Carbonyls

This topic introduces the chemistry of the carbonyl compounds, aldehydes and ketones.

a describe: ☐

(i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$

(ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ or $LiAlH_4$

(iii) the reaction of aldehydes and ketones with HCN and NaCN

b describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones ☐

c describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds ☐

d deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation) ☐

e describe the reaction of CH3CO– compounds with alkaline aqueous iodine to give tri-iodomethane ☐

CARBONYLS

18 Carbonyl compounds

This topic introduces the chemistry of the carbonyl compounds, aldehydes and ketones.

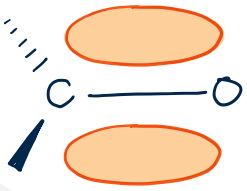
	Learning outcomes Candidates should be able to:
18.1 Aldehydes and ketones	a) describe: (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$ (ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ or $LiAlH_4$ (iii) the reaction of aldehydes and ketones with HCN and NaCN b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation) e) describe the reaction of CH_3CO- compounds with alkaline aqueous iodine to give tri-iodomethane

INTRODUCTION

Collectively, aldehydes and ketones are known as carbonyl compounds.

The properties of aldehydes and ketones are very similar to each other: almost all the reactions of ketones are also shown by aldehydes. But aldehydes show additional reactions associated with their lone hydrogen atom.

The carbonyl double bond is formed by the sideways overlap of two adjacent p orbitals, one on carbon and one on oxygen. Because of its higher electronegativity, oxygen attracts the bonding electrons (in both the σ and the π bonds), creating an electron- deficient carbon atom.



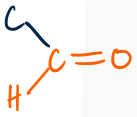
This unequal distribution of electrons is responsible for the ways in which carbonyl compounds react.

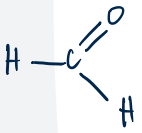
1

ALDEHYDES

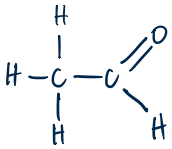
Aldehydes have at least one H attached to the carbonyl group.

Their names end in -al

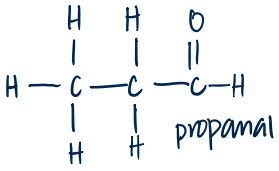




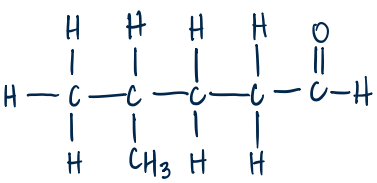
methanal
HCHO



ethanal
CH_3CHO



propanal



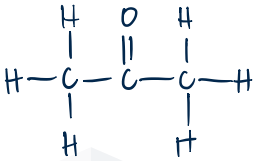
4-methylpentanal

2

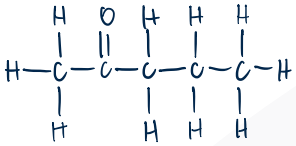
KETONES

Ketones have two carbons attached to the carbonyl group.

