



Breaking the Oxygen Bridge

Cleavage of the C–O Bond in Ethers

Ethers: The Least Reactive Functional Group



The Structure

The C–O bonds in ethers are relatively non-polar compared to alcohols, making them structurally robust.

The Implication

Ethers do not react with common bases, active metals, oxidizing agents, or reducing agents under standard conditions.

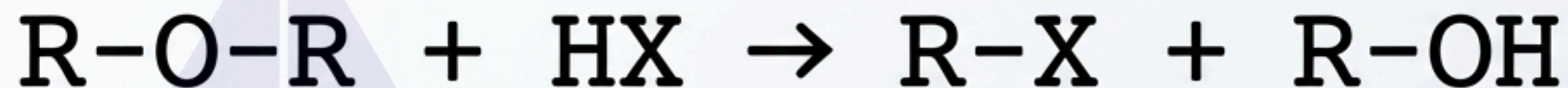
They function as highly stable “**oxygen bridges**” between alkyl/aryl groups.

Forcing the Cleavage

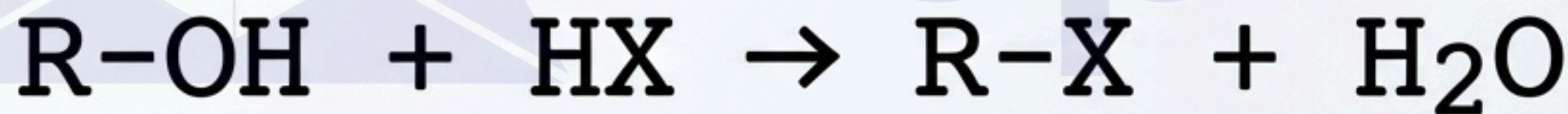


Drastic Conditions Required

Step 1



Step 2



With excess HX at high temperatures, the ultimate products are two alkyl halide molecules and water.



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$$E=mc^2$$



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The Reactivity Hierarchy

HI

Why HI?

Iodide (I^-) is an exceptionally good nucleophile, perfectly suited to attack the protonated oxonium ion.

HBr

HCl

The Mechanism

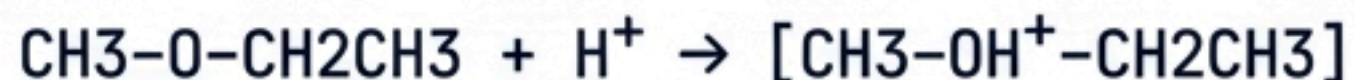
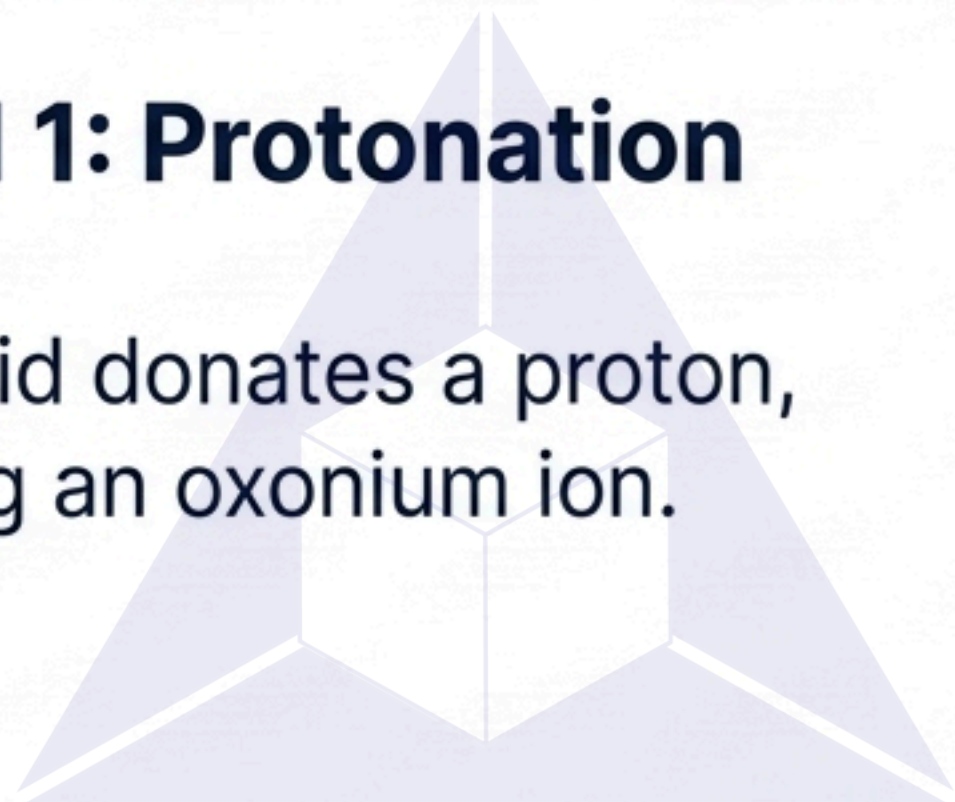
The reaction requires sufficiently acidic reagents for the initial protonation step.

Concentrated HI or HBr at high temperatures is the chemical standard.

Cleaving Dialkyl Ethers

Panel 1: Protonation

The acid donates a proton, forming an oxonium ion.



Panel 2: Nucleophilic Attack (S_N2)

The halide (e.g., I⁻) attacks the least substituted carbon to displace the alcohol.



Mechanism Shift: If a tertiary alkyl group is present, the departure of the leaving group creates a stable carbocation, shifting the mechanism entirely to S_N1.

Alkyl Aryl Ethers: The Uneven Split



Cleavage always occurs at the alkyl-oxygen bond.

Why? The aryl-oxygen bond is significantly more stable and resists breaking. The attack by the I⁻ ion uniquely targets the weaker O-CH₃ bond.

The Phenol Exception

🔑 Core Takeaway

Why doesn't Phenol react further with excess HI to become an aryl halide?

sp^2 Hybridization

The carbon of the phenyl group attached to the oxygen is sp^2 hybridized.

Partial Double Bond

The Aryl-O bond possesses partial double bond character due to resonance delocalization.

The sp^2 hybridized carbon cannot undergo the nucleophilic substitution required to convert into a halide. The cleavage permanently stops at Phenol.



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