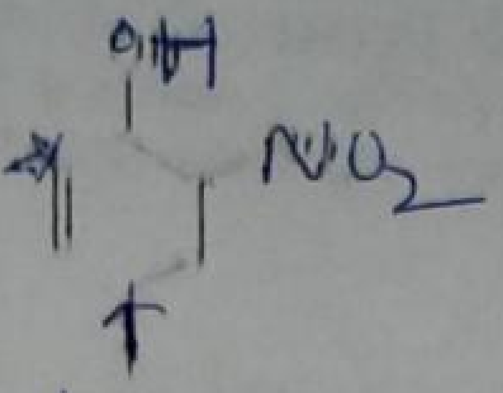
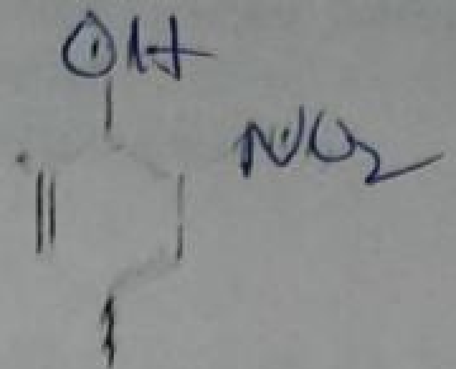
7

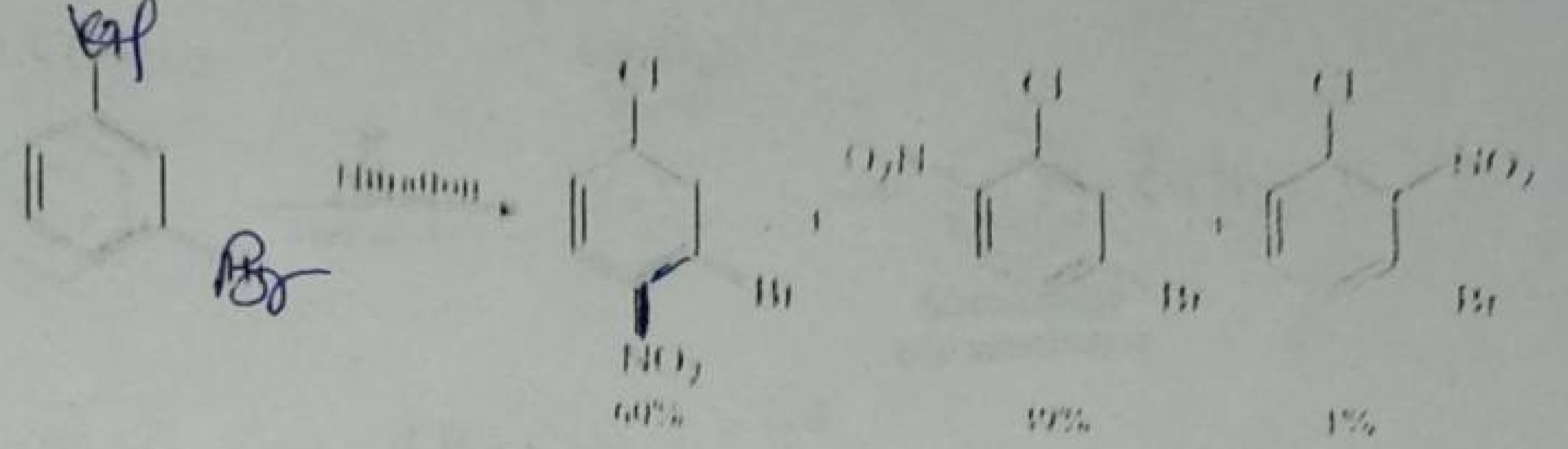




When two gp. occupy m- posn to each other

(v) When the two groups occupy *meta* positions with respect to each other, a third group is least likely to enter between the two groups even when the directing powers of the two groups allow such substitution. This is because of steric hindrance and increases in importance with increase in the size of the groups already present on the ring and with size of the incoming group. For example

