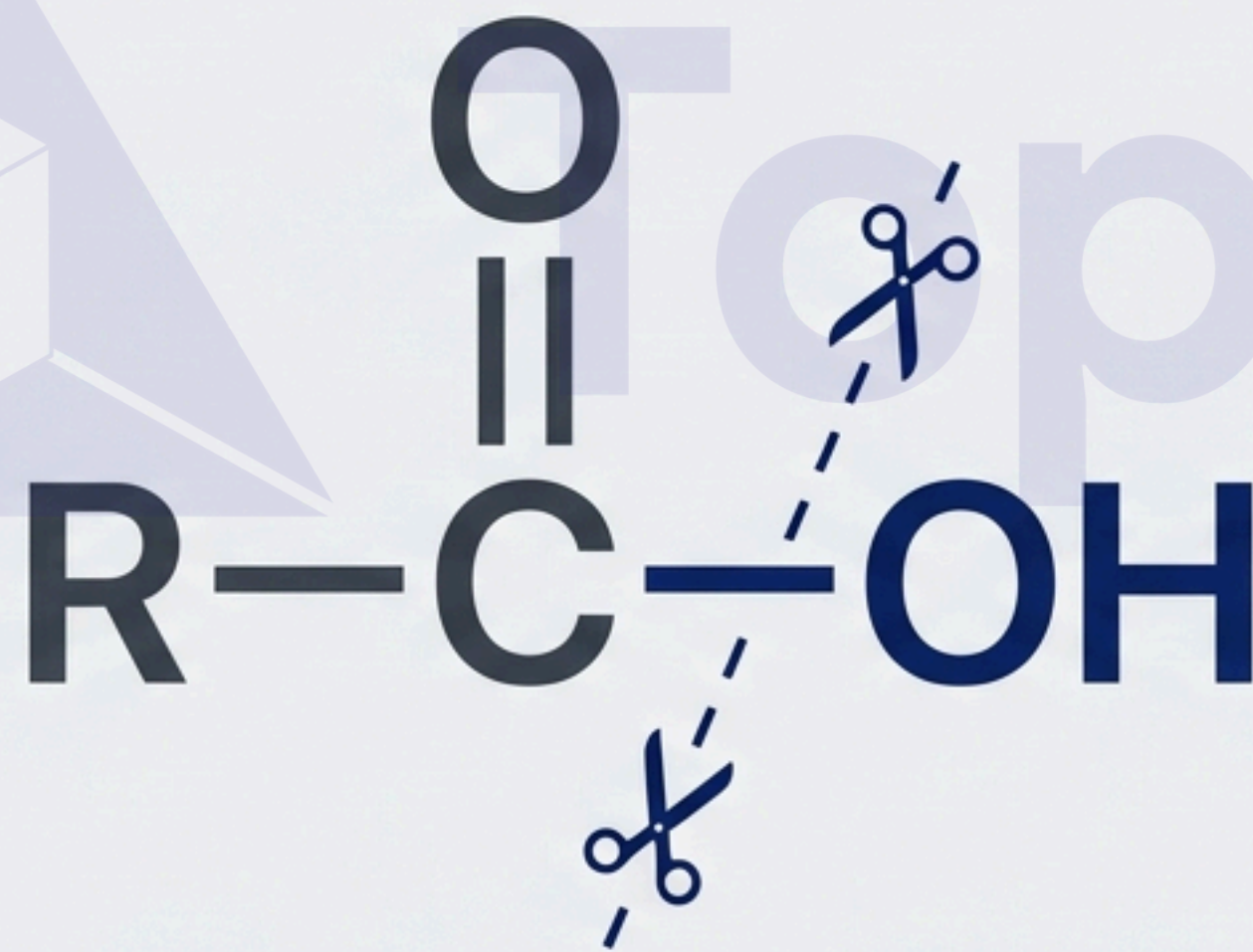


Reactions Involving Cleavage of the C–OH Bond

Nucleophilic Acyl Substitution and the transformation of Carboxylic Acids.



Concept Vocabulary

Nucleophilic Acyl Substitution

The overarching reaction mechanism where an incoming nucleophile replaces the leaving -OH group.

