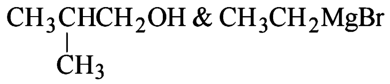
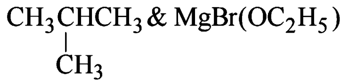
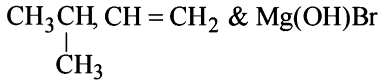
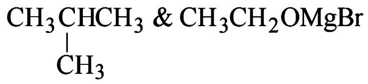
A Fill in the Blanks

1. The halogen which is most reactive in the halogenation of alkanes under sunlight is .... (chlorine, bromine, iodine) *(1981 - 1 Mark)*
2. The compound prepared by the action of magnesium on dry ethyl bromide in ether is known as .... reagent. *(1982 - 1 Mark)*
3. The interaction of elemental sulphur with Grignard reagent gives .... *(1991 - 1 Mark)*
4. Vinyl chloride on reaction with dimethyl copper gives .... *(1997 - 1 Mark)*

B True / False

1. *m*-Chlorobromobenzene is an isomer of *m*-bromochlorobenzene. *(1985 - ½ Mark)*
2. 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)*

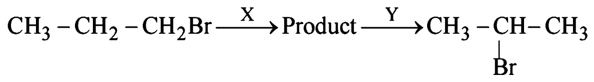
C MCQs with One Correct Answer

1. 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
2. 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
3. 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) $C_2H_6 + Cl_2 \xrightarrow{\text{uv light}}$
4. n-Propyl bromide on treatment with ethanolic potassium hydroxide produces *(1987 - 1 Mark)*
   (a) Propane (b) Propene
   (c) Propyne (d) Propanol
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 *(1988 - 1 Mark)*
   (a) 1 and 2 (b) 2 and 4
   (c) 4 and 2 (d) 2 and 1
6. 1-Chlorobutane on reaction with alcoholic potash gives *(1991 - 1 Mark)*
   (a) 1-butene (b) 1-butanol
   (c) 2-butene (d) 2-butanol
7. The chief reaction product of reaction between *n*-butane and bromine at 130°C is : *(1995S)*
   (a) $CH_3CH_2CH_2CH_2Br$
   (b) 
   $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HBr$
   (c) 
   $CH_3-CH_2\underset{\displaystyle CH_2Br}{\underset{|}{C}}HBr$
   (d) 
   $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}Br_2$
8. Isobutyl magnesium bromide with dry ether and ethyl alcohol gives : *(1995S)*
   (a) 
   $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2OH \;\&\; CH_3CH_2MgBr$
   (b) 
   $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \;\&\; MgBr(OC_2H_5)$
   (c) 
   $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}H,\, CH=CH_2 \;\&\; Mg(OH)Br$
   (d) 
   $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \;\&\; CH_3CH_2OMgBr$
9. $(CH_3)_3CMgCl$ on reaction with D_2O produces : *(1997 - 1 Mark)*
   (a) $(CH_3)_3CD$ (b) $(CH_3)_3OD$
   (c) $(CD_3)_3CD$ (d) $(CD_3)_3OD$.

10. 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)*

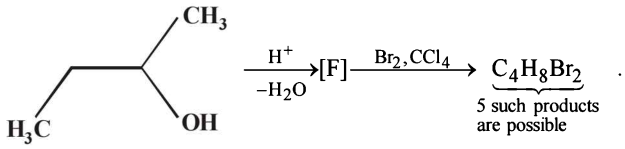
(a) carbanion (b) carbene
(c) free-radical (d) carbocation

11. Identify the set of reagent / reaction conditions 'X' and 'Y' in the following set of transformations *(2002S)*



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

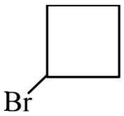
(a) X = dilute aqueous NaOH, 20°C; Y = HBr/acetic acid, 20°C
(b) X = concentrated alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dilute aqueous NaOH, 20°C ; Y = $Br_2/CHCl_3$, 0°C
(d) X = concentrated alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

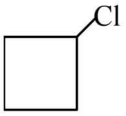
12. 

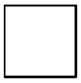
How many structures for F are possible? *(2003S)*

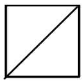
(a) 2 (b) 5
(c) 6 (d) 3

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

(a) 

(b) 

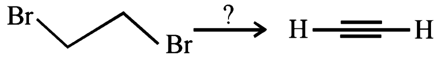
(c) 

(d) 

14. 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

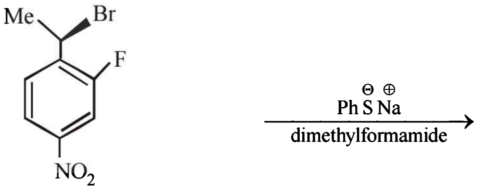
15. The reagent(s) for the following conversion,

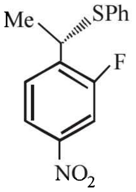


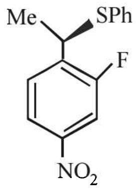
is/are *(2007)*

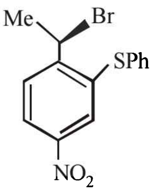
(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn/CH_3OH

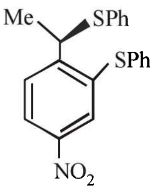
16. The major product of the following reaction is – *(2008)*



(a) 

(b) 

(c) 

(d) 

D MCQs with One or More Than One Correct

1. 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.

