

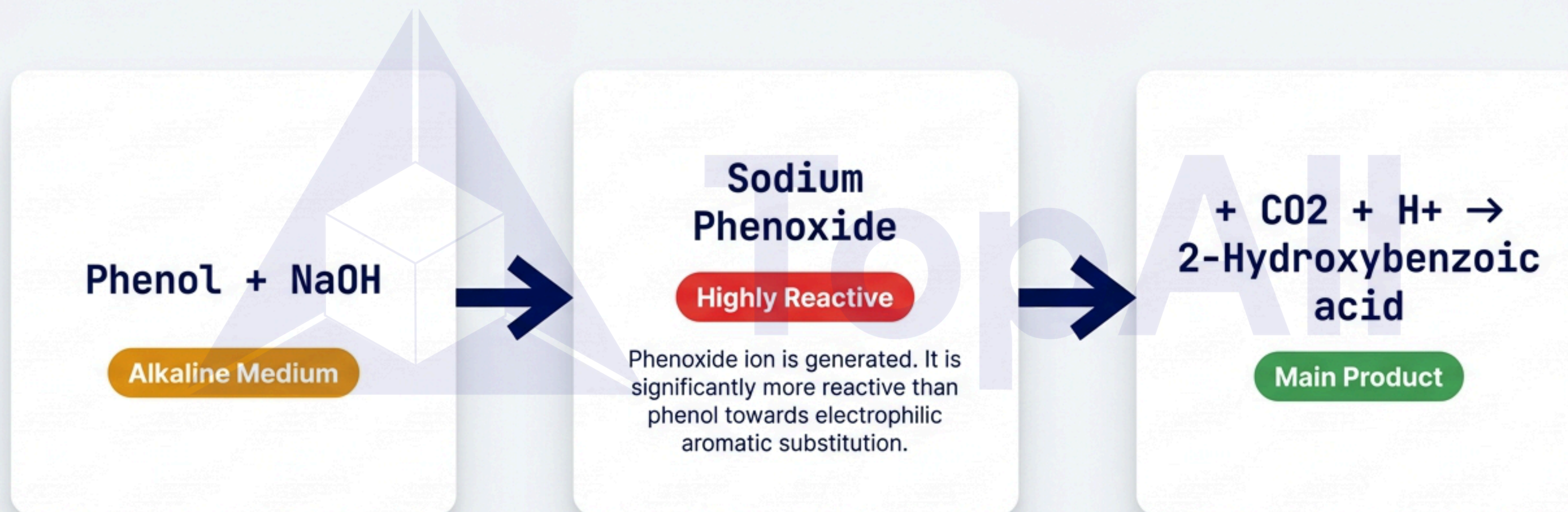
ORGANIC CHEMISTRY: UNIT 7

Kolbe, Reimer-Tiemann and More

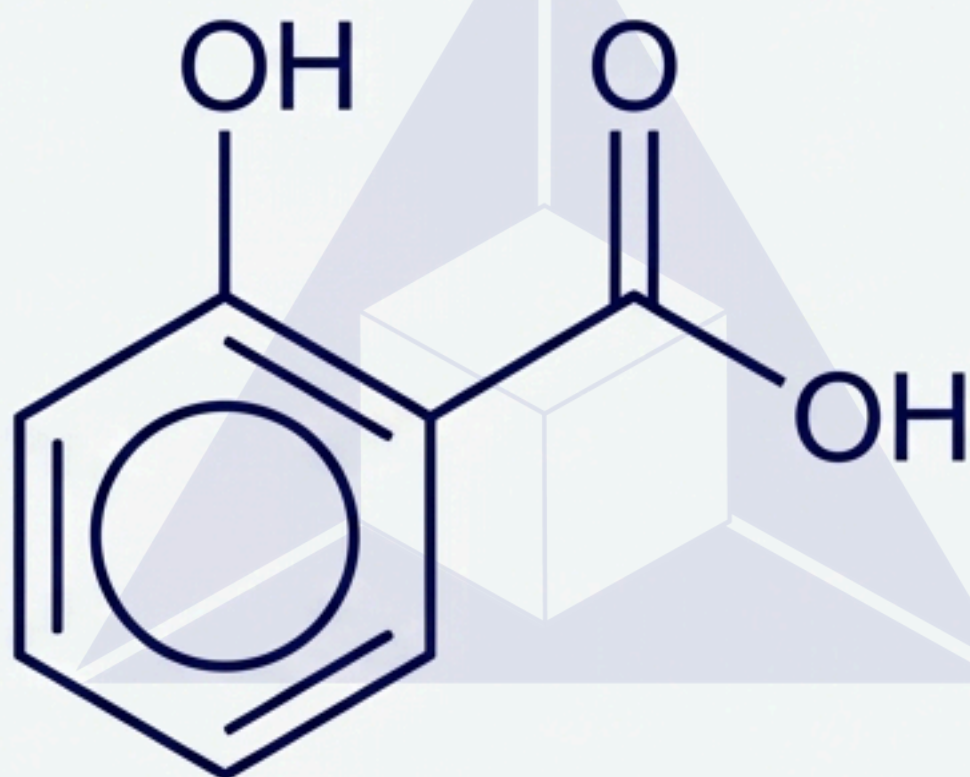
The Special Reactions of Phenol

An analytical breakdown of electrophilic aromatic substitution, reduction, and oxidation pathways in phenolic compounds.

