GE CHEMISTRY SEMESTER-III

Section-B: Organic Chemistry II

AROMATIC HYDROCARBON

Lecture-1

DR. NILOY DAS
ASSISTANT PROFESSOR
DEPARTMENT OF CHEMISTRY
P. R. THAKUR GOVT. COLLEGE

Syllabus

Benzene

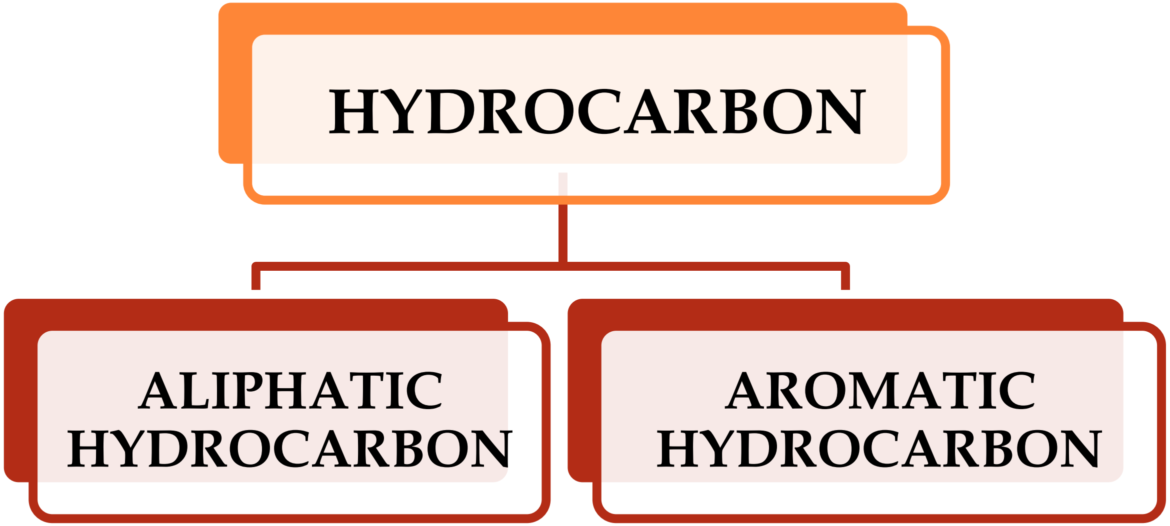
Preparation:

From phenol, by decarboxylation, from acetylene, from benzene sulphonic acid.

Reactions:

1. Electrophilic substitution (general mechanism)
2. Nitration (with mechanism)
3. Halogenations (chlorination and bromination)
4. Sulphonation
5. Friedel-Craft’s reaction (alkylation and acylation) (up to 4 carbons on benzene)
6. Side chain oxidation of alkyl benzenes (up to 4 carbons on benzene).

Quick Overview



HYDROCARBON

ALIPHATIC HYDROCARBON

AROMATIC HYDROCARBON

1. In ancient the word *aromatic* was used to describe fragrant substances such as benzene (from coal distillate), benzaldehyde (from cherries, peaches, and almonds) etc.

2. Today, the word aromatic refer to the class of compounds that contain six-membered benzene-like rings with three double bonds.

BENZENE

History of Benzene

Year1825: Benzene was first discovered by the English scientist Michael Faraday in illuminating gas

Year1845: German chemist A.W. von Hofmann isolated benzene from coal tar.

Year 1861 & 1866: German chemists Joseph Loschmidt and August Kekule von Stradonitz independently proposed a cyclic arrangement of six carbons with alternating single and double bonds but Kekule proposed that due to the oscillation of the double bonds, two equivalent structures in rapid equilibrium.

Year 1931: American chemist Linus Pauling suggested that benzene had a single structure, which was a resonance hybrid of the two Kekule structures.

Continued....

- Benzene (C_6H_6) is a six-membered ring with alternating double and single bond. benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions.
- All the C-C bond lengths in benzene are same (139 pm) and they are in between single bond length(154 pm) and double bond length (134 pm).
- The hybridization of carbons in benzene is sp^2 and all the double bonds are delocalized i.e. the unhybridized p orbital overlaps equally well with the all neighboring p-orbital.
- In resonance term benzene is a hybrid of two equal forms (Fig. 1) and due to this resonance, benzene is more stable and less reactive than a typical alkene.

