

SUBJECT :PHARMACEUTICAL ORGANIC CHEMISTRY- II
II YEAR SEM I
FACULTY- V A N V HARITA

UNIT I

Benzene is one of the most commonly known aromatic compounds with chemical formula C_6H_6 .

Benzene is a naturally occurring substance produced by volcanoes and forest fires and present in many plants and animals, but benzene is also a major industrial chemical made from coal and oil.

Benzene is one of the organic and *simplest aromatic hydrocarbon* and the parent compound of which has about a numerous number of important aromatic compounds. The compound appears like a colourless liquid having a characteristic odour. This compound is primarily utilized for producing polystyrene. It is said to be highly toxic in nature and is also known as a carcinogen; which exposure to this may lead to leukemia.

Structure of Benzene

The structural representation of benzene is as shown in the figure below. The chemical formula for benzene is C_6H_6 , i.e it has 6 hydrogen- H atoms and six-carbon atoms and has an average mass of about 78.112. The structure has a six-carbon ring which is represented by a hexagon and it includes 3-double bonds. The carbon atoms are represented by a corner that is bonded to other atoms.

Benzene Ring Structure

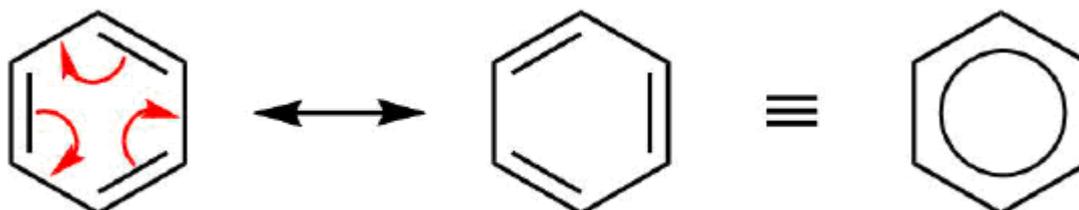
In benzene, the atoms are hydrogens. The double bonds within this structure are mainly separated by a single bond, hence this arrangement is recognized to have conjugated double bonds. A circle is used as an alternative symbol inside the hexagon that is used to represent six pi electrons.

Due to the chemical formula, benzene is categorized as a hydrocarbon. It is a compound consisting of only hydrogen and carbon atoms. The formulas and structure reveal benzene as a pure aromatic hydrocarbon, wherein it is also defined as a compound composing hydrogen & carbon having alternate double bonds in the form of the ring.

When benzene (C_6H_6) was first discovered its low hydrogen to carbon ratio (1:1) led chemists to believe it contained double or triple bonds. Since double and triple bonds rapidly add bromine (Br_2), this reaction was applied to benzene. Surprisingly, benzene was entirely unreactive toward bromine. In addition, if benzene is forced to react with bromine through the addition of a catalyst, it undergoes **substitution reactions** rather than the addition reactions that are typical of alkenes. These experiments suggested that the six-carbon benzene core is unusually stable to chemical modification.

The conceptual contradiction presented by a high degree of unsaturation (low H:C ratio) and high chemical stability for benzene and related compounds remained an unsolved puzzle for many years. Eventually, the presently accepted structure of benzene as a hexagonal, planar ring of carbons with alternating single and double bonds was adopted, and the exceptional chemical

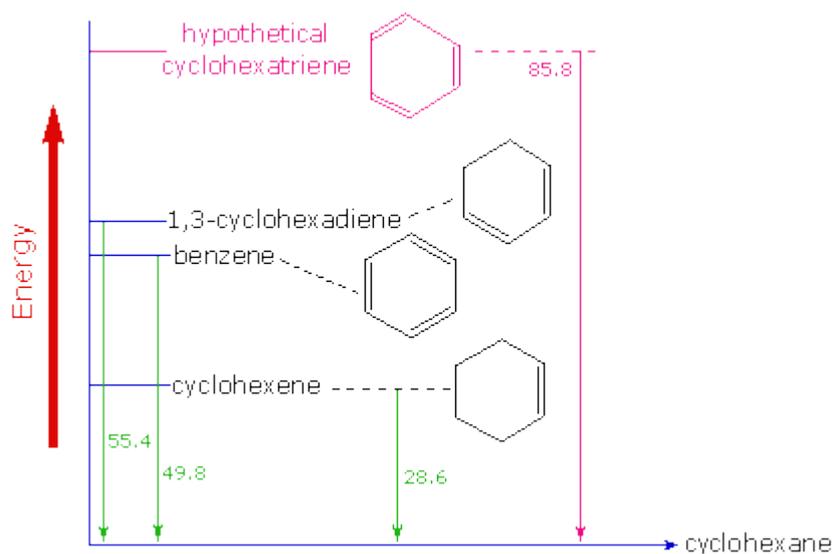
stability of this system was attributed to special resonance stabilization of the conjugated cyclic triene. No single structure provides an accurate representation of benzene as it is a combination of two structurally and energetically equivalent resonance forms representing the continuous cyclic conjugation of the double bonds. In the past, the benzene resonance hybrid was represented by a hexagon with a circle in the center to represent the benzene's pi-electron delocalization. This method has largely been abandoned because it does not show the pi electrons contained in benzene. Currently, the structure of benzene is usually represented by drawing one resonance form with the understanding that it does not completely represent the true structure of benzene.



The six-membered ring in benzene is a perfect hexagon with all carbon-carbon bonds having an identical length of 139 pm¹. The 139 pm bond length is roughly in between those of a C=C double bond (134 pm) and a C-C single (154 pm) which agrees with the benzene ring being a resonance hybrid made up of 1.5 C-C bonds. Each carbon in the benzene ring is sp² hybridized which makes all the C-C-C and H-C-C bond angles in benzene 120° and makes the overall molecule planar.

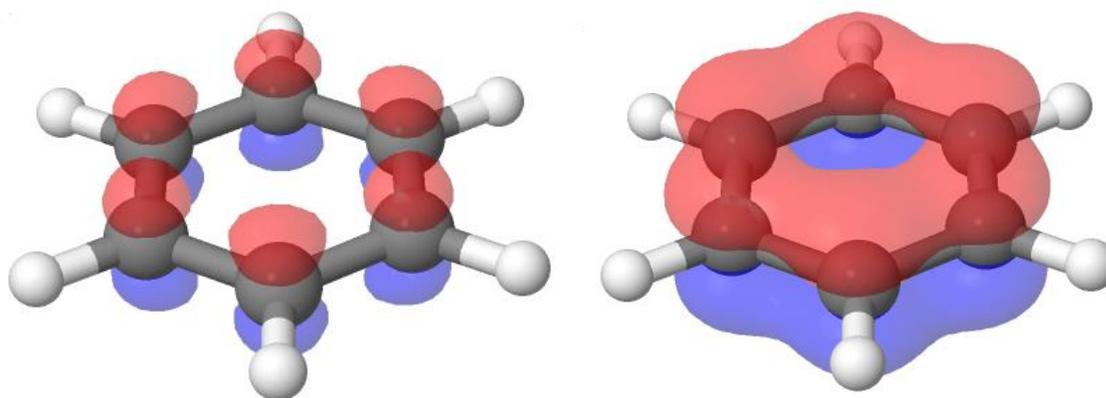
The High Stability of Benzene

In previous polyalkene, examples the electron delocalization described by resonance enhanced the stability of the molecule. However, benzene's stability goes beyond this. Evidence for the enhanced thermodynamic stability of benzene was obtained from measurements of the heat released when double bonds in a six-carbon ring are hydrogenated (hydrogen is added catalytically) to give cyclohexane as a common product. In the following diagram cyclohexane represents a low-energy reference point. Addition of hydrogen to cyclohexene produces cyclohexane and releases heat amounting to 28.6 kcal per mole. If we take this value to represent the energy cost of introducing one double bond into a six-carbon ring, we would expect a cyclohexadiene to release 57.2 kcal per mole on complete hydrogenation, and 1,3,5-cyclohexatriene to release 85.8 kcal per mole. These **heats of hydrogenation** would reflect the relative thermodynamic stability of the compounds. In practice, 1,3-cyclohexadiene is slightly more stable than expected, by about 2 kcal, presumably due to conjugation of the double bonds. **Benzene, however, is an extraordinary 36 kcal/mole more stable than expected.** This sort of stability enhancement is called **aromaticity** and molecules with aromaticity are called aromatic compounds. Benzene is the most common aromatic compound but there are many others. Aromatic stabilization explains benzene's lack of reactivity compared to typical alkenes.



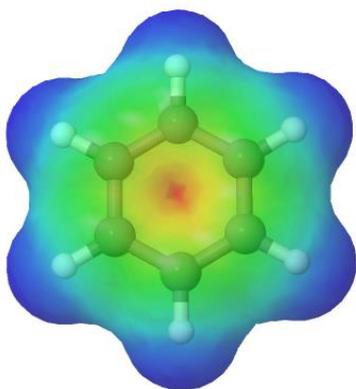
Atomic Orbitals of Benzene

Also, each of benzene's six carbon atoms are sp^2 hybridized and have an unhybridized p orbital perpendicular to plane of the ring. Because each of the six carbon atoms and their corresponding p orbitals are equivalent, it is impossible for them to only overlap with one adjacent p orbital to create three defined double bonds. Instead each p orbital overlaps equally with both adjacent orbitals creating a cyclic overlap involving all six p orbitals. This allows the p orbitals to be delocalized in molecular orbitals that extend all the way around the ring allowing for more overlap than would be obtained from the linear 1,3,5-hexatriene equivalent. For this to happen, of course, the ring must be planar – otherwise the p orbitals couldn't overlap properly and benzene is known to be a flat molecule. An electrostatic potential map of benzene, shown below, shows that the π electrons are evenly distributed around the ring and that every carbon equivalent.



Each carbon in the benzene ring is sp^2 hybridized with a p orbital perpendicular to the ring plane (Left)

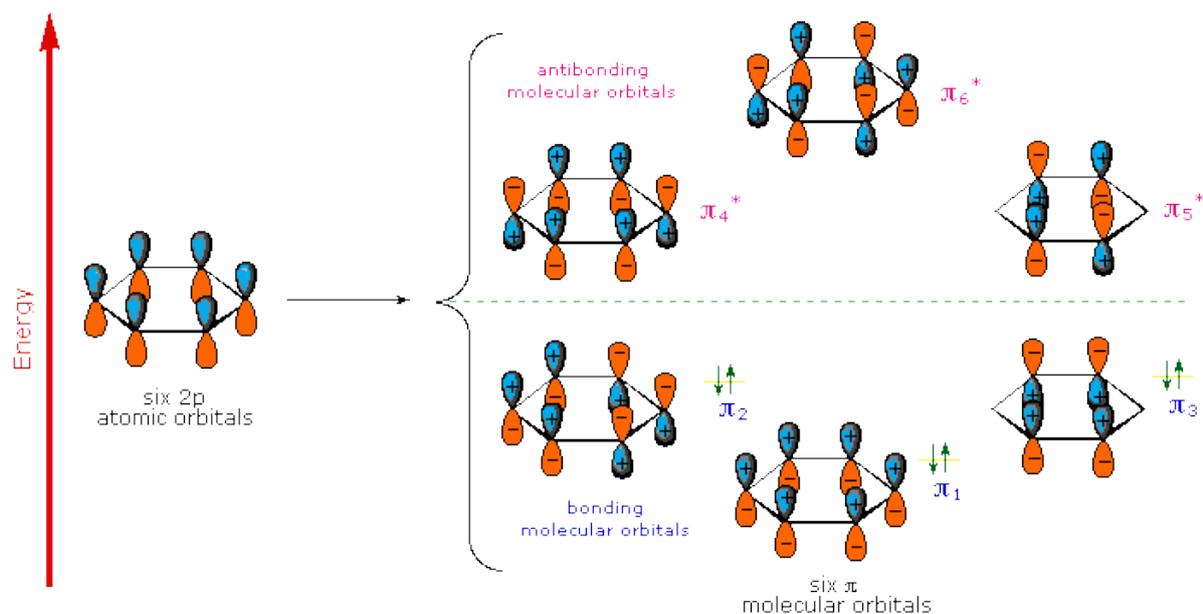
Being planar and cyclic allows benzene's p orbitals to undergo cyclic overlap (Right)



An electrostatic potential map of benzene

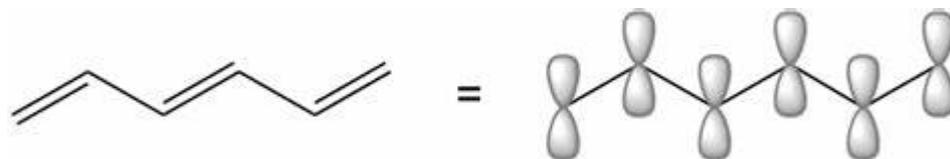
The Molecular Orbitals of Benzene

A molecular orbital description of benzene provides a more satisfying and more general treatment of "aromaticity". We know that benzene has a planar hexagonal structure in which all the carbon atoms are sp^2 hybridized, and all the carbon-carbon bonds are equal in length. As shown below, the remaining cyclic array of six p-orbitals (one on each carbon) overlap to generate six molecular orbitals, three bonding and three antibonding. The plus and minus signs shown in the diagram do not represent electrostatic charge, but refer to phase signs in the equations that describe these orbitals (in the diagram the phases are also color coded). When the phases correspond, the orbitals overlap to generate a common region of like phase, with those orbitals having the greatest overlap (e.g. π_1) being lowest in energy. The remaining carbon valence electrons then occupy these molecular orbitals in pairs, resulting in a fully occupied (6 electrons) set of bonding molecular orbitals. It is this completely filled set of bonding orbitals, or **closed shell**, that gives the benzene ring its thermodynamic and chemical stability, just as a filled valence shell octet confers stability on the inert gases.

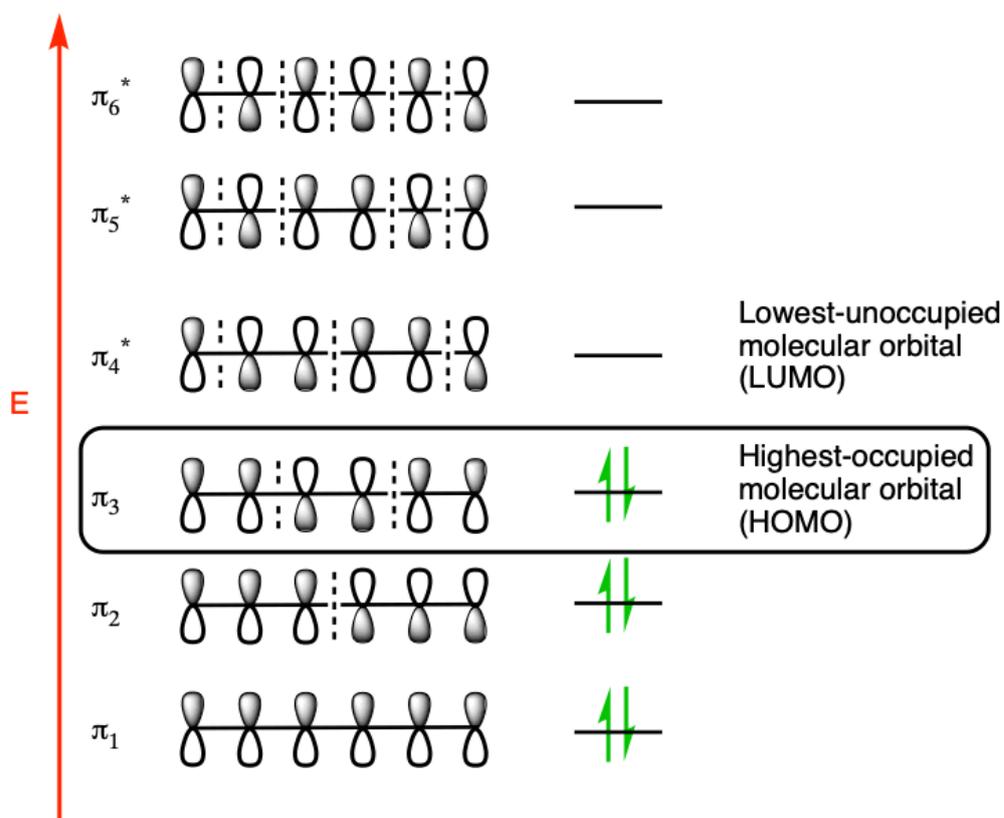


To better see source of the stabilizing aromaticity effect created by the cyclic p orbitals of benzene, the molecular orbitals of 1,3,5-hexatriene must be investigated. The molecule 1,3,5-

hexatriene contains six p orbitals which all overlap but in a linear fashion. As with benzene, this overlap creates 3 stabilized bonding molecular which are completely filled with six p electron. As expected, the conjugation creates a marked increase of stability in 1,3,5-hexatriene but not as much as in benzene.



The Pi Molecular Orbitals Of 1,3,5 Hexatriene



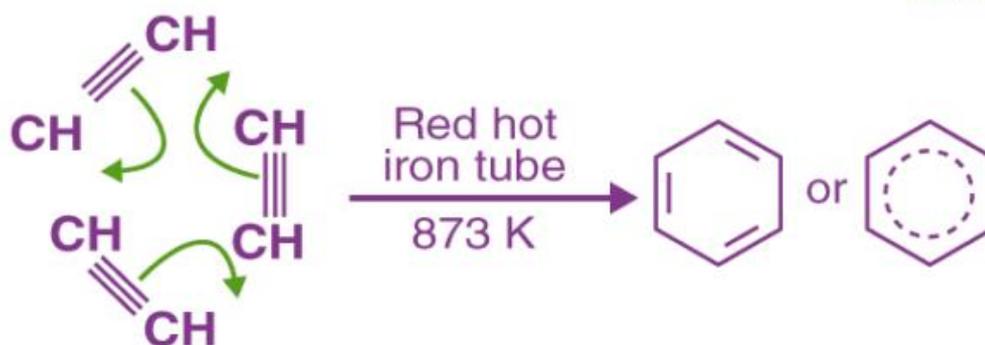
The main difference in stability can be seen when comparing the lowest energy molecular orbital of 1,3,5-hexatriene and benzene: π_1 . In π_1 molecular orbital of 1,3,5-hexatriene there are 5 stabilizing bonding interactions where there are 6 stabilizing bonding interactions in the π_1 of benzene. The sixth bonding interaction is made possible by benzene's p orbitals being in a ring. Because benzene's π_1 molecular orbital has more stabilizing bonding interactions it is lower in energy than the π_1 molecular orbital of 1,3,5-hexatriene. This gives benzene the additional aromatic stability not seen in the acyclic 1,3,5-hexatriene.

The π_1 molecular orbital of benzene (Left) has 6 stabilizing bonding interaction

where 1,3,5-hexatriene's (Right) only has 5

Preparation of benzene from alkynes

Benzene is prepared from ethyne by the process of cyclic polymerization. In this process, Ethyne is passed through a red-hot iron tube at 873 K. The ethyne molecule then undergoes cyclic polymerization to form benzene.

