Chapter 19: Ketones & Aldehydes, Part 2

Nomenclature

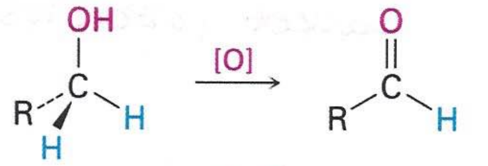
Aldehydes are named by replacing the terminal -*e* of the corresponding alkane name with *–al*
The parent chain must contain the -CHO group, The -CHO carbon is numbered as C1
If the -CHO group is attached to a ring, use the suffix *carbaldehyde*

Ketones are named by replacing the terminal -*e* of the alkane name with *–one*
Parent chain is the longest one that contains the ketone group (smallest ketone # possible)

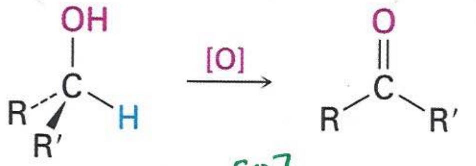
R-C=O (ketones and aldehydes) can be used as a substituent
Aldehyde = Formyl Ketone= Acetyl

Preparation

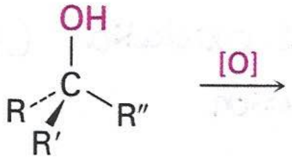
oxidation



1° primary alcohols $\xrightarrow{[O]}$ aldehydes



2° secondary alcohols $\xrightarrow{[O]}$ Ketones



NO Reaction

3° Tertiary alcohols $\xrightarrow{[O]}$ $\emptyset$

common oxidation reagents

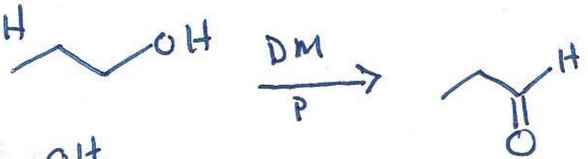
$KMnO_4$ = potassium permanganate

CrO_3 = Chromium Trioxide

$Na_2Cr_2O_7$ = Sodium Dichromate

Dess-Martin periodnane

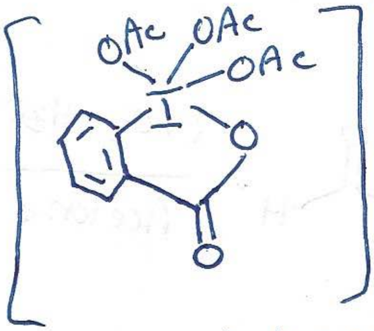
1° OH



aldehydes

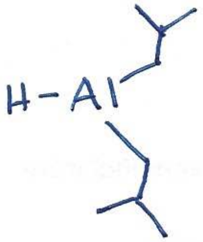
2° OH

ketenes



Periodinane Intermediate

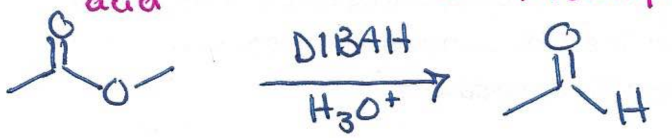
DIBAH Di-isobutyl aluminum hydride



* electrophilic Reduction

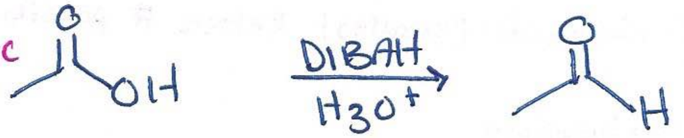
carboxylic acid ÷ ester ——→ Aldehyde

Ester



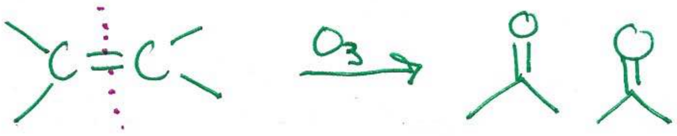
> Aldehydes

carboxylic acid



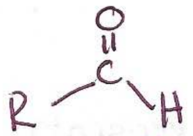
Ozonolysis

alkene



* Detailed mechanism on last page of this packet (ozonolysis)

