

6.

AROMATIC HYDROCARBONS

6.1 Introduction

The term aromatic derived from the Greek word 'aroma' meaning "fragrant", was originally used for a group of compounds which have a pleasant smell. The basic structural unit of aromatic compounds is benzene (C_6H_6) which has a six-member unsaturated cyclic structure. The aromatic compounds have a low hydrogen content and are characterized by a special stability. They undergo substitution reactions more easily than addition reactions. Now the term aromatic compounds stands for the whole series of compounds which contain one or more benzene rings in their molecules. The aromatic **hydrocarbons** include benzene and those compounds of carbon and hydrogen that resemble benzene in their chemical behaviour. All aromatic hydrocarbons (benzene, toluene, naphthalene, anthracene, etc.) are called "**Arenes.**"

6.2 Sources of Aromatic Compounds

Two natural sources of aromatic compounds are coal and Petroleum.

1. **From Coal.** When coal is heated to a high temperature ($1000-1500^\circ C$) in the absence of air, it gives three main products; (i) a gaseous product known as coal gas. (ii) a liquid product known as coal tar, and (iii) a residue which is called coke. **The coal gas** mainly consists of hydrogen, methane, carbon monoxide and ammonia. **Coke** is used in the manufacture of steel and other metals.

Coal tar is rich in aromatic compounds. Coal tar is a black, viscous liquid with a characteristic odour. It is a mixture of large number of naturally occurring neutral, acidic and basic compounds. Coal tar on fractional distillation yields the following four fractions.

(i) **Light Oil.** It distils upto $200^\circ C$ and gives mainly benzene, toluene, xylene besides other products.

(ii) **Middle Oil.** It distils between $200-250^\circ C$, contains naphthalene, phenol, cresols.

(iii) **Heavy Oil.** It distils between $250-300^\circ C$. Its main components are naphthalene and cresols,

(iv) **Anthracene Oil.** It distils between $300 - 350^\circ C$, contains anthracene, phenanthrene and carbazole.

Light Oil fraction is treated with dilute H_2SO_4 to remove basic impurities like pyridine. It is then treated with NaOH to remove acidic impurities like phenol. The oil thus purified on redistillation gives the following fractions.

(i) 90% benzol containing 75% benzene upto $95^\circ C$.

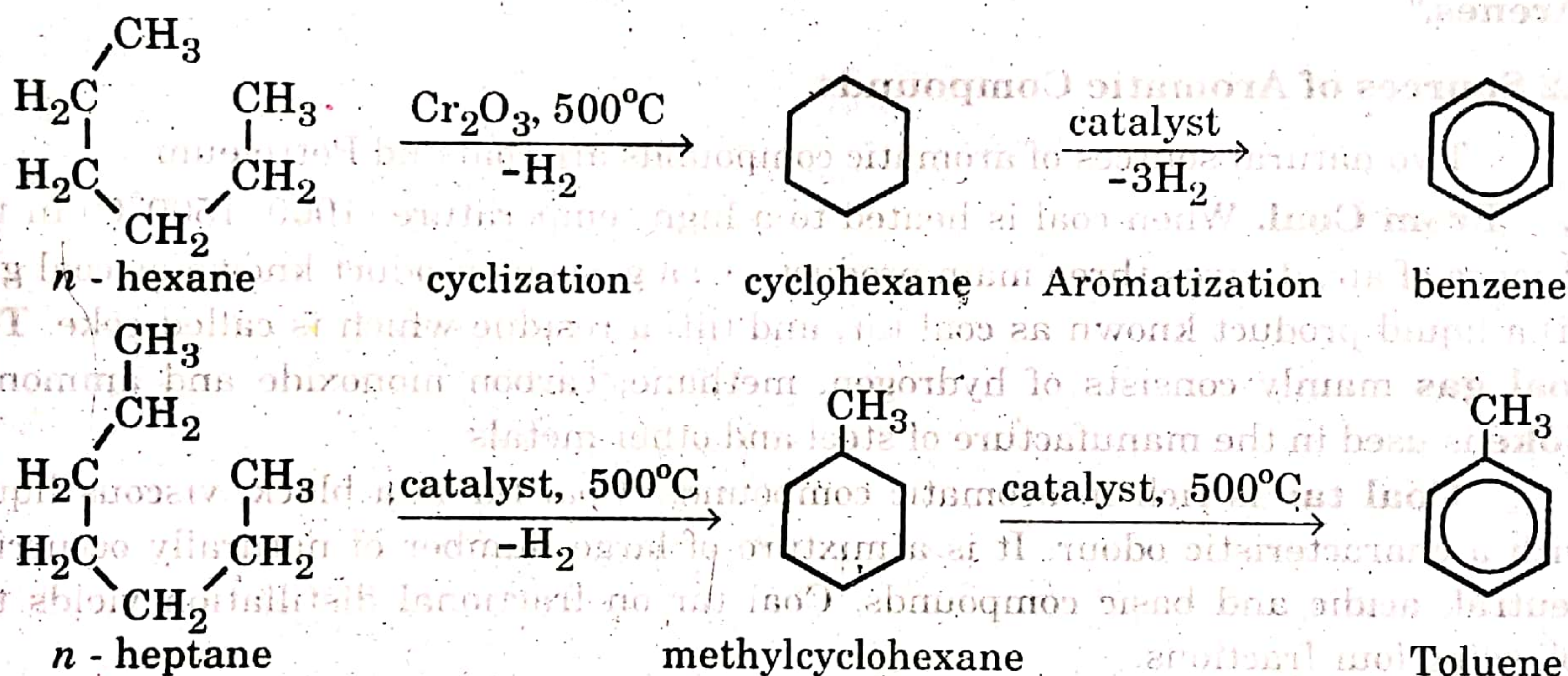
(ii) 50% benzol containing 46% benzene upto 150°C.

(iii) Solvent naphtha upto 200°C.

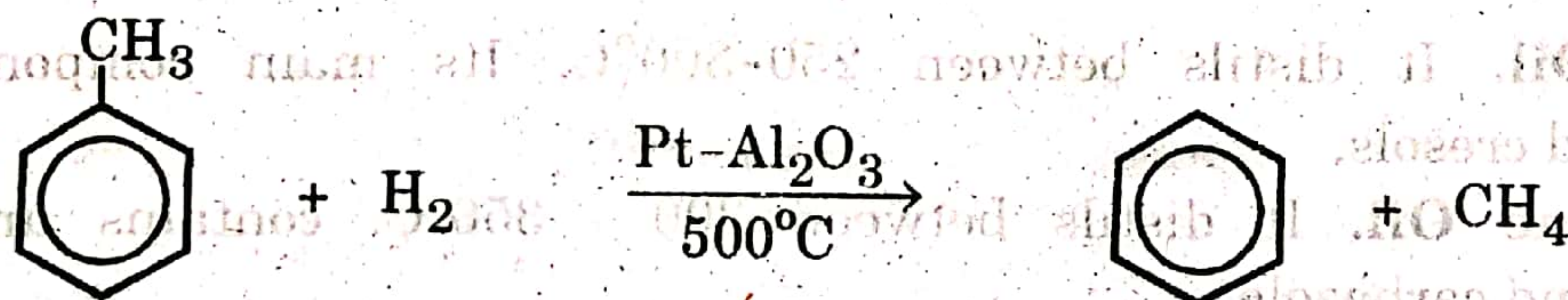
Benzene (b.p. 80°C), toluene (b.p. 110°C) and xylene (135-145°C) are isolated by fractional distillation from the two fractions 90% benzol and 46% benzol.

Over 200 aromatic compounds have been obtained from coal tar. However, benzene, toluene, xylene, naphthalene, anthracene, phenanthrene and some heterocyclic bases are more important.

2. From Petroleum. Petroleum is the major source of aromatic compounds. It contains many aromatic compounds like benzene, toluene, xylene and naphthalene etc. Aromatic hydrocarbons are mainly obtained by the **catalytic reforming** of the aliphatic hydrocarbons present in petroleum which involves cyclization and aromatization under the influence of catalyst such as chromium oxide supported on alumina under pressure and at temperature 500-550°C. The catalytic reforming is also known as **hydroforming**.



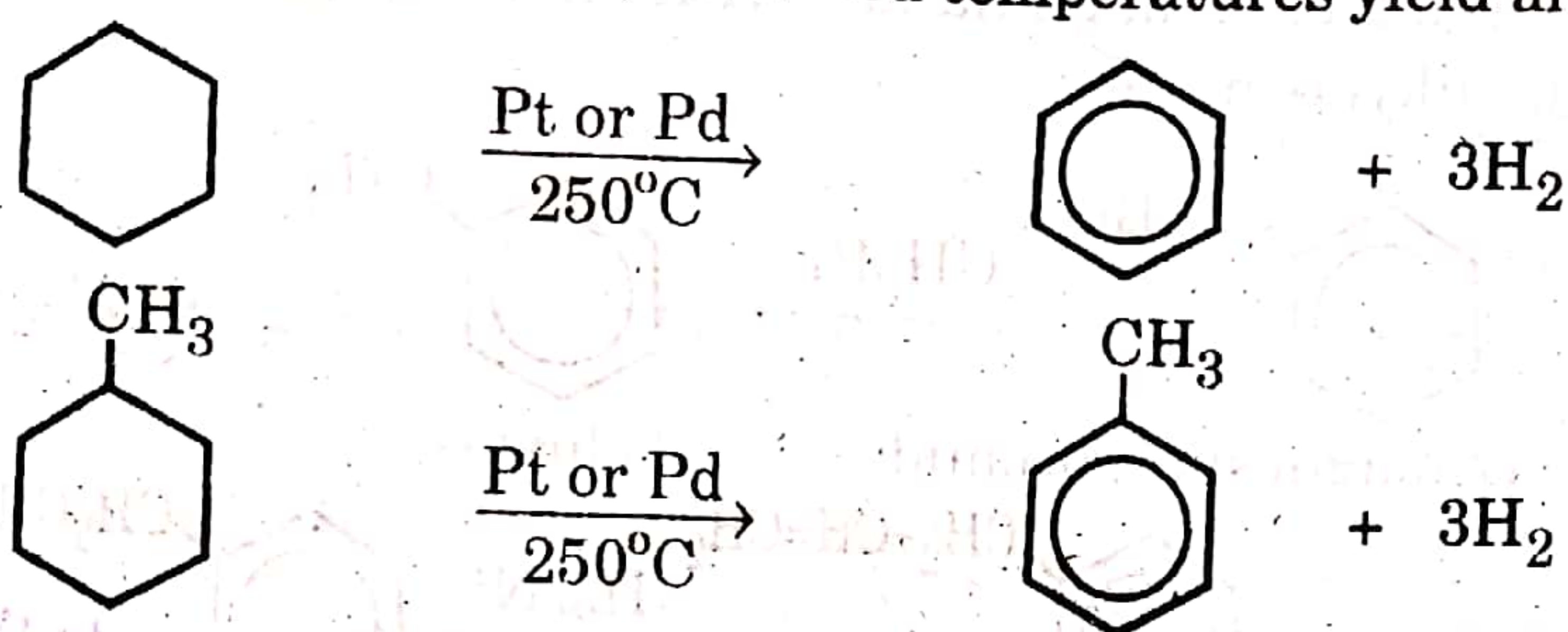
Benzene obtained from reforming operation is in far less amounts as compared to toluene. Therefore, toluene is converted into benzene, which is in much greater demand, by heating toluene with hydrogen under pressure in the presence of a metal oxide catalyst and the process is known as **hydrodealkylation**.



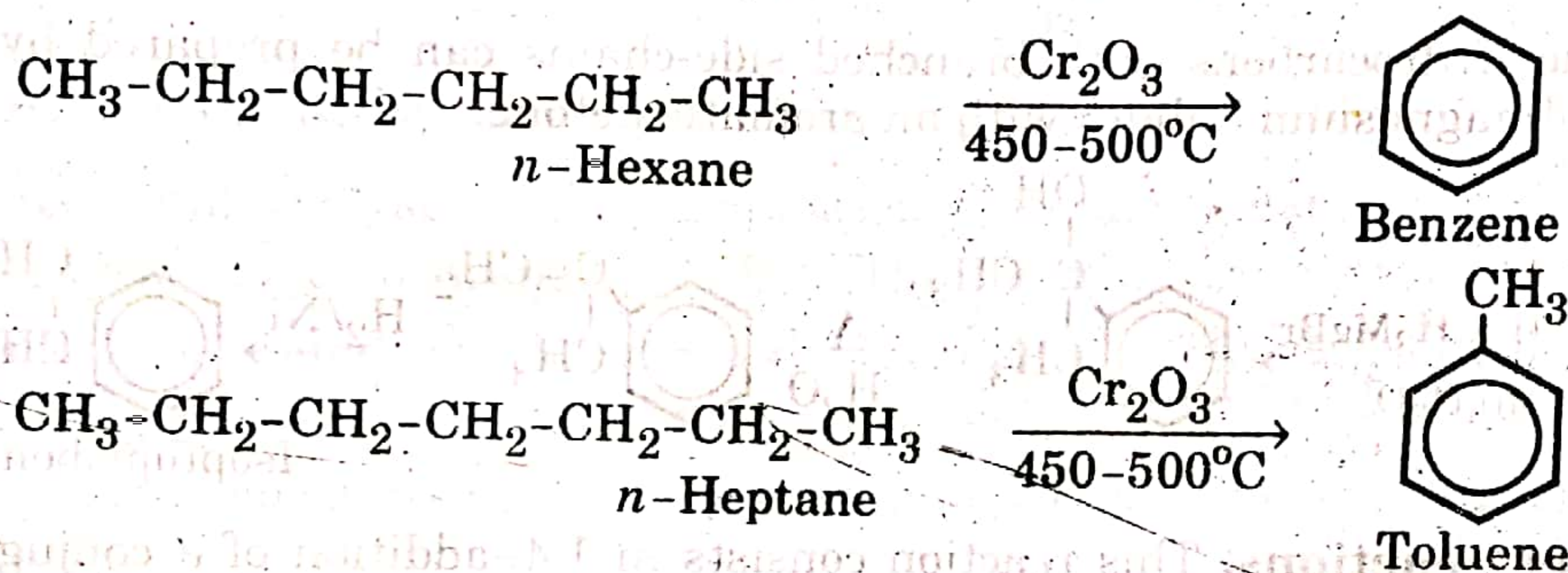
6.3 Preparation of Benzene and its homologues

Benzene and its homologues are obtained on large scale from petroleum and coal tar. The methods of their preparation on laboratory scale are of academic interest only. Some of the methods generally used for their preparation are given below.

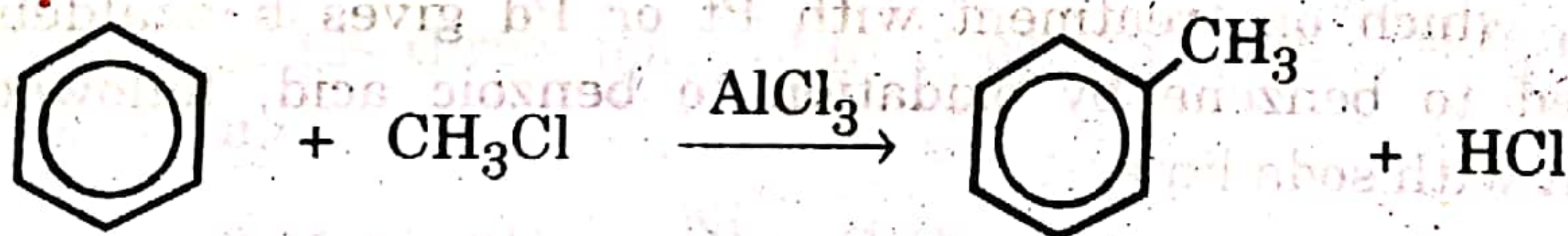
1. **Dehydrogenation of Cycloalkanes.** Cycloalkane and its derivatives on catalytic dehydrogenation at elevated temperatures yield aromatic hydrocarbon.



2. **Cyclization of alkanes.** *n*-alkanes containing six or more carbon atoms on catalytic reforming in the presence of Cr_2O_3 catalyst at elevated temperature under pressure yield aromatic hydrocarbons.

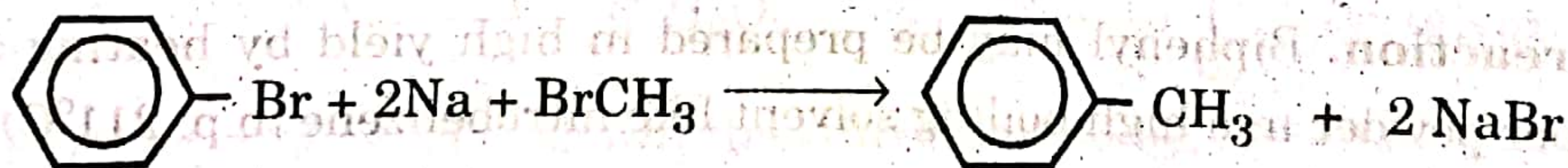


3. **Friedel-Crafts Alkylation.** Benzene and alkyl halides react in the presence of AlCl_3 catalyst to give alkyl substituted benzenes.



This method often gives polysubstituted benzenes, since further alkylation occurs easily.

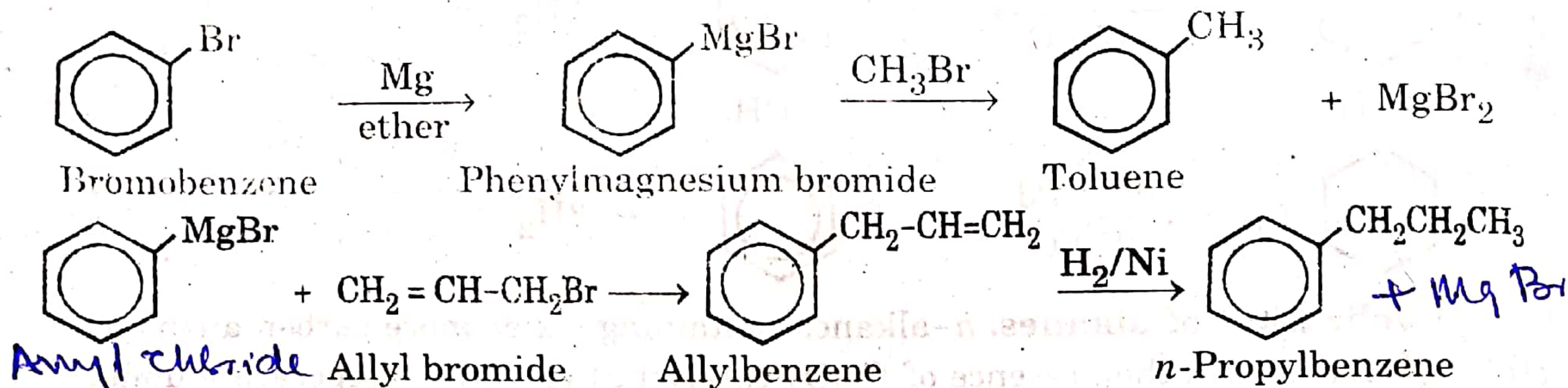
4. **Wurtz-Fittig Reaction.** Fittig extended the Wurtz reaction to the synthesis of alkylaromatic hydrocarbons (arenes). This method consists in heating a mixture of aryl halide and alkyl halide with metallic sodium in ethereal solution to form an alkyl benzene (arene).



The Wurtz - Fittig reaction is particularly important because a long straight chain can be easily introduced into the benzene ring. Further the side products formed have boiling points sufficiently different from those of the arenes which make their separation possible. The yield of alkyl-aryl compound (arene) is usually

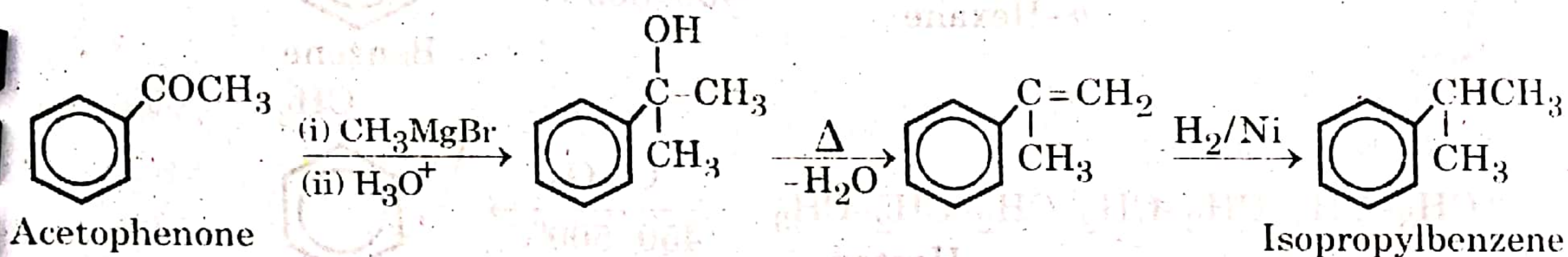
much higher than that of aryl - aryl or alkyl - alkyl compounds.

5. Grignard Synthesis. Coupling of an alkyl halide with an arylmagnesium halide (a Grignard reagent) gives an alkyl benzene.

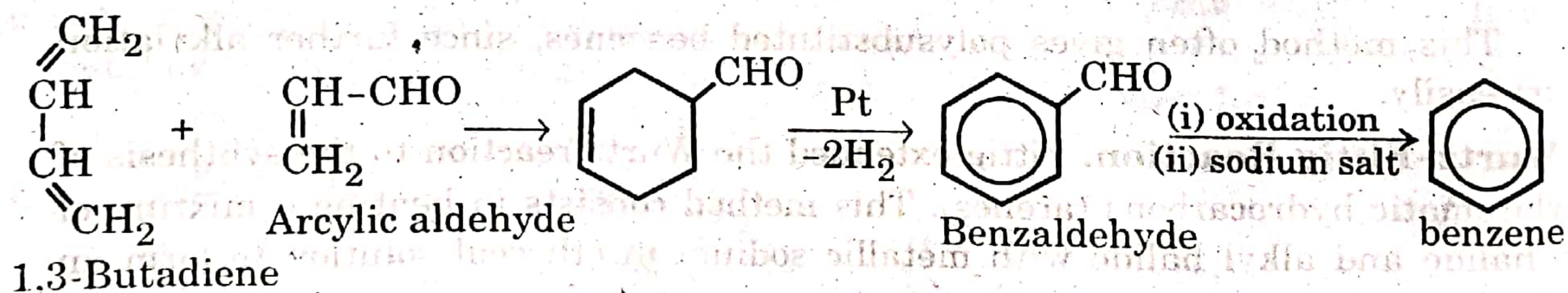


Aryl bromides and aryl iodides are readily converted to Grignard reagent by treatment with magnesium in anhydrous ether. Aryl chlorides are inert toward magnesium.

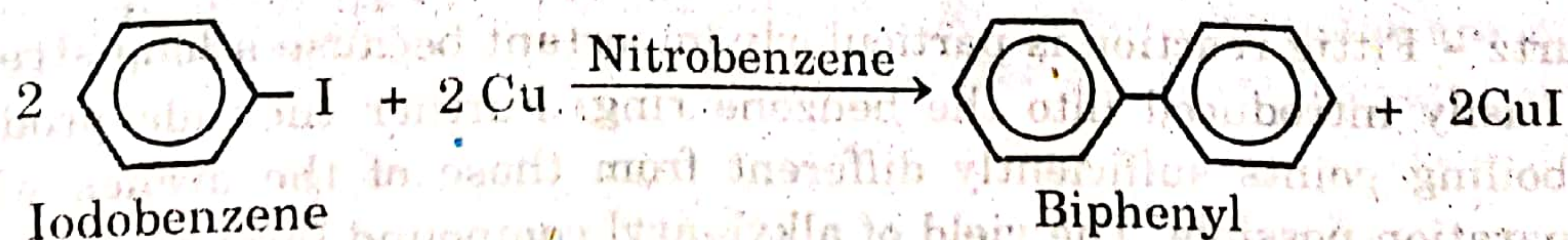
Aromatic hydrocarbons with branched side-chains can be prepared by the reaction of arylmagnesium halides with an aromatic ketone.



6. Diels-Alder reactions. This reaction consists in 1,4-addition of a conjugated diene to an olefin having preferably unsaturated groups attached to it. Thus 1,3-butadiene when heated with acrylic aldehyde undergoes Diels-Alder reaction to give tetrahydrobenzaldehyde, which on treatment with Pt or Pd gives benzaldehyde, which may be converted to benzene by oxidation to benzoic acid, followed by distillation of sodium salt with soda lime.

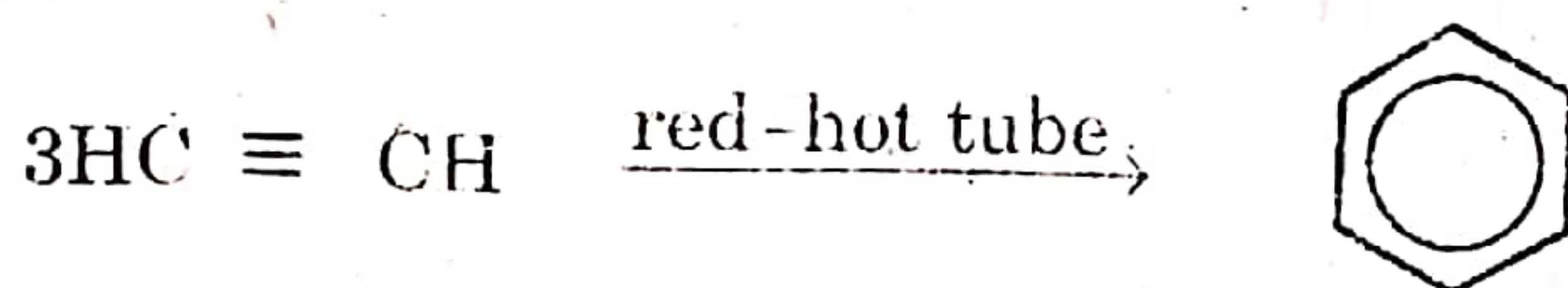


7. Ullman reaction. Biphenyl may be prepared in high yield by heating aryl iodide with copper powder in a high boiling solvent like nitrobenzene (b.p. 211°C).

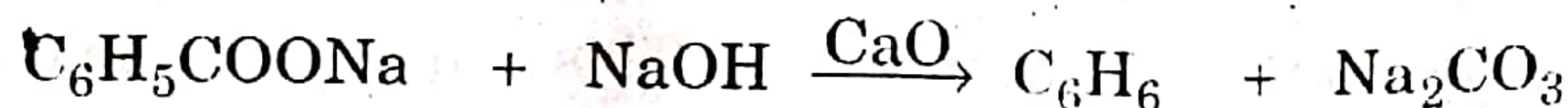


Benzene can also be prepared by the following methods.

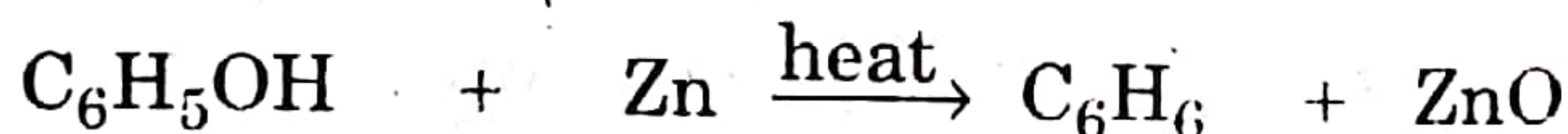
- (i) By passing acetylene through red-hot tube at 500°C.



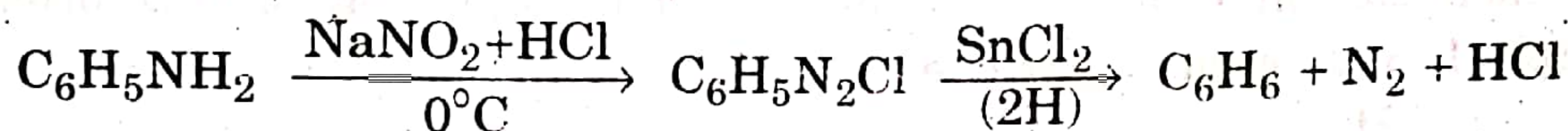
- (ii) By heating benzoic acid or sodium benzoate with soda - lime.



- (iii) By heating Phenol with zinc dust.



- (iv) **From Aniline.** Aniline is diazotized using HCl and NaNO_2 at 0°C to form diazonium salt which on reduction with SnCl_2 gives benzene.

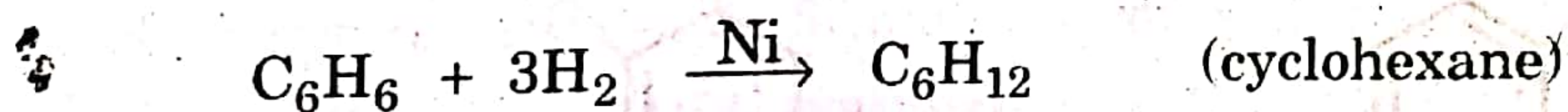


6.4 Structure of Benzene

Elemental analysis and determination of its molecular mass show that the molecular formula of benzene is C_6H_6 . The formula suggests that it is highly unsaturated compound, but its properties are quite different from those of open-chain unsaturated hydrocarbons. It does not decolourise bromine in CCl_4 or cold aqueous potassium permanganate reagents that decolourise unsaturated aliphatic hydrocarbons.

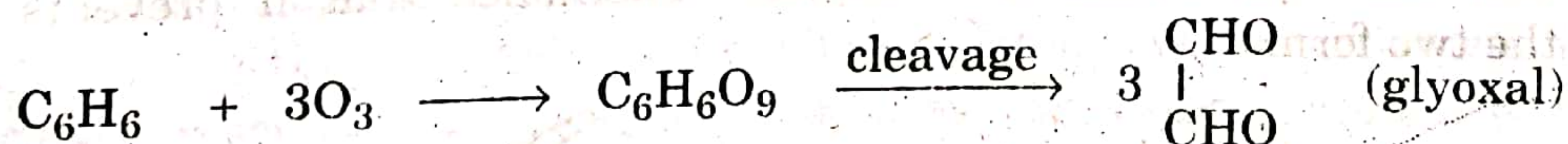
Evidence of Cyclic Structure. Following reactions show the presence of three double bonds and a six-membered carbocyclic ring.

- (i) Benzene adds three moles of hydrogen in the presence of Ni catalyst to form cyclohexane.



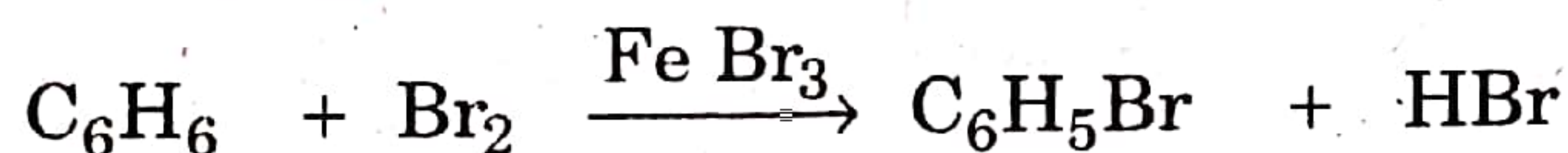
- (ii) Benzene adds three moles of halogen in the presence of sunlight to give benzene hexahalide.

- (iii) Ozone reacts with benzene to form triozone which on cleavage gives three molecules of glyoxal.



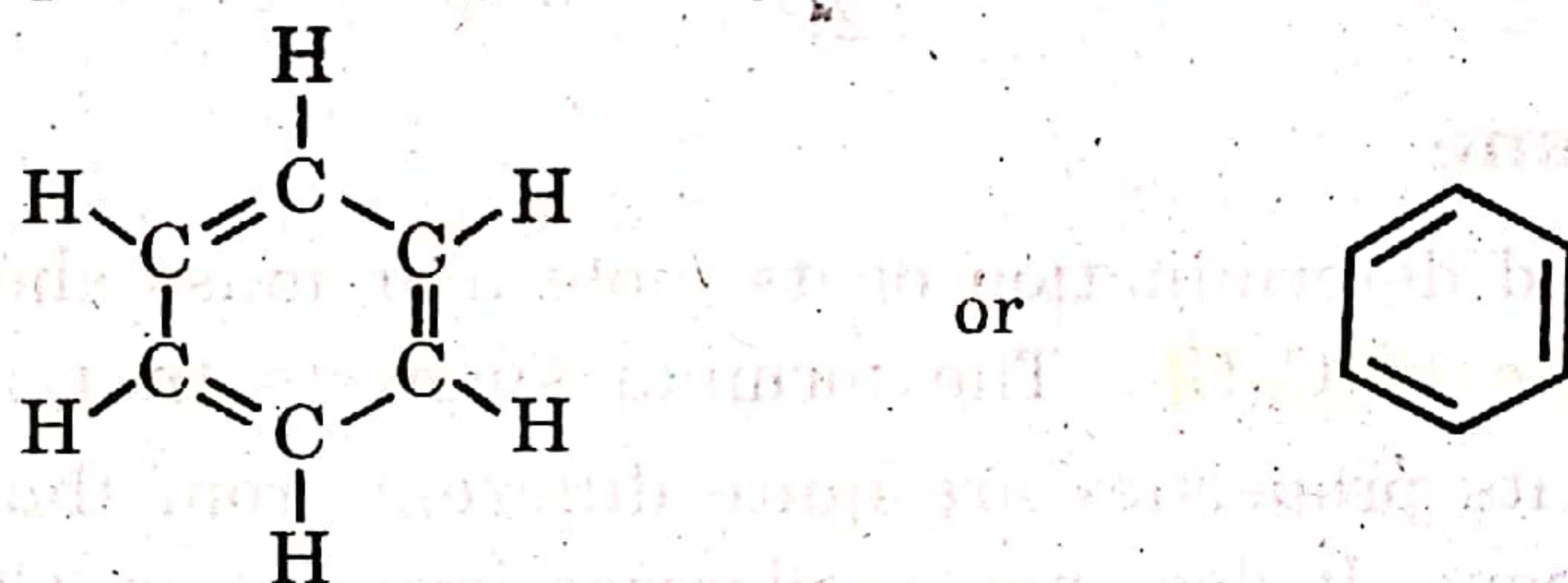
Further studies have shown that three double bonds in benzene are different from the ordinary double bonds, and have a special type of arrangement which is responsible for "unusual" stability of the benzene molecule. The high degree of stability of the benzene molecule is revealed from its heat of hydrogenation. The heat of hydrogenation of benzene is less by 150.5 kJ/mol than predicted for 1,3,5-

cyclohexatriene (hypothetically). The stability of benzene is found in its substitution reactions such as halogenation, nitration, sulphonation etc. For example, benzene reacts with bromine only in the presence of FeBr_3 (catalyst) to give substitution rather than addition reaction.



Benzene forms only one mono substituted product which indicates that all six hydrogen atoms in the benzene molecule are equivalent. This can be possible only if benzene has a cyclic structure of six carbons and to each carbon is attached one hydrogen.

The Kekule's Structure. In 1865, Kekule suggested that benzene is a cyclic compound, with a six-membered ring of six carbons, with alternate double and single bonds and to each carbon is attached one hydrogen. According to this proposal, benzene is simple 1, 3, 5 - cyclohexatriene.

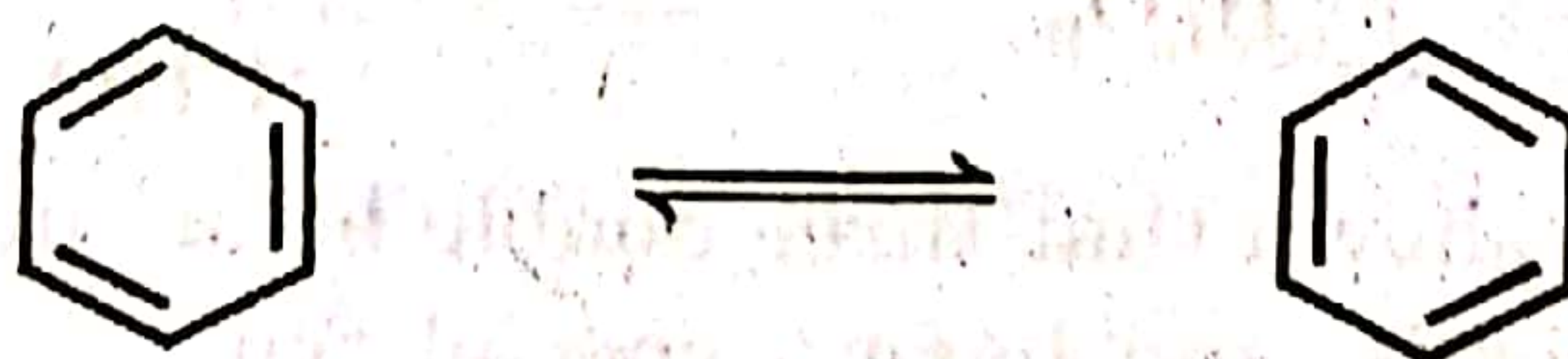


However, the following evidences show that the Kekule structure does not adequately describe the structure of benzene.

- (i) If the Kekule's structure was correct, there should be two different 1, 2 - dibromobenzenes as shown below. In one of them, the two bromine atoms should be on carbons that are connected by a double bond (a), while in the other, the bromines should be on carbons connected by a single bond (b).



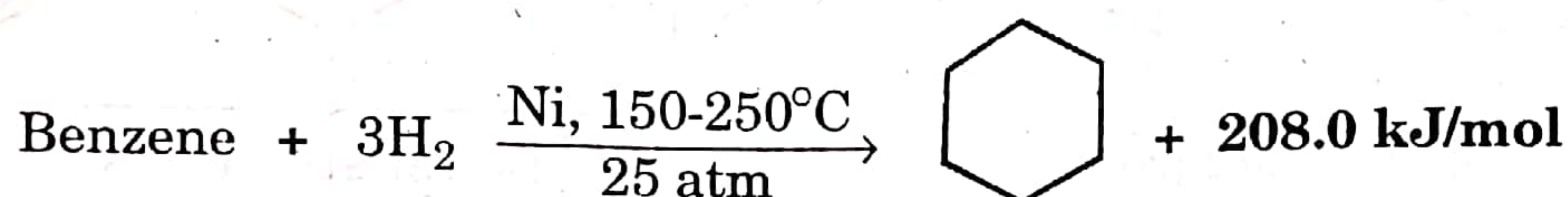
In actual practice, only one, 1,2-dibromobenzene is known. To overcome this objection, Kekule proposed that the two forms of benzene are in a state of dynamic equilibrium, and this equilibrium is so rapidly established that it prevents the separation of the two forms.



We now know that this proposal was wrong and no such equilibrium exists.

(ii) The formula predicts that the heat of hydrogenation of benzene should be approximately 358.5 kJ/mol. In actual practice, the heat of hydrogenation

determined for benzene is only 208 kJ/mol. Thus benzene is more stable than anticipated from its structure suggested by Kekule by an amount of 150.5 kJ/mol.



- (iii) Benzene shows unusual behaviour by undergoing substitution reactions, while on the basis of Kekule's structure it should undergo addition reactions.
- (iv) The bond lengths in 1,3, 5-cyclohexatriene would be 154 pm for the single bond and 132 pm for the double bond. But, in benzene, all C - to - C bonds have the identical length, 139 pm which is intermediate between a single and double bond.

A number of structures for benzene were proposed from time to time. **Dewar** (1867) proposed the '**para - bond**' structure (a). **Claus** also in 1867 proposed the '**three para bond**' structure (b) which abandoned the double bonds altogether. **Armstrong** and **Bayer** (1887) independent of each other, proposed the 'centric formula' (c). According to this formula, the fourth valency of each carbon is directed towards the centre of the ring and reacts upon each other so that the affinity may be uniformly and symmetrically distributed. **Thiele** (1899) proposed that benzene is a conjugated system of '**double bonds par excellence**' in that all the partial valencies are fully neutralised. However, none of them could satisfy all observed properties of benzene and were consequently rejected.



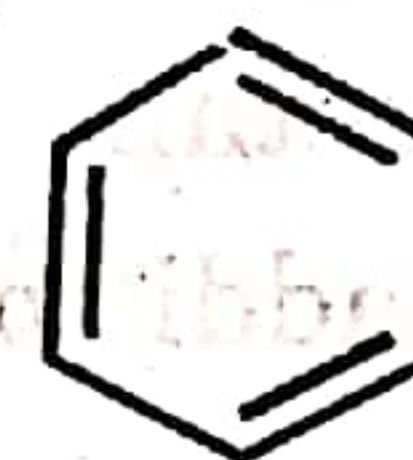
(a)
Dewar



(b)
Claus



(c)
Armstrong
and Bayer



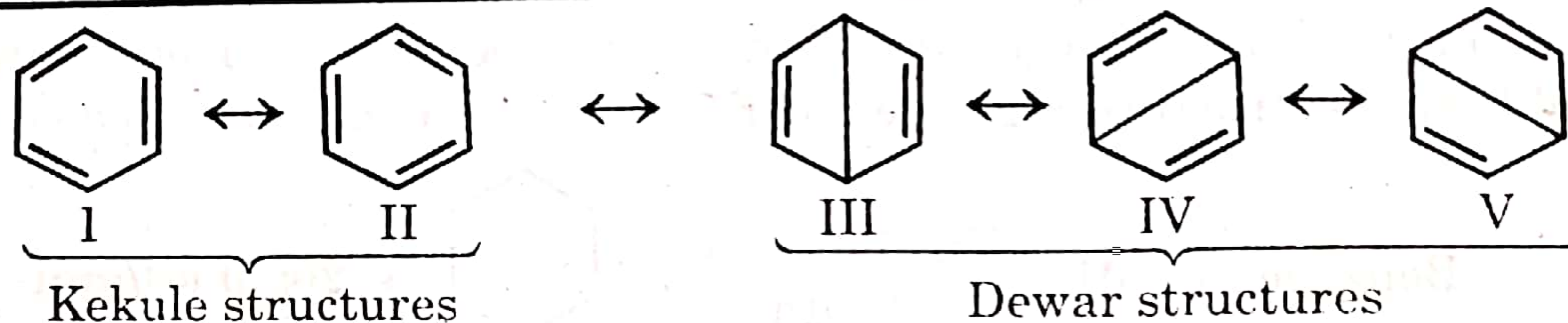
(d)
Thiele

Nonetheless, the Kekule formulation of benzene's structure was an important step forward and, for practical reasons, it is still being widely used today.

3.6 Modern Theories of the structure of Benzene

Wave mechanics provided two methods of approaching the structure of benzene: (i) Resonance method and (ii) Molecular orbital method.

(i) **Resonance method.** The phenomenon in which two or more Lewis structures can be written for a molecule or ion which differ only in the arrangement of electrons is called resonance and these structures are called resonance **contributing structures** or **canonical structures**. The actual structure of the molecule is a resonance hybrid of all the contributing structures. A double headed arrow (\leftrightarrow) between the resonance structures is used to represent the resonance hybrid. The benzene molecule is considered as a resonance hybrid of two Kekule and three Dewar structures.



None of these structures represent benzene satisfactorily. The two Kekule structures make major contribution to the actual benzene molecule. Therefore, benzene is considered as a resonance hybrid of two equal-energy Kekule's structures differing only in the location of the double bonds. The contributing structures exist only in our imagination. All the molecules of benzene have just one structure which cannot be drawn but which resembles the contributing structures to varying degrees. The resonance hybrid is more stable than any of the contributing structures. In other words, the energy of the actual molecule, the resonance hybrid, is less than the lowest energy contributing structure. The difference of energy between the actual molecule and the lowest energy contributing structure is called the **resonance energy**. The benzene is said to be resonance stabilized by an amount of 150.5 kJ/mol which is called the resonance energy of the benzene. The stability due to resonance is so great that the π -bonds of the benzene molecule will normally resist breaking. This explains why does benzene undergo substitution as it wants to retain its stability which is likely to be destroyed if benzene molecule undergoes addition reactions.

Molecular Orbital Method

Spectroscopic measurements show that the molecule of benzene is a regular hexagonal planar with C - C - C bond angle to be 120° and all of its C - C bonds are of equal length which is 0.139 nm (1.39 \AA).

The bond angles of the carbon atoms in the benzene ring suggest that each carbon atom is sp^2 hybridized. Two of these hybrid orbitals are utilized in forming two sigma (σ) bonds with two adjacent carbon atoms due to $sp^2 - sp^2$ overlap and the third one is utilized in forming a sigma (σ) bond with hydrogen due to $sp^2 - s$ overlap. There remains one unhybridized p - orbital on each carbon atom containing one electron, oriented perpendicular to the plane of hexagonal ring structure. The p orbitals are close enough to overlap effectively. The six overlapping p orbitals linearly combine to form six molecular orbitals - three bonding and three antibonding molecular orbitals.

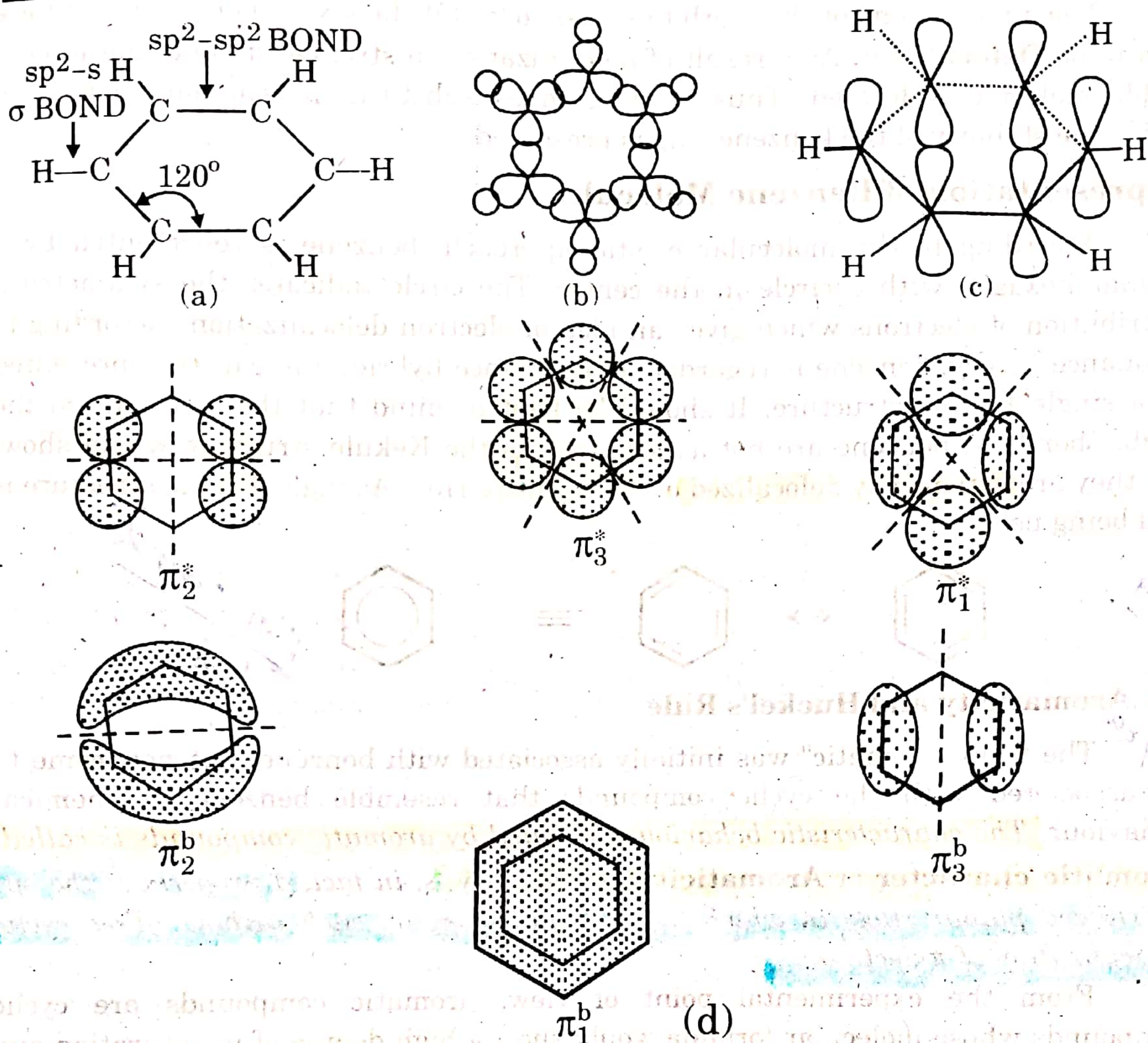


Fig. 6.1 (a) Bond lengths and angles in benzene (b) σ-skeleton (c) Six overlapping p orbitals of benzene (d) Molecular orbitals of benzene.