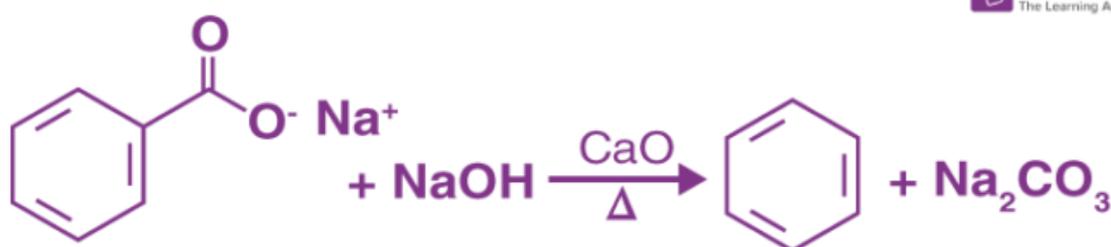


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Preparation of benzene from aromatic acids

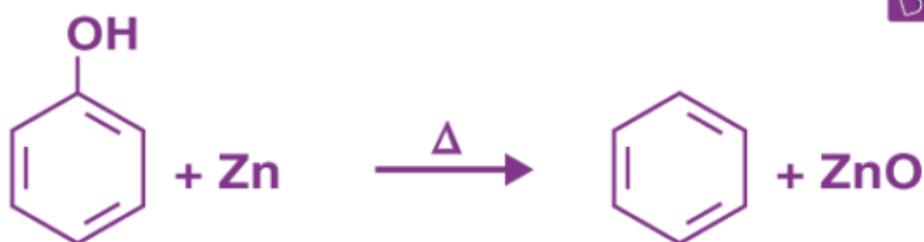
Benzene can be prepared from aromatic acids through decarboxylation reaction. In this process, the sodium salt of the benzoic acid (sodium benzoate) is heated with soda lime to produce benzene along with sodium carbonate.



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Preparation of benzene from phenol

Benzene can be prepared from phenols too through their reduction. In this process vapours of phenol are passed over heated zinc dust. Zinc dust reduces them to form benzene.



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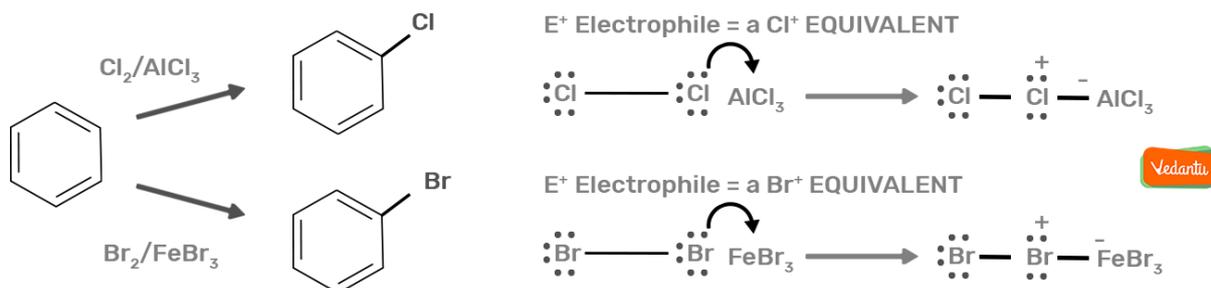
Preparation of benzene from sulphonic acids

Benzene can be prepared from sulphonic acids through their hydrolysis. In this process Benzene sulphonic acid is exposed to superheated steam leading to the formation of benzene.



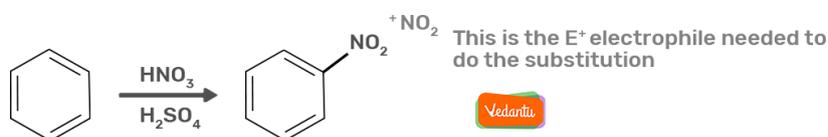
Various Chemical Reactions of Benzene

1. Halogenation of Benzene



By the means of electrophilic aromatic substitution reaction, one hydrogen atom of the arene is substituted by one halogen atom. The reactions mentioned above belong to the category of halogenation reaction. Here we will try to understand the mechanism of the reaction. This reaction is carried out in the presence of a Lewis acid catalyst. Lewis acid is nothing but an electron pair acceptor and the electrons are essentially nonbonding ones.

2. Nitration of Benzene



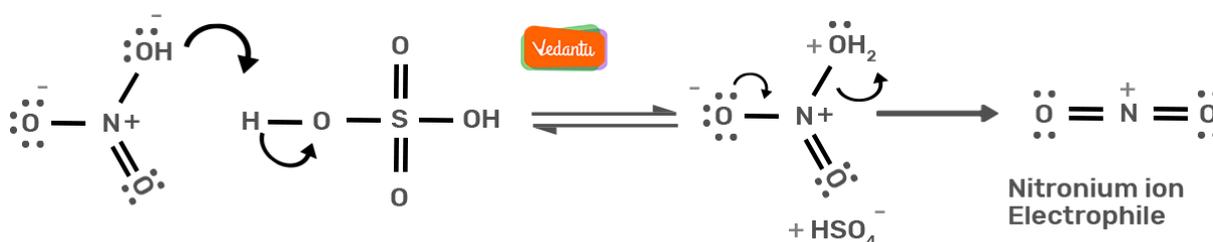
In the reaction nitration of benzene, benzene is treated with a mixture of concentrated nitric acid and concentrated sulfuric acid at a temperature which is not more than 50°C. With the increase in temperature, there is more chance of producing more than one nitro group, -NO₂, that gets substituted onto the ring and results in the formation of Nitrobenzene. The concentrated sulfuric acid acts as a catalyst in this reaction. The "nitronium ion" or the "nitryl cation", NO₂⁺ is the electrophile here. This is produced by the reaction between the nitric acid and the sulphuric acid.

Applications of Nitrobenzene

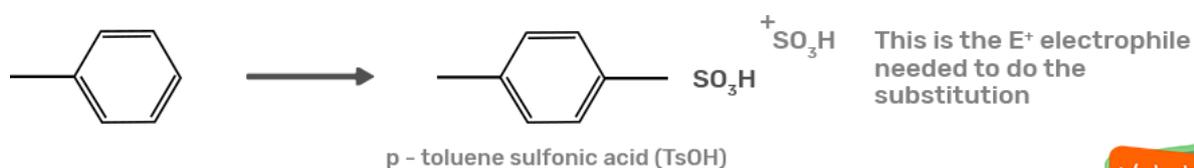
Nitrobenzene is widely used in manufacturing of the chemical, aniline. It finds its application in lubricating oils used in motors and machines. It is also used in manufacturing of dyes, drugs, pesticides, and synthetic rubber.

3. Sulfonation of Benzene

Sulfonation of benzene includes an electrophilic substitution reaction that occurs between benzene and sulfuric acid. There are two equivalent ways of sulfonating benzene:

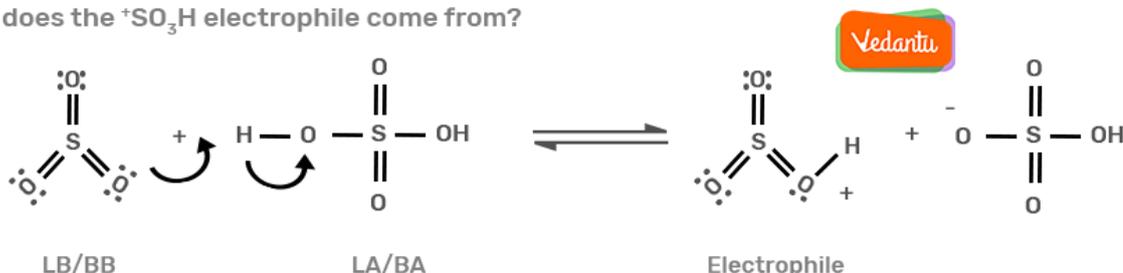


The first way involves heating of benzene under reflux of concentrated fuming sulfuric acid for several hours at 40°C. The product formed is benzenesulfonic acid. The electrophile here is actually sulfur trioxide, SO₃. The sulfur trioxide electrophile can be manufactured in one of the two ways depending on which sort of acid is being used. It can be produced from slight dissociation of concentrated sulfuric acid containing traces of SO₃.

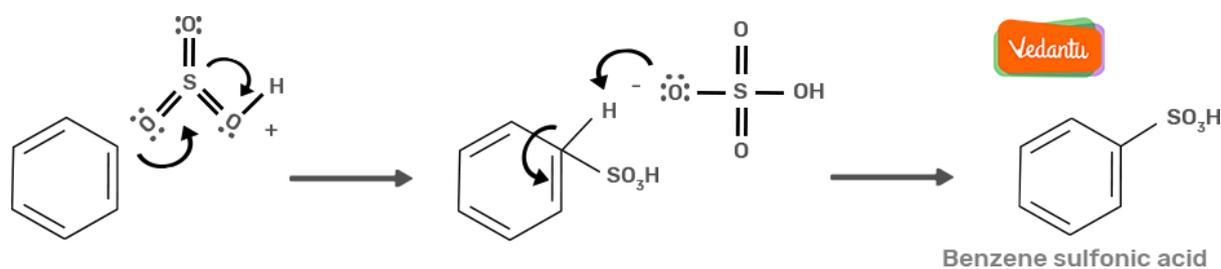




Where does the $^+\text{SO}_3\text{H}$ electrophile come from?



Fuming sulfuric acid, $\text{H}_2\text{S}_2\text{O}_7$, can be considered as a solution of SO_3 in sulfuric acid - and thus it is a much richer source of the SO_3 . Sulfur trioxide is electrophilic in nature because it is a highly polar molecule with a fair amount of positive charge on the sulfur atom. It is this that gets attracted to the ring electrons. The reaction that occurs can be shown as:

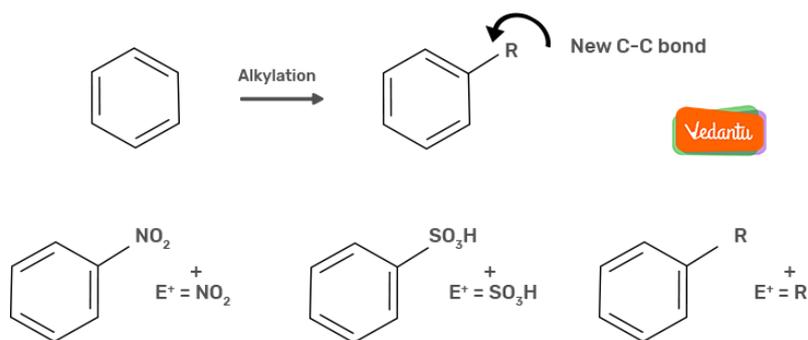


Applications of Halogenation of Benzene

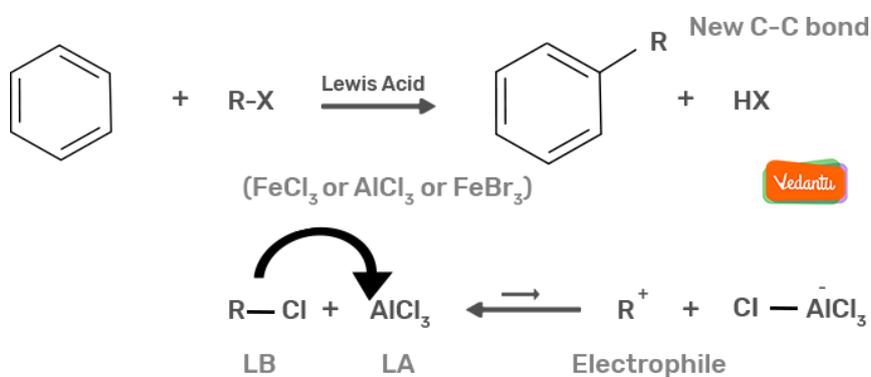
Benzenesulfonic acid is used as an acid catalyst and to standardise dyes. A variety of pharmaceutical drugs are prepared as benzenesulfonate salts and are known as besylates or besylates.

4. Alkylation and Acylation of Benzene

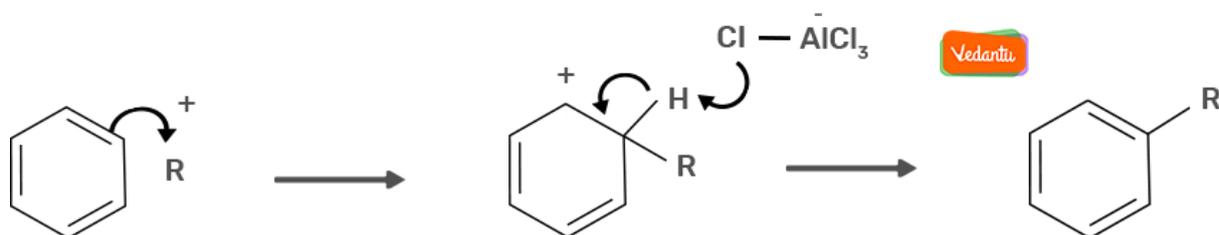
This reaction is popularly known as Friedel-Crafts reaction. The reactivity of haloalkanes gradually increases as you move up the periodic table and polarity also increases. This means that the reactivity of an RF haloalkane is maximum followed by the reactivity of RCl then RBr and finally RI . This denotes that the Lewis acids used as catalysts in Friedel-Crafts Alkylation reactions tend to have similar halogen combinations such as BF_3 , SbCl_5 , AlCl_3 , SbCl_5 , and AlBr_3 , all of which are commonly used in these reactions.

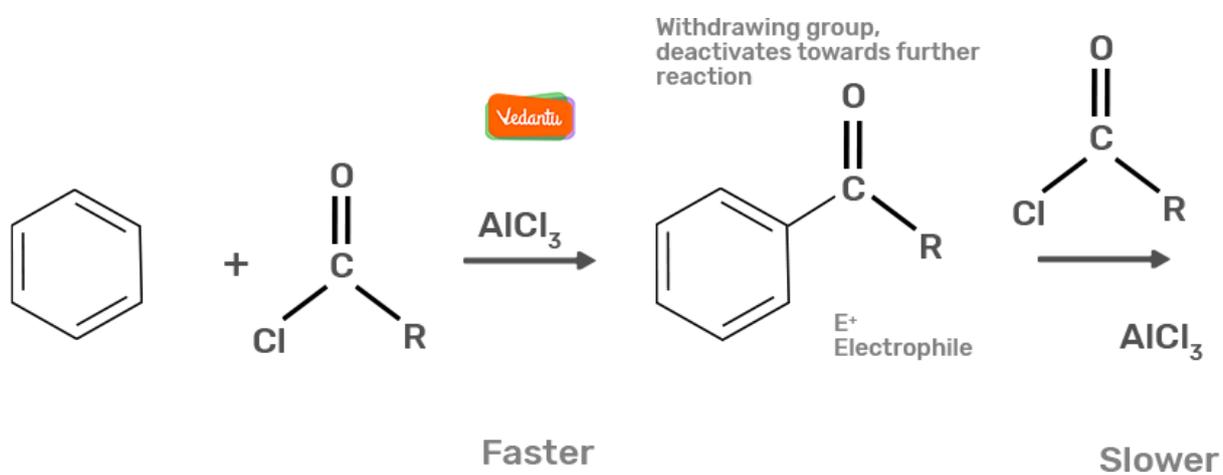
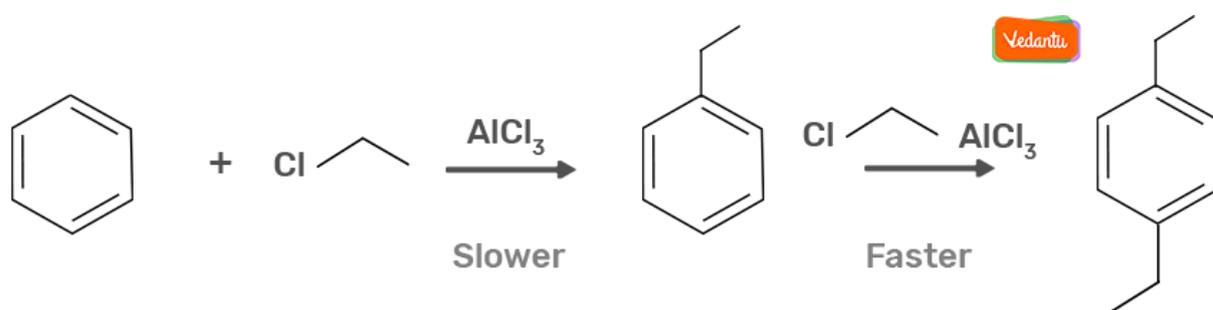
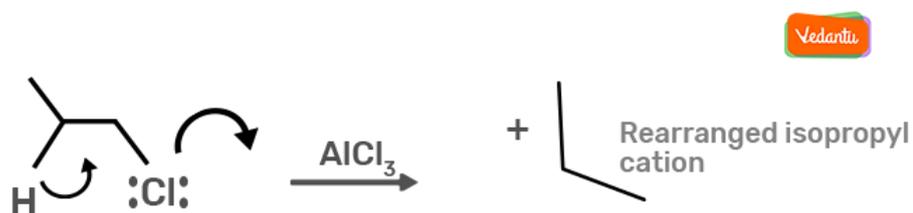
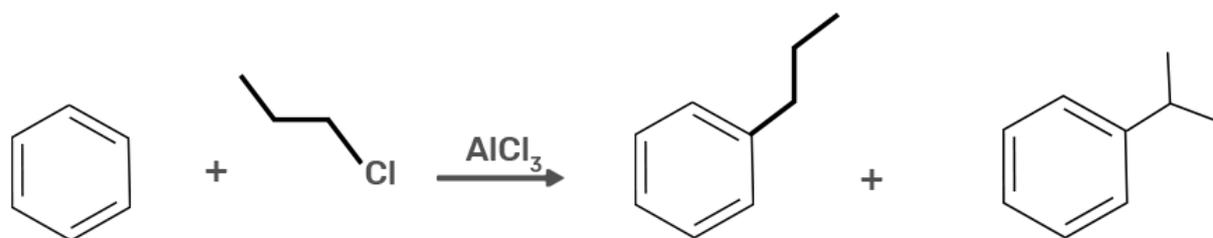
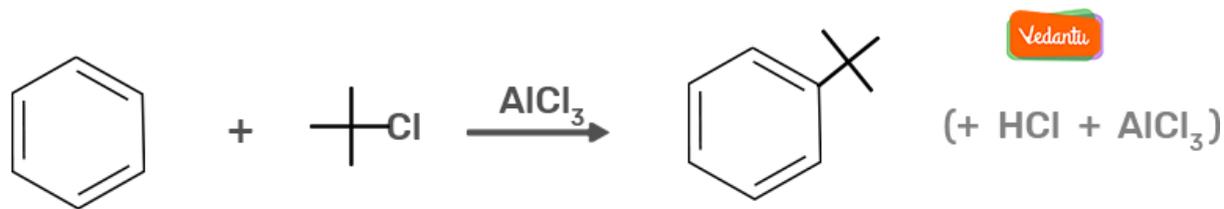


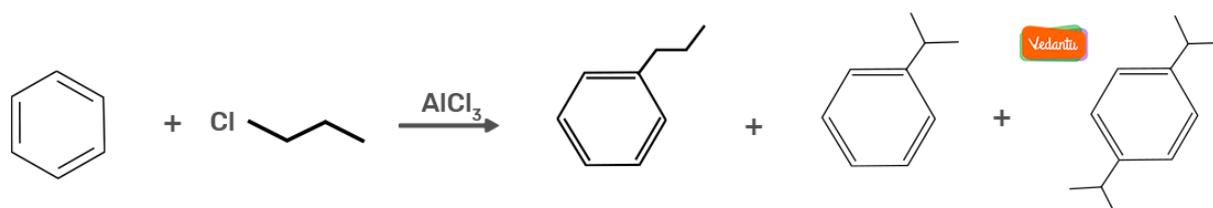
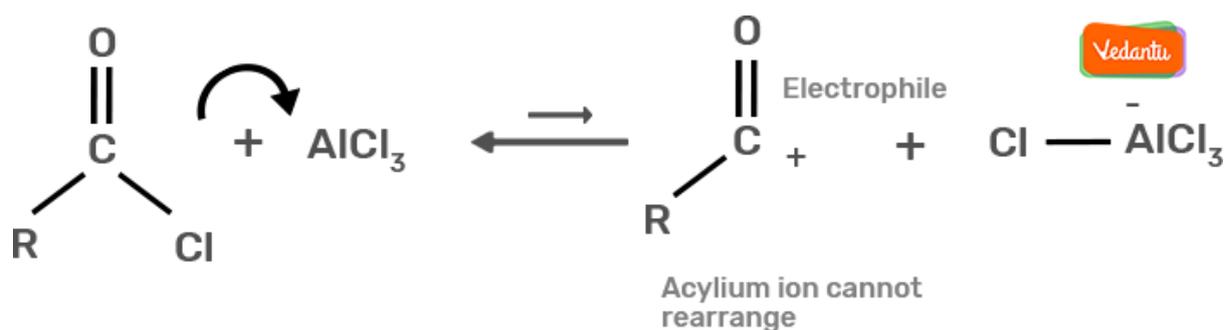
In 1877, the below-mentioned procedure was used to produce alkyl halide but was accompanied by some unwanted supplemental activity that hampered its effectiveness.



