

## UNIT 5: ORGANIC CHEMISTRY II

**Recommended Prior Knowledge:** Unit 1 (Theoretical Chemistry) and Unit 4 (Organic Chemistry I) should have been studied before this unit. Although most of Unit 2 is not immediately relevant to this Unit, some prior discussion of bond energies, acids and bases, and kinetics of reactions, would be beneficial.

**Context:** This unit is a sequel to Unit 4, which should precede it, but it can either precede or follow Units 2 and 3 (but see comment above).

**Outline:** This Unit is the second of two dealing with Organic Chemistry. It covers the properties and reactions of organic compounds with oxygen-containing functional groups: the alcohols, carbonyl compounds and carboxylic acids and some of their derivatives. Finally, it includes a section on tying together the various strands of Organic Chemistry.

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
10.4(a)	recall the chemistry of alcohols, exemplified by ethanol: (i) combustion (ii) substitution to give halogenoalkanes (iii) reaction with sodium (iv) oxidation to carbonyl compounds and carboxylic acids (v) dehydration to alkenes (vi) ester formation	Most of these reactions can be carried out in the laboratory, which will help student to remember the necessary conditions. Provide balanced equations for all reactions (use [O] for the oxygen atoms provided by the oxidising agent) and include essential conditions (e.g. reagent, solvent, temperature). Reactions divide into nucleophilic substitution (ii); redox (i), (iii), (iv); or elimination (v).	C+H 26.3 M 116 R+N 18a.3 P(AS) 28 <a href="#">site 4</a> (alcohols)
10.4(b)	classify hydroxy compounds into primary, secondary and tertiary alcohols	Revise nomenclature and isomerism. Definition and practice with recognising primary, secondary and tertiary R-OH. Mention the chirality of butan-2-ol. Molecular models will prove useful.	C+H 26.1-26.2 M 116 R+N 18a.4
10.4(c)	suggest characteristic distinguishing reactions, e.g. mild oxidation	Primary and secondary alcohols reduce hot acidified dichromate from orange to green, whereas tertiary alcohols give no reaction. If the reaction mixture from the oxidised alcohols is distilled, the distillate will show an acidic reaction ( $\rightarrow$ RCO <sub>2</sub> H) if ROH is primary, but a neutral reaction if ROH is secondary. (In either case the distillate could give an orange ppt with 2,4-DNPH, from an aldehyde or a ketone, so this is not a useful distinguishing reagent). An alternative method is to test for the presence (or absence) of the aldehyde, produced by partial oxidation of the primary alcohol, with Fehling's or Tollens' reagent. Practical work is possible here for competent students.	C+H 26.3 M 116
10.5(a)	describe (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> /H <sup>+</sup>	A good yield of some aldehydes or ketones can be obtained in a preparative experiment (cyclohexanol to cyclohexanone is particularly effective, as also is benzoin (C <sub>6</sub> H <sub>5</sub> CH(OH)COC <sub>6</sub> H <sub>5</sub> ) to benzil). To enhance the production of the aldehyde at the expense of the acid, the Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> solution should be dripped onto the acidified R-OH in a distillation flask which is kept at a temperature just below the b.pt. of the alcohol. Once formed, the more volatile aldehyde distils off, so avoiding further oxidation..	C+H 28.4 M 118 R+N 18a.5 <a href="#">site 4</a> (carbonyls) <a href="#">site 7</a> (N-ch3-07, 15)
10.5(a)	describe (ii) the reduction of aldehydes and ketones using NaBH <sub>4</sub> .	An experiment reducing benzoin with NaBH <sub>4</sub> has been described, which is easily carried out and gives a clean yield of a crystalline product	C+H 26.4, 28.3 M 118 R+N 19.1

