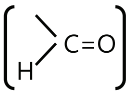
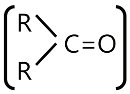
23. ALDEHYDES AND KETONES

CARBONYL COMPOUNDS

1. INTRODUCTION

Carbonyl compounds have a general formula $C_nH_{2n}O$ and contain a >C=O group which is present in aldehydes  $\left(\begin{smallmatrix} \\ H\end{smallmatrix}\!>C=O\right)$ as well as in  $\left(\begin{smallmatrix}R\\ R\end{smallmatrix}\!>C=O\right)$ ketones. They are constituents of fabrics, plastics and drugs. These are also used as reagents and solvents.

1.1 Structure of Carbonyl Compounds

In carbonyl group both the carbon and oxygen atoms are in sp^2 hybridised state. One of the sp^2 hybrid orbital of one carbon atom overlaps with one of the sp^2 hybrid orbital of oxygen atom forming C–O σ-bond. The remaining two sp^2 hybrid orbitals of C atom overlap with either sp^3 orbital of C-atoms (as in ketone) or one with sp^3 orbital carbon and other with s orbital of hydrogen (as in aldehyde forming) 2 more σ-bonds. On the other hand each of two sp^3 hybrid orbitals of 'oxygen' atom contains a lone pair of electrons. Unhybrid orbitals present at the carbon and oxygen atom form π- bond by sideways overlapping. The structure can be represented as:

$$C^* = 1s^2\ \underbrace{2s^1\ 2p_x^1\ 2p_y^1}_{\substack{\downarrow\ sp^2\text{ hybridization}\\ \downarrow\ 3sp^2\text{ hybrid orbital}}}\ \boxed{2p_z^1}\rightarrow\text{Unhybrid orbital}$$

$$O = 1s^2\ \underbrace{2s^2\ 2p_x^2\ 2p_y^1}_{\substack{\downarrow\ sp^2\text{ hybridization}\\ \downarrow\ 3sp^2\text{ hybrid orbital}}}\ \boxed{2p_z^1}\rightarrow\text{Unhybrid orbital}$$

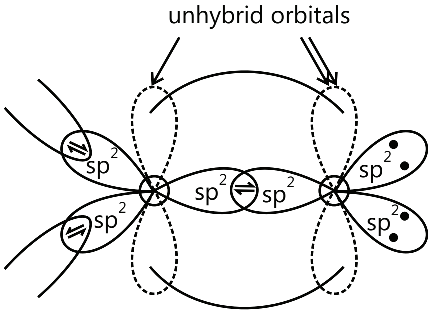
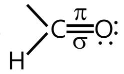


Figure 23.1: Structure of carbonyl compounds

Thus C = O group contains one σ-bond and one π-bond as 

1.2 Bonding in Aldehydes and Ketones

The carbonyl carbon atom is sp^2 hybridized. The unhybridized p-orbital form a π-bond with a p-orbital of oxygen. The double bond between carbons and oxygen is shorter, stronger and polarized.

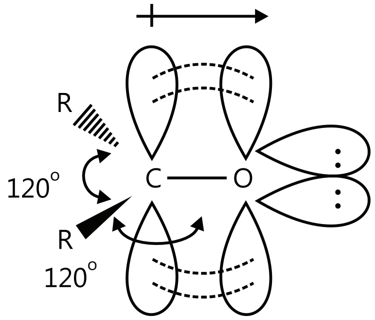
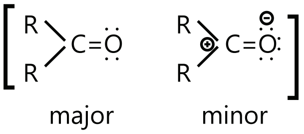


Figure 23.2: Bonding of carbonyl compounds

	Length	Energy
Ketone C =O bond	1.23 Å	178 kcal /mol (745 kJ/mol)
Alkene C = C bond	1.34 Å	146 kcal/mol (611 kJ / mol)

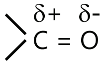
The double bond of the carbonyl group has a large dipole moment because oxygen is more electronegative than carbon.



1.3 Comparison of C=O Bond with C=C Bond

(a) Both atoms in both the cases are in the sp^2 hybridised state.

(b) Both the cases contain one σ-bond and one π-bond.

The difference between C=O and C=C is because of O-atom in carbonyl group is more electronegative than carbon as a result polarity is developed as -> 

Thus, the double bond of the carbonyl group has a large dipole moment. This polarity conforms that there is nucleophilic addition reaction in the carbonyl compound on other hand in alkene (C = C) there is electrophilic addition reaction

2. METHOD OF PREPARATION OF ALDEHYDES AND KETONES

2.1 From Alcohols

2.1.1 By Oxidation of Alcohols

1° Alcohol on oxidation using PCC gives an aldehyde. 2° alcohol gives a ketone on oxidation by $Na_2Cr_2O_7$

$$RCH_2OH \xrightarrow{[O]} R-CH=O$$

MASTERJEE CONCEPTS

- If acidified $K_2Cr_2O_7$ or $KMnO_4$ is used then aldehyde further oxidise to give acid.
- PCC (Pyridinium chloro-chromate in CH_2Cl_2) and Collin's reagent (CrO_3 Pyridine) are used to get aldehyde from 1° alcohol. These reagents do not attack at double bond.

Saurabh Gupta (JEE 2010, AIR 443)

Illustration 1: In the following reaction when we mix Dichromate with Ethanol, the colour of the solution changes from orange to green. Give reason. $CH_3-CH_2-OH+Cr_2O_7^{2-}+H^+$ **(JEE ADVANCED)**

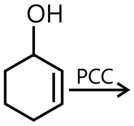
Sol: Dichromate is an oxidizing agent and during the reaction itself undergoes the reduction process and the green colour is due to the formation of reduced chromate Cr^{3+}

Dichromate is a good oxidizing agent, it oxidizes the primary alcohol to Acid and itself gets reduced to Chromium ion (Cr^{+3}).The colour of dichromate is Orange and that of Chromium is green. This is shown by the following equation:

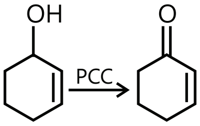
$$CH_3-CH_2-OH+Cr_2O_7^{2-}\text{(Orange)}+H^+\longrightarrow CH_3-COOH+Cr^{3+}\text{(green)}$$

Thus this method is not useful in preparation of aldehydes and ketones.

Illustration 2: Complete the following reaction: **(JEE MAIN)**



Sol: As the alcohol is a 2° alcohol, and PCC is a mild oxidizing agent. So, we get a ketone as a product.



2.1.2 By Dehydrogenation of Alcohols

Dehydrogenation means removal of hydrogen and the reagent used is heated copper.

$$1°\ \text{alcohol}\ (RCH_2OH)\xrightarrow[-H_2]{Cu/300°C}\text{Aldehyde}\ (R-CH=O)$$

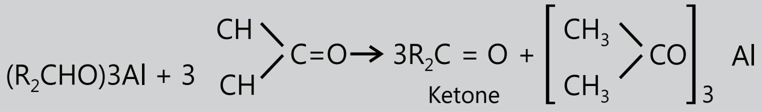
$$2°\ \text{alcohol}\ (R_2CHOH)\xrightarrow[-H_2]{Cu/300°C}\text{Ketone}\ (R_2C=O)$$

$$3°\ \text{alcohol}\xrightarrow[-H_2O]{Cu/300°C}\text{Alkene}$$

MASTERJEE CONCEPTS

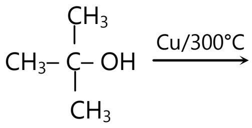
2° alcohol can also be oxidised to ketone by aluminium t-butoxide. During the reaction, 2° alcohol is first refluxed with reagent $[(CH_3)_2CO]_3$ Al, followed by acetone.

$$3R_2CHOH + [(CH_2)_3CO]_3Al \longrightarrow (R_2CHO)_3Al + 3(CH_3)_3C-OH$$



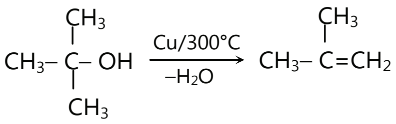
Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 3: Complete the following reaction. **(JEE MAIN)**



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow{Cu/300°C}$$

Sol: It is an example of dehydrogenation of alcohols. The product formed will be an alkene.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[-H_2O]{Cu/300°C} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

MASTERJEE CONCEPTS

As the reaction proceeds at high temperature, so a thermodynamically stable product would be favored in this case.

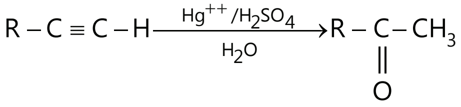
Aman Gour (JEE 2012, AIR 230)

2.2 From Hydrocarbons

2.2.1 Hydration of Alkynes

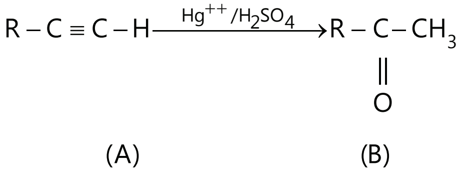
It is the addition of water in the presence of a heavy metal ion. Acetylene on hydration gives aldehyde while any higher alkyne gives ketone.

$$H-C\equiv C-H \xrightarrow[H_2O]{Hg^{++}/H_2SO_4} CH_3-CH=O$$



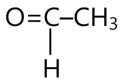
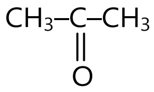
$$R-C\equiv C-H \xrightarrow[H_2O]{Hg^{++}/H_2SO_4} R-\underset{\underset{O}{\|}}{C}-CH_3$$

For example, In the case shown below, by varying the Alkyl (–R) group, the product also varies accordingly.



$$R-C\equiv C-H \xrightarrow{Hg^{++}/H_2SO_4} R-\underset{\underset{O}{\|}}{C}-CH_3$$

(A) (B)

R	A	B
H	H-C≡C-H	 $O=C(H)-CH_3$
CH_3	$CH_3-\overset{\curvearrowright}{C\equiv C}-H$	 $CH_3-C(=O)-CH_3$
$Cl-CH_2$-	$Cl-CH_2-\overset{\curvearrowleft}{C}\equiv C-H$	$Cl-CH_2-CH_2-CH=O$

In the above reaction, the carbonyl group will be formed on that carbon of the alkyne which is easy to attack by the nucleophile (water in this case). Thus, a less crowded carbon will favour the formation of a carbonyl group whereas a more crowded carbon will not favour it. . Therefore, in case (iii), the carbonyl group is formed on that carbon which is easy to attack

MASTERJEE CONCEPTS

- The preparation of carbonyl compounds from the alkyne depends upon the R part and also presence of inductive effect of the group attached to R.
- Carbonyl group will be at the C-atom at which H_2O will attack as a nucleophile

B Rajiv Reddy (JEE 2012, AIR 11)

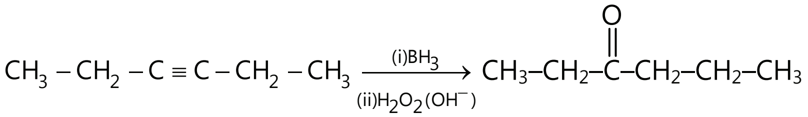
2.2.2 Hydroboration of Alkyne

Hydroboration is a process used to get an aldehyde from a terminal alkyne. Here regents are (i) diborane (B_2H_6) (ii) $H_2O_2(OH^-)$

$R-C=C-H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} R-CH_2-CH=O$ In this reaction, Borane (BH_3) is the electrophile.

$$3R-C\equiv C-H \xrightarrow{BH_3} (R-CH=CH)_3B \xrightarrow{H_2O_2} R\text{–}CH\text{=}CH\text{–}OH \rightleftharpoons R\text{–}CH_2\text{–}CH=O$$

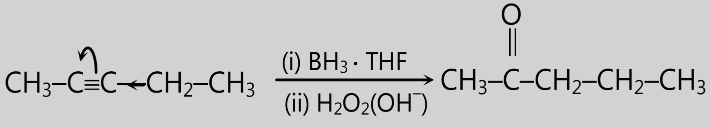
A higher alkyne except a terminal alkyne will give a ketone during hydroboration.



$$CH_3-CH_2-C\equiv C-CH_2-CH_3 \xrightarrow[\text{(ii)}H_2O_2(OH^-)]{\text{(i)}BH_3} CH_3\text{–}CH_2\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_2\text{–}CH_2\text{–}CH_3$$

MASTERJEE CONCEPTS

For an unsymmetrical alkyne ketone will be corresponding to that carbon atom over which electrophile BH_3 will attack. It depends upon the inductive effect and finally the polarization of π-electrons of C=C bond. Hydroboration occurs on the anti-Markownikoff position.



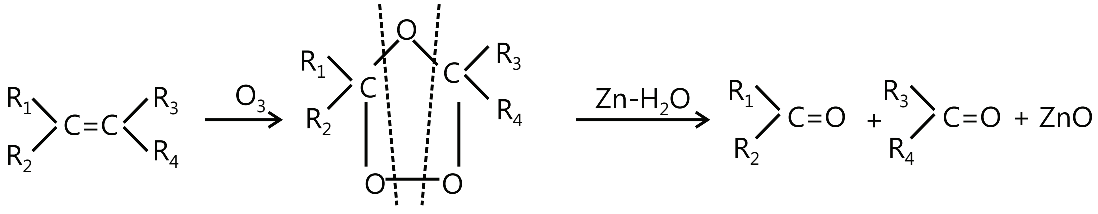
$$CH_3\text{–}\overset{\curvearrowleft}{C}\equiv C \leftarrow CH_2\text{–}CH_3 \xrightarrow[\text{(ii) } H_2O_2(OH^-)]{\text{(i) } BH_3\cdot THF} CH_3\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}CH_2\text{–}CH_2\text{–}CH_3$$

(+ I of ethyl is more than CH_3)

Rohit Kumar JEE 2012, AIR 79

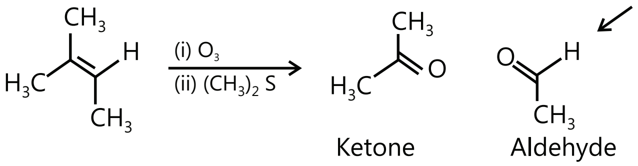
2.2.3 Ozonolysis of Alkenes

Ozonolysis is used to get carbonyl compounds from alkenes. The reaction is -



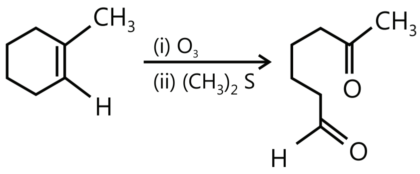
Mono-ozonide

Note: That the carbon-carbon double bond is broken and we are forming a carbon-oxygen double bond on each of the two carbons that originally composed the alkene. The second step in ozonolysis is called the "workup". There are two different types of "workup", and the most common is referred to as the "reductive workup". In this step, we add a reducing agent (commonly zinc metal or dimethyl sulfide) that decomposes the intermediate formed at the end of the ozonolysis reaction (which is called an "ozonide"). The third oxygen of ozone is now attached to what used to be our reducing agent (which may be either zinc oxide (ZnO) or dimethyl sulfoxide (DMSO). Using a "reductive workup" preserves all other aspects of the molecule save the double bond. So if we start with, say, a trisubstituted alkene, as in the example, we will end up with a ketone and an aldehyde. [What happens if the alkene carbon is attached to two hydrogens? It becomes formaldehyde, which is then further converted to carbon dioxide]



note that the H is preserved

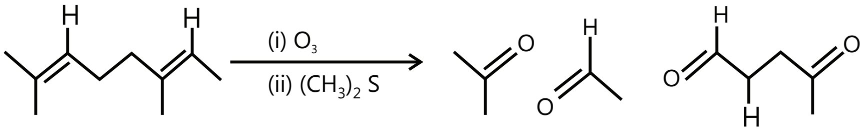
"Reductive workup" merely cleaves the C=C bond and replaces with oxygen



Note: That although $(CH_3)_2S$ is written as the reductant here, it's essentially interchangeable with Zn for our purposes. An interesting consequence of ozonolysis is that if the alkene is within a ring, you end up with a chain containing two carbonyls: Cyclic alkenes becomes chains -If your molecule has multiple alkenes, then you will end up with more than two fragments. For many years, ozonolysis was used as a method for determining the structures of unknown molecules. By "stitching" together the fragments and analysing them, it is then possible to deduce what the original structure was.

