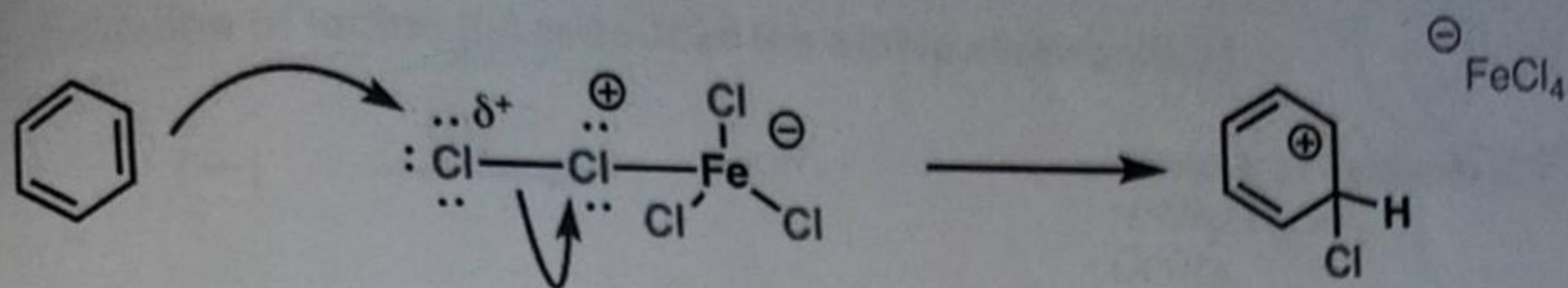
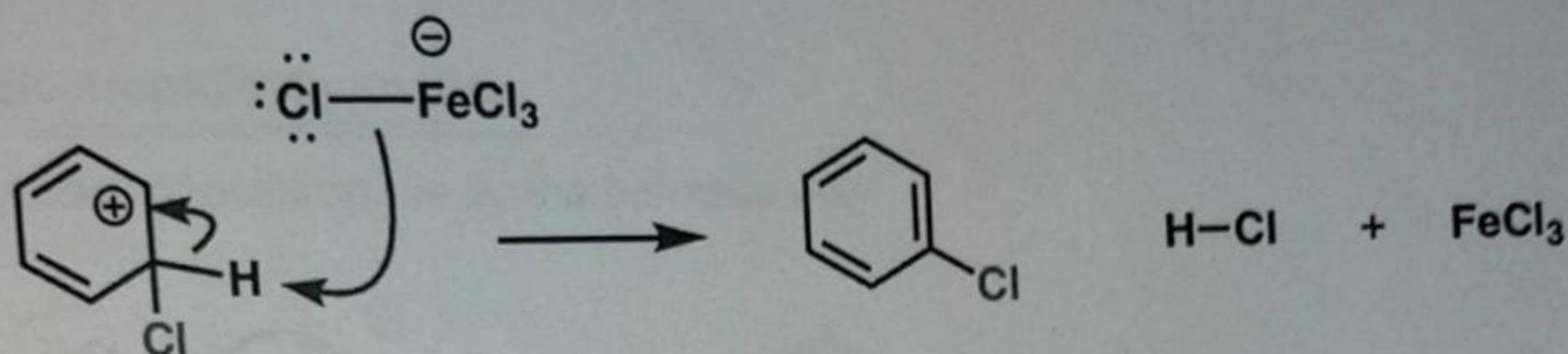


Electrophilic Aromatic Substitution (Chlorination)

Step 1: Attack of the electrophile by benzene

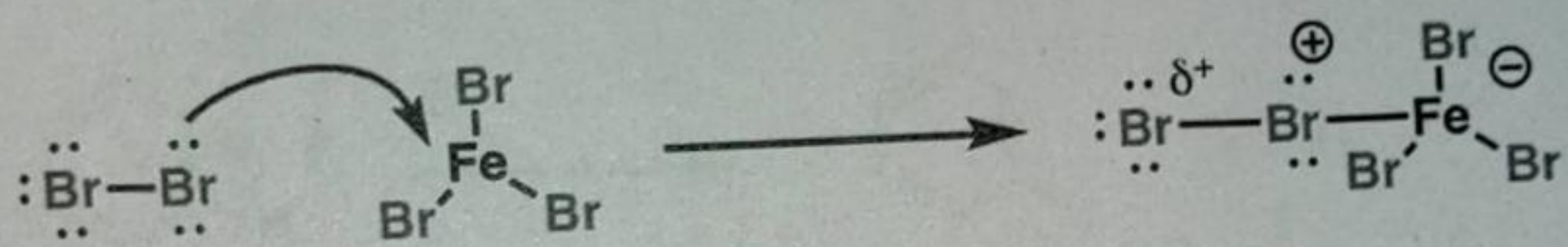


Step 2: Deprotonation (restoring aromaticity)

