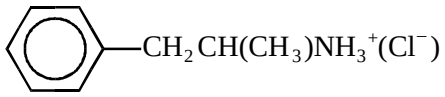
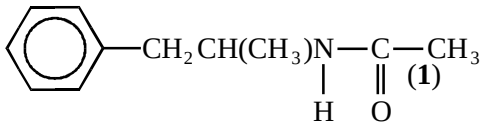
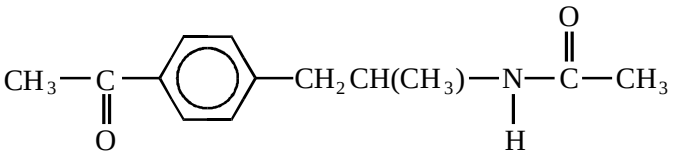
1. (a) (i) $-\ ^*CH(CH_3)-$ **(1)** 1

(ii) (the three) OH group**s** **(1)**
allow adrenalin to form **more** hydrogen bonds with water
(than does benzedrine) **(1)** 2

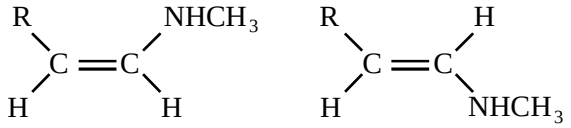
(b) (i)  1

Can use R in place of $C_6H_5CH_2CH(CH_3)-$ in both (i) and (ii)

(ii)  1

(iii) 

substitution(s) in ring at any position(s) **(1)**
production of amide **(1)** 2

(d)  2

(e) (i) $(CH(CH_3)–NH_2)^+$ **(1)** 1

(ii) $(CH_2–NH–CH_3)^+$ / $(CH(OH)CH_2)^+$ **(1)**

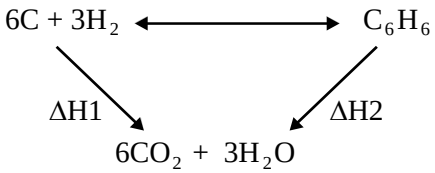
max 1 for (e) if **no** charges shown
must show some structure in answers ie. $C_2H_5N(0)$ 1

[11]

2. (a) (i) The enthalpy / heat / heat energy change / released when 1 mol of benzene is formed **(1)** from its elements **(1)** under standard conditions 2

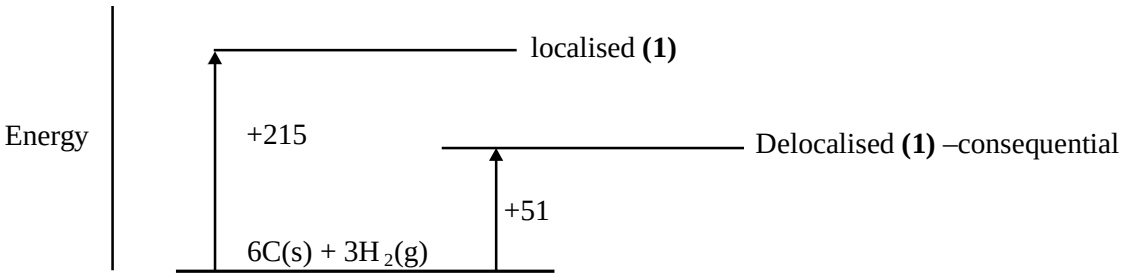
(ii) The enthalpy / heat / heat energy change when 1 mol of benzene burns **(1)** in excess oxygen / burns to form carbon dioxide plus water / is completely oxidized under standard conditions **(1)**
The second mark is not awarded if standard conditions are not mentioned in part (i) or (ii). 2

(b)



For correct cycle shown **(1)** or equivalent equations
$\Delta H1 = 6 \times (-394) + 3 \times (-286) = -3222$ kJ **(1)** for either showing calculation or answer
$\Delta Hf = -3222 - (-3273) = +51$ kJ mol^{-1} **(1)** 3

(c) Benzene has π electrons delocalised **(1)** Therefore bond energy NOT that of C–C or C=C



4

(d) (i) rate = k[benzene][bromine] 1

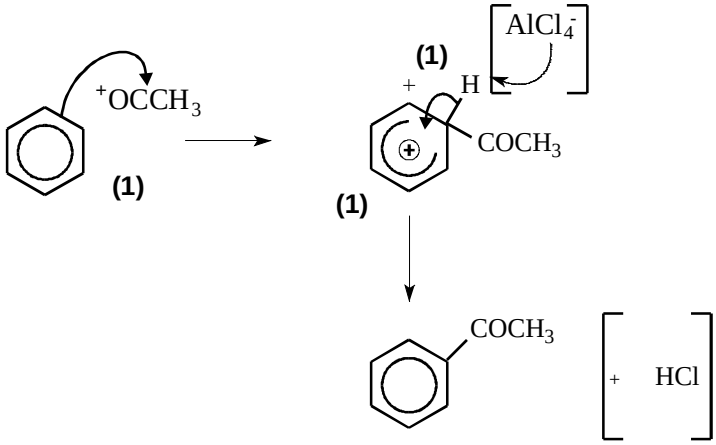
(ii) rate would be decreased **(1)**
E_a *of rate determining step* (or the idea of it) would be increased **(1)** 2

[14]

3. (a) CH_3CO^+ **(1)**

Candidate may not identify electophile but may score this mark if they use the correct electrophile in the mechanism

$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$ ***(1)*** 2

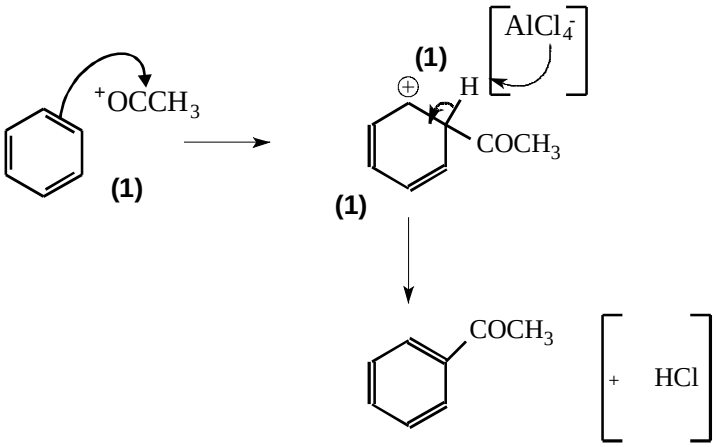


In the mechanism the electrophile can be shown as

$\delta+ \quad \delta-$

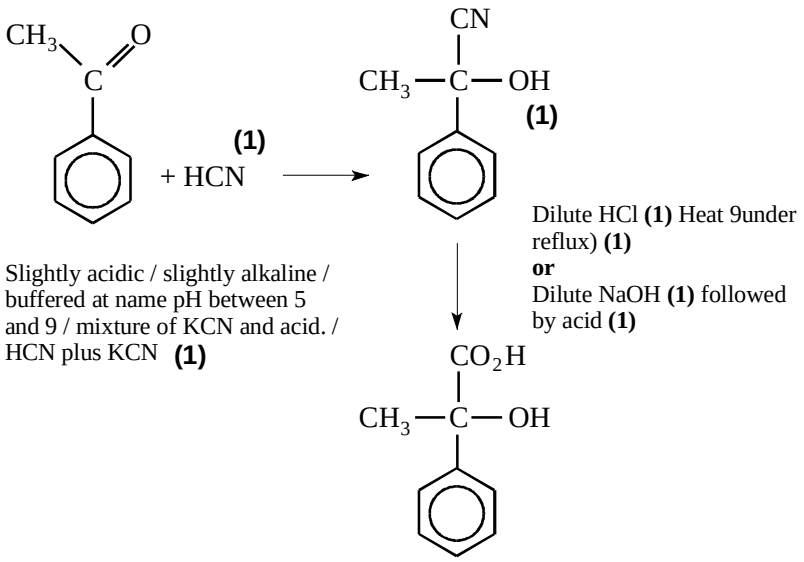
$CH_3CO - Cl^- \rightarrow AlCl_3$

(b) *Notes: The arrow for the first mark should start inside the ring and go to the carbon of the CO group.*
The arrow for the last mark should start on the bond and finish inside the ring.



