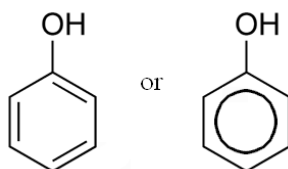


## Year 2, Organic Chemistry, Chapter 15: Phenol

- Phenol (or “Benzenol” or “Carbolic acid”<sup>1</sup>) is a colourless solid and it is the mono-alcohol<sup>2</sup> of Benzene viz. only one “–OH” species has replaced an “H” atom on C<sub>6</sub>H<sub>6</sub>. Phenol, C<sub>6</sub>H<sub>5</sub>OH, is a solid at Room Temperature, and Wikipedia shows the skeletal structure as



- Phenol
  - is an **Alcohol** and displays some of the characteristics of an Alcohol, and
  - it is a **Weak Acid** and has the reactions of a Weak Acid, but
  - it is a **2/4/6 activated Benzene derivative** and most of its reactions are determined by this.
- The great surgeon Lister discovered that Phenol kills “germs” and sprayed it in his operating theatre and in his recovery wards. It did indeed kill “germs” and this saved many lives but, because Phenol ‘burns’ skin, its use has fallen out of favour because the vapour of C<sub>6</sub>H<sub>5</sub>OH is toxic (at even modestly high concentrations).
- Actually any and every alcohol is injurious to living organisms – which is why yeast is killed by Ethanol at a concentration of 12-15% and why “wine” therefore cannot have an ‘alcohol’ content of much more than 14%. *If consumed, Methanol can cause blindness.* It is therefore somewhat surprising that human beings are *rightly* reluctant to spray alcohol in hospitals because of the toxicity of alcohols – *but are apparently more than happy to drink vast quantities of it at weekends!* *Human beings are somewhat strange creatures.*
- When we were talking about Alcohols last year, I told you that the most irresponsible thing that a human being can do is to get drunk/drive a car/and kill another human being. My opinion on this subject has NOT changed.**
- “–OH” has a negative charge and Benzene is surrounded by areas of high electron density and, since a nucleophile cannot naturally attack an electron-rich entity, it is therefore **VERY** difficult to convert Benzene directly into Phenol. However, Phenol can be made by reacting Benzene and Propene in the “Cumene” process<sup>3</sup>. This is a modestly complicated process and you do not need to know the details for ‘A’ level purposes, but I will describe the overall process later on in this Chapter.
- Alcohols are weak Acids, and Phenol is thus a weak acid; but (because some of the electron density of the O atom is locked into the Benzene ring), Phenol is a slightly *stronger* Acid than most Alcohols, but not as strong an Acid as a normal Carboxylic (“–COOH”) Acid.

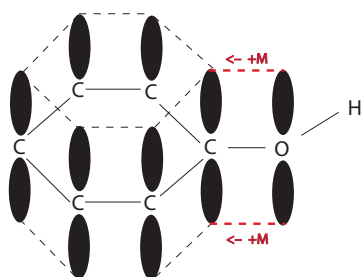
<sup>1</sup> Please do not confuse this with “carboxylic acid”. **Carbolic Acid ≠ Carboxylic Acid.** Carbolic acid soaps are antiseptic (but seem to have gone out of favour with the advent of modern antiseptics). Until the 1960s, every house in the UK used ‘carbolic soap’, and “coal tar” soap (such as Wright’s Coal Tar soap) was very popular. In the 1950s, all young boys used to be given a jolly good scrub with carbolic soap by their mothers on a Saturday night!

<sup>2</sup> An alcohol is an organic species where there is one or more “–OH” species attached to one (or more) of the C atoms in the species.

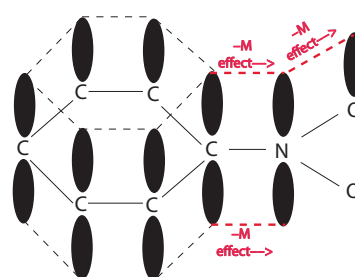
<sup>3</sup> “Cumene” is 1-ethylmethyl Benzene or 2-Phenyl Propane. Wikipedia notes that commercial production of Cumene is by Friedel-Crafts alkylation of Benzene with Propylene.