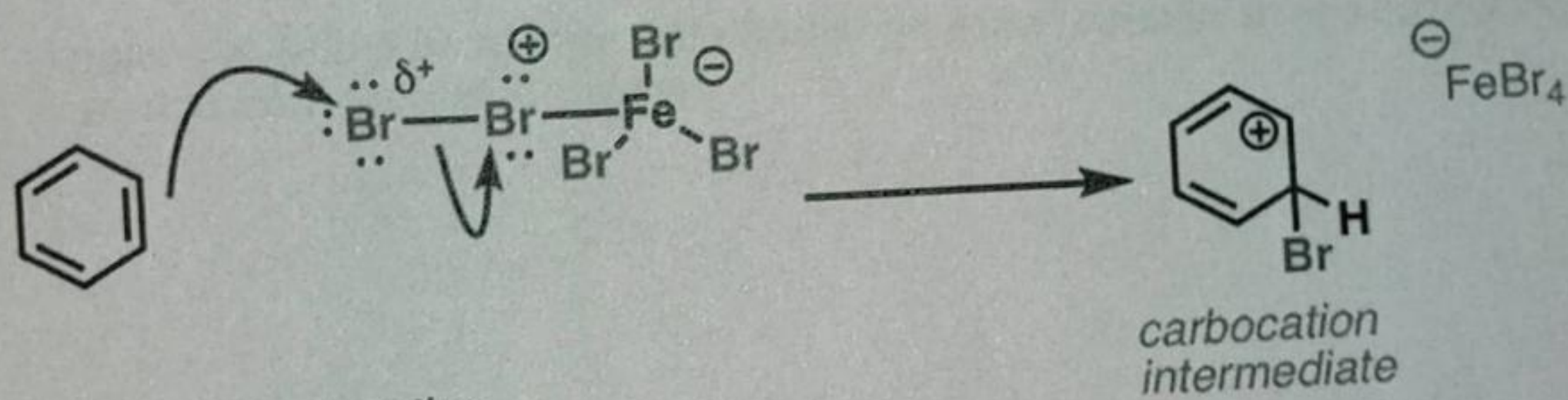


Bromination of Benzene: The Mechanism

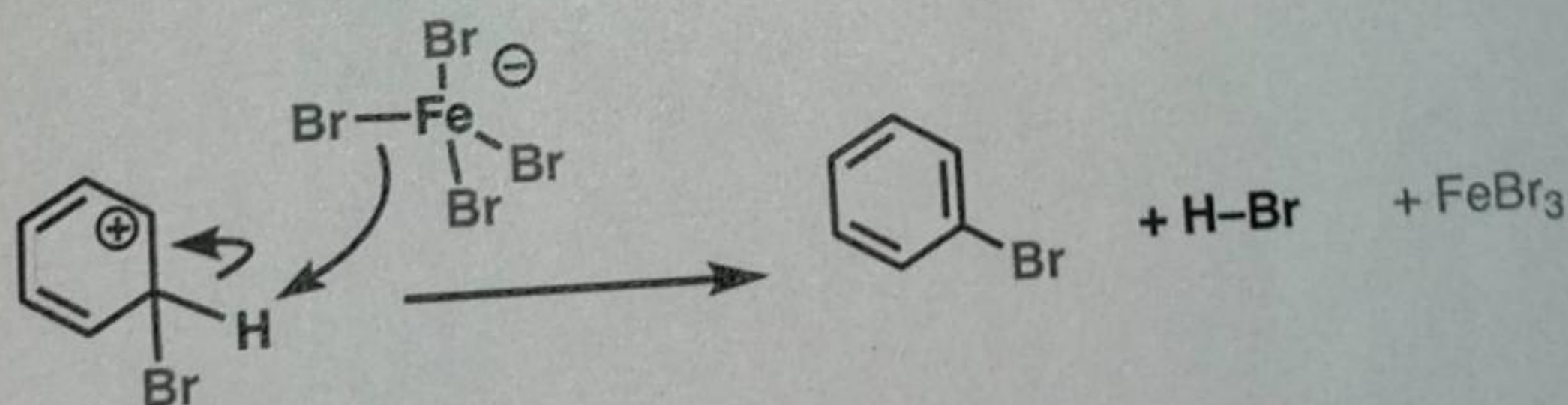
Step 1: Activation of Lewis acid



Step 2: Attack of electrophile by the benzene ring



Step 3: Deprotonation

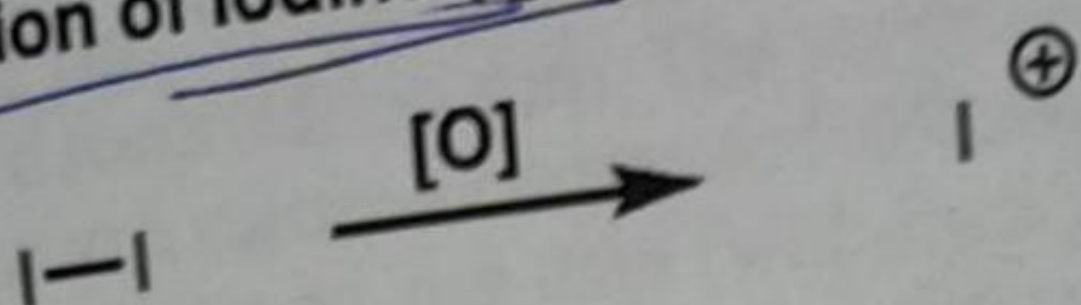


It's also possible to iodinate benzene using I_2 , but the activation step is different. Here, however, it turns out that a Lewis acid catalyst is not sufficient to make iodine an active enough electrophile to react with most aromatic rings.

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Benzene ring
