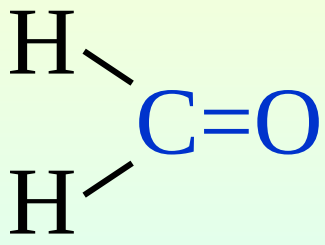
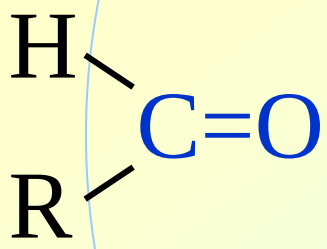
Aldehydes & Ketones

Carbonyl Compounds

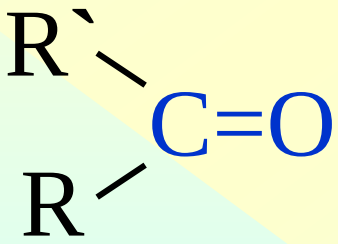
The carbonyl group determines the chemistry of aldehydes & ketones

Aldehydes

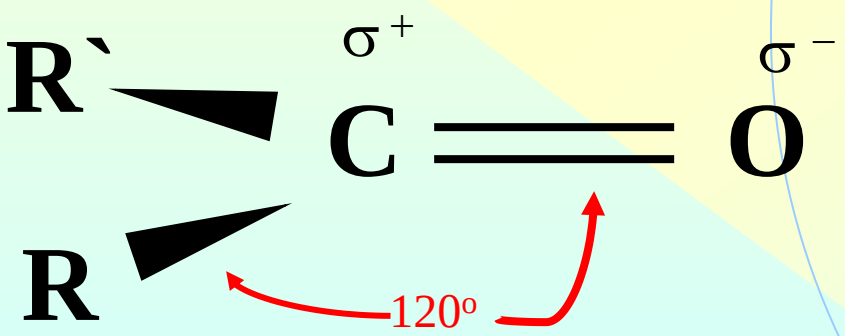


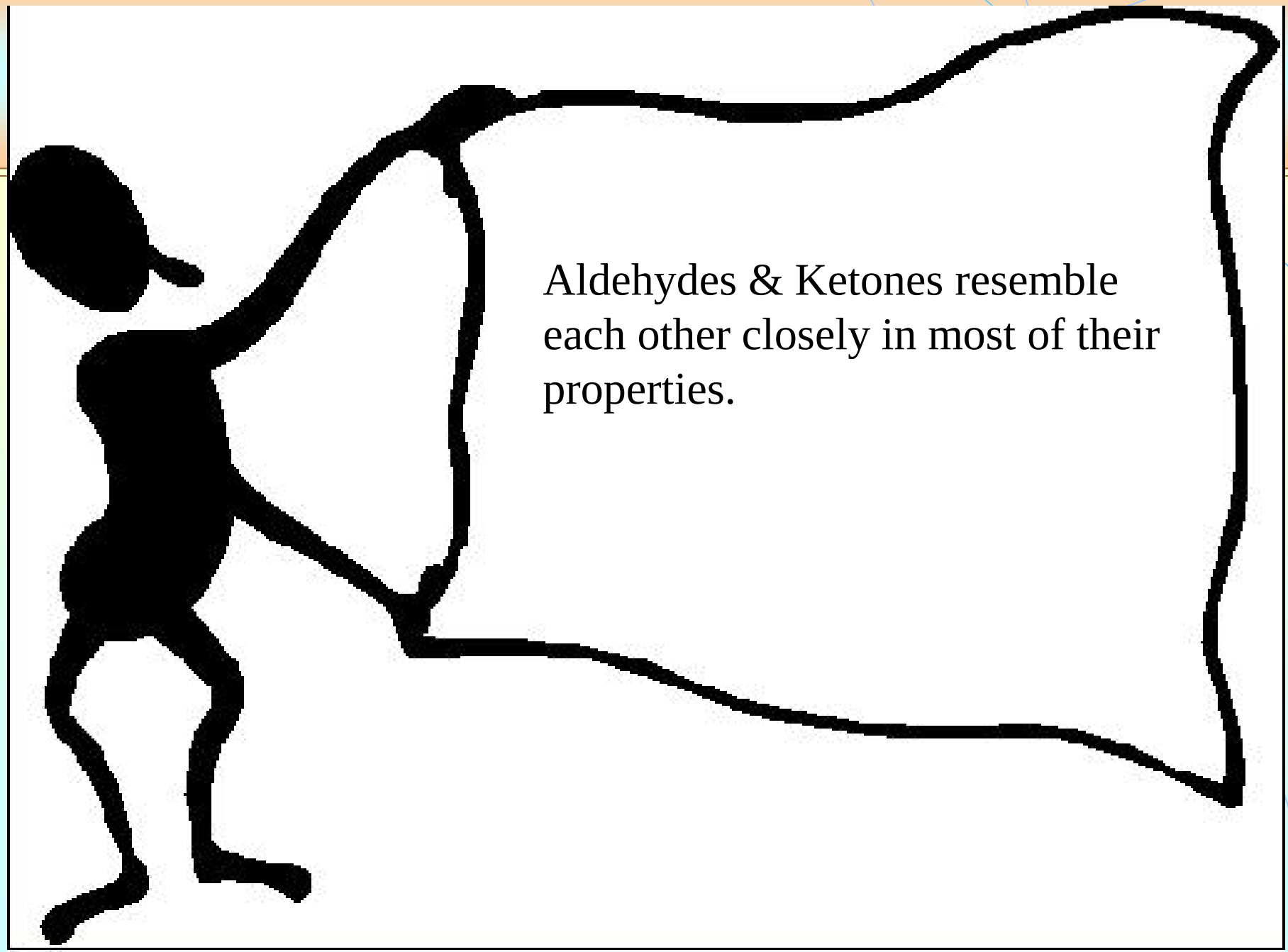


Ketones



A flat molecule due to sp^2 hybridization





Aldehydes & Ketones resemble each other closely in most of their properties.