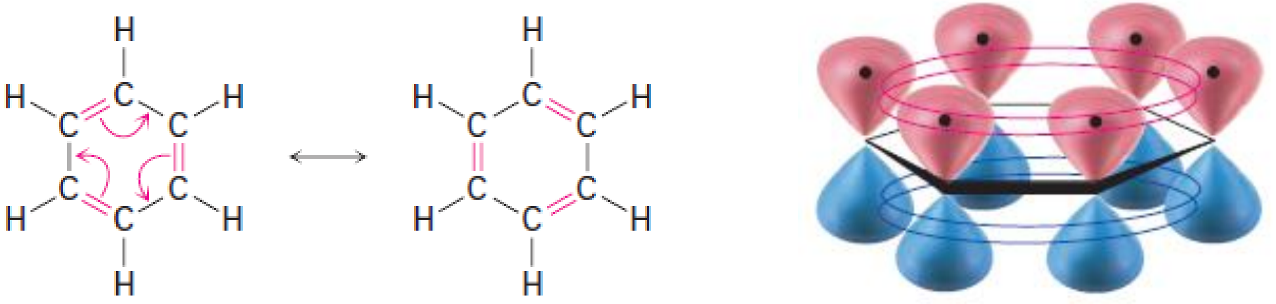


Fig. 1: An electrostatic potential map and orbital picture of benzene

Properties of benzene

A. Benzene is a colorless liquid, m.p. 55°C , b.p. 80°C with a smell
B. Density of benzene is $0.87 gcm^{-3}$
C. It is inflammable and burning with a sooty flame
D. Benzene is a very good solvent for fats, resin, sulphur, iodine etc. but it is immiscible with water

Preparation of benzene

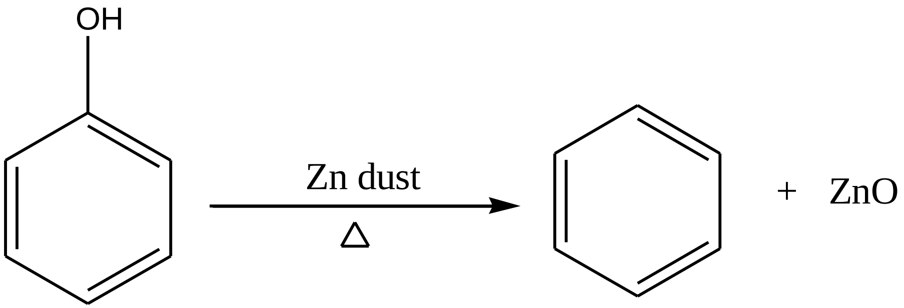
Benzene was first synthesized by Berthelot (1870) by passing acetylene through red hot tube (873 K)

$$3C_2H_2 \longrightarrow C_6H_6$$

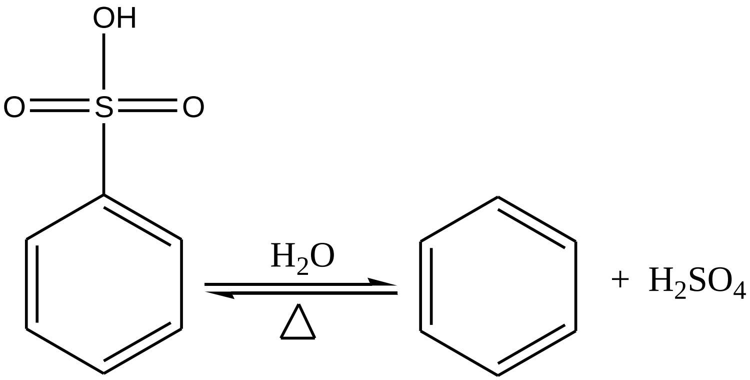
Decarboxylation: In this process sodium benzoate and soda lime (sodium hydroxide and calcium oxide) was heated and benzene was formed after removal of carbon dioxide i.e. decarboxylation.