a stoichiometric amount of an oxidant is used to convert I_2 to I^+ . A common example cited is $[O_2]^+$ which in the presence of additional acid (e.g. H_2SO_4) is a source of the very active oxidant $[O_2]^+$ which converts I_2 to I^+ . [see note below]

Oxidation of iodine (I_2) produces the active electrophile I^+

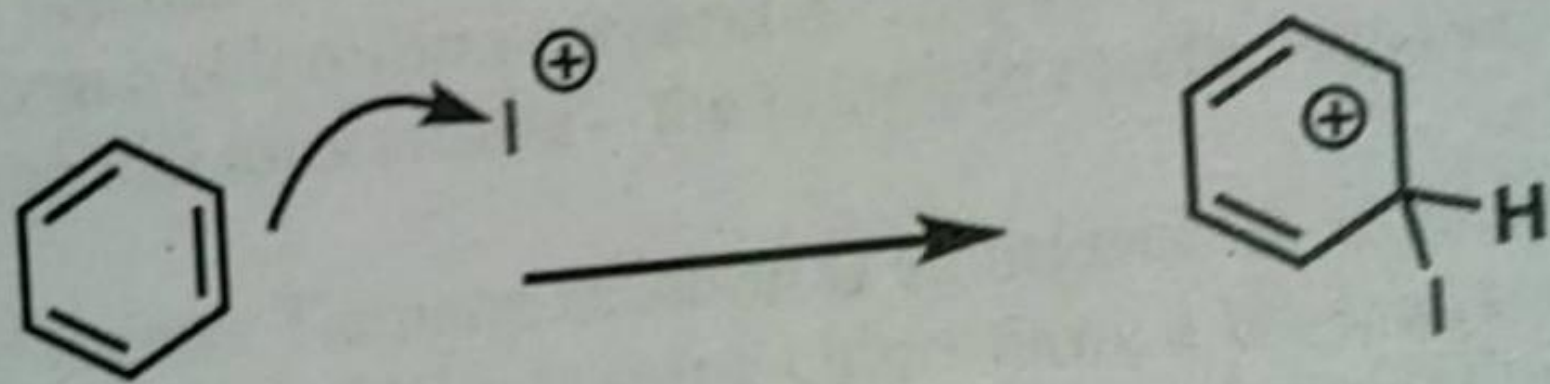


examples of oxidants $[O]$
- HNO_3/H_2SO_4
- $CuBr_2$

Once formed, the benzene ring then reacts with I^+ in the two-step electrophilic aromatic substitution mechanism to give the new carbon-iodine bond.

