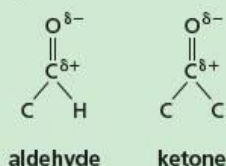


17 Aldehydes and ketones

Functional groups:



The carbonyl group, $>\text{C}=\text{O}$, contained in aldehydes and ketones is both more polarised, and more polarisable, than the $\text{C}-\text{O}$ single bond in alcohols and phenols. This topic introduces the last of our four main reaction mechanisms, nucleophilic addition. This is the characteristic way in which carbonyl compounds react and is due to the highly δ^+ carbon atom that they contain, combined with their unsaturation. Aldehydes are intermediate in oxidation state between alcohols and carboxylic acids and can undergo both oxidation and reduction reactions, but ketones can only undergo reduction reactions.

Learning outcomes

By the end of this topic you should be able to:

- 14.1a)** interpret and use the general, structural, displayed and skeletal formulae of the aldehydes and ketones
- 18.1a)** describe the formation of aldehydes and ketones from primary and secondary alcohols respectively using $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$, the reduction of aldehydes and ketones, e.g. using NaBH_4 or LiAlH_4 , and the reaction of aldehydes and ketones with HCN and NaCN
- 18.1b)** describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones
- 18.1c)** describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds
- 18.1d)** 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)
- 18.1e)** describe the reaction of $\text{CH}_3\text{CO}-$ compounds with alkaline aqueous iodine to give tri-iodomethane.

17.1 Introduction

Collectively, aldehydes and ketones are known as **carbonyl compounds**. The carbonyl group, $>\text{C}=\text{O}$, is a subunit of many other functional groups (see Table 17.1), but the term 'carbonyl compounds' is reserved for those compounds in which it appears on its own.

Table 17.1 Some functional groups containing the carbonyl group

Group	Class of compound
$\text{R}-\text{C}(=\text{O})-\text{R}'$	carbonyl compound
$\text{R}-\text{C}(=\text{O})-\text{OH}$	carboxylic acid
$\text{R}-\text{C}(=\text{O})-\text{OR}'$	ester
$\text{R}-\text{C}(=\text{O})-\text{NH}_2$	amide
$\text{R}-\text{C}(=\text{O})-\text{Cl}$	acyl chloride

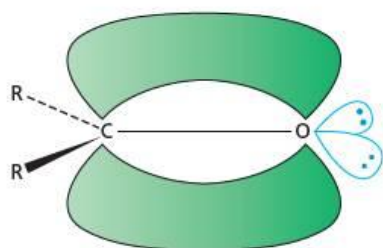
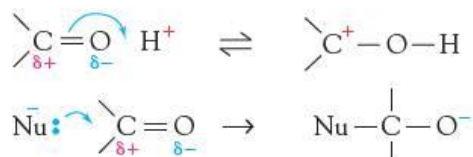


Figure 17.1 Oxygen attracts the bonding electrons away from the carbon atom.

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 bonding of the carbonyl group is similar to that of ethene (see section 14.1). Here, the 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 (see Figure 17.1). This unequal distribution of electrons is responsible for the two ways in which carbonyl compounds react.

- The oxygen of the $\text{C}=\text{O}$ bond can be protonated by strong acids.
- The carbon of the $\text{C}=\text{O}$ bond, on the other hand, is susceptible to attack by nucleophiles, Nu:



The molecules of carbonyl compounds cannot attract one another through intermolecular hydrogen bonds, because they do not contain hydrogen atoms that have a large enough $\delta+$ charge. They can, however, interact with water molecules through hydrogen bonding. The lower members of the series are therefore quite soluble in water (although less so than the corresponding alcohols).

The boiling points of carbonyl compounds are also lower than those of the corresponding alcohols, though significantly higher (by about $40\text{--}50^\circ\text{C}$) than those of the corresponding alkenes. This is due to the dipole–dipole attractions between the molecules (see Figure 17.2). Table 17.2 lists some of these properties.