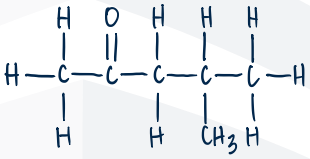
Their names end in -**one**



propanone



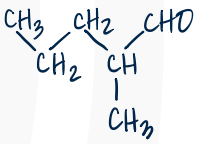
pentan-2-one

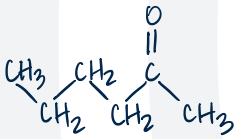


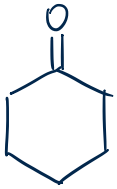
4-methylpentan-2-one

3

SKILL CHECK





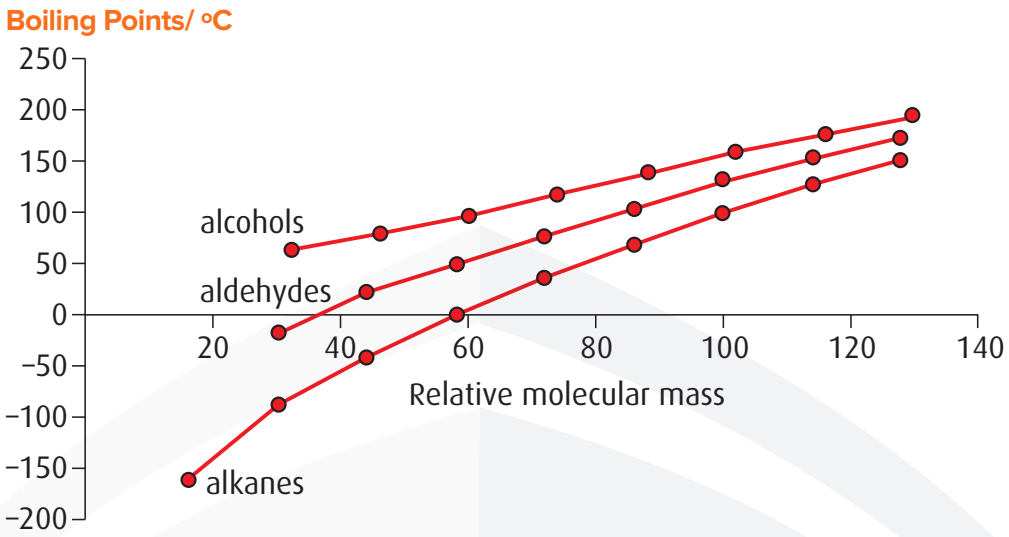


$(CH_3)_3CCHO$

$(CH_3CH_2CH_2)_2C=O$

4

BOILING POINTS



5

BOILING POINTS

Aldehydes have higher boiling points than alkanes, as aldehydes are polar whereas alkanes are non-polar. Aldehydes are polar because of the presence of the very electronegative O atom.

The intermolecular forces between aldehyde molecules are stronger than those between alkane molecules of similar relative molecular mass because of the presence of dipole–dipole interactions between the aldehyde molecules.

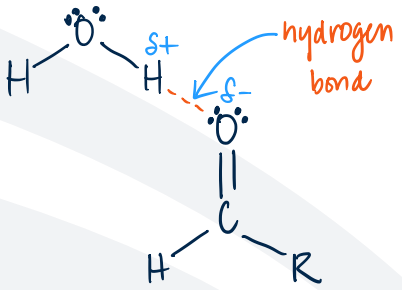
Alcohols are also polar molecules, but, because the O is joined directly to an H atom, they are also able to participate in hydrogen bonding. Hydrogen bonding is a stronger intermolecular force than dipole–dipole interactions.

6

SOLUBILITY

Lower members (methanal, ethanal, propanal, propanone, butanone) are soluble in water because of their polarity and also because they are able to hydrogen bond to water molecules.

The solubility decreases as the hydrocarbon chain gets longer, because of the non-polar nature of the hydrocarbon chain.



Note: aldehydes do not hydrogen bond to each other, but they are able to participate in hydrogen bonding with water.

7

FORMATION OF ALDEHYDES

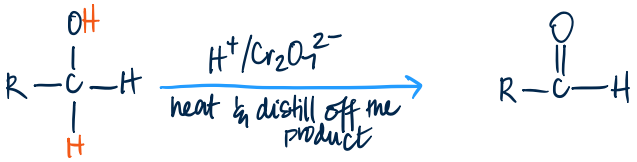
Aldehydes are prepared by the controlled oxidation of a primary alcohol.

Primary alcohols oxidize to aldehydes when heated with acidified potassium dichromate, K2Cr2O7, and the product distilled off. (It is essential to distill off the aldehyde before it gets oxidized to acid.)

Reagent acidified potassium dichromate, $K_2Cr_2O_7$

Condition heat and distill off the product

Type oxidation



8

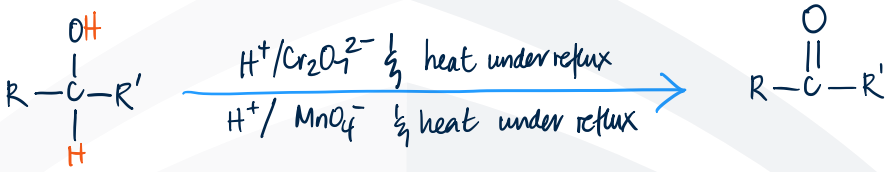
FORMATION OF KETONES

Secondary alcohols when heated (under reflux to get a good yield) with acidified potassium dichromate(VI) or potassium manganate(VII), form ketones.

