2.7 Organic Chemistry: Test Pack

AQA 7405 · Calculator allowed · about 80 minutes

Total Marks

Name: _____ Date: ____ / ____ / _____

Answer ALL questions. Show all your working.

1 This question tests core definitions and nomenclature for alkanes and halogenoalkanes.

(a) State the general formula for the homologous series of alkanes. **(1)**

(b) Define the term homologous series. **(1)**

(c) Give the IUPAC name of the following compound: $BrCH_2CH_2CH(CH_3)CH_3$. **(2)**

(Total for Question 1 is 4 marks)

2 A hydrocarbon, Z, contains only carbon and hydrogen and has a relative molecular mass (Mr) of 84.0. Complete combustion of a 0.420 g sample of Z produced 1.32 g of carbon dioxide and 0.540 g of water.

(a) Calculate the molecular formula of Z. Show your working. **(5)**

(b) A chain isomer of Z, 2-methylpent-2-ene, $CH_3C(CH_3)=CHCH_2CH_3$, does not show E/Z isomerism, even though it is not a terminal alkene. Explain why, with reference to the groups attached to the carbon atoms of the double bond. **(2)**

(Total for Question 2 is 7 marks)

© Revision Library | revisionlibrary.co.uk

3 CFCs (chlorofluorocarbons) such as $CFCl_3$ were once widely used as aerosol propellants and refrigerants, but their use is now banned because they damage the ozone layer in the stratosphere.

Explain, using equations, how $CFCl_3$ catalyses the breakdown of ozone in the stratosphere, and why a small concentration of CFCs can have a disproportionately large effect on ozone concentration.

(Total for Question 3 is 6 marks)

© Revision Library | revisionlibrary.co.uk

4 Pentan-3-ol, $CH_3CH_2CH(OH)CH_2CH_3$, and 2-methylhexan-2-ol, $(CH_3)_2C(OH)CH_2CH_2CH_2CH_3$, are two different classes of alcohol, used here to compare oxidation and dehydration behaviour.

(a) State whether pentan-3-ol is a primary, secondary or tertiary alcohol, and identify the type of carbonyl compound formed when it is oxidised with acidified potassium dichromate(VI) under reflux. **(2)**

(b) State whether 2-methylhexan-2-ol can be oxidised by acidified potassium dichromate(VI), and explain your answer. **(2)**

(c) When heated with concentrated sulfuric acid, 2-methylhexan-2-ol undergoes acid-catalysed dehydration (elimination) to form a mixture of two structural isomers: 2-methylhex-2-ene (the major product) and 2-methylhex-1-ene (a minor product). Give the structural formula of 2-methylhex-2-ene, name the mechanism, and explain, using Zaitsev's rule, why it is the major product. **(3)**

(d) Calculate the atom economy for the formation of 2-methylhex-2-ene (Mr = 98.0) from 2-methylhexan-2-ol (Mr = 116.0) in this dehydration reaction, given that water (Mr = 18.0) is the only by-product. **(3)**

(Total for Question 4 is 10 marks)

© Revision Library | revisionlibrary.co.uk

5 An orange azo dye can be made from benzene in a four-step synthesis, via nitrobenzene, phenylamine and a diazonium salt.

(a) State the reagents and conditions needed to convert benzene into nitrobenzene, and name the type of mechanism involved. **(3)**

(b) State the reagents and conditions needed to reduce nitrobenzene to phenylamine. **(2)**

(c) State the reagents and conditions needed to convert phenylamine into benzenediazonium chloride, and explain why the temperature must be carefully controlled. **(3)**

(d) Benzenediazonium chloride is then reacted with phenol dissolved in sodium hydroxide solution, below 10°C, in a coupling reaction to form an azo dye. State the type of mechanism and describe the observation for this final step. **(2)**

(Total for Question 5 is 10 marks)

© Revision Library | revisionlibrary.co.uk

6 Glycine, H_2NCH_2COOH, is the simplest amino acid. Its carboxylic acid group has pKa1 = 2.34 and its protonated amine group ($-NH_3^+$) has pKa2 = 9.60. The Henderson-Hasselbalch equation is pH = pKa + log10([conjugate base]/[weak acid]).

(a) State the type of structure glycine adopts in aqueous solution at pH values between pKa1 and pKa2 (around neutral pH), and give its structural formula in this form. **(2)**

(b) Using the Henderson-Hasselbalch equation and pKa1 = 2.34, calculate the ratio of the concentration of the zwitterion ($H_3N^+CH_2COO^-$) to the fully protonated cation ($H_3N^+CH_2COOH$) present in a glycine solution buffered at pH 3.34. **(3)**

(c) Predict, with a reason, whether glycine would migrate towards the positive or negative electrode during electrophoresis at pH 12.00 (a strongly alkaline solution, well above pKa2). **(2)**

(Total for Question 6 is 7 marks)

---

7 Benzene reacts with ethanoyl chloride, CH_3COCl, in the presence of anhydrous aluminium chloride, forming phenylethanone (acetophenone) in a Friedel-Crafts acylation reaction.