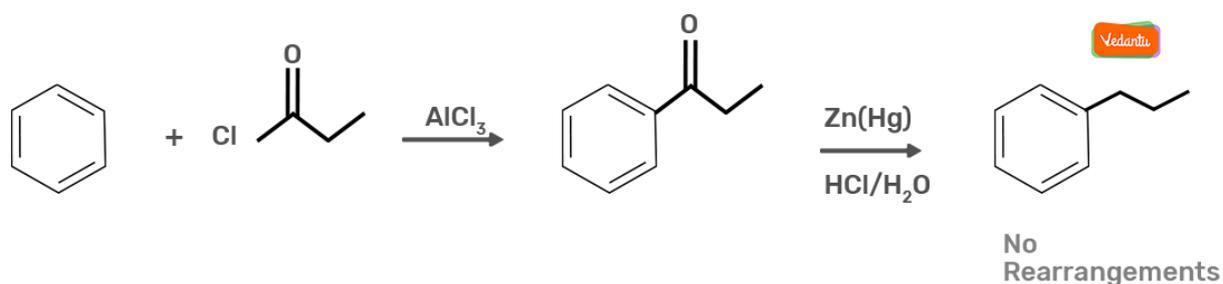
As a remedy to these limitations, a new and improved reaction was devised: The Friedel-Crafts Acylation, also known as Friedel-Crafts Alkanoylation.



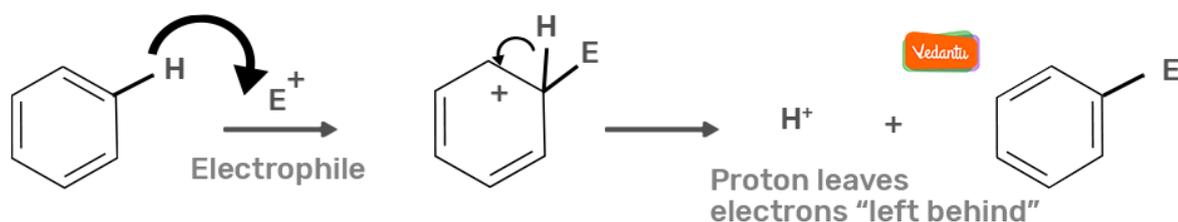




The very first step begins with the formation of the acylium ion that reacts with benzene in the consequent stage. The second step is about the attack of the acylium ion on benzene as a new electrophile that results in one complex structure. The third step involves the removal of the proton in order to ensure that aromaticity returns to benzene. During the third step, AlCl_4 comes back to remove a proton from the benzene ring, thus enabling the ring to return to its aromaticity. In doing so, the original AlCl_3 is regenerated for re-use, along with HCl . Ketone is produced as the first final product of the reaction. This first part of the product is a complex one with aluminum chloride. The final step includes the addition of water to release the final product as the acylbenzene:



Because the acylium ion (as was shown in the first step) is stabilized due to resonance, no rearrangement takes place here (Limitation of this reaction). Also, due to the deactivation of the product, it is no longer prone to electrophilic attack and hence, no longer further reactions will be initiated (another Limitation). However, Friedel-Crafts Acylation may fail with strong deactivating rings.

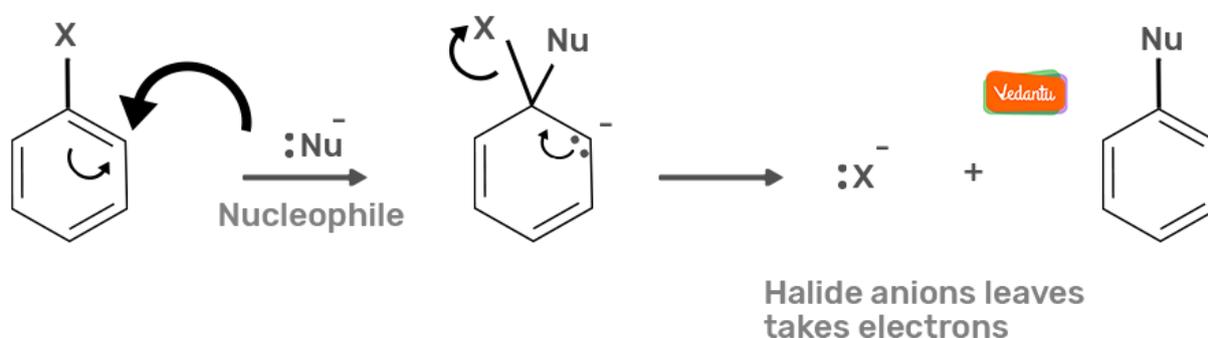


But this alkylation has a couple of drawbacks. These drawbacks include:

1. There are chances of rearrangements
2. The probability of multiple additions can't also be ignored
3. This is not applicable for benzenes with multiple electron-withdrawing groups.

To counter these issues, a Friedel Craft Acylation was introduced. This method of acylation solves the first two problems.

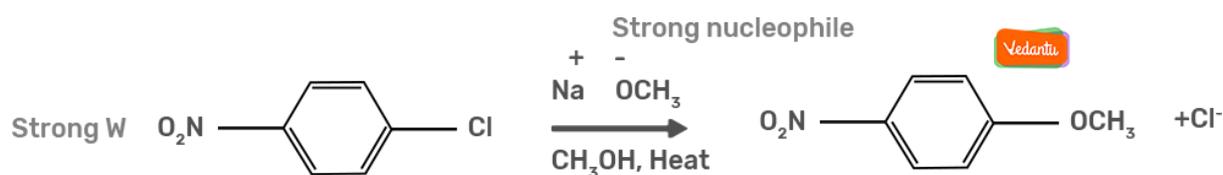
5. Nucleophilic Aromatic Substitution



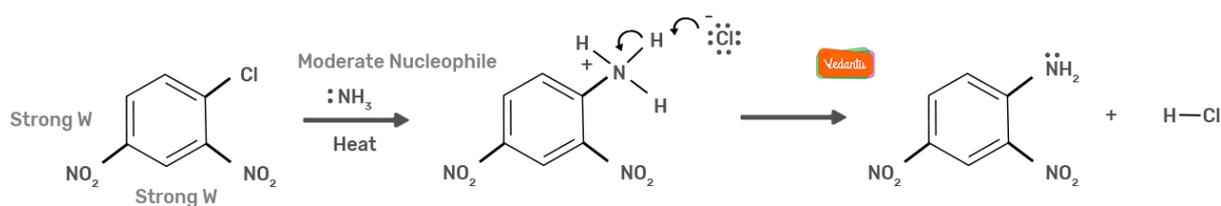
A nucleophilic aromatic substitution involves the substitution reaction where the nucleophile relocates a strong leaving group, like a halide, on an aromatic ring. This reaction mainly follows either of the two mechanisms:

- A. Addition-elimination reaction or
- B. Elimination-addition reaction

The basic principle for this reaction can be stated in the manner where the substituted H atoms "leaves" in the form of a proton, and formally the electrons in the C-H bond are "left behind" and there is a need to complete the bonding with the electron deficient electrophile.



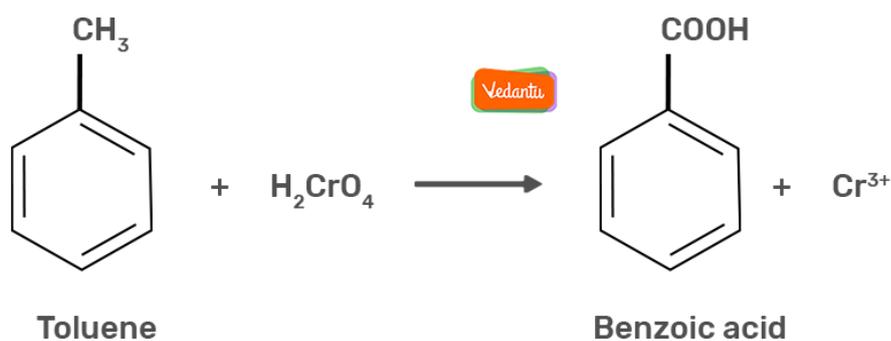
When a nucleophile substitutes, fails to do the replacement for a hydrogen, since the electrons are also supposed to "leave" (the nucleophile brings its own electrons in the form of the hydride anion H^-) there is a need for a better leaving group that can "take" the electrons, need a conventional leaving group such as halide. Electrons are very poor leaving groups.



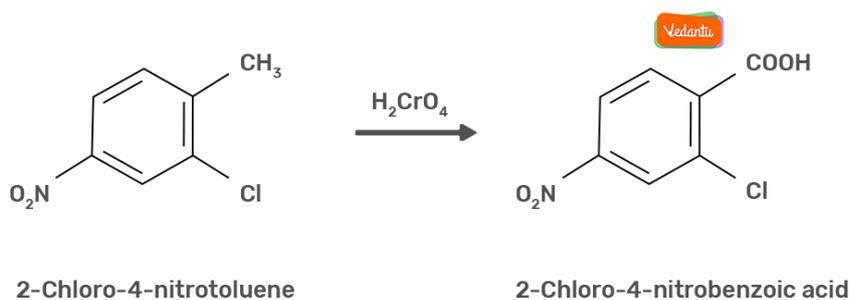
Benzylic Position and Its Impact on Benzene Reactivity

The benzene's aromaticity is responsible for its resistance towards many of the reactions that alkenes typically can take part. However, chemists have found out ways to react benzene following various other methodologies. We begin our discussion of benzene reactions with processes that occur not on the ring directly, but at the carbon immediately bonded to the benzene ring, more accurately called the benzylic carbon.

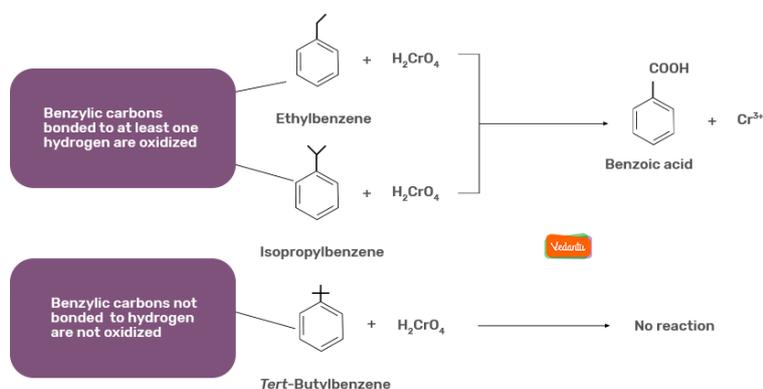
The strong oxidizing agents, such as H_2CrO_4 and KMnO_4 can't even make an impact on benzene. When toluene is treated with these oxidizing agents under extreme conditions, the side-chain methyl group is oxidized to a carboxyl group producing the main byproduct benzoic acid.



The oxidation of the methyl group keeping the aromatic ring unaffected makes it evident that the aromatic ring is extremely stable. Halogen and nitro substituents on an aromatic ring even remain unaffected by these oxidations. For example, chromic acid oxidizes 2-chloro-4-nitrotoluene to produce 2-chloro-4-nitrobenzoic acid. But here as well the nitro and chloro group remain unaffected.



These conditions also allow the oxidation of Ethylbenzene and isopropylbenzene to benzoic acid. Again, the side chain of tert-butylbenzene, devoid of benzylic hydrogen, is unaffected by these oxidizing conditions.



If benzylic hydrogen exists, then the benzylic carbon gets oxidized to a carboxyl group and there is the removal of all other carbons of the side chain. If no benzylic hydrogen is present, as in the case of tert-butylbenzene, then the oxidation of the side chain also does not happen.

Orientation Effects in Substituted Benzenes

Substituted rings are divided into two groups based on the type of the substituent that the ring carries:

- **Activated rings:** the substituents on the ring are groups that donate electrons.
- **Deactivated rings:** the substituents on the ring are groups that withdraw electrons.

Introduction

Examples of activating groups in the relative order from the most activating group to the least activating:

$-\text{NH}_2, -\text{NR}_2 > -\text{OH}, -\text{OR} > -\text{NHCOR} > -\text{CH}_3$ and other alkyl groups

with R as alkyl groups ($\text{C}_n\text{H}_{2n+1}$)

Examples of deactivating groups in the relative order from the most deactivating to the least deactivating:

$-\text{NO}_2, -\text{CF}_3 > -\text{COR}, -\text{CN}, -\text{CO}_2\text{R}, -\text{SO}_3\text{H} > \text{Halogens}$

with R as alkyl groups ($\text{C}_n\text{H}_{2n+1}$)

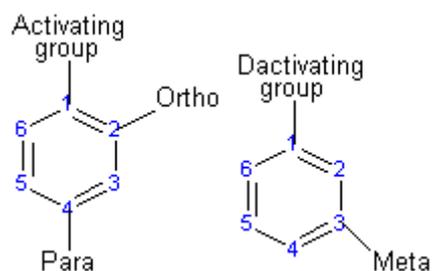
The order of reactivity among Halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:

$\text{F} > \text{Cl} > \text{Br} > \text{I}$

The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen groups, follows the order of electronegativity. The ring that is substituted with the most electronegative halogen is the most reactive ring (less deactivating substituent) and the ring that is substituted with the least electronegative halogen is the least reactive ring (more deactivating substituent), when we compare rings with halogen substituents. Also the size of the halogen affects the reactivity of the benzene ring that the halogen is attached to. As the size of the halogen increase, the reactivity of the ring decreases.

The direction of the reaction

The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4. The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.

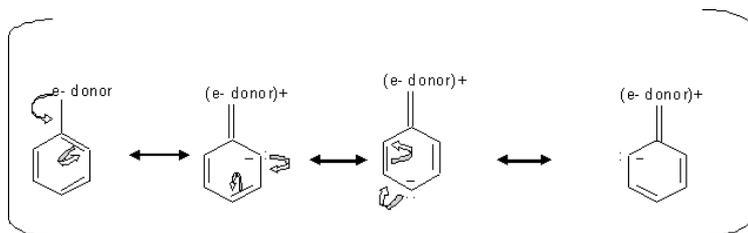


Substituents determine the reaction direction by resonance or inductive effect

Resonance effect is the conjugation between the ring and the substituent, which means the delocalizing of the π electrons between the ring and the substituent. Inductive effect is the withdraw of the sigma (the single bond) electrons away from the ring toward the substituent, due to the higher electronegativity of the substituent compared to the carbon of the ring.

Activating groups (ortho or para directors)

When the substituents like -OH have an unshared pair of electrons, the resonance effect is stronger than the inductive effect which make these substituents stronger activators, since this resonance effect direct the electron toward the ring. In cases where the substituents is esters or amides, they are less activating because they form resonance structure that pull the electron density away from the ring.

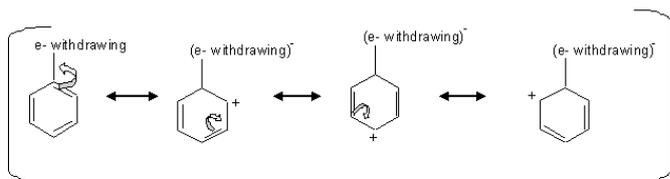


By looking at the mechanism above, we can see how groups donating electron direct the ortho, para electrophilic substitution. Since the electrons localinn transfer between the ortho and para carbons, then the electrophile prefer attacking the carbon that has the free electron.

Inductive effect of alkyl groups activates the direction of the ortho or para substitution, which is when s electrons gets pushed toward the ring.

Deactivating group (meta directors)

The deactivating groups deactivate the ring by the inductive effect in the presence of an electronegative atom that withdraws the electrons away from the ring.



we can see from the mechanism above that when there is an electron withdraw from the ring, that leaves the carbons at the ortho, para positions with a positive charge which is unfavorable for the electrophile, so the electrophile attacks the carbon at the meta positions.

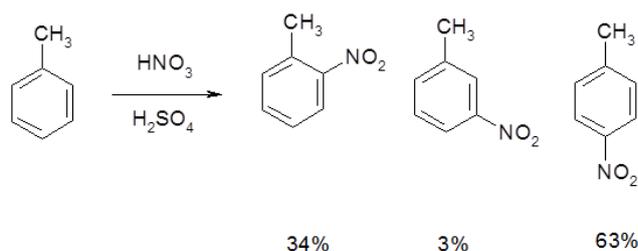
Halogens are an exception of the deactivating group that directs the ortho or para substitution. The halogens deactivate the ring by inductive effect not by the resonance even though they have an unpaired pair of electrons. The unpaired pair of electrons gets donated to the ring, but the inductive effect pulls away the s electrons from the ring by the electronegativity of the halogens.

Substituents determine the reactivity of rings

The reaction of a substituted ring with an activating group is faster than benzene. On the other hand, a substituted ring with a deactivated group is slower than benzene.

Activating groups speed up the reaction because of the resonance effect. The presence of the unpaired electrons that can be donated to the ring, stabilize the carbocation in the transition state. Thus; stabilizing the intermediate step, speeds up the reaction; and this is due to the decrease of the activating energy. On the other hand, the deactivating groups, withdraw the electrons away from the carbocation formed in the intermediate step, thus; the activation energy is increased which slows down the reaction.