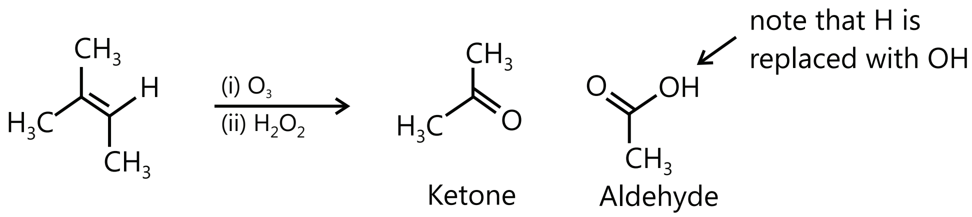
[This was particularly important in the case of unsaturated molecules known as terpenes]. Here's one example:

Molecules with multiple alkenes are cleaved into fragments:



This isn't the end of the story with ozonolysis. There's a second type of workup that can be used, which is referred to as oxidative workup. Instead of using Zn or S $(CH_3)_2$, if we use the oxidant hydrogen peroxide [H_2O_2], any aldehydes that form will be oxidized to give carboxylic acids. Like in the example below – notice that the C-H bond is oxidized to C-OH [but all the other hydrogens remain intact].

"Oxidative workup" oxidized sp^2 hybridized C–H bonds to C–OH as well as cleaving C = C



Typical oxidant used for "oxidative workup" is H_2O_2; this oxidizes any aldehydes to carboxylic acids

MASTERJEE CONCEPTS

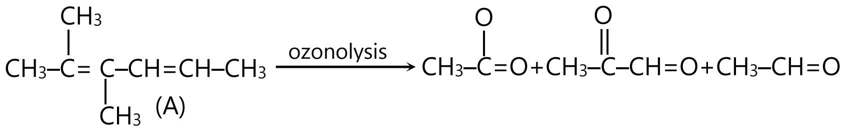
- This method is used because the double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen groups of two carbonyl compounds
- Among the molecules of carbonyl compounds produced:
- If there's a single molecule containing two carbonyl groups, then hydrocarbon will be alkadiene.
- If all the three molecules contain two carbonyl groups, then hydrocarbon will be cycloalkatriene.
- An alternative to using ozone for the oxidative workup is to use the reagent $KMnO_4$, especially in the presence of hot acid; this will lead to the same result.

Krishan Mittal (JEE 2012, AIR 199)

Illustration 4: Which hydrocarbon on ozonolysis gives a mixture of acetone, acetaldehyde and methyl glyoxal?
(a) 2, 3-dimethylhexa-2-4-diene (b) 2, 4-dimethylhex-2,4-diene **(JEE ADVANCED)**

Sol:

(a)

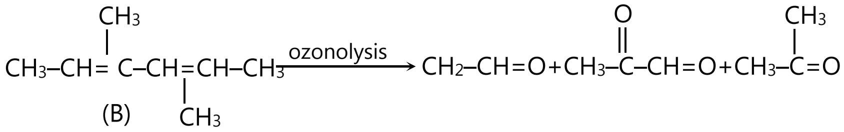


$$CH_3-\overset{CH_3}{\overset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-CH=CH-CH_3 \xrightarrow{\text{ozonolysis}} CH_3-\overset{O}{\overset{|}{C}}=O+CH_3-\overset{O}{\overset{||}{C}}-CH=O+CH_3-CH=O$$

(A)

2, 3-dimethylhexa-2-4-diene

(b)



$$CH_3-CH=\overset{CH_3}{\overset{|}{C}}-CH=\underset{CH_3}{\underset{|}{CH}}-CH_3 \xrightarrow{\text{ozonolysis}} CH_2-CH=O+CH_3-\overset{O}{\overset{||}{C}}-CH=O+CH_3-\overset{CH_3}{\overset{|}{C}}=O$$

(B)

2, 4-dimethylhex-2,4-diene

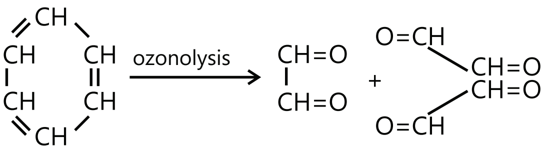
Answer will be both isomeric structures (A) and (B)

Illustration 5: Which hydrocarbon on ozonolysis gives 3 moles of glyoxal **(JEE MAIN)**

Sol: As for formation of 3 moles of glyoxal we require a compound having six carbon atoms and three site of unsaturation so that ozonolysis can occur.so it appears to be an aromatic compound having six carbon backbone. I.e. Benzene

Benzene on ozonolysis gives 3 moles of glyoxal.

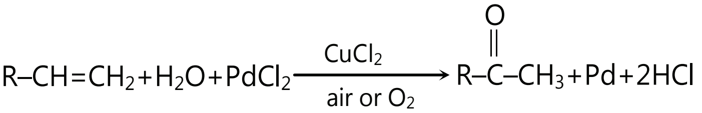
Benzene $\xrightarrow{\text{ozone}}$ Benzenetriozonide



2.2.4 Wacker Process

Alkenes can directly be oxidised to corresponding aldehydes or ketones by treating them with a solution of $PdCl_2$ containing a catalytic amount of $CuCl_2$ in the presence of air or O_2. Apart from ethane, any higher alkene will give a ketone.

$$CH_2{=}CH_2+H_2O+PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} CH_3{-}CH{=}O+Pd+2HCl$$



$$R{-}CH{=}CH_2+H_2O+PdCl_2 \xrightarrow[\text{air or } O_2]{CuCl_2} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3+Pd+2HCl$$

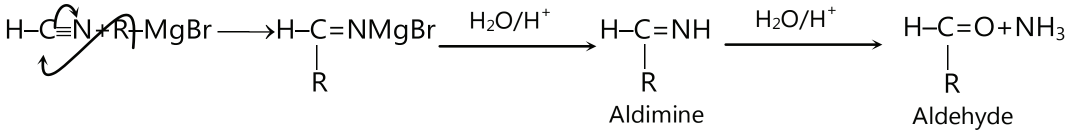
MASTERJEE CONCEPTS

During the reaction $PdCl_2$ is reduced to Pd and $CuCl_2$ is reduced to Cu(I)

T P Varun (JEE 2012, AIR 64)

2.3 From Grignard's Reagent

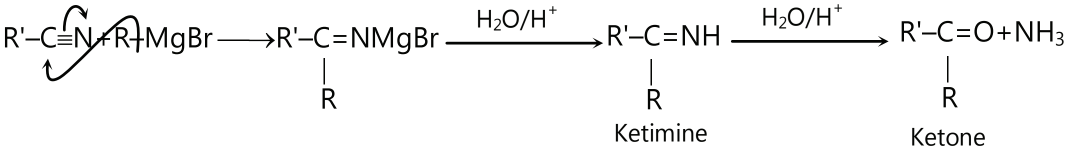
(a) Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives an aldehyde via aldimine



$$H{-}C{\equiv}N+R{-}MgBr \longrightarrow \underset{\displaystyle R}{\underset{|}{H{-}C}}{=}NMgBr \xrightarrow{H_2O/H^+} \underset{\displaystyle R}{\underset{|}{H{-}C}}{=}NH \xrightarrow{H_2O/H^+} \underset{\displaystyle R}{\underset{|}{H{-}C}}{=}O+NH_3$$

Aldimine Aldehyde

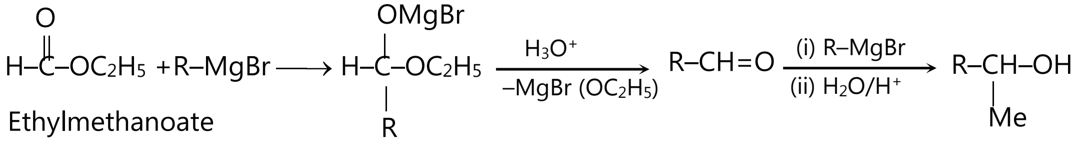
Alkylcyanide by using above process gives ketone via ketimine



$$R'{-}C{\equiv}N+R{-}MgBr \longrightarrow \underset{\displaystyle R}{\underset{|}{R'{-}C}}{=}NMgBr \xrightarrow{H_2O/H^+} \underset{\displaystyle R}{\underset{|}{R'{-}C}}{=}NH \xrightarrow{H_2O/H^+} \underset{\displaystyle R}{\underset{|}{R'{-}C}}{=}O+NH_3$$

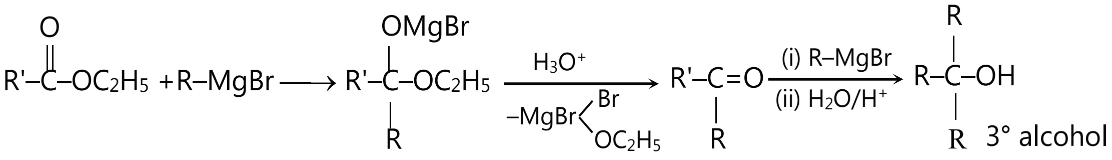
Ketimine Ketone

(b) Alkylformate with Grignard reagent gives 2° alcohol via aldehyde while alkyl alkanoate under similar condition gives 3° alcohol via ketone



$$H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5+R{-}MgBr \longrightarrow H{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}{-}OC_2H_5 \xrightarrow[-MgBr\,(OC_2H_5)]{H_3O^+} R{-}CH{=}O \xrightarrow[(ii)\ H_2O/H^+]{(i)\ R{-}MgBr} R{-}\underset{\underset{\displaystyle Me}{|}}{CH}{-}OH$$

Ethylmethanoate



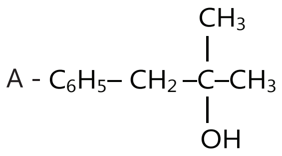
$$R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5+R{-}MgBr \longrightarrow R'{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle OMgBr}{|}}{C}}{-}OC_2H_5 \xrightarrow[-MgBr\langle^{Br}_{OC_2H_5}]{H_3O^+} \underset{\underset{\displaystyle R}{|}}{R'{-}C}{=}O \xrightarrow[(ii)\ H_2O/H^+]{(i)\ R{-}MgBr} R{-}\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{C}}{-}OH$$

3° alcohol

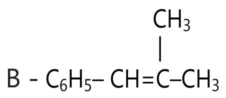
Illustration 6: Complete the following reaction:

$$C_6H_5CH_2CO_2CH_3 \xrightarrow[H_2O]{(i)CH_3MgBr(excess)} A \xrightarrow[\Delta]{H_2SO_4} B$$ **(JEE MAIN)**

Sol: First step is attack of Grignard reagent to form an alcohol, as the starting compound is an ester we end up getting a tertiary alcohol which on treatment with Acid gives an alkene.



$$A - C_6H_5-CH_2-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}-CH_3$$

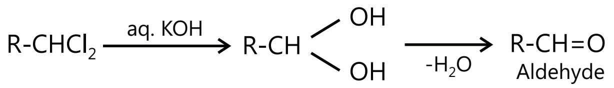


$$B - C_6H_5-CH=\overset{\overset{\large CH_3}{|}}{C}-CH_3$$

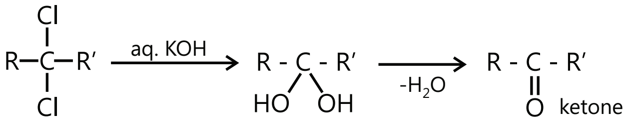
2.4 From Miscellaneous Groups

2.4.1 On Aqueous Alkali Hydrolysis of Gem Di-Halides

Terminal gem dihalides will give an aldehyde while a non-terminal will give ketones as follows

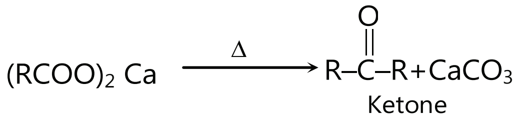


$$R\text{-}CHCl_2 \xrightarrow{aq.\ KOH} R\text{-}CH\begin{matrix} OH \\ OH \end{matrix} \xrightarrow[-H_2O]{} \underset{\text{Aldehyde}}{R\text{-}CH{=}O}$$



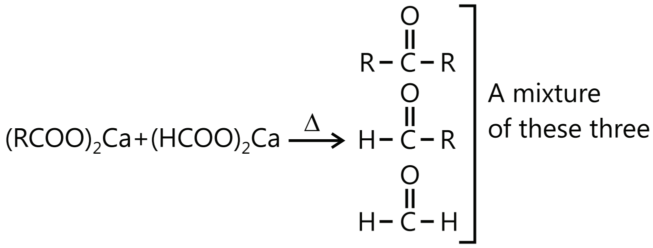
$$R-\overset{\overset{\large Cl}{|}}{\underset{\underset{\large Cl}{|}}{C}}-R' \xrightarrow{aq.\ KOH} R\text{ - }\underset{HO\ \ OH}{C}\text{ - }R' \xrightarrow[-H_2O]{} R\text{ - }\underset{\underset{\large O}{||}}{C}\text{ - }R' \text{ ketone}$$

2.4.2 By Dry Distillation of Calcium Salts of Acid



$$(RCOO)_2\,Ca \xrightarrow{\Delta} \underset{\text{Ketone}}{R-\overset{\overset{\large O}{||}}{C}-R} + CaCO_3$$

On the dry distillation of calcium salt of acid with the calcium salt of formic acid we get a mixture of aldehyde, ketone and formaldehyde



$$(RCOO)_2Ca+(HCOO)_2Ca \xrightarrow{\Delta} \left.\begin{matrix} R-\overset{\overset{\large O}{||}}{C}-R \\ H-\overset{\overset{\large O}{||}}{C}-R \\ H-\overset{\overset{\large O}{||}}{C}-H \end{matrix}\right] \text{A mixture of these three}$$

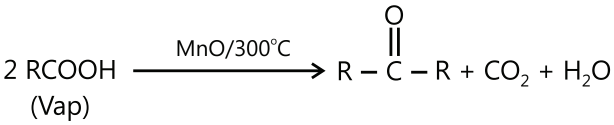
MASTERJEE CONCEPTS

In this reaction, the yield is generally poor due to side reactions viz. formation of formaldehyde and acetone from calciumformate and calcium acetate respectively.

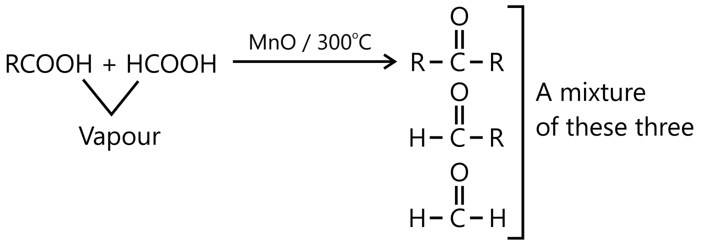
Aishwarya Karnawat (JEE 2012, AIR 839)

2.4.3 On Passing Vapours of Fatty Acids Over Manganous Oxide at 300°C

On passing the mixture of vapours of the fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.



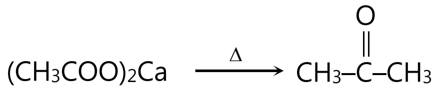
$$\underset{(Vap)}{2\,RCOOH} \xrightarrow{MnO/300^{\circ}C} R-\overset{\overset{\large O}{||}}{C}-R + CO_2 + H_2O$$



$$\underset{\text{Vapour}}{RCOOH + HCOOH} \xrightarrow{MnO\ /\ 300^{\circ}C} \left.\begin{array}{l} R-\overset{O}{\overset{\|}{C}}-R \\ H-\overset{O}{\overset{\|}{C}}-R \\ H-\overset{O}{\overset{\|}{C}}-H \end{array}\right] \text{A mixture of these three}$$

Illustration 7: Complete the following reaction: $(CH_3COO)_2Ca \xrightarrow{\Delta}$ **(JEE MAIN)**

Sol: This method is commonly used for the preparation of a ketone.