Kolbe's Reaction: The Pathway



Understanding Salicylic Acid Formation



The Electrophile

CO₂ is a weak electrophile. It successfully attacks because the phenoxide ion presents a highly activated aromatic ring.

Spatial Positioning

The incoming group is strictly directed to the ortho position. The resonance effect of the "-OH" group makes the ortho/para positions uniquely electron-rich.

Salicylic acid is the foundational precursor for the synthesis of aspirin (acetylsalicylic acid).



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The Reimer-Tiemann Reaction

- 1 Phenol is treated with **chloroform** (CHCl_3) in the presence of sodium hydroxide (**NaOH**). Base + Chloroform
- 2 An intermediate substituted **benzal chloride** is formed on the aromatic ring.
- 3 The **benzal chloride** intermediate is subsequently hydrolysed in the presence of an alkali.
- 4 Final **introduction** of an **aldehyde** ($-\text{CHO}$) group directly at the ortho position.

The Result: Salicylaldehyde

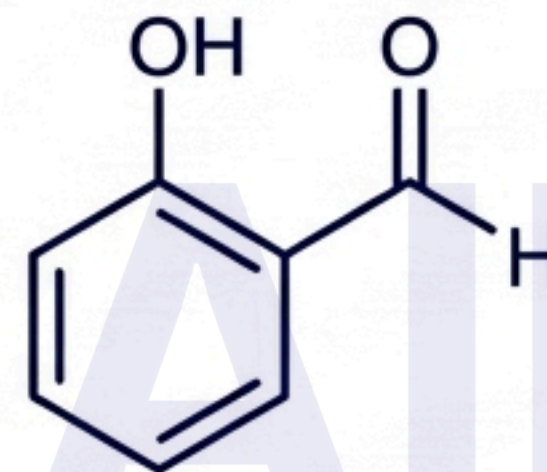
Phenol (C_6H_5OH)



A baseline benzene ring, primarily activated by the resident hydroxyl ("OH") group.



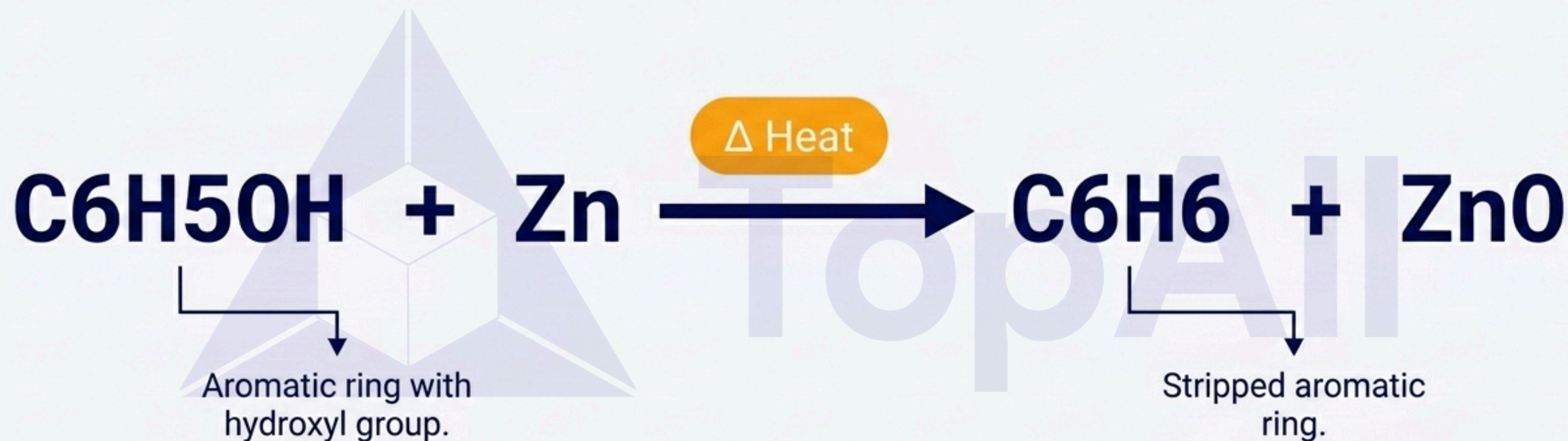
Salicylaldehyde



Ortho-substituted aldehyde group ("CHO") successfully introduced adjacent to the hydroxyl group.

