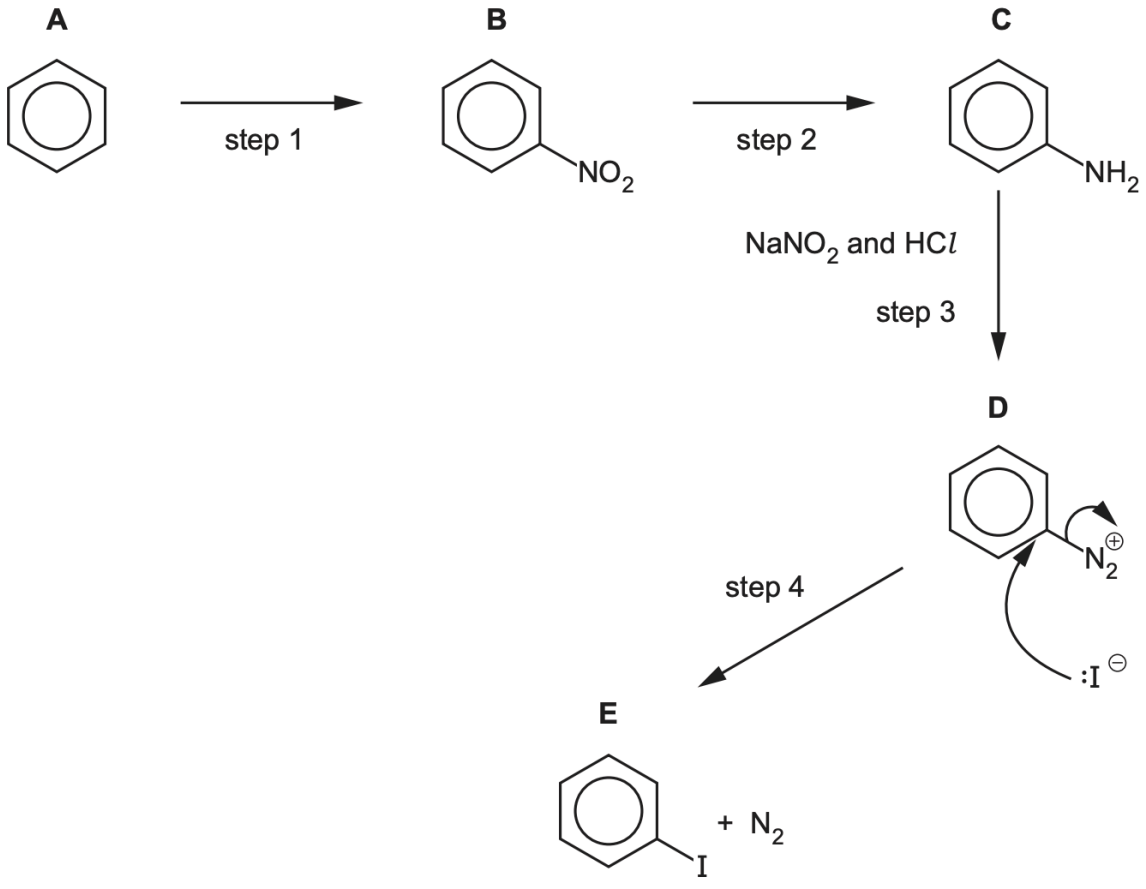
ORGANIC CHEMISTRY

Things to Remember from AS

- Carboxylic acid effervesces with a carbonate (CO2 gas is formed) BUT alcohols do not.
- Both carboxylic acids and alcohols effervesce with reactive metals (H2 gas is formed).
- Positive iodoform test (yellow ppt of iodoform CHI3)
    - Methyl Ketones
    - Aldehydes: only ethanal
    - Alcohols: ethanol + secondary alcohols
- In alkaline conditions, carboxylic acids will always exist as ROO–Na+ (or whichever metal)/ carboxylate ions BUT alcohols will not, as they do not react with OH–. They exist as RO–/alkoxide ions only in when they react with reactive metals.



Step 3 occurs in 2 stages. Write the equations for both stages.

1. $NaNO_2 + HCl = HNO_2 + NaCl$
2. $HNO_2 + C_6H_5NH_2 + H^+ = C_6H_5N_2^+ + 2H_2O$

The I– from KI reacts with D in step 4. Suggest the name for this mechanism

- Nucleophilic substitution

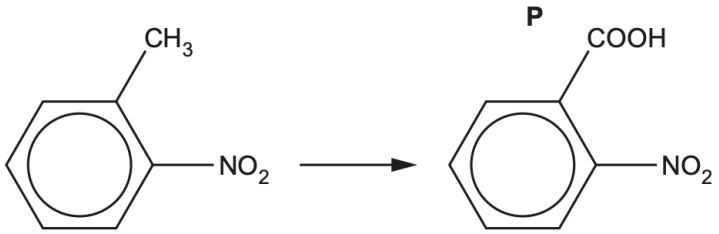
In sunlight, NO_2Cl can undergo homolytic fission to release chlorine radicals which can catalyse the conversion of ozone, O_3 , into oxygen. Complete the mechanism for this process.

initiation (homolytic fission)	NO_2Cl		→ ..... + ...
propagation step 1	..... +	O_3	→ ..... + ...
propagation step 2	..... + ...		→ ..... + ...

- Initiation: $NO_2Cl \rightarrow Cl\cdot + NO_2\cdot$
- Propagation step 1: $Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$
- Propagation step 2: $ClO\cdot + O_3 \rightarrow Cl\cdot + 2O_2$

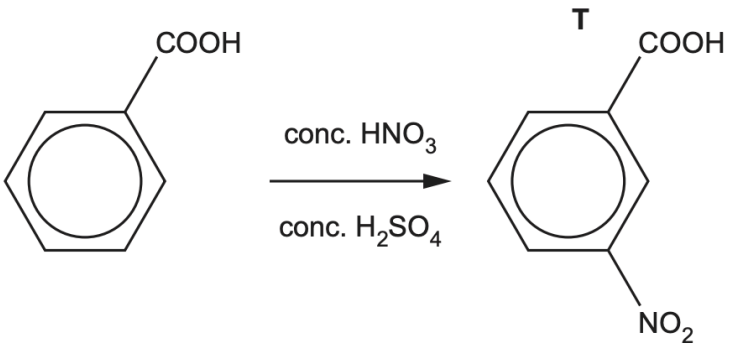
NOTE: For free-radical substitution reactions:

1. Initiation
    - Involves homolytic bond fission to produce radicals.
2. Propagation:
    - Radicals formed in initiation step react with stable molecules to form new radicals.
      Radical + Molecule → New radical + Stable molecule
    - You usually need 2 propagation steps that regenerate the original radical (catalysis).
3. Termination:
    - Radicals combine to form stable molecules.
      Radical + Radical → Stable molecule (no radicals)



Suggest reagents and conditions for this reaction

- Hot / heat / reflux AND (alkaline / acidified / neutral) KMnO4–



Explain why T is the major product in this reaction

- COOH / carboxyl group is electron-withdrawing / electronegative AND 3- and 5- / meta- directing

Methyl red can be synthesised as shown in Fig. 7.1.

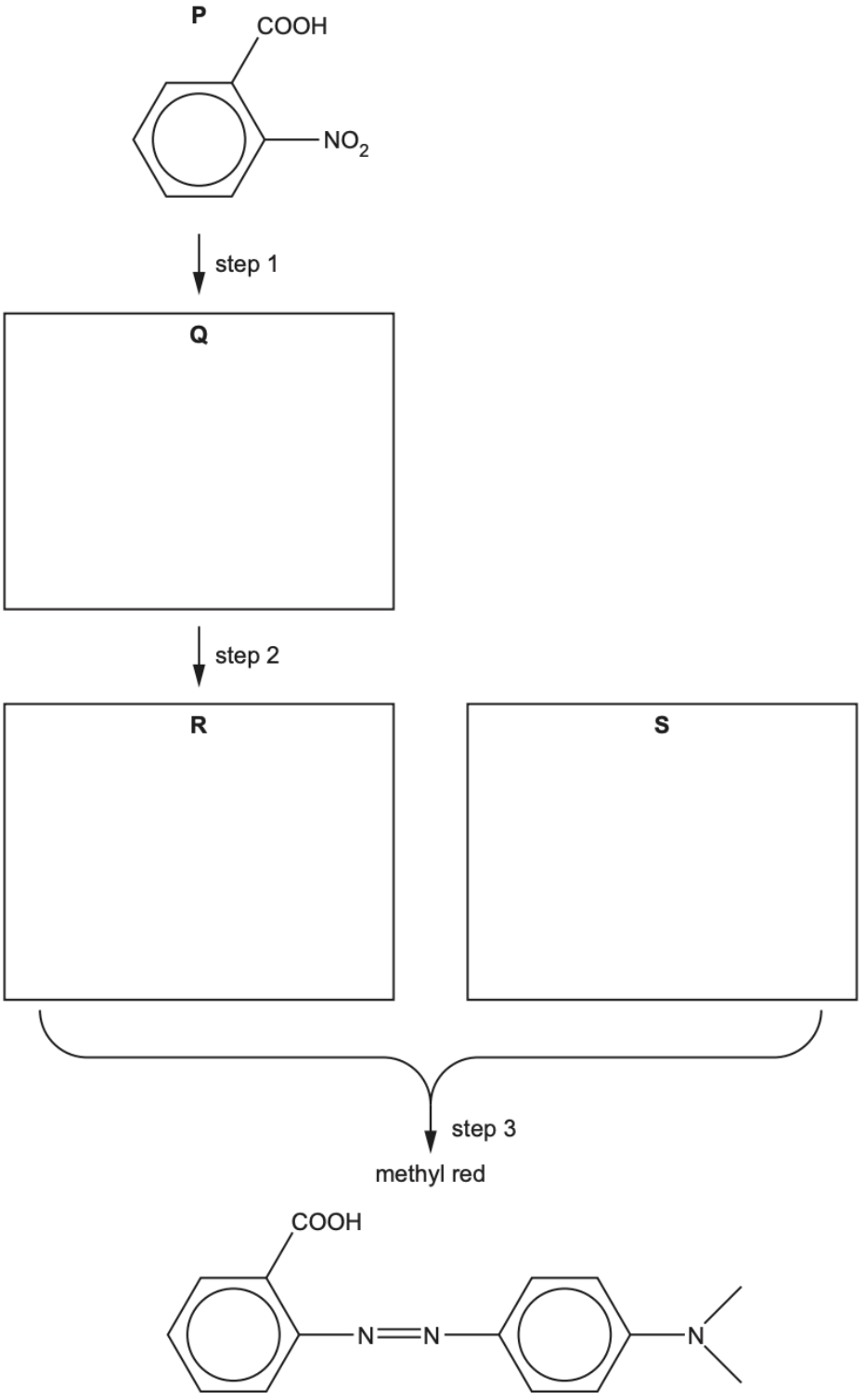
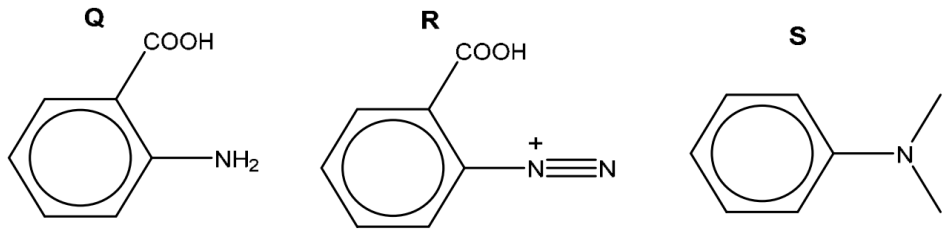


Fig. 7.1

Draw the structures of Q, R and S in the boxes.



