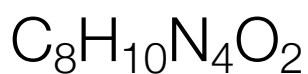
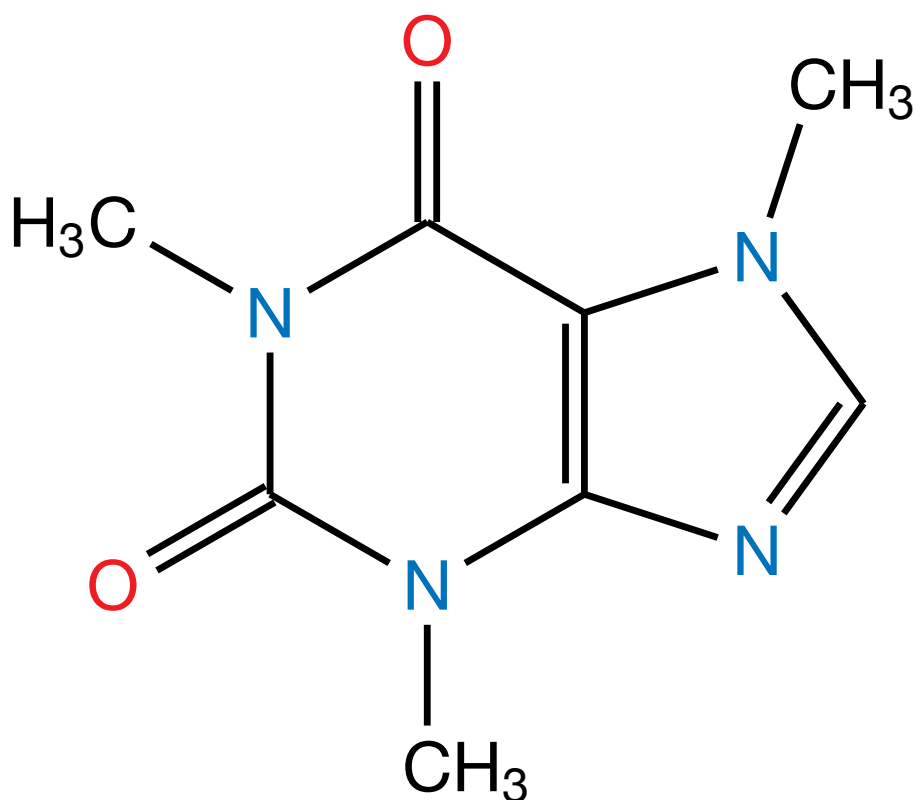


Organic Chemistry



1,3,7-trimethylpurine-2,6-dione

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Caffeine

Chapters 8 to 12

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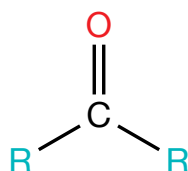
I Aldehydes and Ketones

1 Structure

Aldehydes and ketones have a very similar structure, both revolving around the carbonyl-bearing central carbon atom, with an oxygen atom double-bonded to it.

1.1 Ketones

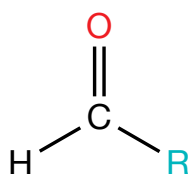
Ketones are the more general form of carbonyls. There exists a central carbon atom, with one oxygen atom double-bonded to it, and two alkyl groups on either side. For ketones specifically, R in this case *cannot* be a hydrogen atom.



The structure of a ketone.

1.2 Aldehydes

Aldehydes are ketones where one or both of the R groups on the central carbon are instead replaced with hydrogen atoms. Methanal, where both are hydrogen atoms, is the simplest aldehyde and the only case (duh) where there are two hydrogens.



The structure of an aldehyde

1.3 Hybridisation

The central carbon in both aldehydes and ketones is sp^2 hybridised, resulting in a planar construction with a bond angle of 120° . As such, the unhybridised p-orbital of the carbon atom is able to overlap with the p-orbital the neighbouring oxygen atom, forming a π -bond.

