ALDEHYDES, KETONES AND CARRBOXYLIC ACIDS CHEMICAL REACTIONS

CHEMICAL REACTIONS

In general, carbonyl compounds undergo nucleophilic addition reactions, which involve the addition of both a nucleophile and a proton across the carbon-oxygen double bond (C = 0). The reactivity of the carbonyl group is a consequence of the oxygen atom's electronegativity, which results in the polarization of the carbon-oxygen double bond. The electrophilic carbon atom in the carbonyl group is sp² hybridized and possesses a flat geometry, making it relatively unobstructed and susceptible to attack from either side of the double bond.

Mechanism



The nucleophile (Nu⁻) approaches the carbonyl group in a direction perpendicular to the plane of the sp² hybridized orbitals of the carbonyl carbon.

During this process, the carbon's hybridization shifts from sp² to sp³. This results in the formation of a tetrahedral alkoxide intermediate.

Reactivity: Aldehydes are more reactive than ketones in nucleophilic addition reactions.



There are two factors which influence the reactivity of ketone and aldehyde.

(i) Inductive effect

(ii) Steric factor

- (i) + I effect of alkyl group decrease the amount of charge on C^+ ($C^+ O^-$). in ketones.
- (ii) Steric effect also causes the less reactivity of carbonyl group.

Nucleophilic addition reactions

(1) Addition of HCN





1 – Amino – 2-Propanol

(2) Addition of NaHSO₃

This reaction is employed to isolate carbonyl compounds from substances that do not contain carbonyl groups.



Chemistry

(3) Reaction with ammonia derivatives

These reactions are either condensation or addition-elimination reactions, and they progress effectively in a mildly acidic environment.

 $\begin{array}{ccc} \mathrm{NH}_3 & \longrightarrow & \mathrm{H}_2\mathrm{Z} \mbox{ (Ammonia derivative)} \\ \\ & > \mathrm{C} = \mathrm{O} + \mathrm{H}_2\mathrm{N} - \mathrm{Z} \frac{-\mathrm{H}}{+\mathrm{Z}} \end{tabular} \rightarrow > \mathrm{C} = \mathrm{N} - \mathrm{Z} + \mathrm{H}_2\mathrm{O} \end{array}$

Addition - elimination (Condensation)

Mechanism

$$>C = OH + NH_2Z \implies C - OH \xrightarrow{IMPE} C - OH_2 \xrightarrow{-H_2O} C = NHZ \xrightarrow{-H^{\oplus}} C = NZ$$

Ammonia derivatives (NH₂Z)

Ζ	=	ОН	\longrightarrow NH ₂ OH (Hy	ydroxyl amine)		
Z	=	NH ₂	\longrightarrow NH ₂ NH ₂ (h	nydrazine)		
Z	=	NHC ₆ H ₅	\longrightarrow NH ₂ NHC ₆ H	45 (Phenyl hydrazine)		
Z	=		\rangle NO ₂ \rightarrow NH ₂ - NH -			
2, 4–Dinitro phenyl hydrazine (DNP) Brady's reagent.						
Z	=	NHCONH ₂	\longrightarrow NH ₂ NHCOM	NH ₂		
			Semi Carb	azide.		
$_{\rm H}^{\rm R}$	C = 0 +	H ₂ NNHC ₆ H ₅	$\rightarrow \frac{R}{H} > C = NNHC_6H_5$	(Aldoxime)		
$_{\rm H}^{\rm R}$	C = 0 +	H ₂ NOH ₂	$\rightarrow \frac{R}{H} > C = NOH_2$	(Hydrazone)		
$_{\rm H}^{\rm R}$	C = 0 +	H ₂ NNHC ₆ H ₅	$\rightarrow \frac{R}{H} > C = NNHC_6H_5$	(Phenyl hydrazone)		



(4) With alcohol and thioalcohol

 $\begin{array}{c} H \\ R \end{array} > C = O + ROH \xrightarrow{HCl(g)} H \\ Hemi - acetal \end{array} \qquad \begin{array}{c} H \\ R \end{array} > C < \begin{array}{c} OH \\ OR \end{array} \xrightarrow{ROH} HCl(g) \\ Hcl(g) \end{array} \xrightarrow{H} C < \begin{array}{c} OR \\ OR \end{array} \\ Acetal \end{array}$

$$R > C = O + 2ROH \xrightarrow{HCl(g)} R > C < OR R > C < OR H2O Ketal$$

Tri ethoxy methane $[HC(OC_2H_5)_3]$ remove the water formed during the reaction and so the reaction proceeds in forward direction.

