

13.1 ALIPHATIC ALDEHYDES AND KETONES

<https://subarnam.com.np/>

Learning outcomes

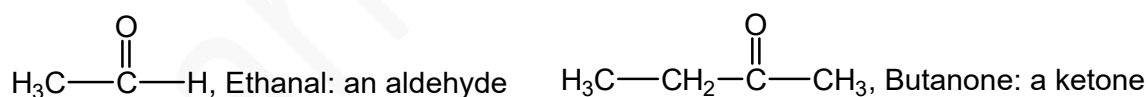
After the lesson, learners should be able to:

- ✓ Write some examples of aliphatic aldehydes and ketones
- ✓ Name the given aldehydes and ketones in IUPAC and common systems
- ✓ Describe briefly the nomenclature and isomerism of aliphatic aldehydes and ketones.
- ✓ Show the preparation of aldehydes and ketones from
 - dehydrogenation, oxidation of alcohols,
 - ozonolysis of alkenes,
 - acid chlorides,
 - gem-dihaloalkanes
 - and catalytic hydration of alkynes
- ✓ State physical properties of aldehydes and ketones.
- ✓ Describe the structure and nature of the carbonyl group.
- ✓ Explain chemical properties of aliphatic aldehydes and ketones,
 - i.e. addition of H_2 , HCN and $NaHSO_3$.
 - Action of aldehydes and ketones with ammonia derivatives, i.e. NH_2OH , NH_2-NH_2 , phenylhydrazine and semicarbazide.
 - Aldol condensation, Cannizzaro's reaction,
 - Clemmensen's reduction and Wolff-Kishner reduction.
 - Action with PCl_5 and action with $LiAlH_4$.
 - Action of methanal with ammonia and phenol.
- ✓ Distinguish between aliphatic aldehydes and ketones by using 2,4-DNP reagent, Tollens' reagent and Fehling's solution.
- ✓ Define formalin and state its uses.

Introduction

These are compounds with the general formula $C_nH_{2n}O$ (for saturated, acyclic aldehydes and ketones) and the functional group $>C=O$. These are also called carbonyl compounds.

If the carbonyl carbon is bonded with at least one hydrogen atom, it is an aldehyde; if it is bonded with two carbon atoms, it is a ketone. e.g.,



In other words, if the carbonyl group is bonded with two alkyl groups, it is a ketone; if it is bonded with one or no alkyl group, it is called an aldehyde.

Nomenclature

Common nomenclature

The common names of the aldehydes are derived from the names of acids they give on oxidation. e.g.:

Formula	Common name	Corresponding acid
HCHO	formaldehyde	HCOOH (formic acid)
CH ₃ CHO	acetaldehyde	CH ₃ COOH (acetic acid)
C ₂ H ₅ CHO	propionaldehyde	C ₂ H ₅ COOH (propionic acid)
CH ₃ CH ₂ CH ₂ CHO	n-butyraldehyde	CH ₃ CH ₂ CH ₂ COOH (n-butyric acid)

The common names of the ketones are obtained by writing the names of the alkyl groups attached to the carbonyl group followed by the word 'ketone'. e.g.

Formula	Common name
CH_3COCH_3	dimethyl ketone (acetone)
$\text{CH}_3\text{COC}_2\text{H}_5$	ethyl methyl ketone
$\text{C}_2\text{H}_5\text{COC}_2\text{H}_5$	diethyl ketone

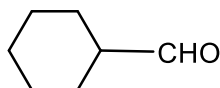
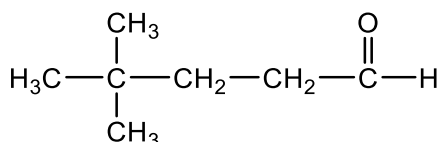
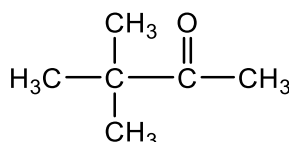
IUPAC nomenclature

In this system, both the aldehydes and ketones are named according to the general rules of IUPAC.

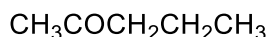
The secondary suffixes of aldehydes and ketones are **-al** and **-one**, respectively. e.g.:

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \rightarrow$ **butanal**

$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 \rightarrow$ **pentan-3-one**



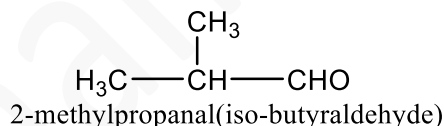
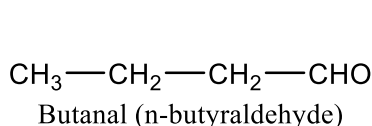
Cyclohexane carbaldehyde



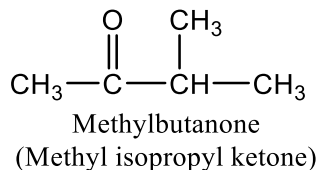
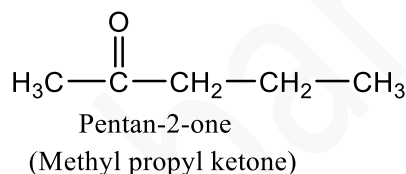
Structural Isomerism in Aldehydes and Ketones

(A) Chain Isomerism

Higher aldehydes and ketones show chain isomerism. e.g., butanal and 2-methylpropanal are chain isomers.



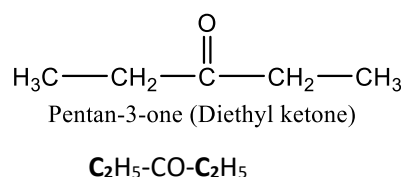
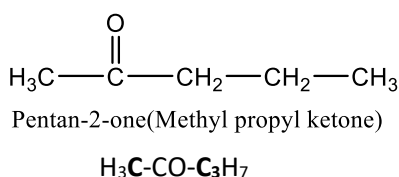
Similarly, pentan-2-one and 3-methylbutan-2-one are chain isomers.



(B) Position Isomerism

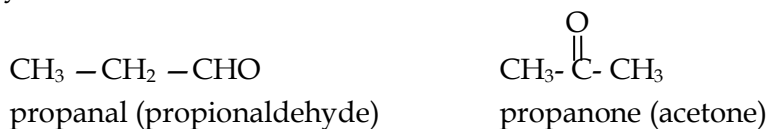
Aldehydes do not show position isomerism. Because the $-\text{CHO}$ group is always located at the end of the carbon chain.

Higher ketones exhibit position isomerism. E.g., pentan-2-one and pentan-3-one are position isomers of each other. These also illustrate **metamerism** because the carbon atoms are distributed differently on the two sides of the carbonyl group.



