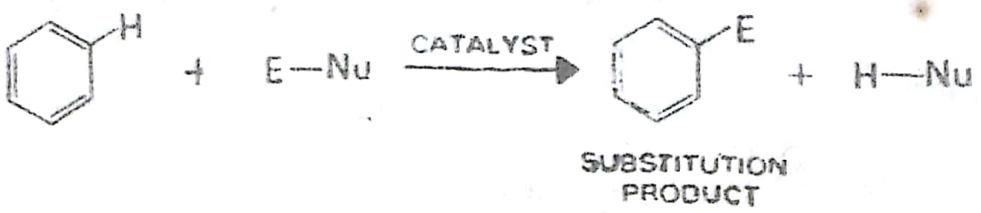
Question 14. Give the general mechanism of electrophilic aromatic substitution.

(Annamalai BSc, 1980 ; Banaras BSc, 1980 ; Jammu BSc, 1980 ; Madurai BSc, 1980 ; Delhi BSc, 1981 ; Jabalpur BSc, 1981 ; Madras BSc, 1981 ; Rajasthan BSc, 1981 ; Saugar BSc, 1981 ; Andhra BSc, 1982 ; Burdwan BSc, 1982 : Jabalpur BSc, 1982 ; Panjab BSc, 1982 : Shivaji BSc, 1982)

ANSWER. The electrophilic aromatic substitution reactions involve the replacement of a hydrogen on an aromatic ring with an electrophile.



All electrophilic substitution reactions follow the same three-step mechanism :

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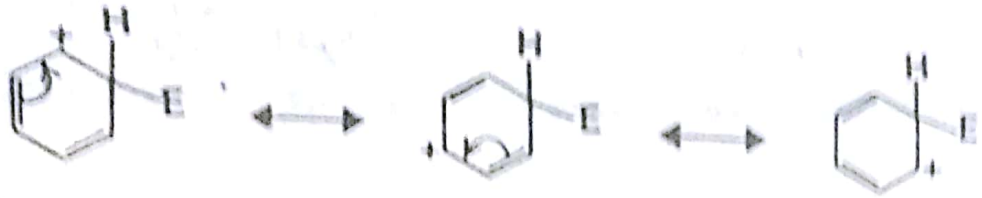
Step 1. Formation of an electrophile.

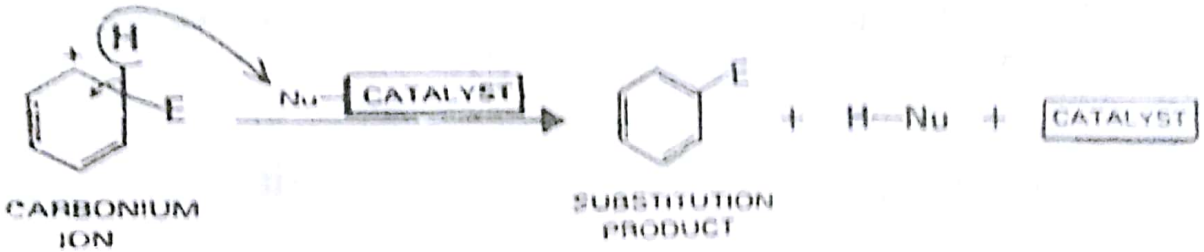
$$E{-}Nu + \boxed{\text{CATALYST}} \longrightarrow E^{+} + Nu\,\boxed{\text{CATALYST}}$$

Step 2. The electrophile attacks the aromatic ring to give a carbonium ion.

Note. The intermediate carbonium ion is resonance stabilised. It is a hybrid of the following structures :



Step 3. Removal of proton gives the product.



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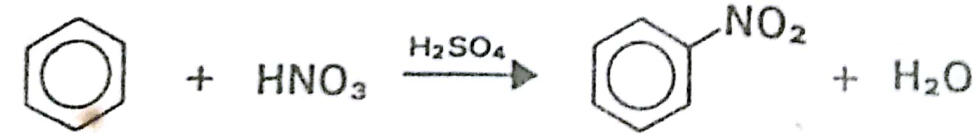
ION PRODUCT

Question 15. Give the mechanism of nitration of benzene.