Reagent acidified potassium dichromate, $K_2Cr_2O_7$
(OR acidified potassium manganate(VII), $KMnO_4$)

Condition heat under reflux

Type oxidation



9

REDUCTION OF ALDEHYDES & KETONES

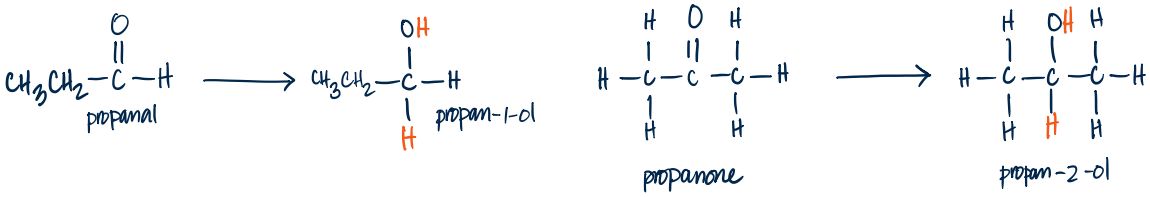
Reagent sodium borohydride, $NaBH_4$(aq) or lithium aluminiumhydride, $LiAlH_4$, in ether.

Condition heat

Type Reduction

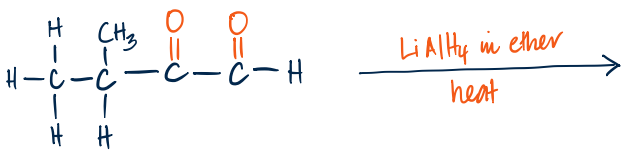
Alternate hydrogen gas over a nickel or platinum catalyst and heat

Aldehydes give primary alcohols, while ketones give secondary alcohols.

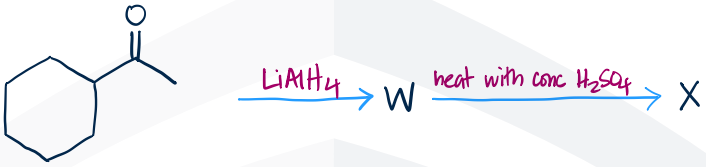


10

SKILL CHECK



Draw molecules **W** and **X.**



11

SKILL CHECK

Draw molecule Q and give the reagents and conditions for reactions **I** and **II**.

12

SKILL CHECK

Name the reagents and the conditions required for the following reactions:

(a) $CH_3-CH=CH-CHO \longrightarrow CH_3-CH=CH-CH_2OH$

(b) $CH_3-CH=CH-CHO \longrightarrow CH_3-CH_2-CH_2-CH_2OH$

13

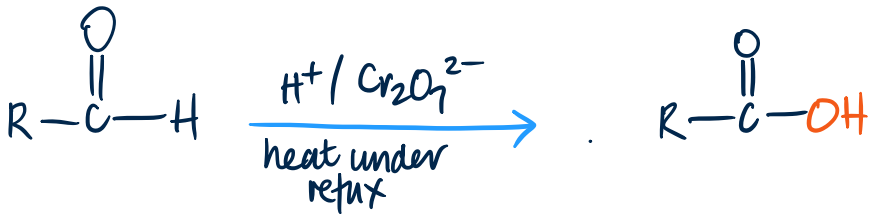
OXIDATION OF ALDEHYDES

Aldehydes are oxidized readily to their corresponding acids by acidified sodium dichromate or manganate (VII). Ketones do not undergo oxidation.

Reagent acidified potassium dichromate, $K_2Cr_2O_7$
(OR acidified potassium manganate(VII), $KMnO_4$)

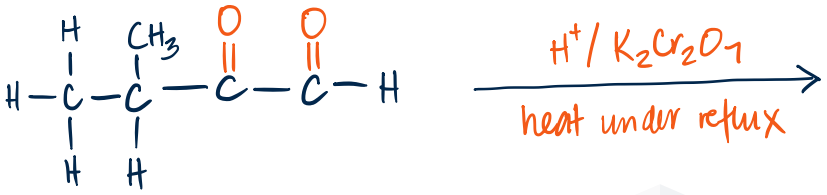
Condition heat under reflux

Type oxidation



14

SKILL CHECK

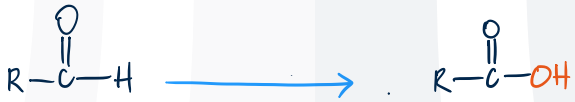


15

OXIDATION OF ALDEHYDES

OXIDATION provides a way of differentiating between aldehydes and ketones.

