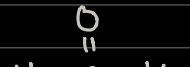
ALDEHYDES + KETONES

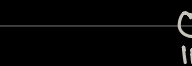
↳ Called carbonyl compounds because they contain the carbonyl group

Aldehydes

where R can be H

1st  methanal

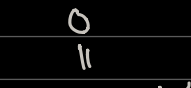
2nd  ethanal

3rd  propanal

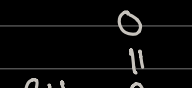
4th  butanal

Example:
written as ... CH_3CH_2CHO for propanal

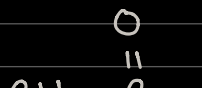
Ketones

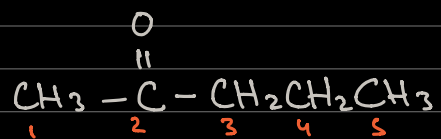


where R cannot be H

1st  propanone or "acetone" or dimethylketone

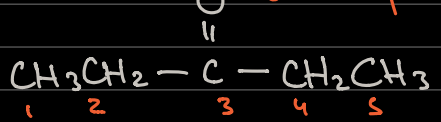
↳ would be written as CH_3COCH_3

2nd  butanone

3rd 

Positional Isomers

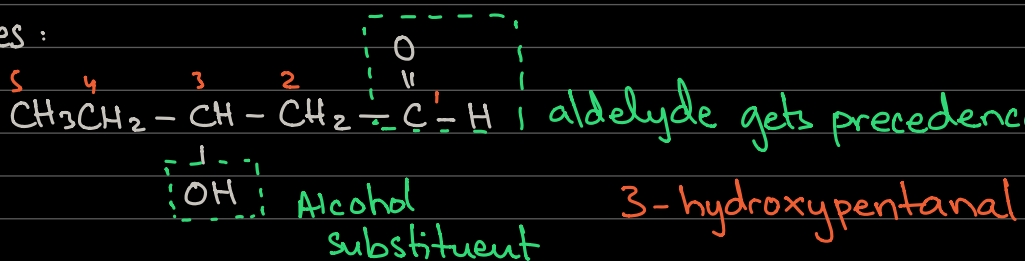
pent-2-one or 2-pentanone

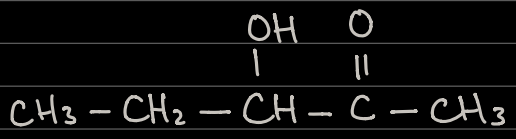


pent-3-one or 3-pentanone

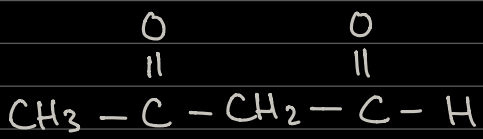
Precedence in naming:
1. Carboxylic Acids
2. Nitriles
3. Aldehydes
4. Ketones
5. Alcohols

Examples:



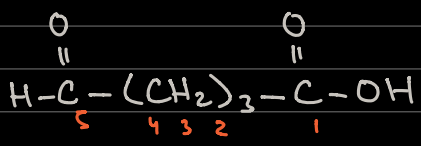


3-hydroxypent-2-one

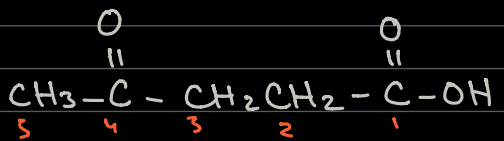


3-oxobutanal

Note: When aldehydes and ketones are substituents, they are called -oxo and are given a number on the chain



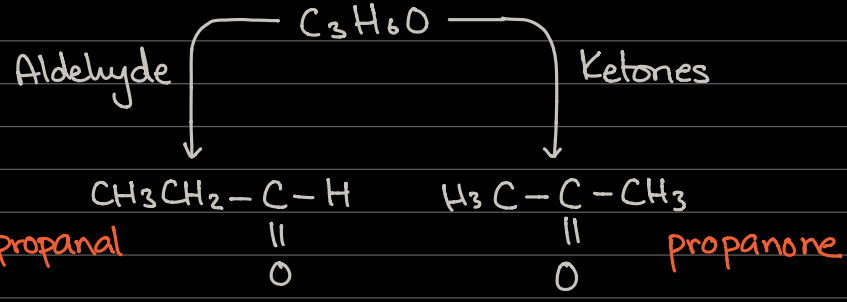
5-oxopentanoic acid



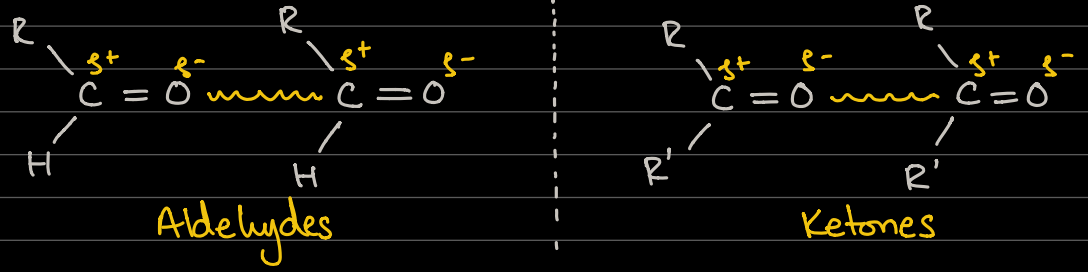
4-oxopentanoic acid

Q. How to differentiate whether an -oxo compound is an aldehyde or ketone?
If -oxo group is on the last / terminal carbon, then it's an aldehyde group, otherwise it's a ketone group

