

Nucleophilic Addition: Mechanism & Reactivity

The molecular blueprint of carbonyl attacks
and the rules of chemical hierarchy.

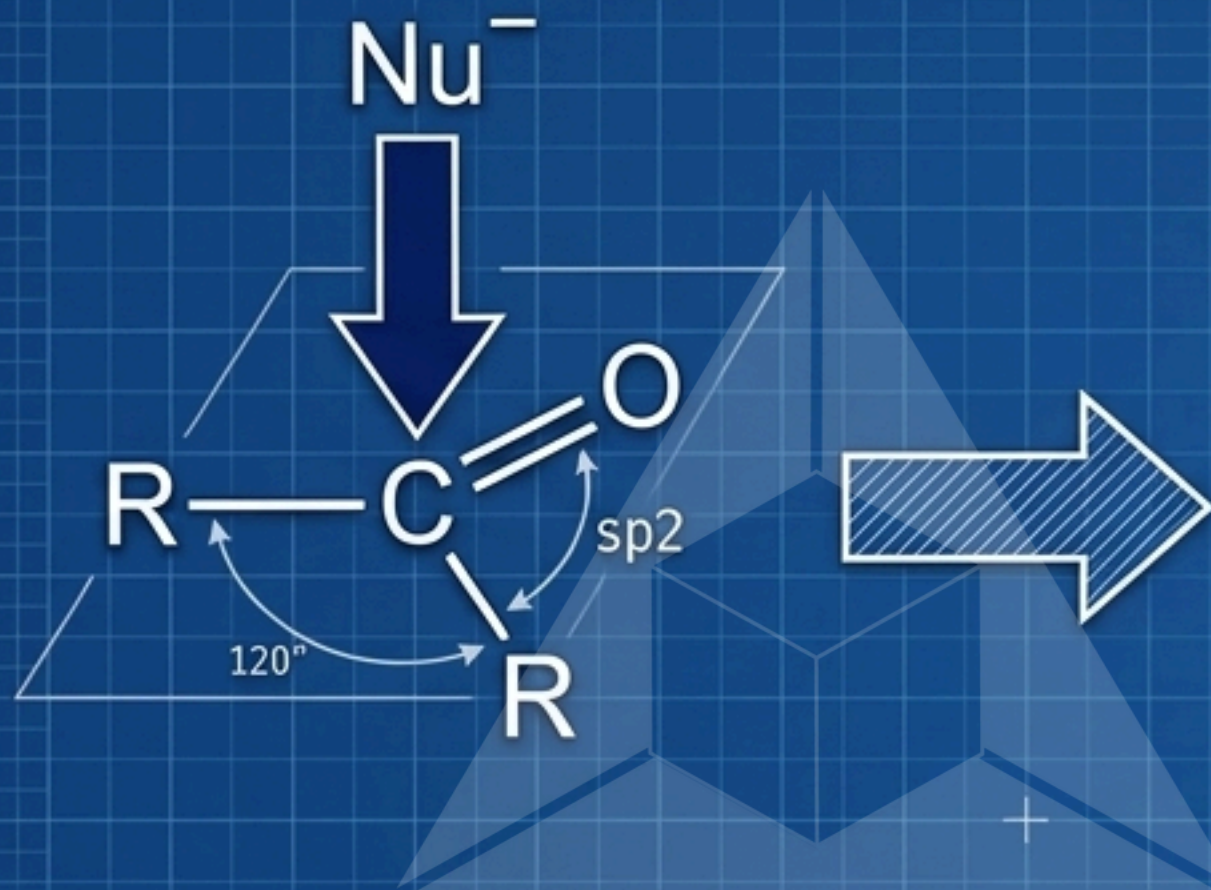
Nucleophilic
Addition

Tetrahedral
Alkoxide

Steric &
Electronic Effects

HORIZONTAL 3-STEP NUCLEOPHILIC ATTACK

