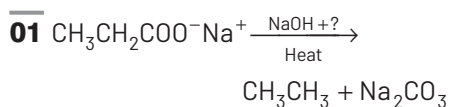


23

Organic Compounds Containing Halogens

TOPIC 1 Haloalkane



Consider the above reaction and identify the missing reagent/chemical. [NEET 2021]

- (a) B_2H_6 (b) Red phosphorus
(c) CaO (d) DIBAL-H

Ans. (c)

In this reaction, removal of carbon dioxide takes place. So, this is a decarboxylation reaction. A decarboxylation reaction takes place with soda lime (NaOH + CaO).

So, missing reagent is CaO.

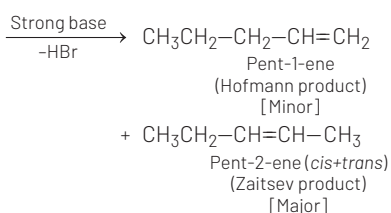
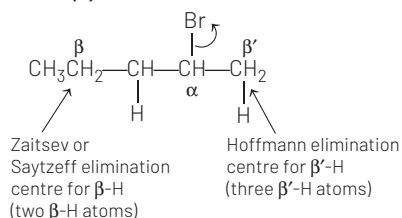
02 Elimination reaction of 2-bromo-pentane to form pent-2-ene is

- β-elimination reaction.
- Follows Zaitsev rule.
- Dehydrohalogenation reaction.
- Dehydration reaction.

[NEET (Sep.) 2020]

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

Ans. (d)



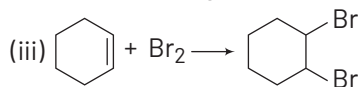
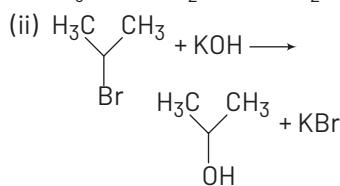
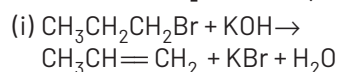
In the above reaction, β-elimination takes place via E_2 mechanism (anti-elimination).

According to Zaitsev rule, β-carbon carrying lesser number of H-atoms get involved in the elimination to give a more substituted alkene (pent-2-ene) as the major product.

Here, loss of HBr, i.e. dehydrobromination (dehydrohalogenation) takes place.

So, 1, 2 and 3 are correct combination.

03 For the following reactions, [NEET 2016, Phase I]

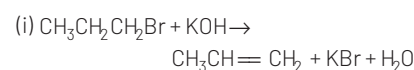


Which of the following statements is correct?

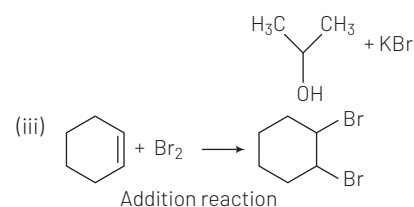
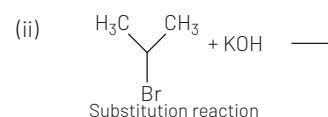
- (a) (i) is elimination reaction, (ii) is substitution and (iii) is addition reaction
(b) (i) is elimination, (ii) and (iii) are substitution reactions

- (c) (i) is substitution, (ii) and (iii) are addition reactions
(d) (i) and (ii) are elimination reactions and (iii) is addition reaction

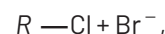
Ans. (a)



Elimination reaction



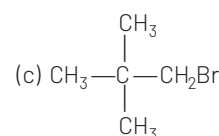
04 In a $\text{S}_\text{N}2$ substitution reaction of the type $\text{R}-\text{Br} + \text{Cl}^- \xrightarrow{\text{DMF}}$



Which one of the following has the highest relative rate?