(C) Functional Isomerism

Aldehydes and ketones can show functional isomerism with one another. e.g.,

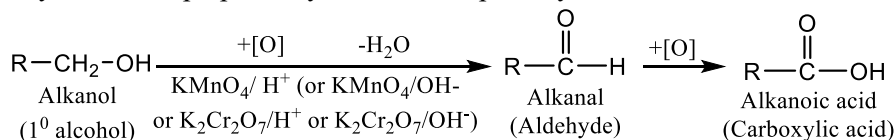


General Methods of Preparation of Aldehydes and Ketones

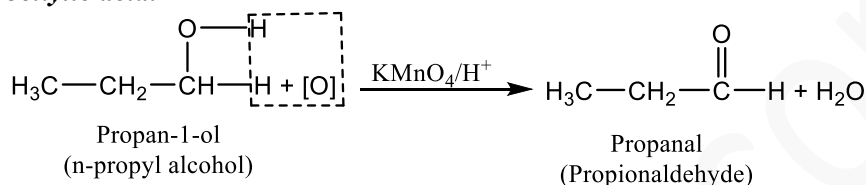
1. From alcohols

a) By oxidation of alcohols

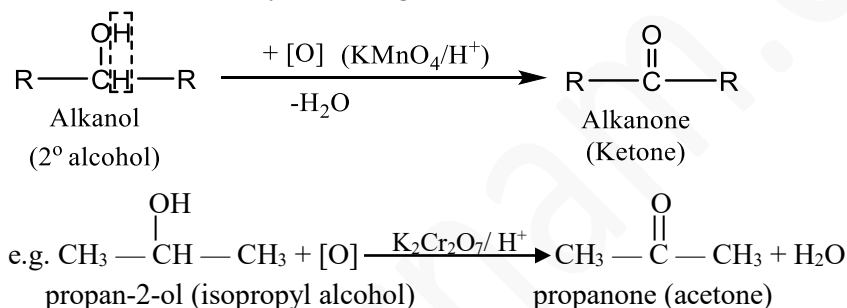
Aldehydes can be prepared by oxidation of primary alcohols with acidified or alkaline KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc.



The aldehyde should be removed by distillation as soon as it is formed; otherwise, it further oxidises to carboxylic acid.



Oxidation of secondary alcohols gives ketones.

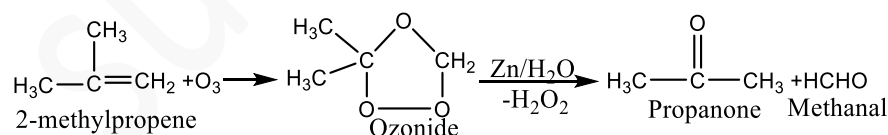


b) Catalytic dehydrogenation of alcohols (studied under the properties of [alcohols](#))

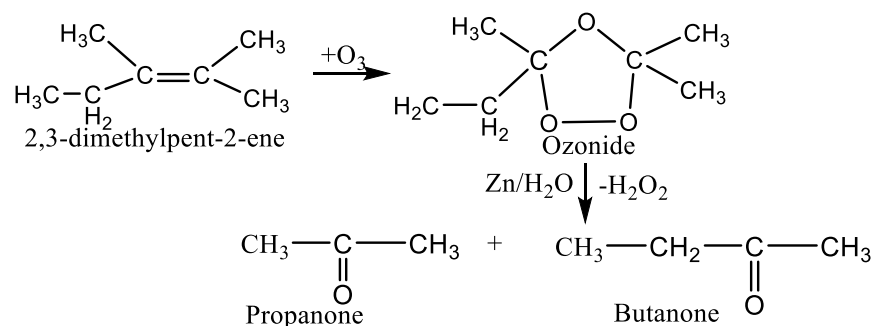
2. From alkenes (by ozonolysis)

Alkenes, on treatment with ozone, give unstable ozonides, which on treatment with zinc and water give carbonyl compounds.

- Alkenes of type $\text{RCH}=\text{CH}_2$ or $\text{RCH}=\text{CHR}$ give aldehydes.

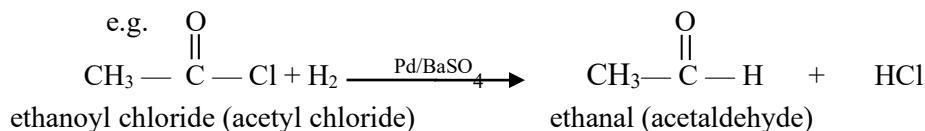
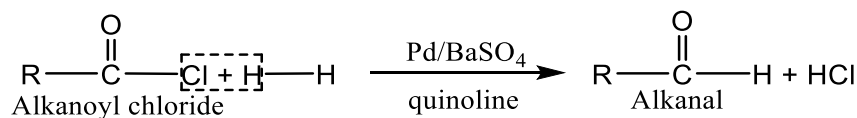


- Alkenes of the type $\text{R}_2\text{C}=\text{CH}_2$, $\text{R}_2\text{C}=\text{CHR}$ or $\text{R}_2\text{C}=\text{CR}_2$ give at least one ketone.

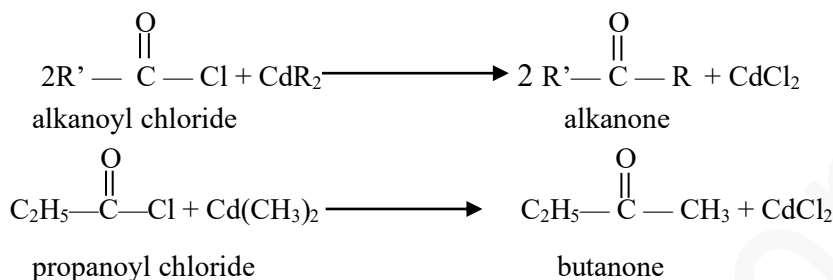


3. From acid chlorides (**Rosenmund's reduction**)

Aldehydes, except formaldehyde, are prepared by reduction of acid chlorides by **Rosenmund's catalyst, i.e., Pd deposited on BaSO₄ and poisoned with quinoline or sulphur to prevent further reduction of aldehydes**. This is called Rosenmund's reduction.



Ketones are prepared by treating acid chlorides with **dialkyl cadmium**.



[Balance the above reaction by the hit-and-trial method]

NOTE: This is a historically valid method, but organocadmium compounds are toxic and not commonly used in modern synthetic chemistry.

