

Organic Chemistry

Aromatic Rearrangements

Faizan Ahmad Khan

Assistant Professor

Department of Chemistry

Dr. H.N Sinha College Of Arts Commerce And Science Patur

Selective Organic Name Reaction

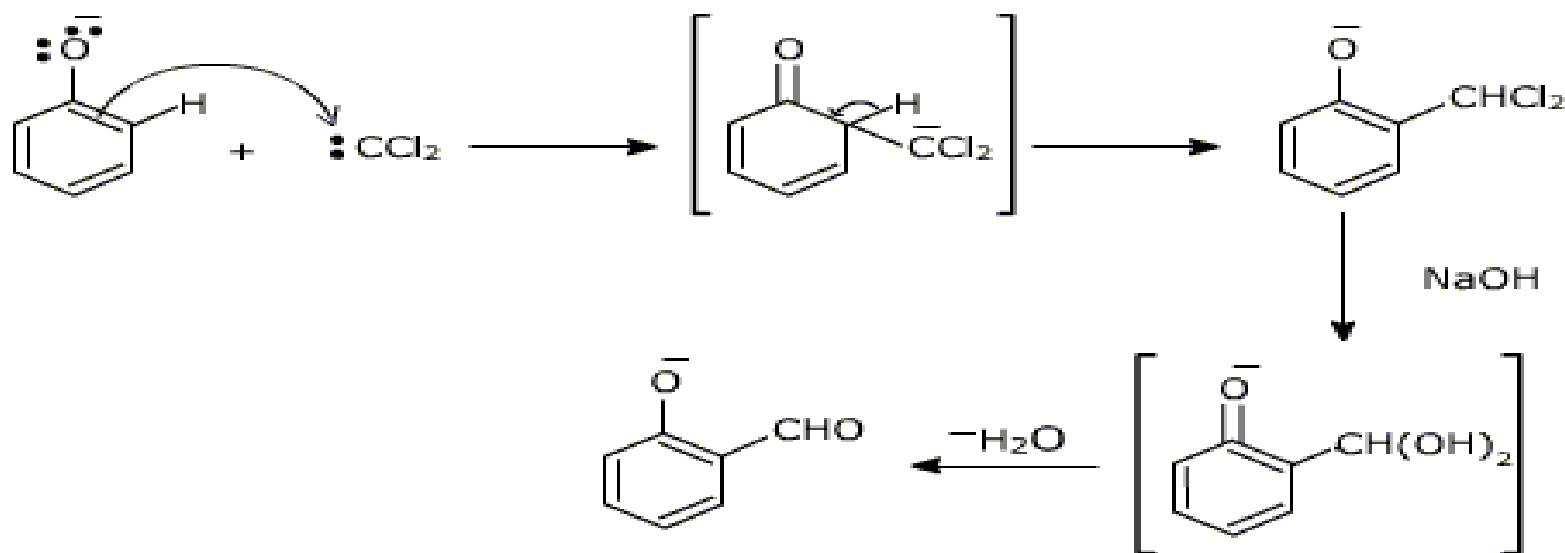
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FRIES REARRANGEMENT

1. Intra molecular Friedal –Craft Acylation
2. Rearrangement of phenolic ester by heating it with Friedal –Craft catalyst.
3. The reaction is catalyzed by Brønsted or Lewis acids such as HF, AlCl_3 , BF_3 , TiCl_4 or SnCl_4 . The acids are used in excess of the stoichiometric amount, especially the Lewis acids, since they form complexes with both the starting materials and products.

