

WORKBOOK ANSWERS

OCR A-level Chemistry A

Organic chemistry and analysis

This Answers document provides suggestions for some of the possible answers that might be given for the questions asked in the workbook. They are not exhaustive and other answers may be acceptable, but they are intended as a guide to give teachers and students feedback.

Module 6 Organic chemistry and analysis

Aromatic compounds, carbonyls and acids

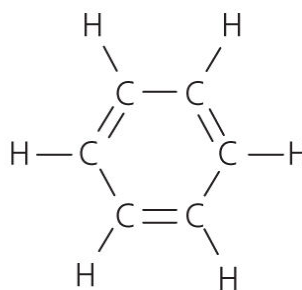
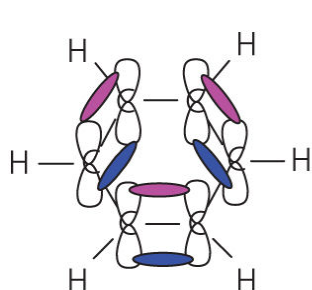
Aromatic compounds

Benzene and aromatic compounds

1a Benzene = $C_6H_6 = 72 + 6 = 78$ % C = $(72/78) \times 100 = 92.3\%$ ✓ [1]

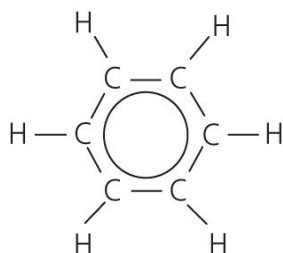
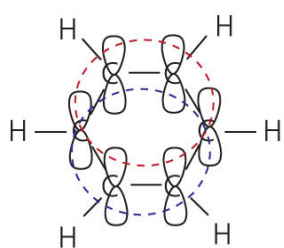
1b

- i Kekulé suggested that adjacent p-orbitals overlap to form π -bonds (as they did in alkenes) such that there were alternating double and single bonds around the ring, as shown below. ✓



✓ [2]

- ii In the delocalised model adjacent p-orbitals overlap and spread around the ring, creating an electron cloud above and below the ring (see below) to form π -bonds above and below the plane. ✓



✓

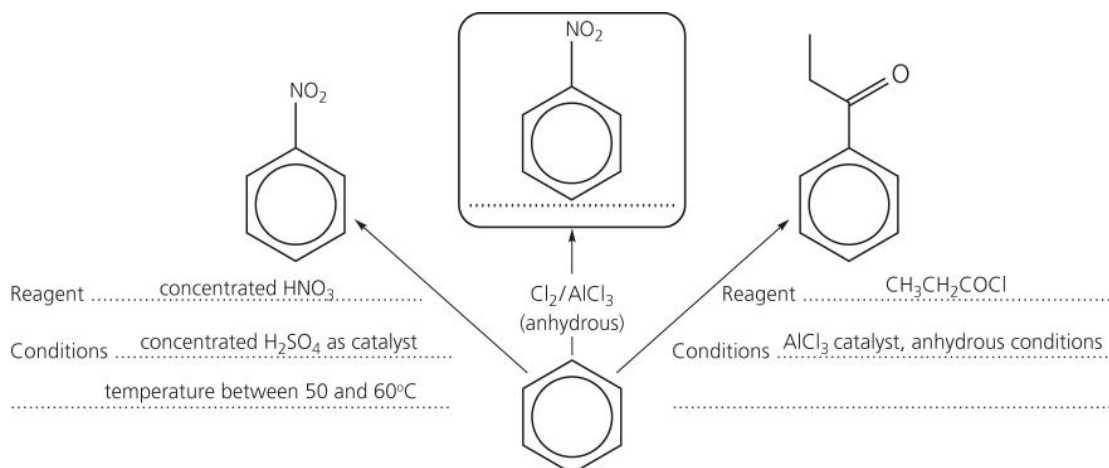
[2]

1c

- i The bond angles in benzene are all 120° . ✓ [1]
- ii A σ -bond is a shared pair of electrons where the two electrons are centred between the two nuclei. ✓ A π -bond is a shared pair of electrons where the two electrons overlap sideways above and below the plane of the two nuclei. ✓ [2]

Electrophilic substitution and phenols

2



3a Reagents and conditions: CH_3Cl and anhydrous AlCl_3 . [2]

3b

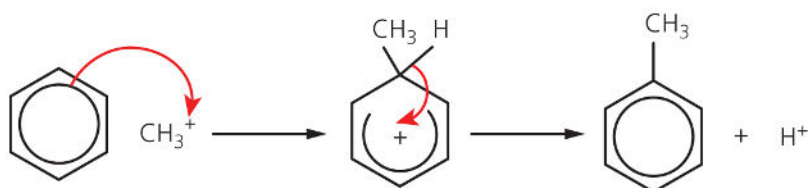
Step 1:

formation of the electrophile



Step 2:

substitution of H by the electrophile



Step 3:

regeneration of the catalyst (halogen carrier)



[1 + 3 + 1 = 5]

4a Phenol is faster because a lone pair of electrons from the oxygen in the OH is delocalised into the ring. ✓ This increases the electron density in the ring, which polarises the Br-Br ✓ and increases the attraction for an electrophile. ✓ [3]

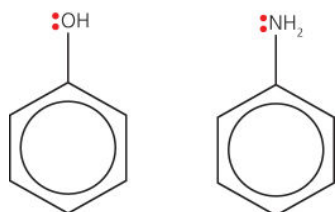
4b The π -electrons in the alkene (cyclohexene) are localised between the two C=C. ✓
Therefore, cyclohexene has high electron density, greater ability to polarise the Br–Br and to attract an electrophile, ✓ so cyclohexene reacts faster than benzene. ✓ [3]

5a Does not react and decolorise bromine (without a halogen carrier). ✓

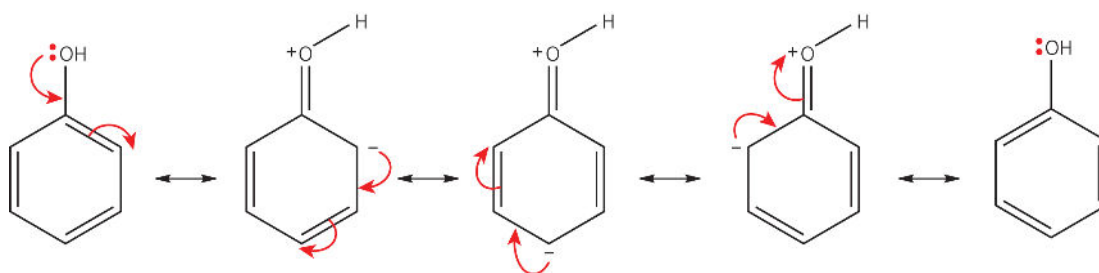
All C–C bond lengths are the same (and intermediate between a C–C and a C=C). ✓

The enthalpy of hydrogenation of benzene is not three times the enthalpy of hydrogenation of cyclohexene. ✓ [3]

5b



The OH group and the NH₂ group each have lone pairs of electrons that can be delocalised into the ring.

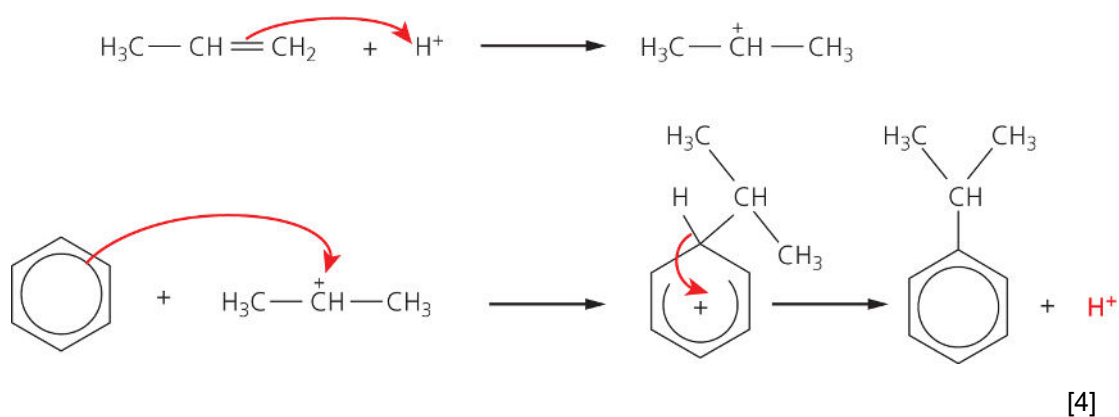


As the electron pair moves around the ring, the negative charge only ever appears at the 2, 4 and 6 positions. This means that electrophiles are directed towards the 2, 4 and 6 positions. [4]

Exam-style questions

1a

i



- ii The H^+ in stage 1 accepts an electron pair ✓, behaves as an electrophile ✓ and adds across the $\text{C}=\text{C}$ bond, forming a secondary carbocation/carbonium ion. ✓ [3]

It could also be argued that the H^+ is a catalyst, as it is regenerated in the second step of stage 1.

- iii When H^+ reacts with propene, the unstable primary carbocation $\text{CH}_3\text{CH}_2\text{CH}_2^+$ will also be formed ✓ as a minor product, which would react to give $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ ✓ [2]

1b

- i Mass spectrum shows molar mass = 58 g mol^{-1} ✓.
 IR shows $\text{C}=\text{O}$ at about 1700 cm^{-1} ✓.
 $\text{C}=\text{O}$ has mass 28, so the rest of the molecule is $58 - 28 = 30 = 2 \times \text{CH}_3$ ✓, so it must be CH_3COCH_3 ✓ [4]

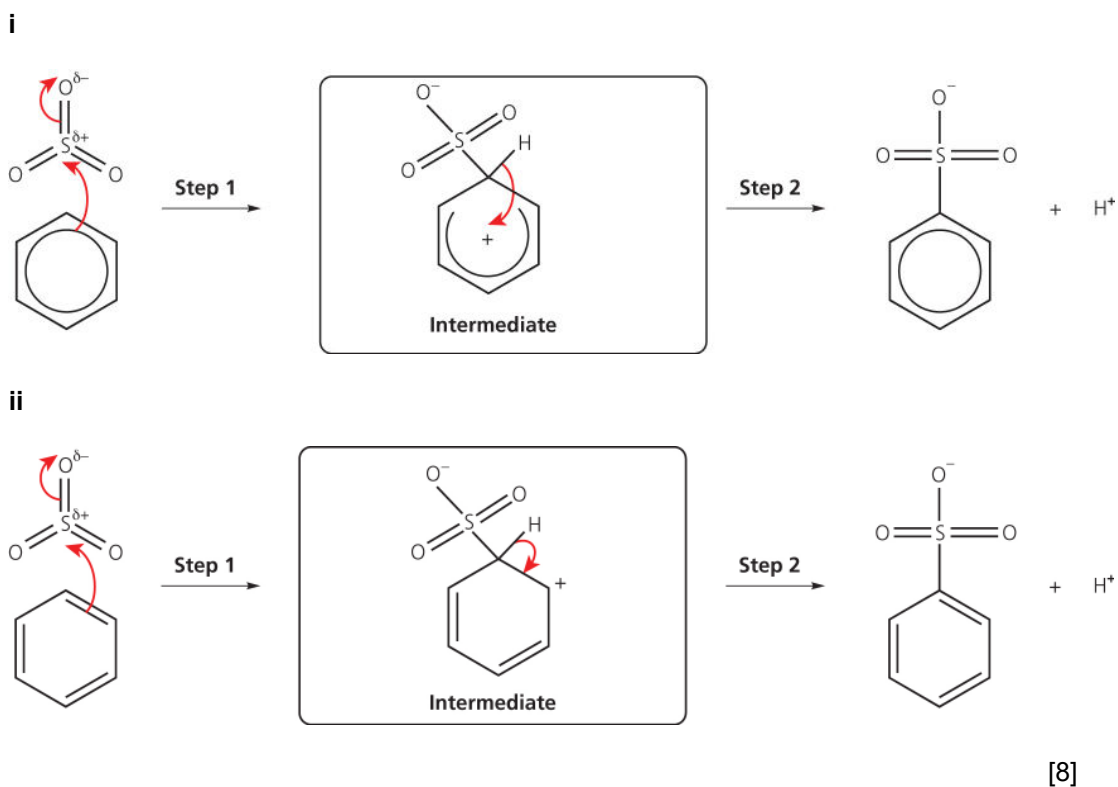
Could also use peak at $m/z = 43$ as evidence for $(\text{CH}_3\text{C}=\text{O})^+(\text{g})$.

