DAY TWENTY NINE

Organic Compounds Containing Halogens

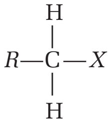
Learning & Revision for the Day

- Alkyl and Aryl Halides
- Polyhalogen Compounds

Alkyl and Aryl Halides

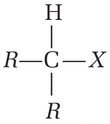
These are formed by the replacement of hydrogen atom(s) from a hydrocarbon (aliphatic or aromatic) by halogen atom(s). These may be classified as mono, di or tri halo compounds depending upon the number of halogen atoms.

1. **Alkyl halides** contain halogen atom(s) attached to sp^3-hybridised carbon atoms of an alkyl group. e.g.



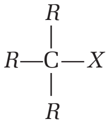
$$R-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-X$$

1° (primary)



$$R-\overset{\overset{\large H}{|}}{\underset{\underset{\large R}{|}}{C}}-X$$

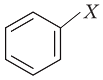
2° (secondary)



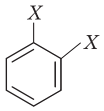
$$R-\overset{\overset{\large R}{|}}{\underset{\underset{\large R}{|}}{C}}-X$$

3° (tertiary)

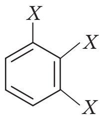
2. **Aryl halides** contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group.



Mono



Di



Tri

Preparation of Alkyl Halides (Haloalkanes)

Alkyl halides can be prepared by using the following reactions:

- Haloalkanes can be obtained from alcohols by the reaction with halogen acids or phosphorus halides (PX_5 or PX_3) or thionyl chloride.

e.g. $$R-OH + \text{dry HCl} \xrightarrow{\text{Anhy. } ZnCl_2} RCl + H_2O$$

$$ROH + \overset{+}{Na}\overset{-}{Br} \xrightarrow{(aq.)\,H_2SO_4} RBr + H_2O + NaHSO_4$$

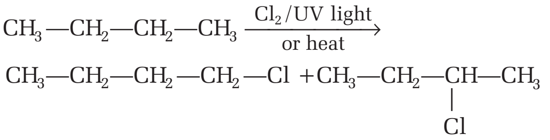
$$3R\text{—}OH + PX_3 \longrightarrow 3\,RX + H_3PO_3$$

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl \quad (X = Cl, Br, I)$$

$$R\text{—}OH \xrightarrow{P(red)/X_2} RX \quad (X_2 = Br_2,\ I_2)$$

$$R\text{—}OH + SOCl_2 \xrightarrow{Pyridine} RCl + SO_2\uparrow + HCl\uparrow$$

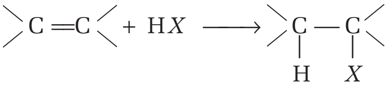
- Alkanes in the presence of sunlight shows free radical halogenation and gives a complex mixture of isomeric mono and polyhaloalkanes which is difficult to separate as pure compounds. e.g.



$$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}}$$

$$CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}Cl + CH_3\text{—}CH_2\text{—}\underset{\substack{|\\ Cl}}{CH}\text{—}CH_3$$

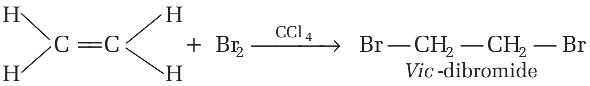
- An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.



In unsymmetrical alkenes (such as propene), only one product predominates as per Markownikoff's rule

$$CH_3CH{=}CH_2 + HI \longrightarrow \underset{\text{(Minor)}}{CH_3CH_2CH_2I} + \underset{\text{(Major)}}{CH_3\,CH(I)CH_3}$$

- Addition of bromine in CCl_4 to an alkene results in the synthesis of *vic*-dibromides. This reaction discharge the reddish brown colour of bromine and is used in the detection of double bond in a molecule.



- **Halide transfer method** is used to prepare alkyl fluoride and alkyl iodide. This includes Finkelstein reaction and Swarts reaction.

These are as follows:

  (i) **Finkelstein reaction** It is used for the conversion of chloroalkane or bromoalkane to iodoalkane.

$$RX + NaI \xrightarrow{Acetone} RI + NaX \qquad (X = Br, Cl)$$

  (ii) **Swarts reaction** (Preparation of alkyl fluorides) Alkyl chloride/ bromide when heated with metallic fluoride such as AgF, Hg_2F_2, CoF_2 or SbF_3 gives alkyl fluoride.

$$CH_3\text{— }Br + AgF \longrightarrow CH_3F + AgBr$$

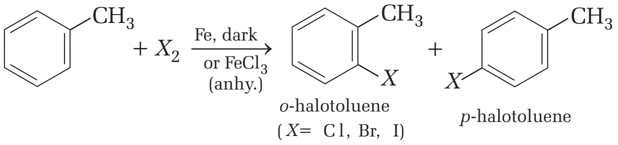
- **Borodine Hunsdiecker reaction** (used to produce alkyl bromide/chloride) proceeds through free radical mechanism and is used to reduce the length of carbon chain. The reaction is mainly used for the preparation of alkyl bromide

$$RCO_2Ag + Br_2 \longrightarrow RBr + CO_2\uparrow + AgBr$$

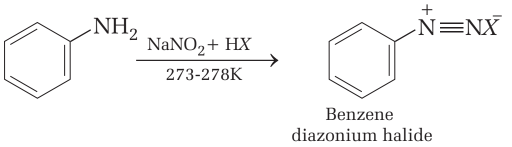
Preparation of Aryl Halides (Haloarenes)

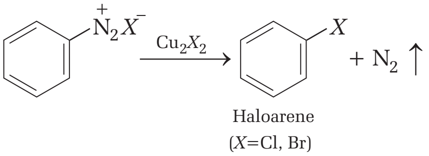
Aryl halides can be prepared by the following reactions.

- Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of a Lewis acids like $FeCl_3$, $FeBr_3$ in dark and at low temperature.

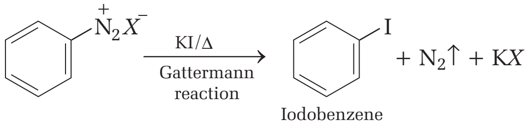


- Aryl halide can be prepared by mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by-Cl or Br. This reaction is called **Sandmeyer's reaction**

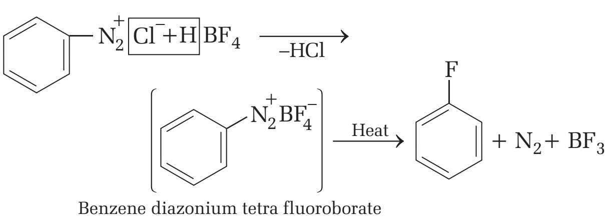




- Iodobenzene is obtained by warming diazonium salt with KI and does not require the presence of cuprous halide.



Fluorobenzene is obtained by using fluoroboric acid, HBF_4.



This reaction is known as **Balz-Schiemann reaction**.

Physical Properties of Haloalkanes and Haloarenes

The physical properties of alkyl and aryl halides are as follows.

- Haloalkanes and haloarenes are polar compounds and have higher boiling point due to dipole-dipole interaction. They have higher boiling points than hydrocarbons of comparable molecular mass.

Decreasing order of boiling point of alkyl halides is as follows:

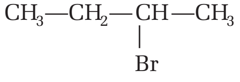
$$RI > RBr > RCl > RF$$

This is because with the increase in size and mass of halogen atom, the magnitude of van der Waals' forces increases.

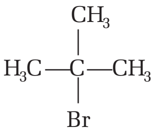
- Straight chain alkyl halides have higher boiling point as compared with branched chain alkyl halide of similar molecular weight, hence boiling points of isomeric haloalkanes decrease with increase in branching due to decrease in surface area. e.g.

$$CH_3—CH_2—CH_2—CH_2—Br$$

B.P./K 375

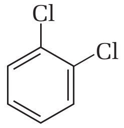


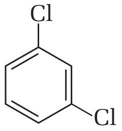
$$CH_3—CH_2—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_3$$

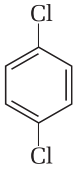


$$H_3C—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}—CH_3$$

B.P./K 364 346







B.P./K	453	446	448
M.P./K	256	249	323

- Bromo and iodo derivatives of hydrocarbons are heavier than water. Lower haloalkanes are very slightly soluble in water but others are insoluble in water because haloalkanes/ haloarenes do not form hydrogen bond with water.

Nature of C—*X* Bond

- Electronegativity of halogen atom is greater than that of carbon atom due to which the shared pair of electrons in C—*X* bond closer to the halogen atom.
- On moving down the group, the carbon - halogen bond length increases.
- In haloarenes, sp^2 hybridised carbon of benzene is bonded to halogen and C—*X* bond is also polar as in haloalkanes due to high electronegativity of halogen.

Chemical Properties of Haloalkanes

Haloalkanes are highly reactive compounds due to the presence of polar R —X bond. The reactions of haloalkanes may be of three types. These are nucleophilic substitution reactions, elimination reactions and reaction with metals. These are as follows.

