MEGA LECTURE · A LEVEL CHEMISTRY

Module 6: Organic Chemistry and Analysis

OCR A Level Chemistry A (H432) — End-of-course synoptic worksheet

SPECIFICATION	TOTAL MARKS	SUGGESTED TIME
6.1 Aromatic compounds, carbonyls & acids · 6.2 Nitrogen compounds, polymers & synthesis · 6.3 Analysis	121	2 hours 25 minutes

www.MegaLecture.com · WhatsApp: +92 323 509 4443

MEGALECTURE · A LEVEL CHEMISTRY

Module 6: Organic Chemistry and Analysis

OCR A Level Chemistry A (H432) — End-of-course synoptic worksheet

SPECIFICATION	TOTAL MARKS	SUGGESTED TIME
6.1 Aromatic compounds, carbonyls & acids · 6.2 Nitrogen compounds, polymers & synthesis · 6.3 Analysis	121	2 hours 25 minutes

Instructions to candidates

- Answer **all** questions in the spaces provided. Show all working in calculations.
- Draw mechanisms with **curly arrows starting from a bond or a lone pair**, and show all relevant dipoles and lone pairs.
- Displayed or skeletal formulae are acceptable unless a specific type of formula is asked for.
- Marks are shown in brackets at the end of each part.
- You may use a scientific calculator and the OCR Data Sheet (IR and NMR chemical shift tables).

Section A — Aromatic Compounds

Spec 6.1.1

A1. The delocalised model of benzene

a. The enthalpy change of hydrogenation of cyclohexene is −120 kJ mol^{-1}. The value predicted for the Kekulé structure of benzene is −360 kJ mol^{-1}, but the experimental value is −208 kJ mol^{-1}. Explain what this tells you about the bonding and stability of benzene. **[3]**

b. X-ray diffraction shows every carbon–carbon bond length in benzene is 0.139 nm. Explain how this evidence contradicts the Kekulé model. **[2]**

c. Explain why benzene undergoes electrophilic *substitution* rather than electrophilic *addition*. **[2]**

A2. Nitration of benzene

a. Write an equation to show the generation of the nitronium ion, NO_2^+, from concentrated nitric acid and concentrated sulfuric acid. **[2]**

b. Draw the full mechanism for the nitration of benzene to form nitrobenzene, including the structure of the intermediate. **[3]**

c. State the reaction conditions and explain why a temperature above 60 °C is avoided. **[2]**

A3. Friedel–Crafts acylation

a. Write the equation for the reaction of benzene with ethanoyl chloride in the presence of an aluminium chloride catalyst. Name the organic product. **[2]**

b. Show, using two equations, how $AlCl_3$ acts as a halogen carrier and is regenerated at the end of the reaction. **[3]**

A4. Phenol

a. Phenol reacts with bromine water at room temperature, whereas benzene does not. State the observation and write an equation for the reaction of phenol with bromine water. **[3]**

b. Explain, in terms of electron density, why phenol is more reactive than benzene towards electrophiles. **[3]**

c. Phenol reacts with aqueous sodium hydroxide but not with aqueous sodium carbonate. Write the equation for the reaction with NaOH and state what this shows about the acidity of phenol relative to carboxylic acids. **[2]**

Section A total: 27 marks

Section B — Carbonyls, Carboxylic Acids and Esters

Spec 6.1.2 / 6.1.3

B1. Nucleophilic addition

a. Draw the mechanism for the reduction of propanone by $NaBH_4$, using H^- as the nucleophile. Name the product. **[3]**

b. Butanone reacts with KCN followed by dilute acid. Name the organic product and state its molecular formula. **[2]**

c. Explain why the product in (b) is formed as a racemic mixture. **[2]**

B2. Identifying carbonyl compounds

a. A student has two colourless liquids, propanal and propanone. Describe a chemical test, with observations for *both* compounds, that distinguishes between them. **[3]**

b. The student then treats each liquid with 2,4-dinitrophenylhydrazine (2,4-DNPH). Describe the observation and explain, in full, how the derivative formed can be used to confirm the exact identity of the carbonyl compound. **[3]**

B3. Carboxylic acids, esters and acyl chlorides

a. Write an equation for the reaction of ethanoic acid with sodium carbonate and state the observation. **[2]**

b. Ethanol and propanoic acid are heated under reflux with a few drops of concentrated sulfuric acid. Name the organic product, write the equation, and state one reason why the yield is less than 100%. **[3]**

c. Compare the acid hydrolysis and alkaline hydrolysis of methyl propanoate. Give the organic products of each and state one advantage of alkaline hydrolysis. **[4]**

d. Give the organic product formed when propanoyl chloride reacts separately with (i) water, (ii) methanol, (iii) methylamine. **[3]**