- ii $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{COCH}_3$ [1]

1c

- i OH^- is a nucleophile in this reaction. [1]
 ii Arenes normally react with electrophiles. Harsh conditions are needed to overcome the repulsion/high activation energy. [1]

2a

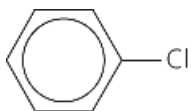


2b

- i Stage 1: must chlorinate first ✓. If nitrated first the major product would be 3-nitrochlorobenzene ✓.

Stage 1: $\text{Cl}_2/\text{AlCl}_3(\text{anhydrous})$ ✓

Intermediate product: chlorobenzene ✓



Stage 2: conc HNO_3 (H_2SO_4)

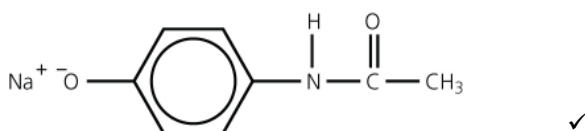
[5]

- ii $\text{ClC}_6\text{H}_4\text{NO}_2 + 6[\text{H}] \checkmark \rightarrow \text{ClC}_6\text{H}_4\text{NH}_2 + 2\text{H}_2\text{O} \checkmark$

[2]

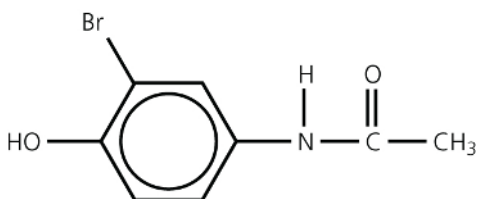
2c

- i Reaction with Na:



Observation: effervescence/bubbles ✓

Reaction with Br_2 :

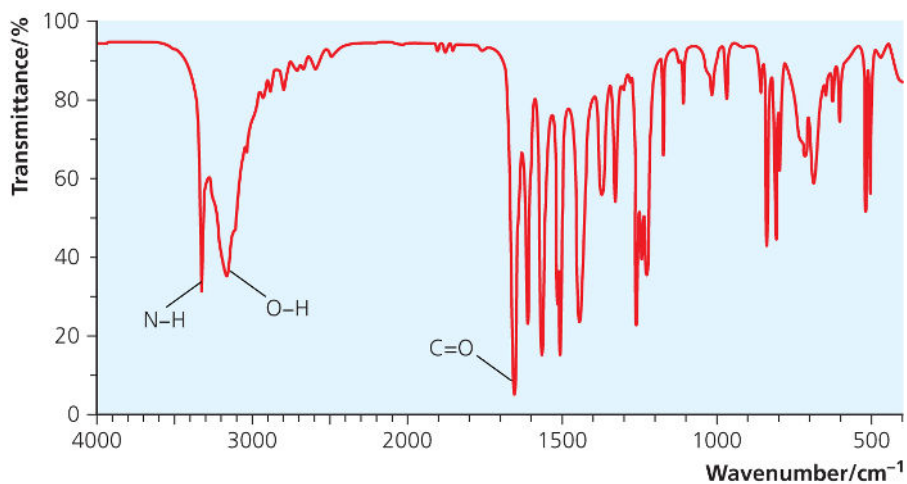


At least one H replaced by a Br anywhere on the ring. ✓

[4]

Observation: decolorises bromine/white precipitate. ✓

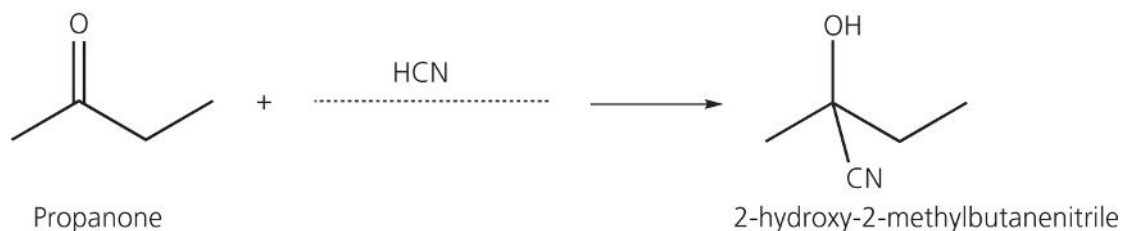
- ii



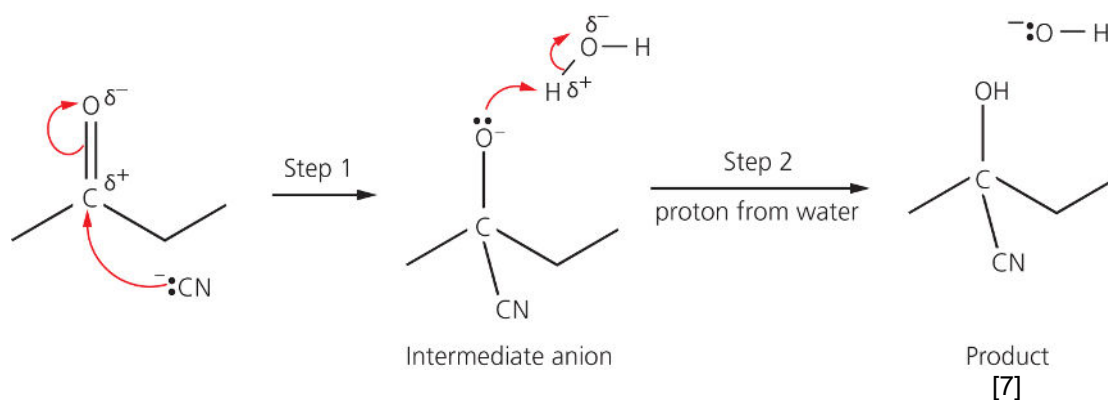
Carbonyl compounds

Reactions of carbonyl compounds

1a

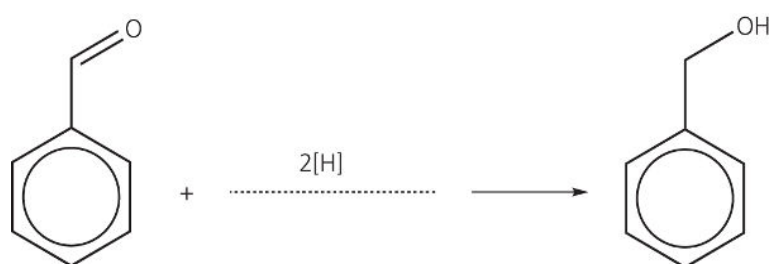


Mechanism is nucleophilic addition. Product is 2-hydroxy-2-methylbutanenitrile. [3]

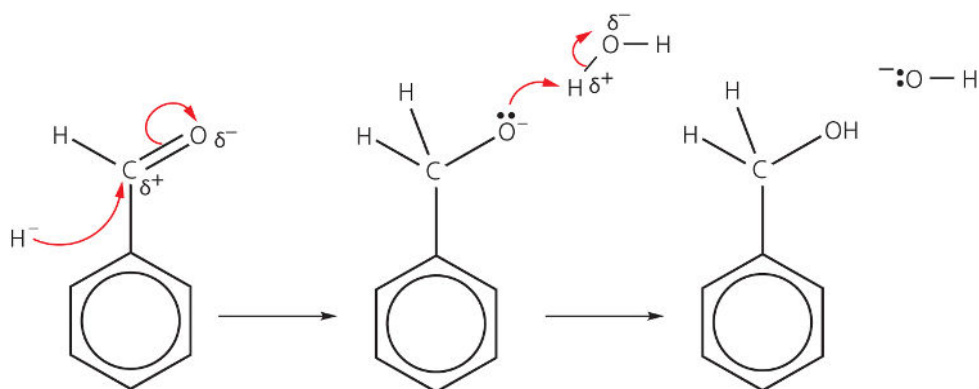


4x ✓ for the mechanism

1b



Mechanism is nucleophilic addition. Product is phenylmethanol. [3]



[7]

4x ✓ for the mechanism

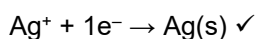
Characteristic tests for carbonyl compounds

- 2a** To 3 cm³ of AgNO₃(aq) add 1 drop of NaOH(aq). A brown precipitate of AgO(s) will be formed. Add dilute NH₃(aq) drop by drop until the precipitate just re-dissolves. ✓
Place in a beaker of water at about 60°C for about 5 minutes. ✓

Split the solution between two test tubes. Add 4 drops of propanal to one test tube and 4 drops of propanone to the other test tube. [3]

- 2b** The test tube with the propanal will produce a silver precipitate/mirror and the one with the propanone will not. ✓ CH₃CH₂CHO + [O] → CH₃CH₂COOH ✓

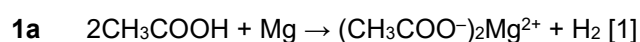
and



[3]

Carboxylic acids and esters

Properties of carboxylic acids



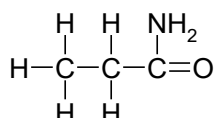
Esters and acyl chlorides

- 2a** Propan-2-ol, CH₃CH(OH)CH₃

- 2b** Thionyl chloride, SOCl₂

- 2c** Dimethylamine, (CH₃)₂NH

- 2d** Propanamide



[8]

Exam-style questions

1a

- i $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ ✓ [1]
- ii Catalyst ✓ [1]
- iii Any H_2O present would push the equilibrium to the left and reduce formation of ester ✓ [1]
- iv mol of ethanol = $6.90/46 = 0.15$ mol ✓
0.15 mol of ethanoic acid = $0.15 \times 60 = 9.0$ g ✓ [2]
- v Heat is required to initiate the reaction ✓, if distilled immediately the volatile compounds would be distilled out and disturb the equilibrium ✓. [2]

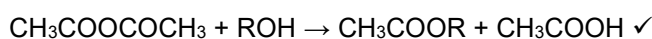
1b

- i $2\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$ ✓ [1]
- ii Use a separating (dropping) funnel and run off the lower aqueous layer ✓ [1]

1c

- i mol of ethanol used = 0.15 mol
mol of ethyl ethanoate produced = $5.28/88 = 0.06$ mol ✓
% yield $(0.06/0.15) \times 100 = 40\%$ ✓ [2]
- ii Use ethanoyl chloride or ethanoic anhydride instead of ethanoic acid ✓. Reaction is not reversible ✓. [2]

2 Acid anhydrides react with alcohol/phenols to produce an ester and carboxylic acid. The equation can be represented as:



$$\text{Atom economy} = \left(\frac{\text{molar mass of desired product (CH}_3\text{COOR)}}{\text{molar mass of all products (CH}_3\text{COOR} + \text{CH}_3\text{COOH)}} \right) \times 100$$

Assume molar mass of CH_3COOR is M , so the only unknown is M . Rearrange the equation and solve for M .

