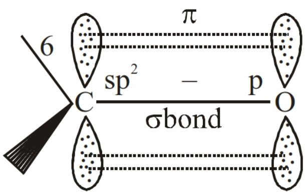
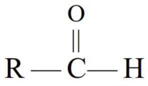
ALDEHYDES KETONES

STRUCTURE OF CARBONYL GROUPS :

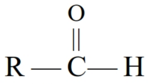
The $>C=O$ bond in aldehyde and ketones is made up of one σ and one π-bond around the carbon oxygen bond.



The electron cloud of the π-bond lies both above and below the $C=O$, σ bond


$R-\overset{\overset{\large O}{\|}}{C}-H$

Aldehyde


$R-\overset{\overset{\large O}{\|}}{C}-H$

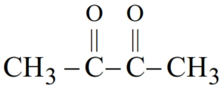
Ketone

NOMENCLATURE OF ALDEHYDE AND KETONES :

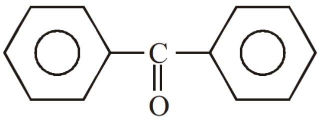
The suffix term for aldehyde is ‘al’ and for ketone is ‘one’.

(a) $\underset{4}{CH_3}-\underset{3}{CH}=\underset{2}{CH}-\underset{1}{CHO}$

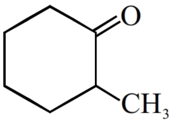
But – 2 – en – 1 – al

(b) 
$CH_3-\overset{\overset{\large O}{\|}}{C}-\overset{\overset{\large O}{\|}}{C}-CH_3$

Butane – 2, 3 – dione

(c) 

Benzophenone

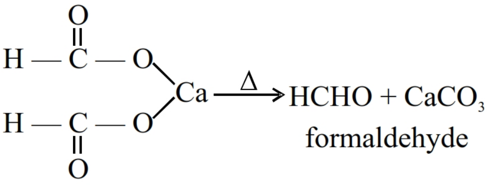
(d) 

2-Methyl-cyclohexanone

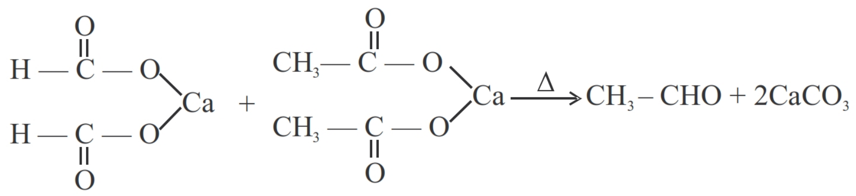
Aldehyde and ketones are functional isomers to each, due to which their properties largely resembles to each other.

GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES:

(1) BY DRY-DISTILLATION OF CALCIUM SALT OF CARBOXYLIC ACIDS :

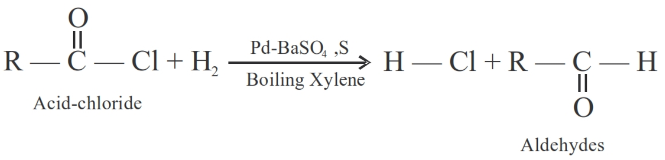
(a) 

Calcium formate

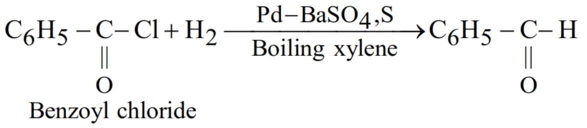
(b) 

2. BY ROSENMUND'S REDUCTION:

Only aldehydes can be synthesised by this reaction.



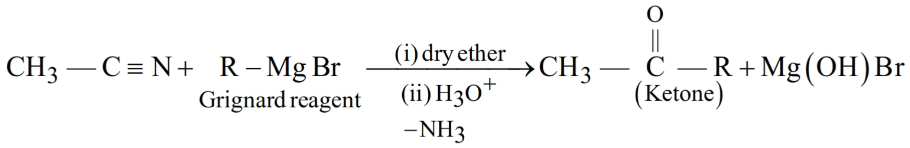
$$\underset{\text{Acid-chloride}}{R-\overset{\overset{O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling Xylene}]{\text{Pd-BaSO}_4\text{,S}} H-Cl + \underset{\text{Aldehydes}}{R-\underset{\underset{O}{\|}}{C}-H}$$