- Aldehydes and ketones are functional group isomers of each other

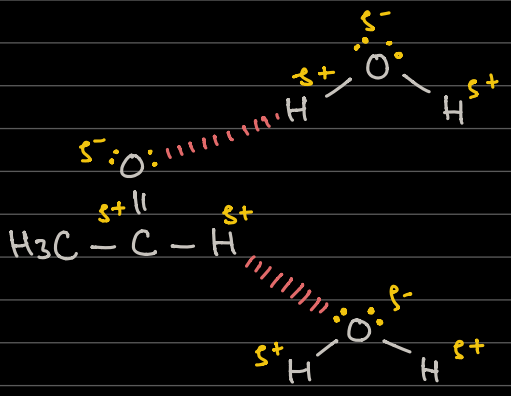


- Main intermolecular force in aldehydes and ketones is the permanent dipole – permanent dipole force of attraction



SOLUBILITY in water

- lower aldehydes (basically the first two: methanal and ethanal) are soluble in water as they can form hydrogen bonds with water

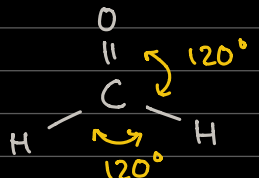


water's H is electron deficient

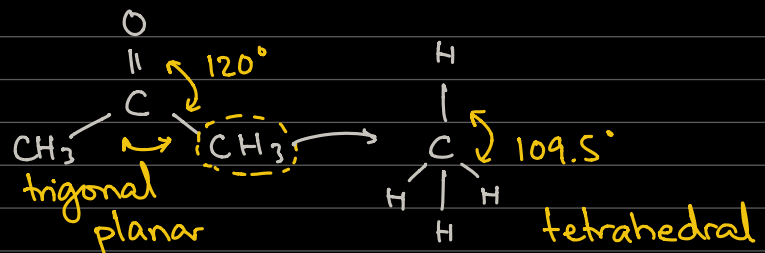
- Solubility in water decreases as the number of carbons increase as VDW (1D-1D) forces start to dominate

- As length of the carbon chain increases, 1D-1D forces increasingly become the more prominent intermolecular force

BOND ANGLES & SHAPES

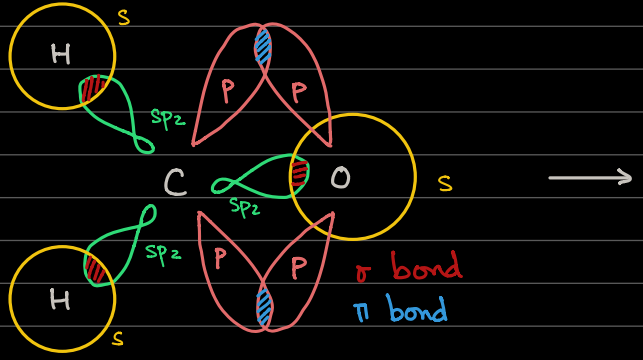


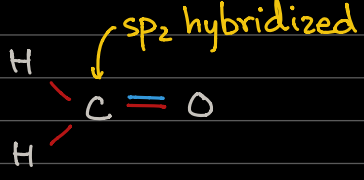
trigonal planar



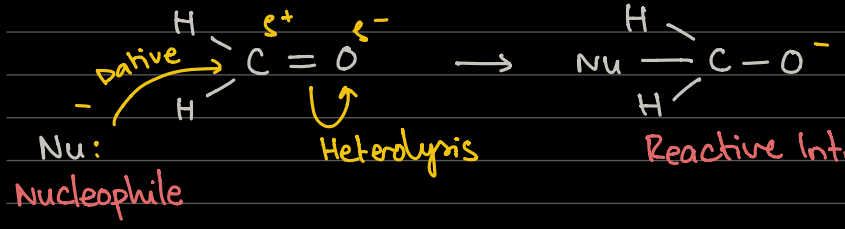
trigonal planar → tetrahedral

C = O = 1σ + 1π bond





REACTIVITY (Nucleophilic Addition):



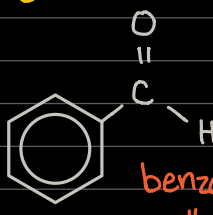
Nucleophile — Reactive Intermediate

USES:

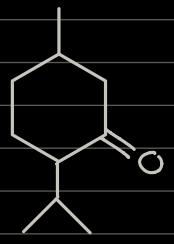
- Ketones have a sweet smell like esters
- Aldehydes have a stringent (sharp + unpleasant) odour