$$69.39 = \left(\frac{M}{M + 60} \right) \times 100 \quad \checkmark \checkmark \checkmark$$

$$69.39(M + 60) = 100M$$

$$69.39M + 4163.3 = 100M$$

$$4163.4 = 30.61M$$

Solving for M gives molar mass of $\text{CH}_3\text{COOR} = 136$ ✓

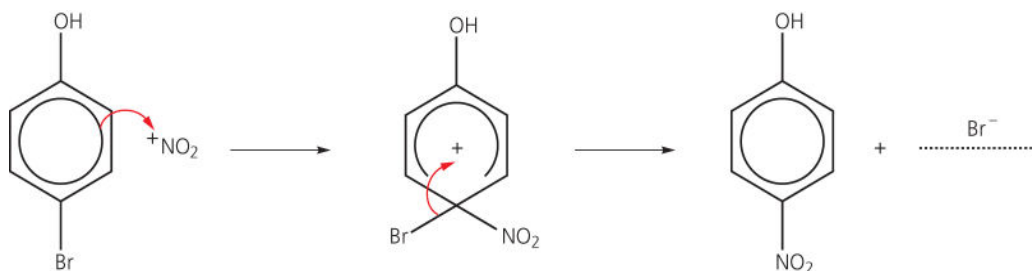
CH_3COO has mass = 59, so mass of R must be $136 - 59 = 77$ ✓

The R group is made up of only C and H, so it must be C₆H₅ (phenyl) ✓

Compound A must be C₆H₅OH ✓

[8]

3a



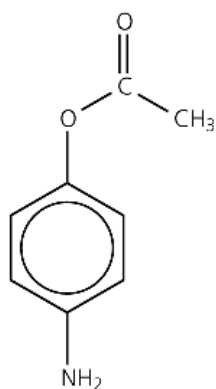
[3]

3b

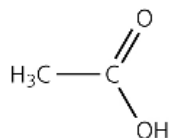
i Reagent A is HCl and reagent B is NaOH [2]

ii $\text{HOC}_6\text{H}_4\text{NO}_2 + 6[\text{H}] \rightarrow \text{HOC}_6\text{H}_4\text{NH}_2 + 2\text{H}_2\text{O}$ [2]

iii



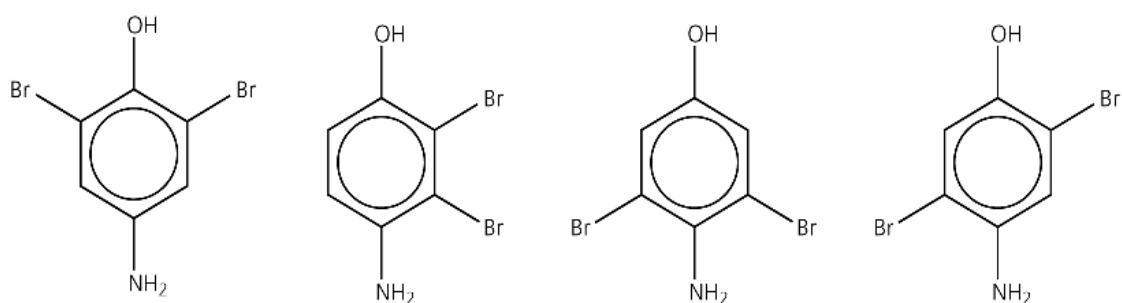
Product 1



Product 2

[2]

3c



[4]

Nitrogen compounds, polymers and synthesis

Amines

Basicity and preparation of amines

1a Compounds with no rings of carbon atoms [1]

1b Compounds with rings of carbon atoms stabilised by delocalised electrons [1]

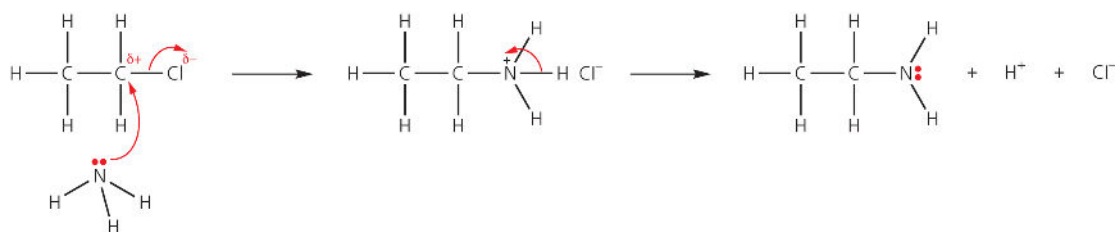
2a

i Ethanol [1]

ii Water reacts with NH_3 to produce an ammonium ion and cannot behave as a nucleophile. [1]

2b

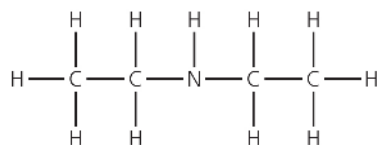
i



[5]

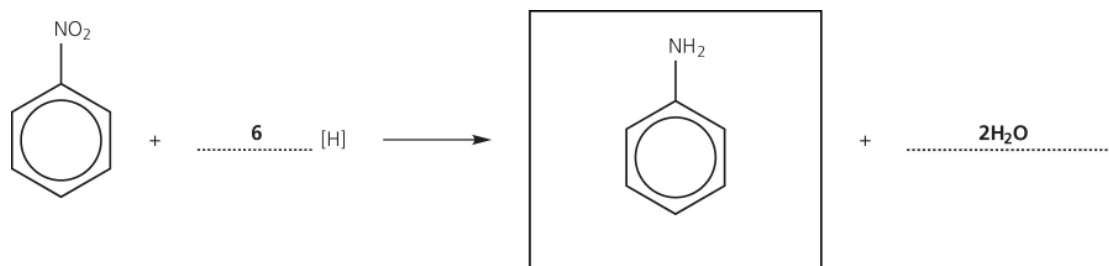
ii $\text{CH}_3\text{CH}_2\text{Cl} + 2\text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Cl}$ ✓ [1]

iii $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ or $(\text{CH}_3\text{CH}_2)_2\text{NH}$ or

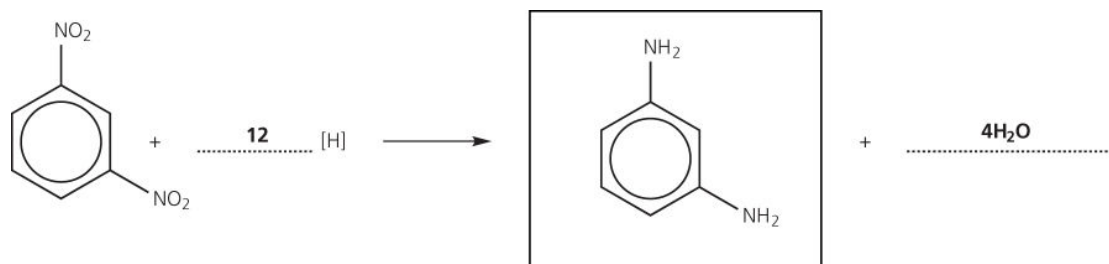


[1]

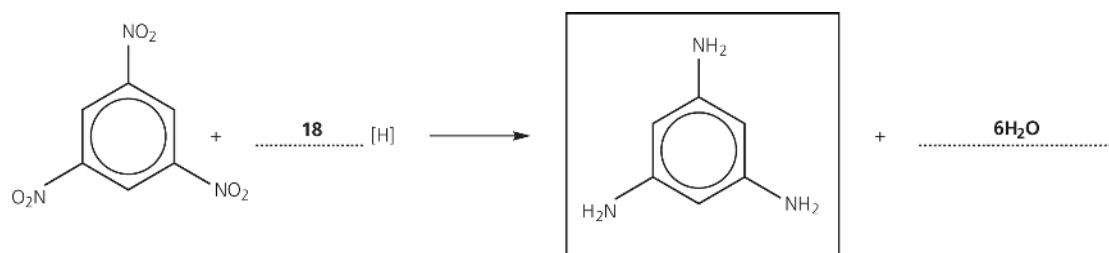
3a



3b

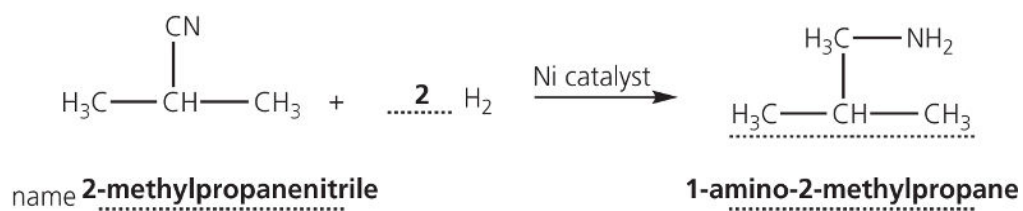
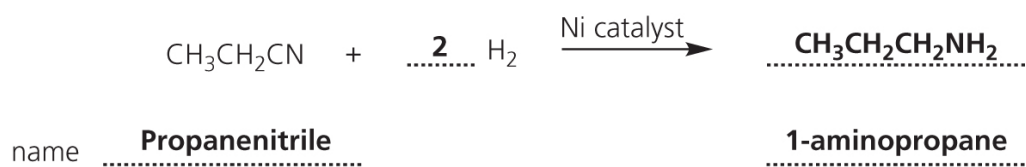


3c



[3]

4 1 mark for each equation and 1 mark for each name:



[6]

Amino acids, amides and chirality

Reactions of amino acids

1a Compound in which the amine group and the carboxylic acid group are attached to the same carbon. [1]

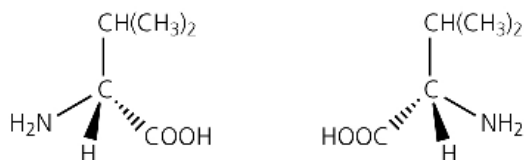
1b $\text{H}_2\text{NCH(R)COOH}$ [1]

Amides and chirality

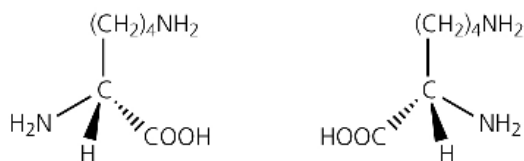
2 *Chiral* compounds are asymmetric and have non-superimposable mirror images. [1]

3a

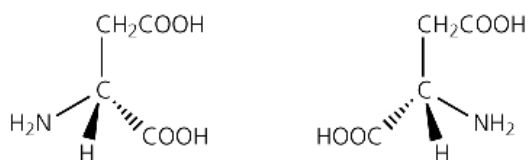
i



ii



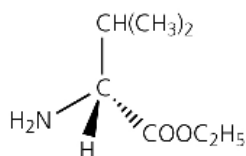
iii



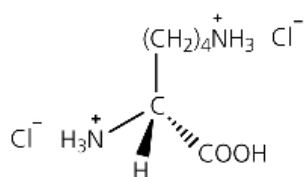
[6]

3b

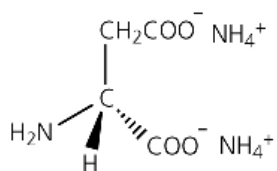
i



ii



iii



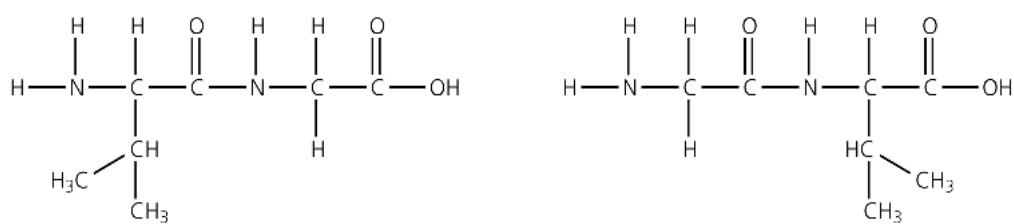
[3]

3c The central C is not bonded to four different atoms or groups: H₂HCH(H)COOH [1]

3d

i C₂H₅NO₂ + C₅H₁₁NO₂ → C₇H₁₄N₂O₃ + H₂O [1]

ii



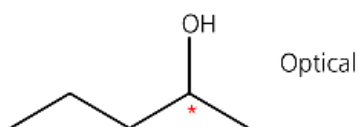
[2]