Aldehydes can be oxidized to carboxylic acids and ketones can not be oxidized.



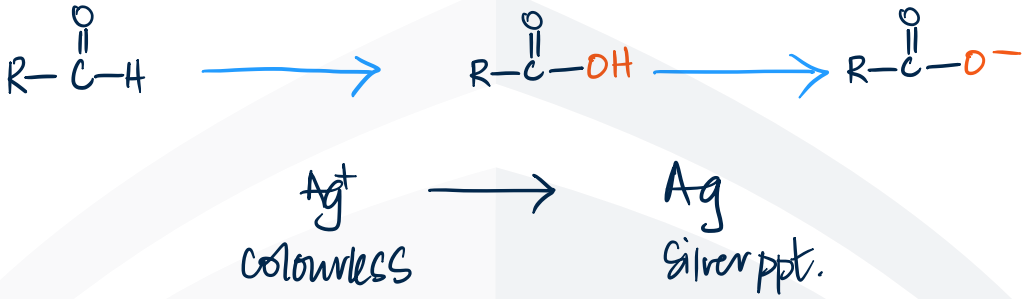
OXIDISING AGENTS	OBSERVATION with ALDEHYDES
Acidified Potassium Dichromate	color changes from orange to green
Acidified Potassium Permanganate	color changes from purple to colorless
Tollen's Reagent	forms a silver ppt.
Fehling's Solution	forms a brick red ppt.

16

TOLLEN'S REAGENT

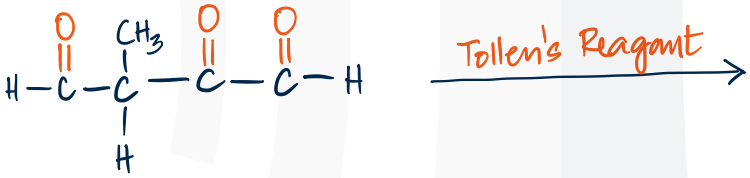
Tollen's Reagent – ammoniacal silver nitrate, contains the diammine silver(I) ion $[Ag(NH_3)_2]^+$ (ligand, complex ion), this acts as a mild oxidizing agent and will oxidize aldehydes but not ketones.

The silver(I) ion is reduced to silver.



17

SKILL CHECK



18

TOLLEN'S REAGENT

The reaction produce a silver ppt (as the silver(I) ion is reduced to silver.)

The test is known as THE SILVER MIRROR TEST.

Aldehydes are oxidised to salt of carboxylic acids as Tollen's reagent is alkaline.

Note: if the container isn't clean, then a black ppt. forms

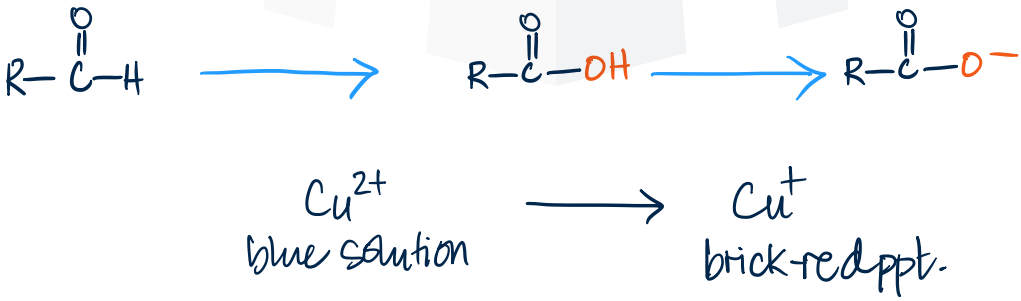
19

FEHLING'S SOLUTION

Fehling's Solution contains copper(II) ions, blue solution.

On warming it will oxidize aldehydes.

Copper(II) is reduced to a brick-red precipitate.