Furthermore, the high electronegativity of the oxygen atom results in it having a partial negative charge, δ^- , while the carbon atom has a partial positive charge, δ^+ . It is this polarisation and permanent dipole that lends aldehydes and ketones their chemical and physical properties.

2 Physical Properties

Both aldehydes and ketones can form intermolecular permanent dipole interactions, thus resulting in stronger electrostatic forces of attraction, and thus higher melting and boiling points than their alkane counterparts.

However, the lack of an H atom attached to the O atom means that there is no possibility for intermolecular hydrogen bonds to be formed. Thus, aldehydes and ketones have lower melting and boiling points than their alcohol and carboxylic acid counterparts.

Furthermore, due to the existence of both a polar and non-polar region, carbonyls are soluble in both polar solvents, like water, and non-polar solvents, like CCl_4 . Their solubility in the former is due to their ability to form favourable solvent-solute interactions in the form of hydrogen bonds, between the partial negatively-charged O atom and the partial positively-charged hydrogen atom in H_2O .

Beyond 5 carbons however, the bulkiness of the alkyl chain prevents further solubility of both aldehydes and ketones.

3 Creation of Aldehydes and Ketones

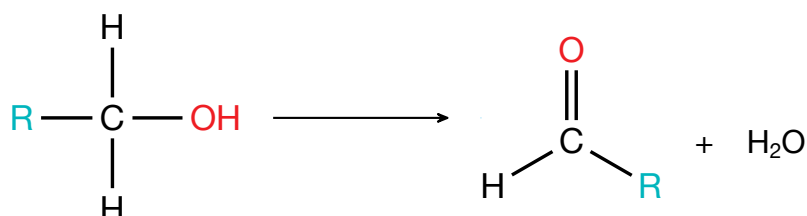
3.1 Oxidation of Alcohols

3.1.1 Oxidation of Primary Alcohols

The details on the mechanics of this reaction can be found [here](#), including the use of $\text{K}_2\text{Cr}_2\text{O}_7$ instead of KMnO_4 .

Conditions: $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 ,
heat with immediate distillation.

Observations: **Orange** $\text{Cr}_2\text{O}_7^{2-}$, turns **green** (Cr^{3+} formed).



3.2 Oxidation of Secondary Alcohols

Secondary alcohols can be oxidised to ketones directly, using either $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .

Conditions: $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 , *OR* KMnO_4 with dilute H_2SO_4 ,
heat under reflux.

Observations: **Orange** $\text{Cr}_2\text{O}_7^{2-}$, turns **green** (Cr^{3+} formed), *OR*
Purple MnO_4^- decolourises (Mn^{2+} formed)

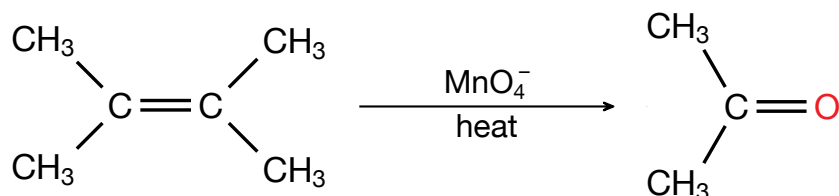


3.3 Oxidative Cleavage of Alkenes

Certain alkenes can undergo strong oxidation, cleaving the double bond. The details are elaborated on [here](#), but only one kind of alkene can form a ketone, where the carbon atom has two alkyl groups substituted, and no hydrogens.

Conditions: Cold KMnO_4 , dilute H_2SO_4 , heat.

Observations: **Purple** KMnO_4 decolourises, forming colourless Mn^{2+} .



Note that alkenes with one hydrogen substituent and one alkyl substituent *will not* form aldehydes, since the hydrogen atom will be oxidised, and instead give a carboxylic acid.

4 Aldehyde and Ketone Reactions

4.1 Nucleophilic Addition

Due to the electronegativity of the oxygen atom, the electron density is drawn towards it. Thus, the carbon atom is able to be attacked by electrophiles due to its partial positive charge.