 $\begin{array}{c} R \\ R \end{array} > C = 0 + 2ROH \xrightarrow{HCl(g)} R \\ \hline H^2O \end{array} \xrightarrow{R} C < \begin{array}{c} SR \\ SR \end{array} \xrightarrow{[0]} R \\ \hline H^2 C < \begin{array}{c} SO_2R \\ SO_2R \end{array} \\ \hline Mercaptan \end{array}$

$$\underset{R}{\overset{R}{\rightarrow}} C = 0 + 2RSH \xrightarrow{HCl(g)} \underset{-H_2O}{\overset{R}{\rightarrow}} C < \underset{R}{\overset{R}{\rightarrow}} C < \underset{SR}{\overset{[0]}{\rightarrow}} \underset{R}{\overset{R}{\rightarrow}} C < \underset{SO_2R}{\overset{SO_2R}{\rightarrow}}$$

Mercaptan (Thio Ketal)

Sulphones Compound

All sulphones' compounds are hypnotic compounds.



Chemistry



Ex. Which compound form more stable hydrate with H₂O?

(A) HCHO	(B) CH ₃ CHO
(C) CH3COCH3	(D) CH ₃ COC ₂ H ₅

[Hint: HCHO since it is more reactive towards this reaction.]

Ans. (A)

Ex. Which carbonyl compound not gives reversible reaction with water?

Sol. Chloral hydrate.



Stable by intra molecular hydrogen bonding.

Wittig Reaction

The Wittig reaction offers a significant and valuable approach to synthesize alkenes. It involves treating aldehydes or ketones with alkylidene phosphoranes, also known as phosphorene's, typically represented as $Ph_3P = CR_2$.



The Wittig reagent, also known as alkylidene triphenyl phosphorane or ylide, is created by reacting a trialkyl or triaryl phosphine, often the latter, with an alkyl halide, typically in a solution. The resulting phosphonium salt is then subjected to a strong base, such as C₆H₅Li, BuLi, NaNH₂, NaH, C₂H₅ONa, and so on.

$$\begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \\ Ph \end{array} + H_{3}C - Br \longrightarrow \left[\begin{array}{c} Ph \\ I \\ Ph \\ Ph \end{array} \right] \xrightarrow{\Theta} C_{6}H_{5}Li \\ Ph \\ Ph \end{array} Ph - \begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \end{array} \xrightarrow{\Theta} C_{6}H_{5}Li \\ Ph - \begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \end{array} \xrightarrow{\Theta} C_{6}H_{2}Li \\ Ph \\ Ph \\ Ph \end{array} Ph - \begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \\ Ph \end{array} \xrightarrow{\Theta} C_{6}H_{2}Li \\ Ph \\ Ph \\ Ph \end{array} Ph - \begin{array}{c} Ph \\ Ph \\ Ph \\ Ph \\ Ph \end{array} \xrightarrow{\Theta} C_{6}H_{5}Li \\ Ph \\ Ph \\ Ph \\ Ph \end{array}$$

Cannizaro's reaction

Aldehydes lacking a hydrogen atom are capable of undergoing this reaction when treated with concentrated NaOH or KOH. The resulting products consist of the salt of a carboxylic acid and an alcohol. In this reaction, one molecule of the carbonyl compound is oxidized to form an acid, while the other is reduced to produce an alcohol. Reactions of this kind are referred to as disproportionation reactions, which are a type of redox reaction.

HCHO + HCHO
$$\frac{\text{conc.}}{\text{NaOH}} \rightarrow \text{HCOONa} + \text{CH}_3\text{OH}$$

Mechanism: (Cannizaro reaction)

(a) Rapid reversible addition of $\overline{O}H$ to one molecule of HCHO.



(b) Transfer of hydride ion to second molecule of HCHO



In a mixed or crossed Cannizaro reaction, the more reactive aldehyde undergoes oxidation, while the less reactive aldehyde experiences reduction.