Section B total: 25 marks

Section C — Nitrogen Compounds, Polymers and Synthesis

Spec 6.2

C1. Basicity of amines

a. Place ammonia, ethylamine and phenylamine in order of increasing base strength. Explain your answer in terms of the availability of the lone pair on the nitrogen atom. **[4]**

b. Write an equation for the reaction of ethylamine with hydrochloric acid and name the salt formed. **[2]**

C2. Preparation of amines

a. Bromoethane is heated with an excess of ammonia dissolved in ethanol in a sealed tube. Write the equation for the formation of ethylamine and explain why a large excess of ammonia is used. **[3]**

b. Describe how nitrobenzene is converted into phenylamine, giving the reagents and conditions for each of the two stages. **[3]**

C3. Amino acids and chirality

a. Draw the zwitterion of alanine, $CH_3CH(NH_2)COOH$, and draw the species present at low pH and at high pH. **[3]**

b. Explain what is meant by a *chiral centre* and state how many optical isomers alanine has. **[2]**

c. Glycine, H_2NCH_2COOH, is not optically active. Explain why. **[2]**

C4. Condensation polymers

Polymer **P** is made from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.
Polymer **Q** is made from hexanedioyl dichloride and 1,6-diaminohexane.

a. Draw the repeat unit of **P** and of **Q**, and name the small molecule eliminated in each case. **[4]**

b. Name the type of linkage present in **P** and in **Q**. **[2]**

c. Explain why condensation polymers can be hydrolysed, whereas addition polymers such as poly(propene) cannot, and comment on the environmental significance of this. **[3]**

C5. Organic synthesis

a. Devise a two-step synthesis of butanoic acid, $CH_3CH_2CH_2COOH$, starting from 1-bromopropane. Give the reagents and conditions for each step and name the intermediate. **[4]**

b. State the reagent you would use to convert the intermediate in (a) into butylamine instead. **[2]**

c. Devise a three-step synthesis of *N*-phenylethanamide, $C_6H_5NHCOCH_3$, starting from benzene. Give reagents and conditions for each step. **[4]**

Section C total: 38 marks

Section D — Chromatography and Spectroscopy

Spec 6.3

D1. Thin-layer chromatography

a. In a TLC experiment the solvent front travelled 7.5 cm and a spot travelled 4.2 cm from the baseline. Calculate the R_f value. **[2]**

b. Explain why (i) the baseline is drawn in pencil, (ii) the solvent level must start below the baseline, (iii) the tank is covered with a lid. **[3]**

c. State what is meant by the *stationary phase* and the *mobile phase* in TLC. **[2]**

D2. Gas chromatography

a. Explain how retention time can be used to identify a component in a mixture, and state one limitation of using retention time alone. **[2]**

b. State how the amount of each component can be determined from a gas chromatogram, and name the technique produced when GC is linked to mass spectrometry. **[2]**

D3. NMR spectroscopy

a. State why TMS is used as the standard reference in NMR spectroscopy. Give three reasons. **[3]**

b. Explain why $CDCl_3$ is used as a solvent rather than $CHCl_3$. **[2]**

c. Explain how a D_2O shake is used to identify O–H and N–H protons. **[2]**

d. State the number of peaks you would expect in the ^{13}C NMR spectra of (i) propan-2-ol, (ii) methylbenzene, (iii) ethyl ethanoate. **[3]**

D4. Structure determination

Compound **X** has the molecular formula $C_4H_8O_2$. The following data were obtained.

Technique	Data
Mass spectrum	Molecular ion peak at *m/z* = 88; major fragments at *m/z* = 43 and 45
Infrared	Strong sharp absorption at 1740 cm^{-1}; no broad absorption between 2500–3300 cm^{-1}
^{13}C NMR	Four peaks
^{1}H NMR	δ 4.12 (2H, quartet); δ 2.04 (3H, singlet); δ 1.26 (3H, triplet)

a. Use the IR data to deduce which functional groups are present and which are absent. **[2]**

b. Deduce the structure of **X**, explaining how each piece of ^{1}H NMR data supports your answer. **[4]**

c. Suggest the identity of the fragment ions at *m/z* = 43 and *m/z* = 45. **[2]**

d. The mass spectrum also shows a small peak at *m/z* = 89. Explain its origin. **[2]**

Section D total: 31 marks

PAPER TOTAL: 121 MARKS

MARK SCHEME — Module 6 Synoptic Worksheet

Award marks independently unless stated. ECF (error carried forward) applies to calculations. Accept correct alternatives.