Electrophilic Iodination

Attack of electrophile by the benzene ring



Deprotonation



note: the actual base here will depend on which counter-ions are floating around from the oxidation step

APPLICATION

*One recent application of this reaction involved a new synthetic route to tris(4-formylphenyl)amine from triphenylamine which by known procedures resulted in a poor chemical yield of 16%. It was found that this low yield was caused by deactivation of the remaining benzene ring by the imine groups on the other two phenyl groups in the third formylation step. The procedure was modified by taking the reaction to a diimine compound followed by hydrolysis to the di-formyl compound and then (with final position reactivated) a separate formylation to the trisubstituted compound.

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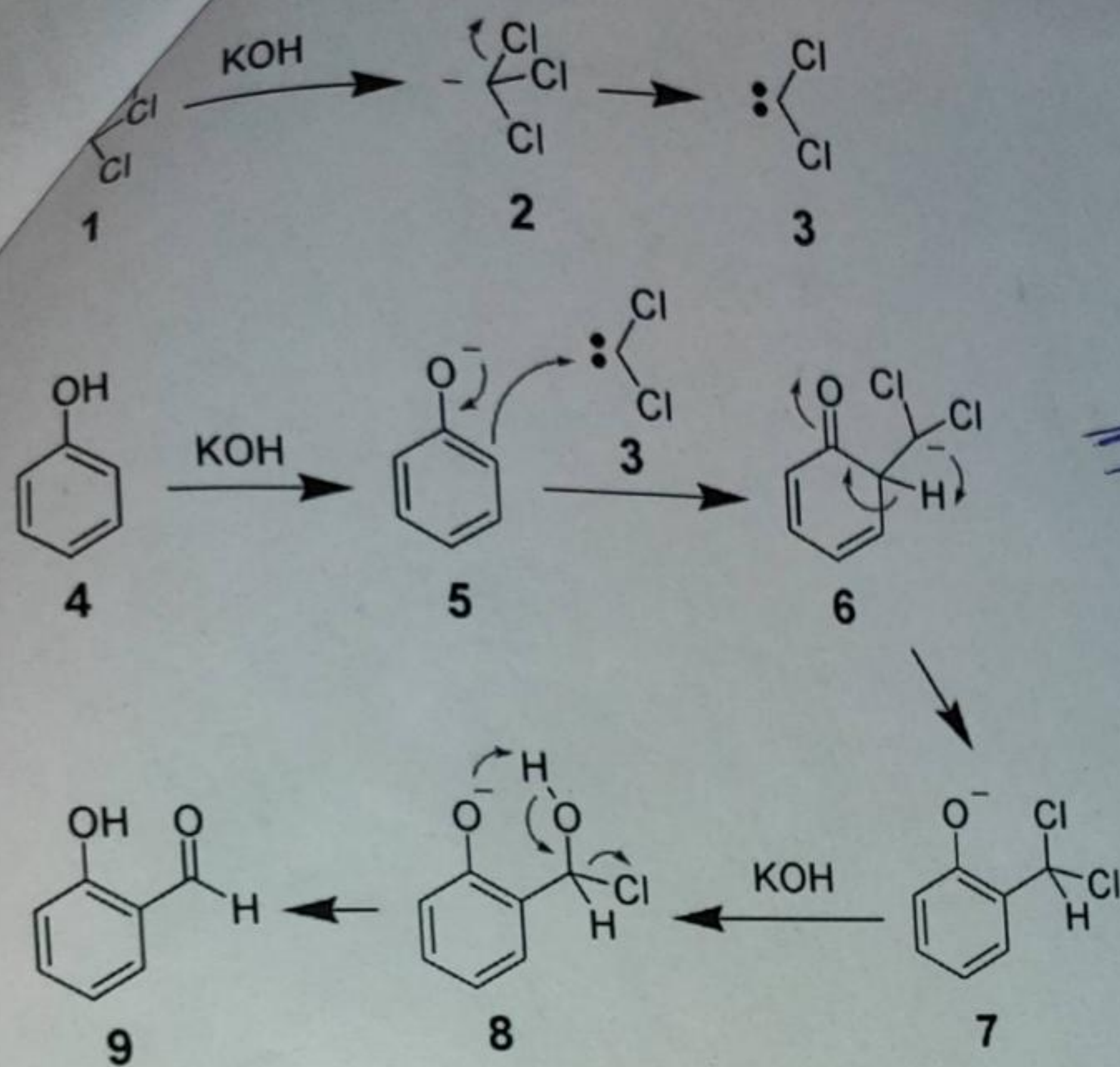
Reimer Tiemann Reaction Mechanism