Suggest reagents and conditions for steps 1 and 2

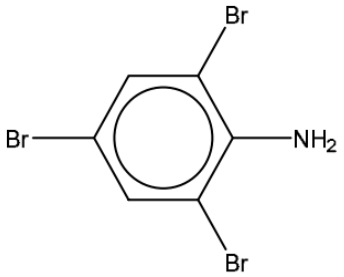
- Step 1: Fe/Sn, conc. HCl AND hot/heat/reflux
- Step 2: HCl + NaNO2 OR HCl + HNO2 AND <= 10˚C

State the relative basicities of phenylamine, $C_6H_5NH_2$, benzylamine, $C_6H_5CH_2NH_2$, and ammonia, NH_3 , in aqueous solution. Explain your answer.

- benzylamine > ammonia > phenylamine
- Basicity linked to p orbital of N / lone pair on N AND being able to bond / accept / donate to / coordinate to a proton / H+
- Benzylamine has R / alkyl / CH2 group AND is electron donating / positive inductive effect / has + I effect
- In phenylamine, p orbital of N / lone pair on N overlaps / incorporated / delocalised in the ring / π-bond system

$C_6H_5NH_2$ reacts readily with Br2 (aq) to form organic product M. State the expected observations for this reaction. Draw the structure of M.

- Observations: white ppt
- Structure:



Suggest why Br2 (aq) reacts with $C_6H_5NH_2$ but not with C_6H_6

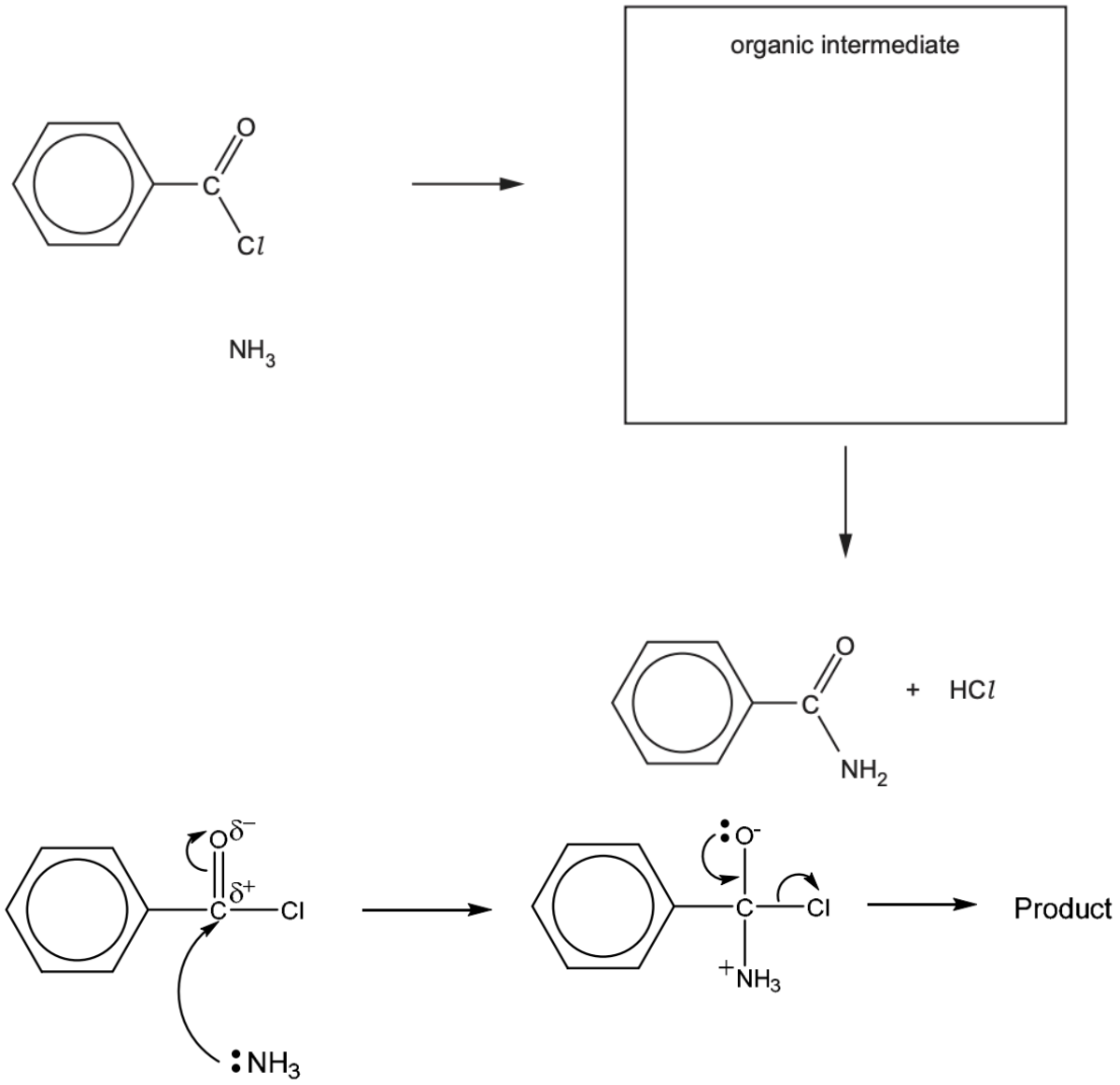
- Because the lone pair of electrons on N atom is delocalised into π-bond system of benzene ring.
- This increases electron density of the ring, so it can polarise the electrophile/ Br2 better.

Explain why benzamide, $C_6H_5CONH_2$, is a much weaker base than ammonia, NH3.

- lone pair / p-orbital on N is delocalised into the C=O group / across the two electronegative O and N.

Complete the mechanism in Fig. 8.1 for the reaction of C_6H_5COCl with NH_3.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles. Draw the structure of the organic intermediate.



M1 / M2 *any two for one mark, all four for two marks:*

- lone pair on N
- correct arrow from lone pair N to C (of C=O)
- correct dipole on C=O
- correct arrow from the C=O bond to O atom

M3 correct intermediate

M4 arrow from $O^{(-)}$ to C–O bond **AND** arrow from C–Cl bond to Cl
ALLOW arrow from anywhere on O^- to C–O bond

State what is meant by isoelectric point.

- pH at which a molecule has no overall charge / is neutral / exists as a zwitterion.

Explain why trichloroethanoic acid, CCl3COOH, is more acidic than ethanoic acid, CH3COOH.

- due to the electron-withdrawing effect/electronegative/ –I effect of chlorine, which stabilises the anion / carboxylate ion OR weakens the O-H bond.

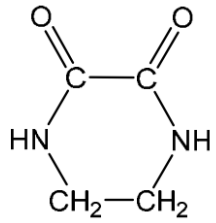
(ii) Samples of $(COCl)_2$ are reacted separately with an excess of warm acidified $KMnO_4(aq)$ and with $H_2NCH_2CH_2NH_2$.

The carbon-containing product from the reaction with $H_2NCH_2CH_2NH_2$ has the molecular formula $C_4H_6N_2O_2$.

Complete the boxes in Fig. 9.1 to suggest the structure of the carbon-containing product in each reaction.

with warm acidified $KMnO_4(aq)$	with $H_2NCH_2CH_2NH_2$

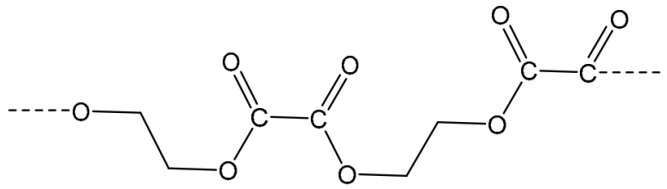
CO_2 [1]



[1]

NOTE: Acyl chlorides are not oxidised to carboxylic acids. They form carboxylic acids by hydrolysis with water (addition-elimination where H2O is added and HCl is eliminated). Oxidation of acyl chlorides by strong oxidising agents forms CO2.

A polyester can be synthesised from the reaction of (COCl)2 with ethane-1,2-diol, HOCH2CH2OH. Draw two repeat units of the polymer formed. Any functional groups should be displayed.



M1 one correct repeat unit (within their structure)
M2 the rest of the structure correct
ecf on one incorrect monomer used
[If structure partly or fully skeletal: continuation bonds must be dashed / wavy / different or have through brackets]

The compound C_6H_6 has many structural isomers. Four suggested structures of C_6H_6 are shown in Fig. 6.1.

Kekulé benzene Dewar benzene Ladenburg benzene delocalised benzene

Fig. 6.1

Using Fig. 6.1, complete Table 6.1 to predict the number of carbon atoms that have sp, sp^2 and sp^3 hybridisation in Kekulé benzene, Dewar benzene and Ladenburg benzene.

Table 6.1

C_6H_6 structure	sp hybridised	sp^2 hybridised	sp^3 hybridised
Kekulé benzene			
Dewar benzene			
Ladenburg benzene			

[2]

	sp	sp^2	sp^3
Kekulé benzene	0	6	0
Dewar benzene	0	4	2
Ladenburg benzene	0	0	6

NOTE:

