A-Level Chemistry

Organic Synthesis

Mark Scheme

Time available: 78 minutes
Marks available: 72 marks

1.

(a) Dehydration

Allow (acid catalysed) Elimination

M1

Conc H_2SO_4

Allow Conc H_3PO_4

M2

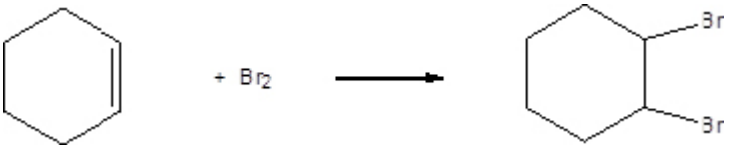
(b) Br_2

Allow bromine (water)

Allow Cl_2 or I_2

Allow O_2 if epoxide route used

M1



allow conseq equation to H_2, H_2O, HBr, HCl. HI and H_2SO_4

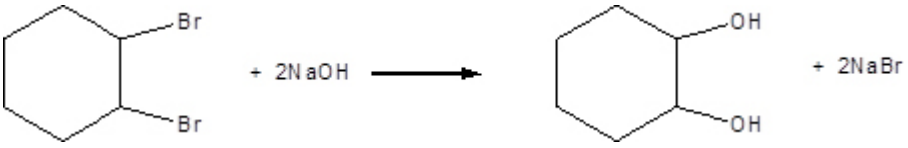
An epoxide is a feasible alternative that could score here and consequentially M3 and M4

M2

NaOH

***Or** KOH or other suitable strong alkali*

M3



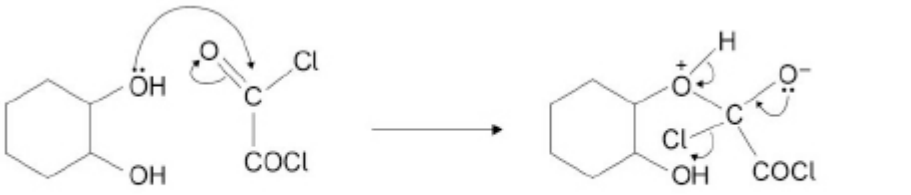
Allow this equation with molecular formulae

M4

(c) **M1** (nucleophilic)addition-elimination

Note lone pair required for M5

M1



M2 curly arrow from lp on O to C
M3 curly arrow from double bond to O
M4 for structure of intermediate
M5 for 3 curly arrows

M2
M3
M4
M5

(d) Less energy used **OR** Better yield

OR *reduces practical losses, simpler plant,*

M1

Less waste **OR** Less pollution

OR *maximises the use of raw materials in the process into useful products, saves resources*

M2

[13]

2. (a) 3-bromo-(2)-methylpropan-1-ol ONLY

3 and 1 are essential, 2 may be omitted, but any other number here is wrong

Ignore hyphens and commas

1

(b) Bromine is more electronegative than carbon

Allow difference in electronegativity if polarity of bond shown

M1

C is partially positive / electron deficient

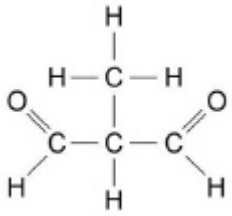
M2 and M3 can be awarded from diagram that shows nucleophilic attack

M2

Lone/electron pair (on the nucleophile) donated to the partially positive carbon

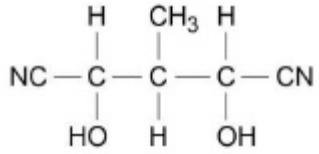
Allow lone pair attracted to / attacks the partially positive carbon

M3

(c) 

Must be displayed with all bonds shown

1

(d) 

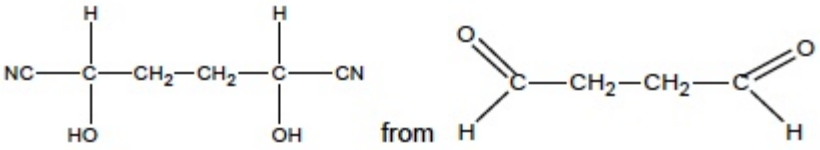
Not need be displayed

See General Marking instructions section 3.12 for penalties for incorrectly drawn bonds such as C–HO or C–NC etc.