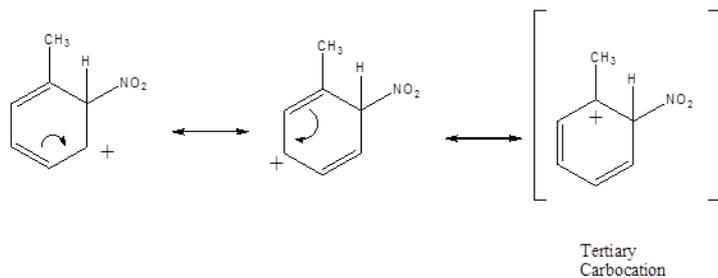
The CH_3 Group is an ortho, para Director



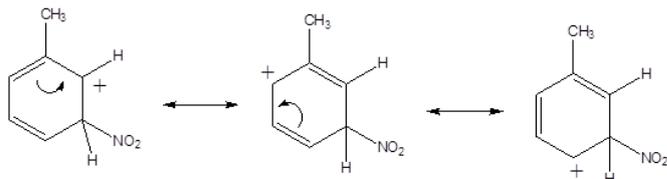
Alkyl groups are Inductive activators

With o/p attack the form a tertiary arenium carbocation which speeds up the reaction

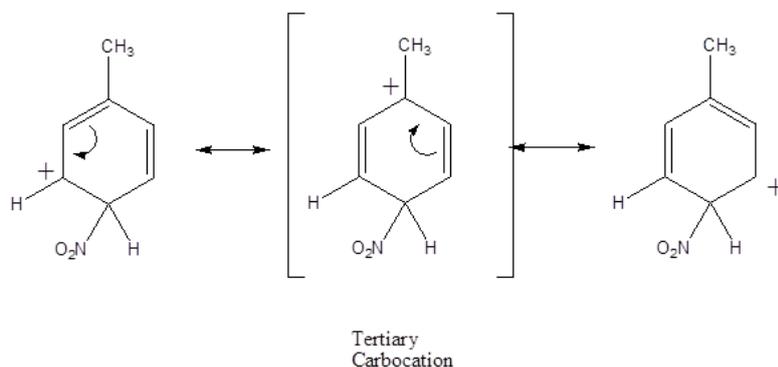
Ortho Attack



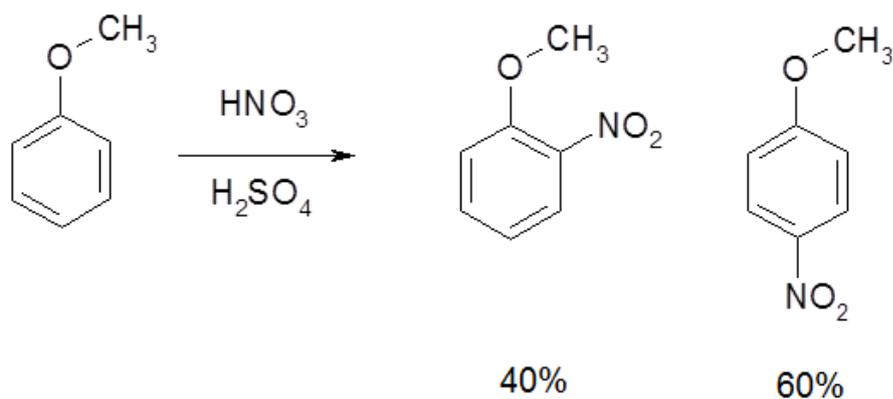
Meta Attack



Para Attack

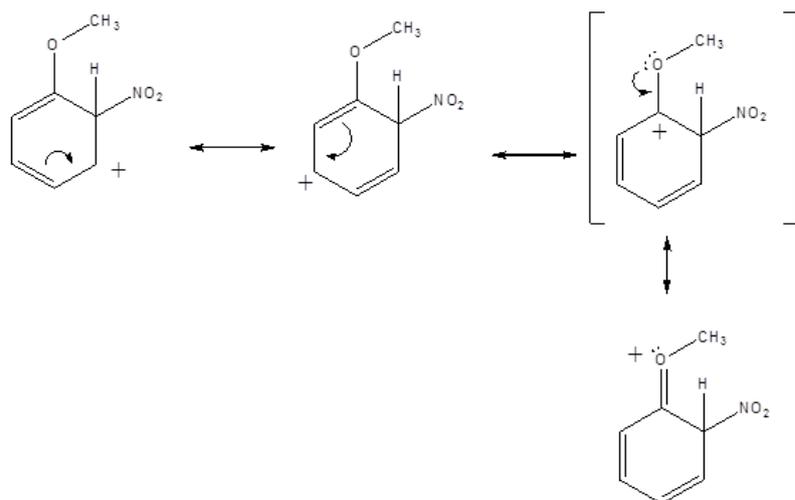


The O-CH₃ Group is an ortho, para Director

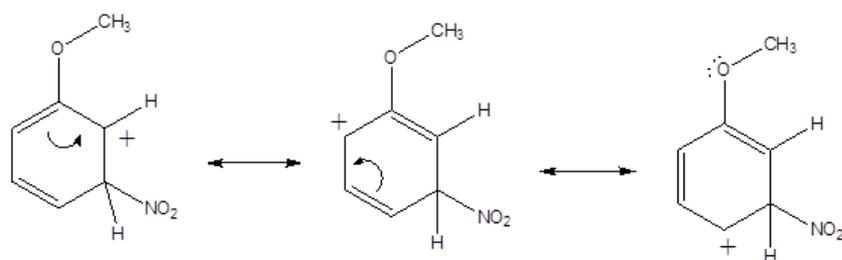


Ortho and Para product produces a resonance structure which stabilizes the arenium ion. This causes the ortho and para products to form faster than meta. Generally, the para product is preferred because of steric effects.

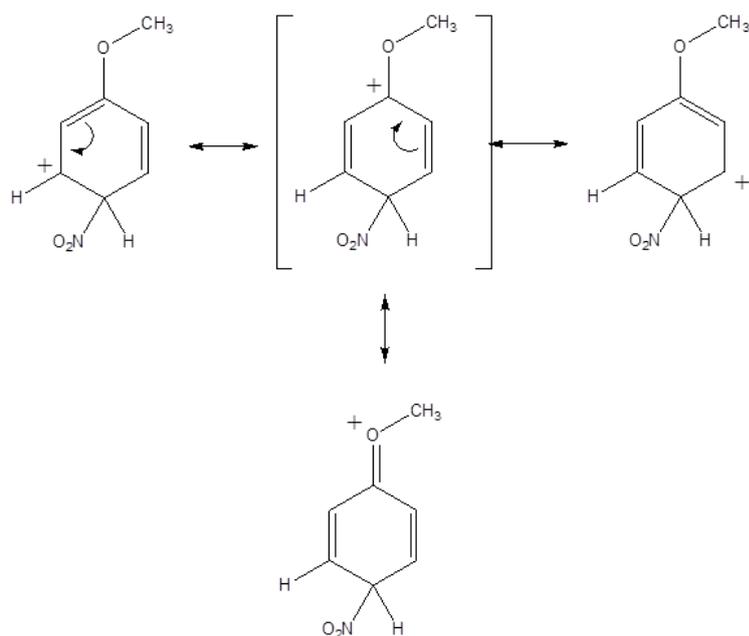
Ortho Attack



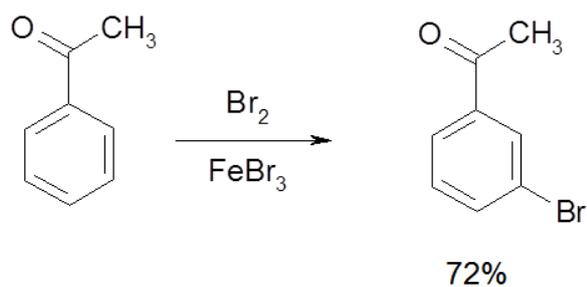
Meta Attack



Para Attack

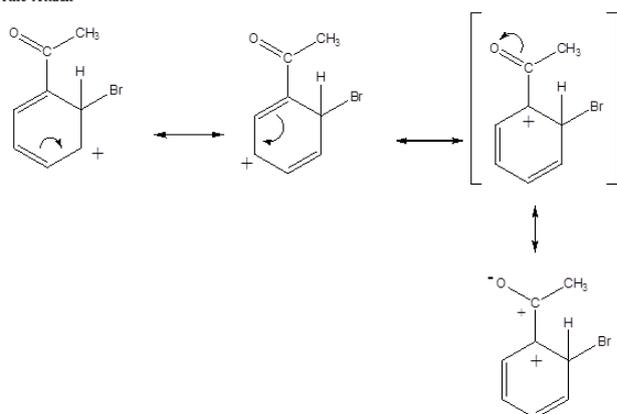


Acyl groups are meta Directors

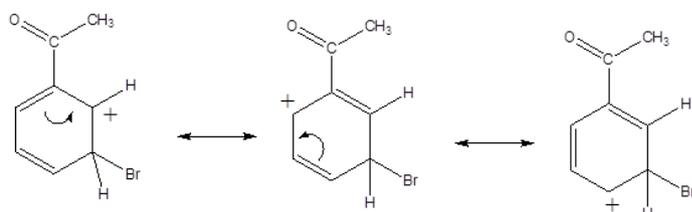


Acyl groups are resonance deactivators. Ortho and para attack produces a resonance structure which places the arenium cation next to an additional cation. This destabilizes the arenium cation and slows down ortho and para reaction. By default the meta product forms faster because it lacks this destabilizing resonance structure.

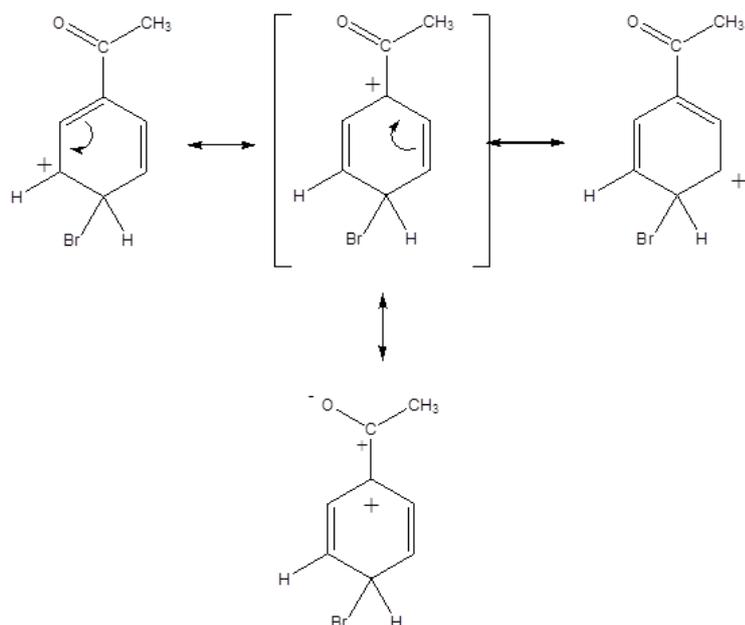
Ortho Attack



Meta Attack



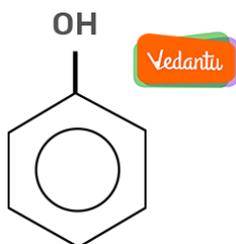
Para Attack



UNIT II

PHENOL

An organic compound is aromatic in nature with the structural formula C₆H₅OH. It is a white crystalline rock that is volatile in nature. The molecule has a phenyl group (-C₆H₅) attached to a hydroxyl group (-OH). It is slightly acidic and needs careful handling due to its tendency for causing chemical burns.



Structure of Phenol

Phenol was first mined from coal tar, but today is manufactured on a large scale (around 7 billion kg/year) from petroleum. It is an important industrial product as a pioneer to various materials and useful compounds. It is principally used to manufacture plastics and related materials. Phenol and its chemical products are very important for the production of Bakelite, polycarbonates, detergents, nylon, epoxies, herbicides such as phenoxy herbicides, and many pharmaceutical drugs.

Properties

Some properties of phenol are listed below.

Chemical formula	C₆H₆O
Molar mass	94.113 g·mol ⁻¹
Appearance	Transparent crystalline solid
Odour	Sweet and tarry
Density	1.07 g/cm ³
Melting point	40.5°C (104.9°F; 313.6 K)
Boiling point	181.7°C (359.1°F; 454.8 K)
Solubility in water	8.3 g/100 mL (20°C)
log P	1.48
Vapour pressure	0.4 mmHg (20°C)
Acidity (pKa)	9.95 (in water), 29.1 (in acetonitrile)

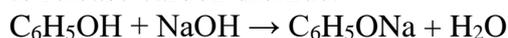
Conjugate base	Phenoxide
UV-vis (λ_{\max})	270.75 nm
Dipole moment	1.224 D

Reactions of phenol

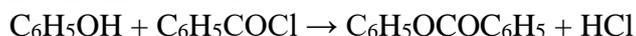
Phenol is extremely reactive to electrophilic aromatic substitution as the oxygen atom's pi electrons give electron density into the ring. By this overall approach, several groups can be attached to the ring, through halogenation, sulfonation, acylation, and other methods.

However, phenol's ring is so powerfully activated—second only to aniline—that chlorination or bromination of phenol will lead to replacement on all carbon atoms para and ortho to the hydroxyl group, not only on one carbon. It reacts with dilute nitric acid at room temperature to produce a mixture of 2-nitrophenol and 4-nitrophenol while with concentrated nitric acid, many nitro groups get replaced on the ring to produce 2, 4, 6-trinitrophenol which is also known as picric acid.

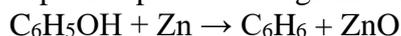
- The aqueous mixture of phenol is weakly acidic and changes blue litmus somewhat to red. It is easily neutralized by sodium hydroxide giving sodium phenate but is weaker than carbonic acid, it cannot be neutralized by sodium bicarbonate or sodium carbonate to release carbon dioxide.



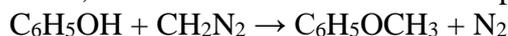
- When a mixture of phenol and benzoyl chloride is shaken in the occurrence of dilute sodium hydroxide solution, phenyl benzoate is produced. This is a case of the Schotten-Baumann reaction:



- Phenol is transformed to benzene when it is distilled with zinc dust, or when phenol vapour is passed over grains of zinc at 400°C:



- In the presence of boron trifluoride (BF_3) phenol is reacted with diazomethane and as a result, anisole is obtained as the main product and nitrogen gas as a byproduct.



- When phenol reacts with iron(III) chloride solution, a powerful violet-purple solution is produced.

Preparation of Phenols

Preparation of phenols from diazonium salts, benzene sulphonic acid, haloarenes, cumene. They are also known as carboic acids. They are weak acids and mostly form phenoxide ions by dropping one positive hydrogen ion (H^+) from the hydroxyl group. Phenol was mainly manufactured from coal tar. Nowadays, with developments in technologies, some new methods have come up for the making of phenols in laboratories. In laboratories, phenol is mainly created from benzene derivatives. Some of the approaches of preparation of phenols are explained below:

- **Preparation of Phenols From Haloarenes:**

Chlorobenzene is an example of haloarenes which is made by mono replacement of the benzene ring. When chlorobenzene is reacted with sodium hydroxide at 623K and 320 atm sodium phenoxide is formed. Finally, sodium phenoxide on acidification makes phenols.

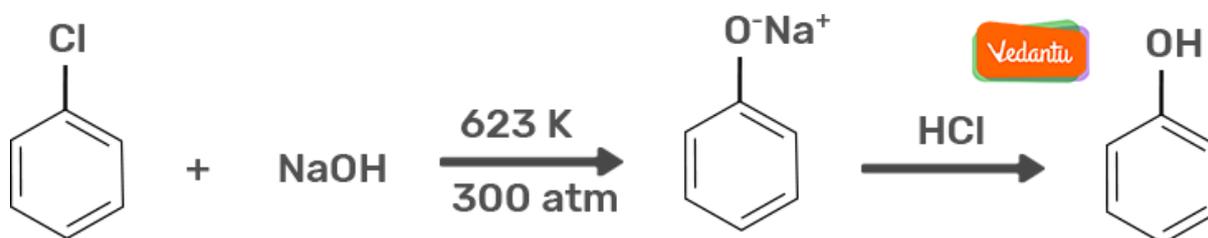


Image: An example of preparation of Phenols from haloarenes

- **Preparation of Phenols from Benzene Sulphonic Acid:**

Benzenesulphonic acid can be acquired from benzene by reacting it with oleum. Benzenesulphonic acid, hence formed, is fused with molten sodium hydroxide at a very high temperature which leads to the development of sodium phenoxide. Lastly, sodium phenoxide on acidification gives phenols.

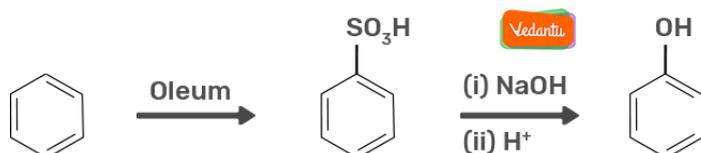


Image: Reaction of preparation of Phenols from Benzene Sulphonic Acid

- **Preparation of Phenols From Diazonium Salts:**

When an aromatic primary amine is fused with nitrous in the presence of HCl(NaNO₂ + HCl) acid at 273 – 278 K, diazonium salts are gained. These diazonium salts are extremely reactive in nature. Upon warming with water, these diazonium salts, to end hydrolyze to phenols. Phenols can also be acquired from diazonium salts by treating it with dilute acids.

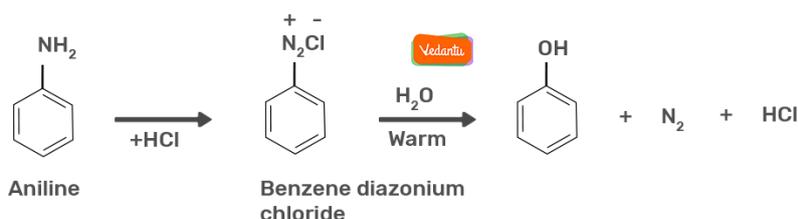


Image: Reaction of preparation of Phenols from Diazonium Salts

- **Preparation of Phenols From Cumene:**

Cumene is an organic compound acquired by Friedel-Crafts alkylation of benzene with propylene. On oxidation of cumene (isopropylbenzene) in the presence of air, cumene hydroperoxide is found. Upon further action of cumene hydroperoxide with dilute acid, phenols are produced. Acetone is also made as one of the by-products of this reaction in large quantities. Therefore, phenols prepared by these techniques need purifications.

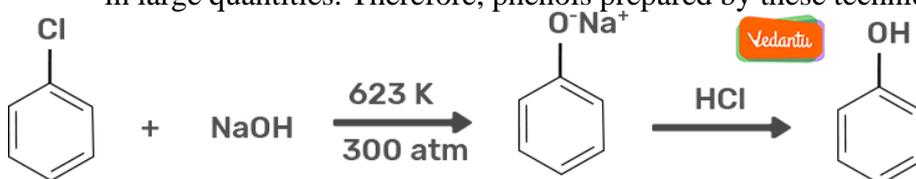


Image: Reaction of Preparation of Phenols from cumene

- **Synthesis of Phenols by the pyrolysis of the sodium salt of benzene sulphonic acid**

You can produce phenols in large amounts by the pyrolysis of the sodium salt of benzene sulphonic acid, by a process known as the Dow process, and by the air oxidation of cumene. Each of these methods is described below. You can also make small amounts of phenol by the peroxide oxidation of phenylboronic acid and the hydrolysis of diazonium salts.