4. From alkynes (by hydration)

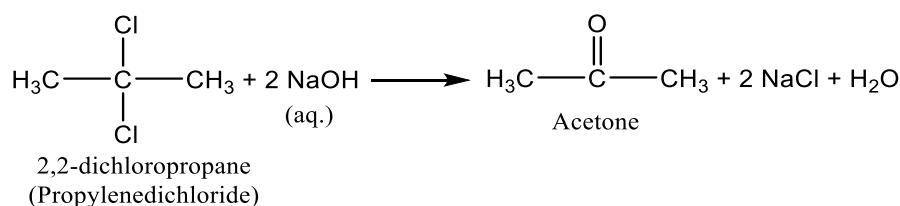
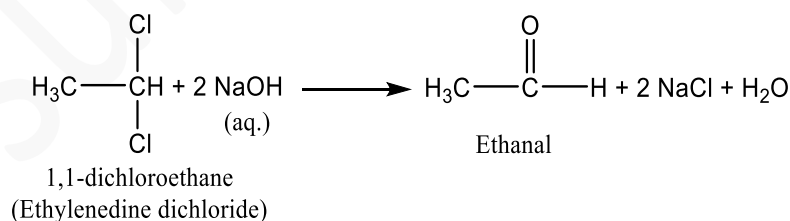
When alkynes are passed through dilute H₂SO₄ in the presence of HgSO₄, carbonyl compounds are obtained.



The addition follows Markovnikov's rule.

5. From gem-dihaloalkanes (refer to hydrolysis of [alkyl halides](#), and chloroform)

Terminal geminal dihalides on hydrolysis with an alkali solution give aldehydes, and **non-terminal** geminal dihalides give ketones. e.g.,

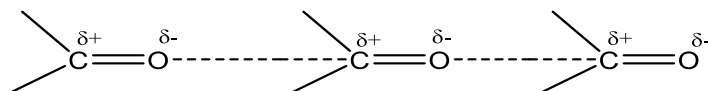


[Practice writing balanced equations for all above types of reactions with different examples.]

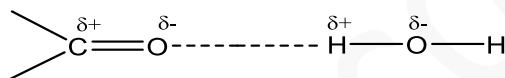
General physical properties of aldehydes and ketones

- Lower aldehydes generally have strong, characteristic odours. Some aldehydes and ketones have pleasant odours and are used in perfumes and flavouring materials.
- Lower aldehydes and ketones are generally volatile liquids. As molecular mass increases, their boiling points increase, and sufficiently higher members may be solids.
- Generally, aldehydes and ketones possess higher boiling points than alkanes and ethers of comparable molecular masses. This is due to the intermolecular dipole-dipole interactions. They **do not form hydrogen bonds with each other, but they can form hydrogen bonds with water.**

The oxygen of the carbonyl group carries a partial negative charge, whereas carbon carries a partial positive charge. The intermolecular force operates as:



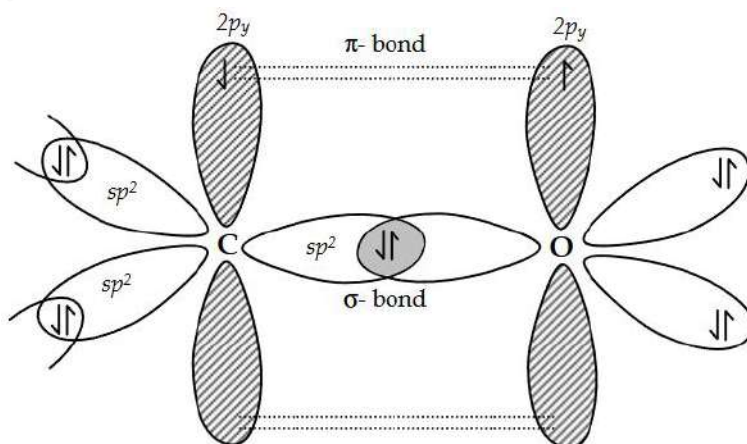
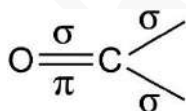
- Lower aldehydes and ketones are appreciably soluble in water because the carbonyl oxygen can form hydrogen bonds with water. The solubility of the carbonyl compounds decreases as we move up the homologous series, as the hydrophobic hydrocarbon portion reduces solubility.



Chemical Properties of Aldehydes and Ketones

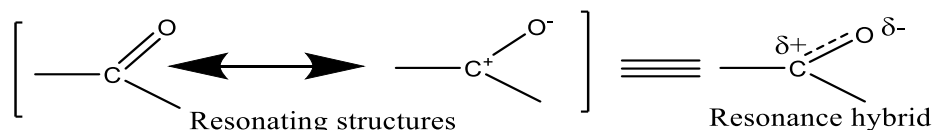
Structure of the Carbonyl Group

In the carbonyl group, both C and O atoms are sp^2 hybridised. One of the p-orbitals of each carbon and oxygen atom remains unhybridized. The three sp^2 hybrid orbitals of carbon lie in a single plane with an angle of about 120° between them. One sp^2 hybrid orbital of C forms one σ bond with a sp^2 orbital of O. The other two sp^2 hybrid orbitals form σ bonds with either carbon or hydrogen. The unhybridized p-orbital of the carbonyl carbon laterally overlaps with the remaining half-filled p-orbital of the O atom to form a π bond.



[Practice drawing the orbital diagram of the carbonyl group.]

The carbonyl group is **highly polarised** because oxygen, being more electronegative than the carbon atom, draws the shared pair of electrons towards itself, developing a partial positive charge (δ^+) in carbon and a partial negative charge (δ^-) in itself.



Nucleophilic Addition Reactions



Why are aldehydes and ketones reactive?

The C=O bond is strongly polar.