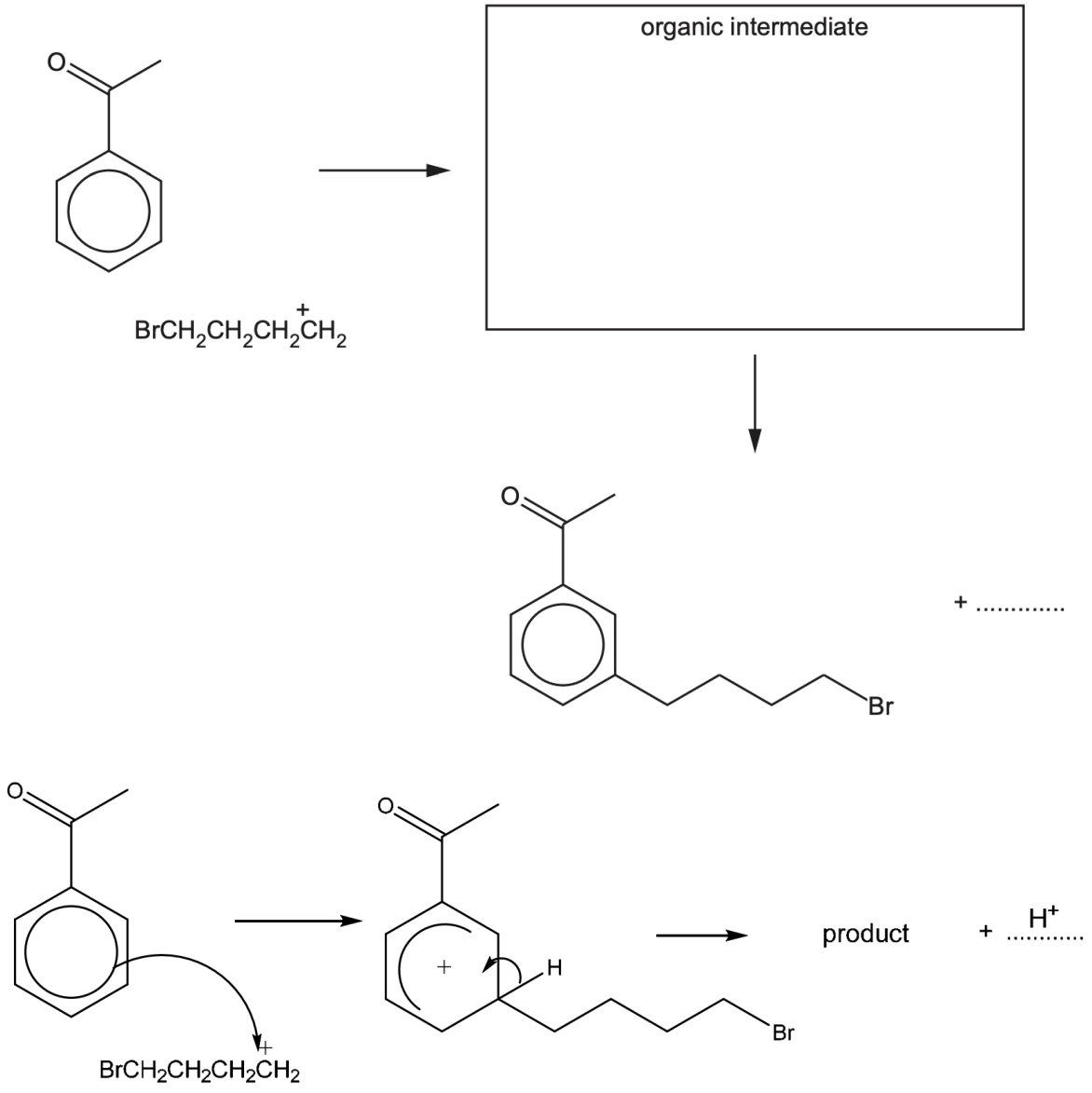
- No. of carbons with single bond = no. of sp3 hybridised carbons
- No. of carbons with double bond = no. of sp2 hybridised carbons
- No. of carbons with triple bond = no. of sp hybridised carbons

Suggest why Dewar benzene and Ladenburg benzene are unstable isomers of C6H6.

- Bond strain/ ring strain

Describe the shape of delocalised benzene. Include the geometry of each carbon, the C-C-H bond angle and the type of bond(s) between the carbon atoms and between the carbon and hydrogen atoms.

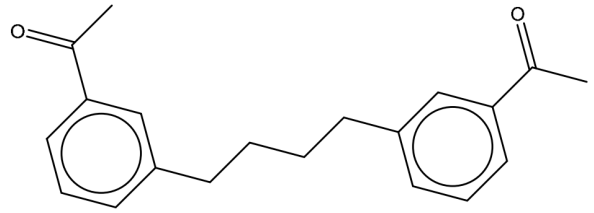
- Geometry: hexagonal/ trigonal planar
- Between C atoms: π-bonds and σ-bonds
- Between C and H atoms: σ-bonds only



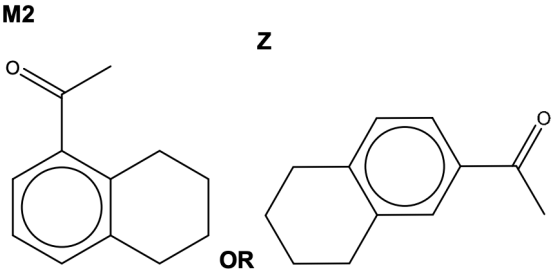
H+ not HBr, since only reaction with already formed electrophile is shown.

This reaction forms small amounts of two by-products, Y ($C_{20}H_{22}O_2$) and Z ($C_{12}H_{14}O$). Suggest structures for Y and Z.

M1 Y



M2 Z



OR

(d) Compound **F**, $C_6H_8O_3$, shows stereoisomerism and effervesces with Na_2CO_3(aq).

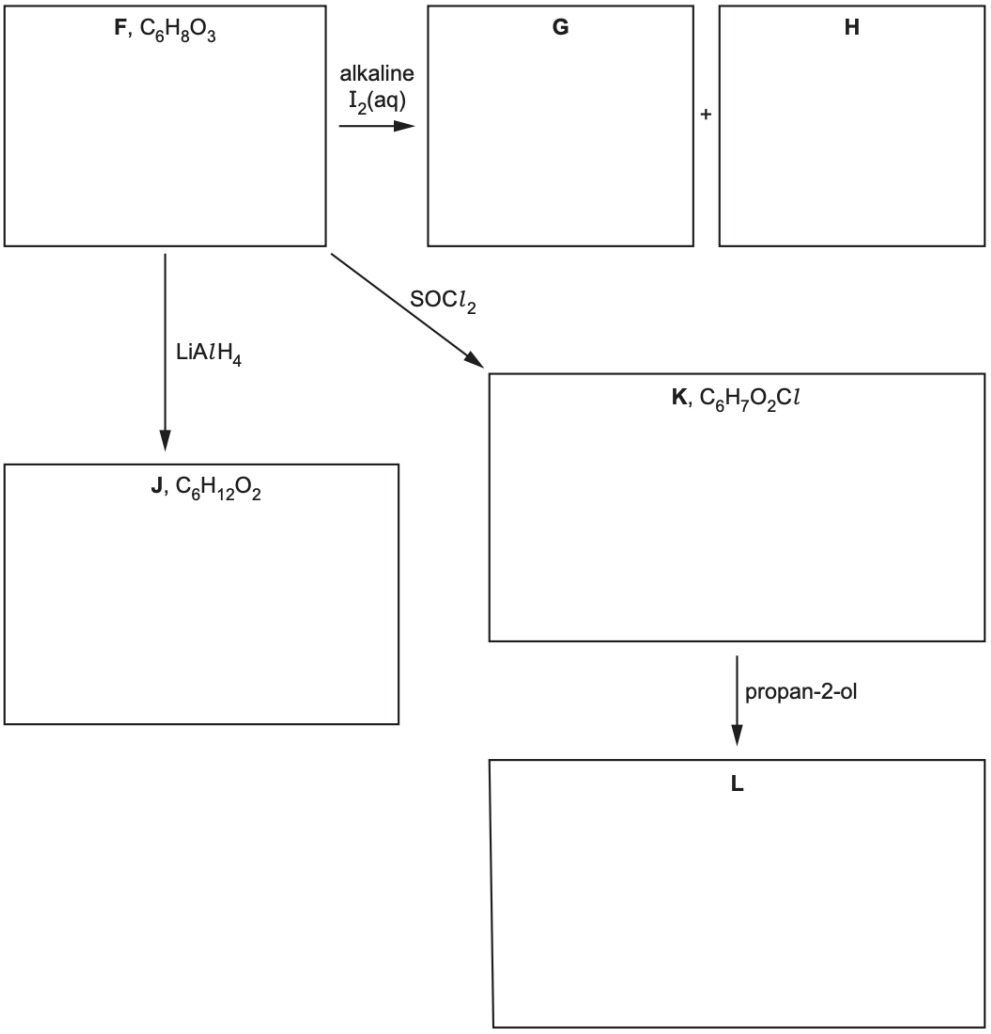
Compound **F** reacts with alkaline I_2(aq) to form yellow precipitate **G** and compound **H**.

Compound **F** reacts with $LiAlH_4$ to form compound **J**, $C_6H_{12}O_2$.

Compound **F** reacts with $SOCl_2$ to form compound **K**, $C_6H_7O_2Cl$.

Compound **K** reacts with propan-2-ol to form compound **L**.

Draw the structures of compounds **F**, **G**, **H**, **J**, **K** and **L** in the boxes in Fig. 7.3.



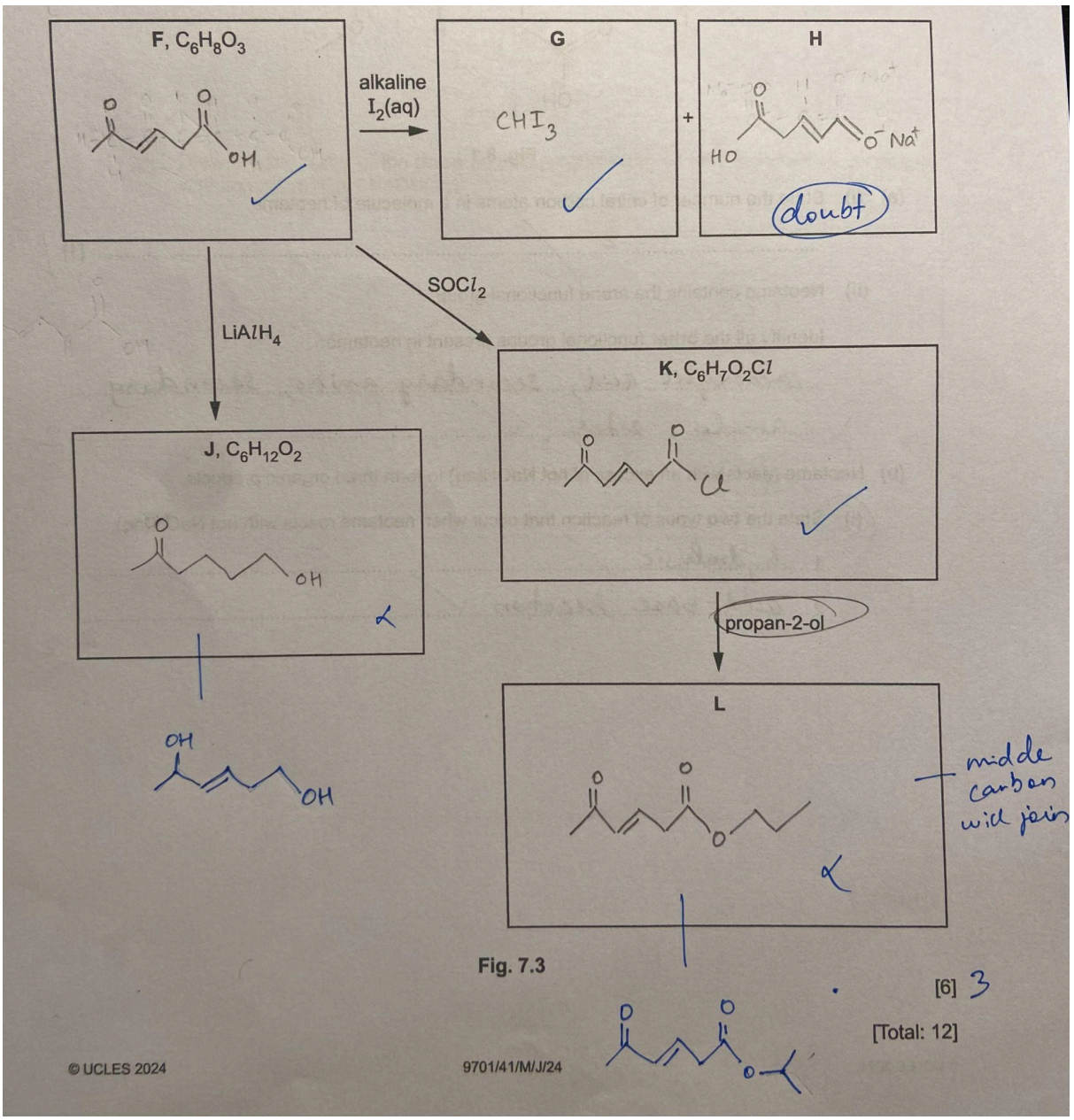
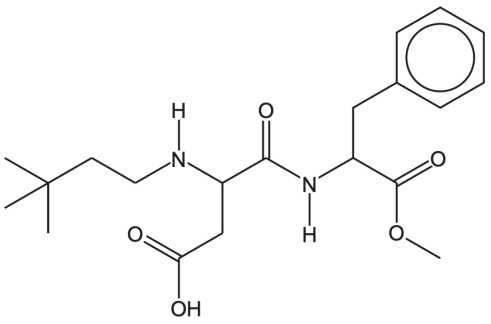


