ALCOHOLS and PHENOLS

(Alkanols)

Alcohols are compounds that have hydroxyl groups bonded to saturated, sp^3 - hybridized carbon atoms; phenols have hydroxyl groups bonded to an aromatic ring.

Both of these classes of compounds can be thought of as organic derivatives of water in which one of the water hydrogens are replaced by an organic substituent: R-O-H, Ar-O-H versus H-O-H.

The geometry around the oxygen atom in alcohols is similar to that of the water molecule, with two lone pairs of electrons:

Alcohols and phenols occur naturally and have a wide range of valuable industrial and pharmaceutical applications. For example, ethanol is used as a fuel additive, an industrial solvent, and a beverage; menthol, an alcohol isolated from peppermint oil, is used as a flavouring agent; BHT (fyi: butylated hydroxytoluene) is widely used as a food additive to prolong shelf life and protect against oxidation.

Nomenclature

Alcohols are named by adding the suffix '-ol' to the alkane stem of the compound. The longest carbon chain that contains the -OH group is chosen as the stem. A digit can precede the '-ol' to describe the position of the –OH group along the chain.
Alcohols can be subdivided into 3 categories: according to the number of carbon atoms attached to the same C-atom as the -OH group, (i.e. the hydroxyl bearing carbon):

	primary (1^0)	**secondary (2^0)**	**tertiary (3^0)**
E.g.	propanol	propan-2-ol	2-methyl propan-2-ol
	butan-1-ol	butan-2-ol	

The hydrogen atoms attached to the same C-atom as the -OH group are readily oxidized and so these three alkanols behave differently to oxidizing agents such as acidified $KMnO_4$ / $K_2Cr_2O_7$.

Assignment: Draw all possible isomers with the formula: C_4H_9OH
(There are five isomers in all: two are primary alcohols, two are secondary alcohols, and one is tertiary alcohol)

Certain commonly occurring alcohols have trivial names that are accepted by IUPAC. The IUPAC name for an alcohol is – ol, where the – e of the alkane is dropped and replaced by – ol.

C_6H_5 - CH_2OH	OH - CH_2CH_2 - OH	CH_3-CH(OH)-CH_3
benzyl alcohol	Ethylene glycol (antifreeze)	isopropyl alcohol
phenylmethanol	ethan-1,2-diol	(Rubbing alcohol)
		(propan-2-ol)
$(CH_3)_3$-C-OH	HO-CH_2-CH(OH)CH_2(OH)	
Tert-butyl alcohol	glycerol, glycerin (strong attraction for water .:	
2-methyl-2-propanol	propan-1,2,3-triol (used in lotions, creams)	

Phenols are named as substituted aromatic compounds, (-phenol is used as the parent name, rather than -benzene). It is also possible to have an -OH on a chain as well as a ring, therefore two types of reactions are possible. Phenol is still used as an antiseptic, 'carbolic acid', in sore throat spray, lip balm, etc. Derivatives of phenol are better germicides, e.g. TCP, 4-chloro-3,5-dimethylphenol is 280 x more effective as phenol.

Assignment: Write structural formulae for the following:
a) 2-methyl propan-1-ol (b) 2-phenylethanol-1-ol (c) 2-methyl phenol (d) prop-2-ene-1-ol

Note: if the -OH group occurs in a side chain, its behavior resembles that of alcohols, but, if the -OH is directly attached to the C_6H_6 ring, then behavior is similar to phenols.

Shape of the Hydroxy Compounds

The geometry around the oxygen atom in alcohols is similar to that of the water molecule, with two lone pairs of electrons.

	:O:	:O:	:O:
	/ \	/ \	/ \
	H H	H_3C H	R H
Bond Angle	104^0	109^0	105^0

Why the increased bond angle in methanol? The CH_3- group is large compared to the H-atom in H_2O, .: more repulsion, hence the atoms are pushed out **.:** ⟶ increasing the bond angle.

Phenol

Phenols have the – OH group directly attached to the ring. One of the lone pairs of electrons on the oxygen atom of phenol become partially incorporated in the delocalised π-electrons of the benzene ring system, i.e. **conjugated**. Thus, electron withdrawal from the oxygen atom facilitates the loss of the proton by weakening the O – H bond.

Diagram: representation of conjugation

Further, the phenoxide ion, $C_6H_5O^{-1}$, is stabilized by the delocalisation of the negative charge through out the ring system.

Because of the delocalisation of the electrons into the benzene ring, thus phenol is more reactive towards electrophiles than benzene, i.e. it is **activated**, and **ortho-, para-, directing**.