- H−C−H → methanal ⟶ aka "Formalin" solution
  ↳ used to preserve biological specimens

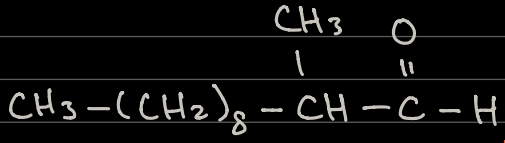
- Aldehydes + ketones are used for food flavorings and perfumes



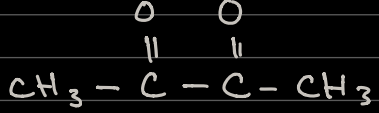
benzaldehyde
"almond flavor"



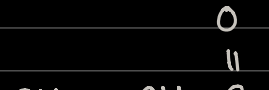
spearmint flavour



Chanel No. 5 perfume



Stale sweat smell



Component of bonfires that makes your eyes water

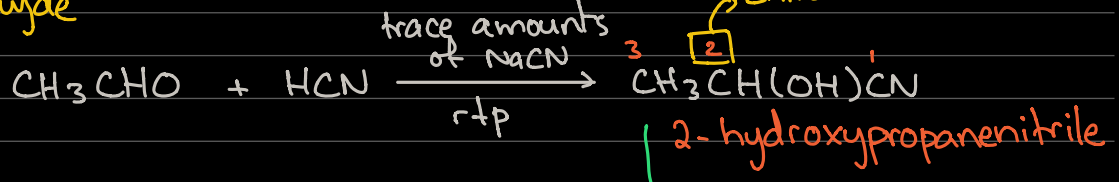
REACTIONS

1. Reactions that are common to both aldehydes and ketones

Nucleophilic Addition [Aldehydes]

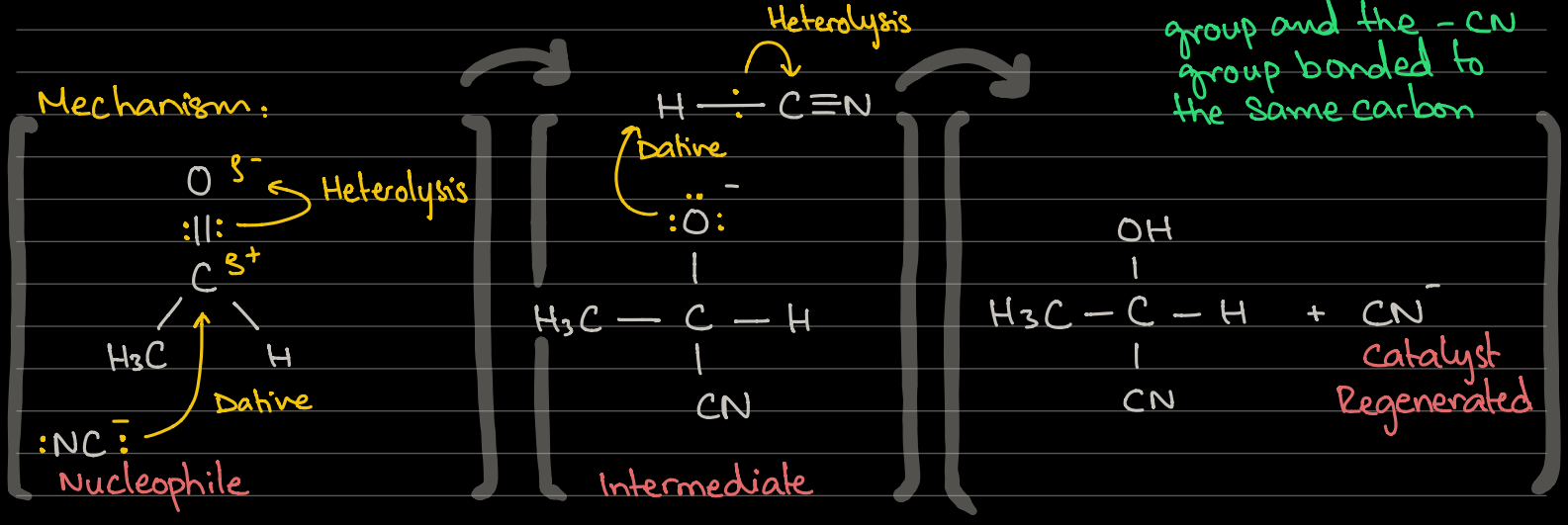
Reagent: HCN (hydrogen cyanide)
Conditions: trace amount of NaCN as catalyst
The catalyst increases the rate of reaction by providing more CN^- ion

Overall Rxns: Aldehyde



Cyanohydrins
organic compounds that have the –OH group and the –CN group bonded to the same carbon

Mechanism:



- The partially positively charged carbon ($C^{\delta+}$) of the aldehyde is electron deficient and attracts the CN^- nucleophile
- The CN^- ion makes a dative bond with the $C^{\delta+}$, and as a result, the C=O double bond breaks heterolytically
- The π electrons in the C=O bond move to the oxygen atom, creating an intermediate with a full negative charge
- The negatively charged oxygen (O^-) gets protonated, by making a dative bond with HCN.