нсно + с ₆ н ₅ сно	NaOH	$HCOONa + C_6H_5CH_2OH$
Oxidized		Reduced
(Sodium format)		(Benzyl alcohol)

Ex: $CH_3CHO + HCHO \xrightarrow{Ca(OH)_2} C(CH_2OH)_4 + (HCOO)_2 Ca, explain mechanism?$

2, 2-Dihydroxy methyl –1, 3-propane diol. (Penta erythritol)

Tishchenko reaction: It is a modified Cannizaro reaction. All aldehydes undergo this reaction in presence of $(C_2H_5O)_3Al$, to form ester.



Reaction With Halogen

Replacement of α -H atoms

Formaldehyde (HCHO) does not exhibit this reaction because it lacks alphahydrogen atoms, and enolization does not occur in HCHO.

$$\begin{array}{c} \alpha \\ CH_2 - C - H + Cl_2 \\ | \\ H \\ 0 \end{array} \xrightarrow{-HCl} CH_2 - C - H \xrightarrow{Cl_2} HCl \xrightarrow{-HCl} CH_2 - C - H \xrightarrow{Cl_2} CH - C - H \xrightarrow{Cl_2} HCl \xrightarrow{-HCl} CCl_3 - C - H \\ | \\ Cl \\ O \\ Cl \\ O \\ Chloral \end{array}$$

Replacement of O-atom of $>_{C = 0}$ **group:** It takes place by PCl₅ or SOCl₂.

$$>C = 0 + PCl_5 \longrightarrow >C < Cl_{Cl + POCl_3}^{Cl}$$

Phosphorus Penta chloride

$$>C = 0 + SOCl_2 \longrightarrow >C < Cl_{Cl + SO_2}^{Cl}$$

Thionyl chloride

Haloform reactions

Chlorine or bromine can substitute one or more alpha-hydrogen atoms in aldehydes and ketones.

For example, acetone can undergo bromination in glacial acetic acid to yield Mon bromoacetone.

 $CH_3COCH_3 + Br_2 \rightarrow CH_3COCH_2Br + HBr (43-44\%)$

Halogenation of carbonyl compounds can be catalyzed by both acids and bases. For instance, let's examine the case of acetone. In an alkaline solution, we can isolate tribromo acetone and bromoform. Interestingly, the addition of a second and a third bromine atom occurs more rapidly than the first. When using aqueous sodium hydroxide, it has been demonstrated that the reaction rate is unaffected by the concentration of bromine but follows a first-order relationship with respect to both acetone and the base, meaning the rate depends on the concentration of these two reactants.

Rate = k [acetone]
$$[OH^1]$$

Aldol Condensation: When a base is present, two molecules of an aldehyde or a ketone can combine in a condensation reaction to form a β -hydroxy aldehyde or a β -hydroxy ketone. This chemical process is known as aldol condensation. In general, carbonyl compounds that have alpha-hydrogen atoms can undergo aldol condensation when treated with dilute NaOH. The resulting compound, known as an aldol, contains both an alcoholic (-OH) and a carbonyl group.

Mechanism of aldol condensation:

This process occurs in two sequential stages:

- Generation of a carbanion.
- > The carbanion then combines with another aldehyde molecule.

Chemistry

Formation of Carbanion: α -H atom of group is quite acidic which can be removed easily as proton, by a base.



Carbanion thus formed is stable because of resonance -



Combination of carbanion with other aldehyde molecule



Aldol condensation is possible between

- **1.** Two aldehydes (Same or different)
- **2.** Two ketones (Same or different)
- One aldehyde and one ketone
 Identical carbonyl compounds
 Different carbonyl compounds
- \rightarrow Simple or self a Idol condensation
- \rightarrow Mixed or crossed a Idol condensation

Simple or Self condensation

$$\begin{array}{c} CH_3 - CH + HCH_2CHO & \xrightarrow{dill} & CH_3 - CH - CH - CHO & \xrightarrow{\Delta} & CH_3 - CH = CH - CHO \\ | & | & | \\ O & OH & H & Crotonaldehyde \end{array}$$