Physical Properties

(Ethanol is a hypnotic, i.e. a sleep producer. It depresses activity in the upper brain even though it gives the illusion of being a stimulant.)

Alcohols change state gradually from liquids ⟶ solids : why?
Lower member alcohols are soluble : why?
Solubility decreases as chain length increases : why?
Alcohols have much higher boiling points than the corresponding alkanes : why?

Explanation

Because of the polarity of the O - H group, this confers a measure of polar character to the molecule as a whole. Alcohols are substantially less volatile, have higher melting points and greater water solubility than the corresponding hydrocarbons. The lower alcohols (C_1, C_2, C_3, and some isomers of C_4) are totally miscible with water, due to hydrogen bonding between the alcohol molecules and water molecules:

As the length of the alkyl chain increases, van-der-Waals attraction predominates between the molecules of the alcohol, and so the miscibility with water decreases. Why????

All alcohols, (recall: H-bonding), have ethers, (recall only dipole-dipole interaction) as isomers.
(As chain length increases, the polar part becomes less significant, i.e the hydrophilic
O - H part is less significant than the “water-insoluble” hydrophobic hydrocarbon backbone.)

The reason for the unusually high boiling points and solubility of alcohols and phenols is due to the fact that like water, they are highly **associated** in solution due to the formation of strong **intermolecular hydrogen bonds with the polar water molecules**. The positively polarised hydroxyl hydrogen atom from one molecule forms a weak hydrogen bond to the negatively polarised oxygen atom of another molecule. The presence of a great many such hydrogen bonds in solution means that extra energy is required to break them during the boiling process, hence higher boiling points. See Table below:

Compound	**propan-1-ol,**	**chloroethane**	**butane**
Formula	C_3H_7OH	Cl– C_2H_5	C_4H_{10}
Molar mass (g mol^{-1})	60	65	58
bp (^{0}C)	97	12.5	-5

Branched chains have lower bp than the straight chain molecules, indicating greater compactness sterically.
The strength of the IMFA’s increases with the size of the molecule, .: increasing boiling point.
(Example: octanol: bp = 195^{O}C).

Hydrogen bonding between —OH groups also has an effect on the viscosity of alcohols, particularly those with more than one —OH group in their molecule; .: ethanol has the same viscosity as water but propan-1,2,3-triol, (glycerine) is very thick, sticky —> this is because of extensive interaction between its molecules which carry three—OH groups.

Isomerism

Alcohols show **chain, positional and optical isomerism**.
Ethers are isomers of alcohols, but they do not contain the –OH group.
C_2H_6O has two isomers: ethanol methoxymethane (dimethyl ether)

Also structural isomerism exhibited:
C_3H_7OH: propan -1-ol propan-2-ol methoxyethane

Assignment: using the structure and bonding in ethers, predict the physical properties you would expect the ether homologous series to possess.

Acidity in alcohols:

Since alkyl groups attached to an -OH are slightly electron-donating (due to positive inductive effect: CH_3—— OH, thus CH_3OH is less acidic than C_2H_5 —— OH, also the ethoxide ion is a stronger base), therefore, the H-atom of the -OH is held more strongly in alcohols, hence alcohols are less acidic in water. Alcohols are neutral, angular, bent around the oxygen atom, cf. H_2O.

$$C_2H_5OH + H_2O \rightleftharpoons C_2H_5O^{-1} + H_3O^{+1} \qquad K_a = 10^{-18}$$

$$HOH + H_2O \rightleftharpoons OH^{-1} + H_3O^{+1} \qquad K_a = 10^{-16}$$

Ethanol is a weaker acid than water, hence the ethoxide ion, $C_2H_5O^{-1}$, is a stronger conjugate base than the OH^{-1} ion.

Most alcohols have a pK_a of 16 -18, .: alcohols are weaker acids, water has a pK_a of 15.8

$$R\text{ - }OH \ + \ H_2O \rightleftharpoons RO^{-1} \ + \ H_3O^{+1} \qquad K_a = 1.0 \text{ x } 10\text{-}^{16}$$

Alkanols are very slightly acidic, as shown by their reaction with an active metal, such as sodium or potassium; hence the **ethoxide ion must be a stronger base than the phenoxide ion**. The metal salts of alcohols are strong bases, (recall: the **alkoxide ion, RO^{-1}, as a strong base**), that are used frequently as reagents in organic chemistry.

Phenols

Phenols contain two functional groups: – the —OH group of the alcohols, and the phenyl ring of the arenes. Their reactions are for the most part the sum of the two sets, but with some modifications.

Nomenclature

If the only other groups on the benzene ring are halogen atoms, nitro, amino or alkyl groups, the compounds are named as **derivatives of phenol** itself:

Example:	4-methylphenol (p-methylphenol)	2-nitrophenol (o-nitrophenol)	2,4,6-trichlorophenol

However, if, the other group is an aldehyde, ketone, or carboxylic acid group, the phenolic —OH becomes a **'hydroxy' substituent:**

Example:	3-hydroxybenzaldehyde (3-hydroxybenzenecarbaldehyde)	2-hydroxybenzoic acid (2-hydroxybenzenecarboxylic acid)

Physical Properties

At room temperature, phenol is pinkish colored crystals, partially soluble, commonly known as carbolic acid, poisonous, and causes blisters on the skin.
B.p = 110.6 ^{O}C. Phenol is weakly acidic in solution : why?

Delocalization of one lone pair of electrons of the oxygen atom into the π- delocalized system of the benzene ring decreases the strength of the -O-H bond in C_6H_5OH, (the withdrawal of electrons from the oxygen atom makes hydrogen more positive), thus permitting proton loss or ionization.
(Recall: Bronsted – Lowry definition: an acid is a proton donor). Hence, phenol is more acidic than alcohols, $K_a = 1.3 \times 10^{-10}$ mol dm $^{-3}$, $pK_a = 10$

$$C_6H_5\text{ - }OH \ + \ H_2O \rightleftharpoons C_6H_5O^{-1} \ + \ H_3O^{+1} \qquad K_a = 1.3 \times 10^{-10} \text{ mol dm}^{-3}$$

(Recall: compounds with a small K_a, or high pK_a are weakly acidic, whereas compounds with a larger K_a, or smaller pK_a are more strongly acidic.)

Phenols are more acidic than alcohols because the phenoxide anion ($C_6H_5O^{-1}$), is resonance - stabilized due to the delocalisation of the negative charge over the whole benzene ring system, hence phenoxide ion is a weak base (Recall: a base is a proton acceptor):

As a consequence of the acidity of phenols, they are thus, soluble in dilute aqueous alkalis:

$$C_6H_5(OH) + NaOH \rightleftharpoons C_6H_5O^{-1}Na^{+1} + H_2O$$

Phenol is visibly acidic. The pH of a 0.1 mol dm^{-3} solution is 5.4, so it will turn universal indicator solution yellow. An old name for phenol is carbonic acid.

Indeed, some phenols, such as the nitro-substituted ones, surpass the acidity of carboxylic acids. When electron-withdrawing group such as the $-NO_2$ are attached to the ring, the resulting phenol is even more acidic as the charge can be even further delocalised:

Order of Acidity

Alcohols ⟶ H_2O → Phenol ⟶ substituted phenol ——— Acid
Ex: nitrophenol R-COOH

⟶
Hydroxy compounds: Acid strength increasing

$C_2H_5O^{-1}$ OH^{-1} $C_6H_5O^{-1}$
<--
Base Strength Increasing

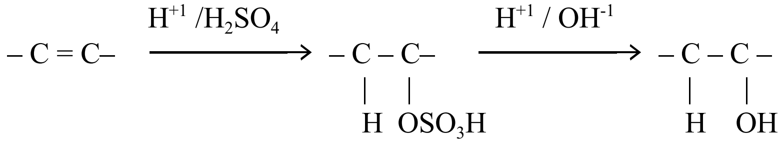
Reactivity of the phenols

Because the -OH group feeds lone pairs of electrons into the C_6H_6 ring, making the π- system more electron rich than it is in benzene, so phenol is more reactive, i.e. the benzene ring is activated to electrophiles – such as bromine. Hence, phenol decolourises bromine in the cold:

Preparation of Alcohols

1. Hydration of an alkene:

Conditions:
Mechanism:
Markovnikov's Rule:



$$-C=C- \xrightarrow{H^{+1}/H_2SO_4} \underset{H\quad OSO_3H}{-C-C-} \xrightarrow{H^{+1}/OH^{-1}} \underset{H\quad OH}{-C-C-}$$

2. Hydrolysis of a halogenoalkane:

Conditions: cold, dilute aqueous alkali:
Mechanism: recall S_N1 or S_N2

$$R-X + OH^{-1} \longrightarrow R-OH + X^{-1}$$

Industrial Methods

1. Catalytic Hydration of ethene: steam is passed over ethene at 300 °C and 60 atm.

$$-C=C- \xrightarrow{Steam} \underset{H\quad OH}{-C-C-}$$

2. Fermentation of sugar:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

Chemical Properties

All alcohols burn well in air, but only the combustion of ethanol is of everyday importance. Ethanol is used as a fuel:

$$C_2H_5OH \quad + \quad 3O_2 \longrightarrow 2CO_2 \quad + \quad 3H_2O$$

Ethanol is marketed as 'methylated spirit' for the use of fuel in stoves, and as a common solvent. This contains about 90 % ethanol, together with 5 % water, 5 % methanol, and pyridine. The poisonous methanol is added to make it undrinkable, and hence exempt from the large excise duty charged on spirits. The pyridine gives it a bitter taste, which makes it unpalatable.

The other **reactions of alcohols can be divided into three groups**:

- reactions involving the breaking of the O – H bond
- reactions involving the breaking of the C – H bond
- oxidation of the – CHOH group (not in tertiary alcohols, these do not contain an H atom attached to the C– atom)

1. Effect of NaOH

- phenol dissolves in alkalis : why?
- benzene is not acidic, but phenol is, why?

$$\text{Phenol} + \text{NaOH} \rightleftharpoons \text{sodium phenoxide} + \text{water}$$

(compare acid + base)

This reaction is reversible: hence the addition of conc. HCl causes a murkiness… pinkish or colorless emulsion observed …

$$\text{sodium phenoxide} + \text{HCl} \rightleftharpoons \text{phenol} + \text{NaCl}$$

2. Reaction with Na_2CO_3

- phenol is a weak acid and can therefore protonate the CO_3^{-2} :

$$C_6H_5OH + CO_3^{-2} \rightleftharpoons C_6H_5O^{-1} + HCO_3^{-1}$$

- i.e. phenol dissolves in $Na_2CO_{3\,(aq)}$, but does not release $CO_{2(g)}$
(unlike a carboxylic acid + $CO_3^{-2} \longrightarrow CO_{2\,(g)}$)

Therefore, phenol is a weaker acid, since the equilibrium in above equation must be displaced to the left. This indicates that not enough H^{+1} present in phenol solution.

3. Reaction with alkali metals (reaction involving the fission of -O-H bond)

Note: in the past we have encountered… $H\text{-}OH + Na \longrightarrow NaOH + \frac{1}{2} H_{2\,(g)}$

We now encounter: $R\text{-}OH + Na \longrightarrow NaOR + \frac{1}{2} H_{2\,(g)}$

This applies to phenols also: $C_6H_5OH + Na \longrightarrow NaOC_6H_5 + \frac{1}{2} H_{2\,(g)}$

However, the reaction with phenol is more violent because of the acidity of the phenol.
This is to say that alcohols are slightly acidic under certain conditions: + active metals.
This is used as a **test for an – OH group**.

C_2H_5ONa, sodium ethoxide is a white solid, soluble in water, to give a strongly alkaline solution, and is soluble in ethanol. The alcohol can be regenerated from the alkoxide salt by addition of water:

$$CH_3ONa \quad + \quad H_2O \longrightarrow CH_3OH \quad + \quad NaOH$$

4. Reaction with PCl_5 (reaction involving - C-O bond fission)

- this reaction is used as a test for the -OH group … reaction gives off $HCl_{(g)}$, which can be tested for by bubbling in $AgNO_{3\,(aq)} \longrightarrow$ white ppte. of AgCl, or test with moist red litmus.

$$C_2H_5OH + PCl_5 \longrightarrow HCl_{(g)} + C_2H_5Cl + POCl_3$$
$$C_6H_5OH + PCl_5 \longrightarrow HCl_{(g)} + C_6H_5Cl + POCl_3$$

5. Reaction with Carboxylic Acids: **Esterification**

Alcohols react with carboxylic acids to form esters, esterification is used in food flavorings and analgesics (methyl salicylate).

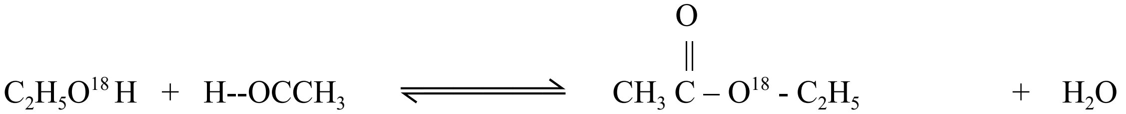
The reaction is catalysed by strong acids, this is an example of **homogeneous catalysis**: the catalyst makes the reactive site more reactive or the leaving group more stable.

The conc. H_2SO_4 plays a dual role:
(1) acts as a catalyst, to increase the rate of the reaction
(2) to shift the position of the equilibrium to the right, acting as a dehydrating agent, absorbs H_2O

Note: phenol does not react with acids to form esters (phenol is already an acid).

