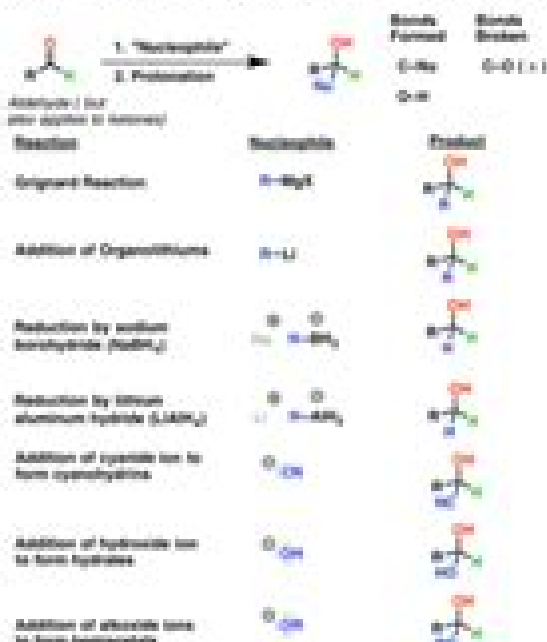


A Simple "Formula" for Seven Key Reactions of Aldehydes & Ketones



Each of these reactions follows a "two-step" pattern: 1) addition 2) protonation

How to draw the mechanism for this pattern:

Step 1 is donation of a lone pair of electrons from the nucleophile to the carbonyl carbon, which leaves a partial positive charge (oxygen is more electronegative than carbon). A bond forms between the nucleophile and carbon, and the carbon-oxygen double bond (π bond) breaks. The oxygen then bears a negative charge.

Step 1: Addition of nucleophile



Step 2: Protonation of oxygen

In the second step of this reaction, H^+ is added the oxygen is protonated to give a neutral hydroxy ($O-H$) group



Specific example: Grignard addition

Step 1: Addition of nucleophile



draw the arrow as coming from the $Hg-C$ bond

What factors affect the reactivity of aldehydes and ketones?

1. Electronic effects

In aldehydes and ketones, the $C=O$ bond is polarized, due to the greater electronegativity of oxygen relative to carbon (3.4 vs. 2.5). The carbon bears a partial positive charge and the oxygen bears a partial negative charge.



Most of the reactions of aldehydes and ketones involve an electron-rich nucleophile forming a bond with the electron-poor electrophile that is the carbonyl carbon of the aldehyde or ketone.

The more electron-poor the aldehyde or ketone, the more reactive it will be with nucleophiles.



the aldehyde is more electron-poor than the aldehyde on the right due to the electron-withdrawing fluorine

2. Steric effects

The larger the group adjacent to the carbonyl carbon, the more difficult it will be for nucleophiles to attack. This is related to an steric hindrance.



Aldehydes are more reactive than ketones largely for this reason.

3. Acid catalysis

When acid (H^+) is added to an aldehyde or ketone it can make the carbonyl carbon more electrophilic (and thus more reactive).



The only "catch" with using acid to accelerate a reaction is that it can't be used with strong base nucleophiles, because it will protonate them reversibly. For instance using strong acid to accelerate a Grignard reaction would not work because Grignard reagents are strong bases; once protonated, they can't be regenerated.

Acid catalysis works well with neutral nucleophiles, the H_2O , ROH , and amines, and also with weakly basic nucleophiles like OH^- .

Synthesis of aldehydes and ketones

Through oxidation of alcohols



Secondary alcohols can also be oxidized to ketones with oxidizing agents such as $K_2Cr_2O_7$ and others.



PCC is a mild oxidant that does not oxidize the aldehyde further to the carboxylic acid.

Hydroboration of alkenes



This first forms the anti, which then tautomerizes to the aldehyde.

Synthesis of Aldehydes and Ketones (continued)

Deprotonation of alkenes



The alkyl water to the more substituted end of the alkene, forming an anti, which then tautomerizes to the ketone.

Oxidative cleavage



Oxidative cleavage cleaves $C-C$ bonds if a "redox-active" reagent is used. $C-H$ bonds attached to the alkene are preserved, leading to aldehydes.

Other Key Reactions of Aldehydes and Ketones

Hydration



Water will add to aldehydes and ketones to give hydrates. Equilibrium favors the starting aldehydes/ketones. The reaction is made faster by acid.

Hydroboration



Alcohols will add to aldehydes/ketones to give hemiacetals. Equilibrium usually favors the starting aldehydes/ketones, except in cases where a ring is formed.

Acetal formation



Treatment of an aldehyde or ketone with an alcohol in acid leads to an acetal. The acetal can be removed by heating with aqueous acid.

Aldehyde as protecting groups



Aldehydes only react with aqueous acid. So forming an acetal is a method of "masking" a carbonyl group.

Wittig Reaction



Aldehydes/ketones treated with a primary amine will give imines. Acid catalysis can be used to promote this reaction.

Enamine formation



Aldehydes/ketones treated with a secondary amine give enamines. Acid catalysis promotes their formation.

Wittig Reaction



Treatment of an aldehydes/ketone with a phosphonium ylide leads to formation of an alkene. This is the Wittig Reaction.

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McMurry, Susan McMurry



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