

17 Carbonyl compounds

The chemistry of carbonyl compounds is only required for AS Level. However, a knowledge of this is expected for some aspects of A Level chemistry, particularly in organic synthesis.

Formation of carbonyl compounds

The oxidation of alcohols by acidified dichromate(VI) was covered in [Chapter 16](#).

- With a primary alcohol ([Figure 17.1](#)) an aldehyde is formed first.

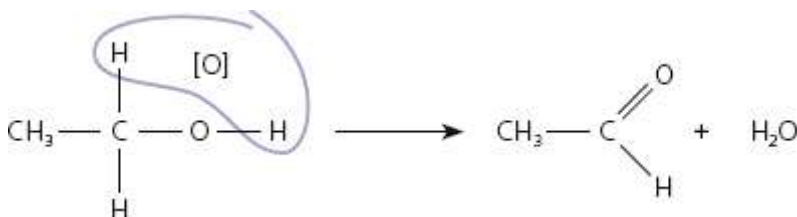


Figure 17.1

- If this is not removed from the reaction vessel, it is oxidised further ([Figure 17.2](#)) to give a carboxylic acid.

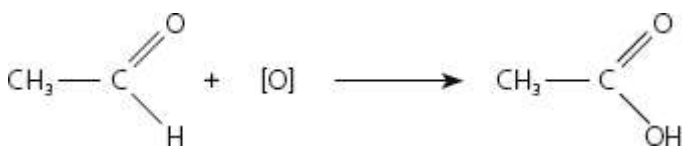


Figure 17.2

- With a secondary alcohol, a ketone is formed ([Figure 17.3](#)). This is not oxidised further.

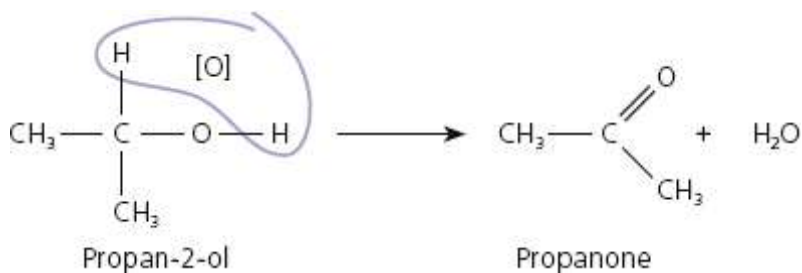


Figure 17.3

Reduction reactions of carbonyl compounds

These are the reverse of the oxidation reactions used in the preparation of carbonyl compounds. They are carried out using sodium tetrahydridoborate (sodium borohydride), NaBH_4 .

With aldehydes such as ethanal the reaction is as shown in [Figure 17.4](#), forming a primary alcohol.

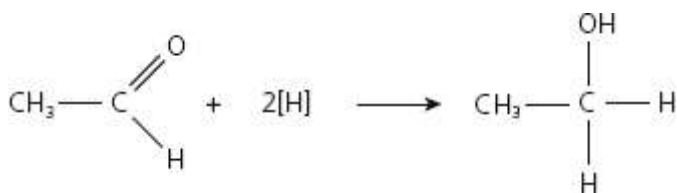


Figure 17.4

With ketones such as propanone ([Figure 17.5](#)) the reaction is very similar. A secondary alcohol is formed.

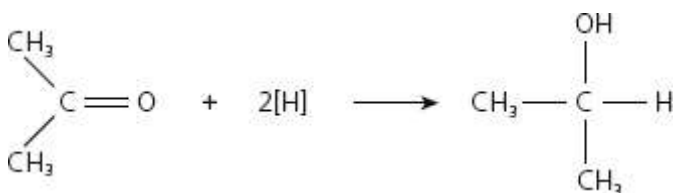


Figure 17.5

NOW TEST YOURSELF

- 1 Complete the table about the oxidation of alcohols.

Alcohol	Type of alcohol (1°, 2°, 3°)	Oxidation product
Butan-2-ol		
2-methylbutan-1-ol		
2-methylbutan-2-ol		
2,2-dimethylpropan-1-ol		

Nucleophilic addition of hydrogen cyanide

In just the same way as alkenes can react by adding a molecule across a C=C double bond, carbonyl compounds can add a molecule across the C=O double bond (Figure 17.6).

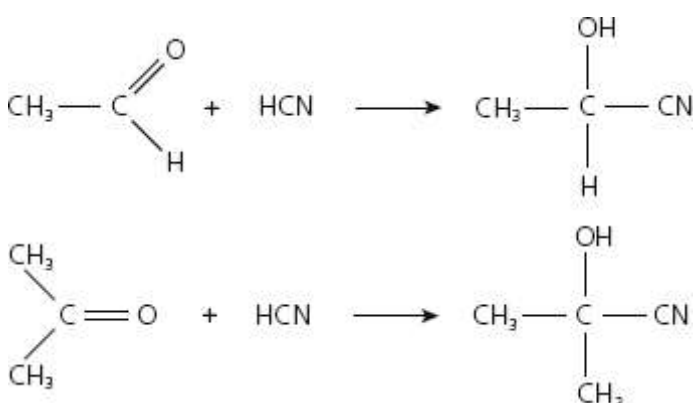


Figure 17.6

For AS Level you need to know the mechanism for the reaction, using hydrogen cyanide as the nucleophile. You may think that this is a strange reactant to choose, but as you saw earlier (page 99), it adds a carbon atom to the chain, which is often an important step in a reaction.