3e asp-val-lys-gly-gly-val-gly [1]

4a



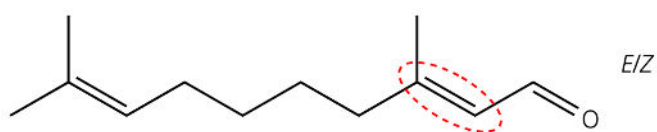
4b



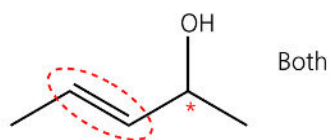
4c



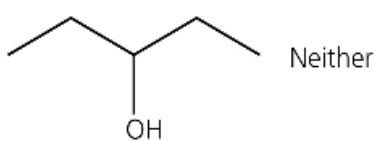
4d



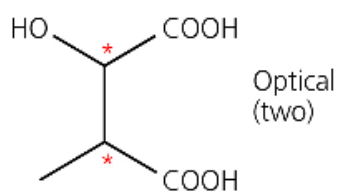
4e



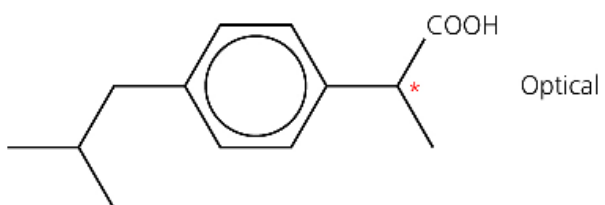
4f



4g

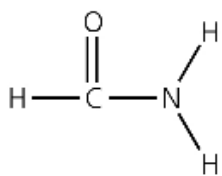


4h



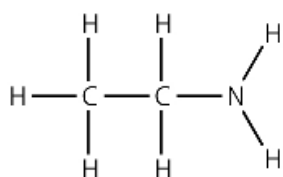
[8]

5a



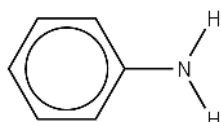
Methanamide

5b



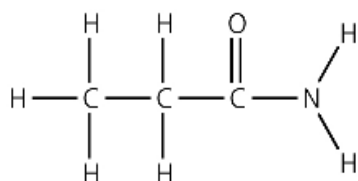
Ethylamine

5c



Phenylamine

5d

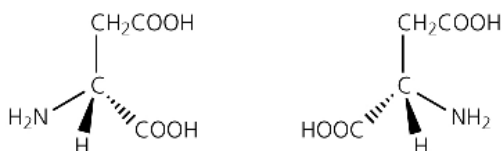


Propanamide

[4]

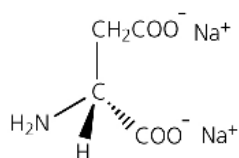
Exam-style questions

1a



[2]

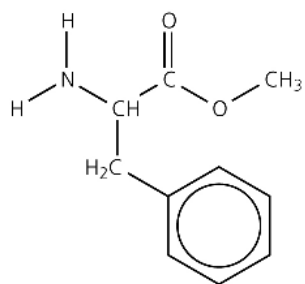
1b



[2]

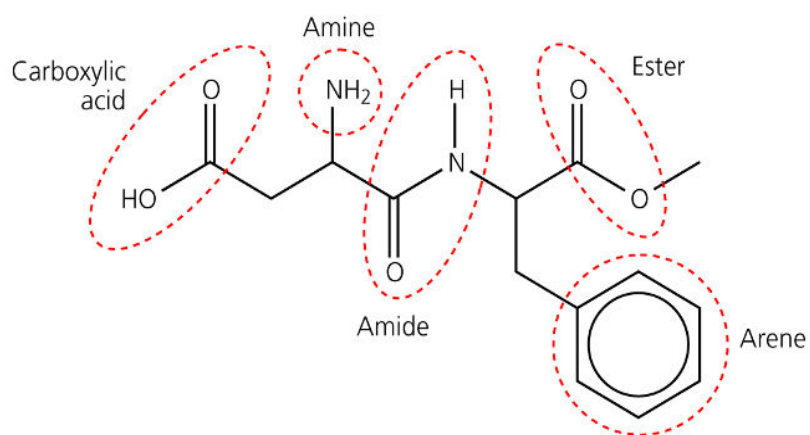
1c

i



[2]

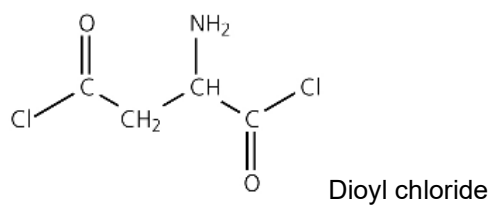
ii



[2 marks for all 5. Lose 1 mark for each error/omission]

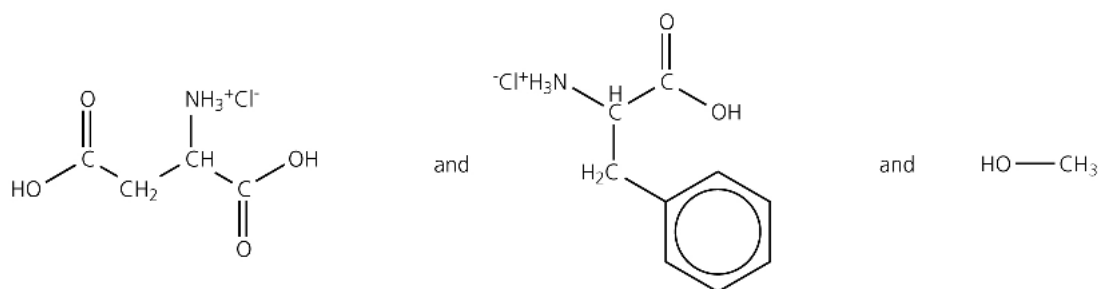
1d

i



[2]

ii



[3]

2a

Element	C	H	O
Mass/%	30.00	3.33	66.67
Ratio	$30.00/12 = 2.50$	$3.33/1 = 3.33$	$66.67/16 = 4.17$
Simplest ratio	$2.50/2.50 = 1$	$3.33/2.50 = 1.33$	$4.17/2.50 = 1.67$
Whole number ratio ($\times 3$)	3	4	5

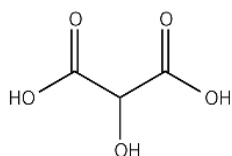
Empirical formula = $C_3H_4O_5$ ✓✓

Empirical mass = $36 + 4 + 80 = 120$, so molecular formula = $C_3H_4O_5$ ✓ [3]

2b

i $C_4H_6O_5$ [1]

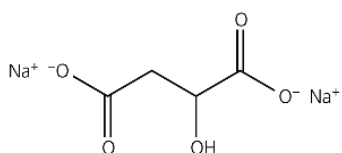
ii



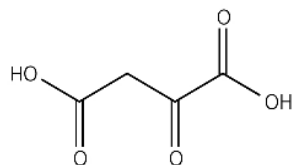
[1]

2c

i



ii

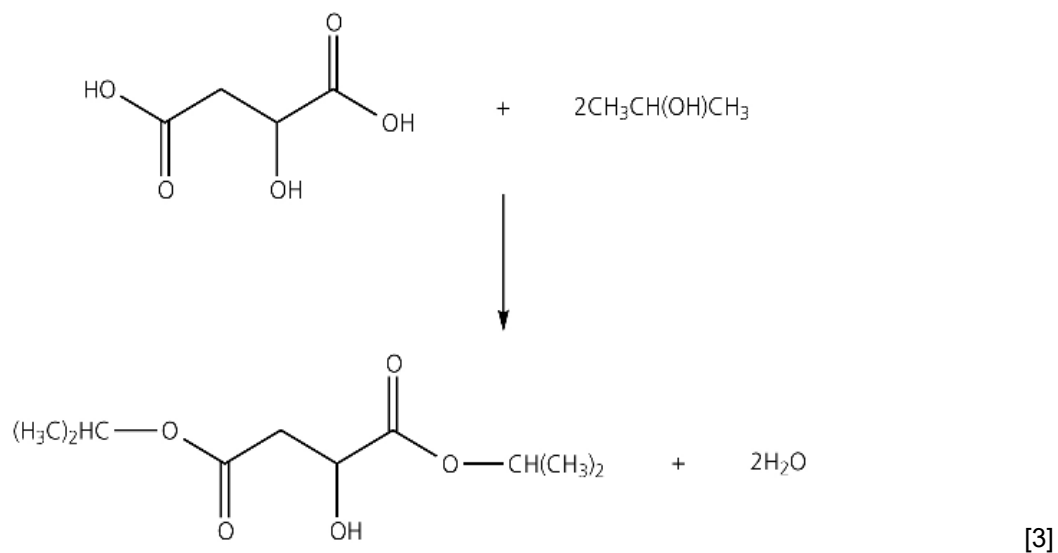


[2]

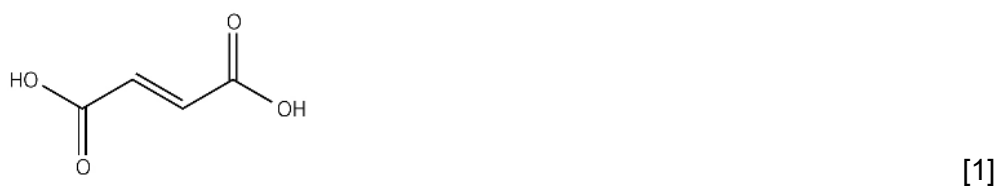
2d

i HCOOH [1]

ii

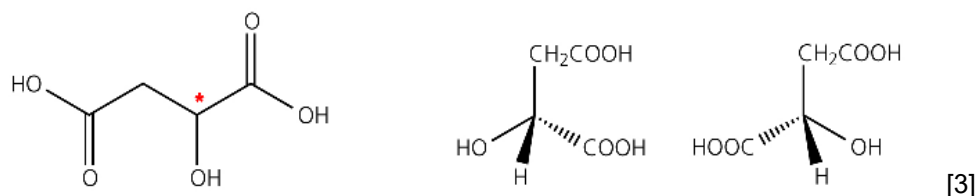


iii

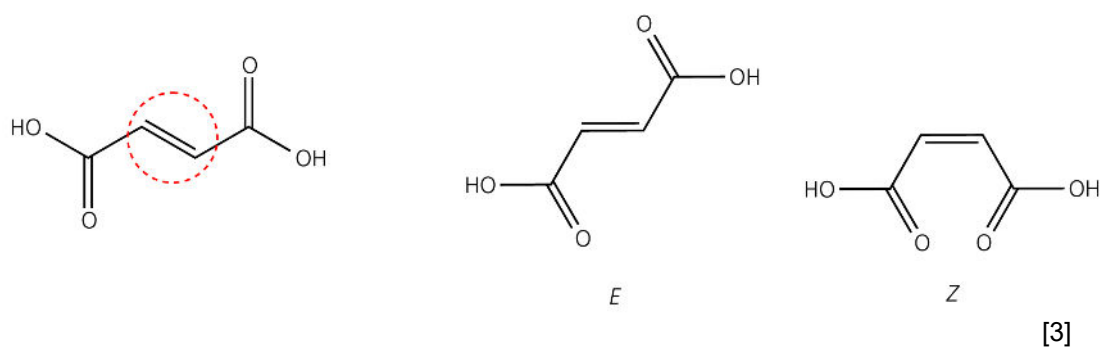


e

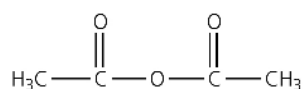
i Malic acid has a chiral carbon and forms two optical isomers.



ii Fumaric acid has a C=C double bond with each carbon bonded to two different atoms or groups and forms *E* and *Z* isomers.