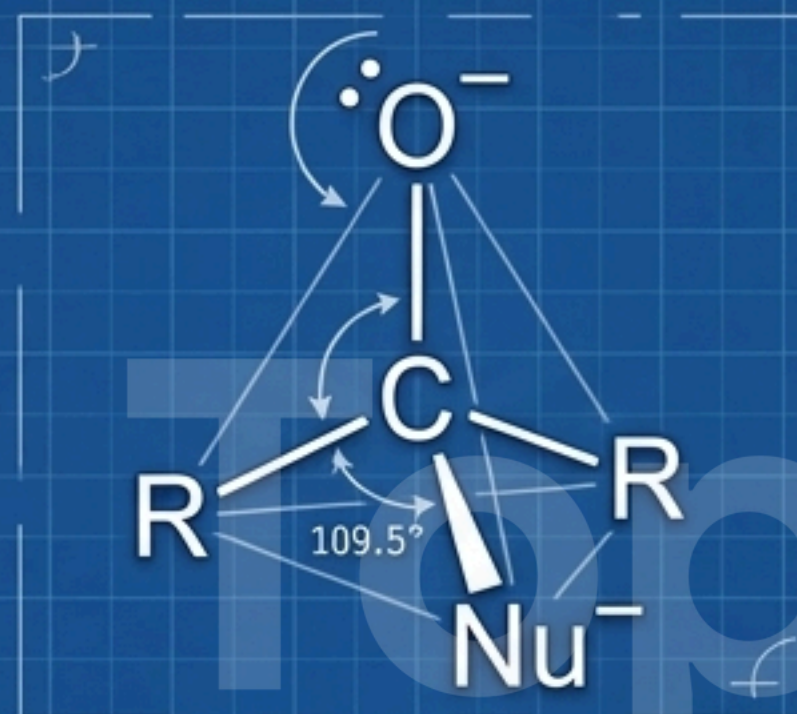
STEP 1: NUCLEOPHILIC ATTACK



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Nucleophile attacks the electrophilic carbon perpendicular to the planar sp² orbitals.

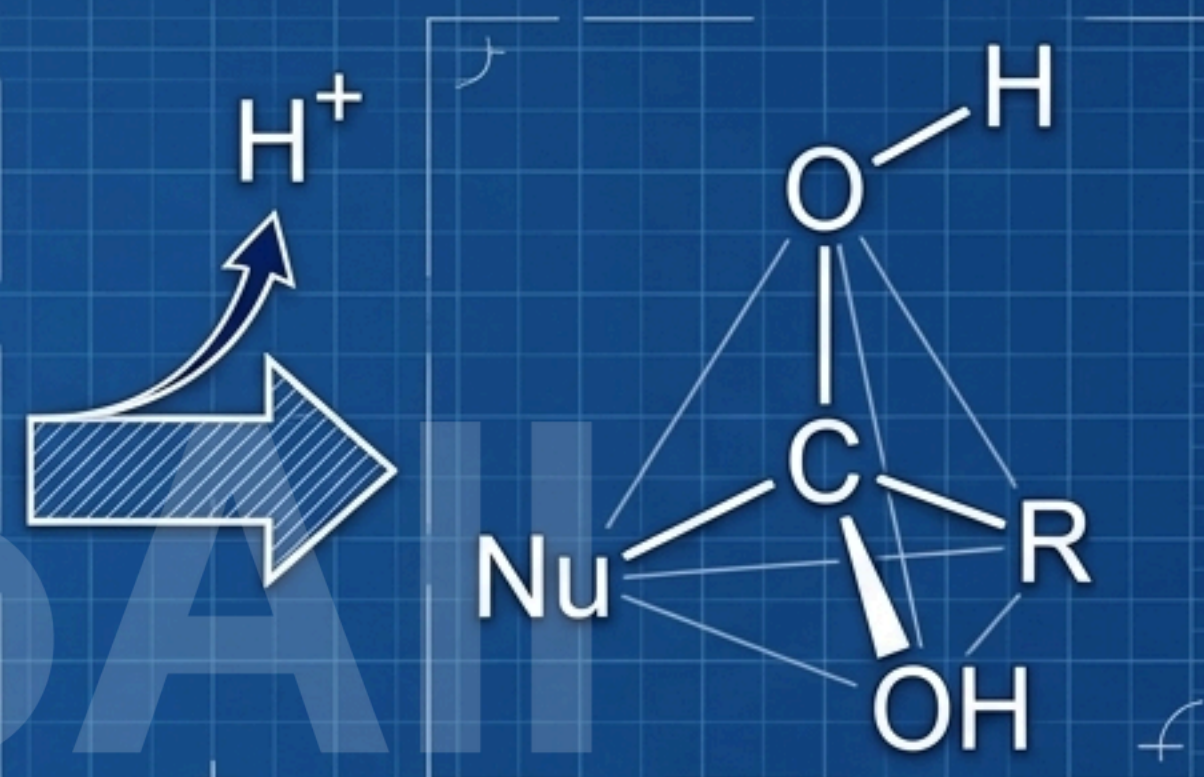
STEP 2: PLANAR-TO-TETRAHEDRAL TRANSITION



