

# Answers

## Chapter 10

### Exercises

- 1 (a) carboxylic acid; butanoic acid  
(b) halogenoalkane; 1,1-dichloropropane  
(c) ketone; butanone  
(d) ester; methyl ethanoate  
(e) ether; methoxyethane  
(f) ester; ethyl pentanoate
- 2 (a)  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$   
(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$   
(c)  $\text{CH}_2\text{CH}(\text{CH}_2)_2\text{CH}_3$   
(d)  $\text{CH}_2\text{BrCH}(\text{CH}_3)\text{C}_2\text{H}_5$   
or  $\text{CH}_2\text{BrCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$   
(e)  $\text{HCOOCH}_2\text{CH}_3$   
(f)  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$   
(g)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$
- 3 A                      4 D
- 5
- |  |                              |
|--|------------------------------|
| $\begin{array}{c} \text{Cl} & \text{Cl} & \text{H} \\   &   &   \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   \\ \text{Cl} & \text{Cl} & \text{H} \end{array}$ | 1,1,1,2,2-pentachloropropane |
| $\begin{array}{c} \text{Cl} & \text{Cl} & \text{Cl} \\   &   &   \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   \\ \text{Cl} & \text{H} & \text{H} \end{array}$ | 1,1,1,2,3-pentachloropropane |
| $\begin{array}{c} \text{Cl} & \text{H} & \text{Cl} \\   &   &   \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{Cl} \\   &   &   \\ \text{Cl} & \text{H} & \text{H} \end{array}$ | 1,1,1,3,3-pentachloropropane |
| $\begin{array}{c} \text{Cl} & \text{Cl} & \text{Cl} \\   &   &   \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   \\ \text{H} & \text{Cl} & \text{H} \end{array}$ | 1,1,2,2,3-pentachloropropane |
| $\begin{array}{c} \text{Cl} & \text{Cl} & \text{Cl} \\   &   &   \\ \text{Cl}-\text{C}-\text{C}-\text{C}-\text{Cl} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array}$ | 1,1,2,3,3-pentachloropropane |
- 6 B
- 7 Benzene is a cyclic molecule with a planar framework of single bonds between the six carbon atoms and six hydrogen atoms. The carbon atoms are also bonded to each other by a delocalized cloud of electrons which forms a symmetrical region of electron density above and below the plane of the ring. This is a very stable arrangement, so benzene has much lower energy than would be expected.
- 8 (a) Similar molar mass will mean molecules have approximately equal London (dispersion) forces and so differences in boiling point can be attributed to differences in dipole-dipole or hydrogen bonding.  
(b) Solubility in hexane will increase with increasing chain length as the non-polar part of the molecule makes a larger contribution to its structure.
- 9 (a)  $\text{C}_5\text{H}_{14}(\text{l}) + 6\text{O}_2(\text{g}) \rightarrow 5\text{CO}(\text{g}) + 7\text{H}_2\text{O}(\text{l})$   
(b)  $2\text{C}_4\text{H}_{10}(\text{g}) + 13\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 10\text{H}_2\text{O}(\text{l})$   
(c)  $\text{C}_3\text{H}_4(\text{g}) + \text{O}_2(\text{g}) \rightarrow 3\text{C}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$
- 10 Bromine + ethane  
*initiation*  
$$\text{Br}_2 \xrightarrow{\text{UV light}} 2\text{Br}^\bullet \text{ bromine radicals}$$
  
*propagation*  
$$\text{Br}^\bullet + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5^\bullet + \text{HBr}$$
  
$$\text{C}_2\text{H}_5^\bullet + \text{Br}_2 \rightarrow \text{C}_2\text{H}_5\text{Br} + \text{Br}^\bullet$$
  
$$\text{C}_2\text{H}_5\text{Br} + \text{Br}^\bullet \rightarrow \text{C}_2\text{H}_4\text{Br}^\bullet + \text{HBr}$$
  
$$\text{C}_2\text{H}_4\text{Br}^\bullet + \text{Br}_2 \rightarrow \text{C}_2\text{H}_4\text{Br}_2 + \text{Br}^\bullet$$
  