1

KCN & (dil) acid

Allow



Allow HCN

Ignore alcoholic solvents

Penalise conc. HCl, H_2SO_4 or any HNO_3

1

[7]

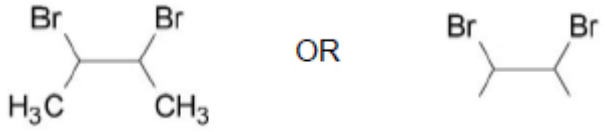
3. (a) 2,3-dimethylbutane(-1,4-)dioic acid

Penalise other numbers.

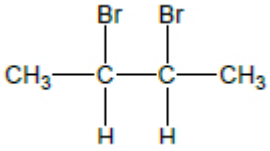
Ignore hyphens, commas, spaces.

1

(b)



Allow displayed formula



1

Step 1:

HBr

1

Electrophilic addition

1

Step 2:

KCN

Not HCN, not KCN with acid.

1

Nucleophilic substitution

1

Step 3:

Hydrolysis

1

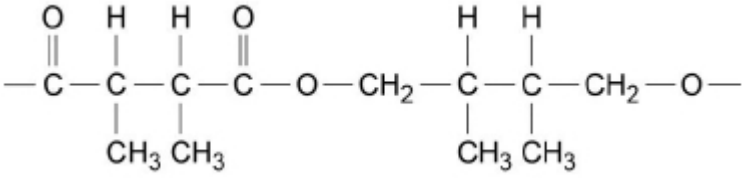
(c)

	Mark
Reagent	1
Observation with **F**	1
Observation with **G**	1

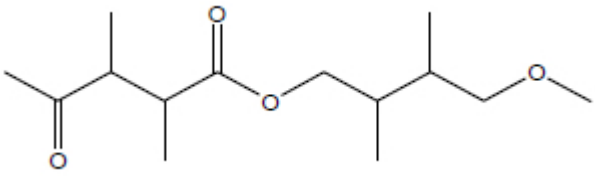
$K_2Cr_2O_7$ & H_2SO_4 (allow acidified)	**Mg**	**Na_2CO_3 or $NaHCO_3$**
F: no visible change	**F:** effervescence	**F:** effervescence
G: orange to green	**G:** no visible change	**G:** no visible change

Named alcohol and conc. sulfuric acid	**Named carboxylic acid and conc. sulfuric acid**
F: pleasant smell	**F:** no visible change
G: no visible change	**G:** pleasant smell

(d)



OR



Two ester groups.

1

One unit only.
Must have trailing bonds.
Ignore n and brackets.

1

(e) Mass of **G** = (1.11×10^3) $cm^3 \times 1.04$ g $cm^{-3} = 1154$ g

65.1 scores 4 marks.

1

Amount of **G** $\frac{1154}{Mr = 118}$ = 9.78 mols

1

Amount of **F** (actual) = $\frac{930}{Mr = 146}$ =

6.37 mol

OR

Expected mass of **F** = 9.78 × (M_r =)

146 = 1428 g

1

% yield = $\frac{6.37}{9.78}$ × 100 = 65.1(%)

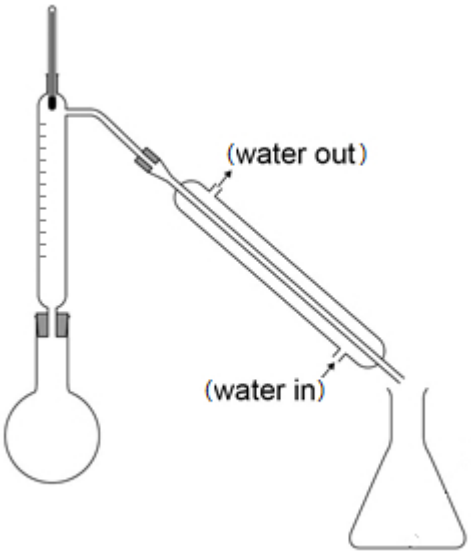
OR

% yield = $\frac{930}{1428}$ × 100 = 65.1(%)

M4 answer must be to 3 significant figures.

1

(f) Fractional distillation



A rough labelled sketch illustrating these points scores the marks.

1

Apparatus for fractional distillation must clearly work with fractionating column.

1

Fractionating column and thermometer.

1

Condenser / water jacket.

Ignore heat source.