2. 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

E Subjective Problems

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.

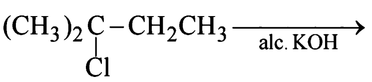
(i) Hexachlorethane, C_2Cl_6, from calcium carbide.
(ii) Chloroform from carbon disulphide.

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

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

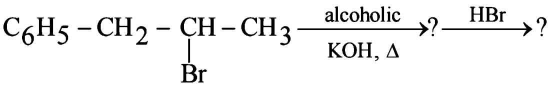
(*i*) chloroform reacts with aniline in the presence of excess alkali *(1981 - ½ Mark)*

(*ii*) bromoethane reacts with one-half of the molar quantity of silver carbonate. *(1981 - ½ Mark)*

(*iii*)  *(1992 - 1 Mark)*

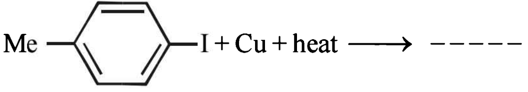
$$(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{C}}-CH_2CH_3 \xrightarrow[\text{alc. KOH}]{}$$

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

(*v*) 

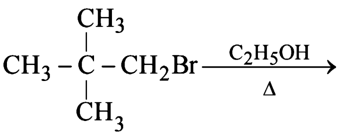
$$C_6H_5-CH_2-\underset{\displaystyle Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{KOH, }\Delta]{\text{alcoholic}} ? \xrightarrow{\text{HBr}} ?$$

(1993 - 1 Mark)

(*vi*) 

(1997 - 1 Mark)

(*vii*) $C_6H_5CH_2CHClC_6H_5 \xrightarrow[\text{heat}]{\text{alcoholic KOH}}$ 2 Products *(1998 - 2 Marks)*

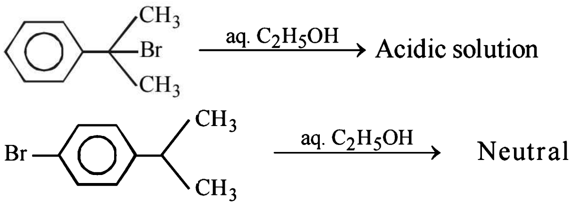
(*viii*)  *(2000 - 1 Mark)*

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

3. 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 presence of Ag^+ ion. Explain. ***(2004 - 2 Marks)***

(*ii*)



solution. Explain. ***(2005 - 1 Mark)***

4. 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)***

5. Write the structure of all the possible isomers of dichloroethene. Which of them will have zero dipole moment? ***(1985 - 2 Marks)***

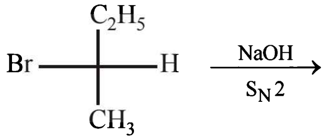
6. What happens when excess chlorine is passed through boiling toluene in the presence of sunlight? ***(1987 - 1 Mark)***

7. What effect should the following resonance of vinyl chloride have on its dipole moment? ***(1987 - 1 Mark)***

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

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. ***(1989 - 4 Marks)***

9. Draw the stereochemical structures of the products in the following reaction : ***(1994 - 4 Marks)***



10. 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)***

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

12. 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)***

H Assertion & Reason Type Questions

1. 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)***

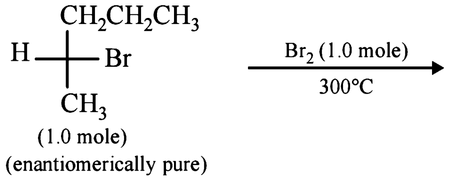
Statement-2 : In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

(a) Statement-1 is True, Statement-2 is True; Statement-2 is a 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

I Integer Value Correct Type

1. The total number of alkenes possible by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is ***(2011)***

2. In the following monobromination reaction, the number of possible chiral products is ***(JEE Adv. 2016)***



Section-B JEE Main / AIEEE

1. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment? **[2003]**

(a) A and $C_6H_5CH_2I$
(b) B and C_6H_5I
(c) Addition of HNO_3 was unnecessary
(d) A was C_6H_5I

2. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is **[2004]**

(a) freon (b) DDT
(c) gammexene (d) hexachloroethane

3. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of **[2005]**

(a) steric hindrance (b) inductive effect
(c) instability (d) insolubility

4. Alkyl halides react with dialkyl copper reagents to give **[2005]**

(a) alkenyl halides (b) alkanes
(c) alkyl copper halides (d) alkenes

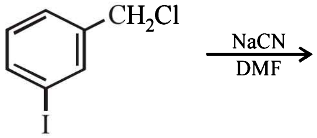
5. Elimination of bromine from 2-bromobutane results in the formation of– **[2005]**
(a) Predominantly 2-butyne
(b) Predominantly 1-butene
(c) Predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

6. Phenyl magnesium bromide reacts with methanol to give **[2006]**
(a) a mixture of toluene and Mg(OH)Br
(b) a mixture of phenol and Mg(Me)Br
(c) a mixture of anisole and Mg(OH)Br
(d) a mixture of benzene and Mg(OMe)Br

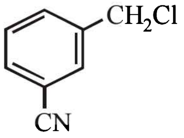
7. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory **[2006]**
(a) by direct fluorination of benzene with F_2 gas
(b) by reacting bromobenzene with NaF solution
(c) by heating phenol with HF and KF
(d) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