*termination*  
$$\text{Br}^\bullet + \text{Br}^\bullet \rightarrow \text{Br}_2$$
  
$$\text{C}_2\text{H}_5^\bullet + \text{Br}^\bullet \rightarrow \text{C}_2\text{H}_5\text{Br}$$
  
$$\text{C}_2\text{H}_5^\bullet + \text{C}_2\text{H}_5^\bullet \rightarrow \text{C}_4\text{H}_{10}$$
  
Overall, these reactions show how a mixture of products is formed.

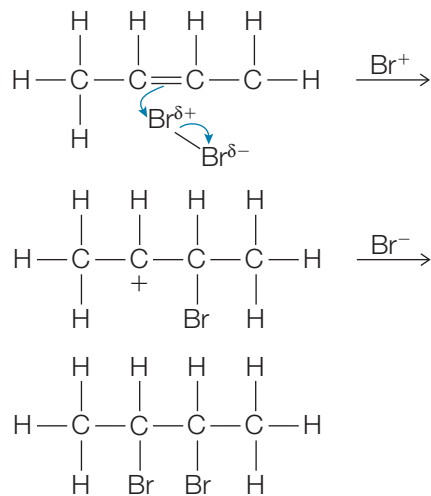
- 11 (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$  butane  
 (b)  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$  butan-2-ol  
 (c)  $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$  2-bromobutane
- 12 (a) No observable change.  
 (b) Burns with very smoky flame.  
 (c) The bromine water changes from brown to colourless.
- 13 (a)  $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2 \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$   
 $2\text{C}_3\text{H}_7\text{OH}(\text{l}) + 9\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 8\text{H}_2\text{O}(\text{l})$   
 (b)  $\text{C}_2\text{H}_5\text{COOH}(\text{aq}) + \text{C}_4\text{H}_9\text{OH}(\text{aq}) \rightarrow$   
 $\text{C}_2\text{H}_5\text{COOC}_4\text{H}_9(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- 14 (a) butanone; orange  $\rightarrow$  green  
 (b) methanal; orange  $\rightarrow$  green  
 (c) no reaction; no colour change
- 15 Nucleophilic substitution involves an electron-rich species (e.g.  $\text{OH}^-$ ) attacking an electron-deficient carbon atom (e.g. in chloroethane), leading to substitution of the halogen functional group by the nucleophile.  
 $\text{C}_2\text{H}_5\text{Cl} + \text{OH}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{Cl}^-$
- 16 Benzene has a very stable structure as a result of its symmetrical ring of delocalized electrons. Addition reactions would involve breaking this ring and therefore decreasing its stability. Substitution reactions in which one or more hydrogen atoms of the ring are replaced by other atoms or groups preserves the aromatic ring structure and therefore its stability.
- 17 (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$  primary  
 $\text{CH}_3\text{CH}_2\text{CHBrCH}_3$  secondary  
 $\text{C}(\text{CH}_3)_3\text{Br}$  tertiary  
 (b) The tertiary halogenoalkane reacts by an  $\text{S}_{\text{N}}1$  mechanism.  
 S = substitution; N = nucleophilic;  
 1 = unimolecular  
 (c)  $\text{RBr} \rightarrow \text{R}^+ + \text{Br}^-$
- 18 C
- 19 (a) The carbon-halogen bond breaks more easily in the iodo- and bromo- derivatives

than in the chloro- derivatives, so these compounds more readily undergo substitution reactions.