The six available electrons fill the three lowest energy bonding orbitals, π₁, π₂ and π₃, while the three antibonding orbitals, π₁^{*}, π₂^{*} and π₃^{*} remain empty when the benzene is in the ground state. The combined effect of six electrons in π₁, π₂ and π₃ orbitals in benzene ring can be represented as a cloud of electrons above and below the ring as shown in Fig. 6.2.

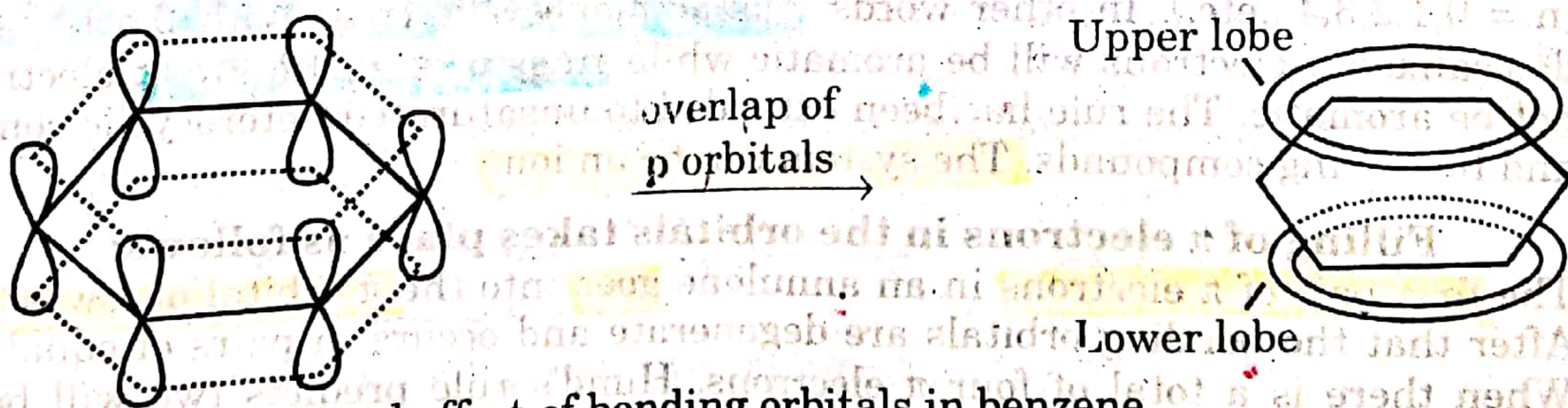
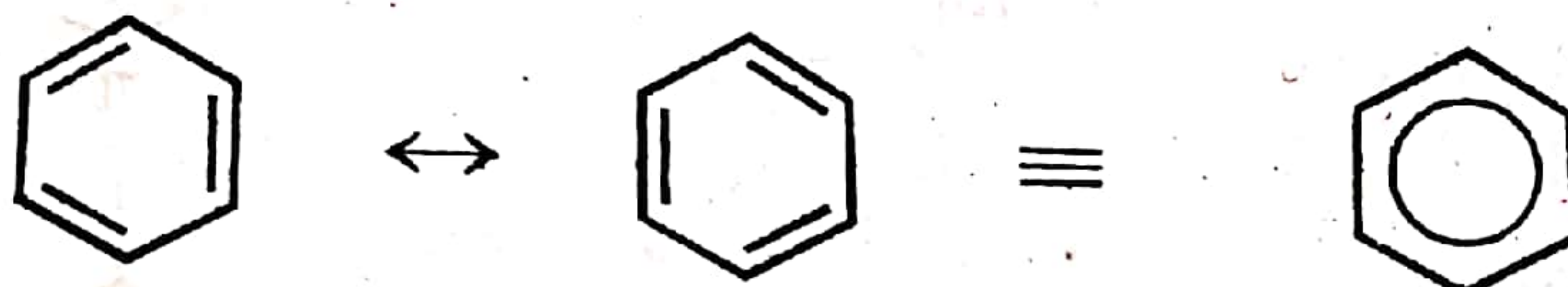


Fig. 6.2 Combined effect of bonding orbitals in benzene.

The six electrons of the p orbitals now cover all the six carbon atoms and are said to be **Delocalized**. As a result of delocalization, a stronger π bond and a more stable molecule is formed. Thus benzene gives substitution reactions readily in which the stability of the benzene ring is preserved.

Representation of Benzene Molecule

According to the molecular orbital approach, benzene is represented by a regular hexagon with a circle in the centre. The circle indicates the symmetrical distribution of electrons which gives an idea of electron delocalization. According to resonance theory, benzene is regarded as resonance hybrid, and can be represented by a single Kekule structure. It should be kept in mind that the electrons in the double bonds in benzene are not as localized as the Kekule structure would show, but they are **extensively delocalized** over the entire ring. A single Kekule structure is still being used.



6.6 Aromaticity and Huckel's Rule

The term "aromatic" was initially associated with benzene, has now come to be associated with the cyclic compounds that resemble benzene in chemical behaviour. **The characteristic behaviour exhibited by aromatic compounds is called.**

Aromatic character or Aromaticity. **Aromaticity is, in fact, a property of the sp^2 hybridized planar rings in which the p orbitals (one on each carbon) allow cyclic delocalization of π electrons.**

From the experimental point of view, aromatic compounds are cyclic compounds whose molecular formula would show a high degree of unsaturation and yet which are resistant to the addition reactions and have the ability to undergo electrophilic substitution reactions like those of benzene. They have the unusual stability (i.e., extra stability): low heats of hydrogenation, low heats of combustion and sufficient resonance energy.

From the theoretical point of view, an aromatic system is one that contains a closed shell of π electrons. **Huckel's rule**, based on molecular orbital calculations, **states that electron rings will constitute an aromatic system only if the number of π electrons in the ring is equal to $4n + 2$** , where n equals zero or a whole number ($n = 0, 1, 2, 3, 4 \dots$ etc.). In other words, **planar monocyclic rings with 2, 6, 10, 14 --- etc. delocalized π electrons will be aromatic while rings of 4, 8, 12, etc. π electrons will not be aromatic.** The rule has been extended to unsaturated heterocyclic compounds and fused ring compounds. **The system can be an ion.**

Filling of π electrons in the orbitals takes place as follows;

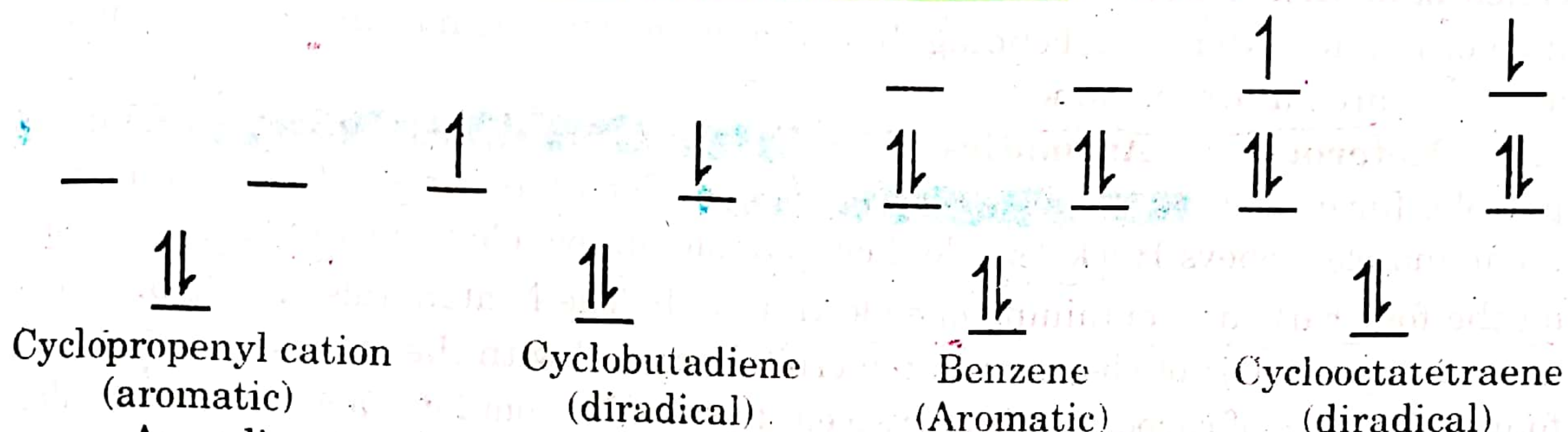
The first pair of π electrons in an annulene goes into the π orbital of lowest energy. After that the bonding orbitals are degenerate and occurs in pairs of equal energy. When there is a total of four π electrons, **Hund's rule predicts two will be in the**

Aromaticity
2, 6, 10, 14

Non-aromatic
4, 8, 12

n = 0, 1, 2, 3, 4 etc

lowest energy orbital but the other two will be unpaired which will be in its degenerate π molecular orbitals, and the system will exist as diradical (a system with two unpaired electrons which makes them unstable).



According to Huckel's rule, annulenes (cyclic conjugated polyenes) will be aromatic, provided their molecules have $(4n + 2) \pi$ electrons and have a planar carbon ring. The ring size of an annulene is indicated by a number in brackets. For example, benzene, a [6] annulene, is aromatic, whereas cyclooctatetraene, [8] annulene is not aromatic.

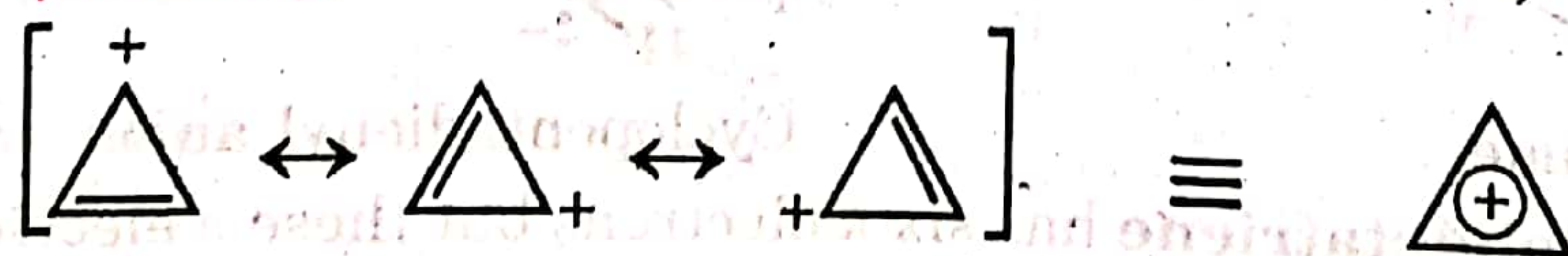
Criteria for Aromaticity. For a compound to be aromatic its molecule must fulfil the following requirements.

1. It must have a cyclic and planar structure.
2. Each atom of the ring must be sp^2 hybridized to provide its unhybridized p orbital for extended π bonding.
3. It must obey Huckel's rule, i.e., it must have $(4n + 2) \pi$ electrons.
4. It must have unusual (special) stability due to the π - electrons delocalization.
5. It must have the ability to undergo substitution rather than addition reactions.
6. It should have equal or approximate equal bond lengths, except when the symmetry is disturbed by a hetero atom or in some other way.
7. It should be able to sustain a ring current induced by an electric magnetic field, i.e., it should be diatropic.

Evidences of Aromaticity:

Let us apply these rules to the various cyclic systems that give evidences of aromaticity.

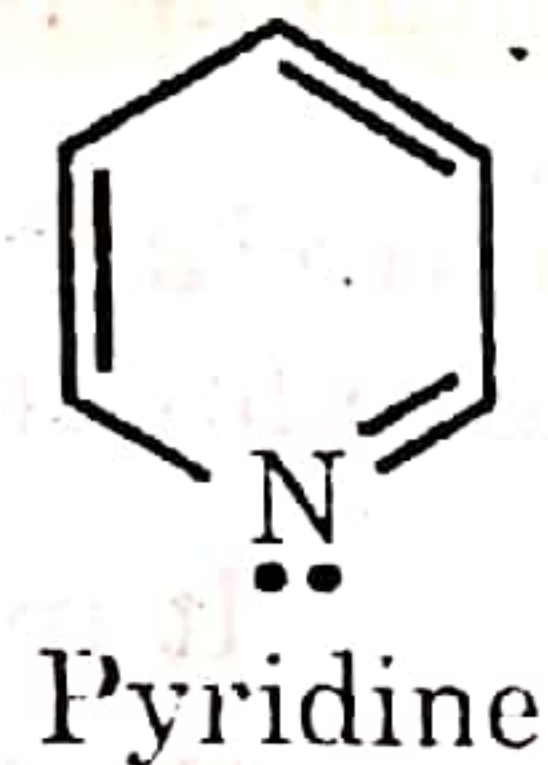
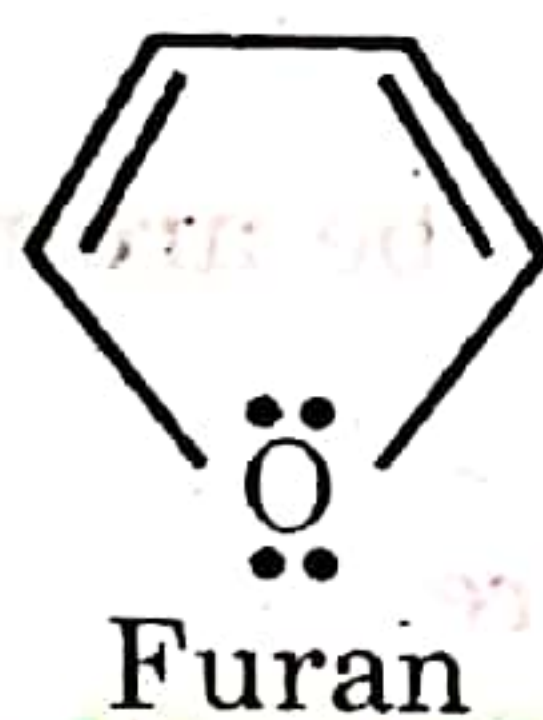
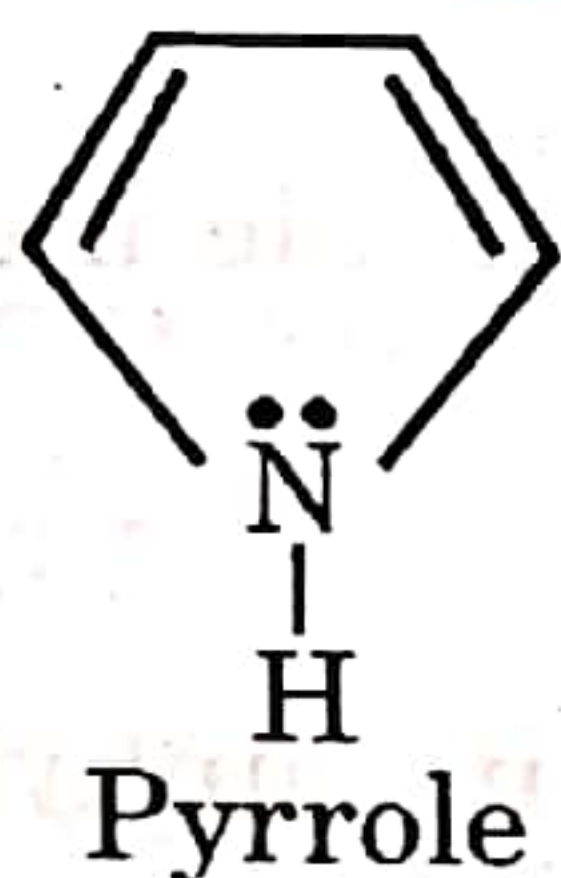
2 π electron system. Cyclopropenyl cation has 2π electrons and $n = 0$, which is in accordance with Huckel's rule. It is reactive and is much more stable than the corresponding acyclic ion. The cyclopropenyl cation is, therefore, aromatic.



2 π electron system; cyclopropenyl cation.

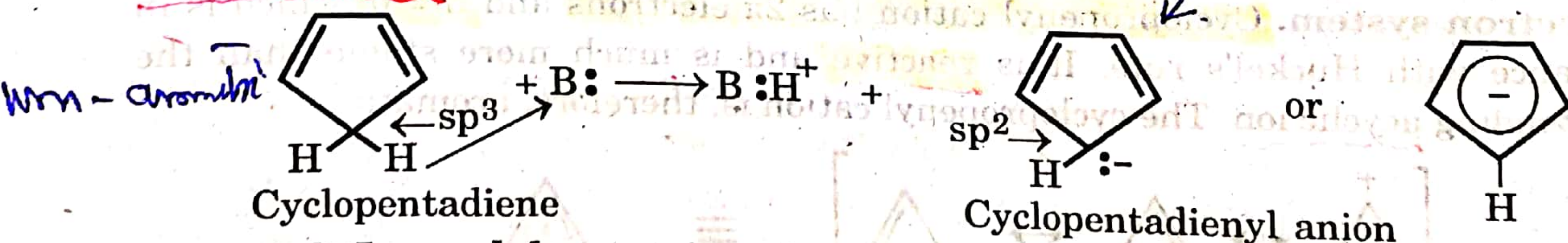
6 π electron system. Benzene is a cyclic and planar. It has 6π electrons and $n = 1$, which is in accordance with Huckel's rule. This set of 6π electrons of benzene is also called **aromatic sextet**. Each carbon atom of the ring is sp^2 hybridized to provide its p orbital for extended π bonding. It is, therefore, benzene has an unusual stability and is an aromatic compound.

Heterocyclic Aromatics: The 5-membered heterocyclic compounds pyrrole, furan and thiophene are cyclic planar. Each has a p orbital on every ring atom and each obeys Huckel's rule. For example, in pyrrole there are four p orbitals on the four carbons, containing one electron each. The N atom (also sp^2 hybridized) has an unused pair of electrons in a p orbital parallel with the other p orbitals. The four π electrons of carbons and the two electrons of N atom form a cyclic π molecular orbital. However, in furan and thiophene, there are two unshared electron pairs with O or S atom. One of these is in a p orbital at right angles to the ring and is not to be counted. Thus pyrrole, furan and thiophene can provide an aromatic sextet and are clearly aromatic.



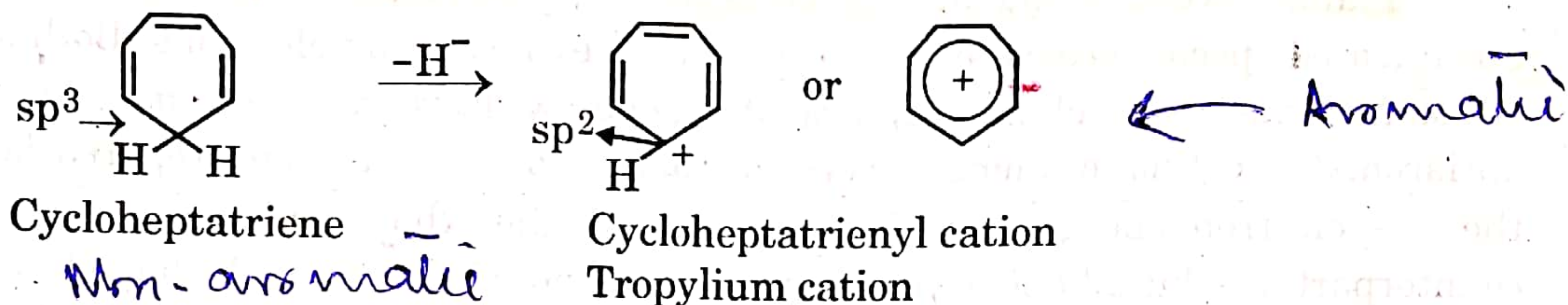
Similarly, in pyridine with three double bonds, each ring atom has a p orbital, containing one electron each, and the six electrons form the π molecular orbital. Therefore, pyridine is aromatic. The unshared electron pair on N atom does not participate in the π overlap.

1,3-cyclopentadiene has a sp^3 hybridized C because of the intervening methylene ($-\text{CH}_2-$) group, making cyclic p orbital overlap impossible. However, it has unexpected acidic properties. Removal of H^+ from this methylene group by a moderately strong base leaves a carbanion whose C is now sp^2 hybridized and has a p orbital capable of overlapping to give a cyclic system of six delocalized π electrons (4π electrons from 2 double bonds plus the two unshared electrons; total 6π electrons). Therefore, 1,3-cyclopentadienyl anion is aromatic but not 1,3-cyclopentadiene.

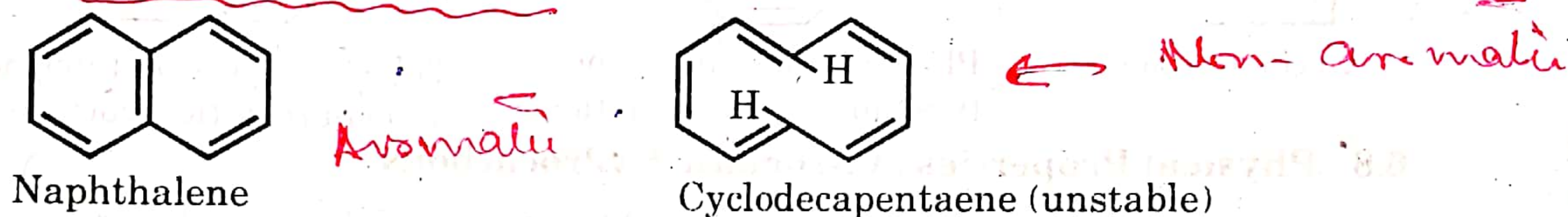


1, 3, 5 - cycloheptatriene has six π electrons but these π electrons cannot be fully delocalized because of the methylene group having sp^3 carbon with no available

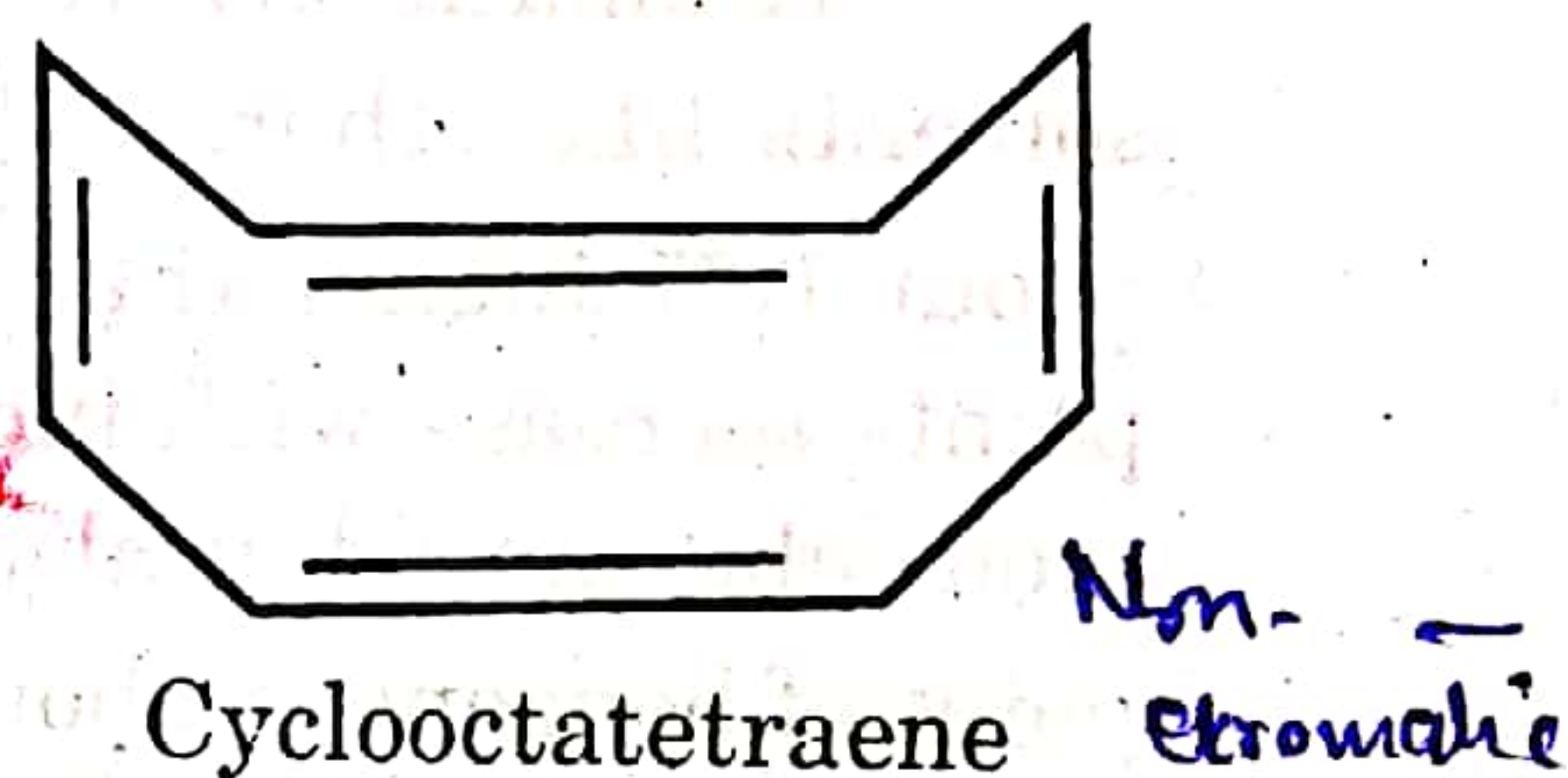
p orbital. However, it can lose a methylene hydrogen along with the pair of bonding electrons, (i.e., as hydride ion) to a suitable reagent, to give the cycloheptatrienyl cation which is quite stable and has 6 π electron system. Therefore, cycloheptatriene cation is an aromatic but not cycloheptatriene.



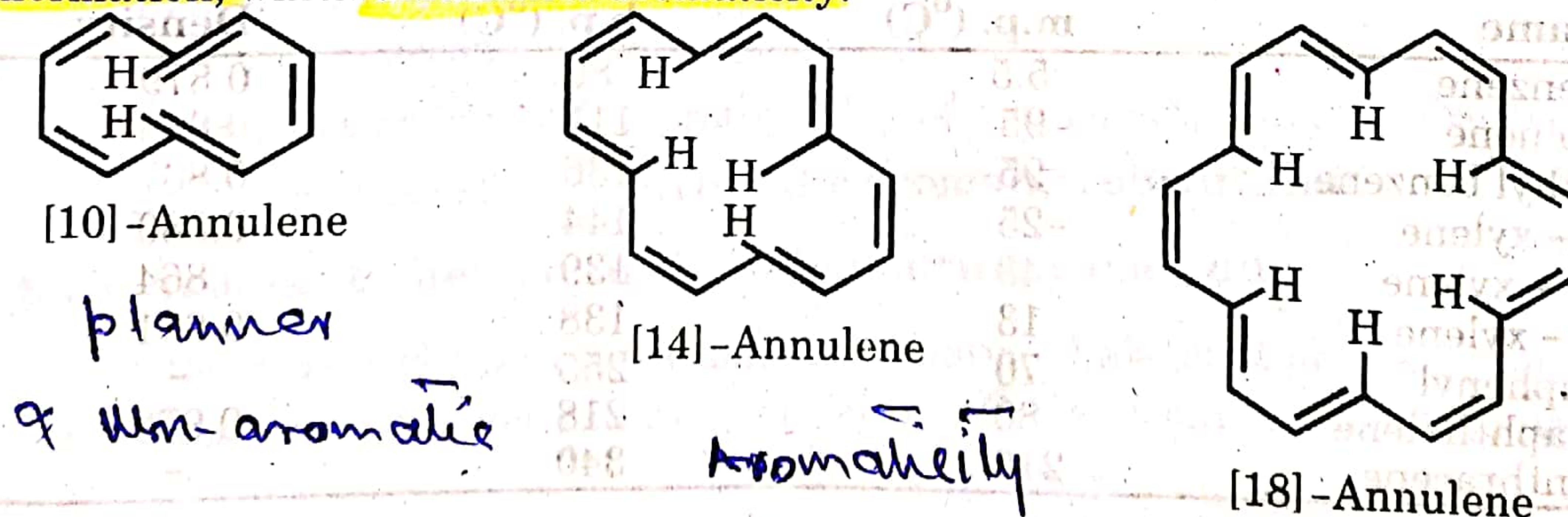
10 π electron system ($n = 2$). Naphthalene has 10 π electron system and is stable aromatic compound. According to Huckel's rule, cyclodecapentaene should be stable aromatic compound but is very unstable because of the non-bonded interaction of the hydrogen inside the planar ring, which force the molecule out of planarity and therefore Huckel rule is not applicable.



Cyclooctatetraene has eight π electrons which is not a Huckel number and, like cyclobutadiene, has two unpaired electrons, in its degenerate π molecular orbitals. It is therefore, nonaromatic and will exist as **diradical**. Further, cyclooctatetraene molecular is not planar, but it is tub-shaped. In view of the instability associated with two unpaired electrons in π molecular orbitals, cyclooctatetraene prefers to have a nonplanar molecule to overcome the angle strain of a planar ring, and gains some stability. Cyclooctatetraene is therefore neither aromatic nor antiaromatic because both these characteristics would require an overlap of parallel p orbitals which is not possible in a tub-shaped molecule. Thus it is simply cyclic polyene.



Annulenes. A [10] annulene would be expected to have the aromatic stability, since 10 is the Huckel number. [10]-annulene is somewhat strained because the hydrogens in the center of the ring are crowded. This steric strain prevents a planar conformation, which diminishes aromaticity.



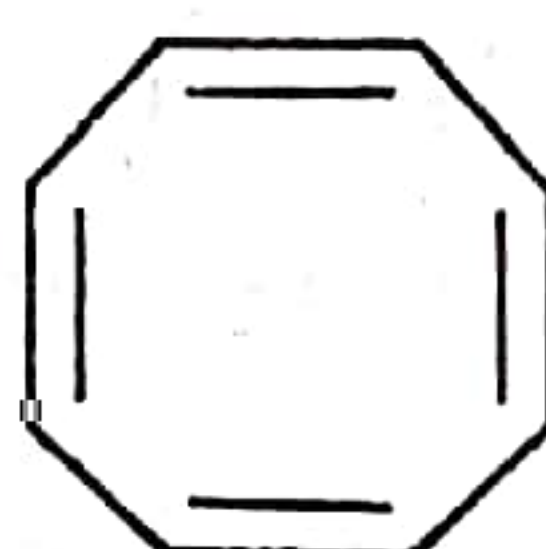
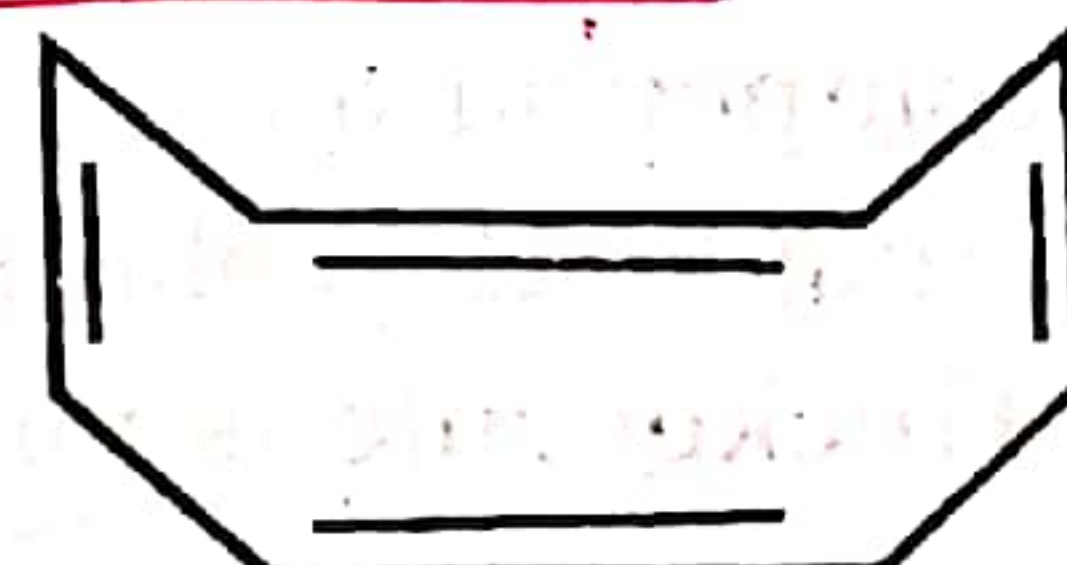
Some of the higher annulenes, e.g., [14] and [18] annulenes obey the Huckel's rule and were found to have the aromatic stability.

6.7 Antiaromaticity

Planar cyclic conjugated species less stable than corresponding acyclic unsaturated species are called antiaromatic. They have $4n\pi$ electrons. Both square cyclobutadiene and planar cyclooctatetraene with 4π electrons should be antiaromatic. Cyclobutadiene is very unstable and has not been prepared because the π - electron energy of cyclobutadiene is higher than that of its open-chain counterpart, 1,3-butadiene. Cyclooctatetraene is not planar but tub shaped in which each double bond is almost perpendicular to its neighbours thereby reducing the π overlap to a very great extent and thus it behaves like a linear polyene.



Cyclobutadiene

Planar cyclooctatetraene
(unstable as an aromatic)Tub-shaped cyclooctatetraene
(a non-aromatic structure)

6.8 Physical Properties of Aromatic Hydrocarbons

Aromatic hydrocarbons are insoluble in water, but soluble in nonpolar solvents like ether, CCl_4 . They are less dense than water, but their densities are about 10% higher than the densities of the corresponding cycloalkanes. The boiling points increase with increasing molecular mass. The melting points depend not only on molecular mass but also on the symmetry of the molecules. For example, the melting point of benzene is about 100° higher than that of toluene. Similarly *p*-xylene has a higher melting point than its ortho and meta isomers.

The aromatic hydrocarbons burn with a luminous smoky flame while the aliphatic hydrocarbons burn with a bluish non-smoky flame. Benzene is a colourless liquid, boils at 80°C and freezes at 5.5°C . It is used as a solvent. The condensed aromatic hydrocarbons are usually solids and water insoluble. Toluene and xylenes are colourless liquids having characteristic odour.

Table 6.1 Physical Properties of Aromatic Hydrocarbons

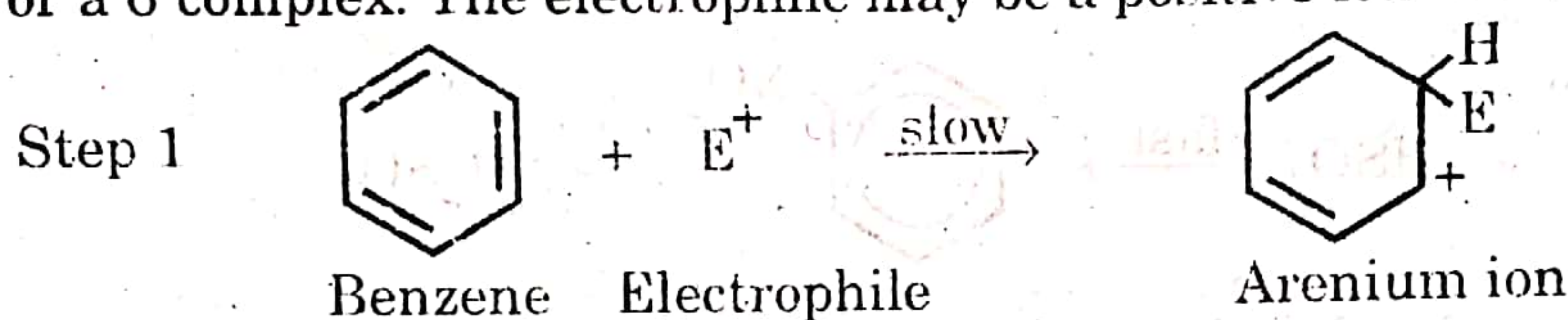
| Name | m.p. ($^\circ\text{C}$) | b.p. ($^\circ\text{C}$) | Density |
|------------------|---------------------------|---------------------------|---------|
| Benzene | 5.5 | 80 | 0.879 |
| Toluene | -95 | 111 | 0.866 |
| Ethyl benzene | -95 | 136 | 0.867 |
| <i>o</i> -xylene | -25 | 144 | 0.880 |
| <i>m</i> -xylene | -48 | 139 | 0.864 |
| <i>p</i> -xylene | 13 | 138 | 0.861 |
| Biphenyl | 70 | 255 | - |
| Naphthalene | 80 | 218 | 0.972 |
| Anthracene | 215 | 340 | - |

6.9 Reactivity of Benzene-Electrophilic Aromatic Substitution

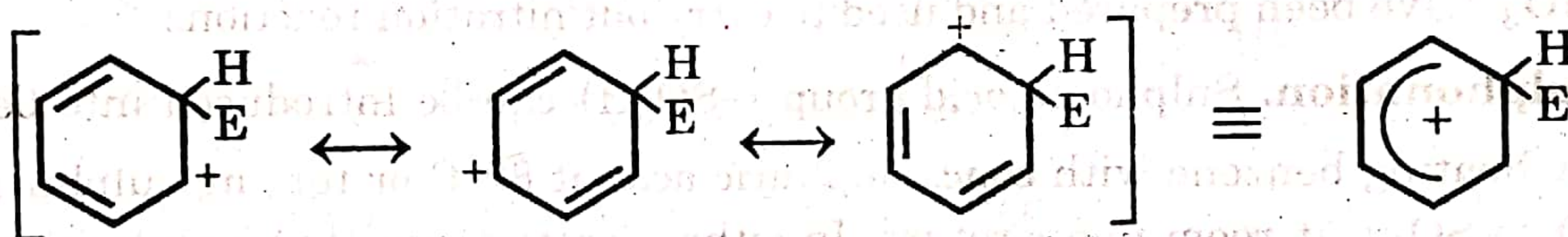
Benzene like alkenes, has a π electron system but benzene has extensively delocalized π electron system which renders benzene stable due to the presence of high resonance energy. The reactivity of benzene is therefore oriented in two directions. Firstly, benzene is susceptible to electrophilic attack, primarily because of its exposed π electrons. Secondly, while benzene is susceptible to electrophilic attack, it undergoes electrophilic substitution reactions rather than addition reactions. Since substitution reactions allow the aromatic sextet of π electrons to be regenerated after attack by the electrophile has occurred.

Mechanism. All electrophilic aromatic substitution reactions follow the same general mechanism that involves two steps.

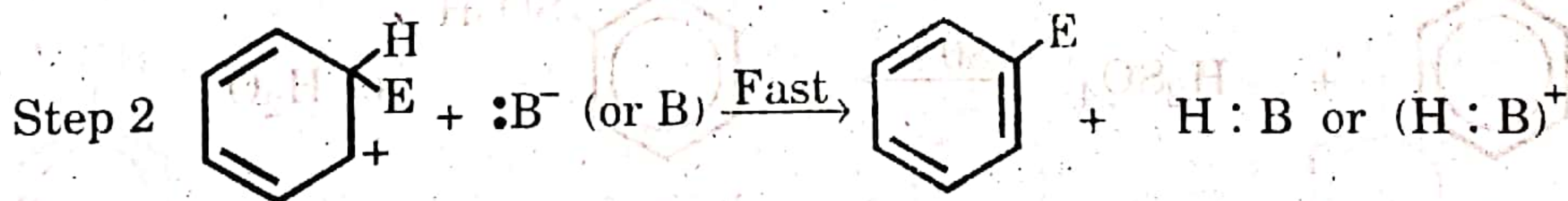
- (i) In the first step, an electrophile attacks the π electron system of the aromatic ring to form a delocalized nonaromatic carbocation known as an arenium ion or a σ complex. The electrophile may be a positive ion or a dipole.



The arenium ion is resonance-stabilized and is a hybrid of the following three-structures.



- (ii) In the second step, the arenium ion loses a proton from the carbon that bears the electrophile, to a base present in the reaction mixture. The electron pair that bonded this proton to carbon becomes a part of the cyclic π electron system and the aromatic sextet will then be restored.



The first step is slower one and therefore is the rate determine step and the reaction is second order.

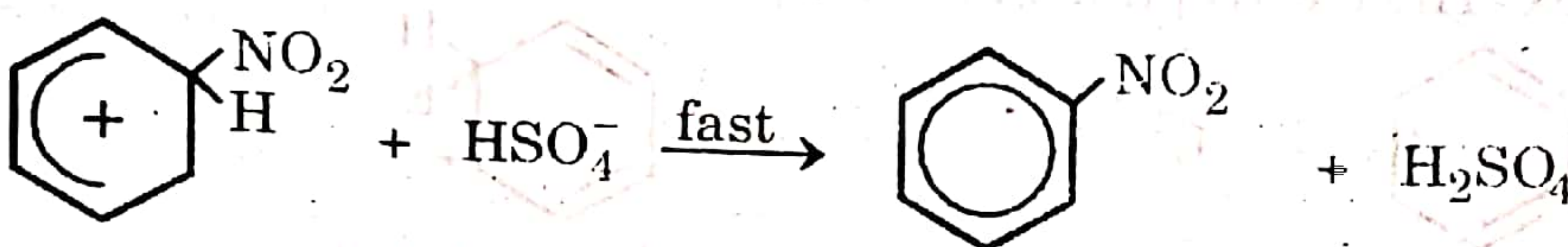
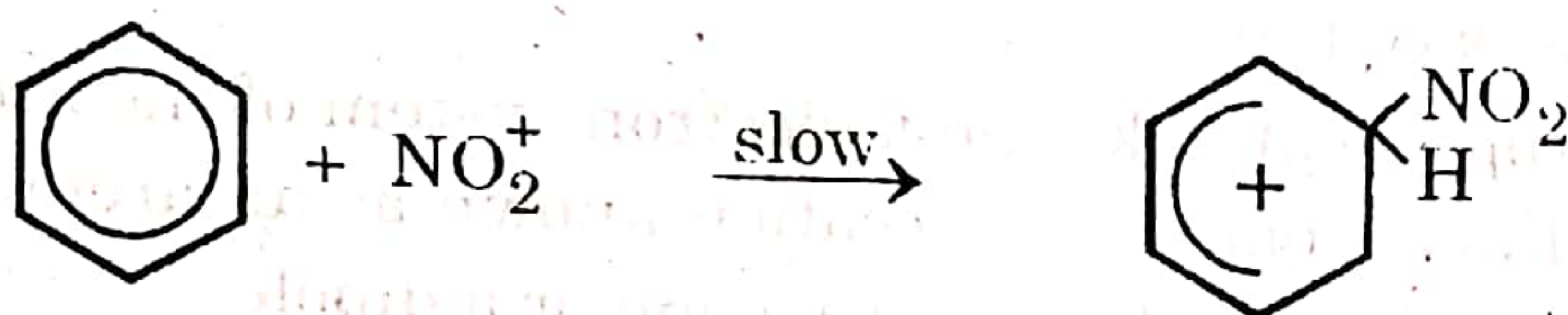
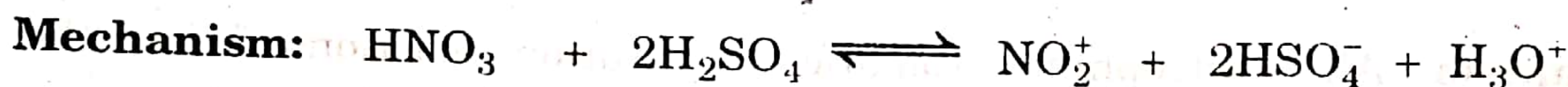
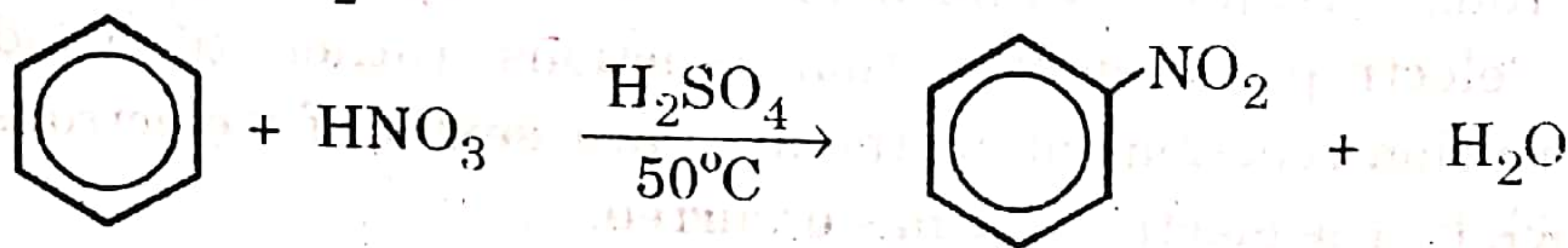
The reaction in which a proton (H^+) of the aromatic ring is substituted by an electrophile (E^+) is called **electrophilic aromatic substitution**.

6.10 Aromatic Electrophilic Substitution Reactions

Benzene undergoes nitration, sulphonation, halogenation and Friedel-Crafts alkylation and acylation reactions. It also undergoes amination, formylation and

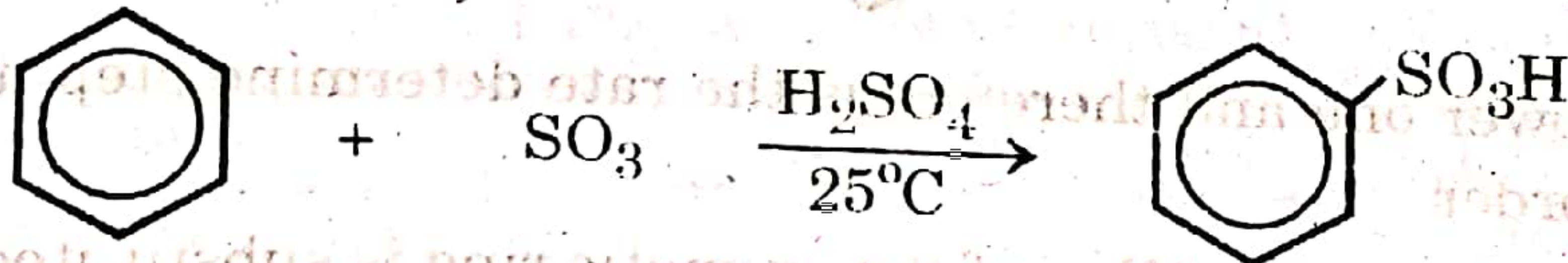
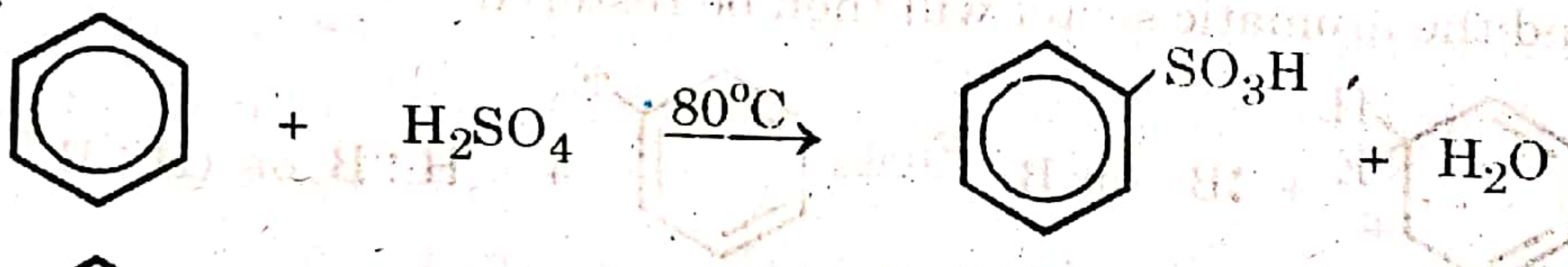
carboxylation reactions.