Further Oxidation



* aldehydes can easily oxidize into carboxylic acids

* ketones are not reactive towards oxidation (inert)

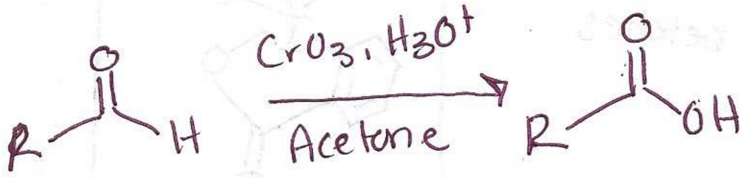
↑ proton can be abstracted during oxidation

Aldehydes Carboxylic Acid

Ketones

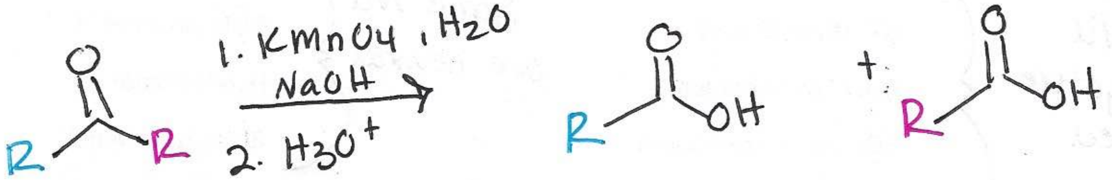
NO Reaction

Example 1



* CrO_3 in aqueous acid is common - oxidation is rapid ÷ has good Yields

Example 2



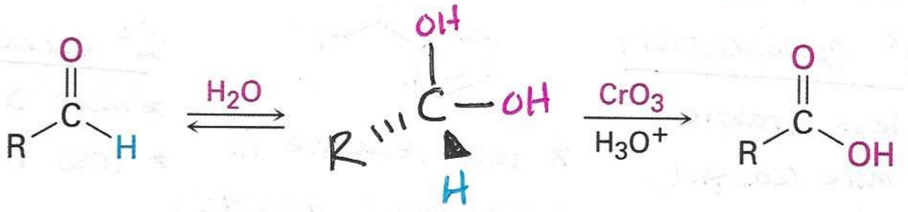
* Ketones are inert to most oxidizing agents but they do undergo a slow cleavage reaction of the C-C bond next to the carbonyl group when treated w/ hot alkaline KMnO4

Aldehyde oxidation occurs through 1,1-diols, also called a hydrate

This is the reversible addition of water to the carbonyl group

Aldehyde hydrate can then be oxidized to become a carboxylic acid

CrO_3 = Chromium trioxide



An aldehyde **A hydrate** **A carboxylic acid**

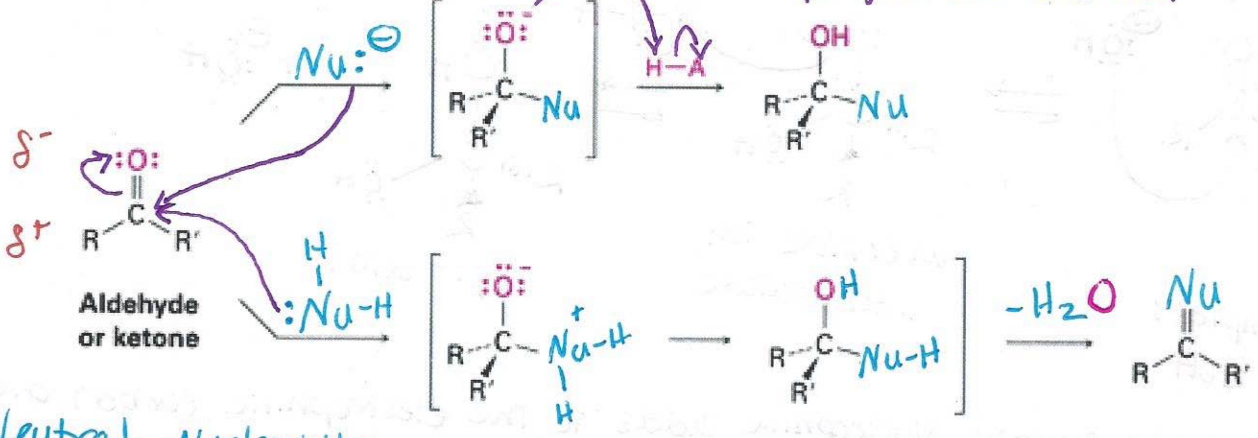
"1,1-diol"

