Unit 13 · Fundamental Principles of Organic Chemistry

ANSWER KEY · FOR TEACHERS

Full marks 34

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Match the columns

1. substrate → **d.** the organic compound that is changed in a reaction
2. electrophile → **e.** a reagent short of electrons, which accepts a pair of electrons
3. nucleophile → **f.** a reagent rich in electrons, which gives a pair of electrons to make a bond
4. free radical → **b.** an atom or group of atoms with an unpaired electron
5. carbocation → **g.** a positive ion with the charge on a carbon atom
6. leaving group → **a.** the group that goes off with the bonding pair, as Br^- does from bromoethane

Each carries 0.5 mark. K · 3

2 Label the diagram

1. Chain
2. Metamerism
3. Geometrical
4. Optical

Each carries 0.5 mark. K · 2

3 Multiple choice

i. **c.** 2,3-dimethylbutane — U · 1

The longest chain has four carbons, with a methyl on carbons 2 and 3: 2,3-dimethylbutane (C_6H_{14}, a chain isomer of hexane).

ii. **b.** to drive off cyanide and sulphide, which would also give precipitates with silver nitrate — U · 1

Cyanide and sulphide ions give silver cyanide (white) and silver sulphide (black); boiling with nitric acid drives them off as HCN and H_2S.

iii. **d.** but-2-ene — A · 1

Each carbon of the C=C must hold two different groups. In but-2-ene each holds H and CH_3; in the others one carbon of the C=C holds two H (or two CH_3).

iv. **d.** $(CH_3)_3C-$ — K · 1

The more branched the alkyl group, the stronger its push: $(CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2- > CH_3-$.

v. **b.** $Fe_4[Fe(CN)_6]_3$ — K · 1

Iron(III) hexacyanoferrate(II), $Fe_4[Fe(CN)_6]_3$. $Fe(SCN)_3$ is the blood red color seen when sulphur is present too.

4 Short answers

a. MARKING SCHEME — U · 2

✓ 3-hydroxybutanal.

✓ –CHO, because the aldehyde is senior to the alcohol (the –OH becomes the prefix hydroxy).

b. MARKING SCHEME — K · 2

✓ $CH_2=CH-CH(CH_3)-CH_3$.

✓ $CH_3CH_2-COO-CH_3$.

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c. MARKING SCHEME U · 2

- ✓ Homolytic: each atom takes one bonding electron, giving free radicals; heterolytic: both electrons go to the more electronegative atom, giving ions.
- ✓ Homolytic happens mostly with non-polar bonds, in the gas phase, with heat, light or a peroxide; heterolytic with polar bonds in polar solvents.

d. MARKING SCHEME A · 3

- ✓ Both N and S are present (as NaSCN).
- ✓ $3NaSCN + FeCl_3 \rightarrow Fe(SCN)_3 + 3NaCl$, blood red.
- ✓ Excess sodium: $NaSCN + 2Na \rightarrow NaCN + Na_2S$.

5 Long answer

ANSWER A · 4

$CH_3CH_2COOH < CH_3COOH < ClCH_2COOH < Cl_3CCOOH$.

An acid is stronger when the ion left after it gives away H^+, $RCOO^-$, is more stable, that is, when its negative charge is spread out.

Chlorine has a −I effect: it pulls electrons, and some of the charge, away from the COO^-, so chloroethanoic acid is stronger than ethanoic acid, and three chlorines pull harder than one, making trichloroethanoic acid the strongest.

The ethyl group has a stronger +I effect than methyl: it pushes more electrons onto the COO^-, so propanoic acid is the weakest.

MARKING SCHEME

- ✓ The correct order.
- ✓ Acid strength depends on how stable (how spread out) the $RCOO^-$ ion is.
- ✓ −I chlorine strengthens the acid, three chlorines more than one.
- ✓ +I alkyl weakens it, ethyl more than methyl.

6 Numerical problems

a. ANSWER A · 4

i. O = 100 − 64.9 − 13.5 = 21.6%. C : H : O = 64.9 ÷ 12 : 13.5 ÷ 1 : 21.6 ÷ 16 = 5.41 : 13.5 : 1.35 = 4 : 10 : 1. Empirical formula $\mathbf{C_4H_{10}O}$ (mass 74), so n = 74 ÷ 74 = 1 and the molecular formula is also $\mathbf{C_4H_{10}O}$.

ii. For example butan-1-ol, $CH_3CH_2CH_2CH_2OH$, and ethoxyethane, $CH_3CH_2–O–CH_2CH_3$: **functional isomers**.

iii. **Butan-2-ol**, $CH_3–C^*H(OH)–CH_2–CH_3$: carbon 2 holds four different groups, H, OH, CH_3 and C_2H_5.

MARKING SCHEME

- ✓ Ratio 4 : 10 : 1.
- ✓ Empirical and molecular formula $C_4H_{10}O$.
- ✓ An alcohol and an ether, named: functional isomers.
- ✓ Butan-2-ol, chiral carbon 2.

b. ANSWER A · 4

i. C : H : O = 62.1 ÷ 12 : 10.3 ÷ 1 : 27.6 ÷ 16 = 5.18 : 10.3 : 1.73 = 3 : 6 : 1. Empirical formula C_3H_6O, mass 58, so n = 1: $\mathbf{C_3H_6O}$.

ii. **Propanal**, CH_3CH_2CHO, and **propan-2-one** (propanone), CH_3COCH_3.

iii. $CH_3–CO–CH_3 \rightleftharpoons CH_2=C(OH)–CH_3$: a hydrogen moves from a CH_3 to the oxygen, and the double bond moves to C=C. The **keto form** (propanone) is over 99.99% at room temperature.

MARKING SCHEME

- ✓ Ratio 3 : 6 : 1.
- ✓ C_3H_6O.
- ✓ Propanal and propanone.
- ✓ The enol $CH_2=C(OH)–CH_3$; the keto form wins.

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7 Think

ANSWER HA · 3

The −I effect of chlorine fades quickly along a chain, after about three bonds it is almost nothing. In 2-chloropropanoic acid the chlorine is on the carbon next to the COOH, so it pulls more charge away from the COO^- and the acid is stronger; in 3-chloropropanoic acid it is one carbon further away. Only 2-chloropropanoic acid has a chiral carbon: its carbon 2 holds four different groups, H, CH_3, Cl and COOH, so it has two mirror-image forms. In 3-chloropropanoic acid each carbon holds two H atoms or is the COOH carbon, so it has no chiral carbon.

MARKING SCHEME

- ✓ The −I effect fades with distance along the chain.
- ✓ Chlorine nearer the COOH stabilizes the COO^- more: the stronger acid.
- ✓ 2-chloropropanoic acid: carbon 2 holds four different groups, so it is chiral.

8 Activity: Hands and molecules

(not marked)

WHAT STUDENTS SHOULD FIND

The two CHBrClF models are mirror images that can't be laid on each other however they are turned, like two hands: the carbon is chiral, and the two are enantiomers. A carbon with two groups the same can always be turned to match its mirror image: it is not chiral. A carbon must hold four different atoms or groups.

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	9	6	16	3	**34**

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