3

(c) *There are several routes through this; all can score full marks*



5

[10]

4. (a) $2S_2O_3^{2-} + I_2 \rightarrow S_4O_{6+}^{2-} + 2I^-$ or clearly stated **(1)**

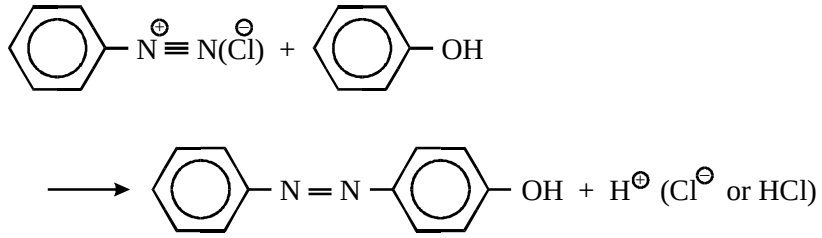
amount of thio = $26.8 \times 0.1 / 1000 = 2.68 \times 10^{-3}$ mol **(1)**
ratio of copper to thio is 1:1 **(1)**
total amount of copper = 2.68×10^{-3} mol $\times$ 10 = 2.68×10^{-2} mol **(1)**
mass of copper = 2.68×10^{-2} mol $\times$ 63.5 g mol^{-1} = 1.70g **(1)**
purity = $1.70 \times 100 / 1.74 = 97.8 / 97.7$ % **(1)** 6
allow 2 to 4 sig figs in final answer mark consequentially

(b) The increase in successive ionisation energies is similar **(1)**
compensated for by bond formation or hydration enthalpy or energy or lattice enthalpy **(1)**
catalysis involves metal ion moving from one oxidation state to another **(1)**
and back **(1)** 4

(c) (i) Sodium nitrite + aq / conc / dilute HCl / hydrochloric acid **(1)**
any temperature between 0 and 10 °C or a range between 0 & 10° C **(1)** 2

(ii) If too cold reaction too slow **(1)**
if too warm product or nitrous acid decomposes / products would be phenol and nitrogen **(1)** 2

(iii)

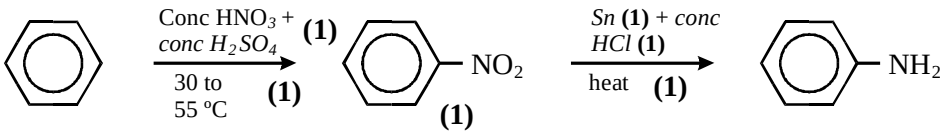


3 structures **(2)**
2 structures **(1)**
Balance **(1)**

It is not necessary to show the full structure for the diazo compound e.g $C_6H_5N_2^+$ is acceptable.

Conditions – phenol in alkali **(1)** yellow / orange / red ppt **(1)** 5

(d)

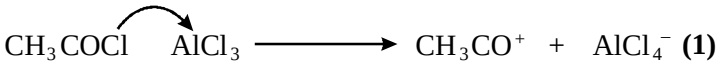


6

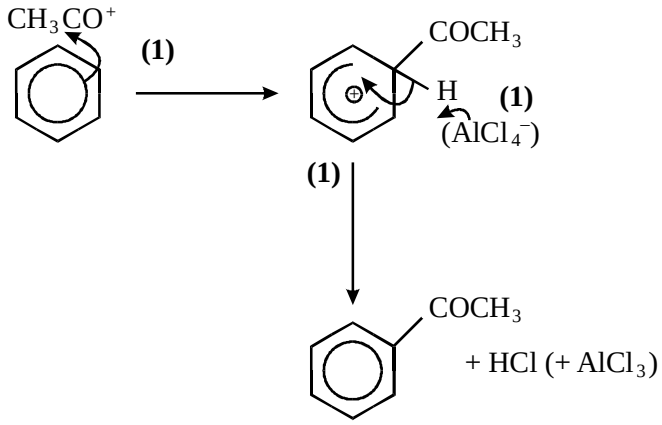
Condition mark depends on reasonable reagents
If give alternative route then – 1 for each error
Name of nitrobenzene acceptable

[25]

5. (a) (i) Aluminium chloride or $AlCl_3$ or iron(III) chloride or $FeCl_3$ **(1)**
catalyst **(1)** 2

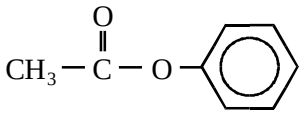


(ii)

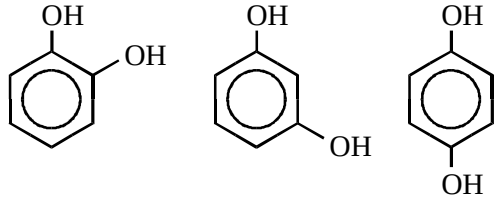


Marks:
formation of electrophile
attack on electrophile from ring
intermediate
removal of proton 4

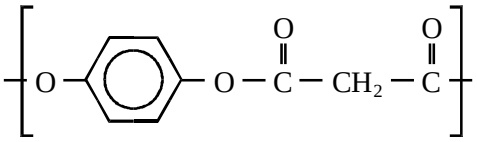
(b) Esterification / condensation **(1)**



(1) 2

(c) (i) 

Three correct 2 marks. 2 correct 1 mark 2

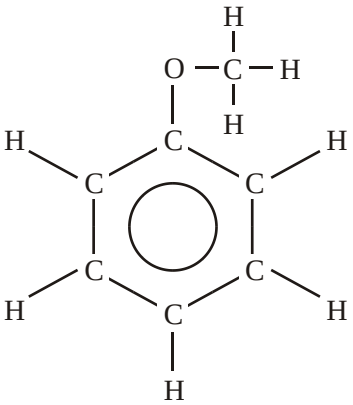
(ii) 

Ester link **(1)**
polymer / with correct benzene ring links **(1)** 2

(d) Benzene diazonium chloride (solution) / ion shown or $C_6H_5N^+{\equiv}N$ **(1)**
Sodium nitrite and hydrochloric acid **(1)**
0–10°C **(1)**
alkaline solution (of phenol) **(1)**

[16]

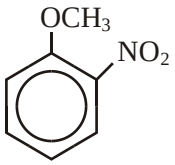
6. (a)



Fully displayed showing all C, H and circle or kekulé structure. 1

(b) Understanding of 'electrophile' – positive/electron deficient entity
ACCEPT Species that accepts a lone pair of electrons **(1)**
Understanding of 'substitution'– exchange/replace for another entity / atom / hydrogen **(1)** 2

(c)



Must contain a hexagon (with ring or kekulé inside)

Bonds must go from ring to O of OCH_3, *and to N of* NO_2 1

(d) C_7H_7OBr)
$C_7H_6OBr_2$) *Any two*
$C_7H_5OBr_3$)
HBr) 2

(e) (i) Methoxybenzenesulph/fonic acid 1

(ii) *Detergents/drugs/dyes* 1

(f) (i) D hydrogen / H_2 **(1)**
E (Raney) nickel / nickle / Ni /Platinum /Pt **(1)** 2

(ii) Addition **(1)**
Reduction **(1)** 2

(g) (i) Petroleum/**crude** oil/coal 1

(ii) Not carcinogenic / (cumulative) poison / toxic use of benzene in schools is illegal 1

[14]

7. (a) (i) Conc. sulphuric acid**(1)**
Conc. nitric acid **(1)** 2

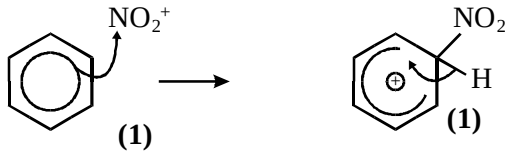
[Conc. must be stated, or implied, for both acids]

(ii) $HNO_3 + H_2SO_4 \rightarrow H_2O + HSO_4^- + NO_2^+$ **(1)**

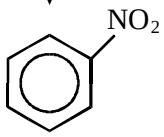
Can be shown in two stages

Or

$HNO_3 + 2H_2SO_4 \rightarrow H_3O^+ + 2HSO_4^- + NO_2^+$ **(1)**



(1) **(1)** **(1) for intermediate**

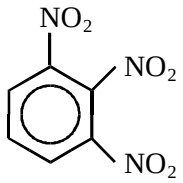


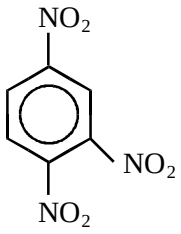
$(+ H^+)$

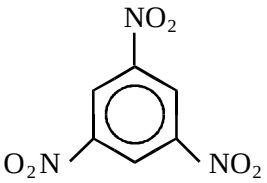
I.e. curved arrow from benzene ring of electrons towards N in NO_2^+ ion **(1)**
Intermediate correctly drawn, including positive charge **(1)**
Curved arrow from C-H bond back into benzene ring **(1)** 4

(iii) Electrophilic substitution 1

(b) 3







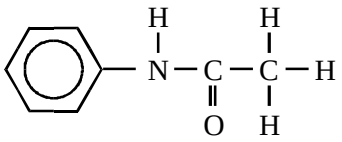
(1) **(1)** **(1)**

Vertical/right hand substituents must be shown with C to N bond
[Mark consequentially on structural formula given for "nitrobenzene" in (a)(ii)]

(c) Tin / iron and concentrated hydrochloric acid/conc. HCl **(1)**
Heat (under reflux) **(1)** 2

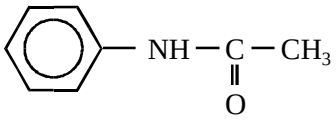
Second mark consequential on correct / "near miss" reagents

(d) (i)



1

Allow:



(ii)
- Dissolve in minimum volume **(1)**
- Of boiling/hot solvent (or any specified solvent other than water) **(1)**
- Filter through a heated funnel **(1)**
- Cool or leave to crystallise **(1)**
- Filter under suction/filter using Buchner funnel **(1)**
- Wash crystals with cold solvent **(1)** 6

NB If no solvent used, no marks available at all in part (d)(ii)

[19]

8. (a) (i) It is non-superimposable on mirror image/ it has a single asymmetric carbon atom 1

(ii) rotates the plane (of polarisation) **(1)**
of (plane–) polarised (monochromatic) light **(1)**
OR
Use a polarimeter **(1)**
rotates the plane (of polarisation) of the light **(1)** 2

(iii) product is an equimolar mixture/racemic mixture **(1)**
so rotations cancel **(1)** 2