Fig. 7.3

[6] 3

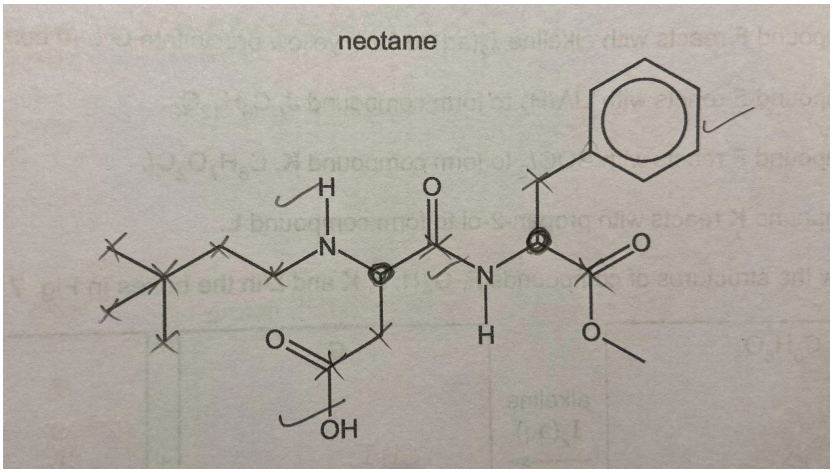
[Total: 12]

neotame



State the number of chiral carbon atoms in a molecule of neotame.

- 2



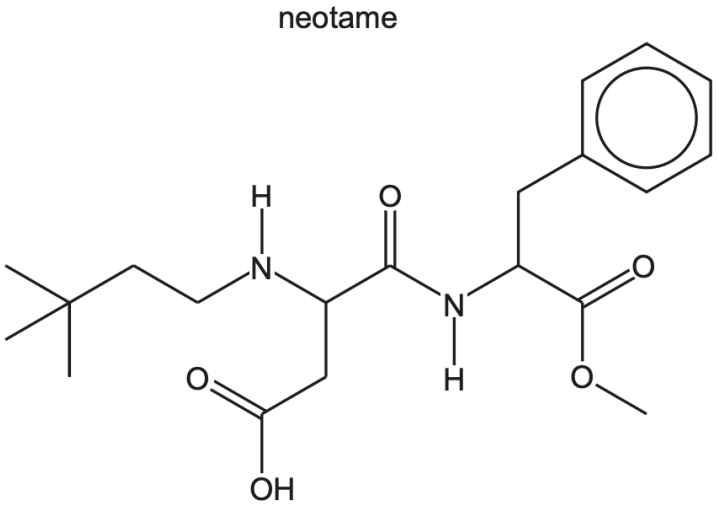
NOTE: C attached to benzene ring cannot be chiral!

Identify all the other functional groups present in neotame.

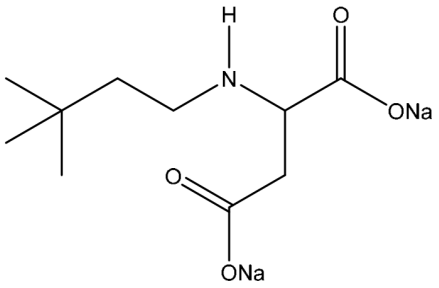
- amide
- amine
- ester
- carboxylic acid / carboxyl

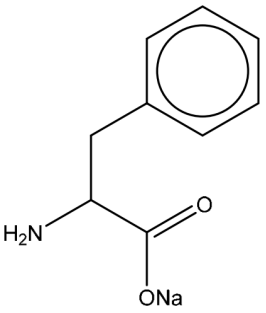
State the two types of reaction that occur when neotame reacts with hot NaOH(aq).

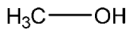
- Hydrolysis
- Acid-base



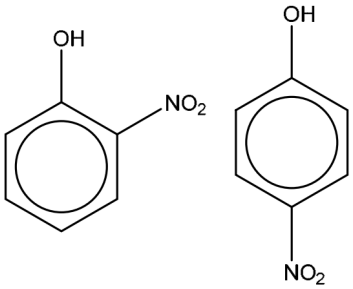
Draw the structures of the three organic products formed from the reaction of neotame with an excess of hot NaOH(aq).



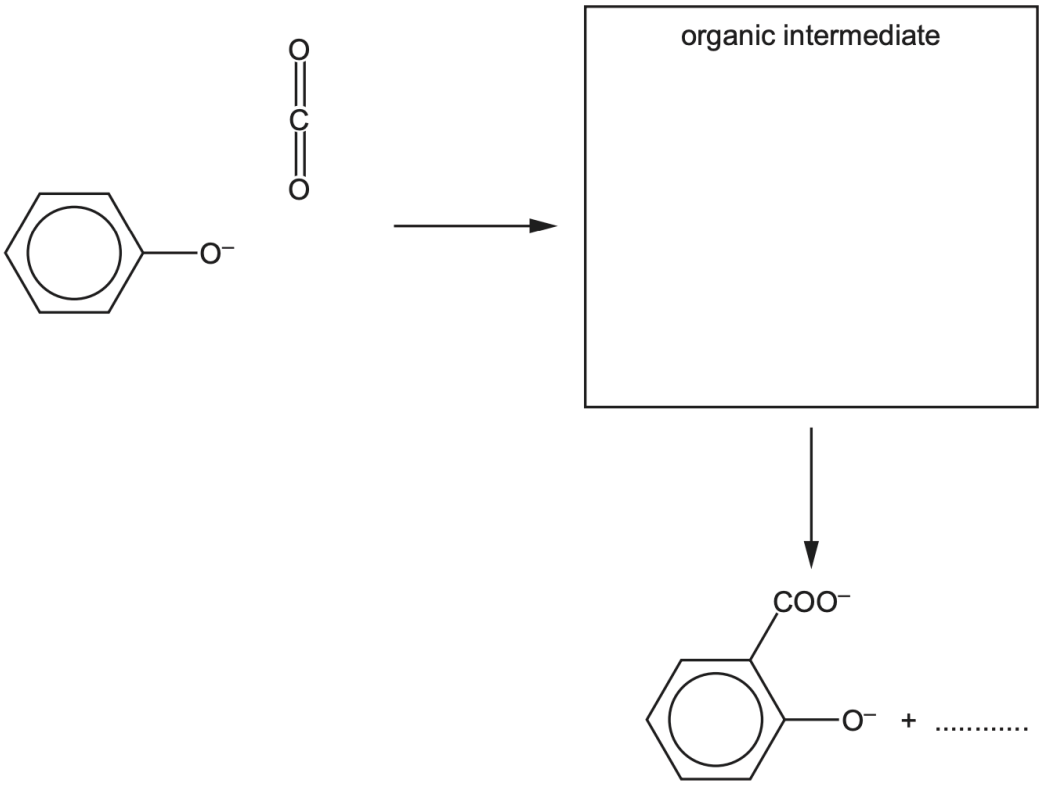


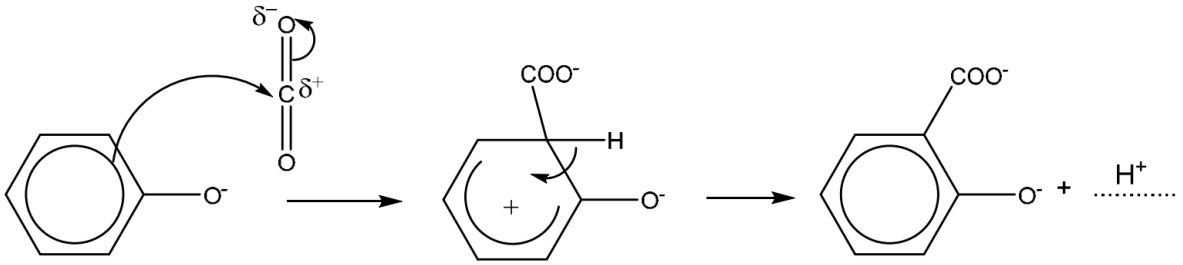


Draw the structures of the two major isomeric organic products formed in the reaction of phenol with dilute HNO3.



Include all relevant curly arrows, dipoles and charges. Draw the structure of the organic intermediate.





Some syntheses use Diels–Alder reactions, which normally involve a diene and an alkene reacting together to form a cyclohexene.

(i) Draw **three** curly arrows in Fig. 9.4 to complete the mechanism for the Diels–Alder reaction between buta-1,3-diene and ethene.

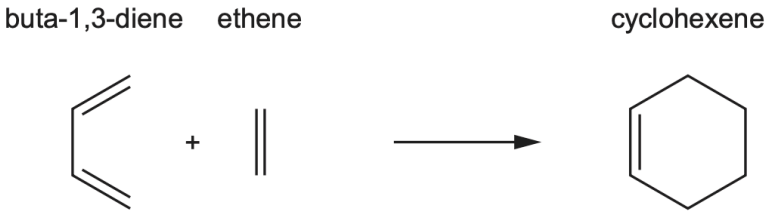
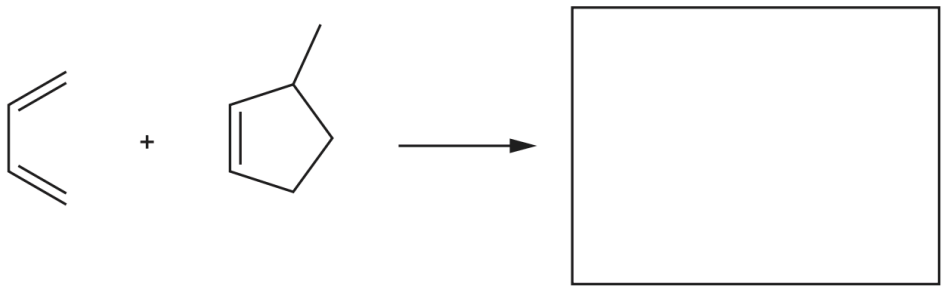


Fig. 9.4

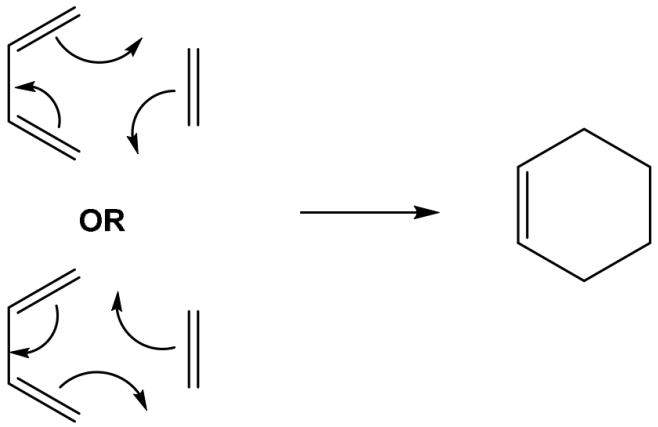
[1]

(ii) Another Diels–Alder reaction of buta-1,3-diene is shown in Fig. 9.5.