- The interesting questions to ask are (i) how do you get a negative “–OH” species to attach to a Benzene ring, and (ii) what happens when you do manage to attach the “–OH” to the Benzene ring, and to answer the second question we need to go back to Chapter 03, Inductive and Mesomeric Effects – and we will need to talk about the “frying-pan-and-its-handle” effect.
- In Chapter 3 we talked about the **positive** and **negative** Mesomeric effects, and let me remind you of them. (Phenol has a positive Mesomeric effect).

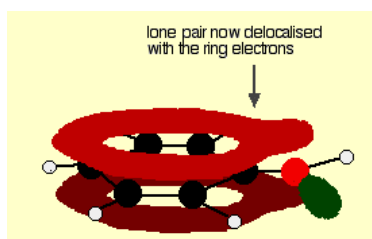
### Positive Effect



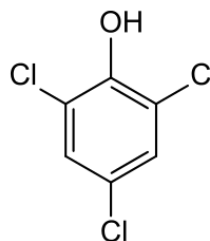
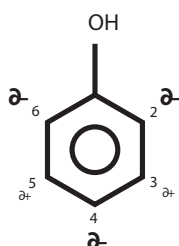
### Negative Effect



- The unhybridised ‘p’ orbital from the Oxygen atom overlaps the unhybridised ‘p’ orbital of the Carbon atom to which it is attached, and the electron gets locked into the delocalised  $\pi$  ring of the Benzene ring (as above). This now creates what used to be called the frying-pan-and-handle effect. Jim Clark’s diagram below just about shows a frying-pan-and-its-handle.



- The positive Mesomeric effect of the “–OH” activates the Benzene ring at positions 2,4 and 6, and this means that an electrophile<sup>4</sup> such as a *positively charged Halide cation* e.g.  $\text{Cl}^+$  or  $\text{Br}^+$  will be attracted to the Benzene ring at positions 2, 4 and 6. That is how you get 2,4-Dichlorophenol and 2,4,6-TriChloroPhenol (TCP).



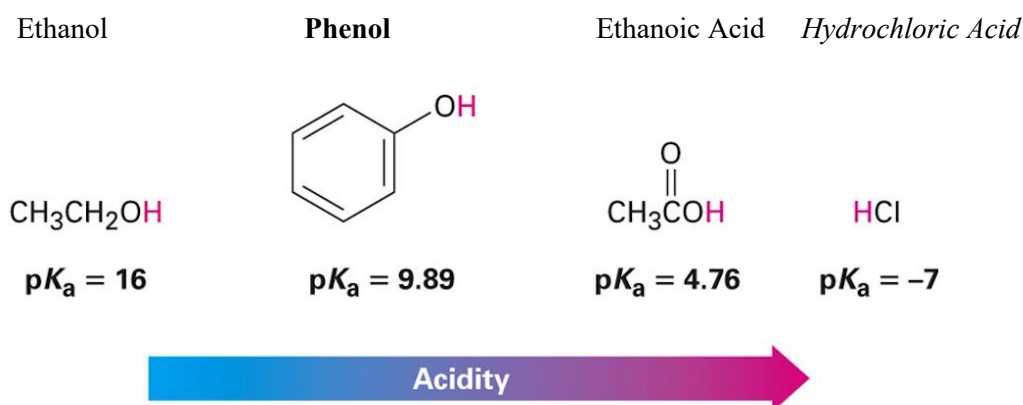
- Dettol contains 2,4,6-trichlorophenol (TCP) and it is a less damaging antiseptic than Phenol<sup>5</sup>, but TCP has gone out of favour because 2,4,6-Trichlorophenol has been shown to be carcinogenic in animals, producing lymphomas, leukaemia, and liver cancer via oral exposure, and it is thus reasonably expected to be a human carcinogen<sup>6</sup>.

<sup>4</sup> To add on to  $\text{C}_6\text{H}_5\text{OH}$  the species has to be an electrophile.

<sup>5</sup> Just as you have 2,4,6-Trichlorophenol, you can have tribromophenol.

<sup>6</sup> Production of TCP in America was stopped in 1975.

