12. ALKYL HALIDES, ARYL HALIDES AND AROMATIC COMPOUNDS

ALKYL HALIDES

1. INTRODUCTION

When hydrogen atoms or atoms of alkanes are replaced by a corresponding number of halogen atoms, the compounds are called halogen derivatives of alkanes.

They are classified according to the number of halogen atoms that replace hydrogen atoms in the alkane.

Monohalogen derivatives: They contain only one halogen atom.

E.g. CH_3Cl Methyl chloride

$CH_3CH(Br)CH_3$ 2-bromopropane

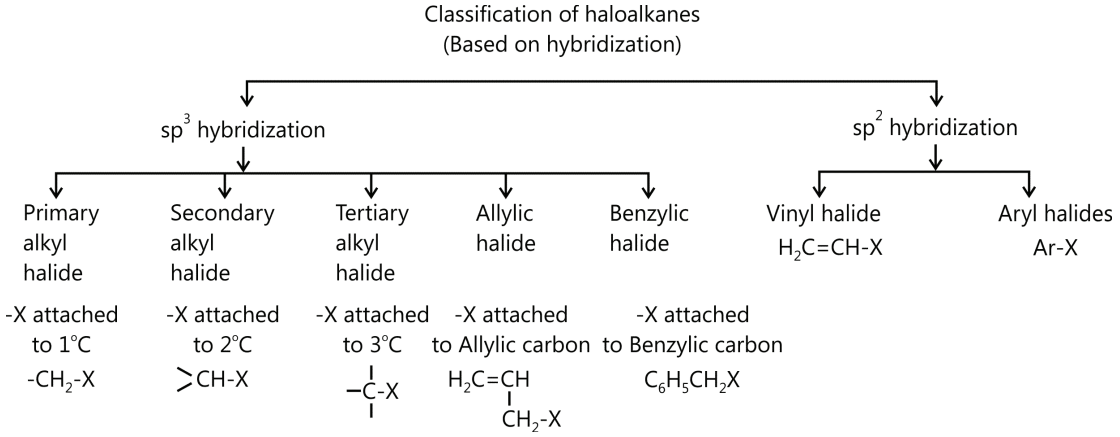
Monohalogen derivatives of alkane are called alkyl halides

Dihalogen alkanes contain two halogen atoms.

Trihalogen alkanes contain three halogen atoms.

Monohaloalkanes

The general formula is RX where R is an alkyl group and X is a halogen.



Flowchart 12.1: Classification of haloalkanes

Common system: 'Alkyl halides' are the monohalogen derivatives of alkanes. These are named by naming the alkyl group attached to halogen and adding the name of the halide. E.g. Methyl halide, Isobutyl halide.

The name of the alkyl group and halide are written as two separate words. The prefixes used to distinguish alkanes like n-, iso-, sec-, tert, etc. are also written.

IUPAC system: Rules for naming haloalkanes that have branches in carbon chains:

The monohalogen derivatives of alkanes are called haloalkanes. The name of haloalkanes are written by prefixing the word 'halo' (bromo or chloro or iodo or fluoro) to the name of the alkane corresponding to the longest continuous carbon chain holding the halogen atom. E.g. Bromoethane E.g. Trichloromethane

(a) The longest continuous chain containing the carbon attached to halogen group is selected as the parent alkane (principal chain or parent chain). While naming alkanes, all the rules that apply to alkane names should be followed.

(b) The carbon atoms are numbered in such a way that the halogen carrying carbon atom gets the lowest number.

(c) The position of the halogen atom and other substituents are indicated by numbers 1,2,3....etc.
E.g. 1-Iodo-2-methylpropane

Dihalo derivatives

(a) When two halogen atoms are attached to the same Carbon-atom, these are called geminal dihalides. Alkylidene dihalides or alkylidene dihalides are also names used for such compounds. E.g. ethlydine dichloride

(b) When two halogen atoms are attached to adjacent Carbon-atoms, they are called vicinal dihalides. As they are prepared from alkenes, they are named as the dihalide of the alkene from which they are prepared. E.g. ethylene dichloride

Polyhalo derivatives: Polyhalo derivative are compounds with multiple halogen atom. These have important application in agricultural industry.

Fully halogenated hydrocarbons are also called perhalohydrocarbons under a common system.

Nomenclature of aryl halides: Aryl halides are termed Haloarenes in IUPAC systems. 'Halo' (bromo or chloro or iodo or fluoro) is prefixed before the name of the aromatic hydrocarbon. In case of disubstituted compounds, the relative positions are indicated by (1,2), (1,3) or (1,4). Ortho, meta and para are also used to indicate the positions. E.g. Chlorobenzene, Bromobenzene.

2. PHYSICAL PROPERTIES OF ALKYL HALIDES

(a) Boiling point: The below chart shows the boiling point of some simple haloalkanes.

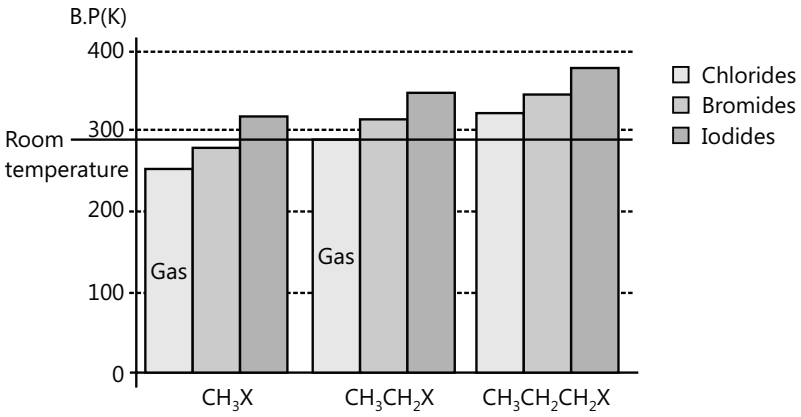


Figure 12.1: Boiling points of haloalkanes

Notice that three of these have b.ps' below room temperature (taken as being about 20° C). These will be gaseous at room temperature. All the other you are likely to come across are liquids.

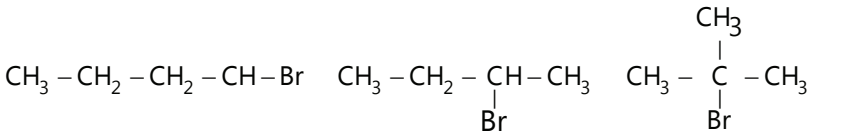
MASTERJEE CONCEPTS

- The only methyl halide which is a liquid is iodomethane.
- Chloroethane is a gas.

The pattern in b.p. reflects the patterns in intermolecular attractions.

Vaibhav Krishnan (JEE 2009, AIR 22)

(b) Boiling point of some isomers: The example shows that the boiling point fall as the isomers go from a primary to a secondary to a tertiary haloalkane.



To put it simply, this is the result of the fall in the effectiveness of the dispersion forces. The temporary dipoles are greatest for the longest molecule. The attractions will also be stronger if the molecules can lie closely together. The tertiary haloalkane is very short and fat, and won't have much close contact with its neighbours.

(c) Solubility of haloalkanes

(i) Solubility in water: The haloalkanes are very slightly soluble in water. In order to dissolve haloalkane in water, you have to break attractions between the haloalkane molecules (van der Waals dispersion and dipole-dipole interactions) and break the hydrogen bonds between water molecules. Energy is released when new attractions are set up between the haloalkane and the water molecules. These will only be dispersion forces and dipole-dipole interactions. These aren't as strong as original hydrogen bonds in the water, and so not as much energy is released as was used to separate the water molecules.

(ii) Solubility in organic solvents: Haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions have the same strength as the ones being broken in the separate haloalkane and solvent.

3. CHEMICAL REACTIVITY OF HALOALKANES

The importance of bond strengths: The pattern in strengths of the four carbon-halogen bonds are:

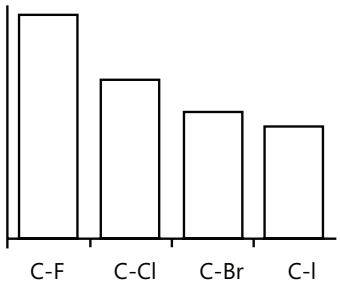


Figure 12.2: Carbon-halogen bond strength

Bond strength falls as you go from C-F to C-I(C-F being the strongest)

MASTERJEE CONCEPTS

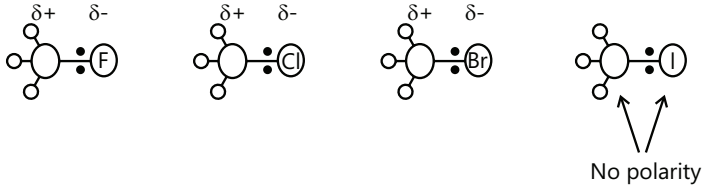
You will find almost as many different values for bond strengths (or bond enthalpies or bond energies) as there are different sources! Don't worry about this-the pattern is always the same. This is why you have got a chart here rather than actual numbers.

Saurabh Gupta (JEE 2010, AIR 443)

In order for anything to react with the haloalkanes, the carbon-halogen bond has got to be broken. As that gets easier when you go from fluoride to chloride to bromide to iodide, the compounds get more reactive in that order. Iodoalkanes are the most reactive and fluoroalkanes are the least. In fact, fluoroalkanes are non-reactive and thus, not considered.

The influence of bond polarity: Out of the four halogens, fluorine is the most electronegative and iodine the least. This means that the electron pair in the C-F bond will be dragged most towards the halogen end.

Let's look at the methyl halides as a simple example:



One of the important set of reactions of haloalkanes is substitute reactions, which involves replacing the halogen by something else. These reactions involve:

(a) The carbon-halogen bond breaking to give positive and negative ions. The ion with the positively charged carbon atom then reacts with something either fully or slightly negatively charged. Or,

(b) Something either fully or negatively charged attracted to the slightly positive carbon atom and pushing off the halogen atom.

The thing that governs the reactivity is the strength of the bonds which have to be broken. It is difficult to break a C-F bond, but easy to break a C-I one.

Illustration 1: (a) Dipole moment of CH_3F is 1.85 D and that of CD_3F is 1.86D. **(JEE MAIN)**

(b) 8-Hydroxy quinoline can be sepated from 4-hydroxy quinolone by steam distillation.

Sol: (a) Both the compound has dipole moment as they do not have structural symmetry but CD_3F has higher dipole moment compared to CH_3F, It is due to the large size of CD_3F, but D is less EN than H. $(\mu = q \times d)$

(b) 8-Hydroxy quinoline can be sepated from 4-hydroxy quinolone by steam distillation as it has higher boiling point due to intermolecular H-bonding.

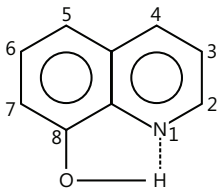
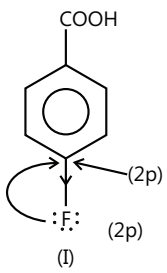


Illustration 2: (a) The pK_a of p-fluorobenzoic acid (I) is 4.14, whereas that of p-chlorobenzoic acid (II) is 3.99.

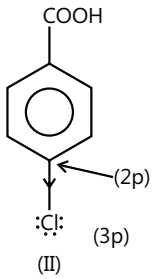
(b) Glycine exists as zwitterion, but PABA does not. **(JEE MAIN)**

Sol: (a) pK_a is a quantitative measure of the strength of an acid in solution. The larger the pK_a value, the more dissociation of the molecules in solution and thus the stronger the acid.

In p-Fluorobenzoic acid + R (resonance effect) is more due to more effective overlap of 2p of F and 2p of C; combined effect of +R and –I, net e^- donating by resonance is slightly more. So, it is a weaker acid than p-chlorobenzoic acid.



In case of p-chlorobenzoic acid +R (resonance effect)is very less, due to less effective overlap of 3p of Cl and 2p of C. Combined effect of +R and –I; net e^--withdrawing effect is more. So, it is a stronger acid than p-fluorobenzoic acid.

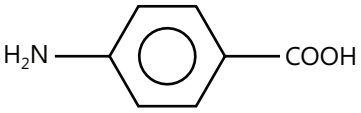


(b) At a particular pH certain organic molecule (amino acids) exist as a Dipolar ion. These are called as Zwitter ion. Zwitter ion contains one positive and one negative charge and thus they are electrically neutral.

Glycine is an amino acid it contains both acidic and basic functional group thus $\left(H_2N-CH-COOH \rightleftharpoons H_3N^{\oplus}-CH_2-COO^{\ominus}\right)$, the aliphatic $\left(-NH_2\right)$ group is sufficiently basic to

(Dipolar or Zwitter Ion)

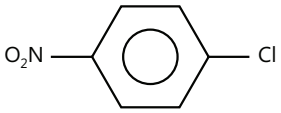
accept $H^{\oplus}$ from $\left(-COOH\right)$ and exists as a dipolar ion (zwitterion),



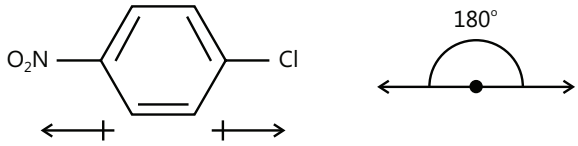
whereas in PABA (p-amino benzoic acid; an aromatic acid, due to presence of electron donating group $\left(-COOH\right)$ is not strong enough to donate $H^{\oplus}$ to a much weaker base $\left(Ar-NH_2\right)$. So, the dipolar ion is not formed.

Illustration 3: Calculate the dipole moment of the following compound:

Given: $\mu_{C-Cl}=1.55D$ $\mu_{C-NO_2}=3.95D$



Sol: Dipole moment is given by μ = q × r



$R^2=P^2+Q^2+2PQ\cos\theta$

$=P^2+Q^2+2PQ\cos180=P^2+Q^2-2PQ;$

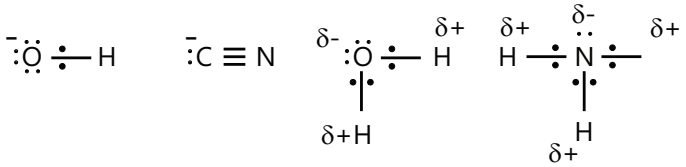
$R^2=\left(P+Q\right)^2;\quad R=\left(P+Q\right)\qquad\therefore R=3.95-1.55=2.4D$

4. CHEMICAL REACTIONS OF ALKYL HALIDES

(a) Nucleophilic substitution reaction

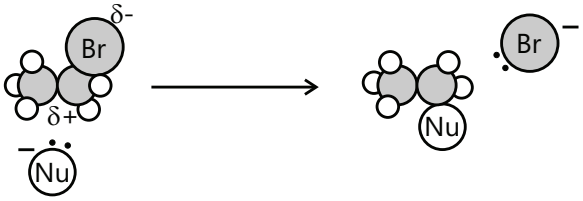
(i) Nucleophilic substitution in primary haloalkanes

Nucleophiles: A nucleophile is a species (an ion or a molecule) which is strongly attracted to a region of positive charge.



Nucleophiles are either fully negative ions, or have a strong –ve charge. Common nucleophiles are hydroxide ions, cyanide ions, water and ammonia. Notice that each of these contains at least one lone pair of electrons either on an atom carrying a full negative charge, or on a very electronegative atom carrying a substantial-charge.

The nucleophilic substitution reaction –an S_N2 reaction: We'll discuss this mechanism by using an ion as a nucleophile because it's slightly easier. The water and ammonia mechanisms involve an extra step which you can read about on the pages describing those particular mechanisms. We'll take bromoethane as a typical primary halogenoalkane. The bromoethane has a polar bond between the carbon and the bromine. We'll look at its reaction with a general purpose nucleophilic ion which we'll call Nu^-. This will have at least one lone pair of electrons. Nu^- could, for example, be OH^- or CN^-. The lone pair on the Nu^- ion will be strongly attracted to the +carbon, and will move towards it and begin making a co-ordinate (dative covalent) bond. In the process, the electrons in the C-Br bond will be pushed even closer towards the bromine, making it increasingly negative.



The movement goes on until the –Nu is firmly attached to the carbon, and the bromine has been expelled as a Br^- ion.

Note: We haven't shown all the lone pairs on the bromine here. These other lone pairs aren't involved in the reaction, and including them simply clutters the diagram to no purpose.

Things to notice: The Nu^- ion approaches the carbon from the far side of the bromine atom. The large bromine atom hinders attack from the side nearest to it and, being –ve would repel the incoming Nu^- anyway. This attack from the back is important if you need to understand why tertiary haloalkanes have a different mechanism. There is obviously a point in which the Nu^- is half attached to the carbon, and the C-Br bond is half way to being broken. This is called a transition state. It isn't an intermediate. You can't isolate it - even for a short time. It's just the mid-point of a smooth attack by one group and the departure of another.

$$\overset{+}{C}H_3 + :\overline{N}u \rightarrow H_3C - Nu$$

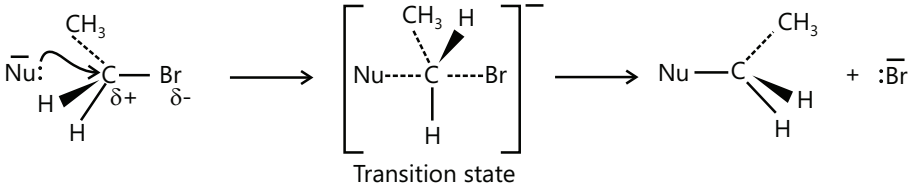
MASTERJEE CONCEPTS

In exam, you must show the lone pair of electrons on the nucleophile (in this case, the Nu^- ion). It probably doesn't matter whether you show them on the departing Br-ion or not.

Aman Gour (JEE 2012, AIR 230)

Technically, this is known as an S_N2 reaction. S stands for substitution, N for nucleophilic, and the 2 refers to the initial stage of the reaction that involves two species –the bromoethane and the Nu^- ion.

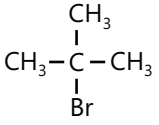
Mechanism: The step-wise mechanism needs to be drawn as shown with very clear details as it gives one a picture of the molecule's arrangement in space.



Transition state

Notice that the molecule has been inverted during the reaction-rather like an umbrella being blown inside-out.

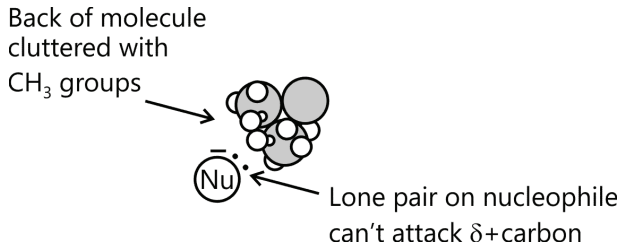
(ii) Nucleophilic substitution in tertiary haloalkanes: Remember that a tertiary haloalkane has three alkyl groups attached to the carbon with the halogen on it. These alkyl groups can be the same or different. Consider a simple one, $(CH_3)_3CBr$ - 2 - bromo-2-methylpropane.



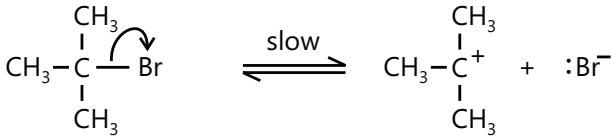
The nucleophilic substitution reaction-an S_N1 reaction

Why is a different mechanism necessary?

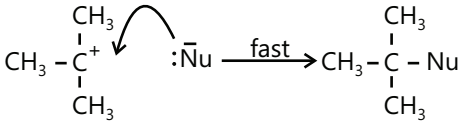
You will remember that when a nucleophile attacks a primary haloalkane, it approaches the +ve C from the side away from the halogen atom. With a tertiary haloalkane, this is impossible. The back of the molecule is completely cluttered with CH_3 groups.



The alternative mechanism: The reaction happens in two stages. In the first, a small proportion of the haloalkane ionizes to give a carbocation and a bromide ion.



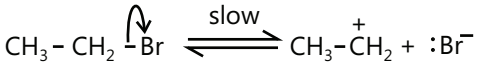
This reaction is possible because tertiary carbocations are relatively stable compared to secondary or primary ones. Even so, the reaction is slow. However, once the carbocation is formed,, it will react immediately when it comes into contact with a nucleophile like Nu^-. The lone pair on the nucleophile is strongly attracted towards the +ve C, and moves towards it to create a new bond.



The speed of the reaction is governed by the ionization of haloalkane. Because this initial slow step only involves one species, the mechanism is described as S_N1 -substitution, nucleophilic, one species taking part in the initial slow step.

Why don't primary halogenoalkanes use the S_N1 mechanism?

If a primary haloalkane uses this mechanism, the first step would be, for example:



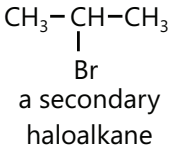
A primary carbocation would be formed, and this is much more energetically unstable than the tertiary one formed from tertiary haloalkanes-and therefore, much more difficult to produce.

This instability brings in a very high activation energy for the reaction involving a primary haloalkane. The activation energy is much less if it undergoes an S_N2 reaction.

(iii) Nucleophilic substitution in secondary haloalkanes: There isn't anything new in this. Secondary haloalkanes will use both mechanisms-some molecules will react using the S_N2 mechanism and other, the S_N1. The S_N2 mechanism is possible because the back of the molecule isn't completely cluttered by alkyl groups and so, the approaching nucleophile can still reach the carbon atom. The S_N1 mechanism is possible because the secondary carbocation formed in the slow step is more stable than a primary one. It isn't as stable as a tertiary one though, and so the S_N1 route isn't as effective as it is with tertiary haloalkanes.

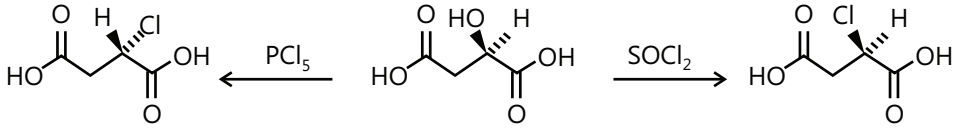
S_Ni mechanism

(i) Reaction of $SOCl_2$ with Secondary Alcohols: The S_Ni Mechanism: Walden noted that when (+)-malic acid treated with PCl_5 , the product was (-) chlorosuccinic acid –a process that proceeded with inversion of stereochemistry. When (+) malic acid was treated with thionyl chloride ($SOCl_2$), the product was (+)-chlorosuccinic acid. This proceeds with retention of stereochemistry.



a secondary haloalkane

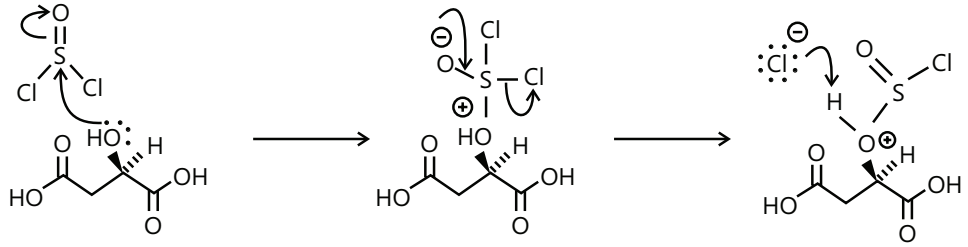
How can we understand this?