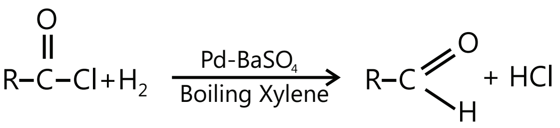


$$\underset{\text{Calcium Acetate}}{(CH_3COO)_2Ca} \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2.5 Methods Used for the Preparation of Aldehydes Only

2.5.1 Rosenmund's Reaction

Here, acid chlorides are reduced to aldehyde With H_2 in boiling xylene using palladium as a catalyst supported on barium sulphate.



$$R-\overset{O}{\overset{\|}{C}}-Cl+H_2 \xrightarrow[\text{Boiling Xylene}]{Pd\text{-}BaSO_4} R-C\begin{smallmatrix} \diagup\!\!\!\!= O \\ \diagdown H \end{smallmatrix} + HCl$$

MASTERJEE CONCEPTS

- Pd catalyst is poisoned by $BaSO_4$ to stop further reduction of aldehyde to alcohol.
- Formaldehyde (HCHO) can't be obtained by this method because HCOCl is unstable at room temperature.
- On reacting acid chloride with dialkyl cadmium, we can obtain ketone.

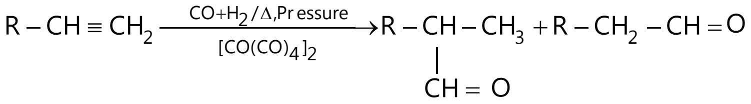
Saurabh Chaterjee (JEE Advanced 2013, AIR)

2.5.2 Stephen's Reduction

$$R-C\equiv N \xrightarrow{SnCl_2/HCl} \underset{\text{Aldimine hydrochloride}}{R-CH=NHHCl} \xrightarrow{H_2O} R-CH=O+NH_4Cl$$

2.5.3 Oxo Process

The Oxo process is also called carbonylation, here the alkene with water gas at high temperature and pressure in the pressure of cobalt carbonyl catalyst to give aldehyde.

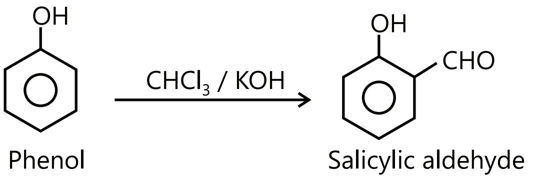


$$R-CH\equiv CH_2 \xrightarrow[{[CO(CO)_4]_2}]{CO+H_2/\Delta,\text{Pressure}} R-\underset{\underset{CH=O}{|}}{CH}-CH_3 + R-CH_2-CH=O$$

2.5.4 Reimer-Teimann Reaction

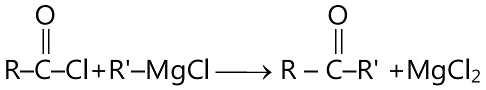
By this, a phenolic aldehyde is prepared

By this method phenolic aldehyde is prepared



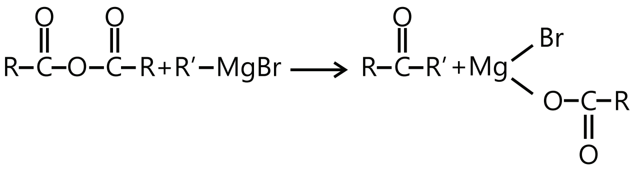
2.6 Methods used for the Preparation of Ketones

(a) Using alkanoyl chloride and Grignard reagent

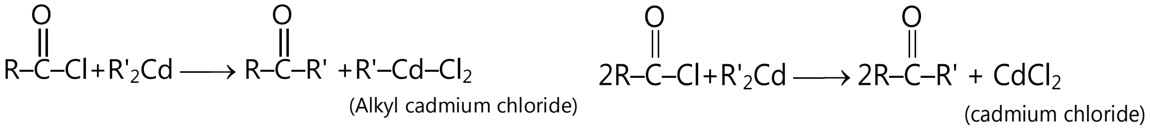


$$R-\overset{O}{\overset{\|}{C}}-Cl+R'-MgCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + MgCl_2$$

(b) Using alkanoic anhydride and Grignard reagent



(c) Using alkanoyl chloride and dialkyl cadmium



$$R-\overset{O}{\overset{\|}{C}}-Cl+R'_2Cd \longrightarrow R-\overset{O}{\overset{\|}{C}}-R' + R'-Cd-Cl_2 \qquad 2R-\overset{O}{\overset{\|}{C}}-Cl+R'_2Cd \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-R' + CdCl_2$$

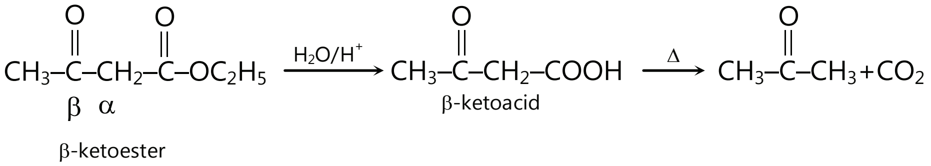
(Alkyl cadmium chloride)

(cadmium chloride)

(d) By acylation or benzoylation of aromatic hydrocarbon (Friedel-Craft Reaction)

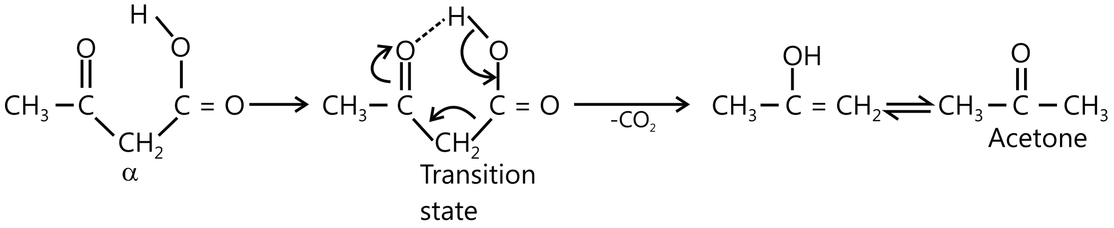
$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{Dry} \underset{\text{(Acetophenone)}}{C_6H_5COCH_3} + HCl; \; C_6H_6 + C_6H_5COCl \xrightarrow[AlCl_3]{Dry} \underset{\text{(Benzophenone)}}{C_6H_5COC_6H_5} + HCl$$

(e) By acid hydrolysis followed by heating of β-Ketoester



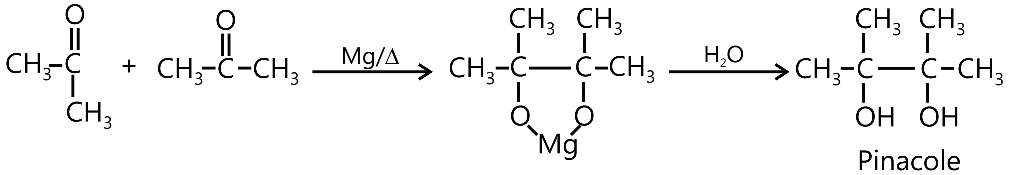
$$\underset{\beta\text{-ketoester}}{CH_3-\underset{\beta}{\overset{O}{\overset{\|}{C}}}-\underset{\alpha}{CH_2}-\overset{O}{\overset{\|}{C}}-OC_2H_5} \xrightarrow{H_2O/H^+} \underset{\beta\text{-ketoacid}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOH} \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-CH_3+CO_2$$

Note: It is β-ketoacid which decarboxylate more readily as it proceeds via six membered cyclic transition-state.



2.7 Pinacol – Pinacolone Rearrangement

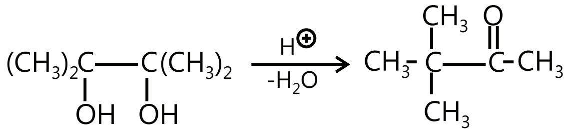
Pinacole is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water



$$CH_3-\underset{CH_3}{\overset{O}{\overset{\|}{C}}} + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{Mg/\Delta} CH_3-\underbrace{\overset{CH_3}{\underset{O}{C}}-\overset{CH_3}{\underset{O}{C}}}_{Mg}-CH_3 \xrightarrow{H_2O} CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

Pinacole

Pinacole undergoes rearrangement in acidic media to give pinacolone



$$(CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2 \xrightarrow[-H_2O]{H^{\oplus}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

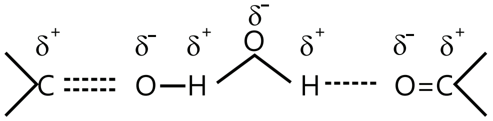
Pinacole Pinacolone

3. PHYSICAL PROPERTIES OF CARBONYL COMPOUNDS

(a) Physical state: Methanal is a pungent smelling gas. Ethanal is a volatile liquid, with a boiling point of 294 K. Other aldehydes and ketones containing up to 11 carbon atoms are colourless liquids while higher members are solids.

(b) Smell: With the exception of lower aldehydes which have unpleasant odours, aldehydes and ketones generally have a pleasant smell. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehyde and ketones have been used in the blending of perfumed and flavourings agents.

(c) Solubility: Aldehydes and ketones up to 4 C-atoms are miscible with water. This is due to the presence of hydrogen bonding between the polar carbonyl group and water molecules as shown below:

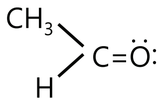


With the increase in the size of alkyl group, the solubility decreases. All aldehydes and ketones are, however, soluble in organic solvents such as ether, alcohol, etc. The ketones are good solvents themselves.

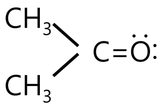
(d) Boiling points: The boiling points of aldehydes and ketones are higher than those of non-polar compounds (hydrocarbons) or weakly polar compounds (such as ethers) of comparable molecular masses. However, their b.p.s' are lower than those of corresponding alcohols or carboxylic acids. This is because all aldehydes and ketones are polar compounds having sufficient intermolecular dipole-dipole interaction between the opposite ends of C = O dipoles.

However, these dipole-dipole interactions are weaker than the intermolecular hydrogen bonding in alcohols and carboxylic acids. Therefore, b.p.s' of aldehydes and ketones are relatively lower than the alcohols and carboxylic acids of comparable molecular masses.

Among the carbonyl compounds, ketones have a slightly higher boiling points than the isomeric aldehydes. This is due to the presence of two electron releasing groups around the carbonyl carbon, which makes them more polar.



Acetadehyde
(μ = 2.52 D, bpt = 322 K)



Acetone
(μ = 2.88 D, bpt = 329 K)

(e) Density: Density of aldehydes and ketones is less than that of water

4. CHEMICAL REACTIONS OF CARBONYL COMPOUNDS

4.1 Nucleophilic Addition Reactions

Addition of a nucleophile and a proton across the (C = O) double bond. The reactivity of the carbonyl group arises from the electronegativity of the oxygen atom and the resulting polarization of the carbon-oxygen double bond. The electrophilic carbonyl carbon atom is sp^2 hybridized and flat, leaving it relatively unhindered and open to attack from either face of the double bond.

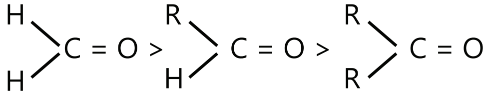


Illustration 8: Why are aldehydes more reactive than ketones? **(JEE ADVANCED)**

Sol: The factors which influence the reactivity of ketone and aldehyde are

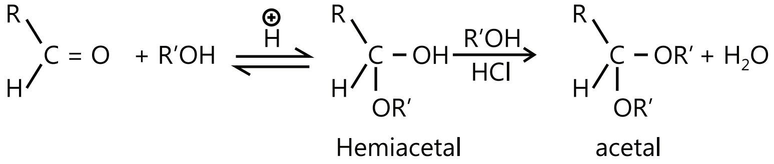
(i) Inductive effect (ii) Steric factor

(i) As alkyl group is electron releasing,+ I effect of alkyl group decreases the amount of charge on C^+ ($C^+ - O^-$). in ketones.

(ii) Steric effect (crowding of bulky group) also causes the less reactivity of carbonyl group of ketone.

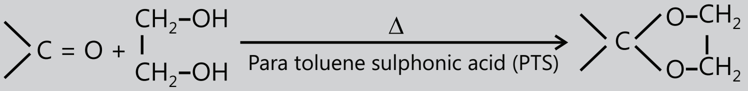
4.1.1 Reaction with Alcohols

Carbonyl compounds react with alcohols in the presence of dry HCl gas to give acetal (if aldehyde) and ketal if ketone via formation of unstable hemiacetal and hemiketal respectively.

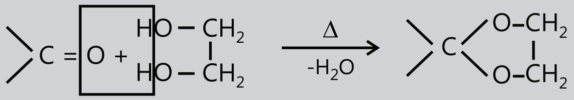


MASTERJEE CONCEPTS

- Acetal is formed to protect aldehyde (as a functional group) and ketal to protect ketone for a long time. Acetal has a functional group 'Ether'.
- Acetal can be decomposed to original Aldehyde by dilute acids.
- On treating with ethylene glycol we get cyclic acetal or ketal (1, 3-dioxolane)



Mechanism

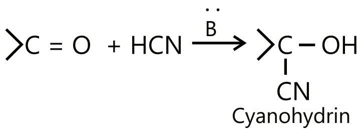


- Acetal formation is found to be more favourable than ketal formation if both the carbonyl groups are present within the molecule.

Mredul Sharda (JEE Advanced 2013, AIR)

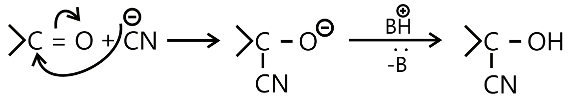
4.1.2 Addition of HCN

It Is a Base Catalyzed Addition



$$>C=O + HCN \xrightarrow{\ddot{B}} >\underset{\underset{\text{Cyanohydrin}}{CN}}{\underset{|}{C}}-OH$$

$$H-C\equiv N \xrightarrow{\ddot{B}} \overset{\oplus}{B}H + \overset{\ominus}{C}N$$



$$>C=O + \overset{\ominus}{C}N \longrightarrow >\underset{CN}{\underset{|}{C}}-O^{\ominus} \xrightarrow[-\ddot{B}]{\overset{\oplus}{B}H} >\underset{CN}{\underset{|}{C}}-OH$$

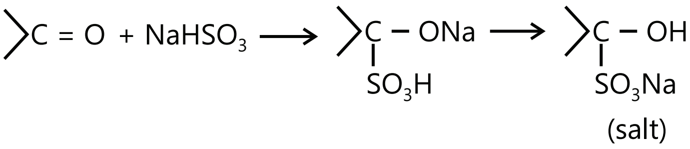
MASTERJEE CONCEPTS

- Addition of HCN over aldehyde gives cyanohydrin and cyanohydrin on acid hydrolysis gives α-hydroxy acid.
- Cyanohydrin on treating with NH_3 (ℓ) followed by acid hydrolysis gives α-amino acid
- In case of ketone cyanohydrin formation is reversible due to bulky group of ketone which hinders the formation.