(Banaras BSc, 1980 ; Jabalpur BSc, 1980 ; Kerala BSc, 1980 ; Manipur BSc, 1980 ; Madras BSc, 1980 ; Maharshi Dayanand BSc, 1980 ; Panjab BSc, 1980 ; Punjabi BSc, 1981 ; Andhra BSc, 1981 ; Baroda BSc, 1981 ; Gulbarga BSc, 1981 ; Mysore BSc, 1981 ; Nagpur BSc, 1981 ; Poona BSc, 1981 ; Osmania BSc, 1981 ; Sri Venkateswara BSc, 1981 ; Shivaji BSc, 1981 ; Guru Nanak Dev BSc, 1982 ; Himachal BSc, 1982 ; Madras BSc, 1982 ; Nagpur BSc, 1982 ; Visva Bharti BSc, 1982)

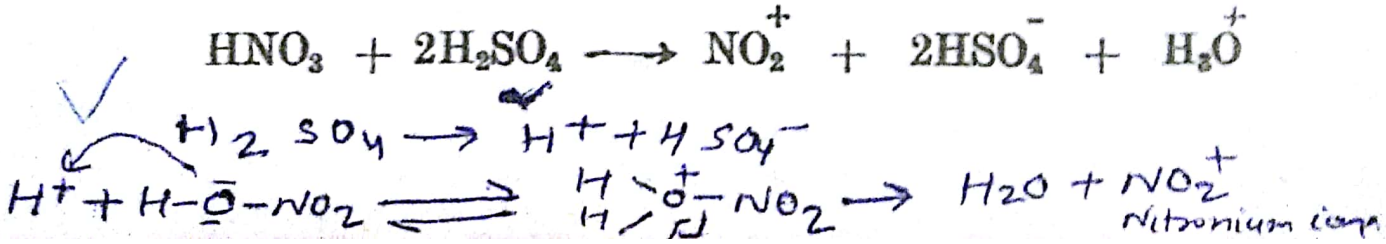
ANSWER. Benzene undergoes nitration when it is treated with concentrated nitric acid in the presence of concentrated sulphuric acid.



BENZENE NITROBENZENE

Mechanism. Three steps are involved :

Step 1. Formation of the electrophile (NO_2^+).



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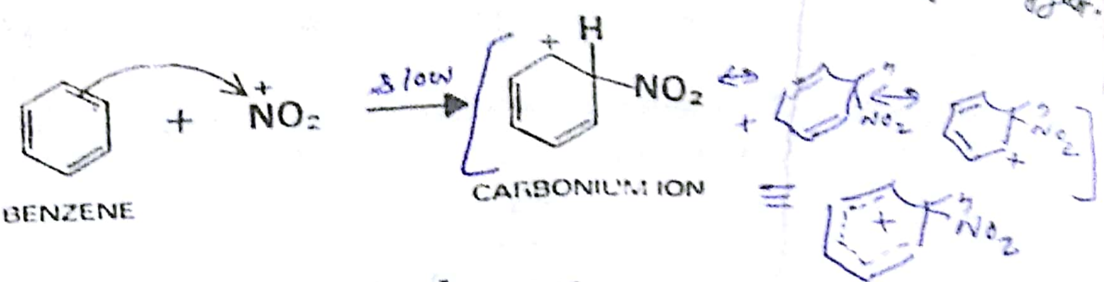
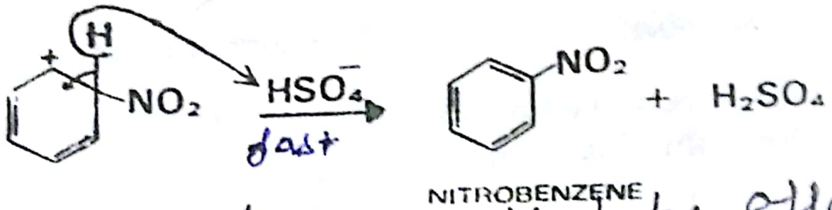
proton का loss slow ie rate determining step का नहीं होता है, so not show isotope effect.

Step 2. The electrophile attacks the benzene ring to give a carbonium ion.



σ-complex wheland Intermediate

Step 3. Removal of proton gives nitrobenzene.



Not show isotope effect

Question 16. Give the mechanism of bromination of benzene.

... BSc. 1980; Calicut BSc. 1980; *Kurukhetra BSc.* 1980 :

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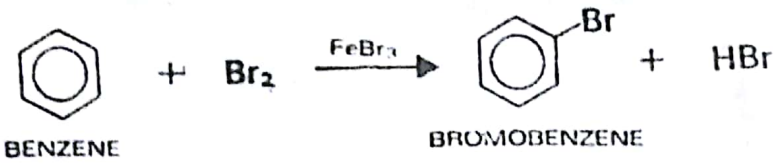
Question 16. Give the mechanism of bromination of benzene.

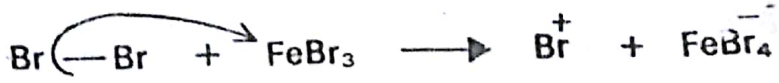
(Annamalai BSc, 1980 ; Calicut BSc, 1980 ; Kurukhetra BSc, 1980 ; Gulbarga BSc, 1981 ; Lucknow BSc, 1982 ; Utkal BSc, 1982)

ANSWER. Benzene undergoes bromination when it is treated with bromine in the presence of ferric bromide ($FeBr_3$).