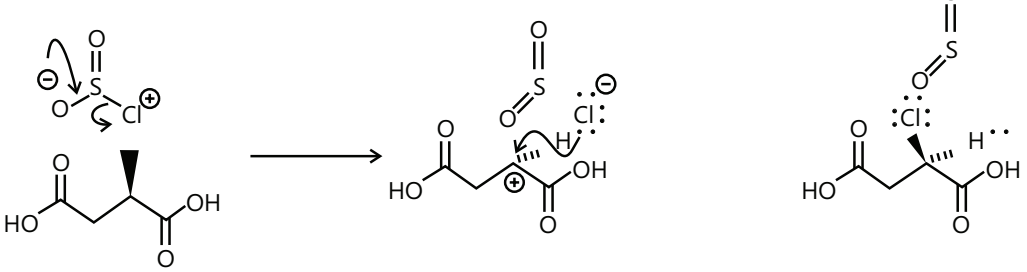
(-)-chlorosuccinic acid (+)-malic acid (+)-chlorosuccinic acid

Inversion Retention

(ii) Why Adding $SOCl_2$ And Pyridine Leads To Inversion (via S_N2): As it turns out, the stereochemistry of this reaction can change to inversion if we add a mild base- such as pyridine.



Attack of OH upon $SOCl_2$ | Expulsion of Cl- to form protonated chlorosulfite | Formation of ''chlorosulfite" (can be Isolated)

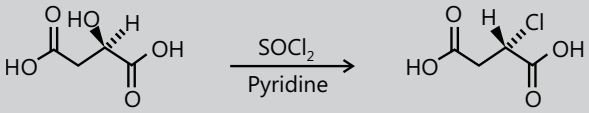


Departure of leaving group to form ''intimate ion pair" | Chloride attacks cabocation on same face of ''Intimate" ion | Loss of SO_2

Both reactions form the "chlorosulfite" intermediate. But, when pyridine (a decent nucleophile) is present, it can attack the chlorosulfite, displacing chloride ion and forming a charged intermediate. Now, if the leaving group departs, forming a carbocation, there's no lone pair nearby on the same face that can attack. In other words, by displacing chloride ion, pyridine shuts down the S_Ni mechanism.

MASTERJEE CONCEPTS

$SOCl_2$ plus alcohol gives retention of configuration, $SOCl_2$ plus alcohol plus pyridine give inversion of configuration (S_N2)



(+)-malic acid

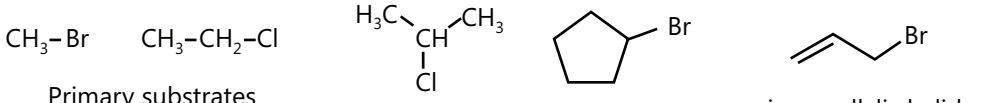
(+)-chlorosuccinic acid
inversion

Saurabh Gupta (JEE 2010, AIR 443)

(iv) Factors affecting nucleophilic substitution reactions:

- **Steric Nature of the Substrate.** Steric accessibility of the electrophilic center in the substrate is probably the most important factor that determines if a nucleophilic substitution will follow a S_N1 or an S_N2 mechanism.

Examples of S_N2 (sterically accessible) substrates

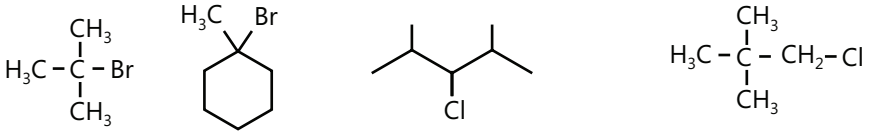


Primary substrates

Unhindered secondary substrates

primary allylic halides

Examples of S_N1(sterically hindered) substrates



Tertiary halides

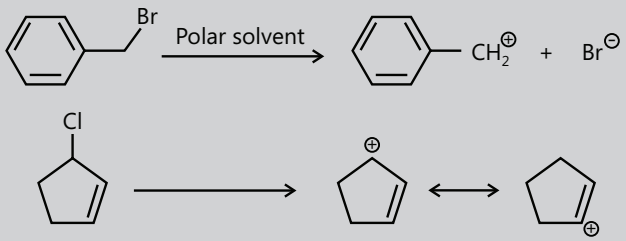
Hindered secondary halides

Hindered primary halides

MASTERJEE CONCEPTS

Some substrates, whether they are sterically hindered or not, may prefer to undergo S_N1 reactions if they can dissociate into very stable carbocations in the presence of the solvent. In most cases, this involves resonance-stabilized cations.

Examples of S_N1 substrates that form stable carbocations



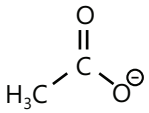
Saurabh Gupta (JEE 2010, AIR 443)

- **Nature of the nucleophile:** Both S_N1 and S_N2 reactions prefer small nucleophiles. Large nucleophiles have more difficulty accessing the electrophilic center in the substrate. They also have an increased tendency to act as Bronsted bases, seeking acidic protons rather than electrophilic centers. This is due to the lower activation energy of acid-base reactions compared to nucleophilic substitutions.

  $^{\ominus}OH \quad CH_3O^{\ominus} \quad CH_3CH_2O^{\ominus} \quad {}^{\ominus}CN \quad RS^{\ominus} \quad R-C\equiv C^{\ominus} \quad Br^{\ominus} \quad I^{\ominus}$

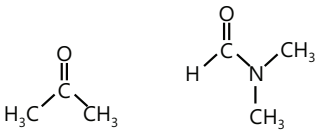
  Small, strong nucleophiles that favor S_N2 reactions are shown below. Most of them have a localized negative charge. It is also better if they are weak bases, such as bromide and iodide ions, but they can be strong bases such as hydroxide and alkoxide ions (conjugate bases of alcohols).

  Weak, small nucleophiles that favor S_N1 reactions are shown below. Notice that several of them are the conjugate acids of strong nucleophiles. They are also typically neutral, but some have a delocalized negative charge.

  $H_2O \quad CH_3OH \quad CH_3CH_2OH \quad RSH \quad NH_3 \quad F^{\ominus}$ 

  Large nucleophiles, especially if they are strong, have a tendency to act as Bronsted bases rather than as nucleophiles. They should be avoided if a nucleophilic reaction is desired.

- **Solvent used:** It has already been mentioned that S_N2 mechanisms are favored by low to moderate polarity solvents such as acetone and N, N-dimethylformamide(DMF). S_N1 mechanisms are favored by moderate to high polarity solvents such as water and alcohols. In S_N1 reactions, quite frequently, the solvent also doubles as the nucleophile. Water and alcohols are prime examples of this practice.

  
  Acetone

  DMF

  S_N2 Solvents

  H_2O Water $\quad CH_3OH$ Methanol $\quad CH_3CH_2$ Ethanol

  S_N1 Solvents

- **Leaving group:** The nature of the leaving group has more of an effect on the reaction rate (faster or slower) than it does on whether the reaction will follow an S_N1 or S_N2 mechanism. The most important thing to remember in this regard is that good leaving groups are weak bases.
  - Except for fluorine, all halogens are good leaving groups
  - Groups that leave as resonance stabilized ions are also weak bases and therefore, good leaving groups.
  - Water is a good leaving group frequently used to prepare alkyl chlorides and bromides from alcohols.

  The OH group in alcohols is not a good leaving group because it leaves as a hydroxide ion, which is a strong base. However, if the hydroxyl group is protonated first with a strong acid, it can leave as a water molecule, which is a good leaving group.

Illustration 4: Prepare the following ethers via Williamson's synthesis.

I. Di-n-propyl ether (A) II. Benzyl methyl ether (B)

III. Phenylethyl ether (C) IV.t-Butyl ethyl ether (D) **(JEE MAIN)**

Sol: Reaction of alcohol with alkyl halide in the presence of base yields ether. This reaction is known as Williamson's Synthesis**.**

I. $n-PrOH \xrightarrow{Na} n-PrO^{\Theta} \xrightarrow{n-PrBr} PrOPr \ (A)$

II. $MeOH \xrightarrow{Na} MeO^{\Theta} \xrightarrow{PhCH_2Br} PhCH_2OMe \ (B)$

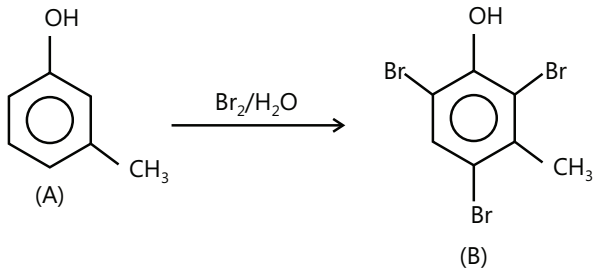
III. $PhOH \xrightarrow{NaOH} PhO^{\Theta} \xrightarrow{EtBr} PhOEt \ (C)$

IV. $t-BuOH \xrightarrow{Na} t-BuO^{\ominus} \xrightarrow{EtBr} t-Bu-OEt\ (D)$

This reaction gives a poor yield because of the bulkiness of t-BuO^-

Illustration 5: An aromatic compound $(A)(C_7H_8O)$ on reaction with Br_2+H_2O gives a white ppt. of compound $(B)(C_7H_5OBr_3)$. Compound (A) is soluble in NaOH. Compound (C), an isomer of (A), also gives the same reaction and gives a white ppt. of compound $(D)(C_7H_5OBr_3)$. Compound (C) is insoluble in NaOH. Identify $(A),(B),(C)$ and (D). **(JEE ADVANCED)**

Sol:



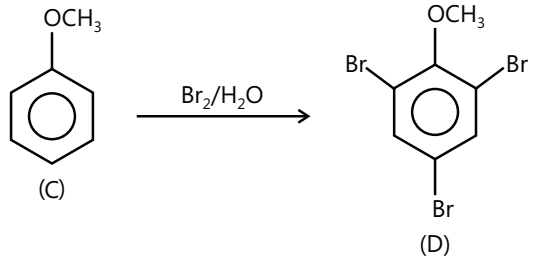
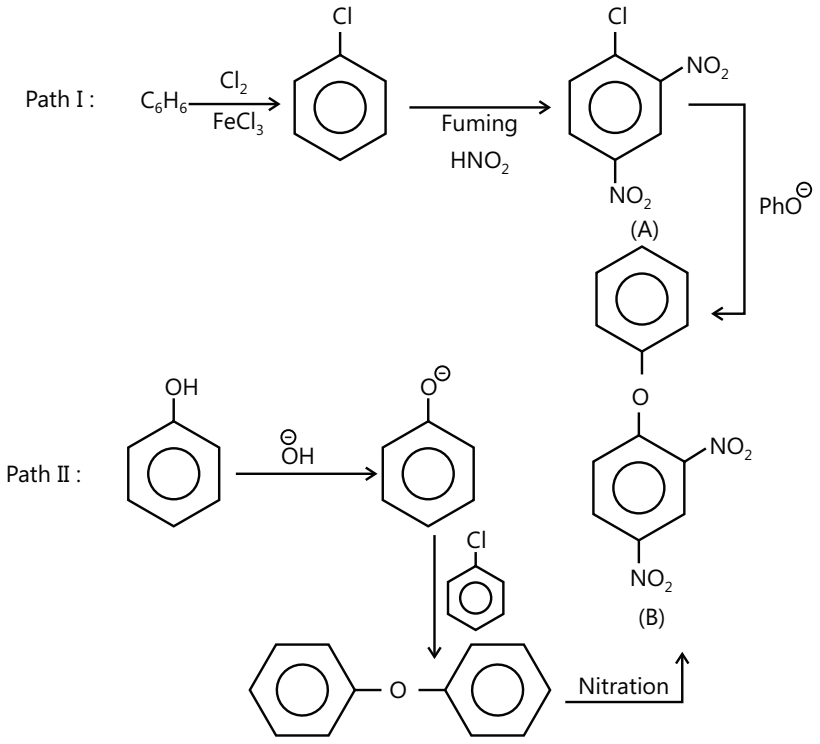
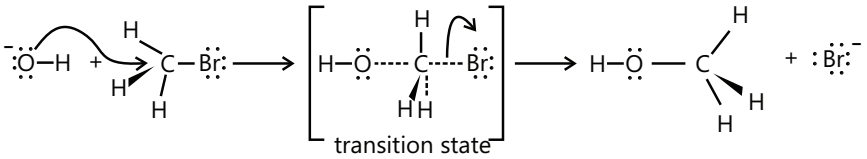


Illustration 6: Starting from C_6H_6 and C_6H_5OH, synthesize phenyl-2,4-dinitrophyneyl ether (B) **(JEE ADVANCED)**

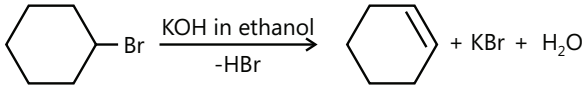
Sol:



(b) Elimination reactions: We have seen that alkyl halides may react with basic nucleophiles such as NaOH via substitution reactions.



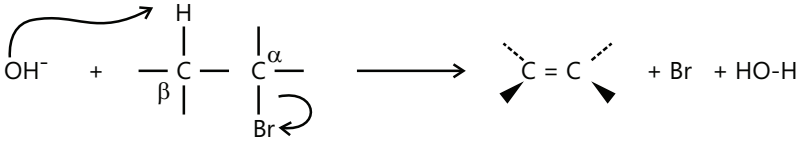
When a 2° or 3° alkyl halide is treated with a strong base such as NaOH, dehydrohalogenation occurs producing an alkene-an elimination (E2) reaction.



There are 2 kinds of elimination reactions, E1 and E2.

E2 = Elimination, Bimolecular (2^{nd} order). Rate $= K[RX][Nu:^-]$

E2 reactions occur when a 2^o or 3 alkyl halide is treated with a strong base such as OH, OR, NH_2^-, H^-, etc.

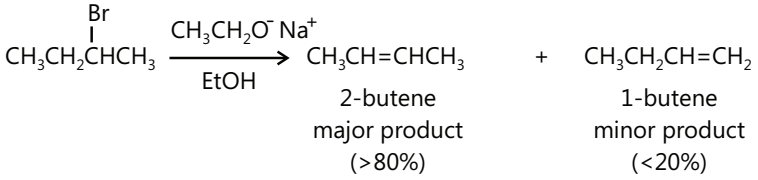


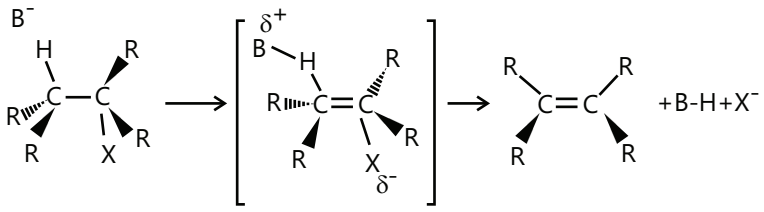
The Nu: removes an H^+ from a β-carbon, the halogen leaves forming an alkene

All strong bases, like OH, are good nucleophiles. In 2° and 3° alkyl halides, the α-carbon in the alkyl halide is hindered. In such cases, a strong base will 'abstract' (remove) a hydrogen ion (H^+) from a β-carbon, before it hits the α-carbon. Thus, strong bases cause elimination (E2) in 2° and 3 alkyl halides and cause substitution (S_N2) in unhindered methyl° and 1° alkyl halides.

In E2 reactions, the Base to H σ bond formation, the C to H σ bond breaking, the C to C π bond formation, and the C to Br σ bond breaking all occur simultaneously. There are no intermediate forms of carbocation. Reactions in which several steps occur simultaneously are called 'concerted' reactions.

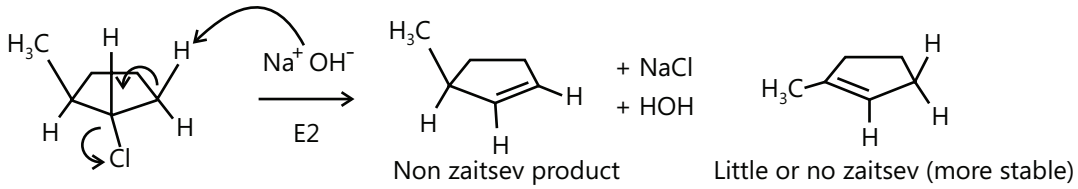
(i) Zaitsev's Rule: Recall that, in elimination of HX from alkenes, the more highly substituted (more stable) alkene product predominates.



- E2 reactions, do not always follow Zaitsev's rule.
- E2 eliminations occur with anti-periplanar geometry, i.e. periplanar means that all 4 reacting atoms- H, C, C, & X- all lie in the same plane. Anti means that H and X (the eliminated atoms) are on opposite sides of the molecules.
- Look at the mechanism again and note the opposite side and same plane orientation of the mechanism:
- When E2 reactions occur in open chain alkyl halides, the Zaitsev product is actually the major product. Single bonds can rotate to the proper alignment to allow the antiperiplanar elimination.
- 

- In cyclic structures, however, single bonds cannot rotate, in regards with the stereochemistry. See the following example.

  E.g. Trans-1-chloro-2-methylcyclopentane undergoes E2 elimination with NaOH. Draw and name the major product.



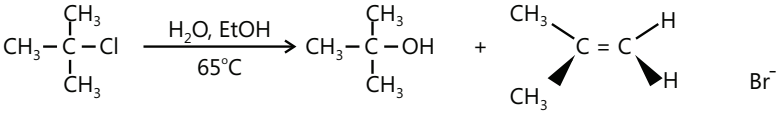
Non zaitsev product is major product

3-methylcyclopentene

Little or no zaitsev (more stable) product is formed

1-methylcyclopentene

(ii) Substitution vs Elimination:

- As with E2 reactions, E1 reactions also produce the more highly substituted alkene (Zaitsev's rule). However, unlike E2 reactions where no C^+ is produced, C^+ arrangements can occur in E1 reactions.
- E.g. t-butyl chloride + H_2O (in EtOH) at 65°C
- 

64% S_N1 product

36% E1 product

- In most unimolecular reactions, S_N1 is preferred to E1, especially at low temperatures.
- If the E1 product is desired, it is better to use a strong base and force the E2 reaction.
- Note that increasing the strength of the nucleophile favors S_N1 over E1. Can you postulate an explanation?

  Mixtures of products are usually obtained.

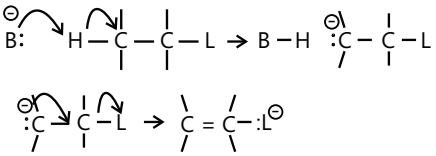
MASTERJEE CONCEPTS

Predicting Reaction Mechanisms

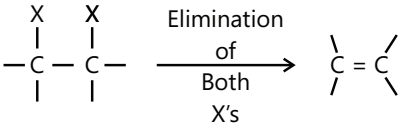
- Non basic, good nucleophiles, like Br^- and I^- will cause substitution not elimination. In 3° substrates, only S_N1 is possible. In Me and 1° substrates, S_N2 is faster. For 2° substrates, the mechanism of substitution depends upon the solvent.
- Strong bases, like OH^- and OR^-, are also good nucleophiles. Substitution and elimination compete. In 3° and 2° alkyl halides, E2 is faster. In 1° and Me alkyl halides, S_N2 occurs.
- Weakly basic, weak nucleophiles, like H_2O , EtOH, CH_3COOH , etc., cannot react unless a C^+ forms. This only occurs with 2° or 3° substrates. Once the C^+ forms, both S_N1 and E1 occur in competition. The substitution product is usually predominant
- High temperatures increases the yield of elimination product over substitution product. $(\Delta G = \Delta H - T\Delta S)$ Elimination produces more products than substitution, hence creates greater entropy (disorder).
- Polar solvents, both protic and aprotic, like H_2O and CH_3CN, respectively, favor unimolecular reactions (S_N1 and E1) by stabilizing the C^+ intermediate. Polar aprotic solvent enhance bimolecular reactions (S_N2 and E2) by activating the nucleophile.

Saurabh Gupta (JEE 2010, AIR 443)

(iii) E1CB elimination: In any E1CB reaction, a base first removes a proton from the α carbon of the substrate to give an intermediate carbanion (a species with a negatively charged carbon). This carbanion then loses the leaving group $\left(^{-}:L\right)$ to form alkene products (s). The E1CB mechanism usually occurs with strong bases and with substrates where groups directly attached to the carbanion center can stabilize that center's negative charge.



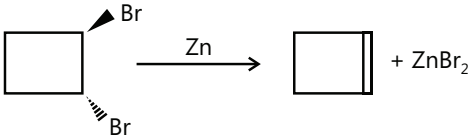
(iv) Elimination of X-X: Alkenes also form from the loss of both X's of a 1,2-dihaloalkane.