8. Reaction of *trans* 2-phenyl-1-bromocyclopentane on reaction with alcoholic KOH produces **[2006]**
(a) 1-phenylcyclopentene (b) 3-phenylcyclopentene
(c) 4-phenylcyclopentene (d) 2-phenylcyclopentene

9. The structure of the major product formed in the following reaction **[2006]**



is

(a)


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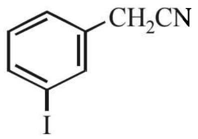

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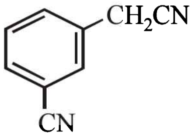

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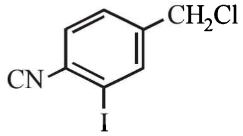
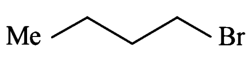


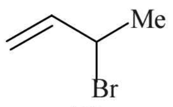
10. Which of the following is the correct order of decreasing S_N2 reactivity? **[2007]**
(a) $R_2CHX > R_3CX > RCH_2X$
(b) $RCHX > R_3CX > R_2CHX$
(c) $RCH_2X > R_2CHX > R_3CX$
(d) $R_3CX > R_2CHX > RCH_2X$.
(X is a halogen)

11. The organic chloro compound, which shows complete sterochemical inversion during a S_N2 reaction, is **[2008]**
(a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
(c) $(CH_3)_2CHCl$ (d) CH_3Cl

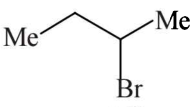
12. Consider the following bromides :



(A)



(B)



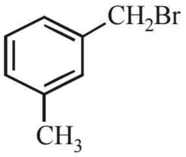
(C)

The correct order of S_N1 reactivity is **[2010]**
(a) B > C > A (b) B > A > C
(c) C > B > A (d) A > B > C

13. How many chiral compounds are possible on monochlorination of 2- methyl butane ? **[2012]**
(a) 8 (b) 2
(c) 4 (d) 6

14. What is DDT among the following ? **[2012]**
(a) Greenhouse gas
(b) A fertilizer
(c) Biodegradable pollutant
(d) Non-biodegradable pollutant

15. Compound (A), C_8H_9Br, gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). **[JEE M 2013]**

(a)


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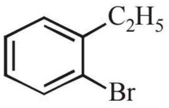
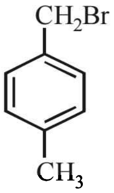


(c)


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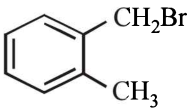


16. In S_N2 reactions, the correct order of reactivity for the following compounds: **[JEE M 2014]**

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

(a) $CH_3Cl > (CH_3)_2CHCl > CH_3CH_2Cl > (CH_3)_3CCl$
(b) $CH_3Cl > CH_3CH_2Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(c) $CH_3CH_2Cl > CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl$
(d) $(CH_3)_2CHCl > CH_3CH_2Cl > CH_3Cl > (CH_3)_3CCl$

17. The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: **[JEE M 2014[**
(a) Acetylene (b) Ethene
(c) 2 - Butyne (d) 2 - Butene

18. The synthesis of alkyl fluorides is best accomplished by : **[JEE M 2015]**
(a) Finkelstein reaction (b) Swarts reaction
(c) Free radical fluorination (d) Sandmeyer's reaction

18

Haloalkanes and Haloarenes

Section-A : JEE Advanced/ IIT-JEE

A **1.** chlorine **2.** Grignard **3.** Thioalcohol **4.** polyvinyl chloride

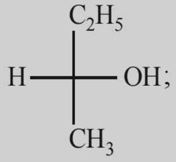
B **1.** F **2.** F

C **1.** (d) **2.** (d) **3.** (a) **4.** **(b)** **5.** (b) **6.** (a) **7.** (b)
8. (b) **9.** (a) **10.** (d) **11.** (b) **12.** (d) **13.** (d) **14.** (a)
15. (b) **16.** (a)

D **1.** (b, e) **2.** (c)

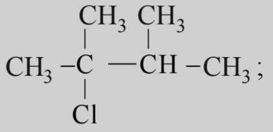
E **8.** CH_2Cl; **Y :** CH_2ClCH_2Cl; **Z :** CH_3CHCl_2

9.



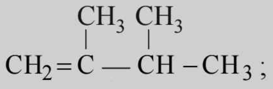
$H-\overset{C_2H_5}{\underset{CH_3}{C}}-OH$;

10.



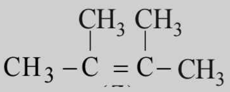
$CH_3-\overset{CH_3}{\underset{Cl}{C}}-\overset{CH_3}{CH}-CH_3$;

[X]



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

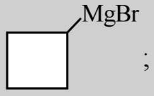
[Y]



$CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_3$

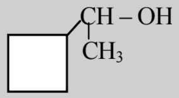
[Z]

12.



[A]

;



[B]

H **1.** (c)

I **1.** **5** **2.** **5**

Section-B : JEE Main/ AIEEE

1. (d) **2.** (b) **3.** (b) **4.** (b) **5.** (c) **6.** (d) **7.** (d)
8. (a) **9.** (b) **10.** (c) **11.** (d) **12.** (a) **13.** (c) **14.** (d)
15. (d) **16.** (b) **17.** (c) **18.** (b)

Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

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

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

2. **Grignard (RMgX)**

3. **Thioalcohol**

4. **polyvinyl chloride.**

B. True/False

1. **False :** *m*-Chlorobromobenzene and *m*-bromochlorobenzene is one and the same compound.