In this method, benzene sulfonic acid is reacted with aqueous sodium hydroxide. The resulting salt is mixed with solid sodium hydroxide and reacted at a high temperature.

The product of this reaction is sodium phenoxide, which is acidified with aqueous acid to make phenol.

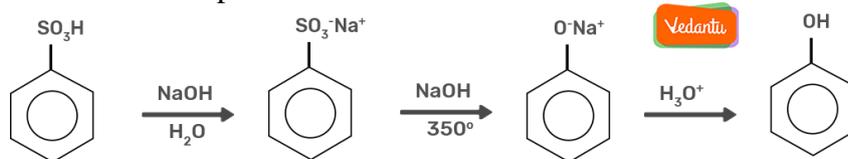


Image: Reaction of synthesis of phenols by the pyrolysis of the Na salt of benzene sulphonic acid

- **Dow Process**

In this process, chlorobenzene is reacted with dilute sodium hydroxide at a temperature of about 300°C and 3000 psi pressure. The following figure exemplifies the Dow process.

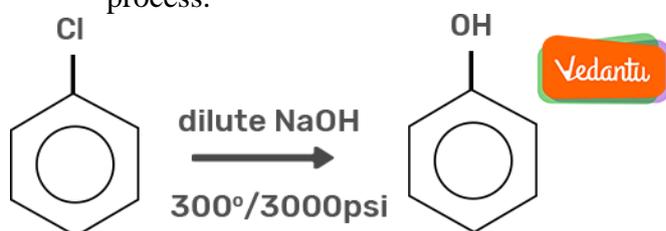


image: Reaction of preparation of phenol by Dow process

- **Air Oxidation of Cumene**

The oxidation of cumene in the presence of air (isopropylbenzene) will lead to the making of both acetone and phenol, as shown in the following figure.

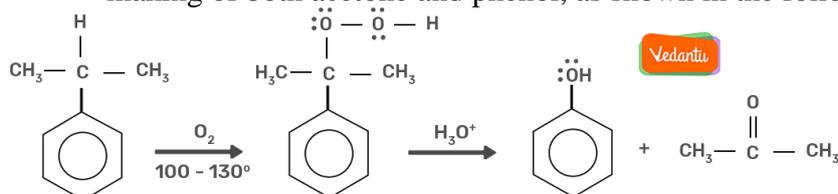


Image: The overall reaction of air oxidation of cumene

The mechanisms for the development and degradation of cumene hydroperoxide need closer looks, which are delivered following the figure.

Cumene Hydroperoxide Formation- The development of hydroperoxide continues by a free radical chain reaction. A radical initiator extracts a hydrogen-free radical from the molecule, making a tertiary free radical. The formation of the tertiary free radical is the first step in the reaction.

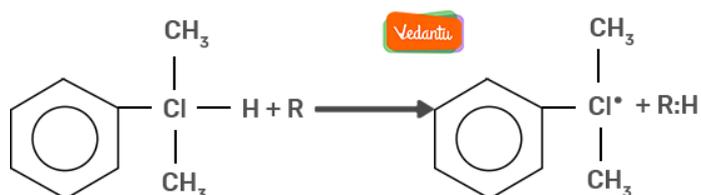


Image: The formation of the tertiary free radical

Further, the free radical is attracted to an oxygen molecule. This attraction yields the hydroperoxide free radical.

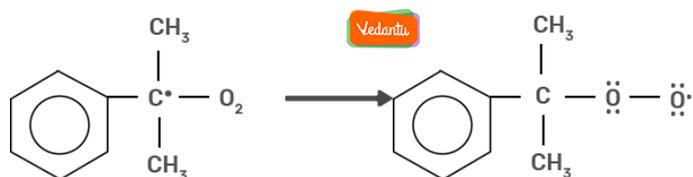


Image: The reaction of formation of hydroperoxide free radical

Lastly, the hydroperoxide free radical extracts a hydrogen-free radical from a molecule of cumene to produce cumene hydroperoxide and a new tertiary free radical.

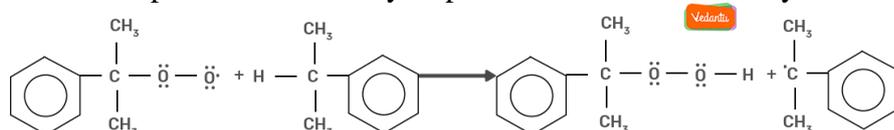


Image: Reaction of formation of cumene hydroperoxide and a tertiary free radical

Cumene Hydroperoxide Degradation- The degradation of the cumene hydroperoxide continues through a carbocation mechanism. In the 1st step, a pair of electrons on the oxygen of the hydroperoxide's "hydroxyl group" is attracted to a proton of the H_3O^+ molecule, making an oxonium ion.

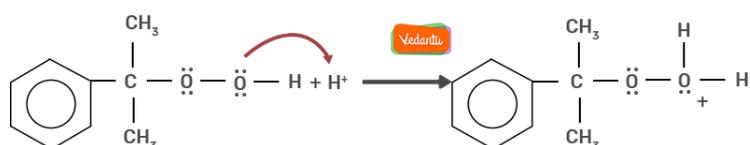


Image: Reaction of formation of an oxonium ion

Next, the oxonium ion develops stability when the positively charged oxygen leaves in a water molecule. This loss of a water molecule yields a new oxonium ion.

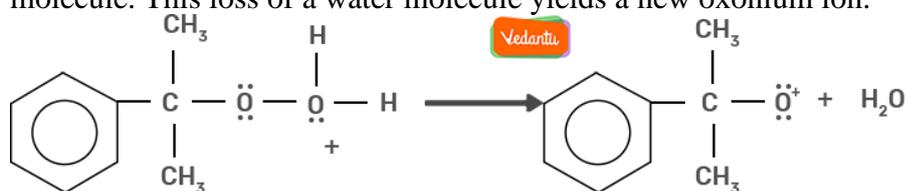


Image: Reaction of formation of new oxonium ion

A phenide ion move to the oxygen atom (which makes a tertiary carbocation) stabilizes the positively charged oxygen. (A phenide ion is a phenyl group with an electron bonding pair accessible to produce a new bond to the ring.)

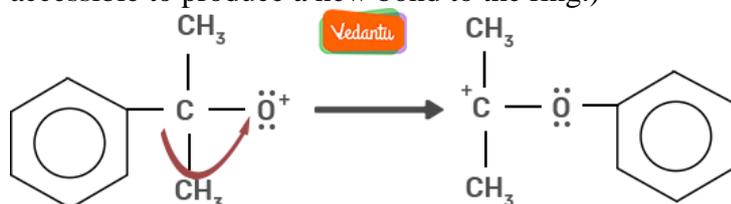


Image: The reaction of formation of a tertiary carbocation from phenyl ion

The carbocation is stabilized via an acid-base reaction with a water molecule, leading to the development of an oxonium ion.

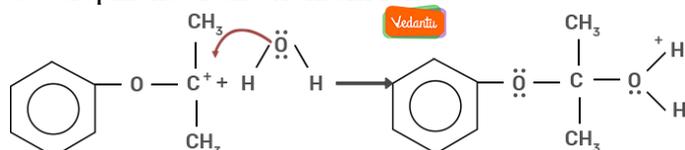


Image: The reaction of formation of oxonium ion

The stability of the oxonium ion is by the loss of a proton.

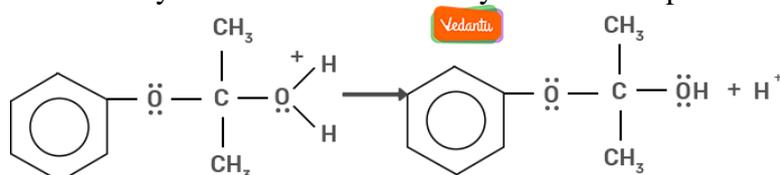


Image: The loss of an electron from oxonium ion

Afterwards, a proton is selected by the ether oxygen in an acid-base reaction, producing a new oxonium ion.

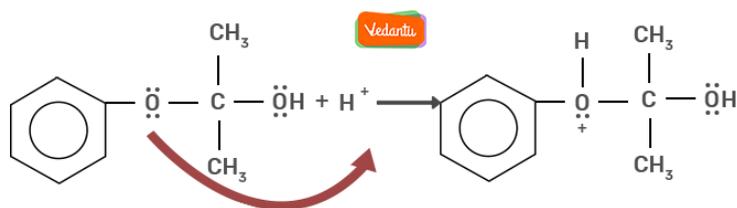


Image: Reaction to form new oxonium ion

The positively charged ether oxygen attracts the electrons in the oxygen-carbon bond toward itself, thus delocalizing the charge over both of the atoms. The fractional positive charge on the carbon attracts the nonbonding electron pair from the oxygen of the OH group, letting the electrons in the original oxygen-carbon bond be released back to the extra electronegative oxygen atom.

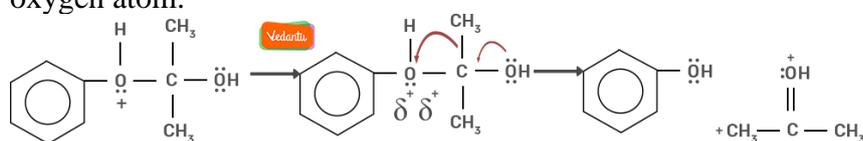


Image: The reaction of formation of phenol

Finally, a proton is lost from the protonated acetone molecule, leading to the development of acetone.

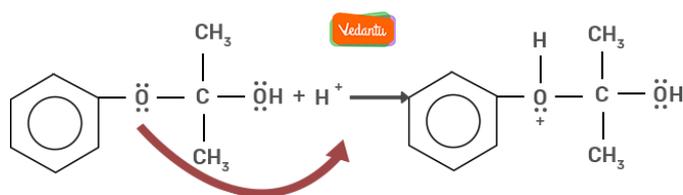


Image: The reaction of formation of acetone

Application of Phenol

Some of the applications of phenol are listed below.

The main uses of phenol, consuming two-thirds of its making, include its transformation to precursors for plastics.

- Condensation with acetone develops bisphenol-A, a key precursor to epoxide resins and polycarbonates.
- Condensation of alkylphenols, phenol, or diphenols with formaldehyde will give phenolic resins, a well-known example of which is Bakelite.

- Partial hydrogenation of phenol will give cyclohexanone, a precursor to nylon. Nonionic detergents are formed by alkylation of phenol to give the alkylphenols, e.g., nonylphenol, which is then exposed to ethoxylation.

Medical

- Phenol is also a useful precursor to a huge collection of drugs, most notably aspirin but also several herbicides and pharmaceutical drugs.
- Phenol is an element in the liquid/liquid phenol-chloroform abstraction technique used in molecular biology for the procurement of nucleic acids from tissues or cell culture samples. Depending on the pH of the solution either DNA or RNA can be mined

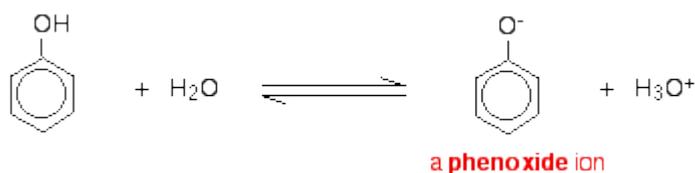
Use

- Phenol is so low-priced that it attracts many small-scale uses. It is a part of industrial paint strippers used in the aviation industry for the removal of polyurethane, epoxy and other chemically resistant coatings.
- Phenol byproducts have been used in the making of cosmetics including hair colourings, sunscreens, skin lightening preparations, as well as in skin toners or exfoliators. Still, due to safety reasons, phenol is banned from use in cosmetic merchandise in the European Union and Canada.

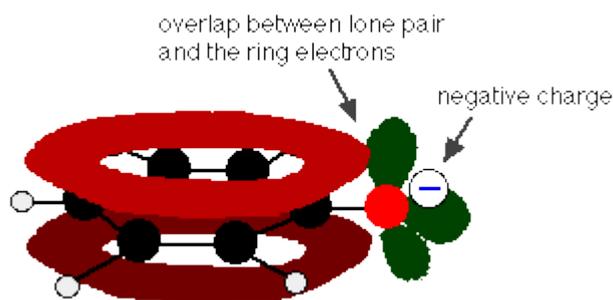
Hence, phenol is an essential chemical which is used for different purposes. In this article, properties along with the important methods of preparation of phenol with reactions and its applications are provided which is helpful for students to understand the important chemicals of organic chemistry.

Why is phenol acidic?

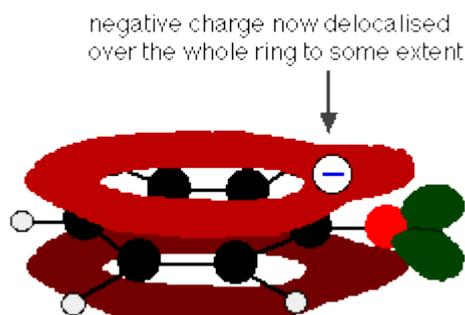
Compounds like alcohols and phenol which contain an -OH group attached to a hydrocarbon are very weak acids. Alcohols are so weakly acidic that, for normal lab purposes, their acidity can be virtually ignored. However, phenol is sufficiently acidic for it to have recognizably acidic properties - even if it is still a very weak acid. A hydrogen ion can break away from the -OH group and transfer to a base. For example, in solution in water:



Phenol is a very weak acid and the position of equilibrium lies well to the left. Phenol can lose a hydrogen ion because the phenoxide ion formed is stabilised to some extent. The negative charge on the oxygen atom is delocalised around the ring. The more stable the ion is, the more likely it is to form. One of the lone pairs on the oxygen atom overlaps with the delocalised electrons on the benzene ring.



This overlap leads to a delocalization which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localized on the oxygen, but is spread out around the whole ion.



Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen. However, oxygen is the most electronegative element in the ion and the delocalized electrons will be drawn towards it. That means that there will still be a lot of charge around the oxygen which will tend to attract the hydrogen ion back again. That is why phenol is only a very weak acid.

Why is phenol a much stronger acid than cyclohexanol? To answer this question we must evaluate the manner in which an oxygen substituent interacts with the benzene ring. As noted in our earlier treatment of electrophilic aromatic substitution reactions, an oxygen substituent enhances the reactivity of the ring and favors electrophile attack at ortho and para sites. It was proposed that resonance delocalization of an oxygen non-bonded electron pair into the pi-electron system of the aromatic ring was responsible for this substituent effect. A similar set of resonance structures for the phenolate anion conjugate base appears below the phenol structures.

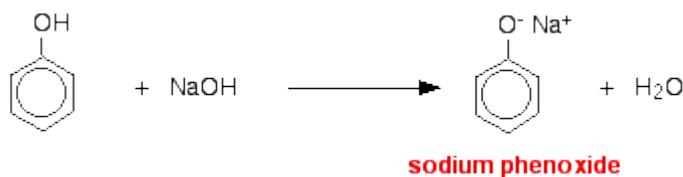
The resonance stabilization in these two cases is very different. An important principle of resonance is that charge separation diminishes the importance of canonical contributors to the resonance hybrid and reduces the overall stabilization. The contributing structures to the phenol hybrid all suffer charge separation, resulting in very modest stabilization of this compound. On the other hand, the phenolate anion is already charged, and the canonical contributors act to disperse the charge, resulting in a substantial stabilization of this species. The conjugate bases of simple alcohols are not stabilized by charge delocalization, so the acidity of these compounds is similar to that of water. An energy diagram showing the effect of resonance on cyclohexanol and phenol acidities is shown on the right. Since the resonance stabilization of the phenolate conjugate base is much greater than the stabilization of phenol itself, the acidity of phenol relative to cyclohexanol is increased. Supporting evidence that the phenolate negative

charge is delocalized on the ortho and para carbons of the benzene ring comes from the influence of electron-withdrawing substituents at those sites.

Properties of phenol as an acid

With indicators

The pH of a typical dilute solution of phenol in water is likely to be around 5 - 6 (depending on its concentration). That means that a very dilute solution isn't really acidic enough to turn litmus paper fully red. Litmus paper is blue at pH 8 and red at pH 5. Anything in between is going to show as some shade of "neutral". Phenol reacts with sodium hydroxide solution to give a colourless solution containing sodium phenoxide.



In this reaction, the hydrogen ion has been removed by the strongly basic hydroxide ion in the sodium hydroxide solution.

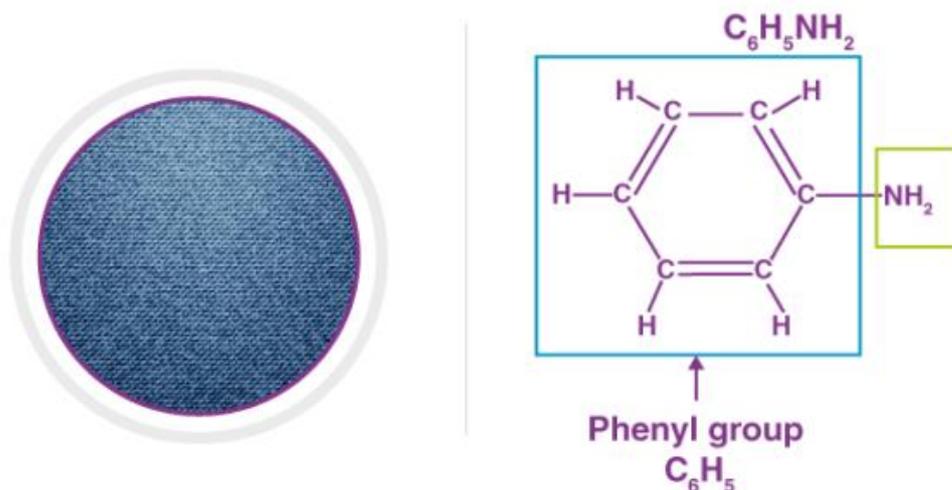
Substituent Effects on the Acidity of Phenols. Electron-donating substituents make a phenol less acidic by destabilizing the phenoxide ion (resonance effect) X OH X= -H -CH₃ -OCH₃ -NH₂ pKa ~ 10 10.3 10.2 10.5 237 Electron-withdrawing substituents make a phenol more acidic by stabilizing the phenoxide ion through delocalization of the negative charge and through inductive effects. X OH X= -H -Cl -Br -NO₂ pKa ~ 10 9.4 9.3 7.2 The influence of a substituent on phenol acidity is also dependent on its position relative to the -OH pKa X= -Cl 9.4 9.1 -NO₂ 7.2 8.4 -OCH₃ 10.2 9.6 -CH₃ 10.3 10.1 X OH OH X 122 238 The effect of multiple substituents on phenol acidity is additive. 2

Anilines

Anilines are the organic compounds in the class of group coming in organic chemistry which are also called as aminobenzene or phenylamine.

Have you ever wondered what is behind the blue colour of the jeans you wear? Yes, this colour is probably due to the chemical compound named aniline, which is used as a dyeing agent in the cloth industry.

These compounds are said to be toxic in nature and also known to be one of the classes of aromatic amines. These are used in a wide variety of industrial and are known to possess all the characteristics of an aromatic compound. The aniline compounds are said to have the formula C₆H₅NH₂ wherein the amino group is supposed to be attached to the Phenyl group.