These dehalogenation reactions do not involve bases. They use metals such as Mg or Zn that react with the halogens (Cl, Br, and/or I) to form metal salts such as MgX_2 or ZnX_2 .Their mechanisms probably involve formation of intermediate organometallic compounds on the metal surface that then eliminate as $^{+}Mg - X$ or $^{+}Zn - X$ and X^{-}

$$BrCH_2 - CH_2Br \xrightarrow[Ether]{Mg} CH_2=CH_2+MgBr_2$$

$$(CH_3)_3\,C - CHBr_2 - CH_2Br \xrightarrow{Zn} (CH_3)_3\,C - CH_2 - CH=CH_2+ZnBr_2$$

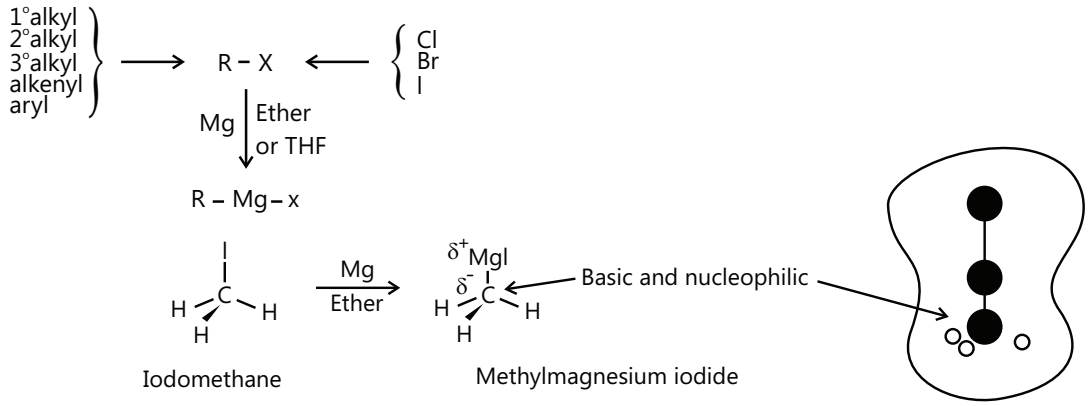


Reaction with organometallic compounds:

(a) Grignard reagent:

(i) Reaction of RX with Mg in ether of THF

(ii) Product is RMgX-an organometallic compound (alkyl-metal bond) Carbanions ($CH_3^{-}Mg^{+}$) are very strong



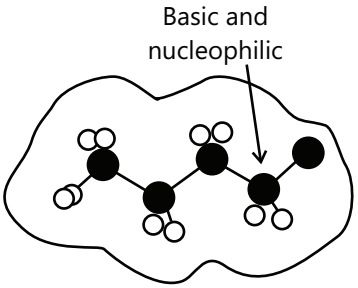
$$CH_3CH_2CH_2CH_2CH_2CH_2Br \xrightarrow[Ether]{Mg} CH_3CH_2CH_2CH_2CH_2CH_2MgBr \xrightarrow{H_2O} CH_3CH_2CH_2CH_2CH_2CH_3$$

1-Bromohexane 1-Hexylmagnesium bromide Hexane (85%)

(iii) Alkylithium (RLi) forms from RBr and Li metal

(iv) RLi reacts with copper iodide to give lithium dialkylcopper (Gilman reagents)

(v) Lithium dialkylcopper reagents react with alkyl halides to give alkanes



$$\underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[\text{Pentane}]{2Li} \underset{\text{Butyllithium}}{CH_3CH_2CH_2CH_2Li} + LiBr$$

$$\underset{\text{Methyllithium}}{2\,CH_3Br + CuI} \xrightarrow{\text{Ether}} \underset{\text{Lithium dimethylcopper (a Gilman reagent)}}{(CH_3)_2Cu^-Li^+} + LiI$$

$$\underset{\text{Lithium dimethylcopper}}{(CH_3)_3CuLi} + \underset{\text{1-Iododecane}}{CH_3(CH_2)_8CH_2I} \xrightarrow[0^\circ C]{\text{Ether}} \underset{\text{Undecane (90\%)}}{CH_3(CH_3)_8CH_2CH_3} + LiI + CH_3Cu$$

(b) Miscellaneous reactions:

(i) Wurtz Reaction: $2R-X+2Na \xrightarrow{\text{Dry ether}} 2NaX+R-R$

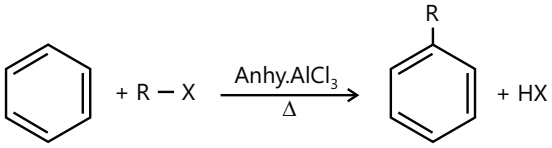
(ii) Formation of Grignard's Reagent $R-X+Mg \xrightarrow{\text{ether}} RMgX$

(iii) Corey House Reaction $R_2CuLi+R'X \xrightarrow{\text{Dry ether}} R-R'+RCu+LiX$

R_2CuLi is prepared as follows:

- (i) $R-Br+2Li \xrightarrow{\text{Dry ether}} LiBr+RLi$
- (ii) $2RLi+CuI \xrightarrow{\text{Dry ether}} R_2CuLi+LiI$

(iv) Friedel Crafts Reaction



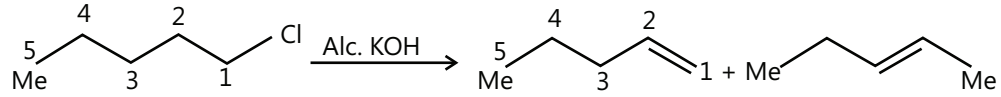
(v) Reduction Reactions

- $R-CI+H_2 \xrightarrow[Pt\,or\,Pd]{Ni} R-H+HCI$
- $R-I+HI \xrightarrow[\Delta]{Re\,dP} R-H+I_2$
- $R-CI+2[H] \xrightarrow{Zn-Cu/alc} R-H+HCl$
- $R-CI+LiAlH_4 \rightarrow R-H+LiCl+AlCl_3$

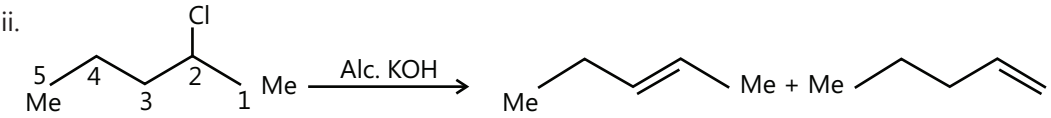
Illustration 7: Identify all the possible alkenes that would be formed on the dehydrohalogenation of the following organic halides with alcoholic KOH. Also, identify the major alkene.

i. 1-Chloropentane ii. 2-Chloropentane **(JEE MAIN)**

Sol:

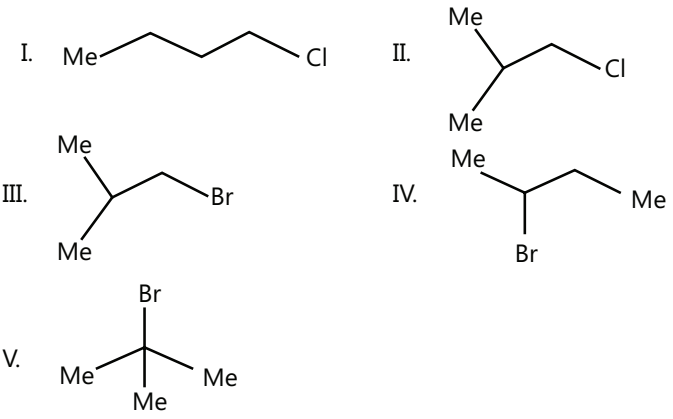
i. 

Pent-1-ene (Minor) Pent-2-ene (Major)

ii. 

Pent-2-ene (Major) Pent-1-ene (Minor)

Illustration 8: Predict the order of reactivity of the following compounds in dehydrohalogenation. **(JEE MAIN)**

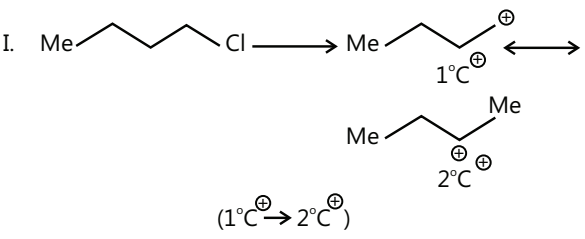


Sol: Stability of carbocation has the influence on reactivity towards dehydrohalogenation. The more stable the carbocation, greater is the reactivity towards dehydrohalogenation.

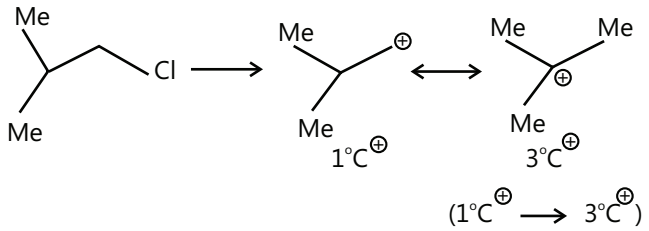
Order of the Stability of carbocation: tert>sec>primary.

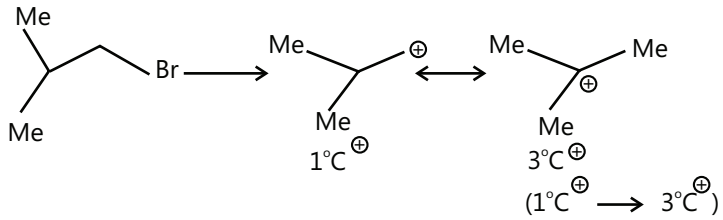
Find out the carbocation formed during each reaction and predict the order of reactivity accordingly.

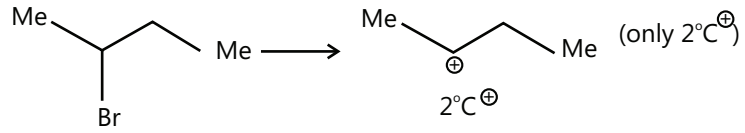
Order of reactivity: $(V) > (III) > (II) > (IV) > (I)$

I. 

(Ease of formation: $3^o > 2^o > 1^o$ carbocation).

II. 

III. 

IV. 

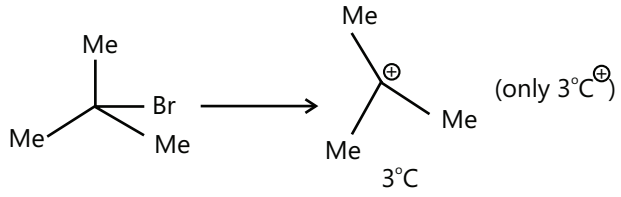
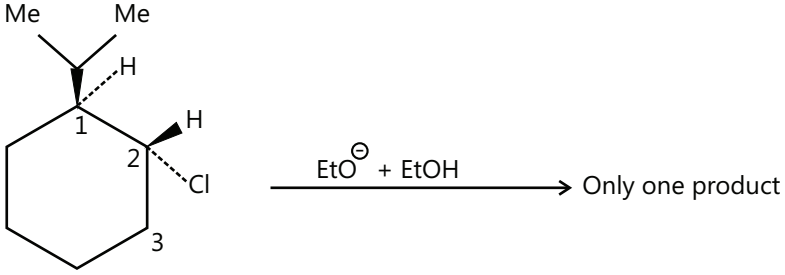
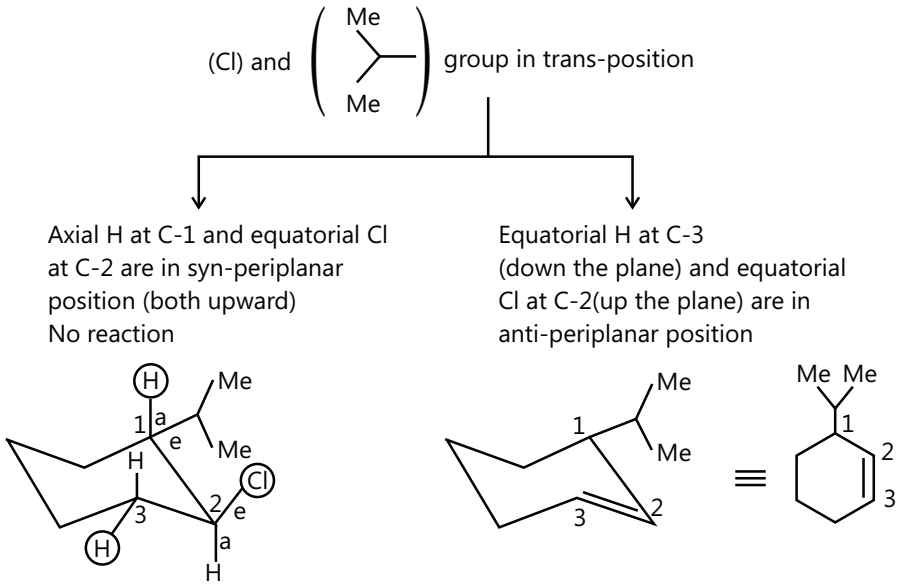
V. 

Illustration 9:  **(JEE ADVANCED)**

trans-1-Isopropyl-2-chloro cyclohexane

Sol: Bulky group at equatorial position imparts stability to the ring. In order to undergo dehydrohalogenation reaction the basic condition to be followed is that the two leaving group has to be in anti periplanar geometry. By using this condition answer the question.

- Here Bulky group has to be in equatorial position (down the plane) as to impart stability and Cl group should also be at equatorial position (up the plane) for trans-configuration.
- In Dehydrohalogenation reaction one important requirement is the orientation of the two leaving atom.
- The two leaving atom has to be in Anti periplanar position.
- Here there are two possibilities, H can be eliminated from C_1 or it can be eliminated from C_3.
- On talking about H at C_1, The H atom occupies axial position and Cl is in equatorial position. Thus the orientation is Syn periplanar (Both upward) so the reaction is not feasible. Thus we only get one product.



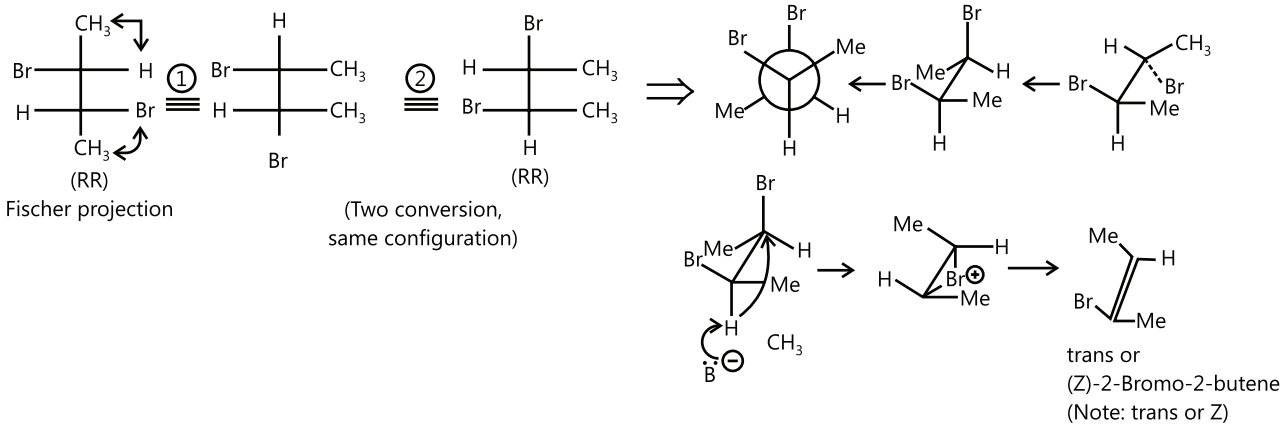
- H atom at C_3 occupies equatorial position and Cl is also in equatorial position thus the orientation is anti, thus we get the product.

Illustration 10: Explain the stereochemistry of the products from E2 dehalogenation with $I^{\ominus}$ of the following.

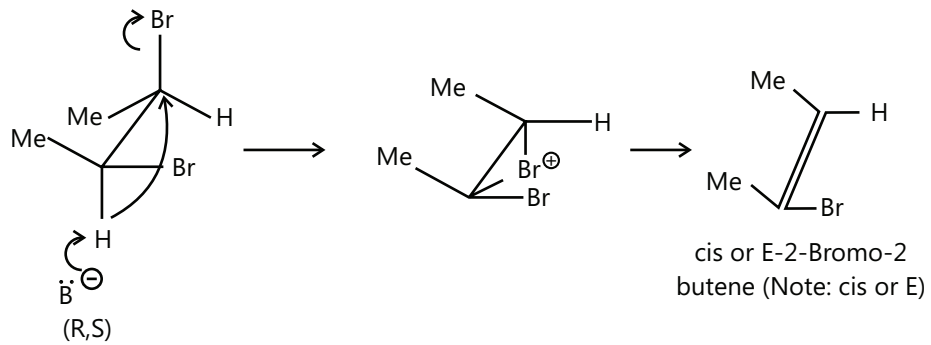
E2-dehydrobromination of (a) R, R-2, 3-dibromobutane and (b) meso-(R,S)-2, 3-dibromobutane. **(JEE ADVANCED)**

Sol: Draw the structure of the compound (a) and (b).In order to undergo dehydrohalogenation reaction the two leaving group has to be in anti periplanar. In order to get this condition interchange the group accordingly**.** Br^- attacks the compound from the bottom side.

(a)



(b)



5. PREPARATION OF ALKYL HALIDES

Numerous ways to make alkyl halides.

1. Free Radical Halogenation

(a) Alkane +Cl_2 or Br_2, heat or light replaces C-H with C-X but gives mixtures

i) Hard to control ii) Via free radical mechanism

(b) It is usually not a good idea to plan a synthesis that uses this method-multiple products

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$
$$\xrightarrow{Cl_2} CH_2Cl_2 + HCl$$
$$\xrightarrow{Cl_2} CHCl_3 + HCl$$
$$\xrightarrow{Cl_2} CCl_4 + HCl$$

Radical Chain Mechanism

Initiation step $\quad Cl-Cl \xrightarrow{h\nu} 2\,Cl\bullet$

Propagation steps (a repeating cycle)

$$\left.\begin{matrix} H_3C-H \\ + \\ Cl\bullet \\ + \\ H_3C-Cl \end{matrix}\right\} \xrightarrow{\text{Step 1}} \left\{\begin{matrix} H-Cl \\ + \\ H_3C\bullet \end{matrix}\right.$$
$$\left\{\begin{matrix} H_3C\bullet \\ + \\ Cl-Cl \end{matrix}\right. \xrightarrow{\text{Step 2}} \left.\begin{matrix} H-Cl \\ + \\ Cl\bullet \end{matrix}\right\}$$

Termination steps

$$\begin{cases} H_3C\bullet + \bullet CH_3 \longrightarrow H_3C-CH_3 \\ Cl\bullet + \bullet CH_3 \longrightarrow Cl-CH_3 \\ Cl\bullet + \bullet Cl \longrightarrow Cl-Cl \end{cases}$$

Overall reaction $\quad CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$

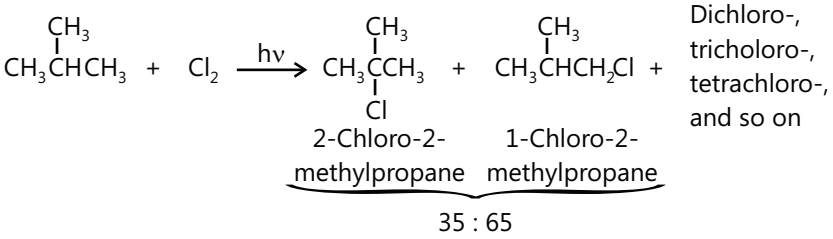
Radical Halogenation: Selectivity

If there is more than one type of hydrogen in an alkane, reactions favor replacing the hydrogen at the most highly substituted carbons

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} + Cl_2 \xrightarrow{h\nu} \underbrace{\underset{\text{1-Chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2-Chlorobutane}}{CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_3}}_{30:70}$$

$$\frac{30\%\left(1^{o}\right)\text{Product}}{6\left(1^{o}\right)H's} = 5\%\text{per}(1^{o})H \qquad \frac{70\%(2^{o})\text{Product}}{4(2^{o})H's} = 17.5\%\text{per}(2^{o})H$$

$$\therefore \quad \frac{17.5\%\text{per}(2^{o})H}{5\%\text{per}(1^{o})H} = 3.5:1 \text{ relative Reactivity}$$

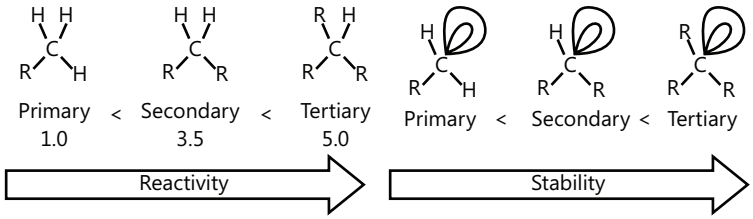


$$\frac{65\%\left(1^{o}\right)\text{Product}}{9\left(1^{o}\right)\text{H's}} = 7.2\%\text{per}(1^{o})\text{H} \qquad \frac{35\%(3^{o})\text{Product}}{1(1^{o})\text{H's}} = 35\%\text{per}(3^{o})\text{H}$$

$$\therefore \ \frac{35\%\text{per}(3^{o})\text{H}}{7.2\%\text{per}(1^{o})\text{H}} = 5{:}1 \text{ relative reactivity}$$

Relative Reactivity

1. Based on quantitative analysis of reaction products, relative reactivity is estimated for
   $Cl_2 : \left(5 : 3.5 : 1 \text{ for } 3^{o} : 2^{o} : 1^{o}\right)$
2. Order parallels stability of radicals
3. Reaction distinction is more selective with bromine than chlorine (1700:80:1 for $3^{o} : 2^{o} : 1^{o}$)



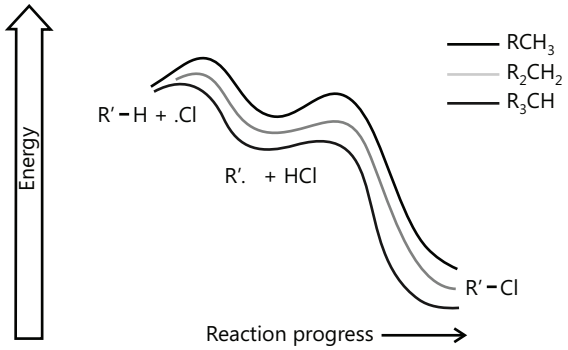
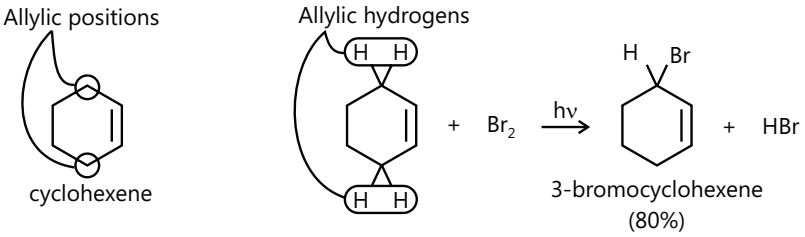
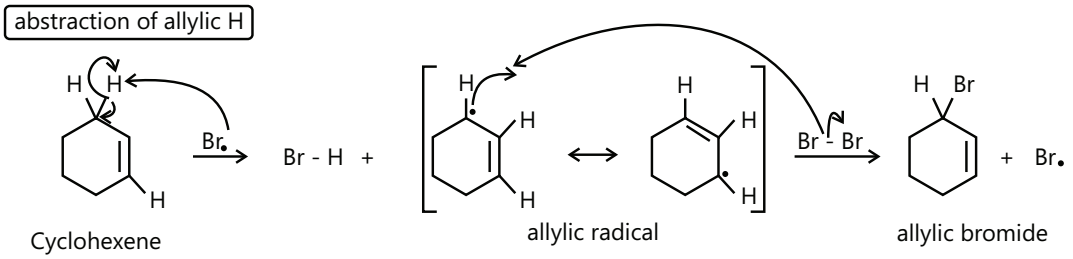


Figure 12.1: Energy profile diagram of different alkyl halide

2. **Allylic Bromination:** (Allylic means adjacent to a C=C double bond)
   The bromination of cyclohexene produces a high yield of 3-bromocyclohexene.



An allylic hydrogen has been substituted for a bromine.
The bromine atom abstracts an allylic hydrogen because the allylic radical is resonance stabilized.
The radical then reacts with a bromine molecule to continue the chain.



3. From Alcohols

(a) Preparation of alkyl chloride: $R-OH+HCl \xrightarrow[ZnCl_2,\Delta]{\text{anhydrous}} R-Cl+H_2O$

(i) $CH_3CH_2-OH+HCl_{(g)} \xrightarrow{\text{anhydrous } ZnCl_2} CH_3CH_2-Cl+H_2O$

(ii) $(CH_3)_2CH-OH + HCl_{(g)} \xrightarrow[ZnCl_2]{\text{anhydrous}} (CH_3)_2CH-Cl + H_2O$

(iii) $(CH_3)_3C-OH + HCl_{(g)} \longrightarrow (CH_3)_3C-Cl + H_2O$

Note: Tertiary alcohols react with HCl(g) even in the absence of anhydrous $ZnCl_2$.

(b) Preparation of alkyl bromides: $R-OH+HBr \xrightarrow[\text{reflux}]{\text{conc.}H_2SO_4} R-Br+H_2O$

(i) $CH_3CH_2-OH+HBr \xrightarrow[\text{reflux}]{\text{conc.}H_2SO_4} CH_3CH_2-Br+H_2O$

(c) Preparations of alkyl iodides: $R-OH+HI \xrightarrow{\text{reflux}} R-I+H_2O$

$CH_3CH_2-OH+HI \xrightarrow{\text{reflux}} CH_3CH_2-I+H_2O$

From alcohols using PX_3 or PX_5

$3R-OH+PCl_3 \rightarrow 3R-Cl+H_3PO_3$

$R-OH+PCl_5 \rightarrow R-Cl+POCl_3+HCl$

From alcohols using $SOCl_2$ (Thionyl chloride) [Darzen's Procedure]

$R-OH+SOCl \xrightarrow[\text{reflux}]{\text{Pyridine}} R-Cl+SO+HCl$

4. Borodine Hunsdiecker Reaction: $RCOOAg+Br_2 \xrightarrow[\text{reflux}]{CCl_4} R-Br+CO_2+AgBr$

Mechanism

$RCOOAg \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^{\ominus} + Ag^{\oplus}$

Step 1 : $R-\overset{\overset{O}{\|}}{C}-O^{\ominus} + Br-Br \longrightarrow R-\overset{\overset{O}{\|}}{C}-O-Br + Br^{\ominus}$

Step 2 : Initiation

$R-\overset{\overset{O}{\|}}{C}-OBr \longrightarrow R-\overset{\overset{O}{\|}}{C}-O^{\bullet} + Br^{\bullet}$

Step 3 : Propagation

$R-\overset{\overset{O}{\|}}{C}-O \longrightarrow R^{\bullet} + CO_2$

Step 4 : Propagation

$R + R-\overset{\overset{O}{\|}}{C}-O-Br \longrightarrow R\,Br + R\,COO^{\bullet}$

Step 5: (a) $R-COO^{\bullet}+R^{\bullet}\rightarrow R-COOR$ (side product)

(b) If ethyl free radical then

$CH_3CH_2^{\bullet}\rightarrow CH_2=CH_2+H$

$H^{\bullet}+CH_3CH_2^{\bullet}\rightarrow CH_3CH_3$

$H^{\bullet}+Br^{\bullet}\rightarrow HBr$

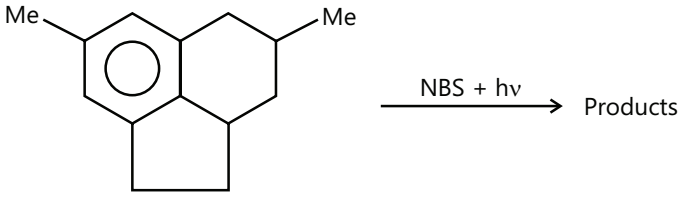
5. Finkelstein Reaction

$$R-Cl+NaI\xrightarrow[\substack{NaCl\\acetone}]{CH_3OH\ \text{or}}R-I+NaCl$$

$$R-Cl+NaBr\xrightarrow{acetone}R-Br+NaCl.$$

The reverse reactions, is not possible because NaCl and NaBr are insoluble in CH_3OH or acetone.