10.5(b)	describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones	The role of a small amount of added NaCN as a homogeneous catalyst should be explained, CN <sup>-</sup> being the attacking nucleophile in the first step, and being regenerated by a proton transfer reaction of RO <sup>-</sup> + HCN in the second step.	C+H 28.3 M 118 R+N 19.2
10.5(c)	describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of carbonyl compounds	The formation of an orange-yellow ppt. is firm evidence. The equation for the reaction including the formula of the product could be given, to interested students, but is not essential.	C+H 28.3 M 118 R+N 19.3 <a href="#">site 7</a> (N-ch3-17) <a href="#">site 21a</a>
10.5(d)	deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation)	Both tests can be carried out in the laboratory. The identities of the reduced products (Cu <sub>2</sub> O and Ag, respectively) should be known. The equations for their formation are not too difficult. Practical work could include the categorisation of a few "unknowns" to the classes of ROH, RCHO or R <sub>2</sub> CO on the basis of the sodium test, reaction with 2,4-DNPH and Tollens reagent.	C+H 31.4-31.5 M 118 R+N 19.4 P(AS) 29 <a href="#">site 21a</a>
10.6(a)	describe the formation of carboxylic acids from alcohols, aldehydes and nitriles	Oxidation of alcohols or aldehydes with an excess of Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + dil H <sub>2</sub> SO <sub>4</sub> . (balanced equations could include [O]). Hydrolysis of RCN with hot dilute H <sub>2</sub> SO <sub>4</sub> . The full balanced equation, giving NH <sub>4</sub> <sup>+</sup> + RCO <sub>2</sub> H, is not difficult.	C+H 29.8 M 119 R+N 20a.1 <a href="#">site 4</a> (carboxylic acids)
10.6(b)	describe the reactions of carboxylic acids in the formation of (i) salts	Titration with NaOH (using phenolphthalein); reaction with Na <sub>2</sub> CO <sub>3</sub> (→ CO <sub>2</sub> : a useful test for RCO <sub>2</sub> H); reaction with Na metal; - all give RCO <sub>2</sub> <sup>-</sup> Na <sup>+</sup> .	C+H 29.3 M 119 R+N 20a.2 P(AS) 30
10.6(b) 10.6(g)	describe the reactions of carboxylic acids in the formation of (ii) esters describe the formation of esters from carboxylic acids, using ethyl ethanoate as an example	The naming of esters, and the translation of names into structural formulae and vice versa, both need practice. Conditions for esterification, which is an equilibrium reaction, usually include an excess of alcohol and the addition of about 10 mole% of conc H <sub>2</sub> SO <sub>4</sub> (to drive the equilibrium over to the ester side). The production of esters in the lab, with subsequent purification using Na <sub>2</sub> CO <sub>3</sub> (aq), drying and distillation, is an excellent way of practicing and improving practical techniques.	C+H 29.3, 29.6 M 120 R+N 20a.2
10.6(h)	describe the acid and base hydrolysis of esters	Acid hydrolysis is the reverse of the above equilibrium – a large molar excess of water (i.e. dilute H <sub>2</sub> SO <sub>4</sub> ) ensures a reasonable yield. Base hydrolysis with NaOH(aq) is faster, and goes essentially to completion, due to the formation of RCO <sub>2</sub> Na. For practical work, the hydrolysis of ethyl benzoate, and subsequent acidification, allows the solid benzoic acid to be isolated in good yield and recrystallised.	C+H 29.6 M 120 R+N 20a.3
10.6(j)	state the major commercial uses of esters, e.g. solvents; perfumes; flavouring.	This could constitute a literature or internet search into the ingredients of some flavouring agents and perfumes and the industrial synthesis of their precursors.	C+H 29.6 M 120 R+N 20a.4
10	Tying together the various strands of Organic Chemistry: <ul style="list-style-type: none"> <li>nomenclature and isomeric compounds</li> <li>recognition of functional groups in unusual environments, and their reactions</li> </ul>	The syllabus content of Unit 5 contains much new knowledge that students need to commit to memory and understand, so allow time at the end to bring together the various functional group reactions that students have been introduced to. Include some practice in: <ul style="list-style-type: none"> <li>the recognition of known reaction types in unusual contexts,</li> <li>the prediction of how a novel, sometimes multifunctional, compound will react with known reagents.</li> </ul>	C+H 31.4-31.5, 31.10-31.11 M 130

	<ul style="list-style-type: none"> <li>identification of reaction types in unusual contexts</li> </ul>	<p>These are just two of the higher level skills that students need to become familiar with.</p> <p>The piecing together of two or more functional group reactions to create a synthesis of a compound from a known starting material is another skill that relies upon a secure knowledge of those reactions.</p> <p>Examples could include:</p> <p><math>\text{C}_2\text{H}_6 \longrightarrow \text{CH}_3\text{CHO}</math> (3 steps)</p> <p><math>\text{C}_2\text{H}_4 \longrightarrow \text{CH}_3\text{CO}_2\text{H}</math> (2 steps)</p> <p><math>\text{C}_2\text{H}_4 \longrightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H}</math> (3 steps)</p> <p><math>\text{C}_2\text{H}_5\text{OH} \longrightarrow \text{CH}_3\text{CH}(\text{OH})\text{CO}_2\text{H}</math> (3 steps)</p> <p><math>(\text{CH}_3)_2\text{CO} \longrightarrow \text{CH}_3\text{CH}=\text{CH}_2</math> (2 steps)</p> <p>Many more can be devised, including those involving functional group transformation in unusual compounds, e.g.</p> <p><math>\text{C}_6\text{H}_5\text{CH}_3 \longrightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5</math> (4 steps)</p>	
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