- (b) The substitution reaction of OH for Cl occurs in both these compounds, displacing  $\text{Cl}^-$  and forming the white precipitate of  $\text{AgCl}$ , which darkens on exposure to air. The tertiary halogenoalkane  $\text{C}(\text{CH}_3)_3\text{Cl}$  isomer reacts more quickly than the primary isomer  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  because it undergoes an  $\text{S}_{\text{N}}1$  mechanism, which is faster.

- 20 Alkenes have a double bond which is an electron-dense region and so is susceptible to attack by electrophiles which are themselves electron deficient. They undergo addition reactions because they are unsaturated; one of the bonds in the double bond breaks and incoming groups can add to the two carbon atoms.

When bromine approaches but-2-ene, it is polarized by the electron density in the double bond. Electrons in the bromine-bromine bond are repelled away from the double bond, leading to the heterolytic fission of the bromine molecule. The  $\text{Br}^+$  product now attaches itself to one of the carbon atoms as the carbon-carbon bond breaks. This produces an unstable carbocation which then rapidly reacts with the  $\text{Br}^-$  ion. The product is 2,3-dibromobutane.

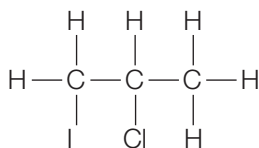
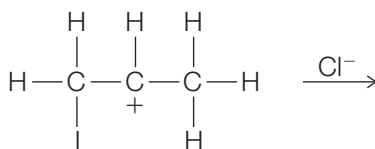
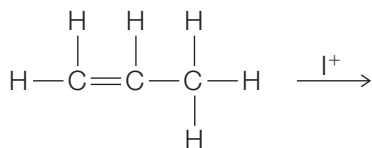


- 21 But-1-ene +  $\text{HBr} \rightarrow$  2-bromobutane

Application of Markovnikov's rule enables us to predict that the electrophile  $\text{H}^+$  will add to

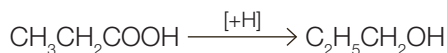
the terminal carbon, forming a secondary carbocation, as this is stabilized by the positive inductive effect of the alkyl groups. Br<sup>-</sup> will then add to carbon 2, forming 2-bromobutane.

- 22** ICl is polarized: I<sup>δ+</sup> Cl<sup>δ-</sup> owing to the greater electronegativity of Cl than I. So when it undergoes heterolytic fission it will form I<sup>+</sup> and Cl<sup>-</sup>. By application of Markovnikov's rule, the I<sup>+</sup> will attach to the terminal carbon, while Cl<sup>-</sup> will add to carbon 2. The product is therefore 1-iodo-2-chloropropane.

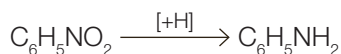


- 23** Concentrated H<sub>2</sub>SO<sub>4</sub> and concentrated HNO<sub>3</sub>. The stronger acid H<sub>2</sub>SO<sub>4</sub> protonates the HNO<sub>3</sub>, leading to production of the nitronium ion NO<sub>2</sub><sup>+</sup>. This is a strong electrophile which reacts with the π electrons of the benzene ring, substituting for H.

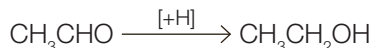
- 24 (a)** Use LiAlH<sub>4</sub> in dry ether and heat. The acid is reduced first to the aldehyde and then to the alcohol.



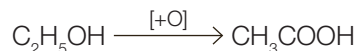
- (b)** Nitrobenzene is heated under reflux with tin and concentrated HCl, and the product is reacted with NaOH.



- (c)** Ethanal is heated with NaBH<sub>4</sub>(aq).

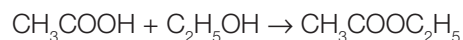


- 25** Start with ethanol. Take one portion and oxidize it using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

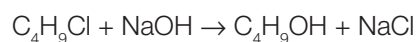


The product is ethanoic acid.

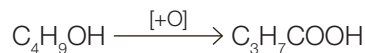
React the ethanoic acid product with another portion of the ethanol by warming it in the presence of some concentrated H<sub>2</sub>SO<sub>4</sub>. The esterification reaction yields ethyl ethanoate.