The mechanism of Reimer Tiemann reaction begins with the deprotonation of chloroform by a strong base to form a chloroform carbanion. This chloroform carbanion quickly undergoes alpha elimination and gives rise to dichlorocarbene – the principle reactive species for this reaction.

The Reimer Tiemann reaction is an organic chemical reaction where phenol is converted into an ortho hydroxy benzaldehyde using chloroform, a base, and acid workup. This name reaction can also be described as the chemical reaction used for the ortho-formylation of phenols.

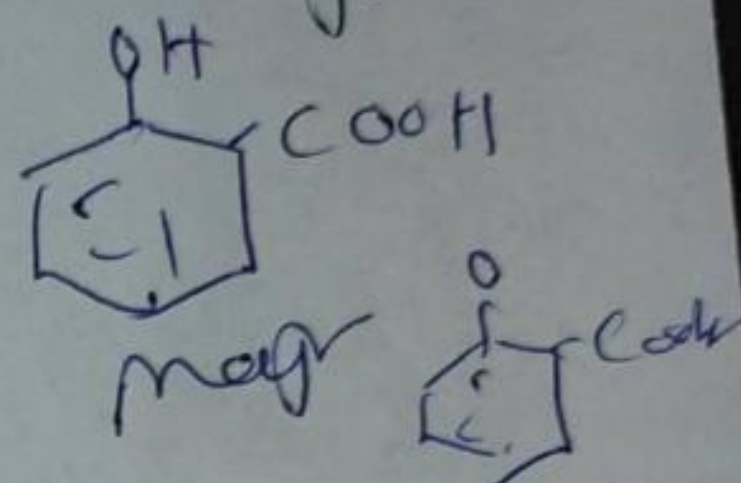
The mechanism of Reimer Tiemann Reaction can be explained in 9 major steps:

- The chloroform is deprotonated by the strongly basic aqueous hydroxide solution, giving the chloroform carbanion.
- This chloroform carbanion readily undergoes alpha elimination, giving dichlorocarbene as the product. As mentioned earlier, the dichlorocarbene is the principle reactive species.
- The aqueous hydroxide also deprotonates the phenol reactant, yielding a negatively charged phenoxide.
- This negative charge is now delocalized into the benzene ring, causing it to be far more nucleophilic.
- This results in a nucleophilic attack on the dichlorocarbene, forming an intermediate dichloromethyl substituted phenol.
- This intermediate is subjected to basic hydrolysis to finally achieve the formation of the desired ortho-hydroxybenzaldehyde.