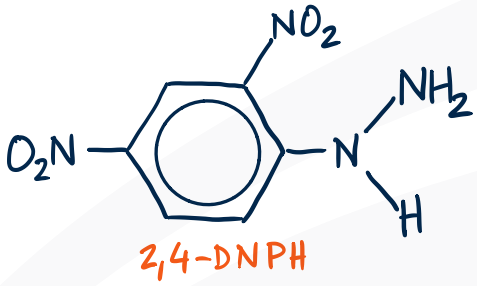


20

CONDENSATION REACTION

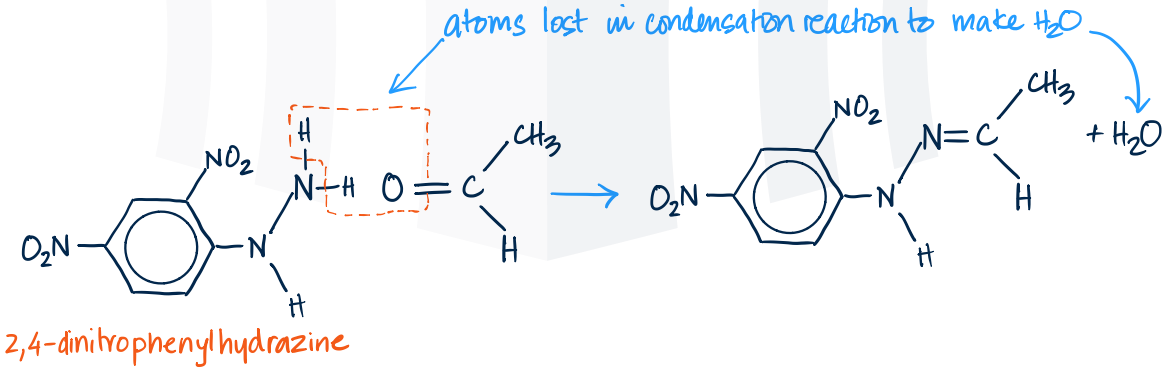
The most important condensation reaction of carbonyl compounds is that with 2,4-dinitrophenylhydrazine (2,4-DNPH).

The products are called hydrazones and are crystalline orange solids, which precipitate out of solution rapidly.



21

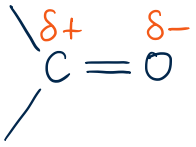
CONDENSATION REACTION



22

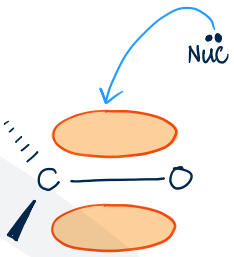
NUCLEOPHILIC ADDITION REACTION

The carbonyl group in aldehydes and ketones is polar because oxygen is much more electronegative than carbon.



The shared electrons in the double bond are drawn towards the oxygen atom. This leaves a slight positive charge on the carbon atom.

As a result, the carbon atom in a carbonyl group is open to attack by nucleophiles.



Both aldehydes and ketones undergo nucleophilic addition reactions.

It involves addition to the **polar** C=O double bond. Nucleophiles attack the positive carbon centre.

23

NUCLEOPHILIC ADDITION REACTION

Carbonyl compounds add on to hydrogen cyanide (HCN) to give nitriles.

The reaction is carried out by treating the carbonyl compound with dilute HCN in an excess of $NaCN_{(aq)}$ (or $KCN_{(aq)}$).

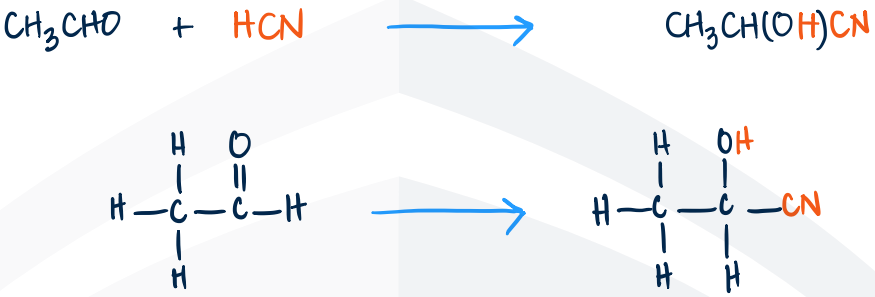
24

NUCLEOPHILIC ADDITION REACTION

Reagent dilute HCN in an excess of $NaCN_{(aq)}$ (or $KCN_{(aq)}$)
OR aqueous sodium cyanide and dilute sulphuric acid (or dilute HCl).

