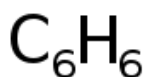


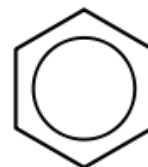
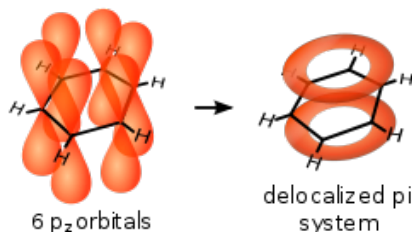
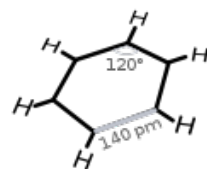
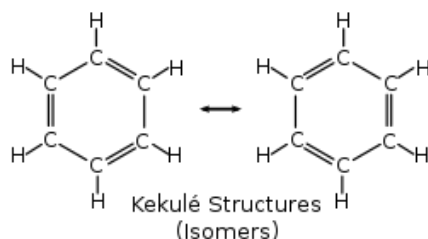
# Aromatic Compounds and Electrophilic Aromatic Substitution

[See online here](#)

Hydrocarbons are compounds exclusively composed of carbon and hydrogen atoms and can be considered aliphatic or aromatic; aromatic compounds will be the primary focus within this article. In general, aromatic compounds exhibit aromaticity, the property in which a conjugated ring of unsaturated bonds, lone pairs, or empty orbitals exhibit increased stabilization compared to ordinary conjugation. In this article, the different properties of an aromatic compound are discussed as well as their different applications; included is a discussion on benzene,  $C_6H_6$ . Unlike ordinary alkenes where addition reaction occurs, aromatic compounds involve electrophilic aromatic substitution (EAS).



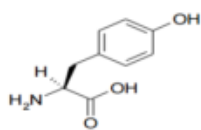
Benzene  
Molecular formula



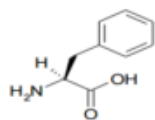
## Aromatic Compounds

Historically, aromatic compounds referred to any compound producing a fragrant smell, such as benzaldehydes which produce the scent of cherries, peaches, and almonds. However, some aromatic compounds were later discovered that do not exhibit this property. Therefore, aromatic compounds are currently classified according to their chemical behavior.

## Biologically relevant examples of aromatic compounds

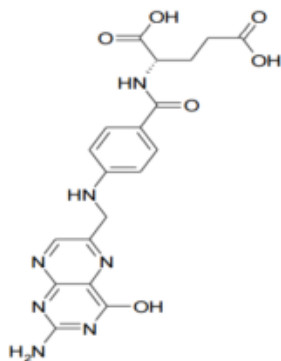


tyrosine



phenylalanine

natural aminoacids



Folic acid, Pteroyl-L-glutamic acid, Vitamin Bc,  
necessary for the production and maintenance  
of new cells

"Aromatic Compounds" by Lecturio.

## Classification of aromatic compounds

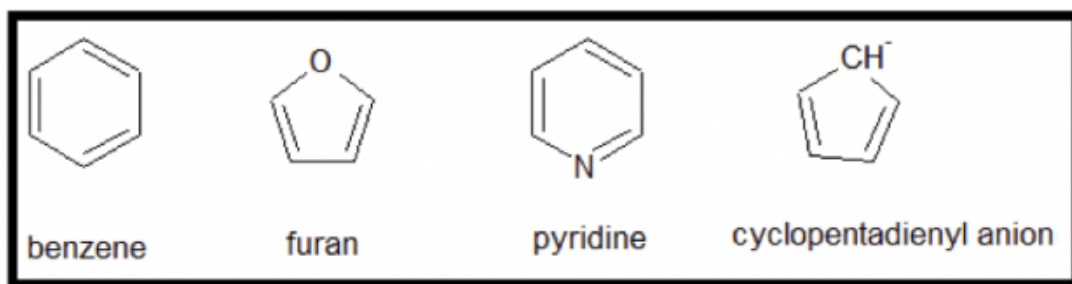
Aromatic compounds are a large family of compounds comprised of a six-membered ring or more complex structure. Notably, aromatic compounds are not limited to hydrocarbons as there are aromatic compounds like thiophene and pyridine which have S and N in their structure. Ions can also be considered aromatic as long as they exhibit the properties noted above.