Class-12th

$$CH_{3} - C - CH_{3} + H - CH_{2} - C - CH_{3} \longrightarrow CH_{3} - C - CH_{2} - CH_{3} - C - CH_{3} - C = CH - COCH_{3} + H_{2}O$$

$$OH \qquad CH_{3} \qquad OH \qquad CH_{3} \qquad Mesityl oxide or$$
Diacetone
$$alcohol$$
4-Methyl -3-pentene-2-one

$$\frac{CH_3}{CH_3} > C = CH - C - CH_3 + 0 < \underbrace{CH_3}_{CH_3} \xrightarrow{HCl \text{ gas } CH_3}_{-H_2O} > C = CH - C - CH = C < \underbrace{CH_3}_{CH_3}$$
Phorone

Mixed or Crossed aldol Condensation

$$CH_{3}CH + CH_{3} - C - \underbrace{Week}_{Base} \text{ Total (4) products} < \binom{(2) \text{ Simple}}{(2) \text{ Mixed}}$$

$$CH_{3} - CH + \overset{\mathbf{C}}{CH_{2}} - COCH_{3} \underbrace{OH}_{Week \text{ base}} CH_{3} - CH - CH_{2} - COCH_{3} \underbrace{-}_{H_{2}O} CH_{3} - CH = CH - COCH_{3}$$

$$(AldOl)$$

Claisen Condensation

When two ester molecules engage in a condensation reaction, the process is referred to as Claisen condensation. The outcome of Claisen condensation is the formation of a β -keto ester.



Chemistry

Following the nucleophilic attack, there is a distinction between aldol addition and Claisen condensation. In Claisen condensation, the negatively charged oxygen regenerates the carbon-oxygen π -bond and removes the OR group.

Mixed Claisen Condensation



Intramolecular Claisen Condensation

Dieckmann condensation: The introduction of a base to a 1,6-diester initiates an intramolecular Claisen condensation within the diester, resulting in the formation of a five-membered ring β -keto ester. This specific type of intramolecular Claisen condensation is known as a Dieckmann condensation.



Perkin Reaction

In the Perkin reaction, the condensation occurs between aromatic aldehydes and aliphatic acid anhydrides in the presence of the sodium or potassium salt of the acid corresponding to the anhydride. This reaction yields α , β -unsaturated aromatic acids.

Class-12th

The acid anhydride should have at least two α -H.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{AcONa}{170-180^{\circ}C} \rightarrow C_6H_5-CH=CH-COOH$$



Knoevenagel Reaction: The Knoevenagel Reaction refers to the condensation of aldehydes and ketones with substances containing an active methylene group in the presence of a basic catalyst. This reaction leads to the formation of α , β -unsaturated compounds. The basic catalyst can be ammonia or one of its derivatives. Various amines, including primary, secondary, and tertiary amines such as aniline, di- or trialkyl amines, pyridine, or piperidine, are commonly employed in this process.



Reformat sky Reaction: A reaction similar to the addition of organometallic compounds to carbonyl compounds is the incorporation of an organozinc reagent into the carbonyl group of an aldehyde or ketone. This chemical process is known as the

Reformat sky reaction, and it leads to the extension of the carbon skeleton of an aldehyde or ketone, resulting in the production of β -hydroxy esters. In this reaction, an aldehyde or ketone is treated with an α -bromo ester in the presence of zinc metal, with benzene being the commonly used solvent. The initial product formed is a zinc alkoxide, which must be subjected to hydrolysis to yield the β -hydroxy ester.



Schmidt Reaction: This reaction occurs when a carbonyl compound reacts with hydrazoic acid in the presence of a concentrated strong acid like sulfuric acid. Aldehydes produce a mixture of cyanide and formyl derivatives of primary amines, while ketones yield amides.

RCHO + HN₃
$$\xrightarrow{H_2SO_4}$$
 RCN + RNHCHO + N₂
RCOR + HN₃ $\xrightarrow{H_2SO_4}$ RCONHR + N₂

Reaction with primary amine

 $>C=O+H_2NR \rightarrow >C=NR+H_2O$ Schiff's Base

Benzoin condensation: The benzoin condensation fundamentally involves the pairing of two aromatic aldehydes with the catalytic assistance of cyanide ions, resulting in the formation of benzoin (I).