Aldehydes have a hydrogen atom attached to the carbonyl group

Two Differences

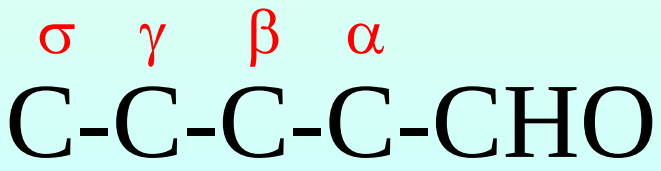
- **a) aldehydes are quite easily oxidized, whereas ketones are oxidized with difficulty**

- **b) aldehydes are usually more reactive than ketones toward nucleophilic addition (the characteristic reaction of carbonyl compounds).**

Aldehydes

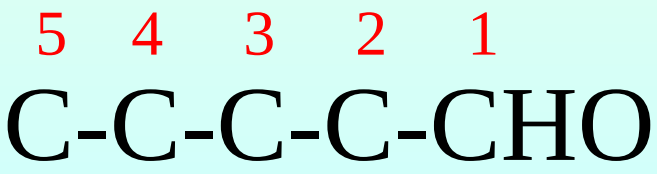
Nomenclature

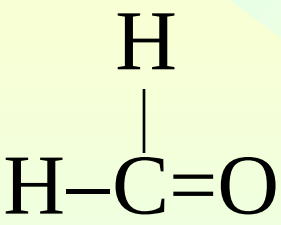
- **Common names**
  - **Derived from the names of corresponding carboxylic acids**
  - **Replace ic with aldehyde**



Nomenclature

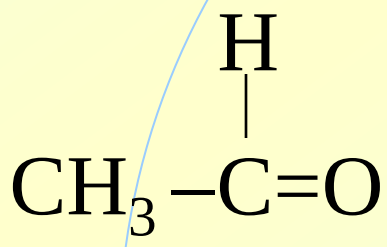
- **IUPAC names**
  - **The longest chain carrying the -CHO group is the parent structure**
  - **Replace -e with -al**





