

a slightly higher 3d energy level. [1] When the electron falls back to the lower 3d level, it loses energy in the form of visible light of a characteristic colour. [1] (max. [2])

(ii) Covalent bonds (within the H₂O molecule) and co-ordinate or dative covalent bonds (from H₂O to metal ion). [1]

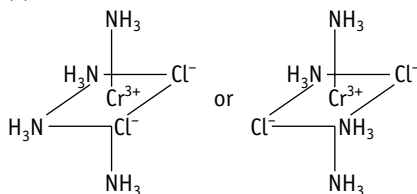
(c) (i) $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$ [1]
 (ii) Copper(II) hydroxide [1]
 (iii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ or $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ [1]
 (iv) Blue +4, green +3, violet +2 (all 3 correct [2], 2 correct [1])

(d) $2\text{VO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5$ [1]

(e) (i) Dioxovanadium(V) [1]

(ii) Tetraammine dichlorochromium(III) [1]

(f)



(only one of the isomers is required: diagram [1], octahedral [1])

59 (a) 4 [1]

(b) 1 : 6 : 2 : 3 [1]

(c) $-\text{COCH}_3$ [1]

(d) The protons responsible for the peak at δ 4.8 are adjacent to a carbon atom with two protons attached. [1] The protons responsible for the peak at δ 2.7 are adjacent to a carbon with only one proton attached. [1] or $-\text{CH}_2\text{CH}-$ [2]

(e) $\text{CH}_3\text{COCH}_2\text{CH}(\text{OCH}_3)_2$ [2]

60 (a) The magnet [1]

(b) The intense peak with the m/e value of 16 [1]

(c) The fact that there is a small peak at $m/e = 17$ ($M_r + 1$) [1]

(d) CH_4^+ [1]

(e) The peaks at $m/e = 12, 13, 14$ and 15 arise from $\text{C}^+, \text{CH}^+, \text{CH}_2^+$ and CH_3^+ . [1] The peak at $m/e = 1$ arises from H^+ . It is impossible to split an atom in a mass spectrometer, so there are no peaks between 1 and 12. [1]

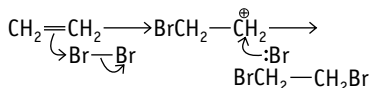
61 (a) (i) Literally a species which is 'nucleus loving'. Something that has a lone pair of electrons and/or is negatively charged. [1]

(ii) Literally a species which is 'electron loving'. Something which is electron deficient and/or has a positive charge. [1]

(iii) When an atom or a group of atoms in a molecule is replaced by something else. [1]

(iv) When two reactants join together to make one product. [1]

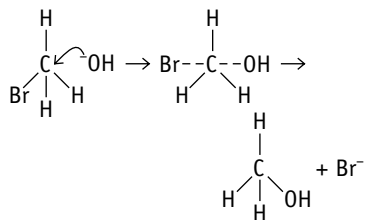
(b)



[3]

(c) (i) Reaction of a haloalkane with aqueous sodium hydroxide, ethanolic potassium cyanide, concentrated aqueous ammonia, silver ethanoate solution or sodium ethoxide. [1]

(ii)



[3]

(iii) S_N2 – The rate-determining step involves the haloalkane and the nucleophile, so the reaction would be second order. [1]

(d) (i) $\text{C}_6\text{H}_{10} + \text{Br}_2 \rightarrow \text{C}_6\text{H}_{10}\text{Br}_2$ [1]

(ii) If an addition reaction took place, the stable ring of delocalised electrons would be broken. [1] Therefore, benzene undergoes substitution reactions, thus retaining the delocalisation energy. Bromine is not sufficiently electrophilic to react with the benzene ring. [1]

62 **A** has a broad absorption at 3350 cm⁻¹, therefore contains an $-\text{OH}$ group. [1] **E** has a broad absorption at 1710 cm⁻¹ and therefore contains a $\text{C}=\text{O}$ group. [1] **B** and **C** have significant bands at 1650 cm⁻¹ and therefore contain $\text{C}=\text{C}$. [1]

A must be butan-2-ol [1], $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ [1]. This undergoes dehydration in the presence of acid to form **B** and **C**, which must be but-2-ene [1] and but-1-ene [1].

B is $\text{CH}_3\text{CH}=\text{CHCH}_3$ [1], **C** is

$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$ [1]

Butan-2-ol (**A**) is optically active as it has an asymmetric carbon atom:

$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$. [1]

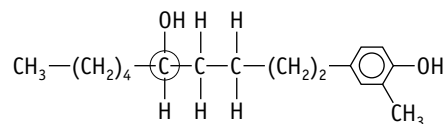
Oxidation of **A** gives **E**. **E** must be a ketone: $\text{CH}_3\text{CH}_2\text{COCH}_3$ [1], butanone [1].