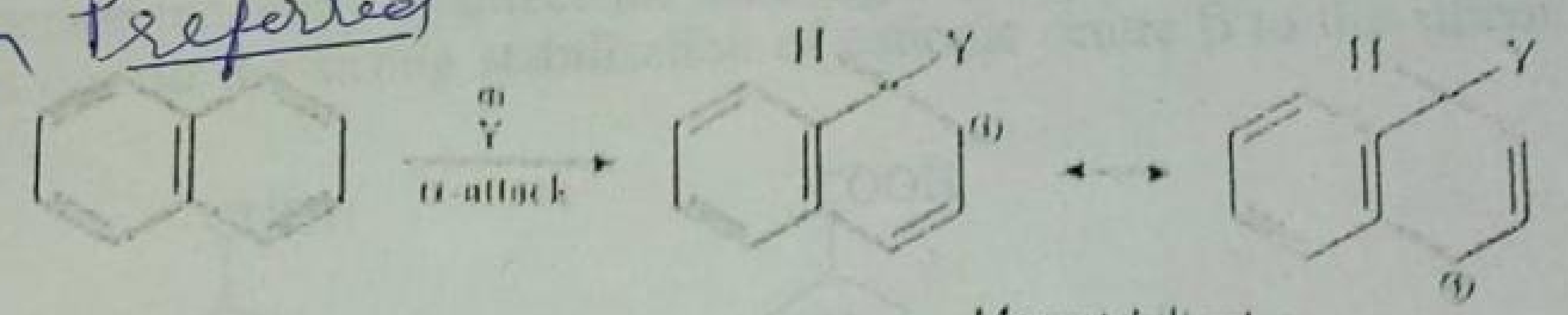
the



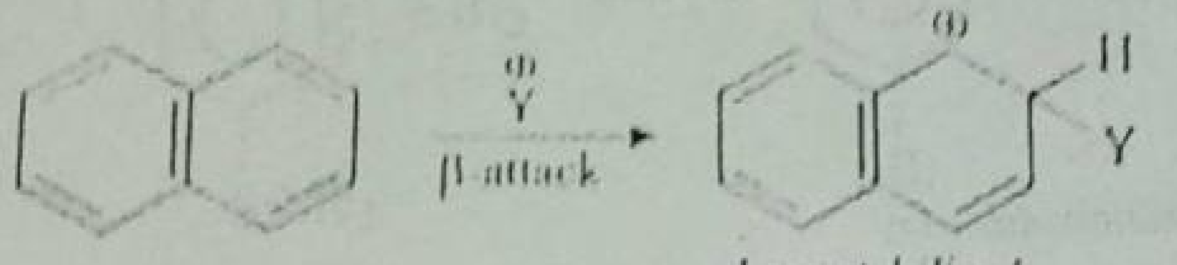
## 6.9 | ORIENTATION IN OTHER RING SYSTEMS

Unlike benzene, in fused ring hydrocarbons the positions are not equivalent, and there is a preferred orientation even in the unsubstituted hydrocarbon. For example, in naphthalene the α-position (position 1) is preferred site of attack, *i.e.*, it is more reactive than the β-position (position 2). This is because the intermediate formed after the attack at α-position is stabilised by two resonating structures retaining one benzene ring, while only one such structure can be written in the case of the attack at β-position.

α-Position Preferred



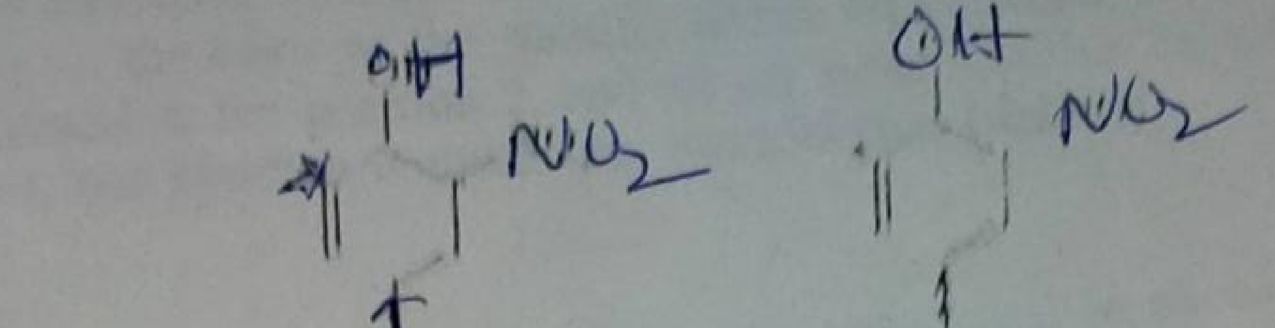
More stabilised



Less stabilised

Under certrain conditions substitution at the β-position predominates. For example, the sulphonation of naphthalene at 80°C, where the reaction does not reach equilibrium, gives mostly α-naphthalenesulphonic acid, whereas at 160°C, where equilibrium is obtained, thermodynamically more stable β-isomer predominates (the α-isomer is thermodynamically less stable because of steric repulsion between the $SO_3H$ group and the hydrogen at the position 8).

Because of more extensive delocalisation of the positive charge in the corresponding arenium ions, naphthalene, anthracene, phenanthrene, and other fused ring polycyclic hydrocarbons are more reactive than benzene in electrophilic substitutions. The orientations in these hydrocarbons can also be predicted and explained on the basis of the stability of the carbocations (arenium ions) formed by the attack of an electrophile.