Figure 17.2 Dipole–dipole attractions in carbonyl compounds

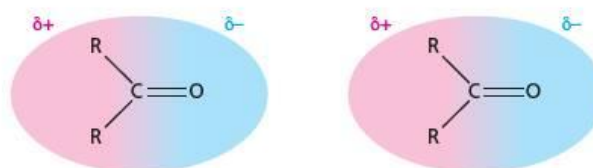
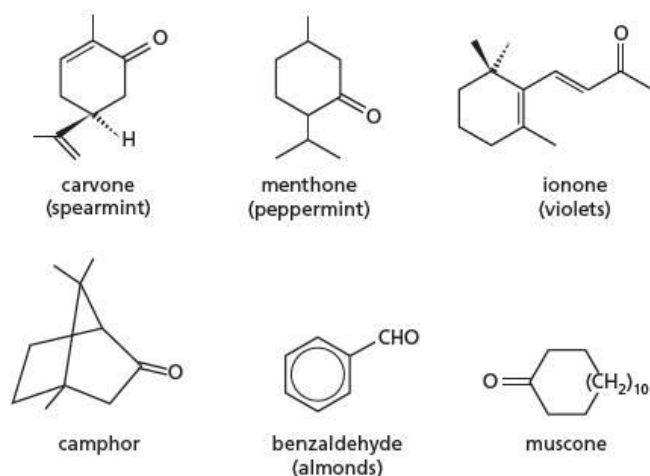


Table 17.2 Properties of some aldehydes and ketones compared with those of alkenes and alcohols

Alkene		Corresponding carbonyl compound			Corresponding alcohol		
Formula	Boiling point/ $^\circ\text{C}$	Formula	Boiling point/ $^\circ\text{C}$	Solubility in 100 g of water/g	Formula	Boiling point/ $^\circ\text{C}$	Solubility in 100 g of water/g
$\text{CH}_3\text{CH}=\text{CH}_2$	−48	CH_3CHO	20	∞	$\text{CH}_3\text{CH}_2\text{OH}$	78	∞
$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	−6	$\text{CH}_3\text{CH}_2\text{CHO}$	49	16	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	97	∞
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	30	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$	76	7	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	118	8
$(\text{CH}_3)_2\text{C}=\text{CH}_2$	−7	$(\text{CH}_3)_2\text{CO}$	56	∞	$(\text{CH}_3)_2\text{CHOH}$	82	∞

Carbonyl compounds have distinctive smells. Ketones smell ‘sweeter’ than aldehydes – almost like esters. Aldehydes have an astringent smell, but often with a ‘fruity’ overtone – ethanal smells of apples, for example. The simplest aldehyde, methanal, has an unpleasant, choking smell. Its concentrated aqueous solution, formalin, is used to preserve biological specimens. Aldehydes and ketones of higher molecular mass have important uses as flavouring and perfuming agents. Figure 25.8 (page 419) includes two carbonyl compounds with benzene rings, vanillin and benzaldehyde, that are used as flavouring agents. Some other carbonyl compounds with pleasant smells are shown in Figure 17.3.

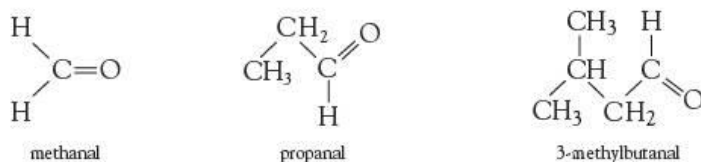
Figure 17.3 Some pleasant-smelling carbonyl compounds, and one that occurs naturally in musk (the basis for perfumes)



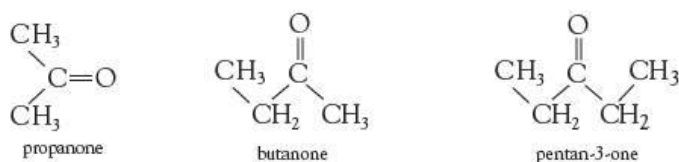
17.2 Isomerism and nomenclature

In one respect, aldehydes and ketones can be considered as positional isomers of each other: in propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, the functional group (carbonyl) is on position 1 of the chain, whereas in propanone, CH_3COCH_3 , it is on position 2. Because of significant differences in their reactions, however, aldehydes and ketones are named differently, and are considered as two separate classes of compounds.

Aldehydes are named by adding '-al' to the hydrocarbon stem:



Ketones are named by adding '-one' to the hydrocarbon stem. In higher ketones, the position of the carbonyl group along the chain needs to be specified:



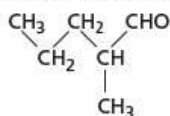
Worked example

Draw structures for the following.

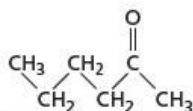
- a** 2-methylpentanal
- b** hexan-2-one

Answer

- a** The five-carbon chain is numbered starting at the aldehyde end:

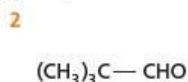
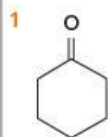


- b**



Now try this

Name the following compounds.