Nucleophilic Addition Reactions of Aldehydes and Ketones

Nucleophilic addition reactions to aldehydes and ketones have two general variations:

Negative Nucleophile

* Tetrahedral intermediate is protonated by water or acid to give an alcohol



Neutral Nucleophile

* Carbonyl oxygen atom is protenated and then eliminated as HO⊖ or water to give a product with a C=Nu

Nucleophiles

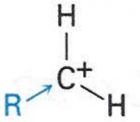
Some Nu are negative charged
- $H\ddot{\underset{..}{O}}:^-$ (hydroxide ion)
- $H:^-$ (hydride ion)
- $R_3C:^-$ (a carbanion)
- $R\ddot{\underset{..}{O}}:^-$ (an alkoxide ion)
- $N{\equiv}C:^-$ (cyanide ion)

Some Nu are neutral
- $H\ddot{\underset{..}{O}}H$ (water)
- $R\ddot{\underset{..}{O}}H$ (an alcohol)
- $H_3N:$ (ammonia)
- $R\ddot{N}H_2$ (an amine)

* neutral has a proten "H" that can be eliminated

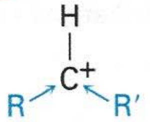
Aldehydes are generally more reactive than ketones in nucleophilic addition reactions

The transition state for addition is less crowded with lower energy for aldehydes than ketones



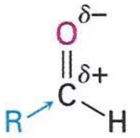
1° carbocation

* less stable
* more reactive



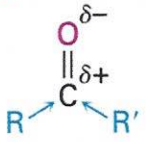
2° carbocation

* more stable
* less reactive



aldehyde

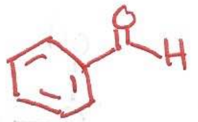
* less stable
* more reactive



Ketone

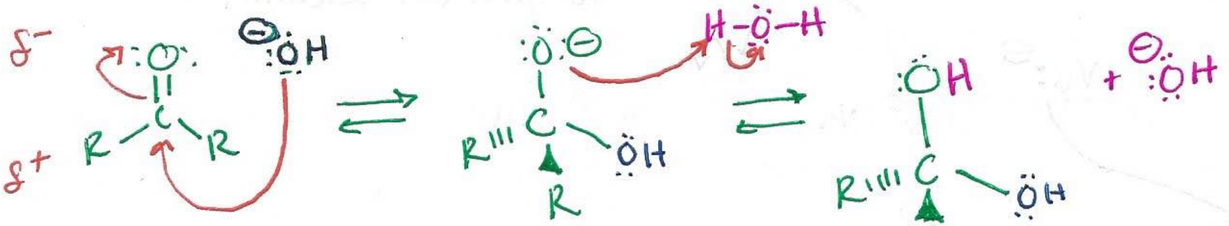
* more stable
* less reactive

* Aromatic Aldehydes like benzaldehyde



* less reactive in nucleophilic addition reactions because of electron donating resonence of the aromatic ring which makes the carbonyl less electrophilic

The nucleophile in a base catalyzed hydration (addition of water) reaction is the hydroxide ion, which is a much stronger nucleophile than water



