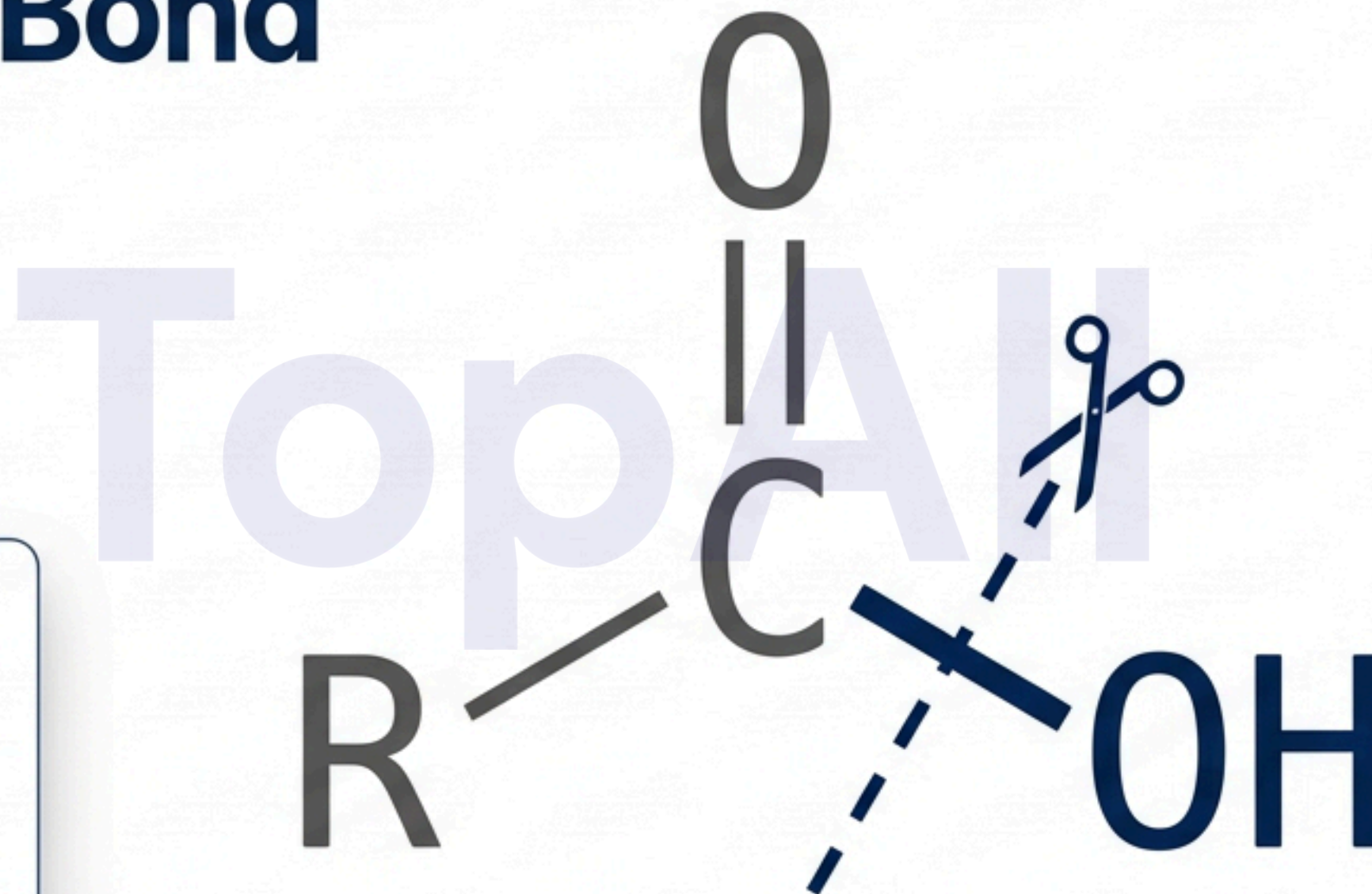


8.9.2 Reactions Involving Cleavage of C–OH Bond

Core Principle

Carboxylic acids undergo substitution reactions where the entire hydroxyl (–OH) group is replaced. This fundamental cleavage paves the way for the formation of vital acid derivatives.