1. **Nitration.** Nitration of benzene is most commonly carried out by heating benzene with a mixture of conc. nitric acid and conc. H_2SO_4 . Concentrated H_2SO_4 increases the rate of reaction by increases the concentration of the electrophile - the nitronium ion, NO_2^+ .

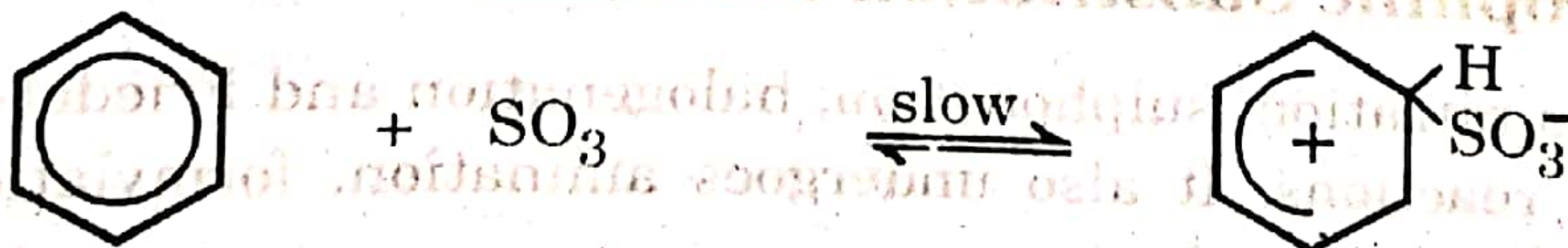
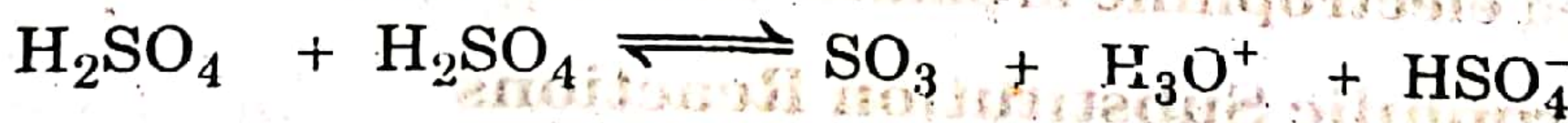


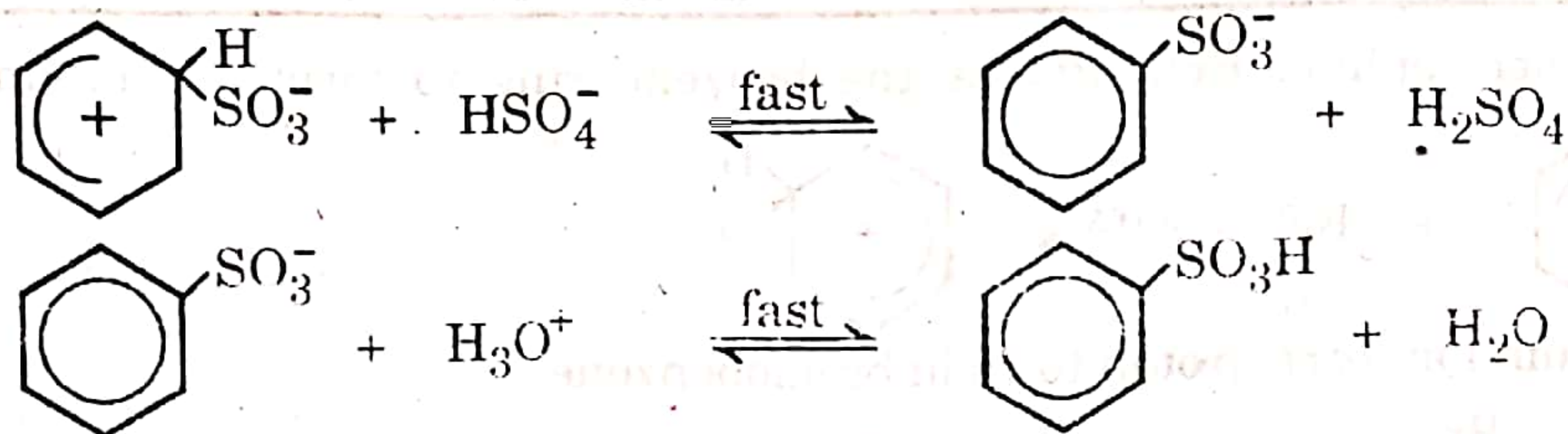
The nitronium ion has been observed spectroscopically in the mixtures of HNO_3 and H_2SO_4 . Recently stable nitronium salts such as $\text{NO}_2^+\text{ClO}_4^-$ and $\text{NO}_2^+\text{NO}_3^-$ have been prepared and used to carry out nitration reactions.

2. **Sulphonation.** Sulphonic acid group ($-\text{SO}_3\text{H}$) can be introduced into benzene ring by heating benzene with conc. sulphuric acid at 80°C or fuming sulphuric acid ($\text{H}_2\text{SO}_4 + \text{SO}_3$) at room temperature. In either reaction the electrophile is sulphur trioxide (SO_3). Although SO_3 is a neutral species, it has an electron deficient sulphur atom due to which it behaves as a strong electrophile. In fuming sulphuric acid, the dissolved SO_3 reacts directly.

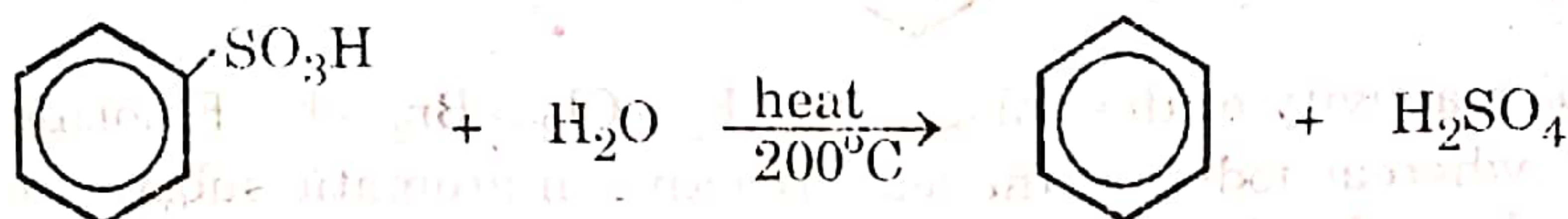


Mechanism: In conc. H_2SO_4 , SO_3 is produced in the following equilibrium.

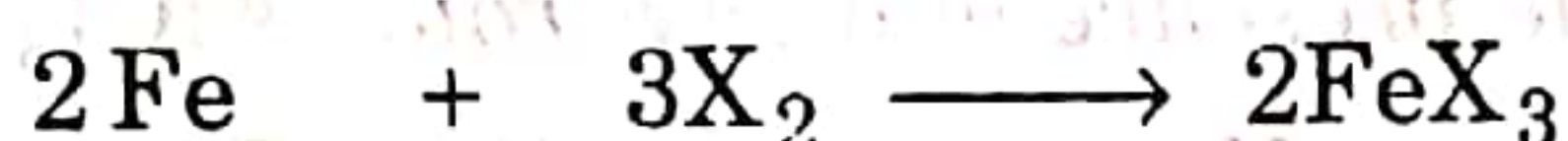




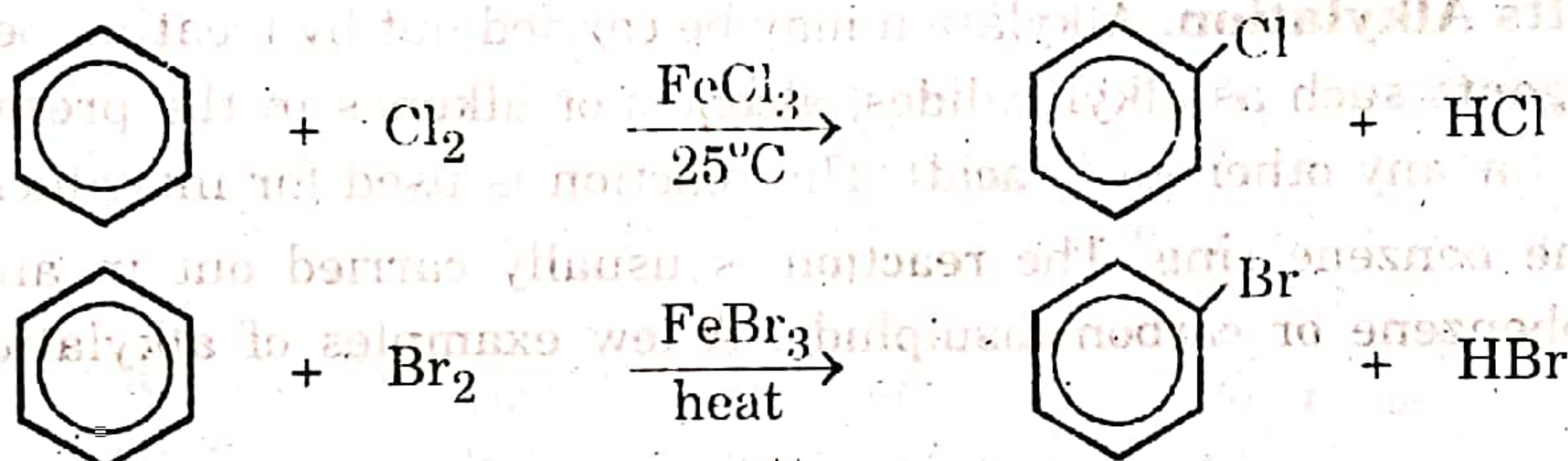
Sulphonation is a reversible process, desulphonation is achieved by treating the benzene sulphonic acid with super heated steam.



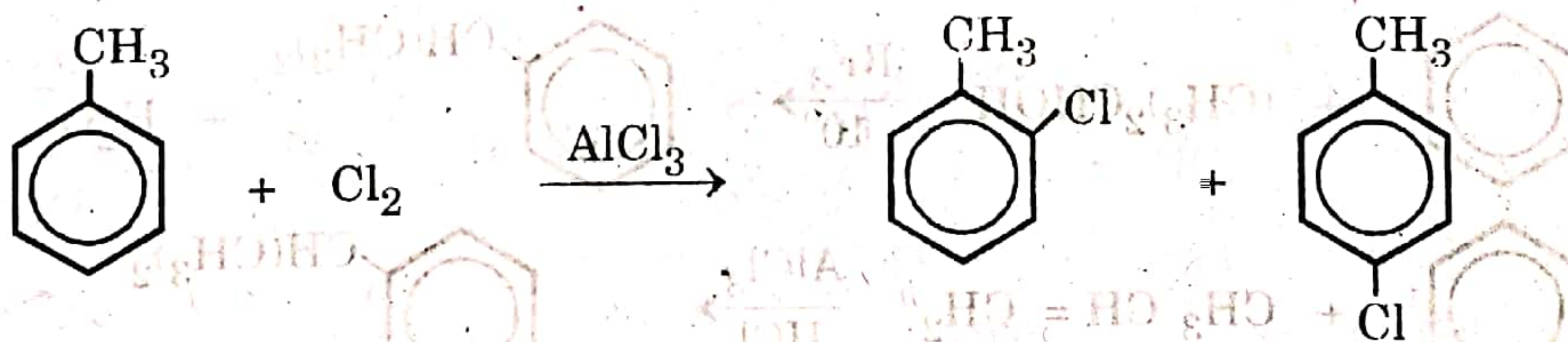
3. Halogenation. The process of substitution of halogen (chlorine or bromine) in place of H atom in benzene ring is called **halogenation**. Benzene reacts with chlorine or bromine in presence of a Lewis acid like FeCl_3 or FeBr_3 to form chlorobenzene or bromobenzene. Most often iron is used as a catalyst, which reacts with halogens to form the required ferric halide.



Since side chain alkylation is catalysed by light, the aromatic halogenation reactions should be conducted in the absence of light.



Toluene reacts with Cl_2 or Br_2 in the presence of AlCl_3 or FeCl_3 to give a mixture of *o*- and *p*-derivatives.

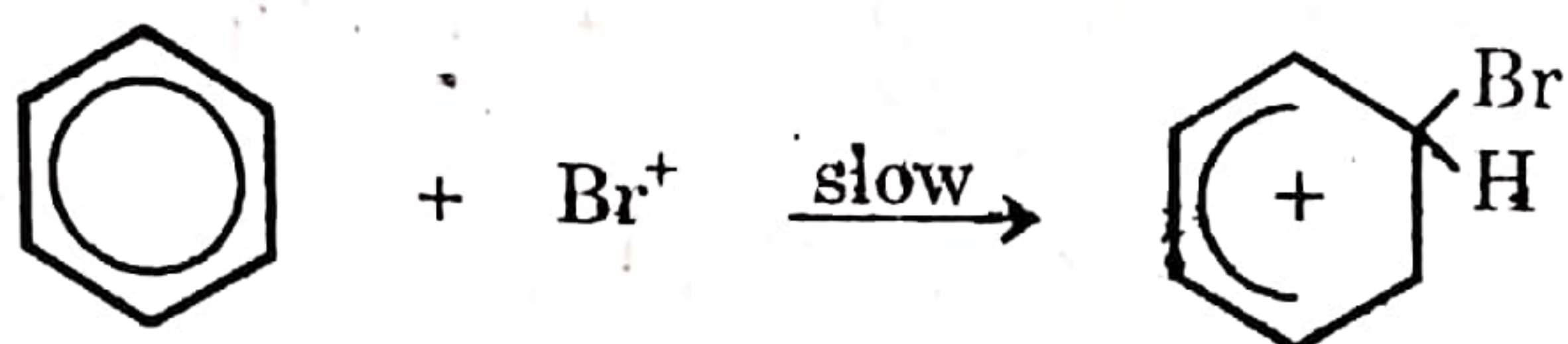


Mechanism: The mechanism of halogenation is similar to the general pattern described already. The actual halogenating agent is halonium ion, X^+ . The mechanism for aromatic bromination is as follows;

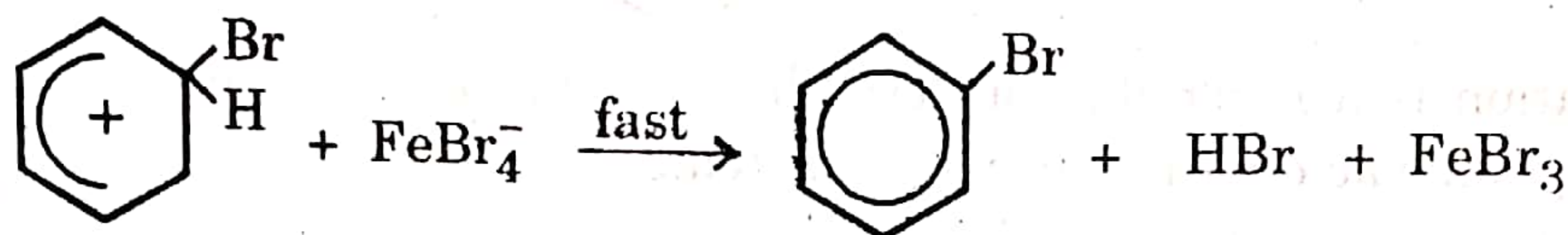
Step 1. Formation of electrophile, halonium ion.



Step 2. The electrophile, Br^+ , attacks the benzene ring to form a arenium ion.



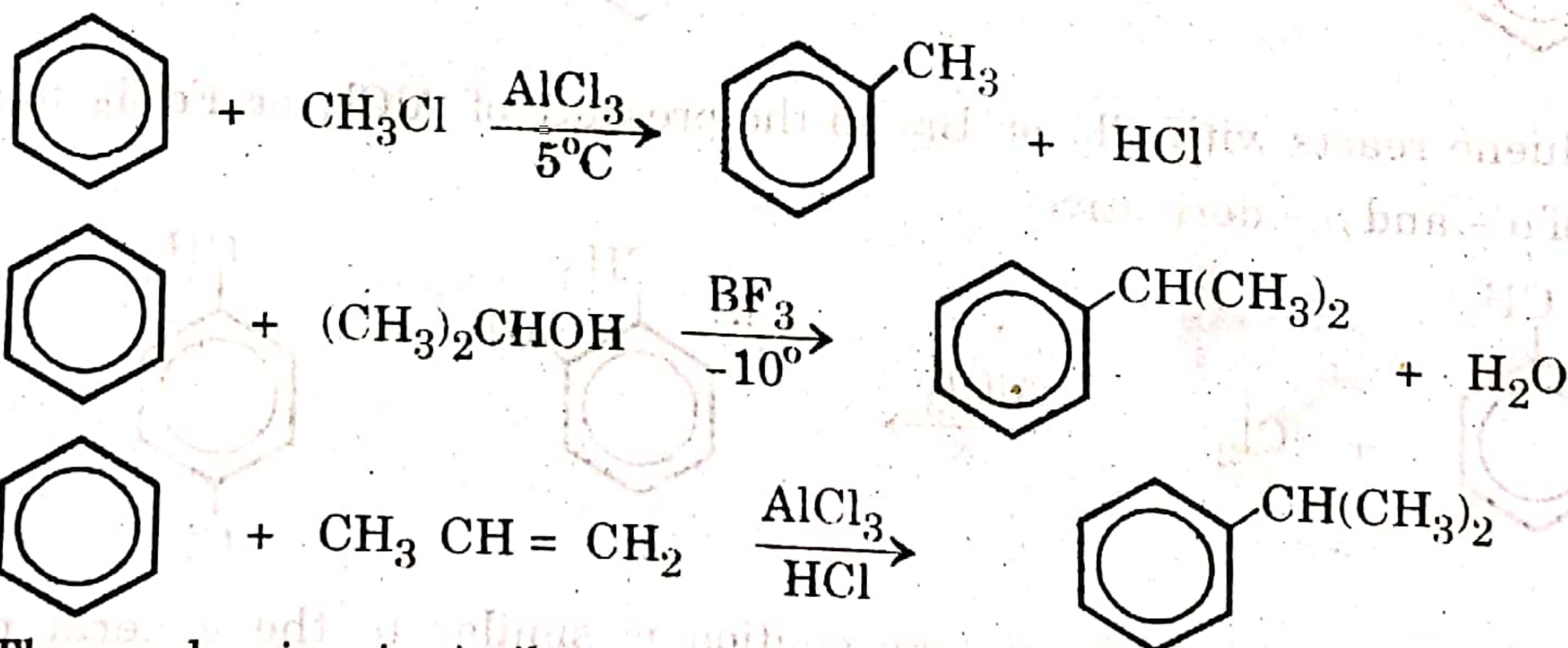
Step 3. Arenium ion loses proton to yield bromobenzene.



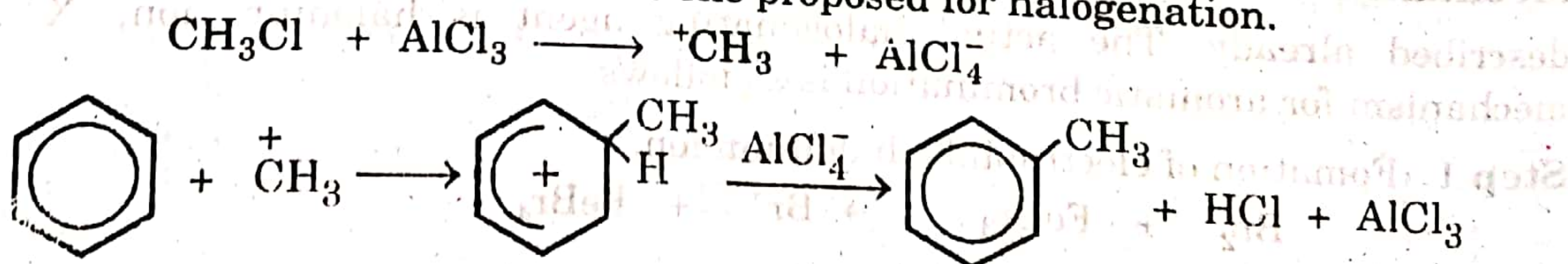
The order of reactivity of the halogens is: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$. Fluorine is too reactive to control, whereas iodine is the least reactive in aromatic substitution. An oxidizing agent such as HNO_3 , HIO_3 or H_2O_2 is generally used to convert iodine into an electrophilic iodinium ion ($\text{I}_2 \xrightarrow{2e^-} 2\text{I}^+$). ICl is a better iodinating agent than iodine itself.

4. Friedel-Crafts reaction. The reaction which, involves the introduction of an alkyl or acyl group into benzene ring in the presence of anhydrous AlCl_3 (or any other lewis acid, i.e., BF_3 , HF , FeCl_3 , ZnCl_2 and H_2SO_4) is called **Friedel - Crafts reaction**. These reactions are classified into two main categories.

1. Friedel-Crafts Alkylation. Alkylation may be carried out by treating benzene with alkylating agents such as alkyl halides, alcohols or alkenes in the presence of anhydrous AlCl_3 (or any other lewis acid). The reaction is used for introducing an alkyl group in the benzene ring. The reaction is usually carried out in an inert solvent like nitrobenzene or carbon disulphide. A few examples of alkylation are given below:

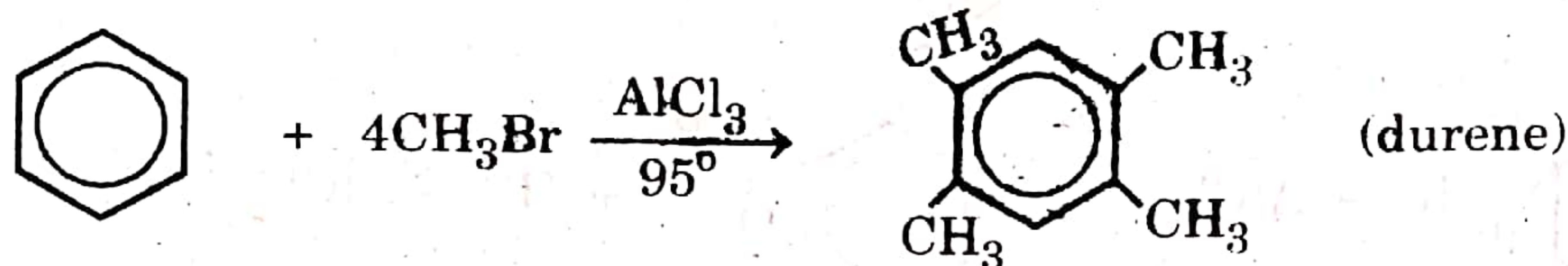


The mechanism is similar to the one proposed for halogenation.

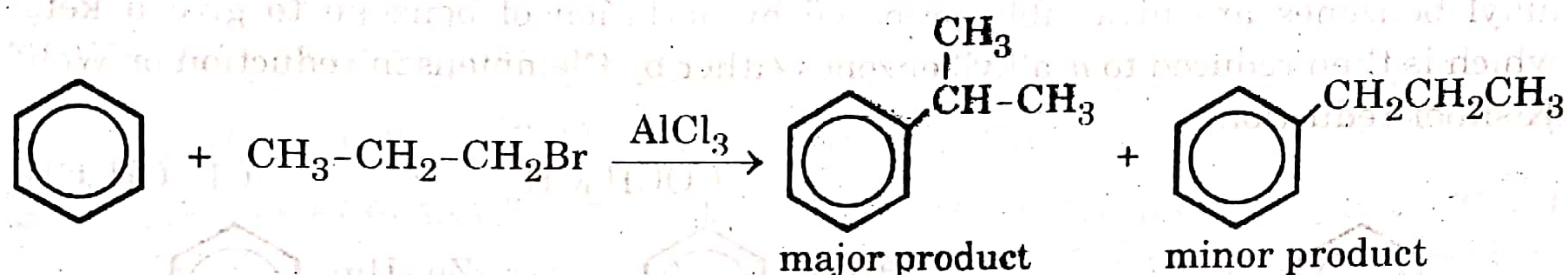


Drawbacks. Friedel - Crafts alkylation has two serious drawbacks:

- (i) It is difficult to stop the reaction when one alkyl group has entered the ring. It often gives poly-alkylated benzenes. For example, benzene with excess of CH_3Br gives 1, 2, 4, 5 - tetramethyl benzene in the presence of AlCl_3 at 95°C .

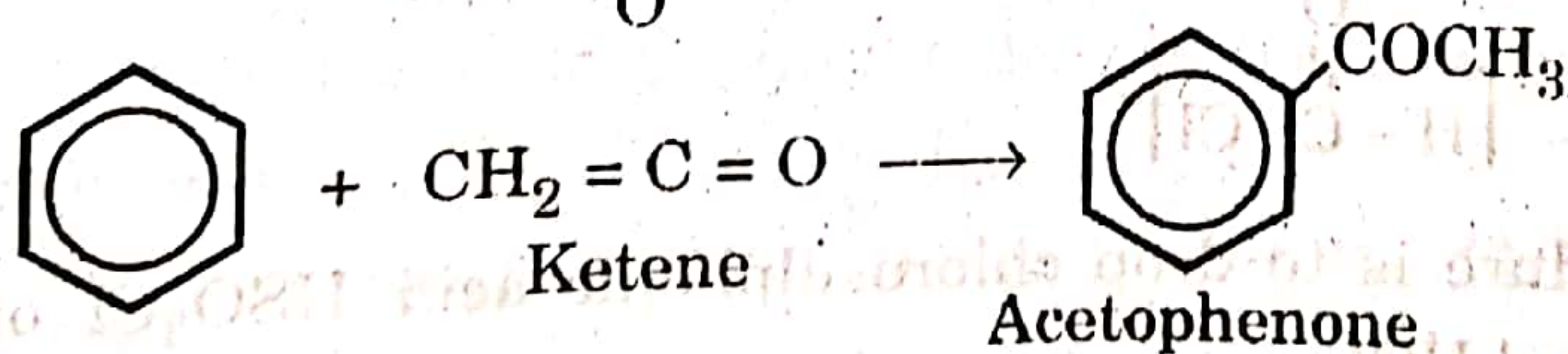
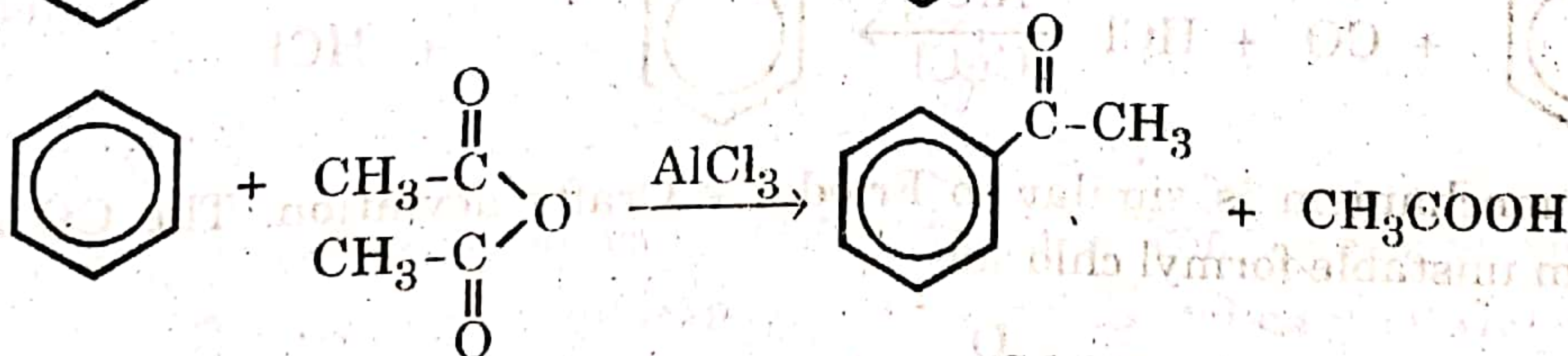
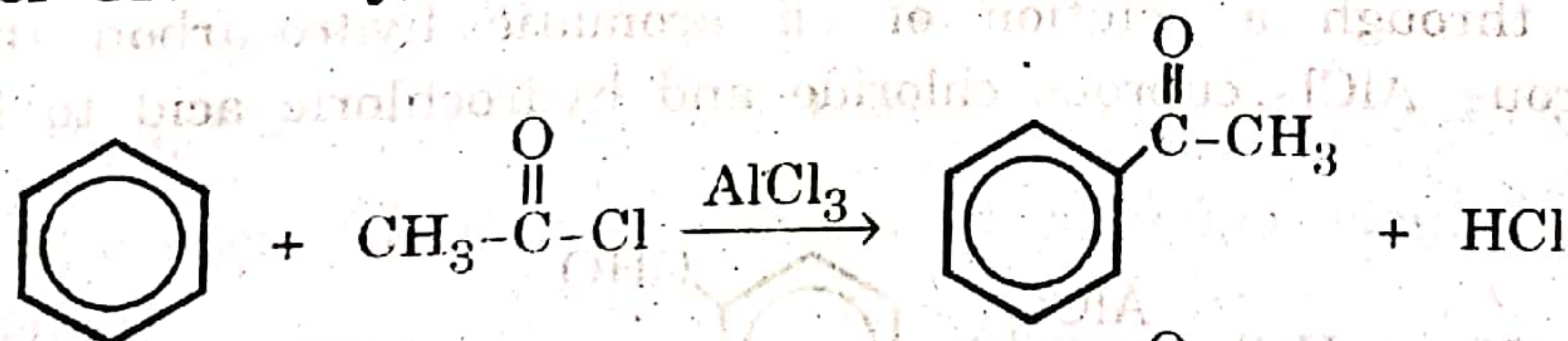


- (ii) The alkyl group often tends to rearrange. For example, when benzene is treated with 1-bromopropane in the presence of AlCl_3 , the product is isopropylbenzene (cumene) rather than the expected *n*-propylbenzene.

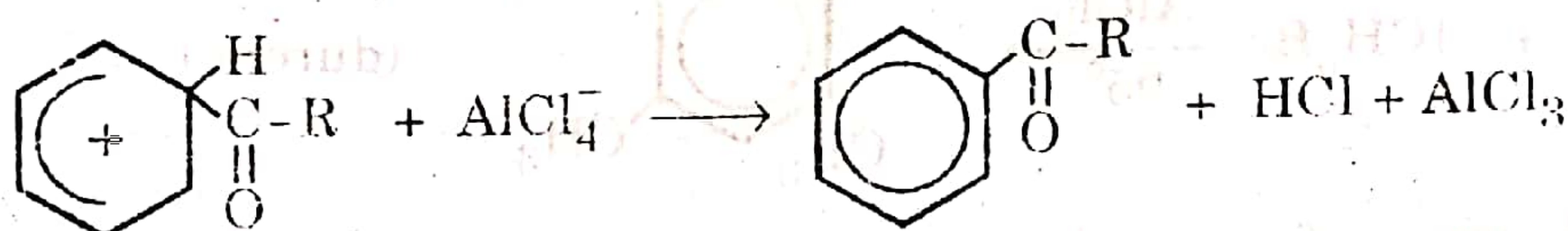
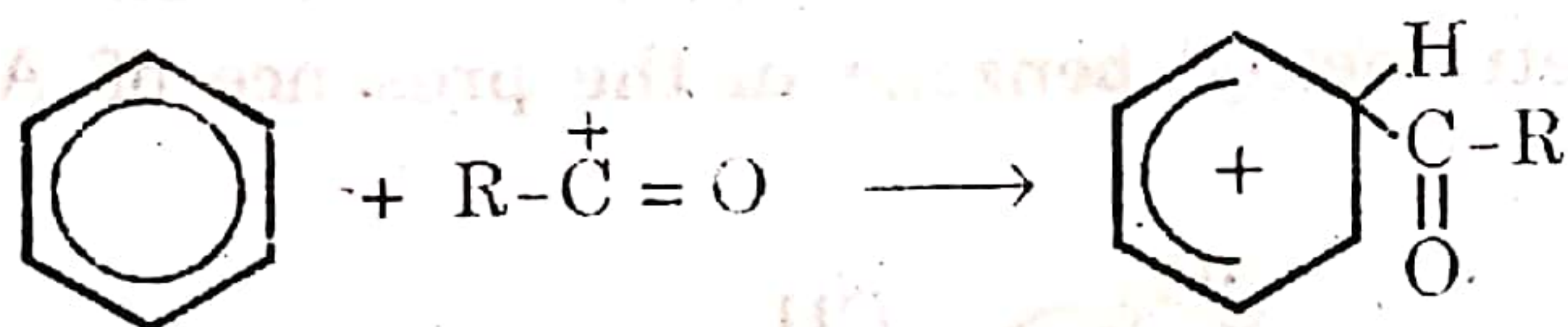
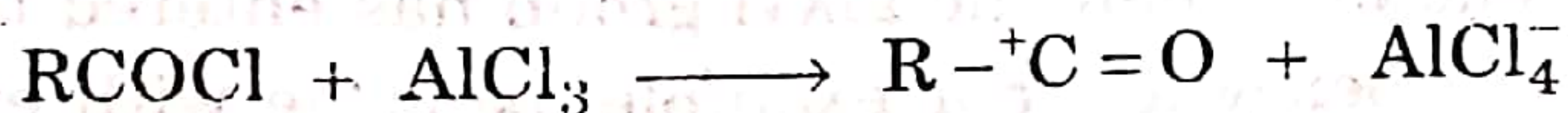


This is because the Friedel-Crafts alkylation involves formation of carbonium ion electrophiles. These carbonium ion can undergo rearrangement before attacking the benzene ring. Rearrangement is usually in the order *primary* \longrightarrow *secondary* \longrightarrow *tertiary* and occurs mostly by migration of H^- but also of R^- .

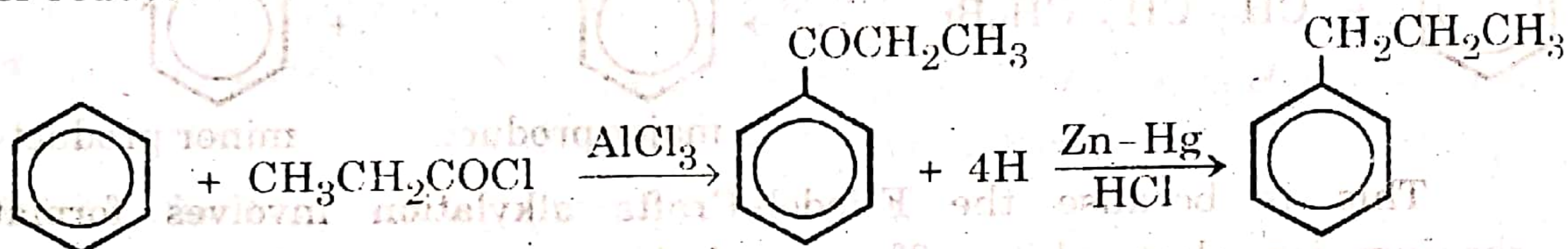
(ii) **Friedel-Crafts Acylation.** A reaction in which an acyl group ($\text{RCO}-$) is introduced into the benzene ring by means of an acid halide or an acid anhydride or a ketenes in the presence of anhydrous AlCl_3 to form aromatic ketones is called **Friedel-Crafts acylation**. A few examples are given below:



The mechanism of acylation involves electrophilic acylium ion ($R - ^+C = O$).

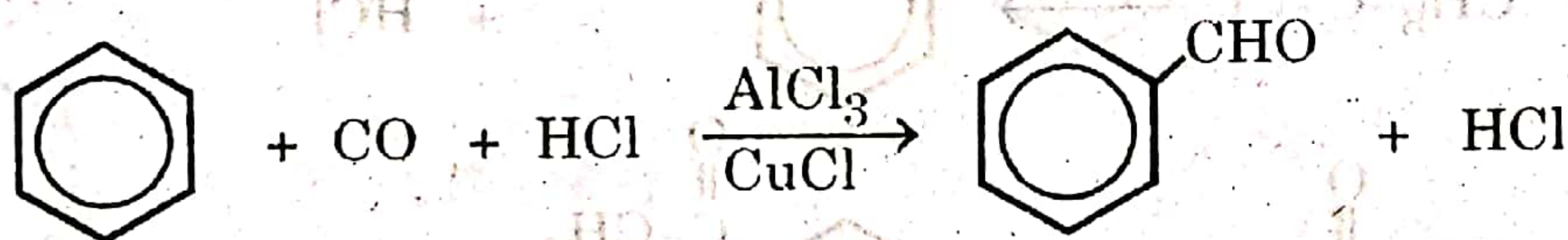


Unlike an alkyl group, an acyl group does not rearrange, nor it allows the introduction of another acyl group in the benzene ring. Therefore, straight-chain alkyl benzenes are invariably prepared by acylation of benzene to give a ketone which is then reduced to *n*-alkylbenzenes either by Clemmensen reduction or Wolff-Kishner reduction.



5. Formylation. Substitution of a formyl group, i.e., aldehyde group ($-CHO$) into an aromatic ring is known as *formylation*. Formylation is similar to acylation, but it is not possible to bring about formylation at ordinary temperatures by the action of formyl chloride or formic anhydride with benzene since formyl chloride is stable only for a short time in $CHCl_3$ at $-40^\circ C$, whereas formic anhydride decomposes slowly at room temperature. Formylation may be accomplished by the following procedures.

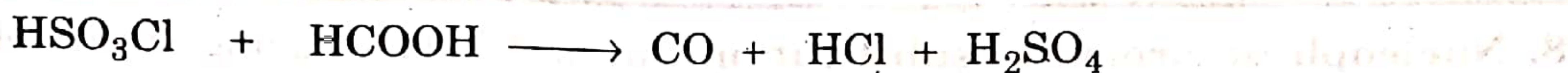
(a) **By Gatterman - Koch reaction.** The reaction is carried out by bubbling carbon monoxide through a solution of an aromatic hydrocarbon (benzene) containing anhydrous $AlCl_3$, cuprous chloride and hydrochloric acid to form an aromatic aldehyde.



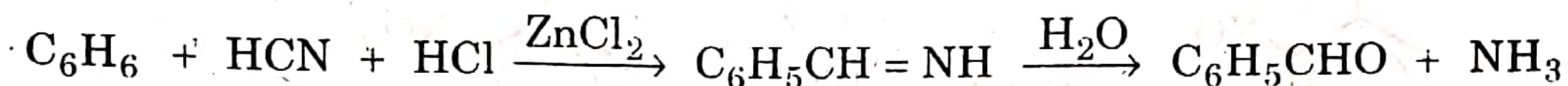
The mechanism is similar to Friedel - Crafts acylation. The CO and HCl react to form unstable formyl chloride.



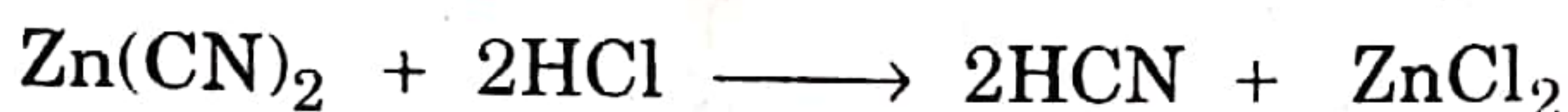
A convenient procedure is to drop chlorosulphonic acid HSO_3Cl on formic acid, which generates CO and HCl .



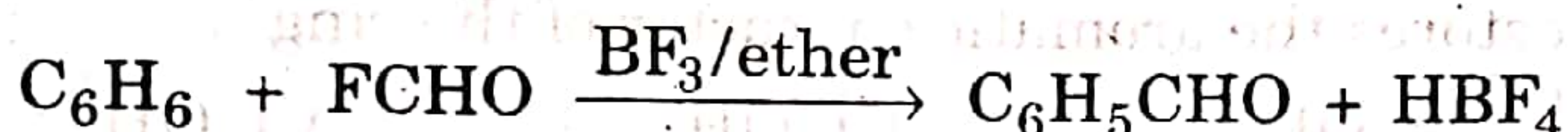
(b) **By Gatterman reaction.** Gatterman used hydrogen cyanide in place of poisonous carbon monoxide as the source of the formyl group. In this procedure, a mixture of hydrogen cyanide and HCl is treated with aromatic compound in the presence of ZnCl_2 .



Direct use of HCN can be avoided by using $\text{Zn}(\text{CN})_2$. HCN is generated *in situ*.



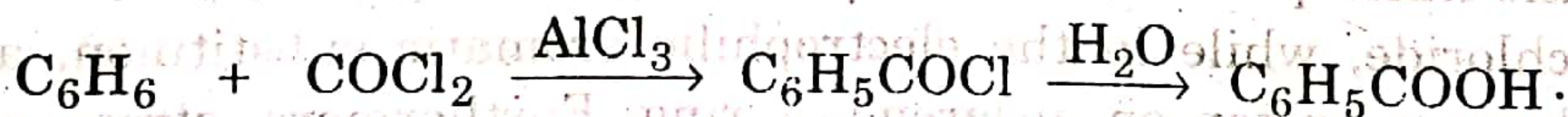
(c) **Formylation with formyl fluoride.** In this method, aromatic rings are formylated with formyl fluoride, HOCF , in the presence of BF_3 in ether. Unlike formyl chloride, formyl fluoride is stable enough for this purpose. This reaction is successful for benzene, alkylbenzenes, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{Br}$ and naphthalene.



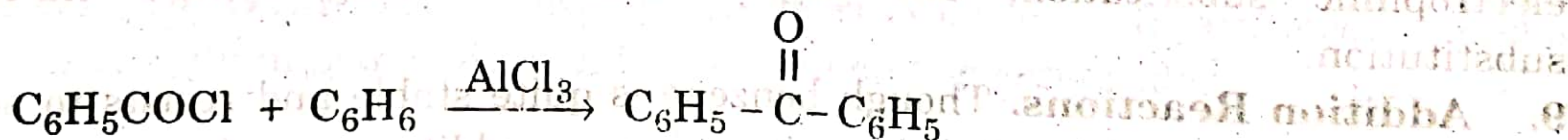
6. Chloromethylation. When certain aromatic compounds are treated with formaldehyde and HCl in the presence of ZnCl_2 , the CH_2Cl group is introduced into the ring in a reaction called **Chloromethylation**. The reaction is related to Friedel-Crafts alkylation and is successful for benzene, alkylbenzenes, alkoxybenzenes and halobenzenes.



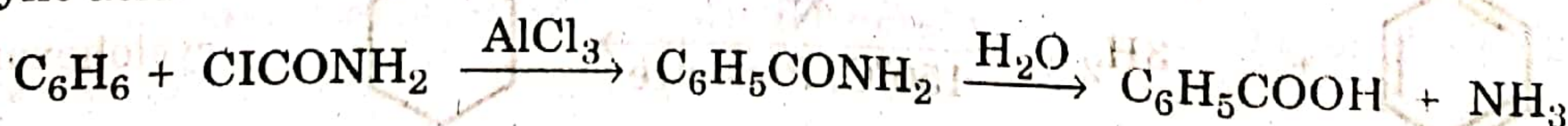
7. Carboxylation. Phosgene (carbonyl chloride, COCl_2) may carboxylate benzene in the presence of anhydrous AlCl_3 . The benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$, initially produced hydrolyzes to the carboxylic acid.



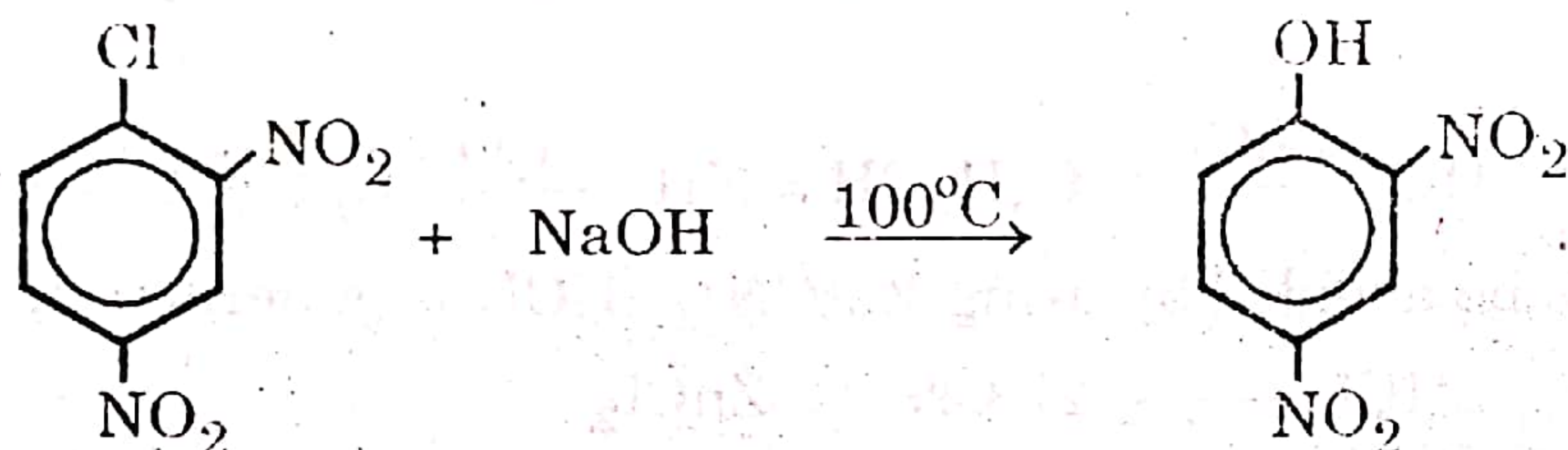
However, in most cases, attacks an other ring to form benzophenone (a ketone).



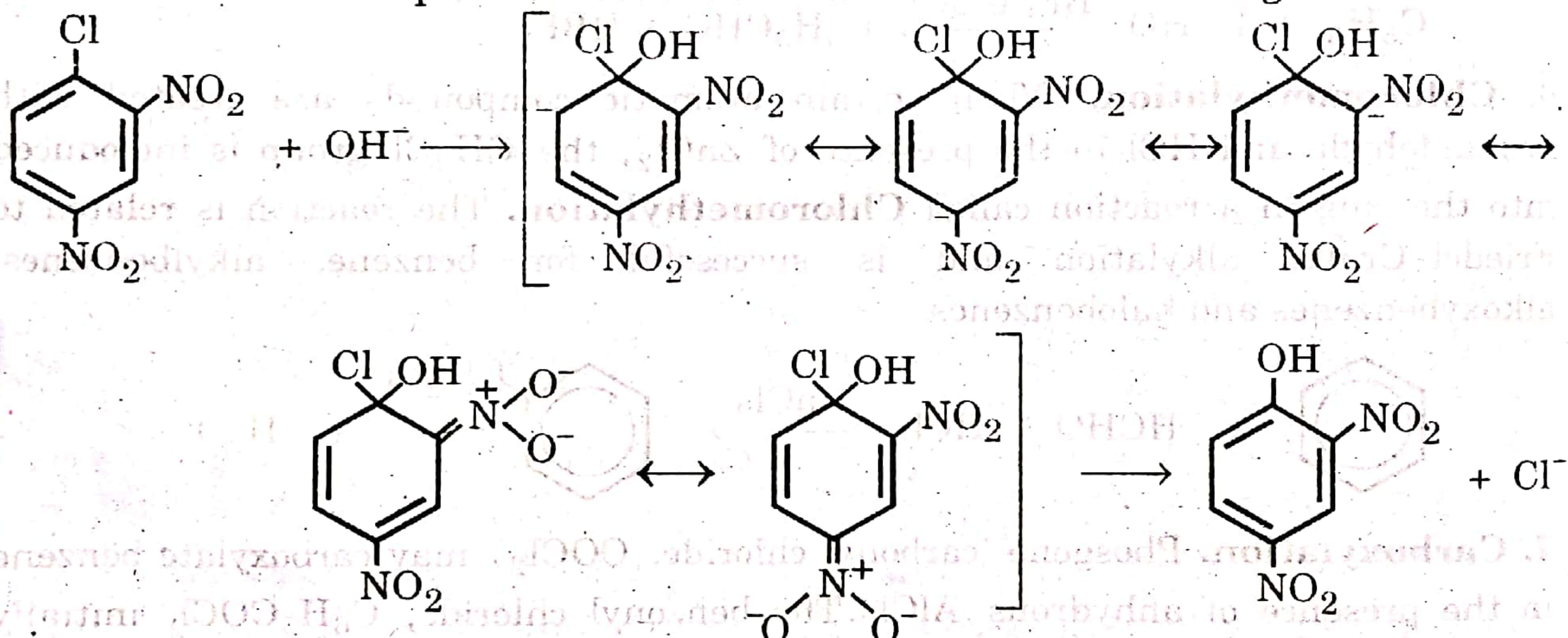
Recently, carbonyl chloride, H_2NCOCl , has been used to prevent the ketone formation. With carbonyl chloride the reaction is called the Gatterman amide synthesis and the product is an amide, which can be hydrolysed to the corresponding carboxylic acid.