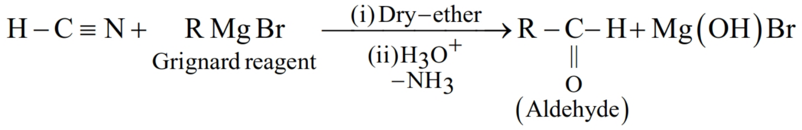
$$\underset{\text{Benzoyl chloride}}{C_6H_5-\underset{\underset{O}{\|}}{C}-Cl} + H_2 \xrightarrow[\text{Boiling xylene}]{Pd-BaSO_4\text{,S}} C_6H_5-\underset{\underset{O}{\|}}{C}-H$$

Note : Formaldehydes can't be obtained by this method. Ketones also can't be synthesised by this reaction.

3. FROM NITRILES :

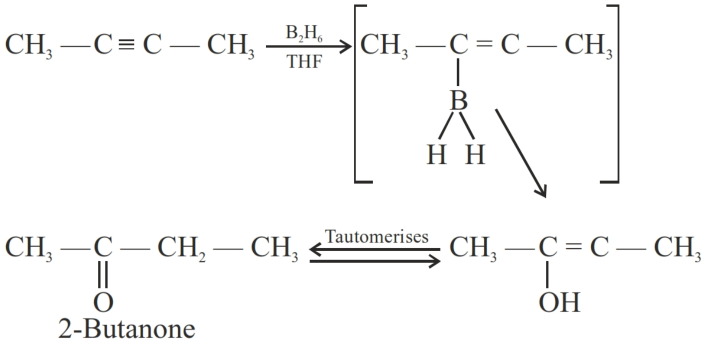
(a) 

$$CH_3-C\equiv N + \underset{\text{Grignard reagent}}{R-MgBr} \xrightarrow[\substack{\text{(ii) } H_3O^+ \\ -NH_3}]{\text{(i) dry ether}} CH_3-\underset{\text{(Ketone)}}{\overset{\overset{O}{\|}}{C}}-R + Mg(OH)Br$$

(b) 

$$H-C\equiv N + \underset{\text{Grignard reagent}}{R\,MgBr} \xrightarrow[\substack{\text{(ii)} H_3O^+ \\ -NH_3}]{\text{(i) Dry-ether}} \underset{\text{(Aldehyde)}}{R-\underset{\underset{O}{\|}}{C}-H} + Mg(OH)Br$$

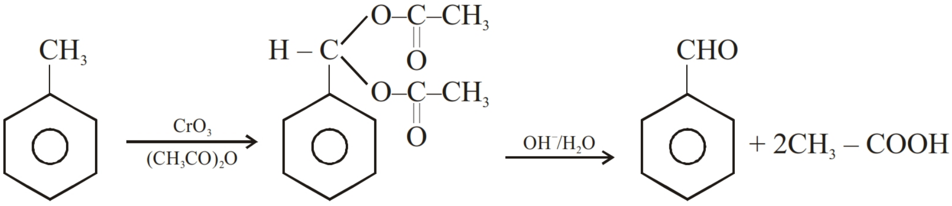
4. BY HYDROBORATION - OXIDATION OF ALKYNES :



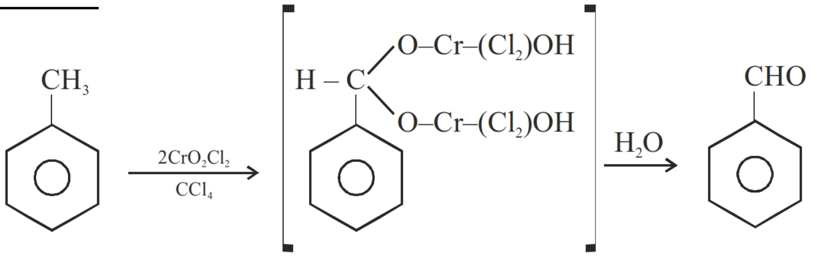
5. WACKER'S PROCESS :

$$CH_2=CH_2+H_2O+PdCl_2 \xrightarrow[\text{air}]{CuCl_2} CH_3CHO+Pd+2HCl$$

6. Oxidation of methyl benzene :



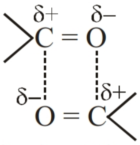
7. Etard Reaction :



Physical Properties :

(1) Boiling - point :

Aldehyde and Ketone molecule are polar molecules due to the presence of carbonyl groups.



