

UNIT 6 • HALOALKANES AND HALOARENES

Preparation of Haloalkanes from Alcohols

Reagents, reactivity trends, and key exceptions in organic synthesis.

Thionyl Chloride (SOCl₂)

The preferred laboratory reagent for synthesizing pure alkyl chlorides.

ZnCl₂ Catalyst

A mandatory addition when reacting primary and secondary alcohols with HCl (Lucas Reagent).

In Situ Generation

Producing unstable reagents (like PBr₃ or PI₃) directly inside the reaction flask by mixing red phosphorus with halogens.

Reagent-Matching Matrix

Tertiary Alcohols (3°)	Conc. HCl	Reacts by simply shaking at room temperature
Primary (1°) / Secondary (2°)	HCl + ZnCl ₂	Requires catalyst to proceed
Alkyl Bromides (R-Br)	Constant-boiling HBr (48%)	Direct substitution
Alkyl Iodides (R-I)	Red P + X ₂ (in situ)	Yields active PBr ₃ or PI ₃ in the mixture



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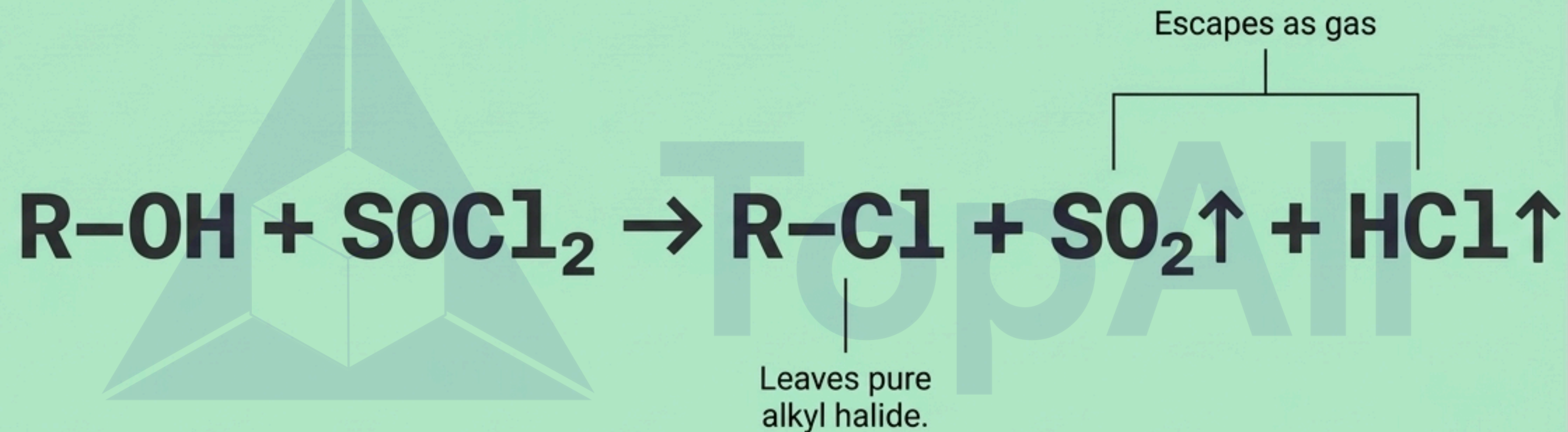