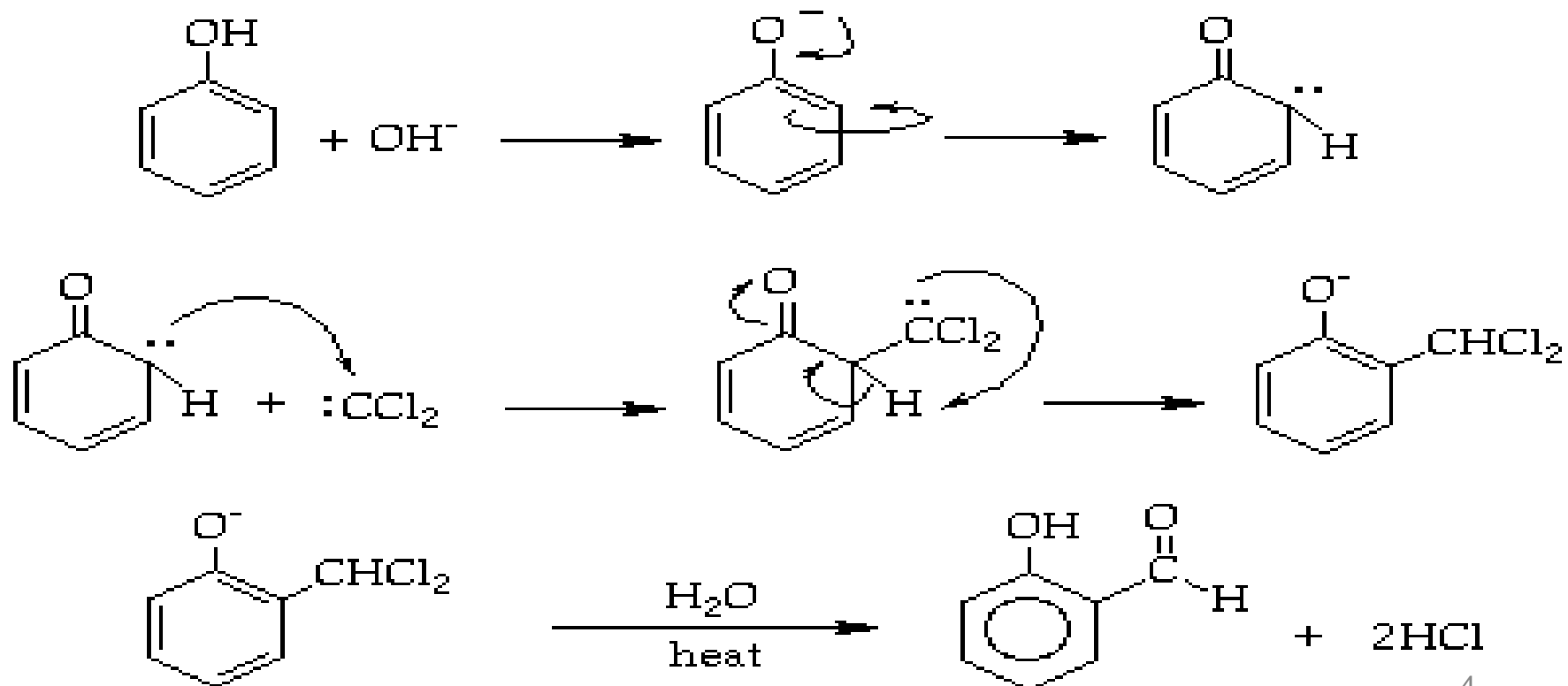
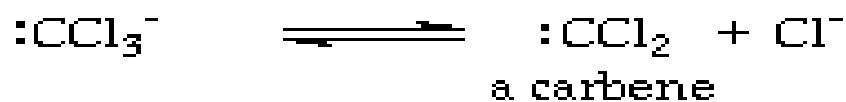
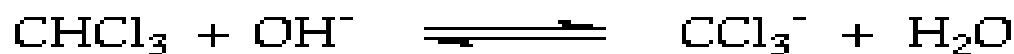
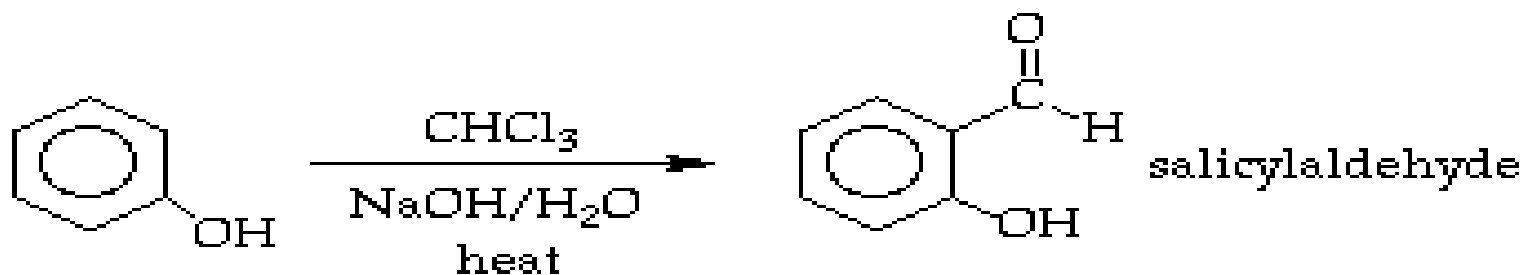
REIMER-TIEMANN REACTION (FROMYLATION)