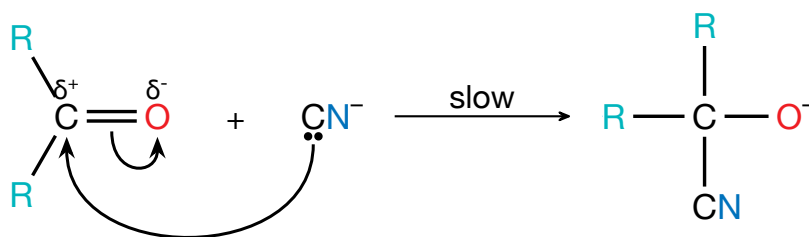
Note that aldehydes will be more reactive than ketones in nucleophilic addition, since they only have one electron-donating alkyl group on the central carbon, whereas ketones have two alkyl groups that are able to inductively donate electrons to stabilise the positive charge, slightly reducing reactivity.

4.1.1 Mechanism of Nucleophilic Addition

The mechanism is a two-step mechanism with the slow step as the first step. Here, the nucleophilic addition of CN to a carbonyl will be illustrated.

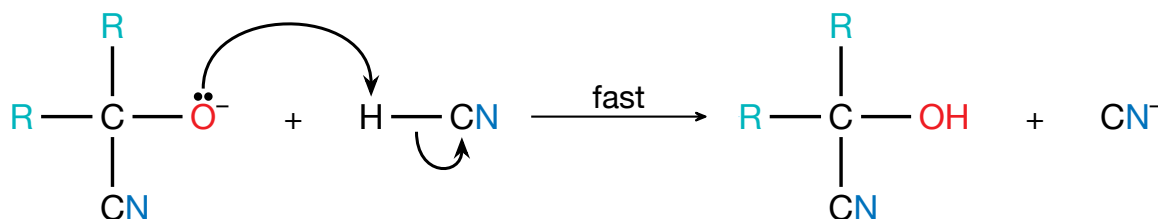
Step 1

Here, the central carbon is attacked by the nucleophile. This also serves to repel the electrons in the π -bond towards the electronegative O atom, forming a stable alkoxide anion.

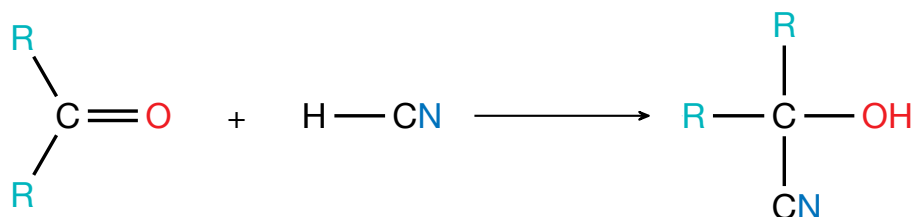


Step 2

Now, the alkoxide ion attacks an undissociated HCN molecule, protonating itself and regenerating the CN^- nucleophile.

