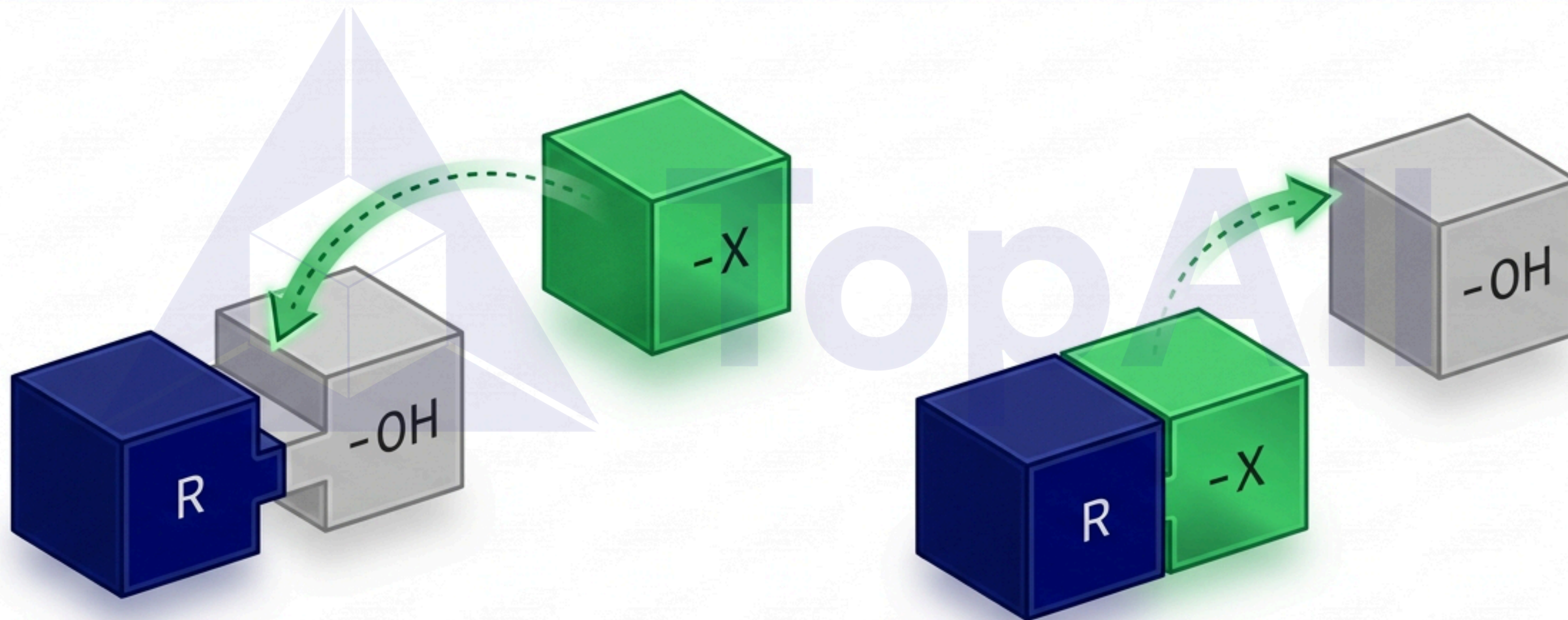