The hydrogen atom bonded to the carbonyl group of aldehydes is typically not readily removable due to its lack of reactivity. However, the addition of a cyanide ion to the carbonyl carbon positions this hydrogen atom in the alpha position of the nitrile, making it relatively more acidic. As a result, a carbanion is generated, which then initiates the attack on the carbonyl carbon of the second aldehyde molecule. This attack, which represents the rate-determining step, leads to the formation of an unstable cyanohydrin of benzoin. This intermediate quickly decomposes into benzoin and hydrogen cyanide.



Benzylic acid rearrangement

The introduction of a potent base to a carbonyl group leads to the generation of an anion. Reversing the charge of this anion can result in the expulsion of the attached group X.



In the scenario of a 1,2-diketone, it is possible for group X to relocate to the neighboring electron-deficient carbonyl carbon, leading to the creation of an α -hydroxy acid.

A prime illustration of this phenomenon can be seen in the reaction of benzil with a potent base, which gives rise to the production of benzilic acid (in the form of a salt), thereby giving rise to the concept of the "benzilic acid rearrangement."



The Beckmann rearrangement

The rearrangement of a ketoxime to form an N-substituted amide under acidic conditions is commonly referred to as the Beckmann rearrangement.



The rearrangement can be catalyzed by a range of acidic substances, including H_3PO_2 , H_2SO_4 , SOCl₂, PCl₅, and others.

Oxidation Reactions: Oxidation reactions:

By K₂Cr₂O₇/H₂SO₄: When primary alcohols are oxidized with K₂Cr₂O₇/H₂SO₄, they initially form aldehydes. Further oxidation of the aldehyde results in the formation of an acid containing the same number of carbon atoms. In contrast, secondary alcohols, when oxidized, yield ketones. Subsequent oxidation of the ketone leads to the production of an acid with fewer carbon atoms.

 $\begin{array}{cccc} R-CH_{2}OH & \stackrel{[0]}{\longrightarrow} & R-CHO & \stackrel{[0]}{\longrightarrow} & R-COOH \\ & (1^{\circ} alcohol) \end{array}$ $\begin{array}{cccc} CH_{3} CH_{2} CH_{2} & CH & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$

(i) 3° alcohol is not oxidised within 2 or 3 minutes.

(ii) 1° and 2° alcohol convert orange colour of K₂Cr₂O₇ to green in 2-3 minutes.

SeO₂ (Selenium Oxide): Oxidation of ketones or aldehydes using SeO2 results in the formation of dicarbonyl compounds. This reaction occurs exclusively in compounds that contain an α -carbon. Notably, formaldehyde (HCHO) does not exhibit this reaction.

$$a \\ CH_{3}CHO + SeO_{2} \longrightarrow H - C - C - H + Se + H_{2}O \\ \| \\ \| \\ 0 \\ 0 \\ G | yoxa |$$

$$a \\ CH_{3} - C - CH_{3} + SeO \longrightarrow H_{3} - C - C - H + Se + H_{2}O \\ \| \\ 0 \\ 0 \\ Methyl G | yoxal (Pyruval de hyde)$$

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Baeyer's Villiger oxidation: Peroxy acids can oxidize both aldehydes and ketones. This chemical transformation, referred to as the Baeyer-Villiger oxidation, is particularly effective when applied to ketones, as it leads to the conversion of ketones into carboxylic esters.

For example, when acetophenone is exposed to a peroxy acid, it is transformed into the ester known as phenyl acetate.



Mechanism:



The outcome of this reaction demonstrates that a phenyl group exhibits a higher inclination to migrate than a methyl group. If it were otherwise, the product would have been C₆H₅COOCH₃ instead of CH₃COOC₆H₅. This propensity for a group to migrate is referred to as migratory aptitude.

Studies of the Baeyer-villager oxidation and other reaction have shown that the migratory aptitude of groups $H > phenyl > 3^{\circ}$ alkyl $> 2^{\circ}$ alkyl 1° alkyl > methyl. In all cases, this order is for groups migrating with their electron pairs, that is, as anions.

Reduction

The wolf kirshner reduction

Heating a ketone or aldehyde in a basic hydrazine solution result in the transformation of the carbonyl group into a methylene group. This chemical alteration is referred to as deoxygenation since it involves the removal of an oxygen atom from the reactant. The specific reaction is recognized as the Wolf-Kishner Reduction.