- The H-C bond in HCN breaks heterolytically to regenerate the CN^- ion and the product cyanohydrin is formed

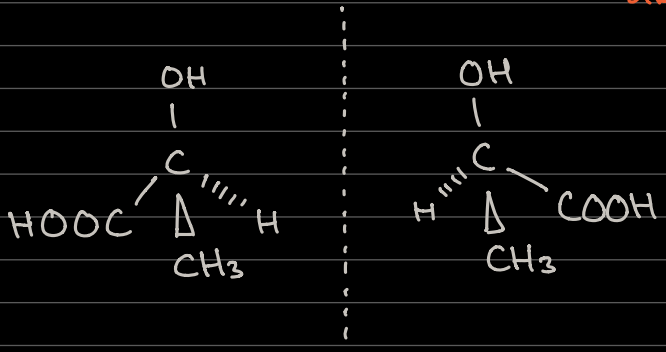
Nitrile —(Reduced to)→ Amines
Nitrile —(Hydrolised to)→ Carboxylic Acid

* : chiral carbons

Example: Hydrolysis of Nitrile

$CH_3-\underset{*}{CH}(OH)-CN \xrightarrow[\text{heat under reflux}]{HCl\ /\ H^+(aq)} CH_3-\underset{*}{CH}(OH)-COOH$

2-hydroxypropanoic acid
aka. "lactic acid"



Note: cannot use Na, ethanol as reducing agent as Na would react with the alcohol

Reduction of nitrile

$CH_3-CH(OH)-CN \xrightarrow[H_2O]{NaBH_4} CH_3-\underset{*}{CH}(OH)-CH_2NH_2$

Nucleophilic Addition [Ketones]

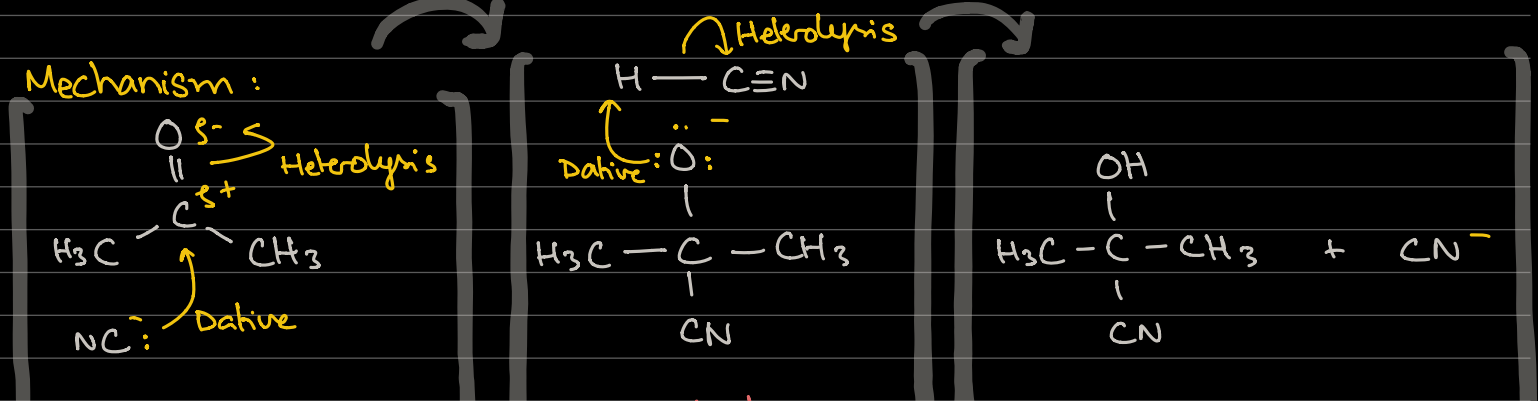
Overall Rxn:

$CH_3COCH_3 + HCN \xrightarrow[\text{rtp}]{\text{trace amount of NaCN}} CH_3-C(OH)(CN)-CH_3$