The Reimer-Tiemann reaction is an organic reaction used for ortho-formylation of phenol. In the reaction a phenol is converted to an ortho-hydroxy benzaldehyde (salicylaldehyde) using chloroform in basic medium.



MECHANISM

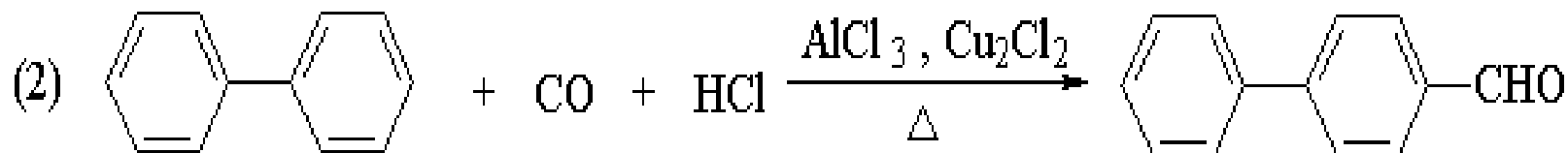
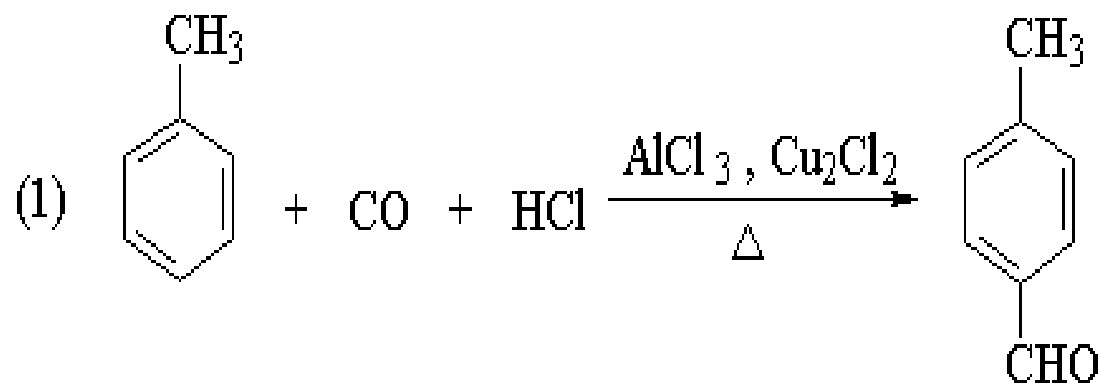
Overall:



- Chloroform is deprotonated by strong base (normally hydroxide) to form the chloroform carbanion. which will quickly alpha-eliminate to give dichlorocarbene which is principle reactive species.
- The hydroxide deprotonates the phenol to give a negatively charged phenolate.
- The negative charge is delocalised into the aromatic ring, making it far more nucleophilic and increases its ortho selectivity.
- Nucleophilic attack of the dichlorocarbene from the ortho position gives an intermediate dichloromethyl substituted phenol.
- After basic hydrolysis, the desired product is formed.