Formation of Anhydrides

Conditions

Requires strong dehydrating agents to force the loss of water.

Mineral Acids (H_2SO_4)

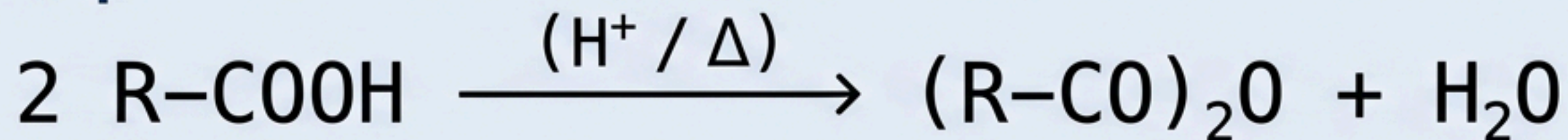
Phosphorus Pentoxide (P_2O_5)

Δ Heating

Concept

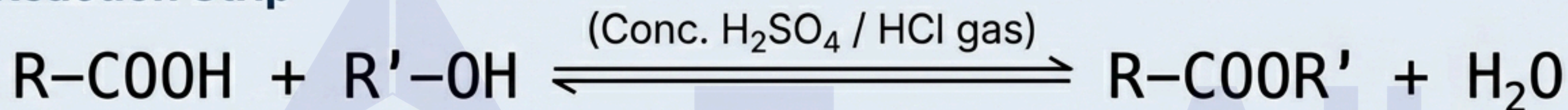
Two molecules of a carboxylic acid condense. One molecule sacrifices its entire $-\text{OH}$ group, while the other loses a proton, losing one molecule of water to form an acid anhydride.

Reaction Strip



Esterification with Alcohols

Reaction Strip



Equilibrium Nature

Fischer esterification is a reversible equilibrium reaction.

Le Chatelier's Application

To drive the reaction forward and maximize ester yield, the water formed must be continuously removed from the reaction mixture.



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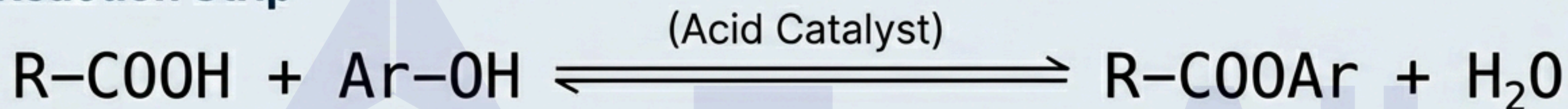
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Esterification with Phenols

Reaction Strip



Aromatic Application

Carboxylic acids react with phenols (aromatic alcohols) to yield aryl esters.

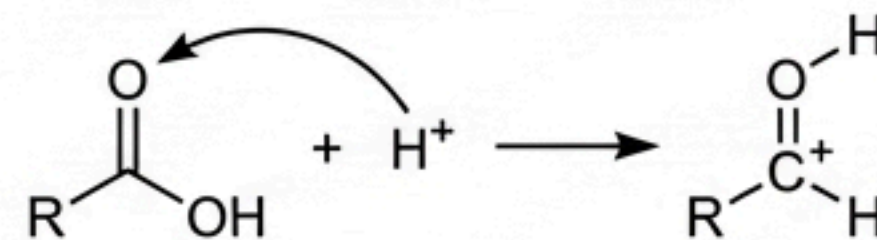
Nucleophilic Distinction

Phenols are less nucleophilic than aliphatic alcohols due to the resonance of the oxygen lone pair into the benzene ring. However, the fundamental C-OH cleavage principle remains identical.