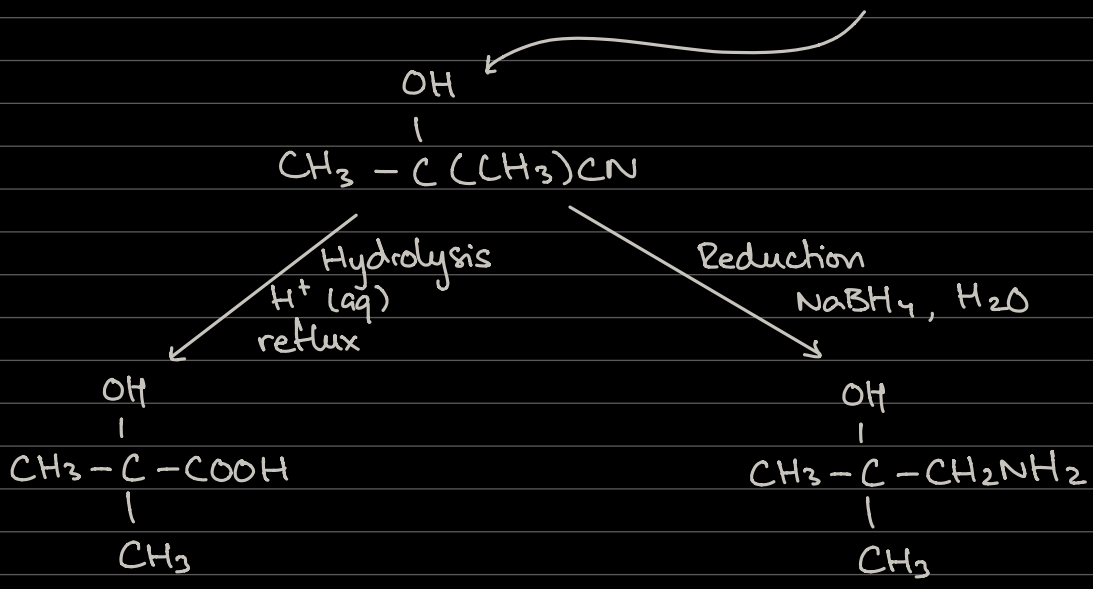
reagent

2-hydroxy-2-methylpropanenitrile

Mechanism:



intermediate



Reduction [Aldehydes + Ketones] by metal hydrides

ie. $NaBH_4$ sodium borohydride, H_2O

$LiAlH_4$ lithium aluminium hydride, anhydrous ether

- very strong reducing agent
- mainly used to reduce carboxylic acids

Aldehydes CH_3CHO —Reduced to→ 1° alcohols CH_3CH_2OH (1° alcohol)

$CH_3CHO \xrightarrow[H_2O]{NaBH_4,\ rtp} CH_3CH_2OH$

Ketones CH_3COCH_3 —Reduced to→ 2° alcohols $CH_3CH(OH)CH_3$ (2° alcohol)

$CH_3COCH_3 \xrightarrow[H_2O]{NaBH_4,\ rtp} CH_3CH(OH)CH_3$

Catalytic Hydrogenation (using $H_2(g)$ as a reducing agent)

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2 \xrightarrow[5atm\ pressure]{Ni\ catalyst} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

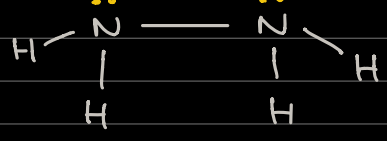
ketone → 2° alcohol

Condensation Rxns of the carbonyl group (for both aldehydes + ketones)

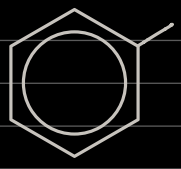
- Compounds based on hydrazine can add across the carbonyl group ($-\overset{\overset{O}{\|}}{C}-$)

- This is used to distinguish aldehydes and ketones from other functional groups

Reagent : 2,4-DNPH
2,4-dinitrophenylhydrazine (aq)



→ Hydrazine

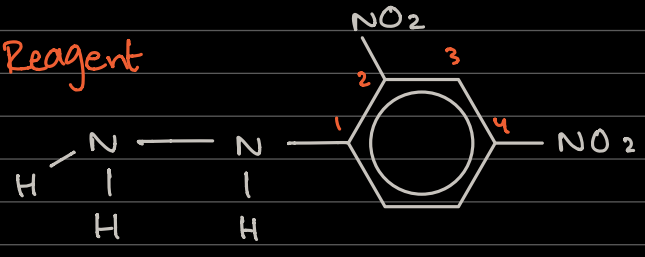


→ Phenyl
When benzene is a substituent its called "phenyl"

Dinitro ⟶ two nitro groups $-NO_2$

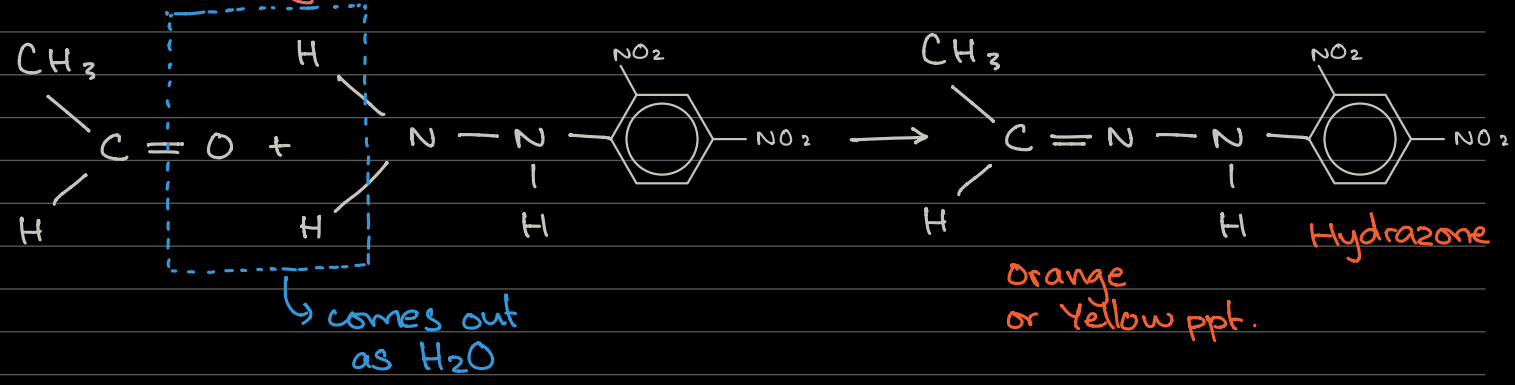
Combining all these above components:

Reagent



→ In aqueous solution

Rxn with Aldehydes:

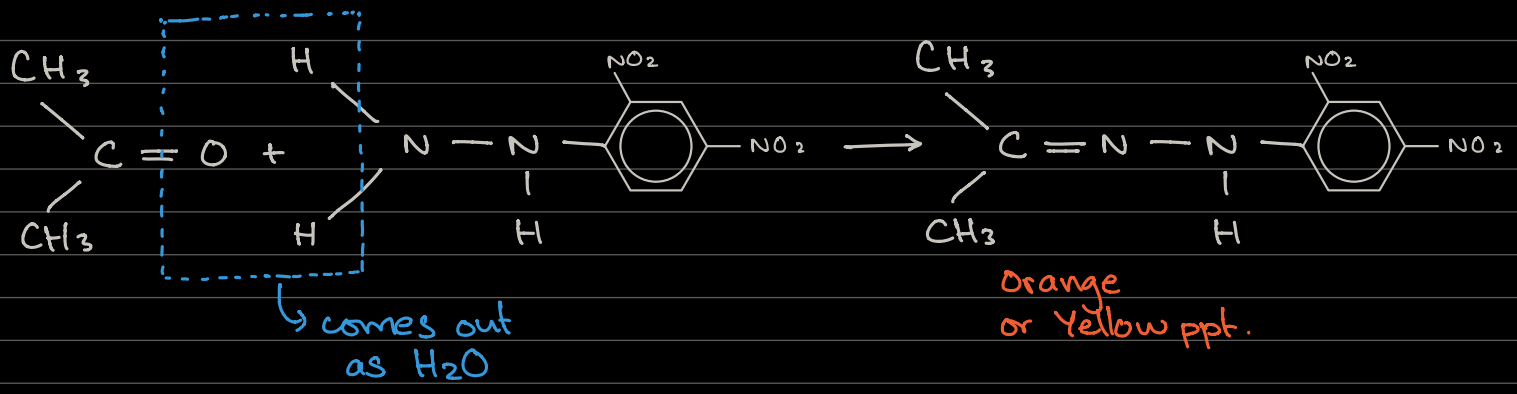


↳ comes out as H_2O

Orange or Yellow ppt.

Hydrazone

Rxn with Ketones:

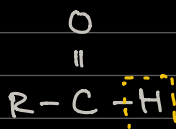


↳ comes out as H_2O

Orange or Yellow ppt.

REACTIONS SHOWN BY ALDEHYDES ONLY

1. Tollens' Reagent test (Silver Mirror Test)



aldehydes behave as reducing agents, as they have a H atom at the end

- A reducing agent is oxidised itself
- Aldehydes are oxidised to carboxylic acids

Reagent: Ammoniacal Silver Nitrate (Tollen's Reagent)

- Tollen's reagent has to be prepared freshly in labs and used immediately, as the Ag gets oxidised readily
- Start with $AgNO_3$

$Ag^+(aq)$ (from $AgNO_3$) $\xrightarrow{aq\ NaOH}$ Ag_2O (Black ppt) $\xrightarrow[\text{until ppt just dissolves}]{aq.\ NH_3\ slowly}$ $2[Ag(NH_3)_2]^+ OH^-(aq)$

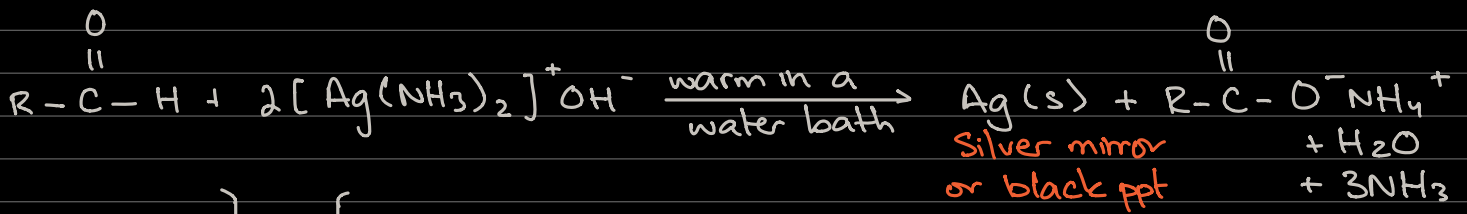
Diammine silver (I)