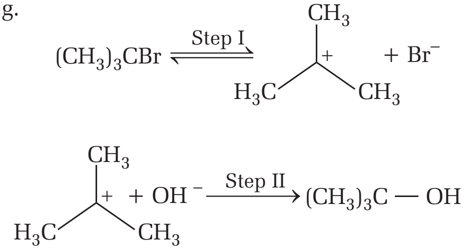
1. Nucleophilic Substitution Reaction

In nucleophilic substitution reactions, a nucleophile reacts with haloalkane having a partial positive charge on the carbon atom bonded to halogen. These reactions proceed either by S_N1 or by S_N2 type of mechanism.

Main features of substitution nucleophilic unimolecular reaction (S_N1) are :

(i) Tertiary alkyl group and polar solvent favours S_N1.
(ii) It follows first order kinetics, rate = k [substrate].
(iii) Carbocation is formed and gets rearranged, if possible.
(iv) Reaction is completed in two steps.
(v) Nucleophile can attack from front and backside. Therefore, racemic mixture can be formed.

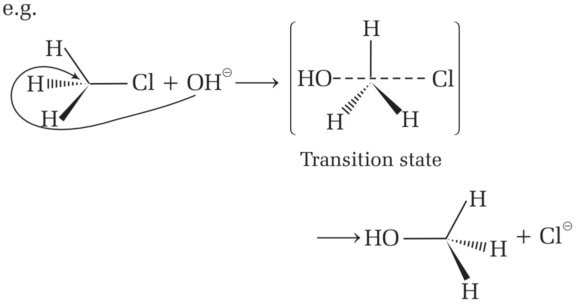
e.g.



Main features of substitution nucleophilic bimolecular reaction (S_N2) are:

(i) Primary alkyl group and non-polar solvent favour S_N2.
(ii) It follows second order kinetics, rate = k [substrate] [nucleophile]
(iii) Carbocation is not formed.
(iv) Reaction is completed in one step.
(v) It involves complete inversion in configuration as the attack of the nucleophile occurs from the backside of reactant.

e.g.



▬ (Wedge solid bond)—towards the viewers

┆ (Dash bond)—away from the viewers

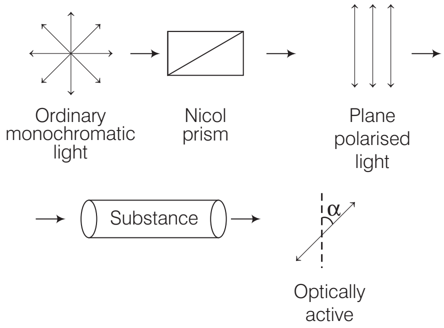
- Reactivity of halides toward S_N2 mechanism is $CH_3X > 1° > 2° > 3°$
- Reactivity of halides towards S_N1 mechanism is $3° > 2° > 1° > CH_3X$.
- In S_N2 mechanism, rate of reactions depends upon the strength of attacking nucleophile.
  The strength of different nucleophiles is

$$CN^- > I^- > OR^- > OH^- > CH_3COO^- > H_2O > F^-.$$

Stereochemical Aspects of Nucleophilic Substitution Reaction

Some basic stereochemical principles and notations are discussed below :

- Certain compounds rotate the plane polarised light when it is passed through solutions. Such compounds are called **optically active** compounds. The angle by which the plane polarised light rotated is measured by an instrument called **polarimeter**.

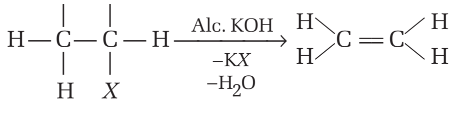


  If plane polarised light rotates in clockwise direction, when passed through a substance, the substance is known as **dextrorotatory** or (+) or (*d*). If it rotates in anticlockwise, the substance is known as **laevorotatory** or *l* or (–).

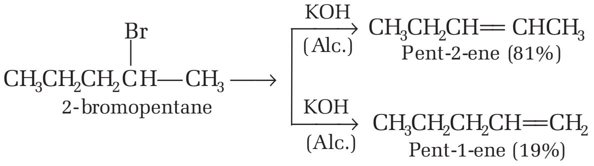
- Chiral carbon has four different groups or atoms attached to it.
- Chiral molecule (Optically active molecule) possesses at least 1-chiral carbon atom.
- Racemic mixture is the equimolar mixture of enantiomers (*dextro* and *laevo*). Racemic mixture is optically inactive due to external compensation. This phenomenon is known as **racemisation.**
- The backside attack by a nucleophile in S_N2 reactions gives rise to a product whose configuration is opposite to the reactant. Therefore, during S_N2 reaction, **inversion of configuration** occurs. This 100% inversion of configuration is known as **Walden inversion**.

2. Elimination Reactions

- When haloalkane having β-hydrogen atom is heated with alc. KOH, β-elimination takes place. e.g.



- If there is possibility of formation of more than one alkene due to availability of more than one α-H-atoms, the elimination of H*X* takes place according to **Saytzeff rule**. It states, "in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms, e.g.



3. Reaction with Metals

Grignard reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.

$$CH_3CH_2Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

NOTE Some Important Reactions of Haloalkanes:

$$R{-}X \xrightarrow{AgNO_2} R{-}NO_2 + AgX$$

$$RX \xrightarrow{NaNO_2 \text{ or } KNO_2} R{-}ONO + KX \text{ or } NaX$$

$$RX \xrightarrow{\text{KCN or NaCN}} RCN + KX \text{ or } NaX$$

$$RX \xrightarrow{AgCN} RNC + AgX$$

Hofmann ammonolysis reaction:

$$RX + NH_3 \longrightarrow RNH_2 + R{-}NH{-}R + R_3N + [R_4N^+]\,Cl^-$$

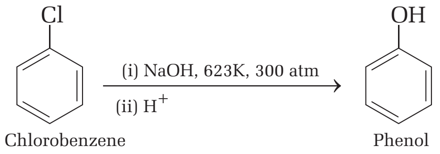
Chemical Properties of Haloarenes

Haloarenes give three types of reactions:

1. Nucleophilic substitution reactions

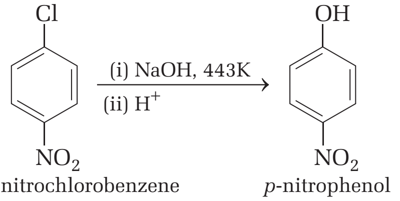
Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions due to resonance effect, difference in hybridisation of carbon atom in $C-X$ bond, instability of phenyl cation and repulsion between electron rich attacking nucleophile and electron rich arenes. Various nucleophilic substitution reactions are as follows

(i)

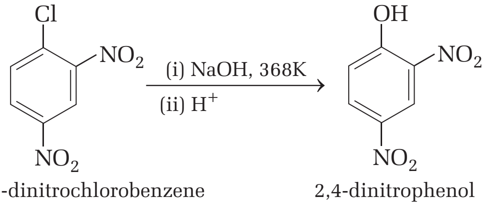


This is known as **Dow's process**.

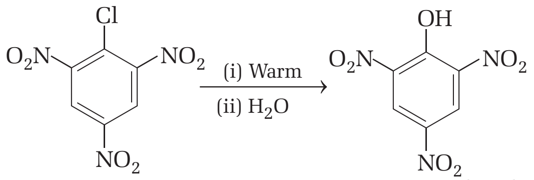
(ii)



(iii)



(iv)



2,4,6-trinitro chlorobenzene

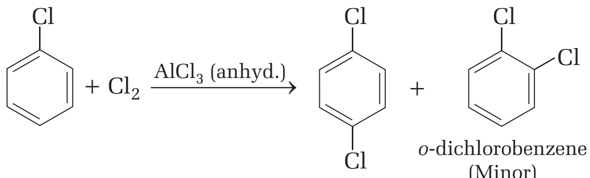
2,4,6-trinitrophenol or picric acid

2. Electrophilic Substitution Reactions

Haloarenes undergo **electrophilic substitution reactions** of benzene nucleus such as halogenation, nitration, sulphonation and Friedel-Crafts alkylation and acylation.