But-2-ene (**B**) exists as the *cis* or *trans* form. [1]

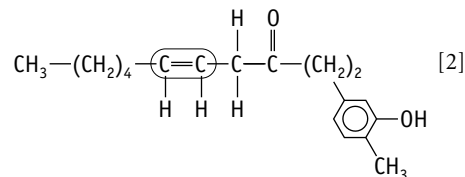
But-1-ene (**C**) reacts with HBr to give **D**. **D** must be $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$ [1], 2-bromobutane [1].

NB To get all the marks, you must give names and structures for all the compounds, and relate them to the information in the question.

63 (a) (i) **E**



F



[2]

(ii) **E**: optical isomerism (chiral)

F: geometric isomerism (*cis/trans*) [2]

(b) (i) Ketone/carbonyl; phenol; arene (any 2 for [2])

(ii) Alcohol/hydroxy/hydroxyl [1]

(iii) Alkene/carbon-carbon double bond [1]

(c) (i) any of the following:
 2,4-DNPH; orange ppt
 PCl_5 ; fumes of $\text{HCl}(\text{g})$
 FeCl_3 ; red/violet
 Br_2 ; white ppt

RCOCl ; fumes of $\text{HCl}(\text{g})$
 NaOH ; solution dissolves
 Na ; bubbles/gas etc [2]

(ii) $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$; green [2]

(iii) $\text{H}^+/\text{MnO}_4^-$; decolorises/green/brown/pink [2]

(d) A suitable dehydrating agent such as concentrated sulphuric acid/concentrated phosphoric acid/aluminium oxide/ceramics/brick dust/absence of air [1] and heat [1].
No credit for just heat with no reagent.

- 64 (a) (i) Fractions are mixtures of hydrocarbons. The compounds in the mixture have similar boiling points. [1]
 or A mixture of compounds with a fairly narrow range of boiling points. [1]
 Primary distillation: crude oil is heated and the vapours passed into a tower or crude oil is heated in a column. [1] The tower is cooler at the top than at the bottom. As the vapours rise up the tower, different fractions/compounds, condense/distil at different temperatures. [1] The fractions with low boiling points rise to the top of the tower. [1] Crude oil is a mixture of many different substances. [1] It has no direct use unless it is separated. The fractions are used as fuels, or feedstock for the chemical industry. [1]

At least 5 of the 6 points are required.

- (ii) Large/long-chain hydrocarbons/alkanes/saturated molecules [1] are broken down into smaller hydrocarbons (saturated), including some alkenes/unsaturated molecules. [1] This is done using heat and a catalyst. [1] Fractions containing large molecules have a limited demand, yet are produced in large quantities. [1] The products of cracking are more valuable/more useful/ in greater demand. [1] Balanced equation with alkane and alkene products. [1]
 e.g. $2C_6H_{14} \rightarrow$
 $CH_4 + 3C_2H_4 + C_2H_6 + C_3H_6$
 or $C_6H_{14} \rightarrow C_4H_{10} + C_2H_4$
- (iii) A free radical is a species/atom/group of atoms/molecule which has an unpaired electron/or a lone electron. [1]
 No mark if ion or free electron mentioned
 $C_6H_{14} \rightarrow CH_3 + C_5H_{13}$ or any equation containing two radicals [1], with at least one but less than six carbon atoms [1].
- (b) (i) $C_6H_{12} \rightarrow C_6H_6 + 3H_2$ [1]
 (ii) $C_6H_{14} \rightarrow C_6H_6 + 4H_2$ [1]

- (iii) Increasing demand for higher octane fuels; provides aromatic feedstock for industry; there is a demand for benzene; or mention of a specific use for benzene or hydrogen. (any 1 for [1])

- (c) Fixed costs: capital investment; rent; rates; interest; depreciation. (any 2 for [2])
 Variable costs: raw materials; fuel; labour; transport; overheads (any 2 for [2])

- (d) (i) Low pressure and a high temperature. [2]
 If the pressure was low, this would force the equilibrium to increase the pressure by moving in a direction which would increase the number of particles, i.e. to the right. [1]
 If the temperature was high, the reaction would move in the endothermic direction, i.e. to the right. [1]

- (ii) Low pressure leads to slow speed of reaction [1]; cost of maintaining high temperature but relevant increase in yield [1]; availability of a catalyst – the cost of this but an increased rate of reaction [1]; use of an excess of steam giving a greater yield [1]. (Any three relevant factors from the list, but each factor must have a reference to the yield, the cost or the rate.)