The reactions are started (Figure 17.7) by the nucleophilic attack on the carbonyl compound by hydrogen cyanide. The C=O bond is polarised, with a

partial positive charge on the carbon atom and a partial negative charge on the oxygen atom.

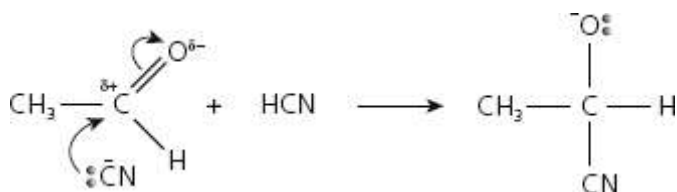


Figure 17.7

Hydrogen cyanide itself is not used in the reaction because it is a highly toxic gas. Instead, sodium cyanide or potassium cyanide is added to the carbonyl compound followed by a small amount of sulfuric acid. This produces hydrogen cyanide in the reaction vessel but also forms cyanide ions, which are important as you will see from the mechanism.

Completing the addition of hydrogen cyanide to an aldehyde

The negative ion formed then picks up a hydrogen ion (Figure 17.8). It could come from a hydrogen cyanide molecule or from the water or the H_3O^+ ions present in the slightly acidic solution.

The negative ion formed then picks up a hydrogen ion to give the hydroxynitrile (or cyanohydrin, as it is sometimes called in older textbooks).

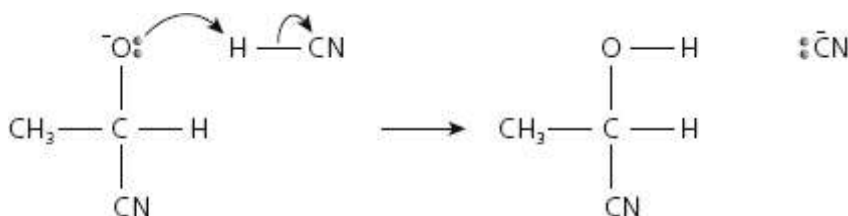


Figure 17.8

Completing the addition of hydrogen cyanide to a ketone

The mechanism for ketones (Figure 17.9) is similar to that for aldehydes. The first stage is a nucleophilic attack by the cyanide ion on the slightly positive carbon atom as above in Figure 17.7. Then the negative ion picks up a hydrogen ion to give the hydroxynitrile.

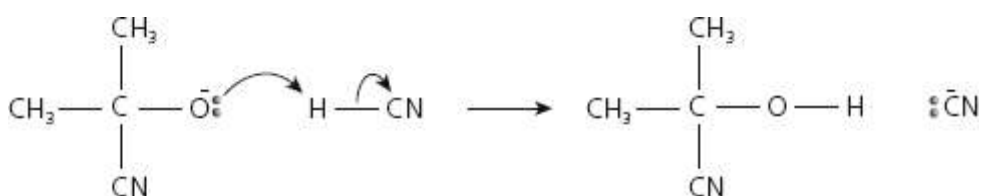


Figure 17.9

NOW TEST YOURSELF

- 2 What is the reagent used for adding hydrogen cyanide to a carbonyl compound?

Chirality

You may have noticed that the product formed with the aldehyde has four different groups attached to the central carbon. You will remember from [Chapter 13](#) that this is a *chiral* carbon atom.

You may also remember that this usually means that the compound exists as a pair of optical isomers that are mirror images of each other. However, the product of this particular reaction is *not* optically active because ethanal is a planar molecule and the mechanism means that attack by the cyanide ion can occur from either above or below the molecule. This produces a 50 : 50 mixture of isomers, so the net result is a lack of optical activity.

NOW TEST YOURSELF

- 3 Give the structure of the product formed when hydrogen cyanide is added to butanal.

Reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH)

- This rather complicated-sounding reagent is used in a simple test for carbonyl compounds. The reaction is called a condensation, or sometimes

a nucleophilic addition–elimination, reaction.

- If a few drops of a suspected carbonyl compound (or a solution of the suspected carbonyl compound in methanol) are added to 2,4-DNPH, a distinct orange or yellow precipitate shows a positive result.

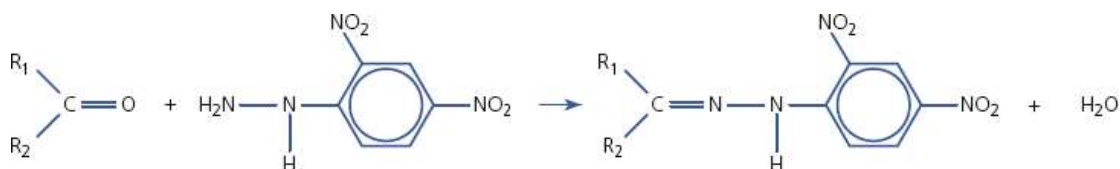


Figure 17.10

- The equation for the reaction is shown in [Figure 17.10](#), but you will not be asked to produce this in an examination.
- The reaction is rather more useful than just testing for a carbonyl compound. If the precipitate is filtered off, washed and recrystallised, the melting point of the crystals obtained is characteristic of the particular aldehyde or ketone that reacted, enabling identification to take place.