[CBSE AIPMT 2008]

- (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$
(b) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2\text{Br}$



- (d) $\text{CH}_3\text{CH}_2\text{Br}$

Ans. (d)

Aprotic solvents like DMF increases the reactivity of nucleophile and favours S_N2 reaction.

The relative reactivity of alkyl halides towards S_N2 reactions is as follows
 $CH_3-X > \text{Primary} > \text{Secondary} > \text{Tertiary}$

However, if the primary alkyl halide or the nucleophile/base is sterically hindered the nucleophile will have difficulty to getting the back side of the α -carbon as a result of this, the elimination product will be predominant. Here, CH_3CH_2Br is the least hindered, hence it has the highest relative rate towards S_N2 reaction.

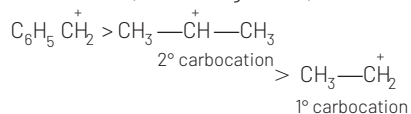
05 Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism?
[CBSE AIPMT 2005]

- (a) Benzyl chloride
- (b) Ethyl chloride
- (c) Chlorobenzene
- (d) Isopropyl chloride

Ans. (a)

Aliphatic S_N1 reaction is carried out in two steps. In form of slow step Step (i) carbonium (carbocation) ion is formed and its formation is based upon the stability

Stability order of carbocation benzylic carbocation (resonating stable)



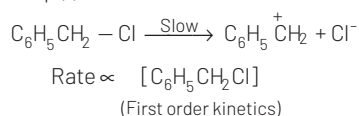
and in step (ii) nucleophile is attracted towards the carbonium ion in form of fast step to give final product.

Hence, in benzyl chloride, ethyl chloride and isopropyl chloride order of S_N1 reaction is benzyl chloride > isopropyl chloride > ethyl chloride.

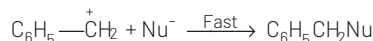
In chlorobenzene, mechanism of S_N1 reaction differ to aliphatic alkyl halide. The aryl halides are much less reactive as compared to alkyl halides, towards nucleophilic reagents in either S_N1 or S_N2 reaction.

The carbon-halogen bond in the aryl halide is quite strong and only forcing conditions can break up this bond.

Hence,
Step (i)



Step (ii)

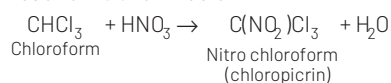


06 Chloropicrin is obtained by the reaction of [CBSE AIPMT 2004]

- (a) steam on carbon tetrachloride
- (b) nitric acid on chlorobenzene
- (c) chlorine on picric acid
- (d) nitric acid on chloroform

Ans. (d)

Chloroform on reaction with nitric acid gives chloropicrin (nitro chloroform). Its reaction is shown below



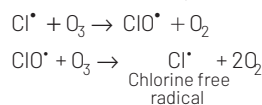
07 Which of the following is responsible for depletion of the ozone layer in the upper strata of the atmosphere?
[CBSE AIPMT 2004]

- (a) Polyhalogens
- (b) Ferrocenes
- (c) Fullerenes
- (d) Freons

Ans. (d)

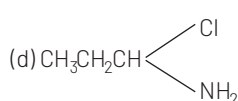
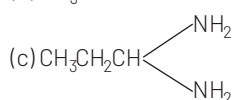
Freons or chlorofluoro carbons are responsible for depletion of the ozone layer in the upper strata of the atmosphere. They are used as propellants, aerosol spray caps, refrigerants, fire fighting reagents, etc. They are stable and chemically inert compounds. They absorb UV-radiation and break down liberating free atomic chlorine which causes decomposition of ozone through free radical reaction. This results in the depletion of the ozone layer.