Section A — Aromatic Compounds

A1 (a) [3]

- Benzene releases 152 kJ mol^{-1} *less* energy than predicted (360 − 208). (1)
- Therefore benzene is 152 kJ mol^{-1} *more stable* / lower in energy than the Kekulé structure. (1)
- This extra stability is due to delocalisation of the six p-electrons above and below the ring. (1)

A1 (b) [2]

- Kekulé predicts alternating C=C (0.134 nm) and C–C (0.153 nm), i.e. two different bond lengths. (1)
- All bonds are identical and intermediate in length, consistent with delocalisation of electrons over all six carbons. (1)

A1 (c) [2]

- Addition would break/disrupt the delocalised π system. (1)
- Substitution preserves delocalisation, so the stable ring is retained (lower activation energy route / energetically favourable). (1)

A2 (a) [2]

- $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$ (1 for NO_2^+, 1 for correct balancing)
- *Allow the two-step version: $HNO_3 + H_2SO_4 \rightarrow H_2NO_3^+ + HSO_4^-$; $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$*

A2 (b) [3]

- Curly arrow from inside the delocalised ring to the N of NO_2^+. (1)
- Intermediate drawn with a horseshoe (broken circle) covering approximately four carbons, a positive charge on the horseshoe, and the sp^3 carbon bearing both H and NO_2. (1)
- Curly arrow from the C–H bond of the sp^3 carbon back into the ring, re-forming the delocalised system and releasing H^+. (1)

A2 (c) [2]

- Reflux/heat at 50–60 °C in a water bath with concentrated H_2SO_4 catalyst. (1)
- Above 60 °C further substitution occurs, producing dinitrobenzene / 1,3-dinitrobenzene, lowering the yield. (1)

A3 (a) [2]

- $C_6H_6 + CH_3COCl \rightarrow C_6H_5COCH_3 + HCl$ (1)
- Product: phenylethanone (accept acetophenone). (1)

A3 (b) [3]

- Generation of the electrophile: $AlCl_3 + CH_3COCl \rightarrow CH_3CO^+ + AlCl_4^-$ (1)
- Regeneration: $AlCl_4^- + H^+ \rightarrow AlCl_3 + HCl$ (1)
- Statement that $AlCl_3$ is regenerated unchanged, therefore it is a catalyst / halogen carrier. (1)

A4 (a) [3]

- Observation: bromine water is decolourised (orange to colourless) and a white precipitate forms. (1)
- Equation: $C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$ (1 for formulae, 1 for balancing)
- *Product is 2,4,6-tribromophenol. No catalyst is required.*

A4 (b) [3]

- Oxygen of the –OH group has a lone pair in a p orbital. (1)
- This lone pair is partially delocalised into / overlaps with the π system of the ring. (1)
- Electron density of the ring increases, so it polarises Br_2 more strongly and attracts electrophiles more readily than benzene. (1)

A4 (c) [2]

- $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ (1)
- Phenol is a weaker acid than carbonic acid, and therefore weaker than carboxylic acids (which do release CO_2 from carbonates). (1)

Section B — Carbonyls, Carboxylic Acids and Esters

B1 (a) [3]

- Curly arrow from the lone pair on H^- to the C of C=O, with δ+ on carbon and δ− on oxygen shown. (1)
- Curly arrow from the C=O bond to the oxygen, giving the negatively charged alkoxide intermediate. (1)
- Alkoxide protonated by H_2O (arrow from O^- lone pair to H of water) → product. Name: propan-2-ol. (1)

B1 (b) [2]

- 2-hydroxy-2-methylbutanenitrile (1)
- C_5H_9NO (1)

B1 (c) [2]

- The C=O group is planar / trigonal planar, so the CN^- nucleophile can attack with equal probability from above or below the plane. (1)
- The product carbon has four different groups (a chiral centre), so equal amounts of the two enantiomers are formed — a racemic mixture with no overall optical activity. (1)

B2 (a) [3]

- Reagent: Tollens' reagent, warmed in a water bath. (1)
- Propanal: silver mirror / grey-black precipitate forms (aldehyde is oxidised to propanoic acid). (1)
- Propanone: no visible change / no reaction (ketones are not oxidised). (1)
- *Allow Fehling's/Benedict's solution: blue to brick-red precipitate with propanal, remains blue with propanone. Allow acidified $K_2Cr_2O_7$: orange to green with propanal only.*

B2 (b) [3]

- Observation: orange/yellow crystalline precipitate with *both* compounds (confirms a carbonyl C=O is present, but not which one). (1)
- The precipitate is filtered and purified by recrystallisation, then dried. (1)
- Its melting point is measured and compared with a database of known 2,4-DNPH derivative melting points to identify the specific carbonyl compound. (1)