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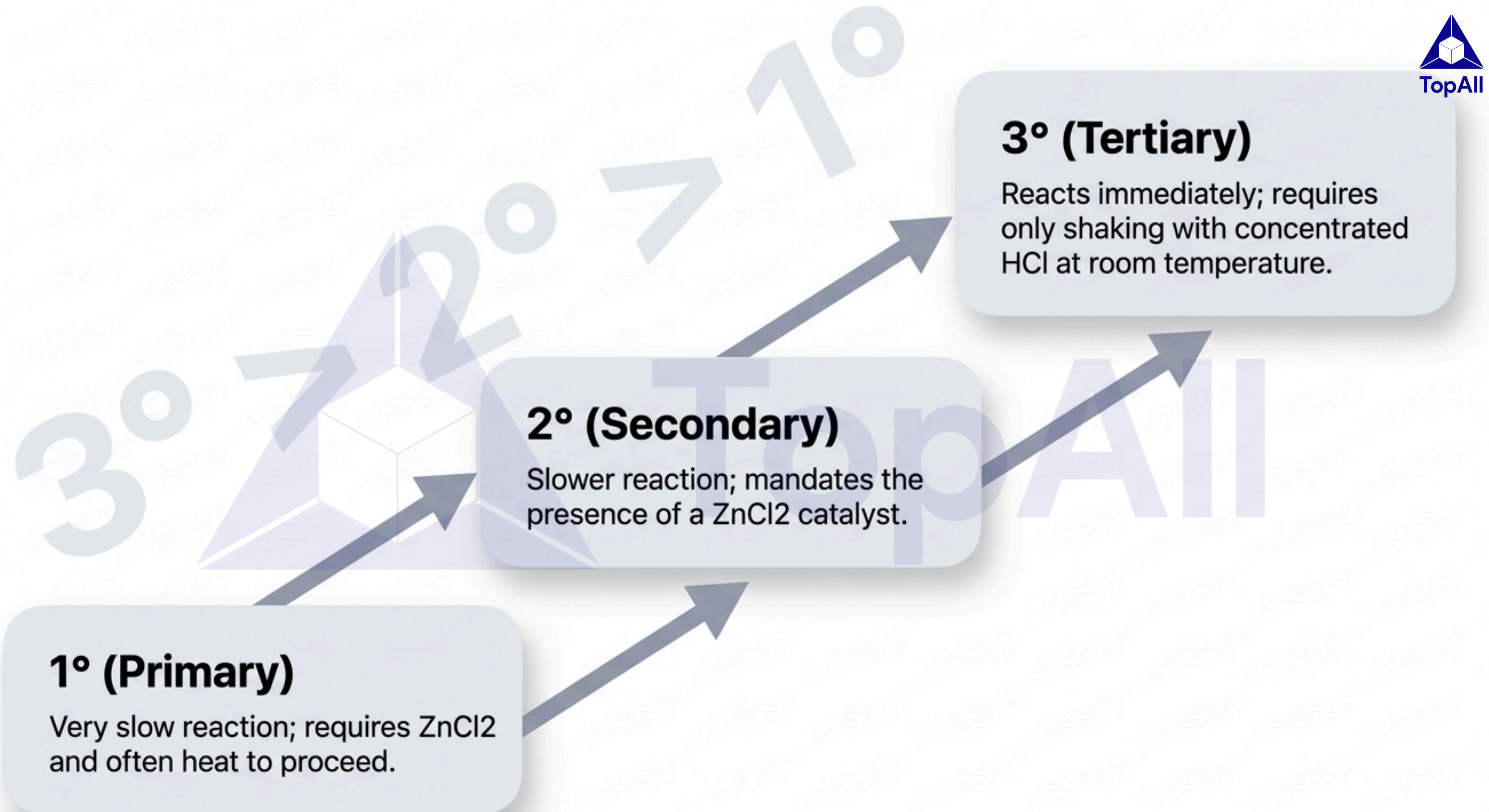
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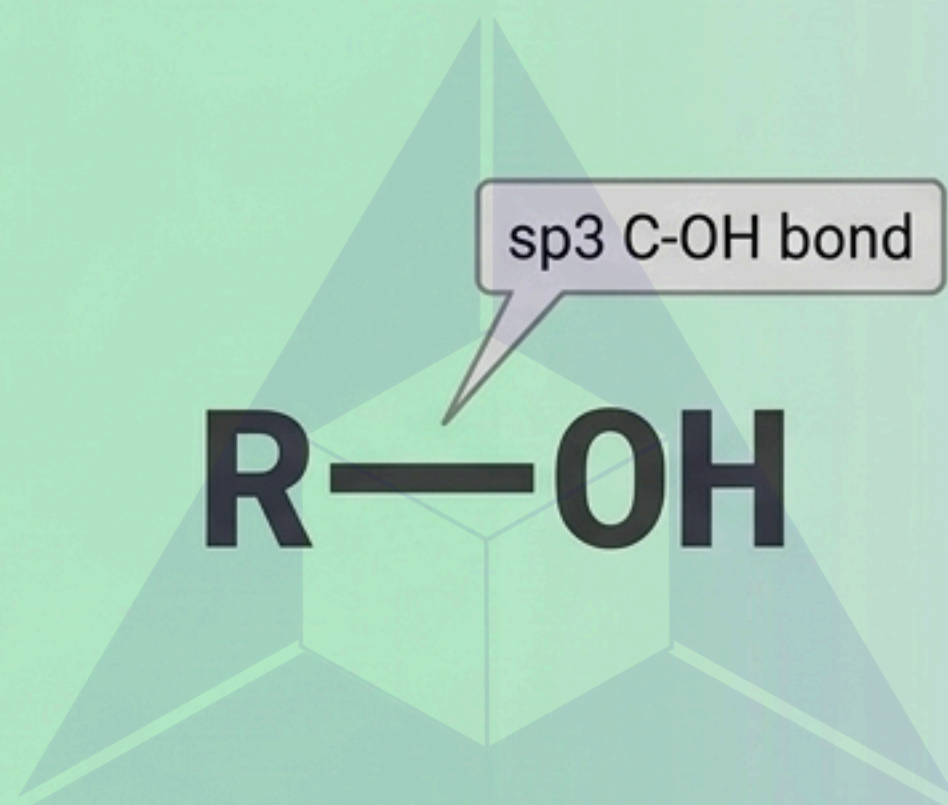