Distinguishing between aldehydes and ketones

In the section on oxidation reactions of hydroxy compounds in [Chapter 16](#), you saw that primary, secondary and tertiary alcohols can be distinguished by looking at their oxidation products. These same reactions enable us to distinguish between aldehydes and ketones.

[Table 17.1](#) summarises the behaviour of the two types of carbonyl compound with different reagents.

Table 17.1

Reagent	Aldehydes	Ketones
Acidified dichromate(VI)	Orange solution turns blue-green	No change in the orange solution

Reagent	Aldehydes	Ketones
Fehling's solution	Blue solution produces an orange-red precipitate of copper(I) oxide	No change in the blue solution
Tollens' reagent	Colourless solution produces a grey precipitate of silver, or a silver mirror is formed on the test tube	No change in the colourless solution

The tri-iodomethane (iodoform) reaction

You saw in [Chapter 16](#) that this reaction is linked to the $\text{CH}_3\text{CH}(\text{OH})-$ group in alcohols. It can also be used to identify the $\text{CH}_3\text{CO}-$ group in carbonyl compounds.

In other words, a positive result – the pale-yellow precipitate of tri-iodomethane (iodoform) – is given by an aldehyde or ketone containing the group shown in [Figure 17.11](#).

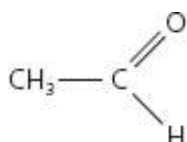


Figure 17.11

Ethanal is the *only* aldehyde to give a positive reaction ([Figure 17.11](#)). Any methyl ketone ([Figure 17.12](#)) will give a positive result.

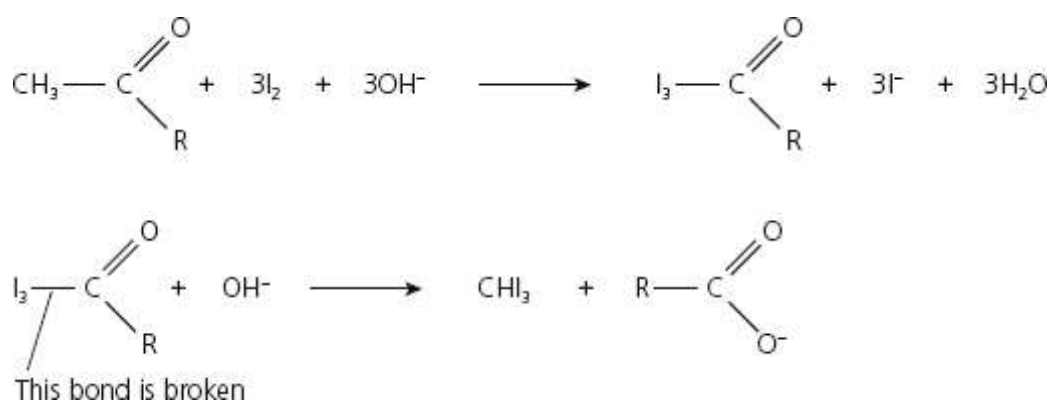


Figure 17.12

NOW TEST YOURSELF

- 4 Compound K was produced by the oxidation of an alcohol J of molecular formula $\text{C}_4\text{H}_{10}\text{O}$. When K is reacted with 2,4-DNPH, a yellow-orange precipitate is formed. K also reacts with Fehling's solution, forming an orange-red precipitate. When treated with alkaline aqueous iodine, no precipitate is formed.

Study the reactions above and use them to deduce the structural formulae of J and K.

REVISION ACTIVITY

- a Why can a primary alcohol be oxidised to an aldehyde and then a carboxylic acid, but a secondary alcohol can only be oxidised to a ketone?
- b Carbonyl compounds react with HCN to form hydroxynitriles (cyanohydrins).
- What sort of reagent is HCN?
 - What type of reaction is this?
- c The iodoform reaction cannot be used to *exclusively* identify a methyl ketone. Explain why.

END OF CHAPTER CHECK

By now you should be able to:

- recall the reactants and conditions by which aldehydes and ketones can be produced
- describe the reduction of aldehydes and ketones using NaBH_4 or LiAlH_4 to form alcohols; the reaction of aldehydes and ketones with HCN , KCN as catalyst and heat to produce hydroxynitriles
- describe the mechanism of nucleophilic addition of HCN with aldehydes and ketones
- describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH reagent) to detect the presence of a carbonyl group and the use of Fehling's and Tollens' reagents to distinguish between aldehydes and ketones
- deduce the presence of a $\text{CH}_3\text{CO}-$ group in an aldehyde or ketone by its reaction with alkaline $\text{I}_2(\text{aq})$