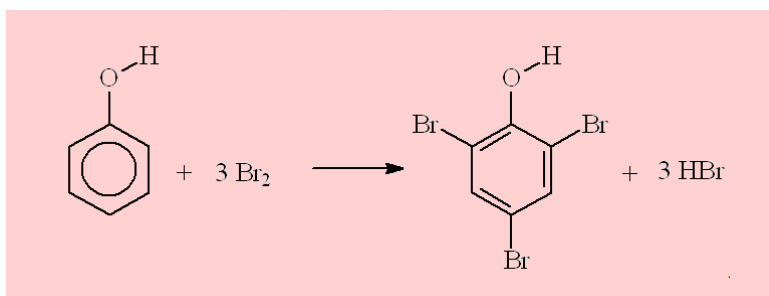
- The O atom in Phenol has an unhybridised 'p' orbital that lies in the same perpendicular plane as the unhybridised 'p' orbitals in Benzene's  $\pi$  ring (and the O atom therefore has a +M effect on the ring). **Phenol's grip on its H atom is then weakened and the H atom can therefore break away as a proton.** Phenol is thus an acid (albeit a weak one).
- Under Brønsted-Lowry's definition, anything that dissociates a proton is an acid (but please remember that the Lewis definition develops the idea of an acid further).
- All Alcohols act like very weak acids, but the +M effect means that because some of the electrons in the O atom of the 'OH' species in Phenol are locked into the  $\pi$  ring of the '-C<sub>6</sub>H<sub>5</sub>' species, then the grip that the O atom has on the H atom is slightly lessened **and the H atom is thus slightly more easily released than it is in a straightforward alcohol.** This means that Phenol acts as a slightly **stronger** acid than does a standard Alcohol. The slide below shows this – and please remember that **the smaller i.e. the lower that a pK<sub>a</sub> value is, the stronger is the acid:**  
**low pK<sub>a</sub>  $\Rightarrow$  low pH  $\Rightarrow$  strong acid.**



Source unknown

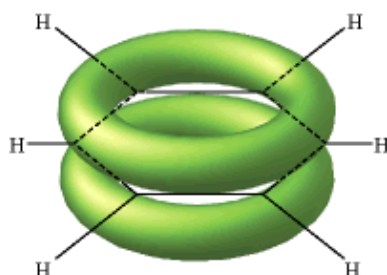
- I am not at all happy with the examiners asking questions about dangerous substances, but they **do** ask such questions, so let us next talk about 2,4,6-Tribromophenol (TBP).
- In a non-polar solvent such as Carbon Disulphide or Tetrachloromethane (which is also now considered to be toxic and is thus no longer used in dry-cleaning), Br<sub>2</sub> will add to Phenol at positions 2 and 4 to give Di-bromophenol, but Phenol will react with Bromine water (Bromine dissolved in Water) to give 2,4,6-Tribromophenol (TBP). If you are asked in the exam (*and the question was asked by OCR in June 2014*) for an equation for the formation of TBP then you should just draw

Phenol dissolved in Water at room temperature will react with brown Bromine Water and give a white precipitate.



Source: Bristol University

- Bromine water is brown, and please could you now spend a few seconds trying to remember the classic test for an unsaturated carbon compound (such as an Alkene or an Alkyne).
- On the front page of Chapter 5 (Alkenes) of the First Year Organic book you will find the statement that “The simplest/the classic test for an alkene is that **it decolourises bromine water immediately**, even in the dark and when ice-cold. An alkene will also decolourise purple potassium permanganate in a few seconds”. Please could you now go back to that Chapter and remind yourself of how Br–Br (or any diatomic Halogen molecule) will react with a double bond.
- The reason for my asking you to do so is that a  $\pi$  bond is in a sense the delocalisation of the electrons in the unhybridised ‘p’ orbitals in each of two overlapping Carbon atoms – and the  $\pi$  ring above and below a Benzene ring is the effect of the delocalisation of the electrons in the unhybridised ‘p’ orbitals in each of the six overlapping Carbon atoms in a Benzene ring



and, if an Alkene (or any unsaturated Carbon compound) will decolourise Bromine Water immediately even in the dark and in freezing conditions, then an activated Benzene compound will also do so. Phenol is a compound derived from Benzene and it will decolourise Bromine Water immediately even in the dark and in freezing conditions.