3a



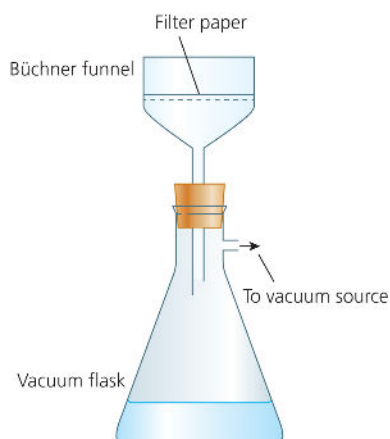
[1]

3b

i CH_3COOH

[1]

ii



[2]

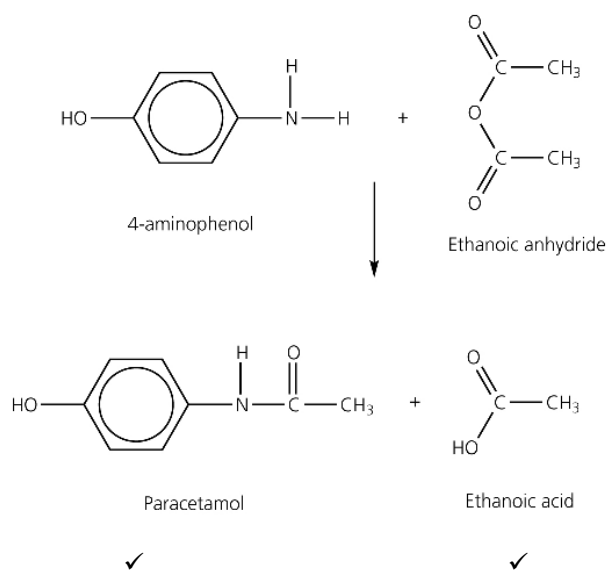
iii mol of 2-hydroxybenzoic acid = $1.05/138 \checkmark = 7.61 \times 10^{-3} \text{ mol} \checkmark$

mol of aspirin = $0.98/180 \checkmark = 5.44 \times 10^{-3} \text{ mol} \checkmark$

% yield = $(5.44 \times 10^{-3}/7.61 \times 10^{-3}) \times 100 = 71.5\% \checkmark$

[5]

3c



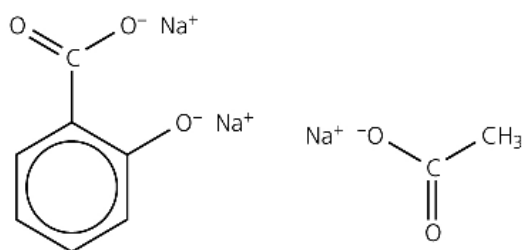
[2]

3d Melting points would be lowered \checkmark and melting would not be sharp but spread over a range of temperatures \checkmark .

[2]

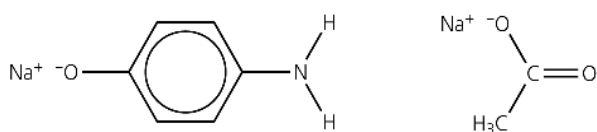
3e

i



[3]

ii



[2]

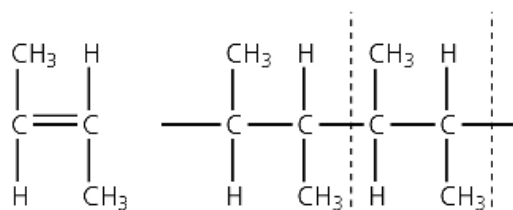
3f $\text{Na}_2\text{CO}_3(\text{aq})$ ✓ reacts with COOH ✓ in aspirin but not with the phenol in paracetamol. [2]

3g Br_2 ✓ reacts on the benzene ring of paracetamol because it is activated by the OH group ✓. [2]

Polyesters and polyamides

Condensation polymers

1a

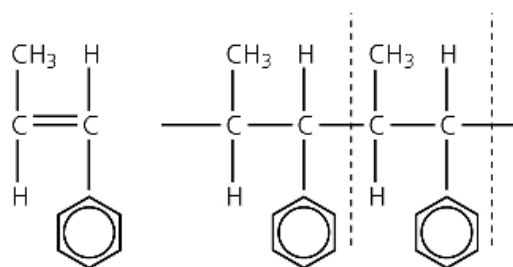


But-2-ene

Repeat unit

[1]

1b

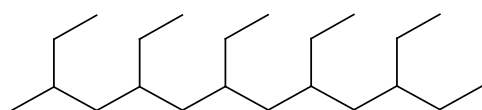


Phenylethene

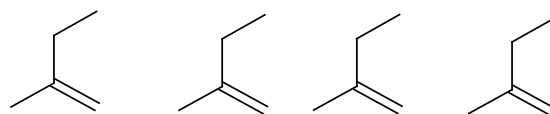
Repeat unit

[1]

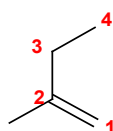
2



polymer



monomer



monomer is 2-methylbut-1-ene

[1]

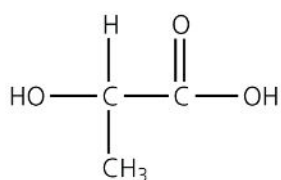
3 A condensation polymer is formed by the elimination of a small molecule such as H₂O or HCl ✓ between monomers to generate a long-chain polymer. ✓ [2]

4a

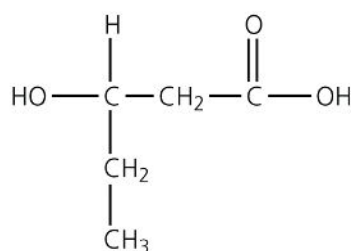
i Ethane-1,2-diol	ii Benzene-1,4-dioyl chloride	iii 1,4-diaminohexane	iv Hexanedioic acid
HO-CH ₂ CH ₂ -OH		H ₂ N(CH ₂) ₆ NH ₂	HOOC(CH ₂) ₄ COOH

[4]

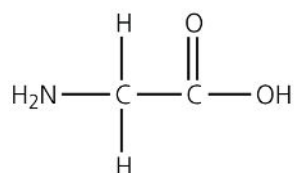
4b



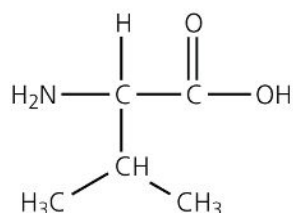
2-hydroxypropanoic acid



3-hydroxypentanoic acid



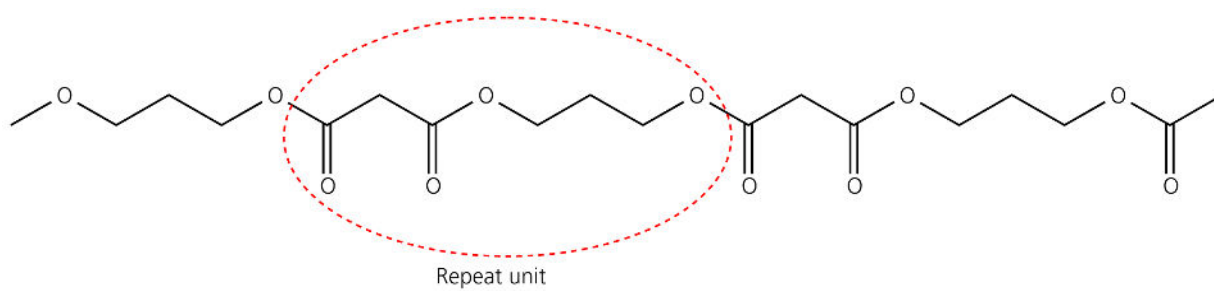
Aminoethanoic acid (glycine)



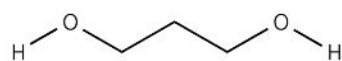
2-amino-3-methylbutanoic acid (valine)

[4]

5a

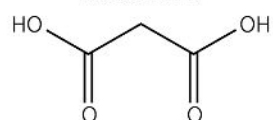


Monomer 1



Propane-1,3-diol

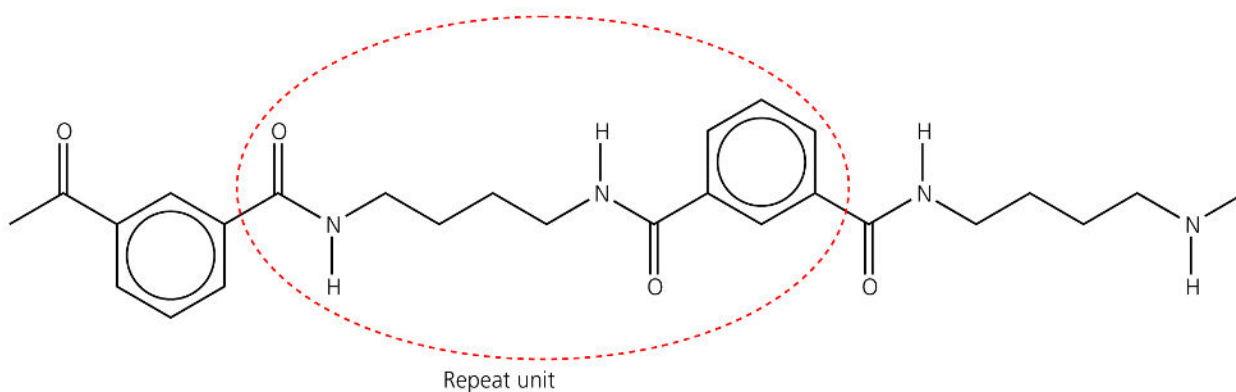
Monomer 2



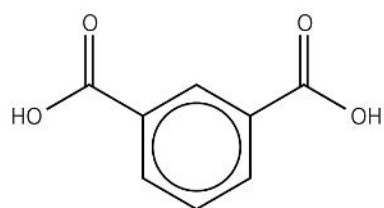
Propanedioic acid

[3]

5b

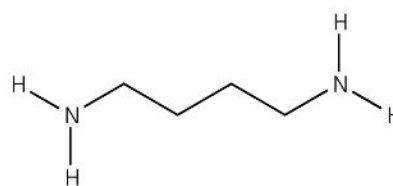


Monomer 1



Benzene-1,3-dioic acid

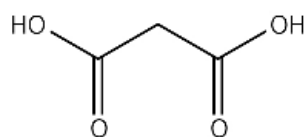
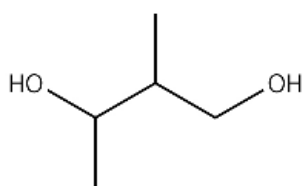
Monomer 2



1,4-diaminobutane

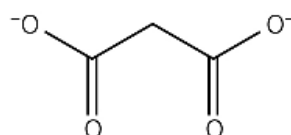
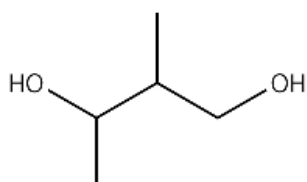
[3]

6a



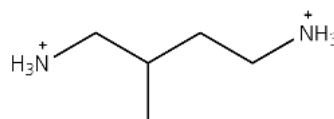
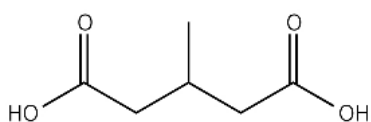
[2]

6b



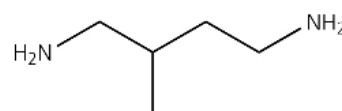
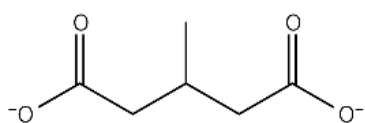
[2]

6c



[2]

6d



[2]

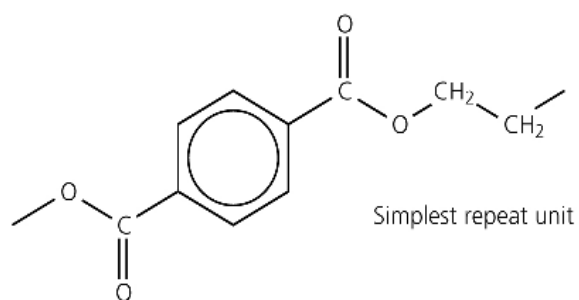
Exam-style question

1a

- i The single monomer ethene, $\text{H}_2\text{C}=\text{CH}_2$, can add together to form an addition polymer ✓. The dioic acid and the diol can react to form a condensation polymer ✓ and condense out H_2O . ✓ [3]

All marks could be achieved by suitable equations.