Predict the product formed in this reaction.

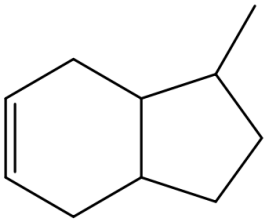


9(c)(i)



All three curly arrows for one mark

9(c)(ii)



Pyrazine is an aromatic compound. The bonding and structure of pyrazine is similar to that of benzene. Describe and explain the shape of pyrazine. In your answer, include:

• the hybridisation of the nitrogen and carbon atoms

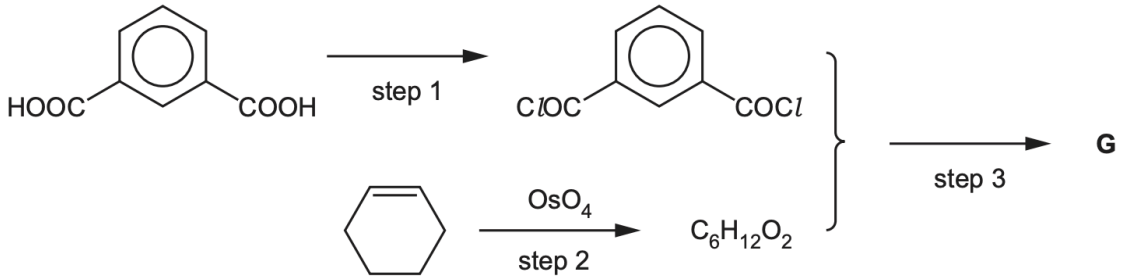
• how orbital overlap forms π bonds between the atoms in the ring.

pyrazine

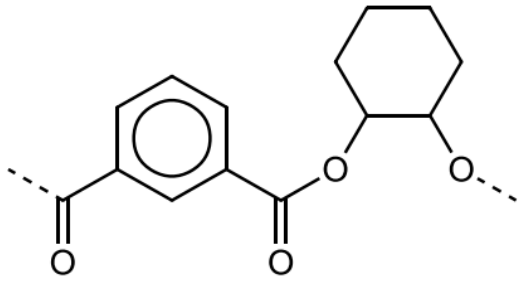
- shape is hexagonal ring planar / trigonal planar / 120˚
- carbons and nitrogens are sp2 hybridised
- a p orbital (from each atom) overlaps sideways/laterally with each other above and below the ring forming π-bonds

(c) Osmium tetroxide, OsO_4, reacts with alkenes in a similar manner to cold dilute acidified MnO_4^-.

Fig. 4.2 shows a proposed synthesis of a condensation polymer **G**.

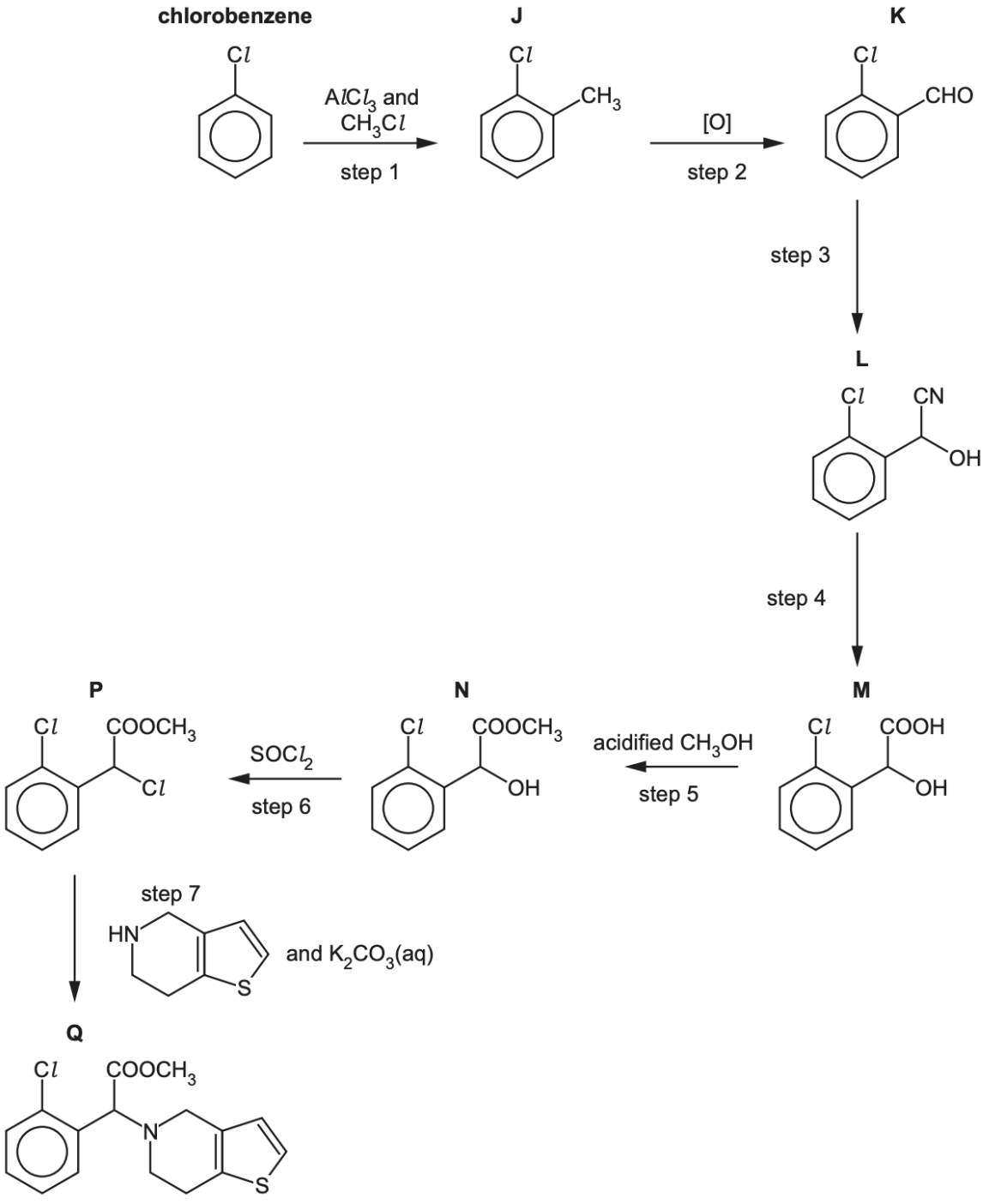


Draw the structure of exactly one repeat unit of the condensation polymer G. The ester linkage should be shown fully displayed.



NOTE:
Alkene + cold dilute KMnO4 = diol

5 Compound **Q** can be synthesised from chlorobenzene in seven steps, using the route shown in Fig. 5.1.



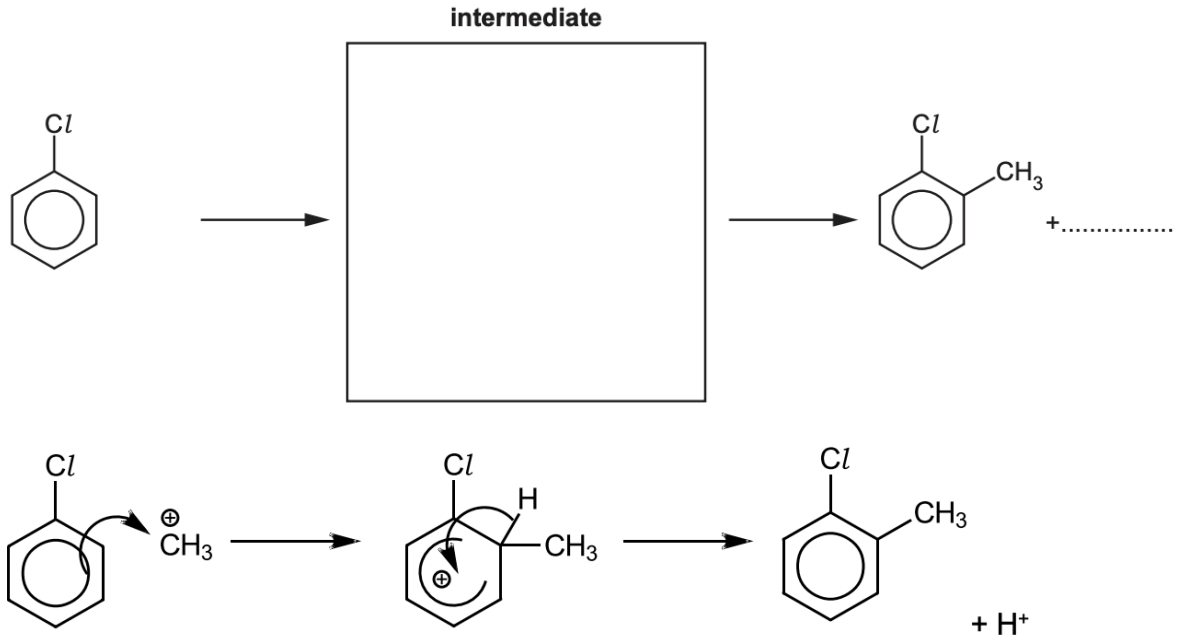
Write an equation for the formation of the electrophile for step 1.

$$AlCl_3 + CH_3Cl \rightarrow AlCl_4^- + CH_3^+$$

(ii) Complete the mechanism in Fig. 5.2 for step 1, the alkylation of chlorobenzene.

Include all relevant curly arrows and charges.

Draw the structure of the intermediate.



curly arrow from inside hexagon to electrophile (CH_3^+)

---

intermediate

---

curly arrow from C—H bond into the hexagon **AND** H^+ formed

Step 2 is an oxidation reaction. Construct an equation for the reaction in step 2. Use [O] to represent an atom of oxygen from an oxidising agent.

- $C_6H_4(Cl)CH_3 + \mathbf{2}[O] \rightarrow C_6H_4(Cl)CHO + H_2O$

Suggest reagents for the conversion of K to M in steps 3 and 4.

- Step 3: HCN and KCN catalyst OR KCN and H2SO4/HCl
- Step 4: H2SO4(aq) OR HCl (aq)

NOTE:

- Aldehyde + HCN (with KCN catalyst) → Hydroxynitrile
- Oxidation of nitriles forms amide!! (NOT carboxylic acid, because the N has to be present). Nitrile to carboxylic acid = hydrolysis with acid.

Identify the type of reaction that occurs in step 5.

- Addition-elimination / condensation

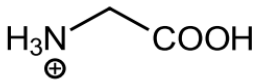
Explain the meaning of optically active.

- A substance able to rotate the plane of plane-polarised light.

Give reasons why it might be desirable to synthesise a single optical isomer for use as a drug.