- Phenol will thus decolourise Bromine Water and the brown colour will disappear immediately to give a white precipitate of  $\text{Br}_3\text{C}_6\text{H}_2\text{OH}$  (as below). However, although an Alkene will decolourise Bromine Water, it will **not** produce the white precipitate that Phenol does.



- In the olden days examiners used to ask questions about tests for different substances in a straightforward way, and I suspect that all this modern stuff about dangerous chemicals is just a disingenuous way of asking you whether you know how to identify a particular chemical. I will therefore tell you/remind you of some of the standard tests for different chemicals (but please remember that **some of these chemicals are really very dangerous things indeed**).

## TESTS FOR DIFFERENT ORGANIC SUBSTANCES

### **An Alcohol group**

#### **Reaction with $\text{PCl}_5$**

An Alcohol will react vigorously with  $\text{PCl}_5$  to form the white fumes of  $\text{HCl(g)}$ . (Phenol will react with  $\text{PCl}_5$ , but less vigorously).

### **1° vs. 2° vs. 3° Alcohols**

#### **Under *GENTLE* Oxidisation**

1°  $\rightarrow$  Aldehydes, and then  $\rightarrow$  Carboxylic Acids

2°  $\rightarrow$  Ketones, and

3° resist gentle oxidation.

(Any alcohol will be converted into a Carboxylic Acid under aggressive oxidation of reflux with acidified  $\text{KMnO}_4$ .)

### **A Halogenoalkane**

Hydrolyse in the presence of  $\text{AgNO}_3$  and a yellowy white ( $\text{AgI}$ )/a creamy white ( $\text{AgBr}$ )/a white ppt ( $\text{AgCl}$ ) of a Silver halide will be formed.

$\text{AgI} < \text{AgBr} < \text{AgCl}$ , where “ $<$ ” = quicker than.



**$\text{AgCl}$  will dissolve in dilute Ammonia**

**$\text{AgBr}$  will dissolve only in concentrated Ammonia**

**$\text{AgI}$  will not dissolve in either**

### **An Alkene**

Brown Bromine water will be decolourised immediately even when ice-cold and in the dark, therefore it cannot be a homolytic bond fission reaction (because that would need uv light to break the  $\text{Br-Br}$  bond).

Phenol can be thought of as having alternating double bonds in it, therefore it will do the same (but a white precipitate will be formed thereby).

An Alkene will turn ice cold, dilute, acidified  $\text{MnO}_4^-$  colourless (but Phenol forms “quinones” which are not part of the ‘A’ Level Syllabus).

### **Oxidising agents**

Dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) :	orange liquid	$\rightarrow$ green.
Tollens $[\text{Ag}(\text{NH}_3)_2]^+$ :	clear liquid	$\rightarrow$ silver ppt.
Fehling's/Benedict's :	blue liquid	$\rightarrow$ brick red.

## Second Year Stuff

### PHENOLS

- will not dissolve easily in Water.
  - are only moderately acidic and therefore do not turn blue litmus paper completely red (as do say HCl or H<sub>2</sub>SO<sub>4</sub>).
  - are a *weakly* acidic Alcohol and thus they will not easily generate CO<sub>2</sub> from CaCO<sub>3</sub>.
- Phenol + FeCl<sub>3</sub> will give a violet/purple colour.  
Phenol + Br<sub>2</sub>(aq) will form a white ppt of Br<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH.  
Phenol + a diazonium salt will give a yellow dye.

### A Carbonyl compound

+ 2,4-dinitro phenylhydrazine will turn a colourless liquid → orangey yellow ppt.  
An Aldehyde will oxidise, a Ketone will not.

### CH<sub>3</sub>CH(OH)–, or CH<sub>3</sub>C–

Tri-iodo methane test : warm (at approx. 40°C) with aqueous alkaline I<sub>2</sub> → pale yellow crystals of CHI<sub>3</sub>.