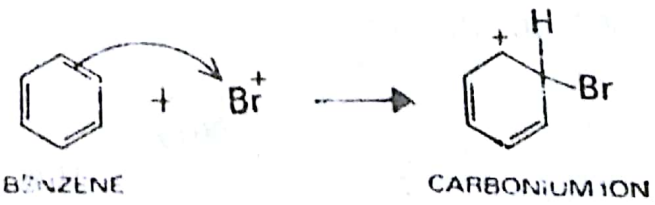


Mechanism. Three steps are involved :

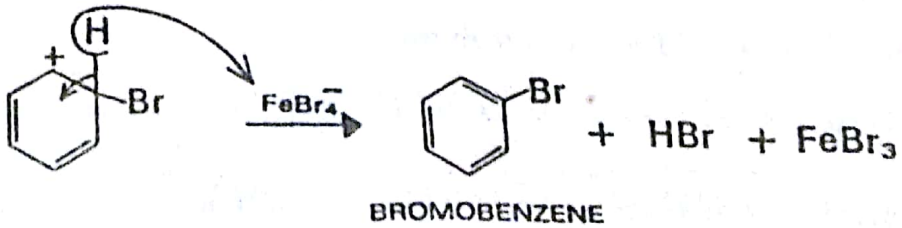
Step 1. Formation of the electrophile (Br^+).



Step 2. The electrophile attacks the benzene ring to give a carbonium ion.



Step 3. Removal of proton gives bromobenzene.



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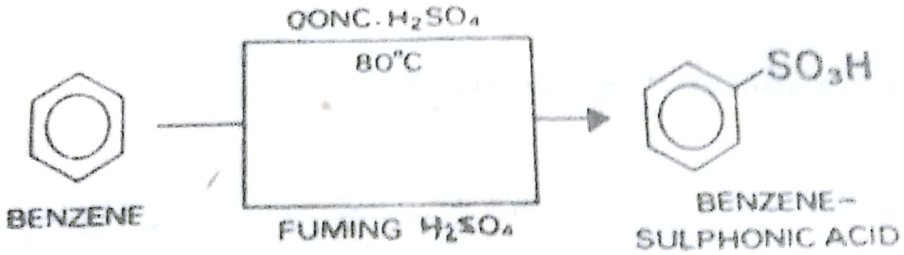
Question 18. Give the mechanism of sulphonation of benzene.

(Bangalore BSc, 1980 ; Indore BSc, 1980; Guru Nanak Dev BSc, 1981; Gulbarga BSc, 1981 ; Maharshi Dayanand BSc, 1981 ; Poona BSc, 1981 ; Udaipur BSc, 1981 ; Himachal BSc, 1982 ; Panjab BSc, 1982)

ANSWER. Benzene undergoes sulphonation when it is treated with concentrated sulhpuric acid at 80°C or fuming sulphuric acid (conc. $H_2SO_4 + SO_3$) at room temperature.



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not show Isotope effect.
rate of C_6H_6 & C_6D_6 are same

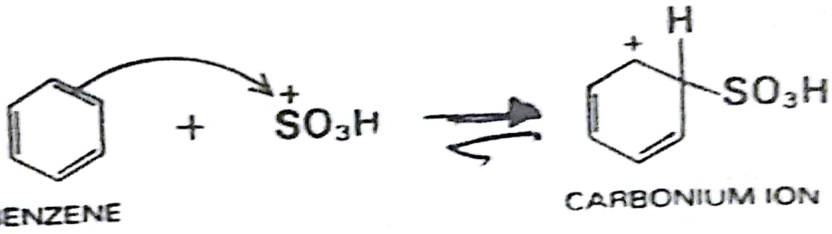
Mechanism. Three steps are involved :

Step 1. Formation of the electrophile ($^+SO_3H$). It is formed by interacuion of two sulphuric acid molecules or by protonation of SO_3.

$$2H_2SO_4 \longrightarrow \overset{+}{S}O_3H + HSO_4^- + H_2O$$

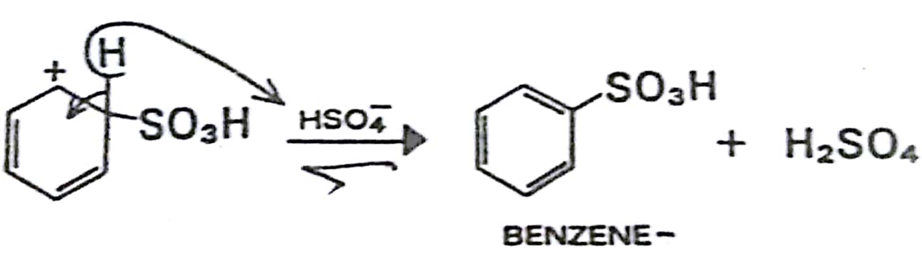
$$SO_3 + \overset{+}{H} \longrightarrow \overset{+}{S}O_3H$$

Step 2. The electrophile attacks the benzene ring to give a carbonium ion. reversible



Reversible
T.S for the
rate deter...
step is the
same
both su...
-nation
desulph...
.oth...