- 26** React the 1-chlorobutane with NaOH in warm aqueous solution to convert it into butan-1-ol.

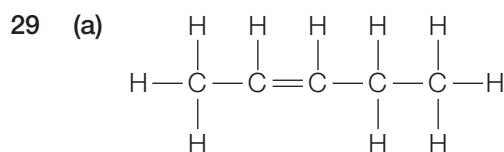
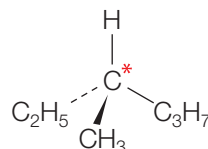


Oxidize the butan-1-ol using acidified potassium(VI) dichromate solution and heat under reflux to allow the reaction to go to completion.

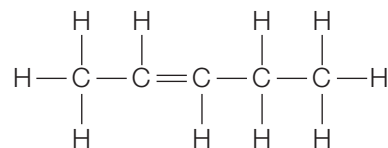


- 27** C

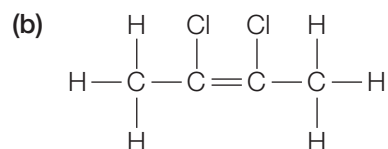
- 28** 3-methylhexane: CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>



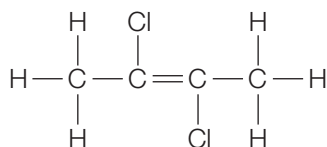
Z-pent-2-ene



E-pent-2-ene



Z-2,3-dichlorobut-2-ene



*E*-2,3-dichlorobut-2-ene

## Practice questions

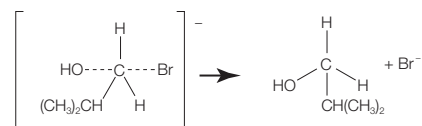
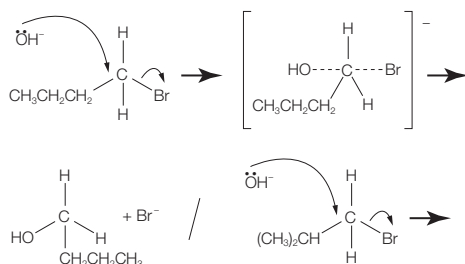
For advice on how to interpret the marking below please see Chapter 1.

- |           |   |           |   |           |   |           |   |
|-----------|---|-----------|---|-----------|---|-----------|---|
| <b>1</b>  | C | <b>2</b>  | C | <b>3</b>  | D | <b>4</b>  | A |
| <b>5</b>  | A | <b>6</b>  | A | <b>7</b>  | B | <b>8</b>  | C |
| <b>9</b>  | B | <b>10</b> | B | <b>11</b> | A | <b>12</b> | C |
| <b>13</b> | A | <b>14</b> | D |           |   |           |   |

- 15 (a)** A: 1-bromobutane  
 B: 2-bromobutane  
 C: 2-bromo-2-methylpropane  
 D: 1-bromo-2-methylpropane [4]

*Penalize incorrect punctuation, e.g. commas for hyphens, only once.*  
*Accept 2-bromomethylpropane and 1-bromomethylpropane for C and D respectively.*

- (b) (i)** C / 2-bromo-2-methylpropane; unimolecular nucleophilic substitution [2]  
**(ii)**  $\text{RBr} \rightarrow \text{R}^+ + \text{Br}^-$  [1]  
*Allow use of 2-bromo-2-methylpropane instead of RBr.*  
**(iii)** A / 1-bromobutane / D / 1-bromo-2-methylpropane



curly arrow going from lone pair/negative charge on O in  $\text{OH}^-$  to C

*Do not allow curly arrow originating on H in  $\text{OH}^-$ .*

curly arrow showing Br leaving

*Accept curly arrow either going from bond between C and Br to Br in 1-bromobutane or in the transition state.*

representation of transition state showing negative charge, square brackets and partial bonds [4]