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Hybridization shifts sp² → sp³. A tetrahedral alkoxide intermediate is formed.

STEP 3: PROTONATION TO PRODUCT



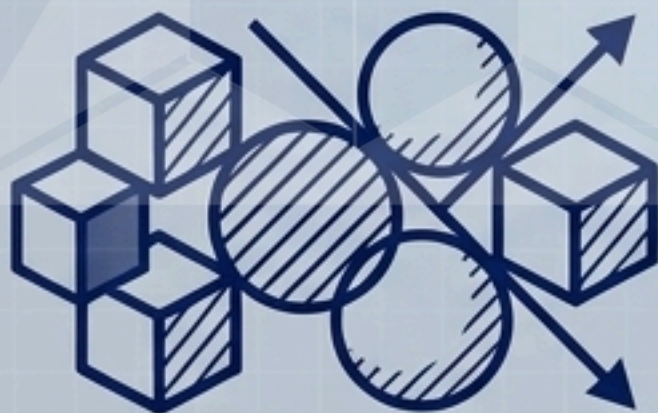
STEP 3: PROTONATION TO PRODUCT

Rapid protonation yields the neutral addition product.

ALDEHYDES > KETONES

In nucleophilic addition, aldehydes fundamentally outpace ketones.

1. THE STERIC FACTOR



Physical crowding and blocked trajectories.

2. THE ELECTRONIC FACTOR



Electrostatic forces and charge manipulation.



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$$E=mc^2$$



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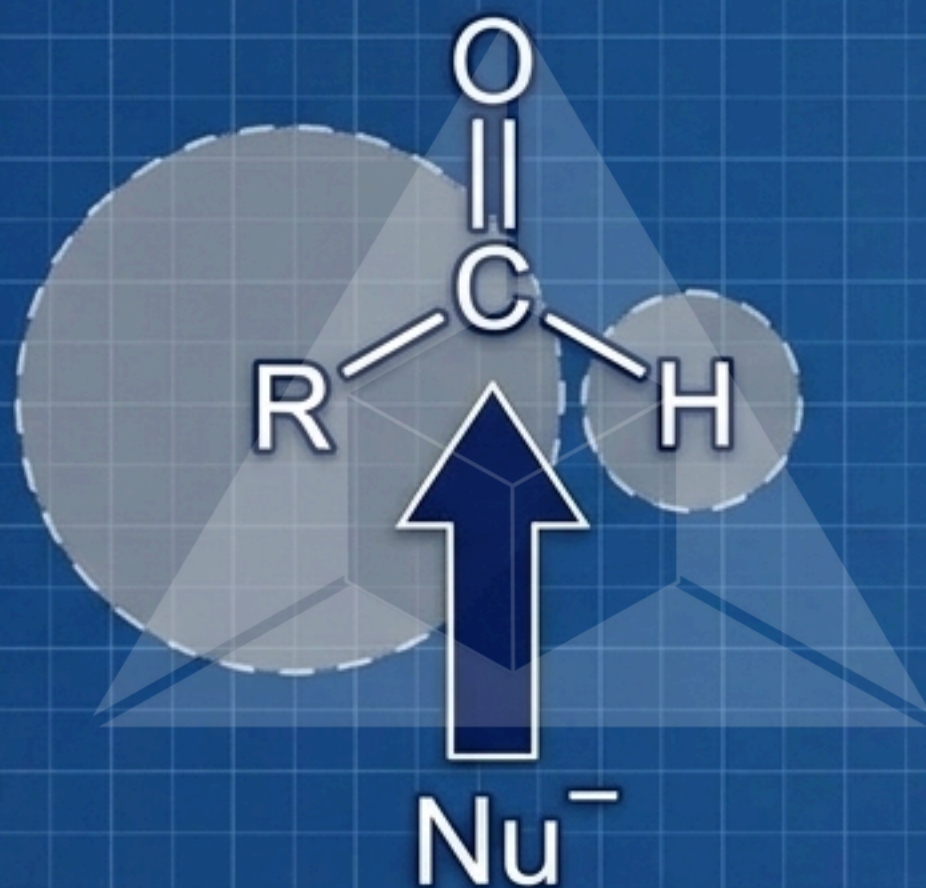
Key Highlights