2. **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.

NOTE : *anti*-Markonikov's rule is applicable only to HBr, but not to HI and HCl.

C. MCQs with One Correct Answer

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

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

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

NOTE : For isomeric alkanes the one having largest straight chain has highest b.p. because of large surface area.

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

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

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

7. (b) **TIPS/Formulae :**

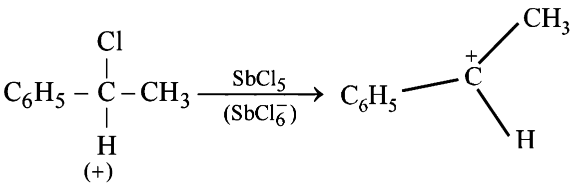
The reaction proceeds via free radical mechanism.

As 2° free radical is more stable than 1°, so $CH_3CH_2CH(Br)CH_3$ would be formed.

8. (b) $(CH_3)_2CHCH_2MgBr\xrightarrow{C_2H_5OH}(CH_3)_2CHCH_3$

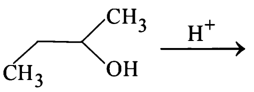
9. (a) $(CH_3)_3C-MgCl+D_2O\longrightarrow(CH_3)_3C-D+Mg(OD)Cl$

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



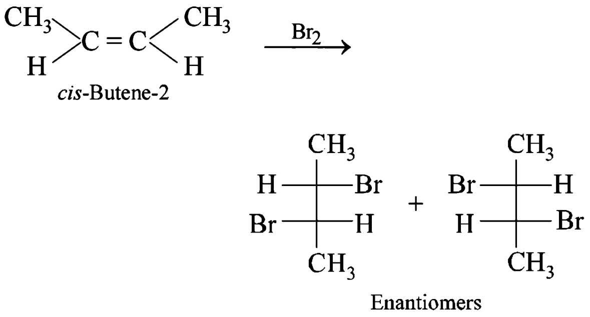
$$\xrightarrow{Cl^-}(+)-+(-)-$$

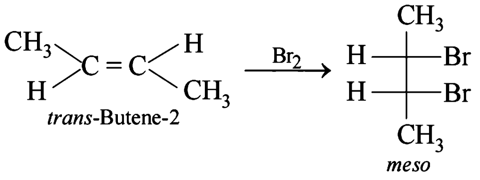
11. (b) Dehydrobromination by strong base (alc. NaOH) followed by Markownikoff addition of HBr.

12. (d) 

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

$$\underset{\text{Butene-1}}{CH_3CH_2CH=CH_2}\xrightarrow{Br_2}\underset{(+)-\text{ and }(-)\text{ enantiomer}}{CH_3CH_2\underset{\underset{Br}{|}}{\overset{*}{C}}HCH_2Br}$$

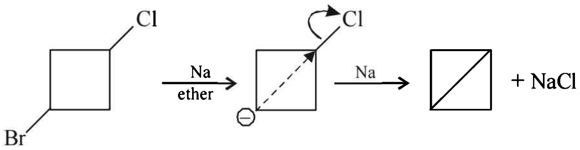




So F can have three possible structures

13. (d) **TIPS/Formulae :**

It is an example of intramolecular Wurtz reaction.



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

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

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

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

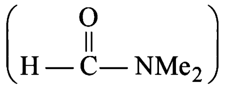
$$\xrightarrow{NaNH_2}CH\equiv CH$$

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

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

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

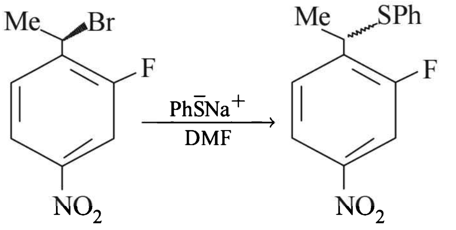
PhS^- is a strong nucleophile and dimethyl formamide



$\left(H-\overset{\overset{O}{\|}}{C}-NMe_2\right)$ is a highly polar aprotic solvent.

These reagent favour S_N2 reactions at 2° benzylic carbon.

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

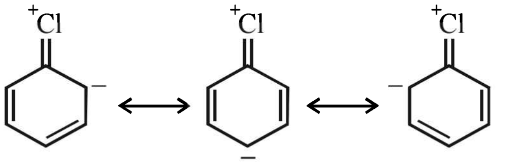


D. MCQs with One or More Than One Correct

1. **(b, e)** **TIPS/Formulae :**

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.

2. **(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.

E. Subjective Problems

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

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

(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.