These are as follows :

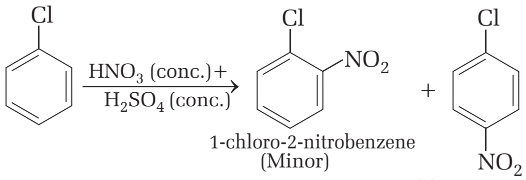
(i) **Halogenation**



o-dichlorobenzene (Minor)

p-dichlorobenzene (Major)

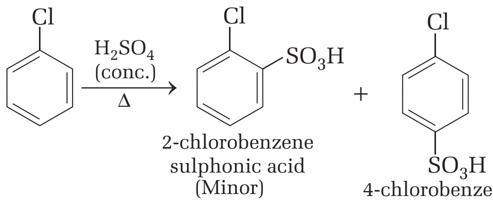
(ii) **Nitration**



1-chloro-2-nitrobenzene (Minor)

1-chloro-4-nitrobenzene (Major)

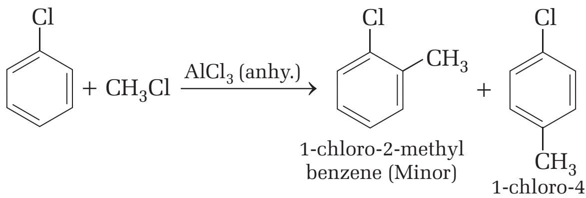
(iii) **Sulphonation**



2-chlorobenzene sulphonic acid (Minor)

4-chlorobenzene sulphonic acid (Major)

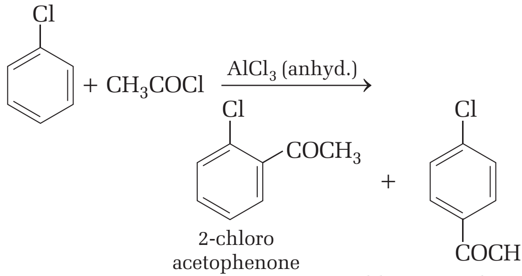
(iv) **Friedel-Craft Alkylation**



1-chloro-2-methyl benzene (Minor)

1-chloro-4-methylbenzene (Major)

(v) **Friedel-Craft Acylation**



2-chloro acetophenone (minor)

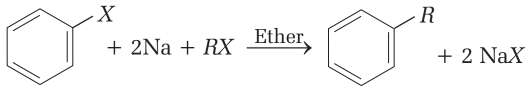
4-chloro acetophenone (major)

Nuclear halogenation takes place by electrophilic substitution mechanism whereas side chain halogenation takes place by free radical mechanism.

3. Haloarenes React with Metals to Produce Higher Alkanes

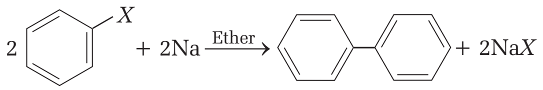
These reaction are as follows:

(i) **Wurtz-Fittig Reaction** A mixture of haloarene and haloalkane, when treated with Na in dry ether gives alkyl arene. e.g.



Alkyl benzene

(ii) **Fittig Reaction** Haloarenes on treatment with Na in dry ether give analogous compounds. e.g.



Diphenyl

Polyhalogen Compounds

The polyhalogenated compounds (PHCs) are any compounds with multiple substitutions of halogens. Some of polyhalogen compounds are given below:

1. Trichloromethane (Chloroform; $CHCl_3$)

- It is employed as a solvent for fats, alkaloids, iodine and other substances.
- It was used as a general anaesthetic but now a days it is replaced by less toxic and safe anaesthetic ether.
- The major use of chloroform today is in the production of the refrigerant, freon.
- It is stored in closed dark coloured bottles, filled completely so that air is kept out because it is oxidised by air in the presence of light.

$$2CHCl_3 + \underset{(Air)}{O_2} \xrightarrow{\text{Light}} \underset{\substack{\text{Phosgene}\\\text{(Poisonous gas)}}}{2COCl_2} + 2HCl$$

2. Tri-iodomethane (Iodoform; CHI_3)

It is prepared by heating ethanol or acetone with sodium hydroxide and iodine or Na_2CO_3 and I_2 in water.

$$CH_3CH_2OH + 6NaOH + 4I_2 \xrightarrow{\text{Heat}} CHI_3 \downarrow + 5\,NaI + HCOONa + 5\,H_2O$$

$$CH_3COCH_3 + 4\,NaOH + 3\,I_2 \xrightarrow{\text{Heat}} CHI_3 \downarrow + 3NaI + CH_3COONa + 3H_2O$$

This reaction is called **iodoform reaction.**

Some of the important characteristic of iodoform are as follows:

(i) It is yellow solid having melting point 119°C.

(ii) It is insoluble in water but soluble in ethanol and ether.

(iii) It is used as antiseptic because it liberates iodine but due to obnoxious (unpleasant) smell, it has been replaced by other medicines.

(iv) Its chemical properties are similar to $CHCl_3$.

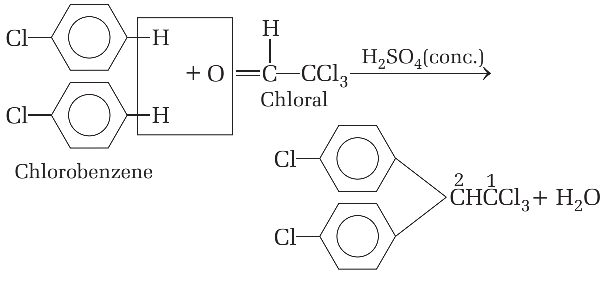
3. Freons (Chlorofluorocarbon; CCl_2F_2)

They are extremely stable, unreactive non-toxic, non-corrosive and easily liquefiable gases.

- It is manufactured from tetrachloromethane by Swarts reaction and used for aerosol propellants, refrigeration and air conditioning purposes.
- Freons deplete the protective ozone layer surrounding our planet, so their use has been banned in many countries.

4. DDT (p,p′-Dichlorodiphenyltrichloroethane)

- It is a powerful insecticide but is not easily biodegradable. Therefore, its long term effects could be potentially dangerous and its use is banned in many countries.
- IUPAC name of DDT is 2,2-*bis* (4-chloro phenyl)– 1, 1, 1-trichloroethane. It is non-biodegradable and slowly changes to another compound DDE by the loss of a molecule of HCl.



(DDT)
p,*p*′-dichlorodiphenyltrichloroethane

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Preparation of alkyl halides in laboratory is least preferred by

(a) halide exchange
(b) treatment of alcohols
(c) addition of hydrogen halides to alkenes
(d) direct halogenation of alkanes

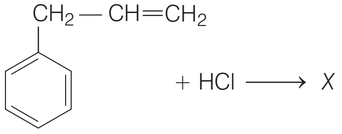
2 The synthesis of alkyl fluorides is best accomplished by ➞ JEE Main 2015

(a) free radical fluorination (b) Sandmeyer's reaction
(c) Finkelstein reaction (d) Swarts reaction

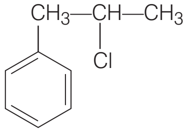
3 Which branched chain isomer of the hydrocarbon with molecular mass 72 u gives only one isomer of mono substituted alkyl halide? ➞ AIEEE 2012

(a) Tertiary butyl chloride (b) *Neo* -pentane
(c) *Iso* -hexane (d) *Neo* -hexane

4 Given, ➞ JEE Main (Online) 2013



X is

(a)


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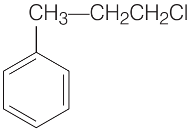

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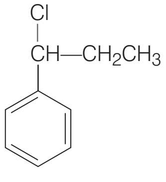

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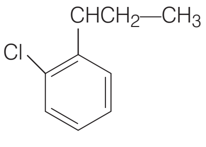
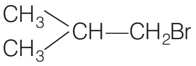


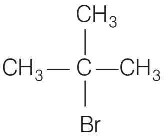
5 Which of the following has highest melting point?

(a) Chlorobenzene
(b) *o*-dichlorobenzene
(c) *m*-dichlorobenzene
(d) *p*-dichlorobenzene

6 Arrange the following compounds, in the increasing order of their boiling points.

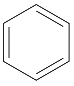
(i) 
$(CH_3)_2CH—CH_2Br$

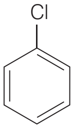
(ii) $CH_3CH_2CH_2CH_2Br$

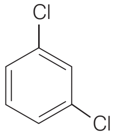
(iii) 
$CH_3—C(CH_3)(Br)—CH_3$

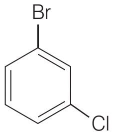
(a) (ii) < (i) < (iii) (b) (i) < (ii) < (iii)
(c) (iii) < (i) < (ii) (d) (iii) < (ii) < (i)

7 Arrange the following compounds in the increasing order of their densities

(i) 

(ii) 

(iii) 

(iv) 

(a) (i) < (ii) < (iii) < (iv) (b) (i) < (iii) < (iv) < (ii)
(c) (iv) < (iii) < (ii) < (i) (d) (ii) < (iv) < (iii) < (i)

8 C—Cl bond is stronger than C—I bond because

(a) C—Cl bond is more ionic than C—I
(b) C—Cl bond is polar covalent bond
(c) C—Cl bond is more covalent than C—Cl
(d) C—Cl bond length is longer than C—I

9 Which of the following alkyl halide is used as a methylating agent ?

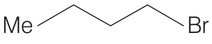
(a) C_2H_5Br (b) C_6H_5Cl (c) CH_3Cl (d) C_2H_5Cl

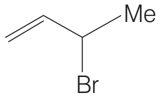
10 The addition of HI in the presence of peroxide catalyst does not follow anti-Markownikoff addition because

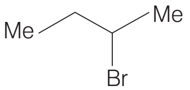
➞ JEE Main (Online) 2013

(a) HI is a strong reducing agent
(b) HI bond is too strong to be broken homolytically
(c) I atom combines with H-atom to give back HI
(d) Iodine atom is not reactive enough to add across a double bond

11 Consider the following bromides,

(*A*) 

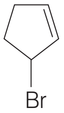
(*B*) 

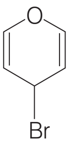
(*C*) 

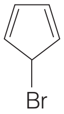
The correct order of S_N1 reactivity is ➞ AIEEE 2010

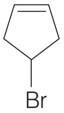
(a) *B* > *C* > *A* (b) *B* > *A* > *C* (c) *C* > *B* > *A* (d) *A* > *B* > *C*

12 The increasing order of reactivity of the following bromides in S_N1 reaction is

I. 