$$C_6H_5COONa \xrightarrow{\text{soda lime}} C_6H_6 + CO_2$$

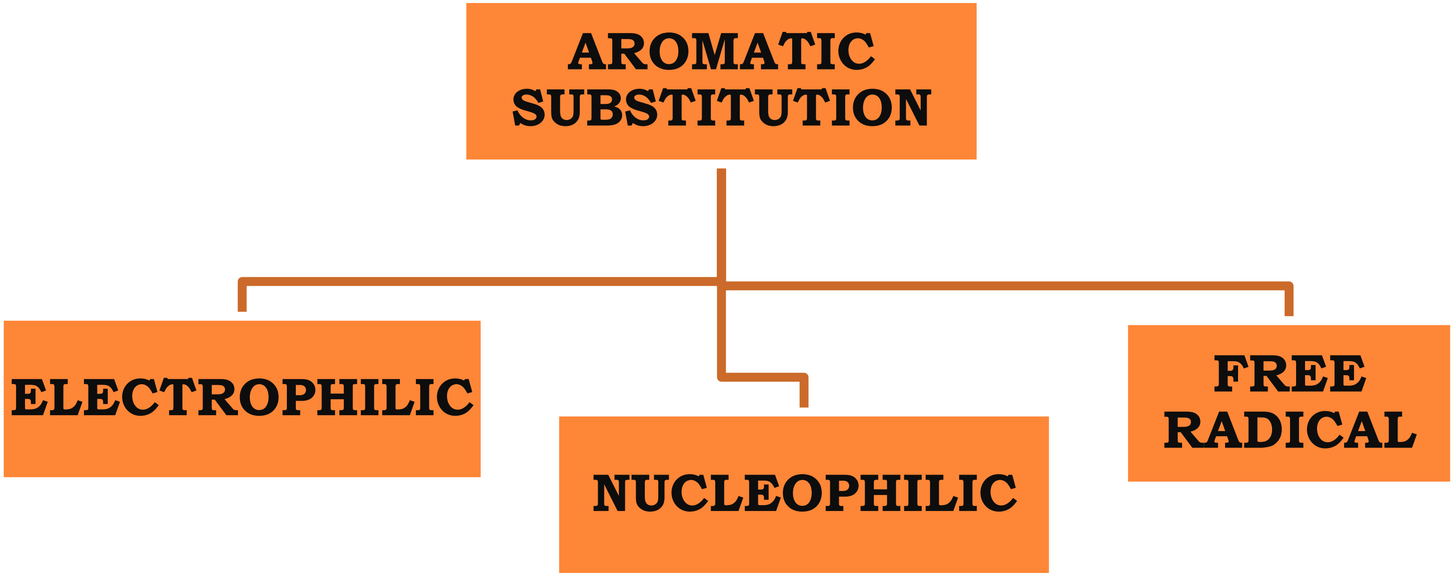
Phenol reacts with Zn dust at high temperature to produce benzene. At high temperature phenol dissociates to form phenoxide ion and proton which accepts electron from Zn metal to form hydrogen radical. After that benzene will form from phenoxide and zinc (cation radical will convert to ZnO.



Hydrolysis sulphonic acid by superheated steam produce benzene and sulphuric acid.



REACTIONS OF BENZENE



AROMATIC SUBSTITUTION

ELECTROPHILIC

NUCLEOPHILIC

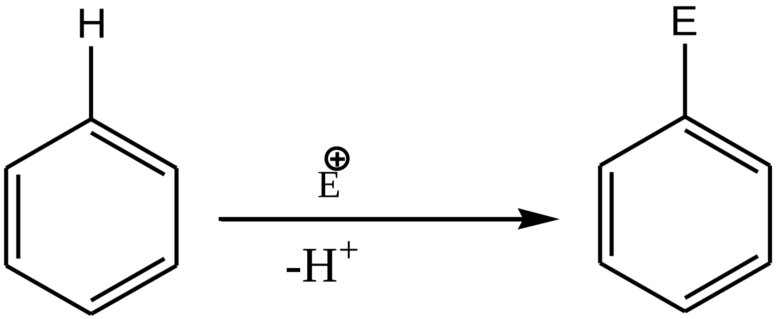
FREE RADICAL

NOTE: The most common reaction in the benzene system is Electrophilic Substitution reaction as benzene is itself a electron rich organic compound.