Note: The mechanism is whereby the -OH is removed from the carboxylic acid, H^{+1} ionizes from the alcohol:

Proof of Mechanism:



$$C_2H_5O^{18}H + H\text{--}OCCH_3 \rightleftharpoons CH_3\overset{\overset{\displaystyle O}{\|}}{C} - O^{18} - C_2H_5 + H_2O$$

labelled oxygen isotope in alcohol

oxygen isotope found in ester, not in water, ethyl ethanoate

Definition: Condensation reaction

Naming Esters:

Phenolic esters can be prepared by the reaction of acid chlorides: benzoyl chloride, C_6H_5COCl or ethanoyl chloride, CH_3COCl

$$C_6H_5COCl + C_2H_5OH \rightleftharpoons C_6H_5COOC_2H_5 + HCl$$

ethyl benzoate
(smell of almonds)

$$C_6H_5COCl + C_6H_5ONa \rightleftharpoons C_6H_5COOC_6H_5 + NaCl$$

(phenol + NaOH)

phenyl benzoate
(no smell visible, why?)

6. Reaction with $FeCl_{3\,(aq)}$

$FeCl_{3\,(aq)}$ is a mild oxidizing agent, (why?, what is the oxidation number of Fe in $FeCl_3$, .: the oxidation number can change to?); it oxidizes phenol to a complex, usually in the blue-violet range, ($[C_6H_5O]_3$ Fe)

The more hydroxy groups attached to the ring, the darker the color of the complex, (quinone). Because, there is no reaction with ethanol, so this can be used as a **test for the hydroxy group, -OH attached to the benzene ring.**
(phenol: violet, O-cresol: blue-violet, resorcinol: deep violet-black)

We have been talking about the reactions of the functional group, but there are a few special reactions undergone by the main chain or ring. You do not abolish the reactions of the chain or the ring by the addition of a functional group.

Nuclear Reactions of Phenol

Phenol reacts with halogens instantly to form a trihalogeno derivative:

$+ Br_2 \longrightarrow$ 2,4,6-tribromo phenol (white, insoluble emulsion)
$+ Cl_2 \longrightarrow$ 2,4,6-trichlorophenol (constituent of the antiseptic TCP lotion)
$+ HNO_3 \longrightarrow$ 2,4,6-trinitrophenol (yellow, picric acid)
$+ H_2SO_4 \longrightarrow$

All reactions are undergone very easily compared to benzene, hence more reactive that benzene. *Why?*

All the products obtained are ortho- and para- , (i.e. 2,4,6-). *Why?*

As a result, phenols are highly reactive substrates for electrophilic aromatic substitution reactions.

Phenol may be reduced (addition of hydrogen is reduction), but with difficulty, in two ways:

a) When phenol vapor is passed over heated zinc dust as catalyst, benzene is formed.

b) If, however, phenol vapor is mixed with hydrogen gas and passed over Ni catalyst as 200°C, then cyclohexanol is produced.

Reactions Undergone by Alcohols Only

I: Dehydration of Alcohols (alkanols): Elimination reactions

Alcohols can be dehydrated (-elimination of water), to give alkenes.

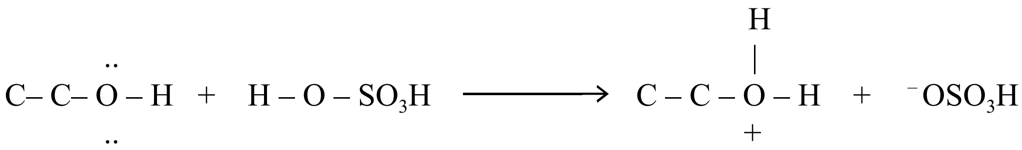
Tertiary alcohols lose water when treated with mineral acid under fairly mild conditions, but primary and secondary alcohols require higher temperature.

Good dehydrating agents include: Al_2O_3, conc. $H_3PO_{4(aq)}$, conc. $H_2SO_{4(aq)}$

Concentrated $H_3PO_{4\ (aq)}$, phosphoric (V) acid is often preferred because, unlike sulphuric acid, it is not also an oxidising agent, and so the formation of by-products is minimised.

Alcohols act as **Lewis bases**, (∵ of the unshared pair of electrons - lone pairs on the oxygen atom of the —OH group), when reacting with conc. acids by accepting protons and forming a protonated alcohol.