II. 

III. 

IV. 

(a) III > I > II > IV (b) III > II > I > IV
(c) II > III > I > IV (d) II > I > IV > III

13 The organic chloro compound which shows complete stereochemical inversion during a S_N2 reaction, is

(a) CH_3Cl (b) $(C_2H_5)_2CHCl$
(c) $(CH_3)_3CCl$ (d) $(CH_3)_2CHCl$

14 The increasing order of reactivity of the following halides for the S_N1 reaction is ➞ JEE Main 2017

I. $CH_3CH(Cl)CH_2CH_3$ II. $CH_3CH_2CH_2Cl$
III. *p*–$H_3CO—C_6H_4—CH_2Cl$

(a) (III)<(II)<(I) (b) (II)<(I)<(III)
(c) (I)<(III)<(II) (d) (II)<(III)<(I)

15 In S_N2 reactions, the correct order of reactivity for the following compounds CH_3Cl, CH_3CH_2Cl, $(CH_3)_2CHCl$ and $(CH_3)_3CCl$ is ➞ JEE Main 2014

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

16 Choose the incorrect statement.

(a) An S_N1 reaction proceeds with inversion of configuration
(b) An S_N2 reaction proceeds with stereochemical inversion
(c) An S_N2 reaction follows second order kinetics
(d) The reaction of *tert*-butyl bromide with OH^- follows first order kinetics

17 $CH_3Br + Nu^- \longrightarrow CH_3—Nu + Br^-$

The decreasing order of the rate of the above reaction with nucleophile (Nu^-) *A* to *D* is

$[Nu^- = (A)\ PhO^-, (B)\ AcO^-, (C)\ HO^-, (D)\ CH_3O^-]$

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

18 In nucleophilic substitution reaction, order of halogens as incoming (attacking) nucleophile is $I^- > Br^- > Cl^-$.

The order of halogens as departing nucleophile should be ➞ JEE Main (Online) 2013

(a) $Br^- > I^- > Cl^-$ (b) $I^- > Br^- > Cl^-$
(c) $Cl^- > Br^- > I^-$ (d) $Cl^- > I^- > Br^-$

19 Match the following and choose the correct option.

	Column I		Column II
A.	S_N1 reaction	1.	*vic*-dibromides
B.	Bromination of alkenes	2.	*gem*-dihalides
C.	Alkylidene halides	3.	Racemisation
D.	Elimination of HX from alkyl halide	4.	Saytzeff rule

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	2	4	(b)	1	3	2	4
(c)	3	2	1	4	(d)	2	4	3	1

20 In alkaline hydrolysis of a tertiary halide by aqueous alkali, if concentration of alkali is doubled, then the reaction rate

(a) will be doubled (b) will be halved
(c) will remain constant (d) cannot say anything

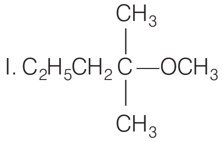
21 Which halide will be least reactive in respect to hydrolysis ?

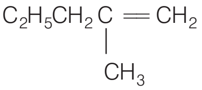
(a) Vinyl chloride (b) Allyl chloride
(c) Ethyl chloride (d) *t*-butyl chloride

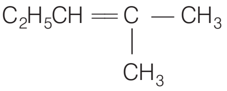
22 A dihaloalkane *X*, having formula $C_3H_6Cl_2$, on hydrolysis gives a compound, that can reduce Tollen's reagent.The compound '*X*' is

(a) 1, 2- dichloropropane (b) 1, 1- dichloropropane
(c) 1, 3- dichloropropane (d) 2, 2- dichloropropane

23 2-chloro - 2-methylpentane on reaction with sodium methoxide in methanol yields ➞ JEE Main 2016

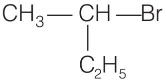
I. 
$C_2H_5CH_2\overset{CH_3}{\underset{CH_3}{C}}-OCH_3$

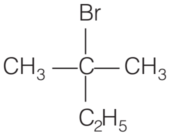
II. 
$C_2H_5CH_2\underset{CH_3}{C}=CH_2$

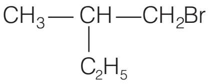
III. 
$C_2H_5CH=\underset{CH_3}{C}-CH_3$

(a) Both I and III (b) Only II
(c) Both I and II (d) All of these

24 Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

I. 
$CH_3-\underset{C_2H_5}{CH}-Br$

II. 
$CH_3-\overset{Br}{\underset{C_2H_5}{C}}-CH_3$

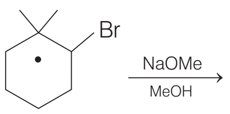
III. 
$CH_3-\underset{C_2H_5}{CH}-CH_2Br$

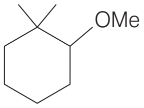
(a) I (b) I, II, III
(c) II, III (d) I, III

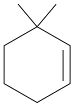
25 A solution of (–) -1-chloro -1-phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of ➞ JEE Main (Online) 2013

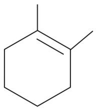
(a) carbene (b) carbocation
(c) free radical (d) carbanion

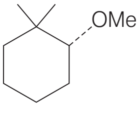
26 The major product of the following reaction is ➞ JEE Main 2018



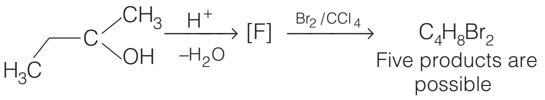
(a) 

(b) 

(c) 

(d) 

27 How many structures of F are possible?



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

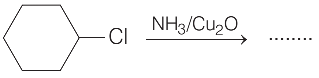
28 The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is ➞ JEE Main 2014

(a) acetylene (b) ethene
(c) 2-butyne (d) 2-butene

29 Aryl halides are less reactive than alkyl halides towards nucleophile due to

(a) resonance (b) stability of carbonium ion
(c) high boiling point (d) None of these

30 Predict the main product in the given reaction :



(a) Phenyl cyanide (b) Nitrophenol
(c) Aniline (d) Hydroxylamine

31 Chlorobenzene can be prepared by reacting aniline with:

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

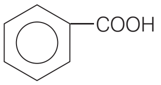
32 The chlorine atom in chlorobenzene is *ortho* and *para* directing because

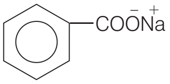
(a) resonance effect predominates over inductive effect
(b) inductive effect predominates over resonance effect
(c) both inductive and resonance effects are evenly matched
(d) only resonance effect and not inductive effect is operating

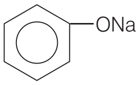
33 The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives predominantly

(a) benzoyl chloride (b) benzyl chloride
(c) *o* - and *p*-chlorotoluene (d) *m*-chlorotoluene

34 Toluene reacts with excess of Cl_2 in the presence of sunlight to give a product which on hydrolysis followed by reaction with NaOH gives

(a) 

(b) 

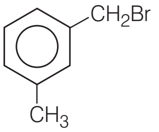
(c) 

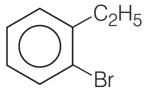
(d) None of these

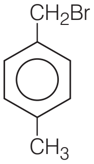
35 The Wurtz-Fittig reaction involves condensation of ➞ JEE Main (Online) 2013

(a) two molecules of aryl halides
(b) one molecule of each of aryl halide and alkyl-halide
(c) one molecule of each aryl halide and phenol
(d) two molecules of a alkyl halides

36 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 Main (Online) 2013

(a)


(b)


(c)


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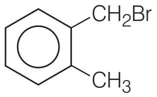


37 CCl_4 is a well known fire extinguisher. However, after using it to extinguish fire, the room should be well ventilated. This is because

(a) it is flammable at higher temperature
(b) it is toxic
(c) it produces phosgene by reaction with water vapour at higher temperature
(d) It is corrosive

38 The reaction of toluene with Cl_2 in the presence of $FeCl_3$ gives X and reaction in presence of light gives Y. Thus, X and Y are

(a) X = benzyl chloride, Y = *m*- chlorotoluene
(b) X = benzyl chloride, Y = *q* -chlorotoluene
(c) X = *m* -chlorotoluene, Y = *p*- chlorotoluene
(d) X = *o* and *p*- chlorotoluene, Y = trichloromethyl benzene

39 Which is not the correct statement?

(a) Chloretone is an insecticide
(b) $COCl_2$ is called phosgene
(c) Chloropicrin is used as an insecticide
(d) CCl_4 is used as fire extinguisher under the name pyrene

40 The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid is

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

Direction (Q. Nos. 41-46) *In the following questions Assertion followed by Reason is given. Choose the correct answer out of the following choices.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct and Reason is incorrect
(d) Both Assertion and Reason are incorrect

41 **Assertion** (A) Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chloride from alcohols.