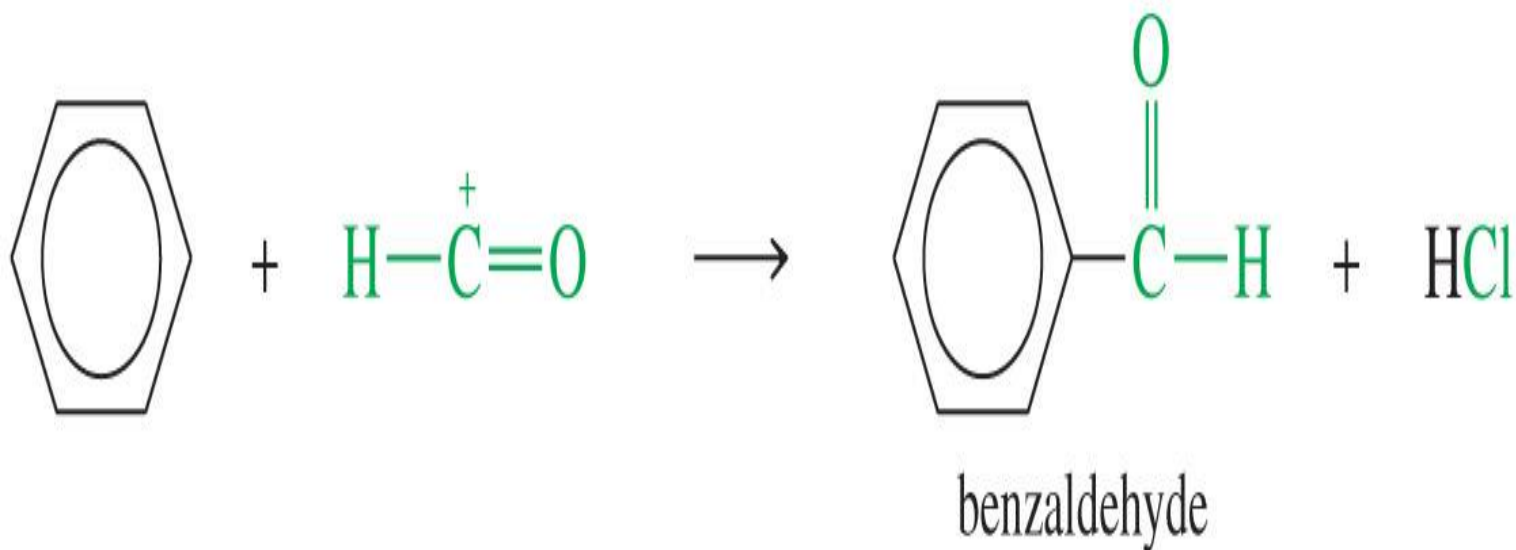
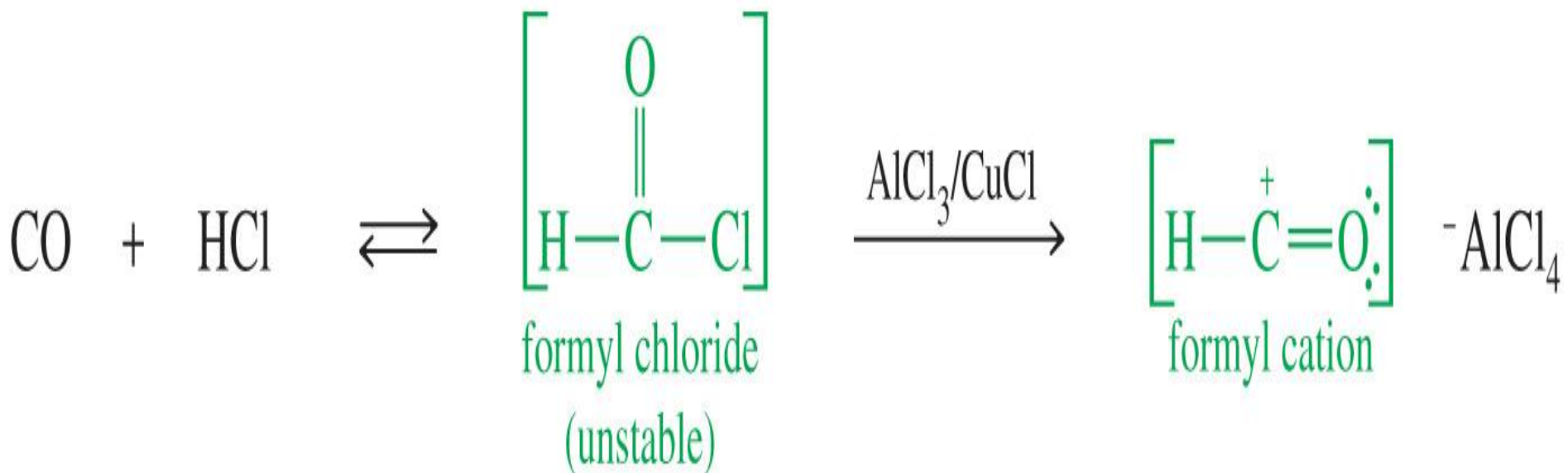
GATTERMANN – KOCH REACTION **(FORMYLATION)**