- 65 (a) $C_6H_{10} + H_2 \rightarrow C_6H_{12}$
 $\Delta H = -120 \text{ kJ}$
 $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$
 $\Delta H = -208 \text{ kJ [1]}$

We would expect the enthalpy of hydrogenation of benzene to be -360 kJ mol^{-1} [1] but benzene is more stable/lower in energy [1] by -152 kJ mol^{-1} [1] due to delocalisation [1] which arises because the p-orbitals overlap giving a symmetrical structure with equal bond lengths [1].
 Cyclohexene undergoes an addition reaction with bromine [1] but benzene undergoes substitution [1] in order to avoid the loss of the delocalisation energy [1].

- (b) Free radical substitution [1]
 $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$ [2] (or equivalent example)

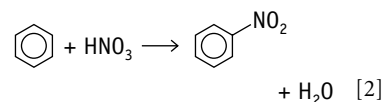
Conditions: (UV) light [1]
 Mechanism should show examples of initiation [1], propagation [1] and termination [1] steps.

Nucleophilic substitution [1]
 $CH_3Br + ^-OH \rightarrow CH_3OH + Br^-$ [2]
 (or equivalent example)

Conditions: warm aqueous NaOH [1] (or equivalent).

Mechanism should show S_N1 , using curly arrows. Including polar C—Br bond [1]; attack by ^-OH (or other nucleophile) on C [1]; departure of Br as Br^- [1].

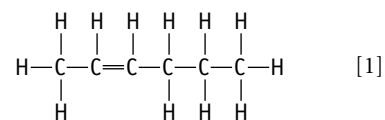
Electrophilic substitution [1]



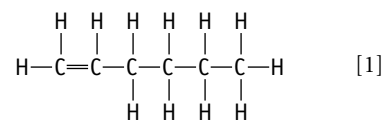
(or equivalent example)

- (c) Reagent: concentrated sulphuric acid or concentrated phosphoric acid. [1]
 Conditions: heat under reflux. [1] (just heat is acceptable)
 The spectrum shown is hex-1-ene. [1]
 The spectrum of hexan-1-ol would have peaks at 3230–3550 (OH) and 1000–1300 (C—O), but no peak at 1620–1680 (C=C) (any 2 for [2])
- 66 (a) (i) C_nH_{2n+2} [1]
 (ii) $12n + 2n + 2 = 170$
 $14n = 168$
 $n = 12$ [1]
 C is $C_{12}H_{26}$ [1]
- (iii) Aircraft fuel/jet fuel/ petrochemicals (any 1 for [1])
 (iv) Gasoline/petrol/naphtha/gases/ LPG (any 1 for [1])
 Lower boiling point/lower M_r / weaker intermolecular forces [1]

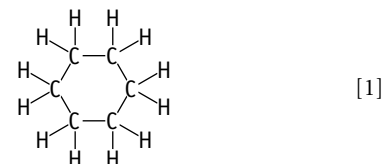
(b) Structure of D



Structure of E



Structure of F



67 (a) Answer should include the following points:

Alkanes

- Undergo substitution to give bromoalkanes and HBr. Several bromoalkanes (mono-, di- etc.) may be formed.
- Example of reactant and products
- React in the presence of sunlight
- React by a free-radical mechanism involving initiation, propagation and termination steps
- Example of mechanism

Alkenes

- Undergo addition to form a dibromo compound only
- Example of reactant and product
- React at room temperature in the absence of sunlight
- React by an electrophilic addition mechanism
- Example of mechanism

(b) Formula of B:

$$\text{C} \frac{82.8}{12} \quad \text{H} \frac{17.2}{1}$$

$$\therefore \text{C } 6.9 \quad \text{H } 17.2$$

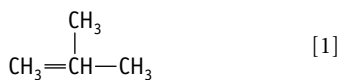
$$\therefore \text{C } 2 \quad \text{H } 5 [1]$$

$$\therefore \text{Empirical formula is } \text{C}_2\text{H}_5 [1]$$

$M_r = 58$, so molecular formula is

$$\text{C}_4\text{H}_{10} [1].$$

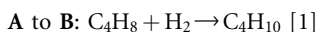
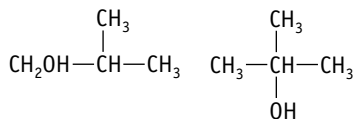
B



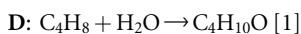
A



C and D



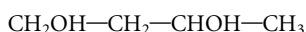
A to C and



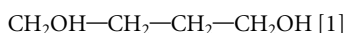
(c) **E** is $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ [2]