Thionyl chloride (SOCl_2) is the preferred laboratory method because the gaseous byproducts (SO_2 and HCl) make purification effortless.

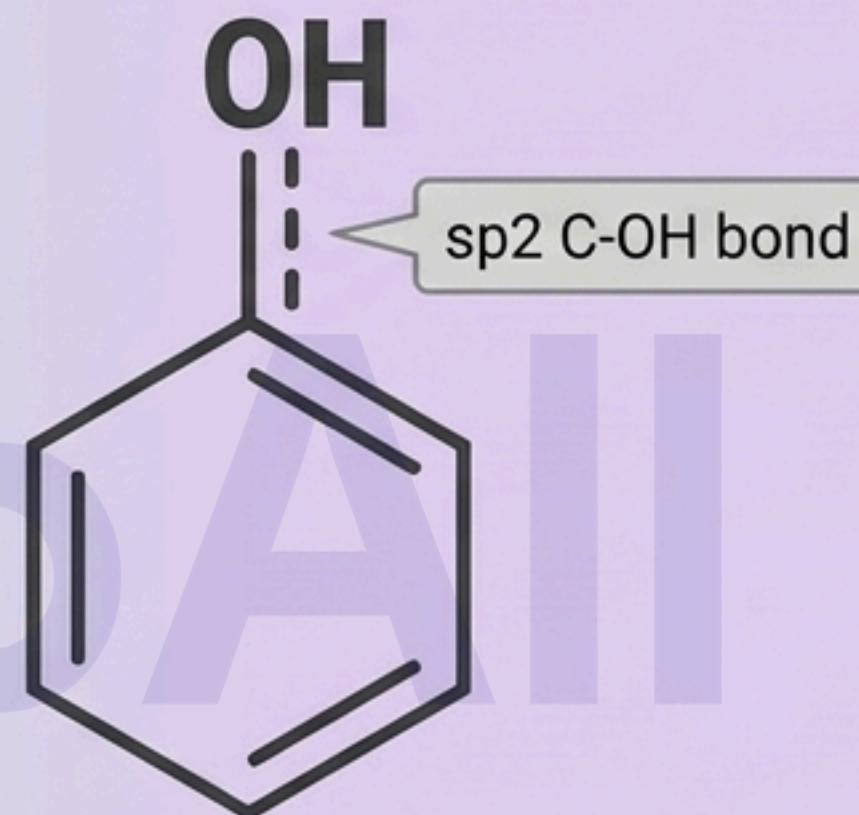


Aliphatic Alcohol



Single bond. Easily cleaved by nucleophiles.

Phenol



Partial double-bond character.

Resonance reinforces the C-O bond in phenols. It is significantly stronger than a single bond and cannot be broken by standard halogen acids or $SOCl_2$.

Watch for this common trap!



This specific method NEVER works for preparing aryl halides from **phenols**. Haloarenes require entirely different preparation methods (like electrophilic substitution) because the reinforced sp² C-O bond resists cleavage.

Key Takeaways

- **SOCl₂ is the gold standard:** Thionyl chloride is the preferred reagent for creating alkyl chlorides because its byproducts (SO₂ and HCl) are gases, leaving behind a highly pure product.
- **Reactivity is strictly 3° > 2° > 1°:** Tertiary alcohols react easily at room temperature, while primary/secondary require a ZnCl₂ catalyst. Crucially, these methods completely fail on phenols due to resonance-stabilized C-O bonds.



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