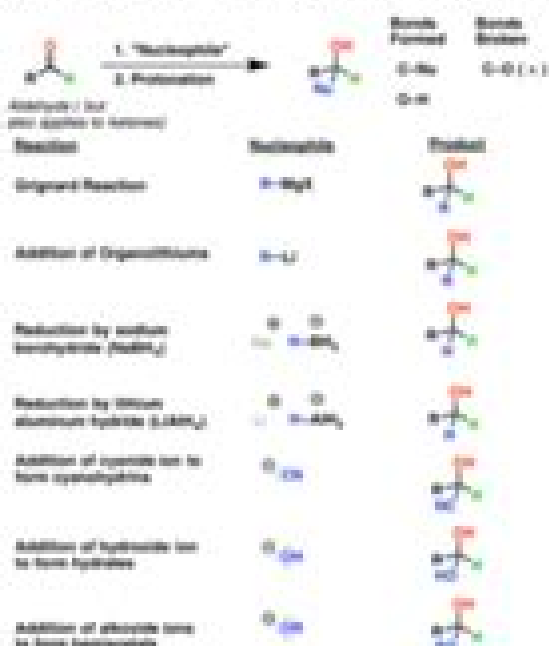


## A Simple "Formula" for Seven Key Reactions of Aldehydes & Ketones



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

How to draw the mechanism for this pattern:

Step 1 is formation of a bond pair of electrons from the nucleophile to the carbonyl carbon, which leaves a partial positive charge (proton is more electronegative than carbon). A bond forms between the nucleophile and carbon, and the carbon-oxygen double bond ( $\pi$  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,  $H_2O$  is added the oxygen is protonated to give a neutral hydroxy ( $OH$ ) group.



Specific example: Grignard addition

Step 1: Addition of nucleophile



draw the arrow as coming from the  $sp^2$  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 carbonyl carbon 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.



### 2. Steric effects

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



### 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 "caveat" with using acid to accelerate a reaction is that it can't be used with strongly basic nucleophiles, because it will protonate them irreversibly. 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 like  $H_2O$ ,  $ROH$ , and amines, and also with weakly basic nucleophiles like  $RO^-$ .

## Synthesis of aldehydes and ketones

Through oxidation of alcohols



Hydroboration of alkenes



## Synthesis of Aldehydes and Ketones (continued)

Oxidation of alkenes



Genetives of alkenes



## Other Key Reactions of Aldehydes and Ketones

Hydration



Acetal formation



Acetal formation



Acetals as protecting groups



Wittig Reaction



Enamine formation



Wittig Reaction



Comments, Questions, Suggestions?

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