Illustration 11: Identify all the possible products. Give the major products and rank the products in decreasing order of reactivity with NBS.



Sol: Reactivity order: $\left(3^{o}\text{allylic}>2^{o}\text{allylic}>1^{o}\text{allylic}\right)$

(I) > (II) = (III) > (IV)

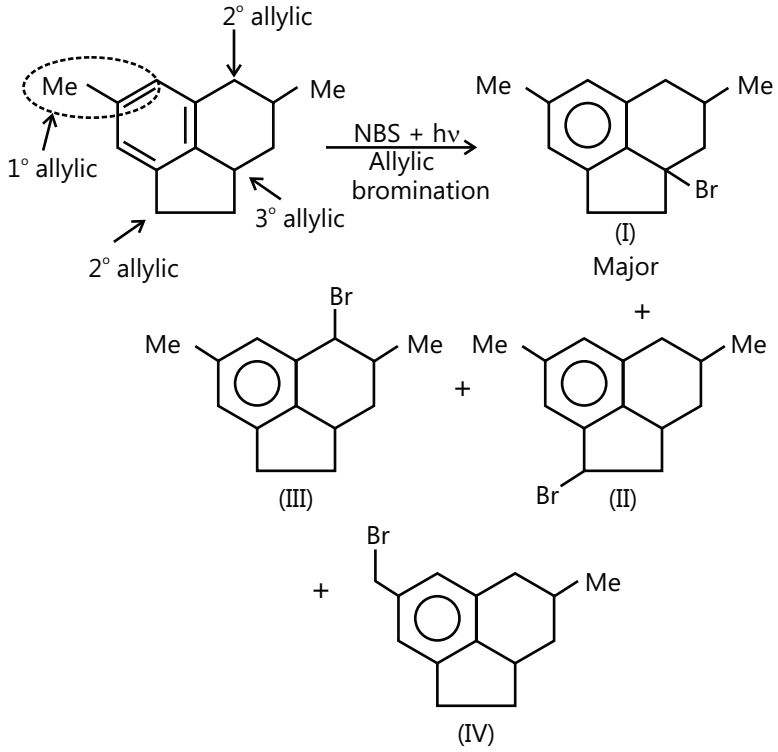
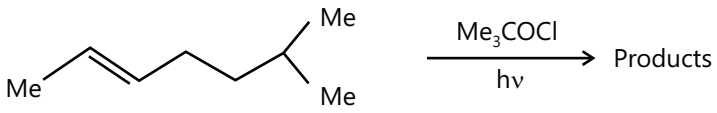


Illustration 12: Identify all the possible products. Give the major products and list them in decreasing order of reactivity with Me_3COCl.



Sol: Reactivity order: $\left(3^o \text{allylic} > 2^o \text{allylic} > 1^o \text{allylic}\right)$

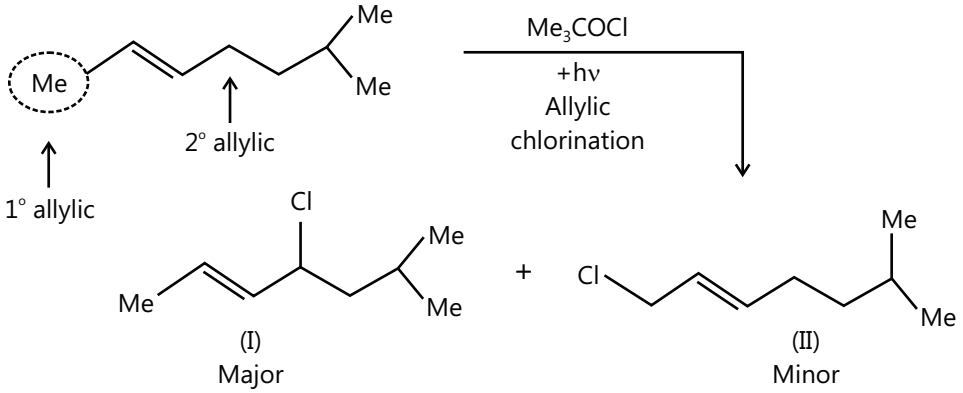
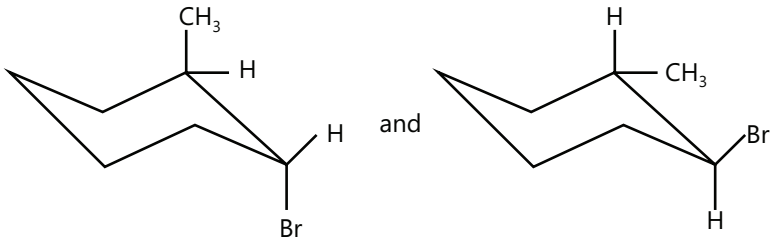


Illustration 13: which of the following will solvolyse faster in S_N1 and why?



Sol: Compound with Substituents on equatorial position are more stable than Diaxial compound. Less stable compound undergoes the reaction faster.

- The rate of S_N1 reaction depends on the difference in energy of the ground state and the transition state.
- In compound (A) both H occupies equatorial position whereas in compound (B) both H occupies axial position
- Compound (A) will solvolyses faster than (B).
- Diaxial compound (A) is less stable than diequatorial compound (B) and thus (A) solvolyses faster.

Illustration 14: Indicate whether the following are S_N1, S_N2, E1, or E2.

1. $\left(CH_3\right)_3 CBr + C_2H_5OH \xrightarrow{60^o C} \underset{(\text{Major})}{\left(CH_3\right)_3 C - OC_2H_5} + \underset{(\text{Major})}{\left(CH_3\right)_2 C = CH_2}$

2. $CH_3CH_2CH_2Br + LiAlH_4 \rightarrow$

3. $CH_3CH_2CH_2Cl + I^{\Theta} \rightarrow$

4. $\left(CH_3\right)_3 CBr + CN^{\Theta}\left(\text{Ethanol}\right) \rightarrow$

5. $CH_3CHBr - CH_3 + \overset{\Theta}{O}H\left(H_2O\right) \rightarrow$

6. $CH_3CHBr-CH_3+\overset{\Theta}{O}H(\text{Ethanol})\rightarrow$

7. $(CH_3)_3CBr+H_2O\rightarrow$ **(JEE ADVANCED)**

Sol: 1. S_N1, 3° halide.

2. $CH_3CH_2CH_3+HBr, S_N2, 1^o$ halide. Nucleophile is H^Θ (hydride ion).

3. $I-CH_2CH_2CH_3, S_N2, 1^o$ halide, I^Θ good nucleophile and poor base.

4. $(CH_3)_2C=CH_2, E2, 3^o$ halide, and CN^- is a strong base, so elimination is predominant over S_N1.

5. $CH_3CHOHCH_3, S_N2$, polar solvent favours substitution.

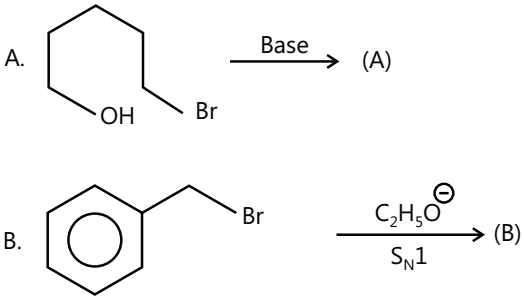
6. $CH_3-CH=CH_2, E2$, less polar solvent favours E2

7. $(CH_3)_3C-OH, S_N1, H_2O$ is not basic enough to remove a proton to give elimination reaction.

Illustration 15: The order of leaving group ability for the following is: 1. $-OAc$ 2. $-OMe$ 3. $-OSO_2Me$ 4. $-OSO_2CF_3$

Sol: Acidic and leaving group order: $CF_3SO_3- > MeSO_3- > AcO- > MeO-$.

Illustration 16: Identify:



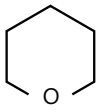
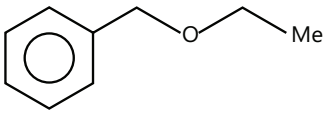
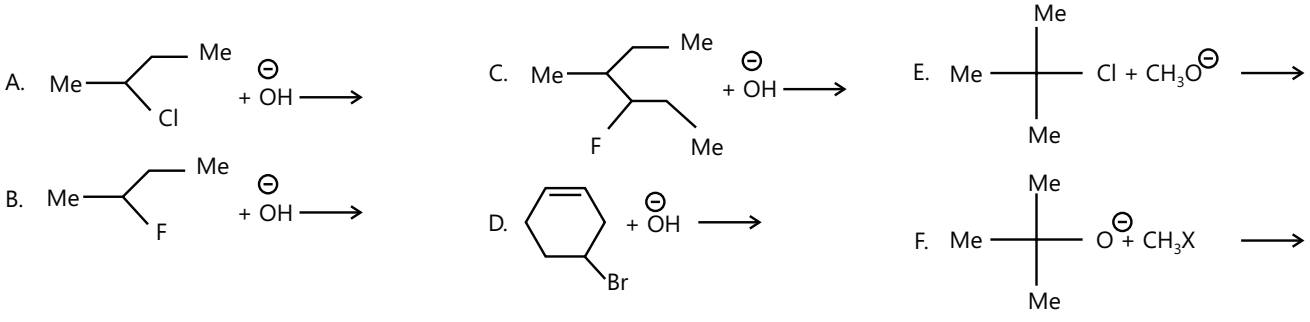
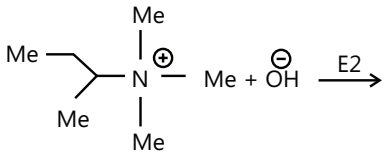
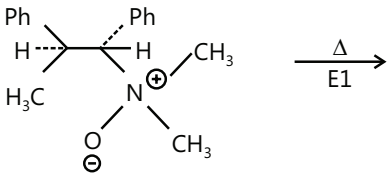
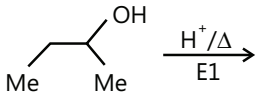
Sol: A.  (A) B.  (B)

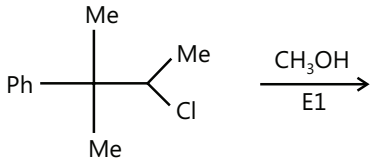
Illustration 17: Give the major products of the following elimination reactions.

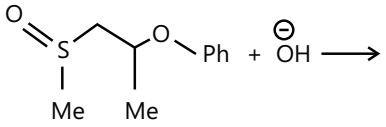


G. 

J. 

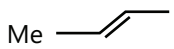
H. 

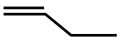
K. 

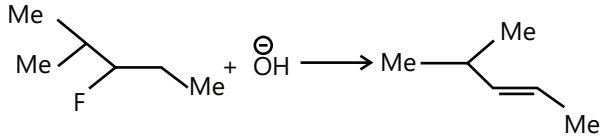
I. 

Sol: E2 elimination follows Hofmann rule and produces Hoffmann product (less substituted alkene-less stable)

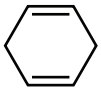
E1 elimination follows Zaitsev's rule and produces Zaitsev's product (more substituted alkene –more stable)

A.  (E2, Saytzeff)

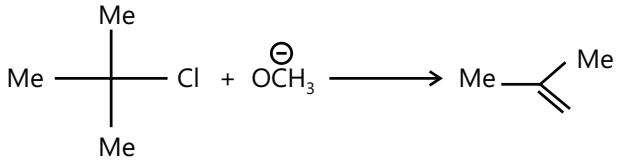
B.  (E2, Hofmann, with F)

C. 

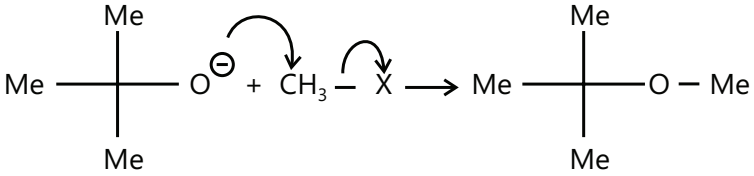
(E2, Hofmann)

D.  (Conjugated double bond) not 

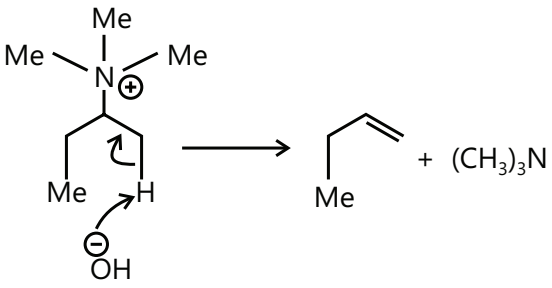
E. CH_3O^{Θ} (nucleophilic cannot attack) 3^oC having high e^- density, hence elimination takes place giving alkene.



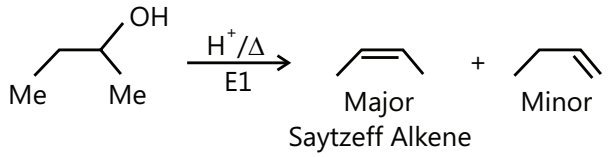
F. Williamson synthesis $\left(CH_3\right)_3C^{\Theta}\left(Nu^{\Theta}\right)$ attacks on 1^oC atom. (S_N2)



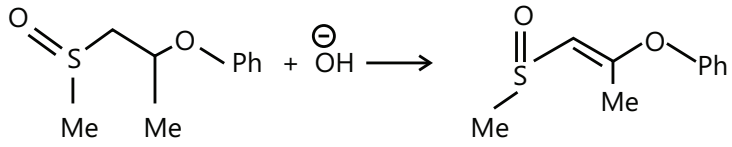
G. Hofmann elimination, less-substituted alkene because the leaving group $\left(CH_3\right)_3N^{\oplus}$ departs as uncharged species.



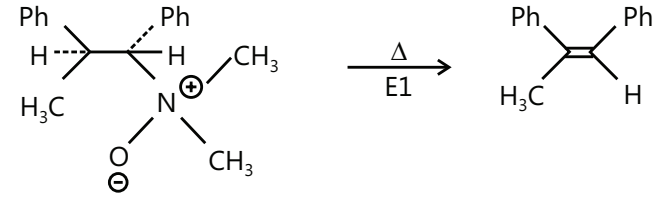
H.



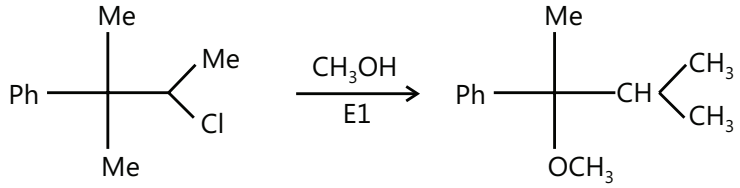
I.



J.



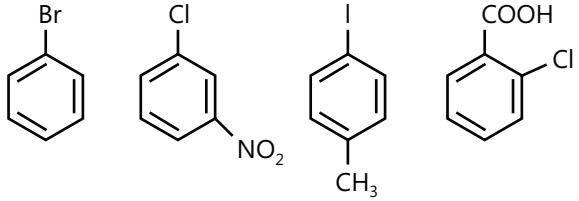
K.



ARYL HALIDES

1. INTRODUCTION

Aryl halides are compounds where halogen is directly attached to an aromatic ring. They have the general formula ArX, where Ar is phenyl substituted phenyl or a group derived from some other aromatic system e.g.

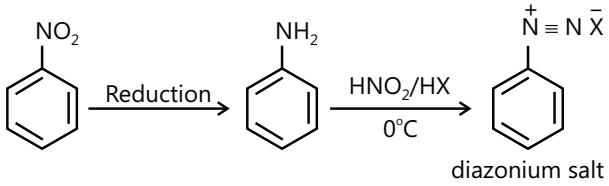


An aryl halide is not just any halogen compound containing an aromatic ring $\left[C_6H_5-CH_2-Cl\right]$ is not an aryl halide for the halogen is not attached to the benzene ring.

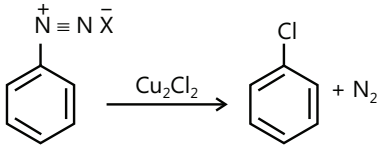
The properties of aryl halides are entirely different from that of Alkyl halides.

2. METHODS OF PREPARATION OF ARYL HALIDES

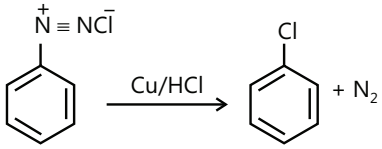
(a) From Diazonium Salts



(i) Sandmeyer Reaction

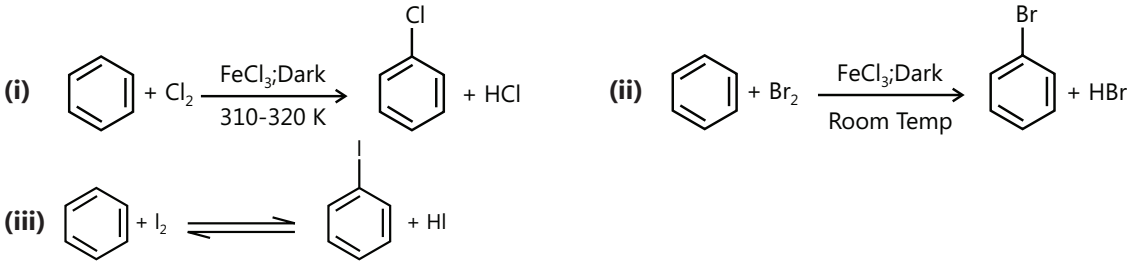


(ii) Gattermann Reaction



The Gatternann reaction is a modification of Sandmeyer reaction. In Sandmeyer reaction, cuprous halides are used which are unstable and difficult to handle, however in Gattermann reaction copper power and hydrogen halide are used.

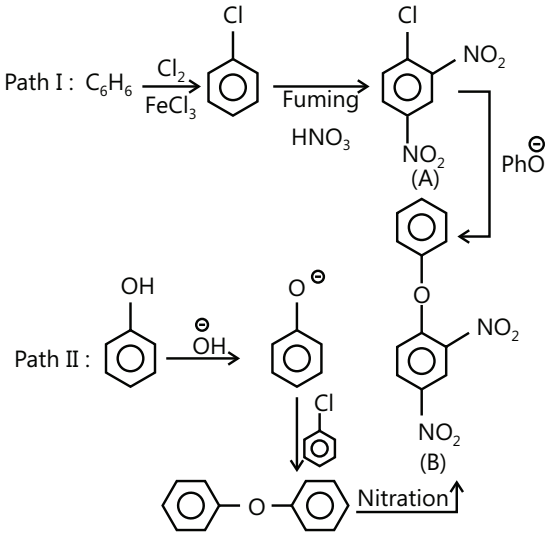
(b) By Direct Halogenation of Aromatic Hydrocarbon



This reaction is reversible due to the formation of HI which is a strong reducing agent. To get iodobenzene, HI must be removed from the reaction mixture. To achieve this some oxidising agent like HIO_3,HNO_3 or HgO is used.

Illustration 18: Starting from C_6H_6 and C_6H_5OH , synthesize phenyl-2, 4-dinitrophenyl ether (B). **(JEE ADVANCED)**

Sol: The Cl of (A) undergoes aromatic nucleophilic displacement because it is activated by two $(-NO_2)$ groups.



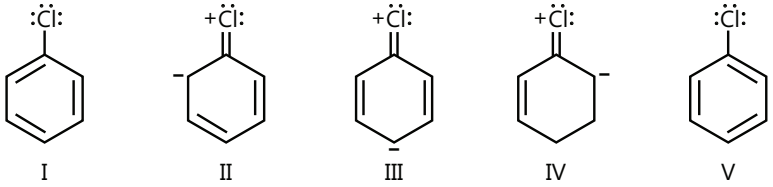
3. PHYSICAL PROPERTIES OF ARYL HALIDES

(a) Aryl halides are colourless liquids and colourless solids with a characteristic odour.

(b) The boiling point of aryl halide follows the order ArI > ArBr > ArCl > ArF

(c) The melting point of p-isomer is more than o- and m-isomer.

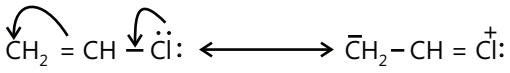
Structure and Reactivity of Aryl Halide and Vinyl Halides: Chlorobenzene is a resonance hybrid of 5 resonating structures.



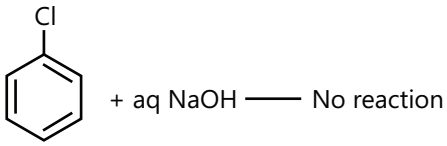
I II III IV V

Contribution by II, III and IV give a double bond character to the carbon-chlorine bond. Hence C-Cl bond in chlorobenzene is strong. As a result, aryl halides are less reactive compared to the corresponding alkyl halide towards nucleophilic substitution reaction.

Similar is the case with vinyl halides.



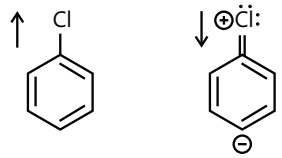
(a) Therefore attempts to convert aryl halides into phenols, ethers, amines with the usual nucleophilic reagents and conditions are unsuccessful. e.g R-Cl+aq.NaOH → ROH+NaCl



(This could however be achieved under vigorous conditions)

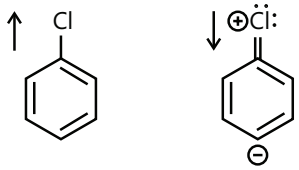
(b) The carbon-halogen bonds of aryl halides and vinyl halides are usually short.

(c) Dipole moments of aryl and vinyl halides are usually small



(d) In chlorobenzene, the chlorine atom is attached to a sp^2hybridized carbon atom whereas in alkyl chloride, the chlorine atom is attached to a sp^3 hydridized carbon atom.

The sp^2 hybridized carbon atom is more electronegative than the sp^3 hybridized carbon atom, thereby the release of electrons to chlorine atoms is less in chlorobenzene and more in alkyl chloride.



(e) The resonating structure of chlorobenzene indicate that the benzene ring carries a –ve charge at o- and p-positions w.r.t. chlorine atom. Thus the benzene ring definitely takes part in electrophilic substitution reactions.

