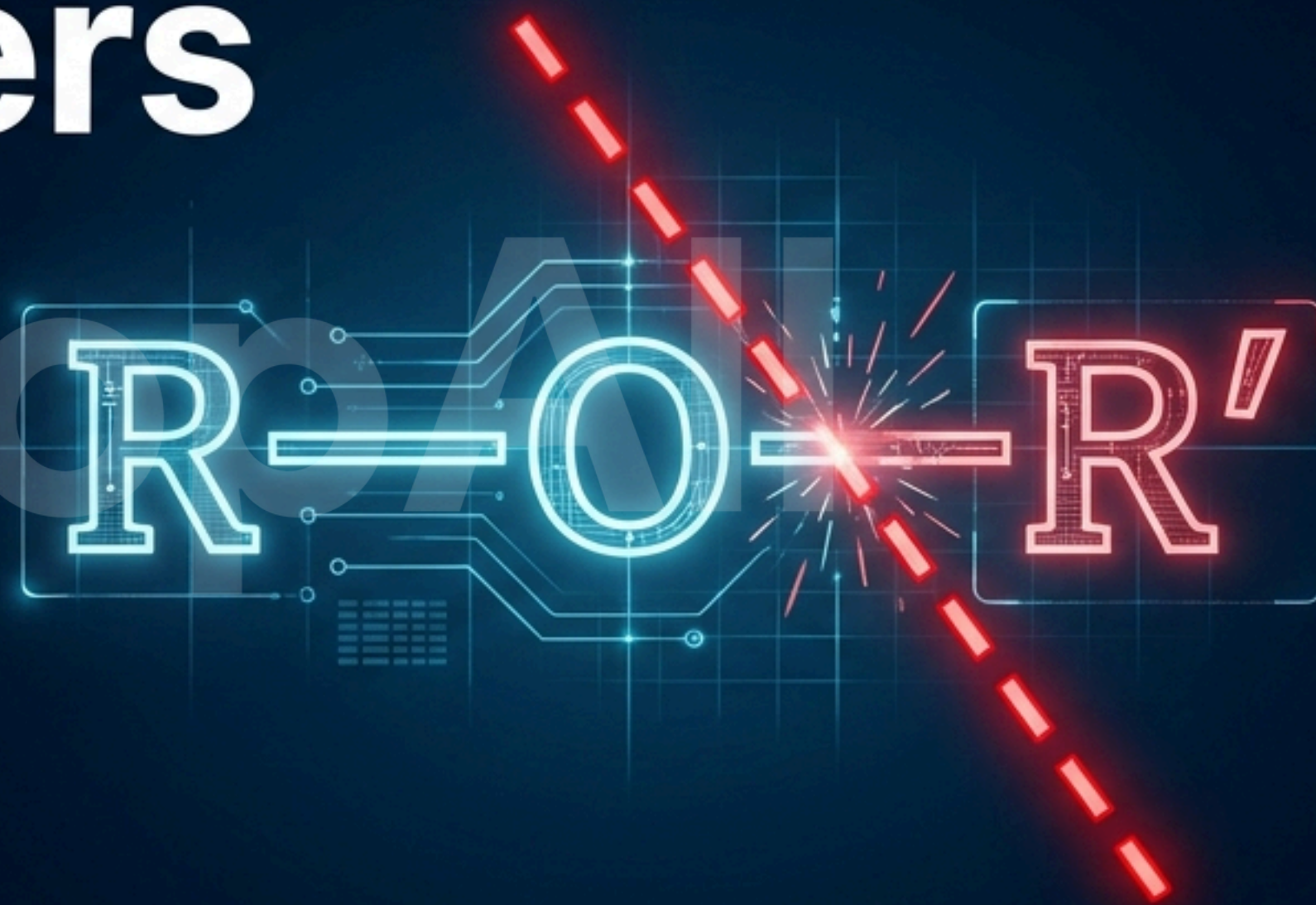


Cleavage of the C–O Bond in Ethers

A diagnostic blueprint for predicting cleavage products in competitive exams.



Key Vocabulary

Oxonium Ion

The highly reactive, positively charged intermediate formed when the ether oxygen accepts a proton.

Protonation

The crucial first step of cleavage; ethers are unreactive until a strong acid donates an H^+ to the oxygen.