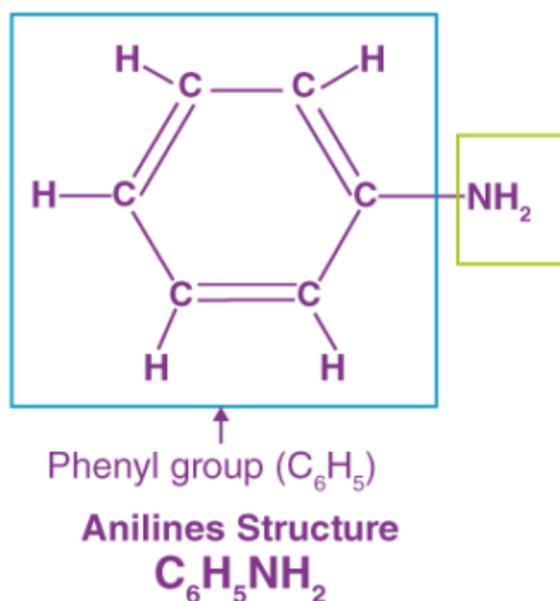


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Anilines – Structure

Aniline, also known as aminobenzene or phenylamine, has 6 carbon (C) atoms, 7 hydrogen (H) atoms, and 1 nitrogen (N) atom in its chemical formula of C_6H_7N or $C_6H_5NH_2$. Because aniline has an amino group in its structure, it is also an amine, hence it is classified as an aromatic amine.

Aniline is a musty, fishy-smelling yellowish to brownish, greasy liquid. -6°C melting point; 184°C boiling temperature; 158°F flash point Water-insoluble and somewhat denser than water. Vapors are more dense than air. Because aniline is an aromatic molecule that combines readily with other aromatic compounds, a low aniline point suggests a low diesel index. A high aniline point suggests a highly paraffinic gasoline with a high Diesel index and excellent ignition quality.



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The above image shows the structure of an Aniline compound. These compounds have the formula $C_6H_5NH_2$ with a phenyl group (C_6H_5) attached to the amino group (NH_2) as shown.

Aniline is in the form of a yellowish and somewhat brownish oily liquid having a musty and a fishy odour. It smells like the odour of a rotten fish. It is a kind of chemical substance which is a flammable liquid and has an unpleasant odour. The compound is soluble in water. It can also be colourless to light brown. It has a chemical formula of $C_6H_5NH_2$ or C_6H_7N and since it has 6 carbon atoms, 1 nitrogen atom and 7 hydrogen atoms in its chemical formula, it is classified under organic compounds.

Anilines – Physical Properties

The physical properties of Anilines are given below-

- Aniline has a boiling of about $184\text{ }^\circ\text{C}$ and melting of about -6 °
- The compound is slightly soluble in water and sometimes freely soluble in the chemicals such as alcohol and ether.
- This organic compound tends to darken when exposed to air and light.
- It is said to be weak base and on its reaction with strong acids, it forms anilinium ion - $C_6H_5-NH_3^+$.
- The compound is said to be toxic when it gets inhaled through the air or gets absorbed into the skin as it produces nitrogen oxides which are harmful to the environment.

Anilines – Reactions

1. Oxidation Reaction- The oxidation reactions of anilines compounds leads to the formation of carbon-nitrogen bonds.
2. Basicity- As it is known that anilines are weak bases. On reaction with strong acids, the compounds form ions of anilinium.
3. Acylation- In acylation reaction, anilines reacts readily with carboxylic acids forming amides.

The other reactions include alkylation reaction, Diazotization, hydrogenation, Wohl-Aue reaction, etc.

Anilines – Uses

Anilines are employed in various fields of science and everyday life as given below-

- Anilines are used in the rubber industry for the processing of rubber chemicals and products such as car tyres, balloons, gloves, etc.
- It is used as a dyeing agent in the manufacture of clothes such as jeans, etc
- It is employed in the production of drugs such as paracetamol, Tylenol, acetaminophen.
- It is used as a pesticide and fungicides in the agricultural industry
- It is utilized in the manufacture of polyurethane which is, in turn, used in the making of plastics.

Basicity of nitrogen groups

In this section we consider the relative basicity of several nitrogen-containing functional groups: amines, amides, anilines, imines, and nitriles.

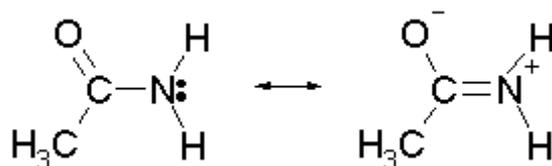
When evaluating the basicity of a nitrogen-containing organic functional group, the central question we need to ask ourselves is: how reactive (and thus how basic) is the lone pair on the nitrogen? In other words, how much does that lone pair want to break away from the nitrogen nucleus and form a new bond with a hydrogen?

Comparing the basicity of alkyl amines to ammonia

Because alkyl groups donate electrons to the more electronegative nitrogen. The inductive effect makes the electron density on the alkylamine's nitrogen greater than the nitrogen of ammonium. Correspondingly, primary, secondary, and tertiary alkyl amines are more basic than ammonia.

Comparing the basicity of alkylamines to amides

With an alkyl amine the lone pair electron is localized on the nitrogen. However, the lone pair electron on an amide are delocalized between the nitrogen and the oxygen through resonance. This makes amides much less basic compared to alkylamines.



In fact, when an amide is reacted with an acid, the protonation occurs at the carbonyl oxygen and not the nitrogen. This is because the cation resulting from oxygen protonation is resonance stabilized. The cation resulting from the protonation of nitrogen is not resonance stabilized.

Basicity of aniline

Aniline is substantially less basic than methylamine, as is evident by looking at the pK_a values for their respective ammonium conjugate acids (remember that the lower the pK_a of the conjugate acid, the weaker the base).

This difference in basicity can be explained by the observation that, in aniline, the basic lone pair on the nitrogen is to some extent tied up in – and stabilized by – the aromatic p system.

This effect is accentuated by the addition of an electron-withdrawing group such as a carbonyl, and reversed to some extent by the addition of an electron-donating group such as methoxide.

In the case of 4-methoxy aniline (the molecule on the left side of the figure above), the lone pair on the methoxy group donates electron density to the aromatic system, and a resonance contributor can be drawn in which a negative charge is placed on the carbon adjacent to the nitrogen, which makes the lone pair of the nitrogen more reactive. In effect, the methoxy group is 'pushing' electron density towards the nitrogen. Conversely, the aldehyde group on

the right-side molecule is 'pulling' electron density away from the nitrogen, decreasing its basicity.

At this point, you should draw resonance structures to convince yourself that these resonance effects are possible when the substituent in question (methoxy or carbonyl) is located at the *ortho* or *para* position, but not at the *meta* position. An imine functional group is characterized by an sp^2 -hybridized nitrogen double-bonded to a carbon. Imines are somewhat basic, with pK_a values for the protonated forms ranging around 7. Notice that this is significantly less basic than amine groups (eg. $pK_a = 10.6$ for methylammonium), in which the nitrogen is sp^3 -hybridized. This phenomenon can be explained using orbital theory and the inductive effect: the sp^2 orbitals of an imine nitrogen are one part s and two parts p , meaning that they have about 67% s character. The sp^3 orbitals of an amine nitrogen, conversely, are only 25% s character (one part s , three parts p). Because the s atomic orbital holds electrons in a spherical shape, closer to the nucleus than a p orbital, sp^2 hybridization implies greater electronegativity than sp^3 hybridization. Finally, recall the inductive effect from section 7.3C: more electronegative atoms absorb electron density more easily, and thus are more acidic. Moral of the story: protonated imine nitrogens are more acidic than protonated amines, thus imines are less basic than amines.

UNIT III

fatty acid, important component of lipids (fat-soluble components of living cells) in plants, animals, and microorganisms. Generally, a fatty acid consists of a straight chain of an even number of carbon atoms, with hydrogen atoms along the length of the chain and at one end of the chain and a carboxyl group ($-\text{COOH}$) at the other end. It is that carboxyl group that makes it an acid (carboxylic acid). If the carbon-to-carbon bonds are all single, the acid is saturated; if any of the bonds is double or triple, the acid is unsaturated and is more reactive. A few fatty acids have branched chains; others contain ring structures (e.g., prostaglandins). Fatty acids are not found in a free state in nature; commonly they exist in combination with glycerol (an alcohol) in the form of triglyceride.

Among the most widely distributed fatty acids are the 16- and 18-carbon fatty acids, otherwise known as palmitic acid and stearic acid, respectively. Both palmitic and stearic acids occur in the lipids of the majority of organisms. In animals palmitic acid makes up as much as 30 percent of body fat. It accounts for anywhere from 5 to 50 percent of lipids in vegetable fats, being especially abundant in palm oil. Stearic acid is abundant in some vegetable oils (e.g., cocoa butter and shea butter) and makes up a relatively high proportion of the lipids found in ruminant tallow.

- recognize the structures of common fatty acids and classify them as saturated, monounsaturated, or polyunsaturated.

Fatty acids are carboxylic acids that are structural components of fats, oils, and all other categories of lipids, except steroids. More than 70 have been identified in nature. They usually contain an even number of carbon atoms (typically 12–20), are generally unbranched, and can be classified by the presence and number of carbon-to-carbon double bonds. Thus, saturated

fatty acids contain no carbon-to-carbon double bonds, monounsaturated fatty acids contain one carbon-to-carbon double bond, and polyunsaturated fatty acids contain two or more carbon-to-carbon double bonds.

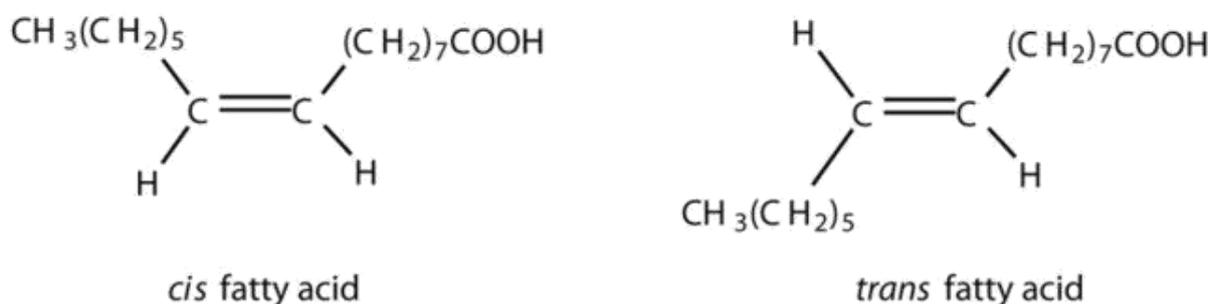


Table [\\(\PageIndex{1}\\)](#) lists some common fatty acids and one important source for each. The atoms or groups around the double bonds in unsaturated fatty acids can be arranged in either the *cis* or *trans* isomeric form. Naturally occurring fatty acids are generally in the *cis* configuration.

Common Fatty Acids Found in Natural Fats

	Abbreviated Structural Formula	Condensed Structural Formula	Melting Point (°C)	Source
	C ₁₁ H ₂₃ COOH	CH ₃ (CH ₂) ₁₀ COOH	44	palm kernel oil
	C ₁₃ H ₂₇ COOH	CH ₃ (CH ₂) ₁₂ COOH	58	oil of nutmeg
	C ₁₅ H ₃₁ COOH	CH ₃ (CH ₂) ₁₄ COOH	63	palm oil
	C ₁₅ H ₂₉ COOH	CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH	0.5	macadamia nut oil
	C ₁₇ H ₃₅ COOH	CH ₃ (CH ₂) ₁₆ COOH	70	cocoa butter
	C ₁₇ H ₃₃ COOH	CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH	16	olive oil
	C ₁₇ H ₃₁ COOH	CH ₃ (CH ₂) ₃ (CH ₂ CH=CH) ₂ (CH ₂) ₇ COOH	-5	canola oil
	C ₁₇ H ₂₉ COOH	CH ₃ (CH ₂ CH=CH) ₃ (CH ₂) ₇ COOH	-11	flaxseed oil
	C ₁₉ H ₃₁ COOH	CH ₃ (CH ₂) ₄ (CH ₂ CH=CH) ₄ (CH ₂) ₂ COOH	-50	liver oil

Two polyunsaturated fatty acids—linoleic and α -linolenic acids—are termed essential fatty acids because humans must obtain them from their diets. Both substances are required for normal growth and development, but the human body does not synthesize them. The body uses linoleic acid to synthesize many of the other unsaturated fatty acids, such as arachidonic acid, a precursor for the synthesis of prostaglandins. In addition, the essential fatty acids are necessary for the efficient transport and metabolism of cholesterol. The average daily diet should contain about 4–6 g of the essential fatty acids.

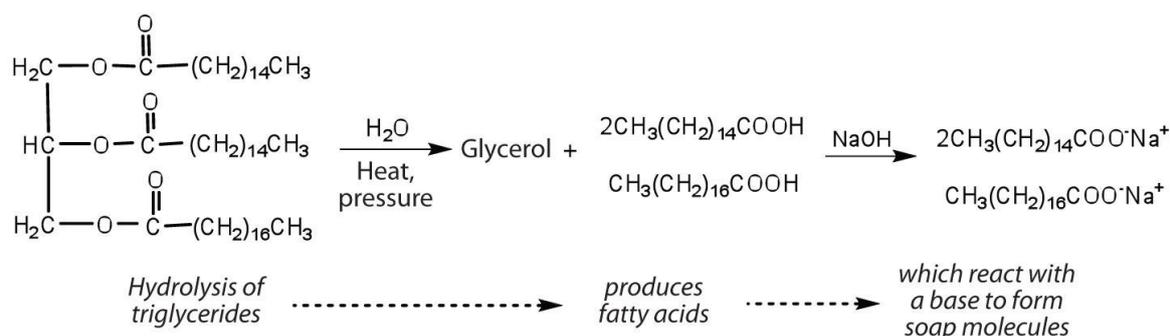
Difference between Fats and Oils

To make you understand how **Oils and fats** are different from each other, here are some major **differences between oils and fats**:

Difference between Fats and Oils	
Fats	Oils
Solid at room temperature	Liquid at room temperature
Saturated and trans are its types	Unsaturated fats like monounsaturated and polyunsaturated are its types
Mostly derived from animal	Mostly derived from plants
Increases cholesterol levels	Improves cholesterol levels
Mainly comes from animal food but also through vegetable oil by process called hydrogenation	Mainly comes from plants or fish
Example: Butter, beef fat	Example:Vegetable oil, fish oil
Contains 9 cal/gm	Contains 9 cal/gm

Chemical Reactions of Fats and Oils

Fats and oils can participate in a variety of chemical reactions—for example, because triglycerides are esters, they can be hydrolyzed in the presence of an acid, a base, or specific enzymes known as lipases. The hydrolysis of fats and oils in the presence of a base is used to make soap and is called saponification. Today most soaps are prepared through the hydrolysis of triglycerides (often from tallow, coconut oil, or both) using water under high pressure and temperature [700 lb/in² (~50 atm or 5,000 kPa) and 200°C]. Sodium carbonate or sodium hydroxide is then used to convert the fatty acids to their sodium salts (soap molecules):



Fat hydrogenation is the process of combining fat — typically, vegetable oils — with hydrogen, in order to make it more saturated.

The process is typically carried out at very high pressure, with the help of a nickel catalyst (that is removed from the final product).

Their partial hydrogenation reduces most, but not all, of these carbon-carbon double bonds. The degree of hydrogenation is controlled by restricting the amount of hydrogen, reaction temperature and time, and the catalyst.^[1] The goal is to turn liquid oils into solid or semi-solid fats that can replace butter and shortening in spreads, candies, baked good, and other products.

What is Rancidity Meaning?

Rancidity in Chemistry, which is also called Rancidification, is a condition that is produced by the aerial oxidation of unsaturated fat present in foods and also other products that are marked by unpleasant flavours or odours. When unsaturated components of a fatty material are exposed to sunlight, they can be converted into hydroperoxides, which break down into esters, volatile aldehydes, ketones, alcohols, and hydrocarbons, some of which have unpleasant odours.

It is also possible in preventing rancidity using some preventive measures.

Examples of Rancidity

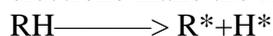
Oil becomes rancid (rancid oil) because of the decomposition of fats it has, or sometimes milk becomes rancid because of not heating it in the humid atmosphere, etc.

How does a Substance Turn Rancid?

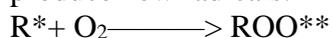
Rancidity, in general terms, is always used for food products that have oil and fatty acids in them. Fatty acids are generally composed of fats, cholesterol and steroids. These are mostly carboxylic acids that consist of a long aliphatic chain. They are either saturated which means there is only a single linkage between the carbon atoms or unsaturated that comprises multiple linkages between the carbon atoms.

The reaction of rancidity typically occurs in three steps, and they are:-

1. **Initiation reaction:** This reaction leads to the formation of the radicals on the food substances because of the external factors like heat and air that stimulates the reaction. A radical can be defined as an atom molecule or ion that has an unpaired electron. These unpaired electrons make the radicals very reactive chemical substances.



2. Propagation reaction: In this stage, the oxygen present in the atmosphere gives rise to the peroxides. These peroxides then react more and more with the unsaturated fatty acids and then produce new radicals.



(peroxide)

Termination reaction: in this stage, the two radicals combine together to form a new single bond.



The fats, lipids and the other compounds are decomposed at the end of the rancidification, thus forming high reactive molecules. This is the reason that the food starts smelling unpleasant and tastes bad after rancidity. In some cases, there is a loss of vitamins due to the process of rancidity.

(Image will be uploaded soon)

Types of Rancidity

There are three types of rancidity. They can be classified as follows:

1. Hydrolytic Rancidity

In some fats, there exists the predominance of short-chain fatty acids. The LIPASE enzyme can break down the linkage between glycerol and fatty acid. A few fatty acids (when not bound to the glycerol) contain flavour that, when present in high concentration, is undesirable (same as in Butter). Long time storage at unrefrigerated temperatures, butter contamination with microbes producing lipases, and more. can accelerate hydrolytic rancidity.

2. Oxidative Rancidity

The large unsaturated fatty acids are more susceptible to oxidation. The oxidation products are given as aldehydes, ketones, and related ones that can give off-flavour at high temperatures (exposure to air, cooking, and some chemical contaminants can accelerate oxidation). Antioxidants are added to the oils to reduce oxidative rancidity.

3. Microbial Rancidity

This type of rancidity takes place when the microorganisms such as bacteria use their enzymes to break down the chemical structures of fat.

Causes and Effects of Rancidity

Unsaturated fatty acids can be found in all solid foodstuffs and oils. These contain carbon-carbon double bonds that can be broken in the air by different reactions between those bonds and oxygen. Besides the shortening of hydrocarbon chains in the lipids, which contain them, the oxygenated products taste and smell different. The polyunsaturated fatty acids, which are supposed to be so good for us, contain a minimum of 2 C=C double bonds, and they are specifically prone to oxidation reactions. They quickly turn rancid compared to the fatty acids containing only a single carbon-carbon bond.

