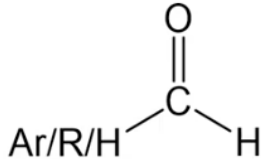
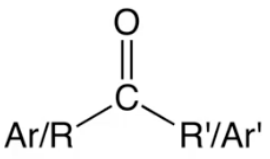


Carbonyl Compounds

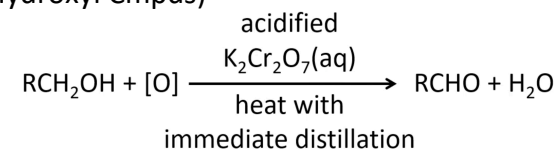
	Aldehydes	Ketone
Structure		
Condensed formula	RCOH	RCOR
IUPAC e.g.	Methane al	Methane one

Properties

- pd-pd i between (polar) molecules of carbonyl compound**
infer the mb/bp of cc vs alkanes/ alcohols and carboxylic acid
- forms hb with water molecules but not itself**
- longer** the non-polar hydrocarbon chain, **greater the hinderance** to hydrogen bond formation with water molecules
- solvent to dissolve polar (hb/ pd-pd i) and non-polar (id-id i) solutes**

Preparation (recap)

- Aldehydes: Mild oxidation of 1^o alcohols to aldehydes (Hydroxyl Cmpds)



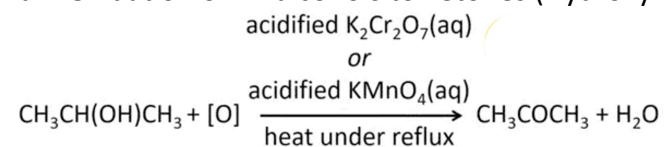
To obtain aldehyde as major product:

- Distil out the aldehyde once it is formed
- Use small amount of mild oxidising agent
- Use large excess of alcohol

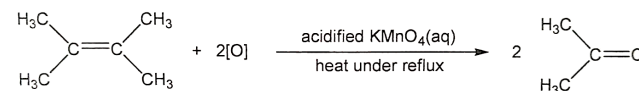
N.B. Alkaline medium does not affect aldehyde

- Ketones

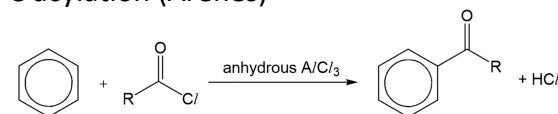
- Oxidation of 2^o alcohols to ketones (Hydroxyl Cmpds)



- Vigorous oxidation of tetra-substituted alkenes (Alkenes)



- FC acylation (Arenes)



Reactions

1. Nucleophilic addition

① R/C: HCN and small amount of $\text{NaOH(aq)} / \text{KOH(aq)}$

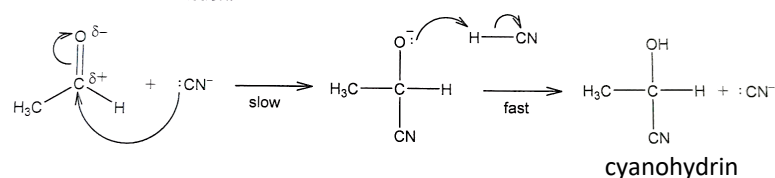
② R/C: HCN and small amount of $\text{NaCN(aq)} / \text{KCN(aq)}$

Initial generation of CN^- :

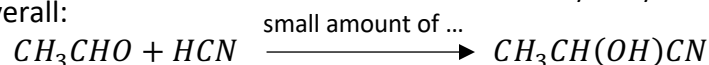
① $\text{HCN} + \text{OH}^- \rightarrow \text{CN}^- + \text{H}_2\text{O}$

② $\text{NaCN} \rightarrow \text{Na}^+ + \text{CN}^-$

Mechanism:



Overall:



N.B. HCN is produced in situ due to its low bp and highly toxic nature → small amount of H_2SO_4 added to KCN(aq) or NaCN(aq) at $10 - 20^\circ\text{C}$

N2020/11/1ii

Suggest two reasons why potassium cyanide in slightly acidic conditions is the preferred method for forming hydroxynitriles from carbonyl compounds (2m).

CN is a weak acid that dissociate partially in water to give a small amount of CN^- as the nucleophile, while KCN is a soluble salt which will give **higher amount of CN^- as the nucleophiles.**

OR

HCN is **gaseous, toxic and will be more difficult to handle** as compared to solid KCN.

OR

The negatively charged CN^- is a **stronger nucleophile** than HCN, and the acidic condition **provides the H^+ to protonate the alkoxide** in step 2.