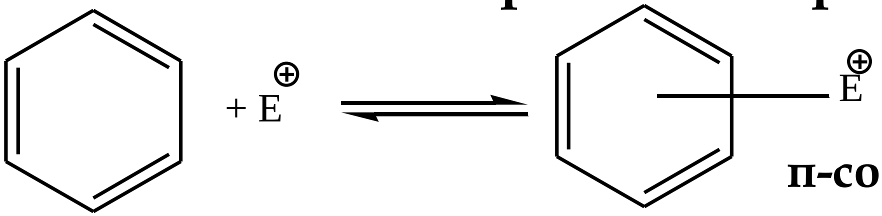
AROMATIC ELECTROPHILIC SUBSTITUTION (AES)

In AES the benzene ring is attacked by an electrophile (E^+) to substitute hydrogen atom to form the substituted product.

This reaction has two steps-1) Addition of electrophile and 2) removal of proton. Among these two steps first step is the slow step (rate determining step or r.d.s.) and second step is very first as after removal of proton it will regain its aromaticity i.e. stability.

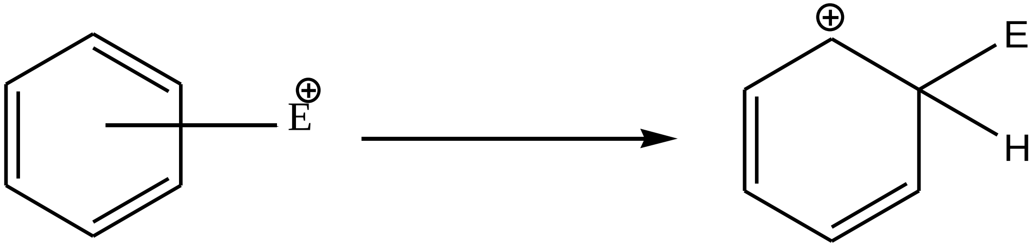


Mechanism: In this mechanism 1st step is the formation of rapidly reversible π-complex. π-complex is a donor-acceptor type complex, where benzene is donor and electrophile is acceptor.



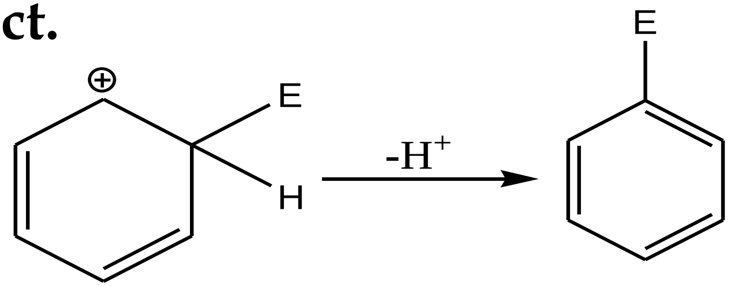
π-complex

π-complex then converted to σ-complex (benzenium ion) to complete the substitution process. It is the intermediate of the AES reaction.



σ-complex

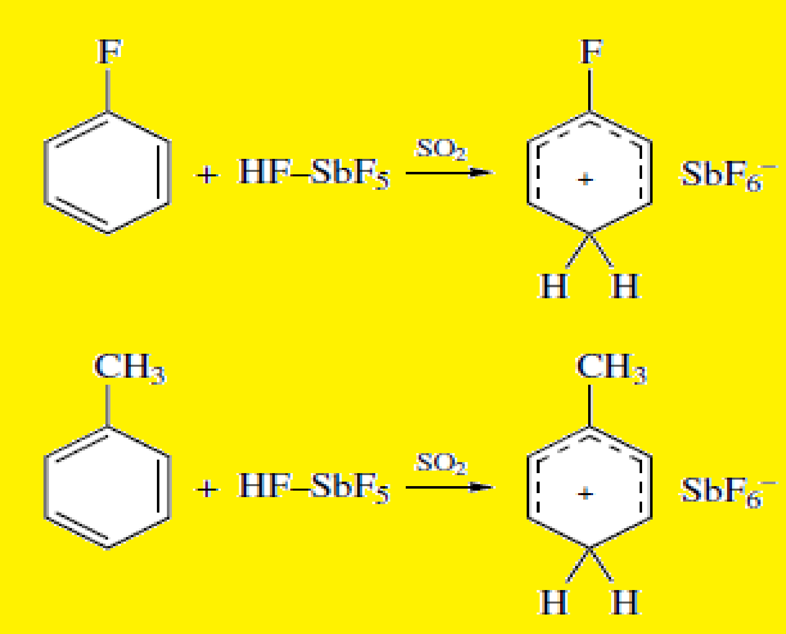
Then removal of proton from this benzenium ion leads to the substituted product.