They form free radical of chlorine in presence of UV-radiation. Such free radical decomposes O_3 as follows :

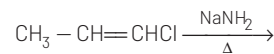
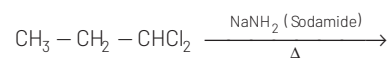


08 When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is [CBSE AIPMT 2002]

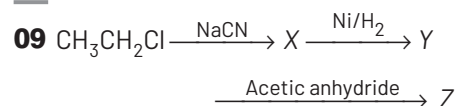
- (a) $CH_3-CH=CH_2$
- (b) $CH_3-C \equiv CH$



Ans. (b)



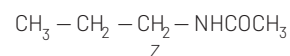
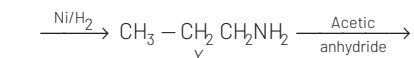
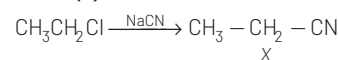
$CH_3-C \equiv CH$
Final product



In above reaction sequence, Z is [CBSE AIPMT 2002]

- (a) $CH_3CH_2CH_2NHCOCH_3$
- (b) $CH_3CH_2CH_2NH_2$
- (c) $CH_3CH_2CH_2CONHCH_3$
- (d) $CH_3CH_2CH_2CONHCOCH_3$

Ans. (a)

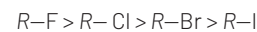


10 Reactivity order of halides for dehydrohalogenation is [CBSE AIPMT 2002]

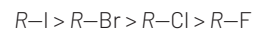
- (a) $R-F > R-Cl > R-Br > R-I$
- (b) $R-I > R-Br > R-Cl > R-F$
- (c) $R-I > R-Cl > R-Br > R-F$
- (d) $R-F > R-I > R-Br > R-Cl$

Ans. (b)

F, Cl, Br and I are the elements of VII A group. In a group atomic radii increases from top to bottom and the bond dissociation energy decreases as



So, during dehydrohalogenation $R-I$ bond breaks more easily than $R-F$ bond. Hence, order of reactivity will be

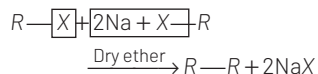


11 An organic compound A (C_4H_9Cl) on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative, then A is [CBSE AIPMT 2001]

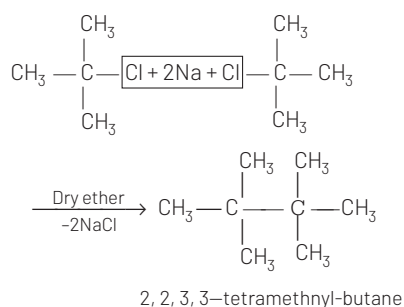
- (a) t-butyl chloride
- (b) s-butyl chloride
- (c) iso-butyl chloride
- (d) n-butyl chloride

Ans. (a)

Alkyl halides react with Na in presence of dry ether to form alkanes. This reaction is known as Wurtz reaction.



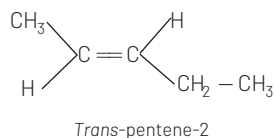
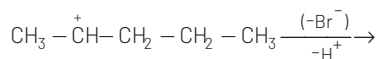
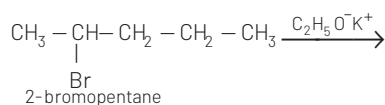
In the given question *t*-butyl chloride $\text{C}_4\text{H}_9\text{Cl}$ is A. It reacts with Na metal in dry ether to form a hydrocarbon that on chlorination gives only one monochloro derivative.



12 2-bromopentane is heated with potassium ethoxide in ethanol. The major product obtained is [CBSE AIPMT 1998]

- (a) 2-ethoxypentane
- (b) pentene-1
- (c) *trans*-pentene-2
- (d) *cis*-pentene-2

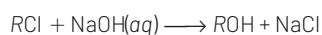
Ans. (c)



13 The alkyl halide is converted into an alcohol by [CBSE AIPMT 1997]

- (a) addition
- (b) substitution
- (c) dehydrohalogenation
- (d) elimination

Ans. (b)



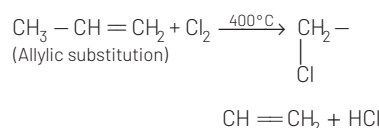
It is an example of nucleophilic substitution reaction.