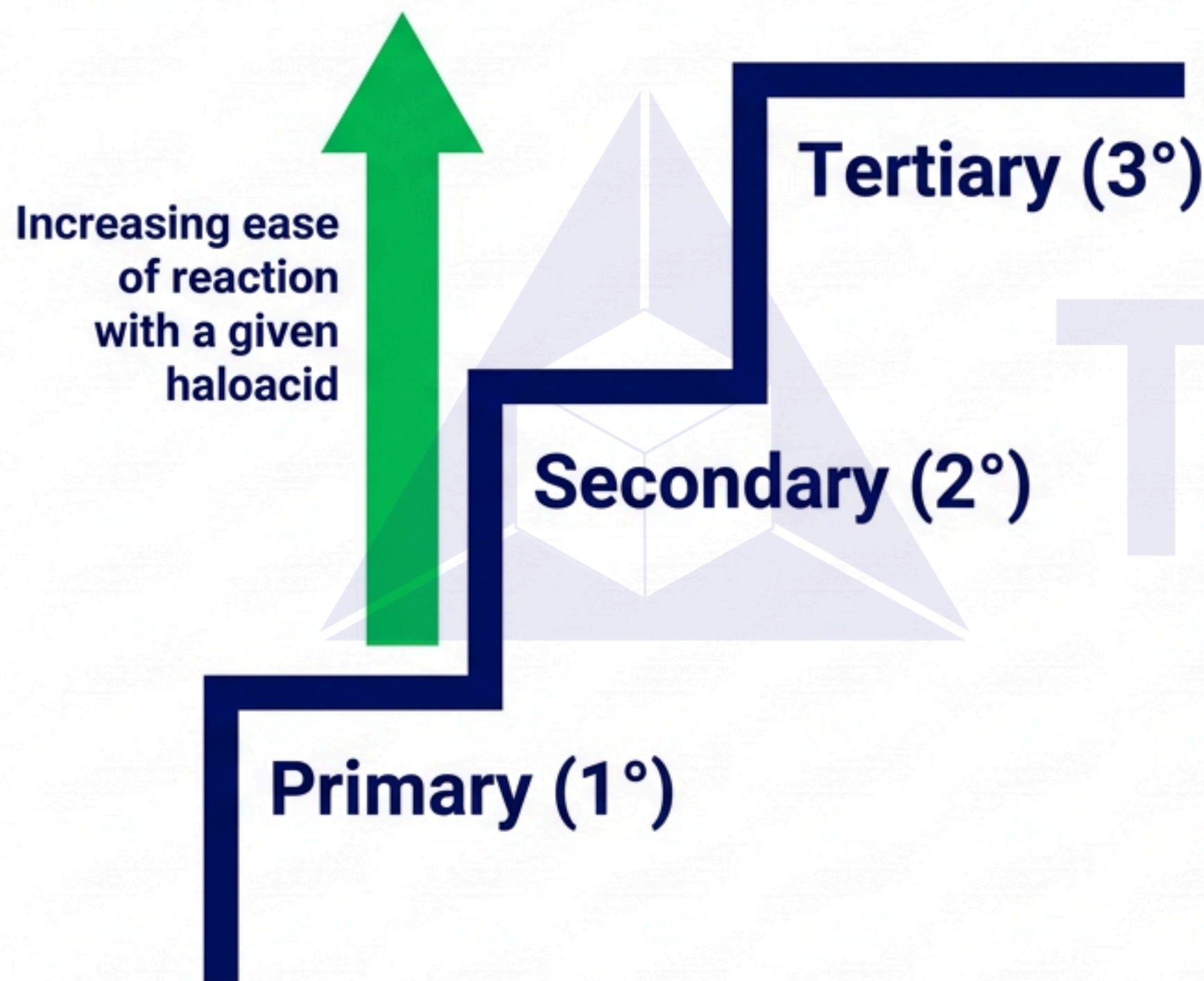