Clemmensen Reduction: The process of converting the carbonyl groups in aldehydes and ketones into methylene groups using amalgamated zinc and concentrated hydrochloric acid is commonly referred to as Clemmensen reduction.



The nature of product depends upon the reducing agent used. It can be summarized as.

(i)
$$> C = \longrightarrow > CH$$

Reducing agents are

- Red P/HI at 150°C

- Zn-Hg/HCl [Clemensen's reduction]

-NH2-NH2/C2H5OH,OH1

(ii) $> C = \longrightarrow > CHO$

[Wolff Kirshner's reduction]

Reducing agents are

— LiAlH₄ (Nice Tron brown)

— Na/C₂H₅OH (Bouveault blank)

— NaH/Benzene (Darzen reaction)

— [(CH₃)₂CHO]₃Al

(Aluminium isopropoxide)

— (CH₃)₂ CHOH (Isopropyl alcohol)

The reduction of a compound using aluminum isopropoxide in an excess of isopropanol is termed MPV (Meerwein-Ponndorf-Verley) reduction. This method selectively reduces specific functional groups, leaving other reducible groups unaffected. $-NO_2$, $-CHCH_2$, -CC-.

Example: $\begin{array}{c} CH_3 \\ CH = CH \end{array} > C = O \xrightarrow{MPV \text{ reduction}} CH_3 \\ CH = CH \end{array} > CHOH$

Reactions given by only aldehydes

Polymerisation: It is a reversible process.

Formaldehyde

(a) $nHCH \xrightarrow{Evaporation} (CH_2O)_{n}, H_2O$ Paraformaldehyde is a linear polymer Formalin Paraformaldehyde which show reducing character with (40% HCHO) n = 6-50 Tolle's reagent, Fehling solution etc. Hydrated white crystal

(b) nHCH $\xrightarrow{\text{Conc.}}$ (CH₂0)_n, H₂0

Poly oxy methylene n > 100



Reaction with ammonia: With the exception of formaldehyde, all other aldehydes undergo addition reactions, whereas formaldehyde experiences an addition-elimination process, which is a condensation reaction.

Condensation $6CH_2O + 4NH_3$ $(CH_2)_6N_4 + 6H_2O$ Reaction Urotropine (Hexamine) White crystalline solid Used in preparation of explosive Used in treatment of urine infection diseases $CH_3 - CH - NH_2$ $CH_3 - CH = NH$ $CH_3 - CH + NH_2$ Addition Conc. H_2SO_4 Acet aldimine II OH Reaction -H₂0 0 Η Used in preparation Acetaldehyde Of cyclic polymer Ammonia CH_3 CH NH ΗN 3H₂0 . 3H2O 3CH₃—CHNH Trimerisation CH HC CH₃ H₃C

Trimethyl hexahydro Triazine trihydrate

Reducing character: Aldehydes are readily susceptible to oxidation, making them potent reducing agents.

Tollen's reagent: It oxidises aldehydes. Tollen's reagent is ammoniacal silver nitrate solution

 $\begin{array}{cccc} (\mathrm{AgNO}_3 + \mathrm{NH}_4\mathrm{OH}) & \longrightarrow & [\mathrm{Ag}(\mathrm{NH}_3)_2]\mathrm{OH} \\ \mathrm{RCHO} + [\mathrm{Ag}(\mathrm{NH}_3)_2]\mathrm{OH} & \longrightarrow & \mathrm{RCOOH} + \mathrm{Ag} + \mathrm{H}_2\mathrm{O} \\ & & & & & \\ & & & & & \\ \mathrm{Silver\ mirror} \\ \mathrm{AgNO}_3 + \mathrm{NH}_4\mathrm{OH} & \longrightarrow & & & & \\ \mathrm{AgOH} & \longrightarrow & & & \\ \mathrm{AgOH} & \longrightarrow & & & \\ \end{array}$

Chemistry

RCHO + Ag₂O
$$\longrightarrow$$
 RCOOH + Ag \downarrow (Silver mirror)

Fehling's solution: It is a mixture of CuSO₄, NaOH and sodium potassium tartrate.