17.3 Reactions of aldehydes and ketones

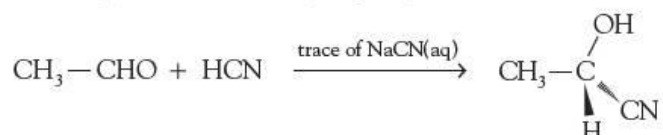
These reactions can be divided into three main groups:

- reactions common to both aldehydes and ketones
- reactions of aldehydes only
- reactions producing tri-iodomethane.

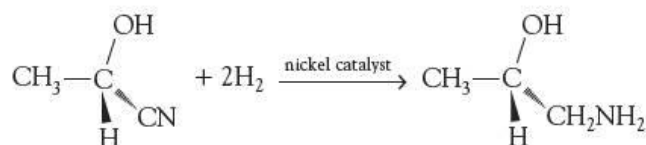
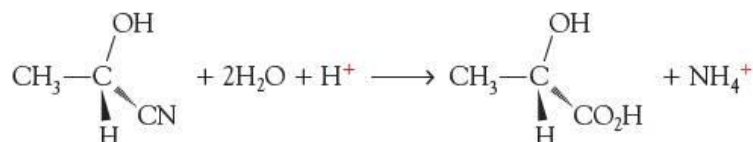
Reactions common to both aldehydes and ketones

Nucleophilic addition of hydrogen cyanide

In the presence of a trace of sodium cyanide as catalyst (or of a base such as sodium hydroxide to produce the salt), hydrogen cyanide adds on to carbonyl compounds:

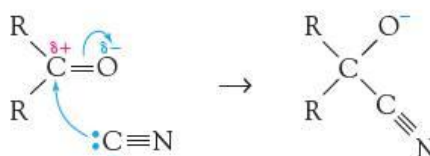


The product is 2-hydroxypropanenitrile. Like the reaction between sodium cyanide and halogenoalkanes (see section 15.3), the reaction is a useful method of adding a carbon atom to a chain, which can be valuable during organic syntheses. Cyanohydrins can be hydrolysed to 2-hydroxycarboxylic acids (see Topic 18) by heating with dilute sulfuric acid, and can also be reduced to 2-hydroxyamines (see Topic 27):

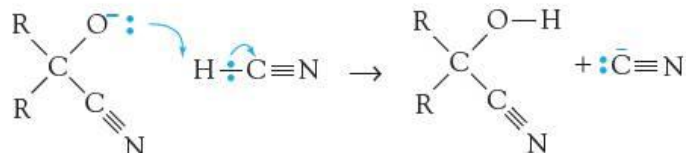


The mechanism of the addition of hydrogen cyanide to carbonyl compounds

Hydrogen cyanide is neither a nucleophile nor a strong acid. Therefore it cannot react with the carbonyl group by either of the routes shown on page 295. However, as we saw in Topic 15, the cyanide ion is a good nucleophile. It can attack the δ^+ carbon of the $\text{C}=\text{O}$ bond:



The intermediate anion is a strong base, and can abstract a proton from an un-ionised molecule of hydrogen cyanide:



So we see that although the cyanide ion is used in the first step, it is regenerated in the second. It is acting as a homogeneous catalyst in this **nucleophilic addition** reaction.

The reduction of carbonyl compounds by complex metal hydrides

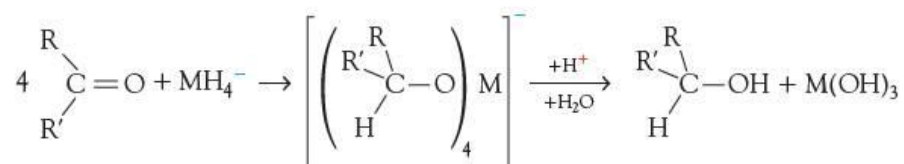
Two complex hydrides, sodium borohydride and lithium aluminium hydride, were discovered in the 1940s, and have proved very useful as reducing agents in organic chemistry. They are ionic compounds which contain the tetrahedral anion $[\text{MH}_4]^-$. Table 17.3 lists some of their properties and how they are used.