**There is a difference between an Alcohol and a Phenol, therefore you can compare the**

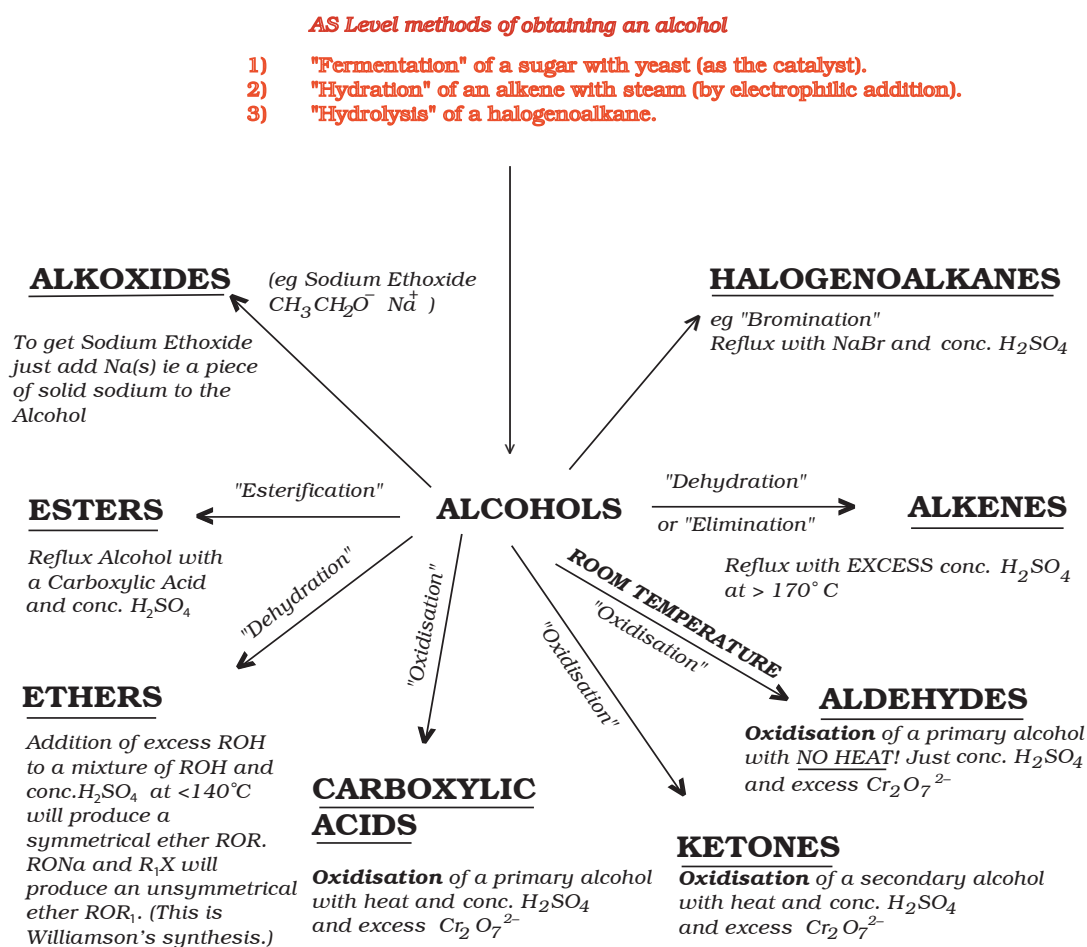
- reactions with PCl<sub>5</sub>
  - reactions with FeCl<sub>3</sub>
  - Acidities
  - States
  - reactions with HCl/HBr/HI
  - reactions with the tri-iodomethane test
  - reactions with C<sub>6</sub>H<sub>5</sub>N<sub>2</sub><sup>+</sup> Cl<sup>–</sup>
  - Solubility
  - reactions with Sodium
  - reactions with an Acyl Chloride
- Sometimes the examiners do ask for tests for different things. You know enough to distinguish between an Alkene and Benzene<sup>7</sup>, and the test for distinguishing Phenol from Ethanol is that Ethanol reacts very *vigorous*ly with PCl<sub>5</sub> to produce HCl(g), **but there is a very slow reaction with Phenol**. Perhaps an even better (and more visible reaction) is that Phenol will react with FeCl<sub>3</sub> to produce a violet colour whereas no colour change is involved with Ethanol (because no reaction has taken place).

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<sup>7</sup> The effect on Bromine water!

## The Reactions of Phenol

- Phenol
  - is an **Alcohol** and displays some of the characteristics of an Alcohol, and
  - it is a **Weak Acid** and has the reactions of a Weak Acid, but
  - it is a **2/4/6 activated Benzene derivative** and most of its reactions are determined by this.
- Alcohols are weak Acids, and Phenol is thus a weak acid; but (because some of the electron density of the O atom is locked into the Benzene ring), Phenol is a slightly *stronger* Acid than most Alcohols, but not as strong an Acid as a normal Carboxylic (“–COOH”) Acid.
- Let us start by revising the reactions of an Alcohol.

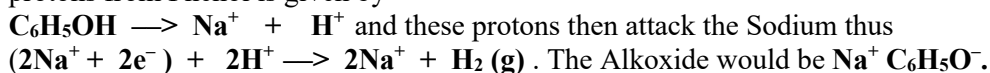


- However, the Benzene ring part of Phenol is not only high in electron density (because it has a big delocalised  $\pi$  ring above it and beneath it); but, in addition, Phenol is **activated** at positions 2,4, 6. The reactivity of the “ $\text{C}_6\text{H}_5-$ ” part of the “ $\text{C}_6\text{H}_5\text{OH}$ ” thus predominate over the reactions that happen as a result of the “–OH” part of the “ $\text{C}_6\text{H}_5\text{OH}$ ”.
- Please remember that
  - Phenol is a **Weak Acid** and will have the reactions of a Weak Acid e.g. it will react with NaOH or KOH to form Water plus the relevant salt
  - Phenol is an **Alcohol** and thus has some of the reactions of an Alcohol
  - Phenyl has a (2/4/6) **Activated Benzene ring** and acts like an Activated Benzene ring.



## Reactions similar to those of an Alcohol

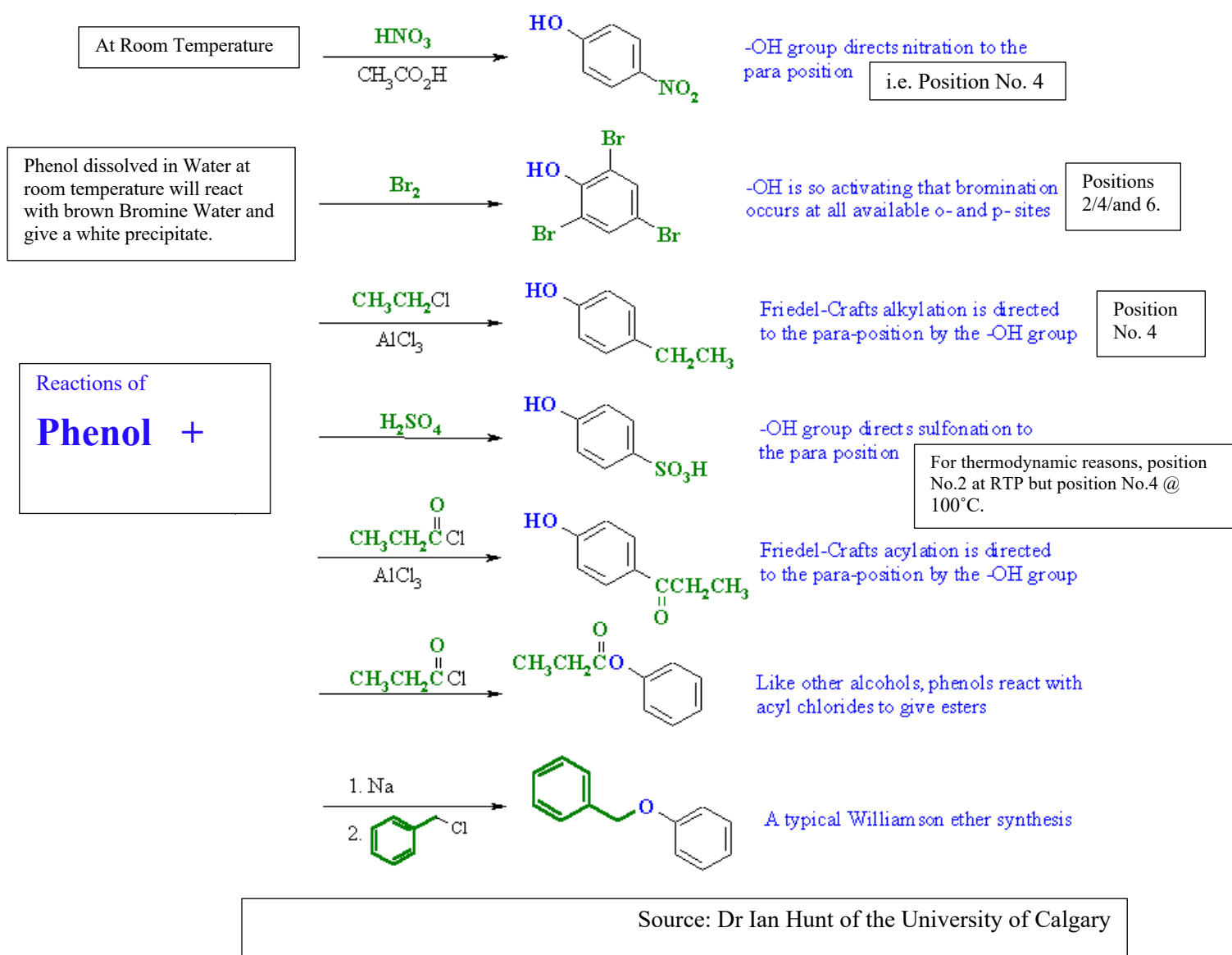
- If a piece of a reactive metal were put into an Alcohol, then an Alkoxide would be formed and Hydrogen gas would be released. Metals consist of positively charged metal ions set in a sea of delocalised electrons, and it is the protons that Alcohols dissociate that react with the electrons in the sea of delocalised electrons of e.g. Sodium to form the Hydrogen gas. The dissociation of the protons from Phenol is given by



The two electrons create the molecular  $\sigma$  bond between the two H atoms.

## Reactions of Phenol where the Benzene ring is predominant

The following diagram from Dr Ian Hunt of the University of Calgary is a nice summary of the reactions of Phenol.





- Different Examination Board require you to know different reactions for Phenol, but the reactions
  - with Sodium metal
  - with Sodium or Potassium Hydroxide
  - with Bromine Water
  - with concentrated  $\text{HNO}_3$  and with concentrated  $\text{H}_2\text{SO}_4$

should be all that you need to know.

### +M effect in Phenol

- The unhybridised 'p' orbital in the O atom in Phenol (i.e. the one that is bonded to the C atom in the  $-\text{C}_6\text{H}_5$ ) overlaps the unhybridised 'p' orbital of the C atom to which it is bonded, and thus the electron therein gets locked into the delocalised  $\pi$  ring of the  $\text{C}_6\text{H}_5$  ring. This increases the electron density on the Benzene ring **and gives a classic '+M' effect** and causes activation at 2/4/6.
- Phenol is involved in EAS reactions, and thus the substitution will take place at 2/4/6.
- However, because Phenol is now activated at 2/4/6, although Phenol will undergo all the same EAS reactions as Benzene, the +M effect/the activation of the ring means that the EAS reactions **will take place with a requirement of much less energy.**
  - the **Nitration** of Phenol will take place with less energy
  - the **Sulphonation** of Phenol will take place with less energy
  - the **Alkylation** of Phenol will take place with less energy
  - the **Acylation** of Phenol will take place with less energy, and
  - the **Halogenation** of Phenol will take place with less energy.

### The Cumene Process : Cumene = “(1-methylethyl) Benzene”

- Some Examining Boards do not expect you to know about the “Cumene Process” while others do. I will therefore cover it only in *brief* detail.
- “Cumene” is **1-methylethyl Benzene**, and it can be made by reacting Benzene with Propene at  $250^\circ\text{C}$  and 30 atmospheres of pressure using  $\text{H}_3\text{PO}_4$  as a catalyst. It is then oxidised by air plus a catalyst into Cumene hydroperoxide which is then reacted with Sulphuric Acid to form Phenol and Propanone.

**NB** For **most** exam boards you do **NOT** need to know that.

- Edexcel however gives the following reaction equation