Fehling solution A- (aq.) solution of CuSO₄

Fehling solution B– Roschelle salt (Sodium potassium tartrate + NaOH)

Fehling solution A + Fehling's solution B (Dark blue colour of cupric tartrate)

$$\begin{array}{cccc} \text{RCHO} + \text{Cu}^{+2} + \text{OH} - &\longrightarrow \text{RCOOH} + \text{Cu}_2\text{O} \\ &&& (\text{Cuprous oxide-Red ppt.}) \\ &&& \text{Cu}^{2+} &\longrightarrow & \text{Cu}^+ \\ &&& (\text{Cupric - Blue}) && (\text{Cuprous - Red ppt.}) \end{array}$$

Benedict's solution: It is a mixture of $CuSO_4$ + sodium citrate + Na_2CO_3 . It provides Cu^{+2} . It is reduced by aldehyde to give red ppt of cuprous oxide.

 $RCHO + Cu^{2+} + OH^{-} \longrightarrow RCOOH + Cu_2O$

(Cuprous oxide-Red ppt.)

Mercuric chloride: HgCl₂ is a caustic sublimate compound. It undergoes reduction when exposed to an aldehyde, resulting in the formation of a white precipitate known as mercurous chloride (Calonal). This mercurous chloride subsequently reacts with additional aldehyde, leading to the formation of a black precipitate composed of mercury (Hg).

 $RCHO + HgCl_2 + H_2O \longrightarrow RCOOH + Hg_2Cl_2 + HCl$ (calomal) $RCHO + Hg_2Cl_2 + H_2O \longrightarrow RCOOH + Hg + HCl$ (black ppt)

Reaction with schiff's reagent: Schiff's reagent is a diluted solution of p-rosaniline hydrochloride or magenta dye. When exposed to SO₂ gas, it loses its pink color, resulting in a colorless solution referred to as Schiff's reagent. Aldehydes can react with this reagent, causing the pink color to reappear.

Reaction of only ketones

Reduction: Acetone is reduced by magnesium amalgam and water to give pinacol.





Reaction with chloroform



Reaction with HNO₂

$$\begin{array}{c} 0\\ CH_3 - C - CH_3 + 0 = N - OH \end{array} \xrightarrow{-H_2O} CH_3 - C - CH = N - OH \end{array}$$

Oximino acetone

Oxidation reaction: According to pop off's rule >C–O group stays with smaller alkyl group.

$$\begin{array}{c} 0\\ H_{3} - CH_{2} - C - CH_{3} \longrightarrow CH_{3}COOH + CH_{3}COOH \end{array}$$

Condensation reaction

(a) In presence of dry HCl - aldol condensation takes place

$$CH_{3} \xrightarrow{CH_{3}} O \xrightarrow{H_{2}O} O \xrightarrow{H_{2}O} O \xrightarrow{H_{3}O} O \xrightarrow{H_{3}O}$$

Mesityl oxide

Class-12th

$$\begin{array}{ccc} CH_3 & CH_3 & CH_3 & 0 \\ I & I & I \\ CH_3 - C = CH - COCH_3 + 0 = C - CH_3 & \begin{array}{c} -H_2O & I & II \\ \hline & -H_2O & I & II \\ \hline & & CH_3 - C = CH - C - CH = C - CH_3 \end{array}$$

$$(Phorone) \text{ or } 2.6\text{-Dimethyl -2,5-} \\ Hepta \text{ diene -4-One} \end{array}$$

(b) In presence of conc. H_2SO_4

$$CH_{3} - \overset{O}{C} - CH_{3} \xrightarrow{Conc. H_{2}SO_{4}}_{Condensation} \xrightarrow{CH_{3}}_{H_{3}C} \overset{CH_{3}}{CH_{3}} \xrightarrow{Mesitylen}_{H_{3}C}$$

$$3CH_3 - C \equiv CH \frac{Fe}{Addition Polymeridstion}$$

Reaction with ammonia

Pyrolysis

$$\begin{array}{c} CH_2 & -C = 0 & \Delta \\ I & I \\ H & CH_3 \\ Aceton \end{array} \xrightarrow{Ketene} \left\{ \begin{array}{c} HCH0 & \Delta \\ HCH0 \\ CH_3CH0 \end{array} \xrightarrow{\Delta} CO + H_2 \\ CH_3CH0 \end{array} \right\}$$