Reason (R) Phosphorus chlorides give pure alkyl halides.

42 **Assertion** (A) *Tert*-butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

Reason (R) In Wurtz reaction, alkyl halides react with sodium in dry sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

43 **Assertion** (A) Alkyl halides are not soluble in water.

Reason (R) Although polar in nature, yet alkyl halides are not able to form H-bonds with water molecules.

44 **Assertion** (A) Tertiary alkyl halides are more reactive than 1° alkyl halides towards elimination.

Reason (R) Positive inductive effect of alkyl groups weakens carbon-halogen bond in 3° alkyl halides.

45 **Assertion** (A) Aryl halides undergo nucleophilic substitution with ease.

Reason (R) The carbon halogen bond in aryl halides has partial double bond character.

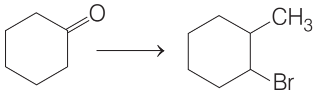
46 **Assertion** (A) Bromobenzene upon reaction with Br_2 / Fe gives 1,4 -dibromobenzene as the major product.

Reason (R) In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in directing the incoming electrophile.

DAY PRACTICE SESSION 2

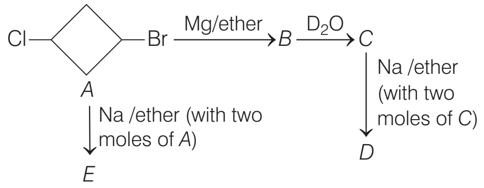
PROGRESSIVE QUESTIONS EXERCISE

1 Which of the following sequence of reagent is best suited for the reaction shown below?

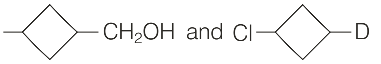


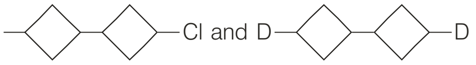
(a) (i) CH_3MgBr, H_3O^+; (ii) H^+ / Δ; (iii) HBr/H_2O_2
(b) (i) CH_3MgBr, H_3O^+; (ii) H^+ / Δ; (iii) HBr
(c) (i) CH_3MgBr, H_3O^+; (ii) HBr;
(d) (i) HBr/$ROOR$; (ii) CH_3MgBr, H_3O^+

2



D and E respectively are

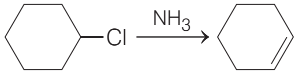
(a) 

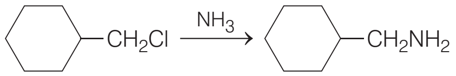
(b) 

(c) 

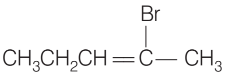
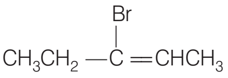
(d) None of the above

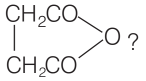
3 Which among the following reaction seems to be incorrect?

(a) $Me_3CCl \xrightarrow{NH_3} Me_3CNH_2$
(b) $Me_3CCl \xrightarrow{NH_3} Me_2C{=}CH_2$
(c) 

(d) 

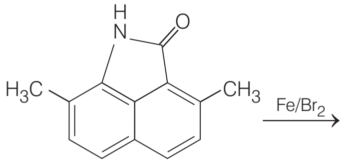
4 An organic compound C_5H_9Br (A) which readily decolourises bromine water and cold alkaline $KMnO_4$ solution and gives $C_5H_{11}Br$ (B) on catalytic hydrogenation. The reaction of A with alcoholic KOH first and then with $NaNH_2$ produces C with evolution of NH_3. C reacts with Lindlar's catalyst to give D and on reaction with Na in liquid NH_3 produces E. D and E are isomeric. The compound A is

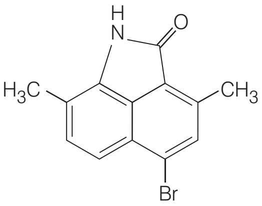
(a)  $CH_3CH_2CH{=}\overset{\displaystyle Br}{\overset{|}{C}}-CH_3$
(b)  $CH_3CH_2-\overset{\displaystyle Br}{\overset{|}{C}}{=}CHCH_3$
(c) Both (a) and (b)
(d) Neither (a) nor (b)

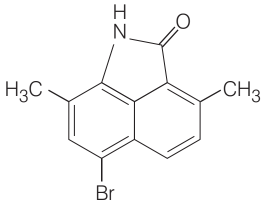
5 The product of which of the following reaction on dehydration gives  $\begin{array}{l}CH_2CO\\ |\\ CH_2CO\end{array}\!\!>O$?

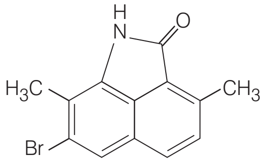
(a) 1, 2-dibromoethane $\xrightarrow{KCN} \xrightarrow{H_3O^+}$
(b) 1, 1-dibromoethane $\xrightarrow{KCN} \xrightarrow{H_3O^+}$
(c) 1, 1, 1-trichloroethane $\xrightarrow{\text{Alkaline hydrolysis}}$
(d) None of the above

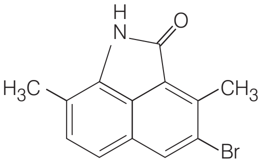
6 Product on monobromination of this compound is



(a) 

(b) 

(c) 

(d) 

7 Iodine from iodoethane can be substituted by cyanide group in a number of ways. Which of the following is true statement?

(a) With AgCN, EtNC while with KCN, EtCN is formed as major product
(b) With AgCN, EtCN and with KCN, EtNC is formed
(c) With either KCN or AgCN, EtNC is formed as major product
(d) With either KCN or AgCN, EtCN is formed as major product

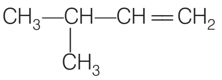
8 A hydrocarbon has molecular mass = 72. It gives a single monochloride and two dichlorides on further photochlorination. The two dichlorides are

(a) $CH_3CCl_2(CH_2)_2CH_3$; $CH_3(CHCl)_2CH_2CH_3$
(b) $(CH_3)_2CCl_2CH_2CH_3$; $(CH_3)_2(CHCl)_2CH_3$
(c) $CHCl_2C(CH_3)_3$; $(CH_3)_2C(CH_2Cl)_2$
(d) $CHCl_2CH_2CH(CH_3)_2$ $CH_3CHClCH_2CHClCH_3$

9 One mole of hydrocarbon (A) reacts with 1 mole of bromine giving a dibromo compound $C_5H_{10}Br_2$. (A) on treatment with cold dilute alkaline $KMnO_4$ solution forms a compound $C_5H_{12}O_2$. On ozonolysis, (A) gives equimolar quantities of propanone and ethanal. The compound (A) is

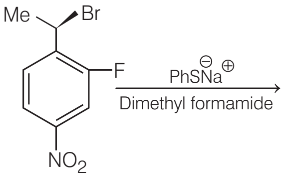
(a) $(CH_3)_2C{=}CHCH_3$ (b) $(CH_3)_2CH{-}CH_2CH_3$

(c) $CH_3CH_2CH{=}CHCH_3$ (d)

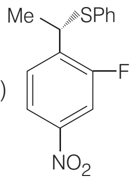


$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH_2$

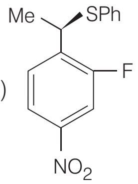
10 The major product of the following reaction is



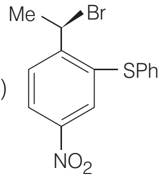
(a)



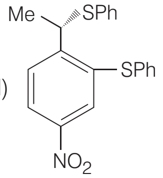
(b)



(c)



(d)



11 Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original lables. 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?