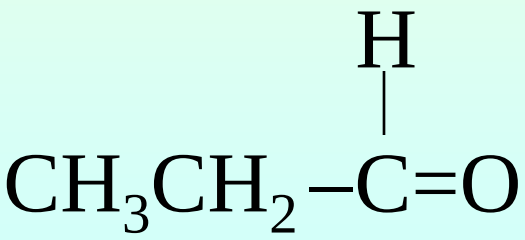
Formaldehyde

Methanal



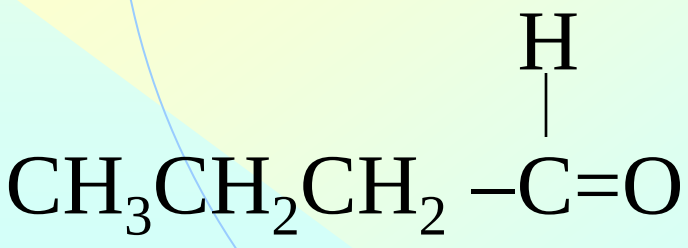
Acetaldehyde

Ethanal



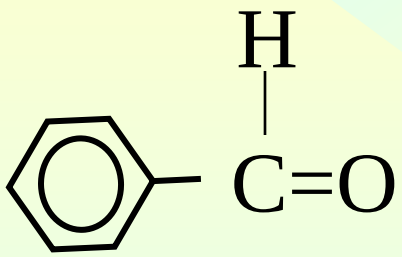
Propionaldehyde

Propanal

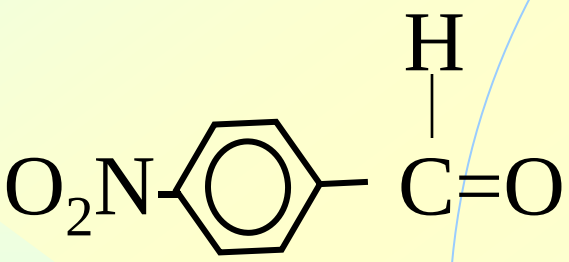


n-Butyraldehyde

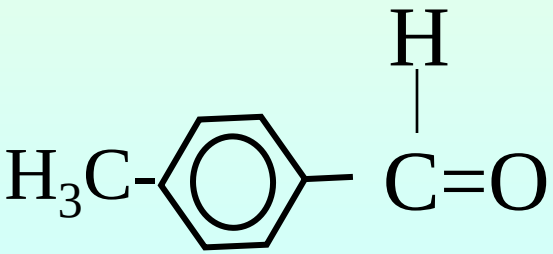
Butanal



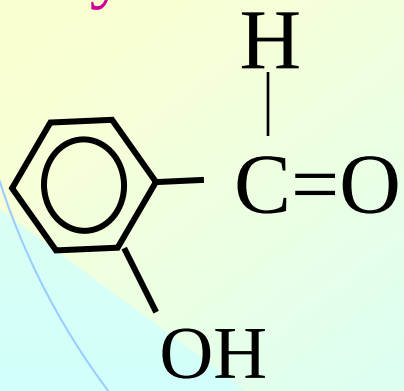
Benzaldehyde



p-Nitrobenzaldehyde

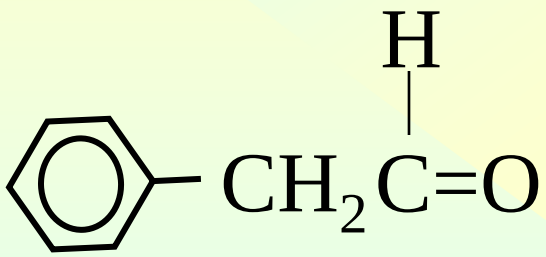


p-Tolualdehyde



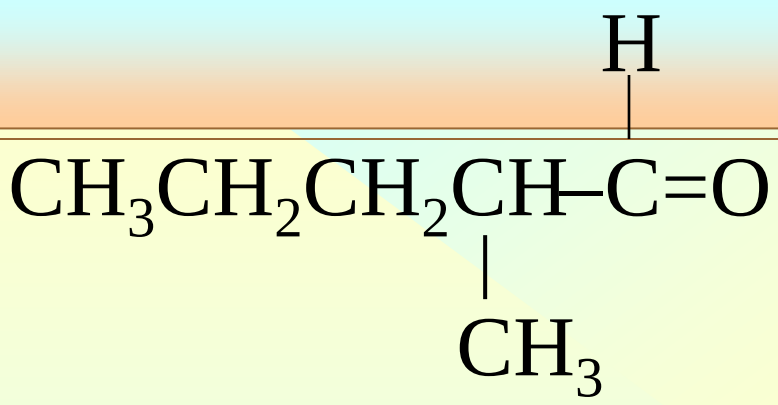
Salicylaldehyde

o-Hydroxybenzaldehyde



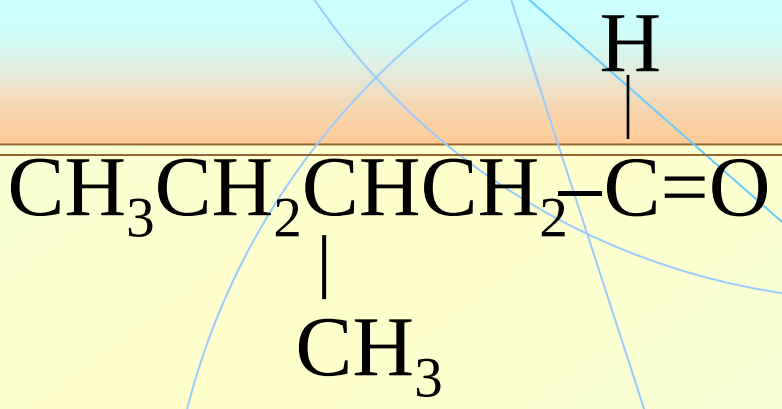
Phenylacetaldehyde

Phenylethanal



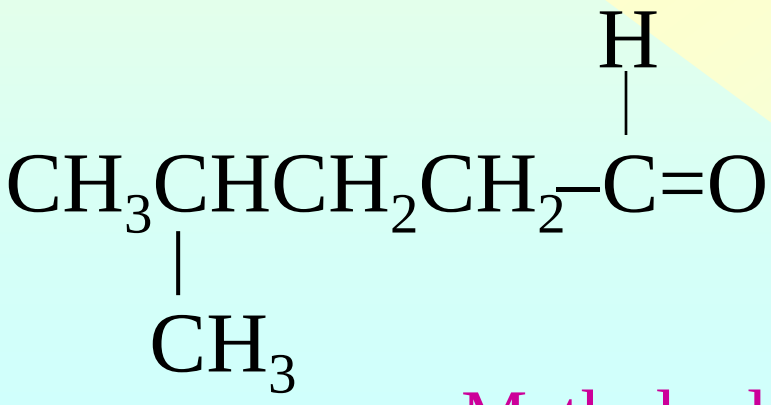
α-Methylvaleraldehyde

2-Methylpentanal



β-Methylvaleraldehyde

3-Methylpentanal



Isocaproaldehyde

γ-Methylvaleraldehyde

4-Methylpentanal

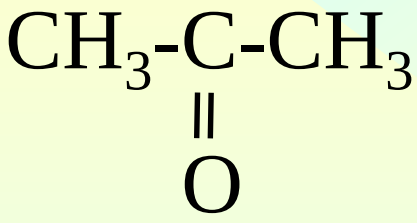
Ketones

Nomenclature

- **Common names**
  - **Derived from the names of the two attached groups to the carbonyl carbon**
  - **Follow with the name ketone**

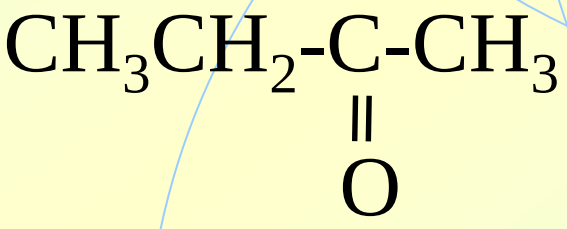
Nomenclature

- **IUPAC names**
  - **The longest chain carrying the carbonyl group is the parent structure**
  - **Replace -e with -one**