(a) State the reagents and conditions needed for this reaction, other than benzene, and name the type of mechanism involved. **(2)**

(b) The electrophile is generated by reaction between ethanoyl chloride and aluminium chloride. Write an equation to show the formation of the electrophile, CH_3CO^+. **(2)**

(c) Outline the mechanism for the electrophilic substitution reaction between benzene and CH_3CO^+, including the role of $AlCl_4^-$ in the final step. **(4)**

(d) Calculate the atom economy of this reaction for the formation of phenylethanone (Mr = 120.0), given Mr(benzene) = 78.0, Mr(ethanoyl chloride) = 78.5, and that HCl (Mr = 36.5) is the only by-product. **(3)**

(Total for Question 7 is 11 marks)

© Revision Library | revisionlibrary.co.uk

Mark scheme · 2.7 Organic Chemistry: Test Pack

Question 1

(a) $C_nH_{(2n+2)}$ cao **B1**

(a) Answer: $C_nH_{(2n+2)}$

(b) a series of compounds with the same general formula and similar chemical properties, in which successive members differ by CH_2, and which show a gradual trend in physical properties oe **B1**

(b) Answer: A series of compounds with the same general formula and similar chemical properties, differing from one member to the next by CH_2, showing a gradual trend in physical properties.

(c) longest chain containing the bromine correctly identified as a 4-carbon (butane) chain, numbered to give bromine the lowest locant (C1) **B1**

(c) 1-bromo-3-methylbutane cao **B1**

(c) Answer: 1-bromo-3-methylbutane

Question 2

(a) moles CO_2 = 1.32/44.0 = 0.0300 mol (= moles of C) **M1**

(a) moles H_2O = 0.540/18.0 = 0.0300 mol, so moles of H = 0.0600 mol **M1**

(a) mass of C + mass of H = (0.0300 x 12.0) + (0.0600 x 1.0) = 0.360 + 0.0600 = 0.420 g, equal to the sample mass, confirming no oxygen is present **M1**

(a) mole ratio C:H = 0.0300:0.0600 = 1:2, empirical formula CH_2 (empirical mass = 14.0) **M1**

(a) 84.0/14.0 = 6, so molecular formula = C_6H_{12} cao **A1**

(a) Answer: C_6H_{12}

(b) E/Z isomerism requires restricted rotation about the C=C double bond and each carbon of the double bond must be attached to two different groups oe **B1**

(b) in 2-methylpent-2-ene the left-hand double-bond carbon is attached to two identical CH_3 groups (the chain methyl and the branch methyl), so this carbon does not have two different groups, and E/Z isomerism is not possible regardless of the groups on the other double-bond carbon oe **B1**

(b) Answer: The left-hand alkene carbon of 2-methylpent-2-ene carries two identical CH_3 groups, so it fails the requirement for two different groups on each double-bond carbon, and no E/Z isomerism is possible.

Question 3

Level 3 A full and logically structured explanation that gives correct equations for the initiation step and both catalytic propagation steps, correctly identifies the chlorine radical as a catalyst that is regenerated, and clearly explains why this repeating cycle allows a small amount of CFC to destroy a disproportionately large number of ozone molecules. **5-6**

Level 2 The answer includes most of the relevant equations and shows some understanding of the radical catalytic cycle, but has minor errors or omissions in the equations, or an incomplete explanation of why the effect is disproportionate. **3-4**

Level 1 Basic, largely qualitative statements, e.g. that CFCs release chlorine radicals which react with and destroy ozone, without correct or complete supporting equations or explanation of the catalytic cycle. **1-2**

Level 0 No relevant content, or the answer does not relate to the question. **0**

Indicative content:

- UV radiation in the stratosphere breaks the weak C-Cl bond in $CFCl_3$ by homolytic fission (initiation): $CFCl_3$ -> $CFCl_2$* + Cl*
- The chlorine radical reacts with ozone: Cl* + O_3 -> ClO* + O_2
- The ClO* radical reacts with a further oxygen species, regenerating the chlorine radical: ClO* + O_3 -> Cl* + $2O_2$ (or ClO* + O -> Cl* + O_2)
- Overall/net reaction: O_3 + O_3 -> $3O_2$ (or O_3 + O -> $2O_2$), so ozone is destroyed
- The chlorine radical acts as a catalyst: it is used up in the first propagation step but regenerated in the second, so it is not permanently consumed
- Because the same chlorine radical is continually regenerated, it can go on to destroy very large numbers of ozone molecules in a repeating chain/catalytic cycle before it is eventually removed, so even a very low steady-state concentration of Cl radicals causes significant, disproportionate ozone depletion

© Revision Library | revisionlibrary.co.uk

Question 4

(a) secondary alcohol **B1**

(a) oxidised to pentan-3-one, a ketone (only one oxidation step is possible) cao **B1**

(a) Answer: Secondary alcohol; oxidised to pentan-3-one (a ketone).

(b) it cannot be oxidised (no colour change is observed) **B1**

(b) because it is a tertiary alcohol: the carbon bonded to -OH has no hydrogen atom attached to it that could be removed in the oxidation step oe **B1**

(b) Answer: It cannot be oxidised, because it is a tertiary alcohol and the carbon bonded to -OH carries no hydrogen atom.