14 When chlorine is passed through propene at 400°C , which of the following is formed?

- (a) PVC [CBSE AIPMT 1993]
- (b) Allyl chloride
- (c) Nickel chloride
- (d) 1,2-dichloro ethane

Ans. (b)

When chlorine gas is reacted with propene at high temperature (400°C), then substitution occurs in place of addition reaction. Hence, allyl chloride is formed



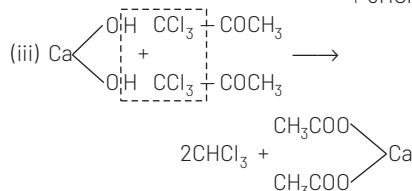
15 Industrial preparation of chloroform employs acetone and [CBSE AIPMT 1993]

- (a) phosgene
- (b) calcium hypochlorite
- (c) chlorine gas
- (d) sodium chloride

Ans. (b)

The industrial preparation of chloroform involves the following steps:

- (i) $\text{CaOCl}_2 + \text{H}_2\text{O} \longrightarrow \text{Ca(OH)}_2 + \text{Cl}_2$
- (ii) $\text{CH}_3\text{COCH}_3 + 3\text{Cl}_2 \longrightarrow \text{CCl}_3\text{COCH}_3 + 3\text{HCl}$

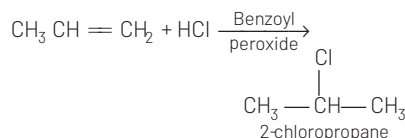


16 When hydrochloric acid gas is treated with propene in presence of benzoyl peroxide, it gives [CBSE AIPMT 1993]

- (a) 2-chloropropane
- (b) alkyl chloride
- (c) no reaction
- (d) *n*-propyl chloride

Ans. (a)

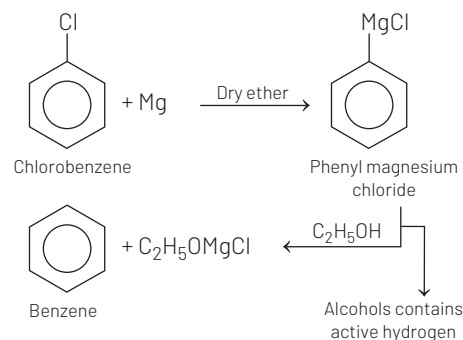
Kharasch effect or peroxide effect is only observed in case of addition of HBr to unsymmetrical alkenes, so the addition of HCl with propene takes place as usual by Markownikoff's rule



17 Chlorobenzene reacts with Mg in dry ether to give a compound (A) which further reacts with ethanol to yield [CBSE AIPMT 1993]

- (a) phenol
- (b) benzene
- (c) ethyl benzene
- (d) phenyl ether

Ans. (b)

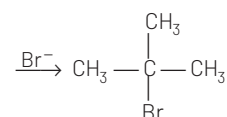
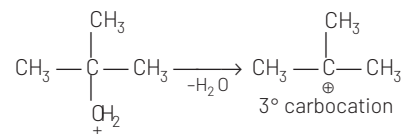
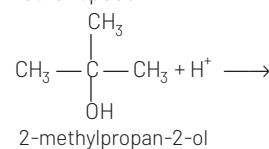


18 HBr reacts fastest with [CBSE AIPMT 1992]

- (a) 2-methyl propan-1-ol
- (b) 2-methyl propan-2-ol
- (c) propan-2-ol
- (d) propan-1-ol

Ans. (b)

2-methylpropan-2-ol gives 3° carbocation, so it reacts with HBr at faster speed.