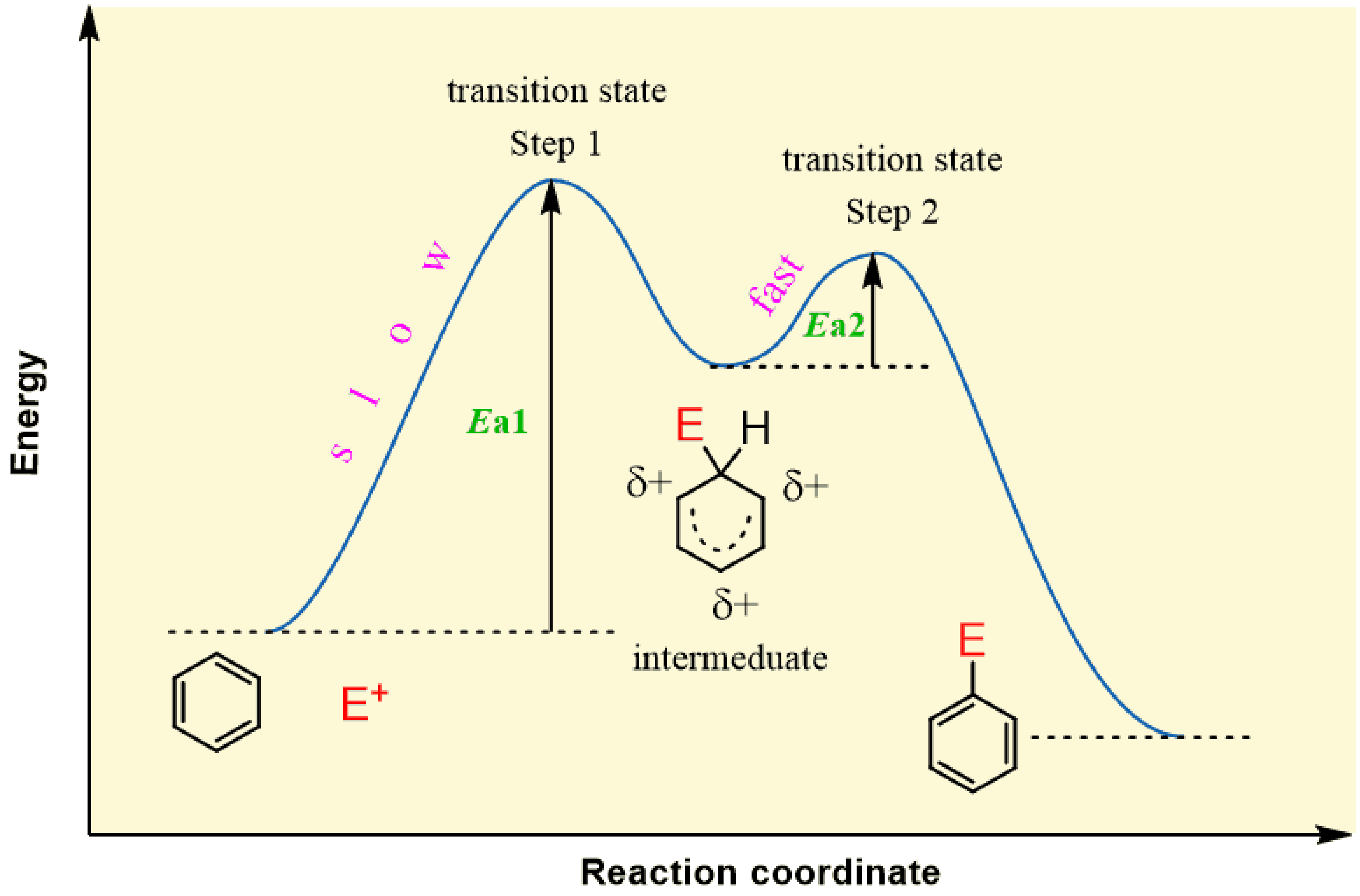
The given mechanistic pathway for the AES reaction can be proved by giving evidence in favor of formation of **σ-complex** as intermediate of AES reaction.