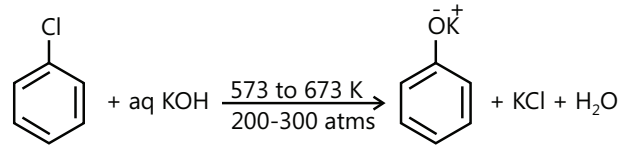
4. CHEMICAL REACTIONS OF ARYL HALIDES

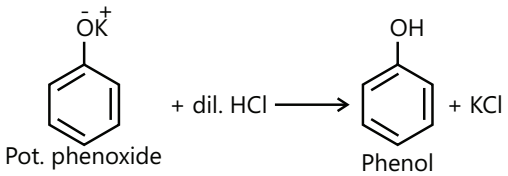
Reaction of Aryl halides can be grouped as:

1. Nucleophillic substitution reactions
2. Electrophillic substitution reactions
3. Miscellaneous reactions

1. Nucleophilic substitution reactions

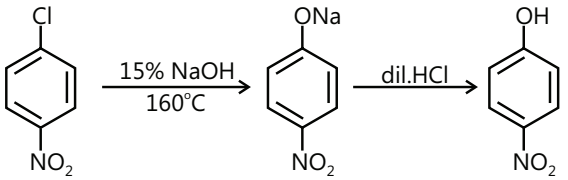
(a) Dow's Process: The presence of a nitro group at ortho or para to chlorine increases its reactivity. Further as the number of such NO_2 groups increases the reactivity is increased.

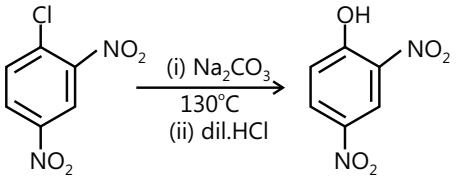


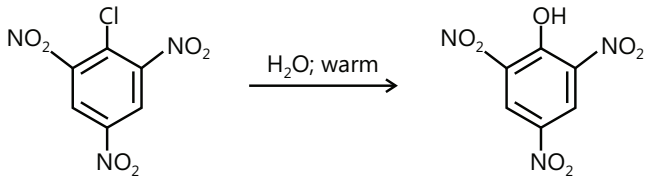


Like NO_2, certain other groups have been found to increase the reactivity of chloro benzene if present at ortho or para to chlorine atom. These groups are,

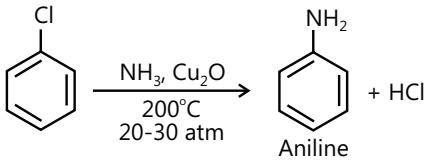
$-\overset{\oplus}{N}(CH_3)_3$, $-CN$, $-SO_3H$, $H-COOH$, $-CHO$, $-\underset{\underset{O}{\|}}{C}-R$



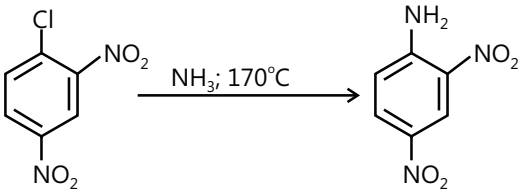


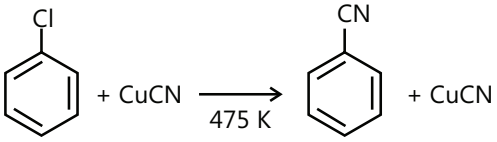


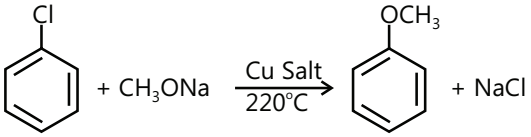
A nitro group at meta position of chlorine has practically no effect on reactivity



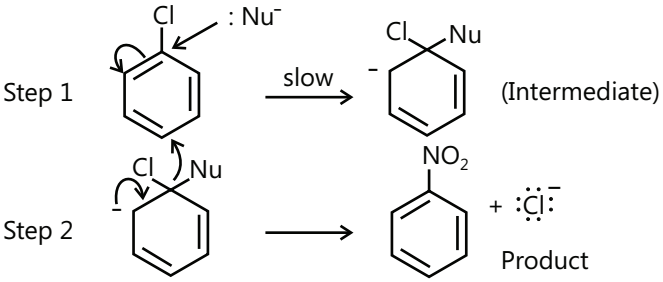
Here again the presence of NO_2 groups at ortho or para position w.r.t. Cl group increases the reactivity.





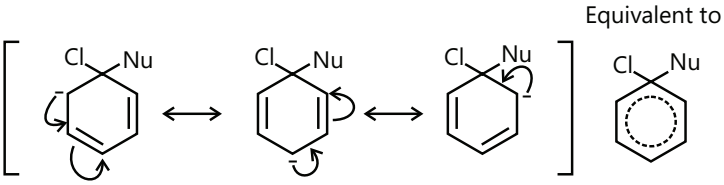


Mechanism: The nucleophilic aromatic substitution reaction can be well explained by a bimolecular mechanism.

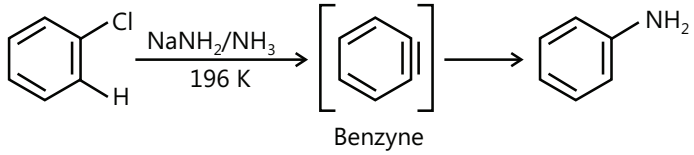


The intermediate carbonium ion is stabilized due to resonance.

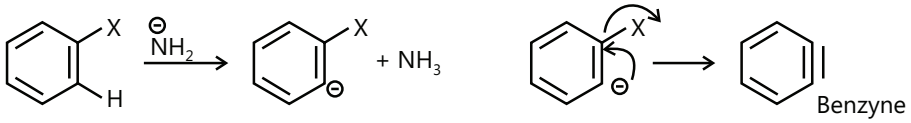
The stability of such carbonium ion can be further increased by –R or –M groups at ortho or para positions.



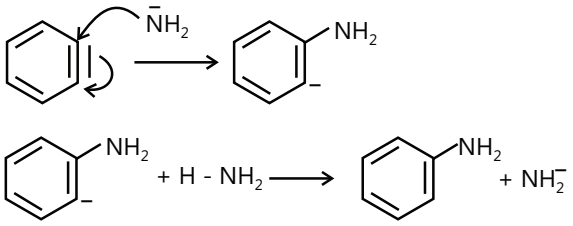
(b) Elimination - Addition Reaction: Reaction with sodamide



This reaction is an elimination- addition mechanism for nucleophilic substitution.

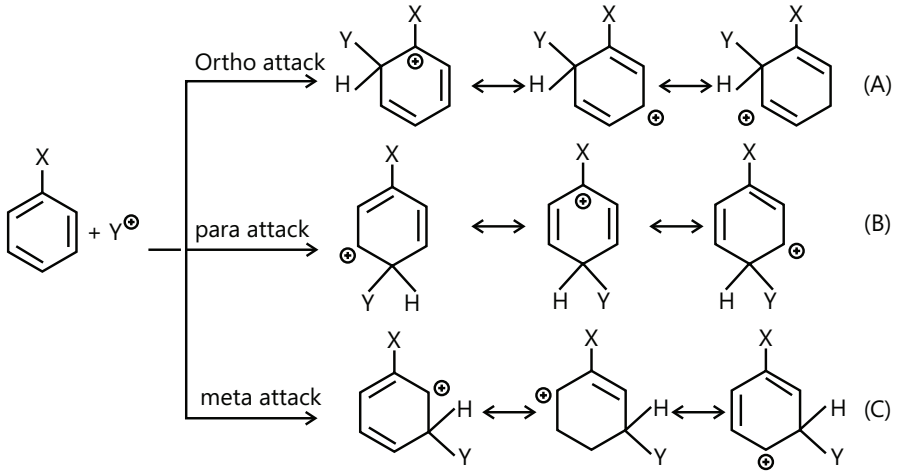


Addition



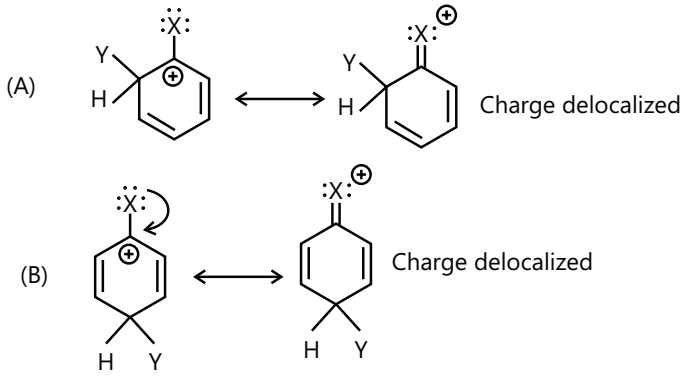
2. Electrophilic Substitution Reaction: Halogens are unusual in their effect on electrophilic substitution reactions: They are electron withdrawing yet ortho and para-directing.

To understand the influence of halogens, let us consider the intermediate formed when an electrophile attacks the halobenzene at ortho, meta and para positions.



In A, B and C if one considers the inductive effect i.e. (-I effect) of X then A and B would be unstable because the (+) charge comes on the carbon atom carrying the halogen atom X. The structure C will be most stable and the (+) charge does not come on the carbon atoms carrying the halogen atom X.

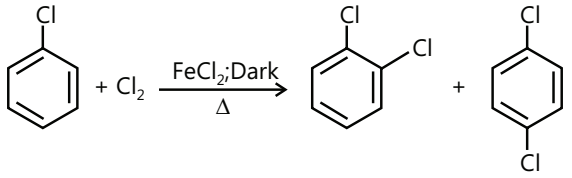
We should therefore expect that halogen atoms attached to the benzene ring would be meta. While directing for electrophilic substitution reactions, the existence of halonium ions have shown that halogen can share a pair of electrons and can accommodate a positive charge. When this idea is applied to the present problem the carbocations formed when an electrophile attacks at ortho or para position i.e. (A) and (B) would be stabilized as below. Whereas the carbocation formed when the electrophile attacks the meta position on halo benzene i.e. C would be destabilized.



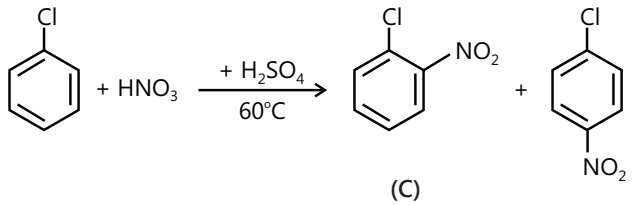
The inductive effect causes electrons withdrawing deactivation- the resonance effect tends to oppose the inductive effect for attack at ortho and para position, and hence makes the deactivation less for ortho and para than for meta. This shows reactivity is controlled by the inductive effect, and orientation is controlled by resonance effect.

Reactions

1. Halogenation

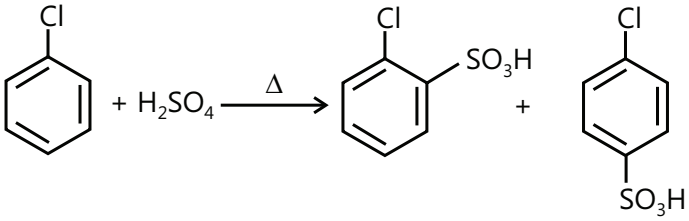


2. Nitration



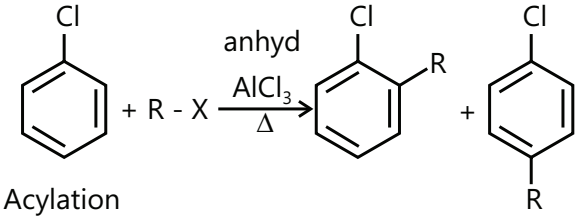
(C)

3. Sulphonation

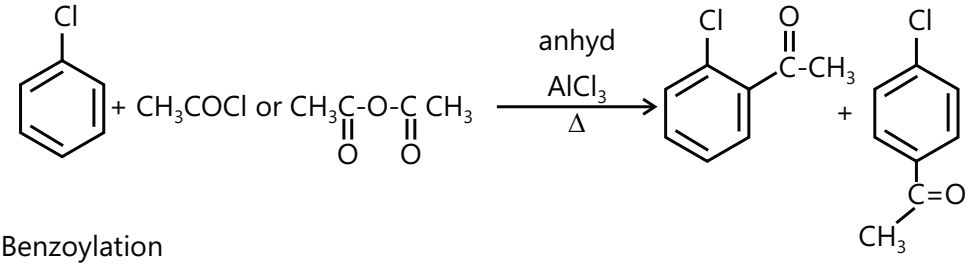


4. Friedel Crafts Reaction

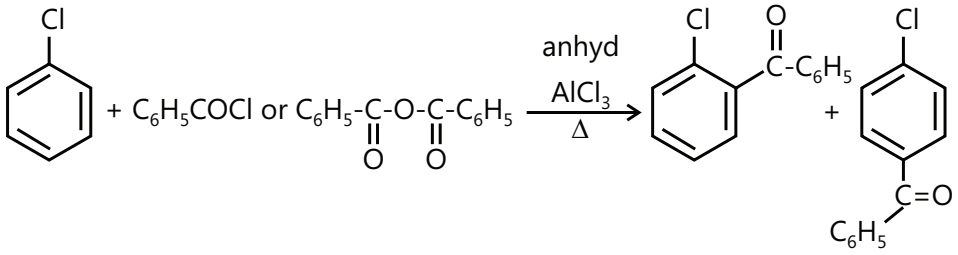
(a) Alkylation



(b) Acylation

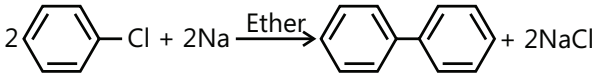


(c) Benzoylation

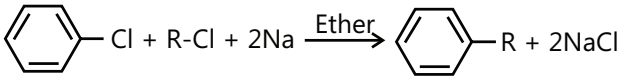


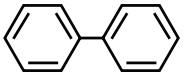
5. Miscellaneous Reactions

(a) Fittig reaction

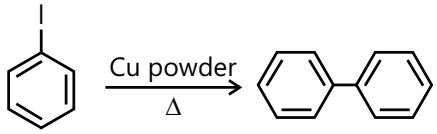


(b) Wurtz-Fittig reaction



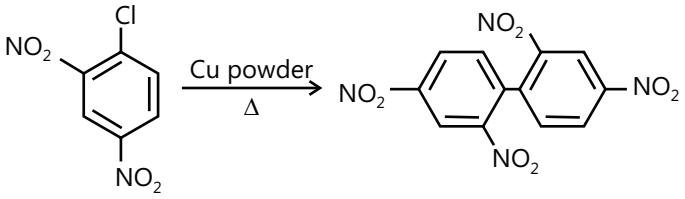
Here side products like R - R and  are also formed

(c) Ullmann's reaction



Biphenyl

Chlorobenzene does not undergo Ullmann's reaction but if a deactivating group is attached to chlorobenzene then the substituted chloro benzene can take part in Ullmann's reaction.



Nucleophilic Substitution Mechanism

Table 12.1: Difference between S_N1 and S_N2

	S_N2	**S_N1**
Reaction	RX + Nu −− > RNu + X	Same
Mechanism	Concerted	Two steps
Intermediate	None	Carbocation
Kinetics	Second-order	First order
Stereochemistry	Complete inversion	Nonspecific
Nucleophile	Important	Unimportant
Leaving Group	Important	Important
Alkyl Group	CH_3 > 1° > 2° > 3° (steric hindrance)	3° > 2° > 1° > CH_3 (carbocation stability)
Occurrence	CH_3, 1°, some 2°	3°, some 2°
Solvent Effects	Variable (Poloreproteic)	Polar, protic

MASTERJEE CONCEPTS

Elimination Mechanisms

Table 12.2: Difference between E1 and E2

	E2	**E1**
Reaction	RX + Base-->C=C	Same
Mechanism	Concerted	Two steps
Intermediate	None	Carbocation
Kinetics	Second-order	First order
Stereochemistry	Anti periplanar	Nonspecific
Base	Important	Unimportant
Leaving Group	Important	Important
Alkene Produced	Zaitsev Rule	Same

Substitution vs. Elimination

Table 12.3: Difference between substitution reaction and elimination reaction

	S_N1	**S_N2**	**E1**	**E2**
CH_3X	No	Good nucl.	No	No
1° (RCH_2X)	No	Good nucl., weak base	No	Strong base, weak nucl.
2° (R_2CHX)	No	Good nucl., weak base	No	Strong base
3° (R_3CX)	Good nucl., weak base	No	Polar solvent, no base or nucl.	Strong base

	Good nucl., strong base, e.g., OH-	**Good nucl., weak base, e.g., I-**	**Poor nucl., strong base, e.g., tBuO-**	**Poor nucl., weak base, e.g., H_2O**
CH_3X	S_N2	S_N2	S_N2	No reaction
$1^o\left(RCH_2X\right)$	S_N2	S_N2	E2	No reaction
$2^o\left(R_2CHX\right)$	E2	S_N2	E2	No reaction
$3^o\left(R_3CX\right)$	E2	S_N1	E2	S_N2

Aishwarya Karnawat (JEE 2012, AIR 839)

Illustration 19: Write the structure of carbocation produced on treatment of a compound (A)($Ph_2CHC(OH)Me_2$) with SbF_5/SO_2. **(JEE MAIN)**

Sol: It is formed by protonation and subsequent elimination of H_2O, followed by H^+ ion transfer to form a more stable carbonium ion.

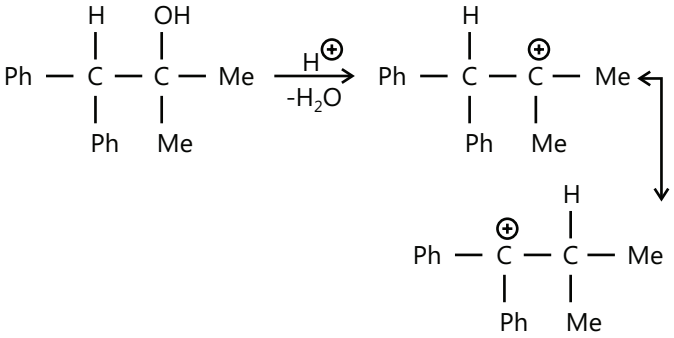
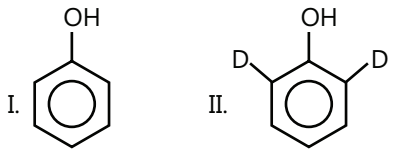
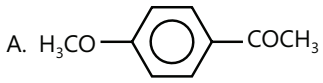


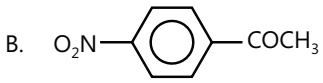
Illustration 20: Which of the following has the greater K_a value **(JEE Advanced)**



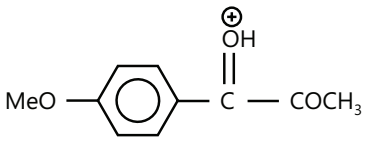
Sol: Deuterium is more e^- donating than H atom. Hence K_a of (i)>(ii).

Illustration 21: Which of the carbonyl groups in (A) and (B) protonate more readily in acid solution and why? **(JEE Advanced)**



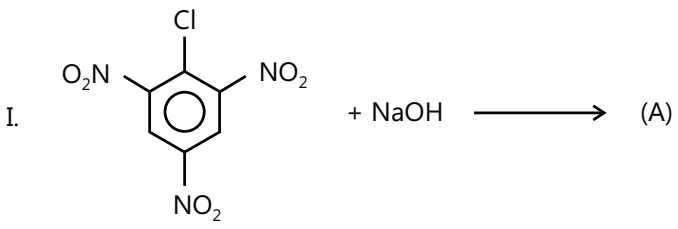


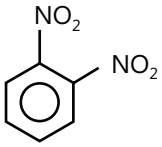
Sol: Protonation of (A) takes place more readily than (B), since protonated (A) is more resonance stabilised than protonated (B).

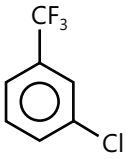


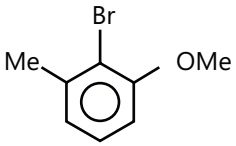
(A) More stable

Illustration 22: **(JEE MAIN)**

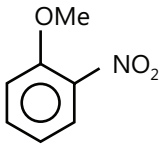


II.  $\xrightarrow[MeOH,\ \Delta]{MeONa}$ (B)

III.  $\xrightarrow[Liq.\ NH_3]{NaNH_2}$ (C)

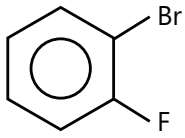
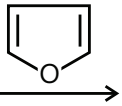
IV.  $\xrightarrow[Liq.\ NH_3]{KNH_2}$ (D)

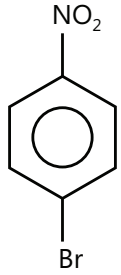
Sol: (I) [due to three e^- -withdrawing (NO_2) groups (C – Cl) bond is weakened.

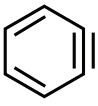
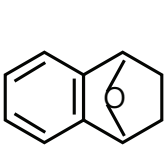
(II) 

(III) [Due to e^- -withdrawing ($-CF_3$) groups, (C – Cl) bond is weakened, so SN reaction takes place.]
(IV) No. reaction since there is no H at o-position that can form benzyne.