Formylation of aromatic hydrocarbon or polycyclic aromatic hydrocarbon with carbon monoxide and hydrogen chloride in the presence of AlCl_3 at high pressure is known as Gattermann-Koch reaction. The other catalysts used are cuprous chloride, HF, BF_3 , trifluoro methane sulphonic acid. The reaction is less accessible due to toxicity of carbon monoxide and high pressure.



The catalyst commonly used is aluminum chloride with cuprous chloride as a carrier. The carrier is not necessary when high pressure is used

MECHANISM

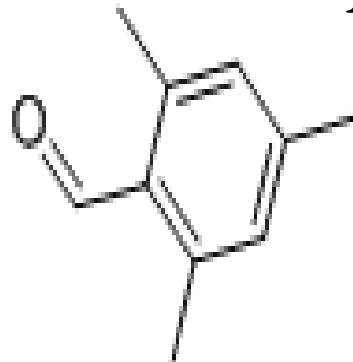


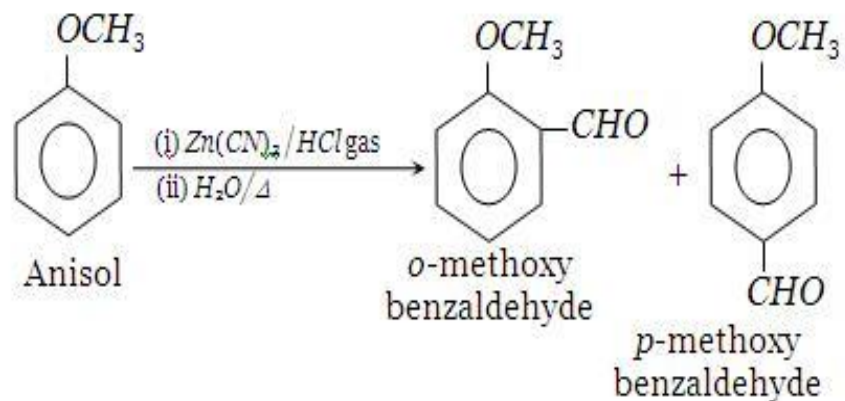
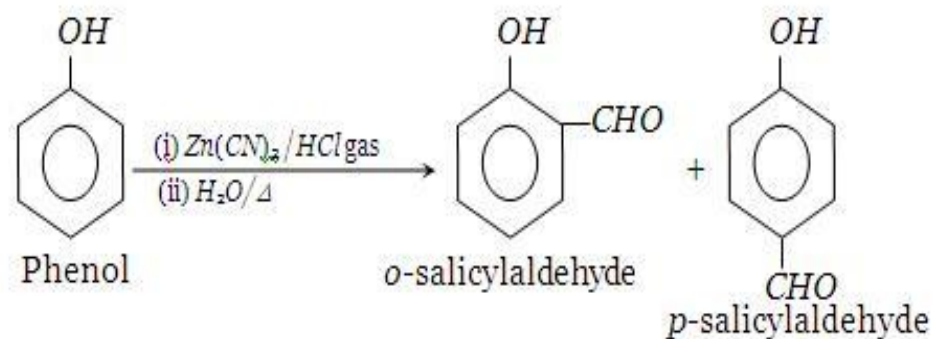