- » Free Study Material, Videos & Infographics
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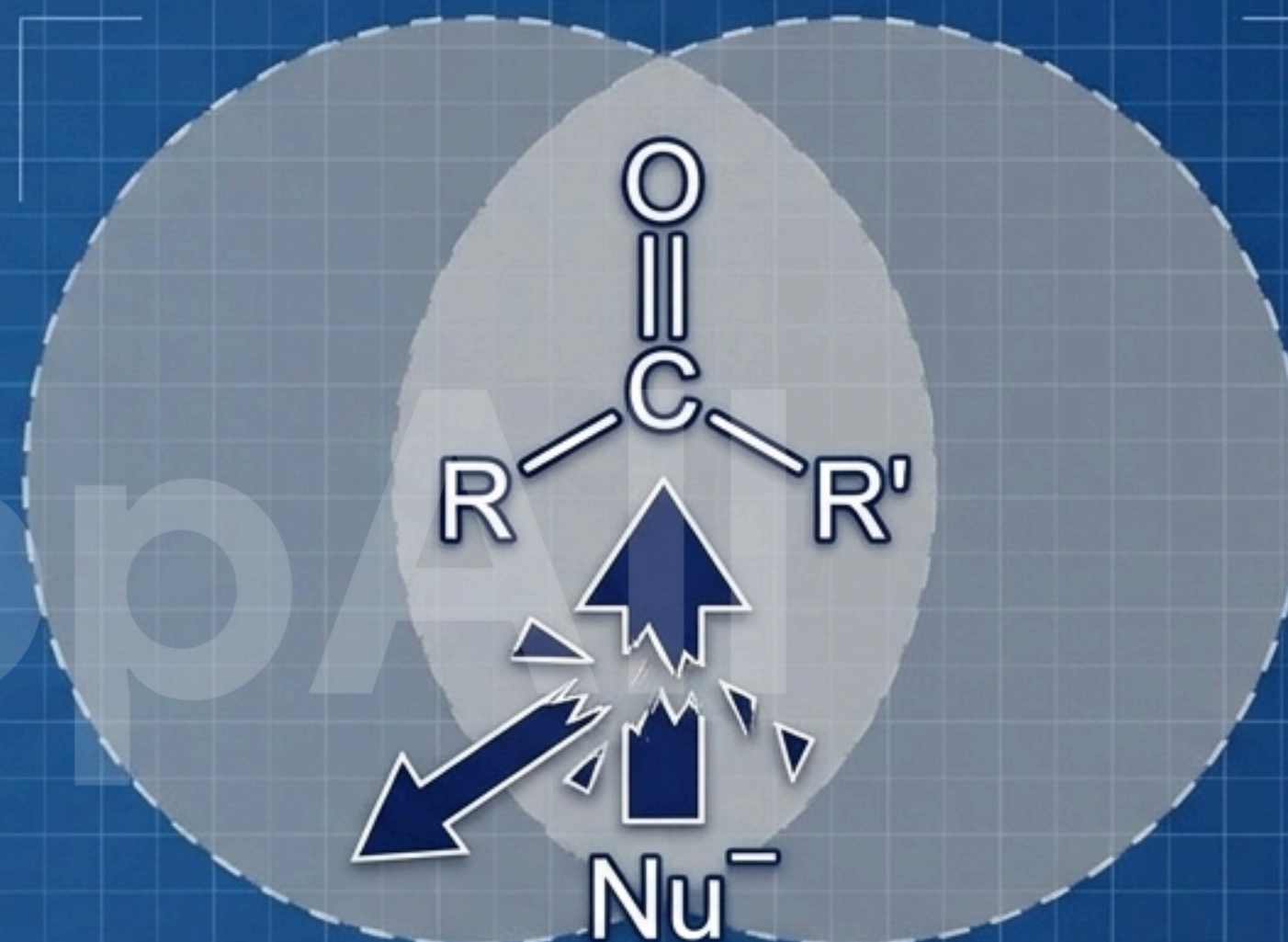
THE PHYSICAL BLOCKADE (STERIC EFFECT)