OR

The slightly acidic conditions will **prevent excessive formation of HCN** which will lower the initial concentration of CN^- (aq) and slow down the reaction)

Reactivity:

- **Aldehydes are generally more reactive than ketones towards NA.**

Presence of more electron donating alkyl groups makes carbonyl carbon less e deficient, reducing the likelihood of attack by nophile

Bulky groups directly bonded to carbonyl carbon hinder the nophile from approaching the e deficient carbonyl carbon

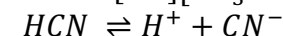
- **Aromatic cc is generally less reactive than aliphatic cc** due to resonance effect contributed by the aromatic ring.
- **Racemic mixture** can be obtained if starting carbonyl compound can be converted into chiral cyanohydrin by NA of HCN. NA can take place above and below the plane as carbonyl carbon is sp^2 hybridised

Purpose of R/C:

① Increase ror

HCN weak acid → POE left → low $[\text{CN}^-]$ in rxn mixture due to partial ionisation → rxn extremely slow → small amount of base react away H^+ → POE right → increase initial $[\text{CN}^-]$ to act as nophile

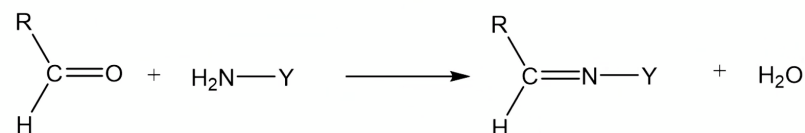
$$\text{Rate} = k[\text{CN}][\text{CH}_3\text{CHO}]$$



② Provide CN^- required for step 1

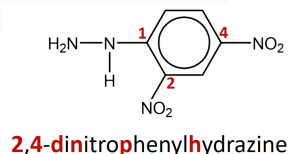
NaCN/ KCN is the catalyst as only HCN is used up.

2. Condensation



R/C: 2,4-dinitrophenylhydrazine (2,4-DNPH)

Observation: Yellow/ orange ppt formed

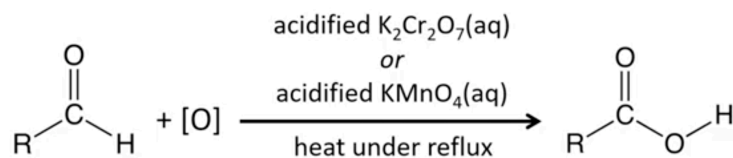


Distinguishing test for carbonyl cmpds.

3. Oxidation

Help to distinguish between aldehyde and aliphatic ketones, aliphatic aldehydes

a. Using $\text{KMnO}_4(\text{aq})$ or $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$

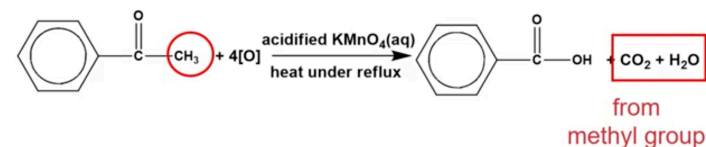
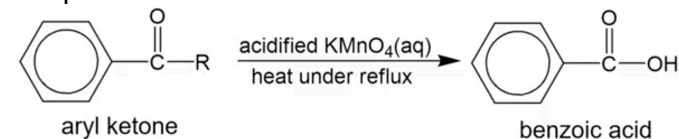


R/C: acidified $\text{KMnO}_4(\text{aq})$ or $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, HUR

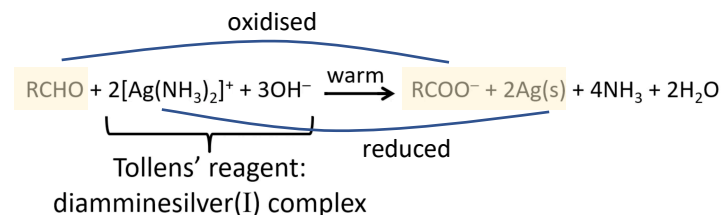
Observation: Purple to colourless or orange to green

Works on aliphatic and aromatic aldehydes and aromatic ketones.

Examples on aryl ketones:



b. Tollens' Reagent



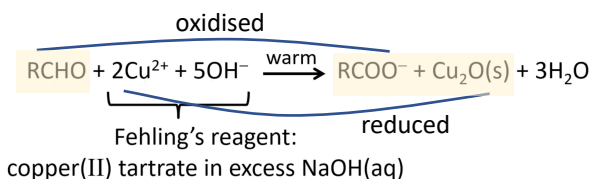
R/C: Tollens' reagent, warm

Observation: Silver mirror (formed on the wall of clean test tube) or grey/ black ppt of Ag

Works on aliphatic and aromatic aldehydes.

N.B. Gives false positive with methanoic acid.

c. Fehling's Reagent



R/C: Fehling's reagent, warm

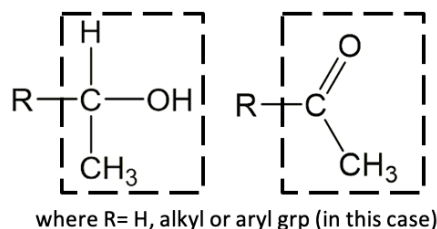
Observation: Brick red ppt of Cu_2O formed

Works on aliphatic aldehydes.

4. Iodoform

R/C: I_2 in NaOH (aq), warm

Observation: (Pale) yellow pppt of tri-iodomethane CHI_3 (with characteristic antiseptic smell) formed



and other compounds formed subsequently the various steps: oxidation, substitution and hydrolysis will give positive iodoform test

5. Reduction

	LiAlH_4	NaBH_4	H_2, Ni catalyst, heat
Characteristics	Stronger RA	Milder RA, selective recdn	Can reduce alkene
Effects	<p>Does not reduce alkenes as electron rich C=C bond in alkenes repel the AlH_4^- nucleophile.</p> <p>Reduces:</p> <ul style="list-style-type: none"> - acids, esters, acid chlorides, and acid anhydrides to primary alcohols - amides to amines - nitriles to primary amines - aldehydes to primary alcohol - ketones to secondary alcohol 		