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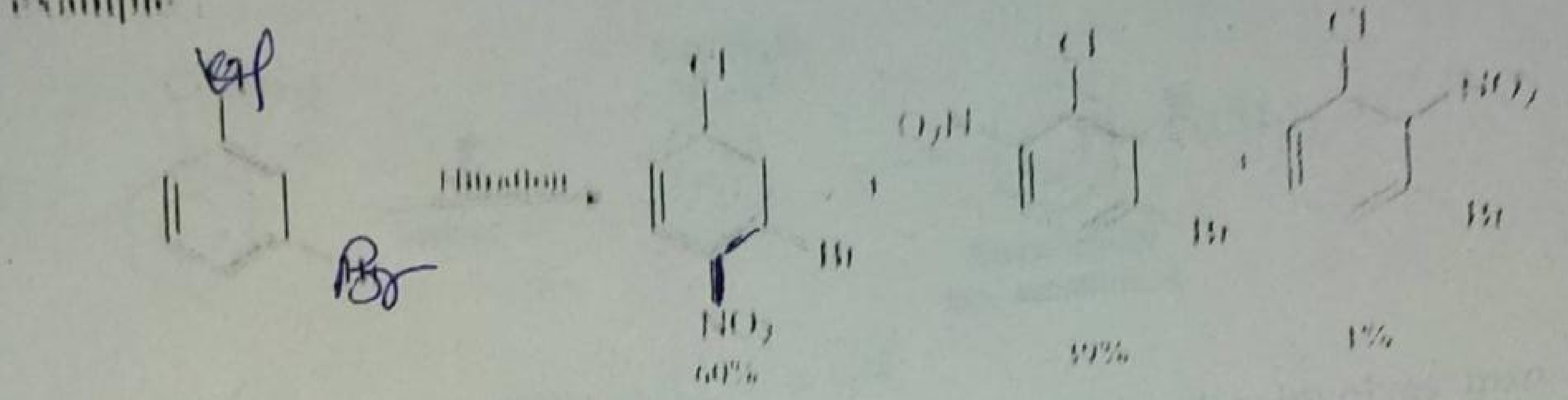

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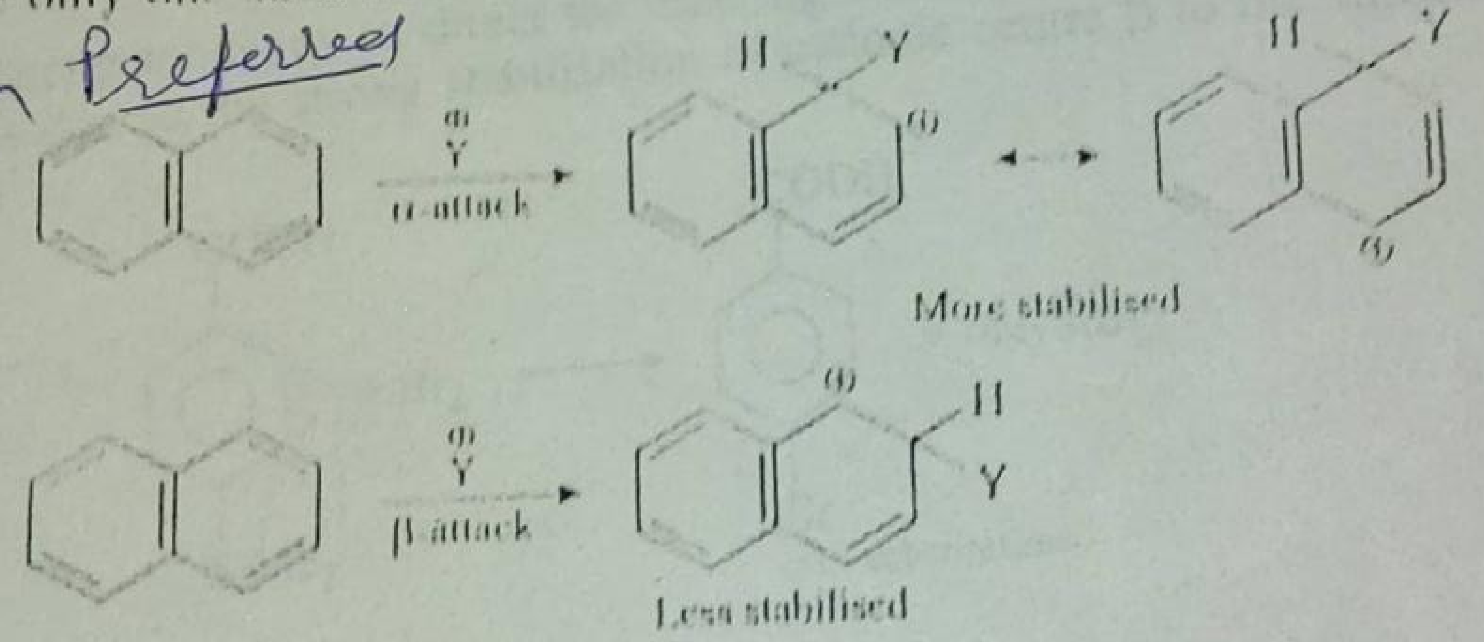
α-Position Preferred