Step 3. Removal of proton gives benzenesulphonic acid.



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BENZENE-SULPHONIC ACID

Question 19. Write a note on : Friedel-Crafts reaction.

(*Delhi BSc, 1980 ; Mysore BSc, 1980 ; Saugar BSc, 1980 ; Aligarh BSc, 1981 ; Bhagalpur BSc, 1981 ; Kurukshetra BSc, 1981 ; Maharshi Dayanand BSc, 1981 ; Rajasthan BSc, 1981 ; Annamalai BSc, 1982 ; Bundelkhand BSc, 1982 ; Calicut BSc, 1982 ; Garhwal BSc, 1982 ; Indore BSc, 1982 ; Meerut BSc, 1982 ; Panjab BSc, 1982 ; Shivaji BSc, 1982 ; Sambalpur BSc, 1982*)

ANSWER. The Friedel-Crafts reaction is of two types :

Friedel-Crafts Alkylation. This involves the treatment of an aromatic compound with alkyl halides in the presence of anhydrous aluminium chloride. The products are ALKYLBENZENES. For example,

BENZENE TOLUENE

Mechanism. Three steps are involved :

Step 1. Formation of the electrophile (CH_3^+).

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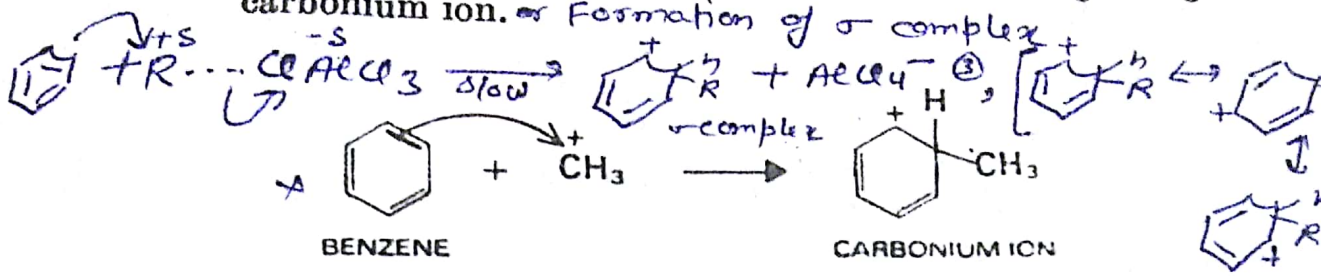
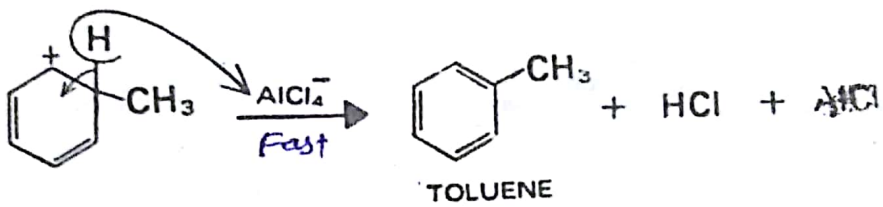
Step 2. The electrophile attacks the benzene ring to give a carbonium ion.



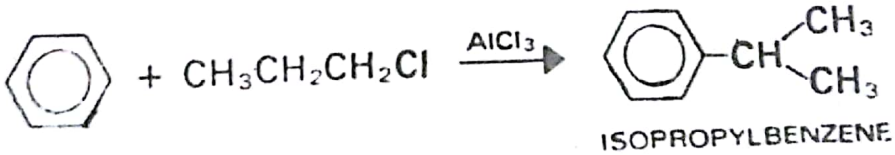
Step 3. Removal of proton gives toluene.



Drawbacks of Friedel-Crafts Alkylation

(1) *Polyalkylation is a serious problem.* It is difficult to stop the reaction when one alkyl group has been introduced. Di- and tri-alkylbenzenes are also formed.

(2) *Rearrangement of alkyl groups is often observed.* For example, when benzene is treated with *n*-propyl chloride in the presence of $AlCl_3$, the product is isopropyl benzene rather than the expected *n*-propylbenzene.



This is because the Friedel-Crafts alkylation proceeds through carboniu ion intermediates, the carbonium ion may undergo rearrangement to more stable carbonium ion before electrophilic attack on an aromat compound.

Friedel-Crafts Acylation. This involves the treatment of

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