Tetrahedral Intermediate

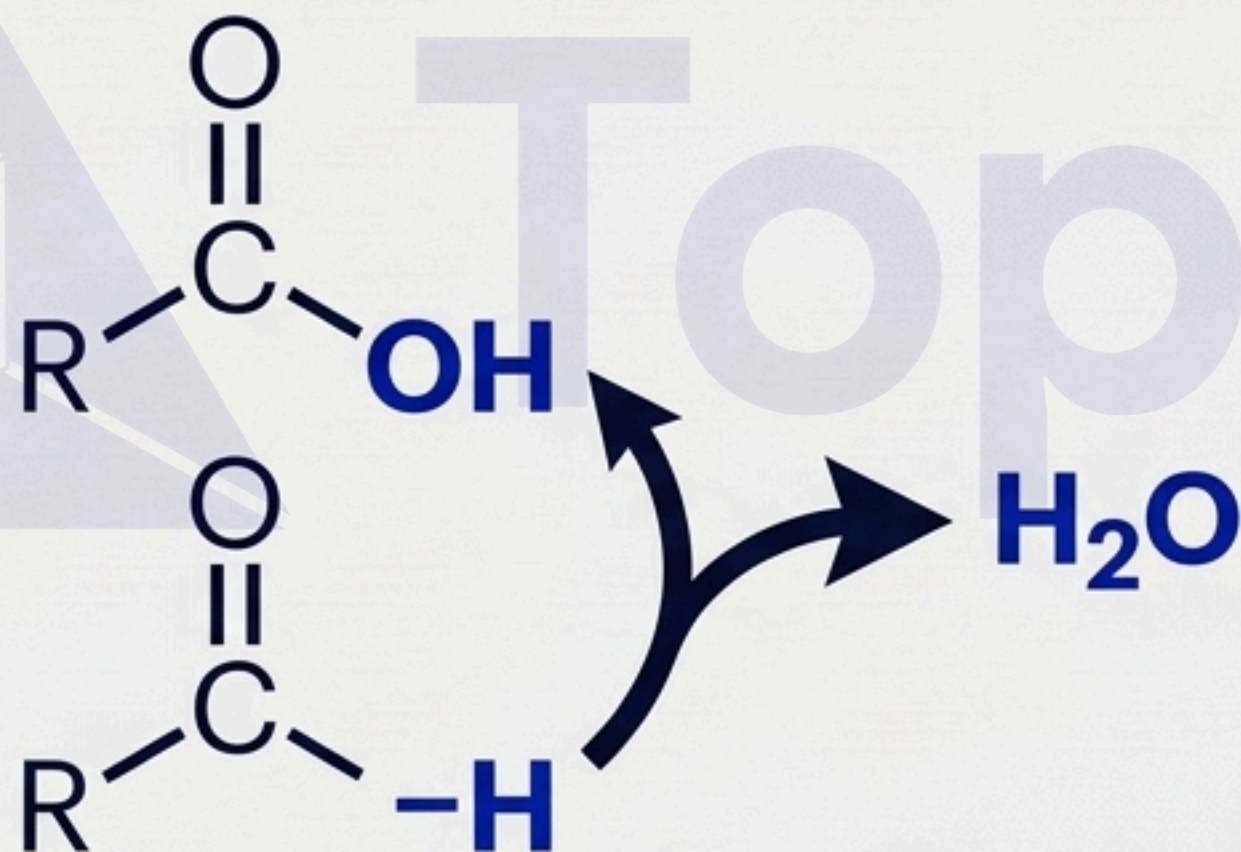
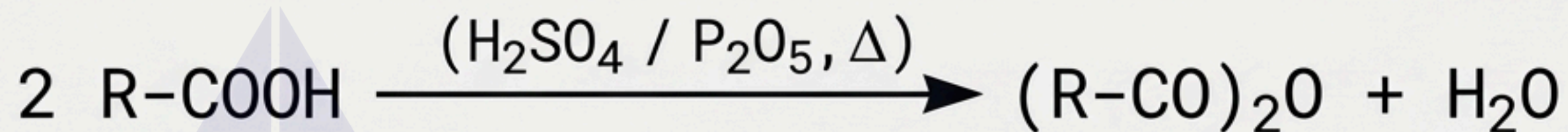
The unstable transition state where the carbonyl carbon is briefly sp^3 hybridized before reforming the double bond.

Esterification Mechanism

The classic, acid-catalyzed 5-step sequence converting an acid and an alcohol into an ester and water.

Anhydride Formation

Condensation of two carboxylic acid molecules.