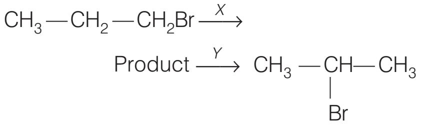
(a) A was C_6H_5I

(b) A was $C_6H_5CH_2I$

(c) B was C_6H_5I

(d) Addition of HNO_3 was unnecessary

12 Identify the set of reagents/reaction conditions x and y in the following set of transformations.



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

(a) X = dilute aqueous NaOH, 20° C; Y = HBr/acetic acid, 20°C

(b) X = conc. 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 = conc. alcoholic NaOH, 80°C; Y = $Br_2/CHCl_3$, 0°C

13 The reaction condition leading to the best yield of C_2H_5Cl are:

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

(b) $C_2H_6 + Cl_2$ (excess) $\xrightarrow[\text{room temp.}]{\text{Dark}}$

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

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

14 (X) on treatment with sodium hydroxide followed by the addition of silver nitrate give white precipitate at room temperature which is soluble in NH_4OH. (X) can be

(a) chlorobenzene

(b) ethyl bromide

(c) benzyl chloride

(d) vinyl chloride

ANSWERS

SESSION 1	**1** (d)	**2** (d)	**3** (b)	**4** (c)	**5** (d)	**6** (c)	**7** (a)	**8** (a)	**9** (c)	**10** (d)
	11 (a)	**12** (d)	**13** (a)	**14** (b)	**15** (b)	**16** (a)	**17** (a)	**18** (b)	**19** (a)	**20** (c)
	21 (a)	**22** (b)	**23** (d)	**24** (a)	**25** (b)	**26** (b)	**27** (d)	**28** (c)	**29** (a)	**30** (c)
	31 (d)	**32** (a)	**33** (c)	**34** (b)	**35** (b)	**36** (d)	**37** (c)	**38** (d)	**39** (a)	**40** (b)
	41 (d)	**42** (a)	**43** (a)	**44** (a)	**45** (d)	**46** (a)				
SESSION 2	**1** (a)	**2** (c)	**3** (a)	**4** (c)	**5** (a)	**6** (b)	**7** (a)	**8** (c)	**9** (a)	**10** (a)
	11 (a)	**12** (b)	**13** (a)	**14** (c)						

Hints and Explanations

SESSION 1

1 By direct halogenation of alkanes a mixture of monohalogen, dihalogen, trihalogen and tetrahalogen substituted product is obtained by this method. These are difficult to separate.

$$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[h\nu]{Cl_2} CH_2Cl_2$$

$$\xrightarrow{Cl_2} CHCl_3 \xrightarrow[h\nu]{Cl_2} CCl_4$$

2 Alkyl fluorides can be prepared by action of metallic fluorides such as AgF, Hg_2F_2 or SbF_3 on corresponding alkyl halide.This reaction is known as Swarts reaction.

$$CH_3Br + AgF \longrightarrow \underset{\text{Methyl fluoride}}{CH_3F} + AgBr$$

When action of NaI/acetone takes place on alkyl chloride or bromide, alkyl iodide forms. This reaction is called Finkelstein reaction.

$$C_2H_5Cl \xrightarrow[\text{acetone}]{\text{NaI}} C_2H_5I + NaCl$$

Free radical fluorination is highly explosive reaction, so not preferred for the preparation of fluoride.

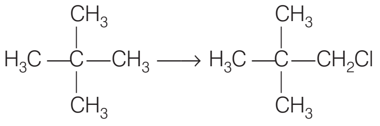
Sandmeyer's reaction is used for the preparation of aryl halides.

3 Molar mass $= 72 = C_nH_{2n+2} = 12n + (2n + 2)$

$$n = 5$$

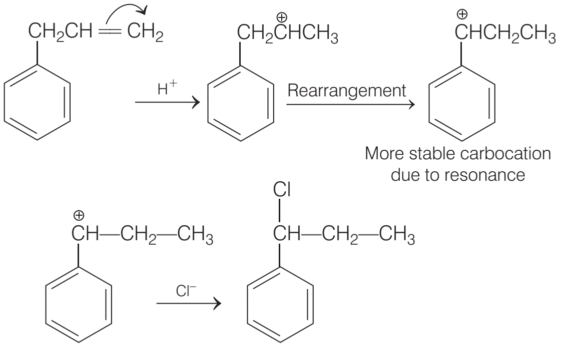
Thus, hydrocarbon is C_5H_{12}.

Since, it gives only single $C_5H_{11}Cl$, thus C_5H_{12} is symmetrical. It is *neo* -pentane.



$$H_3C-C(CH_3)_2-CH_3 \longrightarrow H_3C-C(CH_3)_2-CH_2Cl$$

4



5 *p*-dichlorobenzene has highest melting point because it has symmetrical structure and due to which it can fit well in its crystal lattice. The intermolecular forces of attraction is also strong.

6 Boiling point decreases with branching.

Thus, the correct order is (iii) < (ii) < (i).

7 Densities of alkyl halides decrease in the following order iodide > bromide > chloride > fluoride.

Thus, the correct option is 'a'

8 μ_D for C—Cl bond = 1.56 D

μ_D for C—I bond = 1.29 D

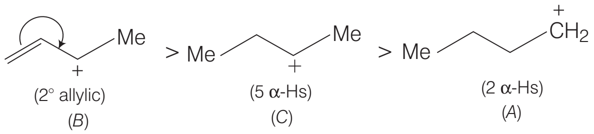
C—Cl bond is more ionic than C—I bond. Among halides, C—*X* bond length increases as the size of halogen increases. Therefore, C—Cl bond is stronger than C—I bond.

9 CH_3Cl is used as methylating agent. The methylating agent is one which is used for the introduction of methyl groups.

10 Addition of HI in the presence of peroxide catalyst does not follow anti-Markownikoff's rule because iodine radicals have more tendency to form I_2 molecule as compared to form free radical of carbon. Thus, iodine atom is not reactive enough to add across a double bond.

$$I^{\bullet} + I^{\bullet} \longrightarrow I_2$$

11 Higher the stability of carbocation, faster is the reaction because S_N1 reactions involve the formation of carbocation intermediate.



12 II is most reactive as it produces an aromatic carbocation while IV is less reactive as it produces a non-resonance stabilised carbocation.III is least reactive than I as former involve an anti-aromatic carbocation.

13 S_N2 reactions are accomplished by complete stereochemical inversion. Since, 1° alkyl halides are most prone to S_N2 reactions, therefore CH_3Cl undergoes complete stereochemical inversion.

14 (i) The rate of S_N1 reaction depends only upon the concentration of the alkyl halide.

(ii) S_N1 reaction proceeds through the formation of carbocation.

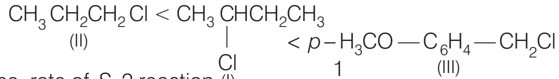
The reactivity is decided by ease of dissociation of alkyl halide.

$$R - X \rightleftharpoons R^{\oplus} + X^{\ominus}$$

Higher the stability of R^+ (carbocation), higher would be the reactivity towards S_N1 reaction.

$p-H_3CO-C_6H_4-\overset{\oplus}{C}H_2$ is the most stable carbocation due to resonance and then $CH_3\overset{\oplus}{C}HCH_2CH_3$ (2° carbocation) while $CH_3CH_2\overset{\oplus}{C}H_2$ (1°) is least stable.

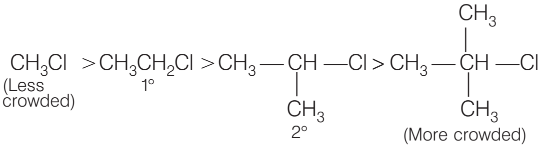
Thus, the correct increasing order of the reactivity of the given halides towards the S_N1 reaction is



$$\underset{\text{(II)}}{CH_3CH_2CH_2Cl} < \underset{\text{(I)}}{CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HCH_2CH_3} < \underset{\text{(III)}}{p\text{-}H_3CO-C_6H_4-CH_2Cl}$$

15 Since, rate of S_N2 reaction $\propto \frac{1}{\text{Steric crowding of C}}$

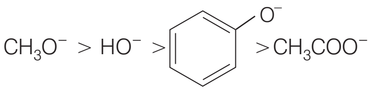
Thus, the correct order is



$$\underset{\text{(Less crowded)}}{CH_3Cl} > \underset{1^\circ}{CH_3CH_2Cl} > \underset{2^\circ}{CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}H-Cl} > \underset{\text{(More crowded)}}{CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}H-Cl}$$

16 S_N1 reactions are accompanied by racemisation. The attack of nucleophile can occur from both the faces with almost equal ease, thereby giving a 50 : 50 mixture of two enantiomers, i.e. racemic mixture.

17 Nucleophilicity order is



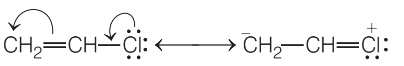
$$CH_3O^- > HO^- > C_6H_5O^- > CH_3COO^-$$

18 The order of departing nature of halides is $I^- > Br^- > Cl^-$. This is because of large size, low electronegativity and nucleophilicity of I^-.

19 A → 3, B → 1, C → 2, D → 4

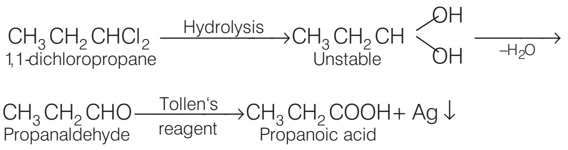
20 Reaction of *tert*-alkyl halides with aqueous alkali gives S_N1 reaction and rate of S_N1 reaction is not based on the concentration of nucleophile (alkali). Hence, reaction rate remains constant.