Vaibhav Krishnan (JEE 2009, AIR 22)

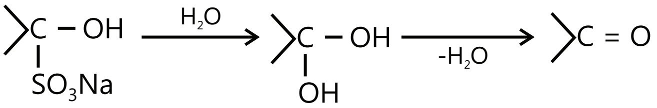
4.1.3 Addition of Sodium Bisulphite ($NaHSO_3$)

This addition is used to isolate carbonyl compounds from the mixture as we get a salt.



$$>C=O + NaHSO_3 \longrightarrow >\underset{SO_3H}{\underset{|}{C}}-ONa \longrightarrow >\underset{\underset{\text{(salt)}}{SO_3Na}}{\underset{|}{C}}-OH$$

The salt on acidification gives carbonyl compounds again

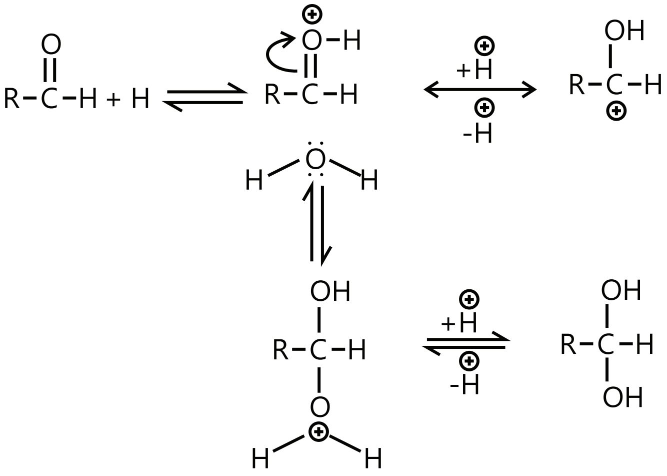


$$>\underset{SO_3Na}{\underset{|}{C}}-OH \xrightarrow{H_2O} >\underset{OH}{\underset{|}{C}}-OH \xrightarrow[-H_2O]{} >C=O$$

4.1.4 Addition of Water

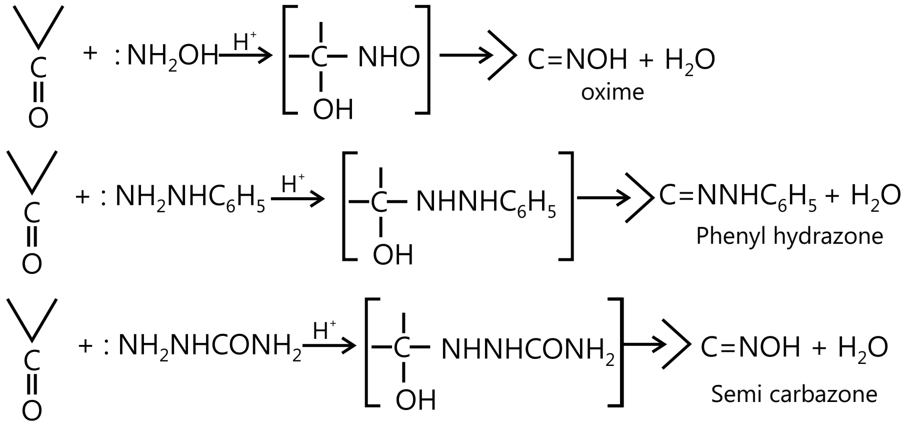
Aldehydes or ketones react with water to form gem-diols. Water is a poor nucleophile and therefore adds relatively slowly to the carbonyl group, but the rate of reaction can be increased by an acid catalyst. Reaction is reversible so removal of water gives back the corresponding carbonyl compound.

Mechanism:



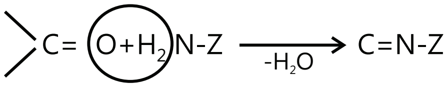
4.2 Addition Elimination Reactions

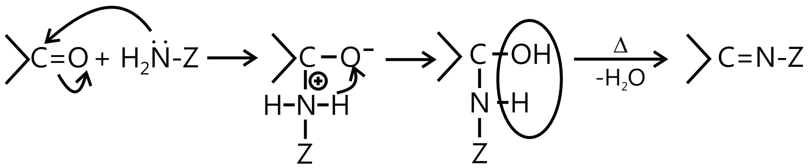
Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and ketones, the product contains a carbon nitrogen double bond resulting from the elimination of a molecule of water from the initial addition products.



Reaction with ammonia derivatives ($H_2\ddot{N}$–Z)**:**

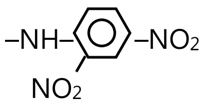
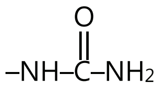
This reaction is a nucleophilic addition followed by water elimination.



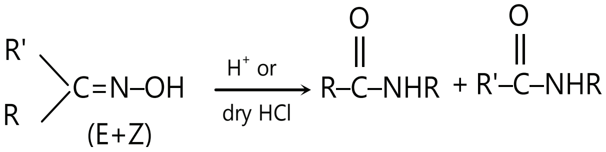


This reaction is carried out in slightly acidic media which will generate a nucleophilic centre for weak base ammonia derivatives. On using strong acidic media lone pair of electrons present at N-atom of ammonia derivatives will accept a proton forming protonated ammonia derivatives which cannot act as a nucleophile for a carbonyl carbon.

$$> CO + H_2N - Z \longrightarrow\ > C = N - Z$$

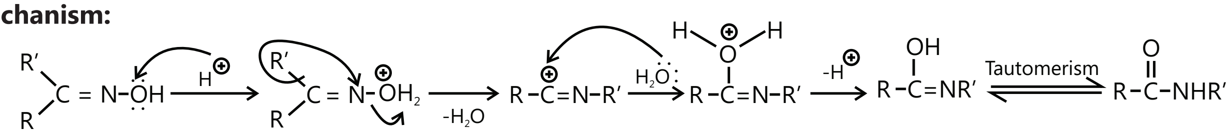
Z		
–OH	Hydroxylamine →	Oxime
–NH	Hydrazine →	Hydrazone
$-NH-C_6H_5$	Phenylhydrazine →	Phenylhydrazone
	2, 4-dinitrophenylhydrazine → (Brandy's reagent) or 2, 4-DNP	2, 4-dinitrophenylhydrazone (Solid orange precipitate)
 $-NH-\overset{O}{\overset{\|}{C}}-NH_2$	Semicarbazide →	Semicabazone

4.3 Beckmann's Rearrangement in Oxime



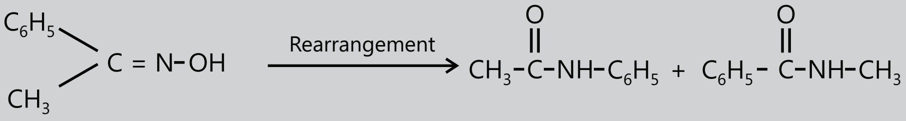
(If R′ is bulkier than R)

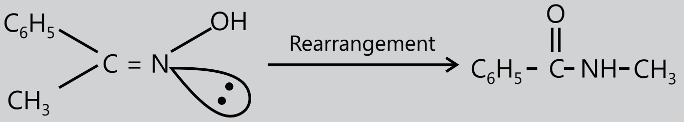
Mechanism:



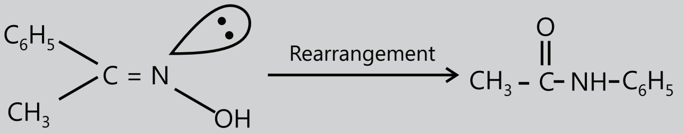
MASTERJEE CONCEPTS

- Brady's reagent is used to distinguish carbonyl compounds from the mixture
- Oxime undergoes Beckmann rearrangement to give its isomer amide.
- In this reaction, the group which is anti –OH group migrates.





(-CH_3 is anti to -OH)

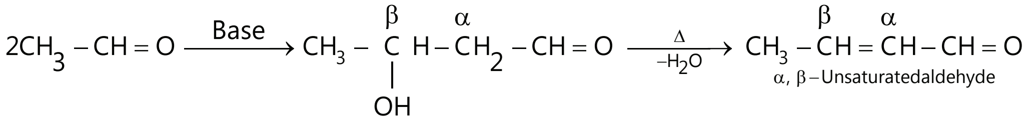


(-C_6H_5 is anti to -OH)

Nikhil Khandelwal (JEE 2009, AIR 94)

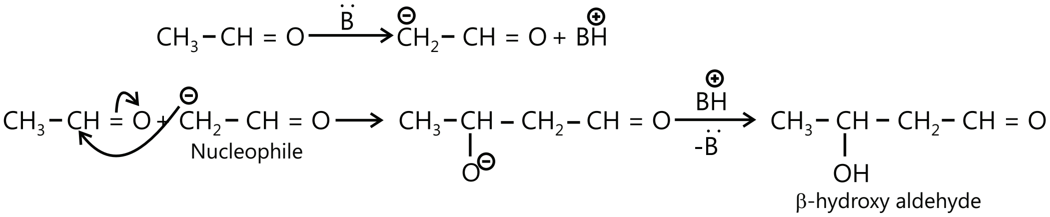
4.4 Aldol Condensation

It is condensation between two moles of carbonyl compounds among which at least one must have α-hydrogen atom in dilute basic media to get α, β-unsaturated aldehyde / ketone via the formation of β-hydroxy aldehyde / ketone.

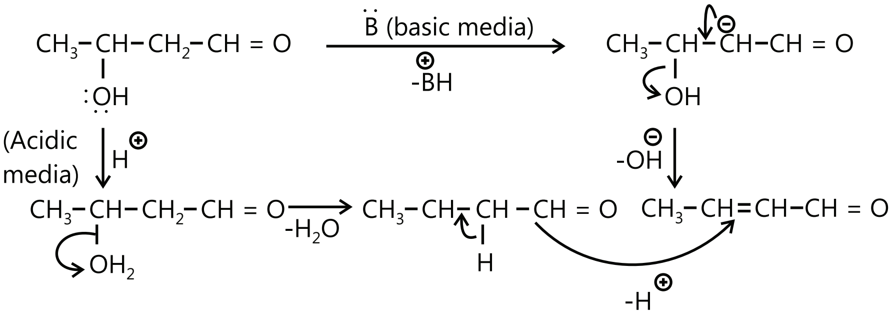


$$2CH_3-CH=O \xrightarrow{\text{Base}} CH_3-\underset{\underset{OH}{|}}{\overset{\beta}{C}}H-\overset{\alpha}{C}H_2-CH=O \xrightarrow[-H_2O]{\Delta} CH_3-\overset{\beta}{C}H=\overset{\alpha}{C}H-CH=O$$

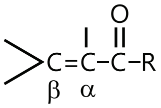
Mechanism:



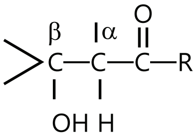
From β-hydroxy aldehyde/ ketone, water is eliminated on using either acidic or basic media.-



Now try to get carbonyl compounds from α,β-unsaturated carbonyl compounds as - keep 'H' at α-position and –OH at β-position of α, β- unsaturated carbonyl compound to get β-hydroxy carbonyl compound.

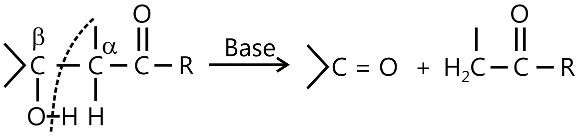


α,β-unsaturated
carbonyl compound

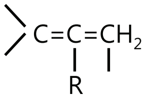


β-hydroxy carbonyl
compound

Now break α and β carbon shown below to get carbonyl compound.



These two carbonyl compounds can be obtained on the ozonolysis of hydrocarbon



4.4.1 Cross Aldol Condensation

On using two type of carbonyl compounds both having α-hydrogen atoms we get a mixture of four condensed products because two types of carbonyl compounds will give two type of carbanions which will be nucleophile for itself and the other molecule.

On using formaldehyde and acetaldehyde during the crossed aldol, all the α-hydrogen atom of acetaldehyde are replaced one by one by the hydroxymethyl group because of the smaller size of formaldehyde to give trihydroxymethylacetaldehyde which undergoes crossed Cannizaro's reaction with formaldehyde to give tetrahydroxymethyl methane and formate ion as a final product

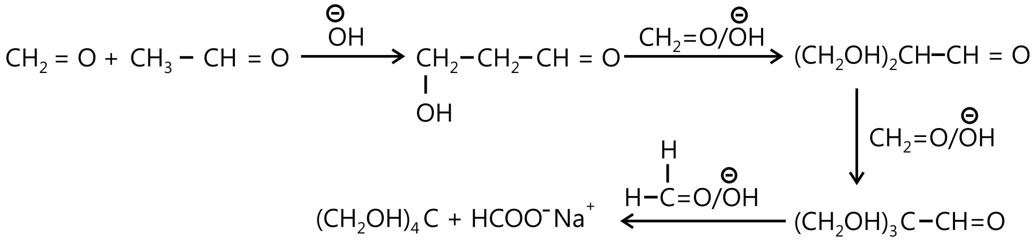
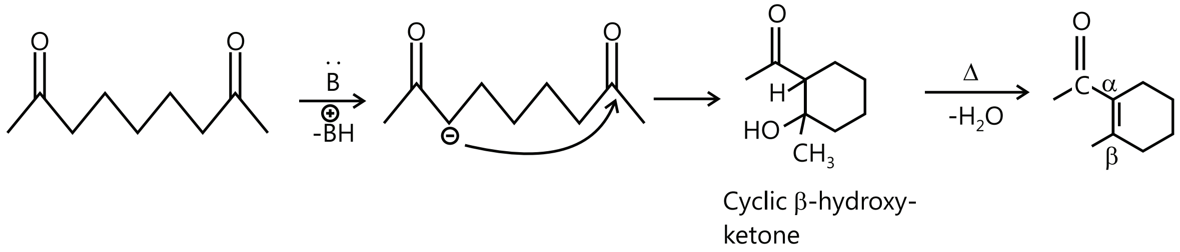


Illustration 9: Show how cinnamaldehyde is prepared by crossed aldol condensation? **(JEE MAIN)**

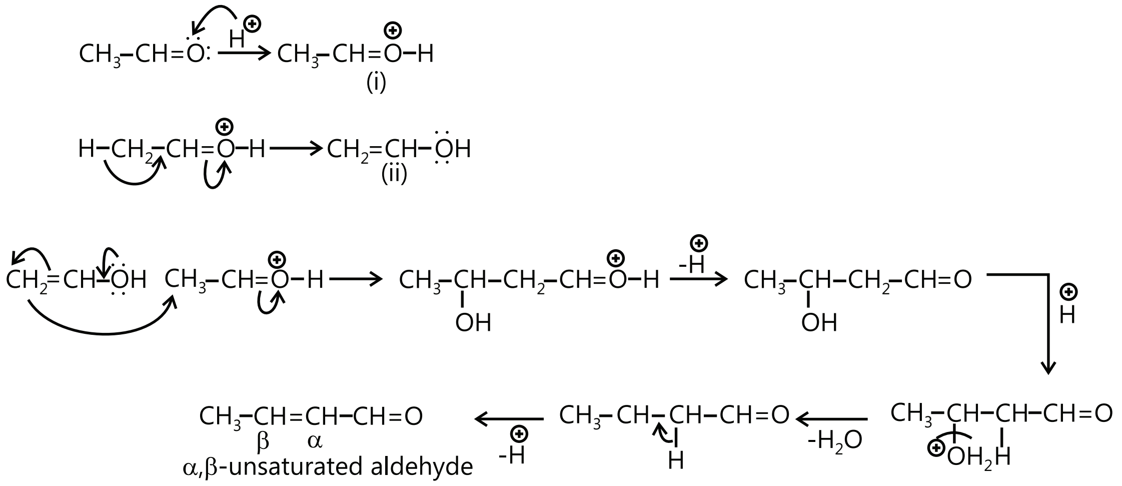
Sol: $C_6H_5CHO + CH_3CHO \xrightarrow[(-H_2O)]{OH^-} \underset{\text{Cinnamaldehyde}}{C_6H_5CH = CH-CHO} + H_2O$

4.4.2 Intramolecular Aldol Condensation

If two carbonyl groups with α-hydrogen atoms are present within the same molecule, then we get cyclic α, β-unsaturated aldehyde / ketones via the formation of cyclic β-hydroxy aldehyde/ketone in presence of basic media



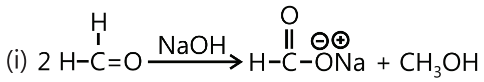
By knowing the product we can get the reactant as in case of intermolecular aldol condensation: Aldol condensation also takes place in acidic media too -



4.5 Cannizaro Reaction

Carbonyl compounds without α-hydrogen atoms undergo disproportionation or redox reactions in strong basic media.

