17 Hydroxy compounds

17.2 Phenol ☐

PHENOLS

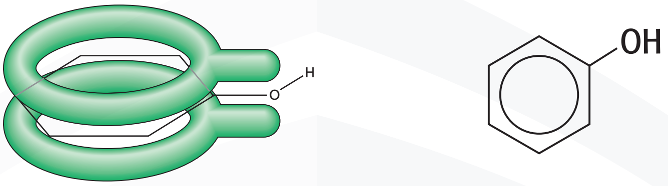
17.2 Phenol	**a) recall the chemistry of phenol, as exemplified by the following reactions:** **(i) with bases** **(ii) with sodium** **(iii) with diazonium salts (see also Section 20.1)** **(iv) nitration of, and bromination of, the aromatic ring** **b) describe and explain the relative acidities of water, phenol and ethanol**

PHENOLS

A phenol group is an —OH group attached directly to a benzene ring.

The C—O bond in phenol is very strong, as a result of the delocalisation of the lone pair of electrons on oxygen over the arene ring. There are no reactions in which it breaks, unlike the situation with the alcohols.

However–OH group in phenol undergoes a variety of reactions.



ACID NATURE

Phenol behaves as a weak acid. The aqueous solution has pH of around 5 or 6. (K_a of the acid is 1.3×10^{-10}).

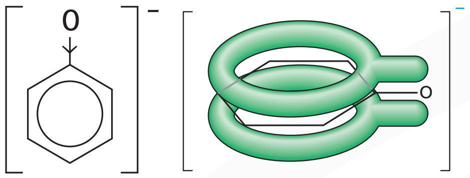
The position of this equilibrium lies well over to the left-hand side. However, phenol is still a stronger acid than water or an alcohol.

This is shown by its small K_a value.

ACID NATURE

Phenol is more acidic than water, with ethanol being the least acidic of the three compounds. (phenol > water > ethanol in terms of acidity).

The phenoxide ion, $C_6H_5O^-$(aq), has its negative charge spread over the whole ion as one of the lone pairs on the oxygen atom overlaps with the delocalised π bonding system in the benzene ring. This makes the ion more stable than an ethoxide ion.



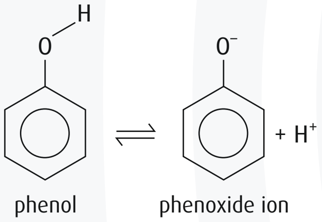
phenoxide ion, with negative charge spread over the whole ion

$CH_3CH_2 \rightarrow O^-$

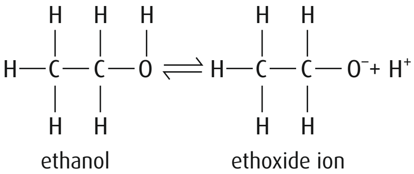
ethoxide ion, with negative charge concentrated on the oxygen

ACID NATURE

The dissociation of phenol may be shown as:



The dissociation of ethanol is:

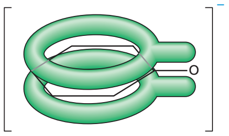


$$CH_3CH_2OH \rightleftharpoons CH_3CH_2O^- + H^+$$

ACID NATURE

We will consider the stability of the anion/conjugate base.

The lone pair on the O– in the phenoxide ion overlaps with the delocalised system in the benzene ring. This spreads out the negative charge in the ion.



The O is thus less negative and the H^+ is not attracted back as strongly. The anion is thus stabilised and phenol is a stronger acid than ethanol.

In ethanol this delocalisation does not occur and indeed the negative charge on the O in the ethoxide ion is increased by the electron-donating alkyl group.

ACID NATURE

The phenoxide ion ($C_6H_5O^-$) is more stable than the ethoxide ion ($C_2H_5O^-$) and hence its formation is favoured.

In the phenoxide ion, the charge is delocalised and is stable. Thus phenol reacts with alkalis unlike alcohols.

Compound	Dissociation in water	p*Ka*
phenol	$C_6H_5OH(aq) \rightleftharpoons C_6H_5O^-(aq) + H^+(aq)$	10.0
water	$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$	14.0
ethanol	$C_2H_5OH(aq) \rightleftharpoons C_2H_5O^-(aq) + H^+(aq)$	16.0

PHENOL IN WATER

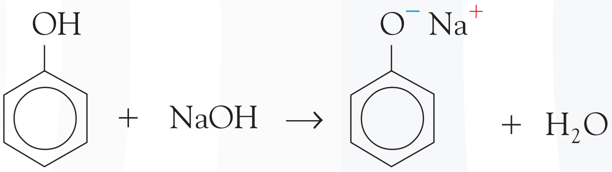
Phenol dissolves very slightly in water to form a weak acidic solution. It is a stronger acid than aliphatic alcohols.

The ring helps weaken the O-H bond and stabilises the resulting phenoxide ion.

Regular alcohols (aliphatic alcohols) do not react with water to form an acidic solution

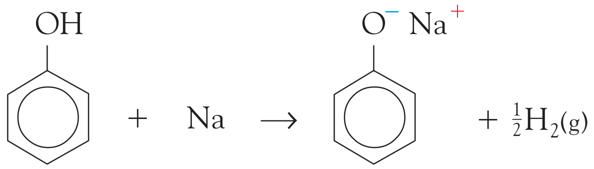
PHENOL IN ALKALIS

Phenols dissolve in aqueous sodium hydroxide:



PHENOL WITH SODIUM

Phenol reacts with sodium metal, giving off hydrogen gas:



sodium phenoxide
(a white solid)

REACTION WITH SODIUM

Phenol reacts with sodium in a similar way to ethanol.

Bubbles of hydrogen form when a small cube of sodium is added to molten phenol or to a solution of phenol in an inert solvent.

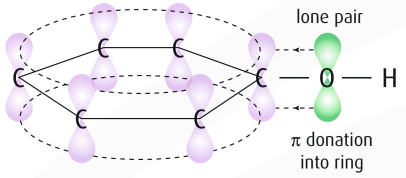
The main product of the reaction is sodium phenoxide.

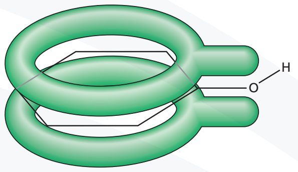
RING REACTIONS WITH PHENOLS

At first sight we might expect the –OH group to be electron-withdrawing due to the high electronegativity of O. However, the –OH group also possesses a lone pair of electrons and overlap of this lone pair into the ring activates the benzene ring.

This π donation into the ring is a bigger effect than the electron withdrawing effect (due to the electronegativity of O).

Therefore there is net donation of electron density into the ring and the ring will attract electrophiles more strongly.



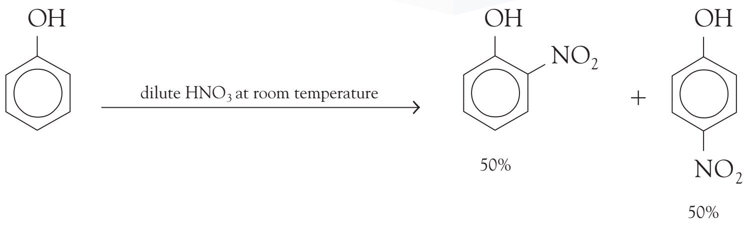


RING REACTIONS WITH PHENOLS

Phenols are more susceptible to electrophilic attack than benzene, owing to the delocalisation of the lone pair of electrons on oxygen.

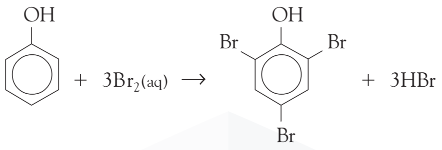
This allows phenol to react with reagents that are more dilute, and also to undergo multiple substitution with ease.

When treated with dilute aqueous nitric acid (no sulfuric acid is needed) phenol gives a mixture of 2- and 4-nitrophenols.

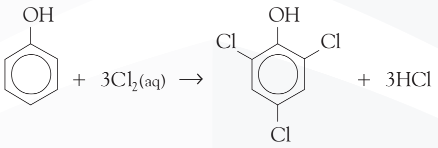


RING REACTIONS WITH PHENOLS

Phenol decolorises a dilute solution of bromine in water at room temperature, giving a white precipitate of 2,4,6-tribromophenol. No aluminium bromide is needed. Contrast this with the conditions needed for the bromination of benzene.

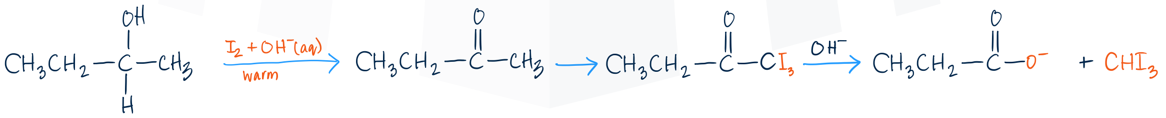


A similar product is formed by the action of chlorine water on phenol.



IODOFORM REACTION

Alcohols that contain the group $CH_3CH(OH)$-, that is, those that have a methyl group and a hydrogen atom on the same carbon atom that bears the OH group, can be oxidised by alkaline aqueous iodine to the corresponding carbonyl compound $CH_3C(O)$-, which is further oxidised a salt of a carboxylic acid (with one less carbon) and a pale yellow ppt of tri-iodomethane.



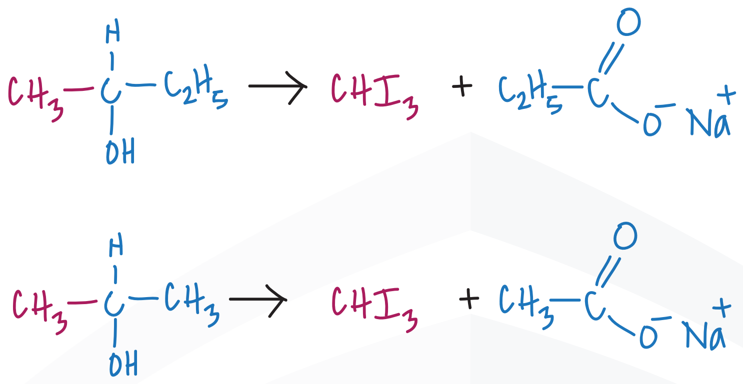
$$CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \xrightarrow[\text{warm}]{I_2 + OH^-(aq)} CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3CH_2-\overset{\overset{O}{\|}}{C}-CI_3 \xrightarrow{OH^-} CH_3CH_2-\overset{\overset{O}{\|}}{C}-O^- + CHI_3$$

The overall reaction is:

$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-X \longrightarrow CHI_3 + X-C(=O)O^-\,Na^+$$

IODOFORM REACTION

Except for ethanol, all the alcohols that undergo this reaction are secondary alcohols, with the OH group on the second carbon atom of the chain, that is, they are alkan-2-ols.

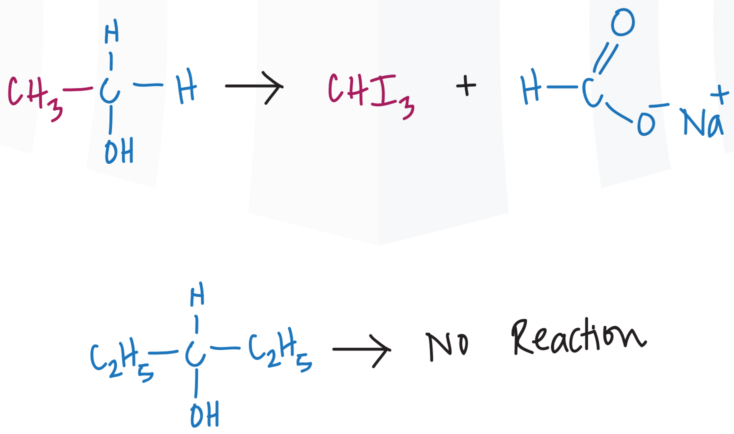


$$CH_3-\overset{H}{\underset{OH}{C}}-C_2H_5 \rightarrow CHI_3 + C_2H_5-C(=O)-O^-\,Na^+$$

$$CH_3-\overset{H}{\underset{OH}{C}}-CH_3 \rightarrow CHI_3 + CH_3-C(=O)-O^-\,Na^+$$

IODOFORM REACTION

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

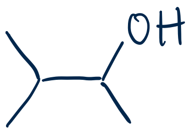


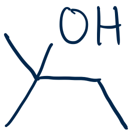
$$CH_3-\overset{H}{\underset{OH}{C}}-H \rightarrow CHI_3 + H-C(=O)-O^-\,Na^+$$

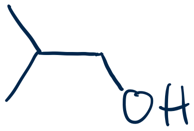
$$C_2H_5-\overset{H}{\underset{OH}{C}}-C_2H_5 \rightarrow \text{No Reaction}$$

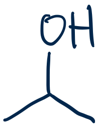
IODOFORM REACTION

Which of these alcohols will undergo the iodoform reaction?





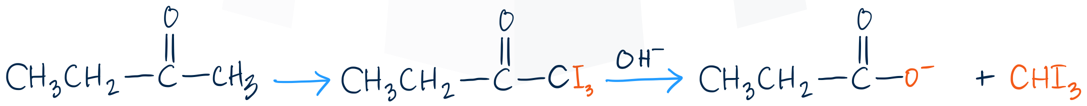




IODOFORM REACTION

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.



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-CI_3 \xrightarrow{OH^-} CH_3CH_2-\overset{O}{\overset{\|}{C}}-O^- + CHI_3$$

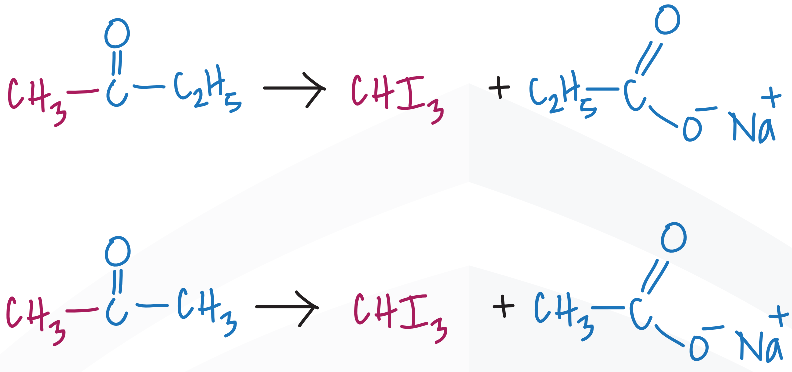
The overall reaction is:

$$CH_3-\overset{O}{\overset{\|}{C}}-X \rightarrow CHI_3 + X-\overset{O}{\overset{\|}{C}}-O^-\,Na^+$$

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.

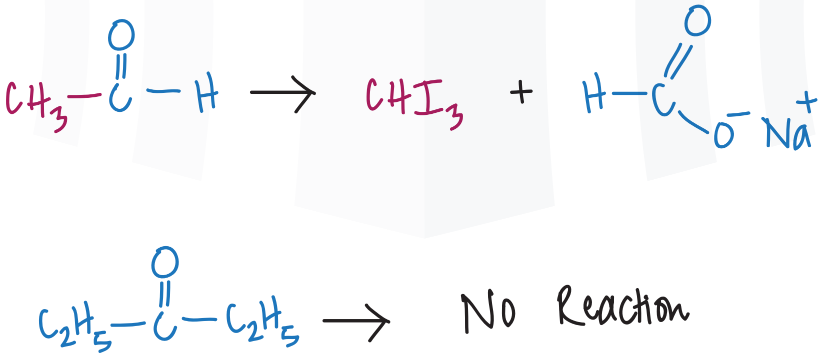


$$CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 \rightarrow CHI_3 + C_2H_5-\overset{\overset{O}{\|}}{C}-O^-\,Na^+$$

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CHI_3 + CH_3-\overset{\overset{O}{\|}}{C}-O^-\,Na^+$$

IODOFORM REACTION

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

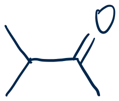


$$CH_3-\overset{\overset{O}{\|}}{C}-H \rightarrow CHI_3 + H-\overset{\overset{O}{\|}}{C}-O^-\,Na^+$$

$$C_2H_5-\overset{\overset{O}{\|}}{C}-C_2H_5 \rightarrow \text{No Reaction}$$

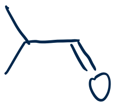
SKILL CHECK 1

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

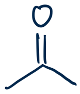


A

B



C



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