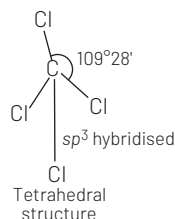
19 In compound 'X' all the bond angles are exactly $109^\circ 28'$, 'X' is [CBSE AIPMT 1991]

- (a) chloromethane
- (b) carbon tetrachloride
- (c) iodoform
- (d) chloroform

Ans. (b)

Carbon tetrachloride (CCl_4) have sp^3 hybridisation and symmetrical

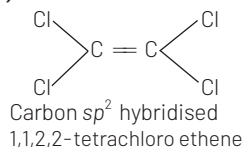
structure, so it have all the bond angle of $109^\circ 28'$.



- 20** The Cl—C—Cl angle in 1,1,2,2-tetrachloroethene and tetrachloromethane will be about [CBSE AIPMT 1988]

- (a) 120° and $109^\circ 28'$
 (b) 90° and 109.5°
 (c) 109.5° and 90°
 (d) 109.5° and 120°

Ans. (a)

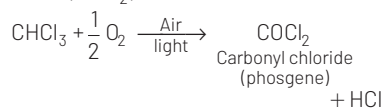


- 21** Phosgene is a common name for [CBSE AIPMT 1988]

- (a) phosphonyl chloride
 (b) thionyl chloride
 (c) carbon dioxide and phosphine
 (d) carbonyl chloride

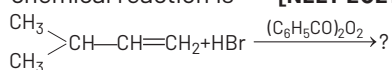
Ans. (d)

Chloroform is slowly oxidised into a poisonous compound called phosgene in the presence of air or light. This compound is also called carbonyl chloride (COCl_2)

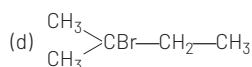


TOPIC 2 Haloarene

- 22** The major product of the following chemical reaction is [NEET 2021]



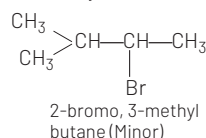
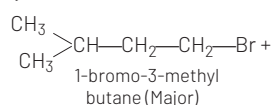
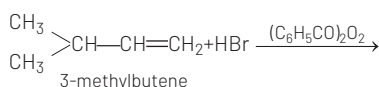
- (a) $\text{CH}_3 \text{ > CH-CH}_2\text{-CH}_2\text{-Br}$
 (b) $\text{CH}_3 \text{ > CH-CH}_2\text{-CH}_2\text{-O-COC}_6\text{H}_5$
 (c) $\text{CH}_3 \text{ > CH-CH(Br)-CH}_3$



Ans. (a)

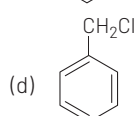
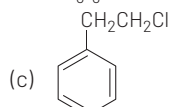
Addition of HBr to an alkene in presence of a peroxide (benzoyl peroxide $[(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2]$) gives an anti-Markownikoff's product.

Anti-Markownikoff's rule states that hydrogen is added to a more substituted carbon atom of an unsymmetrical alkene.



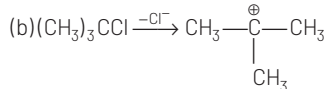
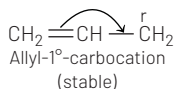
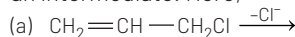
- 23** Which of the following will not undergo $\text{S}_\text{N}1$ reaction with OH^- ? [NEET (Oct.) 2020]

- (a) $\text{CH}_2=\text{CH-CH}_2\text{Cl}$
 (b) $(\text{CH}_3)_3\text{CCl}$

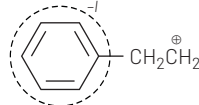
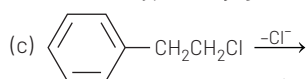


Ans. (c)

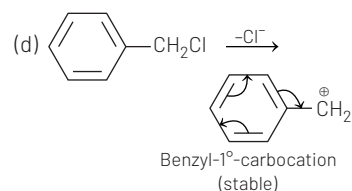
An $\text{S}_\text{N}1$ reaction proceeds through formation of a stable carbocation as an intermediate. Here,



tert-butyl carbocation (stable)
(9 hyper conjugation)

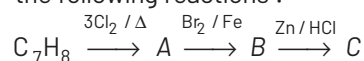


1° -carbocation (less stable due to -I effect of the phenyl group)



So, option (c) will not undergo $\text{S}_\text{N}1$ reaction with OH^- .