Thus , the first step of dehydration is that the acid protonates the -OH group in the alcohol to form a protonated intermediate:



$$C-C-\overset{..}{\underset{..}{O}}-H \;+\; H-O-SO_3H \longrightarrow C-C-\overset{\overset{H}{|}}{\underset{+}{O}}-H \;+\; {}^{-}OSO_3H$$

The protonated alcohol is an important first step to a number of important organic reactions. With concentrated sulphuric acid there are two possible products depending on the conditions used:

CH_3-CH_2-OH_2

Excess acid → Elimination Reaction: $CH_2 = CH_2 + H_2O + H^{+1}$

→ Excess alcohol → Condensation reaction: CH_3-CH_2-O-CH_2-CH_3 + $H_2O + H^{+1}$

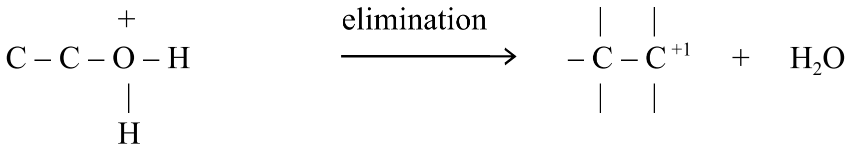
At higher temperatures (> 170°C), and excess conc. H_2SO_4 → alkene

At lower temperatures (< 170°C), and excess alcohol → alkoxy-alkane (ether)

Mechanism of Dehydration (Elimination Reaction)

<u>Definition of an elimination reaction</u>: a multiple bond is formed between two neighbouring atoms and a small molecule is formed from the groups that were originally attached to these atoms and is eliminated.

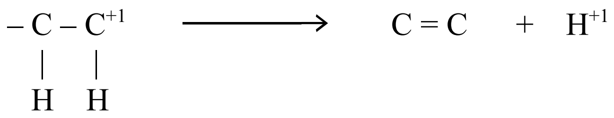
Once the protonated alcohol is formed, the second step is where the protonated intermediate spontaneously loses water via an E1 mechanism,(recall: a unimolecular elimination reaction), to generate a carbocation:



$$C-C-\overset{+}{\underset{\underset{H}{|}}{O}}-H \xrightarrow{\text{elimination}} -\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}{}^{+1} \;+\; H_2O$$

The oxygen–atom is carrying a positive charge, .: it attracts the electrons strongly away form the carbon–atom nest to it, thus forming a carbocation.

The carbocation then immediately loses a proton to form an alkene, i.e. the carbocation is deprotonated:



$$\underset{H}{\overset{|}{-C}}-\underset{H}{\overset{|}{C^{+1}}} \longrightarrow C=C + H^{+1}$$

The elimination reaction is a one-step mechanism.

Note :

1. The hydrogen comes from the place where there are fewest hydrogens to begin with. **Why?**
2. Increasing ease of dehydration:

$$\underrightarrow{R–CH_2\text{-}OH < R_2 — CH\text{-}OH < R_3 — C\text{-}OH}$$

Increasing ease of dehydration
Increasing delocalisation of charge
Therefore, increasing stability of carbocation, hence ease of formation.

Because dehydration of an alcohol involves the formation of a carbocation intermediate:

3^0 carbocation	>	2^0 carbocation	>	1^0 carbocation
most stable				least stable

Because alkyl groups are more electron donating, thus more alkyl groups on the carbocation tend to stabilize the ion by effectively reducing the charge on the carbon-atom. The overall positive charge becomes more "spread out" (delocalized) over the carbocation.

The different classes of alcohols dehydrate under different conditions:

Ethanol ⟶ ethene
propan-2-ol ⟶ prop-1-ene
2-methyl propan-2-ol ⟶ 2-methyl pro-1-ene

Assignment:

Predict the formulas of the main products of the following reactions:
a. butan-2-ol + excess concentrated H_2SO_4
b. propan-1-ol + excess concentrated H_2SO_4

Under **milder conditions**, in the presence of an **excess of an alcohol, an ether is produced:**

Mechanism:

The carbocation formed in the initial stage of the dehydration mechanism above, may then be attacked by a lone pair of electrons on the oxygen atom of another alcohol molecule, acting as a Lewis base:

In the second stage, a proton is eliminated forming an ether:

II: Conversion to Alkyl Halides

If the acid used is **concentrated HCl, HBr or HI**, the halide ion, X^{-1} will displace the H_2O from the protonated alcohol forming an alkyl halide. Therefore the overall product will be the replacement of the hydroxyl group by the halogen.