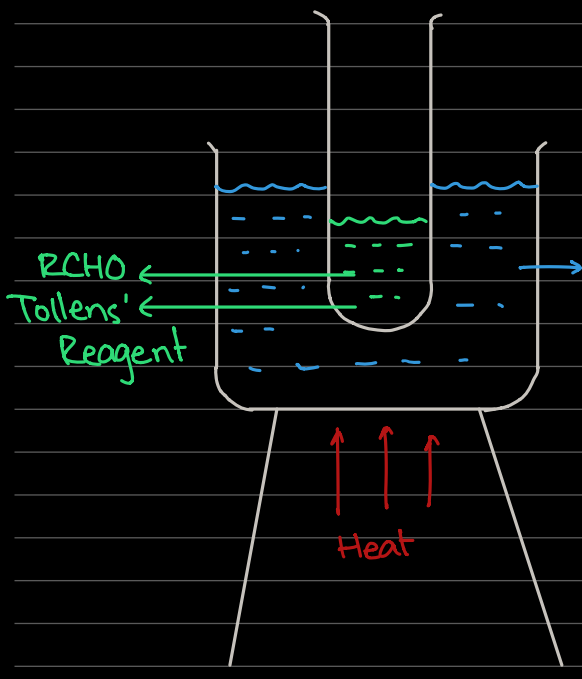
Tollens' Reagent

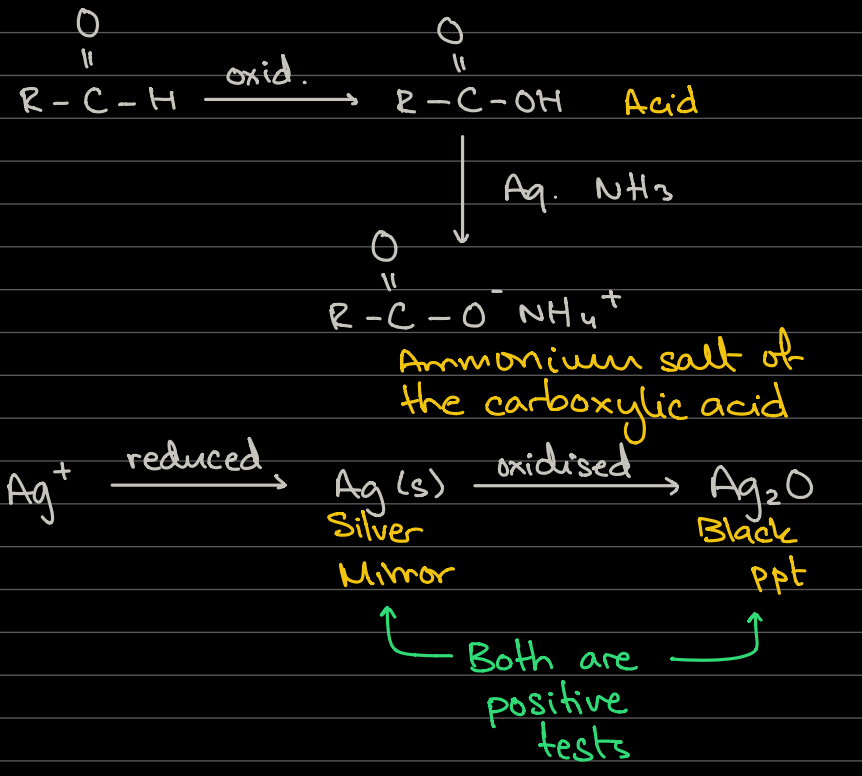
- A ligand is a species that uses its lone pair to make a dative bond with a central metal atom

NH_3 behaves as a ligand

THE REACTION :

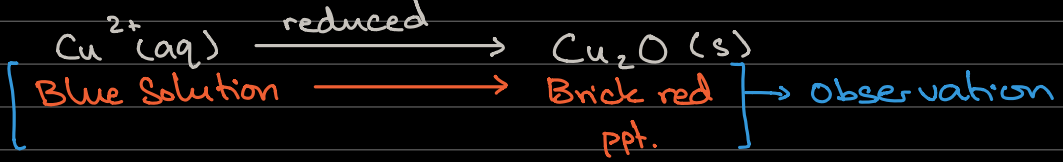




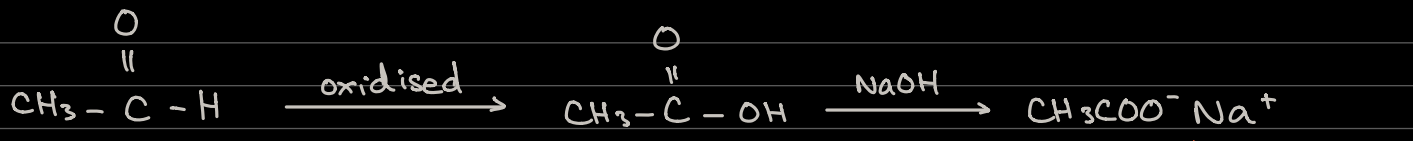


2. Fehlings Solution test (Benedict's test)

Reagent : $CuSO_4$ (aq) and NaOH (aq)
ie. Alkaline $CuSO_4$ (aq)