alkoxide ion Intermediate

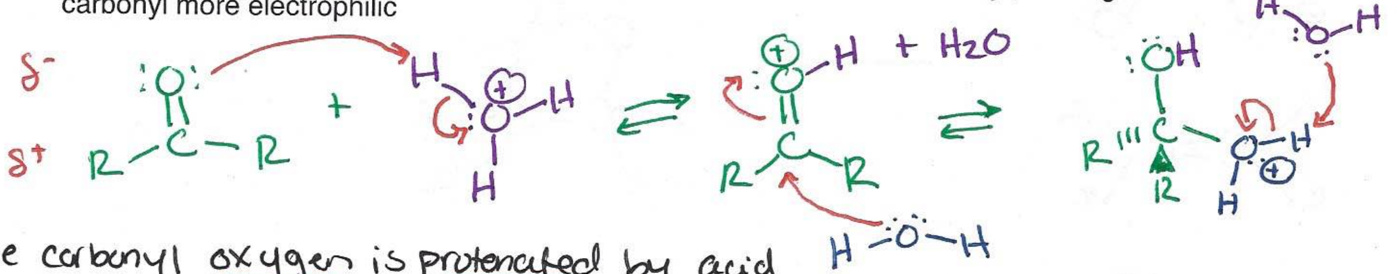
1,1-diol

base examples: NaOH or KOH

① The negatively charged Nucleophile adds to the electrophilic carbon and pushes π electrons from the C=O bond on to the oxygen, making an alkoxide ion

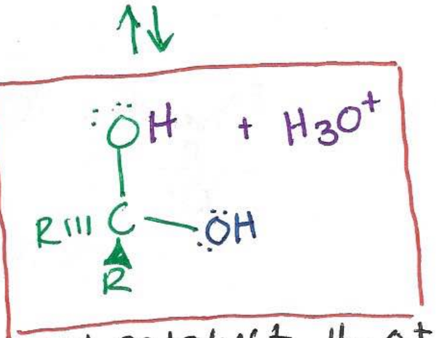
② The alkoxide ion is protenated by water to give the neutral hydrate as the addition product and regenerate the :ÖH⊖

The acid catalyzed addition of water requires the protonation of the carbonyl, making the carbonyl more electrophilic



① The carbonyl oxygen is protonated by acid H_3O^+, making the carbon more strongly electrophilic

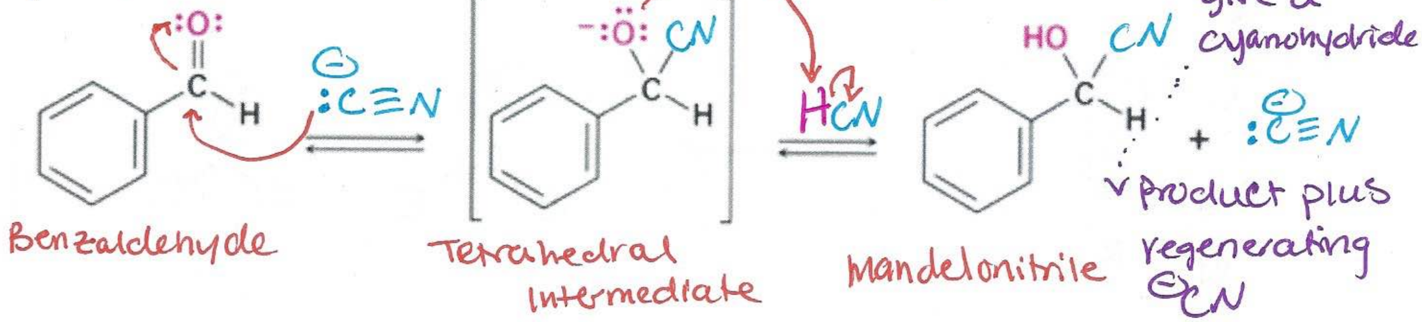
② The neutral Nu: OH_2 adds to the electrophilic C, pushing the π electrons from the C=O on to the oxygen, The oxygen becomes neutral & the Nu: gains the positive ⊕ charge



③ water deprotonates the intermediate giving the neutral hydrate addition product & regenerating the acid catalyst H_3O^+