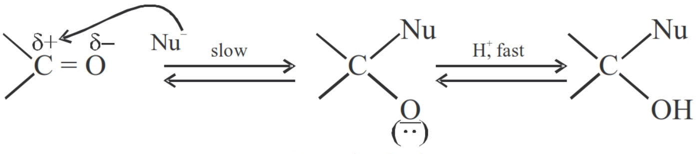
Dipole - Dipole interaction

Among isomeric aldehydes and ketones, ketone have slightaly higher boiling point value

Chemical properties of aldehyde and ketones :

Aldehydes and ketones are highly reactive due to the presence of polarized carbonyl groups. The reaction of aldehyde and ketones can be devided into following categories :

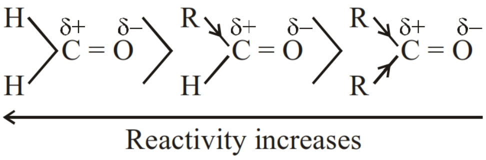
(1) Nucleophilic addition reactions :



The ability of the highly electronegative oxygen to retain the negative charge over it, causes the nucleophilic addition reaction at carbon. In addition, nucleophilic attack causes the formation of stable tetrahedral intermediate.

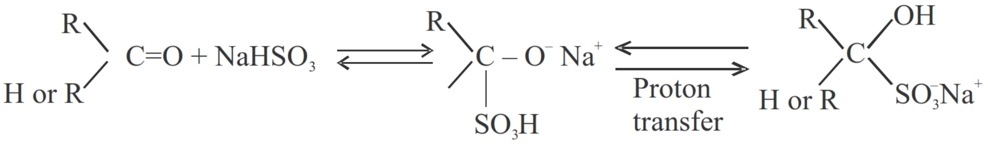
The relative reactivity of aldehydes and ketone is effected by at least given two factors :

(i) Inductive effect (ii) Steric factors



SOME IMPORTANT NUCLEOPHILIC ADDITION REACTION :

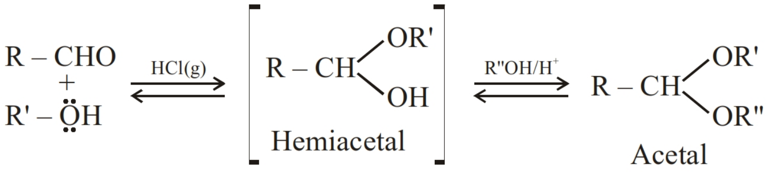
1. ADDITION OF SODIUM BISULPHITE



⇒ The position of equilibrium lies largely to the right for most aldehyde and for most of ketones it lies toward left.

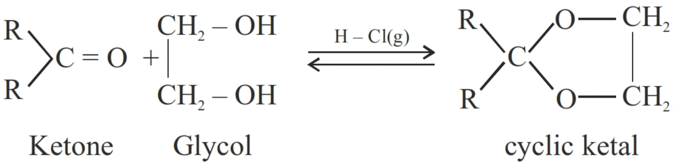
2. ADDITION OF ALCOHOL :

Aldehyde with one molecule of R–OH forms ‘hemiacetal’ and with another molecule it forms acetal.



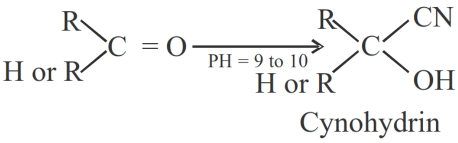
Ketone, similarly forms hemiketal and ketal.

3. WITH DIOL :



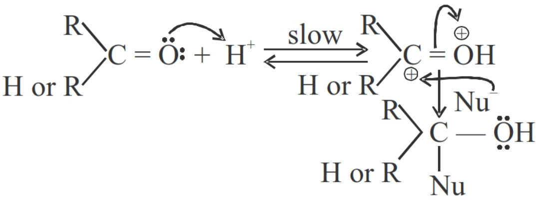
4. WITH HCN :

Cyanohydrins is formed



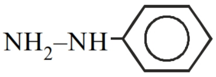
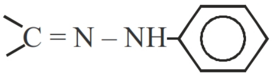
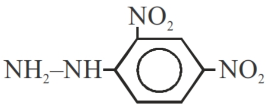
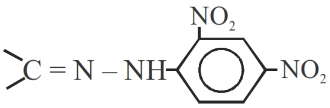
5. ADDITION OF AMMONIA DERIVATIVES :

The addition of ammonia derivative to aldehyde and ketone is catalysed by weak acids.