21 Vinyl chloride is least reactive towards hydrolysis because of the non-reactivity of chlorine atom due to resonance stabilisation. The lone pair of chlorine can participate in delocalisation (resonance) to give two canonical structures.



$$CH_2{=}CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{-}{C}H_2-CH{=}\overset{+}{\underset{..}{Cl}}:$$

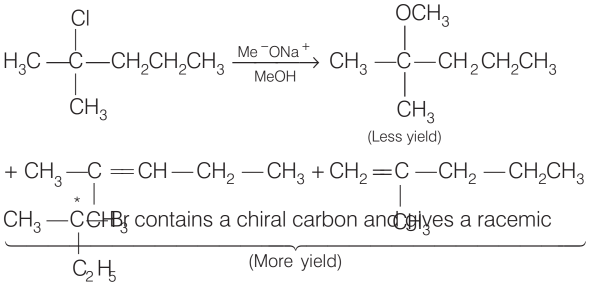
22 The obtained compound reduces Tollen's reagent,therefore, it must be an aldehyde. Thus, it is obvious that both the' —Cl atoms are present at C. Hence, the compound 'X' is 1,1-dichloropropane and the reactions are as follows:



$$\underset{\text{1,1-dichloropropane}}{CH_3CH_2CHCl_2} \xrightarrow{\text{Hydrolysis}} \underset{\text{Unstable}}{CH_3CH_2CH(OH)_2} \xrightarrow{-H_2O}$$

$$\underset{\text{Propanaldehyde}}{CH_3CH_2CHO} \xrightarrow[\text{reagent}]{\text{Tollen's}} \underset{\text{Propanoic acid}}{CH_3CH_2COOH} + Ag\downarrow$$

23 Strong nucleophile (OMe) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.

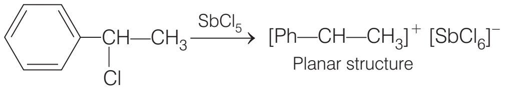


$$H_3C-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_2CH_3 \xrightarrow[\text{MeOH}]{Me^-ONa^+} \underset{\text{(Less yield)}}{CH_3-\overset{\displaystyle OCH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_2CH_3}$$

$$\underbrace{+\,CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH-CH_2-CH_3 + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_2-CH_2CH_3}_{\text{(More yield)}}$$

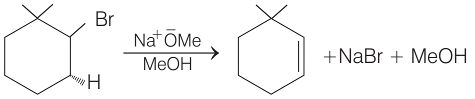
24 $CH_3-\overset{*}{\underset{\displaystyle C_2H_5}{\underset{|}{C}}}H-Br$ contains a chiral carbon and gives a racemic product if it undergoes S_N1 reaction.

25



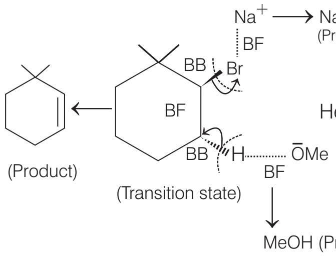
$$C_6H_5-\underset{\displaystyle Cl}{\underset{|}{C}}H-CH_3 \xrightarrow{SbCl_5} \underset{\text{Planar structure}}{[Ph-CH-CH_3]^+[SbCl_6]^-}$$

26 Complete reaction can be represented as



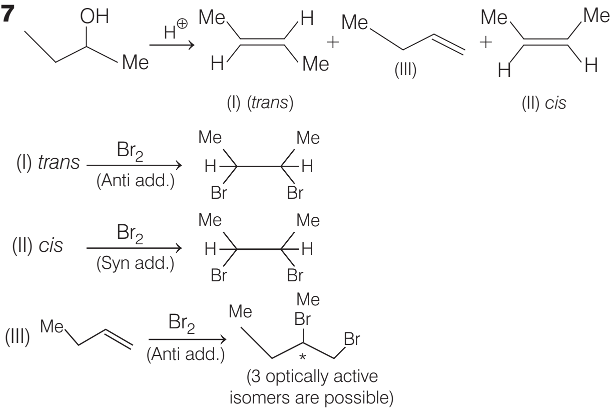
Thus, the given reaction is dehydrohalogenation which is a β-elimination proceeding through E_2 mechanism.

Mechanism The reaction proceeds through the formation of following transition state with simultaneous removal of Br and H-atoms.



Here, BB= Bond breakage
BF= Bond formation

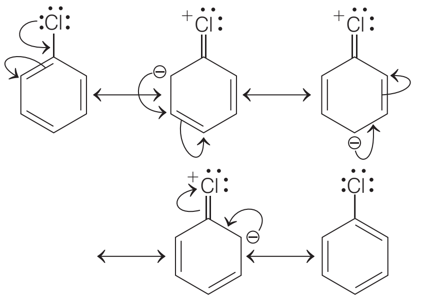
27



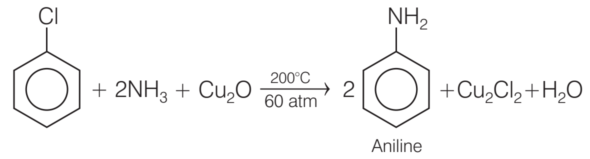
28 The reaction is

$$CH_3-CCl_3 \xrightarrow[\Delta]{6\,Ag} \underset{\text{But-2-yne}}{CH_3-C\equiv C-CH_3} + 6AgCl$$

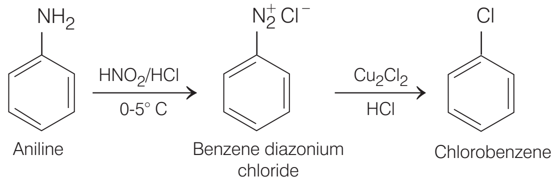
29. Aryl halides are less reactive towards nucleophile than alkyl halides due to resonance.



30

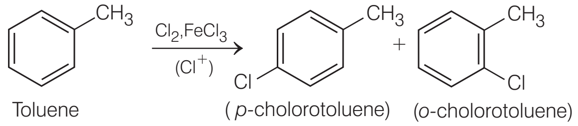


31.



32 Chlorine in chlorobenzene is *ortho*/*para* directing because resonance effect predominates over inductive effect.

33



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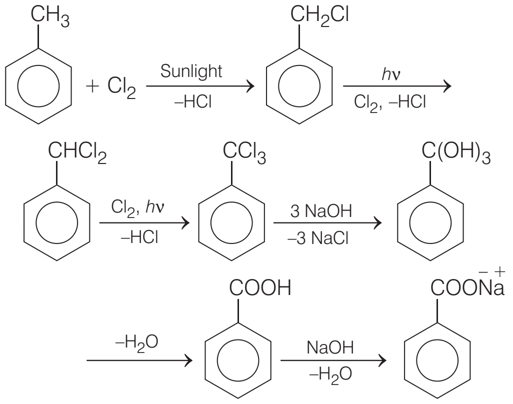
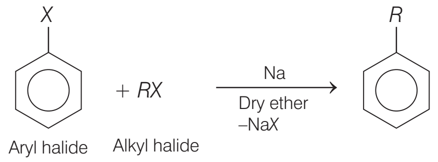
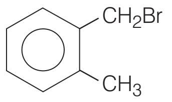


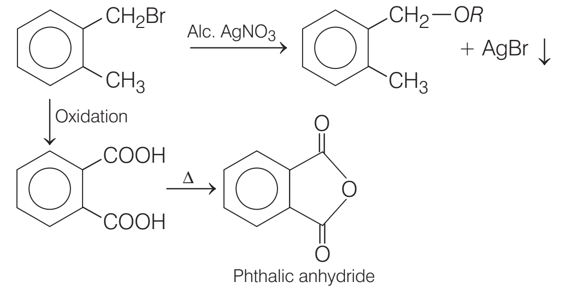
35 When one molecule of alkyl halide undergoes condensation with one molecule of aryl halide in the presence of Na in dry ether, the reaction is called Wurtz–Fittig reaction. e.g.



36 Compound *A* gives a precipitate with alcoholic $AgNO_3$ (here white is misprinting because the colour of precipitate is light yellow), so it must contain Br in side chain. On oxidation, it gives $C_8H_6O_4$, which shows the presence of two alkyl chains attached directly with the benzene nucleus. Since, compound *B* gives anhydride on heating, the two alkyl substituent must occupy adjacent (1, 2) positions. Thus, *A* must be



and the reactions are as follows:



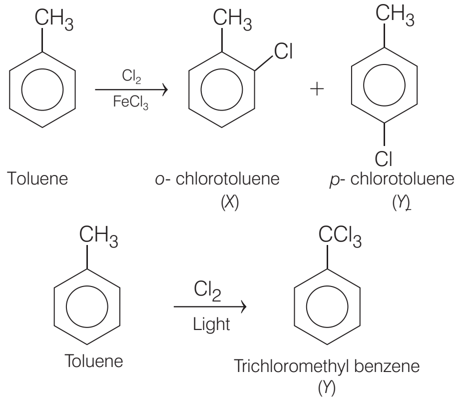
37 CCl_4 at high temperature reacts with water to give phosgene.

$$CCl_4 + H_2O \xrightarrow{500^\circ C} \underset{\text{Phosgene}}{COCl_2} + 2HCl$$

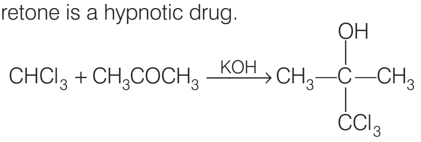
Phosgene is highly poisonous, so after the use of pyrene, CCl_4 to extinguish fire, the room should be well ventilated.