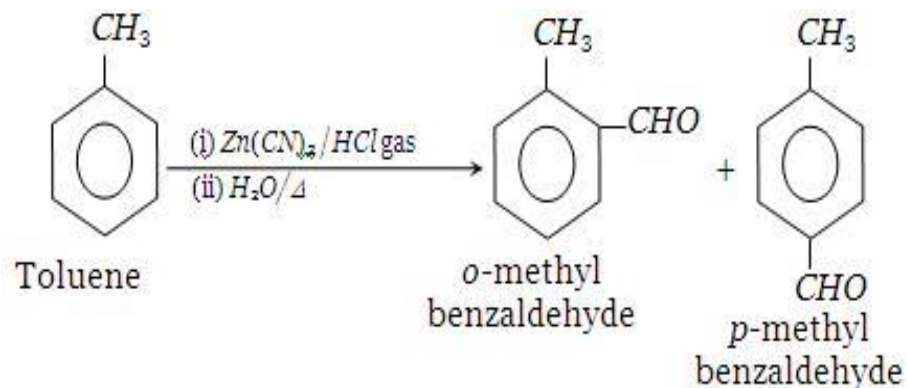
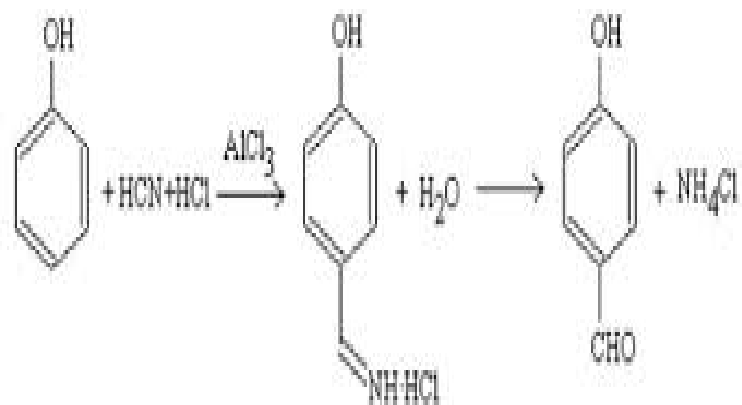
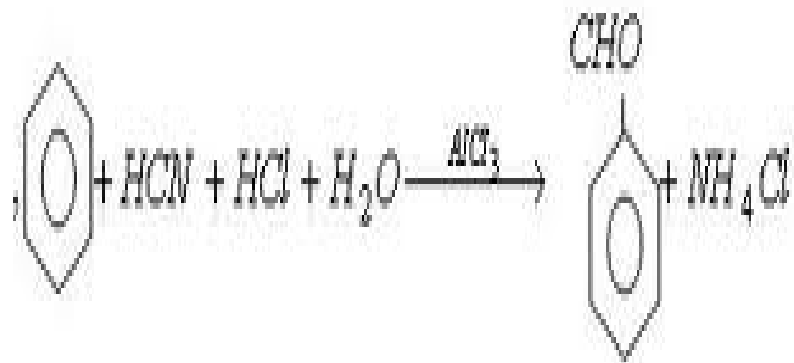
GATTERMANN-ALDEHYDE SYNTHESIS **(FROMYLATION)**

The preparation of aromatic aldehydes containing hydroxyl or alkyloxy groups on the aromatic ring by treatment of the aromatics with hydrogen cyanide and hydrogen chloride in anhydrous solvent (e.g., ether) with or without the presence of a Lewis acid (e.g., ZnCl_2 , AlCl_3) as a catalyst, in which aldimine hydrochloride functions as an intermediate, is generally referred to as the Gattermann aldehyde synthesis or simply as the Gatterman synthesis

