

Hope this is useful. If there are any errors or omissions, please email me at design@adeb.co.uk so I can rectify (and learn from) my mistakes.

Unit 4 Experiments

Chapter 11

	Reactants	Products	Description	Mechanism
1	$\text{CaCO}_3 + \text{HCl}$	$\text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$	This is an example of an experiment which can be followed by weighing the reactants before and during the experiment, with a piece of cotton wool in the flask to prevent entrance or exit of liquids or solids.	The hydrochloric acid is a strong enough acid to displace CO_2 from CaCO_3 , also forming a salt and water.
2	$\text{CH}_3\text{COCH}_3 + \text{I}_2$	$\text{CH}_3\text{COCH}_2\text{I} + \text{HI}$	This is conducted in a flask, timing how long it takes the iodine colour to disappear. The rate of the reaction is proportional to $1/\text{time}$ to disappear.	The reaction is acid catalysed, this is an initial rate mechanism method.
3	$\text{C}_4\text{H}_9\text{Br} + \text{OH}^-$	$\text{C}_4\text{H}_9\text{OH}$	This is the $\text{S}_{\text{N}}1$ (Nucleophilic Substitution, 1 molecule in slow step) mechanism, order one with respect to the bromoalkane.	<ol style="list-style-type: none"> $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$ (slow) $\text{C}_4\text{H}_9^+ + \text{OH}^- \rightarrow \text{C}_4\text{H}_9\text{OH}$ (fast)
4	$\text{C}_4\text{H}_9\text{Br} + \text{OH}^-$	$\text{C}_4\text{H}_9\text{OH}$	This is the $\text{S}_{\text{N}}2$ mechanism, with two molecules in the rate determinant step and order one with respect to the bromoalkane and OH^- . It is essentially a one step process, with a both the hydroxide ion and the bromine temporarily joined to the hydrocarbon group.	<ol style="list-style-type: none"> $\text{C}_4\text{H}_9\text{Br} + \text{OH}^- \rightarrow \text{HOCC}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Br}^-$ (slow)
5	$\text{S}_2\text{O}_3^{2-} + 2\text{H}^+$	$\text{SO}_2 + \text{S} + \text{H}_2\text{O}$	The production of the solid sulphur precipitate means that the solution gets darker as it progresses. The 'obscuring the spot', where rate is proportional to $1/t$, can therefore be used.	Another initial rate mechanism method.

Chapter 12

Benzenes

	Reactants	Products	Description	Mechanism
1	Combustion: Methylbenzene	Bright, sooty flame!	The sooty flame indicates an incomplete combustion, synonymous with a high carbon: hydrogen ratio. All phenols and benzenes have this sooty flame, which can be used as an indicator of the benzene based compounds,	Plain old burning.
2	$\text{C}_6\text{H}_5\text{CH}_3 + \text{KMnO}_4 + \text{H}_2\text{SO}_4$	Nothing happens	You end up with a clear, viscous meniscus floating on top of the solution. For the oxidation to occur successfully, you would need to reflux the solution with sodium carbonate and you would get a dark brown precipitate of manganese oxide.	Nowt.

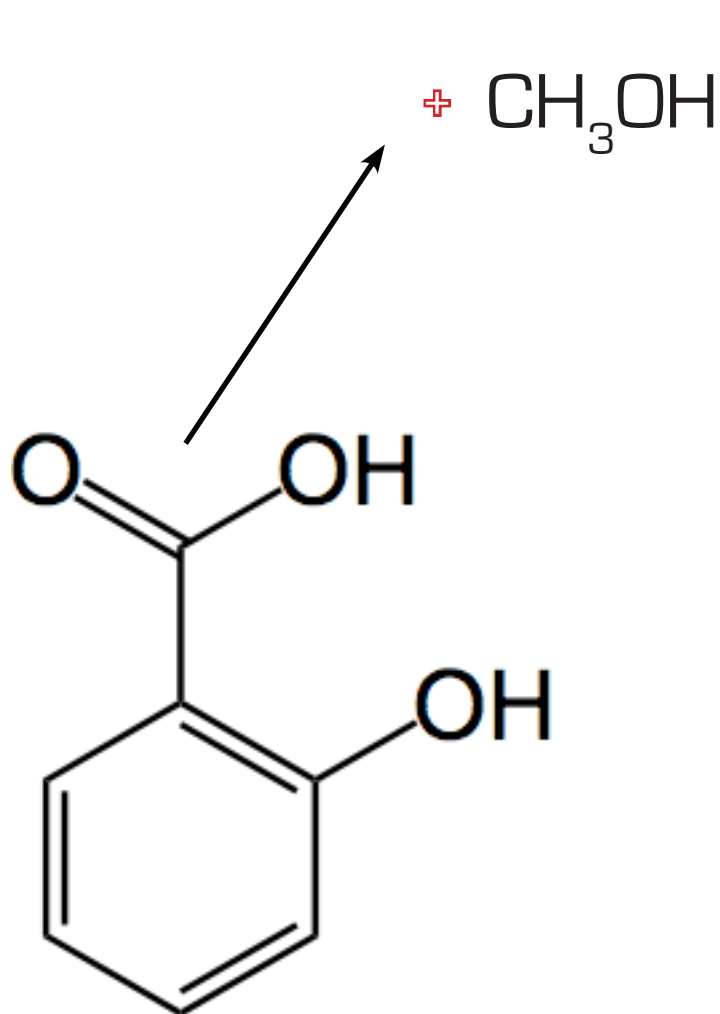
3	$C_6H_5OCH_3 + Br_2$	$C_6H_5OCH_3Br + HBr$	<ul style="list-style-type: none"> Solution goes pale yellow, fumes are misty white when tested with ammonia, indicating the presence of a HHal. Fe catalyst needed for methylbenzene or benzene, but not methoxybenzene ($AlCl_3$ catalyst for Cl). More bromines can be added to the ring by heating. 	An electrophilic substitution.
4	$C_6H_5OCH_3 + SO_3$	$C_6H_5OCH_3SO_3$	<ul style="list-style-type: none"> The tube warms up and the liquid turns pale brown, before forming two layers, green and ochre. Upon the addition of water (removing the H^+ from the HSO_3^- group), there is a milky ppt. A solution of fuming sulphuric acid is used here to provide the attacking molecule, SO_3. Refluxing for several hours is sometimes necessary with benzene, though not with methyl or methoxybenzene. Sulphonation is used to produce drugs detergents and dyes. 	An electrophilic substitution.
5	$C_6H_5OCH_3 + AlCl_3 + CH_3CH_2Cl$	$CH_3CH_2C_6H_5OCH_3 + HCl + AlCl_3$	<ul style="list-style-type: none"> The $AlCl_3$ acts to catalyse the reaction by forming a complex, $R^+AlCl_4^-$, with R being the alkyl group (in this case CH_3CH_2). The R^+ then acts as an electrophile. 	An electrophilic substitution.
7	$C_6H_5OCH_3 + NO_2^+$	$C_6H_5OCH_3NO_2 + H^+$	<ul style="list-style-type: none"> Acidic brown gas evolved, NO_2. Purple layer of fluid formed, colour diffusing downwards The precursor to this is adding H_2SO_4 to the nitric acid, which forms the hydronium ion and NO_2^+, which is an electrophile. Nitration is used to produce explosives and dyes. 	An electrophilic substitution.
8	$C_6H_6 + 3H_2$	C_6H_{12}	<ul style="list-style-type: none"> Done with a Nickel (Ni) catalyst at $200^\circ C$, and usually at 30 atm (to keep the benzene in the liquid phase). Used to produce nylon for clothing etc. 	Nucleophilic Addition.
9	$C_6H_6 + 3Cl_2$	$C_6H_6Cl_6$	<ul style="list-style-type: none"> This reaction must be irradiated with ultraviolet light (hv) to form the Chlorine free radical. The product is 1,2,3,4,5,6-hexachlorocyclohexane! It is used as an insecticide. 	Nucleophilic Addition.

Unit 4 Experiments

Phenols

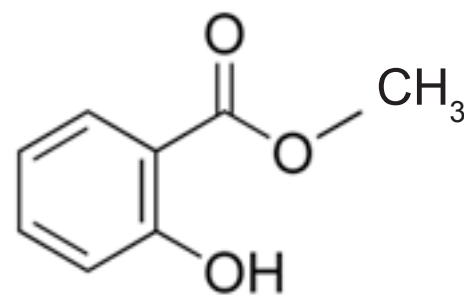
	Reactants	Products	Description	Mechanism
10	Phenol & water	Low solubility	Forms H-Bonds with water, but lower solubility than ethanol due to the arene ring.	H-Bonds.
11	Phenol as acid	Slightly acidic	Formerly known as carbolic acid, the pH is only just less than 7 in water. The reason phenols are acidic and alcohols aren't is because the lone pairs, in their interaction with the delocalised benzene ring, stabilise the anion formed by the dissociation of the H. A phenol is too weak to react with sodium carbonate solution.	Delocalised system stabilisation allow dissociation.
12	Phenol + Na ⁺ OH ⁻	Sodium Phenoxide (C ₆ H ₅ O ⁻ Na ⁺)	This is useful as sodium phenoxide is more reactive than your standard phenol in terms of the reaction of the hydroxyl group, forming a more reactive nucleophile. Sodium Phenoxide, for instance, reacts much more easily with Acyl Chlorides and Acid Anhydrides to form esters.	Electrophilic Substitution.
13	Ethanoic Anhydride + Phenol	Phenyl Ethanoate + Ethanoic Acid	This is a form of esterification, and can be enhanced by the use of a Sodium Phenoxide (above) in place of the phenol. The carbon cation on the acid anhydride attacks the O ⁻ of the hydroxyl group, resulting in one half of the acid anhydride being added to the phenol and the other half forming ethanoic acid. with the H ⁺ eliminated from the hydroxyl group (or sodium ethanoate if sodium phenoxide has been used).	Nucleophilic Addition
14	Phenol + HBr	No reaction	Phenols will not undergo the nucleophilic substitution of the hydroxyl group to form halogenoalkanes, unlike ethanol. This is because the interaction with the delocalised system makes it harder to break the C-O bond.	Nowt.
15	Phenol + Sodium Dichromate + H ₂ SO ₄	No reaction	The hydroxyl group on the phenol cannot be oxidised because of the stability of the benzene ring	Nowt.
16	Substitutions with phenol (i.e bromine, nitric acid)	Multiple substitutions often occur	The delocalisation of electrons from the hydroxyl group into the phenol ring make the ring more nucleophilic, and rendering it more attractive to electrophilic attack	Electrophilic substitution.

Unit 4 Experiments



Acid Catalyst

Heat



Wintergreen

Methylation of the carboxyl group

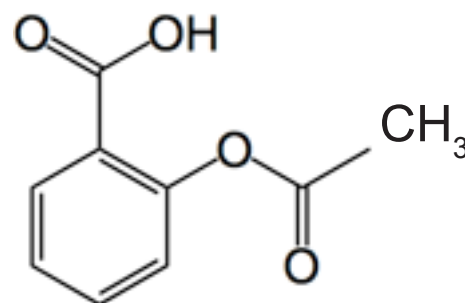
Procedure:

1. Mix the 2-hydroxybenzoic acid (a solid) with methanol and conc sulphuric acid (the catalyst) in a pear shaped flask.
2. Reflux and boil for about an hour.
3. Cool to room temperature and pour it into a separating funnel with cold water. Rinse the flask with ethyl ethanoate (organic solvent) and add this to the separating funnel.
4. Run the lower aqueous layer formed into a conical flask. Add aqueous sodium carbonate to the organic layer, which will produce CO_2 (so let it escape). Again, run off the aqueous layer. Discard.
5. Dry the resultant organic solvent extract with anhydrous sodium sulphate. Leave to dry for 10 mins and then filter out the solid sodium sulphate.
6. Boil off the organic solvent and collect the distillate which boils at 220°C ; oil of wintergreen.



Acid Catalyst

Heat



Aspirin

Ethanoylation of the hydroxyl group

Procedure:

1. Mix the 2-hydroxybenzoic acid (a solid) with the ethanoic anhydride in a pear shaped flask
2. Add phosphoric acid (the catalyst) and reflux with heat
3. Add water into the reflux to hydrolyse the excess ethanoic anhydride (forming ethanol, which boils off)
4. Pour the mixture into a beaker of cold water and stir and rub the sides of the beaker with a glass rod to induce crystallisation. Leave to stand in an ice bath.
4. Collect the product by suction filtration and wash it with a little water, then recrystallize from hot water.
5. Determine purity by testing the melting point; if 'sharp' then purity is reasonable.

Unit 4 Experiments

Chapter 14

	Reactants	Products	Description	Mechanism
1	<p>1. $F^{2+} + Ag^+$</p> <p>2. $CNS^- + Fe^{3+}$</p>	<p>$Fe^{3+} + Ag$</p> <p>$Fe(CNS)^{2+}$</p>	<p>The mixture in 1 (formed by leaving Silver Nitrate and Iron Sulphate solution to mix overnight) is titrated with KCNS, potassium thiocyanate. This leads to the precipitation of solid silver thiocyanate, AgCNS. When all of the silver ions have reacted, the thiocyanate ion turns to the Fe^{3+} ions, forming the deep red iron thiocyanate, $Fe(CNS)^{2+}$. This indicates the end point of the titration.</p>	<p>The fact that the thiocyanate ions 'choose' the silver ions over the iron ones means that when the deep red colour is produced, the silver ions have all been reacted; telling us how many silver ions there were in the eqm solution. This allows us to calculate K_c.</p>
2	N_2O_4	$2NO_2$	<p>Since the first gas is colourless and the second brown, the concentration of the gases can be judged by the intensity of the colour of the gas mixture. This can be observed at different temperatures by placing the mixture in hot or cold water; though our judgement is somewhat hampered by the volume changes incurred.</p>	<p>Warmer temperatures favour the forwards reaction, which is endothermic, leading to a more intense brown colour. Cooling leads to the reverse.</p>

Chapter 15

	Reactants	Products	Description	Mechanism
1	<p>Aldehyde/ Ketone & Water</p>	<p>Soluble for short chains</p> <p>Aldehyde Hydrate formed with aldehydes</p>	<p>Solubility falls as the length of the chain increases. The solubility stems from the fact that although aldehydes and ketones cannot H-bond with themselves, the lone pair on the oxygen means that they can form H-Bonds with water molecules.</p>	<p>The lone pair on the Oxygen of the aldehyde/ ketone facilitates H-Bonding with water molecules.</p> <p>Aldehyde hydrates formed by the addition of water to $C=O$.</p>
2	<p>Aldehyde + Acidified Sodium Dichromate/ Benedict's Solution</p>	<p>Carboxylic Acid + Reduced Sodium Dichromate/ Reduced Benedict's Solution</p>	<p>Colour change orange to green visible as the sodium dichromate is reduced.</p> <p>OR Benedict's solution turns red from blue.</p>	<p>The hydrogen on the carbonyl group is oxidised to OH, forming a carboxylic acid (or a carboxylic acid salt if carried out in alkali conditions).</p>
3	<p>Ketone + Acidified Sodium Dichromate/ Benedict's Solution</p>	No reaction	<p>Solution remains orange, no oxidation having occurred.</p> <p>Benedict's remains blue.</p>	<p>There is no H attached to the carbonyl group, only two alkyl groups, so oxidation cannot occur.</p>

Unit 4 Experiments

4	Aldehyde/ Ketone & Brady's Reagent	Orange Precipitate produced	Brady's Reagent is a mixture of methanol, H_2SO_4 and 2,4-dinitrophenylhydrazine. The orange precipitate formed is X - 2,4-dinitrophenylhydrazone, with X being whatever aldehyde or ketone you started with.	A nucleophilic addition/ elimination reaction with the $C=O$ bond breaking and the Brady's reagent joining on, elimination H_2O in the process.
5	$LiAlH_4$ + Ketone/Aldehyde/ Carboxylic Acid	Alcohol (Secondary/ Primary/ Primary)	Reacts violently if water or alcohol are present, so conducted in carefully controlled conditions.	This is nucleophilic attack by the H^- ion (that's right, H^- ; it's in an ion with Al, a metal, which is a positive ion, and so the H is negative).
6	Carboxylic Acid + Alcohol	Ester + H_2O	Must be done with H_2SO_4 and refluxed with heat, making it quite an expensive procedure.	A nucleophilic addition/ elimination, with H_2O being eliminated. The O in the H_2O comes from the carboxylic acid, and can be traced by using a radioactive isotope.
7	Acyl Chloride + Alcohol	Ester + HCl	Very reactive, requiring no catalysts.	A nucleophilic addition/ elimination, with the ester group replacing the Cl, and the hydrogen coming from the alcohol.
8	Acid Anhydride + Alcohol	Ester + Carboxylic Acid	Moderately reactive and much cheaper than acyl chlorides.	A nucleophilic addition/ elimination. Essentially you are splitting the acid anhydride down the middle, the side that didn't the joining O getting an alcohol stuck onto it, and the other receiving the H eliminated from the alcohol.
9	Acyl Chloride + NH_3	Amide + HCl	The NH_3 acts as a nucleophile, displacing the Cl.	Another nucleophilic addition/ elimination.
10	Hydrolysis of Esters (Ester + H_2O)	Carboxylic Acid + Alcohol	Very slow reaction, and so an acid or base catalyst is used.	Another nucleophilic addition/ elimination, with H^+ as the nucleophile, with the OH^- joining with the displaced alkyl group.