A good example is Linseed oil (turned into rancid oil) because it can be used to harden oil-based paints (for example, artist's 'oil' paints). Also, the hardening reaction results from the polymer formation of these oxygenated fatty acids. It is also believed that walnut oil turns rancid rapidly. For this particular reason, polyunsaturated fatty acid oils should be stored in the refrigerator to slow down the reaction.

Also, some people are sensitive to walnuts that have gone even slightly rancid. The idea that some sort of polymers forming in the stomach is particularly repulsive, and one will not eat any walnuts that smell the slightest bit 'off.' If we notice the labels on the packaged foods that we eat, we can find something called 'BHT' in the ingredients list. The butylated hydroxytoluene scavenges off free radicals, and since rancidification is based on the formation of free radicals, BHT preserves foodstuffs from this particular reaction.

drying oil is an oil that hardens to a tough, solid film after a period of exposure to air, at room temperature. The oil hardens through a chemical reaction in which the components crosslink (and hence, polymerize) by the action of oxygen (not through the evaporation of water or other solvents). Drying oils are a key component of oil paint and some varnishes. Some commonly used drying oils include linseed oil, tung oil, poppy seed oil, perilla oil, and walnut oil. Their use has declined over the past several decades, as they have been replaced by alkyd resins and other binders.

Since oxidation is the key to curing in these oils, those that are susceptible to chemical drying are often unsuitable for cooking, and are also highly susceptible to becoming rancid through autoxidation, the process by which fatty foods develop off-flavors.^[1] Rags, cloth, and paper saturated with drying oils may spontaneously combust (ignite) after a few hours as heat is released during the oxidation process.

Analytical constants of fats and oils

Adulteration of fats and oils is increasing day by day

Several tests are employed in the laboratory to check purity of fats and oils

Some of them are discussed here under

§ Acid value,

§ Saponification value,

§ Ester value,

§ Iodine value,

§ Acetyl value,

§ Reichert Meissl (RM) value

Acid Value

Definition: The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat.

It is a relative measure of rancidity as free fatty acids are normally formed during decomposition of oil glycerides.

Therefore, oils with increased acid number are unsafe for human consumption.

Principle: The acid value is determined by directly titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution.

Analytical Importance: The value is a measure of the amount of fatty acids which have been liberated by hydrolysis from the glycerides due to the action of moisture, temperature and/or lipolytic enzyme lipase.

Saponification Value

Definition: The saponification value is the number of mg of potassium hydroxide required to saponify (hydrolyse) 1 gram of oil/fat.

Principle: The oil sample is saponified by refluxing with a known excess of alcoholic potassium hydroxide solution. The alkali required for saponification is determined by titration of the excess potassium hydroxide with standard hydrochloric acid.

Analytical importance:

The saponification value is an index of mean molecular weight of the fatty acids of glycerides comprising a fat.

Lower the saponification value, larger the molecular weight of fatty acids in the glycerides and vice-versa.

The value is higher for fats containing short chain fatty acids

The saponification numbers of a few fats and oils are given be

Ester value

Definition: The ester value is the number of mg of potassium hydroxide required to saponify the esters in 1.0 g of the substance

Ester value = saponification value - acid value

Iodine number

Definition: The iodine value of an oil/fat is the number of grams of iodine absorbed by 100g of the oil/fat.

Principle: The oil/fat sample taken in carbon-tetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic (**Wijs solution**). The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulfate solution.

analytical importance: The iodine value is a measure of the amount of unsaturation (number of double bonds) in a fat.

- Iodine number is useful to know the relative unsaturation of fats, and is directly proportional to the content of unsaturated fatty acids
- Thus lower is the iodine number, less is the degree of unsaturation
- The iodine numbers of common oils/fats are given below

Analytical constants of fats and oils

<i>Fat/oil</i>	<i>Iodine number</i>
Coconut oil	7 — 10
Butter	25 — 28
Palm oil	45 — 55
Olive oil	80 — 85
Groundnut oil	85 — 100
Cottonseed oil	100 — 110
Sunflower oil	125 — 135
Linseed oil	175 — 200

Acetyl value

Definition: The acetyl value is determined by the milligrams of potassium hydroxide required to neutralize the acetic acid produced when 1 gram of fat or oil is acetylated (hydrolyzed) with acetic anhydride.

Indicates the number of free hydroxyl groups present in the substance.

Principle:

The process consists of acetylating the oil with a measured quantity of acetic anhydride in pyridine decomposing the excess anhydride by boiling with water and then, after the addition of sufficient butyl alcohol to give a homogeneous solution, titrating with alkali.

A control test with the acetic anhydride and pyridine without the oil provides a measure of the acetic anhydride available for acetylation; a similar test with the oil and the pyridine without the acetic anhydride provides a measure of the free fatty acid present.

From the values obtained, the acetyl value or the hydroxyl value of the oil is calculated.

Reichert-Meissl (RM) number

Definition: The Reichert-Meissl value is the number of millilitres of 0.1N aqueous sodium hydroxide /KOH solution required to neutralise steam volatile water soluble fatty acids distilled from 5g of an oil/fat.

Principle: The material is saponified by heating with glycerol sodium hydroxide solution and then split by treatment with dilute sulfuric acid. The volatile acids are immediately steam distilled. The soluble volatile acid in the distillate are filtered out and estimated by titration with standard sodium hydroxide solution.

Analytical Importance:

RM number is useful in testing the purity of butter since it contains a good concentration of volatile fatty acids(butyric acid, caproic acid and caprylic acid)

This is in contrast to other fats and oils which have a negligible amount of volatile fatty acids

Butter has a RM number in the range 25-30, while it is less than 1 for most other edible oils

Thus any adulteration of butter can be easily tested by this sensitive RM number

UNIT IV

Naphthalene is a white crystalline volatile solid with a distinct odor that reminds many people of mothballs. At room temperature, the compound sublimes (turns from a solid to a gas) slowly, generating a highly flammable vapor.

Natural sources of naphthalene include petroleum and coal tar. It is extracted by heating the raw material to a temperature of 200°C to 250°C (392°F to 482°F), resulting in middle oil, a mixture of hydrocarbons. After that, the middle oil is distilled to separate its many components, one of which is naphthalene. This naphthalene is cleaned by washing it in strong acid, then in a sodium hydroxide solution, and finally by steam distillation.

What is Naphthalene?

Before starting with naphthalene, first, you need to understand what an aromatic compound is. Aromatic compounds are the ring compounds that contain a double and single bond in an alternate manner, and follow the huckel rule. Let's come to our main question, what is naphthalene? Naphthalene is an aromatic hydrocarbon, consisting of two or more fused aromatic benzene rings. These are polynuclear aromatic hydrocarbons. In short, naphthalene is

fused with hydrocarbons. In this article, we have covered the all-important points about naphthalene like the use of naphthalene, structure of naphthalene, and resonance in naphthalene.

Structure of Naphthalene

Naphthalene is a member of a polynuclear aromatic hydrocarbon where two aromatic benzene rings are fused together at the ortho position.

The bond length at the double bond position is around 1.36 Angstrom, and the bond length at the single bond position is around 1.40 angstrom. Naphthalene molecule shows the resonance in its structure. It forms a resonance hybrid. Naphthalene molecules show three resonance structures. These structures are known as canonical structures. Naphthalene forms three resonating structures. These structures are shown below for better understanding.

In this structure, the pi electrons are delocalised from one position to another. This delocalisation phenomenon leads to the lowering of the electronic energy of the system. In the naphthalene molecule, the carbon 1 - carbon 2 bond length is shorter than the carbon 2 - carbon 3 bond length. All carbons are sp^2 hybridised and have unused p-orbitals with one electron. In naphthalene, the sigma bond count is eleven.

Properties of Naphthalene:

The physical properties and chemical properties of naphthalene are discussed below:

1. Naphthalene exists in crystalline form.
2. Naphthalene is generally white in color. It is also found in transparent to brownish color.
3. The molecular weight of naphthalene is 128.18 g/mol.
4. Naphthalene is insoluble in water at normal room temperature.
5. Naphthalene has an aromatic odor.
6. The vapor pressure of naphthalene is 0.087 mmHg.

Synthesis of Naphthalene

1. **From Coal Tar-** Naphthalene can be obtained from the coaltar, by making naphthalene crystals. These crystals can be formed by the middle oil fraction. The crystals produced in this process are subjected to sulphuric acid for the purification process. In the end, pure naphthalene crystals are formed.
2. **Haworth Synthesis-** In this process, benzene to naphthalene is produced. The benzene ring is first subjected to the acylation process. This reaction starts with the Friedel craft Acylation of a benzene ring with the succinic anhydride, then a series of reduction reactions undergo. Finally, a naphthalene molecule is produced by dehydrogenation.

Naphthalene in Water

The solubility of naphthalene in water can be determined by its structure. Naphthalene is a polyatomic hydrocarbon. A large number of carbon atoms makes it a hydrophobic molecule. Due to this hydrophobic structure, the naphthalene in water is insoluble. In this article naphthalene, the liquid structure is not discussed in detail.

Naphthalene in Other Solvents

Naphthalene is an organic compound with a melting point of 80°C and a boiling point of 218°C. It sublimates upon heating and is insoluble in water. In other solvents like ethanol, it is not completely soluble. It is very soluble in benzene, ether and chloroform.

Different Forms of Naphthalene

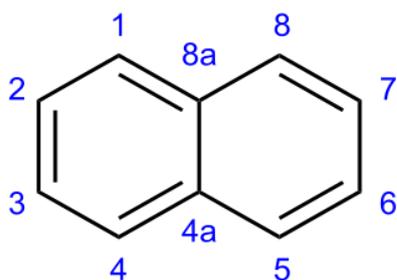
1. Refined naphthalene
2. Alkyl naphthalene
3. Naphthalene solid

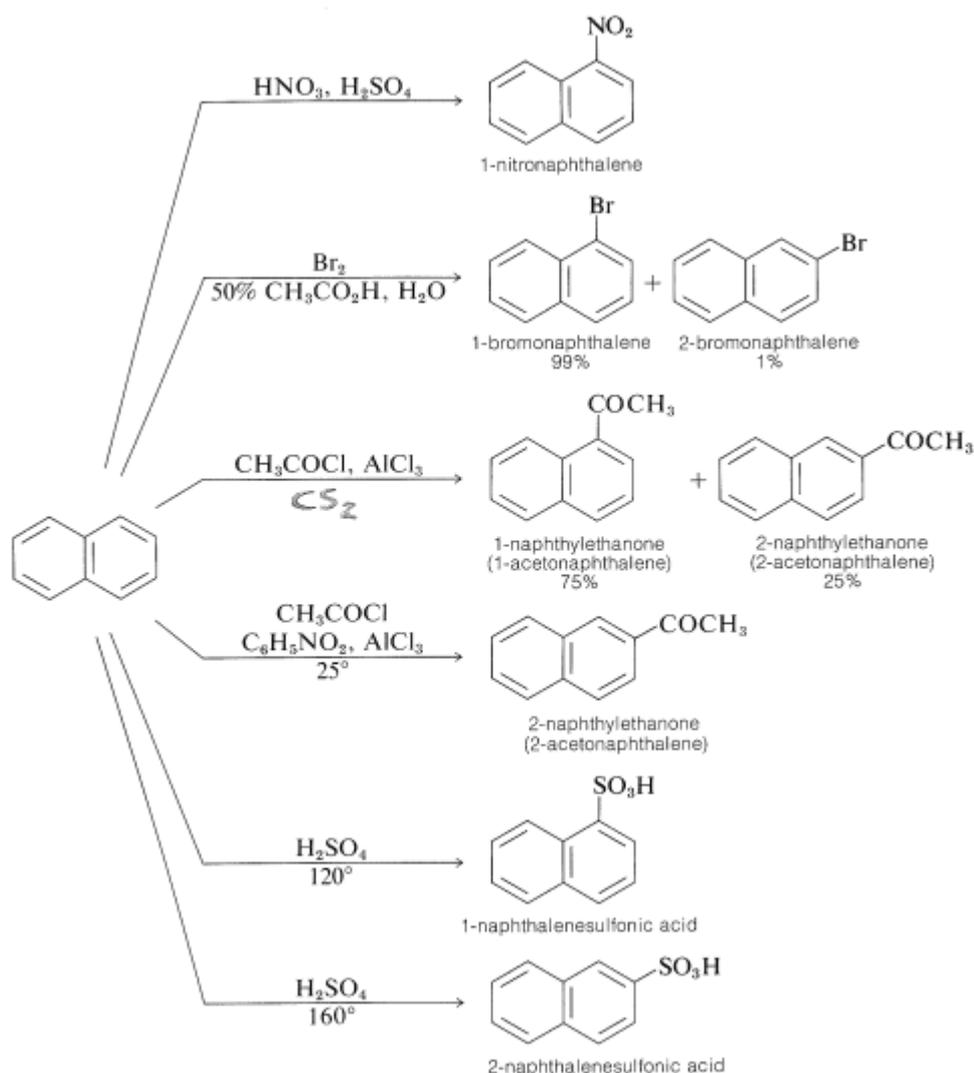
Formula & Structure

The chemical (molecular) formula of naphthalene is pretty easy to remember. It's simply:



The C stands for carbon and the H stands for hydrogen. As such, naphthalene is a **hydrocarbon** since it's composed of hydrogen ('hydro-') and carbon. Its chemical structure is actually really cool.





Anthracene

Anthracene is a colourless crystalline aromatic hydrocarbon utilised in the chemical industry that is created by distilling natural crude oils. Anthracene is a three-fused benzene ring solid polycyclic aromatic hydrocarbon (PAH) with the formula $\text{C}_{14}\text{H}_{10}$. It's a substance found in coal tar. Anthracene is used to make the red dye alizarin as well as other dyes. It is colourless but fluoresces blue (400–500 nm peak) when exposed to ultraviolet light. This article will study the use of anthracene in detail.

Anthracene Sigma Aldrich

Three benzene rings are fused together to form anthracene, a polycyclic aromatic hydrocarbon. A polycyclic refers to a molecule with more than one ring, aromatic refers to a molecule with alternating double-single bonds all over the ring structure, and hydrocarbon refers to a molecule composed entirely of carbon and hydrogen atoms.

It is the three rings that were bound together, as well as the network of alternating double and single bonds that ran all the way around them.

Reactions of Anthracene

1. Anthracene to Anthraquinone

Anthracene is converted to anthraquinone when it is reacted with an oxidising agent like hydrogen peroxide. Anthracene with two carbon-oxygen double bonds at the two middle carbons of the molecule is easily recognised as anthraquinone. Anthraquinone may be formed from direct combustion processes in motor-operated vehicles and engines. They are the extensive category of naturally occurring quinones, together with some of the most crucial native colourants like alizarin, purpurin, munjistin, emodin, chrysophanol, aloe-emodin, physcion, rhein, etc. With over 700 chemicals identified, anthraquinone is the biggest group of natural pigments.

2. Methyl Anthracene

The Elbs reaction is an organic reaction in which an ortho methyl-substituted benzophenone is pyrolyzed to produce a condensed polyaromatic. The reaction is named after Karl Elbs, a German chemist, who also invented the Elbs oxidation. In 1884, the reaction was written. Elbs, on the other hand, misinterpreted the reaction product due to a lack of understanding of naphthalene structure.

3. Dibenzo Anthracene

The action of UV light causes anthracene to photo dimerize. The 4+4 cycloaddition results in a pair of new carbon-carbon bonds connecting the dimer, which is known as Dianthracene (or sometimes paranthracene). Thermally or with UV irradiation below 300 nm, it reverts to anthracene. The behaviour of substituted anthracene derivatives is similar. The presence of oxygen has an effect on the reaction.

4. Magnesium Anthracene

Magnesium anthracene is an organomagnesium compound that is almost always isolated as tetrahydrofuran (THF) adduct with three ligands. The air and water sensitive orange solid $\text{Mg}(\text{C}_{14}\text{H}_{10})(\text{thf})_3$ is made by heating a suspension of magnesium in a thf solution of anthracene.

Use of Anthracene

1. Anthracene is primarily converted to anthraquinone, a dye precursor.
2. Anthracene, an organic semiconductor with a large bandgap, is used as a scintillator for high-energy photon, electron, and alpha particle detectors. Plastics, such as polyvinyl toluene, can be doped with anthracene to create a water-equivalent plastic scintillator for use in radiation therapy dosimetry. The emission spectrum of anthracene peaks between 400 and 440 nm.
3. It is present in wood preservatives, insecticides, and coating materials.
4. Anthracene is widely used as a UV tracer in printed wiring board conformal coatings. The anthracene tracer allows for UV inspection of the conformal coating. Anthracene is also used in anthraquinone use.
5. Anthracene derivatives are used in a number of applications. 1-hydroxyanthracene and 2-hydroxyanthracene are hydroxylated derivatives of phenol and naphthols, and hydroxyanthracene (also known as anthrol and anthracenol) is pharmacologically active. 9,10-dihydroxy anthracene is an example of anthracene with several hydroxyl groups.
6. During combustion processes, anthracene, like many other polycyclic aromatic hydrocarbons, is produced. Tobacco smoke and consumption of food tainted with combustion materials are the primary sources of human exposure.

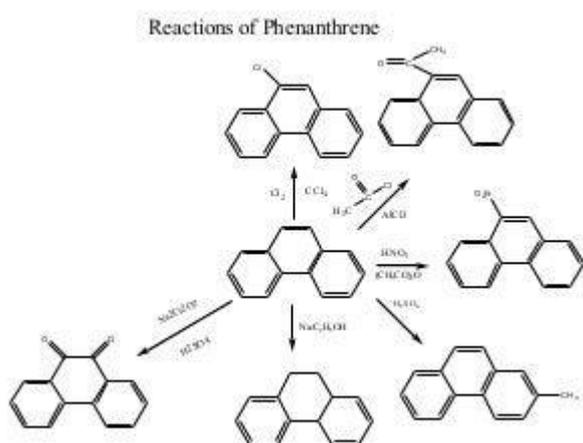
7. Anthracene is non-carcinogenic, as according to several studies it "consistently gives negative results in numerous in vitro and in vivo genotoxicity experiments." Since crude samples were tainted with other polycyclic aromatic compounds, early studies suggested otherwise. It is also easily biodegradable in soil. In the presence of light, it is particularly vulnerable to deterioration.
8. It is also used as a smokescreen, scintillation counter crystals, and inorganic semiconductor research.

Polycyclic aromatic hydrocarbons are addressed as potential starting materials for the abiotic synthesis of materials needed by life's earliest forms. When inhaled, Anthracene can irritate the throat, nose and lungs leading to wheezing and coughing. Contact to the skin may cause irritation, burns, itching which is provoked by sunlight. Regular contact may cause thickening of the skin and changes in pigment. Studies show, Anthracene may turn into an allergy and once the allergy is developed completely in an individual even very low future exposure can cause a skin rash.

Phenanthrene is a polycyclic aromatic hydrocarbon (PAH) with formula $C_{14}H_{10}$, consisting of three fused benzene rings. It is a colorless, crystal-like solid, but can also appear yellow. Phenanthrene is used to make dyes, plastics and pesticides, explosives and drugs. It has also been used to make bile acids, cholesterol and steroids.^[3]

Phenanthrene occurs naturally and also is a man-made chemical. Commonly, humans are exposed to phenanthrene through inhalation of cigarette smoke but there are many routes of exposure. Animal studies have shown that phenanthrene is a potential carcinogen.^[3] However, according to IARC, it is not identified as a probable, possible or confirmed human carcinogen.^[4]

Phenanthrene's three fused rings are angled as in the phenacenes, rather than straight as in the acenes. The compound with a phenanthrene skeleton and nitrogens at the 4 and 5 positions is known as phenanthroline.

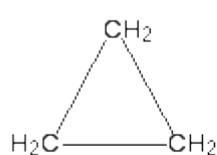


UNIT V

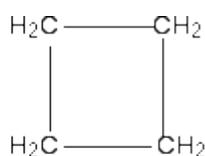
cycloalkanes are cyclic hydrocarbons, meaning that the carbons of the molecule are arranged in the form of a ring. Cycloalkanes are also saturated, meaning that all of the carbon atoms that make up the ring are single bonded to other atoms (no double or triple bonds). There are also polycyclic alkanes, which are molecules that contain two or more cycloalkanes that are joined, forming multiple rings.

Introduction

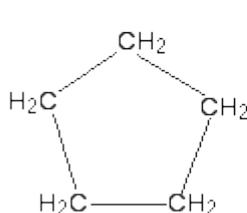
Many organic compounds found in nature or created in a laboratory contain rings of carbon atoms with distinguishing chemical properties; these compounds are known as cycloalkanes. Cycloalkanes only contain carbon-hydrogen bonds and carbon-carbon single bonds, but in cycloalkanes, the carbon atoms are joined in a ring. The smallest cycloalkane is cyclopropane.



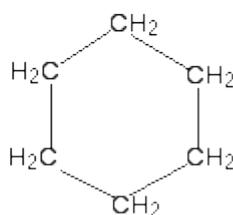
cyclopropane



cyclobutane



cyclopentane



cyclohexane

If you count the carbons and hydrogens, you will see that they no longer fit the general formula C_nH_{2n+2} . By joining the carbon atoms in a ring, two hydrogen atoms have been lost. The general formula for a cycloalkane is C_nH_{2n} . Cyclic compounds are not all flat molecules. All of the cycloalkanes, from cyclopentane upwards, exist as "puckered rings". Cyclohexane, for example, has a ring structure that looks like this:

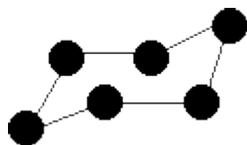
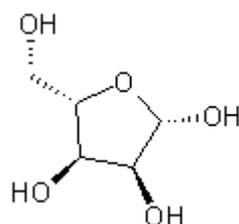
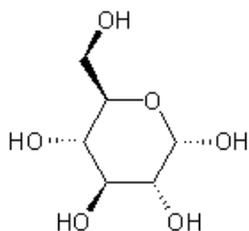


Figure 2: This is known as the "chair" form of cyclohexane from its shape, which vaguely resembles a chair. Note: The cyclohexane molecule is constantly changing, with the atom on the left, which is currently pointing down, flipping up, and the atom on the right flipping down. During this process, another (slightly less stable) form of cyclohexane is formed known as the "boat" form. In this arrangement, both of these atoms are either pointing up or down at the same time

In addition to being saturated cyclic hydrocarbons, cycloalkanes may have multiple substituents or functional groups that further determine their unique chemical properties. The most common and useful cycloalkanes in organic chemistry are cyclopentane and cyclohexane,

although other cycloalkanes varying in the number of carbons can be synthesized. Understanding cycloalkanes and their properties are crucial in that many of the biological processes that occur in most living things have cycloalkane-like structures.



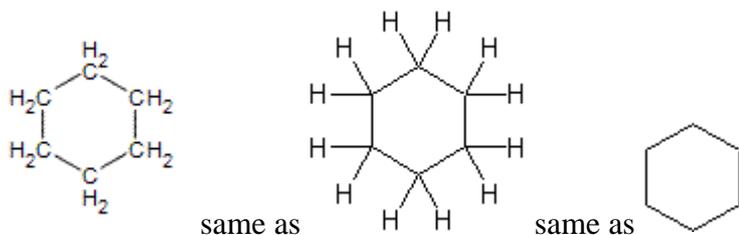
Glucose (6 carbon sugar)

Ribose (5 carbon sugar)

Although polycyclic compounds are important, they are highly complex and typically have common names accepted by IUPAC. However, the common names do not generally follow the basic IUPAC nomenclature rules. The general formula of the cycloalkanes is C_nH_{2n} where n is the number of carbons. The naming of cycloalkanes follows a simple set of rules that are built upon the same basic steps in naming alkanes. Cyclic hydrocarbons have the prefix "cyclo-".

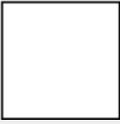
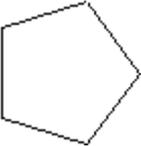
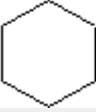
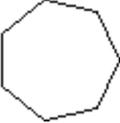
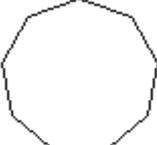
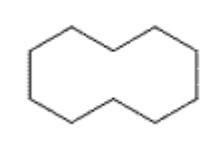
Contents

For simplicity, cycloalkane molecules can be drawn in the form of skeletal structures in which each intersection between two lines is assumed to have a carbon atom with its corresponding number of hydrogens.



Molecular Formula	Basic Structure
C_3H_6	



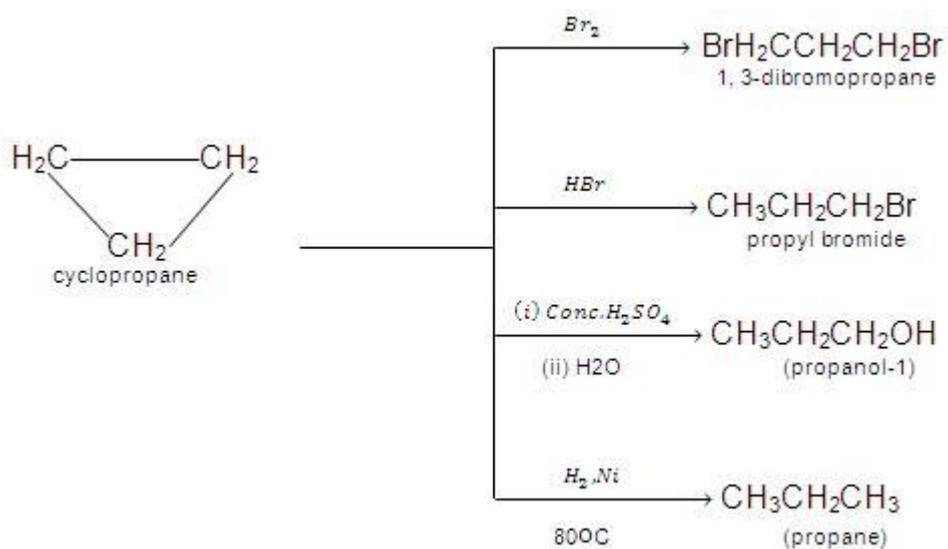
	Molecular Formula	Basic Structure
	C_4H_8	
	C_5H_{10}	
	C_6H_{12}	
	C_7H_{14}	
	C_8H_{16}	
	C_9H_{18}	
	$C_{10}H_{20}$	

IUPAC Rules for Nomenclature

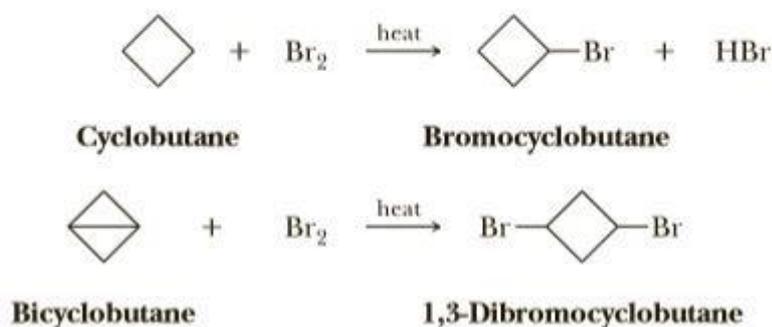
1. Determine the cycloalkane to use as the parent chain. The parent chain is the one with the highest number of carbon atoms. If there are two cycloalkanes, use the cycloalkane with the higher number of carbons as the parent chain.
2. If there is an alkyl straight chain that has a greater number of carbons than the cycloalkane, then the alkyl chain must be used as the primary parent chain. Cycloalkane acting as a substituent to an alkyl chain has an ending "-yl" and, therefore, must be named as a cycloalkyl.

Cycloalkane	Cycloalkyl
cyclopropane	cyclopropyl
cyclobutane	cyclobutyl
cyclopentane	cyclopentyl
cyclohexane	cyclohexyl
cycloheptane	cycloheptyl
cyclooctane	cyclooctyl
cyclononane	cyclononyl
cyclodecane	cyclodecanyl

\



Cyclobutane reacts with bromine to give bromocyclobutane, but bicyclobutane reacts with bromine to give 1,3-dibromocyclobutane. Account for the differences between the reactions of these two compounds.



In 1885, Adolf Baeyer theorized on how to create stability of the first few cycloalkanes, which was derived from the idea that in tetrahedral geometry, there's a normal angle between a pair of carbon atom bonds in 109.28° in methane molecules. In the subject of Tetrahedral Geometry, this concept became very vital and helped us find out that the bond angle for carbon atoms is 109.28° (or 109.50) in methane molecules. Baeyer also found out that these cycloalkanes have distinct bond angles and also different properties and stability at the same time. This is when, based on this, he first thought of proposing Strain Theory.

Overview of Strain theory

This theory, when published, described the cycloalkane reactivity and its stability in great depths. It also told us that the optimum overlap of atomic orbitals is achieved for a bond angle of 109.50°. So in a gist, from this theory, we can conclude that this is the best bond angle for alkanes.

This abundantly efficient and preferable overlap of atomic orbitals gives results where we achieve the highest bond strength and the vastly stable molecule.

The rings in this experiment cause distress on the bond angles as they deviate from the ideal. This also helps us observe that the higher the pressure, the more unstable the system is. Such a higher strain concludes in an increase in reactivity and heat combustion. As Baeyer stated, if we deviate from the bond angle from the perfect bond angle value, which is 109.50°, it will create a strain in the molecule. This will result in a lower variance and a much less unstable solution.

Assumptions of strain theory

This theory is founded on the following assumptions:

- Planar Rings are utilized in all of the ring structures. Unstable Cycloalkanes originate due to divergences from the general tetrahedral angles.
- Large Ring Structures contain negative strains, but these do not exist.
- Since these cycloalkanes have carbon rings with a puckered texture instead of a planar (flat) structure, their bond angles are around 109.50° or less—for example, Cycloheptane, Cyclooctane, and Cyclopentolate.

- These assumptions form the ground basis for comprehending the instability in the cycloalkane ring system.

Baeyer's Strain Theory in Cycloalkanes

- When carbon gets bound to two other carbon atoms in propane, which is an open-chain compound, it is sp^3 hybridized; these hybrid orbitals are usually utilized to form strong sigma bonds.
- Since these carbon atoms are present in the cyclopropane, they do not use these hybrid orbitals to form any bonds; their bent-bond is weaker than a general carbon to carbon bond. This strain is known as the angle strain.
- This ring produces strains with bond angles that deviate from the ideal. We can observe that higher strains result in increased volatility, combustion of heat and reactivity. In simple words, the deviation is directly related to the instability.
- By assuming this, Baeyer discovered that a number of cycloalkanes have different types of bond angles and different properties and stabilities.
- He proposed that the angle in the strain theory is based on this and this theory describes the stability and reactivity.
- The cyclopropane ring is in the shape of a triangle and has a standard tetrahedral structure where the angle is between the two bonds that are compressed to 60° and each of these bonds involved is pulled in by 24.75° .
- What happens is that all three angles become 60° instead of 109.5° , which is the normal bond angle for a carbon atom.
- The deviation or Angle strain of each and every bond is defined by the value of 24.75° .
- In the same way, a cyclobutane is a square with the bond angles of 90° and not 109.5° to make the ring system square with an angle strain of 9.75° .
- When we talk about the cyclopropane and cyclobutane ring systems, a ring pressure is caused by a usual tetrahedral angle.
- In contrast to this Baeyer believed that cyclopropanes are highly stressed and unstable compounds.
- As a result, the triangle ring can be opened up even with a slight provocation, with a release of tension with them. This is true as the cyclopropane undergoes Br_2 ring-opening reactions.
- Cyclopentane, on the other hand, is known to be the least stressed and the most stable. This is why it also has no ring-opening reactions.
- In Cyclohexane, the strain angle is bigger than it is in cyclopentane. This states that if the number of the ring increases, the strain increases with it.
- So, in theory, cyclohexane and higher cycloalkanes become more reactive and unstable as time passes.

- But in contrast to this prediction, cyclohexane and the members of this group turned out to be highly stable, which meant that they go through substitution instead of additional reactions.

As a result, this hypothesis only accounts for the first three adequately. Hence, Cyclopentane > Cyclobutane > Cyclopropane

Limitations

- The Baeyer was not able to describe the impact of an angle pressure in the larger structures.
- According to him, cyclohexane is less stable than cyclopentane, but the reality is the opposite of this.
- He stated that due to negative pressure, larger ring structures are not possible, but they do exist and are highly stable.
- For the removal of angle pressure, larger ring structures are wrinkled (puckered) instead of being planar (flat).

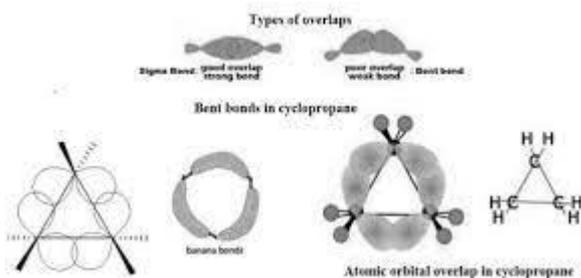
COULSON MOFFIT THEORY

bent bond, also known as a **banana bond**, is a type of covalent chemical bond with a geometry somewhat reminiscent of a banana. The term itself is a general representation of electron density or configuration resembling a similar "bent" structure within small ring molecules, such as cyclopropane (C₃H₆) or as a representation of double or triple bonds within a compound that is an alternative to the sigma and pi bond model.

Bent bonds^{[1][2][3][4]} are a special type of chemical bonding in which the ordinary hybridization state of two atoms making up a chemical bond are modified with increased or decreased s-orbital character in order to accommodate a particular molecular geometry. Bent bonds are found in strained organic compounds such as cyclopropane, oxirane and aziridine.

In these compounds, it is not possible for the carbon atoms to assume the 109.5° bond angles with standard sp³ hybridization. Increasing the p-character to sp⁵ (i.e. 1/6 s-density and 5/6 p-density)^[5] makes it possible to reduce the bond angles to 60°. At the same time, the carbon-to-hydrogen bonds gain more s-character, which shortens them. In cyclopropane, the maximum electron density between two carbon atoms does not correspond to the internuclear axis, hence the name *bent bond*. In cyclopropane, the *interorbital angle* is 104°. This bending can be observed experimentally by X-ray diffraction of certain cyclopropane derivatives: the deformation density is outside the line of centers between the two carbon atoms. The carbon-carbon bond lengths are shorter than in a regular alkane bond: 151 pm versus 153 pm.^[6]

Cyclobutane is a larger ring, but still has bent bonds. In this molecule, the carbon bond angles are 90° for the planar conformation and 88° for the puckered one. Unlike in cyclopropane, the C–C bond lengths actually increase rather than decrease; this is mainly due to 1,3-nonbonded steric repulsion. In terms of reactivity, cyclobutane is relatively inert and behaves like ordinary alkanes.



Sachse – Mohr theory of strainless rings:

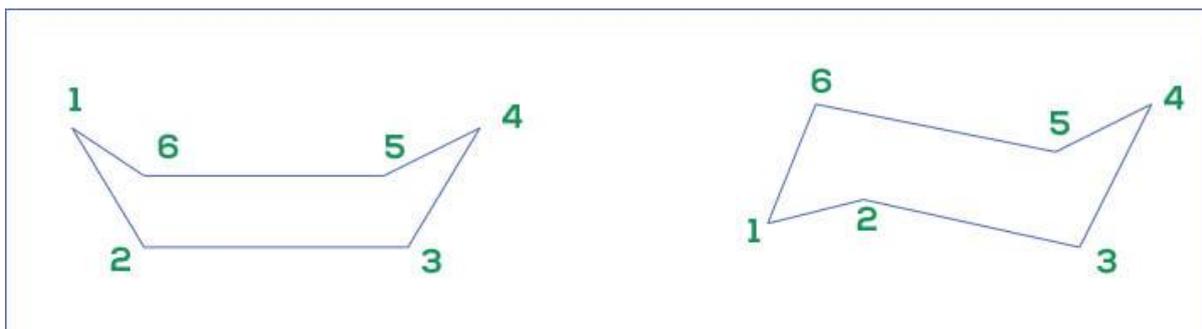
In order to explain the stability of higher cycloalkanes, Sachse and Mohr in 1918 proposed a theory of strainless rings.

According to this Sachse – Mohr theory, the ring with six or more carbon atoms become free from the strain as all the carbon atoms are not forced into one plane. Hence, the carbon atoms occupy different planes where the normal tetrahedral angle is retained. The rings formed are called Strainless rings.

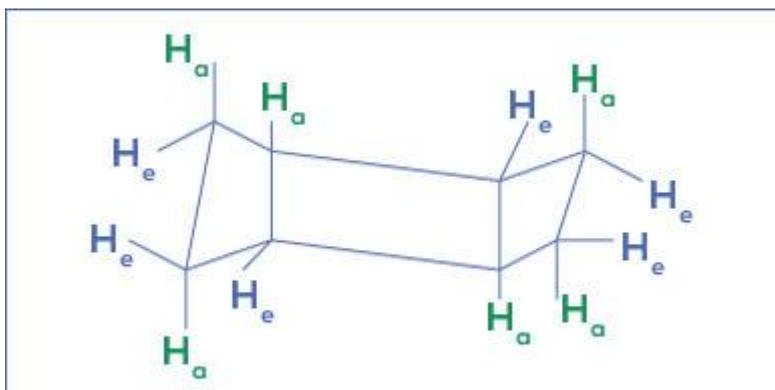
For example, cyclohexane exists in two puckered conformations. They are 'Chair form' and 'Boat form'. Both these forms are without any angle strain. Hence, they are strainless rings.

Chair form of cyclohexane is more stable than the boat form due to the following reasons:

1. In the chair conformation, the adjacent C – H bonds on all the neighbouring carbon atoms are staggered. In the boat form, the adjacent C-H bonds on C₂-C₃ and C₅-C₆ are eclipsed. Hence energy of boat form becomes more than the chair form.
2. Out of the 12 hydrogens, six of them point up or down perpendicular to the plane of the molecule. These are called **axial hydrogens**. The other 6 hydrogens are found either above or below the plane of the molecule. They are equatorial hydrogens. In the boat form, the two axial hydrogen on C₁ and C₄ are closer than in chain form. Hence the energy of boat form is more than chair form.



Boat and chair form of cyclohexane.



Axial and equatorial bonds in cyclohexane