Aldehydes and unhindered ketones react with HCN to yield **cyanohydrins**

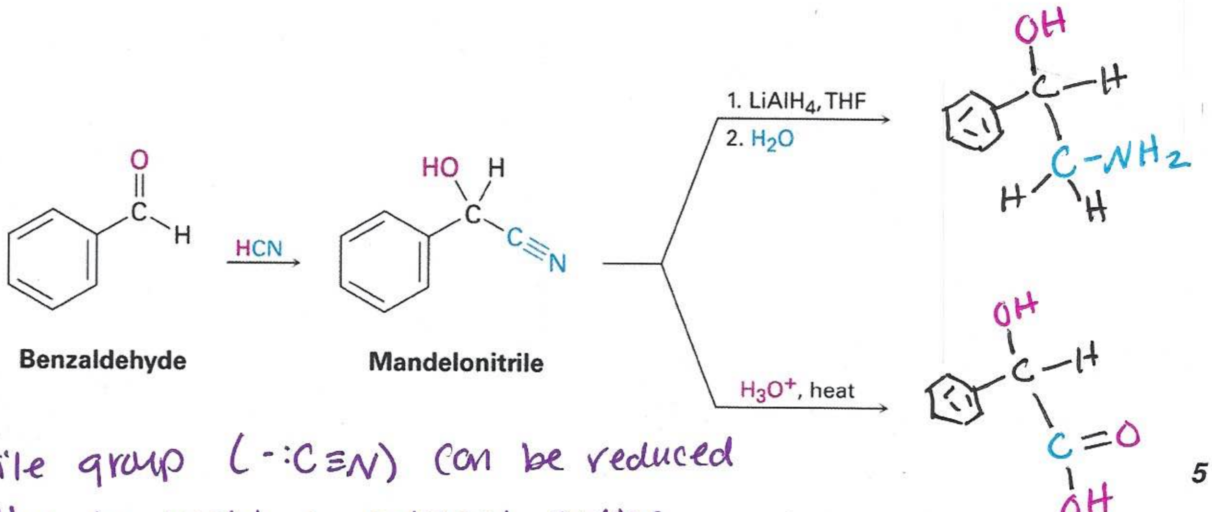
* addition of CN^- cyanide ion takes place via a typical Nu: addition pathway to yield a tetrahedral intermediate that is protonated by HCN to give a cyanohydride



The formation of cyanohydrins is useful because further chemistry can be carried out on the product for example a nitric can be reduced with $LiAlH_4$ to yield a primary amine ~~and~~ OR can be hydrolyzed by hot aqueous acid to make a carboxylic acid