Alkyl-Oxygen Bond

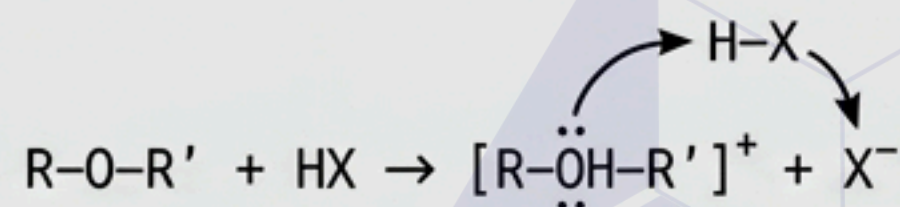
The weaker C-O bond in mixed aromatic ethers. This is the prime target for nucleophilic cleavage.

Aryl-Oxygen Bond

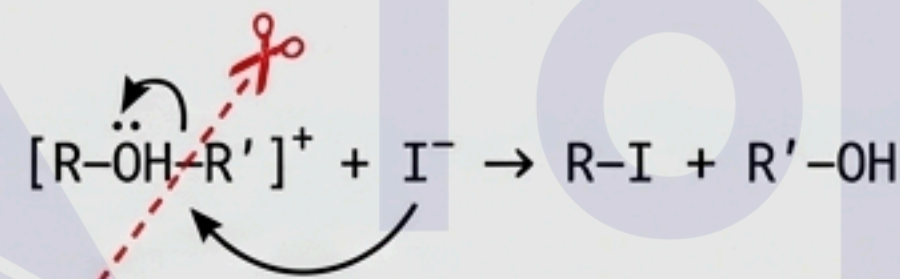
The resonance-stabilized C-O bond attached to a benzene ring. It acts like a locked partial double bond and strongly resists cleavage.

The Baseline Mechanism: 3-Step Cleavage

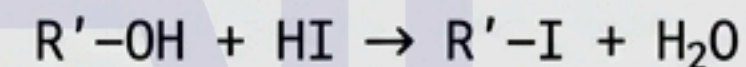
1. Protonation (The Setup)



2. SN2 Attack (The Strike)



3. Excess Acid (The Overkill)



If HI is in excess at high temperatures, the resulting alcohol is also converted to an alkyl halide.



You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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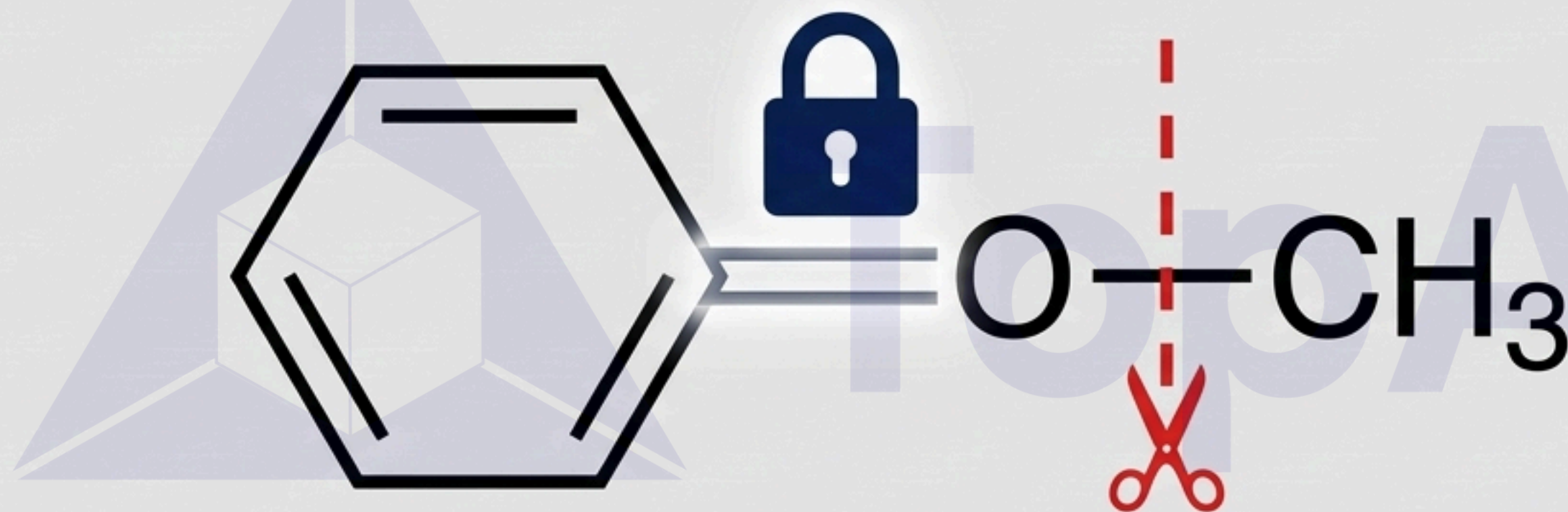
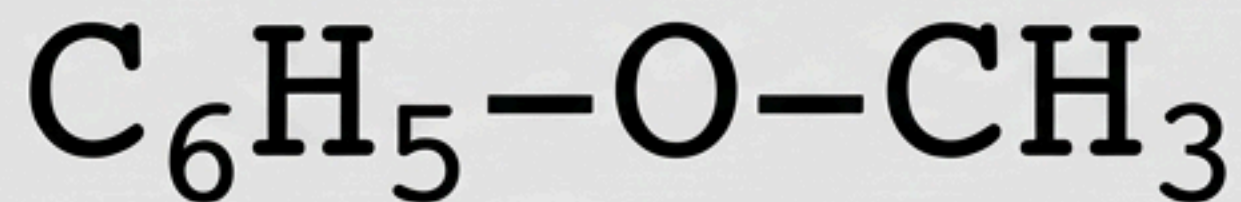
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Alkyl Aryl Ethers: The Locked Bond