Illustration 23: **(JEE MAIN)**

I.  $\xrightarrow{Li/Hg}$ (F) $\xrightarrow{}$  (G)

II.  $\xrightarrow[C_2H_5OH]{KCN,\ \Delta}$ (H)

Sol: I. (F) $\Rightarrow$  $\xrightarrow[Diels\text{-}Alder]{}$  (G)

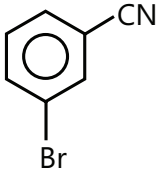
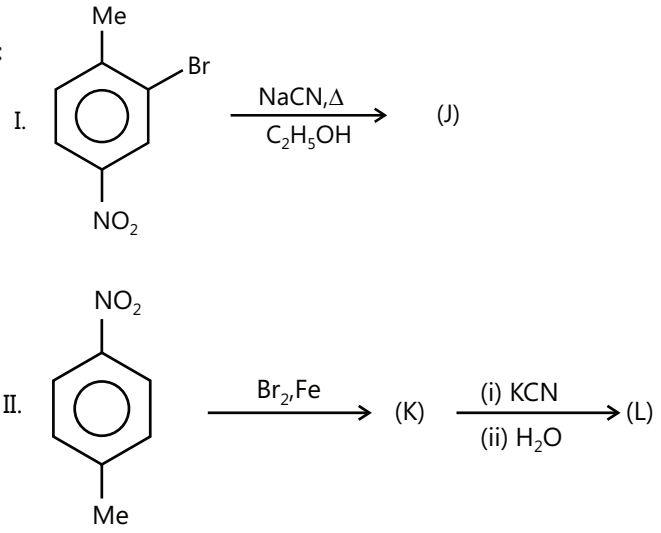
II. (H) $\Rightarrow$ 

Illustration 24:



(JEE ADVANCED)

Sol: I. (J)

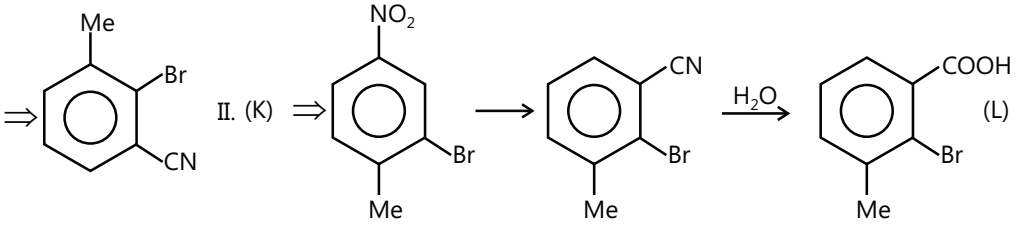
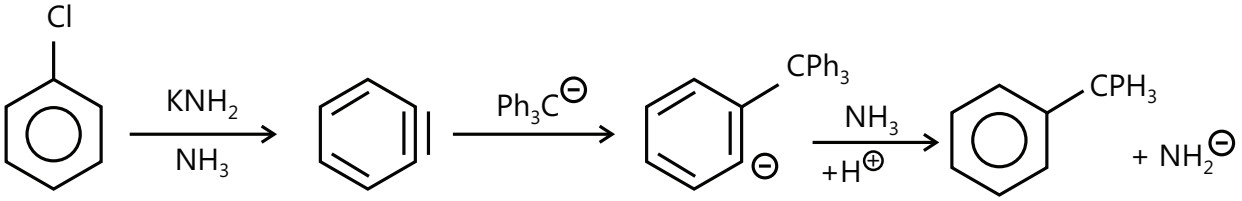


Illustration 25: When a trace of KNH_2 is added to a solution of chlorobenzene and potassium triphenyl methide ($(Ph)_3C^{\ominus}K^{\oplus}$) in liquid NH_3, a rapid reaction takes place to yield a product of formula $C_{25}H_{20}$. What is the product? What is the role of KNH_2 and why is it needed? **(JEE ADVANCED)**

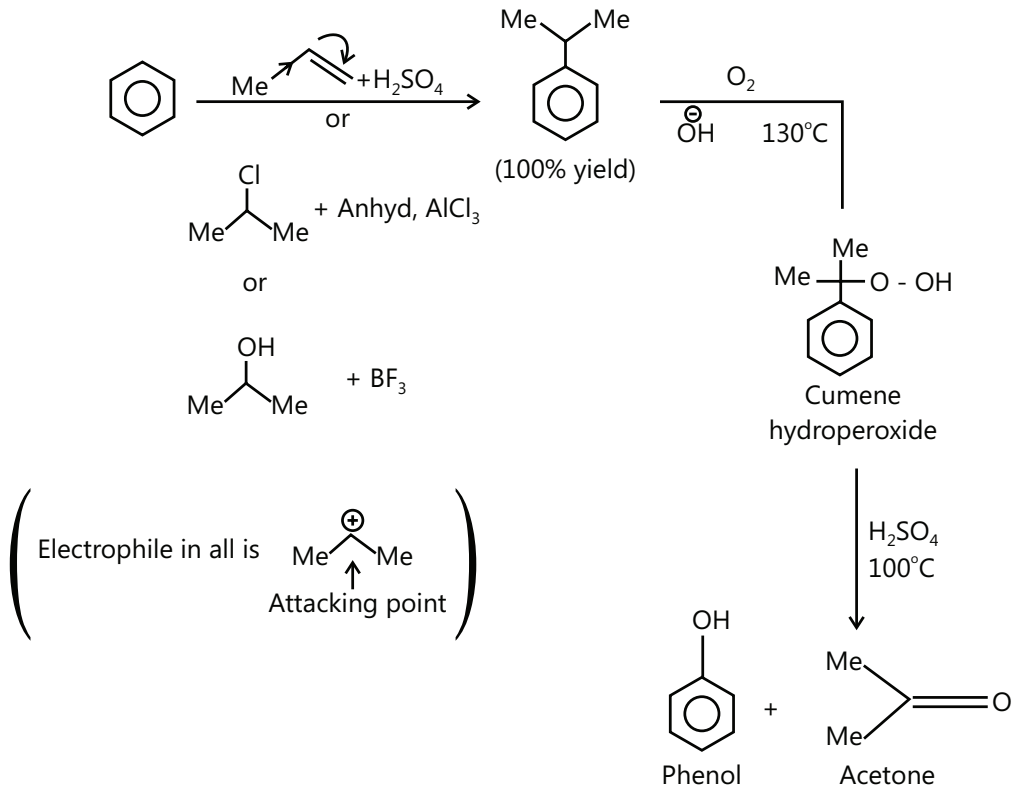
Sol: $C_{25}H_{20}$ suggests that the product is tetraphenylmethane, Ph_4C. KNH_2 is used to produce benzyne which combines with $Ph_3C^-K^+$ to give the final product.



OTHER AROMATIC COMPOUNDS

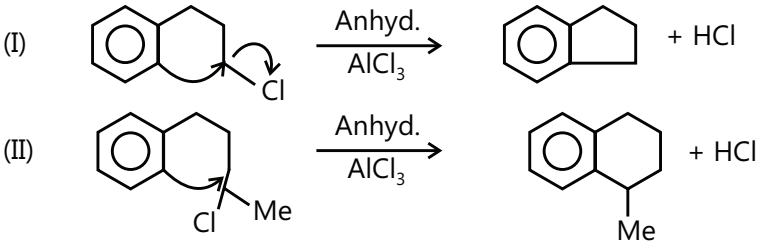
1. PHENOL

This process (to derive phenol) is carried out by the aerial oxidation of cumene to hydroperoxide, which is then decomposed by acid into phenol and acetone (by product).



2. INTRAMOLECULAR FRIEDAL CRAFT REACTION

When both (Ar) group and (R–X) are present within the same molecule, then the intramolecular friedal craft reaction takes place, e.g.,



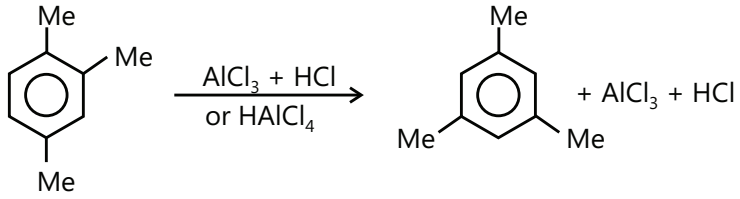
3. LIMITATIONS OF FRIEDAL CRAFT REACTION

(a) As aryl and vinyl halide (CH_2 = CHX) do not form carbocation easily, they are not suitable to be used as the halide component.

(b) Polyalkylation takes place quite often. After the introduction of one alkyl group (an activating group) the ring gets activated for further substitution. Friedal craft acylation does not suffer from this defect since the alkyl or aryl group, being a deactivating group, does not facilitate further substitution.

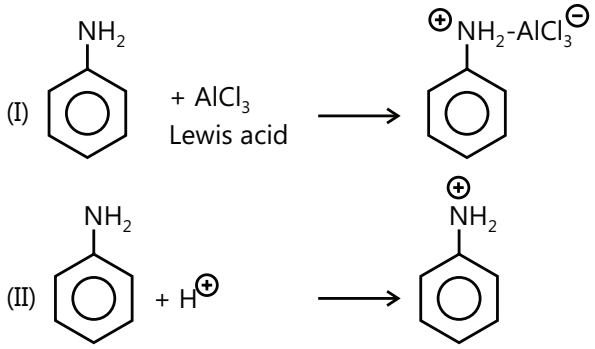
(c) Carbocations formed during the reaction rearrange to yield more stable carbocation.

(d) It is often accompanied by the rearrangement of alkyl group attached to the nucleus e.g., 1, 2, 4-trimethyl benzene rearranges to give mesitylene in friedal craft reaction.

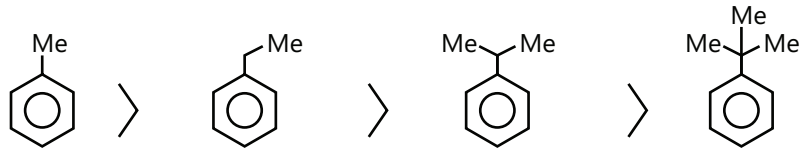


(e) The presence of e^--withdrawing groups (m-directing group) in the ring hinders the Friedal craft reaction, e.g., nitrobenzene and acetophenone do not undergo this reaction. On the other hand, if a strong activating group (e^--donating group) is present in either of the above two compounds, reaction takes place, e.g., o-nitro anisole can undergo this reaction.

(f) The presence of (NH_2), (NHR) and (NR_2) groups also inhibits the reaction. This is because these groups become powerful e^--withdrawing groups reacting with Lewis acid or with protoic acid when the compounds containing these are placed in friedal craft reaction mixtures.



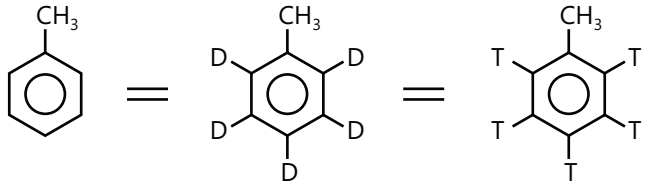
(g) Friedal craft reaction reactivity order of the following compounds is:



Toluene (Three H.C. Structure)	Ethyl benzene (Two H.C. Structure)	Isopropyl benzene (One H.C. Structure)	t-Butyl benzene (No H.C. Structure)

The above reactivity in friedal craft reaction is due to hyperconjugation (H.C.)

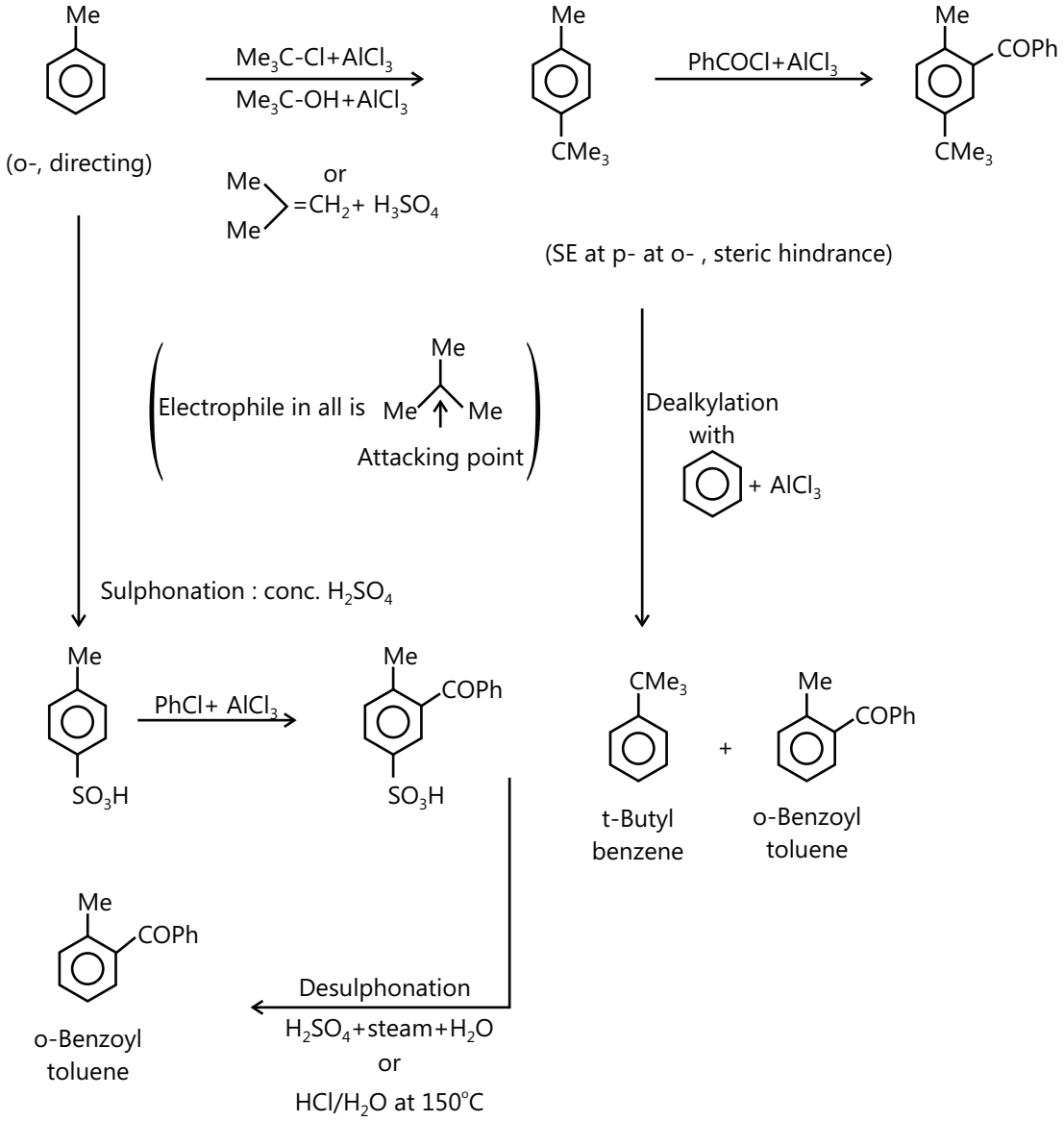
But friedal craft reaction reactivity order of the benzene deuterated or other isotopic label compound is:



Here, again no. (C–H), (C–D), or (C–T) bond break in the first R.D.S. (See mechanism), so primary isotope effect does not take place. So the rate of reaction of the above is almost same.

4. BLOCKING OF P-POSITION BY FRIEDAL CRAFT ALKYLATION

p-position in benzene derivatives can be blocked either by sulphonation and then desulphonation, or by friedal craft alkylation, by the use of bulky t-butyl group. In the dealkylation, benzene or toluene or m-xylene or HF may be used as an acceptor; for example,



To avoid the oxidation of aniline and phenol by nitration, the amino and (–OH) groups are protected by acetylation or benzoylation. The acetyl or benzoyl group is finally removed by hydrolysis to give o-and p-isomers.

Acetylation can be done by any of the following three acetylating reagents.

(a) $(CH_3CO)_2O$ + Glacial acetic acid

(b) $(CH_3CO)_2O$ + Conc. H_2SO_4

(c) CH_3COCl + Pyridine

The benzoylation of alcohol, phenol, aromatic or aliphatic amine with benzoyl chloride (C_6H_5COCl) and NaOH is called **Schotten-Baumann reaction**.

Example:

(i) $ROH + ClCOCH_3 \xrightarrow{Py.} ROCOCH_3 + HCl$

$\xrightarrow[+NaOH]{PhCOCl} ROCOPh + NaCl + H_2O$

(ii)

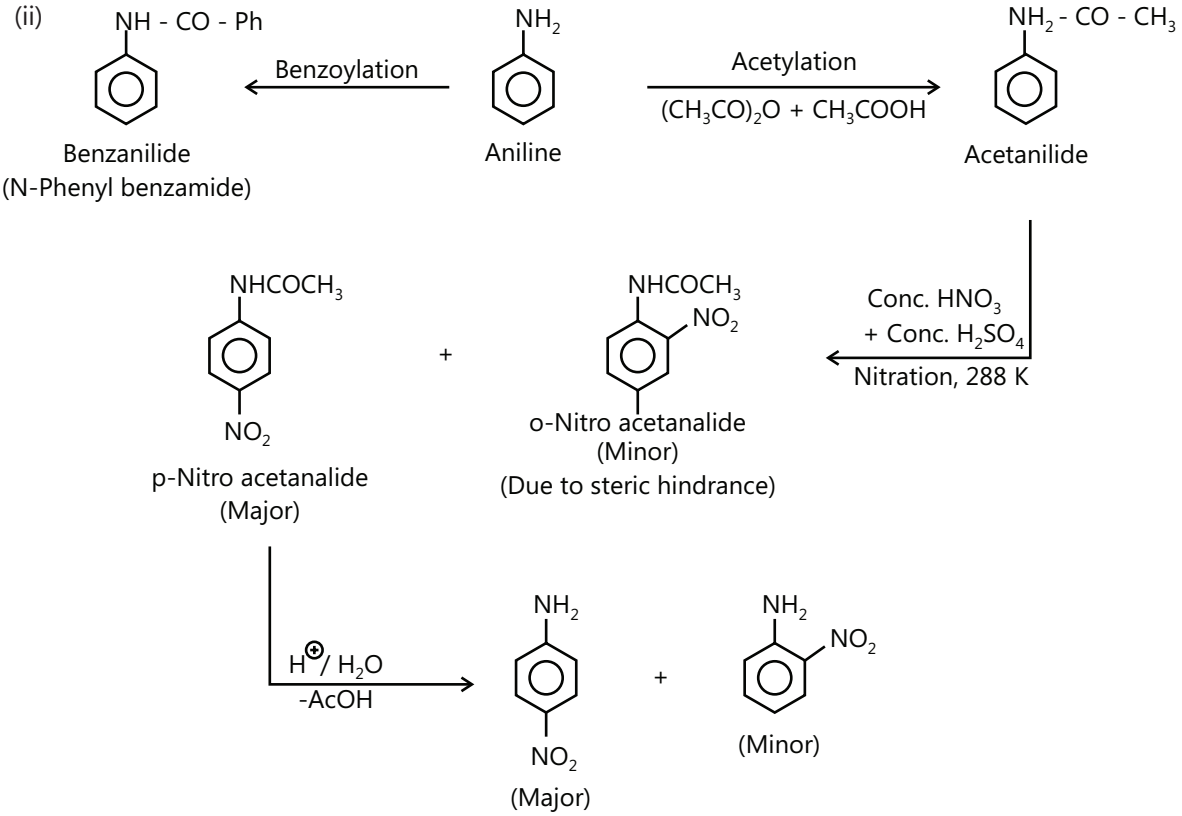
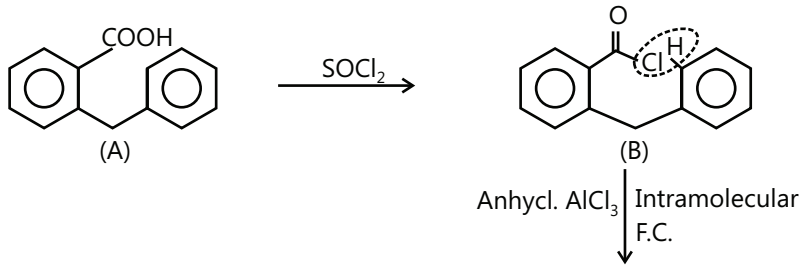
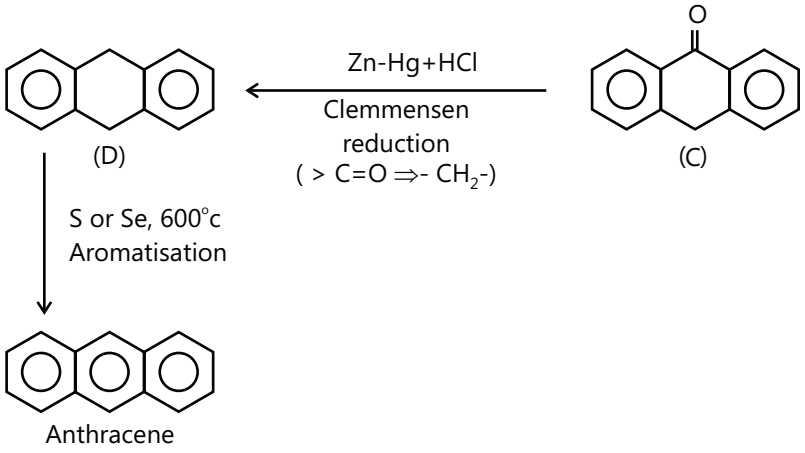


Illustration 26: Complete the following reactions: **[JEE ADVANCED]**

$$\underset{(A)}{o\text{-}HOOC - C_6H_4 - CH_2 - Ph} \xrightarrow{SOCl_2} (B) \xrightarrow[AlCl_3]{Anhyd.} (C) \xrightarrow[+ HCl]{Zn + Hg} (D) \xrightarrow[600^oC]{S \text{ or } Se} (E)$$

Sol:





5. DIRECTIVE/INFLUENCE

Standandard for comparison ⇒ –H in benzene

Class I (o- , p-directing)

i. Very strong activating groups

$$-:\ddot{O}:^{\ominus} > -NR_2 > -N\,HR > -\ddot{O}H$$

ii. Moderately activating groups

$$-OR \Rightarrow -NH-\overset{\overset{O}{\|}}{C}-R > -O-\overset{\overset{O}{\|}}{C}-R$$

iii. Weakly activating group

$$-R > -Ar > -CH=CH_2$$

Class II (m-directing)

i. Very strong deactivating groups

$$-\overset{\oplus}{O}_3 > -\overset{\oplus}{N}HR_2 > -\overset{\oplus}{N}H_3 > -NO_2$$

$$> -CF_3 > -SO_3H > -C\equiv N$$

ii. Moderately activating groups

$$-\overset{\overset{O}{\|}}{C}-H > -\overset{\overset{O}{\|}}{C}-R > -\overset{\overset{O}{\|}}{C} > -\ddot{O}H > -\overset{\overset{O}{\|}}{C}-X >$$

Aldehyde Ketone Acid Acid halide

$$> -\overset{\overset{O}{\|}}{C} > -\ddot{O}-R > -\overset{\overset{O}{\|}}{C} > -\ddot{O}-\overset{\overset{O}{\|}}{C}-R > -\overset{\overset{O}{\|}}{C} > -\ddot{N}H_2$$

Ester Anhydride Amide

iii. Deactivating groups

$$-F > -Cl > -Br > -I \text{ (Due to } -I \text{ effect)}$$

$$-CH_2X > -SR > N=O-\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{\underset{\cdot\cdot}{S}}}-R$$

MASTERJEE CONCEPTS

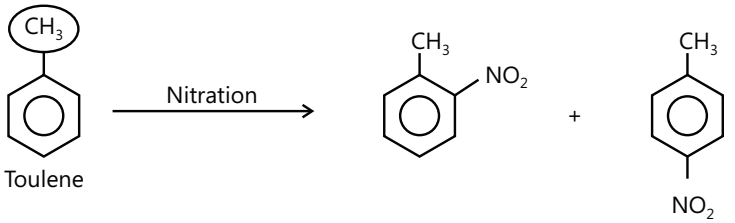
All o^-, p-directing groups except halogens and groups in (iv) are activating groups.

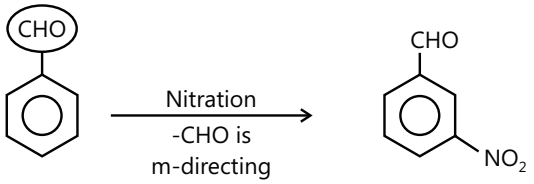
All those substituents which are more reactive than benzene (standard for comparison) are activating.

Vaibhav Krishnan (JEE 2009 AIR 22)

5.1 Directive Influence on Second, Third and Fourth Group

Second group

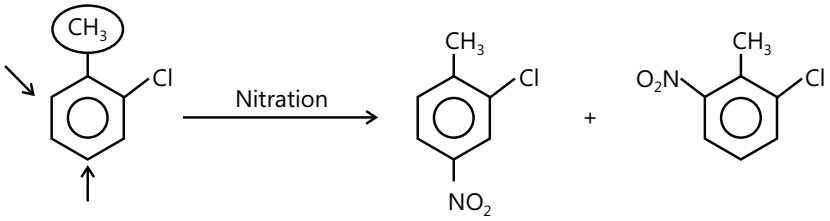




Third group: The position of a third group entering the benzene ring is determined by the nature of two groups already present there.