38 Cl_2 in presence of $FeCl_3$ ⟶ ring substitution

Cl_2 in presence of light ⟶ side chain substitution



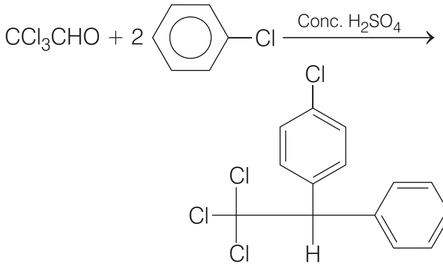
39 Chloretone is a hypnotic drug.



$$CHCl_3 + CH_3COCH_3 \xrightarrow{KOH} CH_3-\underset{CCl_3}{\overset{OH}{C}}-CH_3$$

Chloretone

40



DDT

41 **Correct Assertion** Thionyl chloride is preferred over phosphorus chlorides (tri and penta) for the preparation of alkyl chlorides from alcohols.
Correct Reason Thionyl chloride gives pure alkyl chlorides.

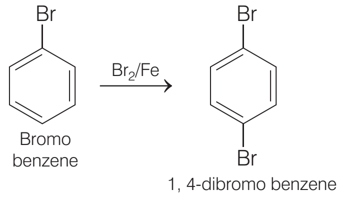
42 Tertiary butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3- tetramethylbutane. In Wurtz reaction, product contain double the number of C-atoms.

43 Alkyl halides are not soluble in water as these are not able to form H-bonds with water molecules.

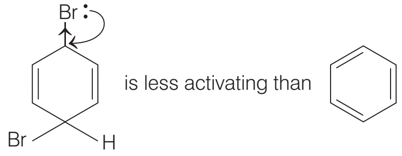
44 Tertiary alkyl halides are more prone to elimination as positive inductive effect of *R*-group weakens C—*X* bond.

45 Aryl halides do not undergo nucleophilic substitution reaction under ordinary conditions. Thus, Assertion I is incorrect. In aryl halides, the carbon-halogen bond has partial double bond character, so it becomes shorter and stronger and cannot be easily replaced by nucleophile.

46

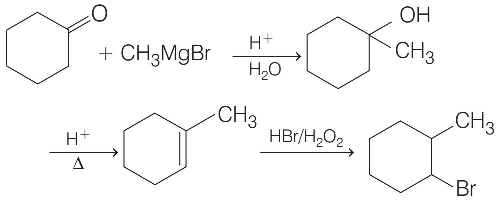


Bromine orientation is controlled by its mesomeric effect, the stabilisation of arenium ion by $+M$ activity. In bromobenzene, the inductive effect of the bromo group is more dominant than the mesomeric effect in the activity of ring.



SESSION 2

1



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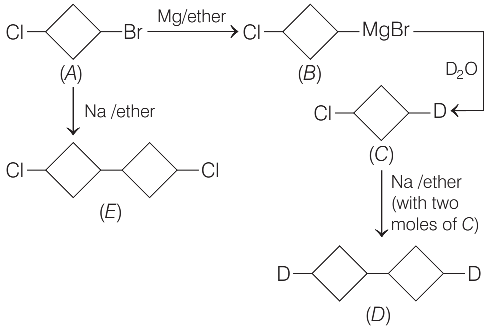
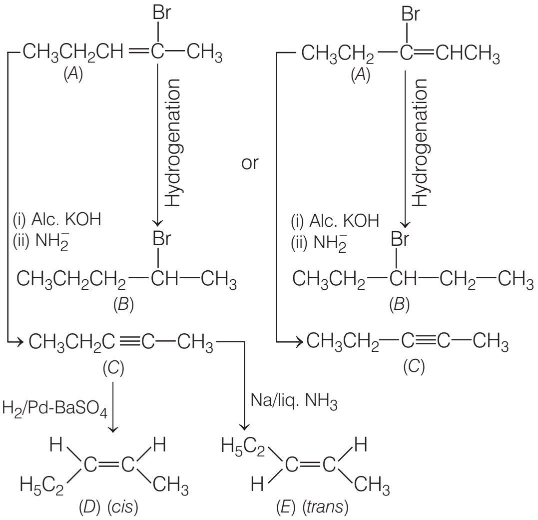


3 Ammonia, being a strong base, favours elimination reaction, rather substitution, when the alkyl halide is 2° or 3°.

4



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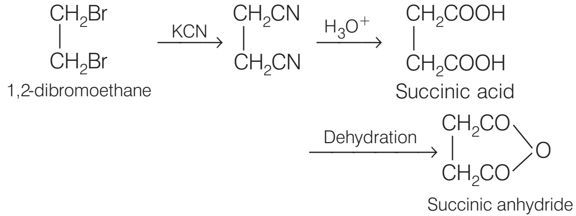

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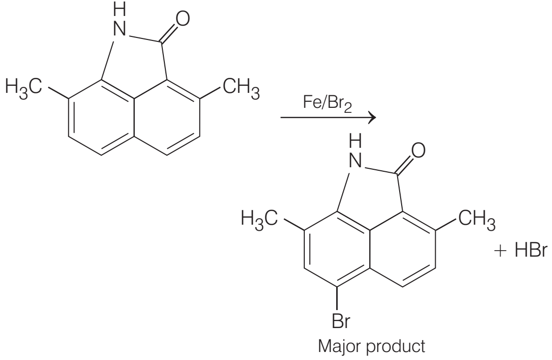


It is an electrophilic substitution reaction so, electrophile must be attacked on *o*/*p*-positions due to higher electron density on these position.

In this ring, the attached —NH-group will have high electron density due to resonance and *ortho* position is blocked, so electrophile is attacked on *para* position.

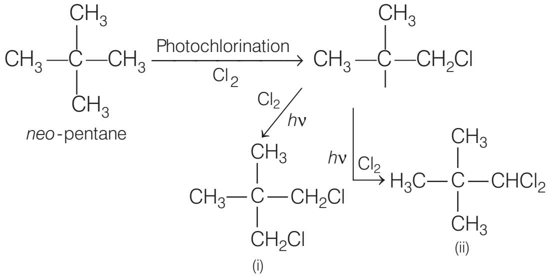
7 With AgCN, due to greater covalency of Ag—C bond, N is the donor atom. In KCN, CN^- exists as free ion and better carbon donor forms the bond.

8 Let the hydrocarbon be C_nH_{2n+2},

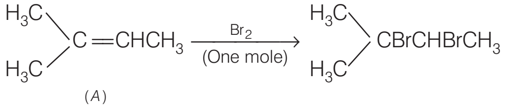
i.e. $12n + 2n + 2 = 72$

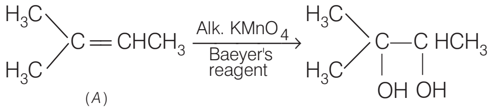
or $n = 5$

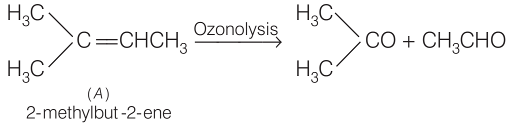
The hydrocarbon is C_5H_{12}. As it forms a single mono chloride, all the hydrogen atoms are equivalent. The compound is $(CH_3)_4C$, i.e. *neo* -pentane.



9 (*A*) adds one mole of Br_2 and thus act as an alkene. (*A*) on ozonolysis forms CH_3COCH_3 and CH_3CHO, thus (*A*) is $(CH_3)_2C{=}CHCH_3$ and the reactions are as follows :







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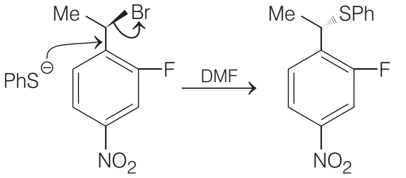
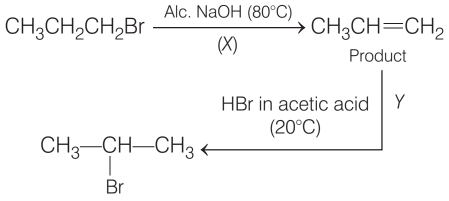


PhS^- is a strong nucleophile and dimethyl formamide (DMF) is a highly polar aprotic solvent.
Condition indicates that bimolecular nucleophilic substitution (S_N2) takes place at 2° benzylic place. Stereochemically, it involves inversion of configuration.

11 In $C_6H_5CH_2$—I, C—I bond is reactive, so it gives yellow precipitate of AgI. On the other hand, C — I bond in C_6H_5I is stable, so it does not give yellow precipitate with $AgNO_3$.

12



13 The best reaction condition leading to the best yield of C_2H_5Cl is (a)

$$C_2H_6 \text{ (excess)} + Cl_2 \xrightarrow{\text{UV-light}} C_2H_5Cl$$

14 $PHCH_2Cl$ forms stable $Ph\overset{\oplus}{C}H_2$ (benzyl C^+) ion. So, the reaction is feasible.