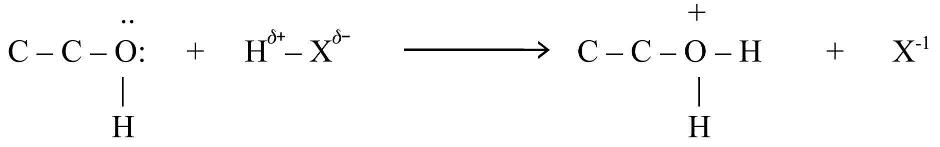
$$R-OH + H\text{-}X \longrightarrow R-X + H_2O \qquad X = Cl, Br, I$$

This is a very useful method for the preparation of alkyl halides, and is used as a **test to distinguish between primary, secondary and tertiary alcohols**. It relies on the fact that alcohols are soluble in the reagent (conc. HCl), whereas the halogenoalkane formed are not, therefore a cloudiness is produced in the solution.

Again, as explained above, the reaction works best for a 3^0 alcohol, the reaction is so rapid with tertiary alcohols that it is often carried out by bubbling the pure $HX_{(g)}$ into a cold solution of the alcohol.

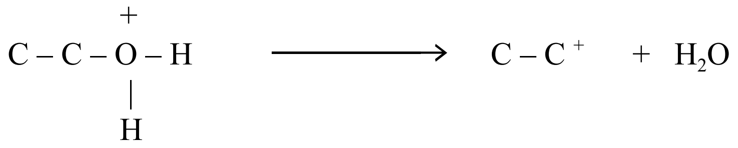
<u>Mechanism for the reaction of alcohols with hydrogen halides</u>

1. The alcohol accepts a proton from the hydrogen halide to form an intermediate:



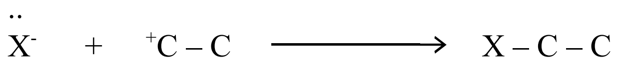
$$C-C-\underset{\substack{|\\H}}{\overset{..}{O}}: + H^{\delta+}-X^{\delta-} \longrightarrow C-C-\underset{\substack{|\\H}}{\overset{+}{O}}-H + X^{-1}$$

2. The intermediate loses water, forming a carbocation:



$$C-C-\underset{\substack{|\\H}}{\overset{+}{O}}-H \longrightarrow C-C^{+} + H_2O$$

3. The nucleophilic halide ion, X^{-1}, approaches the carbocation and bonds with it:



$$\overset{..}{X^{-}} + {}^{+}C-C \longrightarrow X-C-C$$

III: Oxidation of Alcohols

As with most organic compounds, alcohols burn in oxygen to produce CO_2 and H_2O.
Phenols are very sensitive to oxidation, alkaline $MnO_4^{-1}{}_{(aq)}$ oxidises phenol to $CO_{2(g)}$.

Milder oxidation can be done using acidified MnO_4^{-1} / $Cr_2O_7^{-2}$ (wine, Breathalyzer Test — See Notes below)

Primary alcohols will produce **aldehyde as the intermediate**, followed by a **carboxylic acid.**
Example:

Secondary alcohols form a **ketone** when oxidized.
Example:

Tertiary alcohols will **NOT** oxidize
Note: oxidation in the above two cases involves the removal of a hydrogen atom from the carbon to which — OH is attached. Since tertiary alcohols have no such hydrogen, hence they can not be oxidised.
(**DEMO:** 1. Ring of fire 2. Battle field)

Industrially oxidation by air or catalytic dehydrogenation are preferred for economic reasons, and is carried out in the vapour phase, the alcohol is passed over copper as catalyst.

1^0 alcohol $\longrightarrow$ aldehyde ------//------> oxidation does not proceed any further.

2^0 alcohol $\longrightarrow$ ketone.

Assignment

1. Show how you would bring about the following conversions in no more than three stages. Indicate the reagents, conditions and the intermediate products:

a. $H_3CCH_2 = CH_2 \longrightarrow CH_3COCH_3$
b. $H_3CCH_2OH \longrightarrow CH_3CH_2NH_2$
c. $CH_2 = CH_2 \longrightarrow CH_3COOH$
d. $H_3CCHOHCH_3 \longrightarrow CH_3CHBrCH_2Br$

2. Compare the properties of phenol and hexan-1-ol, covering in your answer physical properties and the chemical reactions of both the hydroxyl group and the carbon-containing parts of the molecules. Where possible attempt to relate differences in properties to the differences in structure.

3. Rank the following compounds in order of increasing acidity, and justify your answer:
methanol, phenol, p-nitrophenol, p-methylphenol

4. Assume that you have two unlabelled bottles, one that contains phenol and one that contains ethanol. Describe three chemical tests, that you could carry out in order to label these bottles correctly. Indicate the expected result in each case, and where possible write balanced chemical equations.