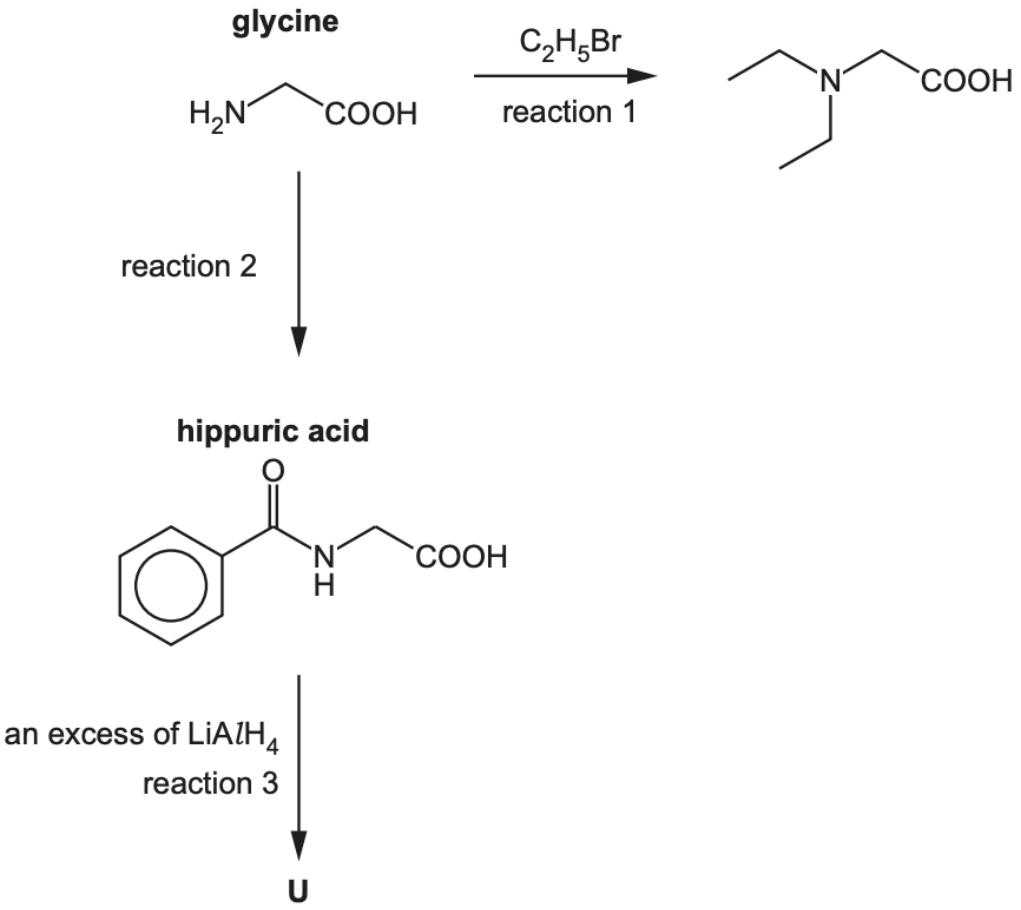
- reduced / different biological activity of 'other' enantiomer
- avoids need to separate the optical isomers to form the pure active isomer
- lower dosage required OR (drug is) more potent
- higher yield (of biologically-active molecule)
- no / less (harmful) side effects OR other isomer can have side effects

Glycine = H_2NCH_2COOH
Draw the structure of glycine at pH4.



NOTE: + charge should be on N!!

Fig. 6.1 shows two syntheses starting with glycine.



State the essential conditions for reaction 1.

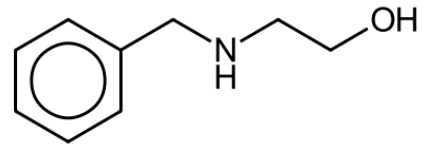
- Ethanol and heat in a sealed tube OR ethanol and high pressure

Identify the reagent used in reaction 2

- Benzoyl chloride

Draw the structure of the organic product U that forms when hippuric acid reacts with an excess of LiAlH4 in reaction 3.

-

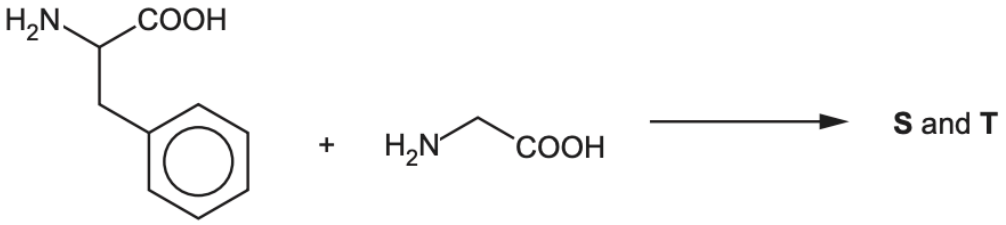


NOTE: the COOH has a carbon- remember that!! Don't directly replace COOH with OH!

A molecule of phenylalanine, **R**, can react with a molecule of glycine to form two dipeptides, **S** and **T**.

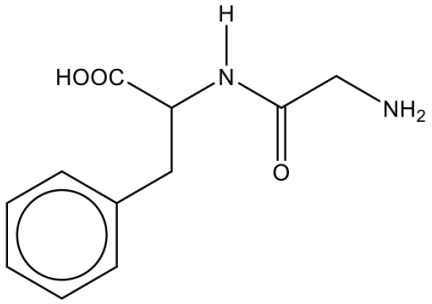
S and **T** are structural isomers.

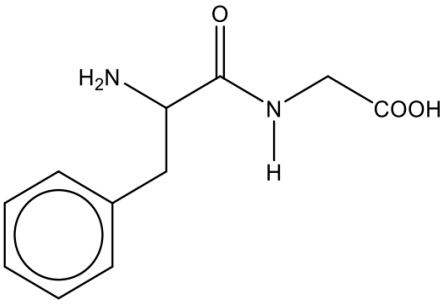
R **glycine**



Draw the structures of these dipeptides. The peptide bond formed should be shown fully displayed.

-

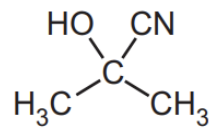




Explain why amides are weaker bases than amines.

- nitrogen lone pair in amides is delocalised with C=O
- lone pair less available for donation / to accept H+ OR less electron density on N / NH2 so less able to accept H+

B



When B is hydrolysed under hot acidic conditions, carboxylic acid C is formed. Draw the structure of C.

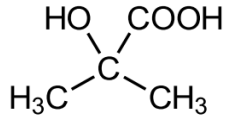


Fig. 4.1 shows two different ways to synthesise propylamine.

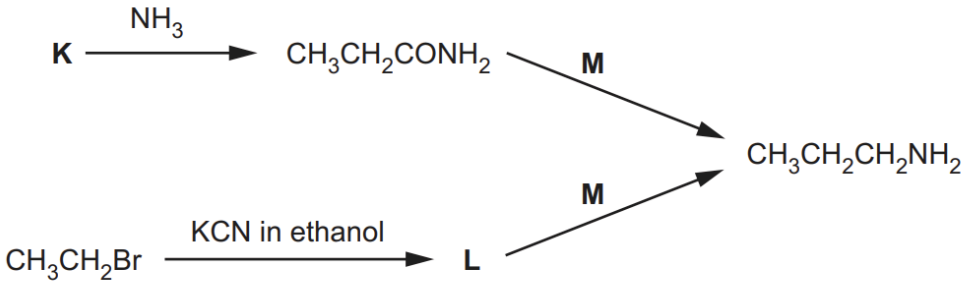


Fig. 4.1

Identify compounds **K** and **L** and reagent **M** from Fig. 4.1.

K = CH_3CH_2COCl / propanoyl chloride

L = CH_3CH_2CN / propanenitrile

M = $LiAlH_4$ **OR** H_2 / Ni / correct names

(c) Compound **N** is shown in Fig. 4.2.

N

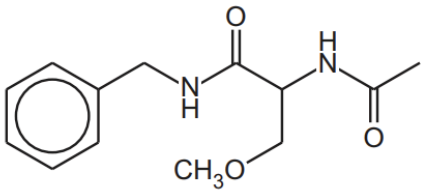


Fig. 4.2

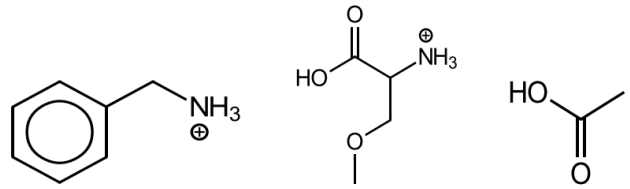
Compound **N** is treated with an excess of concentrated HC*l*(aq).

N undergoes complete hydrolysis to form three organic products.

The products are isolated from the reaction mixture at pH 4.

Draw the structures of the three organic products at pH 4.

Assume that the CH_3O— group does **not** react.



M1: (un)protonated benzylamine
M2: (un)protonated amine as above
M3: ethanoic acid

M4: all amine groups protonated (—NH_3^+) **AND** all acid groups as —COOH

Compound **P** can be synthesised from 1-methyl-4-nitrobenzene by the route shown in Fig. 4.3.

1-methyl-4-nitrobenzene

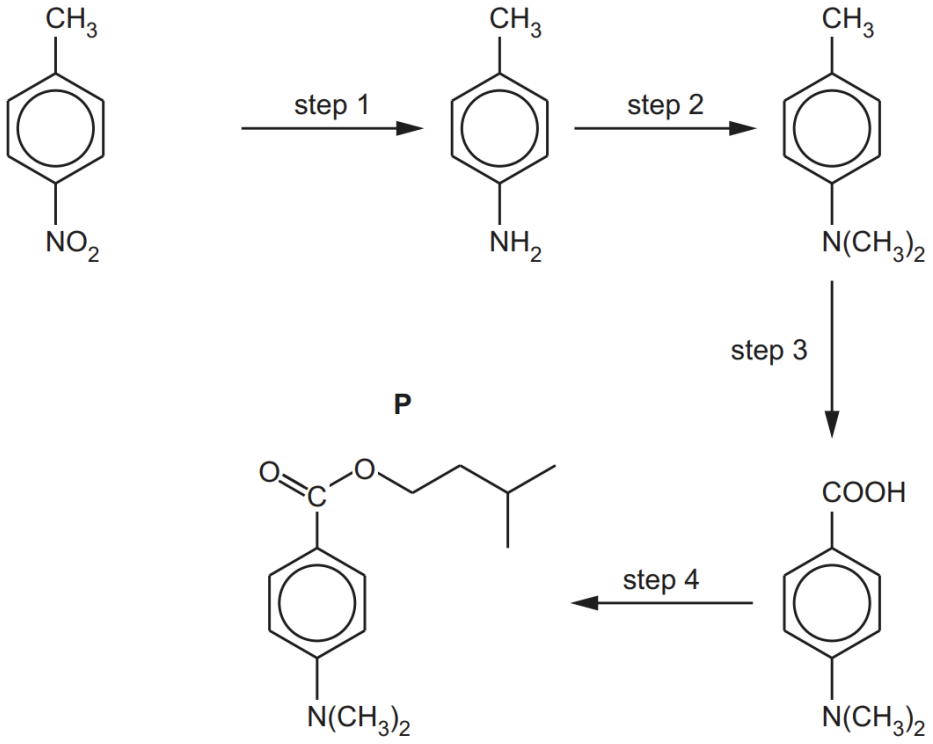
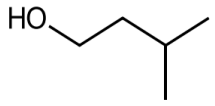
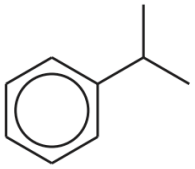


Fig. 4.3

step	reagents and conditions	type of reaction
1	• Sn & **conc**. HCl (+ heat)	reduction
2	• CH_3Br / CH_3Cl / CH_3I (in ethanol)	• (nucleophilic) substitution
3	• **hot** MnO_4^-/$KMnO_4$	• oxidation
4	•  (+ conc. H_2SO_4)	condensation

cumene



Cumene has:

- 6 sp2 carbons
- 3 sp3 carbons

In Friedel–Crafts alkylation of benzene by 1-bromopropane, the CH3CH2CH2 + cation formed in the first step quickly rearranges to form the (CH3)2CH+ cation. Suggest why this is the case. Explain your answer.