(b) $-NH_3^+Cl^-$ on the amino group **(1)**
$-COO^-Na^+$ on the carboxyl group **(1)** 2

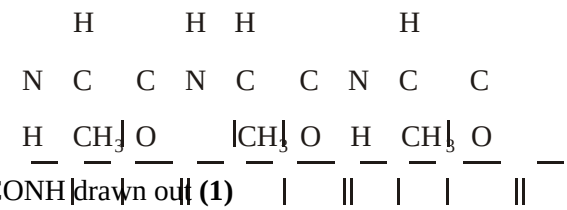
(c) Zwifterion's structure **(1)**
There is ionic attraction between adjacent zwitterions **(1)** 2

(d) (i) (polymer formed by) elimination/ removal of a small molecule/ water (between two monomers) 1

(ii) any ClOC***COCl **(1)** and $H_2N*CH_2*NH_2$ **(1)** 2

(iii) structure consequential on answer to (ii) showing amide link **(1)** and extension of the chain **(1)** 2

(iv)



2

[16]

9. (a) (i) –240 (kJ mol^{-1}) 1

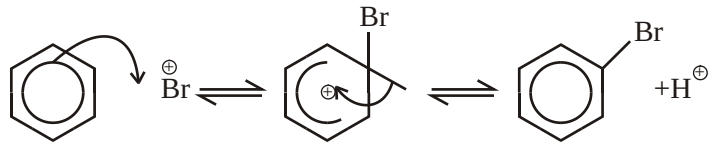
(ii) –360 (kJ mol^{-1})
Penalise incorrect units once only 1

(iii) Overlap of p-orbitals / π (system) **(1)**
(results in) delocalisation **(1)**
makes benzene (more) stable (by 152 kJ mol^{-1}) **(1)**
QWC* 3

(b) (i) $AlBr_3$/ $AIC1_3$ / $FeBr_3$ / Fe
Formula must be correct; no names 1

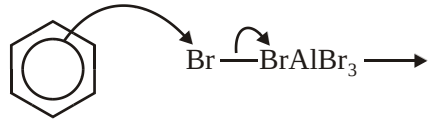
(ii) Ignore curly arrows in this first step; mark species only (consistent with catalyst)

$$Br_2 + AlBr_3 \longrightarrow \overset{\oplus}{Br} + \overset{\ominus}{AlBr_4} \quad \textbf{(1)}$$

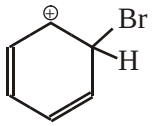


(1) **(1)** structure
(1) arrow

Alternative way of showing part played by catalyst



Allow Kekulé intermediate 4



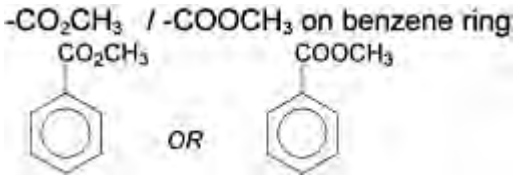
(iii) Electrophilic substitution 1

[11]

10. (a) 6

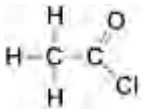
solution	X	Y
Sodium carbonate	fizzing/ effervescence/ bubbles **(1)**	no reaction / no bubbles **(1)**
Brady's reagent (2,4-dinitro phenyl hydrazine)	no change/ (stays) yellow/orange **(1)**	yellow /orange / orange-red or yellow-orange **precipitate /** (crystalline) solid **(1)**
Potassium dichromate + sulphuric acid	no change /(stays) orange **(1)**	Goes from orange to green/ brownish green/dull green **(1)**

(b) (i) 1

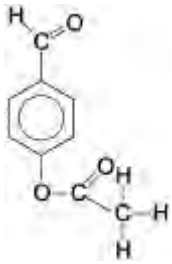


Do not allow if bond is obviously to wrong atom from benzene ring

(ii) 1



(iii) Undisplayed ester + unchanged – CHO **(1)**
Correctly displayed for both groups **(1)** 2



(iv) sulphuric acid / hydrochloric acid 1

(v) Cl (and O) electronegative/electron withdrawing **(1)**
So $C^{\delta+}$ is more/ very susceptible to nucleophilic attack/ more δ+/ more electrophilic **(1)** 2

(c) (i) Electrophiles / electrophilic 1

(ii) $Br^{\delta+}$/ Br^{+}/ $Br^{\delta+}$– $Br^{\delta-}$ 1

(iii) Any substitution product with Br on benzene ring, and other groups unchanged 1

(iv) lone pairs / electrons on **phenolic** group make ring more negative than in benzene / lone pairs on **OH** donated to ring 1

[17]

11. (a) (i) Fuming sulphuric acid / conc.sulphuric acid & sulphur trioxide **(1)**
Warm/(heat under) reflux/ hot/ high temperature **(1)**
[fuming/conc. could appear as a condition]
OR
concentrated sulphuric acid
(heat under) reflux for **several hours (1)** 2

(ii) SO_3/ SO_3H^+ 1

(b) (i)  *OR* C_6H_5Br 1

(ii) Substitution **(1)** Electrophile **(1)** 2

(iii) As **oxygen lone pair** is delocalised into ring / interacts with e^- in ring **(1)**
Benzene ring more attractive to electrophiles/greater electron density/more nucleophilic **(1)** 2

(c) (i) Ethylbenzene/Phenylethane 1

(ii) Aluminium chloride reacts with chloroethane **(1)**
Inducing a positive charge on the ethyl group **(1)**
OR correct equation showing charges
$AlCl_3 + CH_3CH_2Cl \rightarrow AlCl_4 + CH_3CH_2$ **(2)** 2

(d) (i) UV/sun light 1

(ii) 1,2,3,4,5,6-(hexa)chloro cyclohexane 1

[13]

12. (a) (i) $C_6H_5O^-Na^+$ / C_6H_5ONa / $C_6H_5O^-$ 1

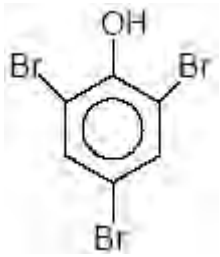
Do not allow covalent O-Na

(ii)

1

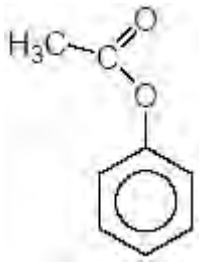
No other Isomer allowed

OR



IGNORE bond to H of OH

(iii)



1

No ring substitution allowed

(b) (i) $NaNO_2$ / sodium nitrate / nitrate(III) **(1)**

conc aq / dil HCl / hydrochloric acid **(1)**

NOT HCI

Any temperature between 0 - 10 °C

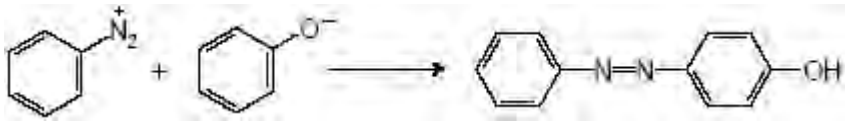
OR range between 0 - 10 °C **(1)**

NOT "less than 10 °C"

IGNORE everything before phenylamine eg starting from benzene

Conditions are dependent on correct or nearly correct reagents 3

(ii)



Correct diazonium ion **(1)** if - $^{+}N=N$ the + must be on correct N

Correct equation **(1)**
IGNORE position of OH group
Can include Cl^- if equation is balanced
ALLOW $+ C_6H_5OH \rightarrow \ldots\ldots\ldots + H^+$ 2

(iii) Alkaline / alkali / sodium hydroxide / NaOH / KOH / potassium hydroxide / sodium carbonate / sodium hydrogencarbonate
IGNORE temperature 1

[9]

13. (a) (i) Chloromethane / bromomethane **(1)**
ALLOW methyl chloride

(anhydrous) aluminium chloride **(1)**
NOT iron (III) chloride / bromide
ALLOW formulae 2

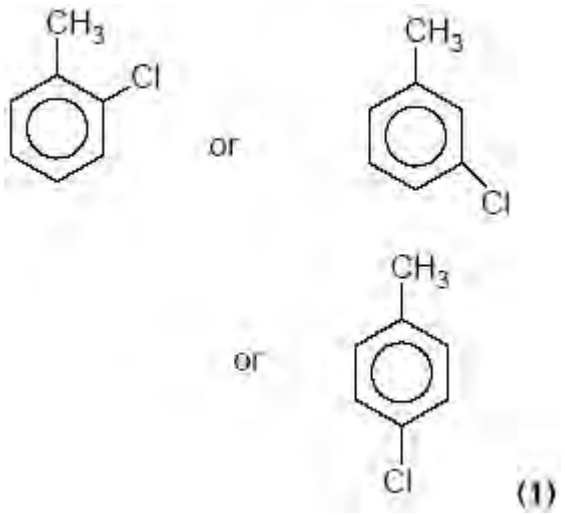
(ii) Substitution **(1)**
Electrophilic **(1)**
In any order

–1 for each extra incorrect type eg addition as well as substitution 2

(iii) $CH_3Cl + AlCl_3 \rightarrow AlCl_4^-$ and CH_3^+ / CH_3^+ $AlCl_4^-$ **(1)**
ALLOW TE with $FeCl_3$

and the positive ion/electrophile is then attracted to the (delocalised) electrons in the benzene ring/negative benzene ring **(1)** 2