Compounds are classified as aromatic if they are able to exhibit the following properties:

- The molecule is cyclic and contains conjugated high or low electron density areas.
- The molecule is very stable compared to their aliphatic counterparts.
- The molecule is planar to allow easier delocalization of the  $\pi$  electrons.
- All atoms in the cycle contain a p-orbital for overlap.
- The molecule follows the Huckel  $4n + 2 \pi$  electron rule where n should be an integer.

The compound is considered to be aromatic if it is able to exhibit all of the properties included in the list. Otherwise, the compound can be classified as either a non-aromatic or anti-aromatic compound.

An aromatic compound is considered a big family of compounds as it comprises of compounds with a **six-membered ring**, to more complex structures. Aromatic compounds are also not limited to hydrocarbons as there are also aromatic compounds like thiophene and pyridine that are considered aromatic, even if they have S and N in their structure. **Ions can also be considered as aromatic**, as long as they will exhibit the properties included above.



"Some aromatic compounds." by Mark Xavier Bailon.

## Biologically relevant examples of aromatic compounds

Steroids are aromatic compounds which are important to biological organisms and include hormones responsible for the growth and the development of physical features. In the pharmaceutical industry, compounds such as atorvastatin, a cholesterol-lowering drug, are also aromatic. Pyridine,  $C_5H_5N$ , is a common aromatic compound present in vitamins and other pharmaceuticals. Most of the essential vitamins we need are also aromatic. Benzene, the most common aromatic compound, is used in manufacturing polystyrene plastics, pesticides, and some pharmaceutical drugs.

### Benzene

**Benzene** is a hydrocarbon with the molecular formula  **$C_6H_6$**  and has a **cyclic structure with alternating or conjugated double bonds**. Although benzene is **unsaturated**, it does not exhibit the relative reactivity of its other alkene and acyclic counterparts. For example, cyclohexene readily reacts with  $Br_2$  to produce 1,2-dibromocyclohexane. Conversely, benzene reacts very slowly with  $Br_2$  to form bromobenzene which still retains the presence of three double bonds, demonstrating the relative stability of benzene.

Another important observation is the **bond lengths in a benzene molecule**. In ordinary compounds, single bonds are expected to be longer than double bonds. However, the bond length analysis of benzene shows that the C to C bond lengths are all equal, regardless of being a single or double bond. The bond angle in each C-C-C segment is  $120^\circ$ , forming a perfect hexagon shape. The electrostatic potential map shows that the electron density is identical in all six carbon-carbon bonds. Each carbon also has a p-orbital that lies perpendicular to the plane of the six-membered ring.

Because of the peculiar properties of benzene, each double bond is not considered to be localized, but rather, overlapping to only one other p-orbital. These properties are only possible if the compound has all p-orbitals equally overlapping adjacent p-orbitals. This overlap of orbitals enables delocalization of the 6  $\pi$  electrons around the ring. Because of this, it is difficult to isolate the 2 possible isomers of benzene. Instead, a circle is included inside the 6 sides of the molecule to indicate delocalization of the  $\pi$  electrons.