- 2° carbocation is more stable due to greater positive inductive effect of alkyl groups.

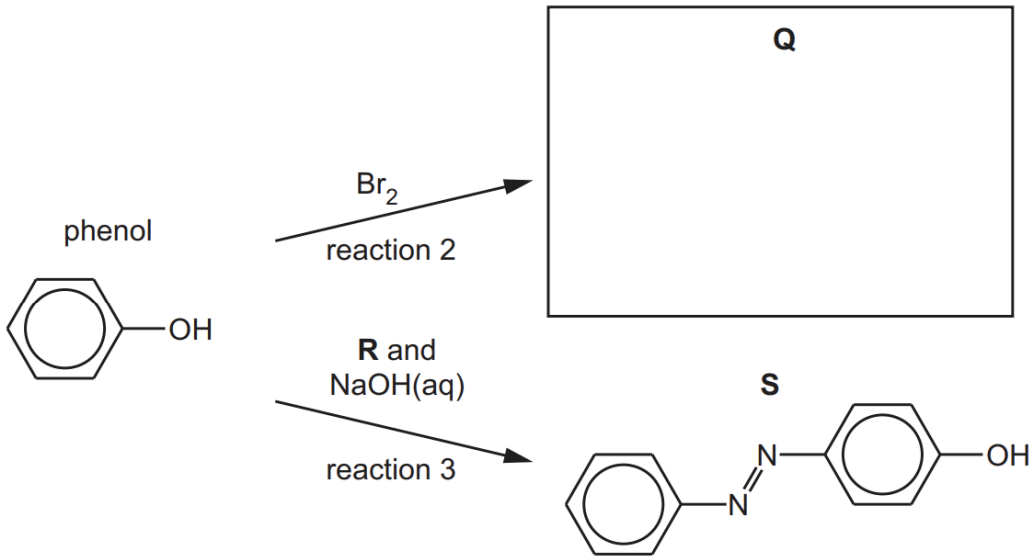
State the conditions for the bromination of phenol. Explain why these conditions are different from those for the bromination of benzene.

Conditions:

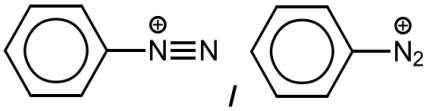
- Aqueous
- Bromine water
- No AlBr3 catalyst needed

Explanation:

- lone pair of e–/p-orbital on oxygen overlap / delocalised with ring / system.
- electron density in ring increases / ring becomes more electron rich (and attracts electrophiles).
- phenol is more reactive so polarises Br2 / bromine / electrophiles more.



Identify organic reagent R.

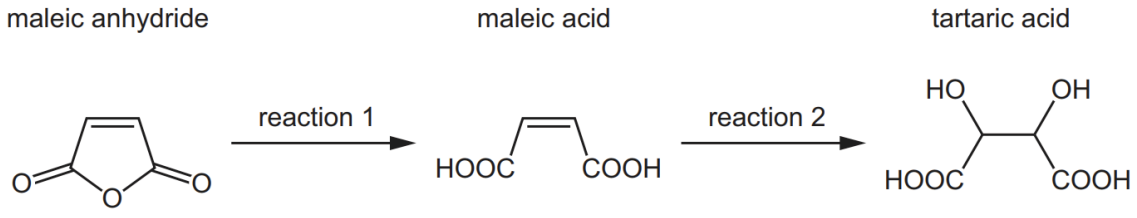
R =  **/** **/ benzene diazonium chloride**

Name the functional group that is formed in reaction 3.

- Azo

(a) Maleic anhydride is an unsaturated cyclic compound used in the formation of several polymers.

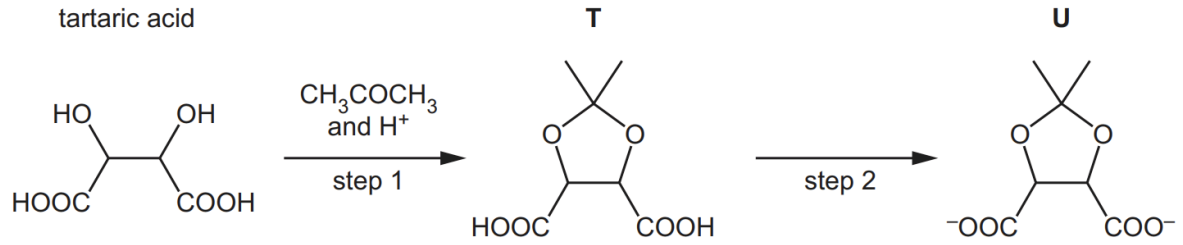
Maleic anhydride can be used to form maleic acid and tartaric acid.



Identify a suitable reagent and the conditions for reaction 2.

- Cold, dilute, acidified KMno4

(b) Compound **U** can be formed from tartaric acid in two steps, as shown in Fig. 6.2.



Suggest the type of reaction that occurs in step 1.

- condensation OR dehydration OR elimination

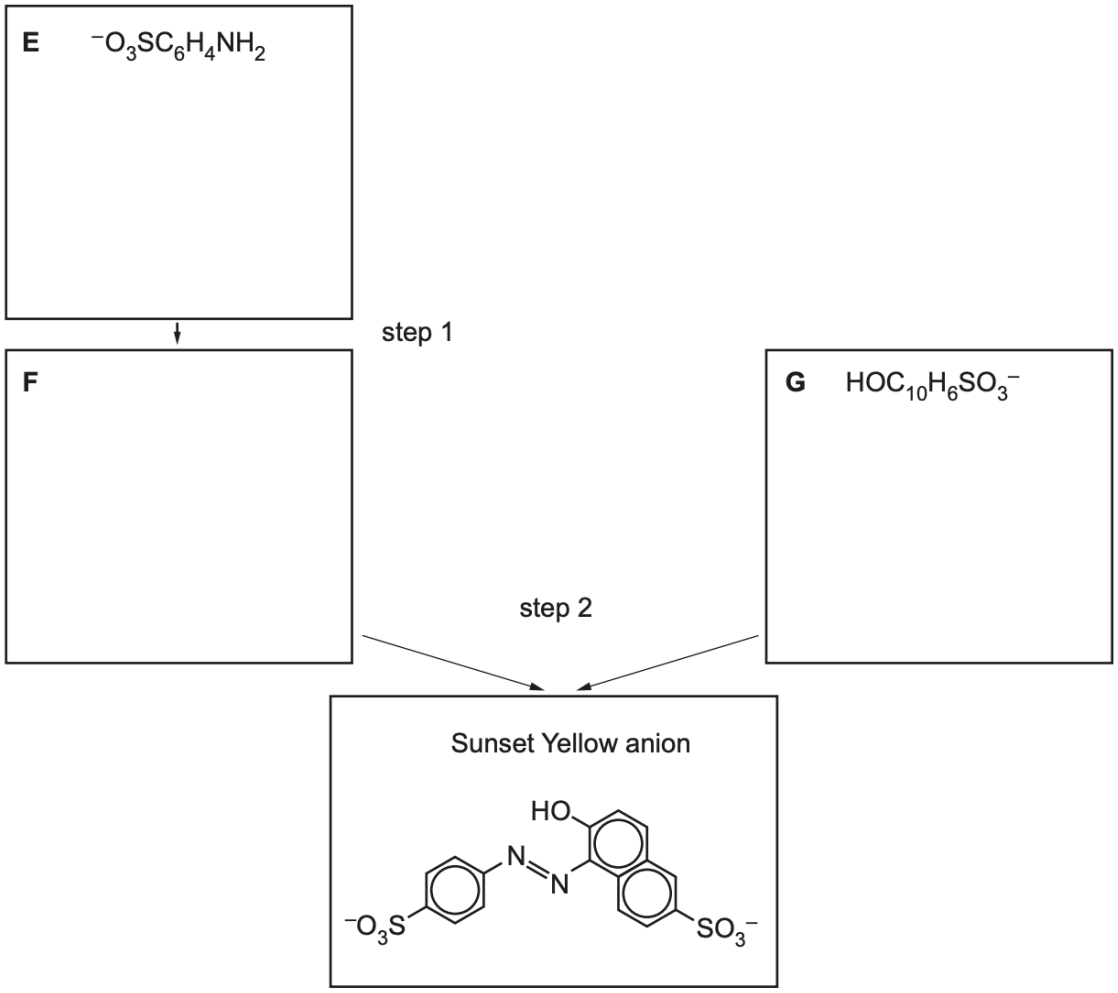
CH3CH2COOH, CH3CCl2COOH and H2SO4 are all acidic. Suggest the trend in the relative acid strength of these three compounds.

- H2SO4 > CH3CCl2COOH > CH3CH2COOH
- H2SO4 is fully dissociated
- CH3CH2COOH / CH3CCl2COOH are partly dissociated / weak acids
- Cl / chlorine is electron-withdrawing / electronegative
- alkyl group (in CH3CH2COOH) is electron donating
- stabilises / destabilises anion OR weakens / strengthens O-H bond
- correct reference to release of / donation of / form H+ / proton

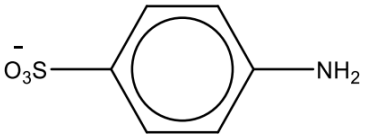
Sunset Yellow is an additive used for colouring foods.

A synthetic route for making Sunset Yellow is shown.

Molecules **E** and **G** each contain one $-SO_3^-$ group. These groups are unchanged in the formation of Sunset Yellow.

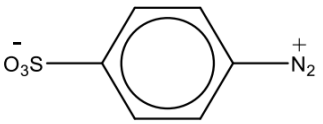


E:

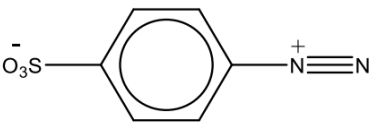


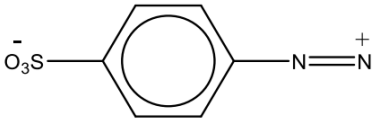
[1]

F:



OR

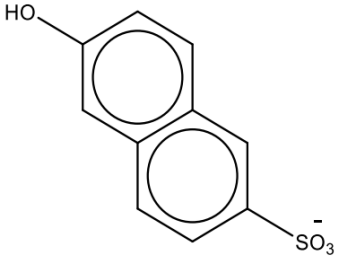




[1]

ECF from E

G



[1]

Suggest suitable reagents and conditions for step 1 and 2.