(b) (i)



(1)

2 (or 3 or 4)-chloro(-1-)methylbenzene **(1)** – *must be consistent with formula*
ALLOW 1-chloro-4-methyl benzene / 1methyl-4-chlorobenzene etc 2

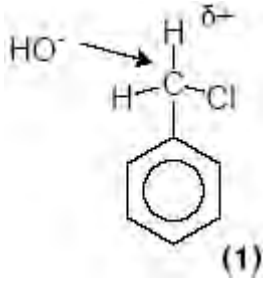
(ii) Chlorine (in an inert solvent) **(1)**
NOT aq/H_2O

iron OR iron(III) chloride **(1)**
Mark independently
ALLOW formulae 2

(c) (i) Substitution **(1)**
Nucleophilic **(1)**
IGNORE hydrolysis
NOT S_N1
NOT hydrogenation 2

(ii) second order

because the halogenoalkane is a primary one / two particles/both reactants are involved in RDS **(1)**
Formulae showing carbon atom has a δ+ with OH^- attacking it



(1)

If S_N1 ALLOW **max 1** *for showing halogenoalkane ionising in slowest step* 2

(d) (Full) oxidation /redox

NOT reduction
NOT partial oxidation 1

(e) **Any 2**
set them on fire/heat **(1)**
both burn with a sooty flame **(1)**

add sodium **(1)**
both give off bubbles of gas /hydrogen/fizz/effervesce/sodium will disappear/white solid forms **(1)**

add PCl_5 **(1)**
misty fumes of HCl **(1)**

nitric and sulphuric acid **(1)** *NOT* nitration
produces yellow/brown/red products **(1)** *NOT* brown gas disappears

If they describe esterification to produce oily drops of the same ester **max 2**
NOT reagents which produce no reaction eg. Brady's reagent
NOT decolorise bromine water
NOT decolorise bromine and iron / iron bromide 4

[19]

14. (a) (i) C_3H_5 **(1)**

7.2 / 24 = 0.3mol CO_2 / 0.3 mol C **(1)**

4.5/18 = 0.25mol H_2O / $\frac{4.5 \times 2}{18}$ = 0.5 mol / g H **(1)**

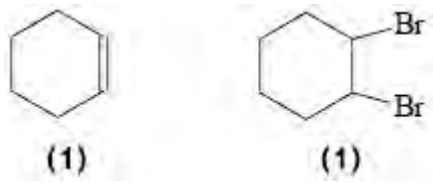
ALLOW deductions based on one calculation

e.g. 0.5g H ∴ 3.6g C ∴ $\frac{3.6}{12}$ = 0.3 mol C.

*Follow through their reasoning – if it logically arrives at the correct ratio **(2)***

e.g. $\frac{4.1}{82}$ mol A → $\frac{4.1}{82}$ × 6 mol C → $\frac{4.1}{82}$ × 6 × 24 dm^3 CO_2 etc 3

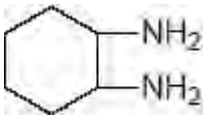
(ii)



(1) (1)

Mark independently
ALLOW other three, four and five membered ring structures
ALLOW fully/partially displayed formulae
NOT open-chain structure with 2 × C=C NOR $C_6H_{10}Br_2$, open chain with one C=C 2

(iii) Structural formula **(1)**

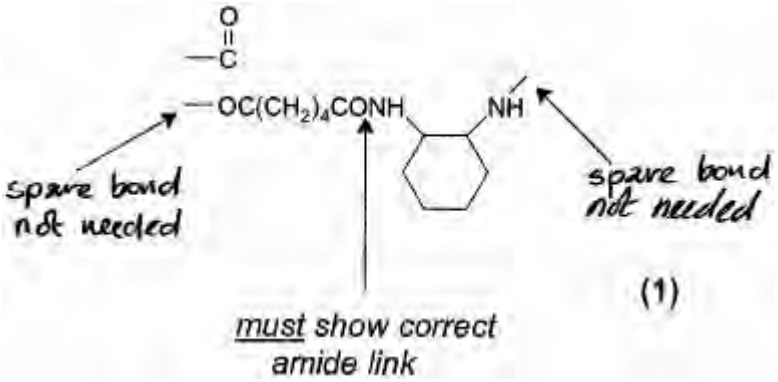


OR T.E. providing correct numbers of bonds
May be in equation

Ethanol/alcohol(ic) and heat / pressure / sealed tube **(1)**

$C_6H_{10}Br_2 + 4NH_3 \rightarrow C_6H_{14}N_2 + 2NH_4Br$ **(2)**
ACCEPT HBr (for**(1)**) 4

(b)



ACCEPT any multiples / partial multiples
ALLOW allowed TE from (iii)
IGNORE 'n's 2

Condensation (polymerisation) **(1)**

[11]

15. (a) Delocalisation / π-systern **(1)**

due to overlap of six *p*-orbitals
OR
Due to overlap of *p*-orbitals around the ring **(1)**

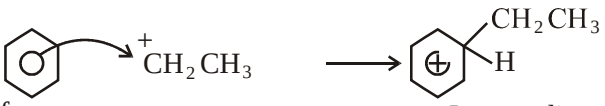
Confers stability / benzene at a lower energy level / more energy needed to break bonds compared with having three separate π / double bonds / cyclohexatriene, Kekule structure **(1)** *Standalone mark* 3

(b) 1st step: sulphuric **and** nitric acid **(1)**
concentrated **(1)**
Intermediate: Nitrobenzene /$C_6H_5NO_2$ **(1)**
2nd Step: Tin / iron **and conc** HCl (followed by addition of alkali) **(1)**
disallow Sn or Fe as catalyst 4

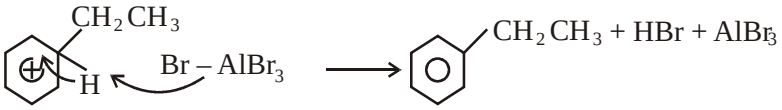
(c) (i) $AlBr_3$ / $FeBr_3$ / $AlCl_3$ / Al_2Cl_6 / $FeCl_3$ / Fe_2Cl_6 1

(ii) $AlBr_3 + CH_3CH_2Br \; CH_3CH_2^+ + AlBr_4^-$ **(1)**

ALLOW $C_2H_5^+$ *in this equation only*

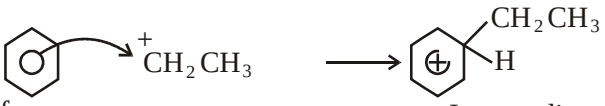


(1) for arrow Intermediate (1)

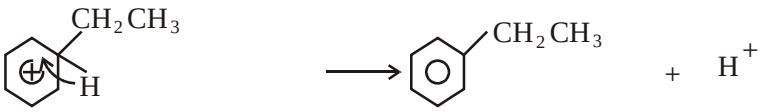


(1) for arrow from C – H bond

OR



(1) for arrow Intermediate (1)



(1) for arrow

(3)

Arrows

Do not allow to $C_2H_5^+$ 4

ALLOW to point / go to + charge

ALLOW C_2H_5 *in intermediate*

(iii) Electrophilic substitution 1

[13]

16. (a) $C_{10}H_8$

ALLOW $(C_5H_4)_2$

NOT $(C_6H_4)_2$ 1

(b) (i) –600

NOT + 600

NOT 600 1

(ii) Naphthalene is more/very stable than double bonds suggest **(1)**
Must be a comparison for the 1st mark

Therefore the electrons/bonds may be/are delocalised
(over the ring system)
OR it is a delocalised system **(1)**

No TE from (i)
Delocalised mark can be given if delocalisation mentioned in (iii) 2

(iii) No
because it is likely to react like benzene / delocalised structure /
no double bonds
OR bromine not a strong enough electrophile without a catalyst

OR "yes but only if **bromine** [NOT bromine solution] and a catalyst" 1

(c) (i) Reagent
2-chloropropane **(1)**
ALLOW 1-chloropropane *OR* other halogenopropanes
NOT chloropropane
NOT bromo-2-propane

ALLOW formula with or without non-systematic name
ALLOW $ClCH(CH_3)_2$ *OR* $(CH_3)_2CHCl$ *OR* $C(CH_3)_2HCl$ *OR* $ClC(CH_3)_2H$

Catalyst
aluminium chloride / $AlCl_3/Al_2Cl_6$
OR aluminium bromide / $AlBr_3$
OR iron(III) chloride/$FeCl_3$ **(1)**
NOT $AlCl_4^{(-)}$
NOT "iron" *on its own*

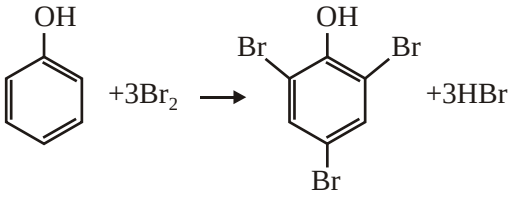
If both correct but wrong way round **1 (out of 2)** 2

(ii) electrophilic **(1)**
substitution **(1)**
Can be given in any order
Mark independently 2

[9]

17. (a) (i) White precipitate OR white suspension OR white solid 1

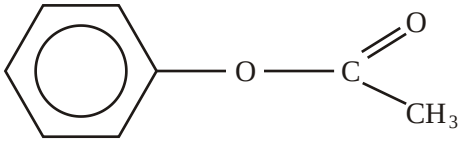
(ii)