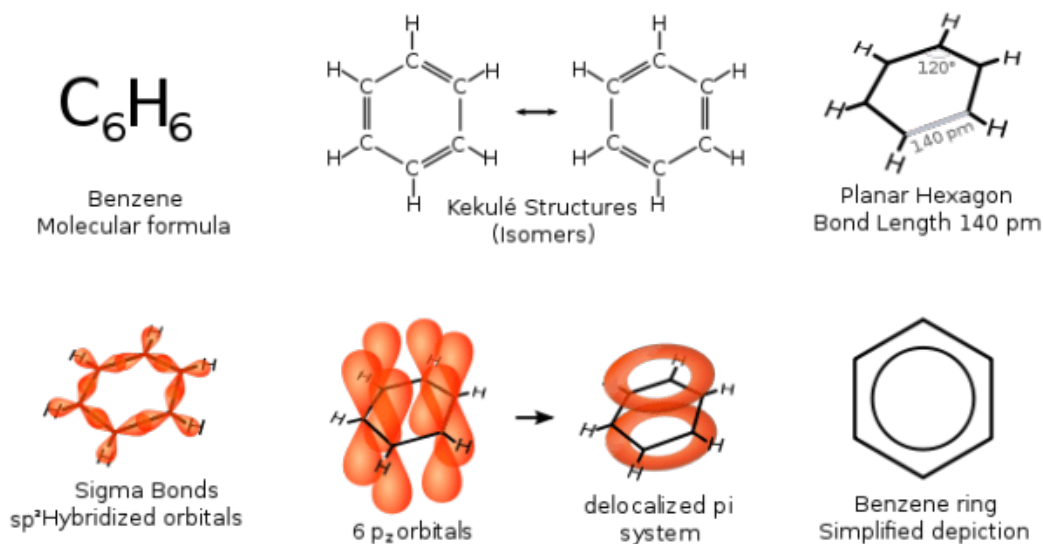
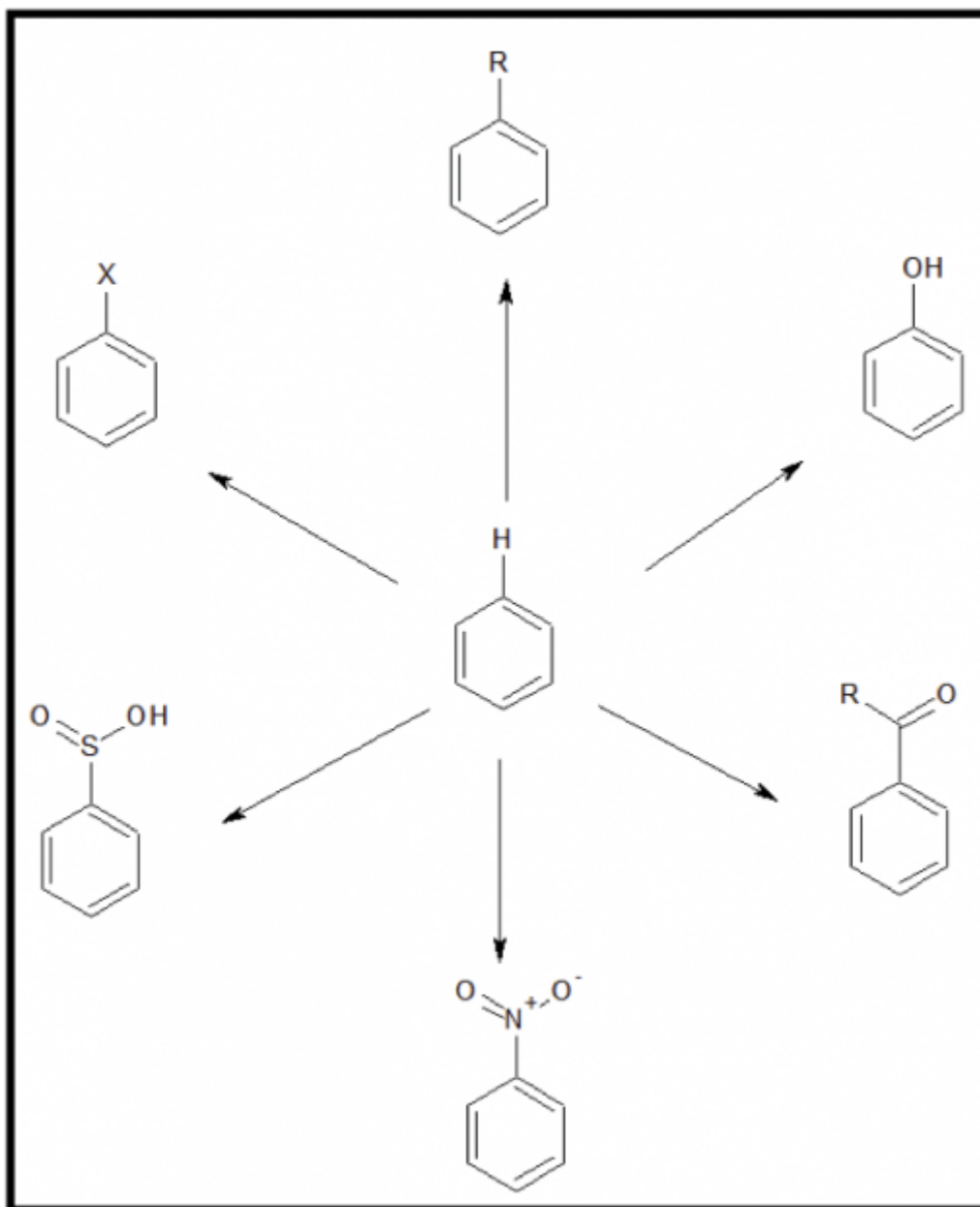