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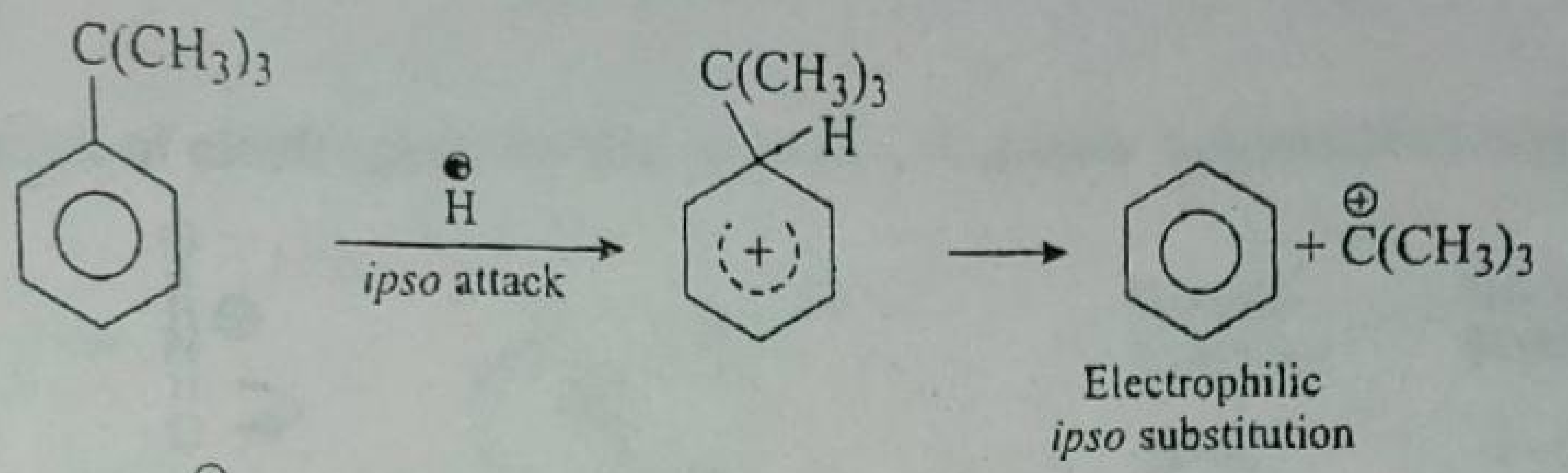
Heterocyclic compounds also have nonequivalent positions and the orientation in their electrophilic ubstitutions can be explained on the basis of the stability of the intermediate formed. Furan, thiophene, nd pyrrole are mainly substituted at the position 2, and all are more reactive than benzene. In pyridine he position 3 is most reactive, but pyridine is much less reactive than benzene.

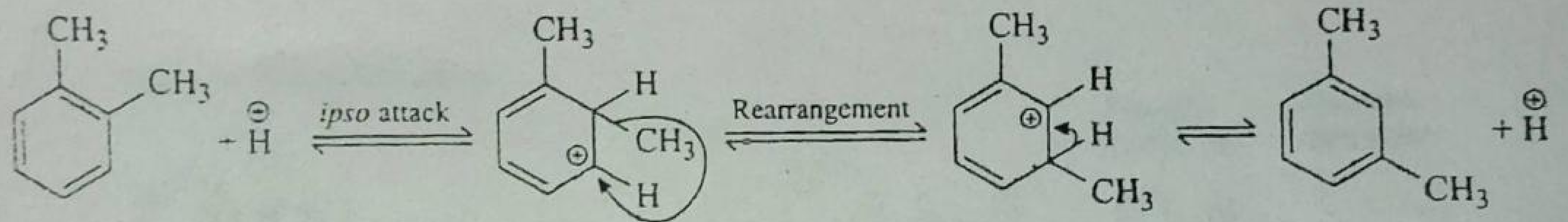
## 6.10 *IPSO* ATTACK

A position which is already occupied by a non-hydrogen substituent in an aromatic ring is called so position (Latin : *ipso*, on itself), the attack on this position is called *ipso* attack (or *ipso* addition), d the aromatic substitution in which a substituent already present is replaced is called *ipso* substitution. r example, protodealkylation of an alkylbenzene (reverse of Friedel-Crafts alkylation). In this reaction tiary alkyl groups are most easily removed, since they depart as stabler carbocations. Thus, *t*-butyl group used to protect the most reactive position in a compound to effect reaction elsewhere. The mechanism as follows :