(c) structural formula $(CH_3)_2C{=}CHCH_2CH_2CH_3$ cao **B1**

(c) elimination (via a carbocation intermediate); Zaitsev's rule states that the more substituted (more stable) alkene is the major product of elimination **B1**

(c) 2-methylhex-2-ene is trisubstituted (three alkyl groups on the two double-bond carbons) compared with the disubstituted 2-methylhex-1-ene, so it is more thermodynamically stable and forms as the major product oe **A1**

(c) Answer: $(CH_3)_2C{=}CHCH_2CH_2CH_3$; elimination via a carbocation, favoured by Zaitsev's rule because it is the more substituted, more stable alkene.

(d) this is an intramolecular elimination (one reactant only), so total reactant Mr = Mr of the alcohol = 116.0 **M1**

(d) atom economy = (Mr of desired product / total reactant Mr) x 100 = (98.0/116.0) x 100 **M1**

(d) 84.5% (3 s.f.) cao **A1**

(d) Answer: 84.5%

Question 5

(a) concentrated nitric acid with concentrated sulfuric acid as catalyst **B1**

(a) warmed at about 50°C (accept 50-60°C) **B1**

(a) electrophilic substitution cao **B1**

(a) Answer: Concentrated HNO_3 with concentrated H_2SO_4 catalyst, warmed at about 50°C; electrophilic substitution.

(b) tin (Sn) and concentrated hydrochloric acid, heated under reflux **B1**

(b) followed by addition of excess sodium hydroxide solution to liberate the free amine cao **B1**

(b) Answer: Sn + concentrated HCl, reflux; then excess NaOH(aq) to liberate free phenylamine.

(c) sodium nitrite ($NaNO_2$) and dilute hydrochloric acid (generating nitrous acid, HNO_2, in situ) **B1**

(c) temperature kept below about 5°C (in an ice bath) **B1**

(c) because the diazonium salt is unstable and decomposes (e.g. to phenol and nitrogen gas) above this temperature oe **B1**

(c) Answer: $NaNO_2$ + dilute HCl, below 5°C (ice bath); the diazonium salt decomposes above this temperature.

(d) electrophilic substitution (the diazonium ion acts as the electrophile, attacking the activated phenoxide ring) **B1**

(d) a bright orange/yellow precipitate of the azo dye forms oe **B1**

(d) Answer: Electrophilic substitution; a bright orange/yellow precipitate (the azo dye) forms.

Question 6

(a) zwitterion **B1**

(a) structural formula $H_3N{+}CH_2COO{-}$ cao **B1**

(a) Answer: Zwitterion; $H_3N{+}CH_2COO{-}$.

(b) rearrange: log10(ratio) = pH - pKa1 = 3.34 - 2.34 = 1.00 **M1**

(b) ratio = $10^{1.00}$ **M1**

(b) 10.0 : 1 (zwitterion : cation) cao **A1**

(b) Answer: 10.0 : 1 (zwitterion to cation)

(c) at pH 12.00, well above pKa2 (9.60), the $-NH_3^+$ group has also lost a proton, so glycine exists mainly as the anion $H_2NCH_2COO{-}$ (overall net negative charge) **B1**

(c) a negatively charged species migrates towards the positive electrode (the anode) oe **B1**

(c) Answer: Towards the positive electrode (anode), because at pH 12.00 glycine exists mainly as the negatively charged anion $H_2NCH_2COO{-}$.

Question 7

(a) ethanoyl chloride with anhydrous aluminium chloride ($AlCl_3$) catalyst, heated under reflux, in the absence of moisture **B1**

(a) electrophilic substitution cao **B1**

(a) Answer: Ethanoyl chloride with anhydrous $AlCl_3$ catalyst, reflux, anhydrous conditions; electrophilic substitution.

(b) correct species: $AlCl_4^-$ **M1**

(b) $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$ cao **A1**

(b) Answer: $CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$

(c) CH_3CO^+ (the electrophile) attacks the delocalised π electron ring system of benzene, forming a new bond to one ring carbon **M1**

(c) this forms a positively charged intermediate (arenium ion/ σ complex), in which delocalisation is disrupted and retained over only the other five carbons **M1**

(c) $AlCl_4^-$ acts as a base and removes an H^+ from the carbon bonded to the $COCH_3$ group **A1**

(c) this restores full delocalisation (aromaticity) of the ring and regenerates the $AlCl_3$ catalyst, forming phenylethanone cao **A1**

(c) Answer: CH_3CO^+ attacks the ring, forming a positively charged arenium ion intermediate; $AlCl_4^-$ removes an H^+ from this intermediate, restoring the aromatic ring, regenerating $AlCl_3$ and forming phenylethanone.

(d) sum of Mr of reactants = 78.0 + 78.5 = 156.5 **M1**

(d) atom economy = (Mr of desired product / sum of Mr of reactants) x 100 = (120.0/156.5) x 100 **M1**

(d) 76.7% (3 s.f.) cao **A1**

(d) Answer: 76.7%

© Revision Library | revisionlibrary.co.uk