Image: "Various representations of Benzene" by Vladsinger. License: [CC BY-SA 3.0](https://creativecommons.org/licenses/by-sa/3.0/)

## Electrophilic Aromatic Substitution Reaction

Electrophilic aromatic substitution (EAS) occurs when **an electrophile reacts with an aromatic ring, substituting one of the H atoms in the ring**. A number of different electrophiles may be used in EAS. Possible electrophiles include halogens (-Cl, -Br, -I), the sulfonic acid group (-SO<sub>3</sub>H), hydroxyl group (-OH), nitro group (-NO<sub>2</sub>), acyl groups (-COR), and alkyl groups (-R). Even with benzene alone, one can come up with some compounds because of the number of possible electrophiles for the reaction.

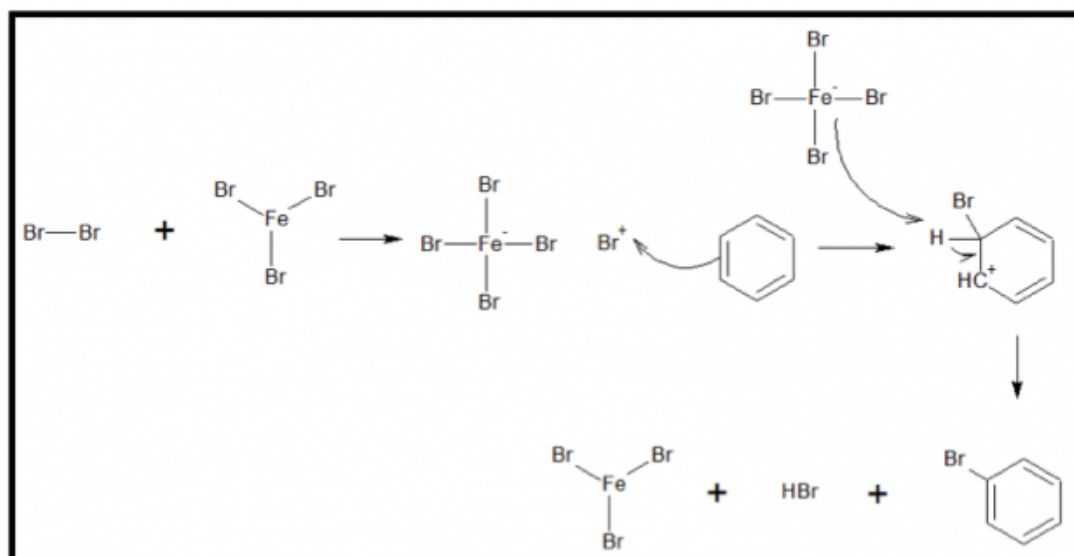


"Electrophilic Aromatic Substitution of Benzene." by Mark Xavier Bailon.

## Halogenation

**Aromatic compounds**, unlike ordinary alkenes, are **less reactive compared to their acyclic counterparts** due to their relative stability afforded by  $\pi$  electron delocalization. In a halogenation reaction known as **bromination**,  $\text{Br}_2$  can readily react with ethane to produce dibromoethane. This is not true for benzene. For the **bromination reaction** to proceed in benzene, a catalyst such as  $\text{FeBr}_3$  is needed which provides a different mechanism for the reaction to proceed.