8. Nucleophilic aromatic substitution. An aryl halide having strong electron-withdrawing groups at ortho or para to the halide may undergo nucleophilic substitution in which the halide ion is replaced by a nucleophile. For example, hydroxide ion can replace chloride from 2,4-dinitrochlorobenzene.



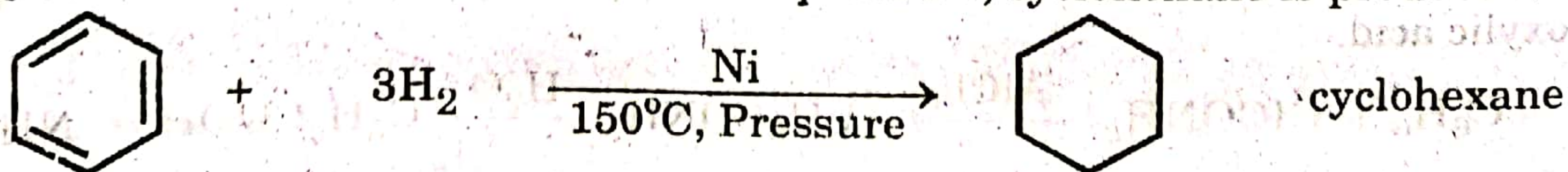
The mechanism of the nucleophilic aromatic substitution involves a negatively charged sigma complex as an intermediate. The negative charge of the complex, delocalized over to the ortho and para position, is stabilized by the electron withdrawing nitro groups through both inductive and resonance effects. Loss of chloride from the complex restores the aromatic character of the ring.



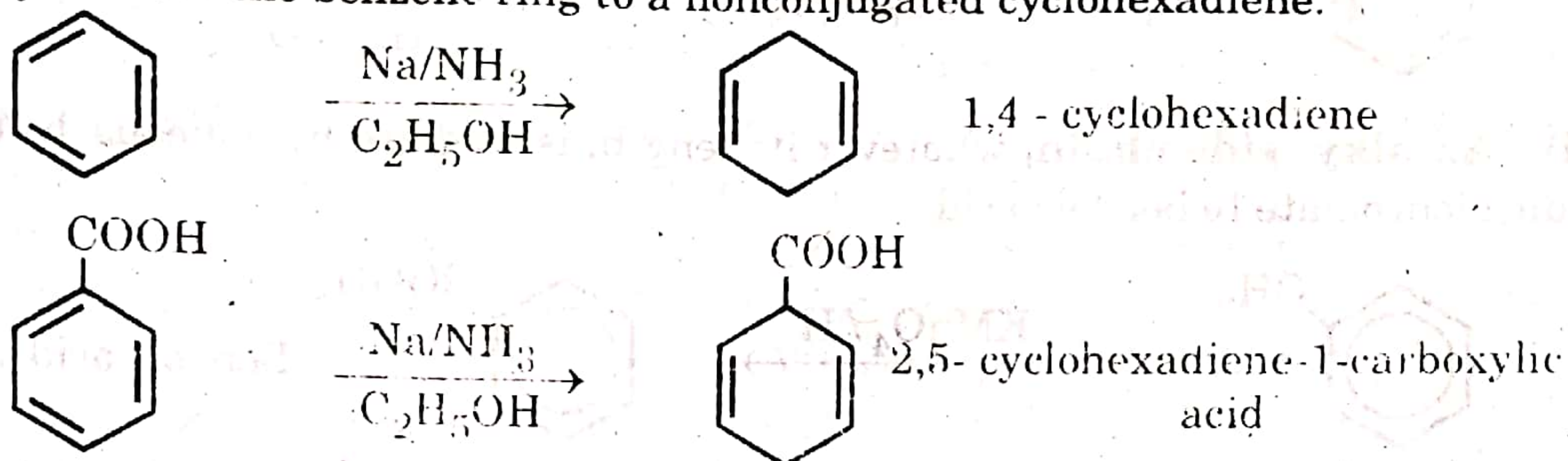
In aromatic nucleophile substitution, a strong nucleophile replaces a leaving group such as chloride, while in the electrophilic aromatic substitution, a strong electrophile replaces a proton on an aromatic ring. Furthermore, strong electron-withdrawing groups such as nitro group, deactivate the aromatic ring toward electrophilic substitution; but they activate the ring toward nucleophilic substitution.

9. Addition Reactions. Though benzene is quite stable and resists to addition, however, under suitable conditions, it undergoes addition reactions, as is evident from the following reactions.

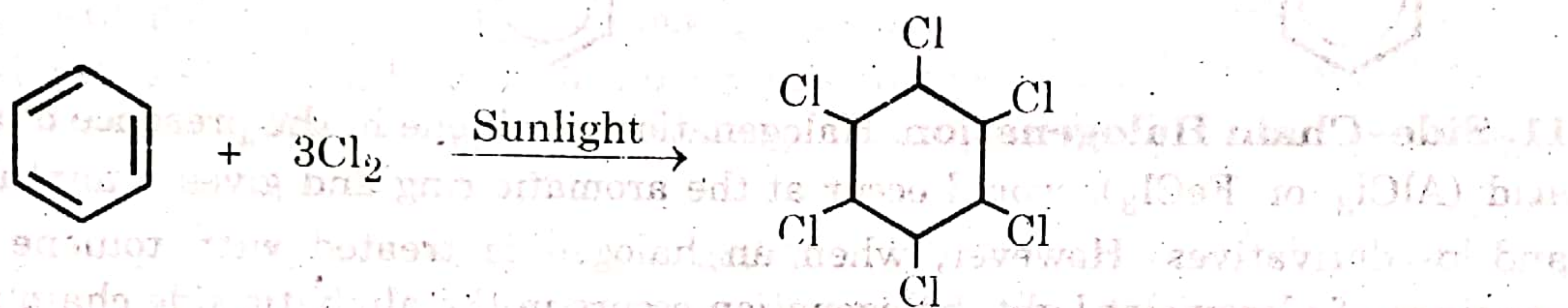
(i) Catalytic Hydrogenation. When a mixture of benzene vapours and hydrogen is passed over a Ni catalyst at 150°C under pressure, cyclohexane is produced.



(ii) **Birch reduction.** Na or Li metal in liquid ammonia in the presence of ethanol partially reduces the benzene ring to a nonconjugated cyclohexadiene.

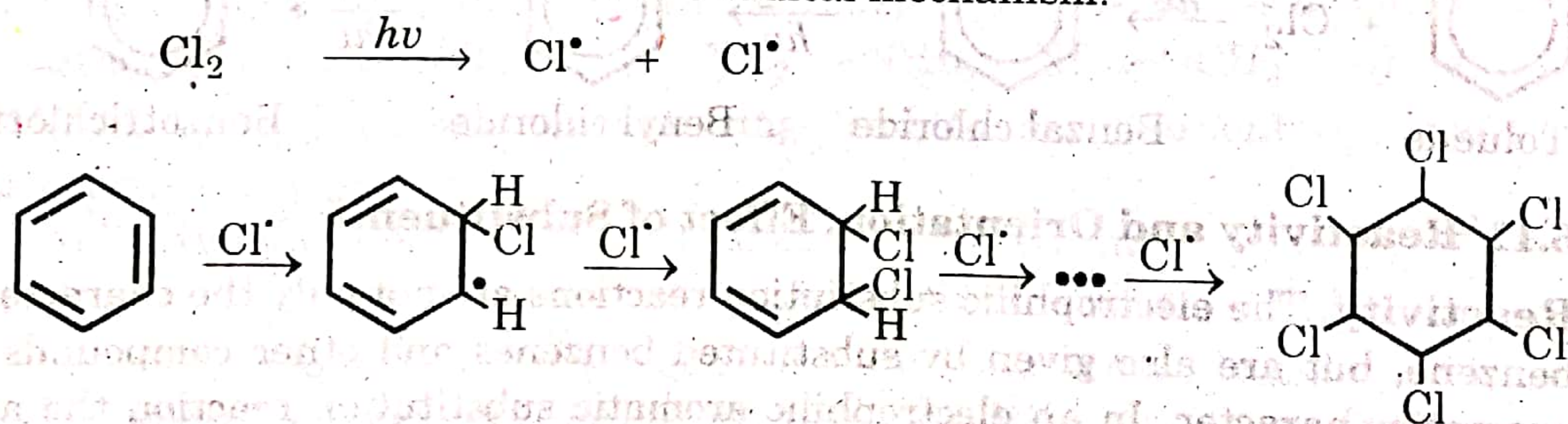


(iii) **Addition of Halogens.** Benzene adds three molecules of chlorine or bromine in the presence of sunlight to form benzene hexachloride or hexabromide.



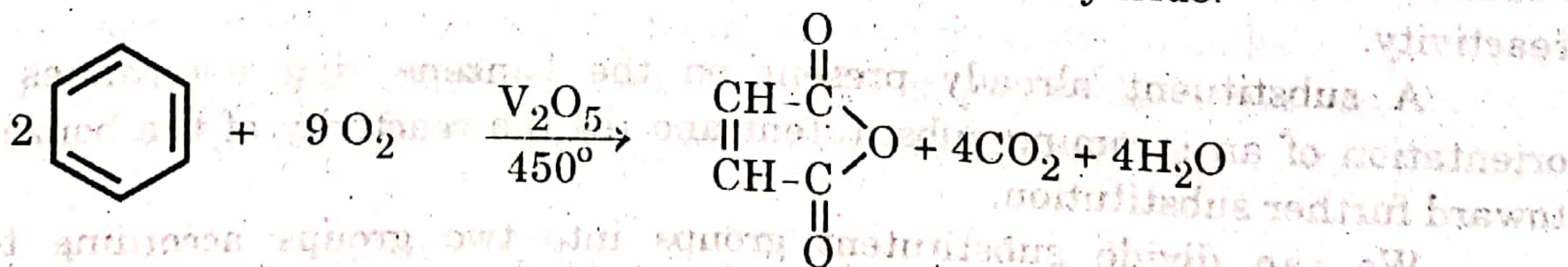
Benzene hexachloride (BHC) is a mixture of eight geometrical isomers and is a powerful insecticide, though only one isomer called γ -isomer, has insecticidal properties. The mixture is sold under the name Gammexane or Lindane or 666.

Mechanism. The reaction involves a free-radical mechanism.

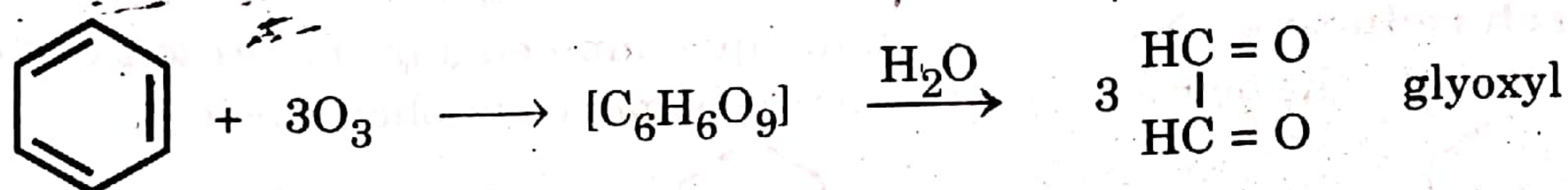


10. Oxidation Reactions. Benzene is resistant to oxidation and is not oxidized by alkaline KMnO_4 or chromic acid at room temperature. However, it can be oxidized under certain conditions, as shown below.

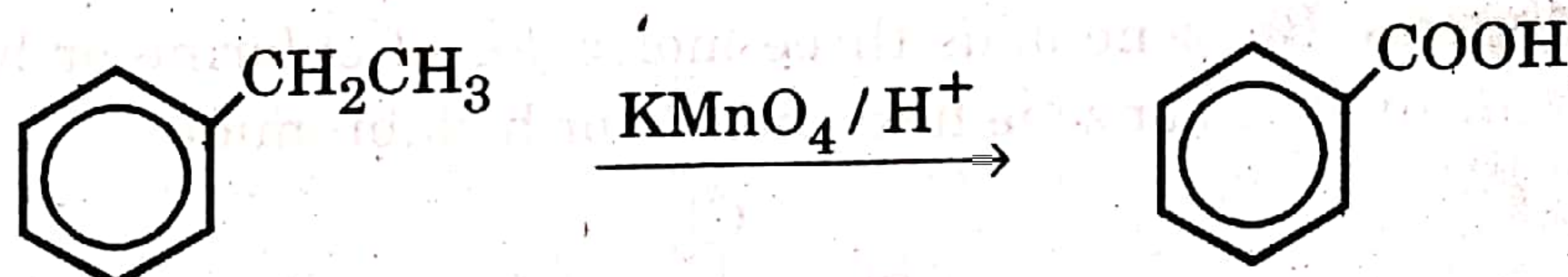
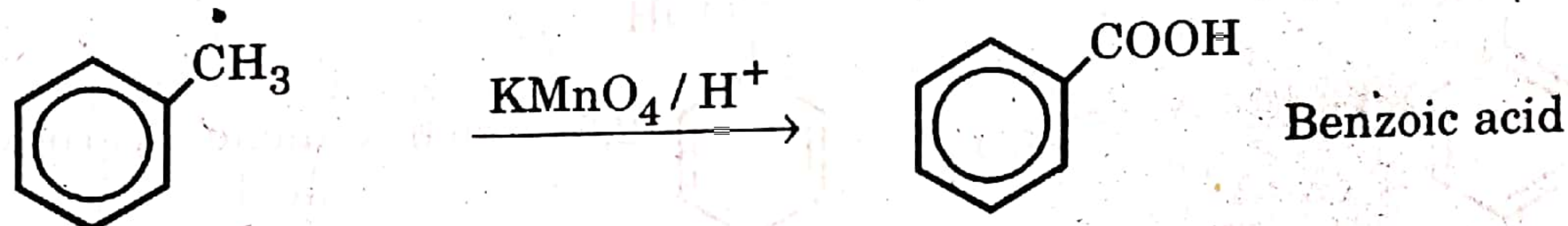
(i) **Catalytic Oxidation.** Benzene undergoes oxidation with air/ oxygen in the presence of vanadium pentoxide at 450°C to form maleic anhydride.



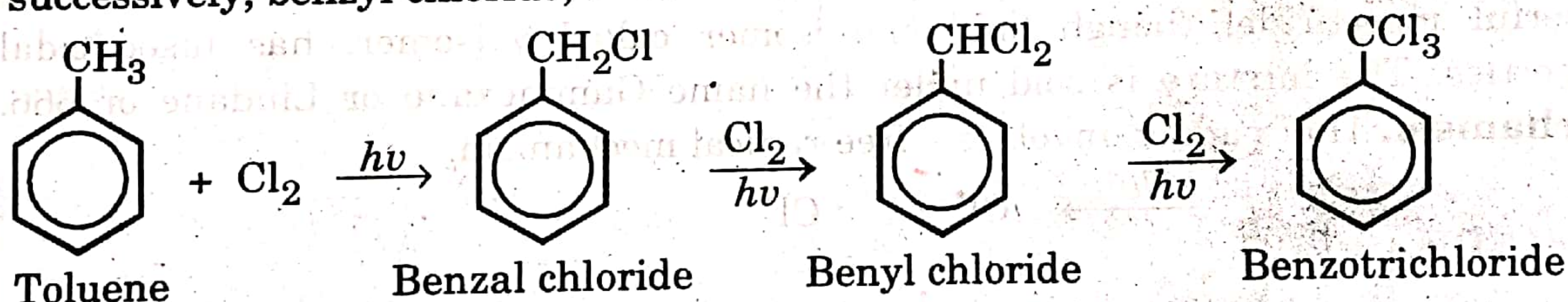
(ii) **Ozonolysis.** Benzene reacts with ozone to give a triozone which on hydrolysis yields glyoxal.



(iii) An alkyl side chain, whatever its length, is oxidized by aqueous KMnO_4 or acidic dichromate to benzoic acid.



11. Side-Chain Halogenation. Halogenation of toluene in the presence of a Lewis acid (AlCl_3 or FeCl_3), would occur at the aromatic ring and gives a mixture of o- and p- derivatives. However, when an halogen is treated with toluene in the presence of ultraviolet light, halogenation occurs in the aliphatic side chain to yield successively, benzyl chloride, benzal chloride and benzotrichloride.



6.11 Reactivity and Orientation: Effect of Substituents

Reactivity. The electrophilic substitution reactions are not only the characteristic of benzene, but are also given by substituted benzenes and other compounds having aromatic character. In an electrophilic aromatic substitution reaction the aromatic ring provides the electron pair out of its aromatic sextet to form a bond with the electrophile. Thus, any substituent group on the aromatic ring that cause an increase in the electron density of the benzene ring will increase its reactivity, since the attack of the electrophile on the aromatic ring is the rate determining step. A substituent that decrease the electron density of the ring will decrease the reactivity.

A substituent already present on the benzene ring determines (i) the orientation of an incoming substituent and (ii) the reactivity of the benzene ring toward further substitution.

We can divide substituent groups into two groups according to their influence on the reactivity of the benzene ring.

1. Activating groups
2. Deactivating groups

Substituent groups that increase the reactivity of the benzene ring relative to benzene itself, are called **activating groups**, and the groups that decrease the reactivity of the ring relative to benzene, are called **deactivating groups**. Thus, an activating group makes the benzene ring to react faster than benzene itself, and a deactivating group makes the benzene ring to react slower than benzene itself, in an electrophilic substitution reaction.

Orientation is a process of determining the relative position of new incoming group in the substituted benzene. We can also divide the substituent groups into two classes to the way they influence the orientation of attack by the incoming electrophile.

1. ortho - para directors

2. meta directors

Substituents which direct the incoming substituent to the ortho and para positions simultaneously, are called **ortho - para directors**, and the substituents which direct the incoming substituent to the meta position are called **meta directors**.

In general, ortho-para directors activate a ring toward electrophilic substitution, whereas meta-directing groups deactivate a ring toward electrophilic substitution. The only exception to the above generalization occurs in halobenzenes, $C_6H_5 - X$, although $-F$, $-Cl$, $-Br$, and $-I$ are ortho - para directors, these substituents deactivate an aromatic ring in electrophilic substitution. On the basis of this generalization, we can divide substituent groups into three classes as follows:

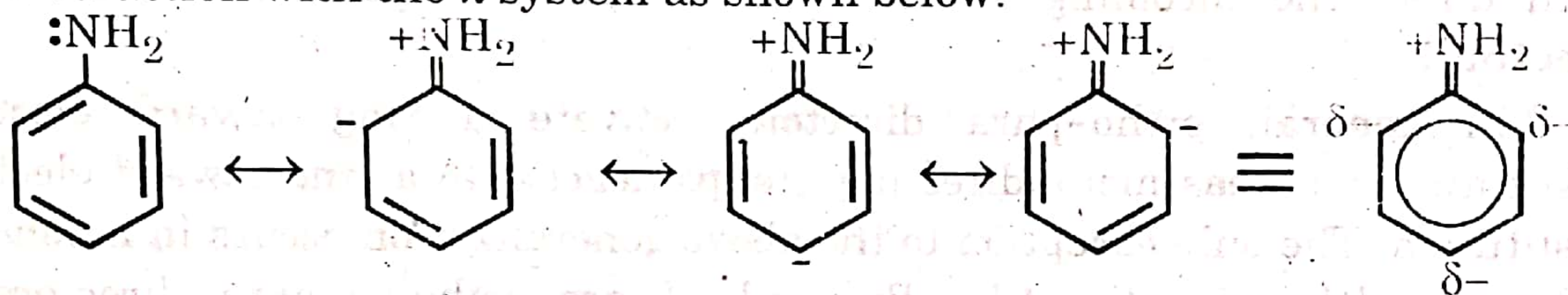
- (i) Substituents such as $-R$, $-OH$, $-NH_2$, $-NHR$, $-NR_2$, $-OCH_3$, $-OR$ and $-NHCOR$ already present on the ring lead to *o*-, *p*-orientation with activation.
- (ii) Halo substituents lead to *o*-, *p*-orientation with deactivation.
- (iii) Substituents such as $-NO_2$, $-SO_3H$, $-COOH$, $-COOR$, $-C=O$, $-CHO$, $-C \equiv N$, $-CF_3$, $-CCl_3$, $-NR_3^+$ lead to meta orientation with deactivation.

Stabilities of sigma complexes (Arenium ion stability). In an electrophilic aromatic substitution reaction on a substituted benzene is to give a disubstituted benzene, the relative yields of the three isomers compounds is to the relative rates of their formation. The rate of a reaction generally depends on the stability of the species formed in the rate-determining step of the reaction. Thus, the rates of formation of the three isomeric disubstituted benzenes and their yields, in an electrophilic substitution reaction, depend on the relative stabilities of the corresponding sigma complexes (arenium ions). The more stable sigma complexes (arenium ion) is formed more rapidly, and thus yields more quantities of the respective isomer.

The influence of the substituent group on the orientation and reactivity of the aromatic ring can be explained on the basis of resonance and inductive effects.

The substituent groups belong to three classes as mentioned above, but to give a broader picture, we divide the substituent groups into five categories.

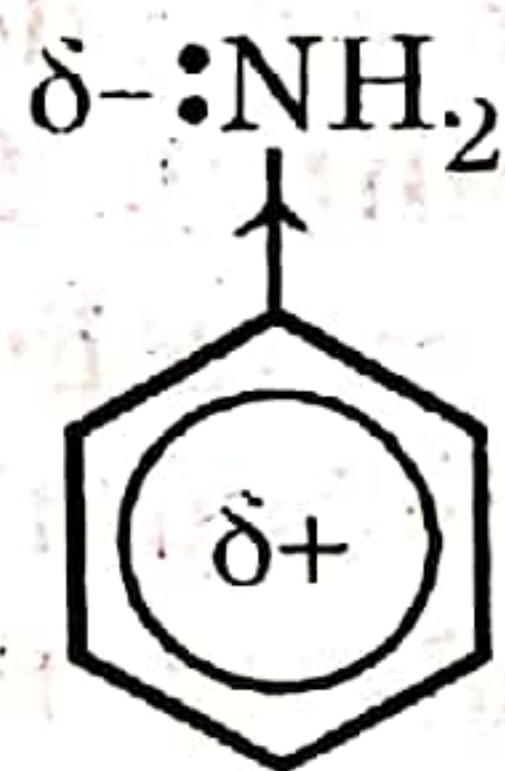
1. **Activating ortho-para directing groups which contain an unshared pair of electrons** on the atom connected to the benzene ring, e.g., $-\text{OH}$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{OCH}_3$, etc. The structural feature of an unshared electron pair on the atom connected to the benzene ring determines the orientation and influences reactivity in electrophilic substitution reaction. An electrophile will attack at those positions at which the electron density is greatest. The unshared electron pair is in a strong position to help the attacking electrophile by making itself available at *o*- and *p*- positions in the benzene ring. For example, the contributing structures for the resonance hybrid of aniline (or any other group of this class) are such that they have the negative charge "concentrated" at the *o*- and *p*- positions in the ring. The unshared electron pair on the N atom attached to the ring is distributed into the ring by interaction with the π system as shown below:



Resonance hybrid

Therefore, an electrophile would naturally attack at the *o*- and *p*- positions rather than at the *m*- positions.

The $-\text{NH}_2$ group exerts an electron-withdrawing inductive effect on the benzene ring and thus deactivates the ring. At the same time, resonance effect exerts an increase of electron density of the ring. Since the resonance effect of the $-\text{NH}_2$ group is stronger than its inductive effect, the net result is that the $-\text{NH}_2$ group activates the ring and makes it to react faster than benzene.



Inductive effect

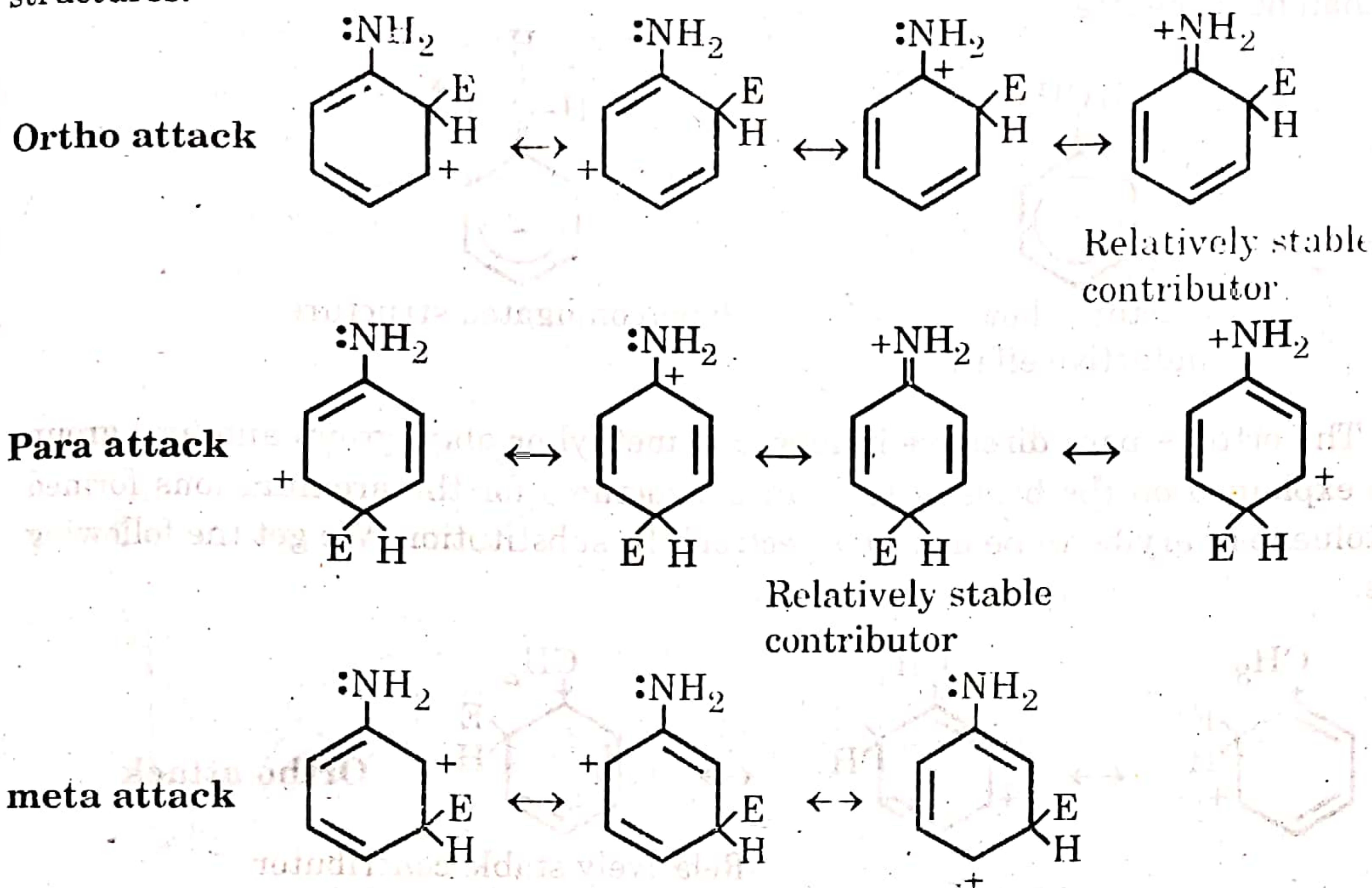


Resonance effect

The orientation and reactivity of the substituted benzenes in an electrophilic substitution reaction can also be explained on the basis of the relative stabilities of the respective intermediate arenium ions (or σ complex). The reaction rate, generally, depends on the stability of the arenium ions. Any group that can donate electrons to the ring will stabilize the arenium ion by dispersing its positive charge and thus increase the reactivity of the ring. An electron-withdrawing group will destabilize the arenium ion by intensifying its positive charge, and thus decrease the reactivity of the ring.

Let us now consider the attack of electrophile on the aniline at the *o*-, *m*-

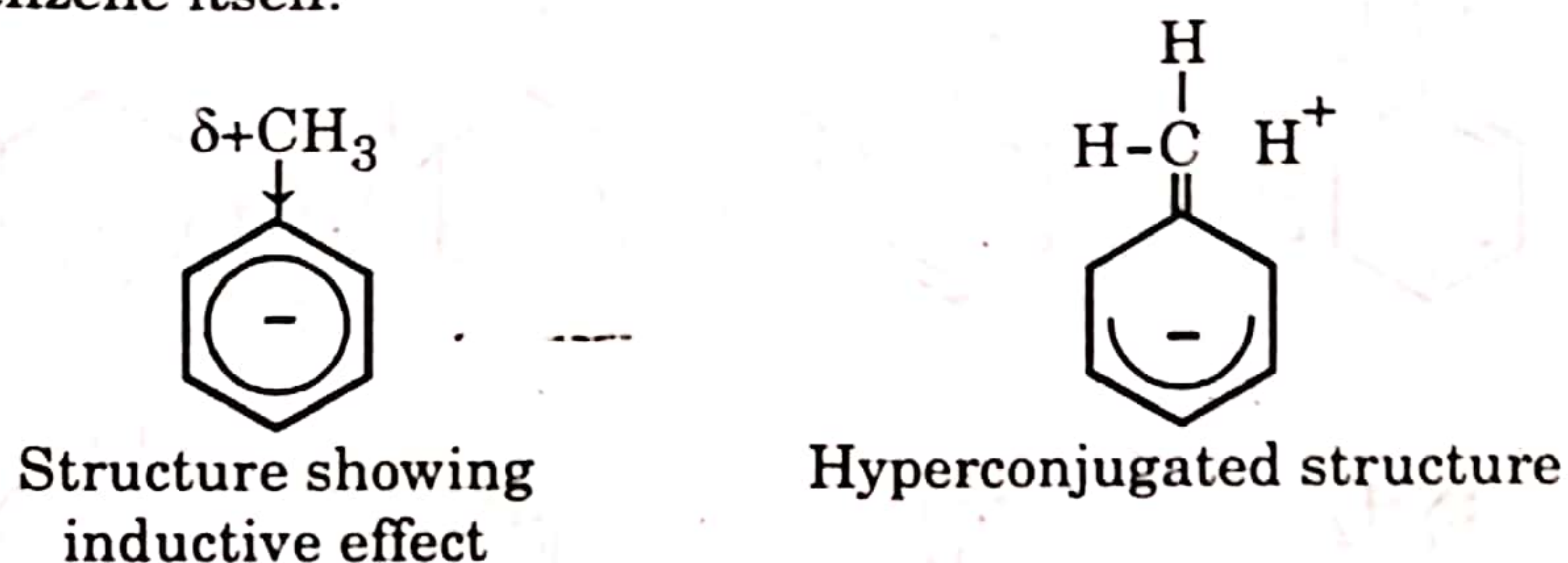
and *p*-positions, the arenium ions has the following resonance contributing structures.



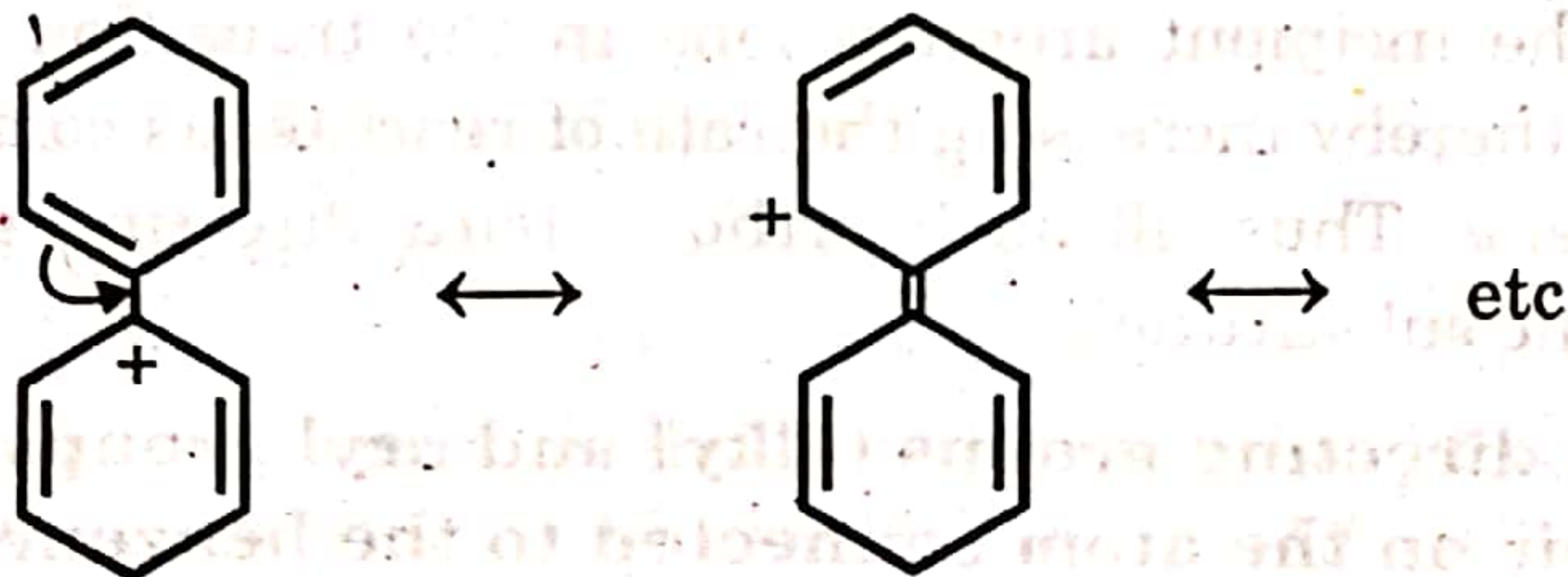
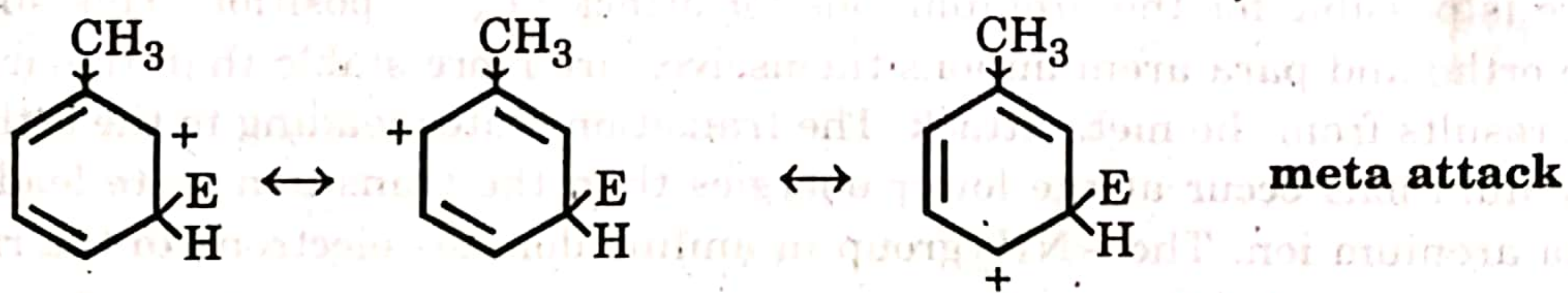
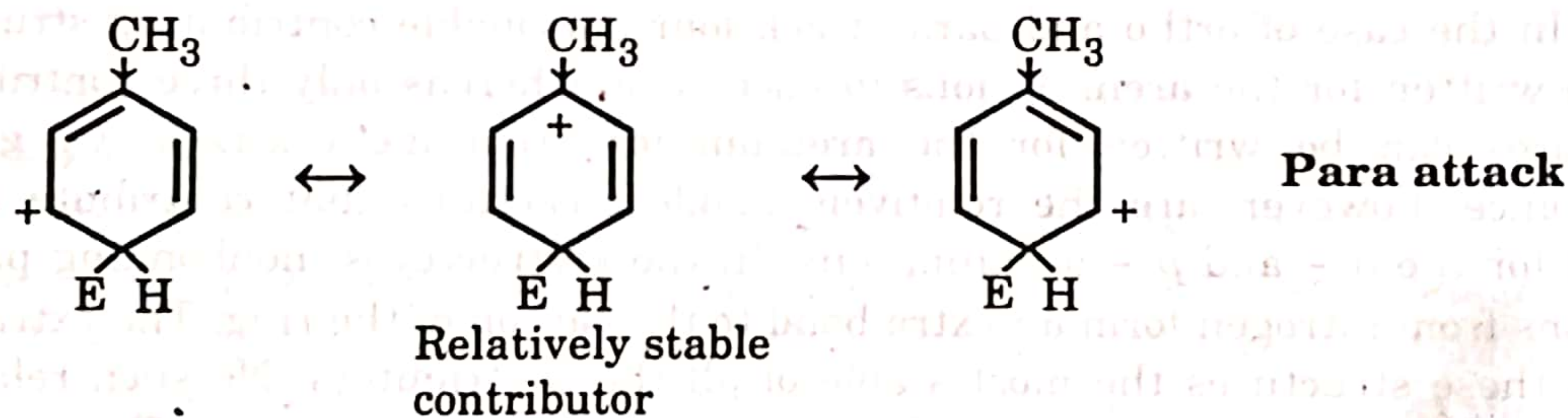
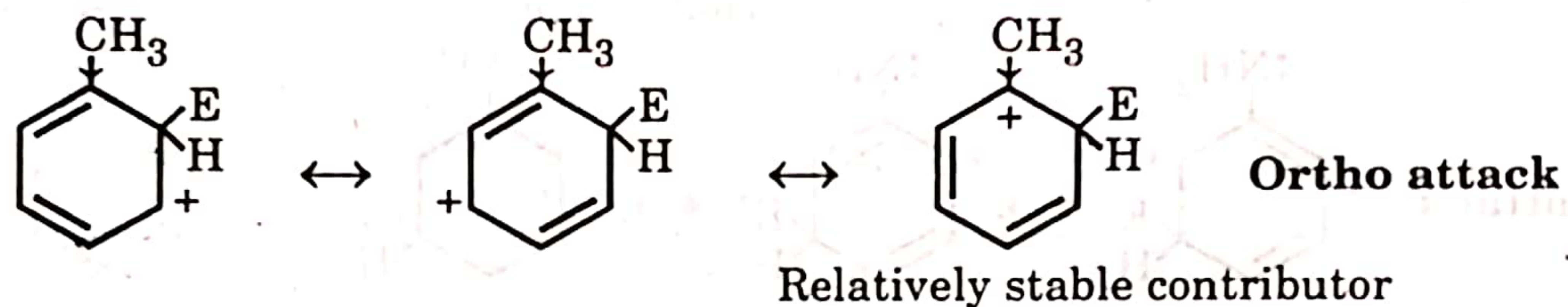
In the case of ortho and para attack four reasonable contributing structures can be written for the arenium ions in each case, whereas only three contributing structures can be written for the arenium ion from meta attack. Of greater importance, however, are the relatively stable structures that contribute to the hybrid for the *o*- and *p*-arenium ions. In these structures, nonbonding pairs of electrons from nitrogen form an extra bond to the carbon of the ring. The extra bond makes these structures the most stable of all the contributors. No such relatively structure is possible for the arenium ions for attack at *m*-position. This suggests that the ortho and para arenium ions themselves are more stable than the arenium ion that results from the meta attack. The transition states leading to the ortho and para arenium ions occur at the lower energies than the transition state leading to the meta arenium ion. The $-NH_2$ group in aniline donates electrons to the ring by resonance effect and stabilizes the incipient arenium ions in the transition states leading to *o*- and *p*-positions, thereby increasing the rate of reaction as compared to the rate of reaction of benzene. Thus all such ortho - para directing groups activate a ring toward electrophilic substitution.

2. Activating ortho and para directing groups (alkyl and aryl groups) that lack an unshared electron pair on the atom connected to the benzene ring. Methyl or alkyl group is electron - releasing by inductive effect. It therefore releases electrons to the benzene ring and thus increases its electron density. It also increases the electron density of the benzene ring through hyperconjugation. Methyl

or alkyl group is therefore an activating group and makes the benzene ring to react faster than benzene itself.

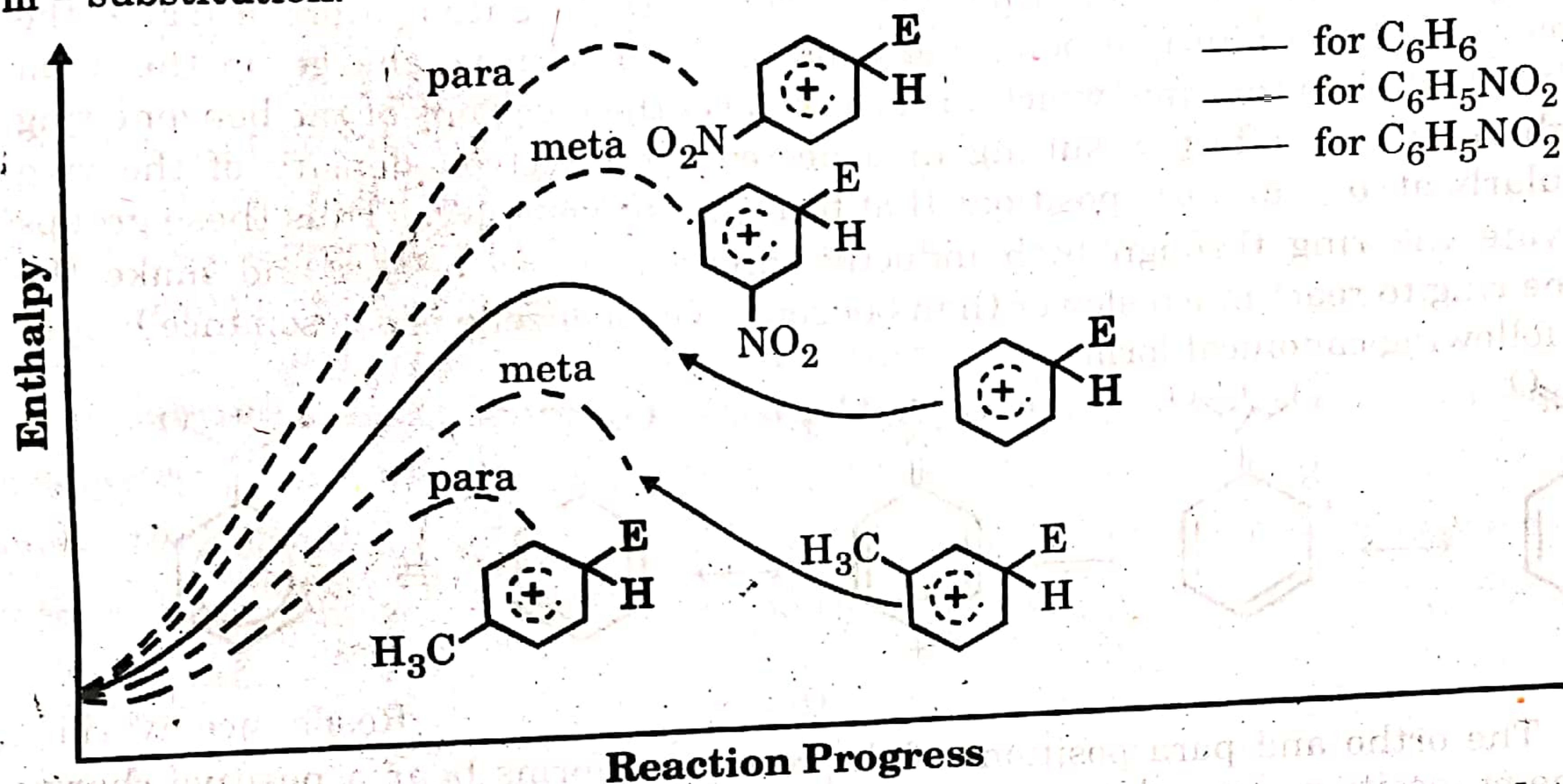


The ortho - para directive influence of methyl or alkyl group and aryl group can be explained on the basis of resonance structures for the arenium ions formed when toluene or arylbenzene undergo electrophilic substitution. We get the following results.

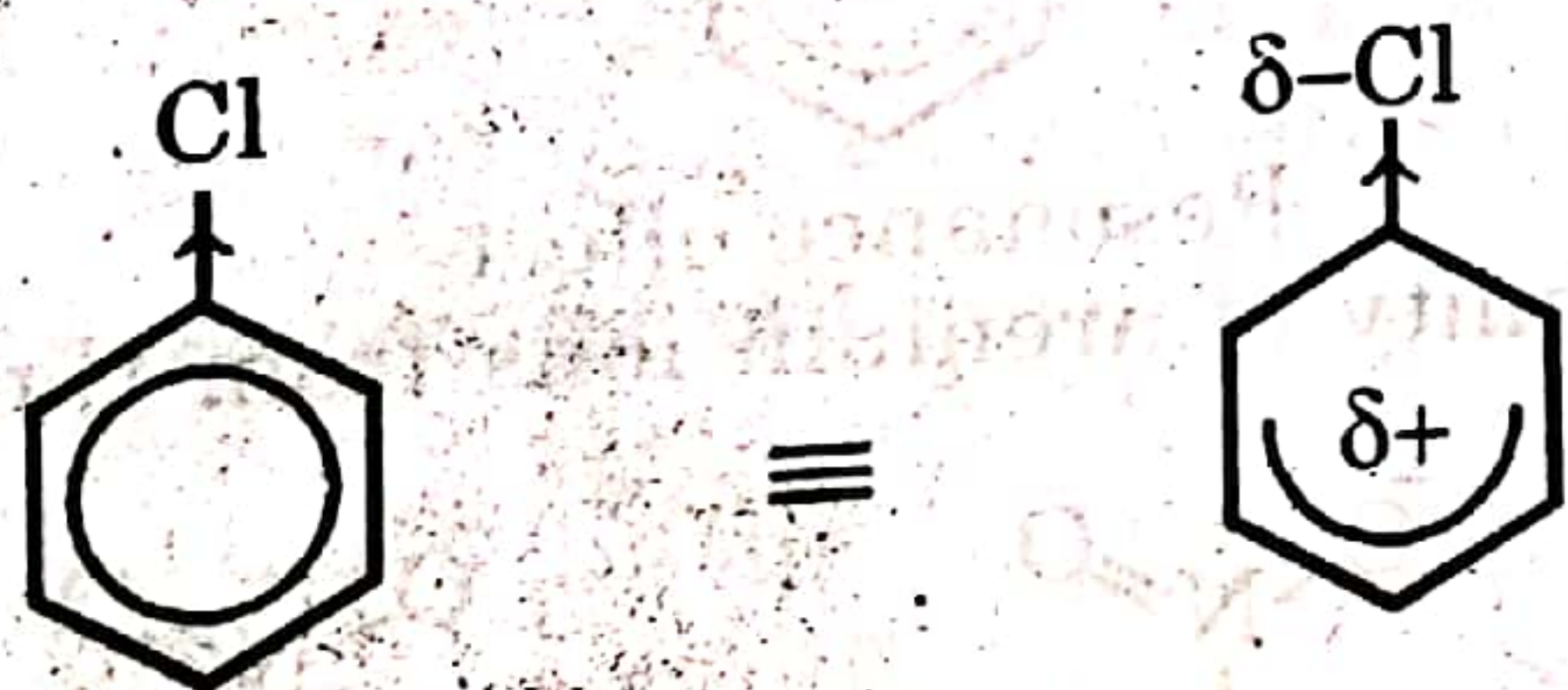


In ortho and para attack there is one contributing structure in each case in which the methyl or aryl group is directly attached to a positively charged carbon of the ring, whereas no such structure can be written when the electrophile attacks the

meta position. These structures are more stable relative to any of the others and therefore, make a large contribution to the resonance hybrid for *o*- and *p*-substituted arenium ions. Thus the *o*- and *p*-substituted arenium ions are more stable, the transition state leading to the arenium ions occurs at lower energy and therefore substitution at ortho and para takes place more rapidly and is preferred to *m*-substitution.