2,4,6-tribromophenol **(1)**
rest of equation if for formation of a tribromophenol **(1)**

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$ scores **(1)** 2

(iii)



C = O in ester must be shown 1

(iv) C (atom) is (very) δ+ because **Cl** highly electronegative
OR Cl electron withdrawing **(1)**
IGNORE references to oxygen

(so C atom) susceptible to nucleophilic attack OR (so C atom) strongly electrophilic **(1)**
IGNORE references to activation energy 2

(b) Sn **and conc** hydrochloric acid (accept conc HCl) OR Fe **and conc** hydrochloric acid (accept conc HCl)
IGNORE any references to NaOH
IGNORE references to Fe or Sn as a catalyst 1

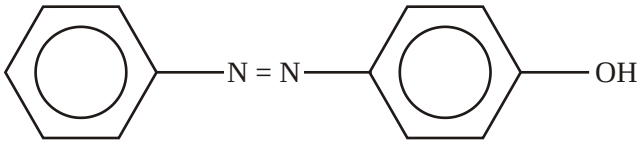
(c) (i)
- Sodium nitrite OR $NaNO_2$ OR sodium nitrate(**III**) **(1)**
  NOT JUST HNO_2
- Hydrochloric acid OR dilute sulphuric acid OR aqueous sulphuric acid 2

ACCEPT HCl if qualified. Do not accept conc. sulphuric acid
Only award the hydrochloric acid mark if $NaNO_2$ or KNO_2 or HNO_2 given as co-reagent

(ii) Below 0 °C : reaction too slow **(1)**

Above 5 °C : product decomposes OR diazonium ion decomposes **(1)** 2
NOT HNO_2 decomposes

(iii)



OR $-O^-$ instead of $-OH$ group 1

(iv) Dissolve in **minimum** volume of boiling solvent OR dissolve in **minimum** volume of hot solvent **(1)**

QWC NOT JUST "small volume"
[*ALLOW* any specified solvent including water]
Filter **hot** OR filter through **heated** funnel **(1)**
Cool or leave to crystallise **(1)**
Filter (under suction) **(1)**
Wash solid with cold solvent (and leave to dry)
OR wash solid with small volume of solvent (and leave to dry) **(1)** 5

[17]

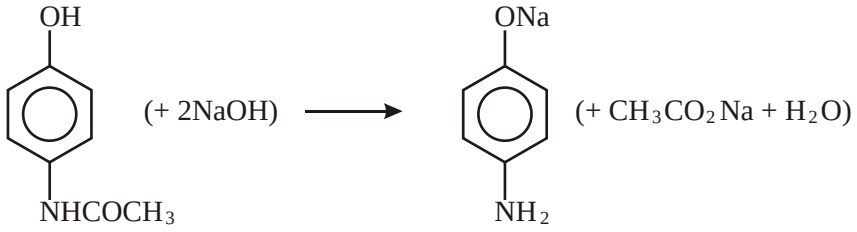
18. (a) Nitric acid / HNO_3 **(1)**
Dilute / 4M acid and boil/heat **(1)** 2

(b) Reduction
ALLOW redox 1

(c) (i) 4(–) aminophenol / 4(–)hydroxyphenylamine
OR 1(–)amino(–)4(–)hydroxybenzene etc
ALLOW para / p etc 1

(ii) Add copper(II) (sulphate solution) / Cu^{2+} **(1)**
Green / brown (precipitate) forms **(1)** 2

(d) (i)



Organic formula fully correct **(2)**
Only one group reacting **(1)** 2

(ii) No because, phenol is not a strong enough **acid** to react with sodium carbonate **(1)**
NOT "because phenol is a weak acid" 1

(e) (i) QWC Van der Waals' and (permanent) dipole – (permanent) dipole, and hydrogen bonds **(1)**

Van der Waals between aromatic rings / everywhere / anywhere **(1)**
(Permanent) dipole force between carbonyl / C=O groups **(1)**
Hydrogen bonds eg between N–H and O=C **(1)** 4

BUT must make it clear which atoms are involved

(ii) QWC Van der Waals total forces in paracetamol are too strong
OR
Hydrogen bonds in water are too strong

ALLOW carbon chain too long / large

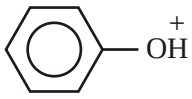
ALLOW because of benzene ring 1

(f) (Broad) OH (stretching absorption from) **(1)**
3750 – 3200 (cm^{-1}) **(1)**

OR
(Broad) NH (stretching absorption from) **(1)**
3500 – 3140 (cm^{-1}) **(1)**
Bond must be specified for 1st mark but range mark is ***not*** *dependent on 1st mark* 2

(g) (i) **$C_8H_9O_2N^+$**
Fully correct with charge 1

(ii) 43–CH_3CO^+ / $C_2H_3O^+$ / $CHNO^+$
93–$C_6H_5O^+$ **(1)**
IGNORE charges unless both negative, then **1 max** *if fully correct*
ACCEPT semi-structural formulae but NOT



2

(h) No gastric / internal bleeding / suitable for younger children 1

[20]

19. (a) (i) Conc(entrated) / fuming sulphuric acid / sulphur trioxide / SO_3 **(1)** 1

*Accept oleum **(1)***

Reject sulphuric acid / H_2SO_4

(ii) Substitution **(1)**

Electrophilic **(1)** 2

(b) (i) To avoid losing too much vanillin (in the filtrate when crystallisation occurs) OWTTE 1

Accept to maximise the yield

Reject answer only referring to saturation

(ii) Insoluble impurities removed by **hot**/ **first** filtration **(1)**

Soluble impurities remain in solution **(1)** 2

(iii) Measure mpt **(1)**

Compare with data OR sharp melting point **(1)** 2

Accept bpt. method can only score 2nd mark

(c) Vanillin is likely to be a product since ……..
IR spectrum of product shows an absorption for aldehyde C=O stretching /vibration **(1)**…
……
at about 1740–1720 cm^{-1} /any value within this range **(1)**
(This is absent in the 2-methoxyphenol IR spectrum) 2

[10]

20. (a) Reagent: chloromethane/CH_3Cl **(1)**

Accept bromomethane/ CH_3Br/iodomethane/ CH_3I

Catalyst: (anhydrous) aluminium chloride/$AlCl_3$/Al_2Cl_6 **(1)**
OR equivalent bromides

Accept iron(III) chloride/ bromide

Reject iron

Mark independently 2

(b) (i) (free) radical substitution 1

(ii) $Cl_2 \rightarrow 2Cl^{\bullet}$ **(1)**

$PhCH_3 + Cl^{\bullet} \rightarrow PhCH_2^{\bullet} + HCl$ **(1)**

$PhCH_2^{\bullet} + Cl_2 \rightarrow PhCH_2Cl + Cl^{\bullet}$ **(1)**

any one of:

$2\ PhCH_2^{\bullet} \rightarrow PhCH_2CH_2Ph$

$PhCH_2^{\bullet} + Cl^{\bullet} \rightarrow PhCH_2Cl$

$2\ Cl^{\bullet} \rightarrow Cl_2$ **(1)**

[IGNORE curly arrows]

If the initiation or propagation steps are wrong, only the termination step can score consequentially on any two of their radicals. 4

Dot must not be on Ph penalise once

P instead of Ph penalise once

(iii) flask and vertical condenser – need not be shown as separate items **(1)** [Ignore direction of water flow; penalise sealed condenser]

gas entry **into liquid** in flask **(1)** [allow tube to go through the side of the flask, but tube must not be blocked by flask wall]

Allow the gas to be bubbled down a tube coaxial with the condenser bore.

*Bubbling gas into a beaker OR other vessel without a condenser **0 (out of 3)***

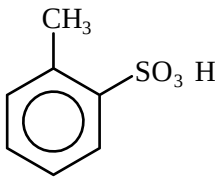
heating from a electric heater/heating mantle/sand bath/water bath/oil bath **(1)** diagram or words
labelling of diagram not necessary
[IGNORE uv source] 3

Reject just 'heat', Bunsen

[10]

21. (a) (i) methylbenzene/phenylmethane 1

(ii)



1

Accept alternative substitution products with –SO_3H group on other ring positions

$SO_3^-\ H^+$

Accept multiple substitutions

Accept Displayed Formulae

Reject bonding to ring through H or O atom

(b) (i) (conc.) nitric acid **(1)**

Accept HNO_3

Reject dilute, HNO_3 (aq)

(conc.) sulphuric acid **(1)** Mark independently 2

Accept H_2SO_4

Reject H_2SO_4(aq)

Reject incorrect formula in conjunction with name

(ii) NO_2^+ 1

Reject $NO_2^{\delta+}$

(c) (i) Substitution **(1)**

Electrophilic / electrophile **(1)** 2

Accept either way round

Reject incorrect type or mechanism in conjunction with correct response

(ii) the ring is more susceptible to attack by electrophiles/ more nucleophilic/ ring has greater electron density **(1)**

as methyl group pushes electrons into ring/ toluene has a dipole moment **(1)** 2