5. (a) Write an equation for the oxidation of pentan-2-ol by acidified potassium dichromate(VI) showing clearly the structure of the organic product. You may use the symbol [O] for the oxidising agent.
(b) Pent-2-ene can be formed by the dehydration of pentan-2-ol. Give the reagent and the conditions used. Outline a mechanism for this reaction.
(c) Alcohols E, F and G are branched-chain isomers of pentanol.
E can not be oxidised by acidified potassium dichromate(VI).
F can be oxidised by acidified potassium dichromate(VI) but can not be dehydrated.
G can be oxidised by acidified potassium dichromate(VI) and can also be dehydrated.
Draw a possible structure for each of the three alcohols.

6. There are four alcohols with the molecular formula, $C_4H_{10}O$, which are structural isomers. Three of the isomers are:
A: butan–1–ol B: butan–2–ol C: 2–methylpropan–2–ol
a. Give the name and structural formula of the fourth isomer.
b. The structural isomer B when reacted with concentrated H_2SO_4 produces a mixture of alkenes.
(i) name the type of reaction. (ii) Give the structural formula and the name of one alkene.
c. $A + Cr_2O_7^{-2} / H^{+1} \longrightarrow X \longrightarrow Y$
(i) Give the name and structure of X. (ii) Give the name and structure of Y.
(iii) If $B + Cr_2O_7^{-2} / H^{+1} \longrightarrow Z$
State the name and the formula of Z. Name the type of reaction in (c)
d. $C + \text{—COOH} \xrightarrow{\text{catalyst}} C_6H_{12}O_2$ (ester)
(i) give the name and structure of the ester formed. (ii) name the carboxylic acid used. (iii) name a suitable catalyst that may be used for the formation of ester.

The Breathalyzer Test ⟶ Green means trouble

The breathalyser test is used to determine whether a person has consumed more than the legally acceptable amount of alcohol for driving a vehicle. The test is based on the assumption that alcohol in the blood, which is absorbed into the blood via the small intestine, is in equilibrium with alcohol vapour in the lungs:

$$C_2H_5OH_{\text{(blood)}} \rightleftharpoons C_2H_5OH_{\text{(lungs)}}$$

The alcohol vapour in breath is analyzed by its reaction with potassium dichromate (VI), $K_2Cr_2O_7$, in the presence of dilute sulphuric acid.

The orange dichromate ions, $Cr_2O_7^{-2}$, are reduced to the green chromium (III) ions, whilst the ethanol is oxidized to ethanoic acid:

$$2Cr_2O_7^{-2}{}_{(aq)} + 3C_2H_5OH_{(aq)} + 16H^{+1}{}_{(aq)} \longrightarrow 4Cr^{+3}{}_{(aq)} + 3CH_3COOH_{(aq)} + H_2O_{(l)}$$

In the breathalyser machine, a known volume of breath is passed through an acidic solution of potassium dichromate (VI) of known concentration.

The decrease in the intensity of the orange colour is measured.

Since this decrease is directly proportional to the decrease in the concentration of the dichromate, the amount of alcohol in the breath sample can be calculated.

The machine then converts breath alcohol to blood alcohol content.

(FYI: the legally intoxicated person has a blood alcohol content of 0.08 % or higher, this equals ~ 1 dm^3 of beer or 0.5 dm^3 of wine for a person weighing 65 kg; and the blood alcohol level decreases by 0.015 % for every hour elapsed after the alcohol is consumed.)

Comparison of Properties of Alcohols and Phenols

Property	Ethanol	Phenol
structure and bonding		
solubility in water		
acidity of solution		
reaction with an alkali: $NaOH_{(aq)}$ (acidity of phenol)		
reaction with a reactive metal: $Na_{(s)}$, (test for –OH group)		
reaction with $Na_2CO_{3(s)}$ (difference between an alcohol and phenol)		
dehydration using excess conc. $H_2SO_{4(aq)}$ —> alkene mechanism of E1 and E2		
dehydration using excess alcohol —> ether		
reaction with $HX_{(aq)}$ (test to distinguish between a 1^0, 2^0 and 3^0 alcohol)		
oxidation using MnO_4^{-1}/H^{+1} or using $Cr_2O_7^{-2}$ / H^{+1}		
esterification using a carboxylic acid + conc. $H_2SO_{4(aq)}$ —> ester		
reaction with $Br_{2(l)}$		
reaction with dilute $HNO_{3\ (aq)}$		
reaction with conc. $HNO_{3\ (aq)}$		
reaction with neutral $FeCl_{3\ (aq)}$: test for –OH on C_6H_6 ring		