ALDEHYDE



One bulky substituent. The nucleophile has an open, unhindered trajectory.

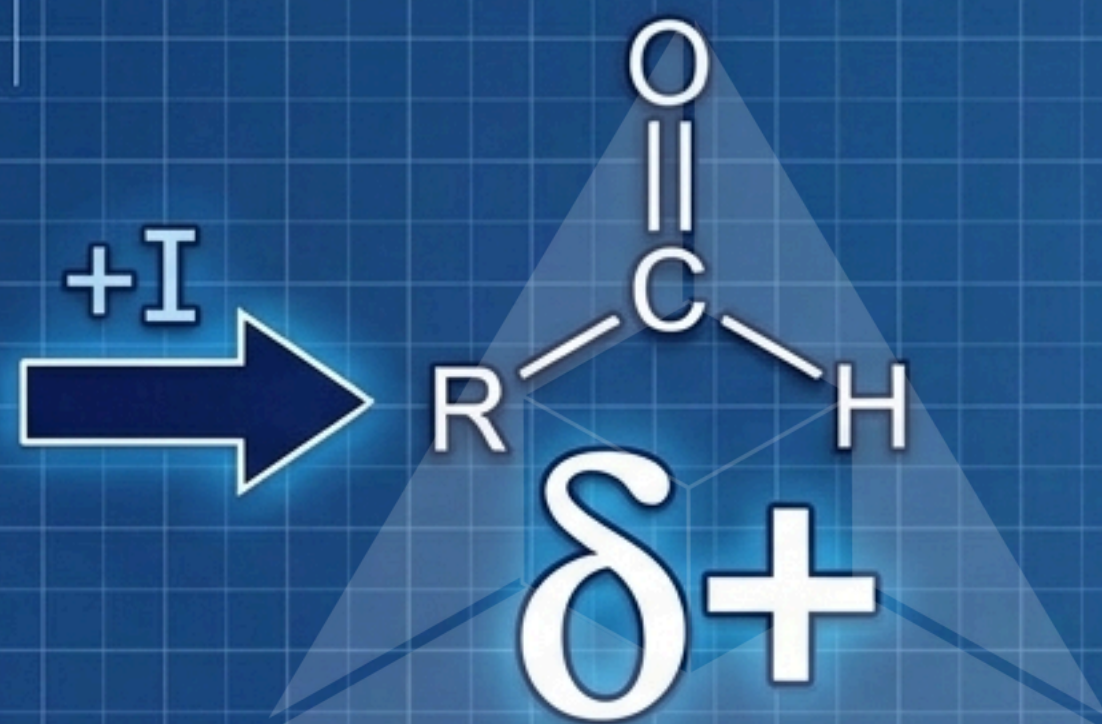
KETONE



Two bulky substituents. Extreme steric hindrance physically blocks the perpendicular attack path.