*Do not penalize if HO and Br are not at  $180^\circ$  to each other.*

*Do not award fourth mark if OH-C bond is represented.*

- (c) (b) (i)** no change as  $[\text{OH}^-]$  does not appear in the rate equation / in the rate determining step  
**(b) (iii)** rate doubles as the rate is proportional to  $[\text{OH}^-]$  /  $\text{OH}^-$  appears in the rate-determining / slow step / first order with respect to  $\text{OH}^-$  [2]

*Award [1] if correctly predicts no rate change for  $\text{S}_{\text{N}}1$  and doubling of rate for  $\text{S}_{\text{N}}2$  without suitable explanation.*

- (d)** rate of 1-bromobutane is faster; C-Br bond is weaker / breaks more easily than C-Cl bond [2]

- (e)** 2-bromobutane / B; (plane-) polarized light shone through; enantiomers rotate plane of plane-polarized light to left or right / opposite directions (by same amount)

*Accept 'turn' instead of 'rotate' but not 'bend'/'reflect'.*

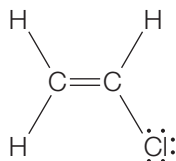
Physical properties identical (apart from effect on plane-polarized light); chemical properties are identical (except with other chiral compounds) [5]

*Do not accept 'similar' in place of 'identical'.*

- 16 (a) Colour change from yellow / orange / rust colour / red / brown to colourless [1]

No mark for change to clear, or for decolorized with no reference to original colour.

- (b) Chloroethene:



No mark if the lone pairs are missing on Cl. Accept lines, dots or crosses for e<sup>-</sup> pairs.

Poly(chloroethene):



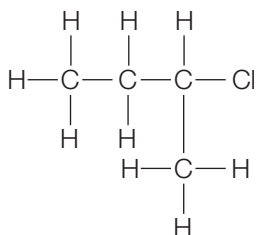
*n* and square brackets are not required.

Continuation bonds must be shown.

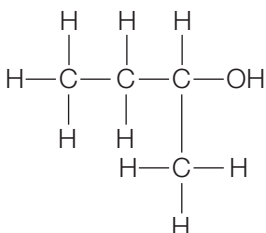
- (c) (hydration of ethene for the manufacture of ethanol /  $\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{OH}$ ; (synthesis of)  $\text{CH}_3\text{COOH}$  / ethanoic / acetic acid; (synthesis of) ethylene glycol / 1,2-ethanediol / ethane-1,2-diol; (synthesis of) drugs / pesticides; (hydrogenation of unsaturated oils in the manufacture of) margarine [2 max]

Accept other commercial applications.

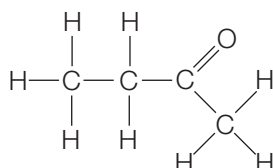
- 17 (a) A:



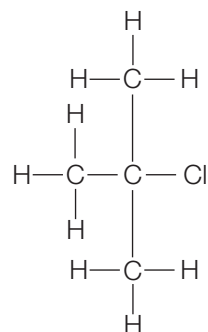
- B:



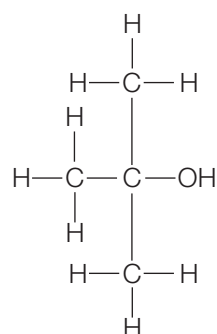
- C:



- D:



- E:



Accept condensed formulas. [5]

Award [1 max] if **A** and **D** are other way round (and nothing else correct). Award [2 max] if **A** and **D** are other way round but one substitution product **B** or **E** is correct based on initial choice of **A** and **D**.

Award [3 max] if **A** and **D** are other way round but both substitution products **B** and **E** are correct based on initial choice of **A** and **D**. M2 (for **B**) and M5 (for **E**) may also be scored for substitution product if primary chloroalkane used. Penalize missing hydrogens once only.