Alkyl aryl ethers always cleave at the alkyl-oxygen bond. The aryl-oxygen bond is stabilized by the sp^2 hybridized carbon of the phenyl group, granting it partial double-bond character. It is too strong to break.

**Guaranteed Products:
Phenol + Alkyl Halide**

Reagent Reactivity: Forcing the Break



Drastic Conditions

Ethers are the least reactive functional group. Cleavage requires high temperatures.



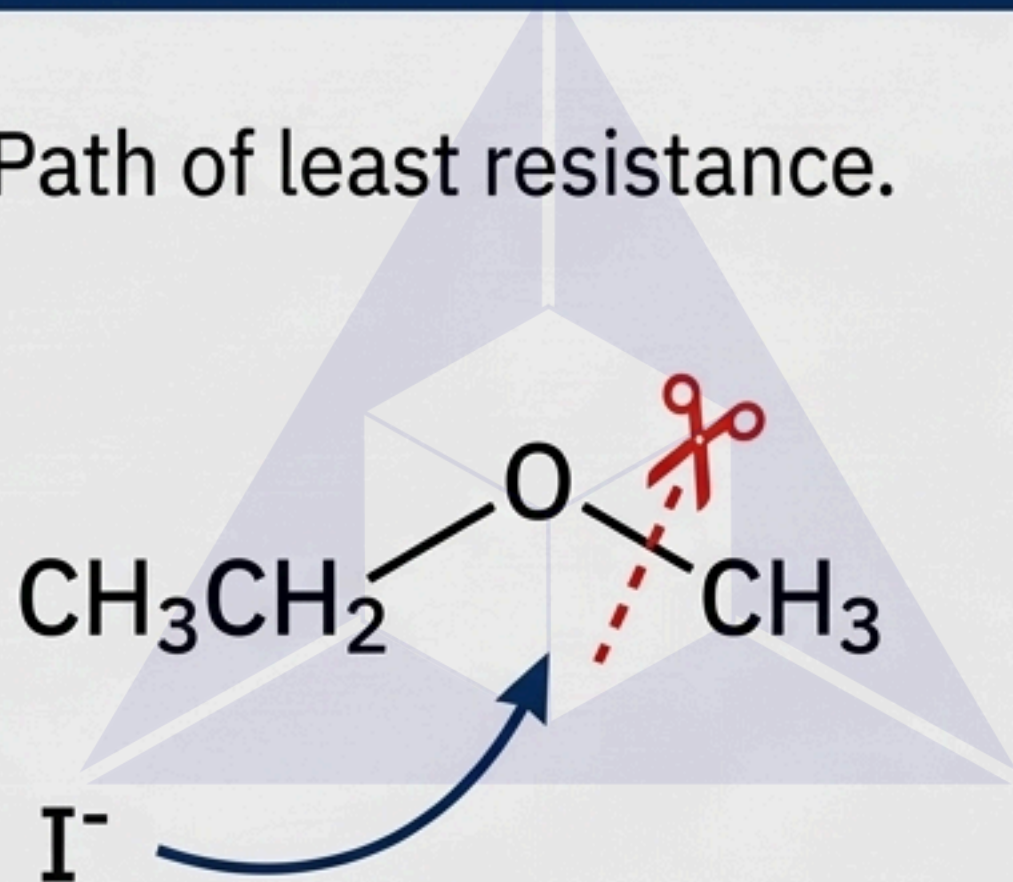
Concentrated Acid

Iodide (I^-) is the most powerful nucleophile and HI is the strongest acid, making it the premier reagent for breaking the tough C–O bond.

The Mechanism Fork: S_N2 vs. S_N1

Primary / Secondary Ethers

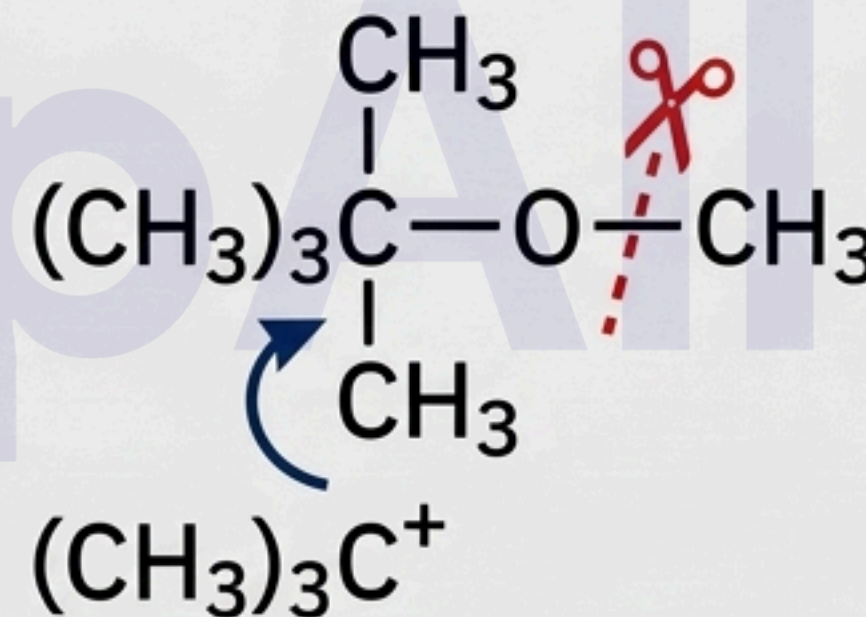
Path of least resistance.



Halide forms on the smaller alkyl group.