The combination of the strongly activating "-OH" group and these specific reagents strictly dictates the ortho-positioning of the new formyl group.

Reduction: Phenol to Benzene



Phenol is converted to pure benzene upon heating with zinc dust. The zinc acts as a potent reducing agent, abstracting the oxygen to form zinc oxide ("ZnO").

Oxidation Pathways

Phenol oxidized with chromic acid
("Na₂Cr₂O₇" / "H₂SO₄").

Yields a conjugated diketone.

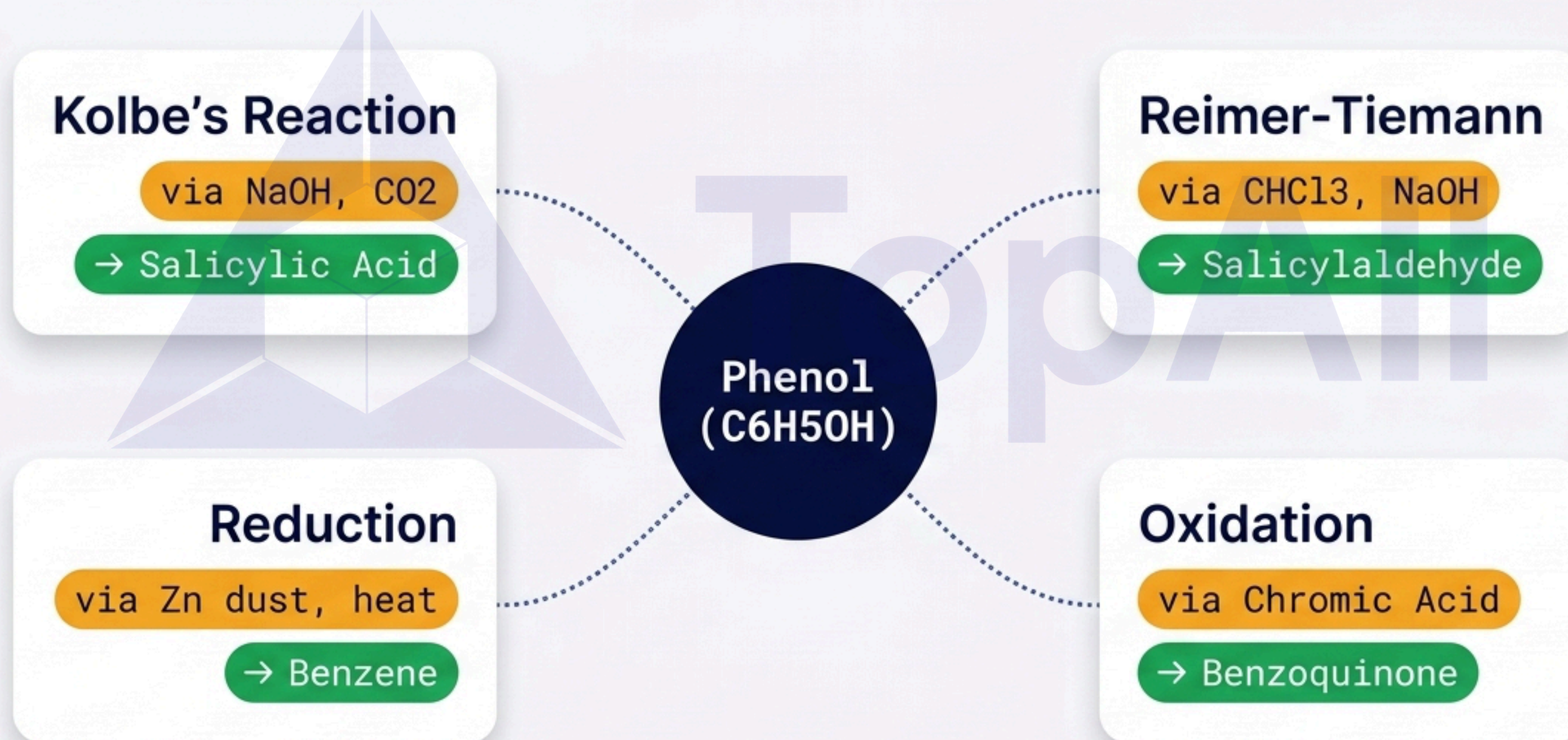


Product: p-Benzoquinone

Warning: Spontaneous Degradation

In the presence of air, phenols are slowly and naturally oxidized into dark-colored chemical mixtures containing various environmental quinones.

Synthesis Map: Special Reactions of Phenol





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