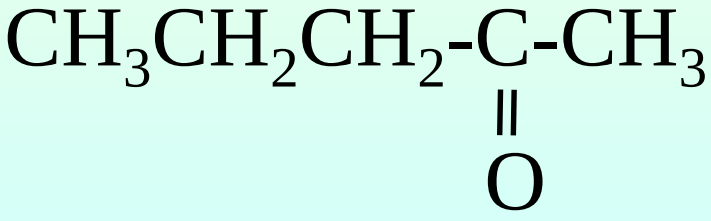
Acetone

Propanone



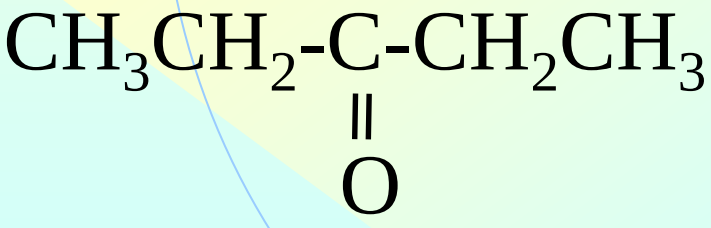
Ethyl methyl ketone

Butanone



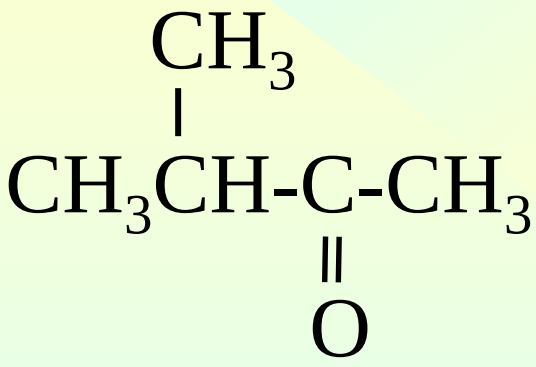
Methyl *n*-propyl ketone

2-Pentanone



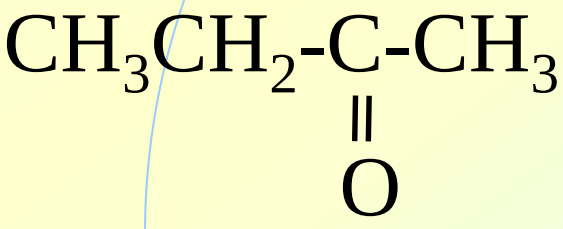
Diethyl ketone

3-Pentanone



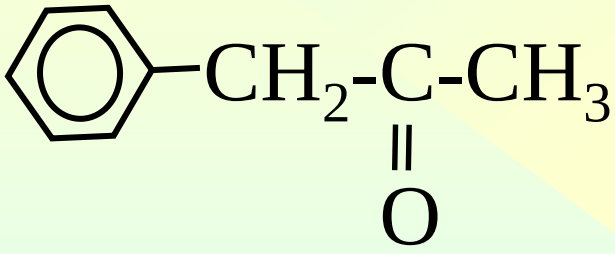
Isopropyl methyl ketone

3-Methyl-2-butanone



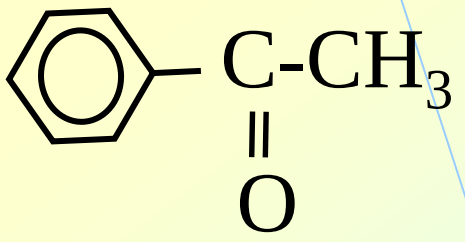
Ethyl methyl ketone

Butanone

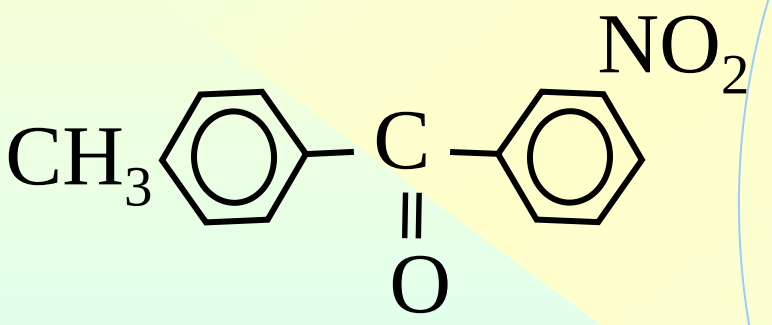


Benzyl methyl ketone

1-Phenyl-2-propanone



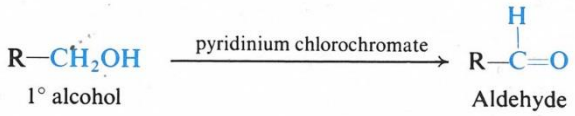
Acetophenone



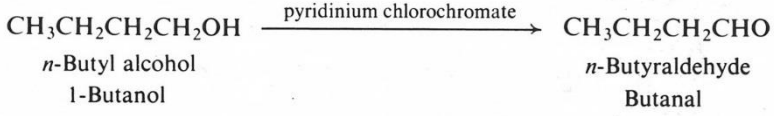
4`-Methyl-3-nitrobenzophenone

PREPARATION OF ALDEHYDES

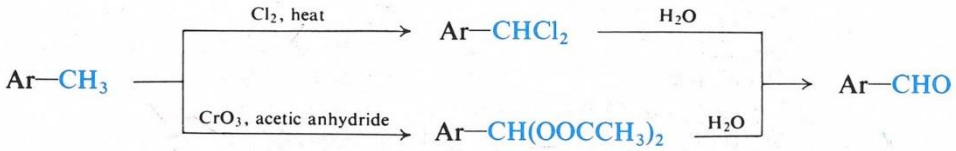
1. Oxidation of primary alcohols. Discussed in Secs. 6.15 and 18.4.



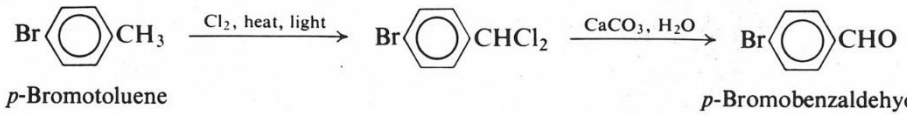
Example:

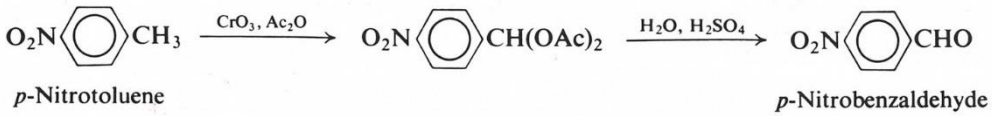


2. Oxidation of methylbenzenes. Discussed in Sec. 18.4.

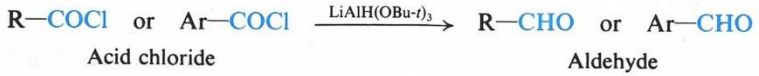


Examples:

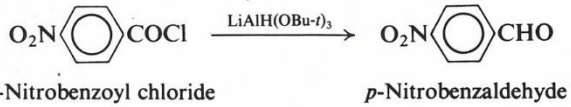




3. Reduction of acid chlorides. Discussed in Sec. 18.4.



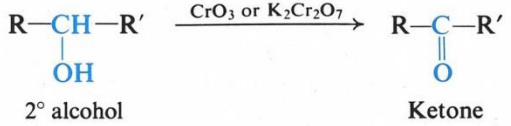
Example:



4. Reimer–Tiemann reaction. Phenolic aldehydes. Discussed in Sec. 24.13.

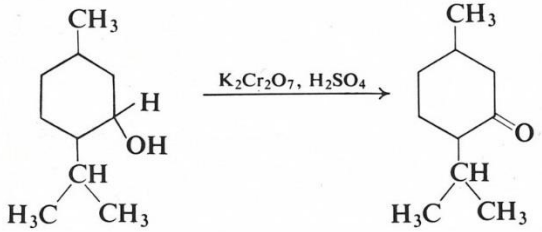
PREPARATION OF KETONES

1. Oxidation of secondary alcohols. Discussed in Secs. 6.15 and 18.4.



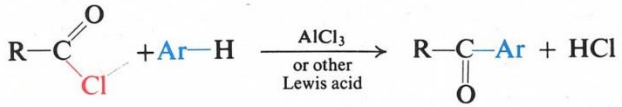
2° alcohol — Ketone

Example:



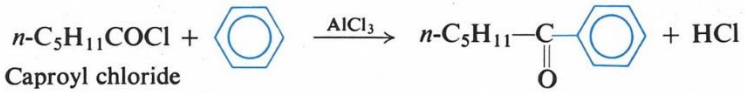
(−)-Menthol — (−)-Menthone

2. Friedel–Crafts acylation. Discussed in Sec. 18.5.



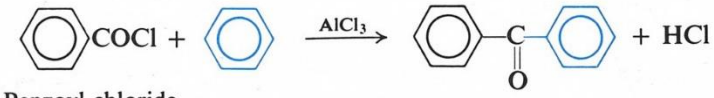
Acid chloride — Ketone

Examples:

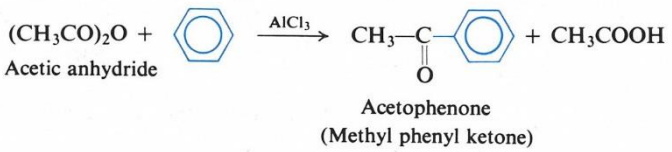


Caproyl chloride — *n*-Pentyl phenyl ketone

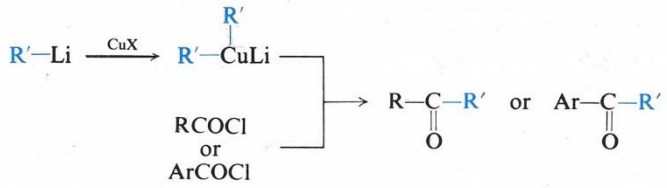
No rearrangement of n-pentyl group



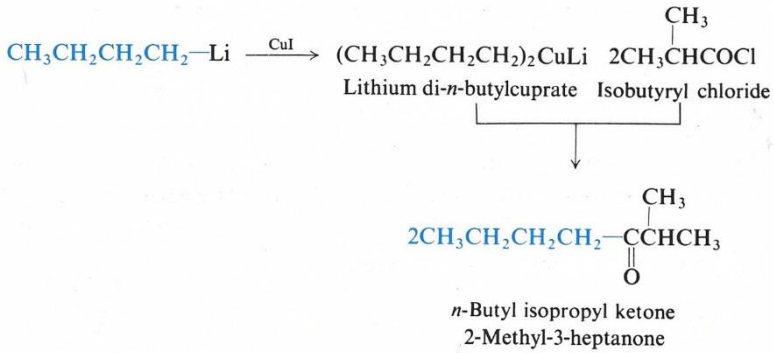
Benzoyl chloride — Benzophenone (Diphenyl ketone)

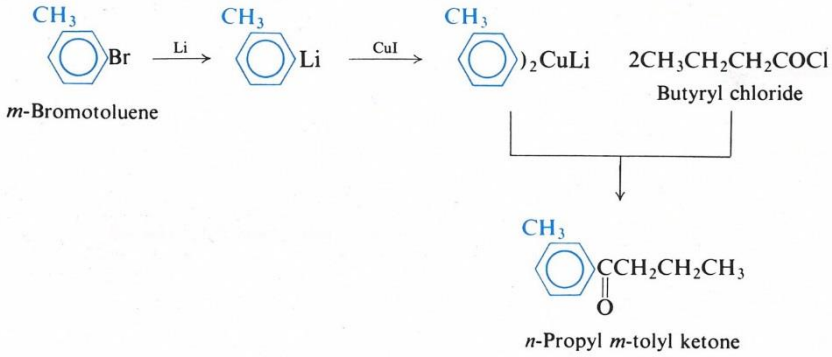


3. Reaction of acid chlorides with organocopper compounds. Discussed in Sec. 18.6.



Examples:



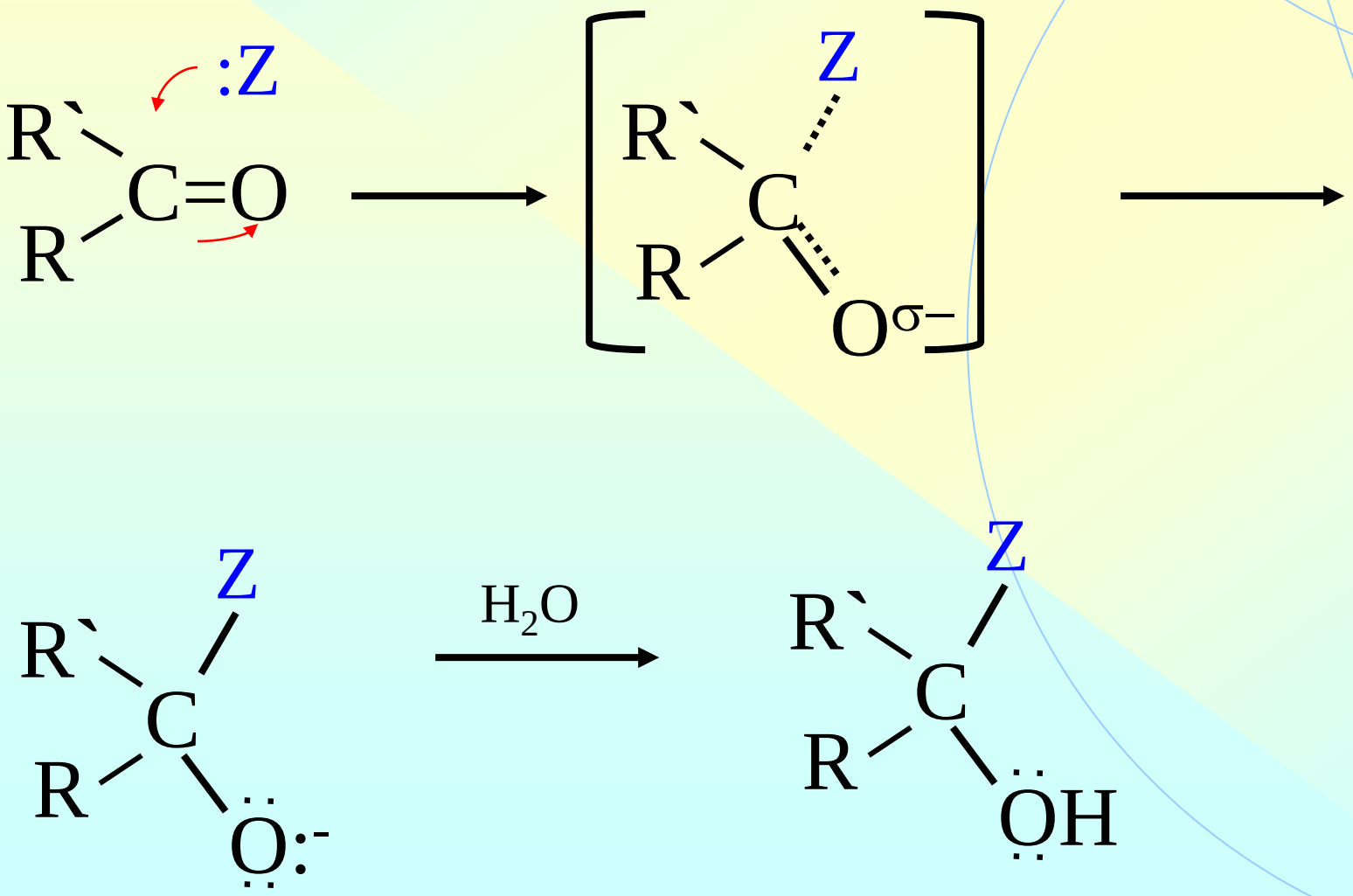


4. Acetoacetic ester synthesis. Discussed in Sec. 25.3.

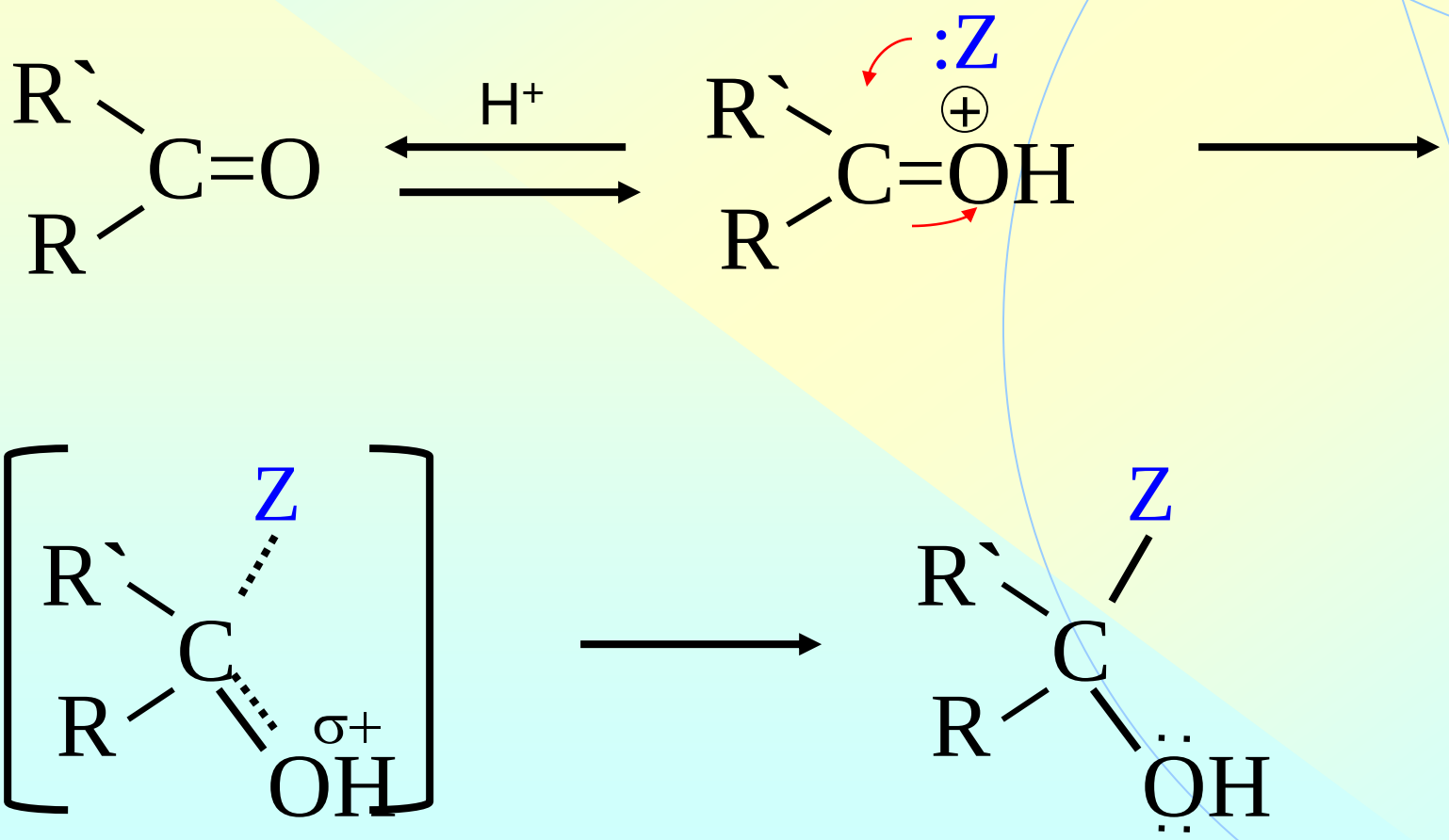
Reactions - Nucleophilic Addition

- The C=O governs the chemistry
  - Provides a site for nucleophilic addition
  - Increasing acidity of the α hydrogens
- Mobile π electrons are pulled strongly toward oxygen
  - Carbonyl carbon – electron-deficient
  - Carbonyl oxygen – electron-rich

The typical reaction of aldehydes and ketones is nucleophilic addition

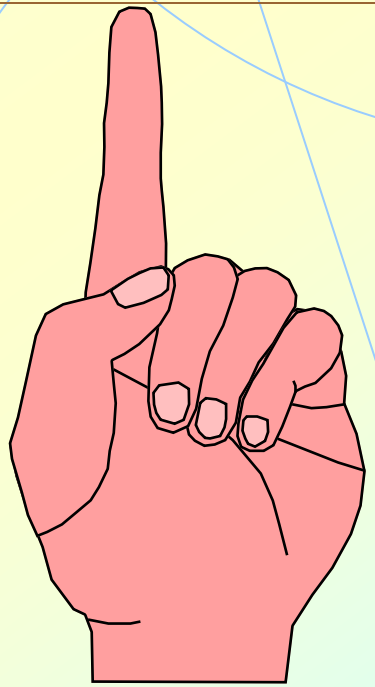

:Z
R`
C=O
R
Z
R`
C
R
Oσ–
Z
R`
C
R
O:-
H2O
Z
R`
C
R
OH

Acid-catalyzed Nucleophilic Addition



$$R-C\equiv \overset{\oplus}{O}$$

Acylium ion



REACTIONS OF ALDEHYDES AND KETONES

1. Oxidation

(a) Aldehydes. Discussed in Sec. 18.8.

$$R{-}CHO \text{ or } Ar{-}CHO \xrightarrow[\text{or } K_2Cr_2O_7]{Ag(NH_3)_2^+ \text{ or } KMnO_4} R{-}COOH \text{ or } Ar{-}COOH$$

Used chiefly for detection of aldehydes

Example:

$$CH_3CHO + 2Ag(NH_3)_2^+ + 3OH^- \longrightarrow 2Ag + CH_3COO^- + 4NH_3 + 2H_2O$$

Tollens' test

Colorless solution — *Silver mirror*

(b) Methyl ketones. Discussed in Sec. 18.21.

$$R{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \text{ or } Ar{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \xrightarrow{OX^-} R{-}COO^- \text{ or } Ar{-}COO^- + CHX_3$$

Haloform reaction

Examples:

$$C_2H_5{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + 3OI^- \longrightarrow C_2H_5COO^- + CHI_3 + 2OH^-$$

Iodoform

Yellow; m.p. 119 °C

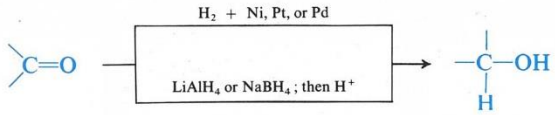
$$CH_3C(CH_3)=CHC(=O)CH_3 \xrightarrow[60\ ^\circ C]{KOCl} CHCl_3 + CH_3C(CH_3)=CHCOOK \xrightarrow{H_2SO_4} CH_3C(CH_3)=CHCOOH$$

4-Methyl-3-penten-2-one

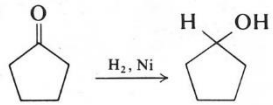
3-Methyl-2-butenoic acid

2. Reduction

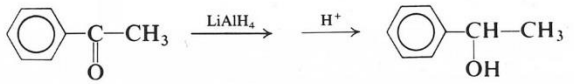
(a) Reduction to alcohols. Discussed in Sec. 18.9.



Examples:

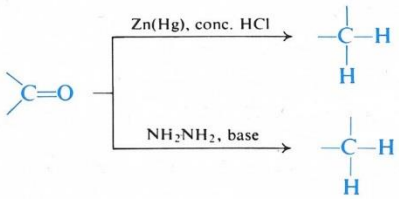


Cyclopentanone Cyclopentanol



Acetophenone α-Phenylethyl alcohol

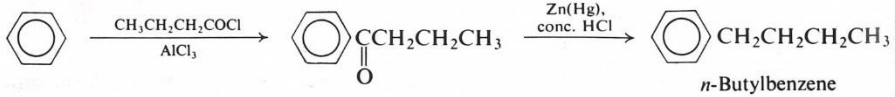
(b) Reduction to hydrocarbons. Discussed in Sec. 18.9.



Clemmensen reduction
for compounds sensitive to base

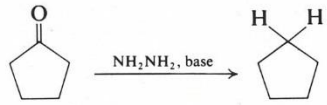
Wolff-Kishner reduction
for compounds sensitive to acid

Examples:



n-Butyrophenone
(Phenyl *n*-propyl ketone)

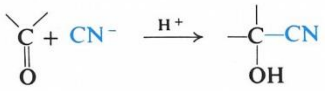
n-Butylbenzene



Cyclopentanone Cyclopentane

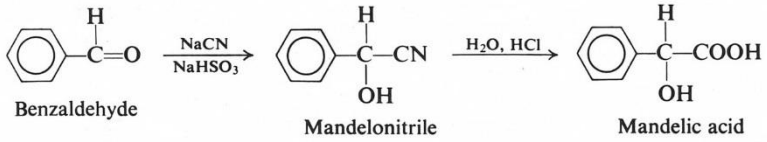
(c) Reductive amination. Discussed in Sec. 22.11.

3. Addition of cyanide. Cyanohydrin formation. Discussed in Sec. 18.10.

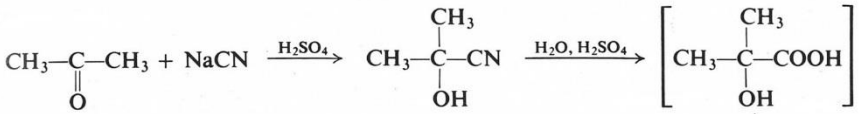


Cyanohydrin

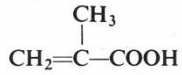
Examples:



Benzaldehyde — Mandelonitrile — Mandelic acid

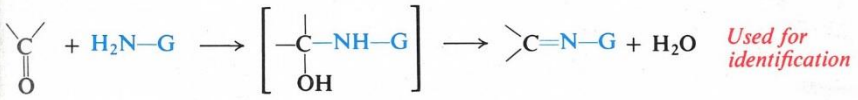


Acetone — Acetone cyanohydrin



Methacrylic acid
(2-Methylpropenoic acid)

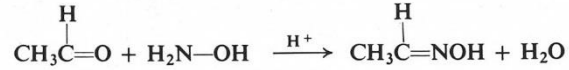
4. Addition of derivatives of ammonia. Discussed in Sec. 18.11.



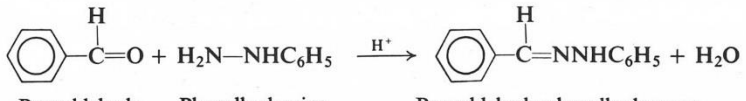
Used for identification

H_2N—G		Product	
H_2N—OH	Hydroxylamine	C=N—OH	Oxime
H_2N—NH_2	Hydrazine	C=N—NH_2	Hydrazone
H_2N—NHC_6H_5	Phenylhydrazine	C=N—NHC_6H_5	Phenylhydrazone
H_2N—NHCONH_2	Semicarbazide	C=N—NHCONH_2	Semicarbazone

Examples:

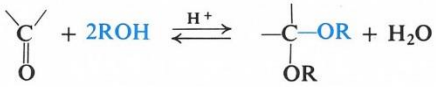


Acetaldehyde — Hydroxylamine — Acetaldoxime



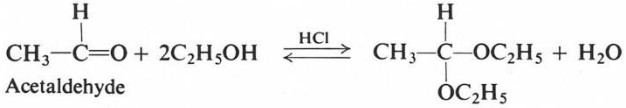
Benzaldehyde Phenylhydrazine Benzaldehyde phenylhydrazone

5. Addition of alcohols. Acetal formation. Discussed in Sec. 18.12.



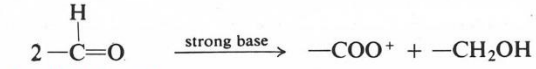
An acetal

Example:



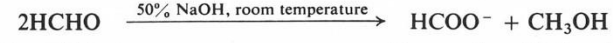
Acetaldehyde Acetal (Acetaldehyde diethyl acetal)

6. Cannizzaro reaction. Discussed in Sec. 18.13.

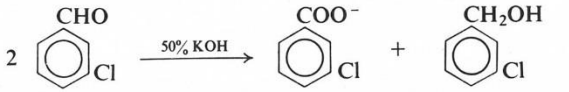


An aldehyde with no α-hydrogens Acid salt Alcohol

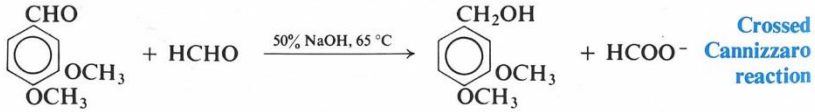
Examples:



Formaldehyde Formate ion Methanol



m-Chlorobenzaldehyde *m*-Chlorobenzoate ion *m*-Chlorobenzyl alcohol



Veratraldehyde 3,4-Dimethoxybenzyl alcohol

3,4-Dimethoxybenzaldehyde

Crossed Cannizzaro reaction


http://web.ukonline.co.uk/stinsv/