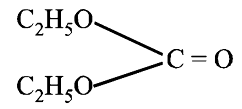
$CHCl_3$ + aq KOH + aniline (i.e. primary amine) $\longrightarrow$ bad smelling isocyanide

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

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

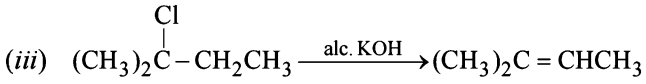
Phenyl isocyanide

(*ii*)



Diethyl carbonate

(*iii*)

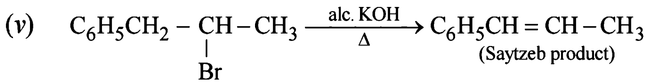


$$(CH_3)_2\overset{\overset{Cl}{|}}{C} - CH_2CH_3 \xrightarrow{alc.\,KOH} (CH_3)_2C = CHCH_3$$

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

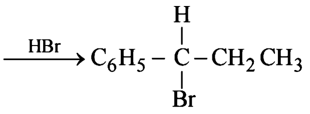
$$\xrightarrow[(-H_2O)]{} CH_3CH_2CHO$$

(*v*)



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

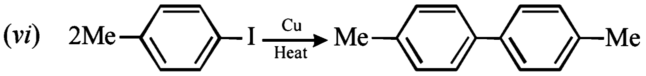
(Saytzeb product)



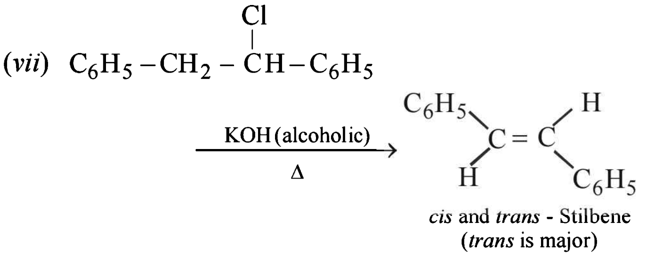
$$\xrightarrow{HBr} C_6H_5 - \overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}} - CH_2CH_3$$

[**NOTE :** $C_6H_5CH_2\overset{+}{C}HCH_3$ 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.]

(*vi*)



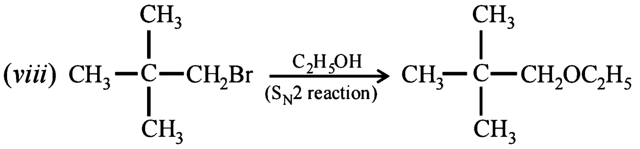
(*vii*)



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

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

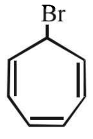
(*viii*)



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

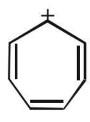
3. (i) **TIPS/Formulae :**

7-Bromo-1,3,5-cycloheptatriene is aromatic whereas 5-Bromo-1,3-Cycloheptadiene is non aromatic.



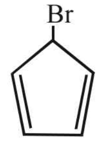
7-Bromo-1,3,5-cycloheptatriene (Triopylium bromide)

Its corresponding cation is



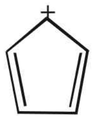
$+ Br^-$

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



5-Bromo-1,3-cyclopentadiene

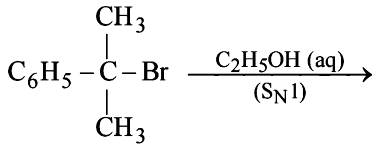
Its corresponding cation is



$+ Br^-$

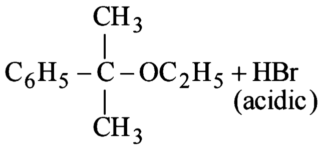
Cyclopentadienyl cation (It has 4 π electrons, hence not aromatic, thus not easily formed)

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

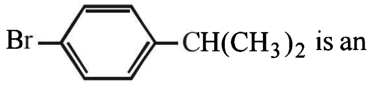


$$C_6H_5 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} - Br \xrightarrow[(S_N1)]{C_2H_5OH\,(aq)}$$

A 3° bromide



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

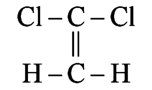


is an aryl halide so it does not undergo nucleophilic substitution reactions. Hence the solution will remain neutral.

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

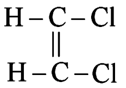
(*ii*) $Al_4C_3 \xrightarrow{H_2O} CH_4 \xrightarrow[\text{sun light}]{Cl_2} CH_3Cl$

5. Dichloroethene exists in three isomeric forms.



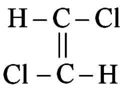
$$\begin{array}{c} Cl-C-Cl \\ \| \\ H-C-H \end{array}$$

1, 1–dichloroethene



$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$

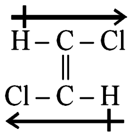
(*cis*)–1, 2–dichloroethene



$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

(*trans*)–1, 2–dichloroethene

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



$$\begin{array}{c} \longmapsto \\ H-C-Cl \\ \| \\ Cl-C-H \\ \longleftarrow\!\!\!+ \end{array}$$

[**NOTE :** Dipole moment is a vector quantity]

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

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

[**NOTE :** This follows free radical mechanism.]

7. **TIPS/Formulae :**

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.