Principal product with steam is $\text{CH}_3-\text{CHOH}-\text{CHOH}-\text{CH}_3$ [1]

Also formed:

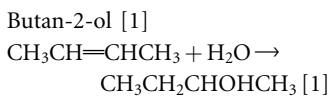
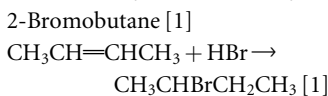
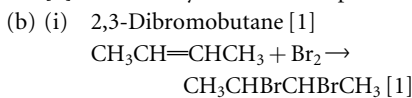


and

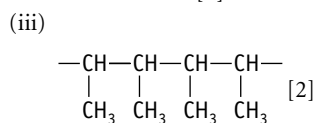


68 (a) Structural isomerism exists when compounds have the same molecular formulae [1] but different structural formulae/arrangement of atoms [1]. [1] for an example.

Cis-trans isomerism exists in alkenes owing to the fact that there is no free rotation round the double bond. [1] [2] for correctly labelled examples.



(ii) Potassium manganate(VII) is an oxidising agent. [1] With cold dilute [1] potassium manganate(VII), butan-1,3-diol is formed. [1] With hot, concentrated [1] potassium manganate(VII), the double bond breaks completely and products could be ethanal/ethanoic acid. [1]



(1 mark for the correct bonds, i.e. no double bonds, extending at either end; 1 mark for the $-\text{CH}_3$ groups branching outwards from the chain.)

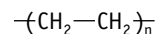
(c) (i) CH_4 is non-polar and has very strong bonds. [1] In the presence of UV light, chlorine splits into chlorine radicals. [1] The free radicals then react with methane, causing C—H bonds to break. [1] The methyl radical formed goes on to react with another chlorine molecule. [1]

(ii) Chlorine is more electronegative than carbon, so the C—Cl bond is polar. [1] Trichloromethane is unsymmetrical so it has a permanent dipole. [1] Tetrachloromethane is symmetrical [1], so the dipoles are balanced and there is no net dipole [1].

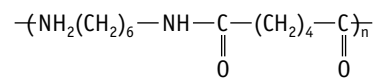
There are 27 marking points giving a maximum of 25 marks.

69 (a) (i) addition polymers:
 e.g. poly(ethene),
 poly(chloroethene) (PVC),
 poly(phenylethene)
 (polystyrene),
 poly(methylmethacrylate)
 (Perspex) [1]
 Condensation polymers:
 e.g. nylon, starch, polyester [1]

(ii) e.g.



poly(ethene) (addition)



nylon 66 (condensation)

(iii) An 'addition' polymer consists of monomers joined by an addition reaction [1].

(b) (i) Addition polymer
 Uses could include: plastic containers, clothing, packaging, children's toys [2].
 Condensation polymer
 Uses could include: fibres, resins [2].

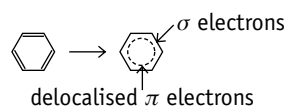
(ii) Addition polymers [1], as condensation polymers may be hydrolysed by aqueous acids [1].

70 Answer should be well organised with an introduction, sections on benzene, carboxylate anions and amides, and a conclusion.

Make the following points:

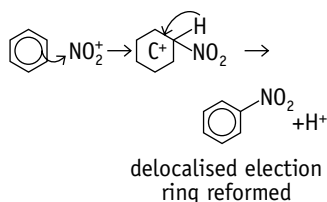
- Delocalisation is the 'spreading out of electrons' over the whole or part of a molecule.
- It arises when a molecule contains π bonds.
- π bonds involve the overlap of p orbitals, at 90° to the plane of the molecule.
- When delocalisation takes place, the overlapping p orbitals extend beyond two carbon atoms.
- This imparts extra stability to a species and therefore affects the reactivity.

Benzene

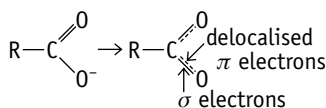


- Each C atom has three σ bonds (bond angle 120°) in one plane. The six 2p orbitals overlap to form a ring above and below the plane.

- Benzene therefore has a planar, symmetrical structure and undergoes substitution reactions, thus retaining the delocalisation energy and the symmetrical structure.
- Examples could include nitration, sulphonation, alkylation, acylation, halogenation.
- With nitration:

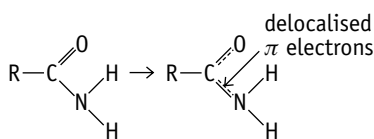


Carboxylate ions



- RCOO^- has a planar structure, with a bond angle of 120° .
- This delocalisation contributes to the acidity of carboxylic acids. The extra stability of the anion means that the O—H bond is more likely to break, and once formed the RCOO^- ion is relatively stable.