$:NH_3$

$^+NH_4$



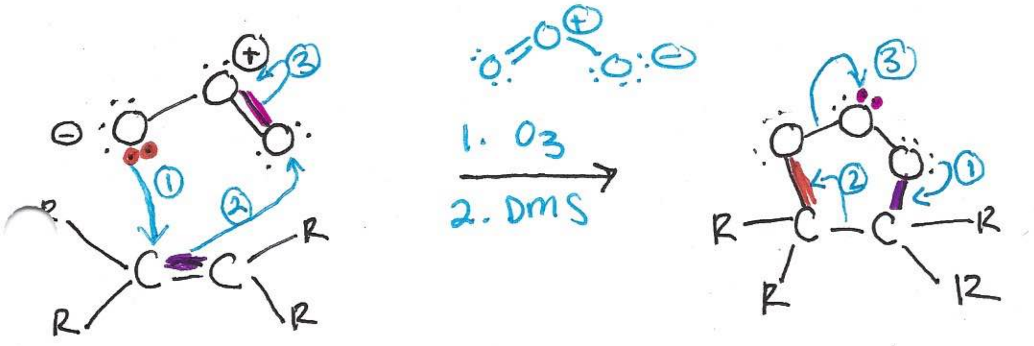
Benzaldehyde

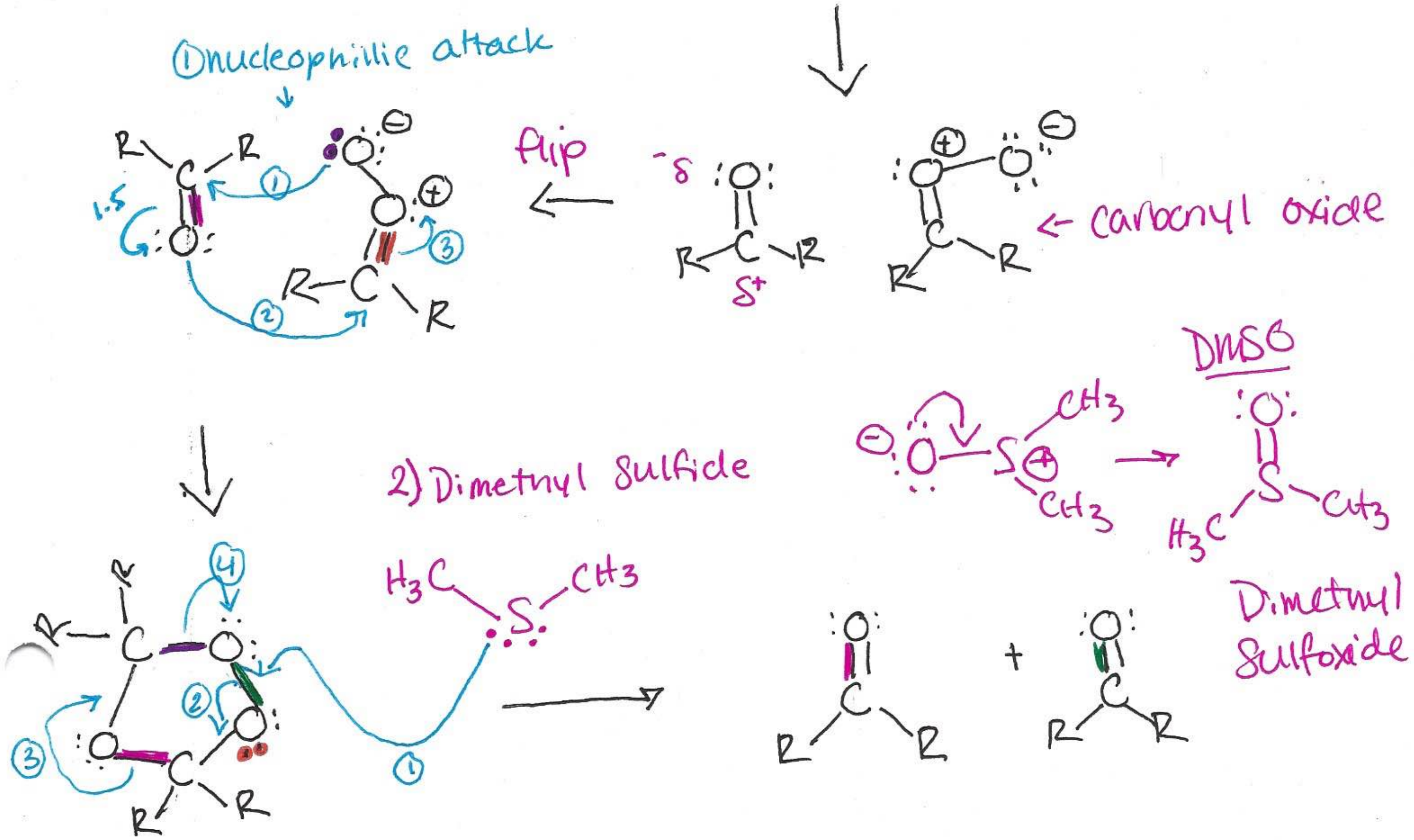
Mandelonitrile

The nitrile group (-:C≡N) can be reduced w/ $LiAlH_4$ to yield a primary amine

Ozonolysis

⊛ oxygen-oxygen bonds are weak



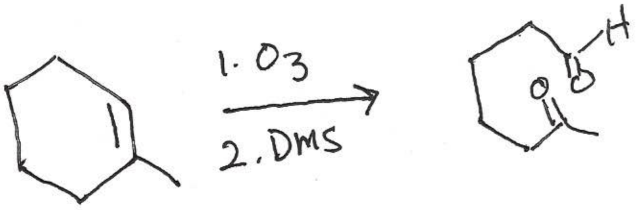


① mention the ultimate plan is alkene to ketones or aldehyde

② Resonance of Ozone (O_3)

③ Follow electrons ¢ add notes

④ bottom line:



Produces an aldehyde and a ketone