Evidence for formation of σ-complex/benzenium ion/Wheland intermediate

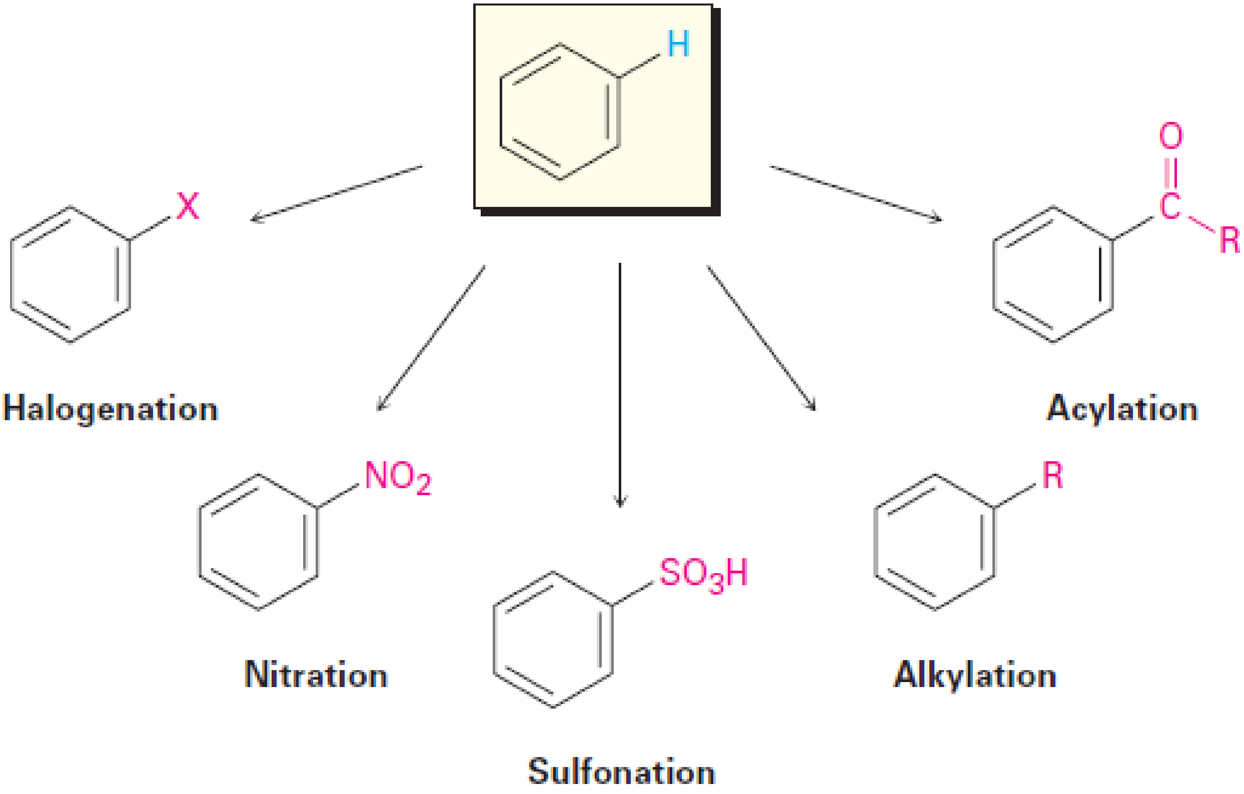
Formation and existence of stable benzenium ion by protonation of the aromatic substrate. This ion can be observed by NMR techniques under stable-ion conditions.



ENERGY PROFILE DIAGRAM FOR AES REACTION



Many different substituents can be introduced onto the aromatic ring by electrophilic substitution. To list some possibilities, an aromatic ring can be substituted by a halogen (Cl, Br, I), a nitro group (NO2), a sulfonic acid group (SO3H), an alkyl group (R), or an acyl group (COR).



THANK YOU