(d) Oxidation 1

Accept partial oxidation

Reject redox

Reject full oxidation

(e) sodium/ potassium dichromate((VI)) **(1)**

Accept $Na_2Cr_2O_7$/ $K_2Cr_2O_7$

sulphuric acid **(1)**
or
Potassium manganate ((VII)) **(1)**

Accept H_2SO_4
dil. or conc.
'acidified dichromate' = 1
or
KMnO4

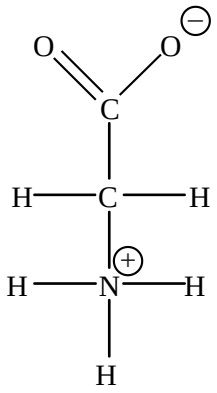
Sulphuric acid **(1)** 2

Accept H_2SO_4
'acidified manganate' = 1
OR
*Potassium manganate ((VII)) **(1)***
*Sodium hydroxide **(1)***

Reject incorrect oxidation numbers
Reject incorrect Formula in conjunction with correct name

[12]

22. (a) (i)



Positive charge must be on the N atom
The minus charge must be on the O in the C—O if no delocalisation shown 1

Accept delocalised carboxylate group with a negative charge shown

Reject compressed structural formula

(ii) (H^+ from) COOH (group) protonates the $–NH_2$(group) 1

Accept transfer of H^+ from COOH to NH_2
Or
"self-protonation"

Reject just "protonation"

Reject just "acid-base reaction"

(iii) **Read the whole answer!**

High energy needed to overcome (strong) **ionic** attractions **(1)**

Accept "ionic bonds" or "ionic lattice" instead of "ionic attractions"

*Reject **just** "intermolecular forces"*
Or H bonding
Or van der Waals' forces etc
award zero overall

between zwitterions **(1)**

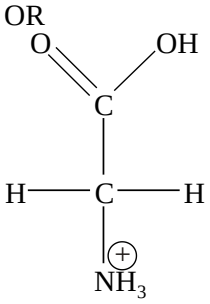
*Accept **between** adjacent species*

Ignore reference to "molecules" if clearly used in the context of attraction between ions 2

(b) (i) $^+NH_3CH_2COOH$ / $^+H_3NCH_2COOH$ / $^+H_3NCH_2COOH$

OR written right to left

OR



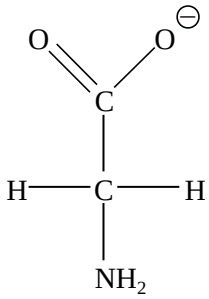
1

Accept $–CO_2H$
OR
$–NH_3^+Cl^–$

Or $–NH_3Cl$

Reject molecular formula

(ii) $NH_2CH_2COO^-$ / $NH_2CH_2CO_2^-$ /

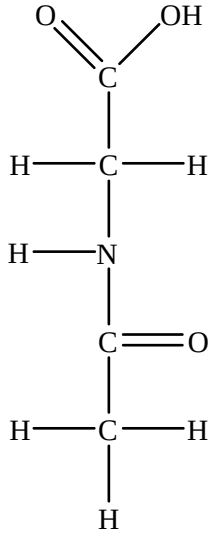


1

Accept —COONa
or
—COO⁻Na⁺

Reject molecular formula

(iii) $CH_3CONHCH_2COOH$/



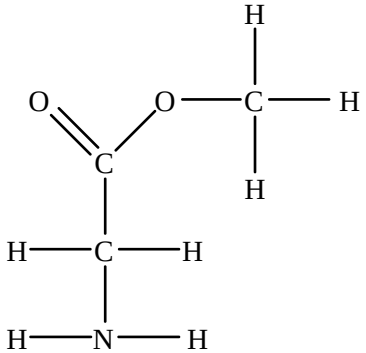
1

Accept $CH_3CONHCH_2CO_2H$

OR 'no reaction' ***(1)***

Reject molecular formula

(iv) $NH_2CH_2COOCH_3$ /



1

Accept $NH_2CH_2CO_2CH_3$

(c) (i) (Glutamic acid molecule) has four different groups attached to a C (atom)
Or
(Glutamic acid molecule) has four different groups attached to a chiral centre

Accept contains an asymmetric carbon (atom)
Or
molecule has no plane of symmetry

*Reject **just** "has a chiral centre"*
Or
***Just** "the molecule is asymmetrical"*

OR
has mirror images which are not superimposable 1

(ii) (the isomers) rotate the plane (or polarisation) of (plane-) polarised light **(1)**

Accept "….rotate plane polarised light"

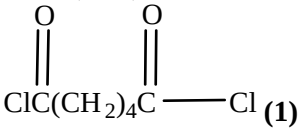
in **opposite** directions **(1)**

Reject just "in different directions"

Ignore any reference to polarimeter 2

(d) $H_2N(CH_2)_6NH_2$ **(1)**

$ClOC(CH_2)4COCl$ /

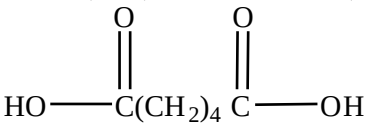


(1)

[Monomers can be given in either order] 2

Accept $NH_2(CH_2)_6NH_2$

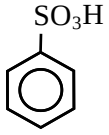
$HOOC(CH_2)_4COOH$ / $HO_2C(CH_2)_4CO_2H$ /



$COOH(CH_2)_4COOH$
Or $COCl(CH_2)_4COCl$

[13]

23. (a) (i)



Bond from benzene ring must be to the sulphur atom
Hydrogen atom must be linked to oxygen 1

Accept $C_6H_5SO_3H$

Accept $C_6H_5SO_2OH$

Reject $C_6H_5HSO_3$

(ii) Fuming sulphuric acid / oleum / sulphur trioxide / SO_3 / sulphur trioxide or SO_3 in sulphuric acid 1

Accept concentrated sulphuric acid / $H_2S_2O_7$

Reject H_2SO_4 / $H_2SO_4(aq)$ / sulphuric acid / dilute sulphuric acid

(iii) (aromatic) Electrophilic substitution 1

Accept Electrophillic / Electrophylic / Eletrophilic substitution

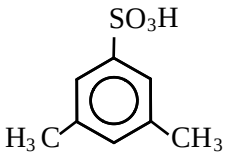
Reject Electrophic substitution

(iv) SO_3/ SO_3H^+
Ignore name if given with formula 1

Accept HSO_3^+

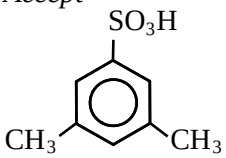
Reject sulphur trioxide / SO_3^+ / SO_3^-

(b) (i)



Allow TE from (a)(i) 1

Accept



Formula for 2,6-dimethyl benzene sulphonic acid

(ii) Reagent X: CH_3Cl **(1)**
Catalyst Y: $AlCl_3$ **(1)**

Allow TE from (b)(i) e.g. CH_3CH_2Cl if an ethylbenzene 2

Accept CH_3Br / CH_3I ***(1)***
Accept Al_2Cl_6/$AlBr_3$/AlI_3 ***(1)***
One correct name and one correct formula (2)
Names for <u>both</u> answers ***(1 max)***

(iii) Hydrogen chloride / HCl 1

Accept answer consequential on (b)(ii), e.g. HBr

Reject hydrochloric acid

(c) (i) 4-chloro-3, 5-**<u>di</u>**methylphenol
3,5-**<u>di</u>**methyl-4-chlorophenol 1

Accept no/wrong punctuation
Allow name based on hydroxybenzene
Allow "cloro" or "methyl"

(ii) Hydrogen bonding interactions between dettol and water are weaker than those between water molecules
OR
Hydrogen bonding interactions between dettol and water are weaker thatn the van der Waals' forces in dettol

Look for good use of scientific language. Answer <u>must</u> include a specific type of intermolecular force 1

Accept hydrogen bonding between dettol and water is weak

Reject dettol molecule is too big

*Accept dettol can only form **one** H-bond with water/only has **one** OH group to H-bond with water*

Reject arguments based on lone pairs of electrons on OH group being delocalised into the ring

[10]

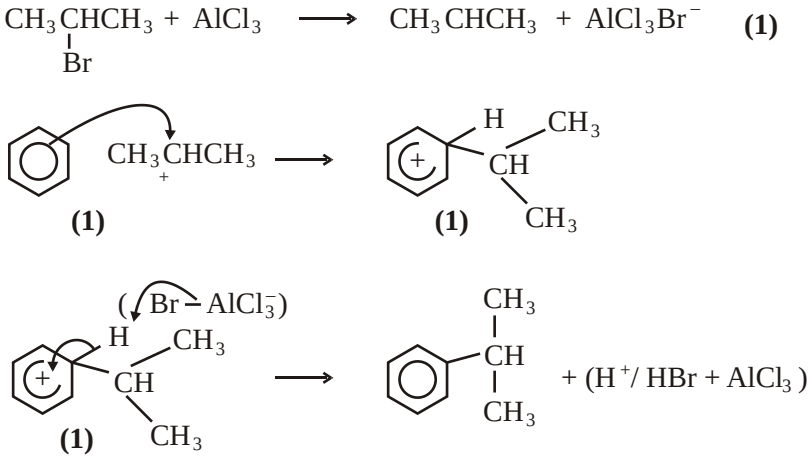
24. (a) (i) (anhydrous) aluminium chloride