B3 (a) [2]

- $2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + H_2O + CO_2$ (1)
- Observation: effervescence / bubbles of gas that turn limewater milky. (1)

B3 (b) [3]

- Product: ethyl propanoate. (1)
- $CH_3CH_2COOH + CH_3CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_3 + H_2O$ (1)
- The reaction is reversible and reaches equilibrium, so it does not go to completion. (1) *Allow: losses on distillation/separation.*

B3 (c) [4]

- Acid hydrolysis (dilute H_2SO_4, reflux): propanoic acid + methanol. (1)
- Alkaline hydrolysis (aqueous NaOH, reflux): sodium propanoate + methanol. (1)
- Acid hydrolysis is reversible / an equilibrium; alkaline hydrolysis is not. (1)
- Advantage: alkaline hydrolysis goes to completion, giving a higher yield. (1)

B3 (d) [3]

- (i) propanoic acid, CH_3CH_2COOH (1)
- (ii) methyl propanoate, $CH_3CH_2COOCH_3$ (1)
- (iii) *N*-methylpropanamide, $CH_3CH_2CONHCH_3$ (1)
- *HCl is produced in each case; misty white fumes observed.*

Section C — Nitrogen Compounds, Polymers and Synthesis

C1 (a) [4]

- Order of increasing base strength: phenylamine < ammonia < ethylamine. (1)
- A base donates/accepts a proton using the lone pair on nitrogen; the more available the lone pair, the stronger the base. (1)
- Ethylamine: the ethyl group is electron-donating (positive inductive effect), increasing electron density on N and making the lone pair more available. (1)
- Phenylamine: the lone pair on N is delocalised into the benzene ring, so it is far less available to accept a proton. (1)

C1 (b) [2]

- $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$ (1)
- Name: ethylammonium chloride. (1)

C2 (a) [3]

- $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$ (1)
- The amine product still has a lone pair on N and is itself a nucleophile, so it can attack further bromoethane. (1)
- Excess ammonia makes it statistically more likely that bromoethane collides with NH_3 than with the amine, reducing formation of secondary/tertiary amines and quaternary salts. (1)

C2 (b) [3]

- Stage 1: heat nitrobenzene under reflux with tin and concentrated hydrochloric acid. (1)
- This reduces the $-NO_2$ group and forms the salt $C_6H_5NH_3^+Cl^-$. (1)
- Stage 2: add excess sodium hydroxide (alkali) to liberate the free amine, phenylamine. (1)

C3 (a) [3]

- Zwitterion: $CH_3CH(NH_3^+)COO^-$ (1)
- Low pH (excess acid): $CH_3CH(NH_3^+)COOH$ (1)
- High pH (excess alkali): $CH_3CH(NH_2)COO^-$ (1)

C3 (b) [2]

- A chiral centre is a carbon atom attached to four *different* atoms or groups. (1)
- Alanine has 2 optical isomers (a pair of non-superimposable mirror images / enantiomers). (1)

C3 (c) [2]

- The central carbon in glycine is bonded to two hydrogen atoms. (1)
- It therefore does not have four different groups, so there is no chiral centre and the mirror images are superimposable. (1)

C4 (a) [4]

- **P** repeat unit: $-[O-CH_2CH_2-O-CO-C_6H_4-CO]-$ with continuation bonds shown at both ends. (1)
- Small molecule eliminated from **P**: water. (1)
- **Q** repeat unit: $-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO]-$ with continuation bonds shown. (1)
- Small molecule eliminated from **Q**: hydrogen chloride, HCl (because a diacyl chloride is used). (1)

C4 (b) [2]

- **P**: ester linkage (polyester — this is PET/Terylene). (1)
- **Q**: amide (peptide) linkage (polyamide — nylon-6,6). (1)

C4 (c) [3]

- Ester and amide linkages contain polar C=O and C–O / C–N bonds, so the carbon is δ+ and open to attack by nucleophiles such as H_2O or OH^-. (1)
- Addition polymers have a saturated, non-polar C–C backbone which is unreactive/inert, so it is not attacked by nucleophiles. (1)
- Condensation polymers are therefore biodegradable and can be chemically recycled back into monomers, whereas addition polymers persist in landfill for a very long time. (1)

C5 (a) [4]

- Step 1 reagent: KCN (or NaCN) in ethanol, heat under reflux. (1)
- Intermediate: butanenitrile, $CH_3CH_2CH_2CN$. (1)
- Step 2 reagent: dilute HCl (or dilute H_2SO_4), heat under reflux. (1)
- Correct recognition that the nitrile is hydrolysed to butanoic acid; the carbon chain is extended by one carbon in step 1. (1)
- *Allow Step 2 as NaOH(aq) reflux followed by acidification with dilute acid.*