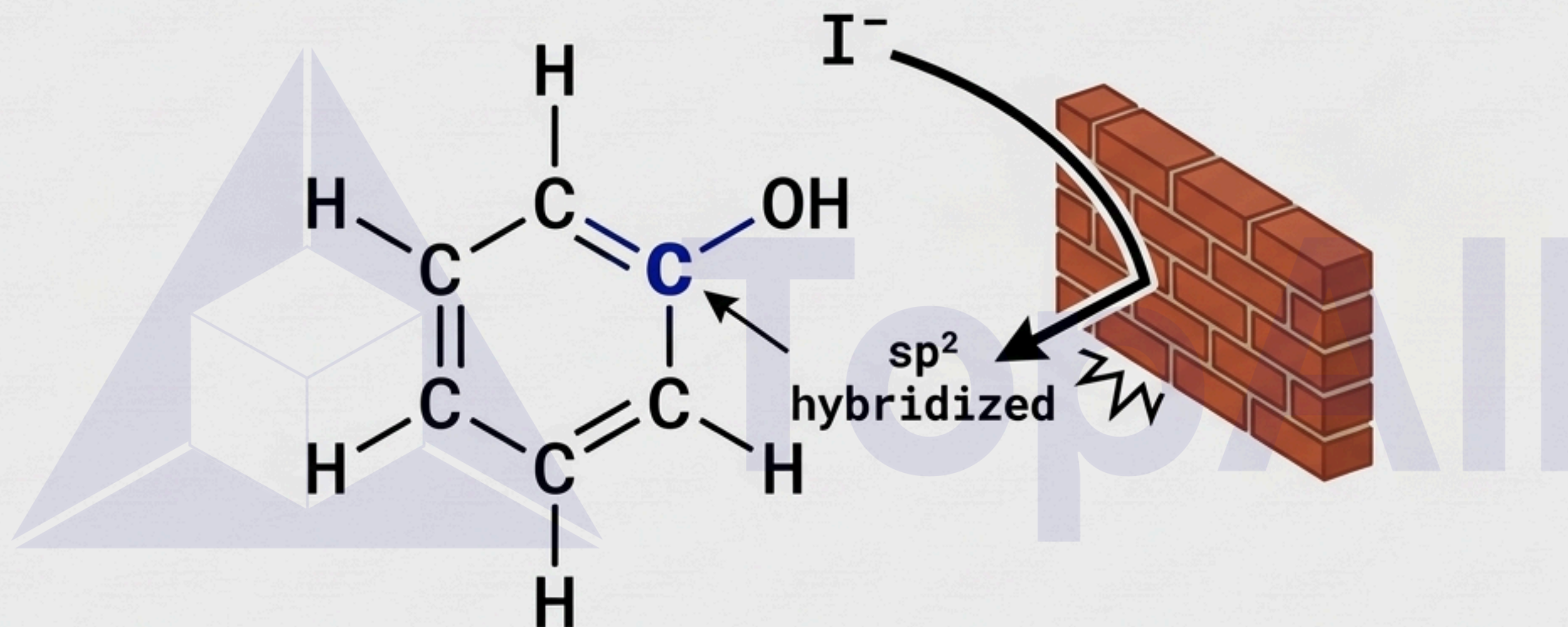
Tertiary Ethers

Carbocation stability reigns supreme.



Halide forms on the tertiary carbon.

The Phenol Dead-End



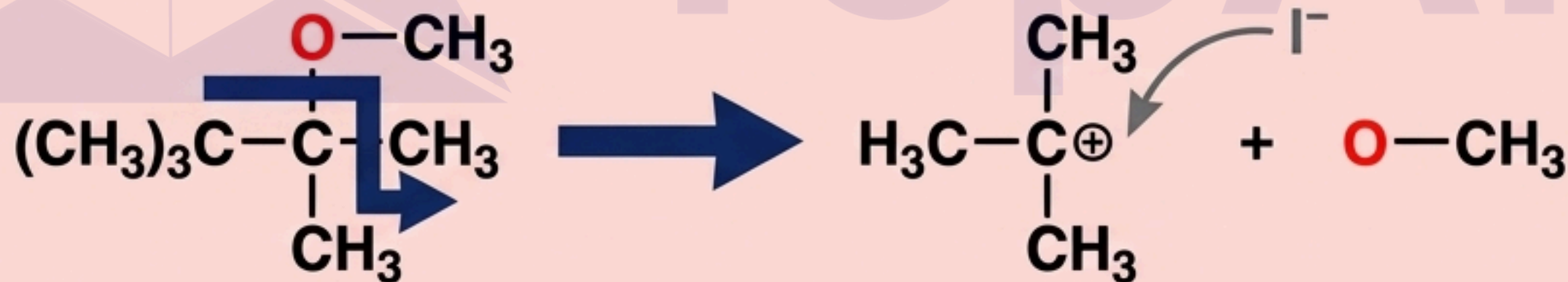
Even with excess HI at high temperatures, the reaction stops at phenol. The sp^2 hybridized carbon of phenol cannot undergo the nucleophilic substitution required to form an aryl halide.

Watch for this: The S_N1/S_N2 Flip

The S_N2 Expectation



The S_N1 Reality



The trap: You learn that the halide goes to the **smaller group**. But the moment a tertiary group is introduced, the rule perfectly reverses. Carbocation stability outranks steric hindrance. The halide goes to the tertiary carbon.

Key Takeaways

- Ethers cleave with concentrated HX (reactivity: $\text{HI} > \text{HBr} > \text{HCl}$) via a 3-step mechanism. Because aryl-oxygen bonds are locked by resonance, alkyl aryl ethers always cleave at the alkyl-oxygen bond to yield phenol.
- The mechanism hinges on the alkyl groups: I^- attacks the smaller group ($\text{S}_{\text{N}}2$) in primary/secondary ethers to avoid steric hindrance, but attacks the tertiary carbon ($\text{S}_{\text{N}}1$) if a tertiary group is present due to carbocation stability.



You've Learned the Theory.

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