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

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

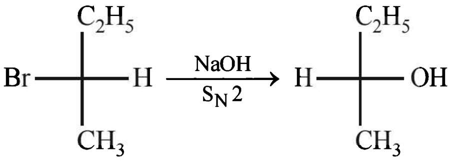
Thus Z should be $\mathbf{CH_3CHCl_2}$ (1, 1-dichlorethane) and Y should $\mathbf{CH_2ClCH_2Cl}$ (1, 2-dichloroethane)

Reactions :

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

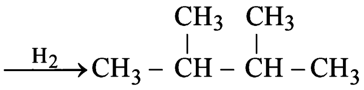
$$\underset{(Y)}{CH_2ClCH_2Cl} \xrightarrow{\text{KOH(aq.)}} \underset{\text{(ethane-1, 2-diol)}}{CH_2OHCH_2OH}$$

9. S_N2 reaction leads to inversion in configuration.



10. Summary of the given facts

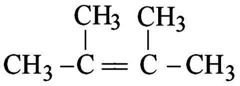
$$\underset{X}{C_6H_{13}Cl} \xrightarrow{(CH_3)_3COK} \underset{\text{Y and Z}}{\text{Two isomeric alkenes}}$$



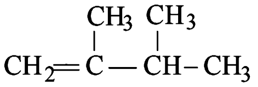
$$\xrightarrow{H_2} CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2,3–Dimethylbutane

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

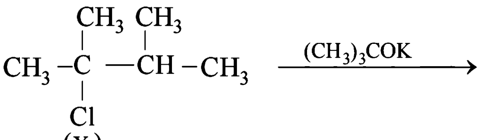


$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3$$



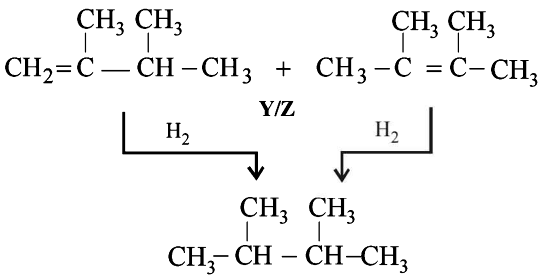
$$CH_2=\overset{\overset{CH_3}{|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Hence the precursor of Y & Z should have following structure which explains all the given facts



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

(X)



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

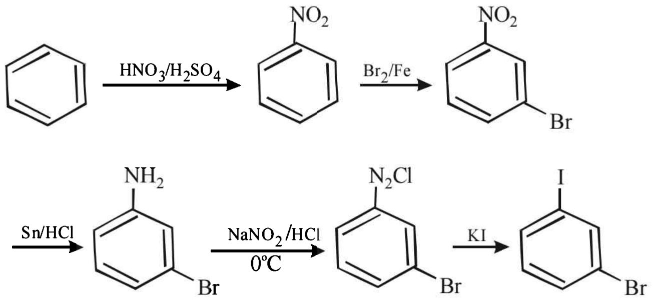
Y/Z

$$\downarrow H_2 \qquad H_2 \downarrow$$

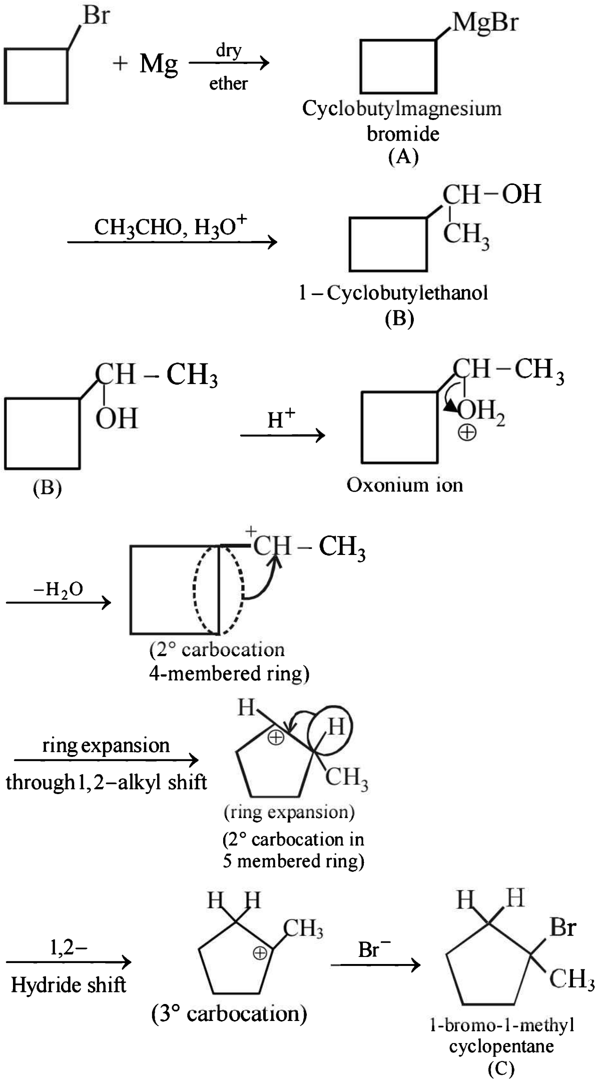
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2, 3 - Dimethylbutane

11.

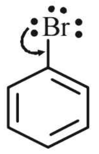


12.