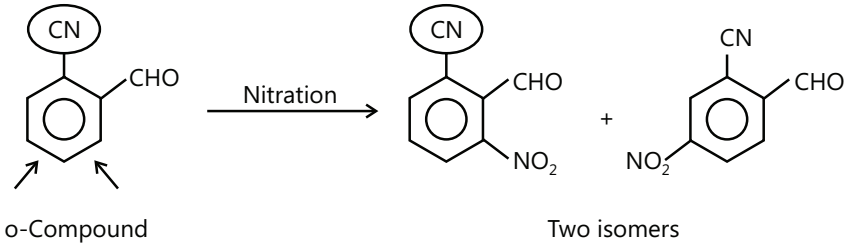
Case I: When both the groups belong to Class I, the directive influence of each group is in the order as given in Table. (When both the groups belong to Class I): Reactivity of ($-CH_3$) > (–Cl).

i.

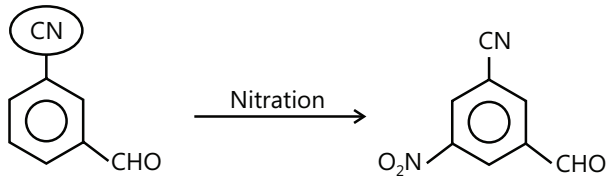


Case II: When both the groups belong to Class II, the third group is introduced only with difficulty. The directive influence of each group is in the order as given in Table. (When both groups are of Class II): Reactivity of (–CN) > (–CHO)

i.



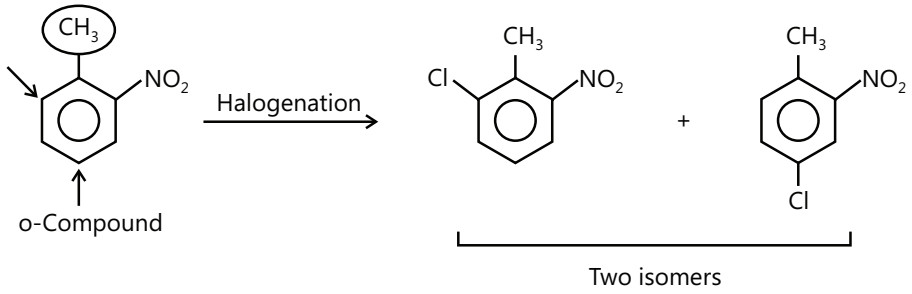
ii.



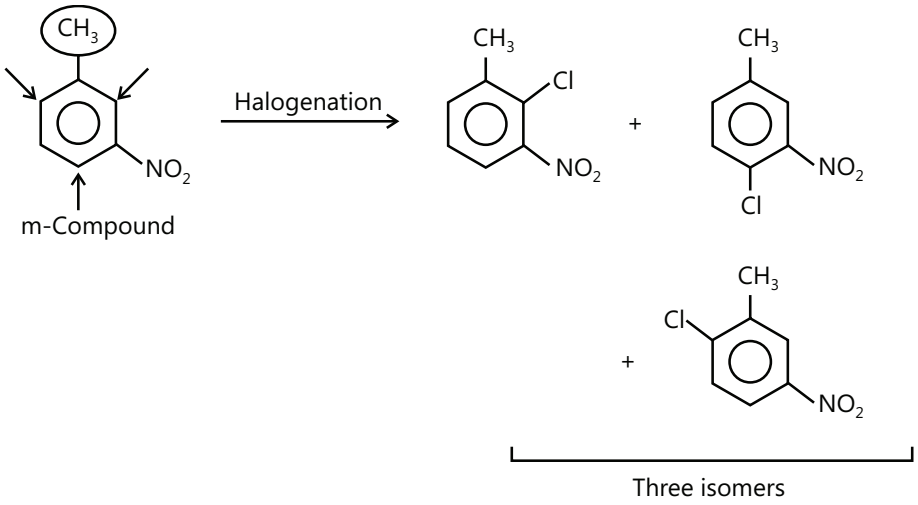
Case III: When groups belongs to Class I and Class II, the directive influence of the group belonging to Class I takes precedence. (When both groups are of Class I and Class II):

(– CH_3) group of Class I directs the substitution.

i.

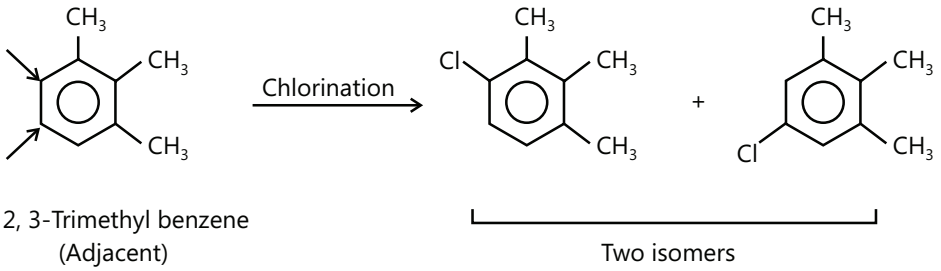


ii.



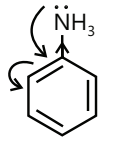
Fourth Group: When a trisubstituted substance is converted to a tetrasubstituted product, adjacent compound (i.e., 1, 2, 3-derivative) gives two, the unsymmetric compound (i.e., 1, 2, 4-derivative) gives three, and the symmetric compound (i.e., 1, 3, 5-derivative) gives only one tetrasubtituted product.

For Example:



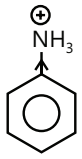
6. RELATIVE REACTIVITIES

All the activating groups render the benzene ring more reactive and the deactivating groups less reactive than benzene towards SE reaction. If a substituent contains a pair of non-bonded e^-'s on the atom directly attached to the benzene ring, and these e^-s being in conjugation with the πe^-s of the benzene ring are delocalized into the ring through π- orbital overlap, then it is called electron donation by resonance or π donation, for example, $\ddot{O}H, -\ddot{N}H_2, -\ddot{B}r:$, etc. They also withdraw e^-s inductively due to the greater electronegativity (EN) of the atom attached to the benzene ring than the EN of H. This is called σ-withdrawing or inductive electron withdrawing.

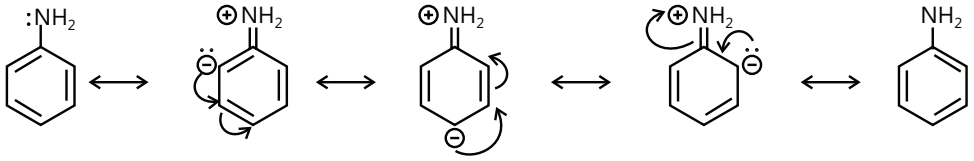


π donation
and σ withdrawing
(or)
e^- donation by
resonance and inductive
e^- withdrawing

σ donation
(or)
(Inductive e^- donation)

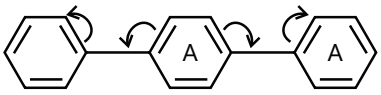


σ withdrawing
(or)
(Inductive e^- withdrawing)



π-donation

Donate $\bar{e}$'s into the ring by resonance (π donation) and withdraw $\bar{e}$'s from the ring inductive (σ withdrawing). But they donate $\bar{e}$'s into the ring less effectively than the very strong activating groups. It means that they are less effective e^- donors by resonance, since they can donate $\bar{e}$'s by resonance in two opposite competitive directions, i.e., into the ring and away from the ring (cross conjugation) and this net resonance effect is decreased. Despite this, $\bar{e}$ donation by resonance is more than $\bar{e}$ withdrawal by inductive effect (σ withdrawal). That is why these groups are moderately activating. ($-CH=CH_2$), ($-CH=CH-R$), ($-CH=CR_2$), and aryl (Ar^-) groups are weakly activating groups. They can donate and withdraw $\bar{e}$s by resonance but are slightly more e^- donating than e^- withdrawing. In case of three isolated rings, the central ring (A) acts as e^- donating by resonance, since it is bonded to two activating Ph group and it can donate e^-s on either side of the ring.



Benzene
(e donation by resonance by ring A on either side)

Alkyls [($-CH_3$), ($-C_2H_5$), and $-CH(CH_3)_2$] are weakly activating groups. An alkyl group is a weak e^- donor inductively (σ donation) and simultaneously e^- donor by hyper conjugation.

The halogens are weakly deactivating groups because they donate e^-'s to the ring by resonance (π donation) and withdraw e^-'s inductively (σ withdrawal). The deactivating characteristic is due to the high EN of halogens, yet they are o^-, p-directing due to e^- donation by resonance (X =–F, –Cl, –Br, –I).

Illustration 27: Given the decreasing order of the relative reactivity towards SE reaction of the following compounds.

(a) I. Benzene, II. Phenol, III. Aniline, IV. Chlorobenzene

(b) I. Acetanilide, II. Aniline, III. Acetophenone, IV. Benzene

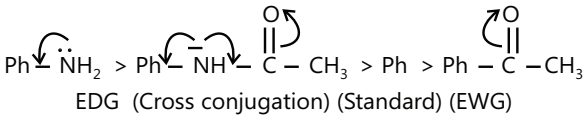
(c) I, 1,3-Dimethyl benzene, II. 1, 4-Dimethyl-benzene, III. Toluene, IV. Benzene, V. 1,3, 5-Trimethyl benzene

(JEE ADVANCED)

Sol: (A) (III) > (II) > (I) > (IV) ($PhNH_2$ > PhOH > PhH > Ph-Cl)

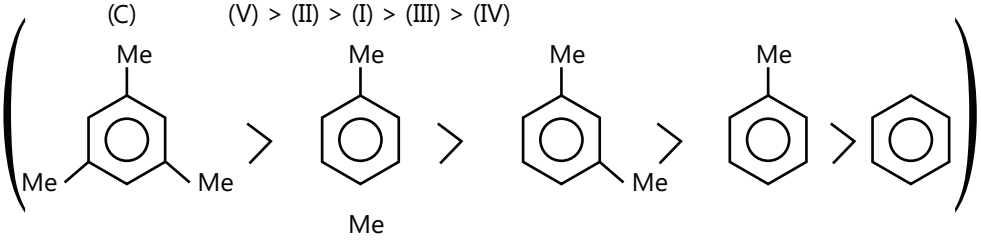
Reactivating of $-NH_2$ > – OH > – H > – Cl

(B) (II) > (I) > (IV) > (III)



(C) (V) > (II) > (I) > (III) > (IV)

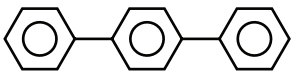
(C) (V) > (II) > (I) > (III) > (IV)

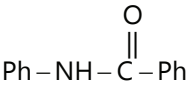


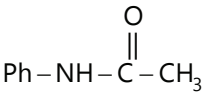
(H.C. Effect)

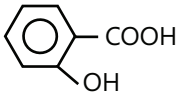
Illustration 28: Indicate by an arrow the position(s) where SE reaction takes place in the following:

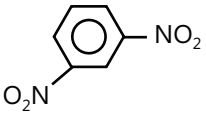
(JEE ADVANCED)

(A) 

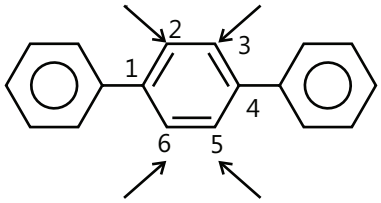
(B) 

(C) 

(D) 

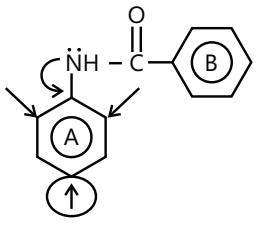
(E) 

Sol: Electrophilic Substitution takes place at position where electron density is maximum. Depending upon the group present and their influence (ortho,meta,para) predict the site of SE

(A) 

1, 4-diphenyl benzene
or
p-terphenyl

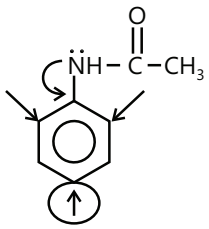
SE reaction takes place at the place indicated by the arrows in the central ring, since it is joined to two activating phenyl rings.

(B) 

Benzanilide

Ring (A) bonded to (–NH–) is activated. So SE reaction takes place at o^- and p-position of ring (A) but p-product is major, since o-positions will be sterically hindered. Ring (B) is bonded to group and is deactivated.

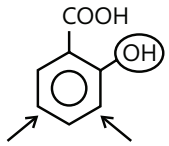
(C)



Acetanilide

Same explanation as in (b), p-product is major.

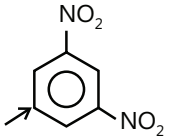
(D)



(o- and p-w.r.t.-OH)

The (–COOH) group is deactivating and m-directing, (–OH) is activating, and o-and p-directing class I (–OH) decides orientation.

(E)

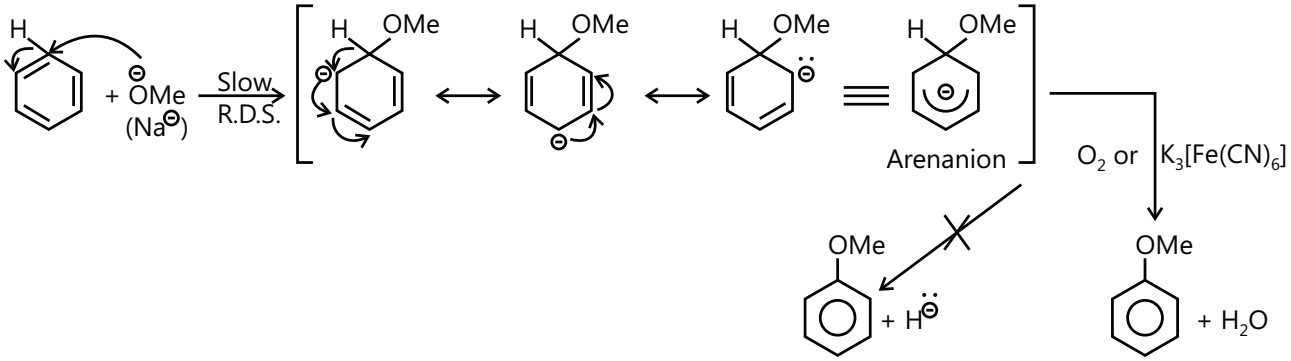


No reaction because of two strongly deactivating ($–NO_2$) groups.

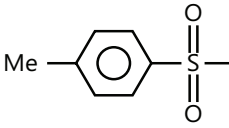
However, the ($–NO_2$) group is m-director; if suitable conditions are employed then ($–NO_2$) directs at m-position.

7. AROMATIC SUBSTITUTION REACTION IN BENZENE

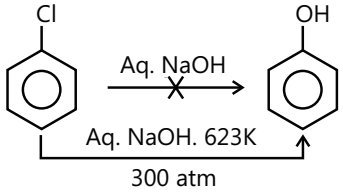
Ar-SN: SN reaction is benzene under ordinary conditions is not possible, since the displacement of $H^{\oplus}$, a very strong base and poor leaving group, is very difficult. This can occur only if an oxidant can convert $H^{\oplus}$ to H_2O. The oxidant O_2 or K_3 $[Fe(CN)_6]$ can convert $H^{\oplus}$ to H_2O.

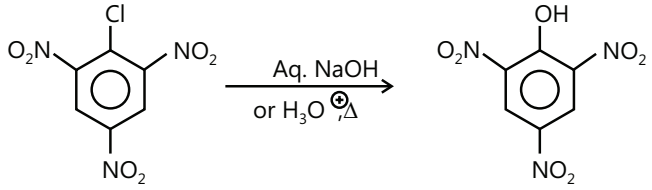


ArSN reactions are possble with ArX and ArOTs, aromatic halides and tosylate (-Ts = p-Toluene sulphonyl group



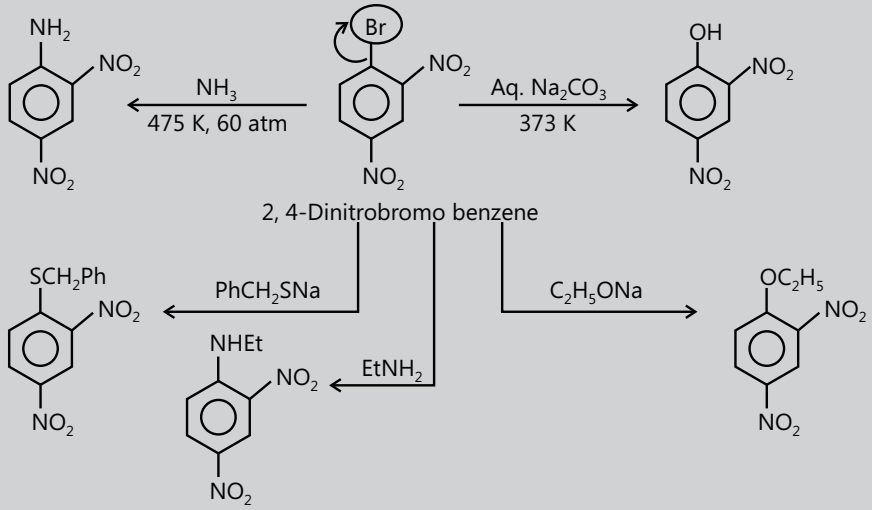
). Both –X and (–OTs) are good leaving groups, especially when EWG (e^--withdrawing groups), such as ($–NO_2$) and (–C ≡N), are present at ortho and/or para to the reacting C atom e.g.,

(I) 

(II) 

MASTERJEE CONCEPTS

Greater the number of these EWG at o-and/or p-position, faster is the reaction and lesser vigorous are required. This is also called addition-elimination reaction (since $Nu^{\oplus}$ adds and –X eliminates)



Nikhil Khandelwal (JEE 2009, AIR 94)

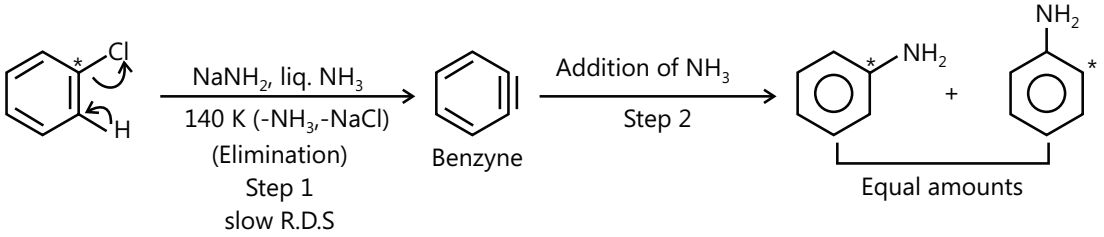
7.1 Aromatic Nucleophilic Substitution

ArX undergoes nucleophilic substitution reaction in the presence of a very strong base such as $NaNH_2$ or KNH_2 in liquid NH_3 at –33°C (140 K). The reaction occurs through the formation of an intermediate called benzyne.

Two important features are :

(i) There is no necessity of an e^--withdrawing group in the ArX.

(ii) The entering group does not always occupy the vacated position. This is called cine substitution.



Step 1: Slow R.D.S: In this reaction, first the elimination of HCl occurs and then the addition of NH_2 takes place, so, this ArSN reaction is called elimination-addition reaction.

When chlorobenzyne (I) with ^{14}C is treated with $NaNH_2$ in liquid NH_3, half of the product has an ($-NH_2$) group attached to ^{14}C (C*) as expected, but the other half has an ($- NH_2$) groups attached to the carbon adjacent to ^{14}C (C*). This observation proves the formation of a benzyne intermediate which has two equivalent C atoms to which the ($-NH_2$) group can be attached. Benzyne has an additional π-bond formed by sideway overlap of sp^2 orbitals alongside the ring. These orbital's that form π- bond cannot overlap with the aromatic π-system because they are not coplanar. The new π-bond is weak because of the poor overlap and hence benzyne is very reactive.

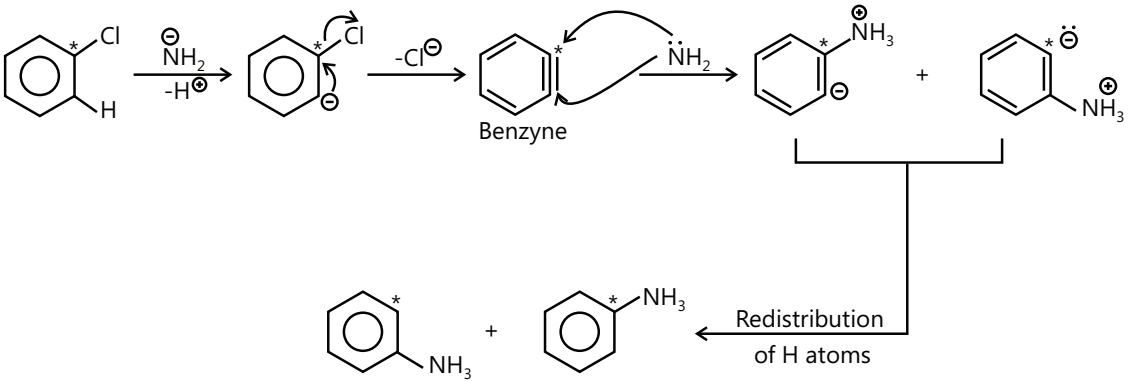
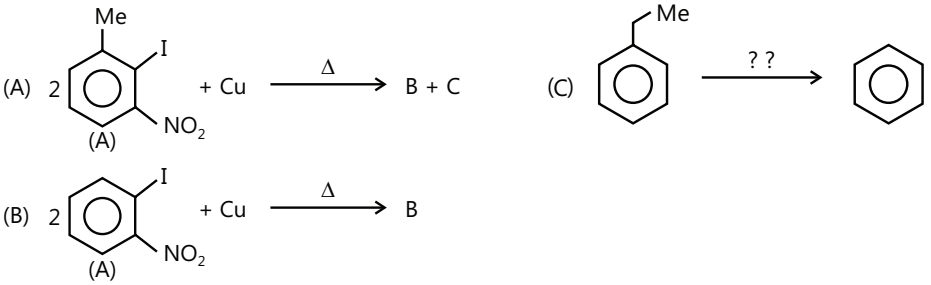
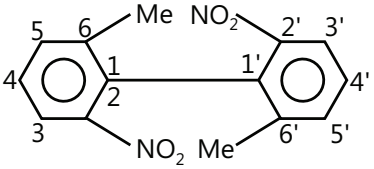


Illustration 29: Complete/Convert the following



Sol: (A) It is Ullmann reaction.



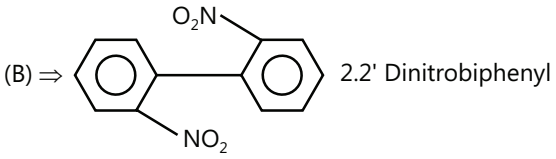
B = (+) form

C = (+) form

(±) 6.6'-Dimethyl-2.2'-dinitro biphenyl

The diphenyl is sterically hindered because of bulky ortho substituents, therefore phenyl rings cannot be coplanar, and the energy barrier for rotation of ($C^1 - C^1$) σ-bond is very high for inter-conversion of enantiomers. The enantiomers are isolable at room temperature. This type of stereoisomerism is due to restricted rotation about a single bond. Such a process in which stereoisomers can be isolated is called atropisomerism and the isomers so formed are called atropisomers.

(B) It is also Ullmann reaction.



In this case, free rotation about the single bond is possible and each ring has vertical plane of symmetry. Hence, it does not show optical isomerism.