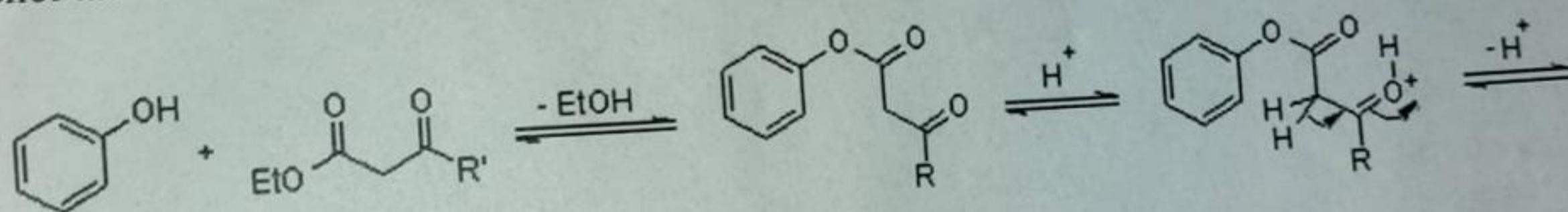
If we use CCl_4 in place

of CHCl_3 then salicylic acid form

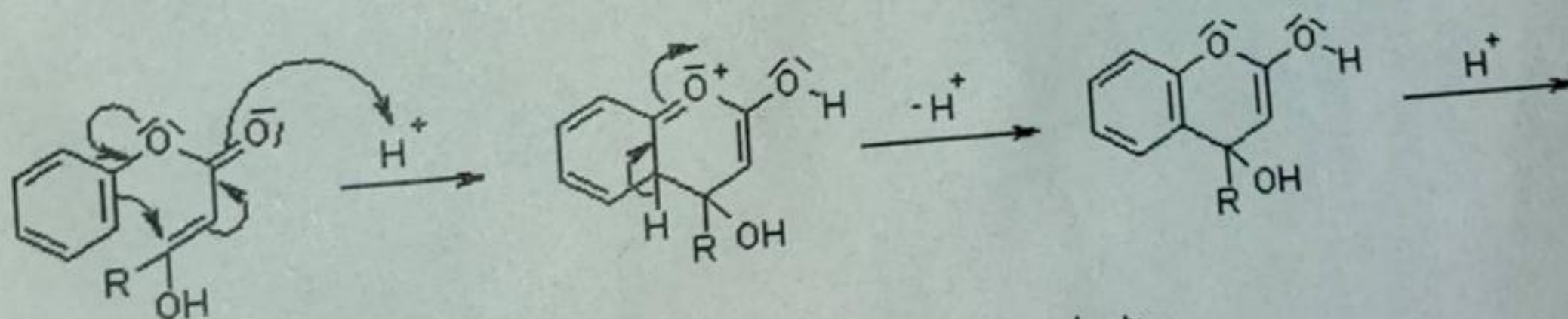


Pechmann Reaction

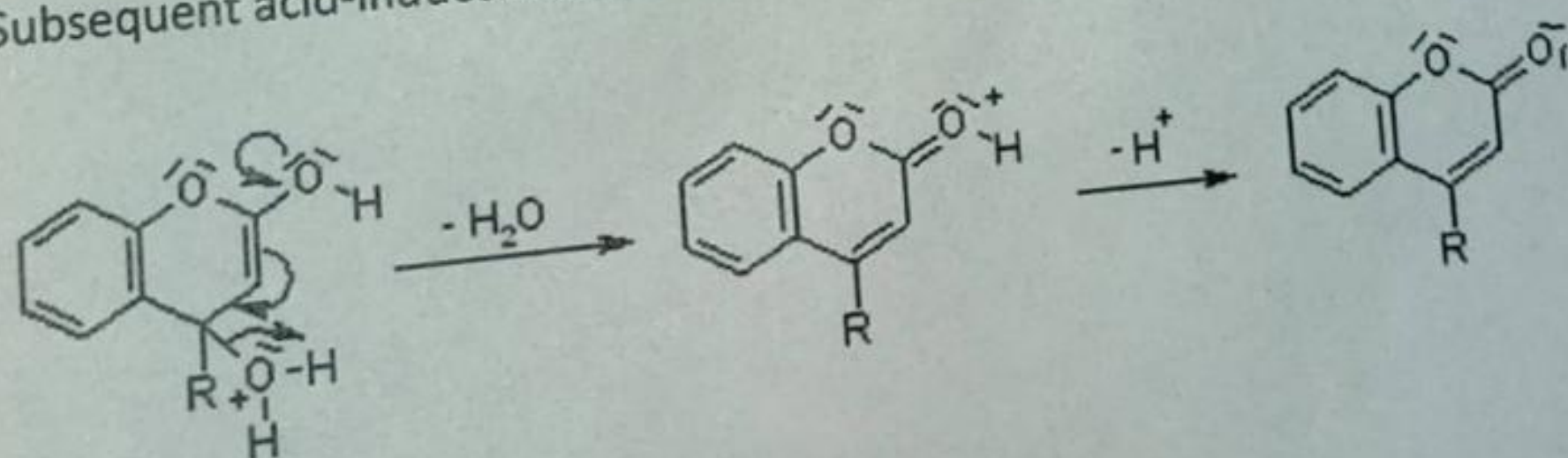
Mechanism of the Pechmann Condensation: The reaction is conducted with a strong Brønsted acid such as methanesulfonic acid or a Lewis acid such as AlCl_3 . The acid catalyses transesterification as well as keto-enol tautomerisation:



A Michael Addition leads to the formation of the coumarin skeleton. This addition is followed by rearomatisation:



Subsequent acid-induced elimination of water gives the product:



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