Table 17.3 Some properties of complex inorganic metal hydrides used as reducing agents in organic chemistry

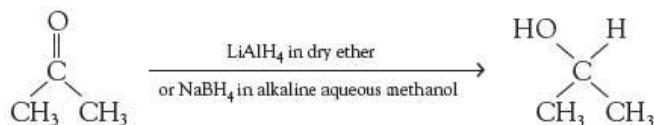
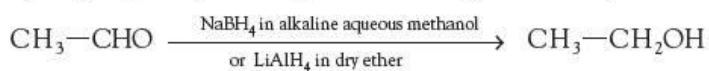
Common name	sodium borohydride	lithium aluminium hydride
Systematic name	sodium tetrahydridoborate(III)	lithium tetrahydridoaluminate(III)
Formula	NaBH_4	LiAlH_4
Solvent used and reaction conditions	methanol–water mixture, room temperature or warming	totally dry ether, room temperature or at reflux (35°C)
How the product is separated	adding acid and extracting the product from the aqueous mixture with an organic solvent such as ether	adding water (with care), then acid, and separating the ether solution of the product from the aqueous layer
Hazards during use	relatively safe in alkaline solution, but evolves hydrogen gas with acids	can catch fire with water or when wet, and ether solvents form explosive mixtures with air
Functional groups that can be reduced, and what they are reduced to	carbonyl compounds (to alcohols)	carbonyl compounds (to alcohols) esters (to alcohols) carboxylic acids (to alcohols) amides (to amines) nitriles (to amines)

As the table indicates, the preferred reagent for the reduction of aldehydes and ketones is NaBH_4 . Although LiAlH_4 will carry out the reduction as efficiently, it is both more hazardous and more expensive than NaBH_4 . However, as the more powerful reductant, it can be used to reduce carboxylic acids and their derivatives, unlike NaBH_4 .

Each reagent works by transferring a nucleophilic hydrogen atom (with its electrons) to the δ^+ carbon of the carbonyl group, forming an intermediate metal alkoxide, which is later decomposed to the alcohol:



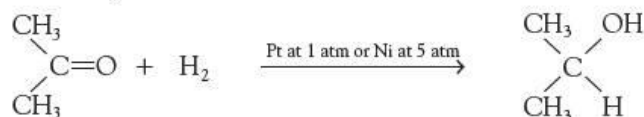
Aldehydes give primary alcohols, while ketones give secondary alcohols:



Because these reagents are nucleophilic, needing a δ^+ carbon to react with, they do not reduce $\text{C}=\text{C}$ double bonds, in contrast to catalytic hydrogenation.

Catalytic hydrogenation

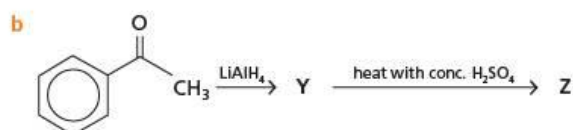
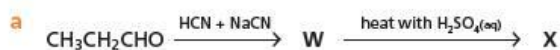
Like alkenes, carbonyl compounds can be reduced by hydrogen gas over a nickel or platinum catalyst:



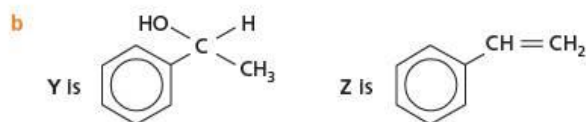
The mechanism is similar to heterogeneous catalysis (see section 8.6).

Worked example

Suggest the structural formulae of the intermediates and products of the following reactions:

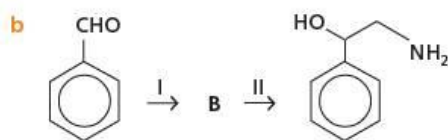
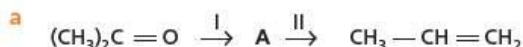


Answer

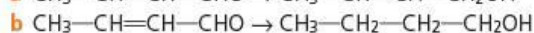
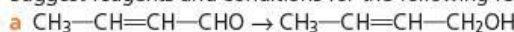


Now try this

1 Suggest reagents for steps I and II in each of the following transformations, and the structures of the intermediates **A** and **B**:

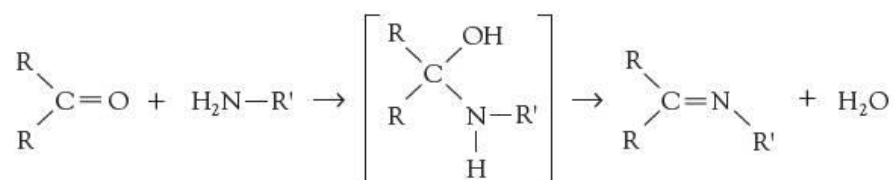


2 Suggest reagents and conditions for the following reactions.



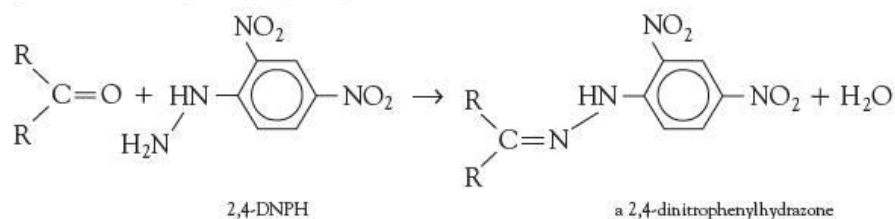
Condensation reactions

Nitrogen nucleophiles readily add on to carbonyl compounds. But usually, the initially formed addition compounds cannot be isolated. They easily lose water to give stable compounds containing a C=N bond:



Reactions that form water (or any other inorganic small-molecule compound) when two organic compounds react with each other are called **condensation reactions**.

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. They can be purified relatively easily by recrystallisation.



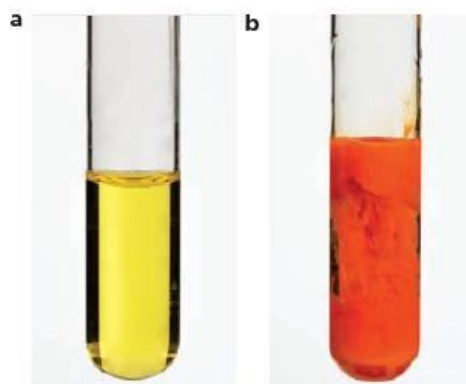
The formation of an orange precipitate when a solution of 2,4-DNPH is added to an unknown compound is a good test for the presence of a carbonyl compound.

If the melting point of a recrystallised sample is measured and compared with tables of known values, the carbonyl compound can be uniquely identified. This is especially useful if the carbonyl compounds have similar boiling points, and so would otherwise be easily confused (see Table 17.4).

Table 17.4 The melting points of some 2,4-DNPH derivatives of carbonyl compounds

Carbonyl compound	Boiling point/°C	Melting point of 2,4-dinitrophenylhydrazone derivative/°C
CH ₃ CH ₂ CH ₂ CH ₂ CHO	103	108
CH ₃ CH ₂ COCH ₂ CH ₃	102	156
CH ₃ CH ₂ CH ₂ COCH ₃	102	144

Figure 17.4 Ethanal reacting with 2,4-DNPH: **a** at the start of the reaction; this forms an orange 2,4-DNPH precipitate, **b**.



Now try this

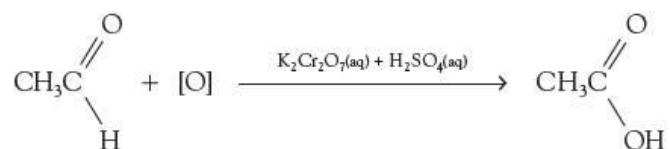
Two isomers **G** and **H** have the molecular formula C₄H₈O. **G** forms an orange precipitate with 2,4-DNPH whereas **H** does not. **H** decolorises bromine water, but **G** does not. On treatment with hydrogen and nickel, both **G** and **H** give the same compound, butan-1-ol. Suggest structures for **G** and **H**.

Reactions undergone only by aldehydes

Aldehydes are distinguished from ketones by having a hydrogen atom directly attached to the carbonyl group. This hydrogen atom is not in any way acidic, but the C—H bond is significantly weaker than usual. The —CHO group is readily oxidised to a —COOH group, making aldehydes mild reducing agents. This oxidation, specific to aldehydes, has been used to design the following tests that will distinguish aldehydes from ketones.

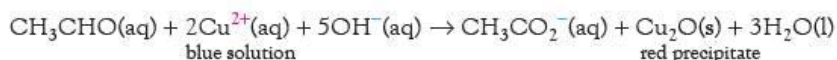
Oxidation by acidified potassium dichromate(VI) solution

It was mentioned in section 16.3 that aldehydes are more easily oxidised than alcohols. The reaction takes place on gentle warming, and the colour of the reagent changes from orange to green.



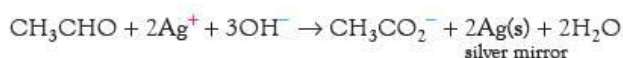
Reduction of Fehling's solution

The bright blue **Fehling's solution** is a solution of Cu^{2+} ions, complexed with salts of tartaric acid, in an aqueous alkaline solution. When warmed with an aldehyde, the Cu^{2+} ions are reduced to Cu^+ ions, which in the alkaline solution form a red precipitate of copper(I) oxide. The aldehyde is oxidised to the salt of the corresponding carboxylic acid:



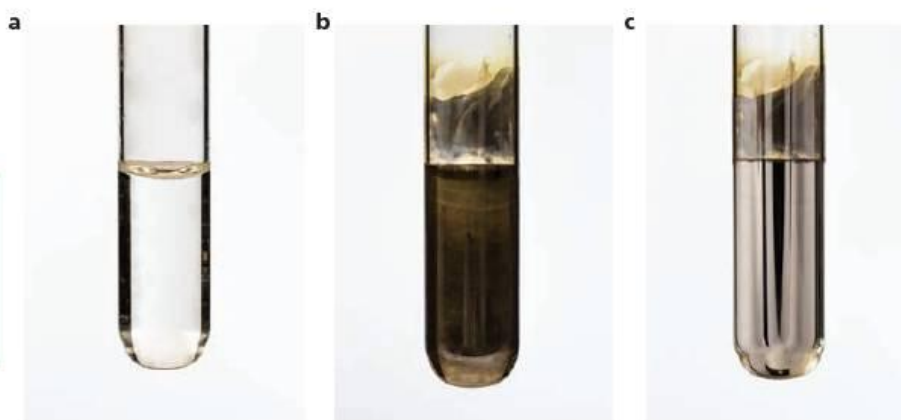
Formation of a silver mirror with Tollens' reagent

Tollens' reagent contains silver ions, complexed with ammonia, in an aqueous alkaline solution. These silver ions are readily reduced to silver metal on gentle warming with an aldehyde. The metal will often silver-plate the inside of the test tube. Once again, the aldehyde is oxidised to the salt of the corresponding carboxylic acid:



A dilute solution of the aldehyde sugar, glucose, was once used to make mirrors for domestic use by means of this reaction.

Figure 17.5 An aldehyde produces a silver mirror with Tollens' reagent.

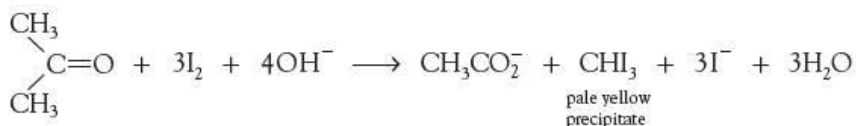


Aldehydes can be distinguished from ketones by one of the following tests:

- aldehydes produce a red precipitate on warming with Fehling's solution
- aldehydes produce a silver mirror on warming with Tollens' reagent.

The tri-iodomethane (iodoform) reaction

Ketones that contain the group —COCH_3 (that is, methyl ketones) undergo the tri-iodomethane (iodoform) reaction on treatment with an aqueous alkaline solution of iodine. Tri-iodomethane, CHI_3 , is a pale yellow insoluble solid, with a sweet, antiseptic 'hospital' smell:



There is one aldehyde, ethanal, that also undergoes the tri-iodomethane reaction:

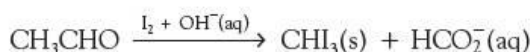


Figure 16.7 shows the results of the iodoform reaction.

The **tri-iodomethane (iodoform) reaction** is thus a very specific test for the $\text{CH}_3\text{CO—}$ group (or the $\text{CH}_3\text{CH}(\text{OH})\text{—}$ group – see Topic 16).

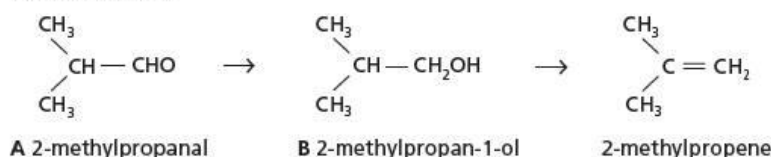
Worked example 1

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**.

Answer

A positive Fehling's solution test means that **A** is an aldehyde. Sodium tetrahydridoborate(III) reduces an aldehyde to a primary alcohol. Concentrated sulfuric acid converts this to the alkene. Therefore:



Now try this

Describe a test (a different one in each case) that you could use to distinguish between the following pairs of compounds.

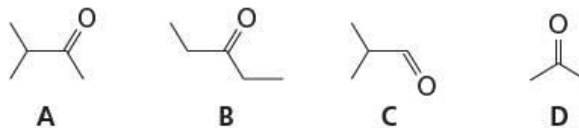
- 1 $\text{CH}_3\text{CH}_2\text{CHO}$ and CH_3COCH_3
- 2 $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$ and $\text{CH}_3\text{CH}_2\text{CHO}$

Now try this

Two carbonyl compounds **E** and **F** have the molecular formula C_4H_8O . **E** gave a yellow precipitate when treated with alkaline aqueous iodine, but **F** does not. Suggest, with a reason, structures for **E** and **F**. Suggest a different test, other than the tri-iodomethane reaction, that could distinguish between these two compounds.

Worked example 2

Which of these carbonyl compounds will undergo the iodoform reaction?



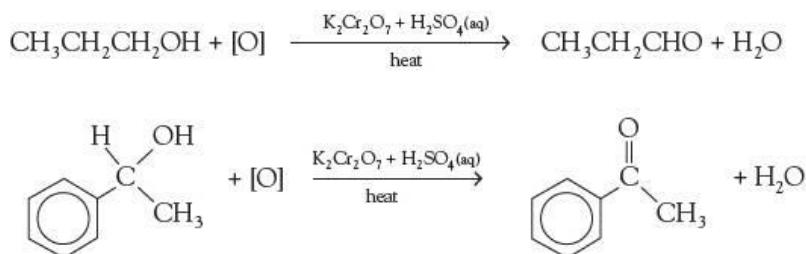
Answer

Only ketones **A** and **D** contain the grouping $\text{CH}_3\text{CO}-$, so these are the only two to give iodoform. **B** contains the grouping $\text{CH}_3\text{CH}_2\text{CO}-$, whilst **C** is an aldehyde.

17.4 Preparing carbonyl compounds

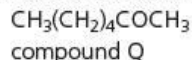
From alcohols, by oxidation

See section 16.3 for details of this reaction. For example:



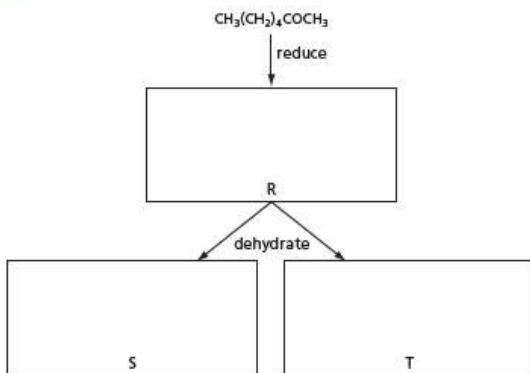
As explained in Topic 16, if an aldehyde is being prepared, the oxidant is added slowly to an excess of the alcohol and the aldehyde is distilled off as it is formed, in order to prevent further oxidation to the acid. (As their molecules are not hydrogen bonded to one another, aldehydes generally have lower boiling points than the corresponding alcohols.) If, however, it is the acid that is required, the reaction mixture is heated under reflux so that any aldehyde that might be formed remains in contact with the oxidising agent, and all is eventually oxidised to the carboxylic acid.

- 2 Compound **Q**, heptan-2-one, is found in some blue cheeses.



- a Compound **Q** may be reduced to **R**. Compound **R** may be dehydrated to give two different products, **S** and **T**.

- i Draw the structural formulae of **R**, **S**, and **T**.



- ii State the reagents that would be used for **each** of these reactions in a school or college laboratory.
- reduction
- dehydration

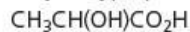
[5]

- b Write the structural formula of the organic compound formed when **Q** is reacted separately with each reagent under suitable conditions. If you think no reaction occurs, write 'NO REACTION'.

Tollens' reagent		
HCN		
$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$		

[5]

- c The first stage of cheese making is to produce 2-hydroxypropanoic acid (lactic acid) from milk.



lactic acid

Other than the use of a pH indicator, what reagent could you use to confirm the presence of some lactic acid in a sample of heptan-2-one? State what observation you would make.

[2]

[Cambridge International AS & A level Chemistry, 9701, Paper 23 Q4 June 2013]