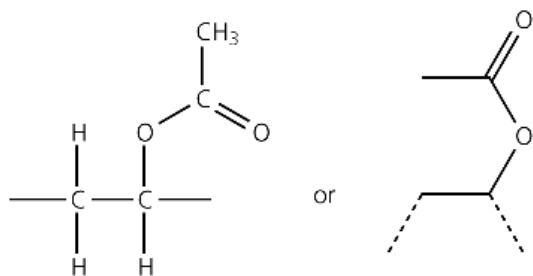
ii



[2]

1b

i

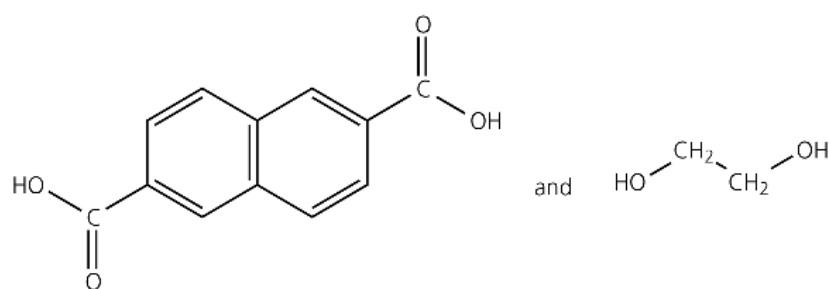


[1]

ii Reagent = dilute HCl or NaOH ✓ Conditions warm gently/reflux ✓

[2]

1c



[2]

Carbon-carbon bond formation

Extending carbon chain length

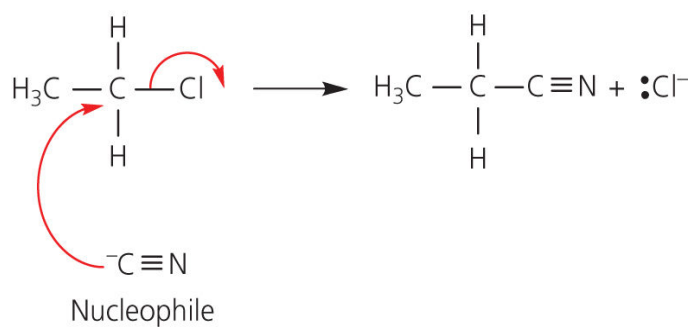


[1]

1b Ethanol

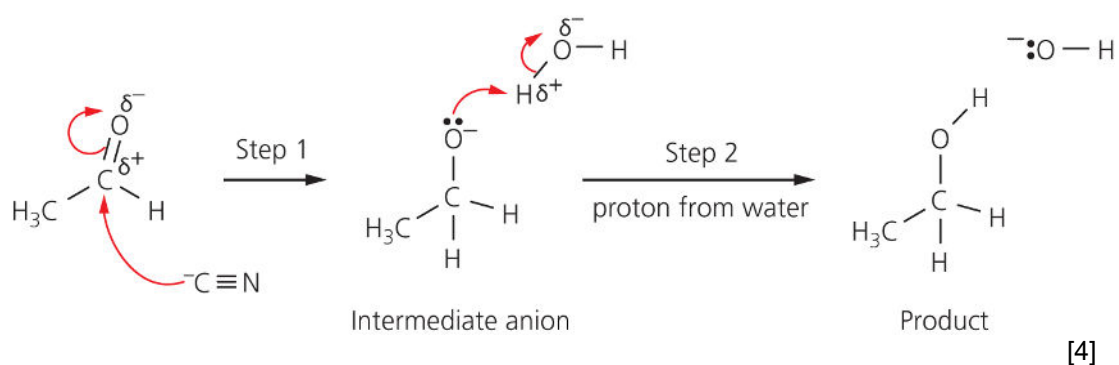
[1]

1c

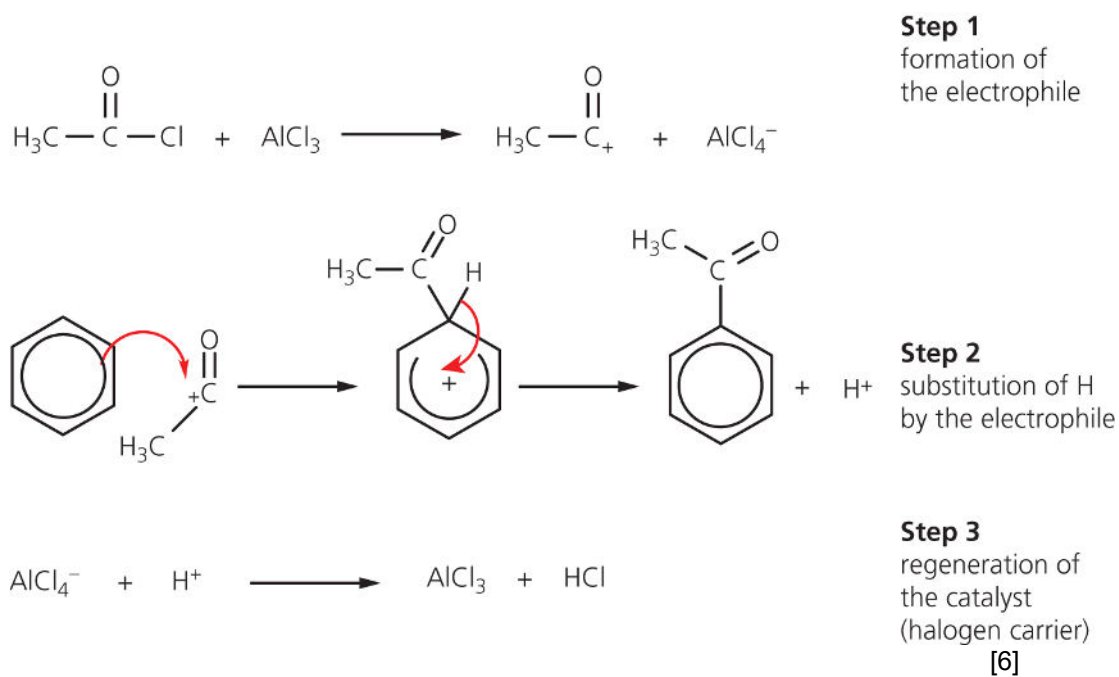


[3]

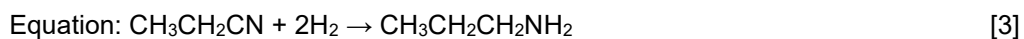
1d



2 Reagents CH_3COCl
 Conditions AlCl_3 (catalyst/halogen carrier) anhydrous
 Mechanism

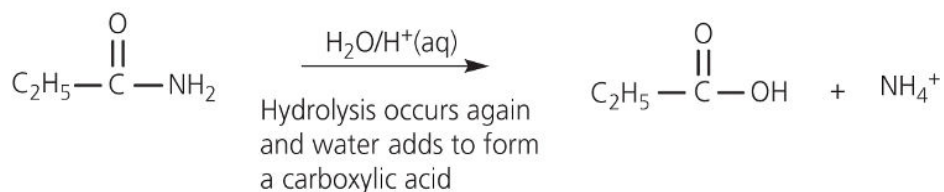
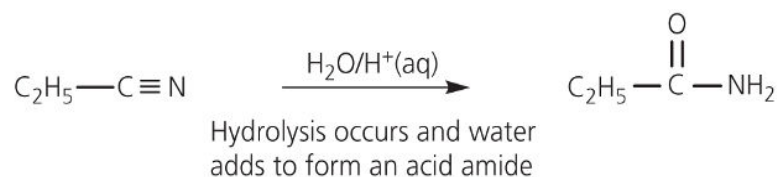


3a Reagent = H_2 , conditions: Ni catalyst

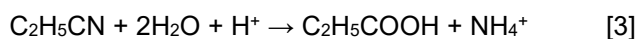


3b Reagent = acid/H⁺, conditions = (aq)

Equation:



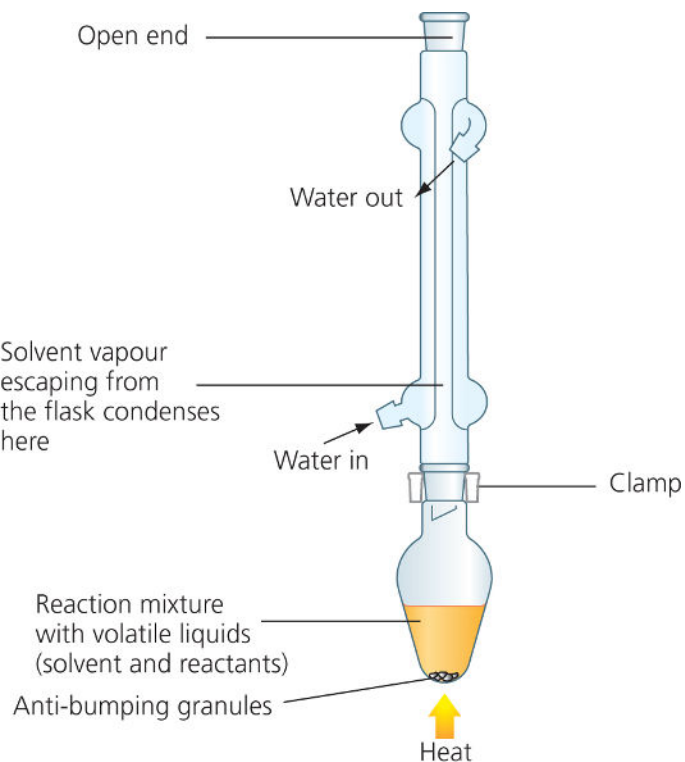
The net reaction for acid hydrolysis is:



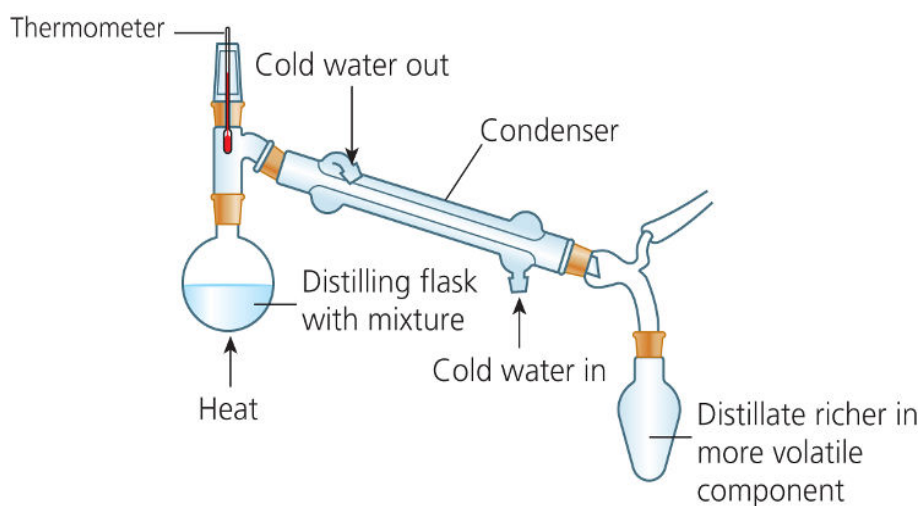
Organic synthesis

Practical skills

1a Reflux



1b Distillation



[2]

Synthetic routes

2a Dissolve impure sample in minimum amount of hot water.