- 24** The compound C_7H_8 undergoes the following reactions :

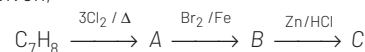


The product 'C' is [NEET 2018]

- (a) 3-bromo-2, 4, 6-trichlorotoluene
 (b) o-bromotoluene
 (c) m-bromotoluene
 (d) p-bromotoluene

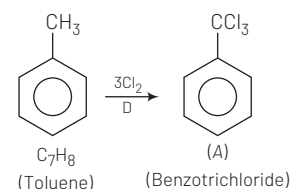
Ans. (c)

Given,

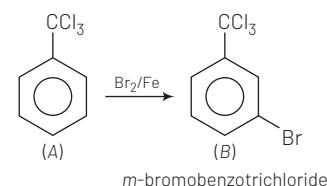


The reaction in the above road map can be explained by the following steps.

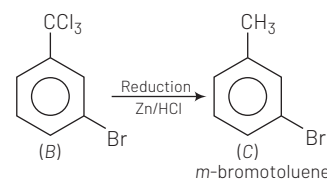
Step I Toluene (A) undergoes side chain halogenation with excess of chlorine to give benzotrichloride (A).



Step II In compound (A), the substituent CCl_3 is an electron withdrawing group, so the electrophile will attack at m-position. Thus, benzotrichloride reacts with bromine in presence of Fe-catalyst to give m-bromobenzotrichloride (B).



Step III m-bromobenzotrichloride undergoes reduction with Zn in presence of HCl to give m-bromotoluene (C).



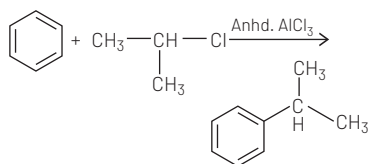
25 Which of the following can be used as the halide component for Friedel-Crafts reaction?

[NEET 2016, Phase II]

- (a) Chlorobenzene
 (b) Bromobenzene
 (c) Chloroethene
 (d) Isopropyl chloride

Ans. (d)

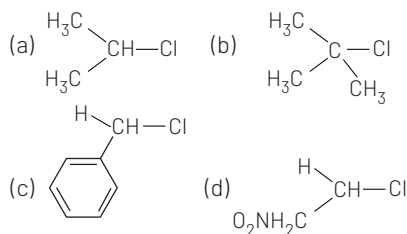
Key Idea In chlorobenzene, bromobenzene and chloroethene, lone pair of halogen is delocalised with π -bonds so it attains double bond character. Thus, these are not suitable as a halide component for Friedel-Crafts reaction.



Other halides, i.e. chloro and bromobenzene along with chloroethene have carbon halogen bond as

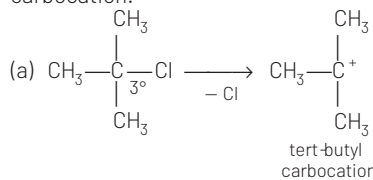


26 In which of the following compounds, the C-Cl bond ionisation shall give most stable carbonium ion? [CBSE AIPMT 2015]



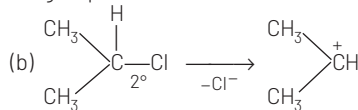
Ans. (c)

The stability of carbocation follow the order $3^\circ > 2^\circ > 1^\circ > \text{methyl}$. More the number of alkyl group attached with the carbon atom carrying the positive charge greater would be the tendency to stabilise positive charge via inductive effect and hence more stable is that carbocation.