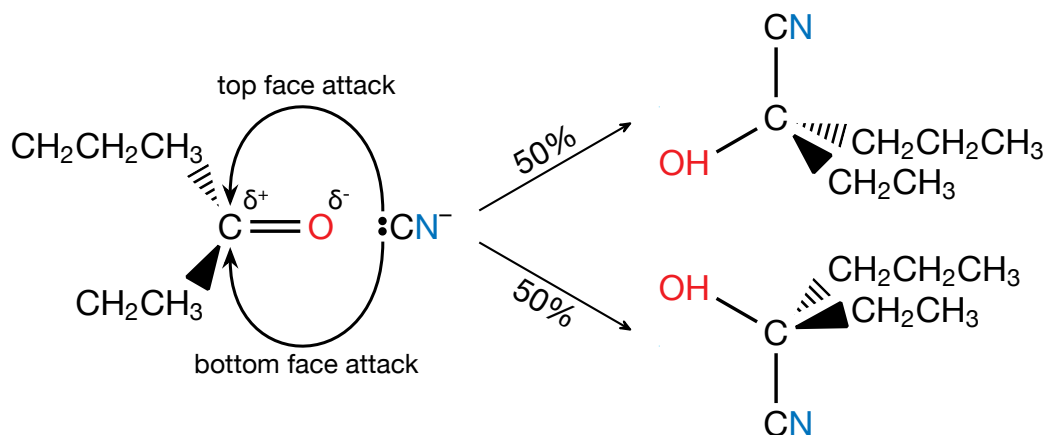


Overall Reaction



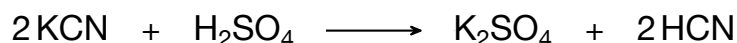
4.1.2 Stereoisomerism of Product

Since the carbonyl is trigonal planar, the nucleophile can attack from either the top or bottom side, with equal probability. Hence, if the product formed is chiral, the resulting solution will be a *racemic mixture*.

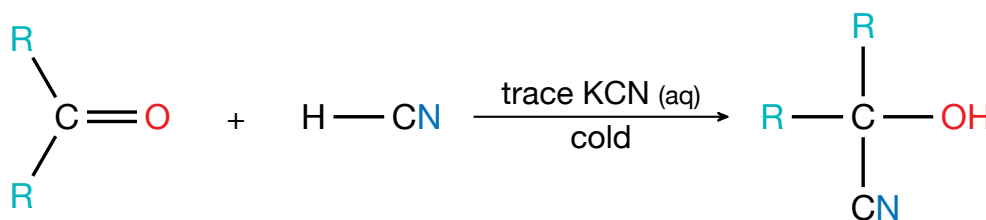


4.1.3 Formation of Nitriles (Cyanohydrins)

The nucleophilic addition of CN to a carbonyl is perhaps one of the more common forms of nucleophilic addition. Since HCN is a toxic gas, it is typically generated *in-situ* by reacting KCN with dilute H₂SO₄.



Conditions: Cold HCN, trace KCN (aq).



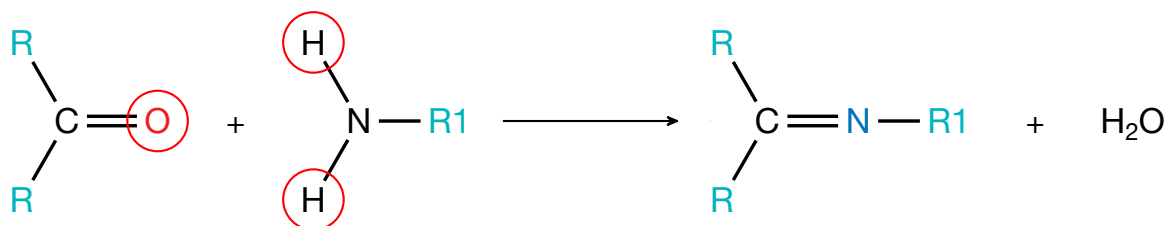
Even though the stated reactant of the reaction above is indeed HCN, simply using pure HCN will result in a dismal rate of reaction — HCN is a weak acid, and as such only partially dissociates in water to give CN⁻ ions, which is the actual electrophile.

Thus, a trace amount of KCN is added, which, as a salt, will completely dissociate in water to give CN⁻ ions, increasing the rate of reaction. Since CN⁻ is regenerated at the end of the reaction, the KCN added actually acts as a catalyst.

The resulting nitrile can be used to create carboxylic acids through hydrolysis, as well as amines through reduction. The details can be found *here*.

4.2 Condensation

Primary amines, which have a nucleophilic nitrogen atom with two attached hydrogen atoms, can undergo an elimination reaction with both aldehydes and ketones, with the removal of H₂O.



The circled atoms form the water that is eventually eliminated.

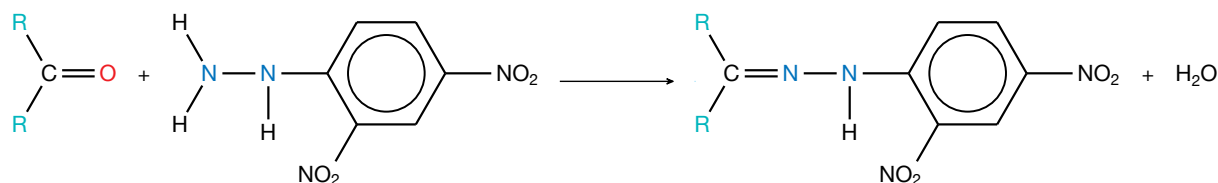
4.2.1 Distinguishing test with 2,4-DNPH

One of the more useful reactions involving this mechanism is the distinguishing test with 2,4-dinitrophenylhydrazine, which is a relatively large molecule with a distinct orange precipitate. This allows for the verification of the presence of an aldehyde or a ketone — both aliphatic and aromatic carbonyls will have a positive result.

The molecule is somewhat complex, but reading it right-to-left is sufficient to deduce its structure — hydrazine is the parent structure, and it has a substituent of 2,4-dinitrophenyl.

Conditions: 2,4-DNPH, room temperature.

Observations: *Orange* precipitate forms with a carbonyl.



4.3 Reduction

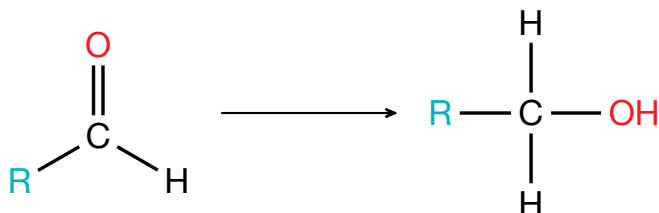
In what is basically the reverse of the oxidation of alcohols, aldehydes can be reduced into primary alcohols, and ketones can be reduced into secondary alcohols.

Clearly, tertiary alcohols cannot be formed like this.

4.3.1 Reduction of Aldehydes

Aldehydes are reduced to primary alcohols. Any of the three reducing agents can be used.

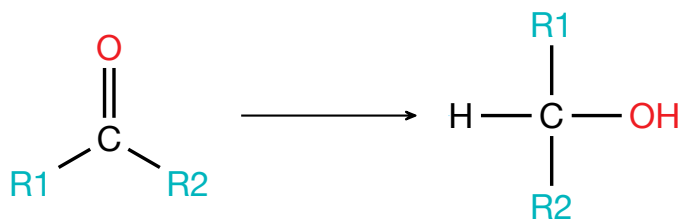
Conditions: LiAlH_4 in dry ether (diethyl ether), *OR*
 NaBH_4 in methanol, *OR*
 H_2 (g), Ni catalyst, high temperature and pressure.



4.3.2 Reduction of Ketones

Ketones are reduced to secondary alcohols. Any of the three reducing agents can be used.

Conditions: LiAlH_4 in dry ether (diethyl ether), *OR*
 NaBH_4 in methanol, *OR*
 H_2 (g), Ni catalyst, high temperature and pressure.



4.4 Oxidation

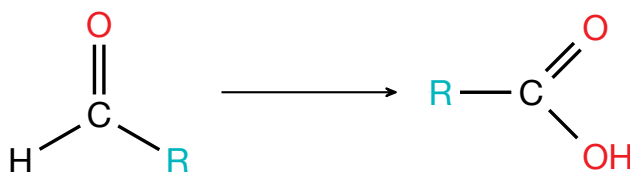
4.4.1 Oxidation of Aldehydes to Carboxylic Acids

As briefly covered in the chapter on *alcohols*, aldehydes can be further oxidised into carboxylic acids.

Also, two special carboxylic acids can be further oxidised, and they are covered above.

Conditions: $\text{K}_2\text{Cr}_2\text{O}_7$ with dilute H_2SO_4 , OR KMnO_4 with dilute H_2SO_4 , heat under reflux.

Observations: **Orange** $\text{Cr}_2\text{O}_7^{2-}$, turns **green** (Cr^{3+} formed), OR **Purple** MnO_4^- decolourises (Mn^{2+} formed)



This reaction can also be used to distinguish aldehydes from ketones, as ketones will *not* undergo further oxidation due to their lack of a hydrogen atom on the central carbon.

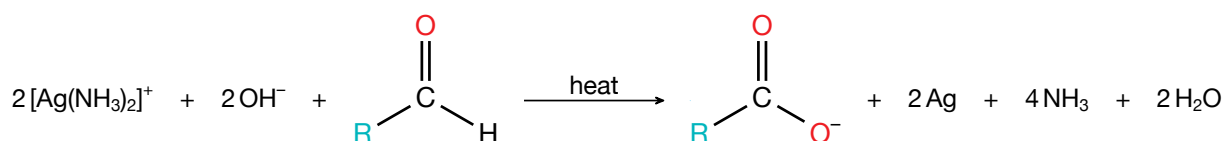
4.4.2 Tollens' Reagent

Tollens' Reagent, or the *silver mirror test*, can also be used to distinguish aldehydes and ketones. Only aldehydes, both aliphatic and aromatic, can react reduce the silver complex to silver metal, while ketones cannot — this is due to the fact that ketones cannot be oxidised.

A positive test results in the depositing of silver metal on the surface of the reaction vessel, hence the silver mirror.

Conditions: Tollens' Reagent, heat.

Observations: **Silver** metal coats the reaction vessel.



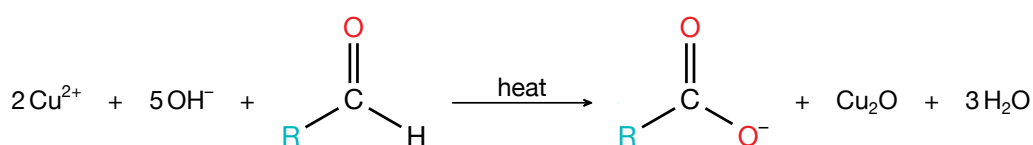
4.4.3 Fehling's Solution

Fehling's Solution, like Tollens' Reagent, relies on the oxidation of the aldehyde, and hence the reduction of itself. In this case, Cu^{2+} is reduced to Cu^+ in the form of Cu_2O , which gives a distinct, brick-red precipitate.

Fehling's Solution is used to distinguish between aliphatic and aromatic aldehydes. Again, since ketones cannot be oxidised, they do not give a positive test for Fehling's Solution.

Conditions: Fehling's Solution, heat.

Observations: *Brick-red*, or *reddish-brown* precipitate is formed.



The aldehyde here cannot be aromatic (aka the R group is a benzene ring). Only normal alkyl-based aldehydes will work.

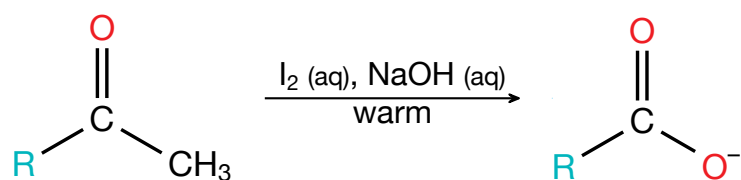
4.4.4 Tri-iodomethane (Iodoform) Formation

Similar to alcohols, ketones and aldehydes can be oxidised by aqueous iodine to give the distinct yellow precipitate, which is useful as a fingerprinting, structural test.

Due to the requirements of having a CH_3 group, ethanal is the only aldehyde that gives a positive result for this test, since the R group will be a hydrogen atom. Otherwise, only terminal ketones will test positive.

Conditions: I_2 (aq), NaOH (aq), warmed.

Observations: *Yellow* precipitate of CHI_3 is formed.



The aldehyde here cannot be aromatic (aka the R group is a benzene ring). Only normal alkyl-based aldehydes will work.