Filter while hot to remove insoluble graphite.

Allow to cool and filter cold solution to remove insoluble benzoic acid.

Wash with cold water and leave overnight to dry.

[4]

2b Melting point: should be sharp melting (at 122°C) if pure (impurities lower the melting point and increase the range over which it melts).

[2]

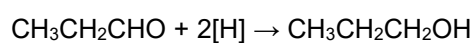
3

Test	Observation	Inference
Add litmus	Turns red	Carboxylic acid or phenol
	Turns blue	Amine
Add Br ₂	Decolorises	Alkene
	Decolorises and white precipitate formed	Phenol
Add Na	Effervescence/bubbles	Carboxylic acid, phenol or alcohol
Add Na ₂ CO ₃ (aq)	Effervescence /gas (CO ₂) given off, bubbles, fizzes	Carboxylic acid
In water bath at about 60°C with AgNO ₃ (aq)/ethanol	White, cream or yellow precipitate formed	Haloalkanes

Test	Observation	Inference
Tollens' reagent/ $\text{Ag}^+(\text{NH}_3)_2$	Silver mirror formed	Aldehyde
Heat with $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$	Colour changes from orange to green	Primary alcohol, secondary alcohol, aldehyde
Add water	White fumes of HCl given off	Acyl chloride
Warm with NaOH(aq)	Smell of NH_3 gas (which turns litmus blue)	Amide

[10]

- 4 Stage 1 Reduce propanal to propan-1-ol with NaBH_4

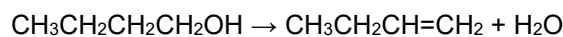


- Stage 2 React alcohol with HBr (made *in situ* from $\text{NaBr}/\text{H}_2\text{SO}_4$)

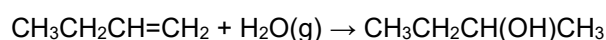


[6]

- 5 Stage 1 React butan-1-ol with hot concentrated H_2SO_4 (approx. 170°C)



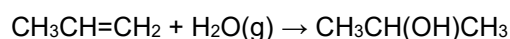
- Stage 2 React but-1-ene with steam in presence of acid (H_3PO_4) catalyst



This will follow the Markownikoff rule.

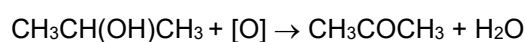
[6]

- 6 Stage 1 React propene with steam in presence of acid (H_3PO_4) catalyst

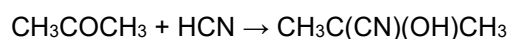


This will follow the Markownikoff rule.

- Stage 2 Reflux with $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ to oxidise propan-2-ol to form propanone

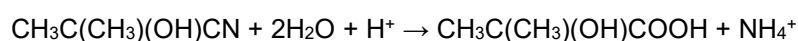


- Stage 3 React propanone with HCN



$\text{CH}_3\text{C}(\text{CN})(\text{OH})\text{CH}_3$ can be written as $\text{CH}_3\text{C}(\text{CH}_3)(\text{OH})\text{CN}$

- Stage 4 Acid hydrolysis of 2-methylpropanenitrile



Exam-style question

- 1a** Ratio C:N:H = 77.42/12 : 15.05/14 : 7.53/1
Empirical formula C:N:H = 6.45:1.075:7.53 = 6:1:7 = C₆NH₇ ✓
Mass spectrum shows molecular ion at $m/z = 93$ so molecular formula also C₆NH₇ ✓
Infrared spectrum shows N–H in region 3300–3500 cm⁻¹ ✓
Compound B is C₆H₅NH₂ ✓ [4]
- 1b** Stage 1 nitration of benzene
Reagent: conc HNO₃ ✓ Conditions: conc H₂SO₄ catalyst / temp 50–60°C ✓
Equation: C₆H₆ + HNO₃ → C₆H₅NO₂ + H₂O ✓
Stage 2 reduction of nitrobenzene
Reagent: Sn and conc HCl ✓ Conditions: warm ✓
Equation: C₆H₅NO₂ + 6[H] → C₆H₅NH₂ + 2H₂O ✓
Stage 3 reaction of phenylamine with acyl chloride
Reagent: CH₃COCl ✓ Conditions: anhydrous/fume cupboard ✓
Equation: C₆H₅NH₂ + CH₃COCl → C₆H₅NHCOCH₃ + HCl ✓ [9]

Analysis

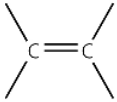
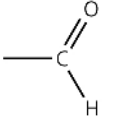
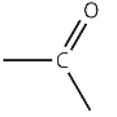
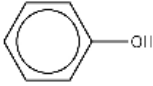
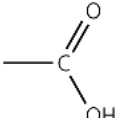
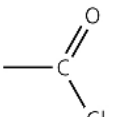
Chromatography and qualitative analysis

Types of chromatography

- 1a** R_f value = (distance travelled by component)/(distance travelled by solvent)
- 1b** retention time — time taken for component to emerge from column after injection of sample into column. [2]
- 2** Quantitative results are difficult to achieve with TLC.
Similar compounds have similar R_f values and spots may overlap. [2]

Tests for organic functional groups

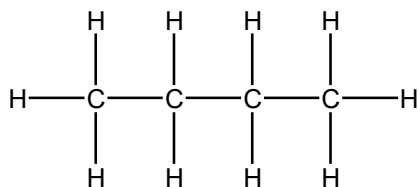
3

Functional group		Reagent/conditions	Observation	Marks
Name	Group			
Alkene		Br ₂ (aq)	Decolorised	2
Haloalkane	R—Cl	Ag(NH ₃) ₂ ⁺ (aq) in water bath at about 60°C/NaOH(aq) + AgNO ₃ (aq)/NH ₃ (aq)	Ag(halide)(s)	2
*Aldehyde		2,4-dinitrophenylhydrazine solution	Orange precipitate	2
		Tollens' test	Silver mirror	2
*Ketone		2,4-dinitrophenylhydrazine solution	Orange precipitate	2
		Tollens' test	No silver mirror	2
*Phenol		Br ₂	Decolorised and white precipitate	2
		Na(s)	Effervescence / bubbles	2
Carboxylic acid		Na ₂ CO ₃ (aq)	Effervescence / bubbles	2
Acid chloride		H ₂ O	White fumes of HCl	2
* Each of these functional groups requires a combination of two tests to confirm its presence				20

Spectroscopy

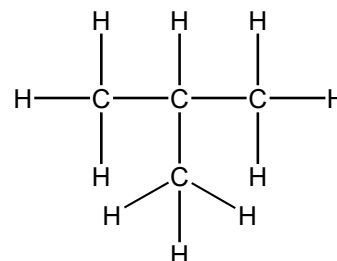
NMR spectroscopy

1



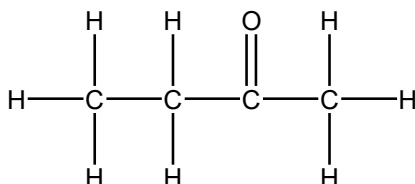
no of peaks in ¹H NMR

no of peaks in ¹³C NMR.....



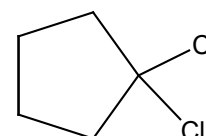
no of peaks in ¹H NMR

no of peaks in ¹³C NMR.....



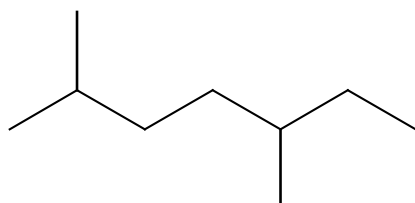
no of peaks in ¹H NMR

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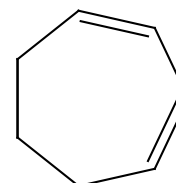
no of peaks in ¹H NMR

no of peaks in ¹³C NMR.....



no of peaks in ¹H NMR

no of peaks in ¹³C NMR.....



no of peaks in ¹H NMR

no of peaks in ¹³C NMR.....

2a hydrogen environments = 1 ✓ carbon environments = 1 ✓ [2]

2b Any three from:

Chemically inert (doesn't react with sample)

Volatile (easy to remove from sample after)

Absorbs at higher frequency than other organic compounds (doesn't overlap with other organic compounds)

Only 1 singlet peak in both ¹H and ¹³C NMR spectra

[3]

2c

Identify the range for the ^1H environment		Identify the range for the ^{13}C environment	
Chemical environment	δ	Chemical environment	δ
$\text{CH}_3\text{CH}_2\text{OH}$	0.5–2.0	$\text{CCH}_3\text{CH}_2\text{OH}$	5–50
CH_3COOH	2.0–3.0	CH_3COOH	160–220
CH_3CHO	2.0–3.0	CH_3CHO	160–220
$\text{C}_6\text{H}_5\text{CH}_3$	2.0–3.0	$\text{C}_6\text{H}_5\text{CH}_3$	110–160
$\text{CH}_3\text{CH}_2\text{OH}$	0.8–12.0	$\text{CH}_3\text{CH}_2\text{NH}_2$	30–70
$\text{CH}_3\text{CH}_2\text{OH}$	3.0–4.2	CH_3CHCH_3	5–50
CH_3COOH	10.2–12.0	$\text{CH}_3\text{CHBrCH}_3$	20–50
$\text{CH}_3\text{CH}_2\text{CH}_3$	0.5–2.0	$\text{CH}_3\text{COOCH}_3$	160–220
$\text{CH}_3\text{COCH}_2\text{CH}_3$	2.0–3.0	CH_3COCH_3	160–220
C_6H_6	6.5–8.0	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	50–90
CH_3CHO	9.0–10.0	$\text{CH}_3\text{-O-CH}_3$	50–90
CH_3OH	3.0–4.2	$\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$	160–220
$\text{CH}_3\text{COOCH}_2\text{CH}_3$	3.0–4.2	$\text{CH}_3\text{CONHCH}_3$	160–220
$\text{C}_6\text{H}_5\text{OH}$	0.8–12.0	$\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$	30–70

- 3 Spectrum 1 is compound C ✓ because it has 2 peaks ✓ in region 5–50 ppm ✓
 Spectrum 2 is compound A ✓ because it has 3 peaks ✓ (in the region 0–70 ppm) ✓
 Spectrum 3 is compound D ✓ because it has 2 peaks ✓ in region 90–160 ppm ✓
 Spectrum 4 is compound E ✓ because it has 4 peaks ✓ in region 90–60 ppm ✓
 Spectrum 5 is compound B ✓ because it has 4 peaks ✓ in region 5–50 ppm ✓

4 82.76% C and 17.24% H gives

ratio C : H = 82.76/12 : 17.24/1

C : H = 6.90 : 17.24

so ratio 1 : 2.5 so empirical formula is C_2H_5 . ✓

Empirical mass = 29 molar mass = 58 so molecular formula is C_4H_{10} ✓

It could be butane or methylpropane. ^{13}C NMR has 4 peaks: butane has 4 different C environments ✓ whereas methylpropane only has 2 C environments ✓. Therefore, it is butane. [4]

5a i If undeuterated solvents were used (e.g. $CHCl_3$), the H would absorb and interfere/overlap with the spectrum of the sample. ✓

ii If deuterated solvents (e.g. $CDCl_3$) are used, the 2D absorbs at frequencies that do not interfere/overlap with the spectrum of the sample. ✓ [2]

$CDCl_3$ or any other deuterated solvent ✓

5b

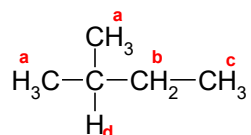
Number of H on adjacent C	Type of splitting
1	Doublet (2)
2	Triplet (3)
3	Quartet (4)
4	Pentet/quintet (5)*

[2]

* Multiplet would suffice

5c

There are 4 different H environments in methylbutane (labelled a to d) The peak ratio will be



$H_a : H_b : H_c : H_d$

6 : 2 : 3 : 1

[2]

5d

Compound	CH ₃ CH ₂ OH			CH ₃ COOCH ₃			HCOOCH ₂ CH ₃		
Number of peaks	3			2			3		
Ratio of peak areas	3 : 2 : 1			1 : 1			1 : 2 : 3		
Type of H and δ value and splitting	CH ₃	0.5–2.0	Triplet	CH ₃ (on left)	2.0–3.0	Singlet	H	2.0–3.0	Singlet
Type of H and δ value and splitting	CH ₂	3.0–4.2	Quartet	CH ₃ (on right)	3.0–4.2	Singlet	CH ₂	3.0–4.2	Quartet
Type of H and δ value and splitting	OH	0.5–12	Singlet				CH ₃	0.5–2.0	Triplet
Marks				1	1		1	1	1

5e A labile proton is a proton that is easy to exchange with other protons in the solvent, such as in O–H or N–H. These are difficult to assign as they appear in a wide range. If solvent is deuterated the proton in the O–H or in the N–H and the deuterated proton exchange and the ¹H peak disappears from the spectrum.