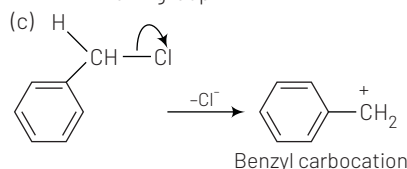


This carbocation is more stable due to nine α -hydrogen and (nine

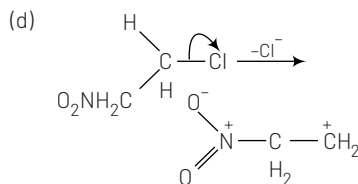
hyperconjugative structures) three α groups.



2° carbocation containing 6 α -hydrogen showing six hyperconjugative structure along with two α group.



It has slightly lesser stability as compared to 3° -alkyl carbocation due to presence of three electron donating alkyl group in 3° -alkyl carbocation. Although the stabilities of 3° and benzyl carbonium ion are almost same and cannot be compared in solution but whenever a comparison is made between **Resonance** (the cause of stability in benzyl carbonium ion) and **No bond resonance** (the cause of stability in 3° carbonium ion) then the former is always preferred hence here in this question benzyl carbonium ion is more stable than 3° carbonium ion.



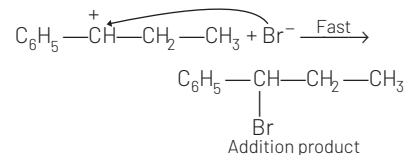
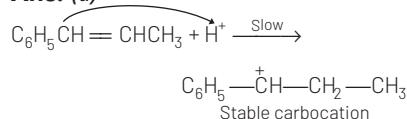
1° carbocation less stable than all present here.

27 The reaction of $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ with HBr produces

[CBSE AIPMT 2015]

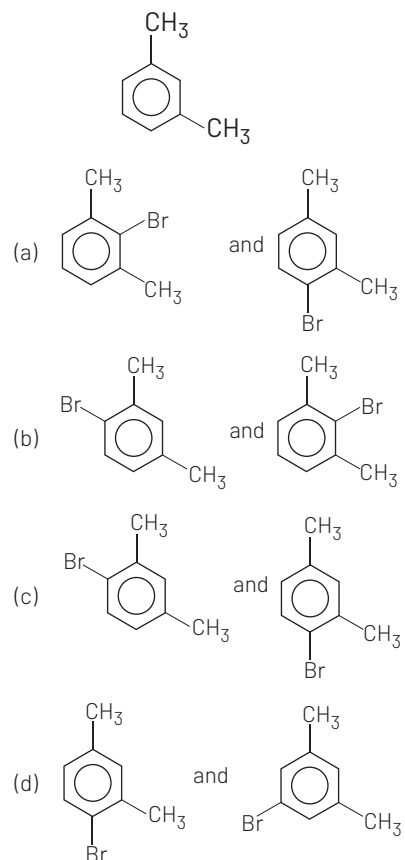
- (a) $\text{C}_6\text{H}_5-\text{CH}(\text{Br})-\text{CH}_2\text{CH}_3$
 (b) $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}(\text{Br})-\text{CH}_3$
 (c) $\text{C}_6\text{H}_5-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$
 (d) $\text{C}_6\text{H}_5-\text{CH}(\text{Br})-\text{CH}=\text{CH}_2$

Ans. (a)



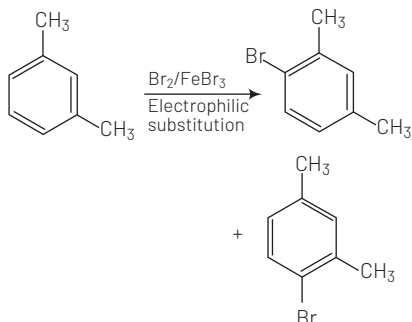
Electrophilic addition reaction takes place via more stable carbocation.