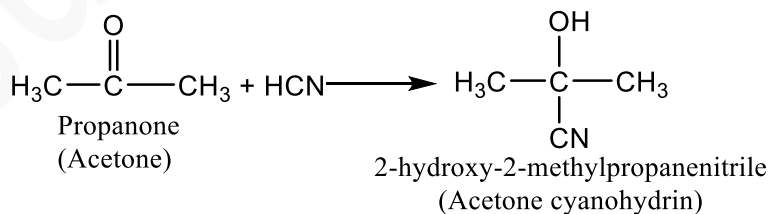
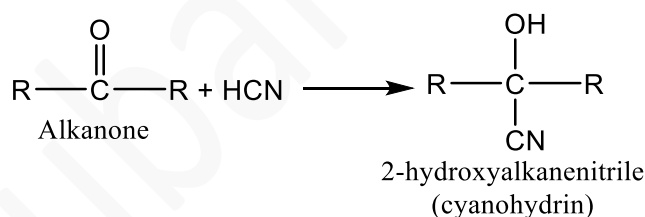
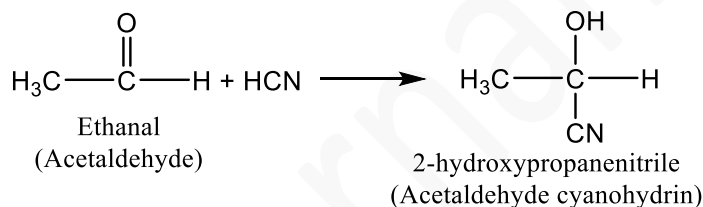
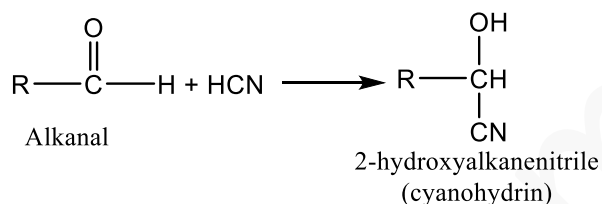
Carbonyl carbon $\rightarrow \delta^+$

Carbonyl oxygen $\rightarrow \delta^-$

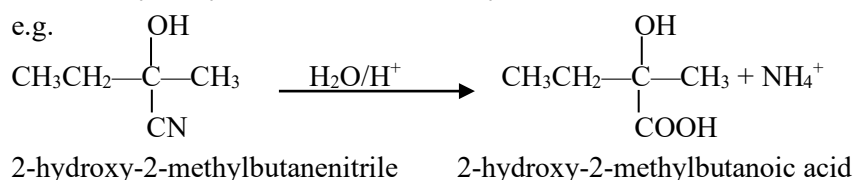
Therefore, nucleophiles attack the carbonyl carbon.

1. Addition of hydrogen cyanide (HCN)

Aldehydes and ketones react with HCN (prepared in situ by mixing NaCN and H_2SO_4 under controlled conditions) to give cyanohydrins.

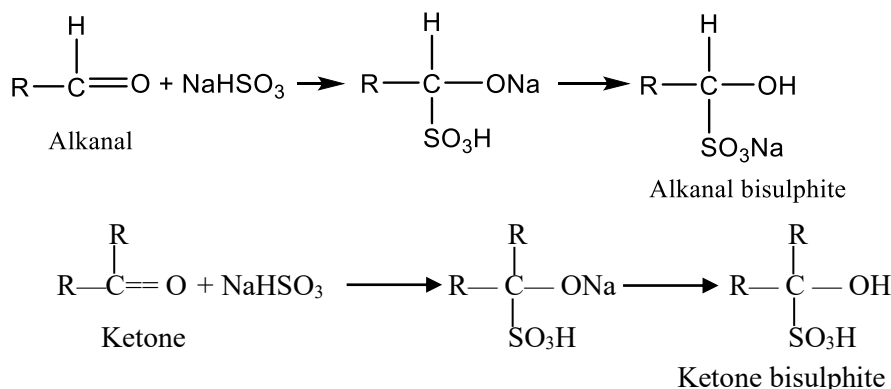


Cyanohydrins, on hydrolysis (acidic or basic), give 2-hydroxy acids. (Simply, the cyanide/nitrile(-CN) group, on hydrolysis, produces carboxylic acids).



2. Addition of sodium bisulphite (NaHSO₃)

Aldehydes and many ketones react with saturated sodium bisulphite solution to form crystalline bisulphite addition products.

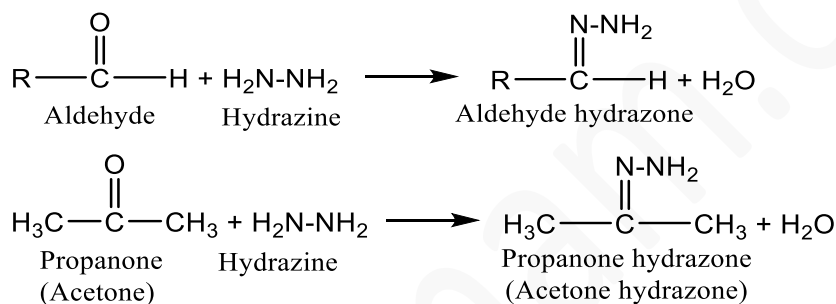


Nucleophilic addition followed by elimination (Addition of ammonia derivatives)

Aldehydes and ketones react with ammonia derivatives to form an addition product, which, on elimination of water, gives the final product. For simplicity and from an examination point of view, these reactions are shown in single steps.

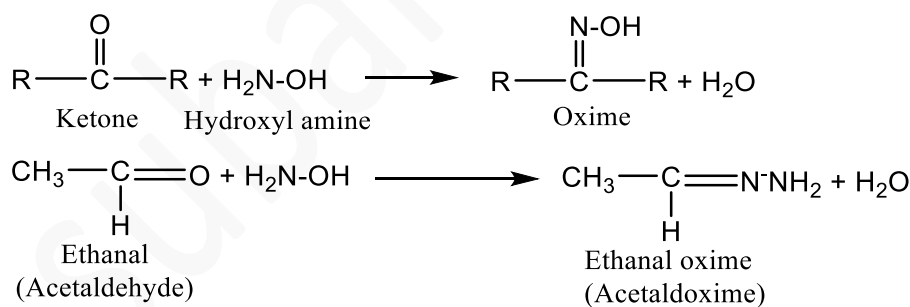
1. Reaction with hydrazine (NH₂NH₂)

Aldehydes or ketones react with hydrazine to give hydrazones.



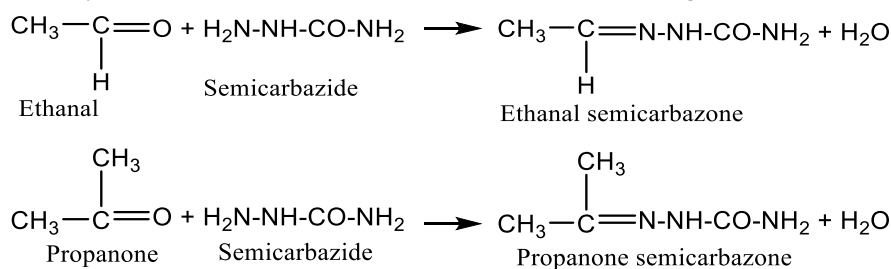
2. Reaction with hydroxylamine (NH₂OH)

Aldehydes or ketones react with hydroxylamine to give oximes.