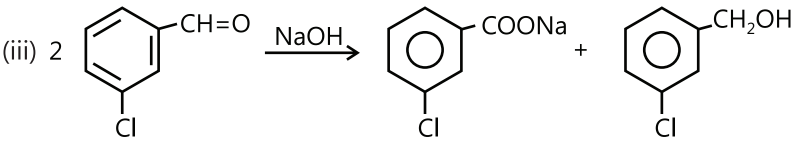
The reactions are intermolecular Cannizzaro reactions



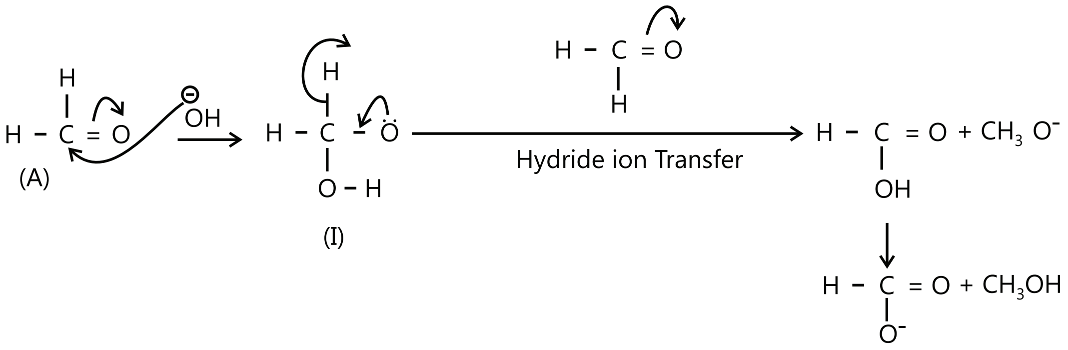
$$\text{(i)}\ 2\,H-\overset{H}{\overset{|}{C}}=O \xrightarrow{NaOH} H-\overset{O}{\overset{\|}{C}}-\overset{\ominus\oplus}{ONa} + CH_3OH$$

$$\text{(ii)}\ 2\,C_6H_5CH=O \xrightarrow{NaOH} \underset{\text{Sodiumbenzoate}}{C_6H_5CO\overset{\ominus\oplus}{ONa}} + \underset{\text{Benzylalcohol}}{C_6H_5CH_2OH}$$

(iii) 2



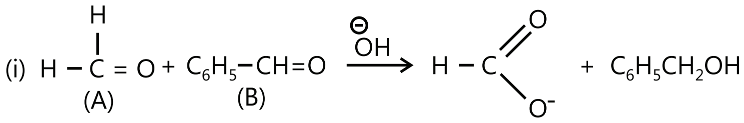
Mechanism: By this mechanism, it is clear that acid is corresponding to that carbonyl compound over which $\bar{O}H$ is going easily as a nucleophile

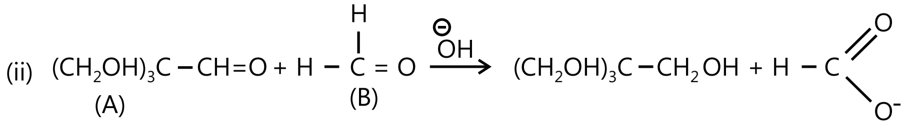


Note: It is observed that a hydride ion transfer from (I) to Carbonyl compound (B) is a rate determining step.

4.5.1 Crossed Cannizaro Reaction

On using two types of carbonyl compounds without α-hydrogen atom, the acid will be corresponding to that aldehyde over which $\bar{O}H$ will approach without any hindrance.

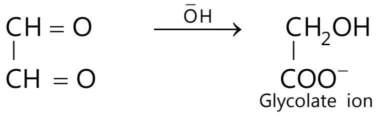




In case (i) , $\bar{O}H$ will easily go to (A) and in case (ii) it will go to (B) hence acid will be formate ion in both the cases.

4.5.2 Intramolecular Cannizaro Reaction

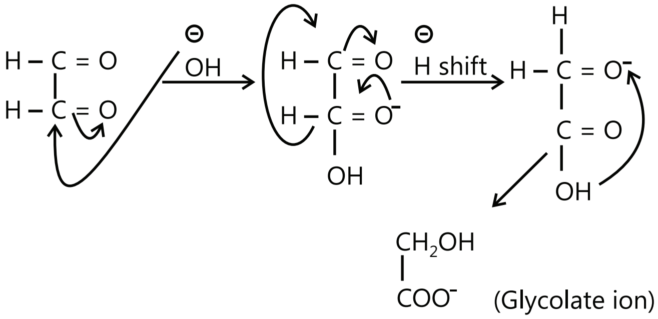
Here two carbonyl groups (without α-hydrogen atom) are present within the same molecule.



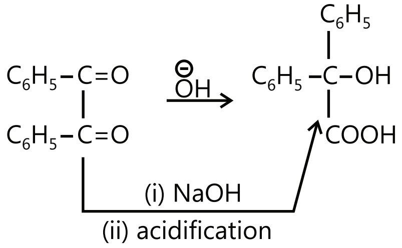
$$\begin{matrix} CH=O \\ | \\ CH=O \end{matrix} \xrightarrow{\bar{O}H} \begin{matrix} CH_2OH \\ | \\ COO^- \end{matrix}$$

Glycolate ion

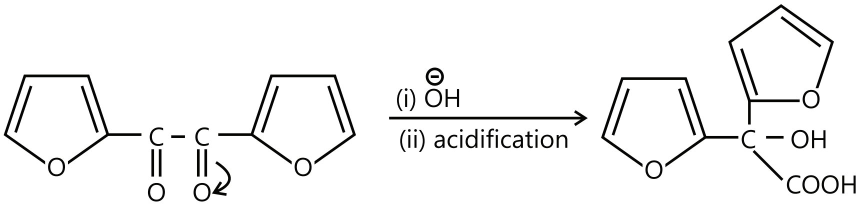
Mechanism:



4.5.3 Benzil – Benzilic Acid Rearrangement



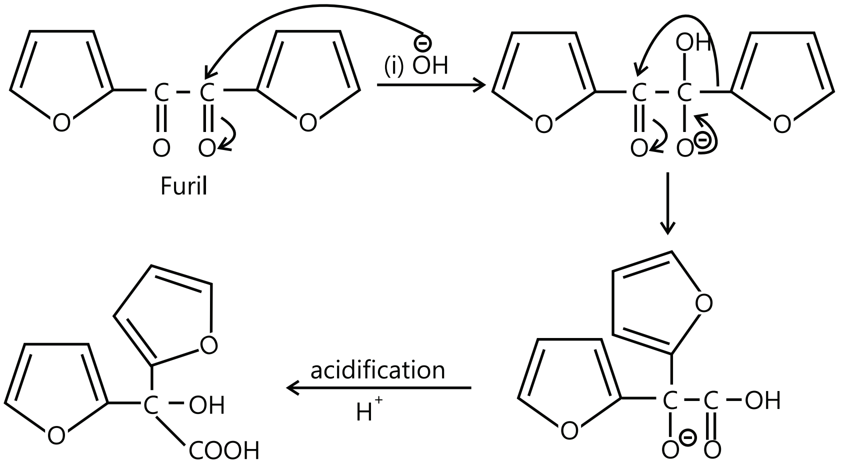
Other example is



Furil

Furilic acid

Mechanism:

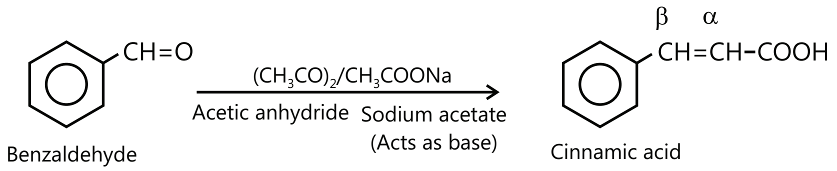


Furilic acid

Furilic acid

4.6 Perkin Reaction

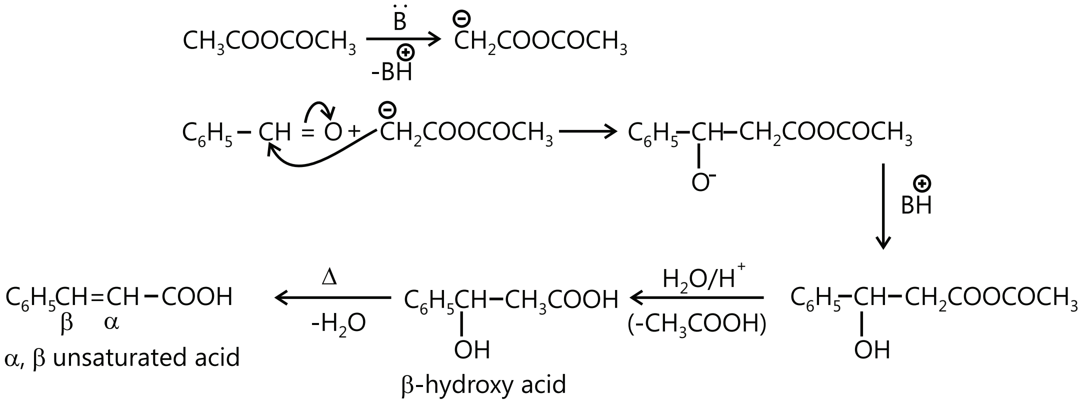
When an aromatic aldehyde like benzaldehyde is treated with an anhydride in the presence of the sodium salt of an acid from which an anhydride is derived we get α, β-unsaturated acid e.g.



Benzaldehyde

Cinnamic acid

Mechanism:



$$CH_3COOCOCH_3 \xrightarrow[-\overset{\oplus}{B}H]{\ddot{B}} \overset{\ominus}{C}H_2COOCOCH_3$$

$$C_6H_5-CH=O + \overset{\ominus}{C}H_2COOCOCH_3 \longrightarrow C_6H_5-\underset{O^-}{\underset{|}{C}H}-CH_2COOCOCH_3 \xrightarrow{\overset{\oplus}{B}H} C_6H_5-\underset{OH}{\underset{|}{C}H}-CH_2COOCOCH_3$$

$$C_6H_5-\underset{OH}{\underset{|}{C}H}-CH_2COOCOCH_3 \xrightarrow[(-CH_3COOH)]{H_2O/H^+} C_6H_5\underset{OH}{\underset{|}{C}H}-CH_3COOH \xrightarrow[-H_2O]{\Delta} \underset{\beta\quad\alpha}{C_6H_5CH=CH-COOH}$$

β-hydroxy acid

α, β unsaturated acid

MASTERJEE CONCEPTS

By knowing α, β-unsaturated acid we can get an idea about the anhydride used in the Perkin reaction. This can be done by keeping 'H' at α and –OH at β-carbon atom followed by breaking α, β carbon as given below. By this we can know about acid and it will be anhydride of this only.

Saurabh Gupta (JEE 2010, AIR 443)

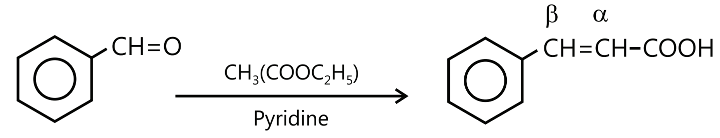
Illustration 10: Complete the reaction; $C_5H_5CHO + CH_3 - COOC_2H_5 \xrightarrow[\text{heat}]{NaOC_2H_5 \text{ in absolute } C_2H_5OH} (D)$ **(JEE MAIN)**

Sol: It is an example of Perkin reaction**.**

The product D is: (D) $C_6H_5-CH = CHCOOC_2H_5$

4.7 Knoevenagel Reaction

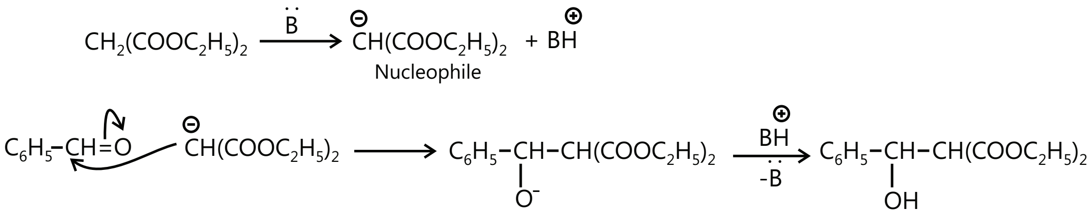
It is the preparation of α, β-unsaturated acid with a carbonyl compound using a malonic ester in the presence of a pyridine base



Benzaldehyde

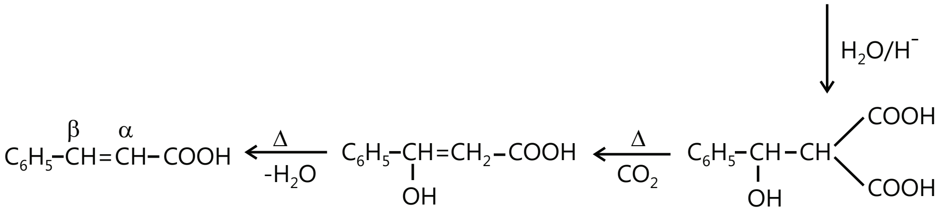
Cinnamic acid

Mechanism:



$$CH_2(COOC_2H_5)_2 \xrightarrow{\ddot{B}} \underset{\text{Nucleophile}}{\overset{\ominus}{C}H(COOC_2H_5)_2} + \overset{\oplus}{B}H$$

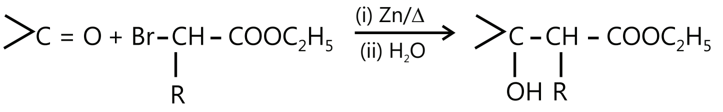
$$C_6H_5-CH=O \quad \overset{\ominus}{C}H(COOC_2H_5)_2 \longrightarrow C_6H_5-\underset{O^-}{\underset{|}{C}H}-CH(COOC_2H_5)_2 \xrightarrow[-\ddot{B}]{\overset{\oplus}{B}H} C_6H_5-\underset{OH}{\underset{|}{C}H}-CH(COOC_2H_5)_2$$



$$C_6H_5-\overset{\beta}{CH}=\overset{\alpha}{CH}-COOH \xleftarrow[-H_2O]{\Delta} C_6H_5-\underset{OH}{CH}-CH_2-COOH \xleftarrow[CO_2]{\Delta} C_6H_5-\underset{OH}{CH}-CH(COOH)_2$$

4.8 Reformatsky Reaction

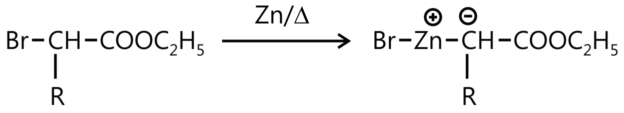
When a carbonyl compound and a halogenated ester are heated with zinc followed by treating it with water we get β-hydroxy ester.



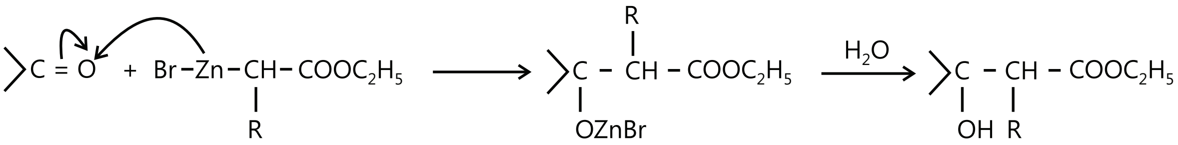
$$>C=O+Br-\underset{R}{CH}-COOC_2H_5 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } Zn/\Delta} >\underset{OH}{C}-\underset{R}{CH}-COOC_2H_5$$

α-halogenated ester α-halogenated ester

This reaction can be represented as -



$$Br-\underset{R}{CH}-COOC_2H_5 \xrightarrow{Zn/\Delta} Br-\overset{\oplus}{Zn}-\overset{\ominus}{\underset{R}{CH}}-COOC_2H_5$$

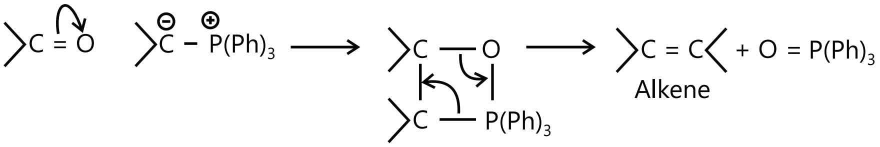


$$>C=O+Br-Zn-\underset{R}{CH}-COOC_2H_5 \longrightarrow >\underset{OZnBr}{C}-\overset{R}{CH}-COOC_2H_5 \xrightarrow{H_2O} >\underset{OH}{C}-\underset{R}{CH}-COOC_2H_5$$

β-hydroxyester

4.9 Wittig Reaction

The Wittig Reaction is used in order to get an alkene from a carbonyl compound using phosphourus ylide via the formation of cyclic structure betaine.

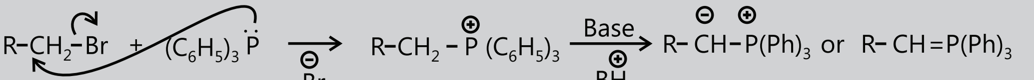


Alkene

Betaine

MASTERJEE CONCEPTS

Phosphourus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as -

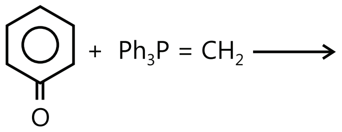


$$R-CH_2-Br+(C_6H_5)_3\ddot{P} \xrightarrow[-\overset{\ominus}{Br}]{} R-CH_2-\overset{\oplus}{P}(C_6H_5)_3 \xrightarrow[-\overset{\oplus}{B}H]{Base} R-\overset{\ominus}{CH}-\overset{\oplus}{P}(Ph)_3 \text{ or } R-CH=P(Ph)_3$$

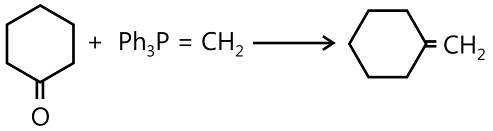
Phosphorous ylide

Neeraj Toshniwal (JEE 2009, AIR 21)

Illustration 11: Complete the following reaction: **(JEE MAIN)**

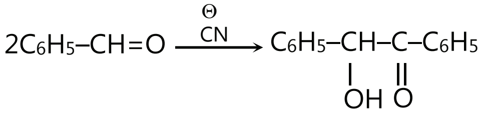


Sol: The above reaction is the Wittig reaction.



4.10 Benzoin Condensation

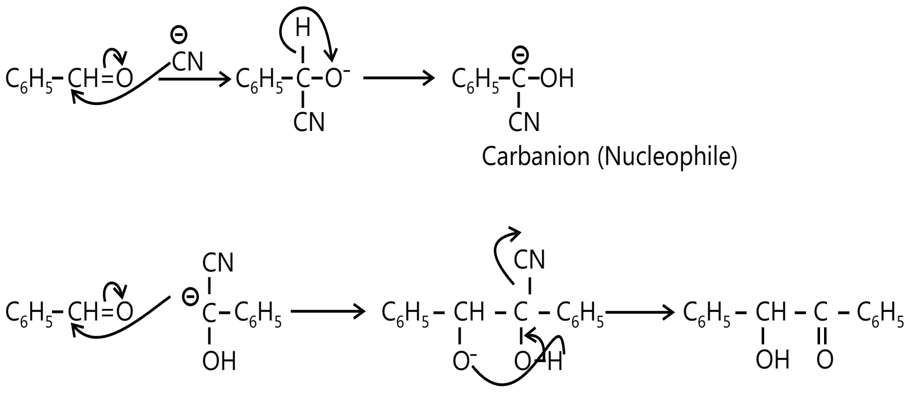
During this reaction, benzoin is obtained when an ethanolic solution of benzaldehyde is heated with a strong alkali like potassium cyanide or sodium cyanide.



$$2C_6H_5{-}CH{=}O \xrightarrow{\overset{\ominus}{CN}} C_6H_5{-}\underset{OH}{\underset{|}{CH}}{-}\underset{O}{\underset{||}{C}}{-}C_6H_5$$

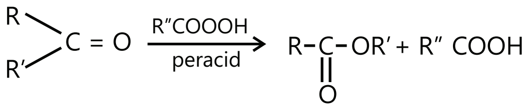
(Benzoin)

Reaction Mechanism:



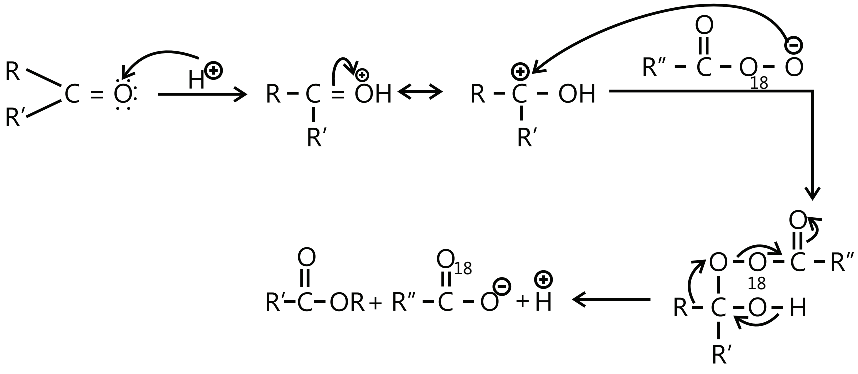
4.11 Baeyer-Villiger Oxidation

It is preparation of an ester from a ketone using peracid-



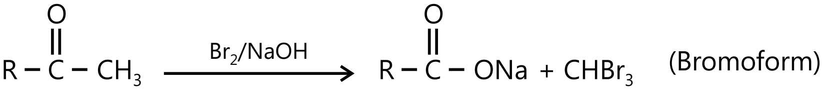
$$\begin{matrix}R\\R'\end{matrix}\!>C=O \xrightarrow[\text{peracid}]{R''COOOH} R{-}\underset{O}{\underset{||}{C}}{-}OR' + R''\ COOH$$

Mechanism:



4.12 Haloform Reaction

Acetaldehyde and methylalkyl ketones react rapidly with halogens (Cl_2, Br_2, or I_2) in the presence of an alkali to give a haloform and acid salt.

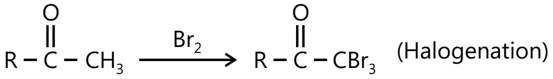


$$R-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{Br_2/NaOH} R-\overset{O}{\overset{||}{C}}-ONa + CHBr_3 \quad \text{(Bromoform)}$$

In this reaction $-CH_3$ of $CH_3-\overset{O}{\overset{||}{C}}-$ group is converted into a haloform, as it contains an acidic hydrogen atom and the rest of alkyl methyl ketone gives an acid salt having a carbon atom corresponding to alkyl ketone.

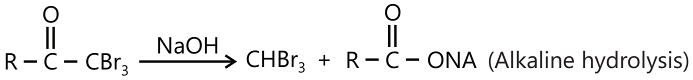
Preparation of haloform from methylketone involves two steps

(a) Halogenetion



$$R-\overset{O}{\overset{||}{C}}-CH_3 \xrightarrow{Br_2} R-\overset{O}{\overset{||}{C}}-CBr_3 \quad \text{(Halogenation)}$$

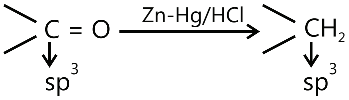
(b) Alkali hydrolysis



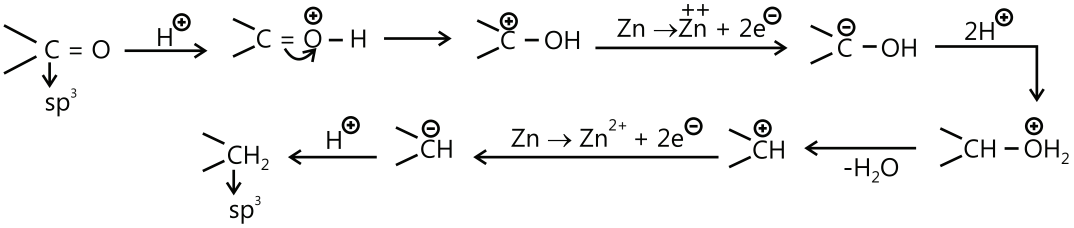
$$R-\overset{O}{\overset{||}{C}}-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-\overset{O}{\overset{||}{C}}-ONA \quad \text{(Alkaline hydrolysis)}$$

4.13 Clemmensen Reduction

Used to get alkane from carbonyl compounds.

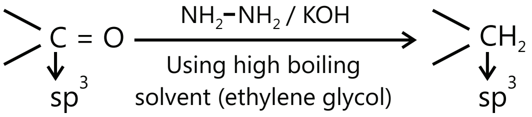


Mechanism:

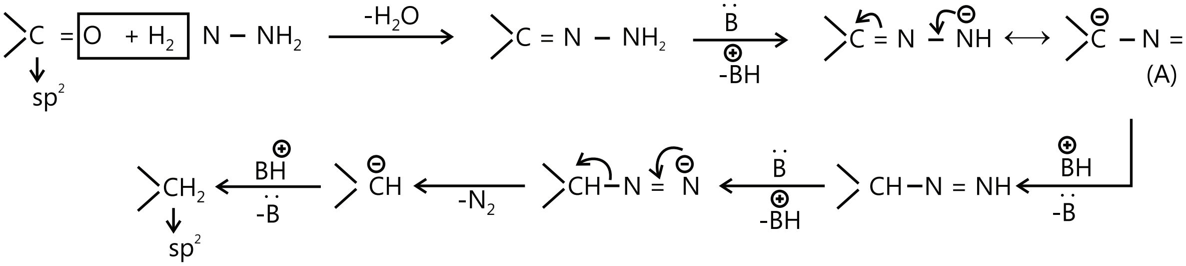


4.14 Wolf Kishner Reduction

Used to get alkane from carbonyl compounds

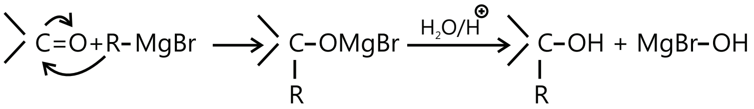


Mechanism:



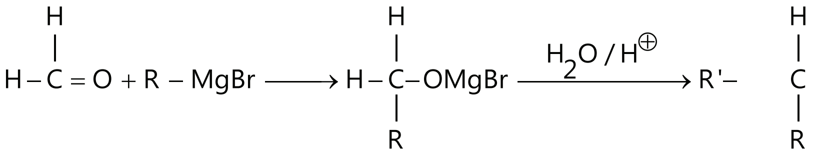
4.15 Addition of Grignard Reagent Over Carbonyl Compounds

It gives alcohol



$$>C=O+R-MgBr \longrightarrow >\underset{R}{C}-OMgBr \xrightarrow{H_2O/H^{\oplus}} >\underset{R}{C}-OH + MgBr-OH$$

(i) When formaldehyde is treated with Grignard reagent

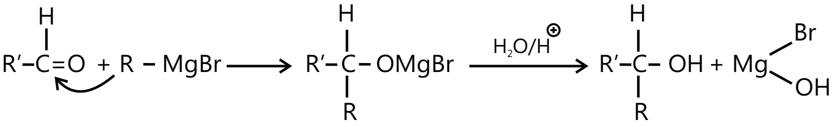


$$H-\overset{H}{C}=O+R-MgBr \longrightarrow H-\underset{R}{\overset{H}{C}}-OMgBr \xrightarrow{H_2O/H^{\oplus}} R'-\underset{R}{\overset{H}{C}}$$

1°alcohol

Followed by acid hydrolysis, a primary alcohol is obtained

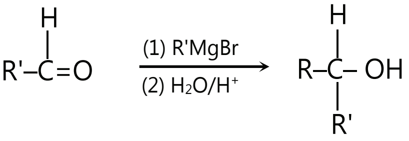
(ii) When an aldehyde except formaldehyde is treated with Grignard reagent followed by hydrolysis, we get 2° alcohol



$$R'-\overset{H}{C}=O + R-MgBr \longrightarrow R'-\underset{R}{\overset{H}{C}}-OMgBr \xrightarrow{H_2O/H^{\oplus}} R'-\underset{R}{\overset{H}{C}}-OH + Mg\begin{matrix}Br\\OH\end{matrix}$$

2° alcohol

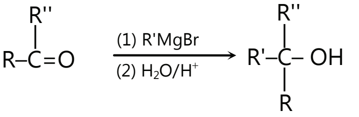
This 2° alcohol is also obtained as -



$$R'-\overset{H}{C}=O \xrightarrow[(2)\ H_2O/H^+]{(1)\ R'MgBr} R-\underset{R'}{\overset{H}{C}}-OH$$

2° alcohol

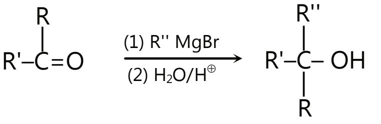
(iii) When a ketone is treated with Grignard reagent followed by acid hydrolysis, it gives 3° alcohol



$$R-\overset{R''}{C}=O \xrightarrow[(2)\ H_2O/H^+]{(1)\ R'MgBr} R'-\underset{R}{\overset{R''}{C}}-OH$$

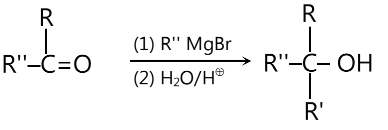
3° alcohol

This 3° alcohol is also obtained by using the following two methods



$$R'-\overset{R}{C}=O \xrightarrow[(2)\ H_2O/H^{\oplus}]{(1)\ R''\ MgBr} R'-\underset{R}{\overset{R''}{C}}-OH$$

3° alcohol



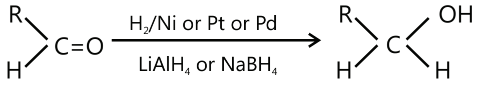
$$R''-\overset{R}{C}=O \xrightarrow[(2)\ H_2O/H^{\oplus}]{(1)\ R''\ MgBr} R''-\underset{R'}{\overset{R}{C}}-OH$$

3° alcohol

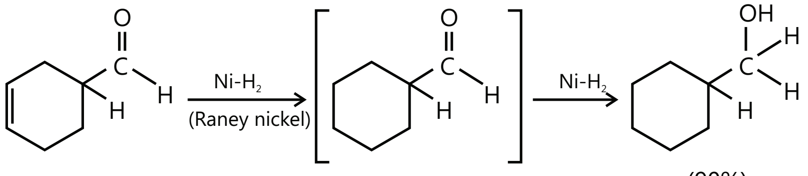
Note: 2° alcohol on oxidation gives a ketone

4.16 Reduction of Carbonyl Compounds

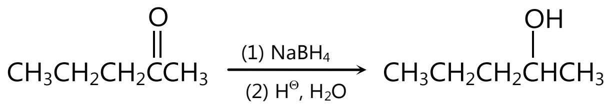
(a) Reduction to alcohols



e.g.

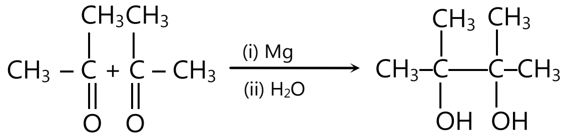


(90%)



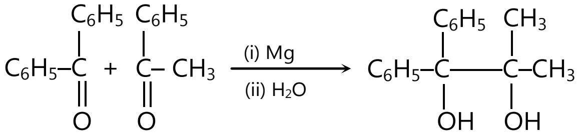
$$CH_3CH_2CH_2\overset{\overset{\Large O}{\|}}{C}CH_3 \xrightarrow[(2)\ H^{\ominus},\ H_2O]{(1)\ NaBH_4} CH_3CH_2CH_2\overset{\overset{\Large OH}{|}}{C}HCH_3$$

(b) Reduction to pinacols



$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}+\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ Mg} CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

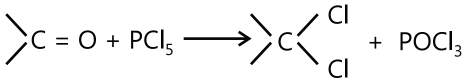
e.g.



$$C_6H_5-\underset{\underset{O}{\|}}{\overset{\overset{C_6H_5}{|}}{C}}+\underset{\underset{O}{\|}}{\overset{\overset{C_6H_5}{|}}{C}}-CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ Mg} C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{C_6H_5}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

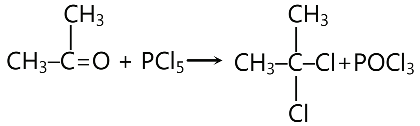
4.17 Reaction with PCl_5

Carbonyl compounds give geminal dihalides



(a) $CH_3CH{=}O+PCl_5 \rightarrow CH_3{-}CHCl_2+POCl_3$

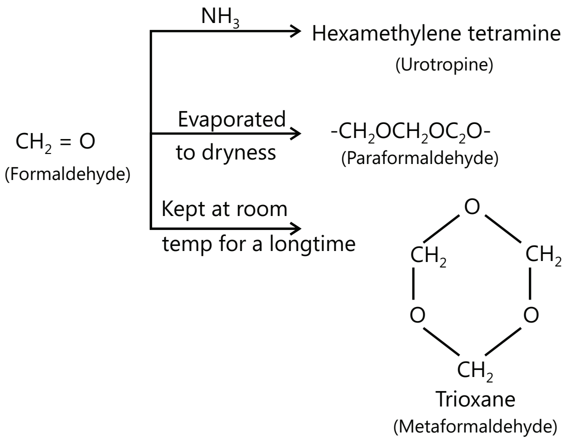
(b)



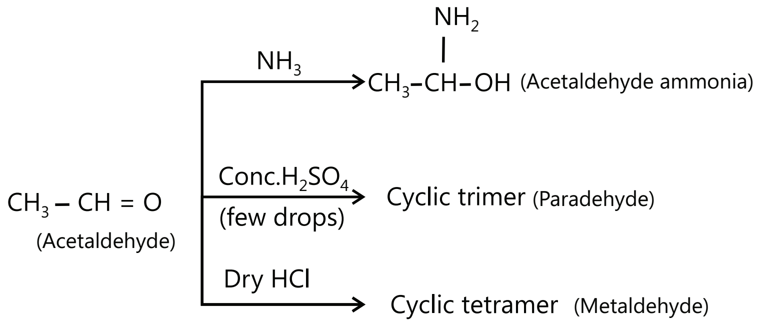
$$CH_3-\overset{\overset{CH_3}{|}}{C}{=}O + PCl_5 \longrightarrow CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl+POCl_3$$

4.18 Other Reactions

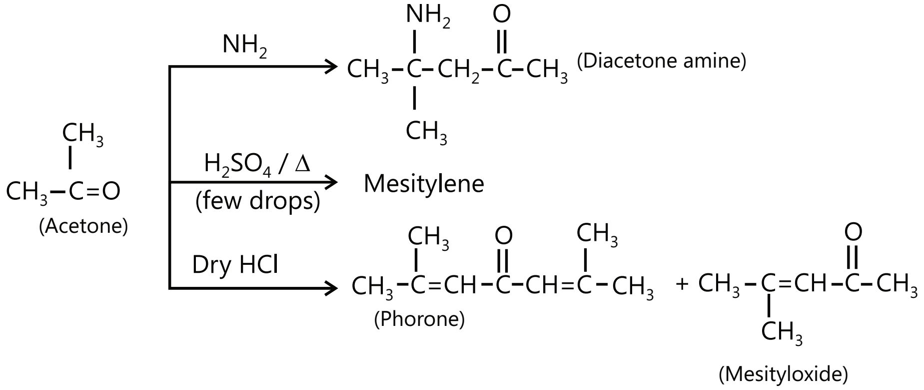
(a)



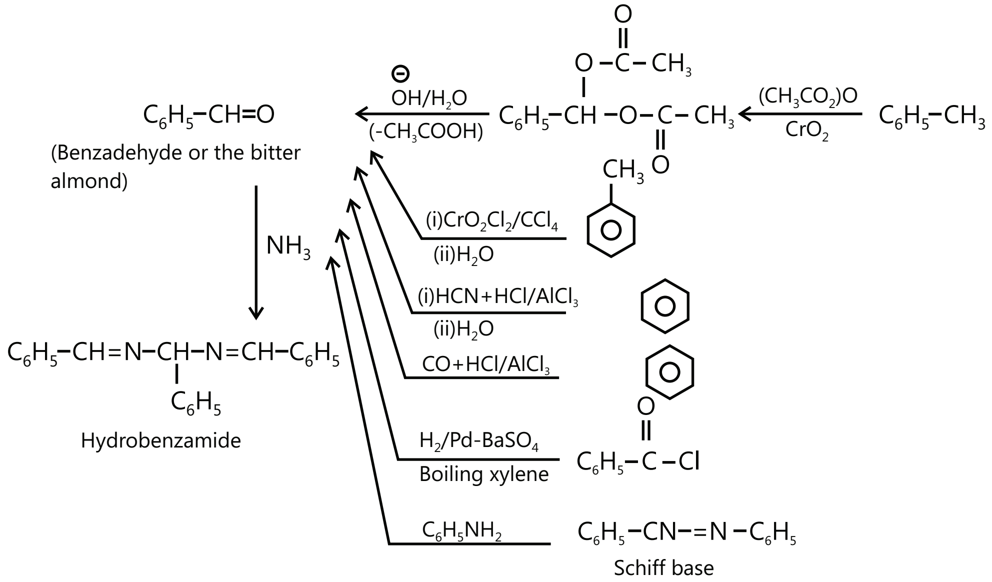
(b)


NH3
NH2
CH3–CH–OH (Acetaldehyde ammonia)
Conc.H2SO4
(few drops)
Cyclic trimer (Paradehyde)
CH3 – CH = O
(Acetaldehyde)
Dry HCl
Cyclic tetramer (Metaldehyde)

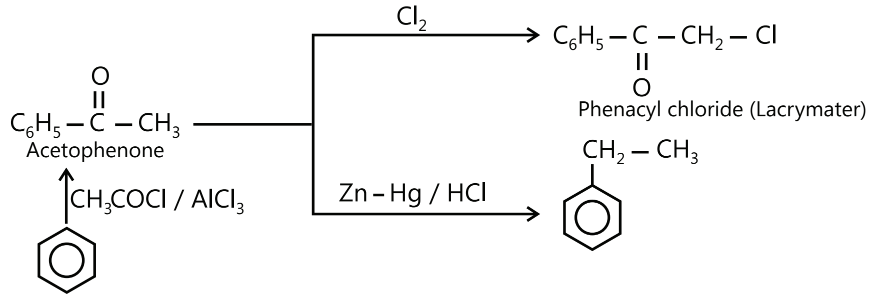
(c)


NH2
NH2 O
CH3–C–CH2–C–CH3 (Diacetone amine)
CH3
CH3
CH3–C=O
(Acetone)
H2SO4 / Δ
(few drops)
Mesitylene
Dry HCl
CH3 O CH3
CH3–C=CH–C–CH=C–CH3
(Phorone)
+ CH3–C=CH–C–CH3
O
CH3
(Mesityloxide)

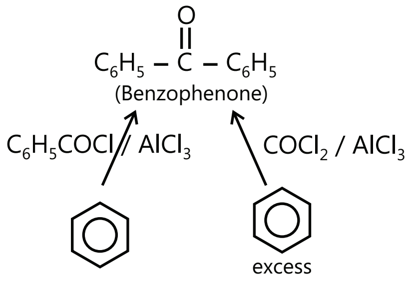
(d)


C6H5–CH=O
(Benzadehyde or the bitter almond)
⊖ OH/H2O
(-CH3COOH)
O
O–C–CH3
C6H5–CH–O–C–CH3
O
(CH3CO2)O
CrO2
C6H5–CH3
NH3
CH3
(i)CrO2Cl2/CCl4
(ii)H2O
(i)HCN+HCl/AlCl3
(ii)H2O
CO+HCl/AlCl3
H2/Pd-BaSO4
Boiling xylene
O
C6H5–C–Cl
C6H5NH2
C6H5–CN–=N–C6H5
Schiff base
C6H5–CH=N–CH–N=CH–C6H5
C6H5
Hydrobenzamide

(e)


Cl2
C6H5 – C – CH2 – Cl
O
Phenacyl chloride (Lacrymater)
O
C6H5 – C – CH3
Acetophenone
CH3COCl / AlCl3
Zn – Hg / HCl
CH2 – CH3

(f)



4.19 Some Important Reagents used for the Identification of Aldehydes

(a) **Tollen's reagent:** It is ammoniacal silver nitrate solution, prepared by the addition of ammonium hydroxide to $AgNO_3$ solution. During the reaction, first Ag_2O is formed which is dissolved in ammonium hydroxide to give Tollen's reagent

$$2AgNO_3 + 2NH_4OH \longrightarrow Ag_2O + NH_4NO_3 + H_2O$$

$$Ag_2O + 4NH_4OH \longrightarrow 2[Ag(NH_3)_2]OH + 3H_2O$$

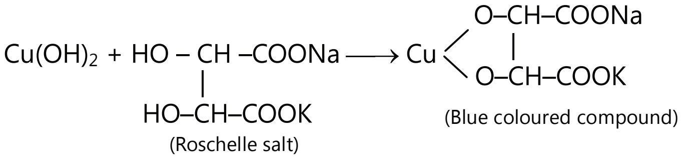
Tollen's reagent is a weak oxidizing agent. It gives Ag mirror test with an aldehyde.

$$R-CH=O + 2Ag(NH_3)_2^{\oplus} + 3OH^- + \longrightarrow RCOO^- + 2Ag + 2NH_3 + 2H_2O$$

$$R-CH=O + 2Ag_2O \longrightarrow R-COOH + 2Ag(\text{Silver})$$

(b) **Fehling's solution:** It is an alkaline solution of cupric ion complexed with sodium potassium tartarate. Two solutions are kept by naming Fehling solution (I) ($CuSO_4$ solution) and Fehling solution (II) (Alkaline solution of sodium potassium tartarate). When these two solutions are mixed we get deep blue coloured solution.

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4$$



$$Cu(OH)_2 + \underset{\substack{|\\ \text{HO–CH–COOK} \\ \text{(Roschelle salt)}}}{\text{HO – CH –COONa}} \longrightarrow Cu\begin{cases}\text{O–CH–COONa}\\ \quad\;\; | \\ \text{O–CH–COOK}\end{cases}$$

(Blue coloured compound)

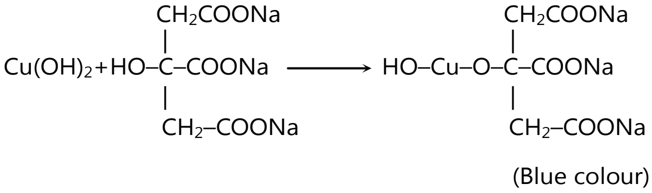
Equal volume of both the solutions are heated with aldehyde to give red brown precipitate of cuprous oxide (Cu_2O) which confirms the presence of aldehyde.

$$R-CHO + \underset{\text{blue}}{2CuO} \longrightarrow RCOOH + Cu_2O(\text{Redppt})$$

$$RCHO + 2Cu_2 + +3OH^- \longrightarrow RCOO^- + \underset{\text{(Red ppt)}}{2Cu^{\oplus}} + 2H_2O$$

(c) **Benedict solution:** It is solution of $CuSO_4$, Sodium citrate and sodium carbonate. It also consists of two solutions. Solution (I) is alkaline solution of sodium citrate and solution (II) is $CuSO_4$ solution.

$$CuSO_4 + 2NaOH \rightarrow Cu\,(OH)_2 + Na_2SO_4$$



$$Cu(OH)_2 + HO-\overset{\substack{CH_2COONa\\ |}}{\underset{\substack{|\\ CH_2-COONa}}{C}}-COONa \longrightarrow HO-Cu-O-\overset{\substack{CH_2COONa\\ |}}{\underset{\substack{|\\ CH_2-COONa}}{C}}-COONa$$

(Blue colour)

Aldehyde gives positive test with Benedict solution

$$RCH=O + \underset{\text{(Blue)}}{2Cu^{2+}} + 3OH^- \longrightarrow RCOO^- + \underset{\text{(Red ppt.)}}{2Cu^+} + 2H_2O$$

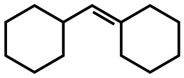
(d) **Schiff's Reagent:** It is a dilute solution of p-rosaniline hydrochloride. Its red colour has been discharged by passing SO_2. Aldehyde restores red colour when treated with Schiff's reagent (Magenta solution in H_2SO_3).

5. USES OF ALDEHYDES AND KETONES

In the Chemical industry, aldehydes and ketones are used as solvents, and reagents for the synthesis of products. Formaldehyde is known as formalin (40%) solution used to preserve biological specimens and to prepare Bakelite, urea-formaldehyde glues and other polymeric products. Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs. Benzaldehyde is used in perfumery and in dye industries. Many aldehydes and ketones, e.g. butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

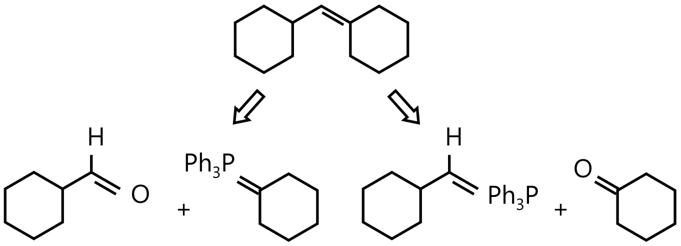
PROBLEM-SOLVING TACTICS

Problem 1: Identify the reagents to prepare the compound below using a witting reaction



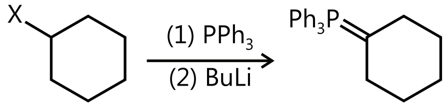
Sol: Begin by focusing on the carbon atom of the double bond. One carbon atom must be a carbonyl group, while the other must be the Wittig reagent. This gives two potential routes to us to explore.

Step 1: Using a retrosynthetic analysis, determine the two possible sets of reactants that could be used to form the C=C bond



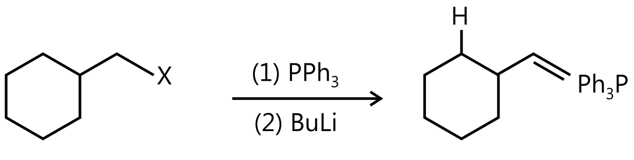
(Method 1) (Method 2)

Let's compare these two methods, by focusing on the Wittig reagent in each case. Wittig reagent is prepared by an S_N2 process, and we therefore must consider steric factors during its preparation. Method 1 requires the use of a secondary alkyl halide.



2° Alkyl halide

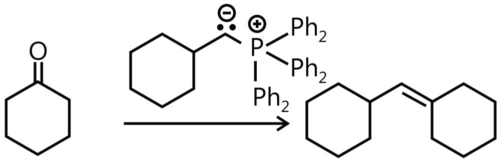
But method 2- requires the use of a primary alkyl halide



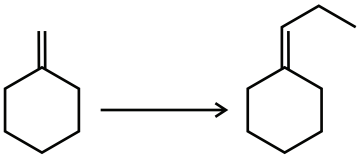
1° Alkyl halide

Step 2: Consider how you would make each possible Wittig reagent, and determine which method involves the substituted alkyl halide

Method 2 is likely to be efficient, because a primary alkyl halide will undergo S_N2 more rapidly than a secondary alkyl halide. Therefore, the following would be the preferred synthesis.