⇒ Due to protonation, the ease of nucleophilic addition becomes faster.

6.

AMMONIA DERIVATIVE USED		PRODUCT OBTAINED	
Strucutre	Name	Strucutre	Name
NH_2OH	Hydroxylamine	$>C=N-OH$	Oxime
NH_2-NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
	Phenyldrazine		Phenylhydrazone
	2,4-Dinitro-phenyldrazine		2,4-Dinitrophenyl-hydrazone
$NH_2CONHNH_2$	Semicarbazide	$>C=NNHCONH_2$	Semicarbazone

7. OXIDATION OF ALDEHYDE AND KETONES

Oxidation

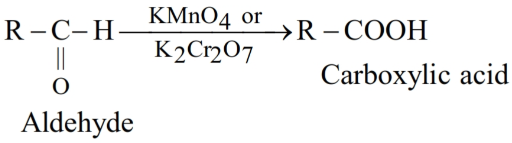
(A) Strong Oxidising agents

(1) $KMnO_4$ (2) $K_2Cr_2O_7$
(3) HNO_3

(B) Weak Oxidizing agents

(i) Fehling solution
(ii) Tollen's Reagent
(iii) Benedict solution

(A) Strong Oxidising agents :

(a) 

$$\underset{\text{Aldehyde}}{R-\underset{\underset{O}{\|}}{C}-H} \xrightarrow[K_2Cr_2O_7]{KMnO_4 \text{ or}} \underset{\text{Carboxylic acid}}{R-COOH}$$

(B) Oxidation by weak oxidising agents :

The given reactions are also used to distinguish between aldehyde and ketones.

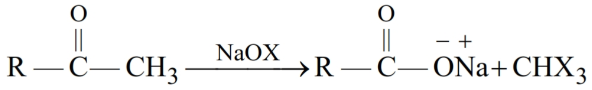
(i) By Tollen's reagent :

$$R-CHO+2\underset{\text{Tollen's reagent}}{\left[Ag(NH_3)_2\right]^+}+3OH^- \longrightarrow R-COO^-+2H_2O+4NH_3+\underset{\Rightarrow\text{Silver mirror test}}{2Ag\downarrow}$$

(ii) Fehling's solution :

$$R-CHO+2Cu^{2+}+5OH^- \longrightarrow R-COO^-+\underset{\text{Brown}}{Cu_2O}+3H_2O$$

(C) Oxidation of methyl ketones by Haloform reaction :



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaOX} R-\overset{\overset{O}{\|}}{C}-\overset{-}{O}\overset{+}{Na}+CHX_3$$

8. REDUCITON :

Reduction : → (a) To alcohol
→ (b) To alkane

(A) To alcohols :

$$R-CHO \xrightarrow[NaBH_4]{LiAlH_4 \text{ or}} R-CH_2-OH$$

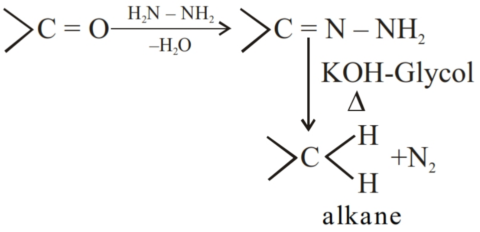
(B) To alkane :

(i) Clemmenssen's reduction:

$$>C=O \xrightarrow[HCl]{Zn\text{-}Hg} >CH_2 + H_2O$$

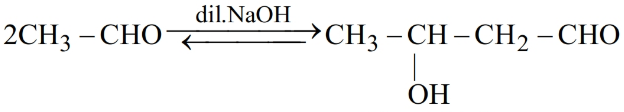
alkane

(ii) Wolff-kishner reduction:



9. REACTION INVOLVING α-HYDROGEN (ALDOL-CONDENSATION REACTION) :

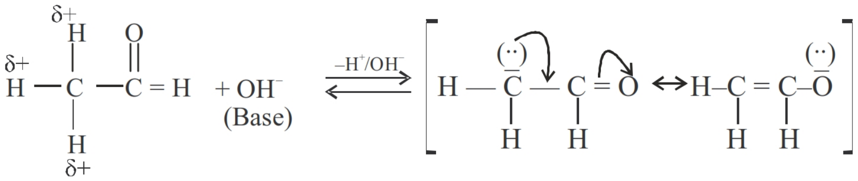
Aldehyde and Ketones having α H undergoes condensation in presence of these dilute base to form aldol. Thus reactions are also called as aldol condensation reactions.