H. Assertion & Reason Type Questions

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



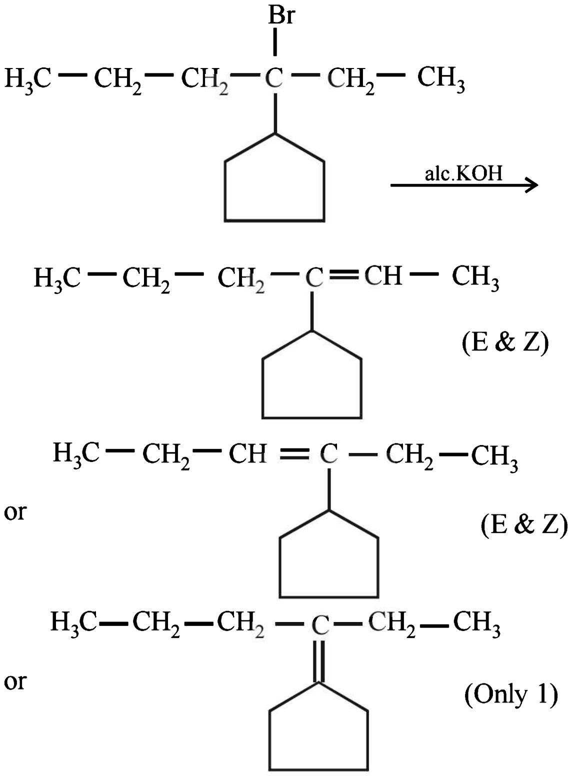
(–I effect, + M effect)

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.

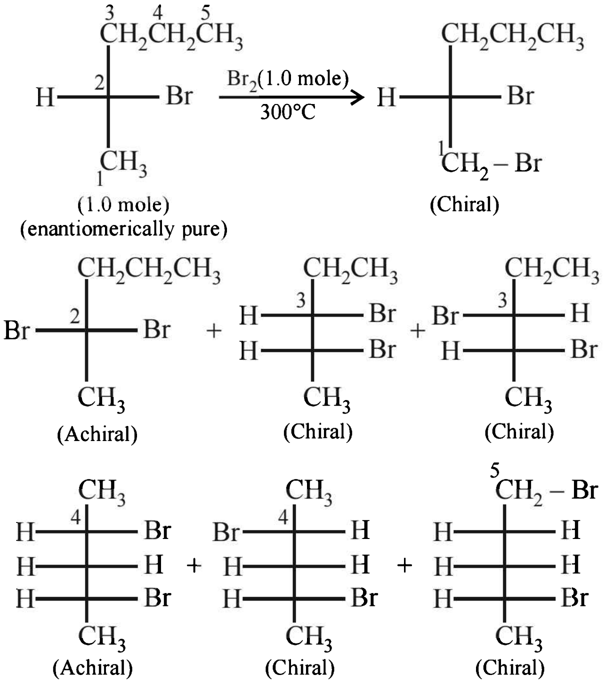
I. Integer Value Correct Type

1. 5

Total no. of alkenes will be = 5



2. (5)



Section-B JEE Main/ AIEEE

1. **(d)** $C_6H_5I \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{HNO_3/H^+}$

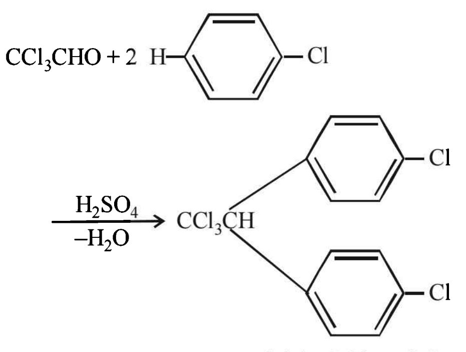
$C_6H_5OH \xrightarrow{AgNO_3}$ No yellow ppt.

$C_6H_5CH_2I \xrightarrow{NaOH} C_6H_5CH_2ONa \xrightarrow{HNO_3/H^+}$

$C_6H_5CH_2OH \xrightarrow{AgNO_3}$. yellow ppt.

Since benzyl iodide gives yellow ppt. hence this is compound B and A was phenyl iodide (C_6H_5I).

2. **(b)** DDT is prepared by heating chlorbenzene and chloral with concentrated sulphuric acid



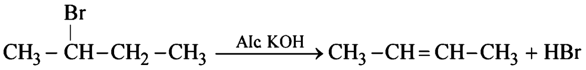
1,1,1-trichloro–2,2 bis
(p-chlorophenyl) ethane
or
DDT

3. **(b)** Due to steric hindrance tertiary alkyl halide do not react by S_N2 mechanism they react by S_N1 mechanism. S_N2 mechanisam is followed in case of primary and secondary alkyl halides
The order is
$CH_3-X > CH_3-CH_2X > (CH_3)_2CH.X > (CH_3)_3C-X$

4. **(b)** In Corey House synthesis of alkanes alkyl halide react with lithium dialkyl cuprate

$$R'X + LiR_2Cu \longrightarrow R'-R + RCu + LiX$$

5. **(c)**

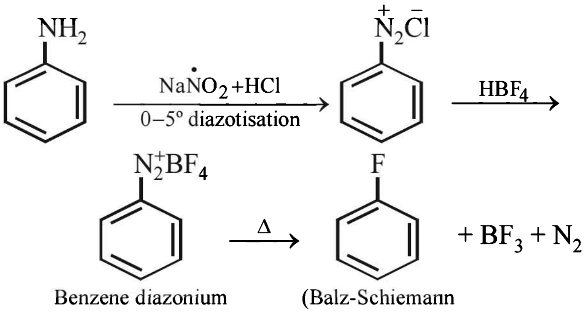


$$CH_3-\overset{Br}{\overset{|}{C}H}-CH_2-CH_3 \xrightarrow{\text{Alc KOH}} CH_3-CH=CH-CH_3 + HBr$$

The formation of 2-butene is in accordance to **Saytzeff's rule**. The more substituted alkene is formed.