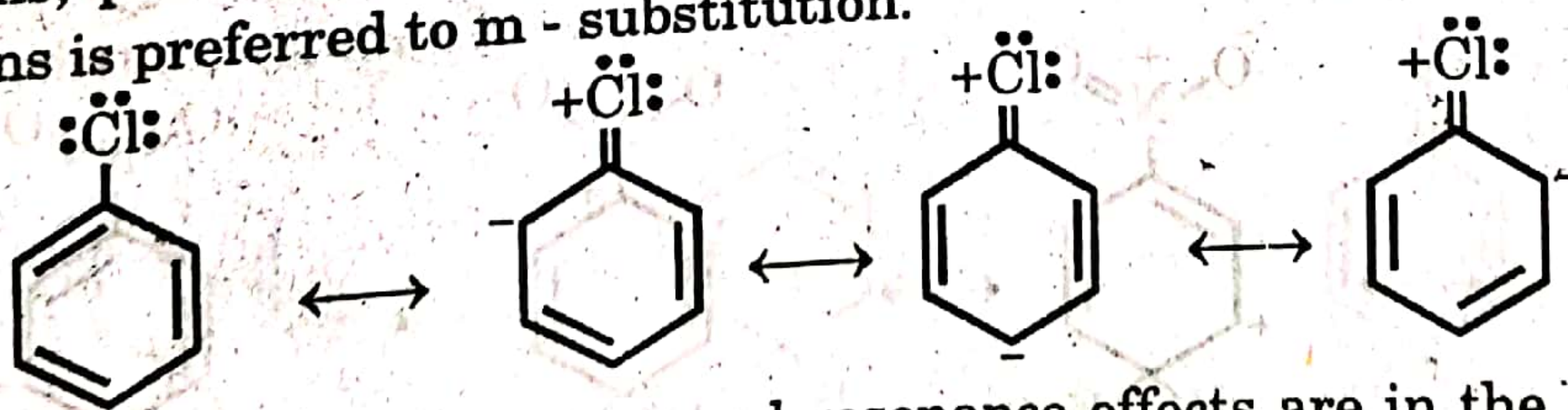


3. Deactivating ortho and para directing halo substituents bonded to the ring. The halo groups are highly electronegative and therefore exert an electron-withdrawing effect on the benzene ring. This would result in reducing the overall electron availability on the ring and thereby deactivate it towards electrophilic attack.



Inductive effect of chloro group deactivates ring

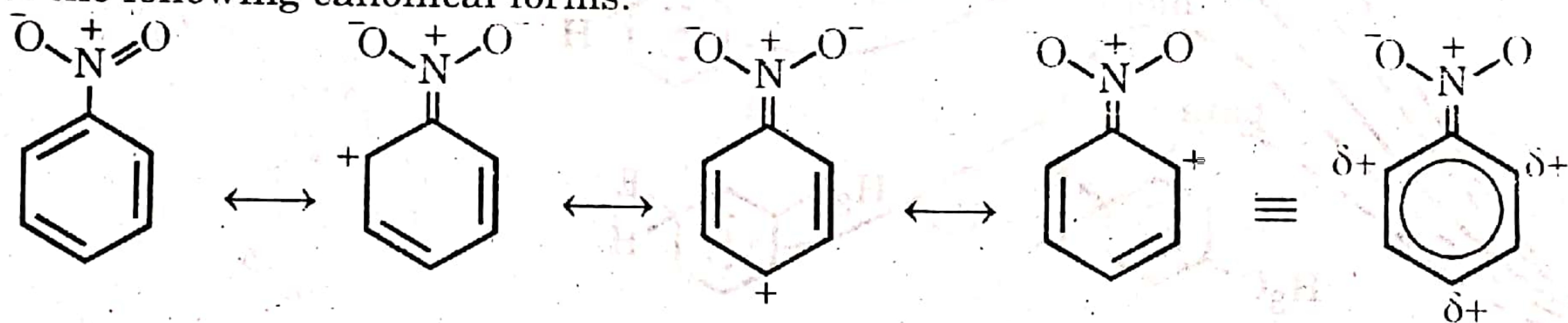
On the other hand, the unshared electron pair on the halogen atom may be donated to the ring through its resonance effect and thereby making it richer in electrons, particularly at *o*- and *p*-positions. Thus substitution at *o*- and *p*-positions is preferred to *m*-substitution.



Although, the inductive and resonance effects are in the opposite directions, but the inductive effect causes a deactivation of the ring, whereas the resonance

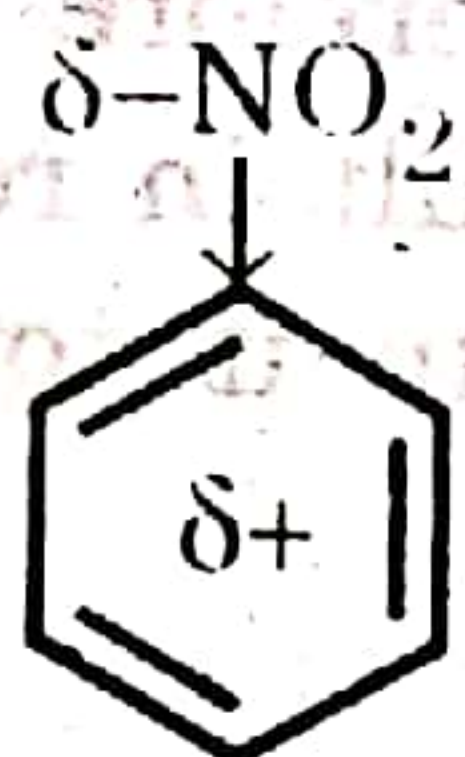
effect, determines the position of the attack, with the result that substitution occurs at ortho and para positions with deactivation.

4. Deactivating meta directing groups that lack an unshared electron pair on the atom connected to the ring, e.g., $-\text{NO}_2$, $\text{C}\equiv\text{N}$, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{CHO}$, and $-\text{COR}$. These groups are electron-withdrawing. In these substituents the atom directly attached to the ring is also bonded to another highly electronegative atom by a multiple bond. The electronegative atom attracts the electron pair of the multiple bond and thus places a positive charge on the atom directly attached to the ring, which in turn attracts the electrons of the benzene ring through resonance effect, resulting in a decrease of electron density of the ring particularly at *o*- and *p*-positions that bear a positive charge. Thus these groups deactivate the ring through both inductive and resonance effects and make the benzene ring to react much slower than benzene. Nitrobenzene is a resonance hybrid of the following canonical forms.

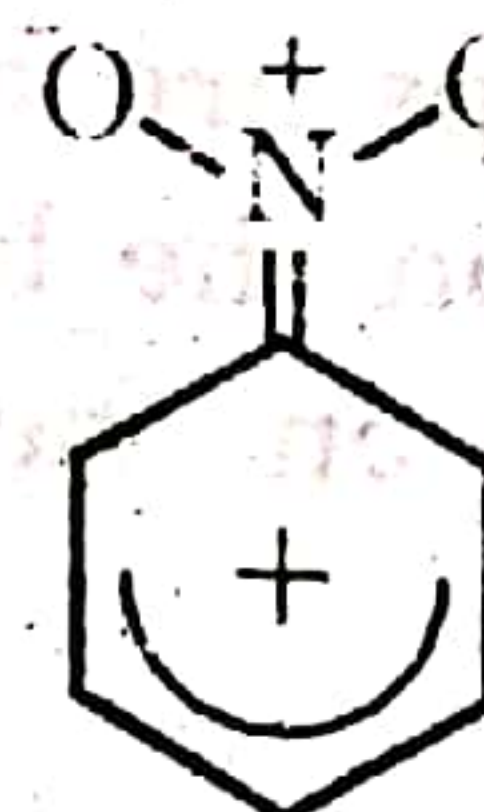


Resonance hybrid

The ortho and para positions of the resonance forms bear a positive charge and the *m*-positions are relatively unaffected, therefore, substitution occurs at meta positions under drastic conditions with deactivation.

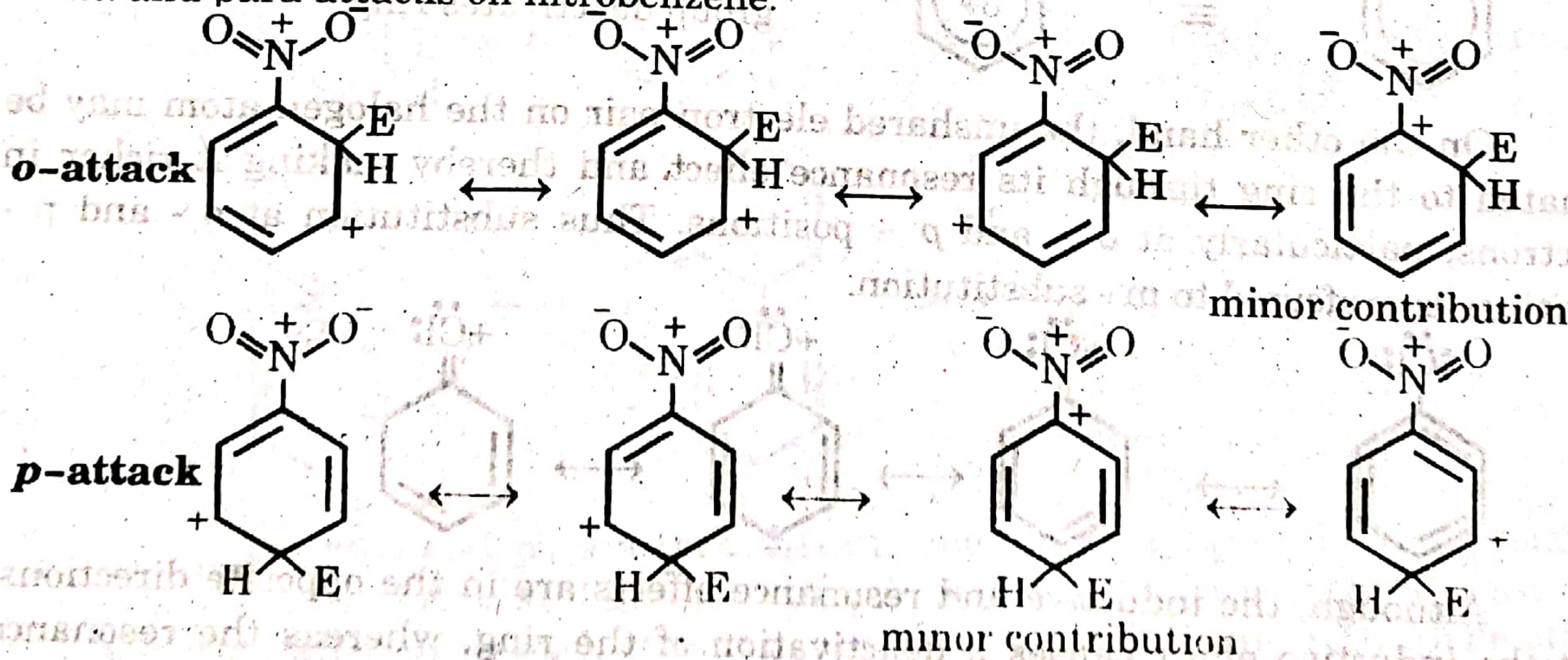


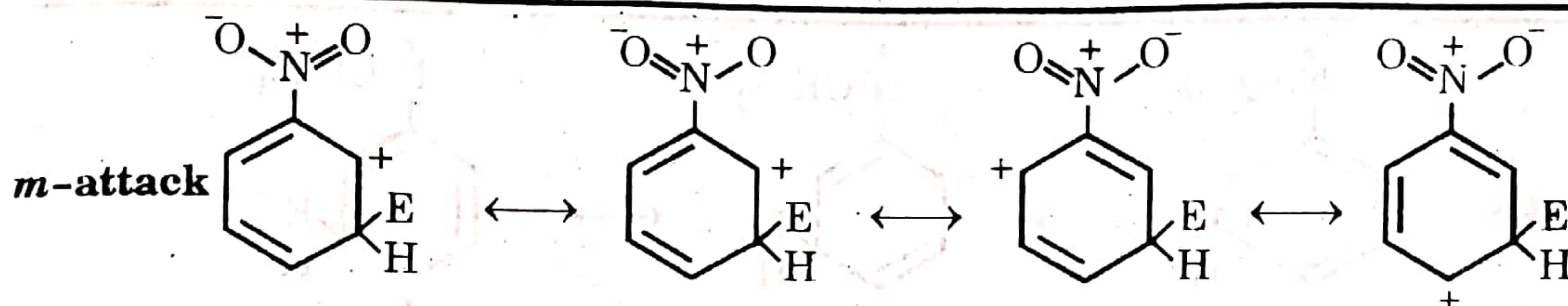
Inductive effect



Resonance effect

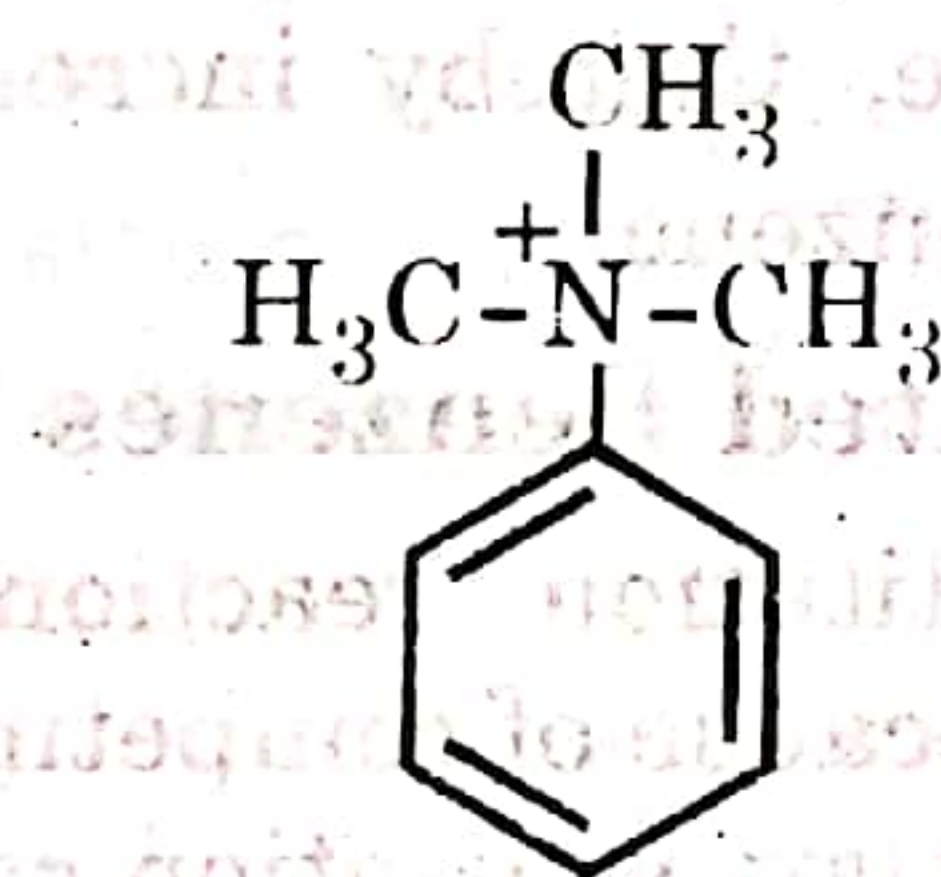
Let us now consider the resonance stability of arenium ions from the ortho, meta and para attacks on nitrobenzene.



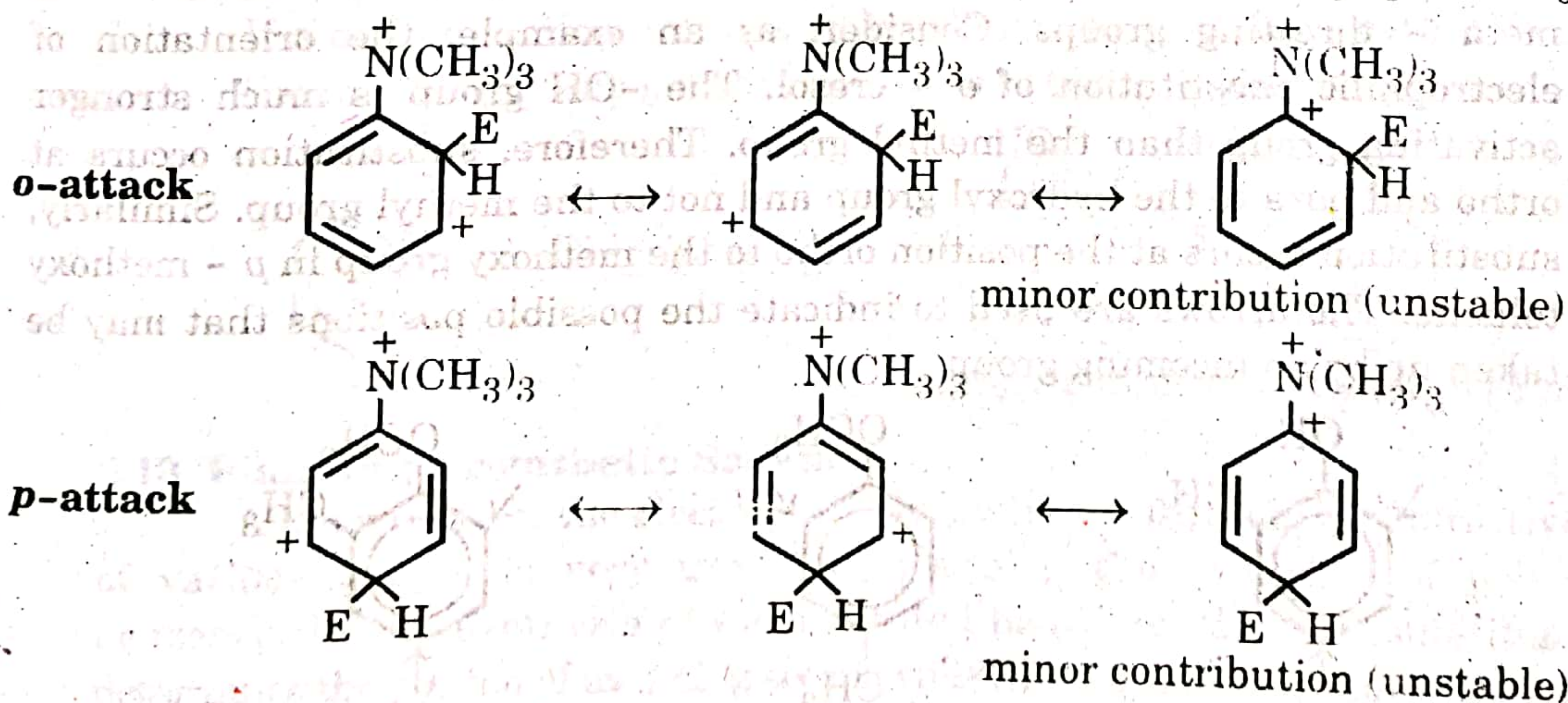


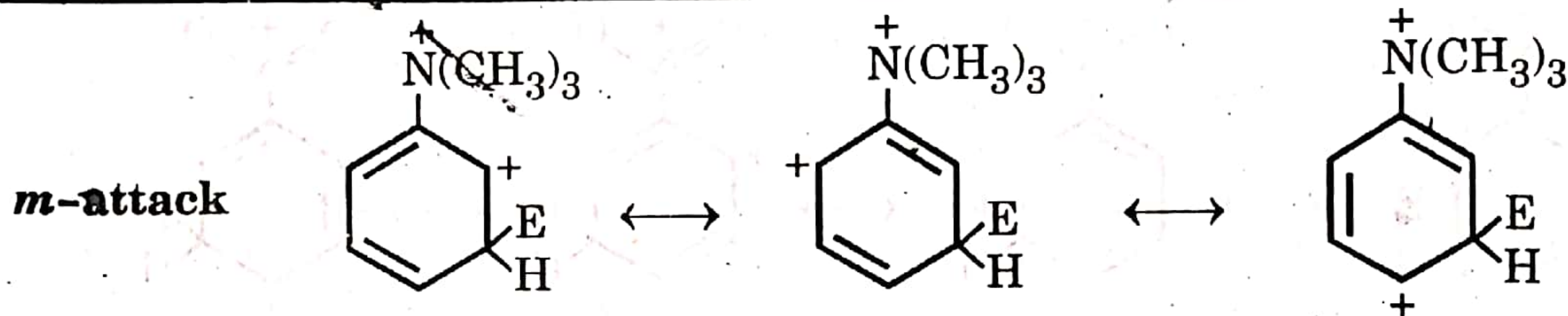
Each arenium ion has four resonance contributing structures but the arenium ions resulting from the ortho and para attacks have one resonance structure each, which is highly unstable because the two positive charges are located on two adjacent atoms. Therefore, the arenium ion resulting from the meta attack is relatively more stable than the each hybrid resulting from ortho and para attacks. Hence the transition state resulting from ortho or para attacks has higher energy than the transition state arising from meta attack. The nitro group (or other group of this category) is therefore not only deactivating but also meta directing.

5. **Deactivating meta groups with a positive charge on the atom directly connected to the ring**, e.g., $^+\text{N}(\text{CH}_3)_3$, $^+\text{NR}_3$, $^+\text{PR}_3$, etc. These groups are also electron - withdrawing and exert an inductive effect away from the benzene ring and thus lower the electron density on the ring. For example, $^+\text{N}(\text{CH}_3)_3$ (trimethyl ammonium ion):



The electron - withdrawing inductive effect of such groups deactivates the ring towards electrophilic attack because they tend to decrease the electron density on the ring. Such groups are also meta directive. This can be seen by considering the arenium ions resulting from the ortho, meta and para attacks on $\text{C}_6\text{H}_5-\text{N}^+(\text{CH}_3)_3$.





Each arenium ion has three contributing structures but the arenium ions resulting from the *o* - and *p* - attacks has one structures each, which is highly unstable because they have positive charges located on adjacent atoms. whereas the arenium ion resulting from meta attack has no such structure. Thus, the arenium ion resulting from the meta attack on $C_6H_5N(CH_3)_3$ is relatively more stable than the arenium ions of the *o* - and *p* - attacks because of the destabilization of the later.

The $-N(CH_3)_3$ group is therefore meta directing.

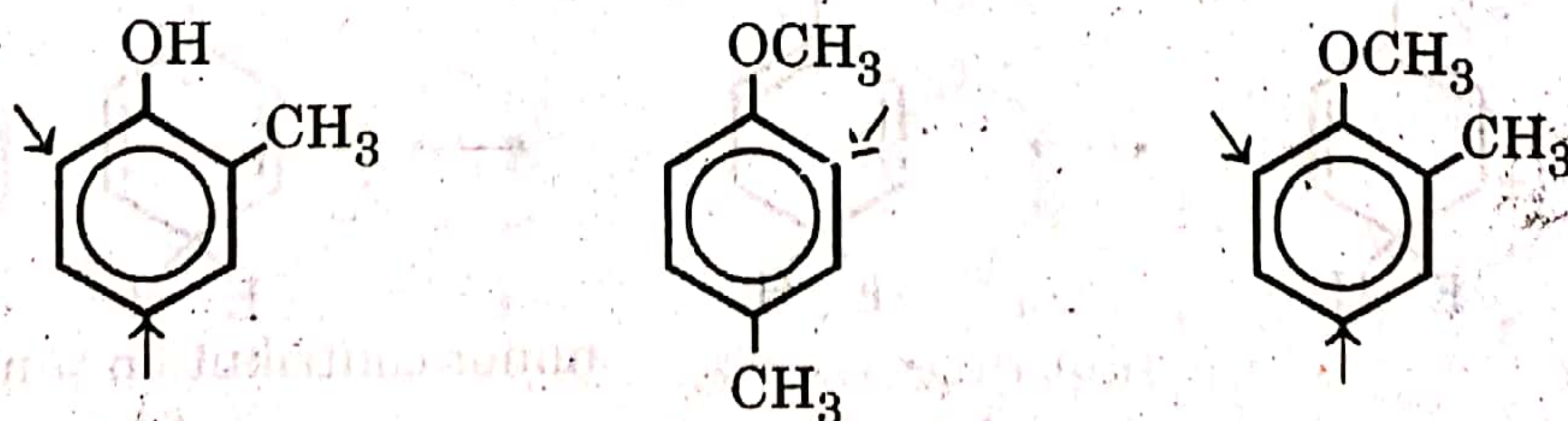
Note: (i) All *m* - directors are electron - withdrawing and destabilize the incipient arenium ion in the transition state. They therefore diminish the rate of reaction as compared to the rate of reaction of benzene.

(ii) Most ortho para directors are electron - donating. They stabilize the incipient arenium ion in the transition state, thereby increasing the rate of reaction as compared to the rate of reaction of benzene.

6.12 Orientation in Disubstituted Benzenes

Electrophilic aromatic substitution reactions of disubstituted benzenes usually give a mixture of products because of competing orientation influence of both substituents. However the following generalization can be made:

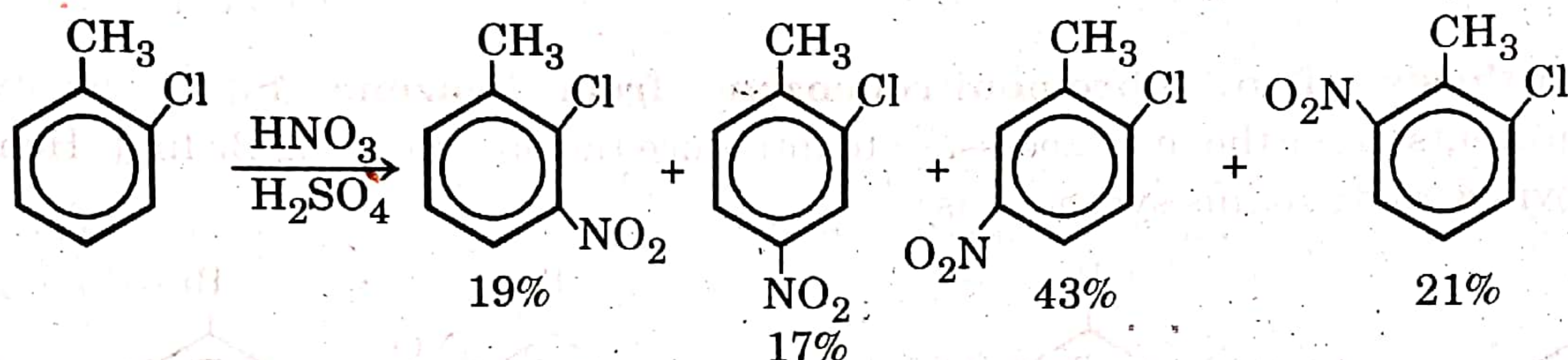
1. When the directive influence of two substituents oppose each other, the more powerful activating group generally controls the orientation. The various groups can be arranged in the order of decreasing activation of the ring are as follows: $-OH > -NR_2 > NH_2 > -OR > -COOR > -NHCOCH_3 > -C_6H_5 > -CH_3$ meta - directing groups. Consider, as an example, the orientation of electrophilic substitution of *o* - cresol. The $-OH$ group is much stronger activating group than the methyl group. Therefore, substitution occurs at ortho and para to the hydroxyl group and not to the methyl group. Similarly, substitution occurs at the position ortho to the methoxy group in *p* - methoxy toluene. The arrows are used to indicate the possible positions that may be taken up by an incoming group:



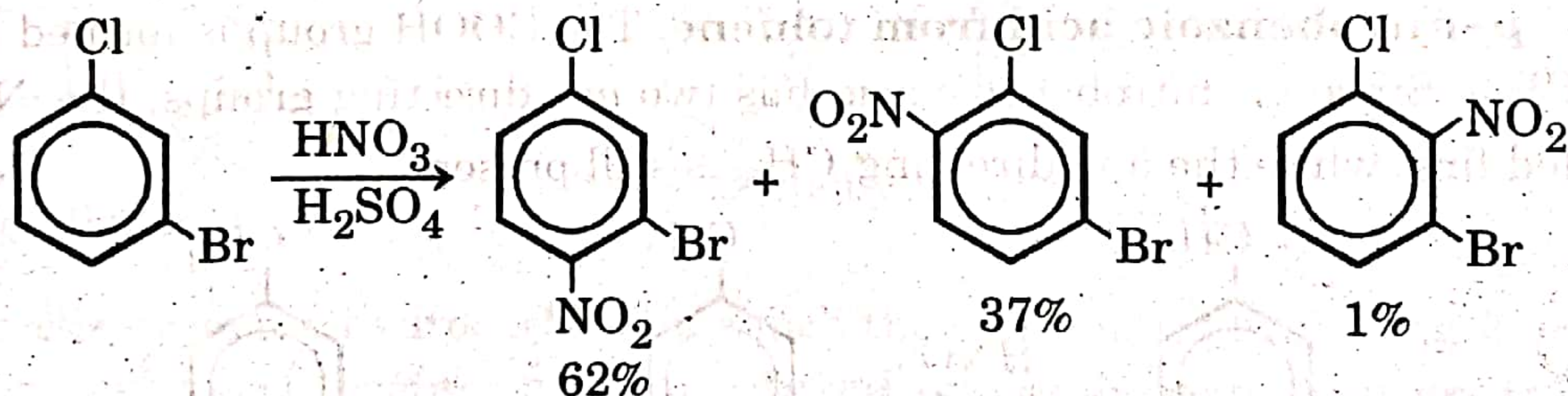
2. If there is competition between an ortho - para group and meta directing group, the *op*-director determines the orientation of the incoming group. For example:



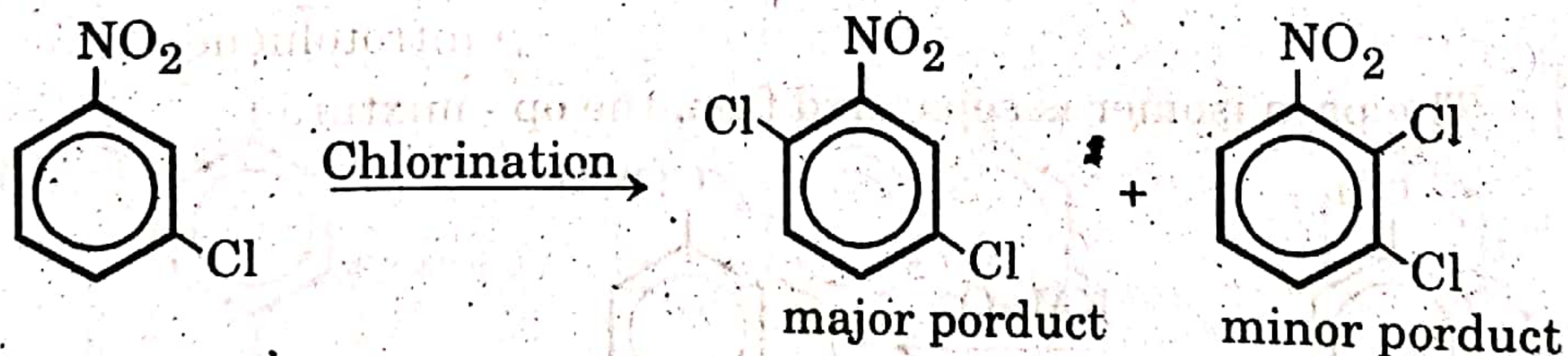
3. When two groups having about the same directing ability are in competition with each other, the attacking electrophile may enter each of the available positions giving all the four isomers in reasonable proportions, e.g.,



4. When two groups having about the same ability are present meta to each other, substitution does not occur to an appreciable extent between these groups if another position is open. This is because of greater steric hindrance at this position due to the bulk of the substituents and the electrophile.



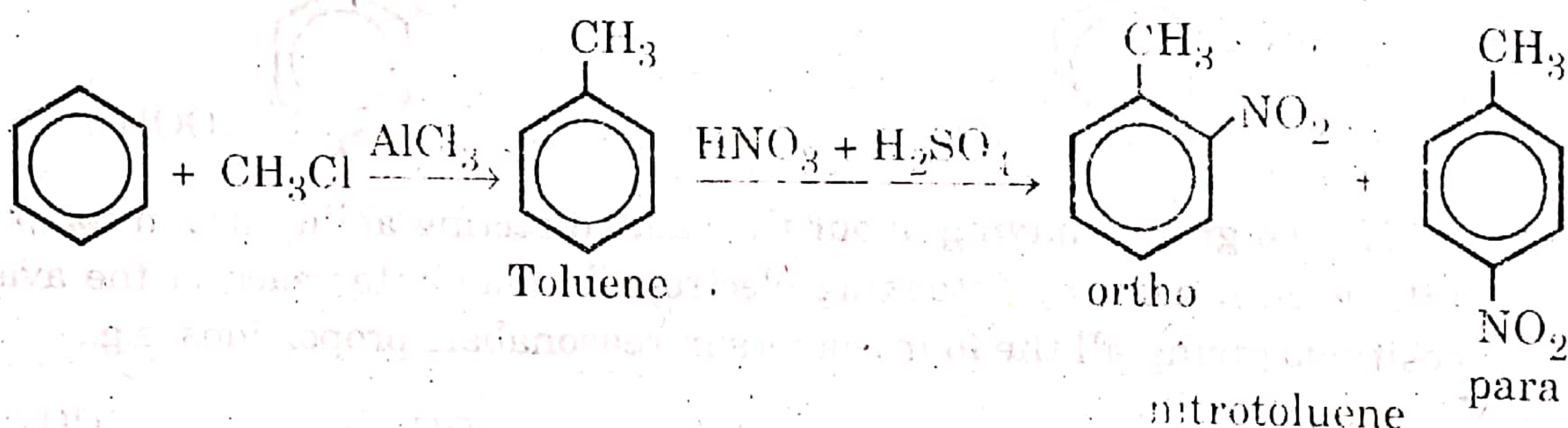
5. If a meta directing group is situated meta to an ortho - para directing group, the incoming group goes mainly ortho to the *m* - director.



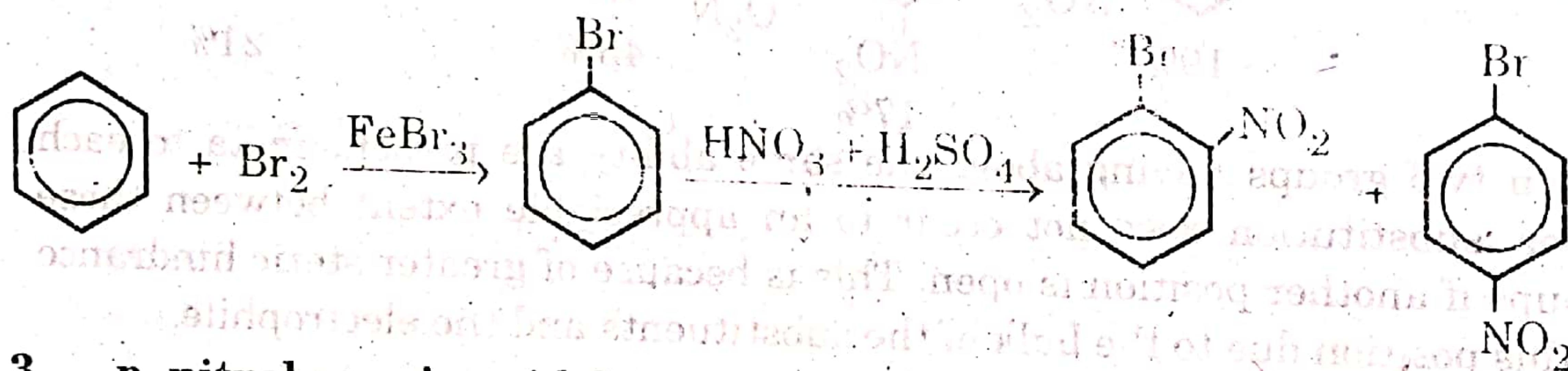
6.13 Planning a Synthetic Scheme

A knowledge of the electrophilic aromatic substitution and directive influence of various groups is very useful in planning the synthesis of polysubstituted benzenes. In the synthesis of disubstituted benzenes, the first substituent present determines the position of incoming second substituent. A few examples are given below:

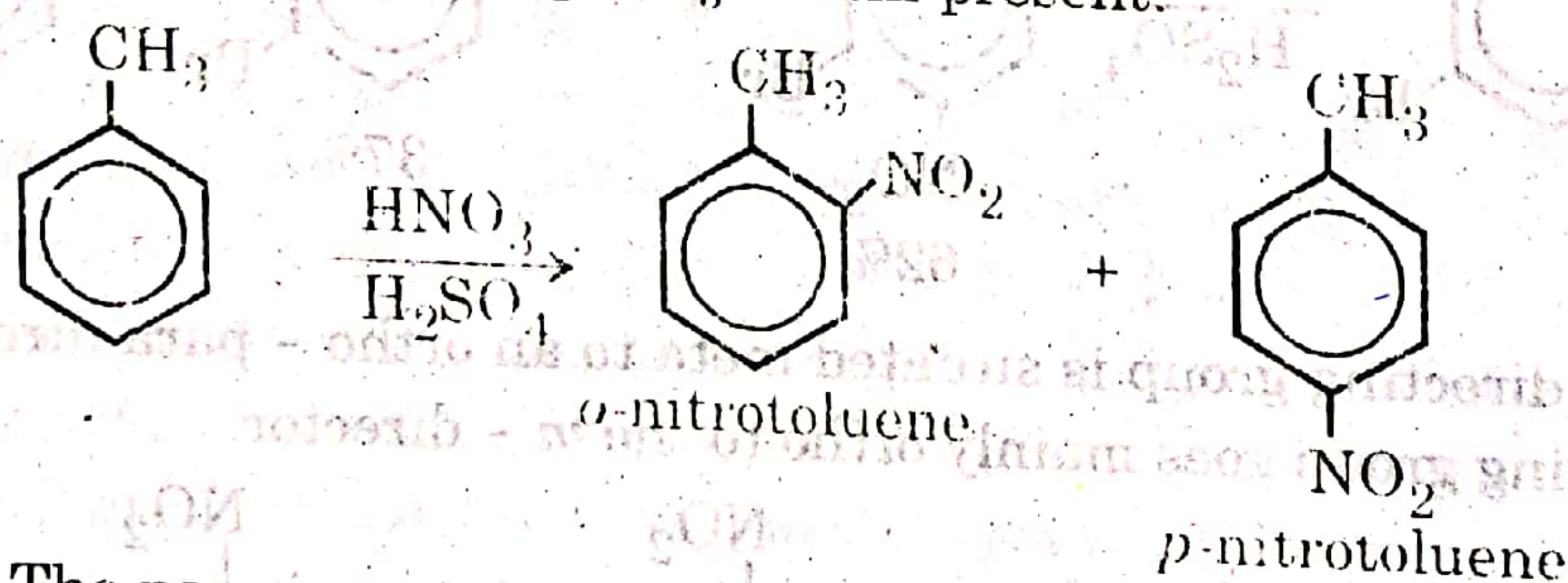
1. **Synthesis of *p*-nitrotoluene from benzene.** Since the two substituents are para, it is necessary to introduce the *o*p - directing methyl group first, because the nitro group is meta directing. The *p*-nitrotoluene is separated from the *o*p - mixture by fractional distillation.



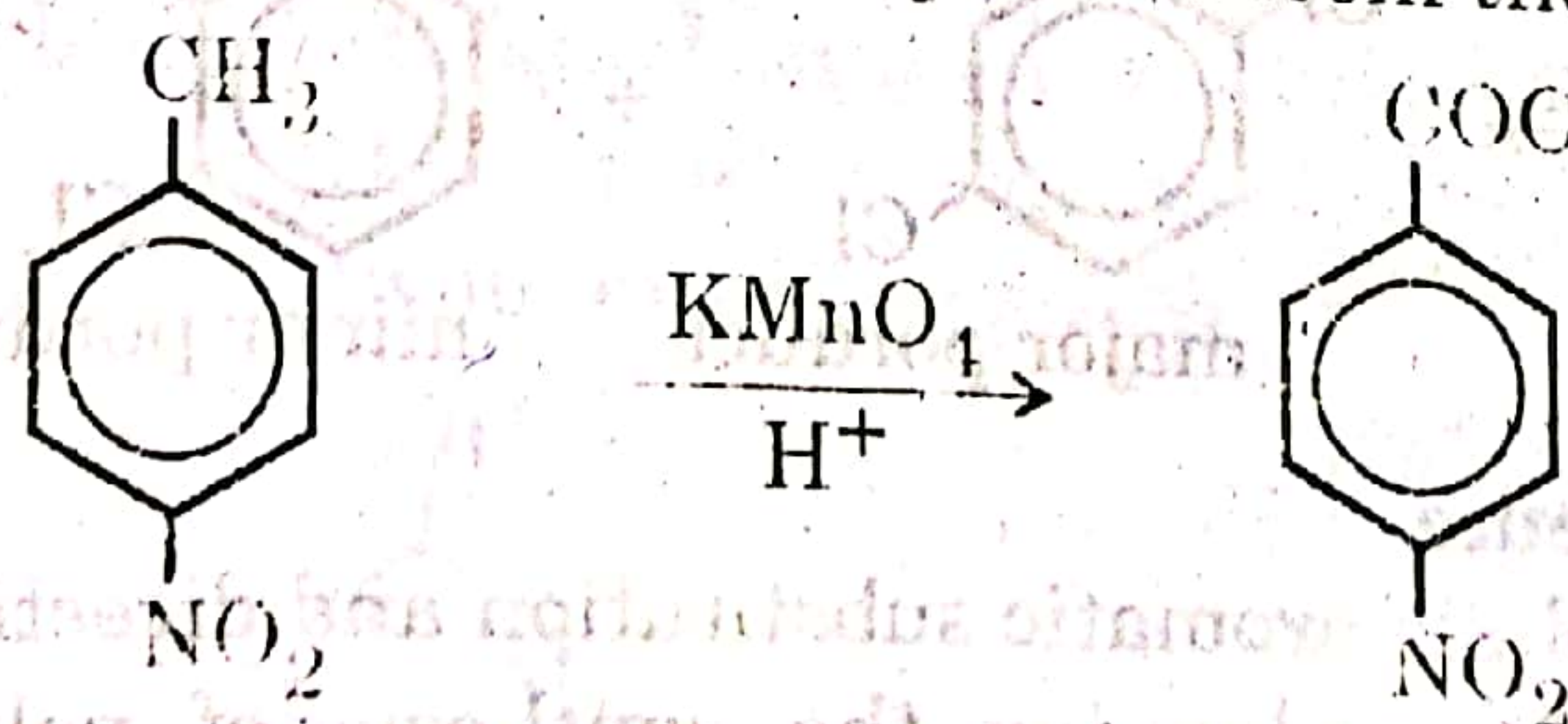
2. **Synthesis of *o*-bromonitrobenzene from benzene.** Since the two substituents are ortho, it is necessary to introduce the *o*p - directing Br first. Hence the obvious route to this synthesis is:



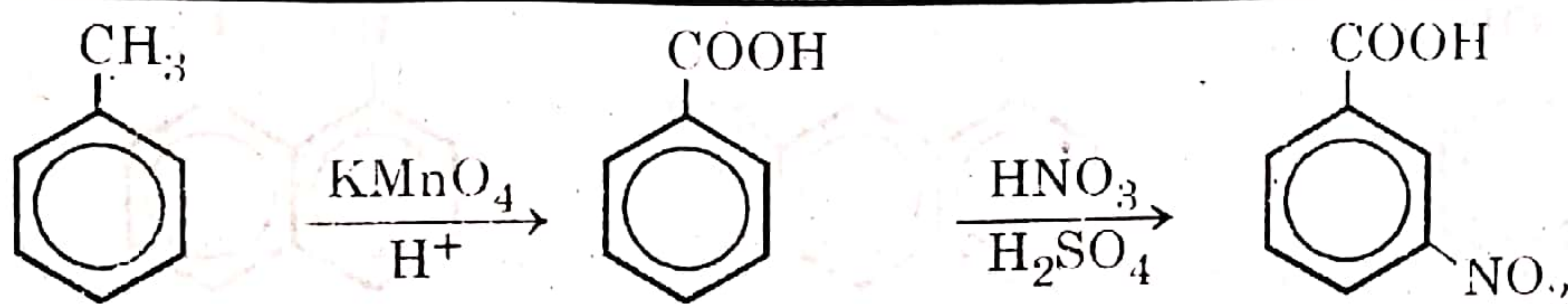
3. ***p*-nitrobenzoic acid from toluene.** The COOH group is formed by oxidation of CH₃. Since *p*-nitrobenzoic acid has two *m*-directing groups, the NO₂ must be added first while the *o*p - directing CH₃ is still present.



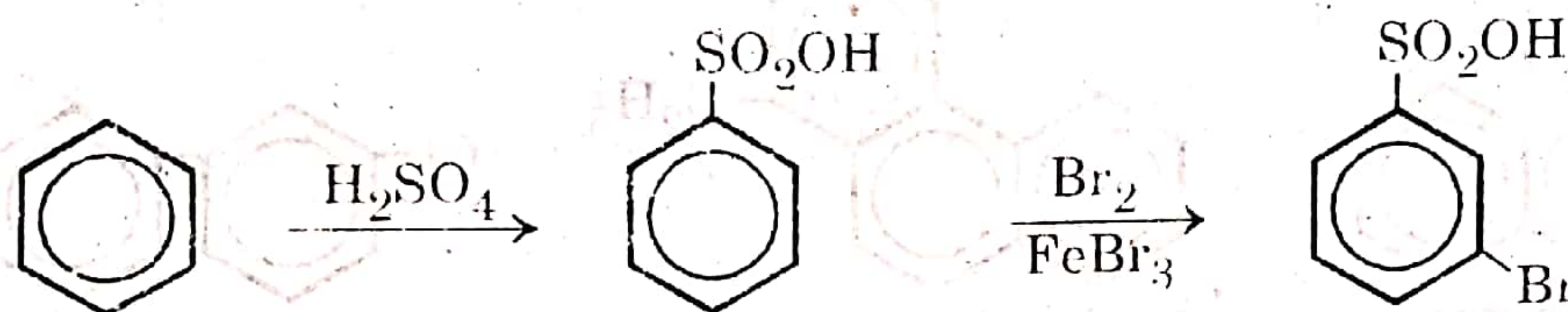
The para isomer is separated from the *o*p - mixture.



4. ***m*-nitrobenzoic acid from toluene.** Since the substituents are meta, and NO₂ is introduced when the *m*-directing COOH is present.