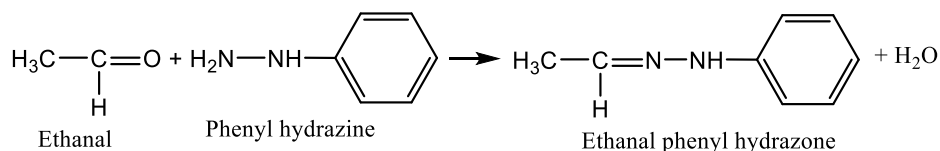
3. Reaction with Semicarbazide (NH₂NHCONH₂)

Aldehydes and ketones react with semicarbazide to give semicarbazone.



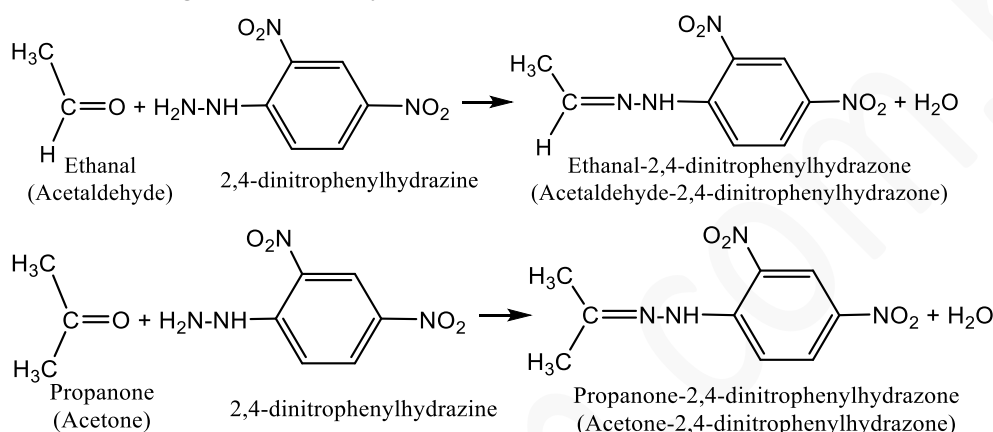
4. Reaction with phenylhydrazine (NH₂NH-C₆H₅)

Aldehydes and ketones, on treatment with phenylhydrazine, give phenylhydrazones.



5. Reaction with 2,4-dinitrophenylhydrazine (**2,4-DNP** or 2,4-DNPh) (the 2,4-DNP test)

When aldehydes and ketones are treated with 2,4-dinitrophenylhydrazine, a **yellow, orange or red crystalline precipitate** of the corresponding 2,4-dinitrophenylhydrazone is obtained. It is a characteristic reaction of carbonyl compounds. Thus, it serves as a **test for carbonyl compounds**. But it does not distinguish an aldehyde from a ketone.



★ **2,4-DNP:** Aldehyde or ketone → yellow/orange/red precipitate

✗ **Cannot distinguish aldehyde from ketone**

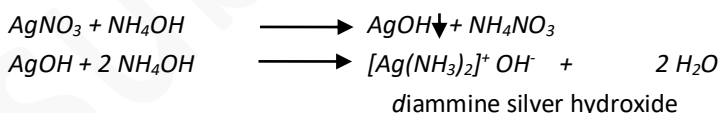
Oxidation of aldehydes

1) **Oxidation with Tollens' reagent**

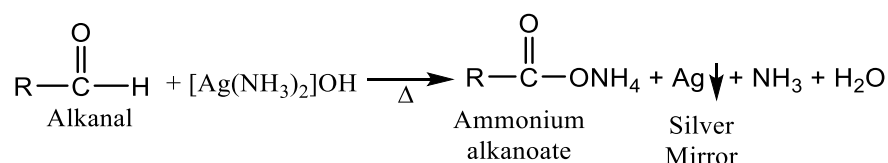
The Tollens' reagent is an ammoniacal silver nitrate solution - [Ag(NH₃)₂]OH.

Extra info for advanced learners

Tollens' reagent is prepared by adding ammonium hydroxide solution to silver nitrate solution till a precipitate formed initially dissolves. The reactions involved are:



When an aldehyde is heated with Tollens' reagent, Tollens' reagent is reduced to free metallic **silver** in the form of a mirror, and the aldehyde is oxidised to a carboxylate salt. The reaction, therefore, is widely known as the **silver mirror test**.

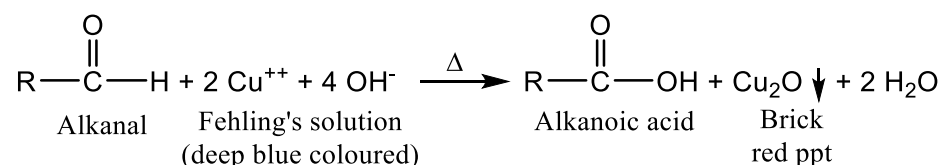


Ordinary ketones do not undergo these reactions. Therefore, aldehydes can be distinguished from ketones and other organic compounds by the silver mirror test in the laboratory.

2. Oxidation with **Fehling's solution**

The alkaline solution of copper sulphate complexed with tartrate ions (Rochelle salt) is called Fehling's solution.

When an aldehyde is heated with Fehling's solution, a **red** precipitate of cuprous oxide (Cu_2O) is obtained.



Aliphatic aldehydes generally give a positive Fehling's test, whereas ordinary ketones do not.

Aromatic aldehydes such as benzaldehyde generally do not give a positive Fehling's test.

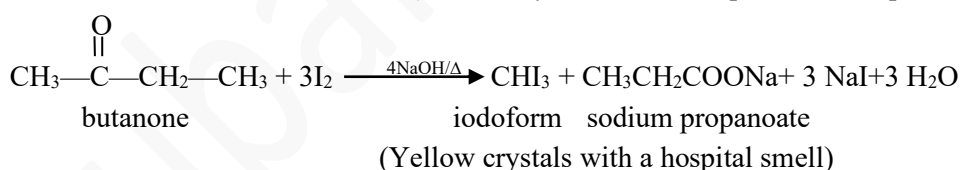
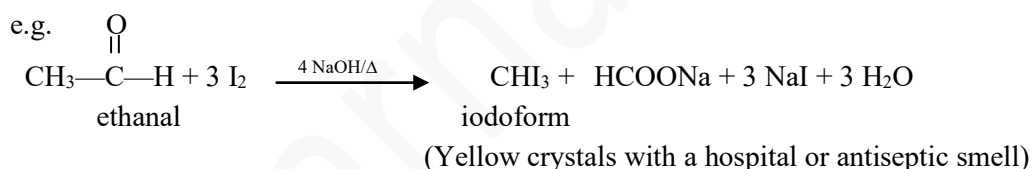
Benedict's solution is similar to Fehling's solution and is obtained by mixing CuSO_4 solution with Na_2CO_3 solution and sodium citrate. Benedict's solution reacts similarly to Fehling's solution only with aldehydes.