5f Alcohol, carboxylic acid, amine and amide.

Combined techniques

6a Infrared spectroscopy can be used to identify functional groups.

6b Chromatography can be used to separate components in a mixture.

6c Mass spectrometry can be used to determine molar mass.

6d GC is used to separate components ✓ and MS uses fragmentation ions ✓ to match with computer database ✓ to identify the component. ✓

6e ¹³C NMR is used to identify carbon environments.

6f ¹H NMR is used to identify hydrogen environments ✓ and splitting patterns ✓ give information about neighbouring environments. ✓

7 Step 1 IR shows peak in region 3200–3600 cm⁻¹ indicating an alcohol.

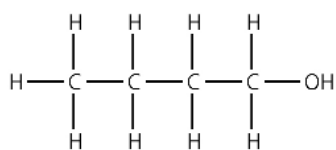
Step 2 MS has molecular ion peak at $m/z = 74$ showing molar mass to be 74 g mol⁻¹

Step 3 OH functional group has mass = 17, molar mass = 74 therefore the rest of the molecule = 74 – 17 = 57. (Assuming only one –OH group is present)

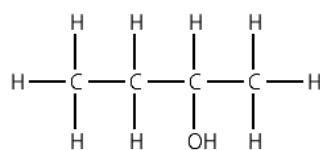
Step 4 The rest of the molecule is the carbon & hydrogen hence it must be made up of 4 carbons (48) and 9 hydrogens so the formula is C₄H₉OH.

Step 5 ¹³C NMR shows there are 3 different C environments.

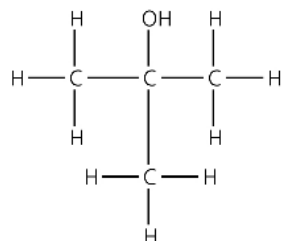
Step 6



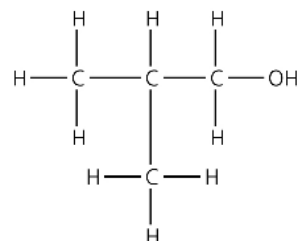
4 C environments



4 C environments

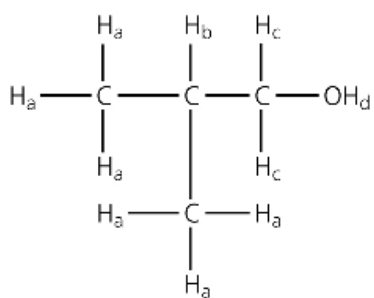


2 C environments



3 C environments

Step 7



H_a is split into a doublet, as it is next to C–H.
Chemical shift is 0.5–2.0 as next to C in chain.

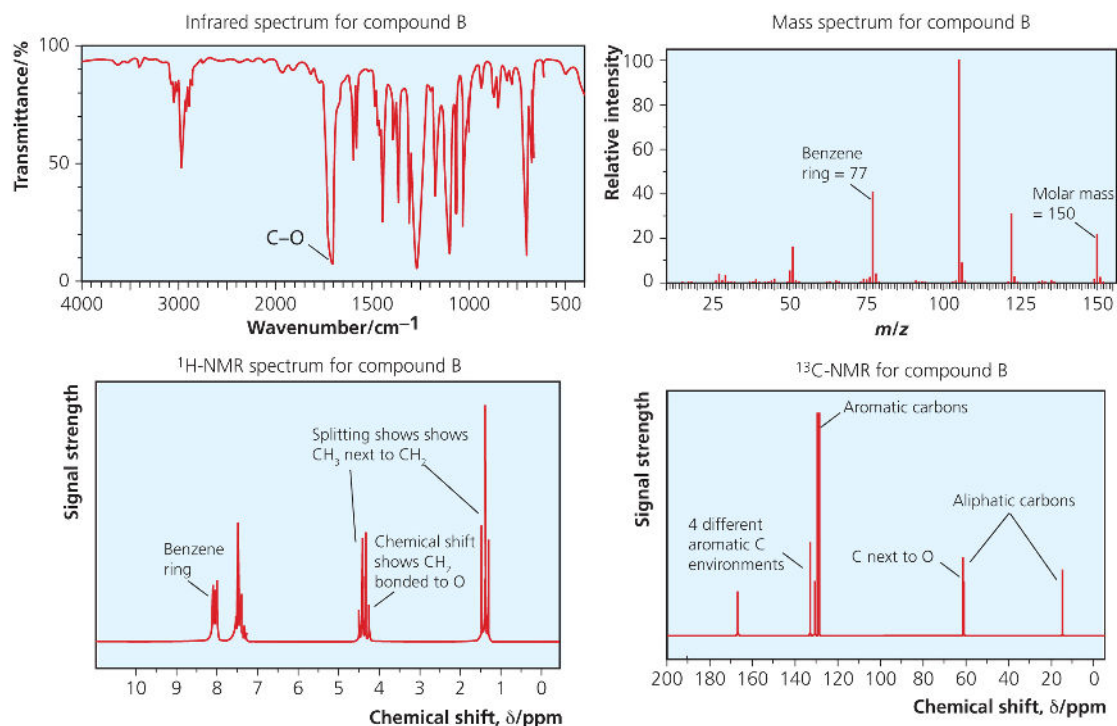
H_b is split into a multiplet, as it is next to 8H_s, but in different environments.

H_c is split into a doublet, as it is next to C–H.
Chemical shift is 3.0–4.2 as next to O.

H_d is a singlet.

Hence the compound is methylpropan-1-ol.

- 8 There are numerous ways this can be approached. It is possible to simply label key features on each spectrum and to use them to build the unknown molecule. However, a much better approach is to write out each step in full and explain your logic, so that the marker/examiner can follow your approach.



A possible mark scheme is:

- C=O identified in IR ✓
- Molar mass deduced from MS ✓
- Benzene ring deduced from either MS or ^1H NMR ✓
- CH_3CH_2 deduced from peaks at 1.2 and 4.3 in IR ✓
- CH_2 bonded to an O deduced from chemical shift in IR ✓
- Four different C environments in benzene ring deduced from peaks around 130 in ^{13}C NMR ✓

Compound B is $\text{C}_6\text{H}_5\text{COOCH}_2\text{CH}_3$. ✓

There are many different ways in which the chemical could have been identified

Exam-style questions

1a

- Each peak was counted as a separate ester ✓ [1]
- Similar compounds have similar retention times ✓ and peaks might overlap so that what looks like one peak may be made up of more than 1 ester ✓ [2]

- 1b Mass spectrum shows molecular ion = 150 ✓ Ester group COO has mass = 44, rest of molecule has mass = 106 and consists of 8C (96) and 10H, molecular formula is $\text{C}_9\text{H}_{10}\text{O}_2$. ✓✓

^{13}C NMR shows nine different C environments. ✓

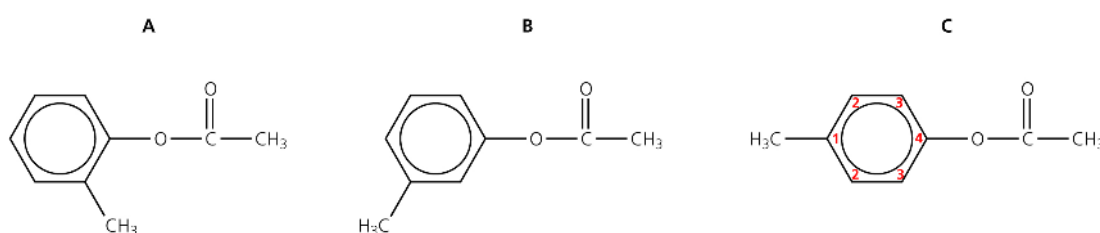
^1H NMR shows aromatic carbons. ✓

^{13}C NMR shows that each of the aromatic carbons are non-equivalent. ✓

Chemical shifts: ^1H NMR shows the aliphatic protons in region 2–3 ppm, so must be either HC– bonded to a C=O and/or a benzene ring ✓ (or a N) and four aromatic protons, so must be two aromatic protons substituted ✓.

Hence it contains:

- a benzene ring with a methyl group attached ✓
- a methyl group attached to C=O of the ester which is attached to the ring ✓



Isomers A and B each have six different carbon environments in the benzene ring and one for each of the aliphatic carbons, giving a total of nine peaks.

Isomer C would have four peaks due to the aromatic carbons and one for each of the aliphatic carbons, giving a total of seven peaks. ✓✓✓

A would have 9, B would 9 and C would have 7.

So it is either A or B [13]

1c The fragmentation pattern in the mass spectra ✓ of the two isomers could be identified using a computer database. ✓ [2]

2a Instant decolorisation of Br_2 suggest it contains an alkene group, C=C. ✓

Reaction with $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ indicates either a primary alcohol, a secondary alcohol or an aldehyde. ✓✓ [3]

2b Mass spectrum shows molecular ion at $m/z = 132$

Wet tests show either primary alcohol, secondary alcohol or aldehyde but infrared spectrum shows must be aldehyde ✓, because there is a peak at approx. 1700 cm^{-1} and there isn't a peak in region $3200\text{--}3600\text{ cm}^{-1}$. ✓

Mass of compound = 132, mass of functional groups (C=C = 24 + C=O = 28) = 52 so the rest of the molecule has a mass of $132 - 52 = 80$. ✓

The rest of the compound is C and H, hence 6C and 8H. ✓

Molecular formula = $\text{C}_6\text{H}_8 + \text{C}=\text{C} + \text{C}=\text{O} = \text{C}_9\text{H}_8\text{O}$.

Mass spectrum: peak A $m/z = 132 = \text{C}_9\text{H}_8\text{O}^+(\text{g})$ ✓

peak B $m/z = 103 = \text{C}_8\text{H}_7^+(\text{g})$ ✓

(Allow $\text{C}_7\text{H}_5\text{O}^+$)

peak C $m/z = 77 = \text{C}_6\text{H}_5^+(\text{g})$ ✓

C_6H_5 is benzene ring with 1 H substituted C_6H_5-

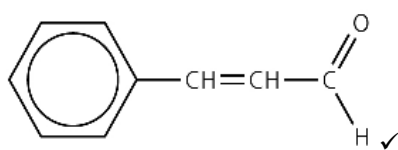
C_8H_7 must be benzene ring attached to C_2H_2 : $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-$ ✓

(Allow $\text{C}_6\text{H}_5\text{CO}$)

$\text{C}_9\text{H}_8\text{O}$ must be $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-$ attached to CHO ✓

(Allow $\text{C}_6\text{H}_5\text{COCHCH}_2$, which can be ruled out because it is a ketone.)

To give $\text{C}_6\text{H}_5-\text{CH}=\text{CHCHO}$:



[10]