Condition heat under reflux

Type nucleophilic addition



25

NUCLEOPHILIC ADDITION STEP 1

CN^- (from NaCN or KCN) acts as a nucleophile and attacks the slightly positive carbon atom.

One of the C=O bonds breaks; a pair of electrons goes onto the O and gets a negative charge.

26

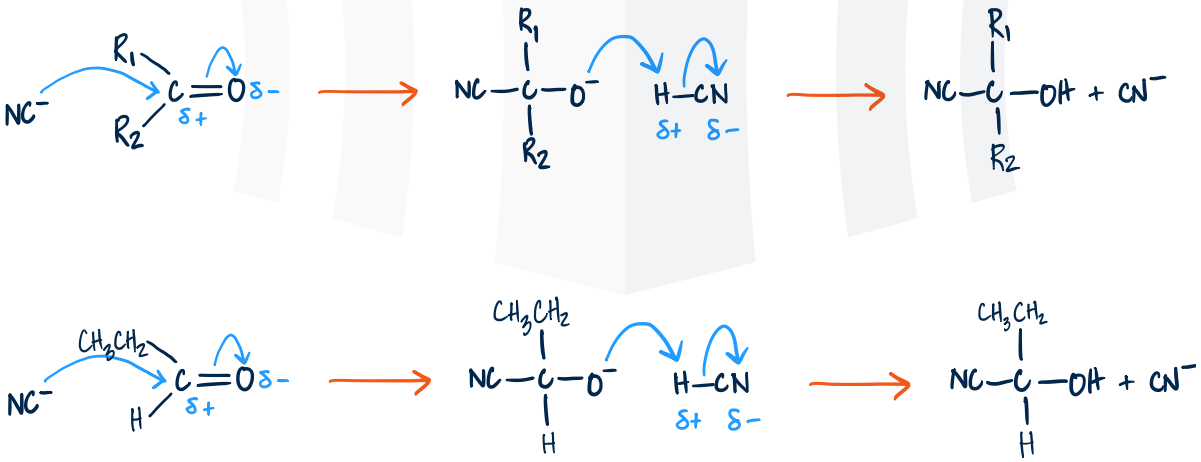
NUCLEOPHILIC ADDITION STEP 2

A pair of electrons from the O with a —ve charge is used to form a bond with H from HCN.

Overall, there has been an addition of HCN.

27

NUCLEOPHILIC ADDITION

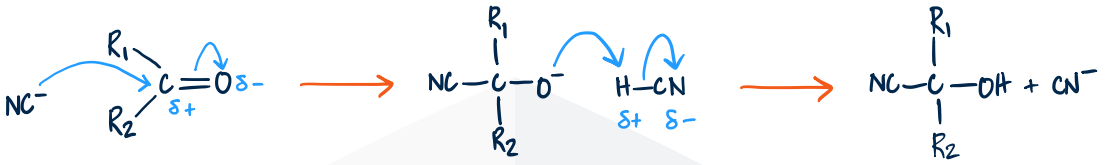


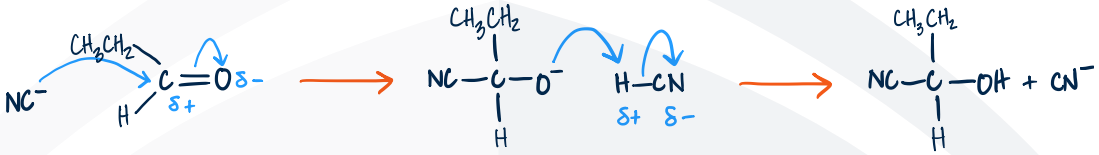
28

NUCLEOPHILIC ADDITION

Note: HCN is a **weak acid**; HCN $\rightleftharpoons$ H^+ + CN^- therefore, a **few CN^- ions** produced.

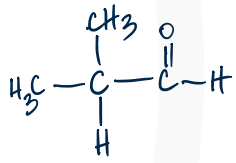
The reaction is catalyzed by CN^- ions from NaCN (or KCN).