[Name or formulae] 1

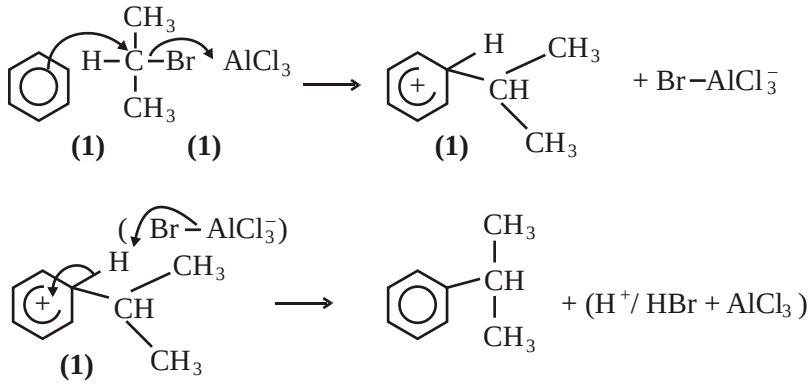
Accept Al_2Cl_6
Accept $AlBr_3$ $FeBr_3$
Accept $FeCl_3$

Reject Fe

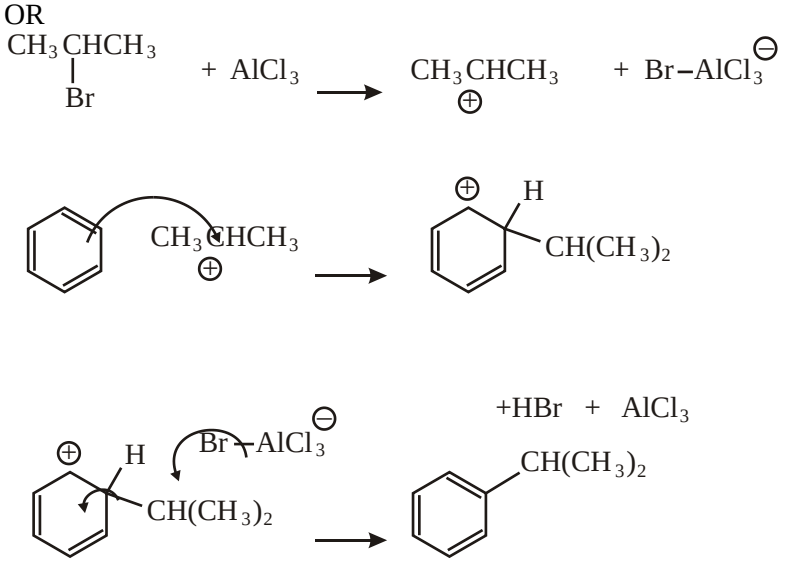
(ii)


CH3CHCH3 + AlCl3 → CH3CHCH3 + AlCl3Br−
Br
(1)
CH3CHCH3
+
(1)
H
CH3
CH
CH3
(1)
(Br – AlCl3−)
H
CH3
CH
CH3
(1)
CH3
CH
CH3
+ (H+/ HBr + AlCl3)

OR


CH3
H–C–Br
CH3
AlCl3
(1)
(1)
H
CH3
CH
CH3
(1)
+ Br–AlCl3−
(Br – AlCl3−)
H
CH3
CH
CH3
(1)
CH3
CH
CH3
+ (H+/ HBr + AlCl3)

OR



Equation for formation of electrophile **(1)**
IGNORE if incorrect arrows added at this point

First arrow must be from C=C or from or within ring
to C with + and can point to + **(1)**

Correct intermediate as shown in mechanism above **(1)**

Second arrow from C–H bond into ring **(1)** 4

Accept either a delocalised or Kekule ring

If $CH_3CHBrCH_3 \rightarrow CH_3CH^+CH_3 + Br^-$ loses 1st mark but can score 2nd, 3rd and 4th marks

(b) (i) $CH_3CH_2CH^{2+}$ 1

Accept $C_2H_5CH_2^+$

Reject $C_3H_7^+$

(ii) secondary carbocation is more stable than primary **(1)**

primary carbocation ($CH_3CH_2CH_2^+$) rearranges to produce
a secondary carbocation
OR
primary carbocation ($CH_3CH_2CH_2^+$) turns into a secondary
carbocation
OR
a description of the rearrangement e.g. a hydrogen atom
moves from the middle to the end **(1)** 2

Reject any reference to stability of intermediate /product

(c) (i) **First mark**
sodium nitrite /sodium nitrate(III)/$NaNO_2$ **(1)**

Second mark
hydrochloric acid / HCl(aq) **(1)**
IGNORE concentration of acid
2nd mark is conditional on $NaNO_2$ or HNO_2 2

Reject HNO_2

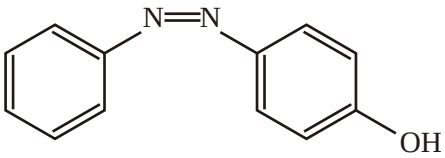
Reject HCl/hydrogen chloride

(ii) below 0 °C reaction is too slow **(1)**

above 10 °C the product/benzenediazonium ions decomposes /hydrolysed **(1)** 2

Accept HNO_2 decomposes

(iii)



N=N link, can be shown linear **(1)**
IGNORE other atoms
Remainder correct **(1)** 2

IGNORE position of OH group.

Accept —ONa or O^- instead of OH

Reject —N=N—O—

(d) (i) QWC

First two
add 2,4-dinitrophenylhydrazine/Brady's reagent **(1)**
orange/yellow ppt **(1)**
Allow this second mark if the name of the reagent is slightly incorrect e.g. 2,4-diphenylhydrazine

Accept 2,4-dnp(h)

Accept any combination of yellow and orange
Must be ppt

Reject just "Red ppt"

Reject "solid" for "ppt"

OR
IR absorption due to C=O stretch **(1)**
at 1700 cm^{-1} **(1)**

Third mark
Does not give a silver mirror with ammoniacal silver nitrate (or Tollens' reagent)

Accept no change with Tollens'

OR
no red ppt/stays blue with Fehling's or Benedict's solution

Reject Iodoform

OR
$H^+/Cr_2O_7^{2-}$ does not change from orange to green/stays orange

OR
H^+/MnO_4^- does not change from purple to colourless/stays purple **(1)** 3

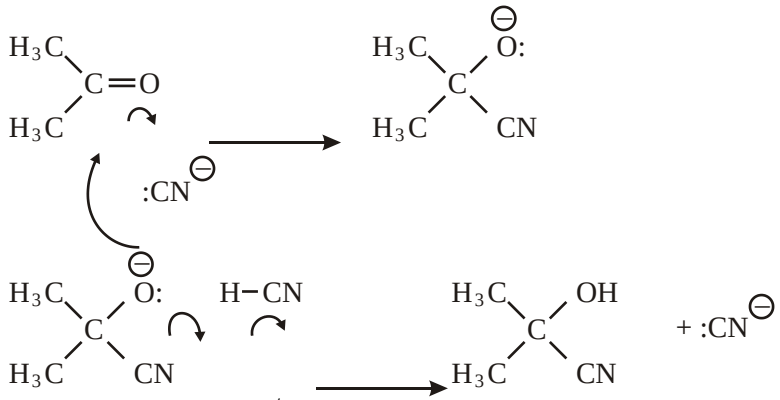
(ii) the C=O group is polar **and** the nucleophile attacks the δ^+ carbon **(1)**

whereas C=C is non-polar/electron-rich, the double bond/π-bond is attacked by electrophiles **(1)**

OR
C=O is polar **and** C=C is non–polar **(1)**

Nucleophile attacks the δ^+ carbon in C=O **and**
electrophiles attack the π/double bond in C=C, which is electron rich/non-polar **(1)** 2

(iii)



both curly arrows in 1st diagram, attack by cyanide, arrow must start from C or –ve charge on C **not** N and –ve charge must be present somewhere on ion; lone pair not essential. Arrow must start from bond between C and O and point towards the O **(1)**

Accept curly arrow from O to H^+

Intermediate – lone pair not essential but negative charge is essential **(1)**

Arrow from O (lone pair not needed) or negative charge to HCN or H^+, this can be shown on the diagram of the intermediate **(1)**
If HCN is used the arrow from H–CN bond is required

Any other ketone or aldehyde, **max (2)** 3

[22]

25. (a) (i) The activation energy for the reaction is high **or** to ensure that more molecules have $E \geq E_a$. 1

Accept $E > E_a$

Reject to overcome E_a ***alone***

Reject reactants kinetically stable; reactants thermodynamically stable

(ii) protonates the alcohol **(1)**

Reject 'as a catalyst' alone

providing H_2O as the leaving group which is more easily displaced by the bromide ion/is a better leaving group than hydroxide **(1)**

OR

reacts with NaBr **(1)**

to give HBr (which is the attacking reagent) **(1)** 2

(iii) H-bonding between water and the alcohol not strong enough to overcome hydrophobic interactions /effect of alkyl group **(1)**

acid and alcohol form ionic species/$C_4H_9OH_2^+$ which is more soluble **(1)** 2

Accept butyl group

(iv) Removes acid 1

Accept neutralises HCl /HBr

Accept neutralises acid

(v) Removes water 1

Accept absorbs water
Accept dries the product

(vi) Electric heating mantle **or** sand bath **or** oil bath **(1)**

Accept water bath

Reject heat under reflux

Reject no naked flame

Reject fume cupboard

because the alcohol/reaction mixture/bromobutane is flammable **or** because the heating is uniform and less likely to crack the flask **(1)**
This mark is conditional on the first being scored. 2

Reject 'volatile' for 'flammable'

(b) QWC

EITHER

Intermediate (ion) in S_N1 is planar **(1)**

Accept intermediate carbocation is a planar molecule

*intermediate **molecule alone** loses this mark*

equal attack (by hydroxide ions) from either side **(1)**
produces a racemic mixture **(1)**

Reject attack by bromide ions

Note: Statement that the S_N2 mechanism is consistent with the information cannot score any marks.