Problem 2: Propose an efficient synthesis for the following

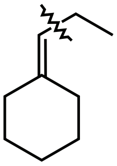


Sol: Always begin a synthesis problem by asking the following two questions.

Step 1: Inspect whether there is a change in the carbon skeleton and /or a change in the identity or location of the functional group.

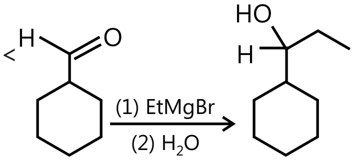
1. Is there any change in the carbon skeleton? Yes. The product has two additional carbon atoms.

2. Is there any change in the functional groups? No. Both the starting material and the products have a double bond in the exact same location. If we destroy the double bond in the process of adding the two carbon atoms we will need to make sure that we do so in such a way that we can restore the double bond. Now, let's consider how we might install the additional two-carbon atoms. The following C–C bond is the one that needs to be made. In this chapter, we have seen a C–C bond-forming reaction, let's consider each one as possible.

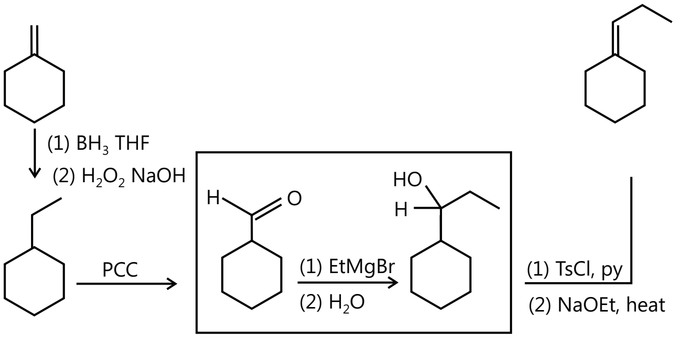


Step 2: When there is a change in the carbon skeleton, consider all of the C–C bond-forming reactions and all of the C-C bonds. Breaking the reaction that you have formed so far.

We can immediately rule out cyanohydrin formation, as that process installs only one carbon atom, not two. So, let's consider forming the C–C bond with either a Grignard reaction or a Wittig reaction. A Gignard reagent won't attack a C–C double bond into a functional group that can be attacked by a Grignard reagent, such as a carbonyl group.

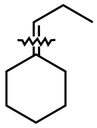


This reaction can indeed be used to form the crucial C–C bond. To use this method of C–C bond formation, we must first form the necessary aldehyde, then perform the Grignard reaction, and then finally restore the double bond in its proper location. This can be accomplished with the following reagents.

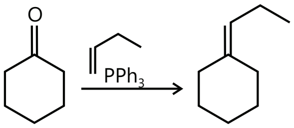


C-C bond forming reaction

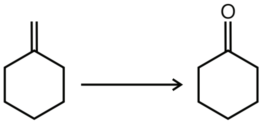
This provides us with a four-step procedure, and this answer is certainly reasonable. Let's now explore the possibility of proposing a synthesis with a Wittig reaction. Recall that a Wittig reaction can be used to form a C=C bond, so we focus on the formation of this bond



This bond can be formed if we start with a ketone and use the following Wittig reagent.

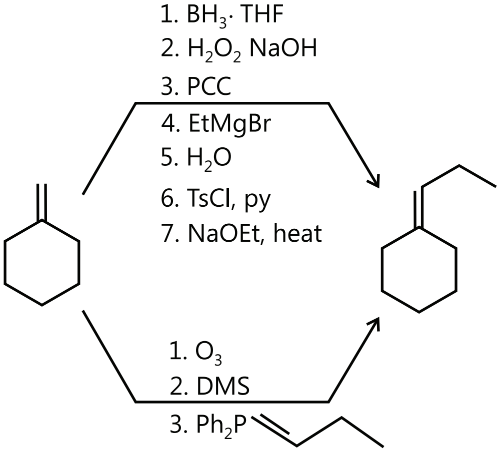


To use this reaction we must first form the necessary ketone from the starting alkene.

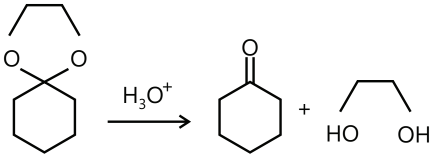


This can be accomplished with ozonolysis. This gives a two-step procedure for accomplishing the desired transformation: Ozonolysis followed by a Wittig reaction. This approach is different from our first answer. In this approach, we are not attaching a two-carbon chain, but rather, we are first expelling a carbon atom and then attaching a three-carbon chain

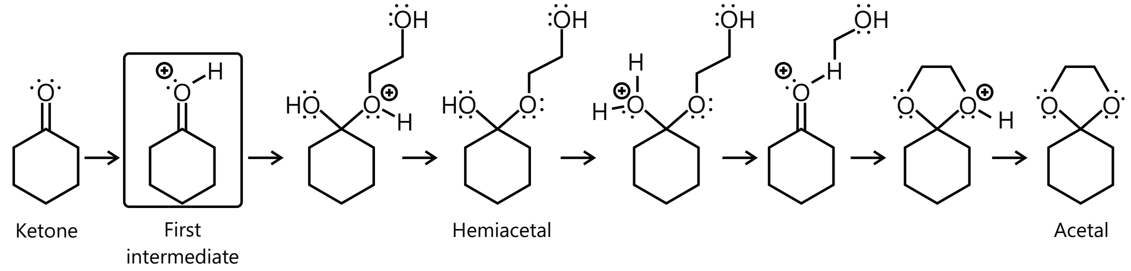
In short, there are two plausible methods have been discovered. Both methods are correct answers to this problem, however the method employing the Wittig reaction is likely to be more efficient, because it requires fewer steps.



Problem 3: Propose a mechanism for the following transformation:

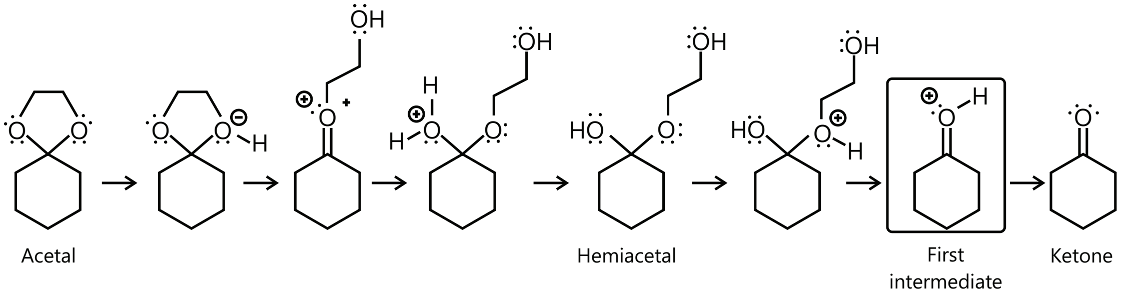


Sol: This is a hydrolysis reaction in which a cyclic acetal is opened to form a ketone. We therefore expect the mechanism to be the reverse of acetal formation. Begin by considering all of the intermediates in acetal formation

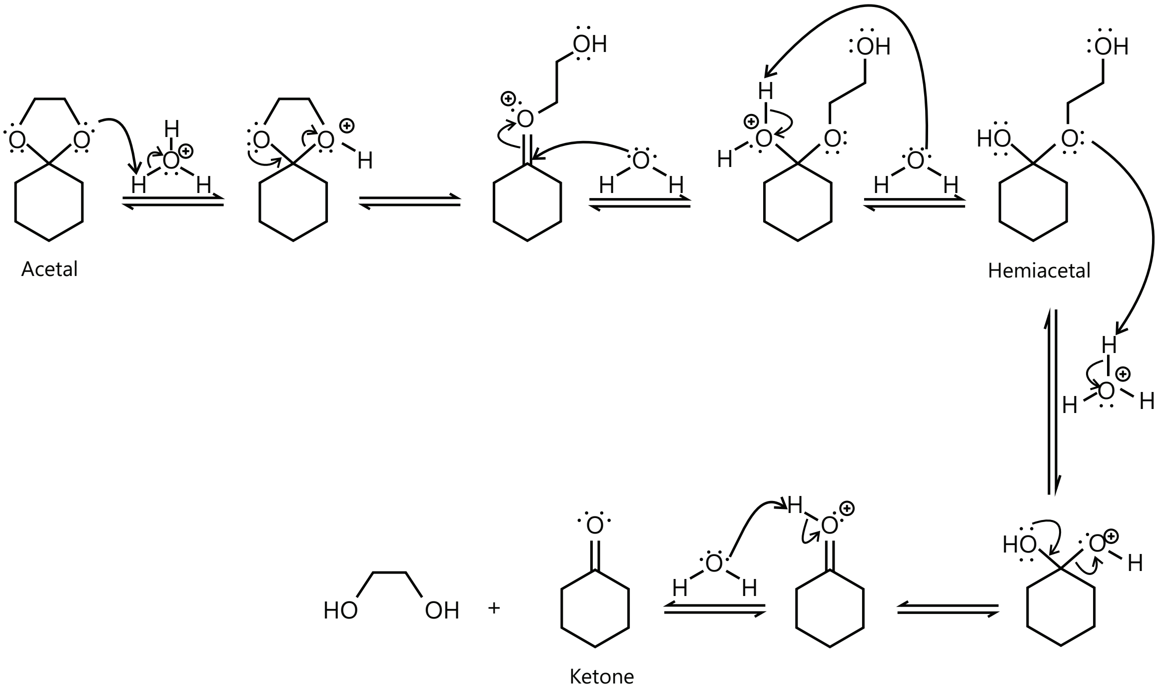


Step: 1 Draw all intermediates for acetal formation in reverse order

We simply draw all of these intermediates in reverse order so that the first intermediate above (Highlighted) becomes the last intermediate of the hydrolysis mechanism.



Hydrolysis of the acetal must involve these intermediates, in the order shown above. If any of the intermediates has a negative charge, then a mistake has been made. With the intermediates placed in the correct order, the final step is to draw the reagents and curved arrows that show how each intermediate is transformed into the next intermediate. Begin with the acetal, and work forward until reaching the ketone. Make sure to use only the reagents that are provided, and obey the master rule for proton transfer. For example this problem indicates that H_3O^+ is available. This means that H_3O^+ should be used for protonating, and H_2O should be used for deprotonating. Do not use hydroxide ions, as they are not present in sufficient quantity under acid-catalyzed conditions, Application of these rules gives the following answer?

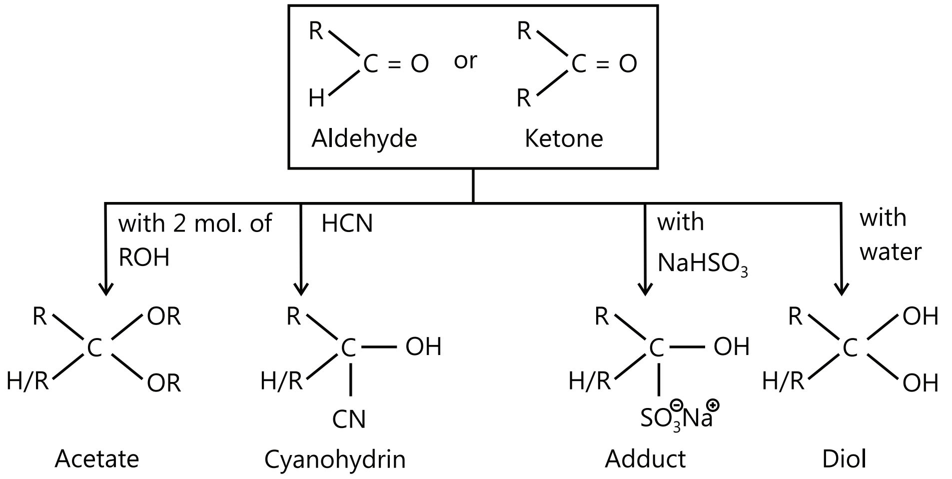


Step: 2 Draw the curved arrows and necessary reagents for each step of the mechanism

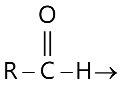
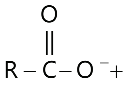
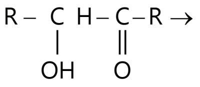
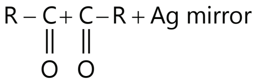
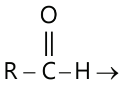
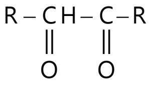
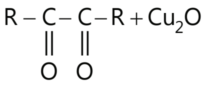
Notice the use of equilibrium arrows, because the process is governed by an equilibrium, as noted in the previous section.

POINTS TO REMEMBER

Nucleophilic Addition Reactions:



Reagents used to identify Aldehyde and Ketone:

No.	Reagent	Reactant	Product
1.	**Tollen's Reagent:** (Ammoniacal solution of $AgNO_3$) $\left[Ag(NH_3)_2\right]^{\oplus}\overset{\ominus}{O}H$ Also known as silver mirror Test.	 $R-\overset{O}{\overset{\|}{C}}-H\rightarrow$	 $R-\overset{O}{\overset{\|}{C}}-O^{-}+$ Ag Silver mirror
		α,β -Unsaturated Aldehyde. $RCH=CH-CHO\rightarrow$ α -hydroxy ketone  $R-\underset{OH}{\underset{\|}{C}}H-\underset{O}{\underset{\|}{C}}-R\rightarrow$ Ketone	$R-CH=CH-COO^{\ominus}+$ Ag mirror  $R-\underset{O}{\underset{\|}{C}}+\underset{O}{\underset{\|}{C}}-R+$ Ag mirror No reaction
2.	**Fehling's solution:** Ammoniacal solution of $CuSO_4+$ Rochelle salt. i.e. – sodium potassium tartarate	 $R-\overset{O}{\overset{\|}{C}}-H\rightarrow$ α,β -Unsaturated aldehyde $R-CH=CH-CHO\rightarrow$ α - hydroxyl ketone  $R-\underset{O}{\underset{\|}{C}}H-\underset{O}{\underset{\|}{C}}-R$ Ketone	$RCOO^{-}+Cu_2O$ (Red ppt) $R-CH=CH-COO^{\ominus}+Cu_2O$  $R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R+Cu_2O$ No red ppt.
3.	**Schiff's reagent** Containing rosaniline hydrochloride in H_2O, whose red colours is decolurised with SO_2.	Schiff's reagent + Aldehyde	Red colour of dye is restored.

No.	Reagent	Reactant	Product
4.	**Benedicts's solution:** (Ammoniacal solution of $CuSO_4$ + sodium citrate) $[Cu(NH3)_4]_2 + (OH^{2-})_2$	$R-\overset{O}{\overset{\|}{C}}-H \rightarrow$ α,β -Unsaturated aldehyde $R-CH=CH-CHO \rightarrow$ α -hydroxy ketone $R-\underset{OH}{\underset{\|}{C}}H-\underset{O}{\underset{\|}{C}}-R \rightarrow$ Ketone	$RCOO^- + \underset{\text{(Red ppt)}}{Cu_2O}$ $R-CH=CH-COO^- + \underset{\text{(Red ppt)}}{Cu_2O}$ $R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R + \underset{\text{(Red ppt)}}{Cu_2O}$ No reaction (No red ppt)
5.	**Haloform or Indoform** or Hypohalite oxidation $NaOH + x_2$ Or KOH $x_2 = I_2$ Or $Ca(OH)_2$	Aldehyde or ketone containing 3 α H atom (methyl ketone) $CH_3-\overset{O}{\overset{\|}{C}}-H \rightarrow$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow$	$CH_3-\overset{O}{\overset{\|}{C}}-O^- + \underset{\text{(yellow)}}{CHI_3}$ $CH_3-\overset{O}{\overset{\|}{C}}-O^- + \underset{\text{(yellow)}}{CHI_3}$

Important Reaction Flow Chart: