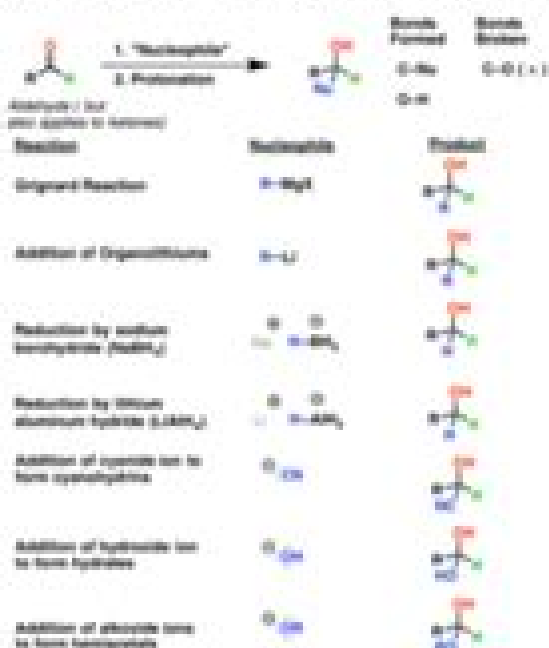


A Simple "Formula" for Seven Key Reactions of Aldehydes & Ketones



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 (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_2O is added the oxygen is protonated to give a neutral hydroxyl (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 (2.4 vs. 3.5), 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 "catalyst" 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 alkyne



Synthesis of Aldehydes and Ketones (continued)

Oxymercuration of alkyne



Genetypers of alkyne



Other Key Reactions of Aldehydes and Ketones

Hydration



Hydroxymethylation



Acetal formation



Acetals as protecting groups



Wittig formation



Enamine formation



Wittig Reaction



Acs Study Guide First Semester Organic

Yicheng Fang



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