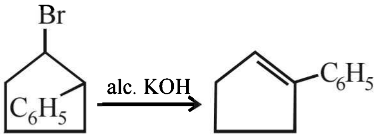
6. **(d)** $CH_3OH + C_6H_5MgBr \longrightarrow CH_3O.MgBr + C_6H_6$

7. **(d)**



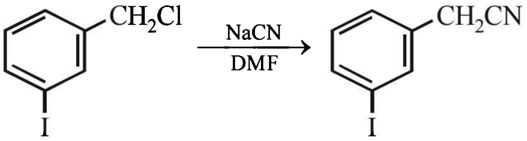
Benzene diazonium tetrafluoroborate (Balz-Schiemann reaction)

8. **(a)** The reaction is dehydrohalogenation



1-phenyl cyclopentene

9. **(b)**



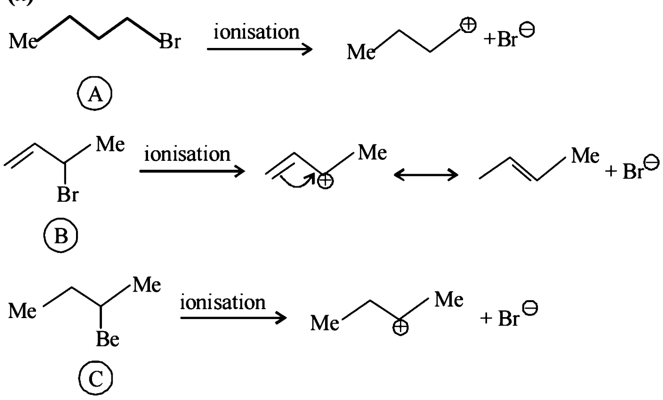
Nuclear substitution will not take place.

10. **(c)** In S_N2 mechanism transition state is pentavelent. For bulky alkyl group it will have sterical hinderance and smaller alkyl group will favour the S_N2 mechanism. So the decreasing order of reactivity of alkyl halides is $RCH_2X > R_2CHX > R_3CX$

11. **(d)** S_N2 reaction is favoured by small groups on the carbon atom attached to halogen.
So, the order of reactivity is
$CH_3Cl > (CH_3)_2CHCl > (CH_3)_3CCl > (C_2H_5)_2CHCl$

NOTE : S_N2 reaction is shown to maximum extent by primary halides. The only primary halides given is CH_3Cl so the correct answer is (d).

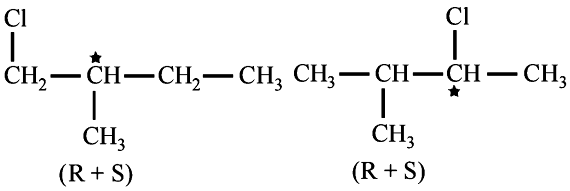
12. **(a)**



Since S_N1 reactions involve the formation of carbocation as intermediate in the rate determining step, **more is the stability of carbocation higher will be reactivity of alkyl halides towards S_N1 route.** Now we know that stability of carbocations follows the order : 3° > 2° > 1°, so S_N1 reactivity should also follow the same order.

3° > 2° > 1° > Methyl **(S_N1 reactivity)**

13. **(c)**



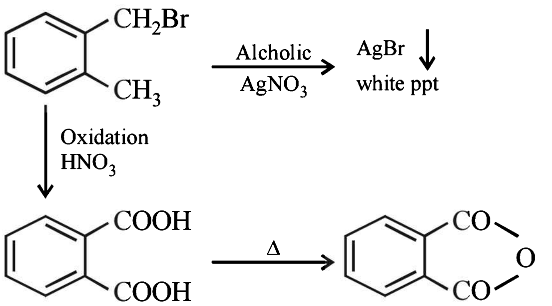
$$\overset{Cl}{\overset{|}{C}H_2}-\underset{\underset{CH_3}{|}}{\overset{\star}{C}H}-CH_2-CH_3 \qquad CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\star}{\overset{\overset{Cl}{|}}{CH}}-CH_3$$

(R + S) (R + S)

Four monochloro derivatives are chiral.

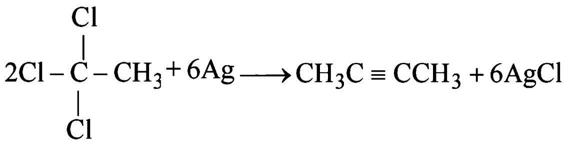
14. **(d)** DDT is a non-biodegradable pollutant.

15. **(d)**



16. **(b)** Steric congestion around the carbon atom undergoing the inversion process will slow down the S_N2 reaction, hence less congestion faster will the reaction. So, the order is
$CH_3Cl > (CH_3)CH_2-Cl > (CH_3)_2CH-Cl > (CH_3)_3CCl$

17. **(c)**



$$2Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3 + 6Ag \longrightarrow CH_3C\equiv CCH_3 + 6AgCl$$

1, 1, 1-trichloroethane 2-butyne

18. **(b)** Alkyl fluorides are more conveniently prepared by heating suitable chloro– or bromo-alkanes with organic fluorides such as AsF_3, SbF_3, CoF_2, AgF, Hg_2F_2 etc. This reaction is called **Swarts reaction**.

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr$$
$$2CH_3CH_2Cl + Hg_2F_2 \longrightarrow 2CH_3CH_2F + Hg_2Cl_2$$