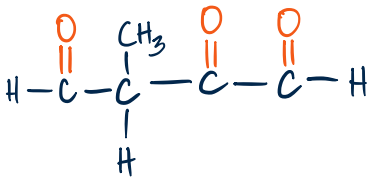
29

SKILL CHECK



2-methylpropanal

$NaCN_{(aq)}$ in $HCN_{(aq)}$, heat under reflux



$NaCN_{(aq)}$ in $HCN_{(aq)}$, heat under reflux

30

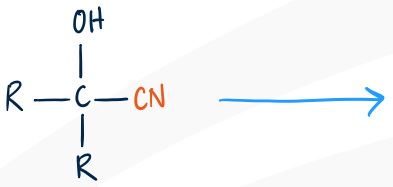
HYDROLYSIS

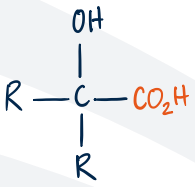
The product of nucleophilic addition, the hydroxy-nitrile, are hydrolyzed by heating under reflux with a dilute acid.

Reagent dilute hydrochloric acid, dil. HCl, (or dilute sulphuric acid)

Condition heat under reflux

Type hydrolysis





$CH_3CH(OH)CN + 2H_2O + H^+ \longrightarrow CH_3CH(OH)CO_2H + NH_4^+$

31

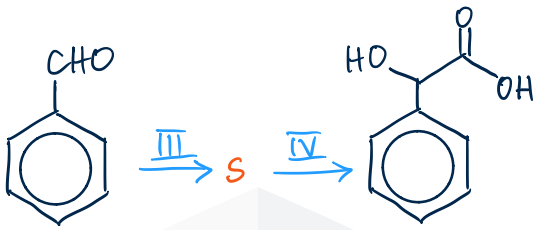
SKILL CHECK

Draw molecules **A** and **B**.

32

SKILL CHECK

Draw molecule **S** and give the reagents and conditions for reactions **III** and **IV**.



33

SKILL CHECK

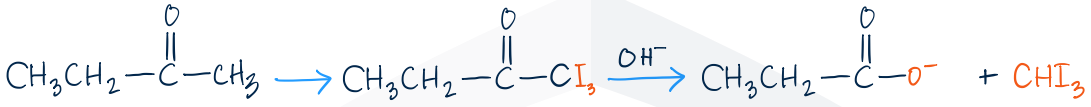
Compound **A** has the molecular formula C_4H_8O. It reacts with Fehling's solution. On treatment with sodium tetrahydridoborate(III) it gives **B**, which on warming with concentrated sulfuric acid gives 2-methylpropene. Identify **A** and **B**.

34

IODOFORM REACTION

Carbonyl compounds containing CH_3CO- group, that is, those that have a methyl group on the same carbon atom that bears the oxygen atom, can be oxidised by alkaline aqueous iodine to a salt of a carboxylic acid (with one less carbon) and a pale yellow ppt of tri-iodomethane.

The tri-iodomethane (iodoform) reaction is thus a very specific test for the CH_3CO— group (or the $CH_3CH(OH)$— group.



The overall reaction is:

35

IODOFORM REACTION

Except for ethanal, all the carbonyls that undergo this reaction are methyl ketones, with the carbonyl group on the second carbon atom of the chain, that is, they are alkan-2-ones.

The reaction can be use to obtain an acid having one carbon less.

36

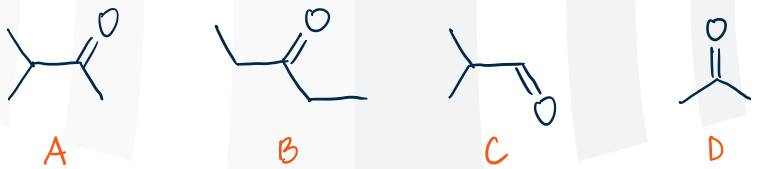
IODOFORM REACTION

The exception, ethanal, is the only aldehyde to give the pale yellow precipitate of tri-iodomethane (iodoform) with alkaline aqueous iodine:

37

SKILL CHECK

Which of these carbonyl compounds will undergo the iodoform reaction? Draw all the organic products.



38