Role of Acid Catalyst

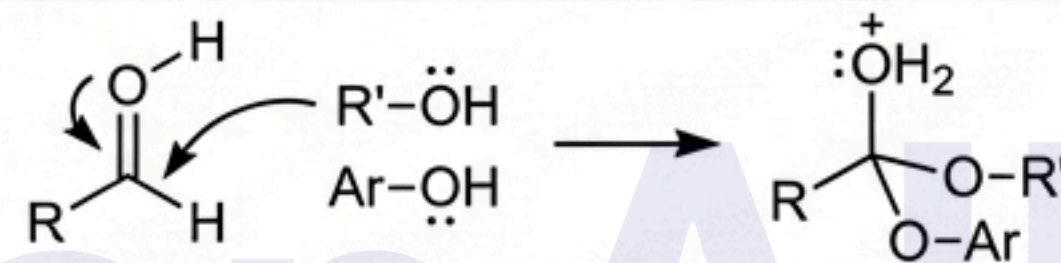
Step 1: Protonation (Activation)

The acid catalyst donates a proton to the carbonyl oxygen, increasing the electrophilicity of the carbonyl carbon.



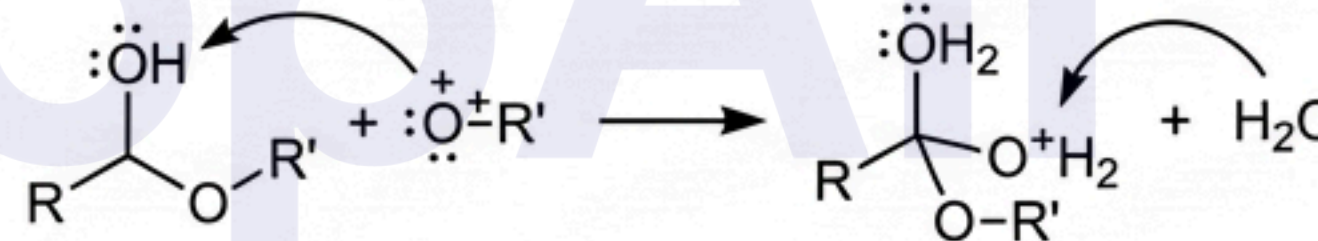
Step 2: Nucleophilic Addition (Attack)

The alcohol/phenol attacks the activated carbonyl carbon, forming a tetrahedral intermediate.



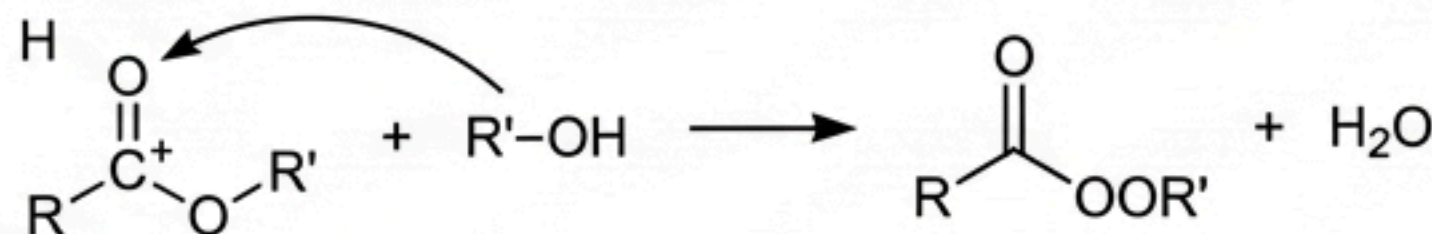
Step 3: Proton Transfer (Transfer & Elimination)

A proton shifts to the hydroxyl group, converting it into $-O^+H_2$ (an excellent leaving group). It is eliminated as neutral water.



Step 4: Deprotonation (Regeneration)

The protonated ester loses a proton to yield the final neutral ester product.



Key-Takeaway Panel

Without the acid catalyst, the carbonyl carbon is not electrophilic enough to be attacked by weak nucleophiles like alcohols.

Final Recap: Condensation-Type Conversions

	Anhydride Formation	Aliphatic Esterification	Phenolic Esterification
Nucleophile/ Reactant	2 nd Carboxylic Acid	Alkyl Alcohol (R-OH)	Phenol (Ar-OH)
Bond Cleaved	Acid C–OH	Acid C–OH	Acid C–OH
Byproduct	H ₂ O	H ₂ O	H ₂ O

Regardless of the reactant (acid, alcohol, or phenol), all three reactions are unified by a nucleophilic acyl substitution mechanism that relies on the precise cleavage of the carboxylic acid's C–OH bond and the elimination of water.



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