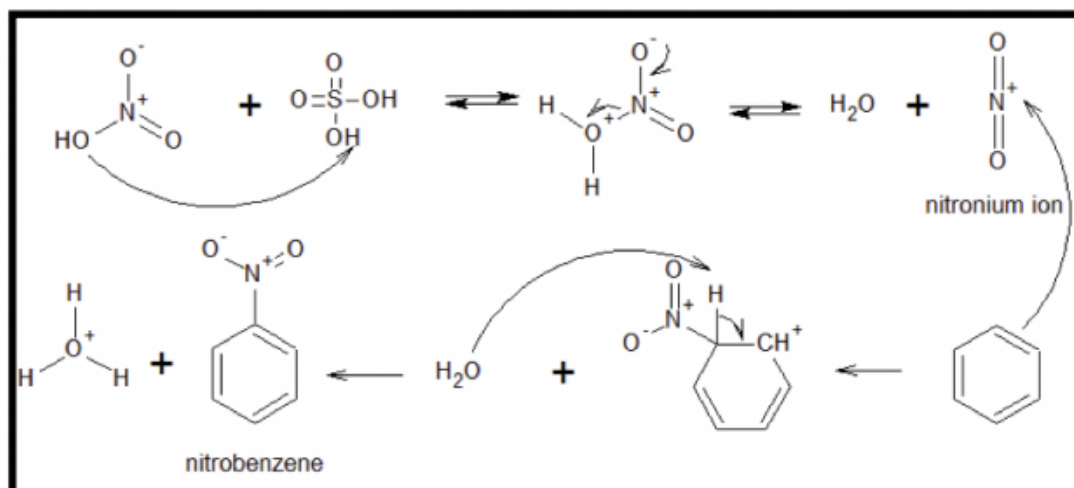
The 1st step in the reaction is the polarization of the  $\text{Br}_2$  molecule by  $\text{FeBr}_3$ . In the process, a more electrophilic molecule is produced in the form of  $\text{FeBr}_4^- \text{Br}^+$ . The presence of  $\text{Br}^+$  makes  $\text{FeBr}_4^- \text{Br}^+$  more electrophilic than an ordinary  $\text{Br}_2$  molecule. The  $\text{FeBr}_4^- \text{Br}^+$  will then attack the benzene molecule and a base will remove the proton in the process. Below is the mechanism of the reaction:



"Bromination Reaction of Benzene." by Mark Xavier Bailon.

## Nitration

Nitration of aromatic rings can be achieved **using a mixture of concentrated nitric and sulfuric acids**. The electrophile in the reaction is the nitronium ion,  $\text{NO}_2^+$ , which is produced by the protonation and loss of water in the form of  $\text{HNO}_3$ . Just as in halogenation, a carbocation intermediate is produced when the nitronium ion interacts with the benzene ring. Upon loss of a proton, the neutral substitution product nitrobenzene is produced. Below is the basic mechanism for the nitration of benzene:

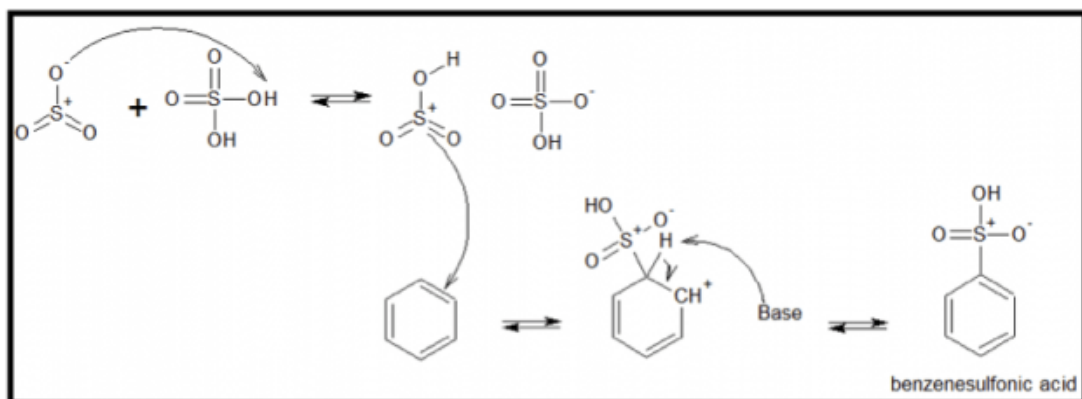


"Nitration Reaction of Benzene." by Mark Xavier Bailon.