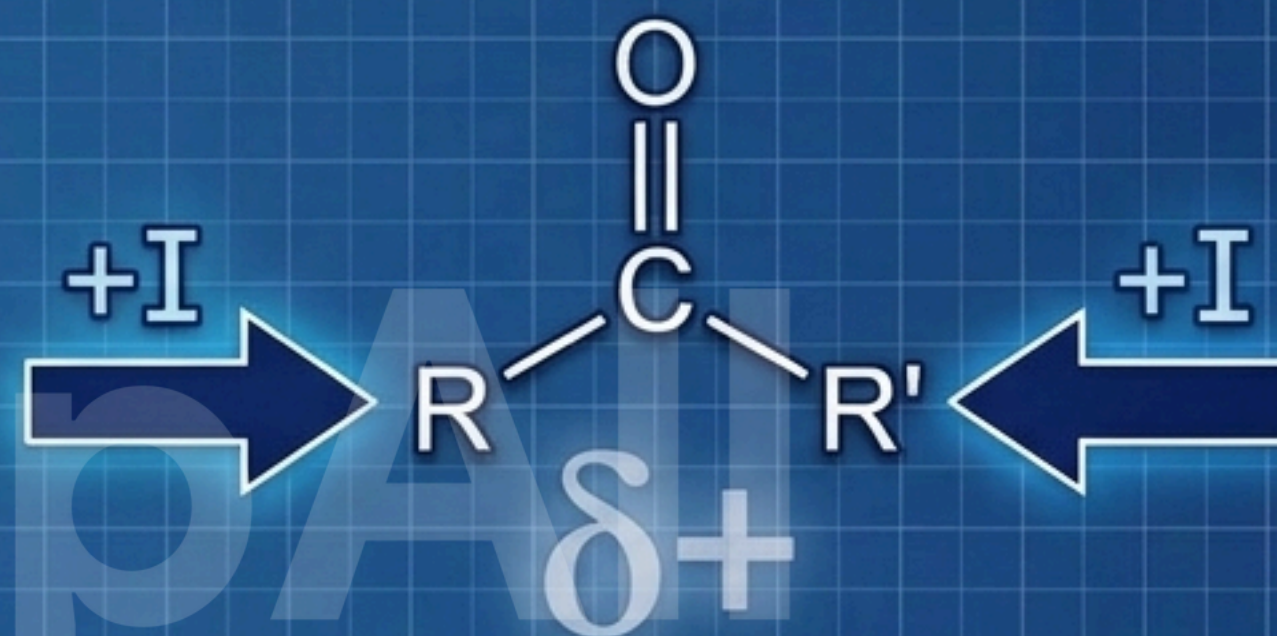
THE CHARGE DILUTION (ELECTRONIC EFFECT)