[Note: Iodoform test for aldehydes and ketones is not mentioned in the syllabus, but frequently questions have been asked in the NEB examinations.]

Iodoform test (test for $\text{CH}_3\text{CO}-$ group)

Methyl ketones ($\text{R}-\text{CO}-\text{CH}_3$) and ethanal (acetaldehyde) react with iodine in the presence of alkali to produce iodoform. Compounds containing the $\text{CH}_3\text{CO}-$ group give the iodoform test; ethanal is the only aldehyde that gives this test.

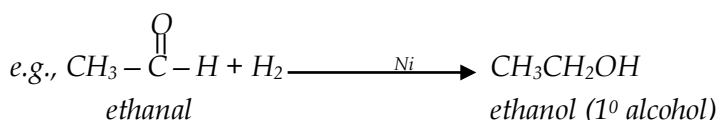
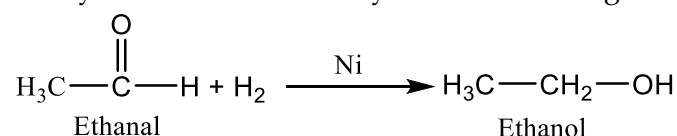


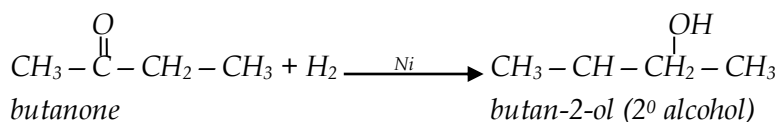
[compare iodoform test of carbonyl compounds with [alcohols](#)]

Reduction of Aldehydes and Ketones

1. Reduction by H_2/Ni (Catalytic reduction) (or addition of H_2)

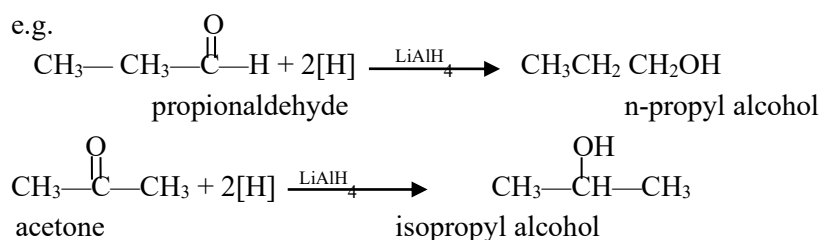
Catalytic reduction of aldehydes and ketones gives primary and secondary alcohols, respectively.





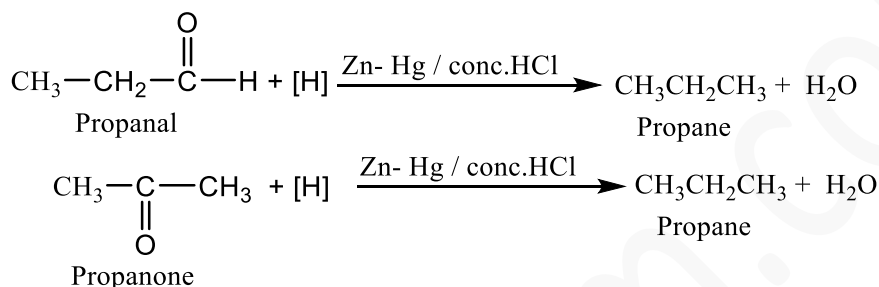
2. Reduction with LiAlH_4

Aldehydes give primary (1°) alcohols, and ketones give secondary (2°) alcohols by reduction with lithium aluminium hydride (LiAlH_4).



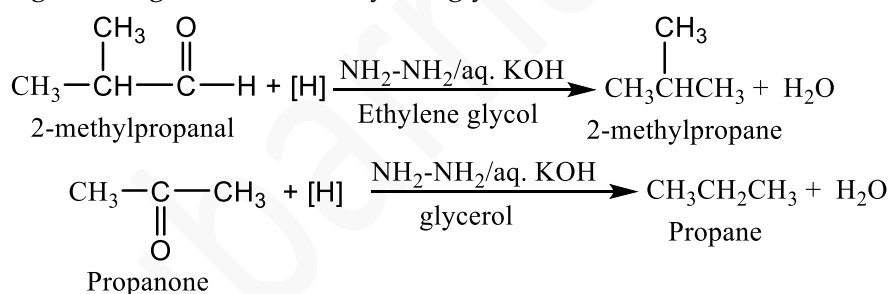
3. Clemmensen's reduction

Aldehydes and ketones are **reduced to alkanes** by zinc amalgam in concentrated HCl. The reaction is known as Clemmensen's reduction.



4. Wolff - Kishner reduction

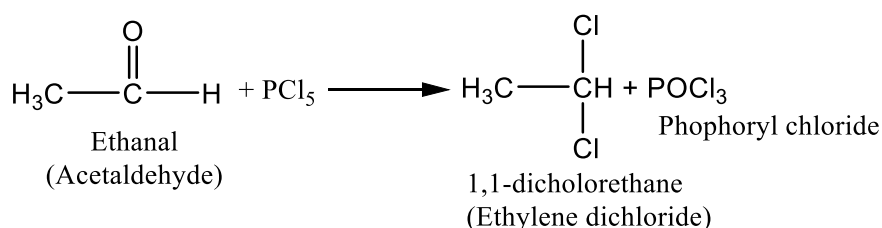
Aldehydes and ketones are **reduced to alkanes** by a mixture of hydrazine and a strong base in a high-boiling solvent like ethylene glycol.