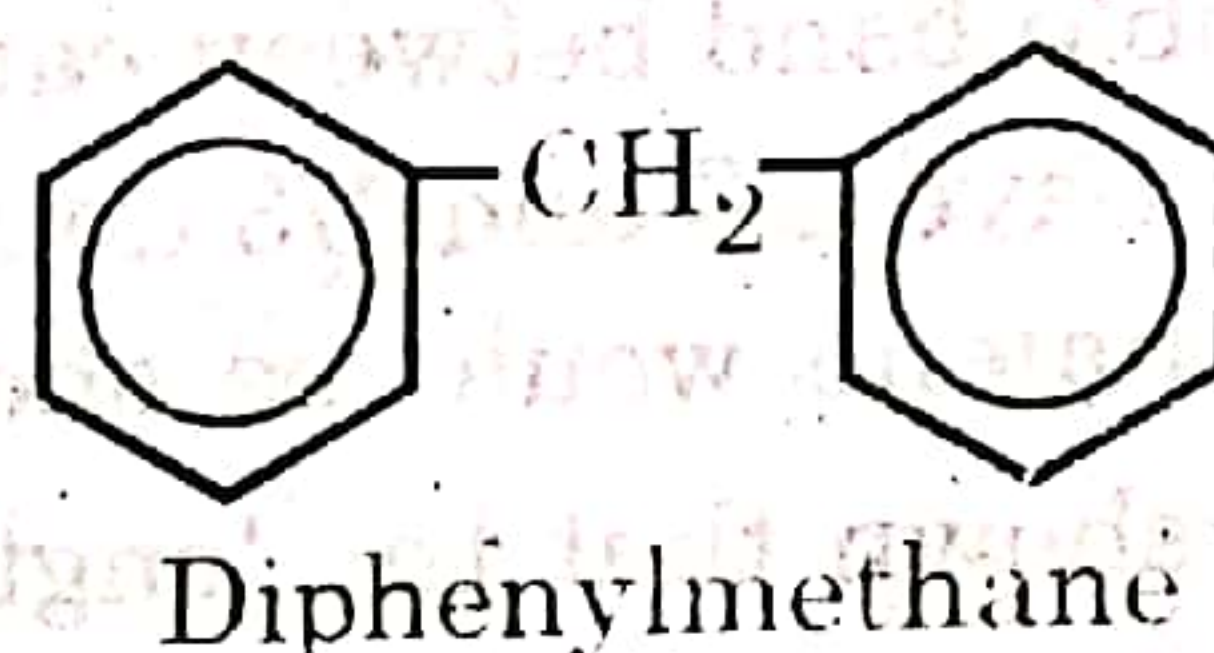
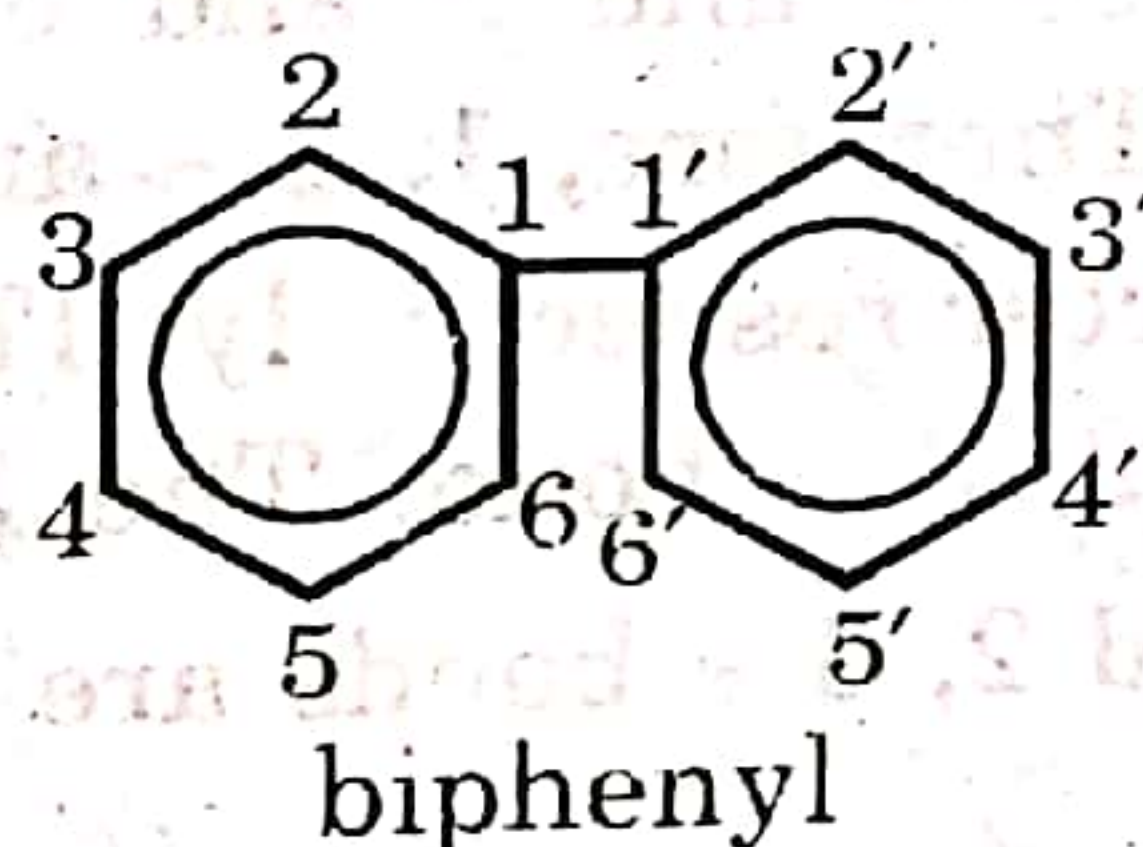
5. **Meta-bromobenzene Sulphonic acid from benzene.** Since the substituents are meta, the *m* - SO₃H is introduced first, because SO₃H is a *m* - director.



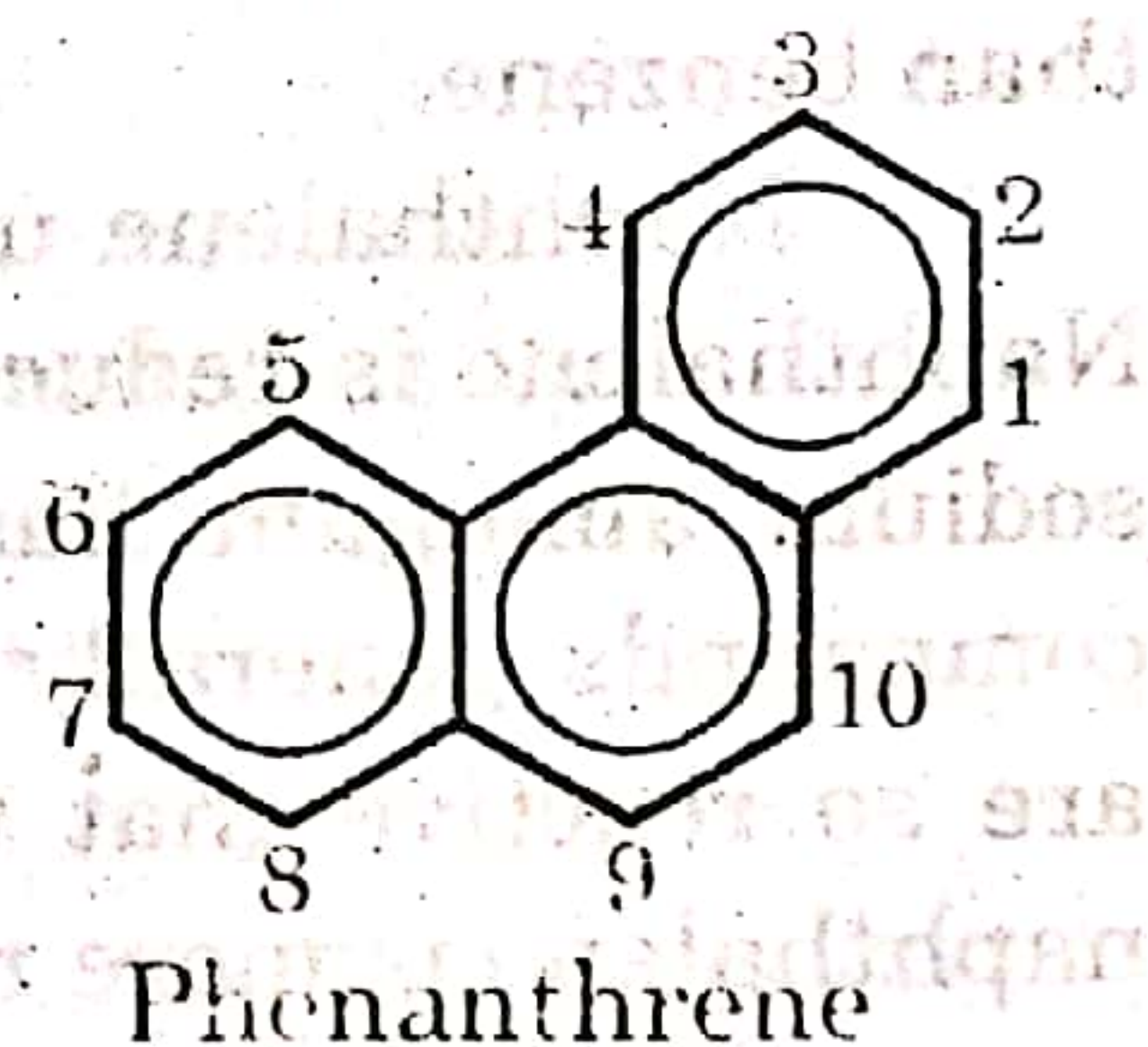
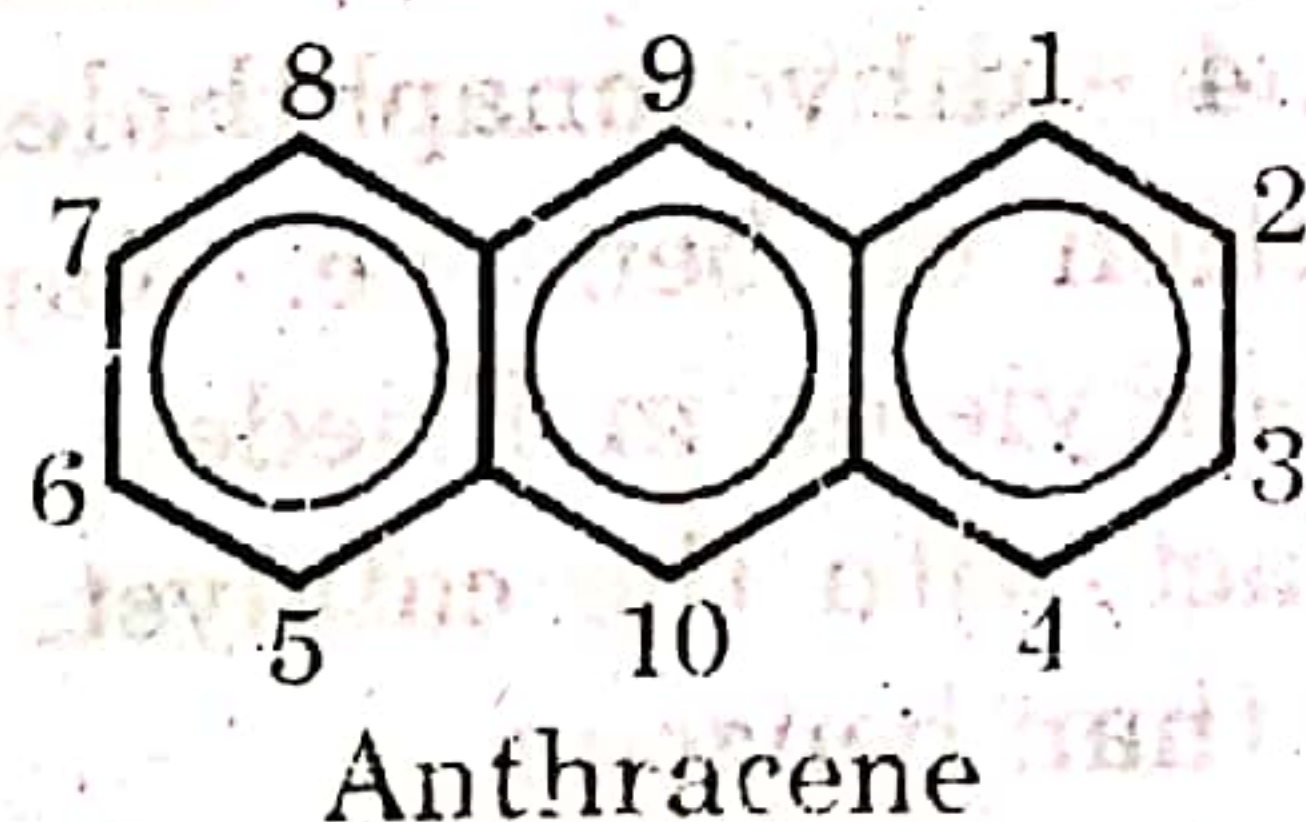
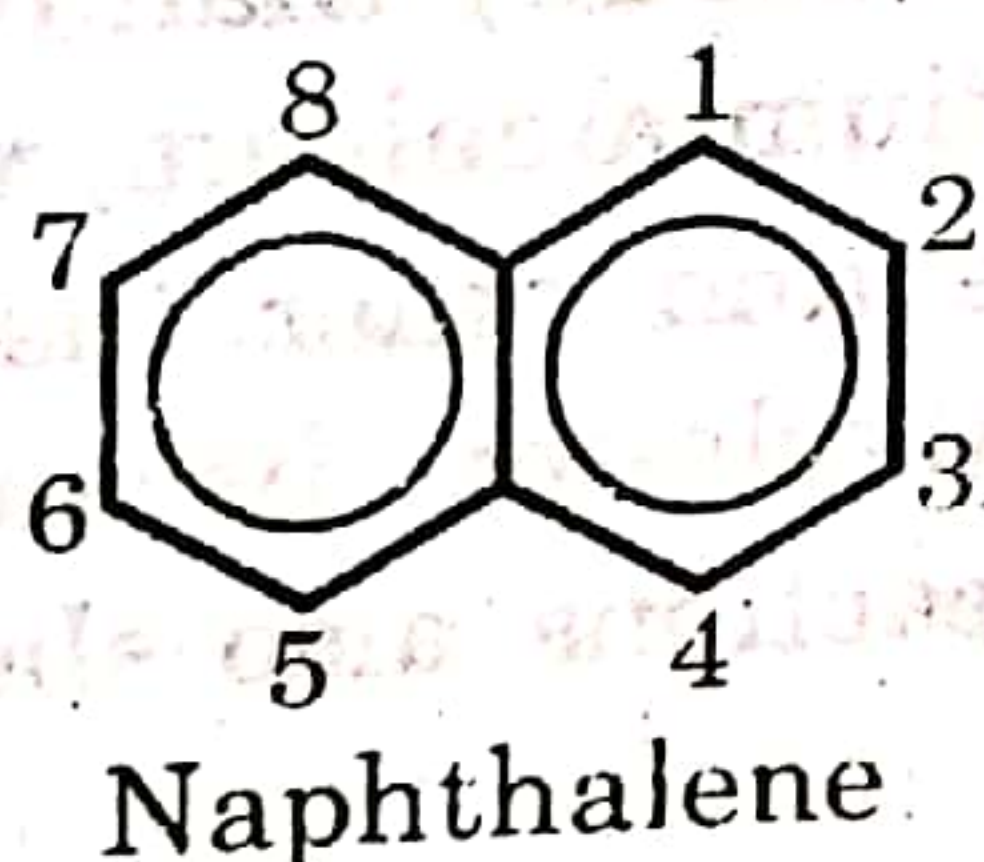
6.14 Polycyclic Aromatic Hydrocarbons

Aromatic hydrocarbons containing more than one benzene ring in their molecules are called polycyclic aromatic hydrocarbons. They may be divided into two main classes:

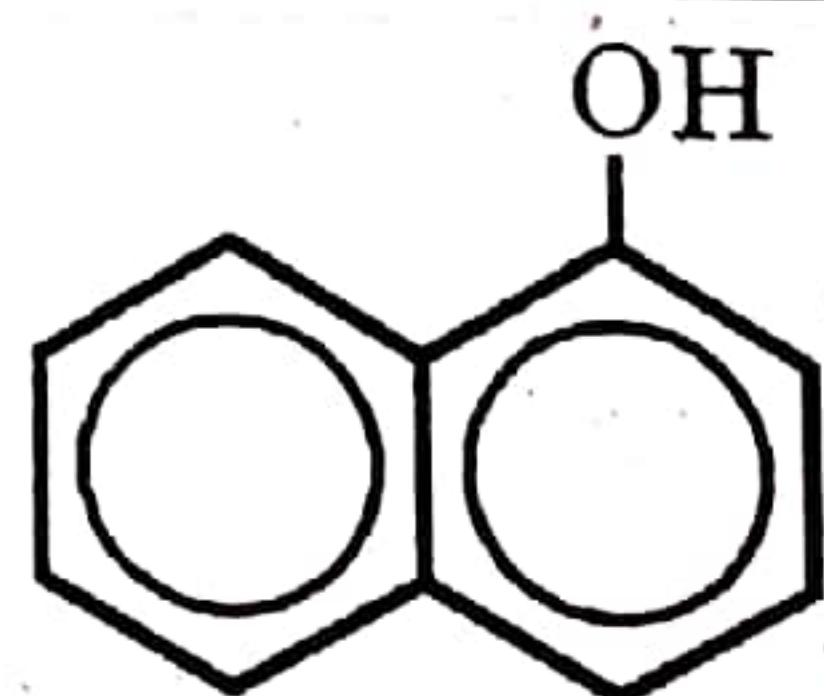
- (i) Polycyclic aromatic hydrocarbons which have **isolated** rings, e.g., biphenyl, diphenylmethane. These are considered as phenyl-substituted benzenes and methane and are treated like other substituted benzenes and methanes.



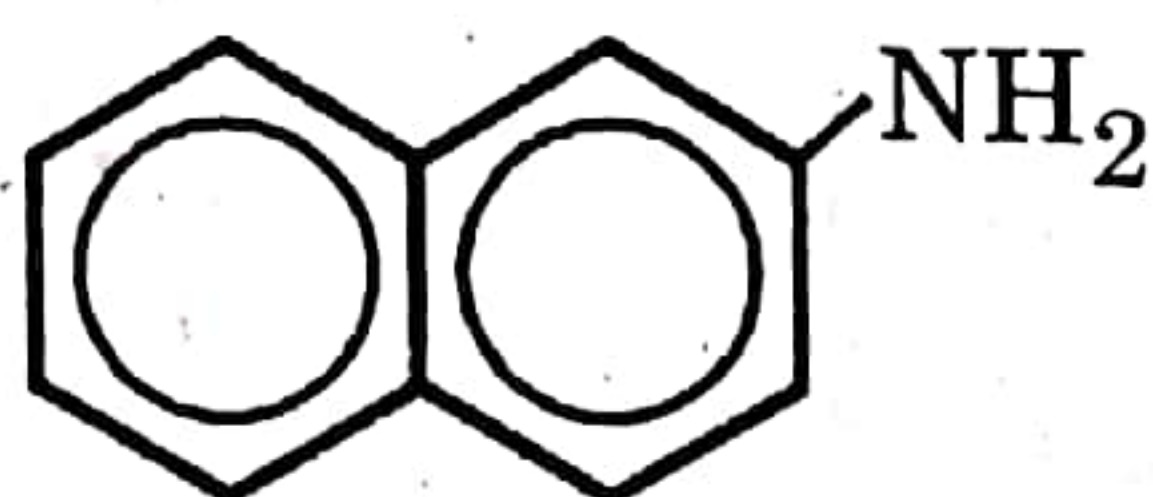
- (ii) Polycyclic aromatic hydrocarbons in which the benzene rings sharing 2 ortho carbons are fused together are called **fused or condensed ring aromatic hydrocarbons**, e.g., naphthalene, anthracene and phenanthrene.



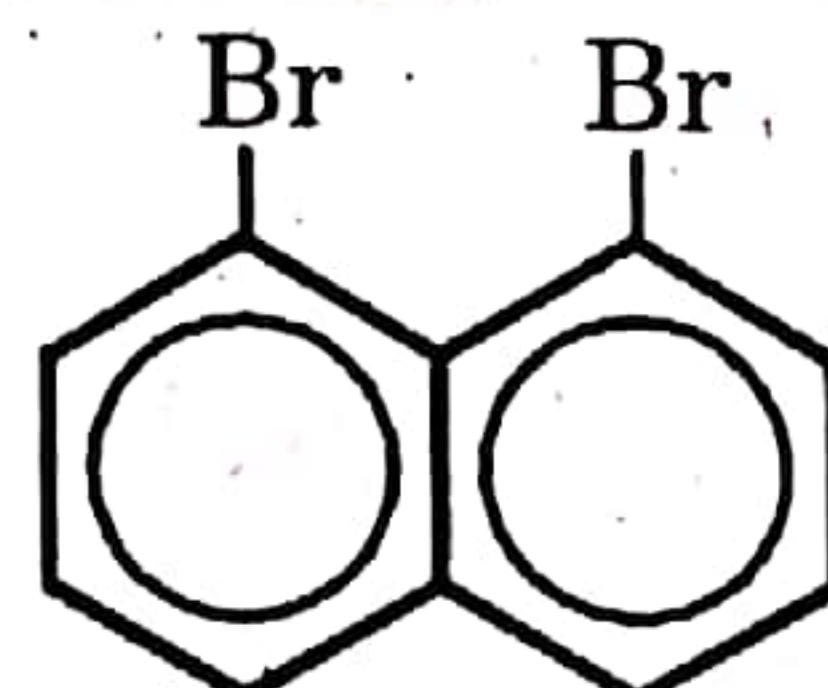
Nomenclature. In the IUPAC system of nomenclature, numbers are assigned only to those positions of the fused ring aromatic hydrocarbons at which substitution can occur, as shown in the above structures. Positions 1 and 2 of the naphthalene ring system are usually designated as α and β , respectively



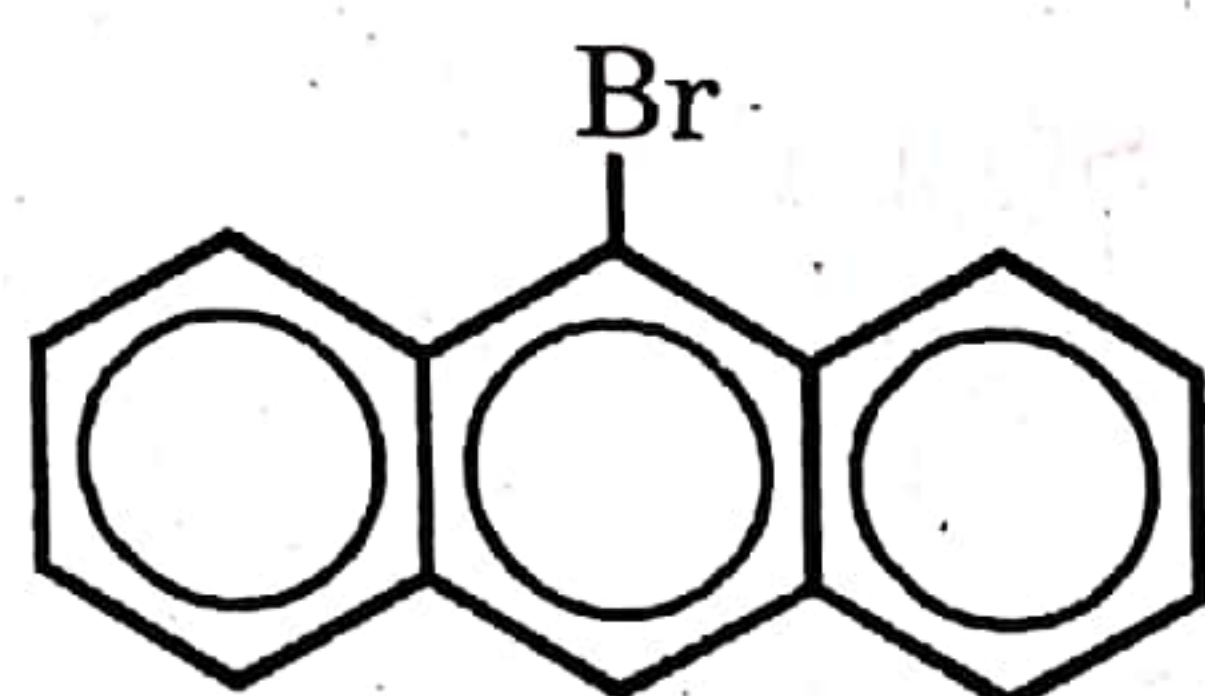
α -naphthol
1-naphthol



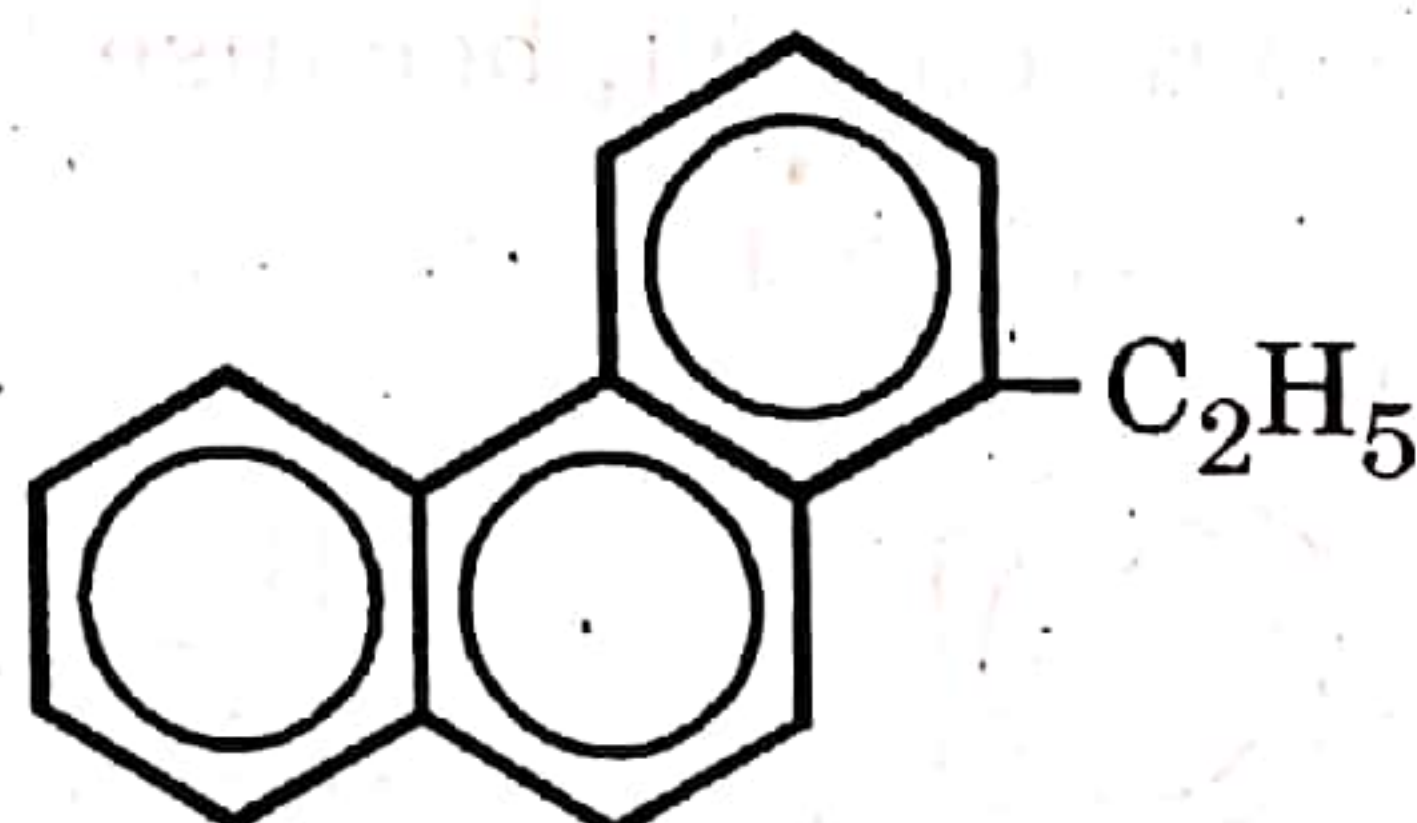
β -naphthylamine
2-aminonaphthalene



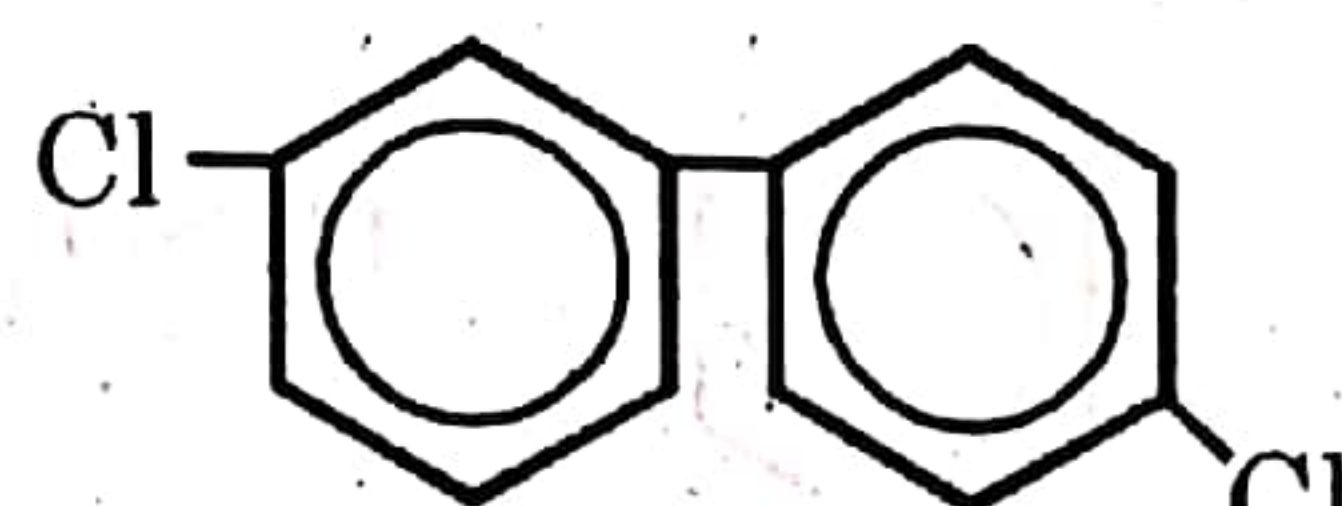
1,8-dibromonaphthalene



9-bromoanthracene



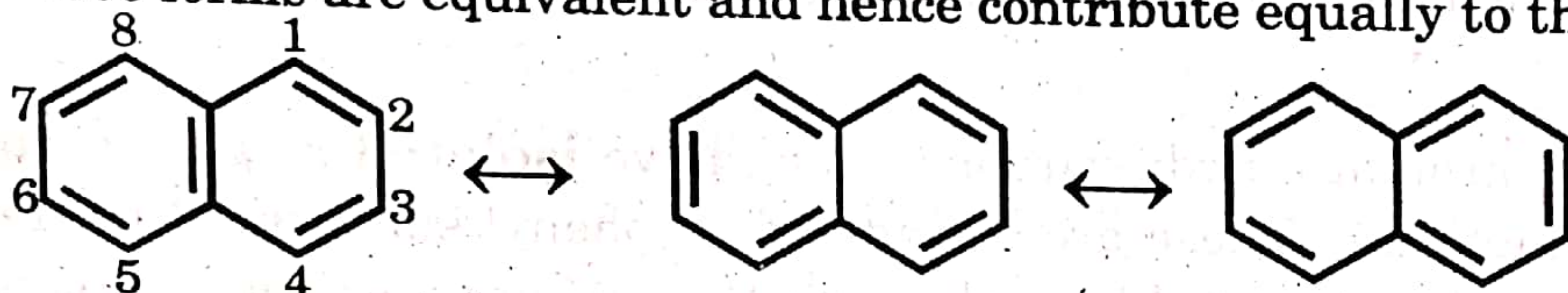
1-ethylphenanthrene



3,4'-dichlorobiphenyl

Reactivity and Orientation in polycyclic hydrocarbons

Naphthalene is a resonance hybrid of the following three canonical forms. All the three forms are equivalent and hence contribute equally to the hybrid.



Two structures have double bond between carbons 1 and 2 and only one structure has the double bond between carbons 2 and 3. Therefore, 1, 2 - and 2, 3 - bonds in naphthalene have $2/3$ and $1/3$ double bond character respectively. Thus, the 1, 2 - bond of naphthalene would be shorter than the 2, 3 - bond. The X - ray diffraction study has shown that the lengths of 1, 2 - and 2, 3 - bonds are 1.36 \AA (0.136 nm) and 1.42 \AA (0.142 nm) respectively.

The resonance energies of benzene and naphthalene are 150.5 kJ/mol and 255 kJ/mol . When the aromatic character of one ring of naphthalene is destroyed, only 105 kJ of resonance energy is sacrificed, which is much less than the 150.5 kJ/mol that would be sacrificed for benzene. This shows that naphthalene is more reactive than benzene.

Naphthalene undergoes oxidation and reduction more readily than benzene. Naphthalene is reduced to 1, 4 - dihydronaphthalene by sodium amalgam, whereas sodium amalgam has no action on benzene. Naphthalene and other fused ring compounds generally give poor yields in Friedel - Crafts alkylation, because they are so reactive that they react with the catalyst. These reactions also show that naphthalene is more reactive than benzene.

In fused ring systems, the positions are not equivalent and there is usually a preferred orientation. In naphthalene, the position 1 is relatively more reactive than the position 2. This can be explained in terms of the resonance structures of the arenium ion formed by electrophilic attack at the 1 - position as compared to the 2 - position.

(384.5 - 255.0) of resonance energy. On the other hand, if the reaction occurs at 9- or 10 positions, the aromatic character of one ring (i. e., central ring) is destroyed, leaving behind two benzene rings. In this way, anthracene will sacrifice 50.0 kJ/mol (351.0 - 2 × 150.5) and phenanthrene will sacrifice 83.5 kJ/mol (384.5 - 2 × 150.5) of resonance energy. Thus both hydrocarbons required to sacrifice less resonance energy for a reaction at 9- or 10- position than at 1- or 2- position. That is why 9- and 10- position of anthracene and phenanthrene are more reactive than any other positions

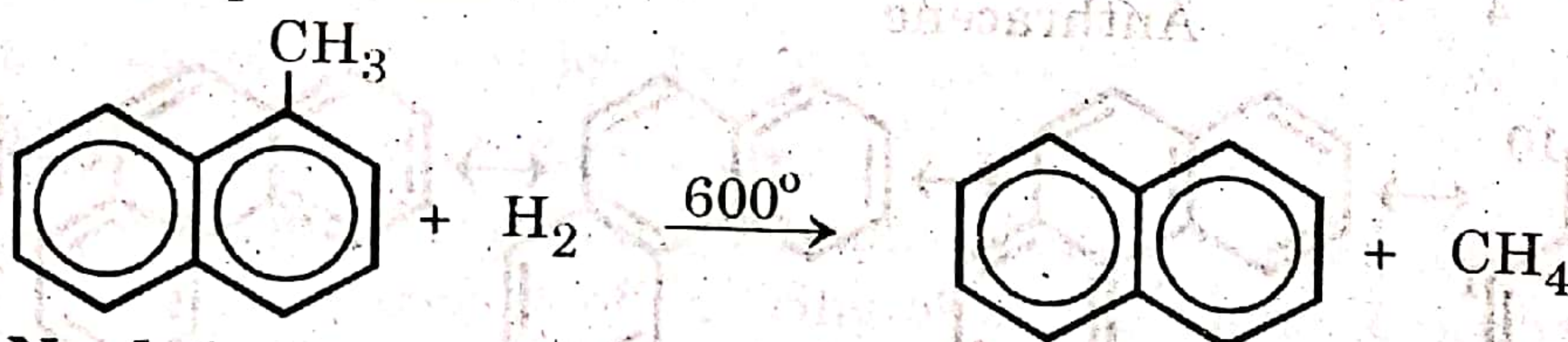
The loss of resonance energy of benzene, naphthalene phenanthrene, anthracene in a reaction is 150.5, 105, 83.5 and 50.0 kJ/ mole respectively. Therefore, the order of their reactivity is anthracene > phenanthrene > naphthalene and benzene

6.15 NAPHTHALENE

Manufacture

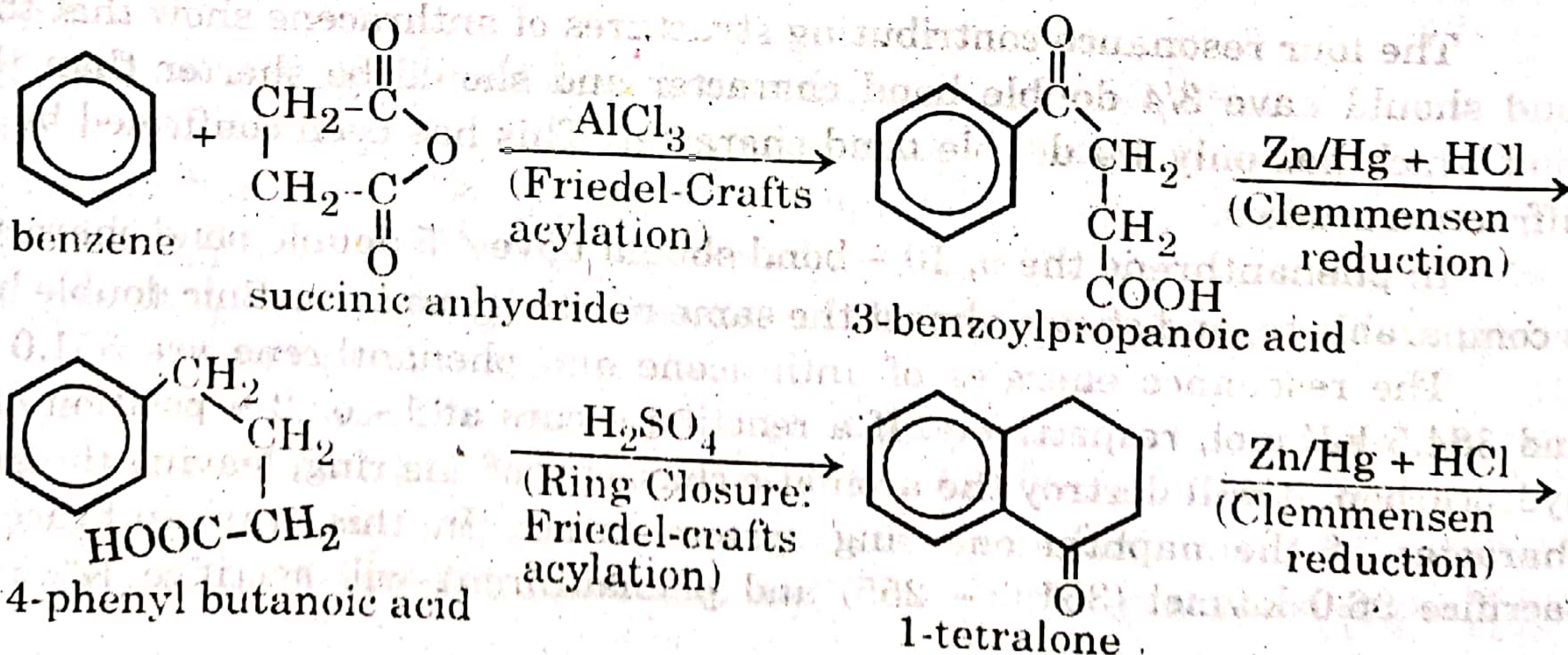
1. From Coal tar. Naphthalene is present to the extent of 10% in coal tar. When middle oil fraction (195–230°C) is cooled, naphthalene crystallises out and is separated by centrifuging. The crude naphthalene is melted and treated with conc. H_2SO_4 to remove basic impurities, and then washed with aq. NaOH to remove phenols and excess H_2SO_4 and finally sublimed to get pure naphthalene (m.p. 80°C).

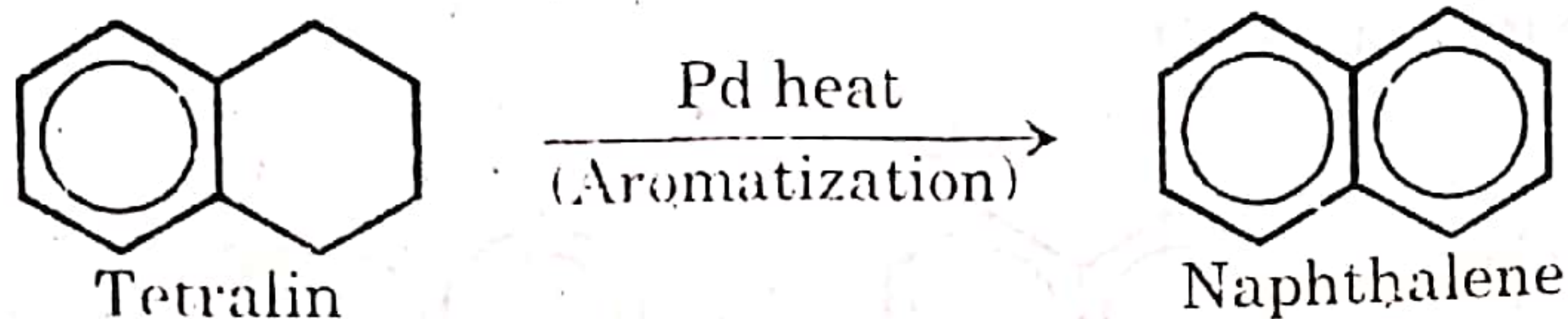
2. From petroleum. The middle oil distillates of petroleum on catalytic cracking and catalytic reforming give naphthalene and methylnaphthalenes. The methylnaphthalenes on heating to about 600°C in the presence of hydrogen are dealkylated to give naphthalene.



Synthesis of Naphthalene. Haworth synthesis.

It may be synthesized by the following route:



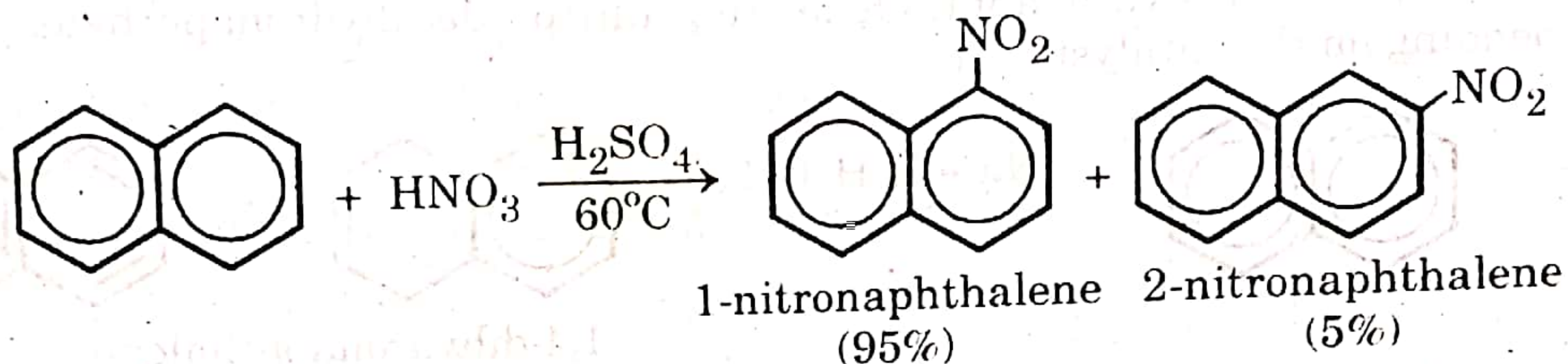


Properties

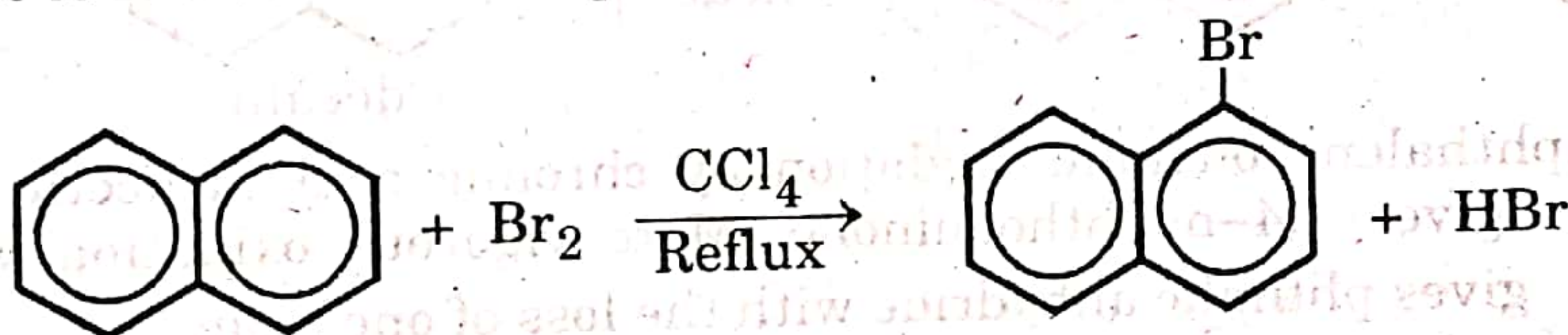
(Physical). Naphthalene is a colourless solid, mp 80°C , bp 218°C . It has a familiar odour of moth balls. It is very volatile and sublimes slowly at room temperature. It is insoluble in water and is soluble in ether and benzene. It burns with a smoky flame.

Electrophilic Substitution Reactions of Naphthalene

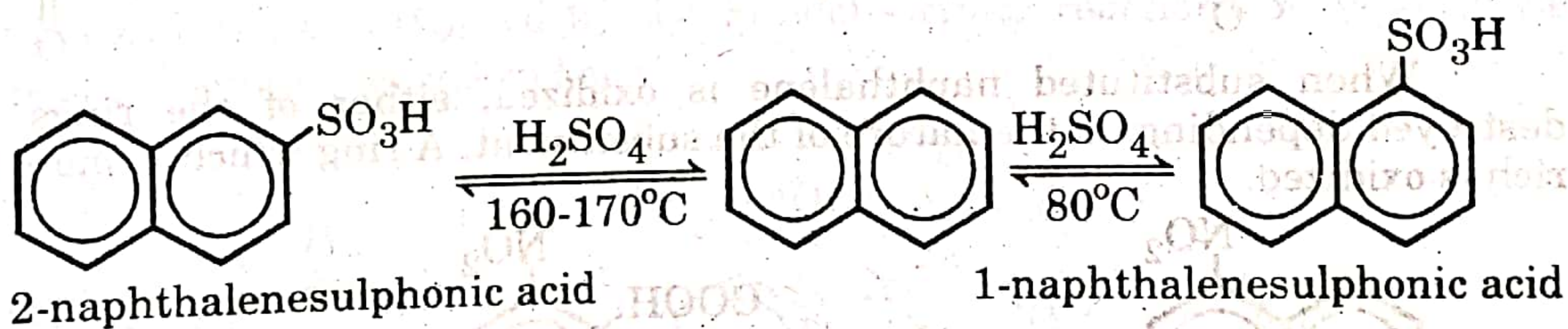
1. Nitration. Naphthalene on warming with a mixture of conc. HNO_3 and H_2SO_4 gives 1-nitronaphthalene as the major product.



2. Halogenation. Naphthalene reacts with Cl_2 and Br_2 in CCl_4 solution without a catalyst to form 1-chloronaphthalene or 1-bromonaphthalene.

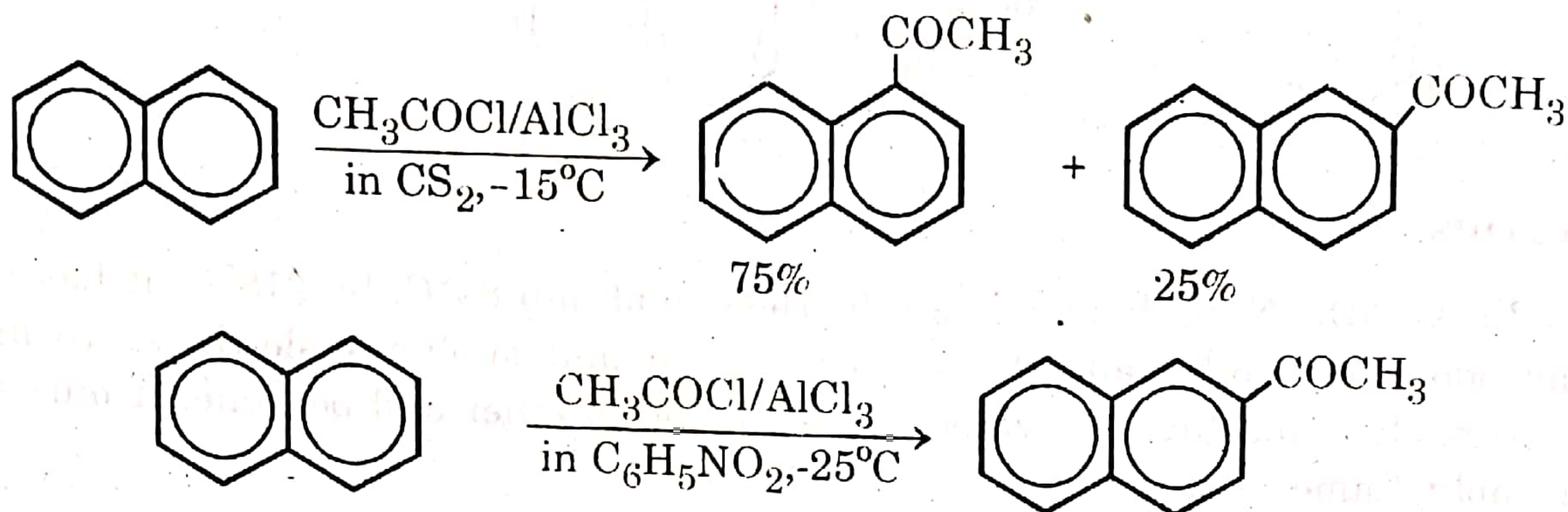


3. Sulphonation. Sulphonation of naphthalene at 80°C gives 1-naphthalenesulphonic acid, whereas at 160°C gives 2-naphthalenesulphonic acid. The reaction is reversible. At high temperature the stable product 2-naphthalenesulphonic acid dominates.