From Alcohols to Haloalkanes

The fundamental toolkit for replacing the -OH group with a halogen.



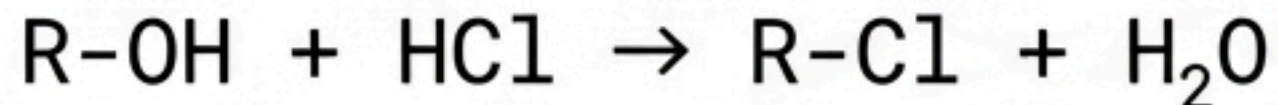
The Substrate Rule: The Reactivity Ladder



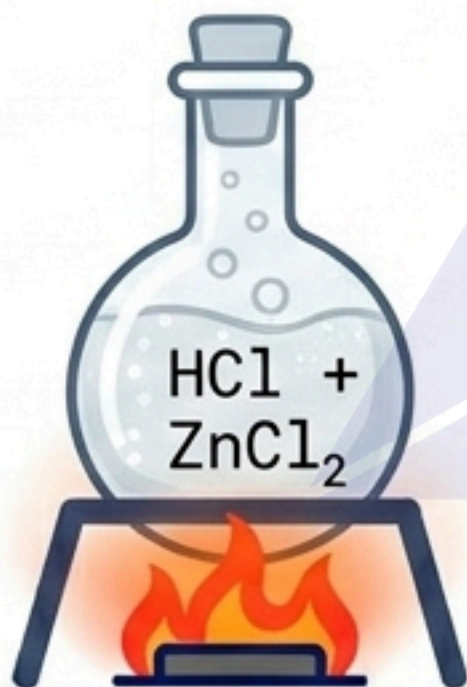
The order of reactivity of alcohols with a given haloacid **strictly** follows the degree of carbon substitution.

Reactivity: $3^\circ > 2^\circ > 1^\circ$

Tool #1: Concentrated Halogen Acids



Requires Catalyst



Primary and secondary alcohols require the presence of a zinc chloride (ZnCl_2) **catalyst** to react with HCl.

Room Temp



Tertiary alcohols are **highly reactive**; the reaction is conducted by simply shaking the alcohol with concentrated HCl at room temperature.

- Bromides: Require constant boiling with HBr (48%).
- Iodides: Require heating with NaI or KI in 95% orthophosphoric acid.



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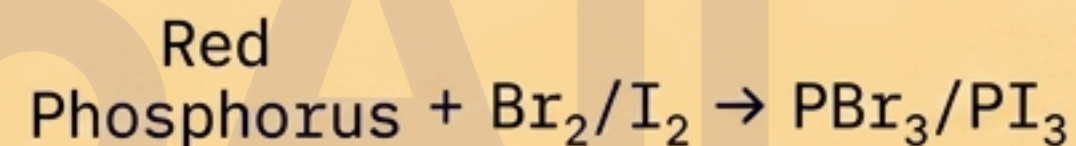
Tool #2: Phosphorus Halides

Standard Reagents



PCl_3 and PCl_5 can directly replace the hydroxyl group of an alcohol with a chlorine atom.

In Situ Generation



Phosphorus tribromide and triiodide are highly unstable. They are generated in situ (produced directly in the reaction mixture).

Tool #3: Thionyl Chloride (SOCl_2)



Industry
Preferred



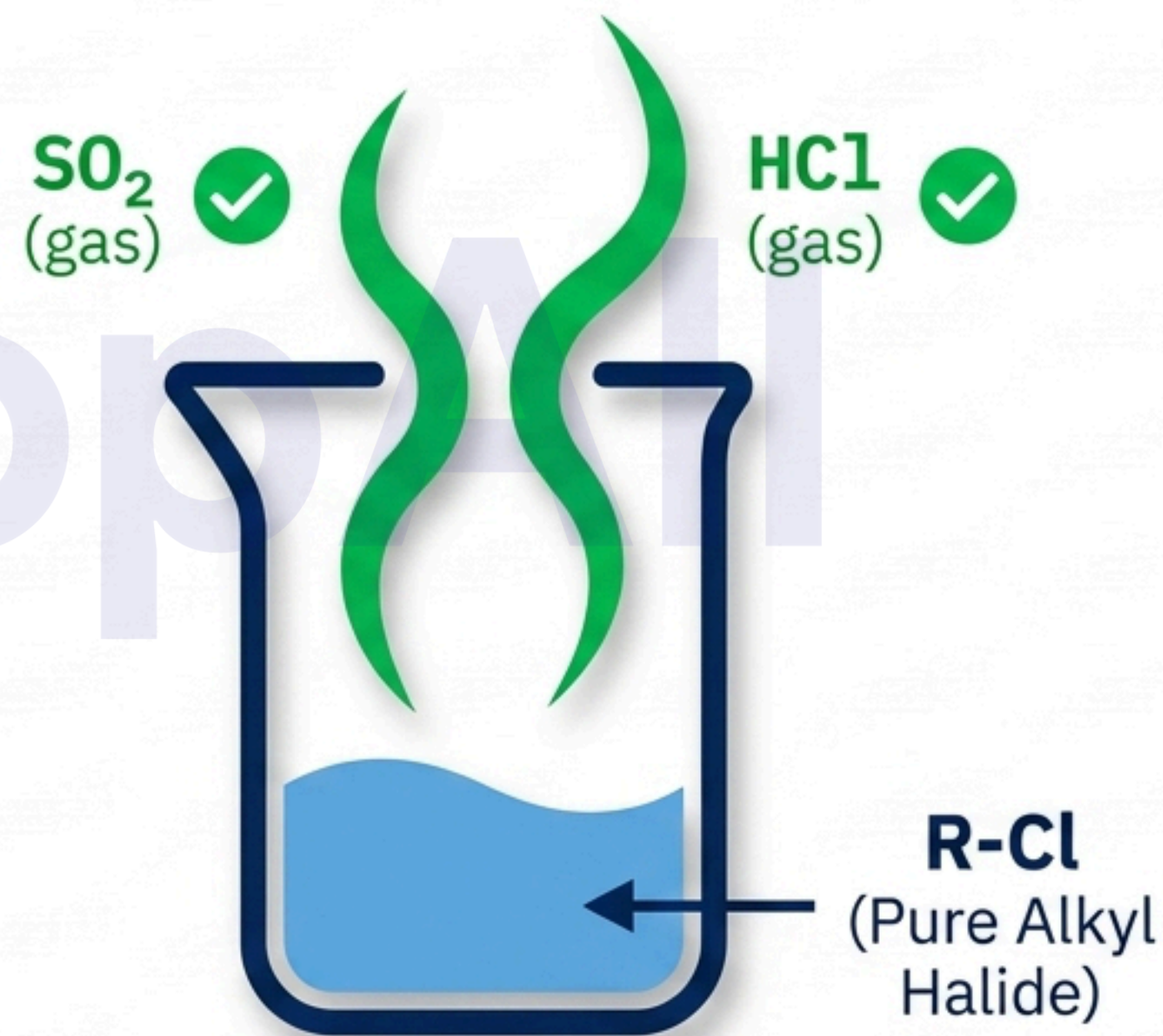
Thionyl chloride is the preferred reagent for synthesizing alkyl chlorides from alcohols. It reliably replaces the hydroxyl group while yielding highly specific, easily managed by-products.

The Thionyl Chloride Advantage

Why is SOCl_2 preferred over Halogen Acids or Phosphorus Halides?

- The two by-products of the reaction (SO_2 and HCl) are strictly gaseous.
- They naturally escape the reaction mixture, leaving behind a pure liquid alkyl halide.

No complex separation or purification steps are required.



Reagent Synthesis Matrix



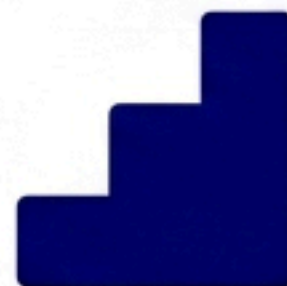
Reagent Class	Conditions & Notes	By-products	Verdict
Halogen Acids (HX)	Needs ZnCl_2 for 1°/2°, room temp for 3°	Liquid H_2O	Good, but needs catalyst for lower degrees.
Phosphorus Halides (PX_3 / PX_5)	Bromides/Iodides must be made in situ with Red P	Liquid phosphorus acids	Reliable, but yields liquid by-products.
Thionyl Chloride (SOCl_2)	Standard conditions	Gaseous $\text{SO}_2\uparrow$, $\text{HCl}\uparrow$	Best overall; produces pure product natively.

High-Yield Exam Summary



Core Reaction

$\text{R-OH} \rightarrow \text{R-X}$.
Achieved via HX,
 PX_3/PX_5 , or SOCl_2 .



The Golden Rule

Reactivity order of
alcohols with
haloacids is **strictly**
 $3^\circ > 2^\circ > 1^\circ$.



The Champion Reagent

SOCl_2 is preferred
because its by-
products (SO_2 , HCl)
are escapable gases.



Exam Alert

Note: These methods are NOT applicable for preparing aryl halides because the carbon-oxygen bond in phenols has partial double bond character.



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