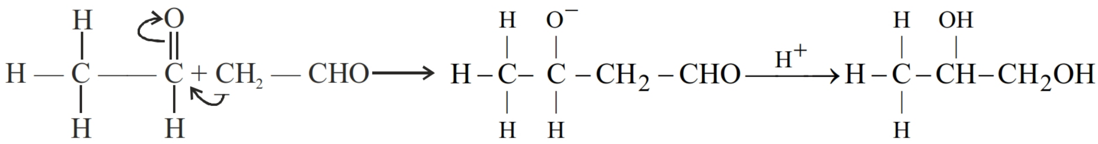
$$2CH_3-CHO \underset{}{\overset{dil.NaOH}{\rightleftharpoons}} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

(Acetaldol)

Mechanism :

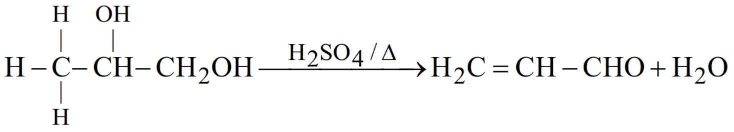


2nd Step :



[Aldol]

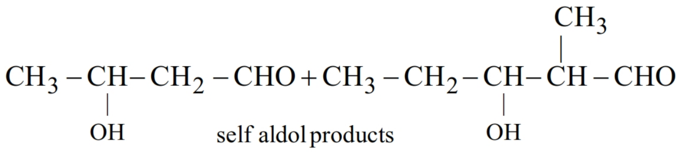
Note: The aldol formed may undergo dehydration in presence of dilute acids, upon heating.



$$H-\underset{H}{\overset{H}{C}}-\overset{OH}{CH}-CH_2OH \xrightarrow{H_2SO_4/\Delta} H_2C=CH-CHO+H_2O$$

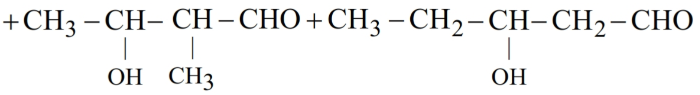
Cross Aldol condensation reaction:

$$CH_3-CHO+CH_3-CH_2-CHO \xrightleftharpoons{Na-OH}$$



$$CH_3-\underset{OH}{CH}-CH_2-CHO+CH_3-CH_2-\underset{OH}{CH}-\overset{CH_3}{CH}-CHO$$

self aldol products

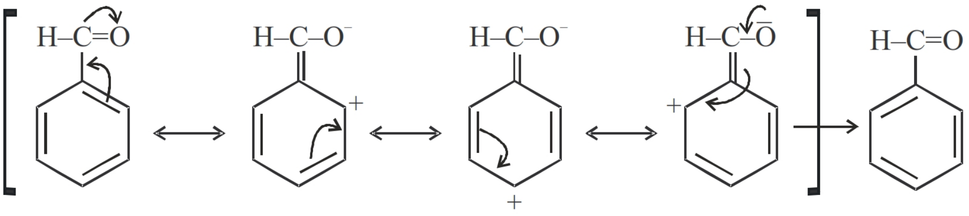


$$+CH_3-\underset{OH}{CH}-\underset{CH_3}{CH}-CHO+CH_3-CH_2-\underset{OH}{CH}-CH_2-CHO$$

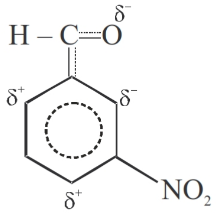
cross aldol products

Electrophilic Substitution reaction :

Aromatic aldehydes and ketones, gives rise to electrophilic substitution reaction at meta position. The carbonyl groups acts as deactivating, group for incoming electrophiles



Resonance hybrid:



(1) Nitration: