UNIT 9: ARENES, PHENOLS AND CARBOXYLIC ACID DERIVATIVES

Recommended Prior Knowledge: The AS Units 4 and 5 (Organic Chemistry) should have been completed, along with the sections in AS Units 1 and 2 dealing with π-bonds and enthalpy changes. Parts of A2 Unit 7A (ionic equilibria involving acids and bases) would be useful background to work on the acidities of carboxylic acids.

Context: These two sub-units can be studied on their own, or in conjunction with each other. They should be studied before the other Organic Chemistry Unit 10, but can come before or after the other A2 Units.

Outline: Sub-unit 9A covers the chemistry of benzene, methylbenzene, and phenol, and introduces the important mechanism of electrophilic substitution.
Sub-unit9B covers the tri-iodomethane reaction, and the chemistry of acyl chlorides. It brings together several trends involving halogeno compounds: the relative ease of hydrolysis of chloroalkane, chloroarenes and acyl chlorides; and the relative acidities of chlorinated carboxylic acids.

UNIT 9A: ARENES AND PHENOLS

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
10.1(a)	interpret, and use the nomenclature, general formulae and displayed formulae of the following classes of compound: *(i)* arenes *(ii)* halogenoarenes *(iii)* phenols	Revision of the general rules of nomenclature should precede a closer study of the naming of substituted benzene rings (including the 1,2-, 1,3- and 1,4- positional isomers); and the naming of benzene ring-containing compounds where the ring is considered a side-chain (e.g. phenylethene). Even in displayed formulae, the benzene ring can be drawn as a hexagon-with-an-inscribed-circle – localised double bonds, or individual C and H atoms, need not be shown.	M 109, 113 C+H 27.2 R+N 16.28, 16.35
10.1(c) 10.1(d)	*(i)* describe the shape of the benzene molecule explain the shape of the benzene molecule in terms of σ and (delocalised) π carbon-carbon bonds.	Benzene is a regular planar hexagon, with 120° bond angles. A large molecular model would help with this explanation. The bonding is best described by first constructing the σ-framework, using 3 electrons from each C atom, and then "delocalising" the remaining 6 electrons by forming a 6-centre orbital through overlap of the unused p-orbital on each carbon atom. The fact that this gives a more stable system is best illustrated by calculating the $\Delta H_{hydrogenation}$ of the hypothetical "cyclohexatriene" (assuming itsΔH_{hydr} to be three times the ΔH_{hydr} for ethene), and comparing that to the experimental value for benzene. (Students could do the ΔH calculations themselves). Practical work comparing the reactivities of methylbenzene and cyclohexene towards $KMnO_4$(aq) and Br_2(aq) will reinforce this idea.	**site 16** (organic chemistry: benzene)
10.2(j)	describe the chemistry of arenes as exemplified by the following reactions of benzene and methylbenzene: *(i)* substitution reactions with chlorine and bromine *(ii)* nitration *(iii)* oxidation of the side-chain to give a carboxylic acid.	The need for powerful reagents should be emphasised: The necessity of a Lewis acid catalyst (e.g. $AlCl_3$), and pure *non-aqueous* Cl_2 or Br_2 for halogenation, and *concentrated* nitric acid with a *concentrated* sulfuric acid catalyst for nitration. Mention the possibility of polysubstitution – hence the temperature for nitration must be kept below 55^oC. The nitration of methyl benzoate is a suitable example for a class practical, giving an easily recrystallisable solid product. Oxidation of alkyl side chains (not just CH_3 – higher ones are oxidised too) by heating for hours with $KMnO_4$ (aq) + OH⁻, shows how stable the benzene ring is compared to the usually unreactive alkyl groups.	M 113 C+H 27.3 R+N 16.29 P(A2) 19 **site 4** (arenes) R+N 16.33

10.2(k)	(i) describe the mechanism of electrophilic substitution in arenes, using the mononitration of benzene as an example. (ii) describe the effect of the delocalisation of electrons in arenes in such reactions.	The general electrophilic substitution mechanism involving the addition of an electrophile E^+, giving the Wheland intermediate, and subsequent elimination of H^+, should be described. The equation for the production of the electrophile NO_2^+ should include 2 moles of H_2SO_4: $$2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + NO_2^+$$ The production of other electrophiles could also be mentioned, e.g. $$Cl_2 + AlCl_3 \longrightarrow AlCl_4^- + Cl^+$$ Although the Wheland addition intermediate is analogous to that formed between ethene and an electrophile, the re-forming of the delocalised sextet of π electrons is the driving force for the elimination of the proton in the second step, unlike the addition of an anion in the case of ethene. The delocalisation of the (+) charge in the intermediate can be represented by a 'horse shoe' drawn inside the hexagon, with the (+) charge at its 'closed' end.	M 114 C+H 27.3 R+N 16.30 **site 8** (aromatics + plastics)
10.2l	predict whether halogenation will occur in the side-chain or aromatic nucleus in arenes depending on reaction conditions..	Both reactions need the halogen to be *anhydrous*. With a Lewis acid such as $AlCl_3$, nuclear substitution occurs; in the absence of a Lewis acid, but in the presence of UV light, free radical substitution occurs in the side chain, on the carbon atom adjacent to the ring, thus phenylethane gives 1-choro,1-phenylethane, not 1-chloro,2-phenylethane. Point out that this is due to the stability of the benzylic radical formed as an intermediate. This could be a good point to revise the mechanism of free radical substitution in alkanes (Unit 4).	M 113 C+H 27.3 R+N 16.32
10.2m	apply the knowledge of positions of substitution in the electrophilic substitution of arenes.	The directing effects of groups do not need to be learnt, but students should know that it is the group *already attached* to the ring that determines the position of substitution. The most likely questions on this topic will involve the application of knowledge from orientation examples stated in the question to a new situation. Practice by using questions from past papers (e.g. 9701/04 June 2008)	M 114 C+H 27.3
10.4e	recall the chemistry of phenol, as exemplified by the following reactions: (i) with bases (ii) with sodium (iii) nitration, and bromination, of the aromatic ring.	Unlike alcohols, phenols are acidic enough to dissolve in NaOH(aq), and be re-precipitated on the addition of HCl(aq) [The intrinsic solubility of phenol in water sometimes masks this effect - the use of the less soluble thymol makes for a more impressive demonstration]. Phenol reacts vigorously with sodium, after warming gently to melt the solid. The ready nitration (using *dilute* nitric acid with no sulfuric acid) and bromination (with bromine *water* and no Lewis catalyst) shows how much more reactive to electrophilic substitution is the aryl ring in phenol. Unfortunately, carrying out this reaction in the laboratory often produces intractable tars. Explain the enhanced reactivity in terms of delocalisation of the oxygen's lone pair over the ring. This ties in with the explanation that will be used for phenol's enhanced acidity.	M 117 C+H 27.5 R+N 18.7, 18.9 R+N 18.8 **site 21a**
10.4f	explain the relative acidities of water, phenol and ethanol	Explain that ethanol ionises slightly less easily than water (due to the inductive effect of the ethyl group), but phenol ionises much more readily – universal indicator paper turns orange-red in a solution of phenol. The explanation should be in terms of the extra stability of the phenoxide anion, due to delocalisation of charge over the aryl ring. Explain that phenol is a much weaker acid than carboxylic acids, however. In the latter case the (-) charge of the anion is shared equally between two electronegative (electron-attracting) oxygen atoms, so making the anion particularly stable.	M 117 C+H 27.5 R+N 18.10