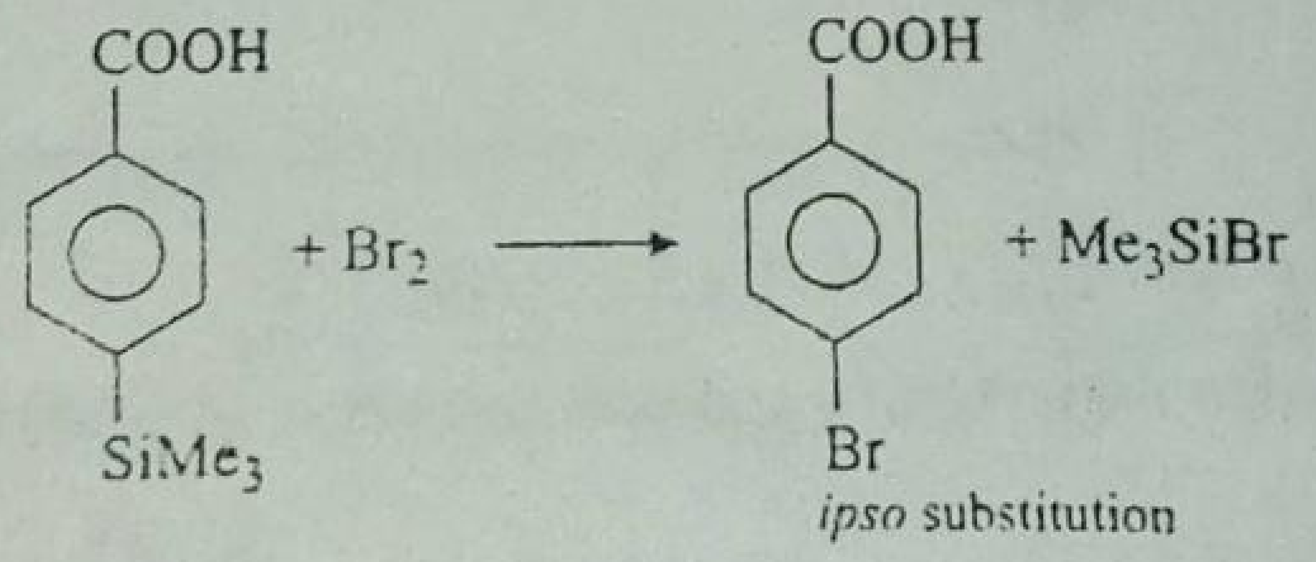
$$(CH_3)_3\overset{\oplus}{C} \longrightarrow (CH_3)_2C{=}CH_2 + H^{\oplus}$$

The rearrangement of alkylbenzenes leading to their isomerisation also involves *ipso* attack. For xample, *o*-xylene isomerises to *m*-xylene as follows :

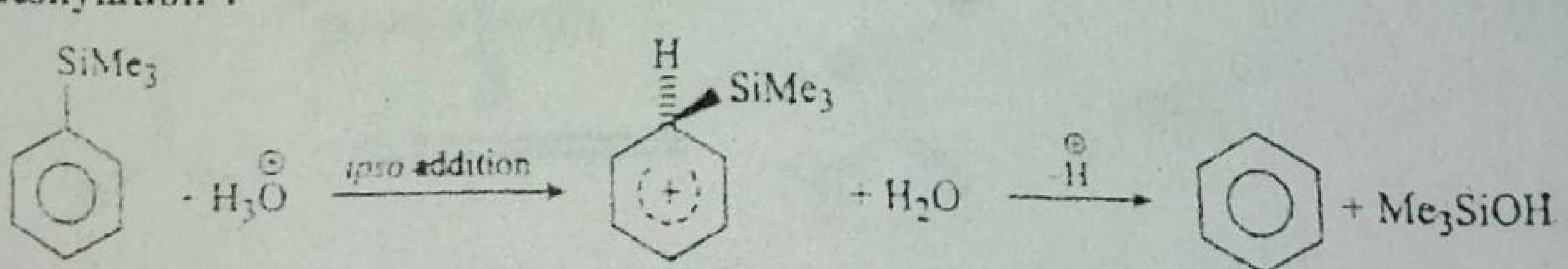


Silyl group has a strong tendency to direct the entering electrophile to the position occupied by it, *i.e.*, *ipso* position. This is due to the strong stabilisation of cationic centre β to the silicon.