ALDEHYDE



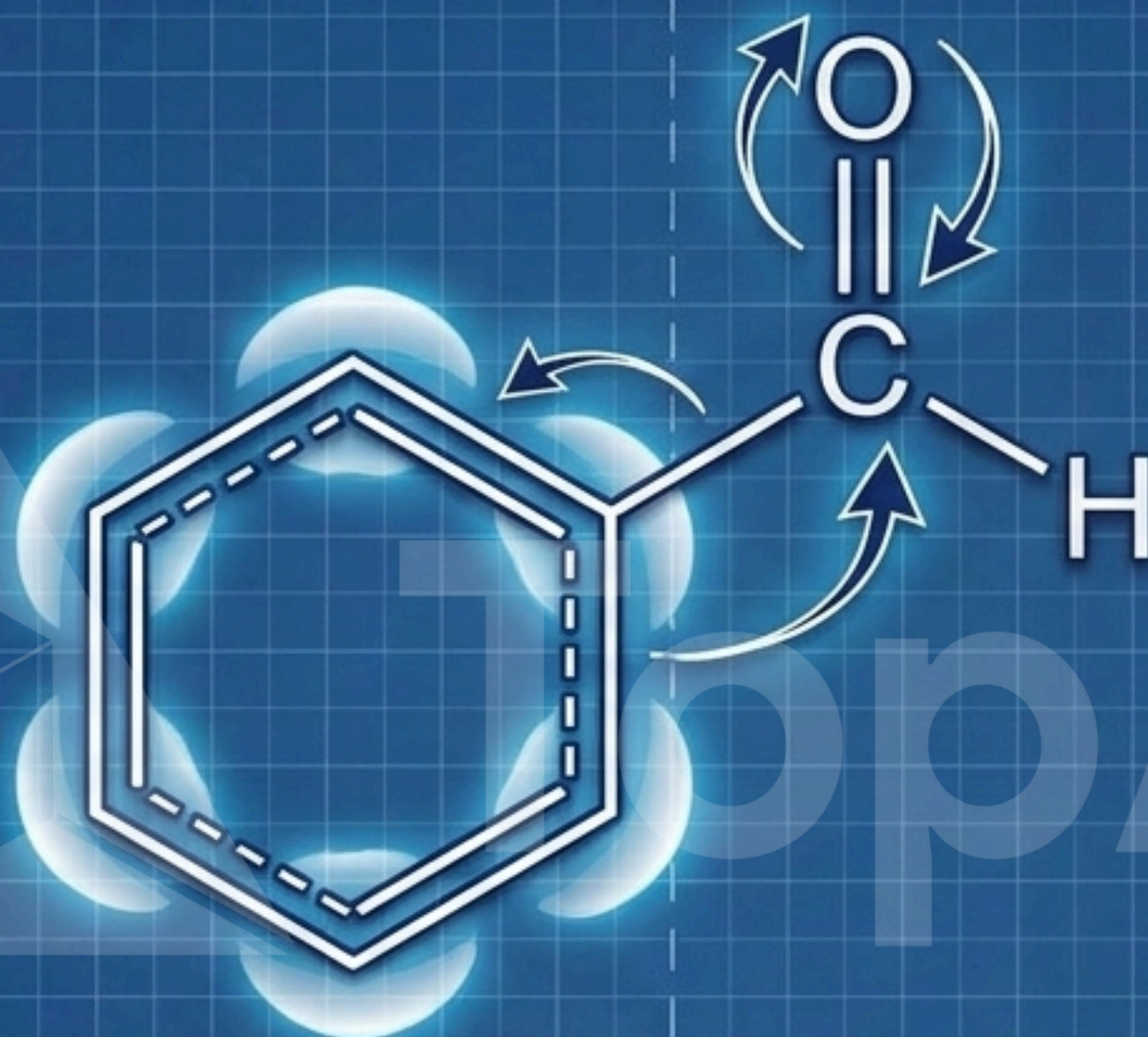
A single alkyl group provides mild electron donation. The carbon remains highly electrophilic (electron-hungry).

KETONE



Dual alkyl groups aggressively pump electron density into the carbon, neutralizing its positive charge and destroying its electrophilicity.

THE AROMATIC MODIFIER: BENZALDEHYDE



Benzaldehyde < Propanal

The benzene ring acts as a massive internal electron donor. By delocalizing its π -electrons into the carbonyl group via resonance, it drastically reduces the electrophilic starvation of the central carbon.

Watch for this: The Reactivity Trap

When asked why aldehydes are more reactive than ketones, exam options will often tempt you to choose only steric hindrance or only the electronic (+I) effect.

Do not fall for the “Either/Or” fallacy. You must always cite BOTH. They act simultaneously.

-  **Steric: 2 alkyl groups physically block the attack.**
-  **Electronic: 2 alkyl groups reduce carbonyl electrophilicity.**

Key Takeaways

- Nucleophilic addition transforms a planar sp^2 carbonyl carbon into a tetrahedral sp^3 alkoxide intermediate via a strict perpendicular attack.
- Aldehydes naturally outpace ketones in reactivity due to a dual mechanism: less steric hindrance (fewer bulky groups blocking the path) and higher electrophilicity (fewer electron-donating alkyl groups neutralizing the charge).



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