UNIT 9B: CARBOXYLIC ACIDS DERIVATIVES

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
10.4(d) 10.5(e)	deduce the presence of a $CH_3CH(OH)$- group in an alcohol from its reaction with alkaline aqueous iodine to form tri-iodomethane. describe the reaction of CH_3CO- compounds with alkaline aqueous iodine to give tri-iodomethane.	These are two A2 additions to the reactions of alcohols and carbonyls that were studied at AS level. Test tube experiments involving various known, and the identification of "unknown", compounds can be carried out (in conjunction with other tests, such as sodium metal, Tollens' reagent and 2,4-DNPH). These can form a useful revision of the AS part of the course. It is important to appreciate that apart from tri-iodomethane, the other product is the sodium salt of the carboxylic acid. Balanced equations should be taught.	M 118 C+H 26.3, 28.3 R+N 19.5 **site 7** (N-ch3-16)
10.6(c)	explain the acidity of carboxylic acids and of chlorine-substituted ethanoic acids in terms of their structures.	If sub-unit 7A has been previously taught, acidities can be related to K_a and pK_a values for weak acids, illustrated by equations showing the acid-anion equilibrium. Measuring the pH of 0.1 mol dm^{-3} solutions of various acids will give student a feel for the trends. The pK_a of an "unknown" acid can also be measured using the continuous variation method described in sub-unit 7A. The explanation should be in terms of the stability of the anion, through delocalisation over *two* electronegative oxygen atoms. This delocalisation of negative charge becomes even more effective if electronegative elements such as chlorine are present. Thus the chloroethanoic acids become increasingly more acidic as more chlorine atoms are present in the molecule.	M 119 C+H 29.1 R+N 20.5 **site 4** (A2: carboxylic acids)
10.6(b)	*(iii)* describe the formation of acyl chlorides (from carboxylic acids)	The reagent of preference is $SOCl_2$, since both by-products are gases. Other possibilities are PCl_3 and PCl_5. The reaction can be carried out in the lab (e.g. with $C_6H_5CO_2H$) if a fume cupboard is available – the product can be used without distillation to make benzamide.	M 120 C+H 29.3 R+N 20.6
10.6(d) 10.6(e)	describe the hydrolysis of acyl chlorides describe the reactions of acyl chloride with alcohols, phenols and primary amines.	Explain that acyl chlorides readily react with nucleophiles, due to the highly $\delta+$ carbon atom they contain. The formation of esters from alcohols or phenols is often carried out in the presence of a base (e.g. dissolving the phenol in NaOH(aq), or adding pyridine), which absorbs the HCl by-product. The formation of benzamide from benzoyl chloride + conc NH_3(aq) [fume cupboard!] produces an easily re-crystallised solid product.	M 120 C+H 29.4 R+N 20.7, 20.8 P(A2) 23, 25, 26
10.6(g)	describe the formation of esters from acyl chlorides using phenyl benzoate as an example.	The reaction between benzoyl chloride and phenol dissolved in NaOH(aq) (the Schotten-Baumann procedure) gives a solid product that can be recrystallised. Emphasise that the usual esterification route is not available for phenols, due to the poor nucleophilicity of the oxygen atom. The reactions between benzoyl chloride and ethanol, or between ethanoyl chloride and phenol, are suitable lab practicals, producing high boiling liquid esters that can be purified by simple distillation.	M 120 C+H 29.4 R+N 20.9
10.6(f) 10.3(c)	explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides. interpret the reactivity of chlorobenzene with particular reference to hydrolysis and the relative strength of the C-Hal bond.	For acyl chlorides the explanation should be based on the presence of the highly $\delta+$ carbon atom in the carbonyl group, flanked by the two electronegative atoms oxygen and chlorine. Acyl chlorides also display the advantage of being able to use the addition-elimination mechanism for their reactions with nucleophiles, thus lowering the activation energy (cf. the different reactivities of CCl_4 and $SiCl_4$). For aryl chlorides, the lack of reactivity is due to two effects: the geometry of the molecule precludes nucleophilic attack on the back side of the C-Cl carbon atom (hence no possibility of an S_N2 reaction); and the partial overlap of the 3p lone pair on chlorine with the ring π electrons strengthens the C-Cl bond. Students could make a practical comparison of the reactions of organic chlorides with NaOH(aq) or	M 115, 120 C+H 29.4 R+N 20.10 C+H 27.4

| | | H_2O (at room temperature with acyl/alkyl chlorides, after heating under reflux for an hour or two for alkyl/aryl chlorides), followed by the identification of Cl^- with $AgNO_3$ + HNO_3, to demonstrate this difference in reactivity. | |