C5 (b) [2]

- $LiAlH_4$ in dry ether, followed by dilute acid. (1)
- Accept H_2 with a nickel (or platinum) catalyst, high temperature and pressure. (1)

C5 (c) [4]

- Step 1: concentrated HNO_3 and concentrated H_2SO_4 at 50–60 °C → nitrobenzene. (1)
- Step 2: Sn and concentrated HCl, reflux. (1)
- Then excess NaOH(aq) → phenylamine. (1)
- Step 3: ethanoyl chloride, CH_3COCl, at room temperature (or ethanoic anhydride) → *N*-phenylethanamide. (1)

Section D — Chromatography and Spectroscopy

D1 (a) [2]

- R_f = distance moved by spot ÷ distance moved by solvent front = 4.2 ÷ 7.5 (1)
- = 0.56 (no units) (1)

D1 (b) [3]

- (i) Pencil is insoluble in the solvent, so the baseline will not move or interfere with the spots (ink would run). (1)
- (ii) If the solvent were above the baseline the samples would dissolve into the solvent reservoir instead of moving up the plate. (1)
- (iii) The lid saturates the tank with solvent vapour, preventing evaporation from the plate and giving reproducible R_f values. (1)

D1 (c) [2]

- Stationary phase: the thin layer of silica (SiO_2) or alumina on the plate, which adsorbs the components. (1)
- Mobile phase: the liquid solvent that moves up the plate, carrying the components with it. (1)

D2 (a) [2]

- The retention time of the unknown is compared with the retention time of a known standard run under identical conditions; a match suggests the same compound. (1)
- Limitation: different compounds can have very similar or identical retention times, so identification is not conclusive. (1)

D2 (b) [2]

- The area under each peak is proportional to the amount of that component; a calibration curve made from standard solutions of known concentration is used to find the concentration. (1)
- GC–MS (gas chromatography–mass spectrometry). (1)

D3 (a) [3]

- All 12 hydrogen atoms are in the same environment, so TMS gives a single sharp peak. (1)
- It is chemically inert / non-toxic and does not react with the sample. (1)
- It is volatile and easily removed, and its peak is well away from (upfield of) almost all other signals, defined as δ = 0. (1)

D3 (b) [2]

- $CDCl_3$ contains deuterium, not ^1H. (1)
- It therefore produces no peak in the ^1H spectrum, so the solvent does not obscure or add to the sample's signals. (1)

D3 (c) [2]

- The sample is run, then a few drops of D_2O are added and the spectrum re-run. (1)
- Labile O–H / N–H protons exchange with deuterium, so their peak disappears (or shifts) in the second spectrum. (1)

D3 (d) [3]

- (i) Propan-2-ol: 2 peaks (the two CH_3 carbons are equivalent). (1)
- (ii) Methylbenzene: 5 peaks (CH_3, ipso C, ortho pair, meta pair, para C). (1)
- (iii) Ethyl ethanoate: 4 peaks. (1)

D4 (a) [2]

- Absorption at 1740 cm^{-1} indicates a C=O group is present; the value is typical of an ester rather than a carboxylic acid or ketone. (1)
- The absence of a broad absorption at 2500–3300 cm^{-1} shows that no O–H group of a carboxylic acid (or alcohol) is present. (1)

D4 (b) [4]

- Structure: ethyl ethanoate, $CH_3COOCH_2CH_3$. (1)
- δ 4.12, 2H, quartet: OCH_2 — shifted downfield by the adjacent electronegative oxygen; split into 4 by the 3 neighbouring H of the CH_3 (n + 1 rule). (1)
- δ 2.04, 3H, singlet: CH_3 next to C=O — no neighbouring hydrogens on the adjacent carbon, so no splitting. (1)
- δ 1.26, 3H, triplet: CH_3 of the ethyl group — split into 3 by the 2 H of the adjacent CH_2. (1)
- *Ratio 2:3:3 accounts for all 8 hydrogens; four carbon environments is consistent.*

D4 (c) [2]

- *m/z* 43 = CH_3CO^+ (the acylium ion). (1)
- *m/z* 45 = $C_2H_5O^+$ / $OCH_2CH_3^+$. (1)

D4 (d) [2]

- This is the M+1 peak. (1)
- It arises because about 1.1% of carbon atoms are the ^{13}C isotope, so a small proportion of molecules have a mass one unit higher. (1)

END OF MARK SCHEME · 121 marks