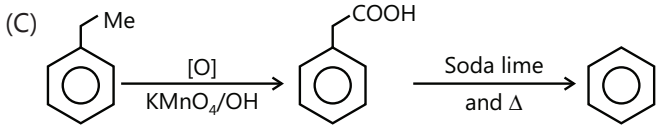
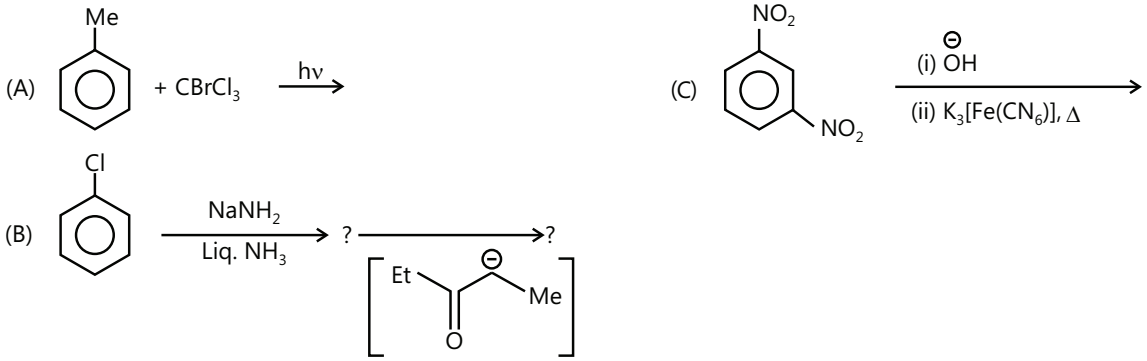


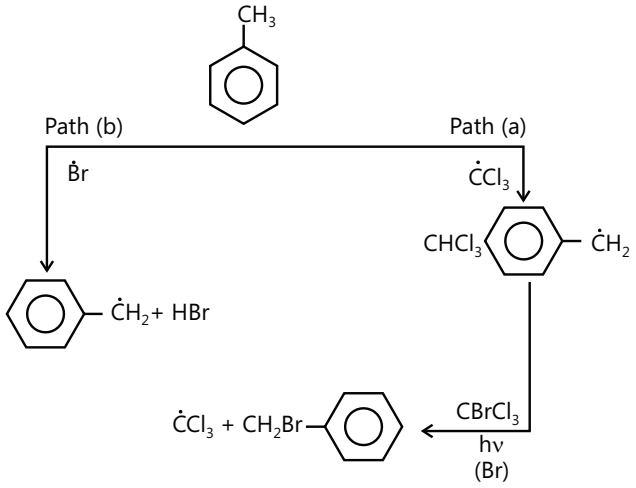
Illustration 30: Complete the following reactions: **(JEE ADVANCED)**



Sol: (A) Reaction proceeds by free radical mechanism because in the presence of light, radicals are formed. (C – Br) bond is weaker than (C – Cl) bond and hence (C – Br) bond breaks to give Br^-.

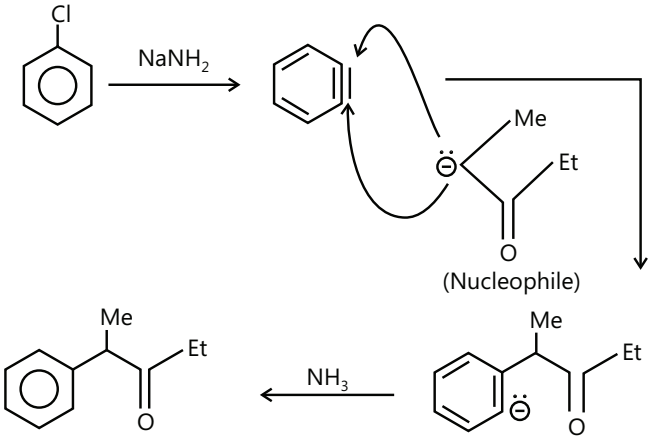
$$CBrCl_3 \xrightarrow{h\nu} Br\bullet + \bullet CCl_3$$

Attack by $\left(\bullet CCl_3\right)$ on toluene occurs at the Me side chain and not in the ring because (C – H) bond of Me is weaker than (C – H) bond of the ring. Moreover, benzyl radical is more stable than aryl radical.



Path (A) is favourable because the formation of $CHCl_3$ is more stable than the formation of HBr. It is because (C – H) bond in $CHCl_3$ is stronger than (H – Br) bond.

(B) It is an example of ArSN (elimination-addition) reaction via benzyne.



(C) It is an example of ArSN (addition-elimination) reaction due to the presence of strongly EWG [two ($-NO_2$) groups]. H atom at o- and p- to ($-NO_2$) group will be most activated and is attacked by nucleophile $\left(\overset{\ominus}{OH}\right)$ at these positions. K_3 $[Fe(CN)_6]$ is an oxidising agent to remove proton from the complex

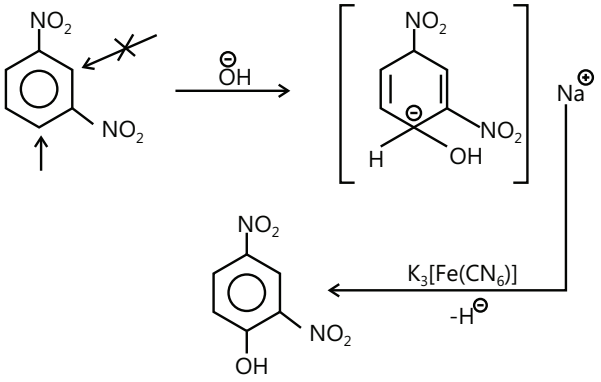
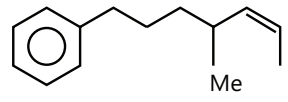
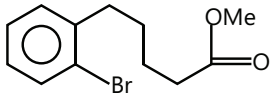


Illustration 31: **(JEE ADVANCED)**

(i) 

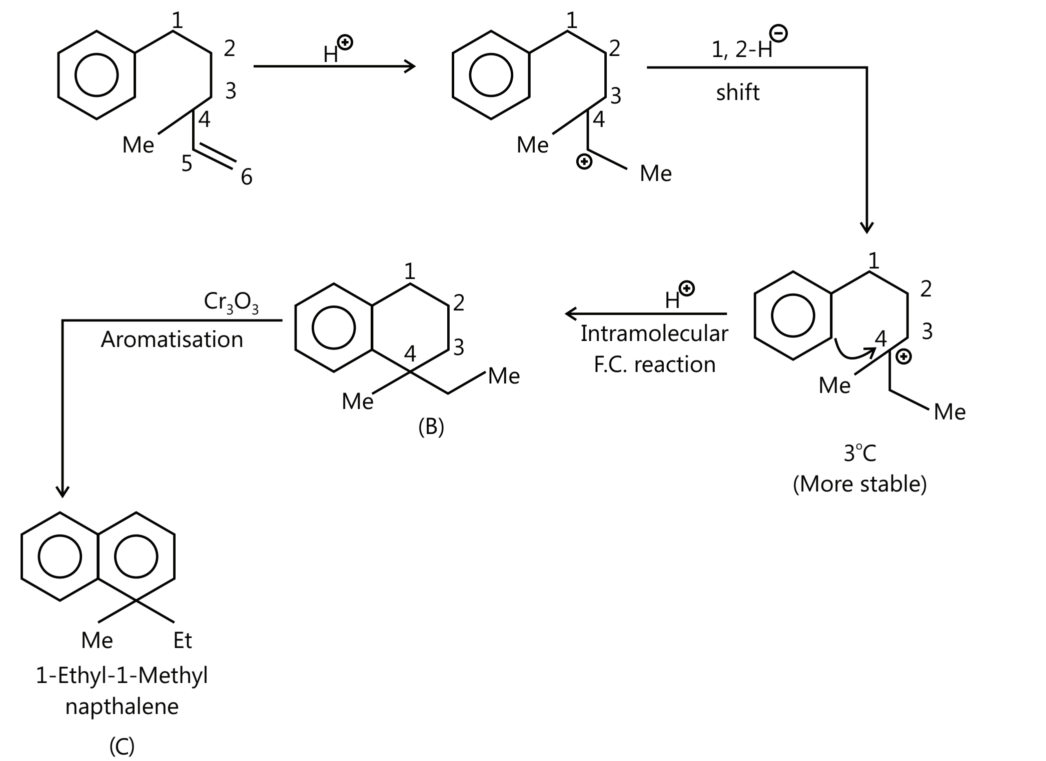
$\xrightarrow{H^{\oplus}}$ (B) $\xrightarrow[\text{or } Mo_2O_3]{Cr_2O_3 \text{ or } V_2O_5}$ (C)
773K. 10-20 atm

(ii) 

$\xrightarrow[2.\ H_3O^{\oplus}]{1.\ \text{Excess of } NaOH_2.NH_3}$ (G)

Sol: These reaction are example of intermolecular friedal craft alkylation reaction.

(i)



(ii)

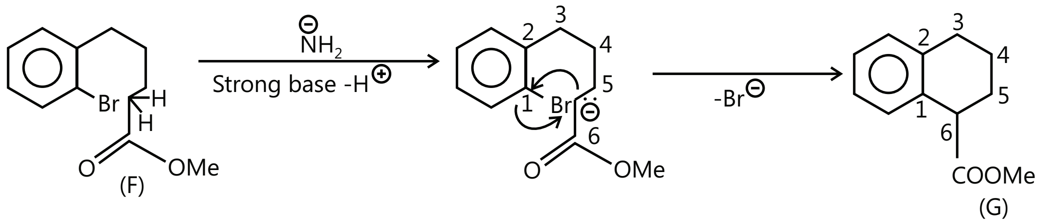
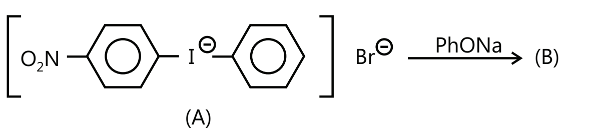
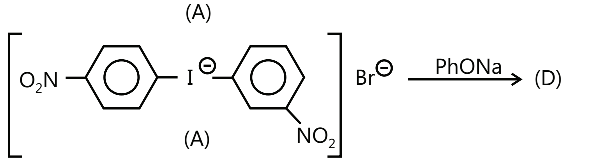


Illustration 32: Indicate the position where ArSN reaction will take place and explain why. **(JEE ADVANCED)**

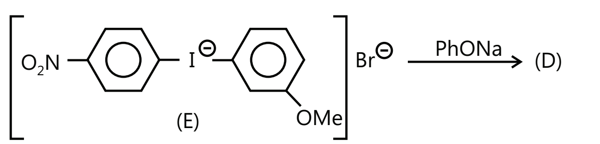
(i)



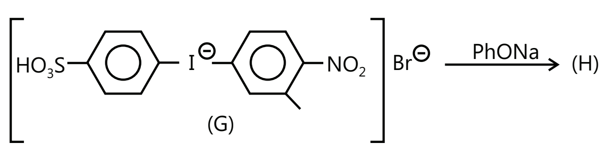
(ii)



(iii)



(iv)



Sol: ArSN (addition-elimination) reaction takes place in the ring which contains strong EWG at o- or / and p to the eliminating group.

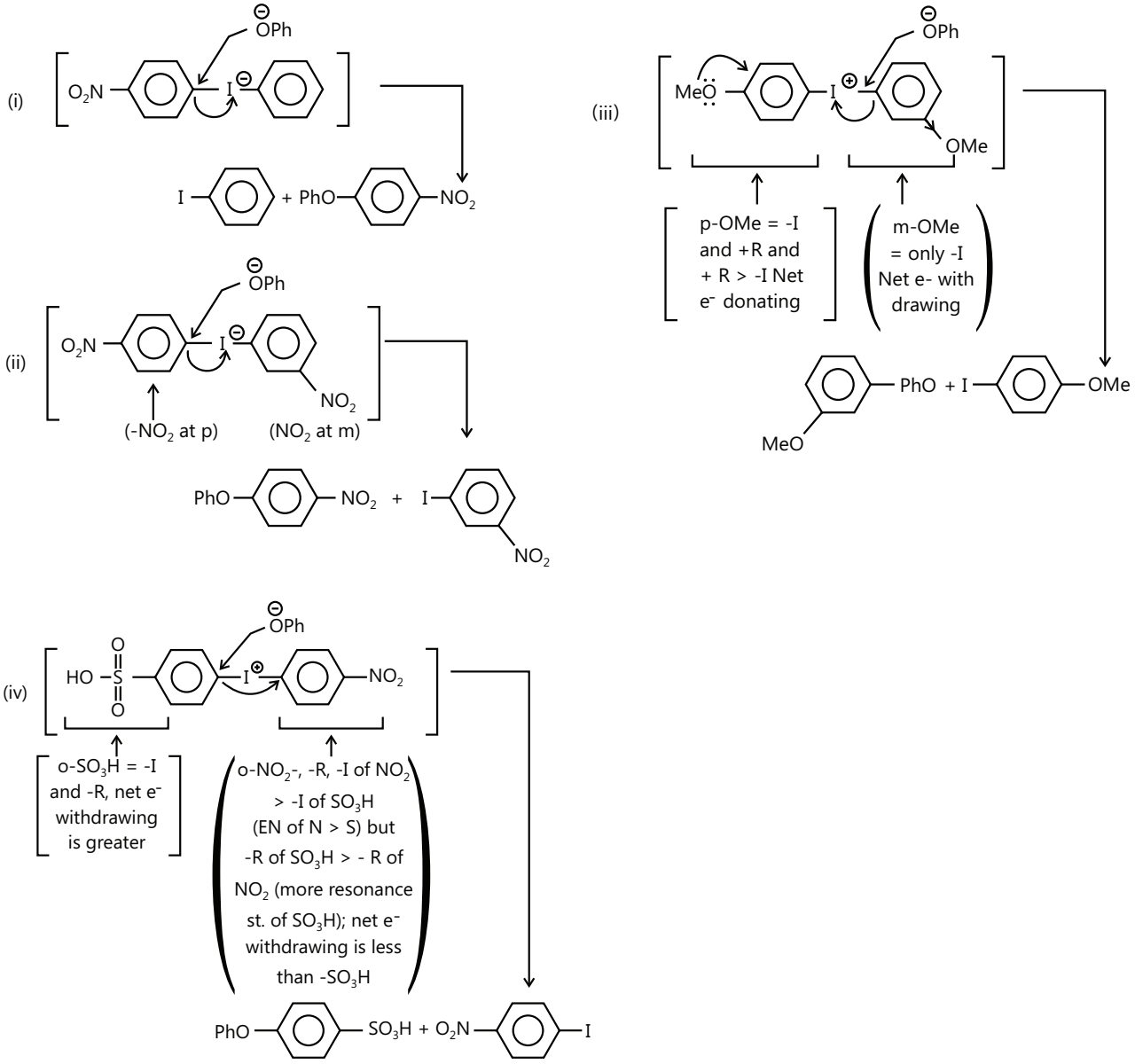
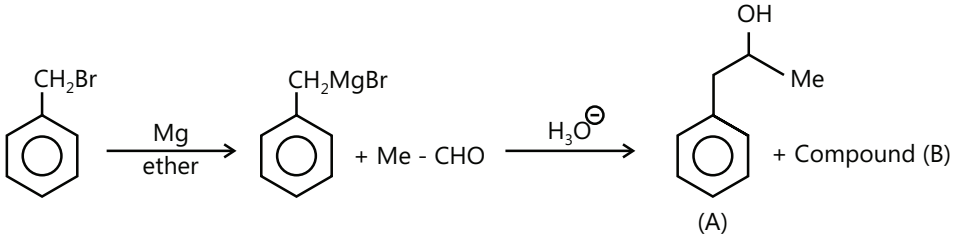
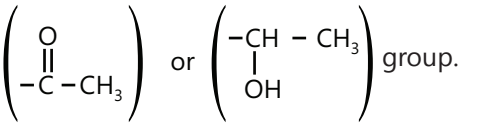


Illustration 33:



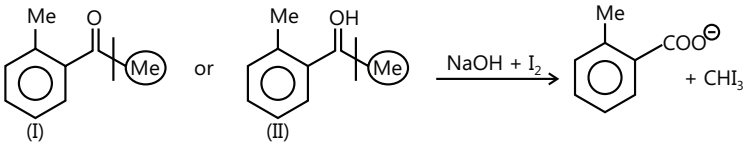
Compound (B) is an isomer of (A). Compound (B) shows positive iodoform test and gives o-toluic acid. What is (B)? Explain its formation. **(JEE ADVANCED)**

Sol: (B) is an isomer of (A) and shows iodoform reaction, therefore, the side chain must contain either



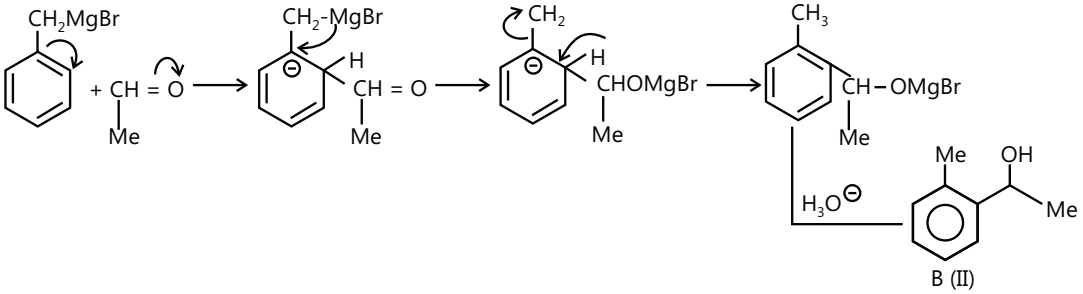
group.

Compound (B) may be:



But (I) is not an isomer of (A) (molecular formula $C_9H_{10}O$), (II) is an isomer of (A). Hence, compound (B) is (II).

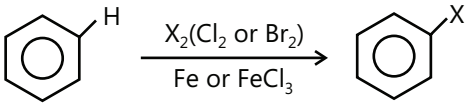
Formation of (II): It involves the rearrangement. The (CH_3CHO) group is attached to o-position of the ring, due to the polarisation of (Me-HC=O ↔ Me-CH-O) in which o-position of the ring behaves as the nucleophilic centre.



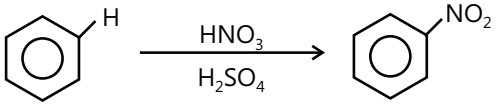
POINTS TO REMEMBER

1. Electrophilic substitution reaction:

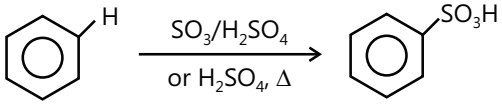
(a) Halogenation – Addition of Cl or Br : need a Lewis acid catalyst (Fe or $FeCl_3$)



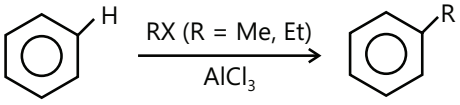
(b) Nitration



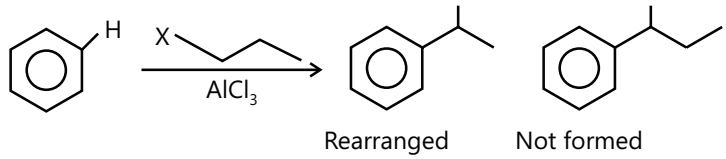
(c) Sulfonation



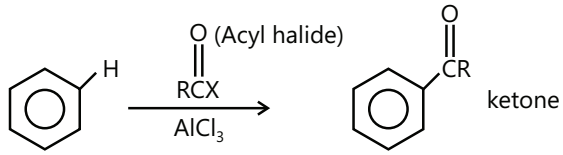
(d) Friedel – Crafts Alkylation – Substitution of methyl (Me) or ethyl (Et) need Lewis acid catalyst.



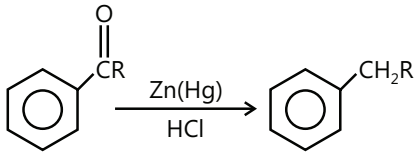
Why does R have to be Me or Br ? Longer alkyl chains attach at most substituted carbon.



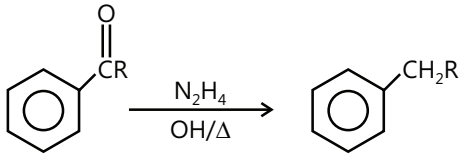
(e) Friedel-Craft Acylation – Substitution of acyl group (RC = O) for H : Need Lewis acid catalyst.



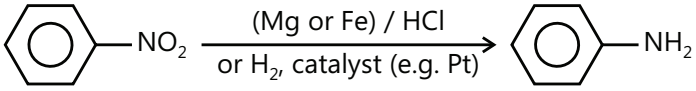
2. Clemmensen reduction



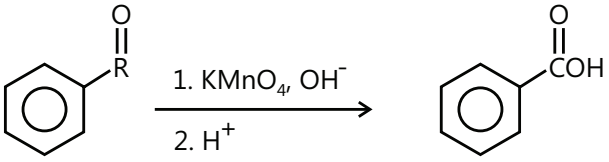
3. Wolf-Kishner reduction



4.

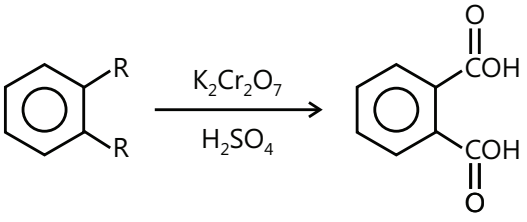


5.



Carboxylic acid

6.



Dicarboxylic acid

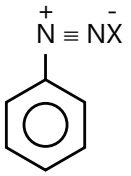
Flow Chart:

Nucleophilic substitution

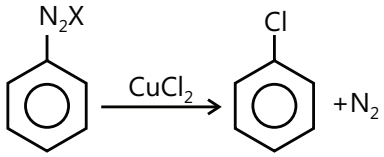
S_N1	S_N2	S_Ni
• Neucleophilic substitution • Unimolecular reaction • Two step • Primary Alkyl halide uses this mechanism • Retention of configuration	• Neucleophilic substitution • Bimolecular reaction • One step • Primary Alkyl halide uses this mechanism • Inversion of configuration	• Reaction of $SOCl_2$ with secondary alcohol • Retention of configuration when only $SOCl_2$ is used • When $SOCl_2$ and pyridine is used, inversion of configuration

Preparation of Aryl Halide:

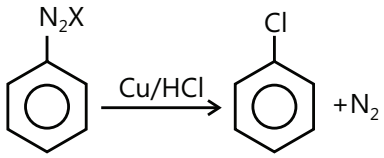
(1) From diazonium salt



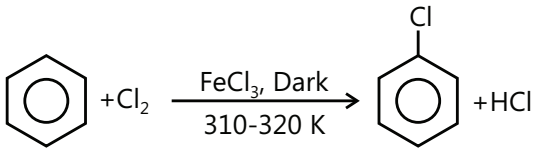
(a) Sandmeyer reaction :



(b) Gattermann reaction :



(2) Direct halogenation of aromatic hydrocarbon



Elimination reaction

E1

- Unimolecular elimination
- Two step process
  - Ionization
  - Deprotonation
- Take place with tert. Alkyl halide
- In competition with S_N1 reaction because they share a common carborcationic intermediate
- Occurs in
- Absence of base
- No antiperiplanar requirement

E2

- Bimolecular elimination
- Single transition state
- Takes place with primary and secondary alkyl halide
- Competes with S_N2 reaction mechanism
- Antiperiplanar requirement
- Requires strong base

E1CB

- Elimination unimolecular conjugate base
- Poor leaving group and acidic hydrogen eliminate to form addition bond
- Two step process
- Compounds must have a acidic hydrogen on its β-carbon and poor leaving group on σ-carbon
- Carbanion intermediate

Reactivity of Aryl Halide:

Electrophilic substitution reaction →
- Halogenation
- Nitration
- Sulphonation
- Fridal craft Alkylation/ Acylation / Benzylation

} Takes place at ortho and para position to chloro group

Nucleophillic substitution reaction → Presence of groups like NO_2, -CN, $-SO_3H$, -CHO at o-or para position increases the activity of chlorobenzene