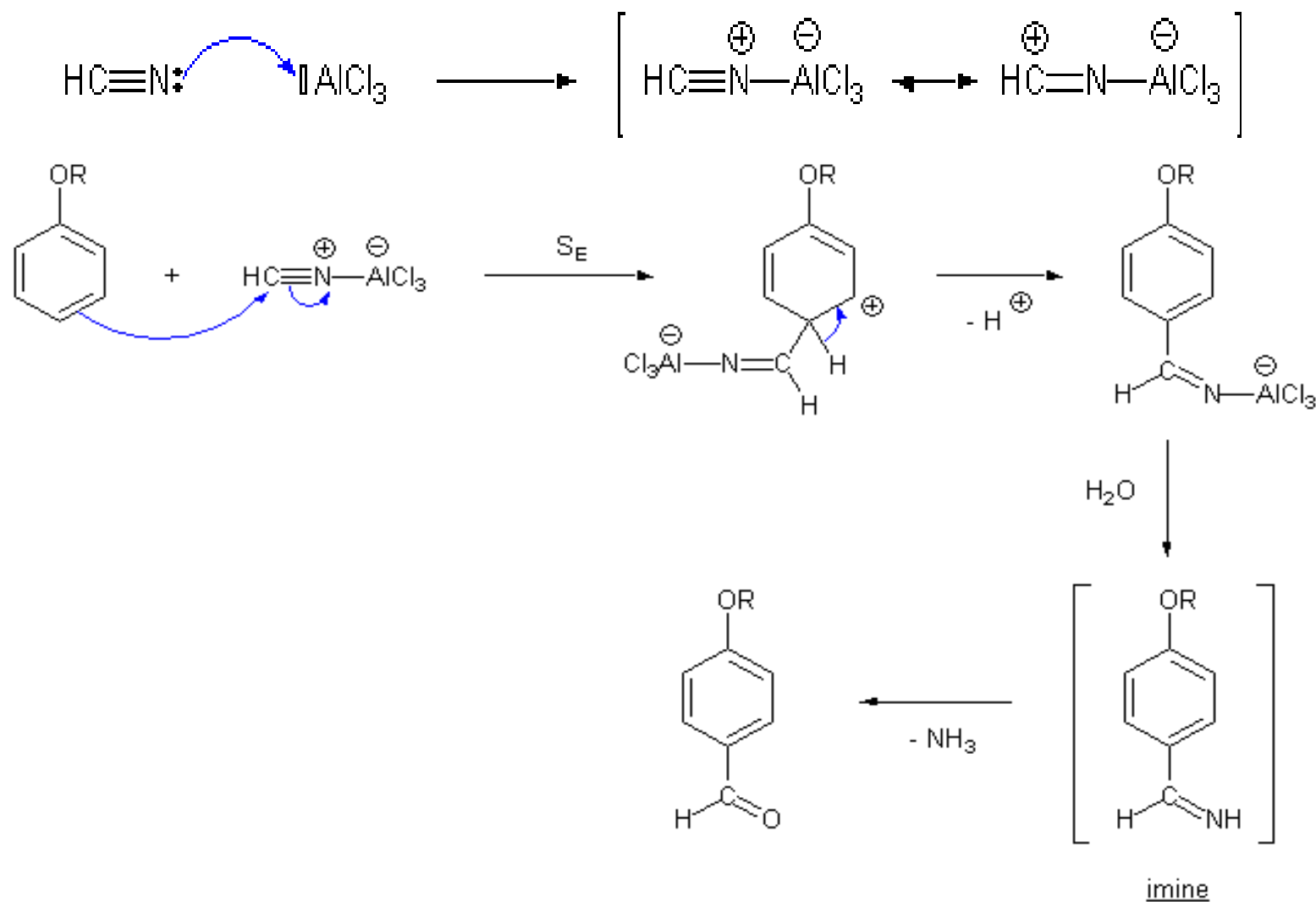
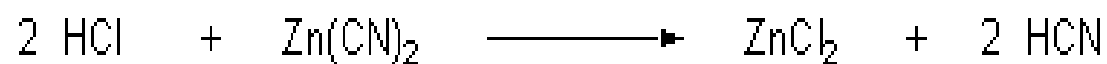
This is an alternative to Gattermann – Koch Reaction in which HCN is used instead of CO.

This reaction is useful in the preparation of aromatic aldehydes with hydroxy, alkoxy, and even multi-alkyl groups, such as mesitaldehyde (2,4,6-trimethyl-benzaldehyde)





MECHANISM





THANK

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