Amides



- The lone pair of electrons on nitrogen overlaps with the π electrons in the C=O bond.
- The amide group is planar, and relatively unreactive. The delocalised lone pair is not available for bonding, so amides are very weak bases.
- The amide bond is particularly stable owing to delocalisation, and is known as a 'peptide link'.

71 (a) (i) $\text{C}:\text{H} = \frac{90.56}{12} : \frac{9.44}{1}$
 $= 7.55 : 9.44$ [1]
 $= 1 : 1.25$
 $= 4 : 5$

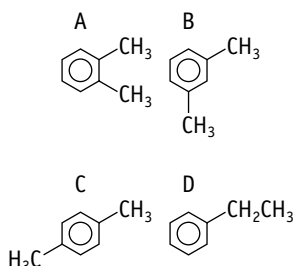
Therefore the empirical formula is C_4H_5 [1]

(ii) Empirical formula
 mass = $(12 \times 4) + 5 = 53$

Molecular mass = 106

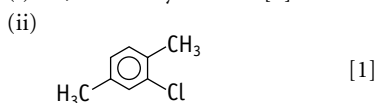
\therefore molecular formula = C_8H_{10} [1]

(iii) There are four possible isomers:



[1] for each correct isomer.

(b) (i) 1,4-Dimethylbenzene [1]



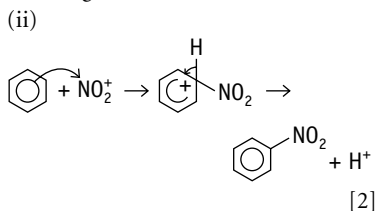
(c) (i) Free radical substitution. [1]

(ii) All the side chain H's could be substituted. [1]

72 (a) (i) $\text{CH}_2\text{Br—CH}_2\text{Br}$ [1]



(b) (i) Each carbon atom in the benzene ring has a p orbital which overlaps with others to form a delocalised π orbital extending in a ring above and below the plane of the molecule. [1] Each C atom contributes one electron to this π orbital, and the six electrons are thus delocalised around the ring. [1]



(c) (i) Warm **A** and **B** with complexed silver ions in ammoniacal solution (Tollen's reagent). **A** will give a silver mirror, **B** will not react. (Other possible tests include Fehling's or Benedict's solutions, or the iodoform reaction.)

[1] for the test; [1] for the results expected.

(ii) **D** [1]

(iii) **C** [1]

(iv) **C** [1]

(v) **C** and **E** [1]

73 (a) Concentrated nitric acid [1];
 concentrated sulphuric acid [1];
 electrophilic substitution [1].

(b) $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ [2]

$$\text{percentage of H} = \frac{5}{227} \times 100 = 2.2\% \text{ [1]}$$

74 (a) (i) The C—Br bond in 2-bromopropane is polar



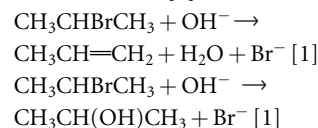
and therefore attracts nucleophiles. [1]

In bromobenzene, the C—Br bond is less polar [1]; the π electrons in the benzene ring repel nucleophiles [1]; a lone pair of electrons on the Br atom is partially delocalised into the π -electron ring on the benzene [1] and this strengthens the C—Br bond [1]. (any 3 for [3])

(ii) 2-Bromopropane reacts faster. [1] The intermediate is more stable in the case of 2-bromopropane [1] owing to the stabilising inductive effects of adjacent alkyl groups [1].

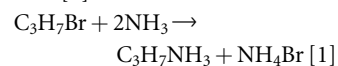
(b) (i) **W** is $\text{CH}_3\text{CH=CH}_2$ [1]
X is $\text{CH}_3\text{CH(OH)CH}_3$ [1]
 The alcohol has the higher boiling point due to hydrogen bonding. [1]

The alkene would decolorise bromine water. [1]

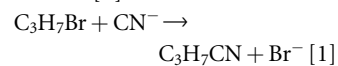


(ii) Formation of **W**: elimination reaction. [1]
 Formation of **X**: substitution reaction. [1]

(c) (i) Concentrated aqueous ammonia [1]; heat in a sealed tube [1].



(ii) A carbon atom is added by using a nitrile intermediate, CN^- ions (from KCN) [1] in ethanol [1].



Then hydrolysis [1] using $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ [1]