- Positive for aldehydes only

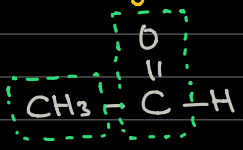


$$CH_3CHO + \underbrace{2Cu^{2+}(aq) + 5OH^-(aq)}_{\text{Fehling's solution}} \xrightarrow[\text{water bath}]{\text{heat in}} CH_3COO^- + Cu_2O + 3H_2O$$

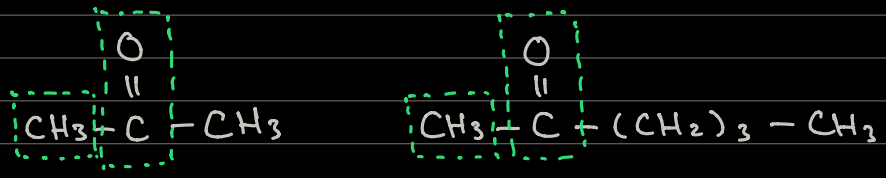
ppt. Brick red

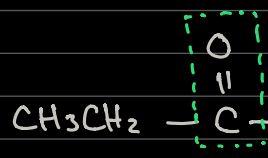
3. Iodoform test

- Aldehydes give a positive iodoform test when a carbonyl group and a methyl group are bonded to the same carbon
- Ethanal is the only aldehyde that gives a positive iodoform test



- All methyl ketones show a positive iodoform test

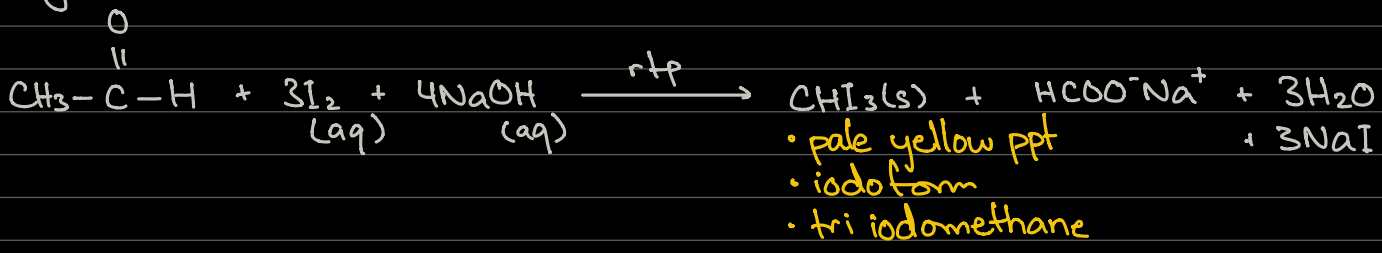




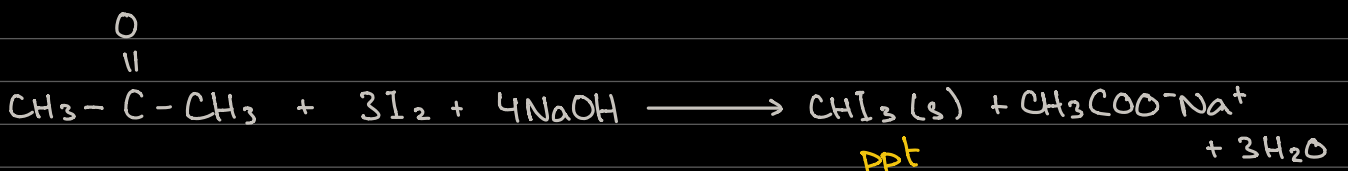
→ does not return a positive iodoform test
- missing methyl group

Reactions:

Aldehyde



Ketone



Note: Iodoform test was only in the syllabus from 2016 onwards

IS X A CARBONYL COMPOUND? $-\overset{O}{\overset{\|}{C}}-$

add 2,4-DNPH

Orange ppt

Tollen's Reagent → No Rxn ← Fehling's Solution

↓

KETONE

Silver Mirror — Brick Red ppt

↓ ↓

ALDEHYDE

Distinguish between ....

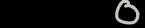
$CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$	$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$	$CH_3CH_2CH_2-\overset{OH}{\overset{\|}{}}$
propanal	propanone	propanol
Aldehyde	Ketone	1° Alcohol
Tollens Reagent ↳ Silver Mirror	Iodoform ↳ Yellow ppt.	Na(s) ↳ Bubbles of colorless gas which extinguishes a burning splint with a pop sound

$CH_3CH_2CH_3$	$CH_2=CH_2$
propane	ethene
Alkane	Alkene
add Br_2 (aq) in the dark ↳ No Rxn.	add Br_2 (aq) in the dark ↳ Bromine will be decolorised

CH_3CH_2OH
ethanol
Alcohol

1. $Na(s)$
   ↳ H_2 gas

2. $SOCl_2$
   ↳ white fumes of HCl



CH_3-C-H
ethanal
Aldehyde

1. 2,4-DNPH
   ↳ orange ppt.

2. Fehling's
   ↳ Brick red ppt.

3. Tollens'
   ↳ Silver Mirror

Note: Cannot use $K_2Cr_2O_7/H^+$ as it would oxidize both of these compounds