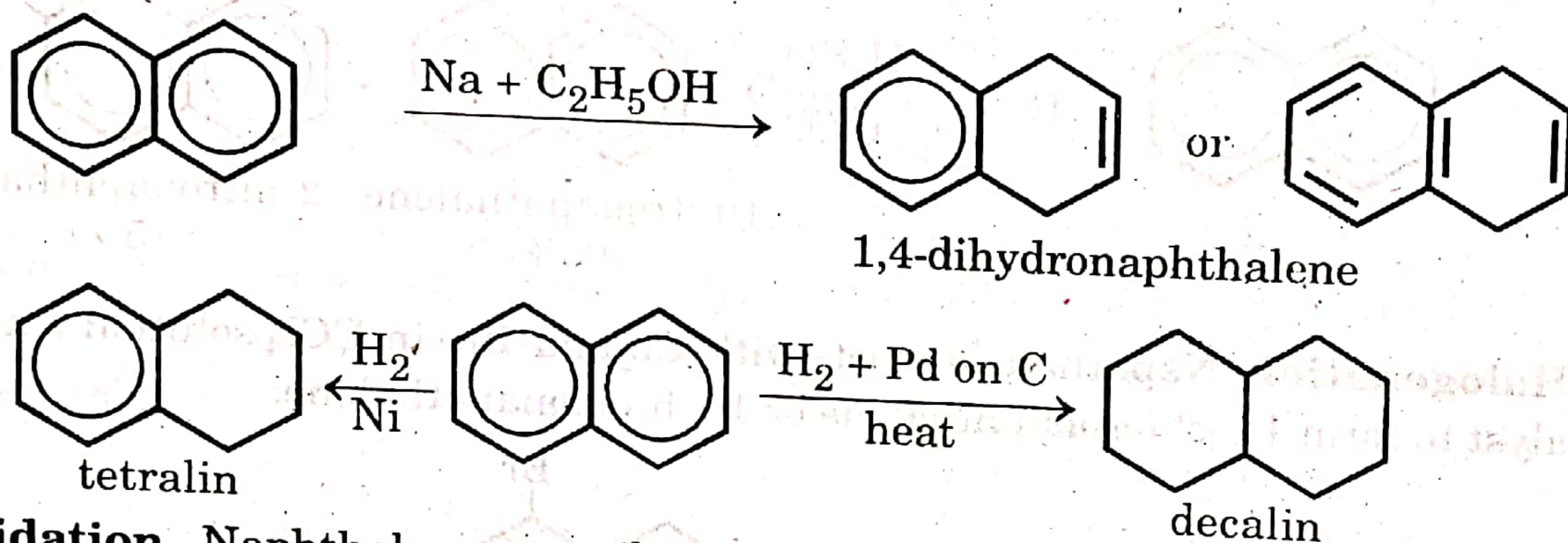


4. Friedel - crafts Acylation. Naphthalene reacts with acetylchloride (or benzoyl chloride) in the presence of AlCl_3 at -15°C in CS_2 solution to give mixture of 1- and 2-acylnaphthalene. If nitrobenzene is used as solvent, 2-

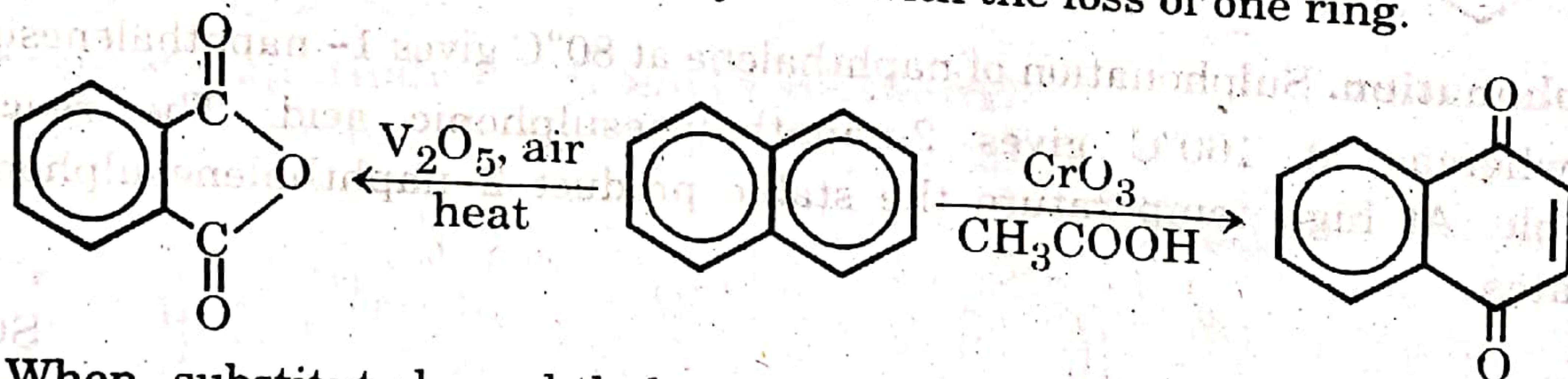
acylnaphthalene is the main product.



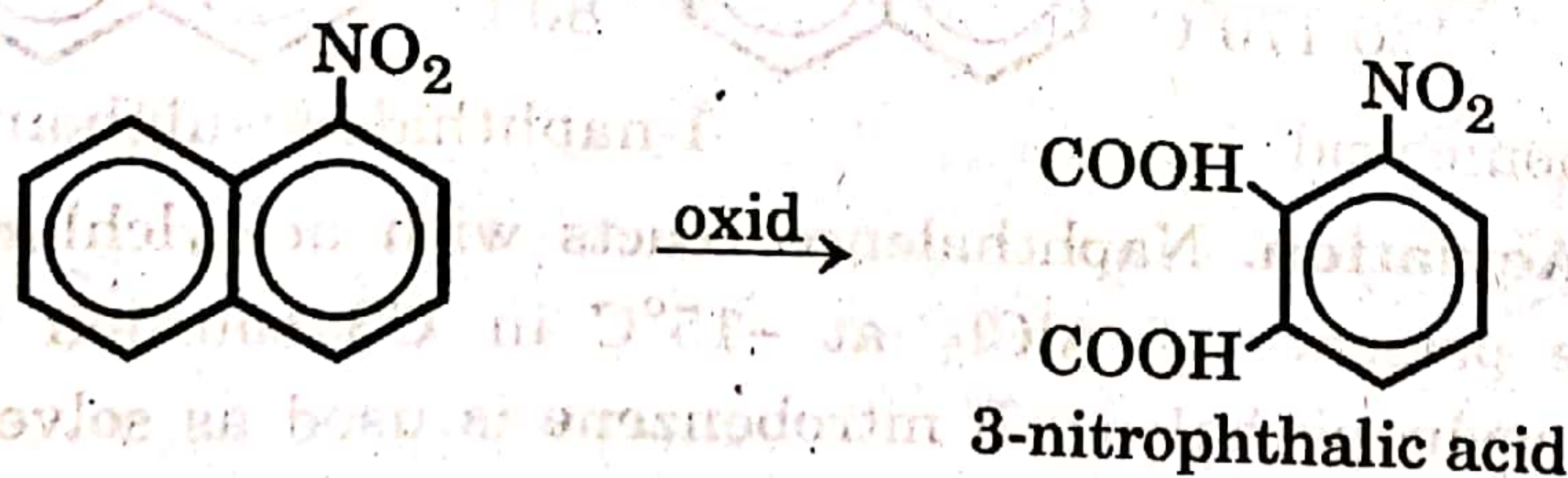
5. Reduction. Naphthalene can be reduced either partially or completely depending on the nature of the reducing agent employed. Reduction of naphthalene with sodium and alcohol or NH_3 gives 1,4-dihydronaphthalene. Catalytic hydrogenation gives 1,2,3,4-tetrahydronaphthalene (tetralin) or decahydronaphthalene (decalin) depending on the catalyst used.

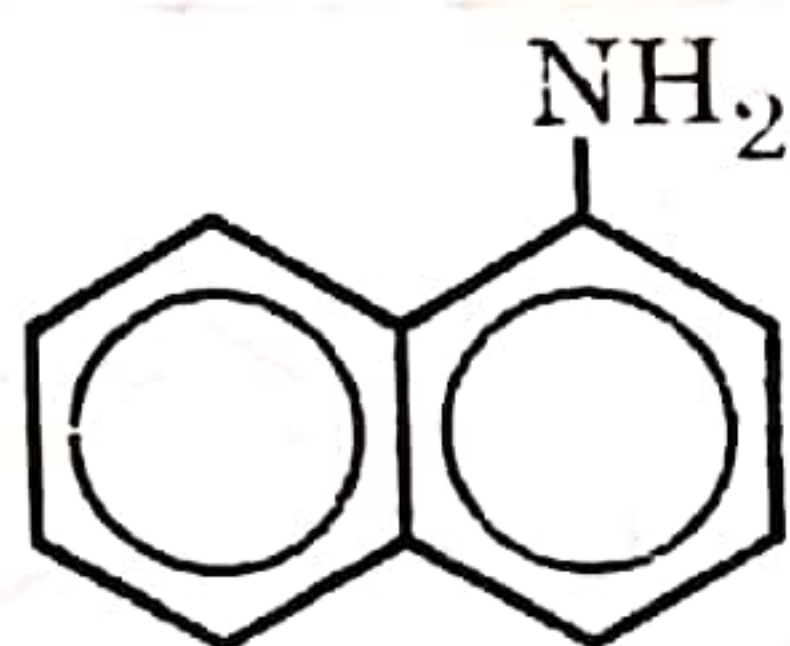


6. Oxidation. Naphthalene on mild oxidation by chromic acid in acetic acid or ($\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$) gives 1,4-naphthoquinone. More vigorous oxidation with air (oxygen) and V_2O_5 gives phthalic anhydride with the loss of one ring.

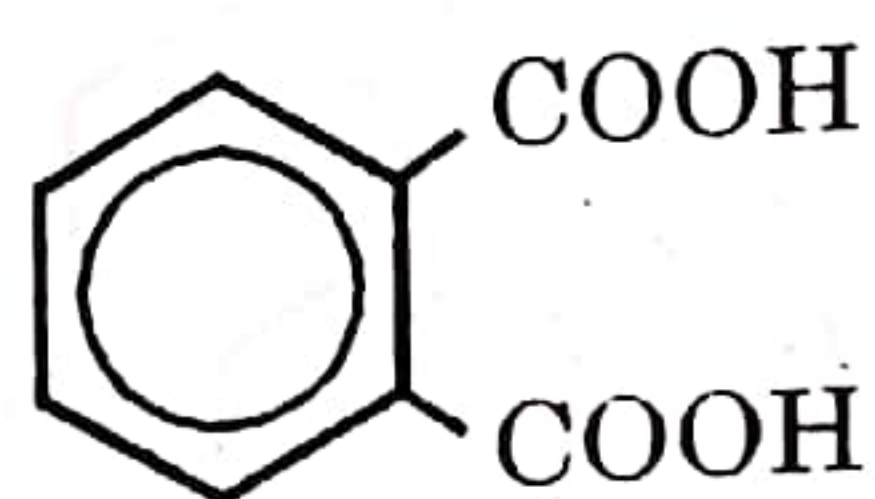


When substituted naphthalene is oxidized, either of the rings may be destroyed depending on the nature of the substituent. A ring which is more electron





oxid \rightarrow



Phthalic acid

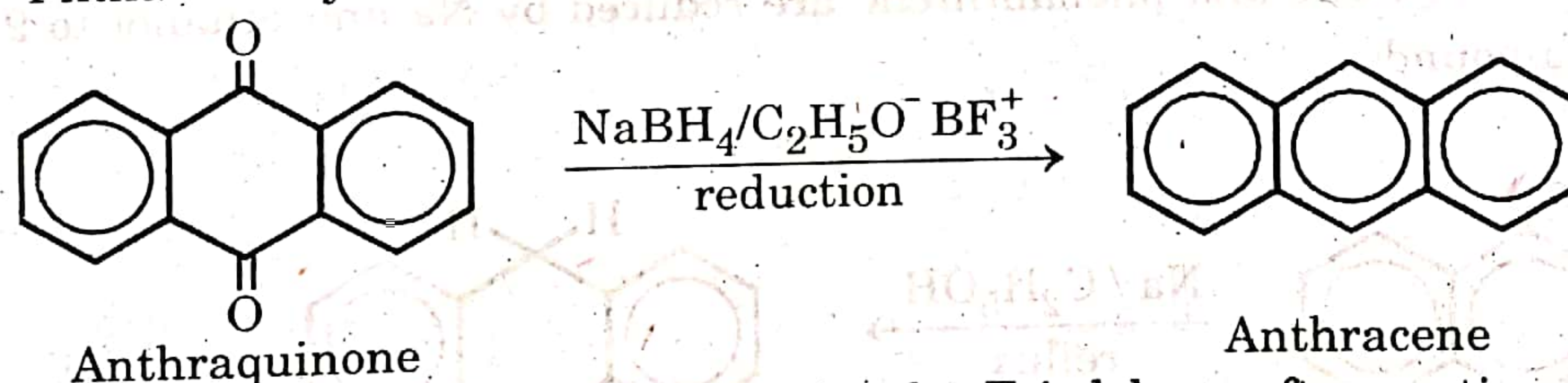
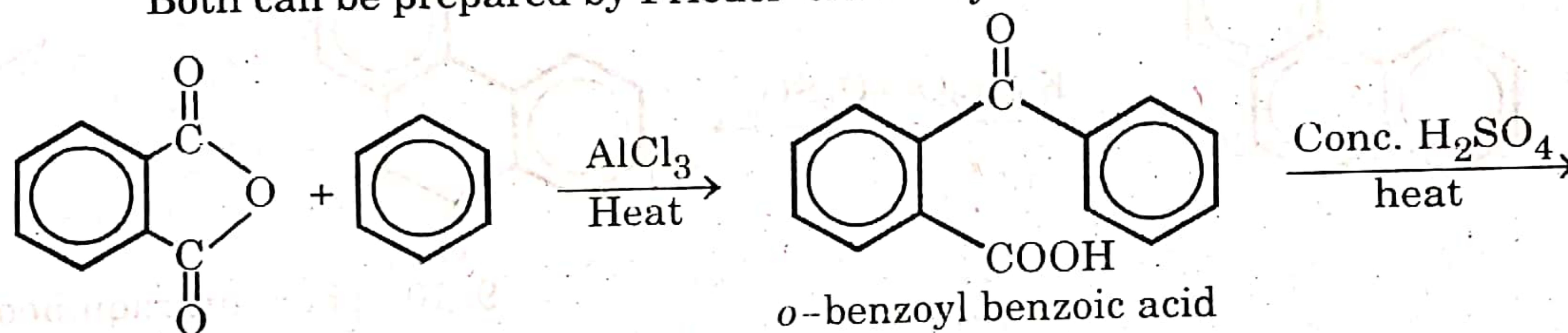
6.16 Anthracene and Phenanthrene

Anthracene and phenanthrene are isomeric fused ring aromatic hydrocarbons. In anthracene, three benzene rings are fused in a linear manner, whereas in phenanthrene the rings are fused angularly.

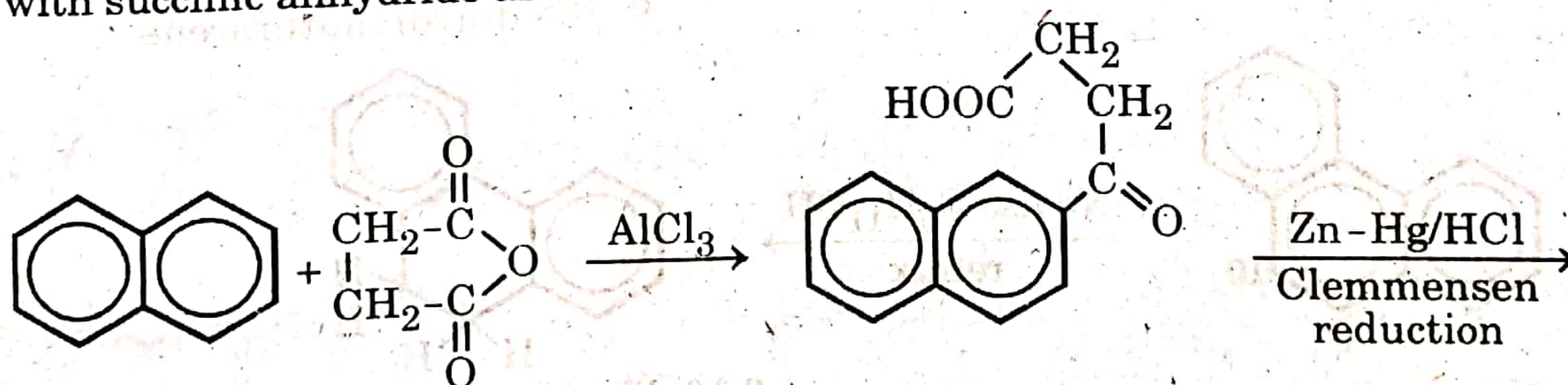
Isolation from Coal-tar. Anthracene and phenanthrene are present in the anthracene oil fraction (bp. 300-350°C) of coal tar. When anthracene oil is cooled, crude anthracene crystallises out which also contains phenanthrene. The crude anthracene is washed with solvent naphtha which dissolves phenanthrene. The remaining solid, anthracene is washed with pyridine to remove carbazole. Finally, anthracene is purified by sublimation. Phenanthrene is recovered from its solution in solvent naphtha.

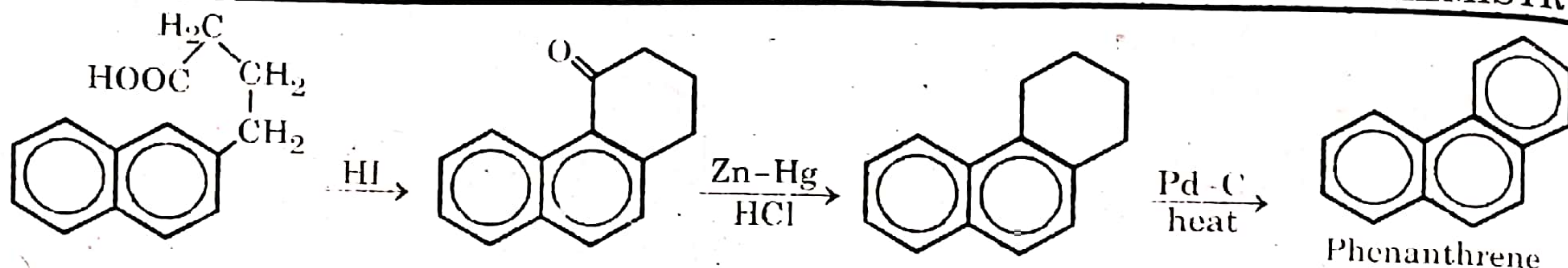
Preparation of Anthracene and phenanthrene

Both can be prepared by Friedel-Crafts acylation reactions as shown below:



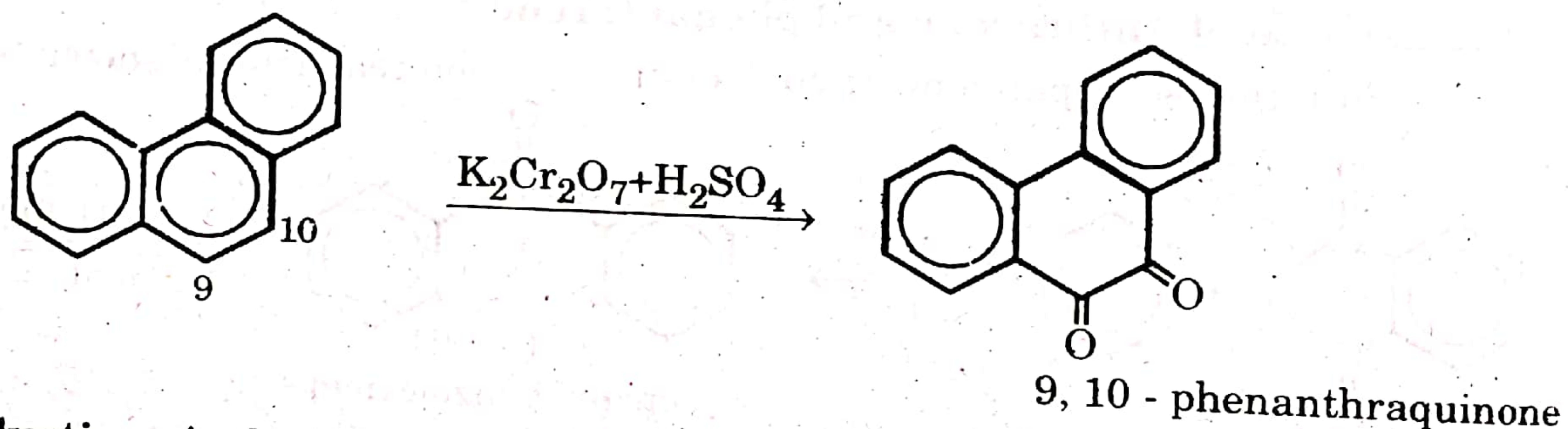
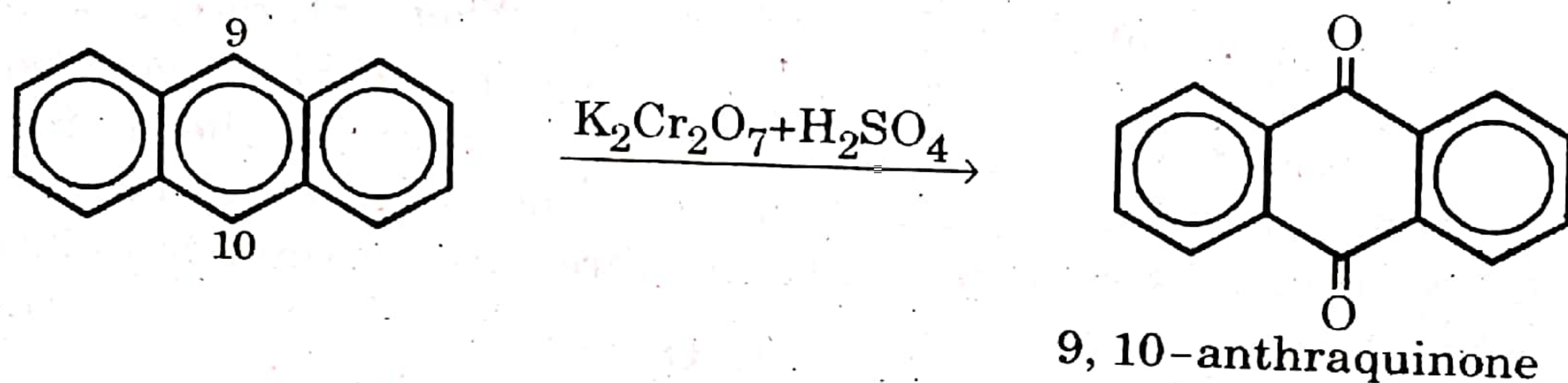
Phenanthrene can be prepared by the Friedel-Crafts reactions of naphthalene with succinic anhydride as shown below:



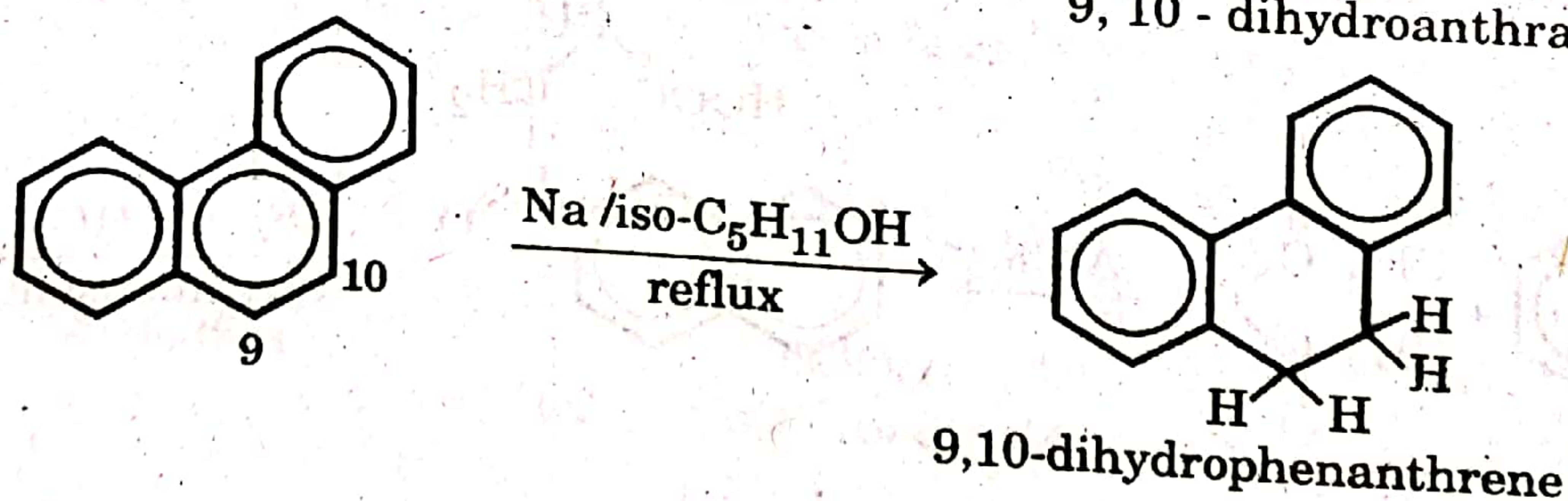
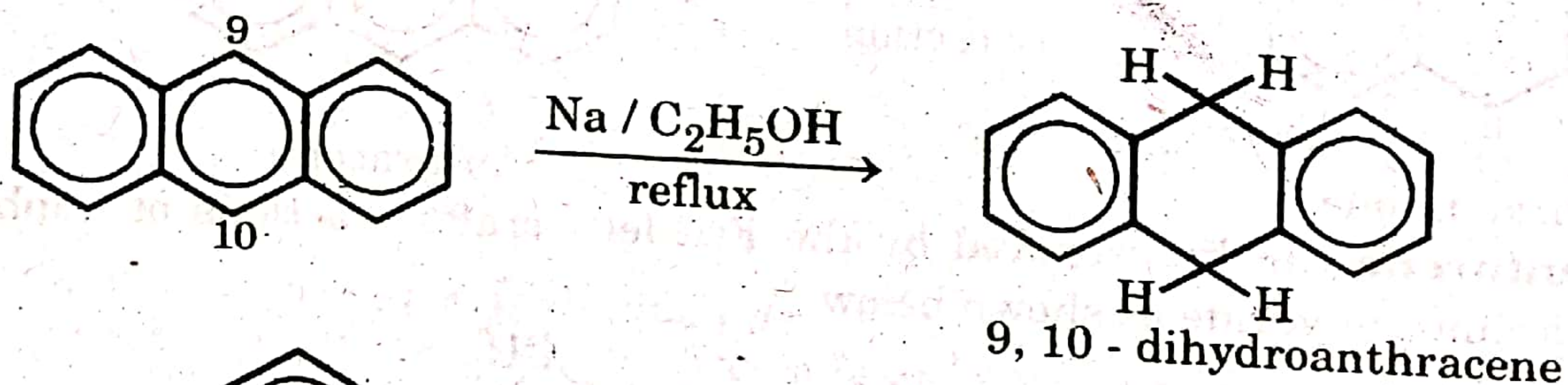


Reactions. The greater reactivity of 9- and 10- position of anthracene and phenanthrene is seen in the following reactions:

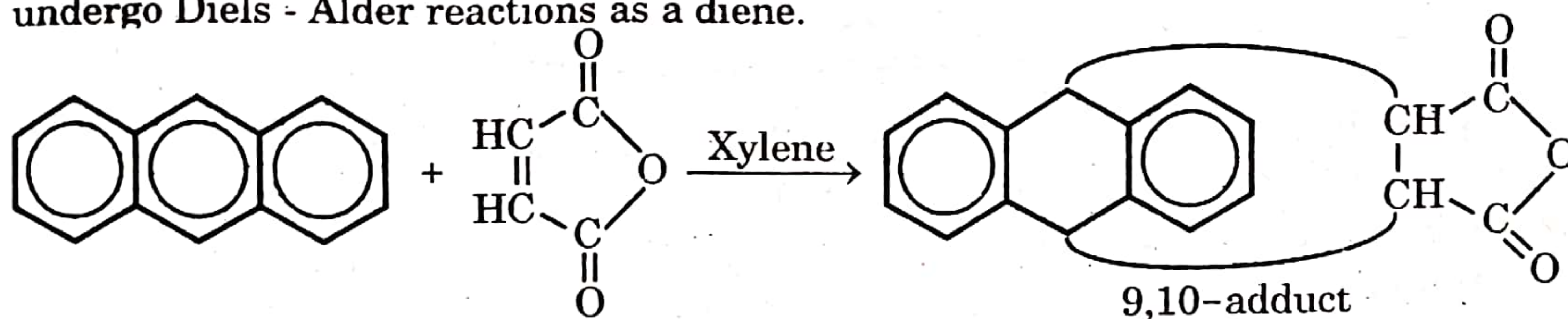
1. Oxidation. Anthracene and phenanthrene are oxidized by $K_2Cr_2O_7 + H_2SO_4$ to 9, 10 - quinones.



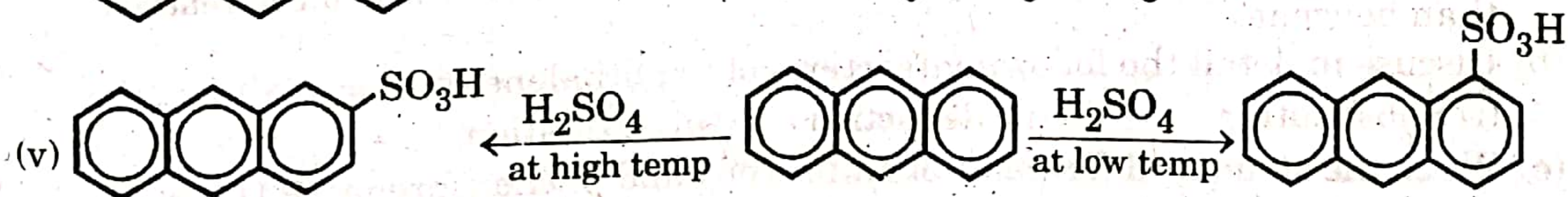
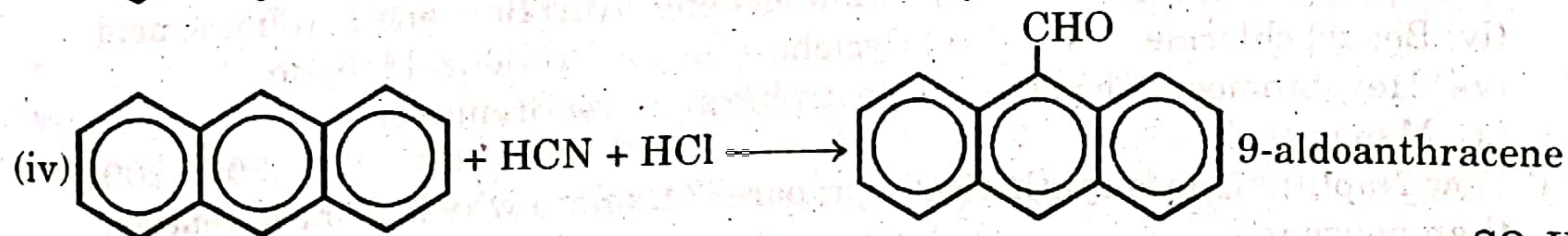
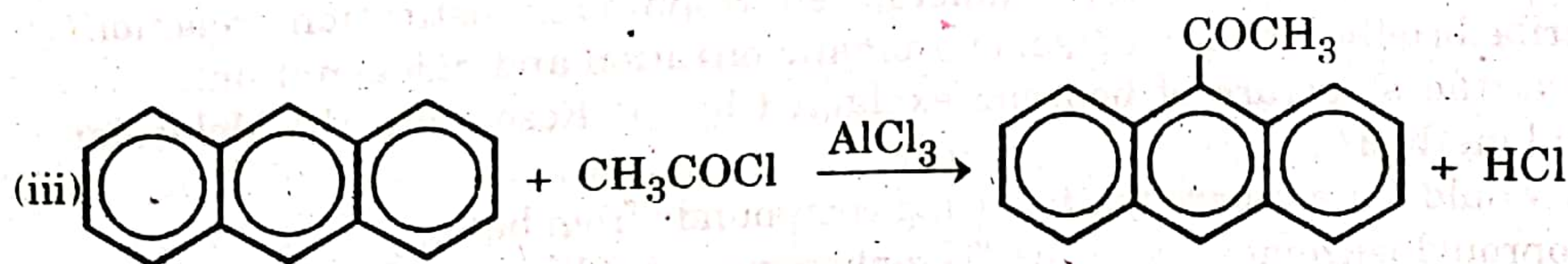
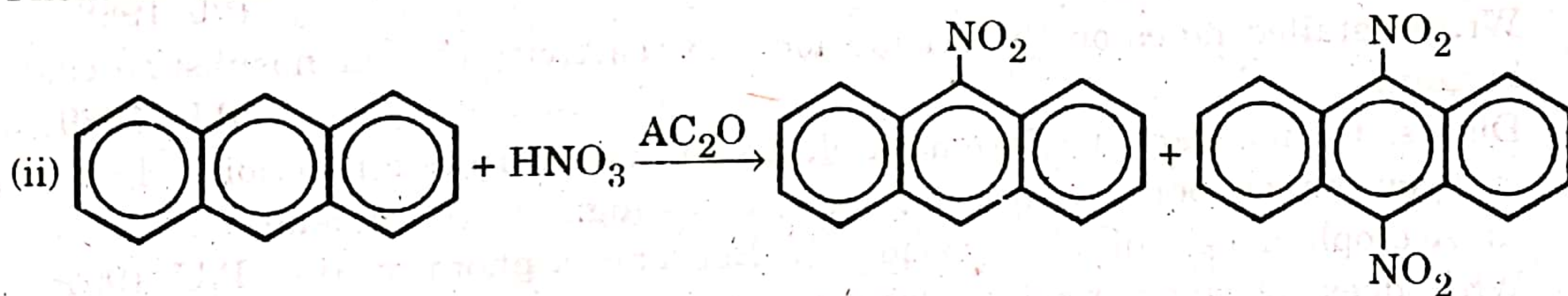
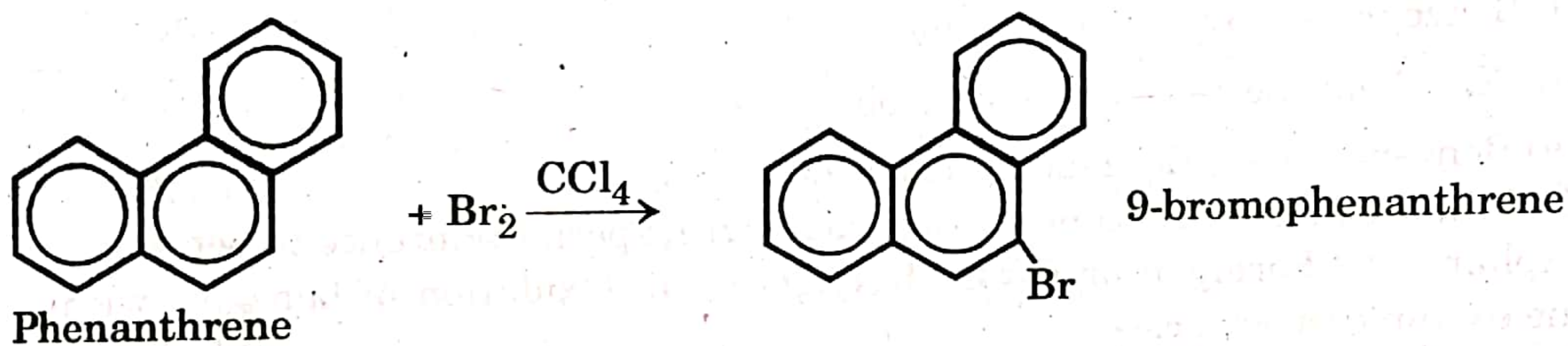
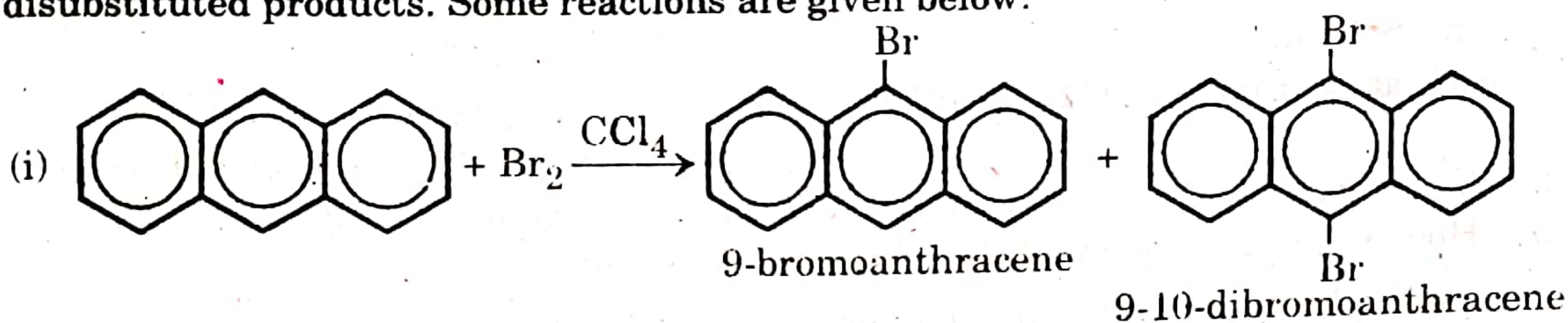
2. Reduction. Anthracene and phenanthrene are reduced by Na and ethanol to 9, 10 - dihydro compounds.



3. Diels - Alder Reaction. 9, 10 - positions of anthracene behave like a diene and undergo Diels - Alder reactions as a diene.



4. Electrophilic Substitution Reactions with anthracene and phenanthrene occur most readily at 9 - position. Anthracene also frequently gives 9, 10 disubstituted products. Some reactions are given below.



QUESTIONS

1. Write the structural formulae of the following compounds.

| | |
|-----------------------------------|--------------------------|
| (a) <i>m</i> - Chloronitrobenzene | (b) Picric acid |
| (c) Benzenesulphonic acid | (d) Resorcinol |
| (e) Bromobenzene | (f) Catechol |
| (g) <i>o</i> - Toluidene | (h) Meistylene |
| (i) 9 - bromoanthracene | (j) Phenanthrene |
| (k) 3 - Phenylpentane | (l) 1, 2- diphenylethane |
| (m) Styrene | (n) Anisole |
2. What is aromaticity? How will you deduce the structure of benzene?
(P. U. 1999), B. Z. U. M. 1989.
3. (a) Give mechanism of Acylation and Nitration of the benzene ring.
(b) How will you bring about the following conversions:
 - (i) Naphthalene \longrightarrow α - aminonaphthalene.
 - (ii) Benzene \longrightarrow *o* - nitrotoluene
 - (iii) Nitrobenzene \longrightarrow *m* - dinitrobenzene
 - (iv) Benzene \longrightarrow Benzenehexachloride
4. (a) Explain the modern concept of aromaticity with special reference to benzene. (P.U. 2001)
(b) Explain: - (i) Formylation (ii) Carboxylation (iii) Oxidation of benzene, with one example in each case.
5. Write detailed notes on the orientation and reactivity of a monosubstituted benzene. (P.U.1988)
6. Discuss the mechanism of aromatic electrophilic substitution reactions. How will you convert benzene into each of the following: (i) Toluene (ii) Acetophenone (iii) Maleic acid (iv) Benzene sulphonic acid. P.U. 1989
7. Why does benzene readily undergo electrophilic substitution reaction? Describe briefly the mechanism of aromatic nitration and halogenation. P.U. 1991
8. How is the structure of benzene explained by (a) Resonance (b) Molecular orbital method?
9. How would you prepare the following compounds from benzene?

| | | |
|----------------------------|--------------------|------------------------------|
| (i) Isopropylbenzene | (ii) Acetophenone | (iii) Benzene sulphonic acid |
| (iv) Benzyl chloride | (v) Cyclohexane | (vi) Benzaldehyde |
| (vii) Hexabromocyclohexane | (viii) Nitrohexane | (ix) Bromobenzene |
| (x) Maleic acid. | | |
10. (a) How Naphthalene is synthetically prepared? Explain why it is more reactive than benzene? (P.U. 1994,2001,2002)
(b) Discuss in detail the following reactions of naphthalene:-
(i) Substitution (ii) Reduction (iii) Oxidation.
(c) Write the structural formulas of anthracene and phenanthrene. (P.U. 1988)

11. (a) How is Anthracene prepared from coal tar and synthesized in the laboratory?
 (b) Give the electrophilic substitution reactions of Anthracene with the following:-
 (i) Br_2 (ii) conc. H_2SO_4 (iii) CH_3COCl (iv) $\text{HCN} + \text{HCl}$
 (v) $\text{Na} - \text{Hg} + \text{alcohol}$ (vi) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ (P.U. 1989)
12. Write resonance structures of naphthalene, anthracene, and phenanthrene. Show why 1-position in naphthalene and 9,10-positions in anthracene and phenanthrene are reactive.
13. Discuss the mechanism of Friedel - crafts reactions. What are its limitations?
14. What is aromaticity? Discuss Huckel rule for aromaticity.
15. How will you distinguish between ethylbenzene and *o* - xylene?
- Hint:** Ethylbenzene gives benzoic acid (mp. 122°C) on oxidation with KMnO_4 .
o - xylene gives phthalic acid (mp. 184°C).
16. Account for aromaticity observed in :
 (a) 1, 3 - cyclopentadienyl anion but not 1, 3 - cyclopentadiene
 (b) 1,3, 5 - cycloheptatrienyl cation but not 1,3 - cycloheptatriene
 (iii) Cyclopropenyl cation (iv) The heterocyclic pyrrole and pyridine.
17. Explain: (a) all *m*-directors are deactivating (b) Most *o* - and *p* - directing substituents make the ring more reactive than benzene itself - they are activating. (c) the halogens are, *op* - directors but are deactivating.
18. Discuss the following reactions of benzene:
 (a) Halogenation (b) Nitration (c) Chloromethylation
 (d) Friedal-Crafts reaction (e) Gatterman-Koch reaction (P.U. 1998)
19. How will you prepare the following compounds from toluene? (i) Benzoic acid
 (ii) Benzyl bromide (c) *m*-Nitrobenzoic acid (P.U. 2000)

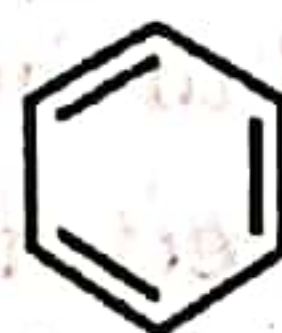
SHORT QUESTIONS

1. Benzene is a planar molecule with bond angles of 120° . All 6C-to-C bonds have the identical length, 139 pm. Is benzene the same as 1,3,5-cyclohexatriene?

Ans. No. The bond lengths in 1,3,5-cyclohexatriene would alternate 154 pm for the single bond and 132 pm for the double bond. The C-to-C bond in benzene is intermediate between a single and double bond.

2. What are annulenes?

Ans. The name annulene has been proposed as a general name for monocyclic compounds having alternating single and double bonds. The ring size of annulene is indicated by a number in brackets. The benzene is [6] annulene and cyclooctatetraene is [8] annulene. Huckel's rule predicts that annulene



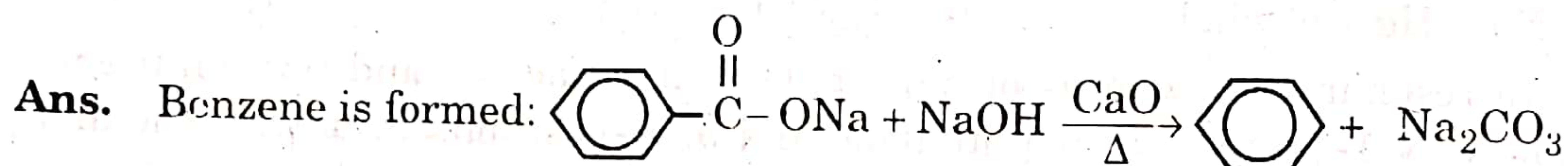
Benzene
[6] Annulene



Cyclooctatetraene
[8] Annulene

will be aromatic, provided their molecules have $(4n+2)$ pi electrons and have a planar ring. Thus, [6] annulene is aromatic whereas [8] annulene is not aromatic.

3. What happens when sodium benzoate is heated with sodalime?

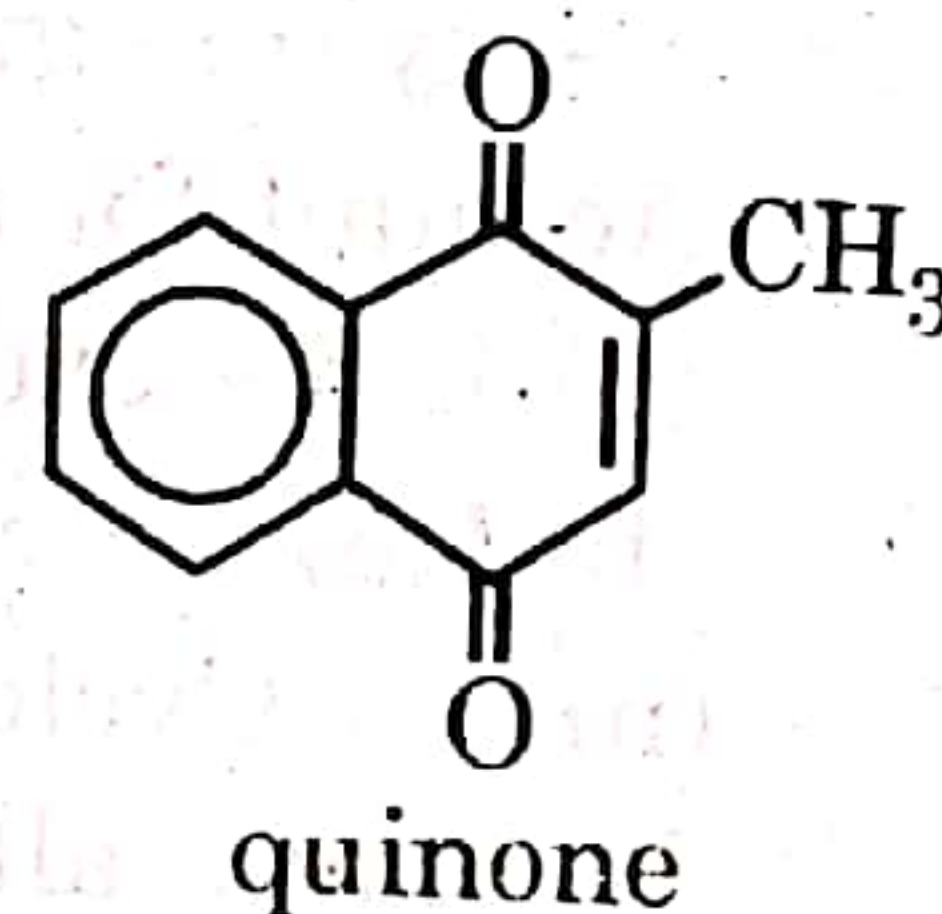


4. Is the benzenonium ion, $\left[\text{C}_6\text{H}_5\text{C}^+\begin{matrix} \text{H} \\ \text{E} \end{matrix}\right]$, flat.

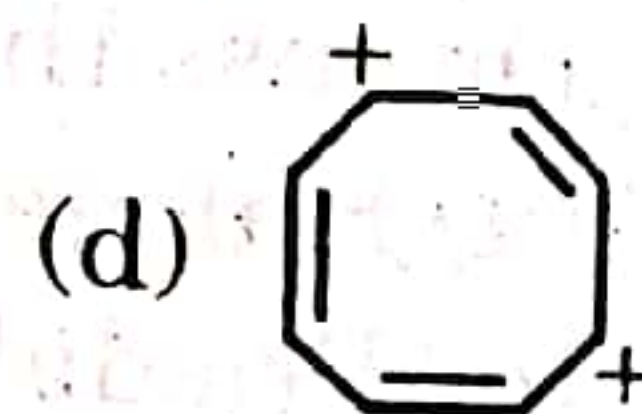
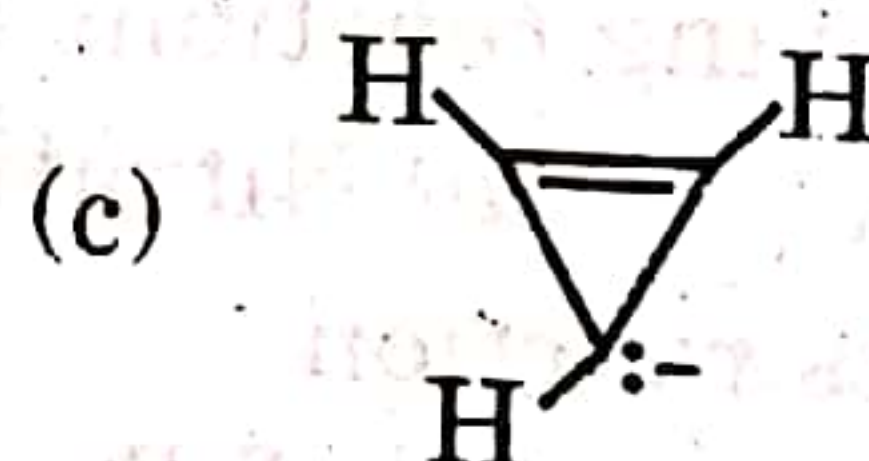
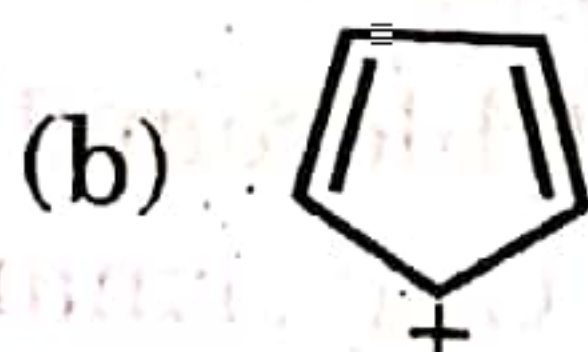
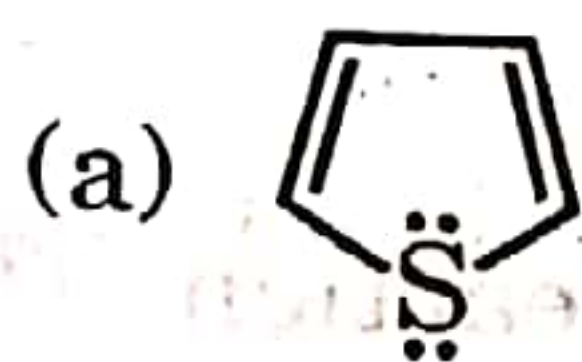
Ans. No. The C bonded to E and H is tetrahedral.

5. Why cannot 2-naphthalenecarboxylic be formed by oxidation of 2-methylnaphthalene?

Ans. Oxidation is an electrophilic attack and CH_3 is activating. The CH_3 -substituted benzene ring is more susceptible to oxidation than is the side chain CH_3 . The product is a quinone.



6. Use the Huckel rule to indicate whether the following planar species are aromatic or antiaromatic:



Ans. (a) aromatic. There are two π electrons from each $\text{C}=\text{C}$ and 2 from an electron pair on S to make an aromatic sextet. (b) and (c). Antiaromatic. They have $4n(n=1)$ π electrons. (d) aromatic. There are 6 π electrons.

7. Explain aromaticity and antiaromaticity in terms of MO energy levels.

Ans. Aromaticity is observed when all bonding MO's are filled and nonbonding MO's, if present empty or completely filled. Huckel's rule arises from this requirement. A species is antiaromatic if it has electrons in antibonding MO's or if it has half filled bonding or nonbonding MO's, provided it is planar.

8. Explain: All *m*-directors are deactivating.

Ans. All *m*-directors are electron-attracting and destabilize the incipient benzenonium ion in the transition state. They therefore diminish the rate of reaction as compared to the rate of reaction of benzene.

9. Explain: Most *op*-directing substituents make the ring more reactive than benzene itself—they are activating.

Ans. Most *op*-directors are on balance, electron donating. They stabilize the incipient benzenonium ion in the transition state, thereby increasing the rate of reaction as compared to the rate of reaction of benzene. For example, the

ability of the $-\ddot{\text{O}}\text{H}$ group to donate electrons by extended p orbital overlap (resonance) for outweighs the ability of the OH group to withdraw electrons by its induction effect.

10. Compare the activating effects of the following *op*-directors.

$-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}:$ and $-\ddot{\text{O}}\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$. Explain your answer.

Ans. The order of activation is $-\text{O}^- > -\text{OH} > -\text{OCOCH}_3$. The O^- , with a full negative charge, is best able to donate electrons, thereby giving the very stable uncharged intermediate,



In OCOCH_3 , the C of the

$\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$ has +ve charge and makes demands on the $-\ddot{\text{O}}-$ for electron

density, thereby diminishing the ability of this $-\ddot{\text{O}}-$ to donate electrons to the benzenonium ion.

11. What are arenes?

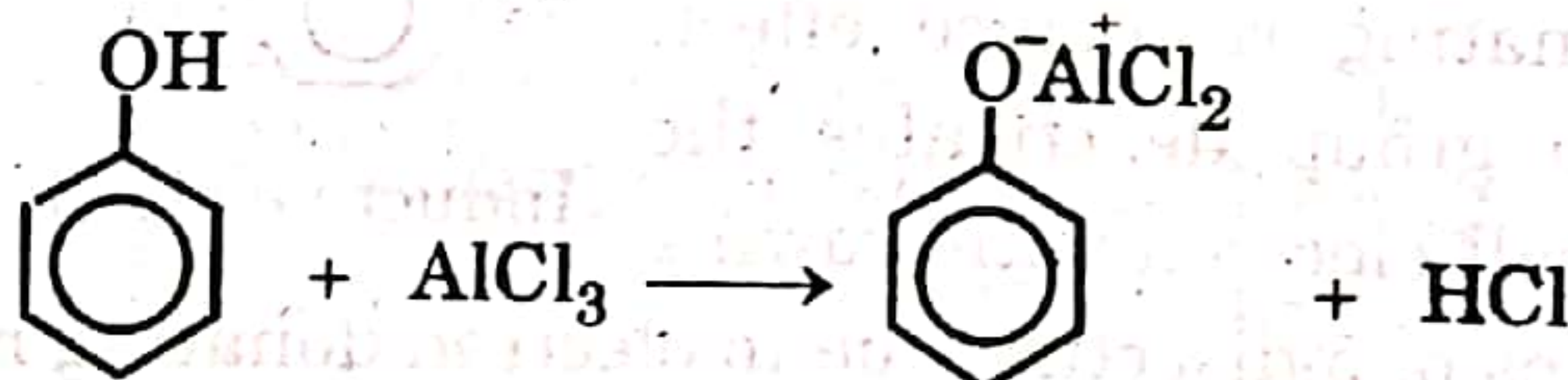
Ans. Benzene derivatives with saturated or unsaturated C-containing side chains are called **arenes**. Examples are cumene or isopropylbenzene $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, and styrene or phenylethene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$.

12. In monoalkylating C_6H_6 with RX in AlX_3 an excess of C_6H_6 is used in Friedel-Craft alkylation reaction. Explain.

Ans. The monoalkylated product, $\text{C}_6\text{H}_5\text{R}$, which is more reactive than C_6H_6 itself since R is an activating group, will react to give $\text{C}_6\text{H}_4\text{R}_2$ and $\text{C}_6\text{H}_3\text{R}_3$. To prevent polyalkylation an excess of C_6H_6 is used to increase the chance for collision between R^+ and C_6H_6 and to minimize collision between R^+ and $\text{C}_6\text{H}_5\text{R}$.

13. The alkylation of $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{NH}_2$ with RX in the presence of AlCl_3 catalyst gives poor yield. Explain.

Ans. OH and NH_2 groups react with initially with AlCl_3 (the Lewis acid) and inactivate the catalyst. That is why the yields of Friedel-Crafts reaction with phenol and aniline are very poor.



14. $\text{C}_6\text{H}_5\text{NO}_2$, but not C_6H_6 is used as a solvent for the Friedel-Craft alkylation of $\text{C}_6\text{H}_5\text{Br}$. Explain.

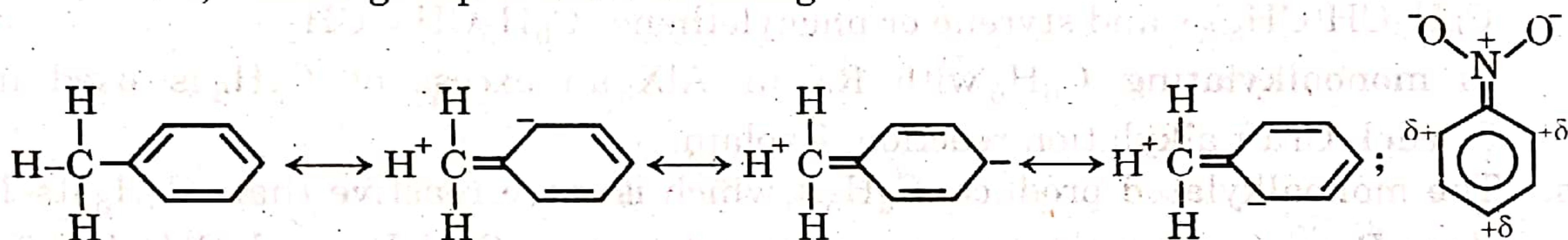
Ans. C_6H_6 is more reactive than $\text{C}_6\text{H}_5\text{Br}$ and would preferentially undergo alkylation. $-\text{NO}_2$ is so strongly deactivating that $\text{C}_6\text{H}_5\text{NO}_2$ does not undergo Friedel-Craft alkylation or acylation.

15. Draw a conclusion about the stability and aromaticity of naphthalene from the fact that the experimentally determined heat of combustion is 255 kJ mol^{-1} per ring is less than the 150 kJ mol^{-1} resonance energy of benzene.

Ans. The difference of 255 kJ mol^{-1} is naphthalene's resonance energy. Naphthalene is less aromatic than benzene because a resonance energy of 127 kJ mol^{-1} per ring is less than the 150 kJ mol^{-1} resonance energy of benzene. Naphthalene is more stable than benzene because resonance energy of naphthalene (255 kJ/mole) is higher than the resonance energy of benzene (150 kJ/mole).

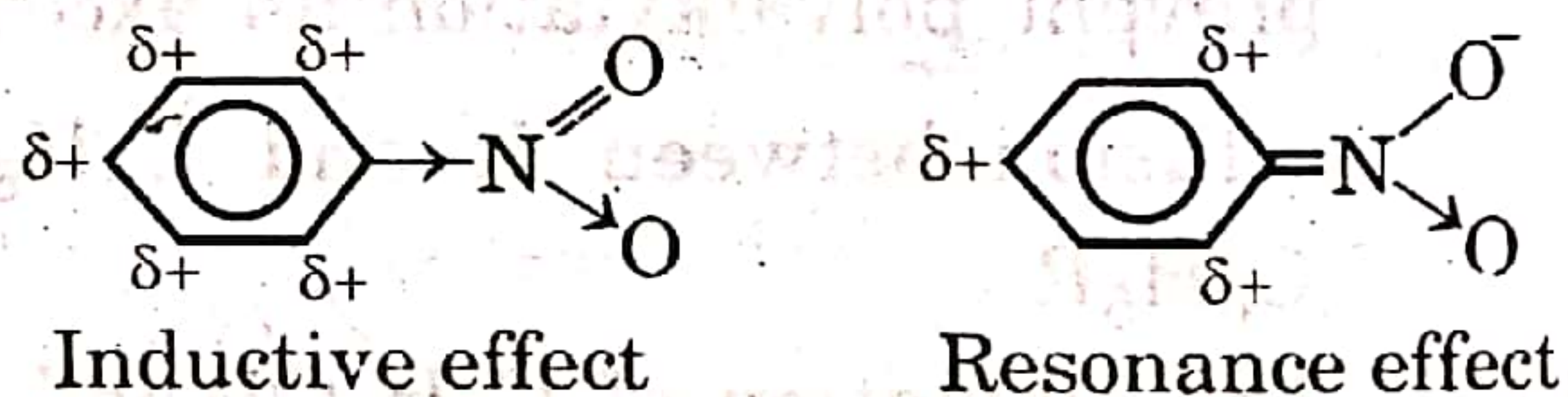
16. Why a methyl group is *o*-, *p*-directing and a nitro group is meta directing.

Ans. Methyl (or alkyl) group is electron-donating by inductive effect. When it is substituted on benzene, it therefore, releases electrons and creates partial negative charge at 2,4 and 6-position (ortho and para) at the benzene ring through resonance (or hyperconjugation). *o*- and *p*-positions attract the incoming electrophile, therefore, a methyl group is *o*-, *p*-directing. Nitro group is electron withdrawing by inductive effect and produces partial positive charge at 2,4 and 6-positions at the benzene ring due to resonance which leaves meta position more susceptible to attack by an electrophile. Thus, a nitro group is meta directing.



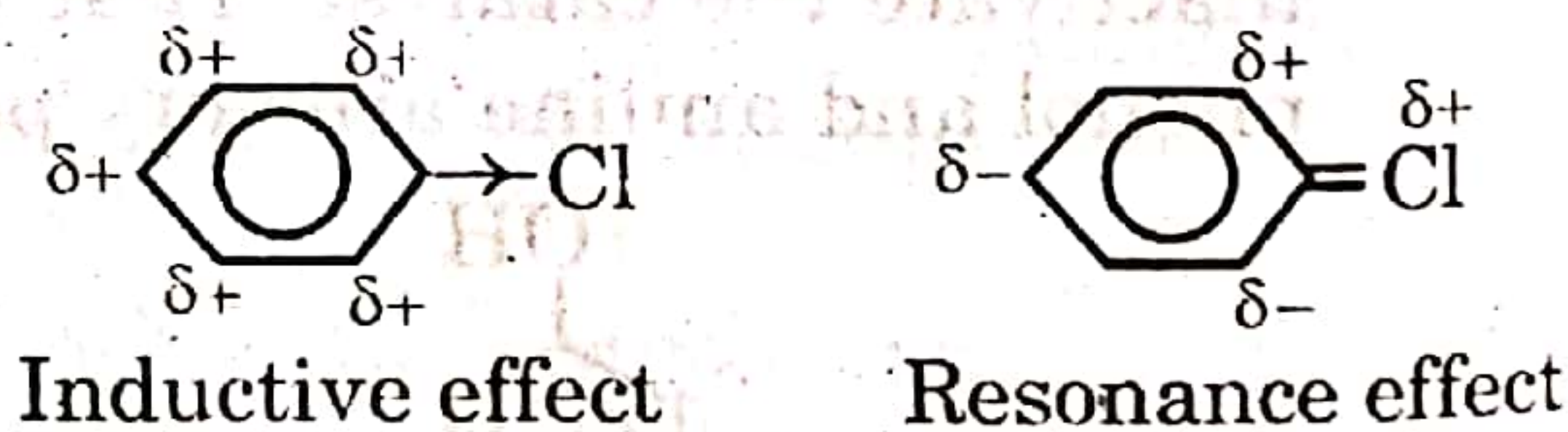
17. Why a nitro group is both deactivating and meta directing?

Ans. A nitro group has electron-withdrawing inductive effect as well as electron-withdrawing resonance effect, hence *o*-NO₂ group deactivates the ring and is *m*-directing



18. Explain why a chloro group is deactivating but *o*-, *p*-directing.

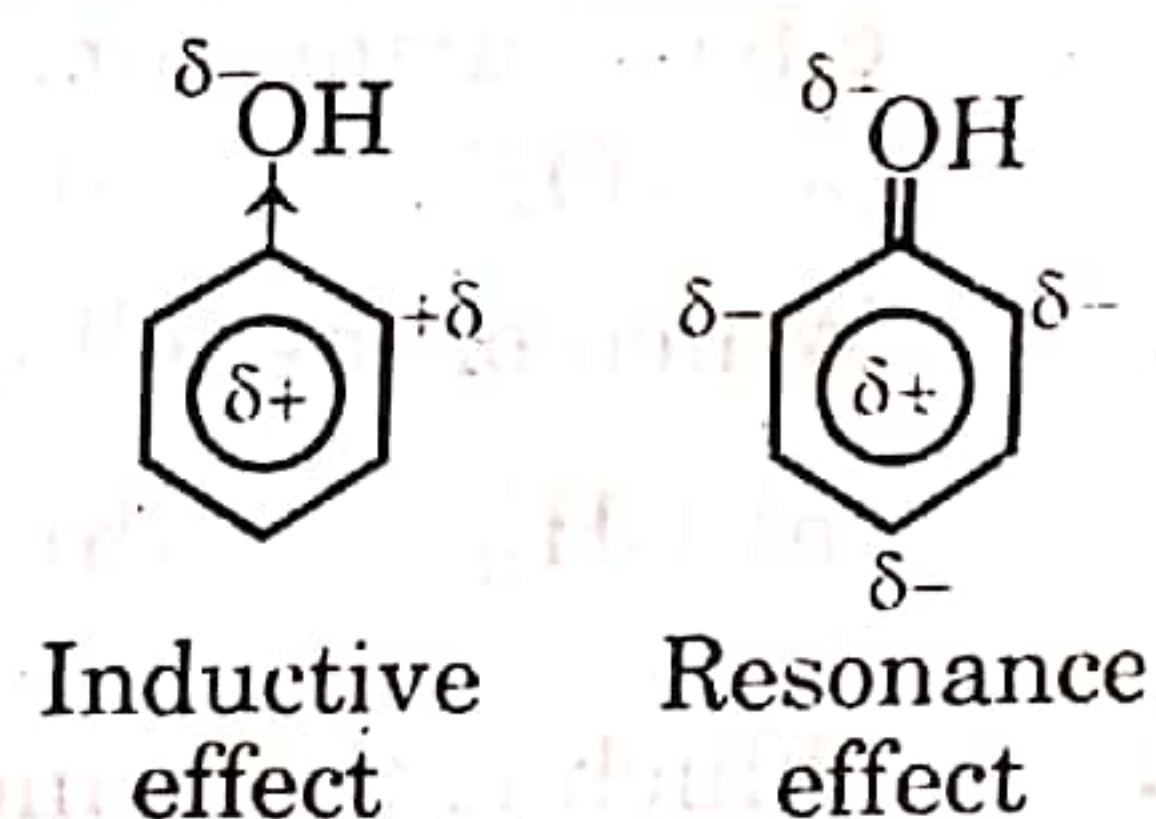
Ans. Chloro group has a stronger electron withdrawing inductive effect due to its strong electronegativity which dominates the electron-donating resonance effect. Hence a chloro group deactivates the ring due to overall electron withdrawing effect but remains *o*-, *p*-directing due to electron donating resonance effect.



19. Explain why a hydroxyl group is activating but *o*-, *p*-directing?

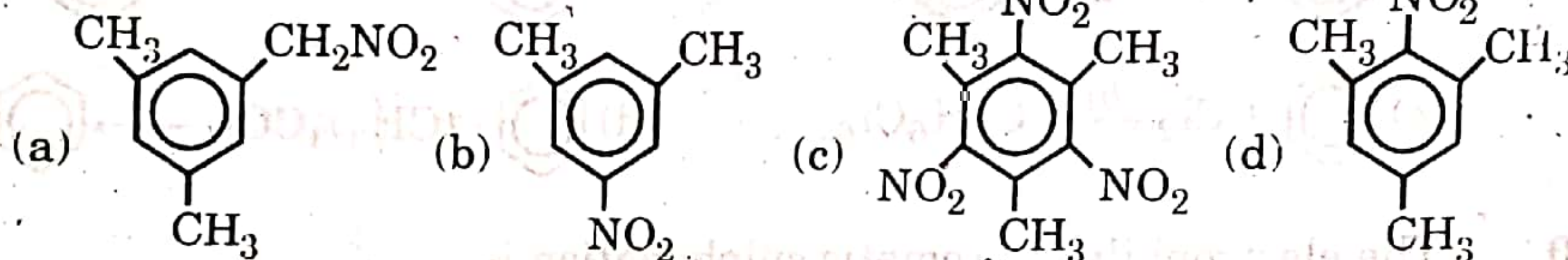
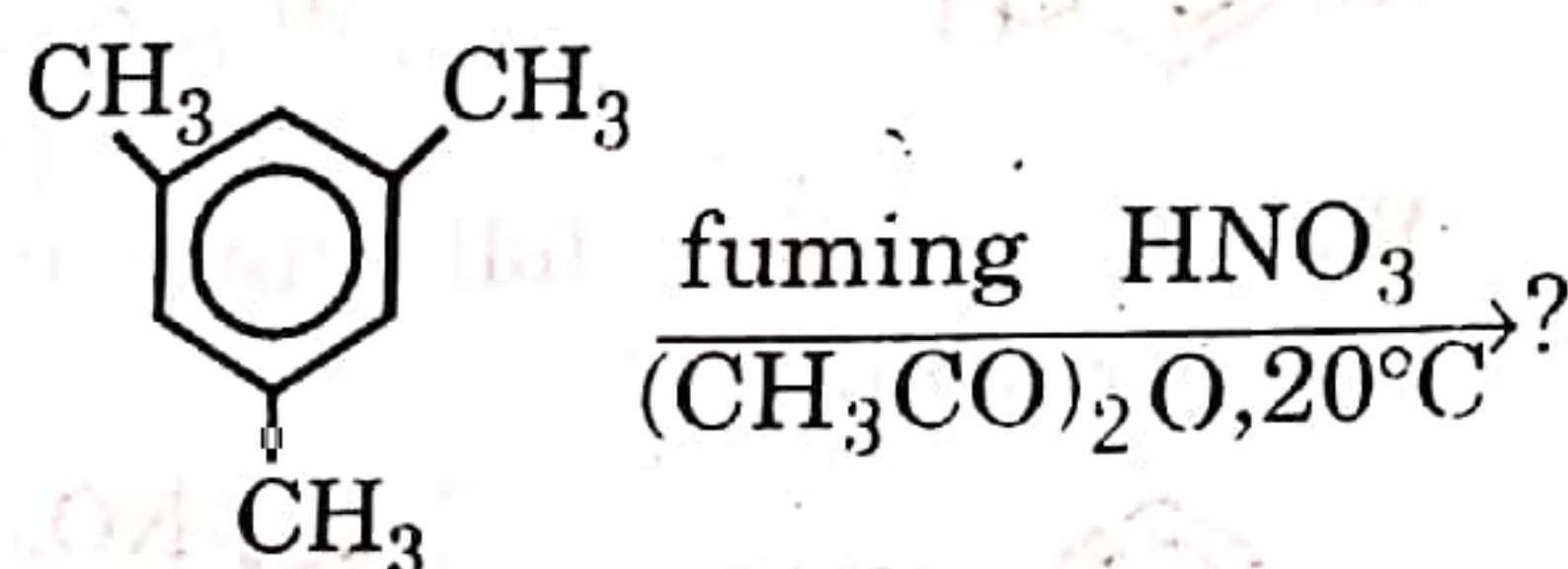
Ans. In phenol, since O atom of -OH group is more electronegative than C atom of the ring, the -OH group exerts an electron-withdrawing inductive effect thus deactivates it. At the same time a lone pair of electrons on O atom of the -OH group is delocalized over to the ring, resulting in an increase in electron

density at the positions 2,4 and 6, which are actually *ortho* and *para* positions. Thus it activates through resonance effect. Since the resonance effect of the -OH group is stronger than its inductive effect, the net result is that -OH group activates the ring. Hence -OH group is activating, but *o*, *p*-directing.



Multiple Choice Questions

1. Which is the major product of the reaction:



Ans:(d)

2. Which of the following functional groups is not *ortho*, *para* directing and activating?

(a) -R (b) -OH (c) -NR₂ (d) -COR

Ans:(d)

3. If each of the following reagents are added to benzene only one of the them would react. Which reagent is the one that would react?

(a) O₃/Zn, H⁺ (b) hot KMnO₄ solution
(c) cold Br₂/CCl₄ solution (d) HI

Ans:(a)

4. The nucleophilic aromatic substitution reaction that can occur on a benzene ring is affected by the substituent group (s) present. Which one of the following statements describes such a substituents group and its effects.

(a) -COOH, electron releasing, activates the ring.
(b) -NO₂, stabilizes carbanion, activates the ring.
(c) -R, destabilizes carbanion, electron withdrawing.
(d) -CHO, destabilizes carbanion, deactivates the ring.

Ans:(b)

5. Which of the following statements concerning the Friedel-Crafts alkylation is not correct?

(a) It involves the use of a Lewis acid.
(b) It involves the introduction of an alkyl group into benzene ring.
(c) Both aryl and alkyl halides may be used to initiate the reaction with the aromatic compound.

(d) The reaction is referred to as an electrophilic aromatic substitution.

6. Which of the following groups below is considered to have a deactivating



Ans:(c)

effect during substitution?

- (a) -OH (b) -NH₂ (c) -CH₃ (d) -CN

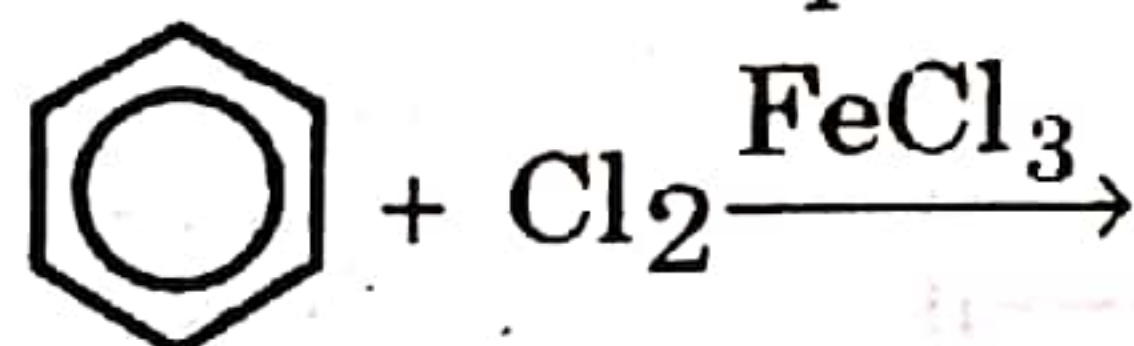
Ans:(d)

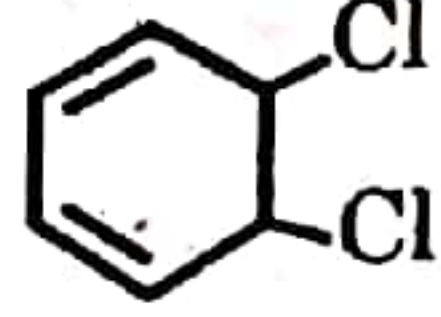
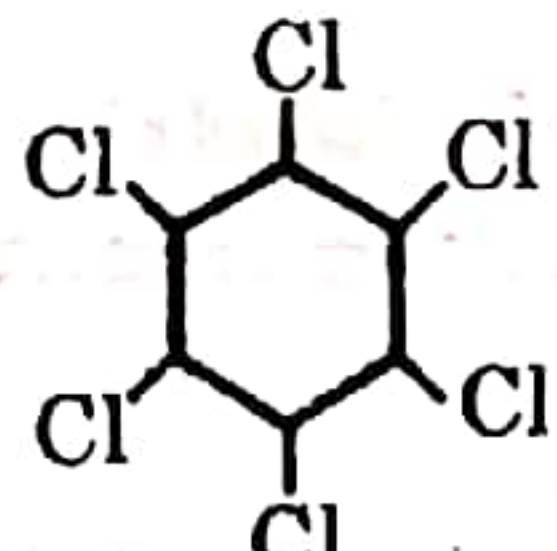
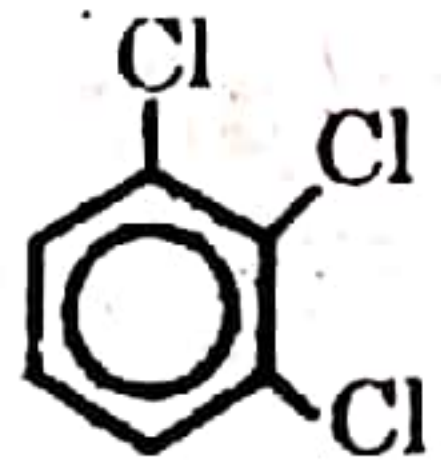
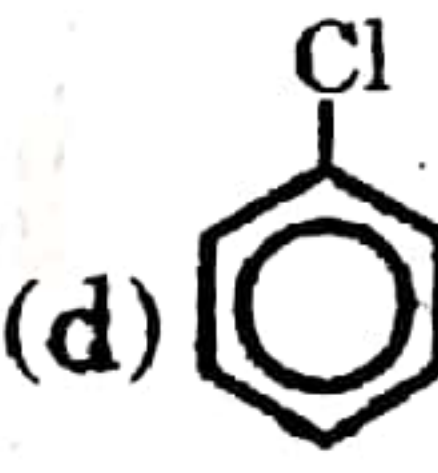
7. Which of the following is the most stable carbocation?

- (a) CH₃⁺ (b) (CH₃)₃C⁺ (c)  (d) 

Ans:(c)

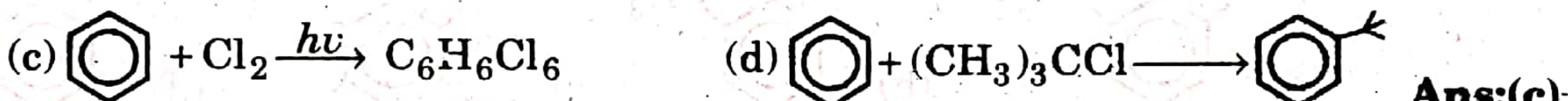
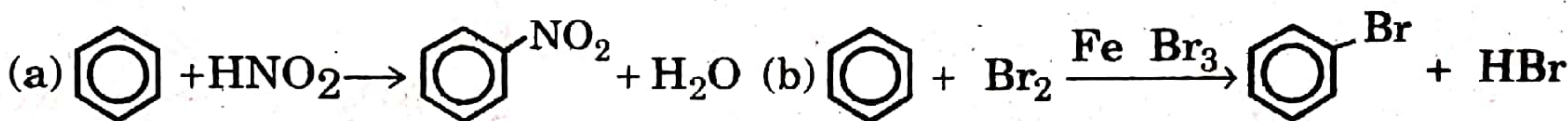
8. Which is the principal product of the given reaction?



- (a)  (b)  (c)  (d) 

Ans:(d)

9. Which of the following is not an example of electrophilic aromatic substitution



Ans:(c)

10. The electrophile in aromatic sulphonation is

- (a) H₂SO₄ (b) HSO₄⁻ (c) SO₃⁺ (d) SO₃

Ans:(d)

11. The nitrating species in aromatic nitration is:

- (a) HNO₃ (b) NO₃⁻ (c) NO₂⁺ (d) NO₂

Ans:(c)

12. Which of the following is the most reactive hydrocarbon?

- (a) Benzene (b) Anthracene
(c) Naphthalene (d) Phenanthrene

Ans:(b)

13. Which of the following is the most stable hydrocarbon

- (a) Benzene (b) Anthracene
(c) Naphthalene (d) Phenanthrene

Ans:(d)

14. Which of the following can accomplish Friedel-Crafts alkylation?

- (a) CH₃Cl (b) (CH₃)₂CHOH
(c) CH₃CH=CH₂ (d) All of the given:

Ans:(d)

15. Which positions of anthracene and phenanthrene are more reactive.

- (a) 1-and 2 (b) 1-and 9- (c) 9-and 10- (d) 2-and 9-

Ans:(c)

16. Which of the following substituents present on the benzene ring would not lead to meta orientation with deactivation?

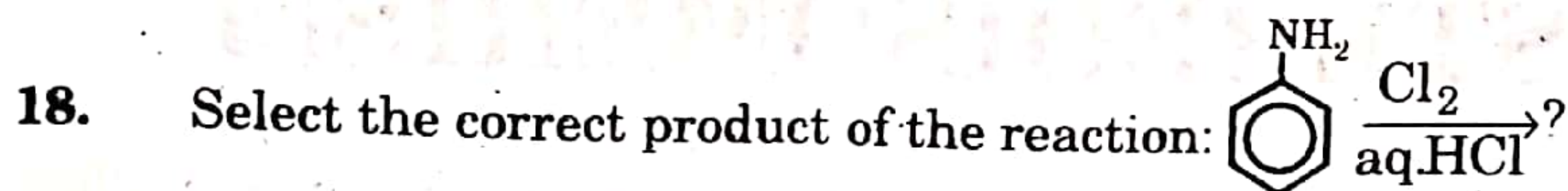
- (a) -NO₂ (b) -OH (c) -CHO (d) -COOH

Ans:(b)

17. During nitration, which of the following can form more than one product in significant yield?

- (a) *p*-nitrotoluene (b) Methoxyacetanilide
(c) *p*-dichlorobenzene (d) 1,3,5-trichlorobenzene.

Ans:(b)



- (a) *o*-chloroaniline (b) 2,6-dichloroaniline
 (c) 2,4,6-trichloroaniline (d) *p*-chloroaniline

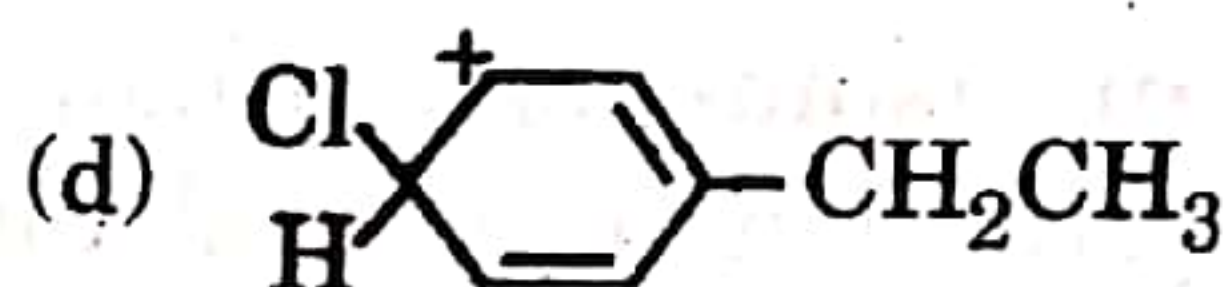
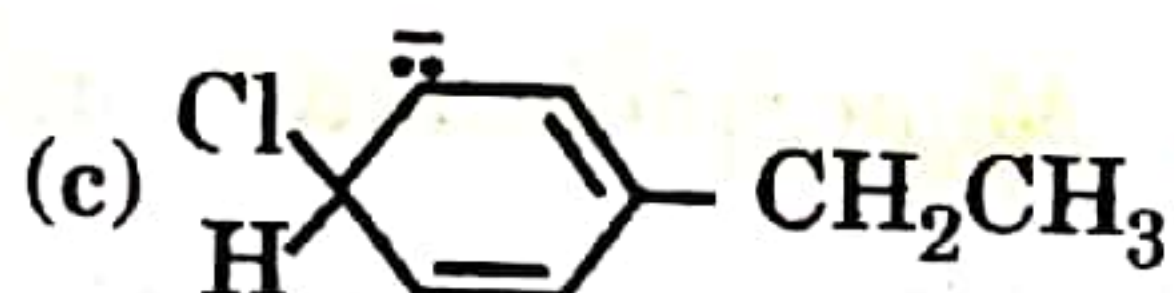
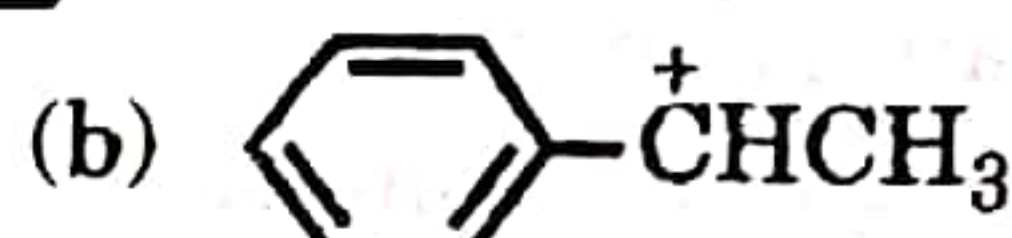
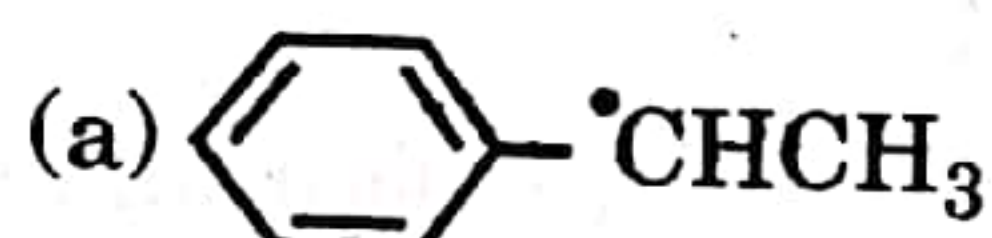
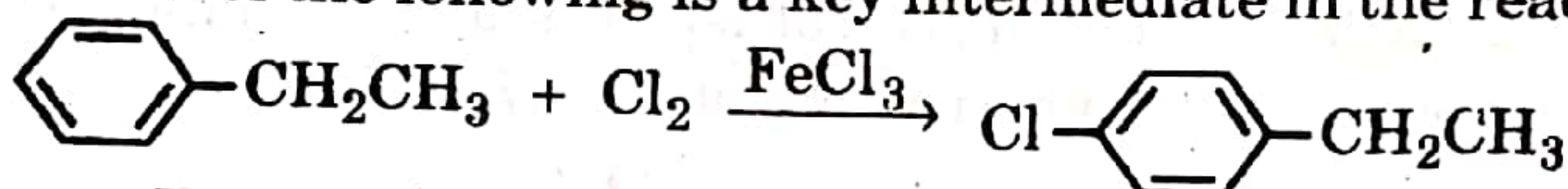
Ans:(c)

19. Which xylene gives 3 monobromo derivatives?

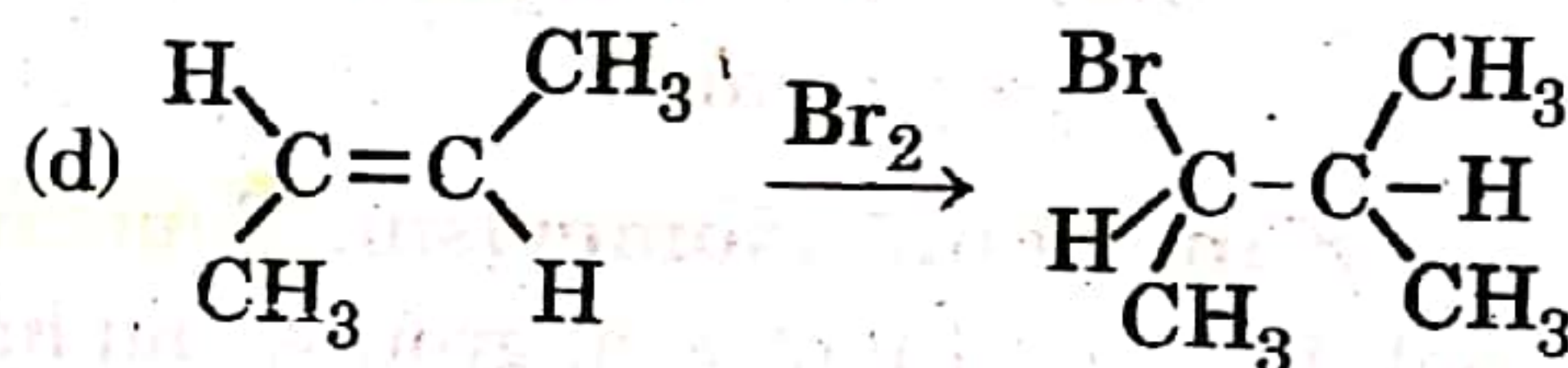
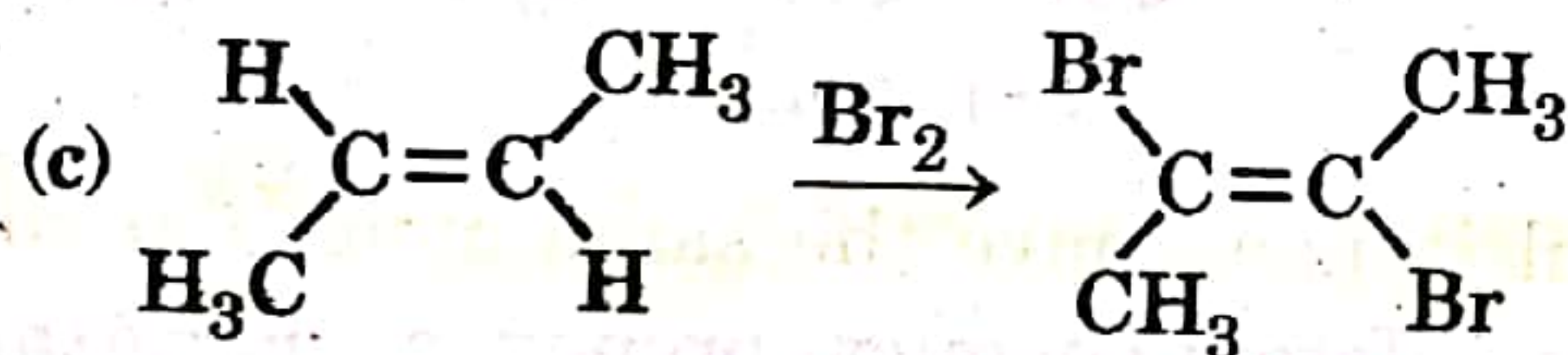
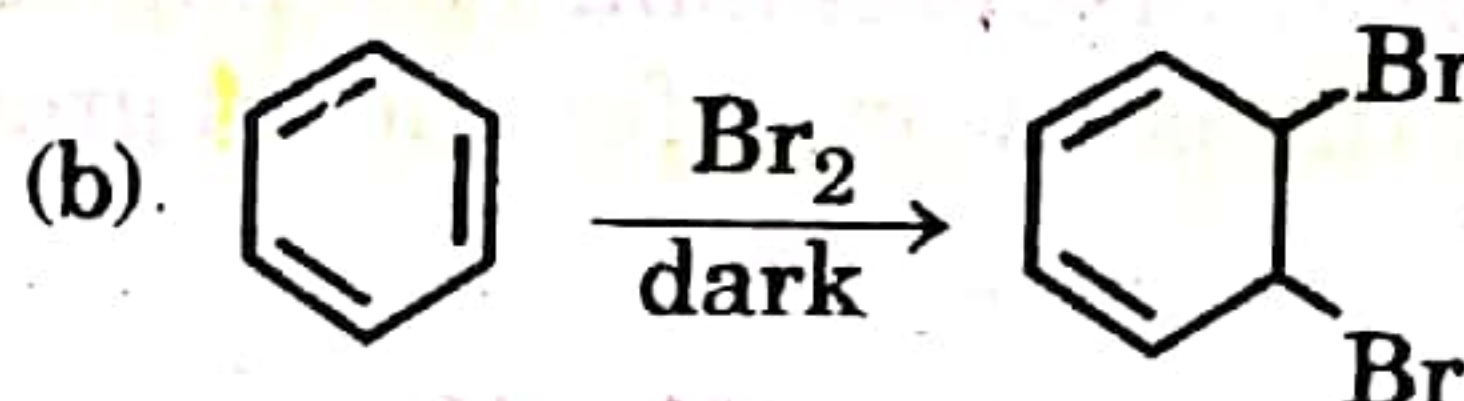
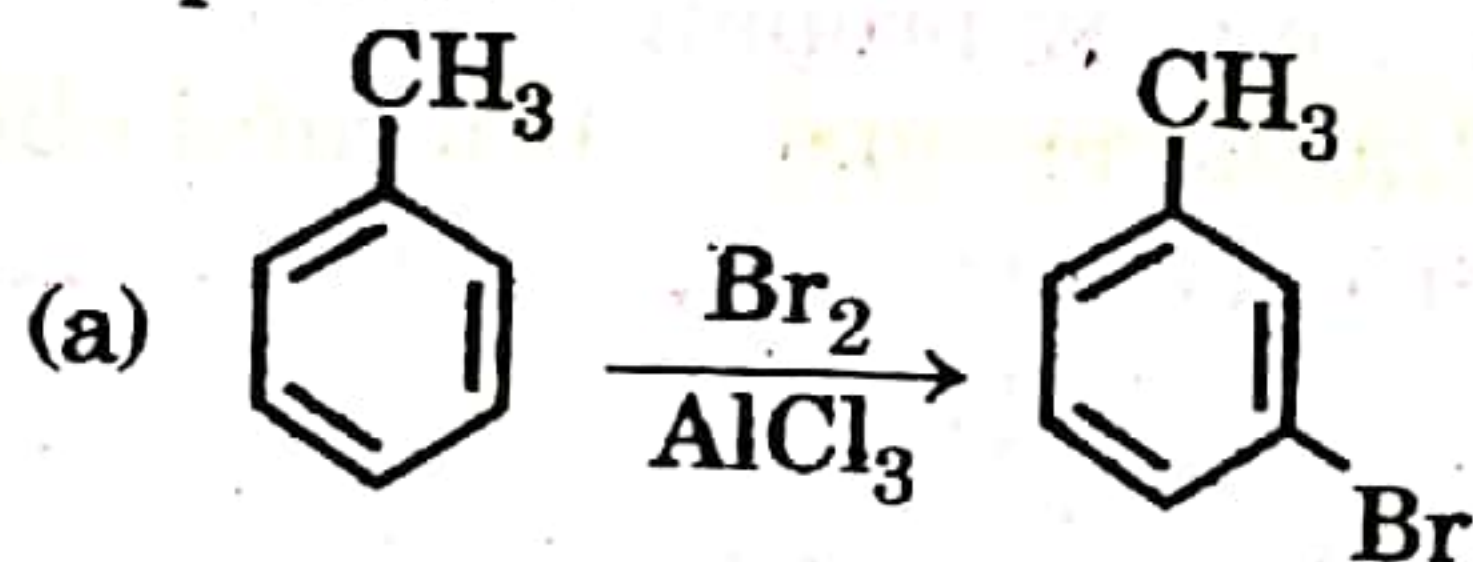
- (a) ortho xylene (b) meta xylene
 (c) para xylene (d) All of the above

Ans:(b)

20. Which of the following is a key intermediate in the reaction:



21. Which of the following reactions yield the indicated compound as a major product.



Ans: (d)