OR

S_N2 involves attack from one side **(1)**

so configuration of the product would be inverted **(1)**

leading to retention of optical activity **so must be SN1 (1)**

Accept forms one optical isomer only

Statement that the reaction is S_N1 alone scores zero. 3

(c) (i) Orange → green 1

(ii) $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ **(1)**

$\underline{(3CH_3CH(OH)CH_2CH_3 \rightarrow 3CH_3COCH_2CH_3 + 6H^+ + 6e^-)}$
$Cr_2O_7^{2-} + 3CH_3CH(OH)CH_2CH_3 + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3COCH_2CH_3$ **(1)**

No consequential marking on incorrect equations. 2

Accept C_4H_9OH and C_4H_8O

Accept equation having non-cancelled H^+ ions

Reject equation having non-cancelled electrons

(iii) The broad peak/absorption/trough around 3400 cm^{-1} due to –OH **(1)**

Accept 3230 – 3550

Reject broad transmission

has disappeared in the product to be replaced by C=O at 1700 cm^{-1} **(1)**

Accept 1680 – 1750

If no reference to both groups responsible for the peaks then max **(1)**

OR

If no reference to both wavenumbers responsible for the peaks then max **(1)** 2

(d) (i) Addition of barium ions pulls equilibrium to r.h.s. **(1)**

increases $[H^+]$ **and** so lower pH/the pH falls **(1)** stand-alone mark 2

Reject '..so gets more acidic'

(ii) lower pH/pH falls 1

Reject 'mixture is more acidic' for 'lower pH'

[20]

26. (a) (i) **Step 1**

Reagent

Fuming sulphuric acid / sulphur trioxide/sulphur(VI) oxide/oleum **(1)**

Accept $SO_3/H_2S_2O_7$

Reject (Concentrated) sulphuric acid/H_2SO_4

Conditions

Reflux / heat **(1)**

Only allow heat for this mark if the reagent is reasonable (e.g. conc sulphuric acid)

Accept if just stated temperature must be above 75 °C

Step 2

Reagent

Sodium hydroxide **(1)** 3

Accept sodium carbonate/sodium
Accept hydrogencarbonate/sodium

Reject sodium chloride

(ii) **Step 1**

(electrophilic) substitution **(1)**

Accept sulphonation

Reject Nucleophilic substitution

Step 2

neutralisation or acid-base **(1)** 2

(b) (i) Friedel-Craft(s)

Accept phonetic spelling 1

Accept alkylation

(ii) Reagent
$C_{12}H_{25}Cl$
OR
$C_{12}H_{25}Br$ **(1)**

Accept (1-)chlorododecane
$C_{12}H_{25}I$

Catalyst
$AlCl_3$ **(1)** 2

Accept Al_2Cl_6
Accept Aluminium chloride

Reject $AlCl_4$

Reject $AlCl_4^-$

[8]

27. (a) Electrophilic substitution **(1)**
IGNORE extras eg Friedel Craft, alkylation UNLESS contradictory

1-chloro-(2)-methylpropane **(1)**
IGNORE punctuation

Accept (2)-methyl-1-chloropropane
Accept $CH_3CH(CH_3)CH_2Cl/CH(CH_3)_2CH_2Cl$
Accept "Bromo"/"iodo" for "chloro"

Reject 1-methyl-2-chloropropane

Reject missing "1" from position of Cl in name

Catalyst
$AlCl_3$/aluminium chloride **(1)** 3

Accept Al_2Cl_6, $AlBr_3$, $FeBr_3$

(b) $LiAlH_4$ is a source of H^- / hydride ion **(1)**

Hydrogen might reduce/attack benzene ring/ H^- won't attack
region of negative charge/ H^- can attack (δ^+) C in keto group **(1)** 2

Reject comments on conditions or safety eg temperature, pressure

Reject $LiAlH_4/H^-$ is a more powerful reducing agent

Reject H^- is a nucleophile/a stronger nucleophile

Reject any mention of attack on carboxylate ion (for 2nd mark)

(c) **Note:** although many candidates have calculated the empirical formula, this is not required.

Molecular formula of ibuprofen = $C_{13}H_{18}O_2$ **(1)**

Allow if given at end

Allow marks for masses and number of moles if answers are rounded to 2 SF in "OR" but method is correct.

EITHER

$M_r = 206$ (1)

$1\text{ g} = \frac{1}{216}\text{ mol} = 4.854 \times 10^{-3}\text{ mol}$

mass CO_2 produced from 13 C

$= 13 \times 44 \times 4.854 \times 10^{-3} = 2.78$ g **(1)**

mass H_2O from 18 H

$= 9 \times 18 \times 4.854 \times 10^{-3} = 0.787$ g **(1)**

OR

Mass C $= \frac{(2.78 \times 12)}{44} = 0.758$g

Mass H $= \frac{(0.786)}{9} = 0.0873$g **(1)**

Moles C $= \frac{(0.758)}{12} = 0.0632$

Moles H = 0.0873 **(1)**

Ratio C:H = 0.0632: 0.0873 = 13:18 **(1)** 4

(d) (i) (Aspirin and ibuprofen) both contain same (types of) **bond(s)**(so absorb at same frequency/wavenumber) 1

Accept list of at least 4 bonds which are present in both

Reject "groups" for "bonds"

(ii) Data is required for mark

Y = paracetamol
Peak at 3500–3300 (N–H)
IGNORE mention of amine

OR 3500–3140 (N–H or amide)

OR 3750–3200 ((phenolic) O–H)

OR Only **Y** has peaks above 3000 cm^{-1} (so must contain different type of bond to X and Z) 1

Reject C–H in arene = 3030 as present in both

Reject 1700–1630 (amide)

(iii) <u>57 in Ibuprofen</u>

$C_4H_9^+$ /$CH_3CH(CH_3)CH_2^+$/$CH(CH_3)_2CH_2^+$

OR

$C_2O_2H^+$/CCO_2H^+ **(1)**

Accept structural or displayed formulae

Do not allow lines at
15 (CH_3^+)
76 ($C_6H_4^+$)
43 ($C_3H_7^+$ or CH_3CO^+)
45 ($COOH^+$)
as present in both

<u>Aspirin</u>

59 **(1)** $OCOCH_3^+$ /$C_2H_3O_2^+$ **(1)**

OR

121 **(1)** $C_6H_4CO_2H^+$ **(1)**

OR

180 **(1)** $C_9H_8O_4^+$ (parent ion) **(1)**

OR

137 **(1)** $C_6H_4(CO_2H)O^+$ **(1)**

Penalise no/wrong charges once only 3

[14]

28. A

[1]

29. B

[1]

30. D

[1]

31. B

[1]

32. A

[1]

33. B

[1]

34. C

[1]

35. D

[1]

36. (a) B 1

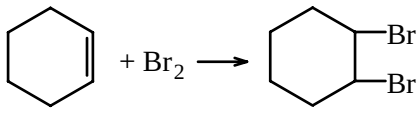
(b) B 1

(c) A 1

(d) D 1

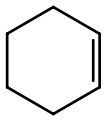
[4]

37. (a) (i)

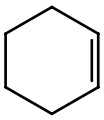


1

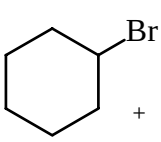
(ii)



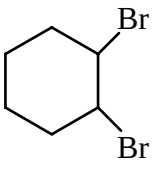
$\delta+ \quad \delta-$
$Br—Br$ **(1)**



$Br—Br$ **(1)**



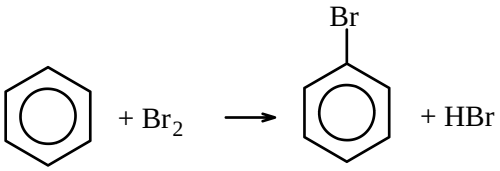
Br^-



(1)

3

(b) (i)



1

(ii) $Br_2 + FeBr_3 \rightarrow Br^+ + FeBr_4^- / \delta+ \quad \delta-$
$Br—FeBr_4$ **(1)**

Step 1
Arrow from ring towards Br+ **(1)**
Intermediate **(1)**
Step 2
Arrow from bond, ring to H, to inside ring (and from $FeBr_4^-$ to H^+) and formation of products **(1)**

4

(iii) $FeBr_4^- + H^+ \rightarrow FeBr_3 + HBr$ 1

(c) (i) QWC

Both attacked by an electrophile **(1)**
Due to stability of delocalised ring **(1)**
benzene attacked by (stronger electrophilic) Br^+
rather than $Br^{\delta+}$ in Br_2 **(1)**

3

(ii) QWC

Cyclohexene

Addition of Br^- does not involve bond breaking /results in more exothermic reaction than loss of H^+ **(1)**

Benzene

No Br^- available in benzene reaction **(1)** Stability of ring regained by loss of H^+ **(1)** 3

(d) Three / 3 1

[17]