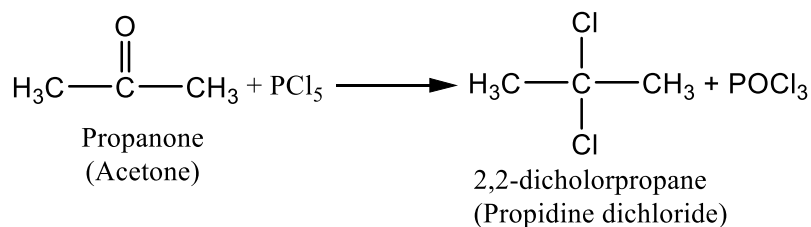


Other reactions of aldehydes and ketones

Reaction of Aldehydes and Ketones with PCl_5

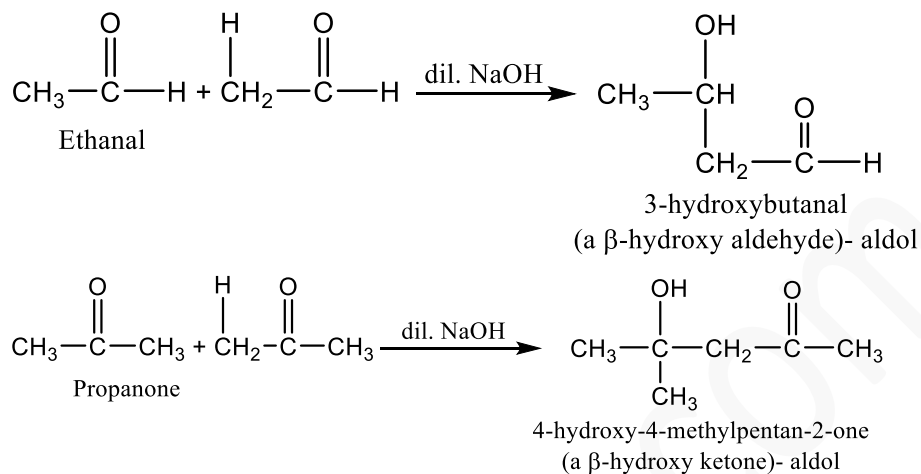
Aldehydes and ketones give geminal dichlorides on treatment with PCl_5 . They give terminal and non-terminal geminal dichlorides, respectively.





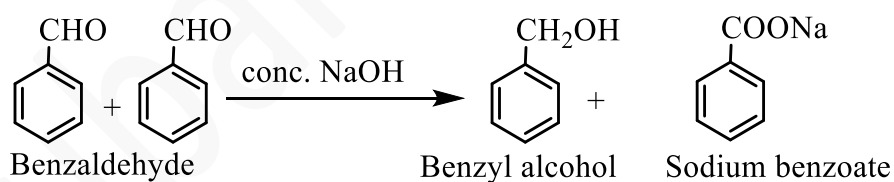
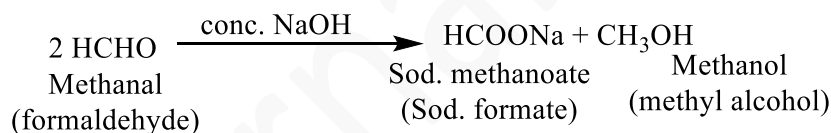
Aldol Condensation

Aldehydes or ketones having α -hydrogen atoms, when treated with dilute bases such as NaOH undergo a condensation reaction to give β -hydroxy aldehydes or ketones, called **aldols**.



Cannizzaro's reaction

Aldehydes that do not contain α -hydrogen atoms (like formaldehyde, benzaldehyde), undergo disproportionation when treated with a concentrated aqueous alkali solution (e.g. 50% NaOH), forming an alcohol and a carboxylate salt.



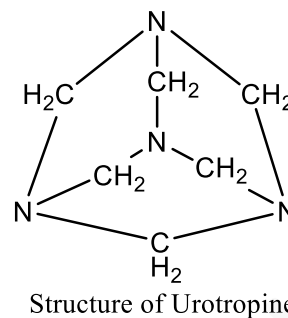
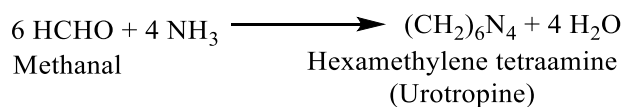
Remember

α -H present $\rightarrow$ Aldol

α -H absent $\rightarrow$ Cannizzaro

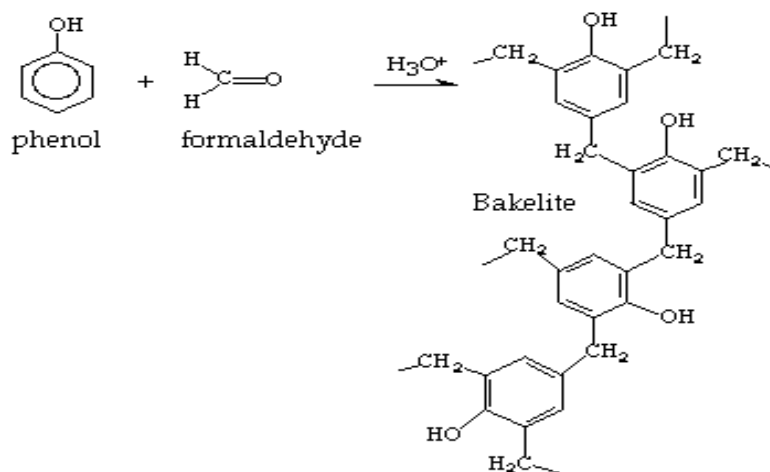
Reaction of Methanal with Ammonia

Methanal (formaldehyde) reacts with ammonia, giving hexamethylene tetramine, also called Urotropine, which is used as medicine (urinary antiseptic) and in some industries.



Reaction of Formaldehyde with Phenol

Formaldehyde reacts with phenol in an acidic medium, forming phenol-formaldehyde resin or **Bakelite**. Bakelite is a **thermosetting plastic**, so it is used in **electrical appliances** (switches, plugs), **handles of cooking utensils**, etc.