**Bromodesilylation :**



**Protodesilylation :**



## 6.11 SOME IMPORTANT NAME REACTIONS INVOLVING AROMATIC ELECTROPHILIC SUBSTITUTION MECHANISM

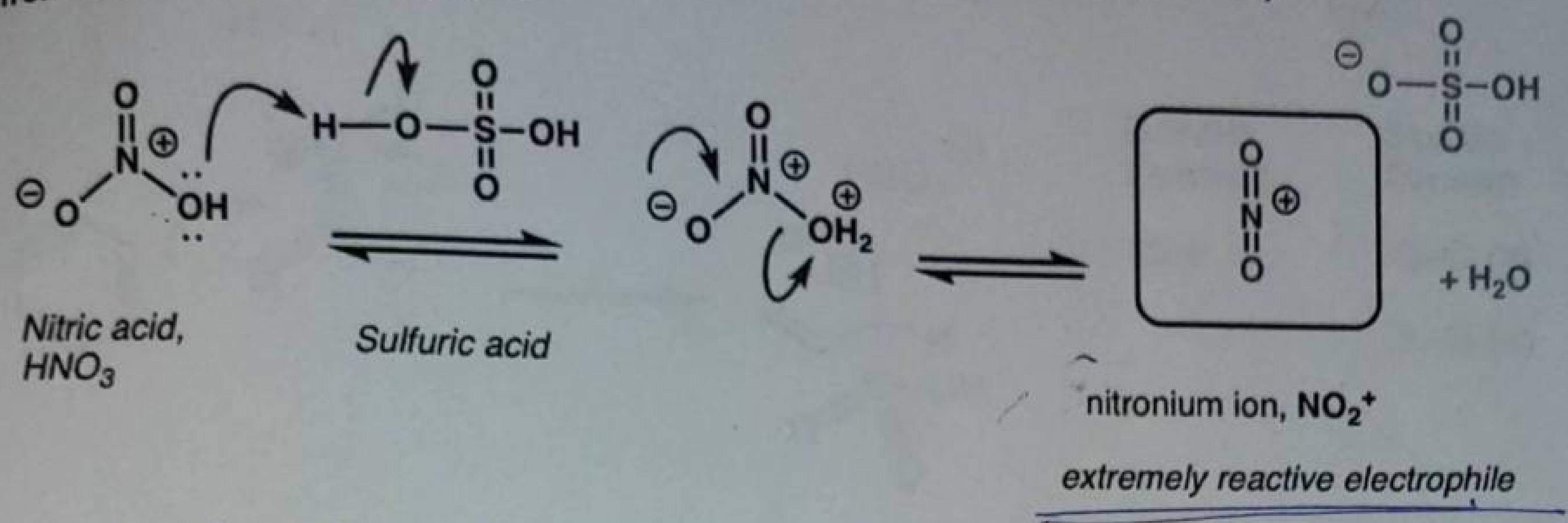
### 1. Vilsmeier-Haack Reaction

Formylation of active aromatic compounds, like phenolic ethers and dialkylanilines in *o* and *p*-ositions, with disubstituted formamide and phosphorus oxychloride is called Vilsmeier or Vilsmeier-Haack

# Aromatic Nitration

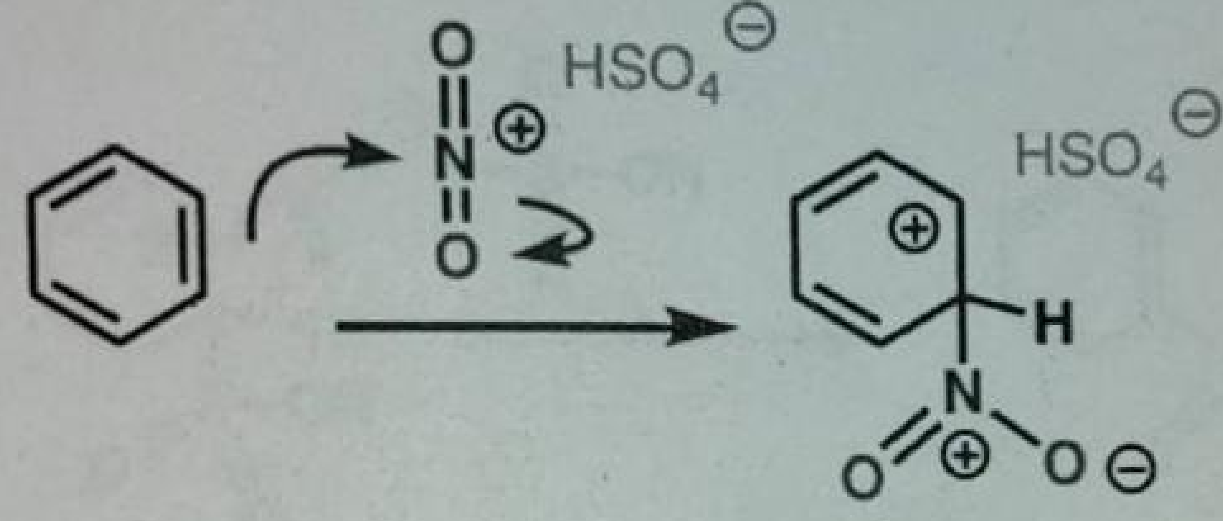
## Nitration of benzene

**Step 1: Generation of the highly reactive electrophile, $NO_2^+$ (the nitronium ion) from nitric acid and sulfuric acid**



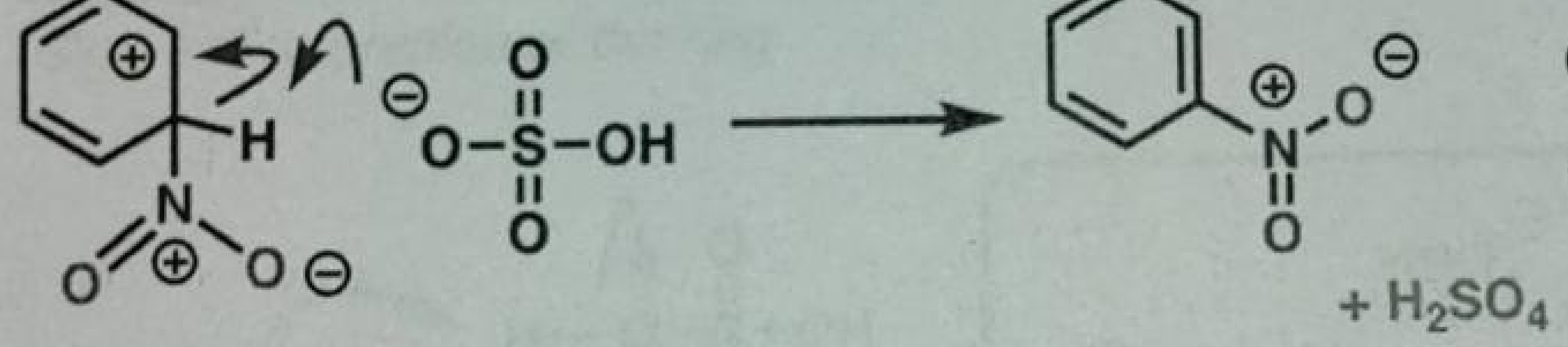
Reagent of Nitration → nitric and sulphuric acid