- (b)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COOCH}_3 + \text{H}_2\text{O}$

[1] for reactants and [1] for products.

(concentrated) sulfuric acid /  $\text{H}_2\text{SO}_4$

Do not accept just  $\text{H}^+$  or acid.

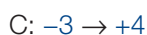
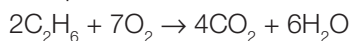
methyl propanoate [4]

## Challenge yourself

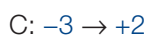
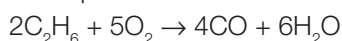
- 1 All four C atoms in the molecule are  $\text{sp}^3$  hybridized because they form four single bonds

which are tetrahedrally arranged. The nitrogen atom is also  $sp^3$  hybridized, as its four electron domains are also tetrahedrally arranged. Note that here the hybridization also includes the lone pair on the nitrogen atom.

- 2 Complete combustion:



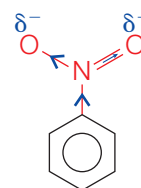
Incomplete combustion:



- 3 *Heterolytic* describes breaking of the bond, producing two *different* products. The products are ions, and the reaction mechanism involves attraction of the electron density of the  $C=C$  double bond to the positive ion.
- 4 The repeating unit in polystyrene is  $-CH(C_6H_5)-CH_2-$
- 5 The cyanide ion,  $CN^-$ , and ammonia,  $NH_3$ , are nucleophiles that react with halogenoalkanes in substitution reactions. They act as ligands with transition metal ions, forming complexes such as  $[Cu(NH_3)_4(H_2O)_2]^{2+}$  and  $[Cu(CN)_4]^{3-}$ . They act as Lewis bases by donating a lone pair of electrons. For example:
- $$NH_3 + BCl_3 \rightarrow NH_3BCl_3$$
- 6 The order of the reaction with respect to each reactant can be deduced from experiments in which the concentration of each reactant in turn is changed, and the initial rate of the reaction then measured. If, for example, the concentration of halogenoalkane is doubled while the concentration of  $OH^-$  remains constant, and the rate is found to have doubled, then it indicates that the reaction is first order with respect to halogenoalkane. Examples of this type of experiment and the interpretation of the results are given in Chapter 6.
- 7 With bromine water, the water can also take part in the second part of the reaction because of its lone pairs. The carbocation is attacked by water in competition with  $Br^-$ , and the major

product is 2-bromoethanol,  $CH_2BrCH_2OH$ . The bromine water is decolorized from brown. The relative concentration of bromoethanol and 1,2-dibromoethane depends on the strength of the bromine water used.

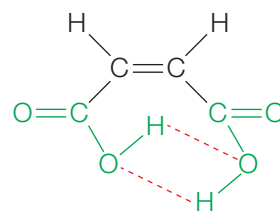
- 8 The  $-NH_2$  group in phenylamine is electron donating due to conjugation of the lone pair of electrons on N with the ring electrons. As a result, the electron density of the ring is increased, making it more susceptible to electrophilic attack. In contrast, the  $-NO_2$  group in nitrobenzene is electron withdrawing due to the electronegativity of the nitrogen and oxygen atoms.



Also, the electrons in its double bond conjugate with the  $\pi$  electrons in the ring, causing the electron density of the ring to be decreased, making it less susceptible to electrophilic attack.

- 9 In both square planar and octahedral compounds, geometric isomers can arise due to groups having the possibility of being in adjacent (*cis*) or in across (*trans*) positions. In tetrahedral compounds, all positions are adjacent to each other, so these isomers are not possible.

10



*cis*-butenedioic acid  
melting point  $139^\circ C$

The *cis* isomer, maleic acid, has a lower melting point as it forms fewer intermolecular bonds. The *cis* isomer is much more soluble in water than the *trans* isomer, and its density is less. *cis*-Butenedioic acid is a stronger acid because when  $H^+$  is lost, the *cis* anion is more stable than the *trans* form.