1

[20]

4. (a) M1 NaOH

Only score M2 if M1 gained, but mark on from hydroxide. Mention of acid loses M1 & M2

1

M2 Aqueous/(warm)

Ignore alcoholic / conc / dil.

1

M3 (Fractional) distillation or described

Not just evaporation; not reflux

Allow chromatography

1

(b) M1 S is $CH_3CH(CN)CH_2CH_3$

Allow without brackets

1

Step 3

M2 KCN (mark on from CN^-)

Not HCN, not KCN with acid

1

M3 Alcoholic / (aqueous)

Allow ethanolic

Can only score M3 if M2 gained

1

Step 4

M4 H_2

$LiAlH_4$

Na

Can only score M5 if M4 gained

1

M5 Ni or Pt or Pd

Ethoxyethane or ether

$LiAlH_4$ with acid loses both M4 and M5

Ignore 'followed by acid'

Na

Ethanol

NOT $NaBH_4$ OR Sn/HCl

Penalise other extras as list

Ignore pressure or temperature

1

[8]

5.

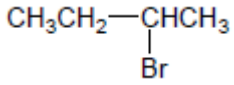
Step 1

HBr

In any step, if wrong reagent or extra wrong reagent, can only score mechanism mark,but if $AlCl_3$ added in Step 3, lose M7 but can score M8 & M9

M1

1



M2

1

electrophilic addition

If 1-bromobutane structure given for M2 then 1-aminobutane structure for M5, penalise M2 and M5 but mark M8 consequentially

M3

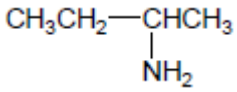
1

Step 2

NH_3

M4

1



If 1-bromobutane structure given for M2 then 2-aminobutane structure for M5, penalise M2, M5 and M8

M5

1

nucleophilic substitution

If 2-bromobutane structure given for M2 then 1-aminobutane structure, penalise M5 and M8

M6

1

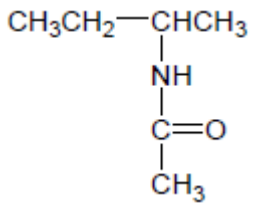
Step 3

CH_3COCl or $(CH_3CO)_2O$

Allow C_2H_5 for CH_3CH_2

M7

1



M8

1

(nucleophilic) addition-elimination

Not allow (electrophilic) addition-elimination

M9

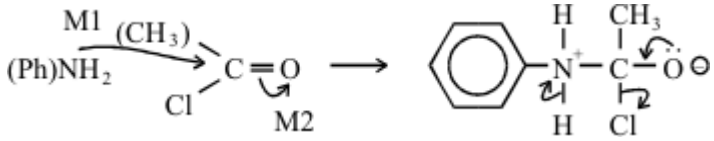
1

[9]

6. (a) CH_3COCl or $(CH_3CO)_2O$ **(1)**

$AlCl_3$ or H_2O or CH_2SO_4 loses this mark
CH_3COOH loses reagent and M3, M4 = max 3

nucleophilic addition–elimination **(1)**



M3: structure
M4: 3 correct arrows
Allow M1 for attack on CH3-C^+=O
Penalise Cl^- removing H^+

6

(b) Conc HNO_3 **(1)**

Conc H_2SO_4 **(1)**

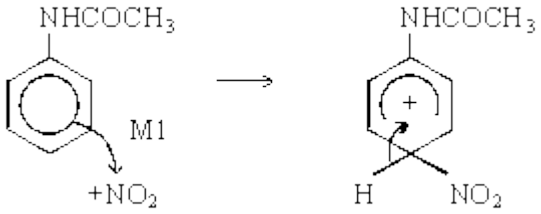
$HNO_3 + 2\ H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2\ HSO_4^-$ **(2)**

(or H_2SO_4) **(or $H_2O + HSO_4^-$)**

HNO_3 / H_2SO_4 scores 1

Any 2

electrophilic substitution **(1)**



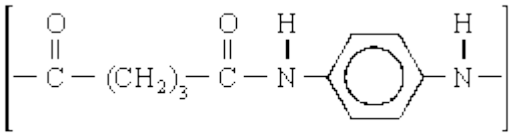
M2 structure

M3 arrow

6

(c) Sn **(or Fe)** / HCl or Ni / H_2 **(1)**

NOT $LiAlH_4$ $NaBH_4$



(1) **(1)**

3

[15]