**Step 2: Attack of electrophile by the aromatic ring (rate-determining step)**



| Bonds Formed | Bonds Broken |
|---|---|
| C–N | C–C (π) |
| | N–O (π) |

**Step 3: Deprotonation**

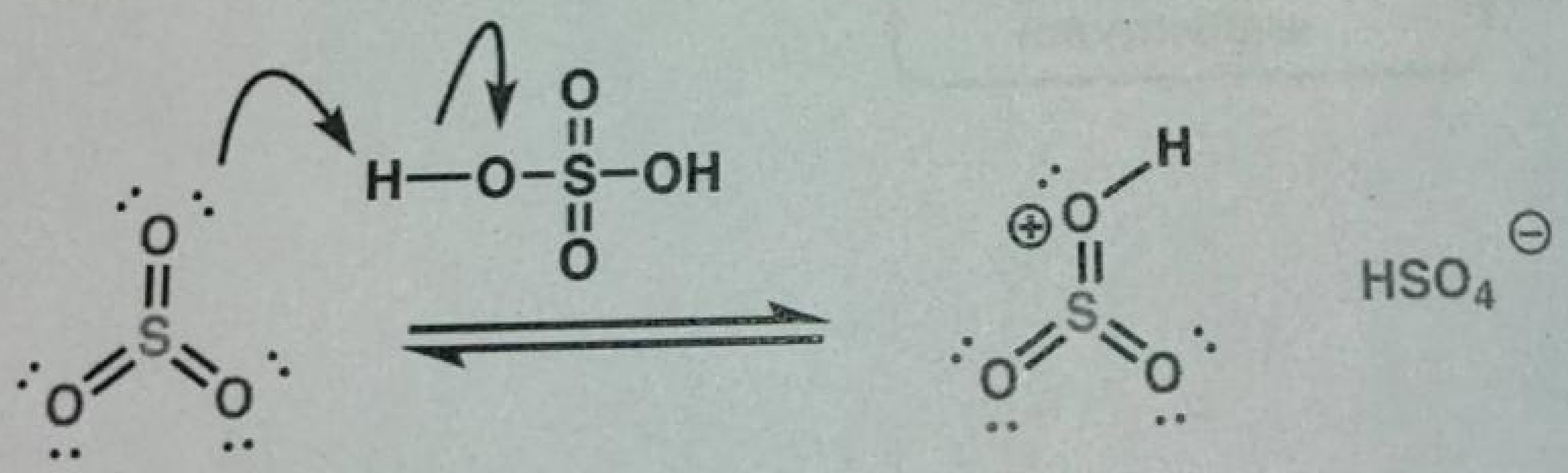


| Bonds Formed | Bonds Broken |
|---|---|
| C–C (π) | C–H |
| O–H | |

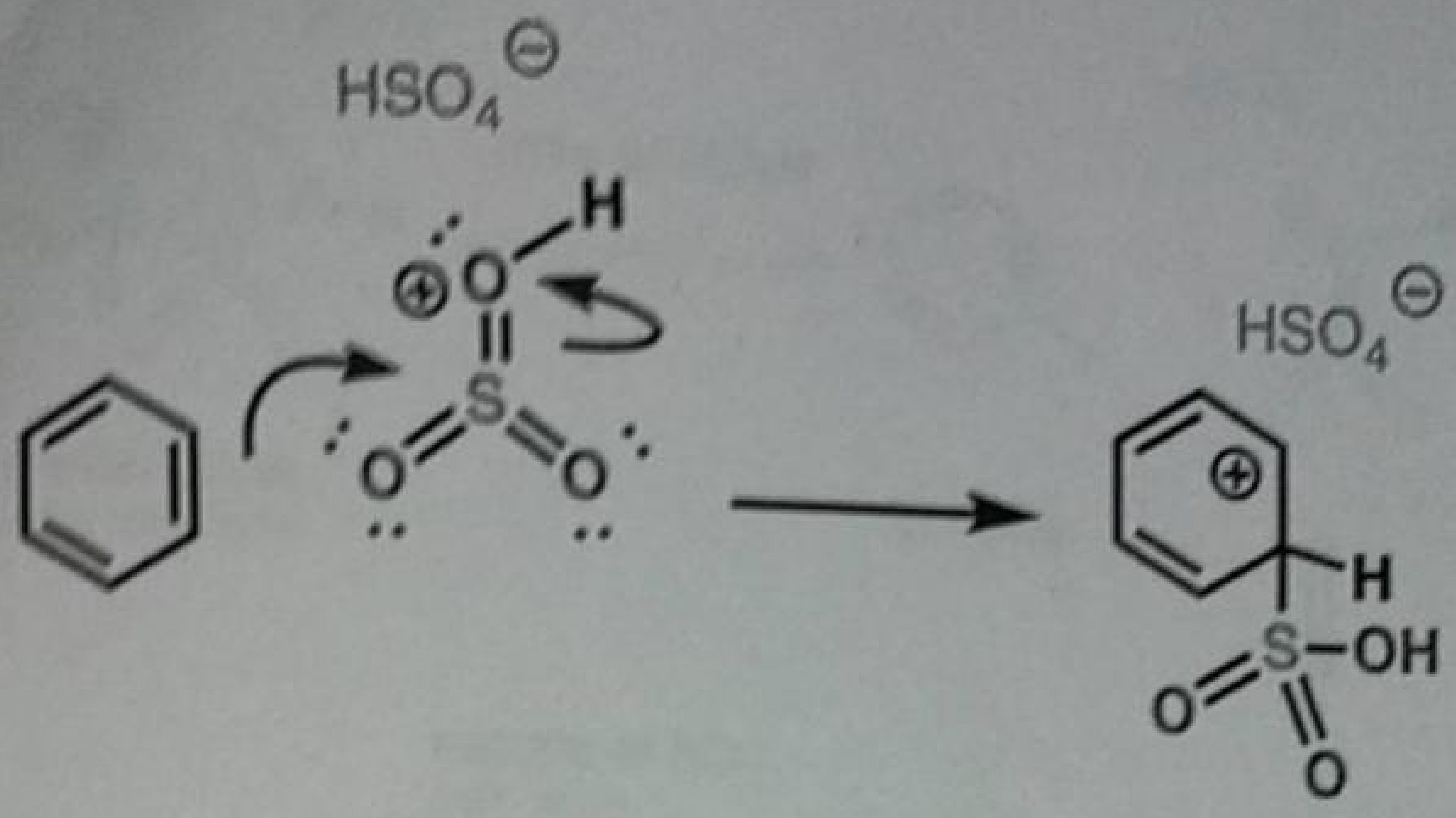
*the base here can be the sulfonate ion ($HSO_4^-$) or water*