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$$E=mc^2$$



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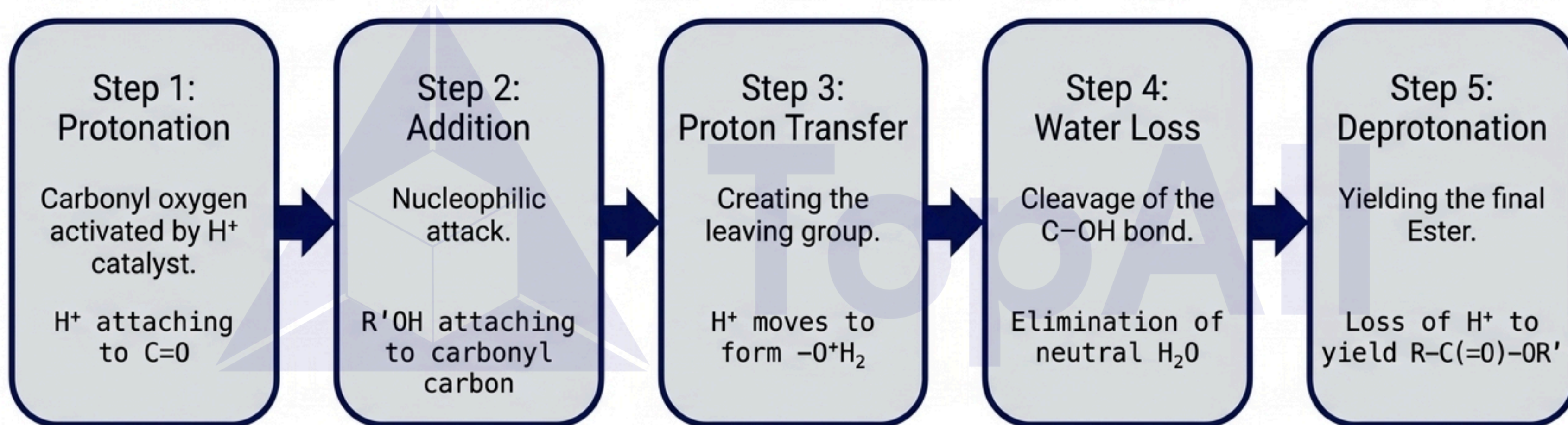
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The 5-Step Esterification Mechanism



Halogenation of the Acyl Group

Reagent

Main Product

Byproducts

PCl₅

R-COCl

POCl₃ + HCl

PCl₃

R-COCl

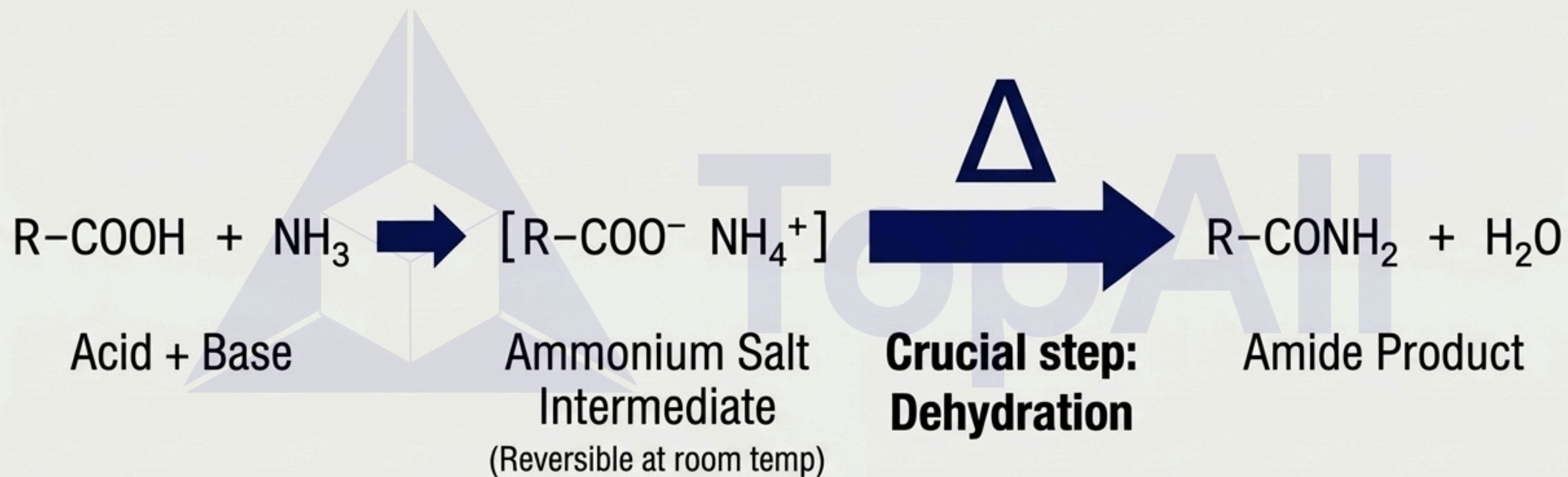
H₃PO₃

SOCl₂

R-COCl

SO₂(g)↑ + HCl(g)↑

Amide Formation via Ammonia



High-Yield Exam Concept

Watch for this: The Thionyl Chloride Advantage

When replacing the -OH group with a halogen to form an acid chloride, **SOCl_2 (Thionyl Chloride)** is **strictly preferred** over PCl_3 or PCl_5 in laboratory and exam settings.

The "Why": Both byproducts (SO_2 and HCl) are gaseous and naturally escape the reaction mixture.

The Result: This leaves pure acyl chloride behind without requiring any complex downstream purification.

Summary: C–OH Cleavage

- The C–OH bond in carboxylic acids is cleaved via **Nucleophilic Acyl Substitution**, allowing the –OH group to be replaced by other incoming nucleophiles (such as alcohols, halogens, or ammonia).
- The specific reaction conditions dictate the final product: use acidic dehydrating agents for anhydrides/esters, thionyl chloride for exceptionally pure acid chlorides, and heat (Δ) with ammonia to yield amides.



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