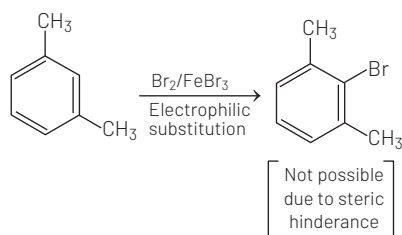
28 What products are formed when the following compound is treated with Br_2 in the presence of FeBr_3 ? [CBSE AIPMT 2014]



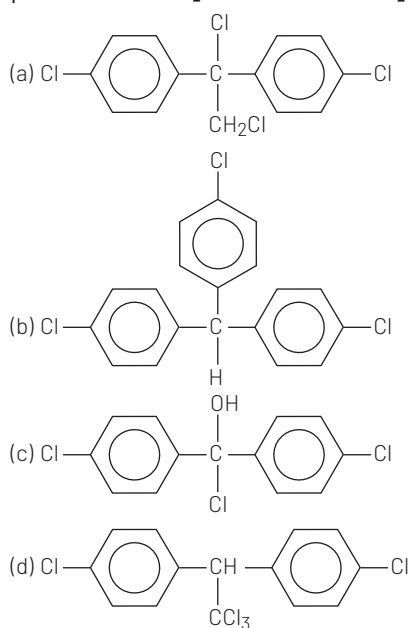
Ans. (c)

CH_3 is a *o/p*-directing group, thus electrophilic substitution reaction of toluene

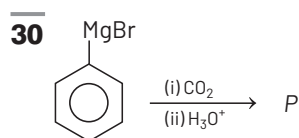
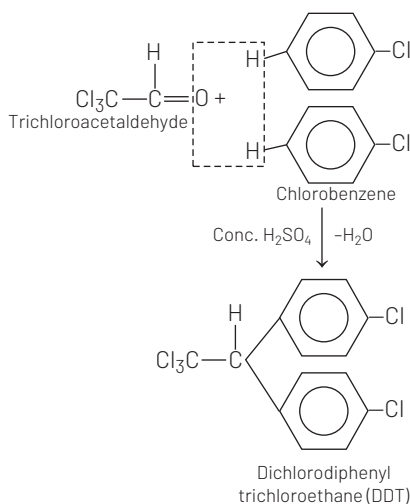




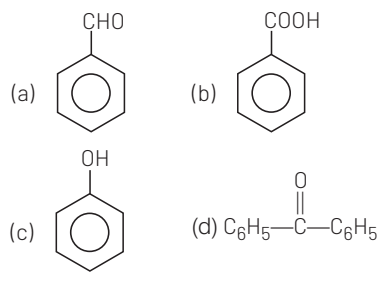
29 Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in the presence of sulphuric acid and produces **[CBSE AIPMT 2009]**



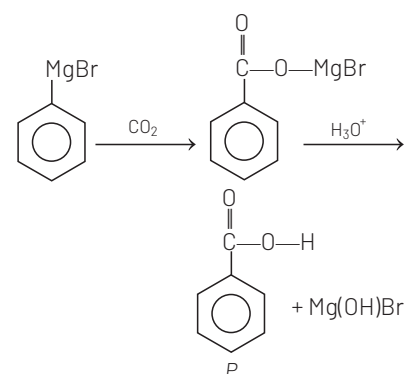
Ans. (d)



In the above reaction product 'P' is **[CBSE AIPMT 2002]**



Ans. (b)



31 Replacement Cl of chlorobenzene to give phenol requires drastic conditions but chlorine of 2, 4-dinitro chlorobenzene is readily replaced. This is because **[CBSE AIPMT 1997]**

- (a) NO_2 makes the ring electron rich at *ortho* and *para*-positions
- (b) NO_2 withdraw electrons from *meta*-position
- (c) NO_2 donates electrons at *meta*-position
- (d) NO_2 withdraw electrons from *ortho/para*-positions

Ans. (d)

$-\text{NO}_2$ group is electron withdrawing group, so it deactivates the benzene ring. Due to electron withdrawing nature of $-\text{NO}_2$ group, it develops positive charge at *o/p* position. This cause easier for the removal of $-\text{Cl}$ -atom.