Aromatic sulphoration → active electrophile is $SO_3$

**Sulfur trioxide ($SO_3$) is activated through protonation with $H_2SO_4$**

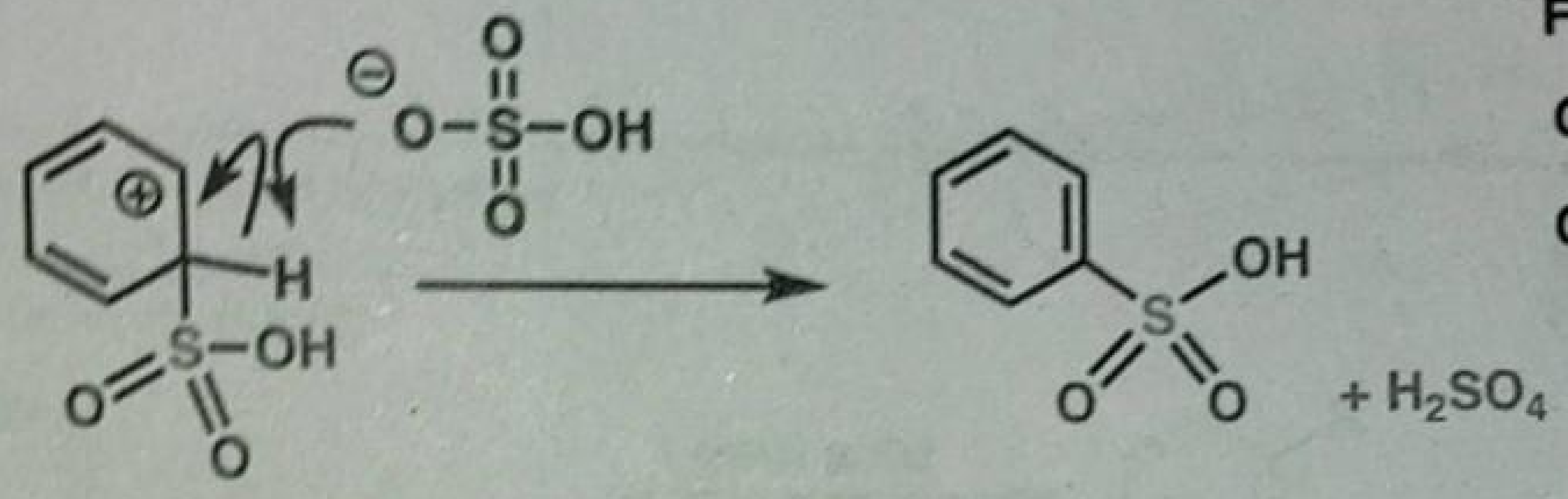


### Step 2: Attack of electrophile by the aromatic ring (rate-determining step)



| Bonds Formed | Bonds Broken |
|---|---|
| C–S | C–C (π) |
| | S–O (π) |

### Step 3: Deprotonation To Restore Aromaticity



| Bonds Formed | Bonds Broken |
|---|---|
| C–C (π) | C–H |
| O–H | |

**In the presence of strong acid, sulfonation can be reversed** → especially at high temp

*Step 1: Protonation of the ring*