## Sulfonation of Benzene

A sulfonation reaction of aromatic rings is achieved by **reacting benzenes with fuming sulfuric acid** (a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$ ). The electrophile for the reaction is either  $\text{HSO}_3^+$  or neutral  $\text{SO}_3$ , depending on the reaction conditions. This reaction mechanism is similar to the bromination and nitration reactions previously discussed. A sulfonation reaction is favored in the presence of strong acids, while desulfonation is favored in hot,

dilute aqueous acids. The mechanism for sulfonation is as follow:



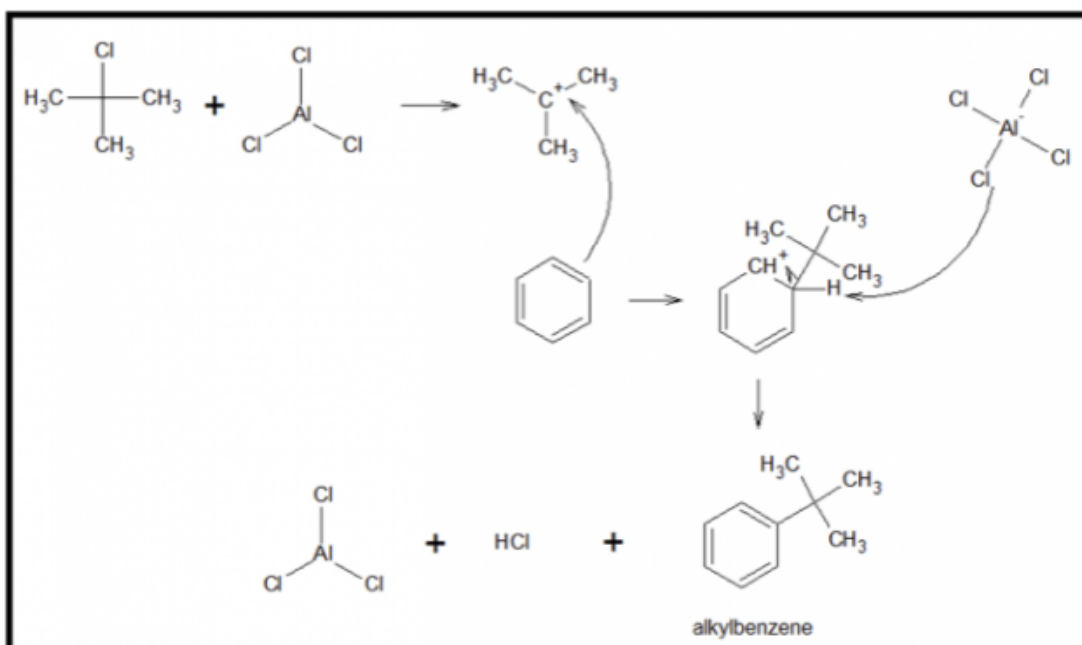
"Sulfonation Reaction of Benzene." by Mark Xavier Bailon.

## Hydroxylation

A hydroxylation reaction of aromatic rings is very difficult to achieve in ordinary reaction conditions and requires **the presence of biological enzymes**. An example of a hydroxylation reaction catalyzed through a biological pathway is the hydroxylation of p-hydroxyphenylacetate using the enzyme p-hydroxyphenylacetate-3-hydroxylase to produce 3,4-dihydroxyphenylacetate. The process requires molecular oxygen plus the coenzyme-reduced flavin adenine dinucleotide, FADH<sub>2</sub>.

## Alkylation Reaction

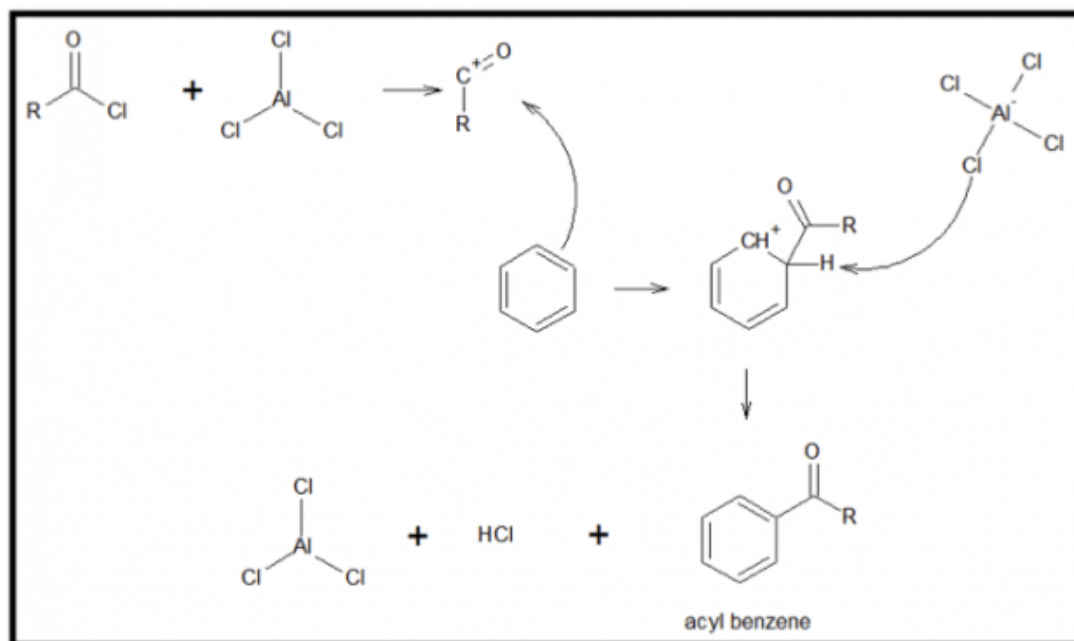
An alkylation reaction **proceeds when an alkylchloride is combined with  $\text{AlCl}_3$** .  $\text{AlCl}_3$  enables the dissociation of R-X to produce the carbocation that will serve as the electrophile. The electrophile then attacks the benzene ring and the reaction is completed by proton loss. The mechanism of the reaction is shown below:



"Alkylation of Benzene." by Mark Xavier Bailon.

## Acylation Reaction

The mechanism of the acylation reaction is similar to the alkylation reaction. The alkyl halide is just replaced by an acyl halide. For example, for the acylation reaction of benzene, the first step is the generation of a strong electrophile by the interaction between the acyl chloride and the  $\text{AlCl}_3$  molecule. The acyl cation is then stabilized by rearrangement in the acyl cation with the  $+$  charge present in the C atom. The  $+\text{C}$  then interacts with the double bond in the benzene molecule, forming a carbocation that can be stabilized by abstracting one of the protons using the  $\text{AlCl}_4^-$  ion produced in the first step. The mechanism for acylation is shown in the figure below:

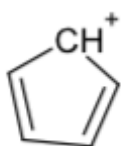


"Acylation of Benzene." by Mark Xavier Bailon.

## Review Questions

The correct answers can be found below the references.

**1. Which of the following property of an aromatic compound is violated by the**

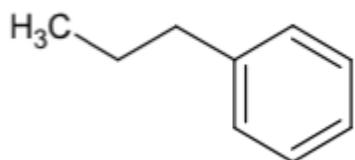
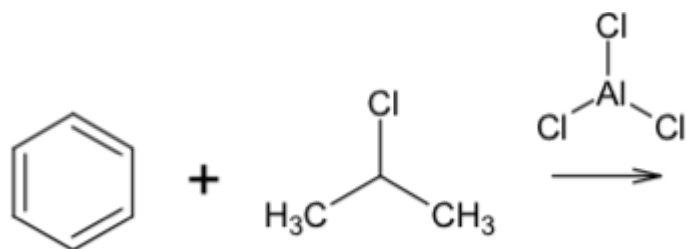


**cyclopentadienyl cation below?**

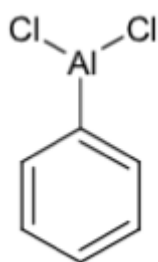
- A. Planar
- B. Conjugated double bond
- C. All atoms in the cycle contain a p-orbital.
- D. Huckel rule ( $4n + 2 \pi$  electrons)

**2. Which of the following compounds will be produced by the reaction below?**

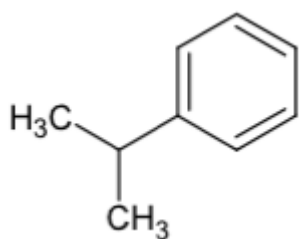




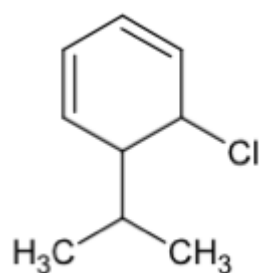
A.



B.



C.



D.

## References

McMurry, J. (2008). Organic Chemistry. 7th ed. USA. Brooks/Cole, Thomson Learning Inc.

Carey, F. (2000). Organic Chemistry. 4th ed. USA. McGraw-Hill Companies, Inc.

**Correct answers:** 1D, 2C

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