Formalin and its uses

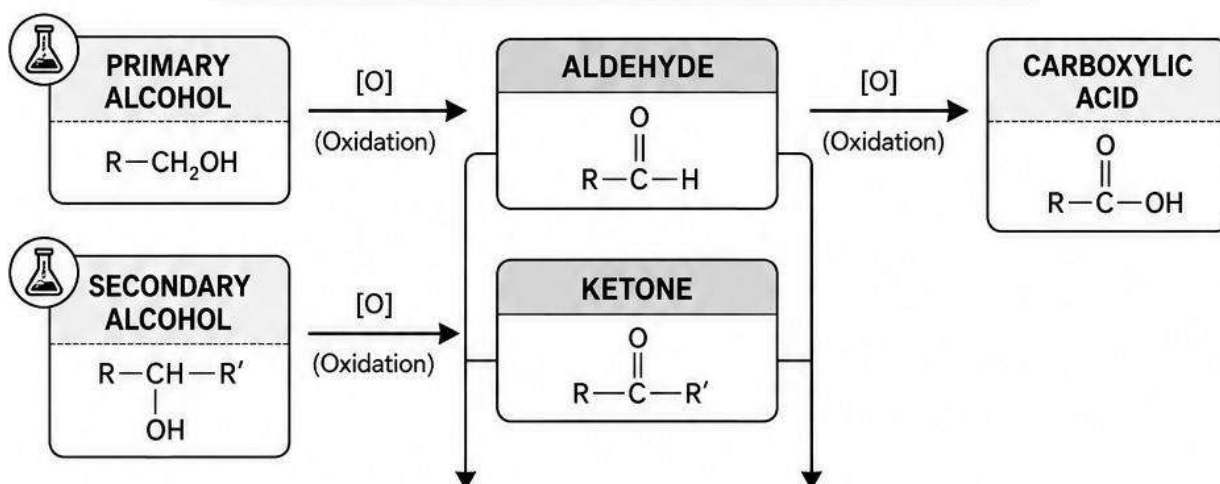
Formalin is a **37% (to 40%) formaldehyde solution** in water (usually stabilised with a small amount of methanol). It is used to **preserve museum specimens** in biology laboratories and as an antiseptic.

<https://subarnam.com.np/>

*** ... ***

REACTION MAP

ALDEHYDES AND KETONES



REACTIONS OF ALDEHYDES AND KETONES

1	H_2 (Ni/Pt)	$\rightarrow$ ALCOHOL	From Aldehyde $\text{R}-\text{CH}_2\text{OH}$	From Ketone $\text{R}-\underset{\text{OH}}{\text{CH}}-\text{R}'$	(Reduction)
2	HCN	$\rightarrow$ CYANOHYDRIN	$\text{R}-\underset{\text{CN}}{\text{CH}(\text{OH})}-\text{R}'$		(Nucleophilic addition)
3	NaHSO_3 (Satd.)	$\rightarrow$ BISULFITE ADDITION COMPOUND	$\text{R}-\underset{\text{SO}_3\text{H}}{\text{CH}(\text{OH})}-\text{R}'$		(Addition compound)
4	NH_2OH	$\rightarrow$ OXIME	$\text{R}-\underset{\text{R}'}{\text{CH}}=\text{NOH}$		(Condensation)
5	NH_2NH_2	$\rightarrow$ HYDRAZONE	$\text{R}-\underset{\text{R}'}{\text{CH}}=\text{NNH}_2$		(Condensation)
6	$\text{C}_6\text{H}_5\text{NHNH}_2$ (Phenyl hydrazine)	$\rightarrow$ PHENYLHYDRAZONE	$\text{R}-\underset{\text{R}'}{\text{CH}}=\text{NNHC}_6\text{H}_5$		(Condensation)
7	SEMICARBAZIDE ($\text{NH}_2\text{NHCONH}_2$)	$\rightarrow$ SEMICARBAZONE	$\text{R}-\underset{\text{R}'}{\text{CH}}=\text{NNHCONH}_2$		(Condensation)
8	PCl_5	$\rightarrow$ GEM-DICHLORIDE	$\text{R}-\underset{\text{R}'}{\text{CH}}\text{Cl}_2$		(Substitution)
9	Zn(Hg)/HCl	$\rightarrow$ ALKANE	$\text{R}-\text{CH}_2-\text{R}'$		(Reduction)



LEGEND

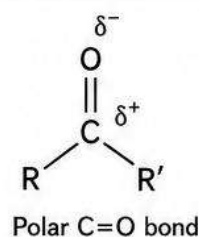
[O] = Oxidizing agent

R, R' = Alkyl or aryl groups



KEY POINTS

- Primary alcohol $\rightarrow$ Aldehyde $\rightarrow$ Carboxylic acid (on oxidation)
- Secondary alcohol $\rightarrow$ Ketone (on oxidation)
- Aldehydes are easily oxidized; ketones are resistant to oxidation.
- Aldehydes and ketones undergo nucleophilic addition reactions due to the polar C=O bond.



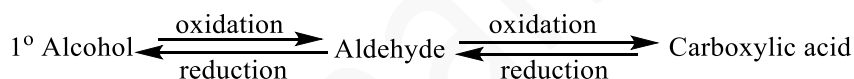
Aliphatic Aldehydes and Ketones - Chapter Summary

1. Aldehydes and ketones are **carbonyl compounds** containing the $>\text{C}=\text{O}$ group. Aldehydes have the general structure $\text{R}-\text{CHO}$, while ketones have $\text{R}-\text{CO}-\text{R}'$.
2. Aldehydes and ketones are named using the suffixes -al and -one, respectively.
3. Aldehydes and ketones show chain isomerism and functional isomerism; ketones also show position isomerism. Aldehydes and ketones with the same molecular formula are functional isomers.
4. Aldehydes are commonly prepared from primary alcohols, and ketones from secondary alcohols, by oxidation or dehydrogenation.

Common oxidizing agents: KMnO_4/H^+ ; $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$; $\text{KMnO}_4/\text{OH}^-$

5. Other methods to prepare aldehydes and ketones include ozonolysis of alkenes, Rosenmund reduction, gem-dihalide hydrolysis and alkyne hydration.
6. The $\text{C}=\text{O}$ bond is polar, making the carbonyl carbon partially positive and susceptible to attack by nucleophiles.
7. They undergo important nucleophilic addition reactions with HCN , sodium bisulphite and ammonia derivatives.
8. Aldehydes are readily oxidised to carboxylic acids, while ketones generally resist oxidation under mild conditions.
9. H_2/Ni and LiAlH_4 reduce aldehydes to primary alcohols and ketones to secondary alcohols. Clemmensen and Wolff-Kishner reductions convert the carbonyl group into $-\text{CH}_2-$.

Common reducing agents: H_2/Ni and LiAlH_4



10. Aldehydes and ketones containing α -hydrogens can undergo the aldol condensation, while aldehydes without α -hydrogen can undergo the Cannizzaro reaction.
11. 2,4-DNP detects aldehydes and ketones; Tollens' reagent gives a silver mirror with aldehydes; and Fehling's solution generally gives a brick-red precipitate with aliphatic aldehydes (not ketones).

Test	Aldehyde	Ketone
2,4-DNP	Yellow/orange/red ppt.	Yellow/orange/red ppt.
Tollens'	Silver mirror	No reaction
Fehling's	Brick-red Cu_2O ppt.	No reaction

12. Methyl ketones and ethanal give the iodoform test, producing a yellow precipitate of CHI_3 .
13. Methanal is used to prepare formalin and phenol-formaldehyde resin (Bakelite).

...