- Step 1: HNO2 OR NaNO2 + HCl, T ⩽ 10 °C
- Step 2: NaOH(aq) / alkaline conditions

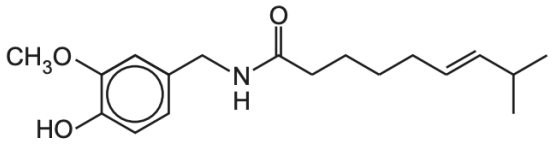
Define buffer solution

- a solution which resists changes in pH when small quantities of acid or base are added

(b) Complete the equation for the reaction of capsaicin with an excess of Br_2(aq) in the dark.

Draw the structure of the organic product in the labelled box.

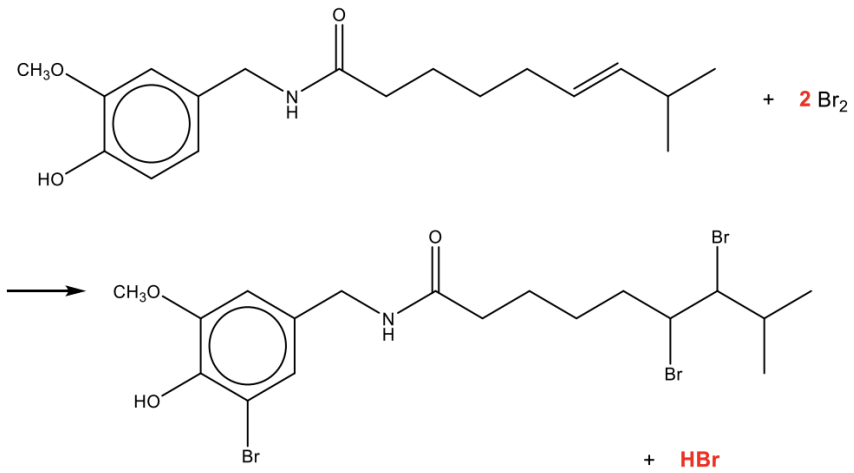
capsaicin



+ .....Br_2 ⟶

organic product

+ .....



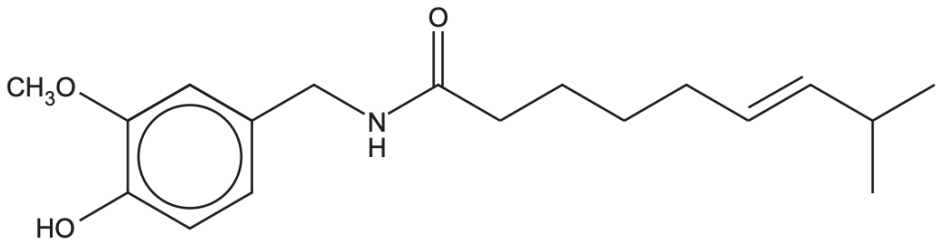
M1: HBr [1] u / c
M2: structure of the organic product[1]
M3: correct balanced equation [1] ecf

When capsaicin is treated with reagent J under suitable conditions one of the products is methylpropanoic acid, CH3CH(CH3)COOH. Identify reagent J and any necessary conditions.

- hot AND concentrated AND acidified AND KMnO4

(e) (i) Capsaicin is heated with an excess of hot aqueous NaOH.

capsaicin

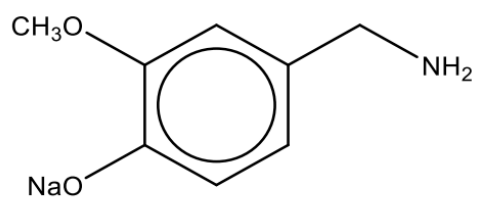


Draw the structures of the two organic products **H** and **K**.

H $C_8H_{10}NO_2Na$

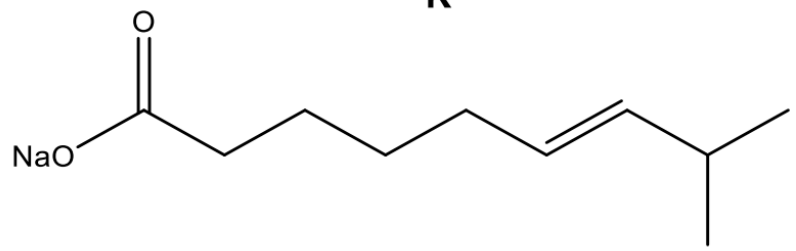
K $C_{10}H_{17}O_2Na$

H



[1]

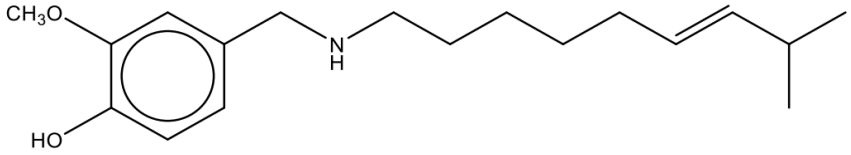
K



[1]

Draw the structure of the organic product L formed when capsaicin is treated with LiAlH4 in dry ether.

L



[1]

NOTE: carboxylic acid to acyl chloride = nucleophilic substitution

Suggest the relative ease of hydrolysis of benzoyl chloride, chlorobenzene and chloroethane when added separately to water at 25°C.

- Chlorobenzene (hardest to hydrolyse) < chloroethane < benzoyl chloride (easiest to hydrolyse)
- correct link to: strengthening C-Cl bond OR weakening C-Cl bond OR C-Cl bond has partially double bond character OR C-Cl is more difficult to break
- Chlorobenzene: lone pair / p-orbital on Cl overlaps / delocalised / incorporated with ring
- Benzoyl chloride: C of C-Cl has most electron deficient OR has an electronegative oxygen atom / two electronegative atoms / electron withdrawing C=O group
- Chloroethane: electron donating effect / positive inductive effect of alkyl / R group

(b) C_6H_5COCl reacts with phenol, C_6H_5OH, to give the ester phenyl benzoate, $C_6H_5COOC_6H_5$.

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.

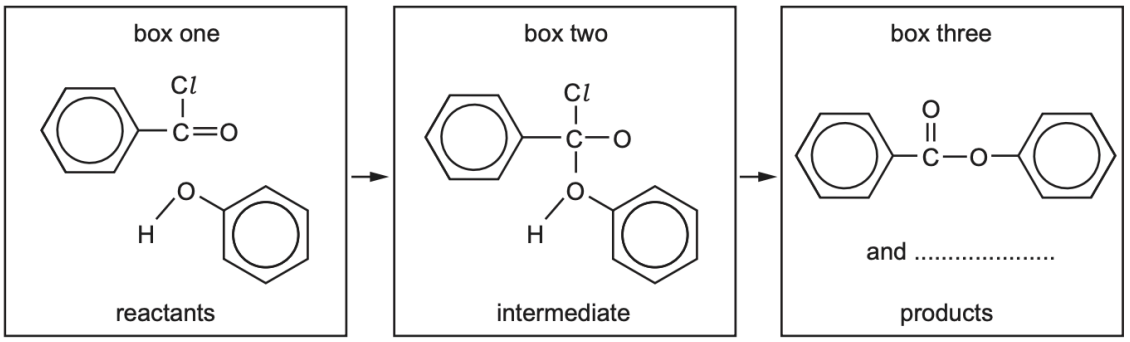
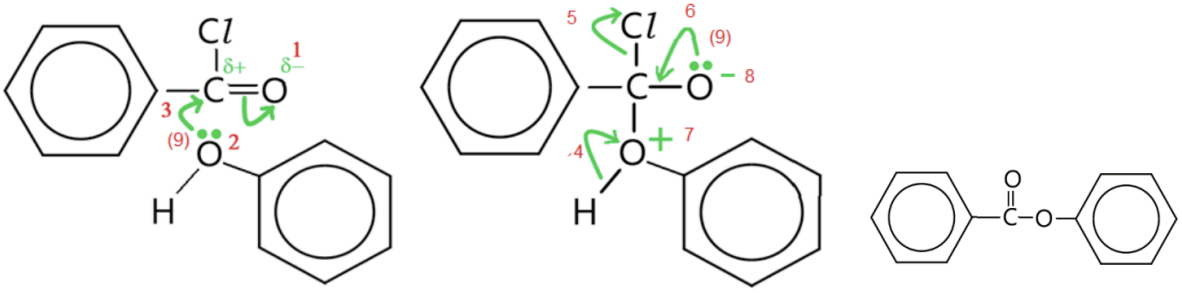


Fig. 9.1

(i) Complete the mechanism in Fig. 9.1 and include:

- all relevant dipoles (δ+ and δ–) and full electric charges (+ and –) on the species in box one and in box two
- all relevant lone pairs on the species in box one and in box two
- all relevant curly arrows to show the movement of electron pairs in box one and in box two
- the formula of the second product in box three.



and HCl [10]

The red numbers refer to points 1 to 10 in the verbal MS that follows.

---

box one:
- 1 dipole on C=O
- 2 curly arrow from O of phenol to C of acyl chloride
- 3 curly arrow from bond of C=O to O of acyl chloride

box two:
- 4 curly arrow from O-H bond to what was O of phenol
- 5 curly arrow from C-Cl bond to what was Cl of acyl chloride
- 6 curly arrow from O to reform C=O
- 7 + charge on what was O of phenol
- 8 – charge on what was O of acyl chloride
- 9 curly arrow start close to LP for bullet 3 OR 6 (from LP on O)

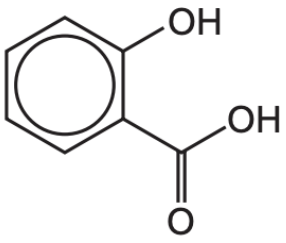
box three:
- 10 HCl / H^+Cl^-

any two [1] any five [2] any eight [3] all ten [4]

Name this mechanism.

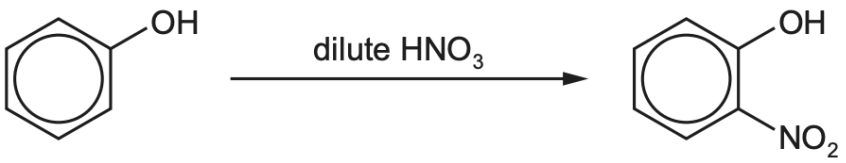
- Addition-elimination

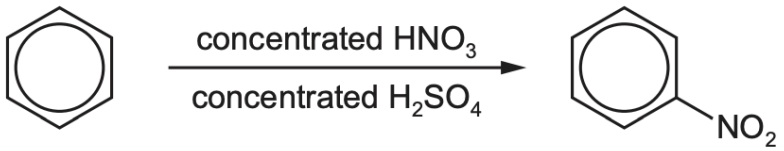
K



Explain why phenol is a weaker acid than K

- O—H bond weaker / more easy to donate H+ in K
- Owing to negative inductive / electron withdrawing effect of C=O / COOH group
- Carboxylate anion stabilised / phenoxide anion is less stabilised





- p-orbital on oxygen overlaps with ring / π system OR lone pair of e– on oxygen is delocalised into the ring.
- electron density in ring increases.
- attracts/polarises electrophile better.

Advantage of condensation polymers over addition polymers

- biodegradable/ easily hydrolysed

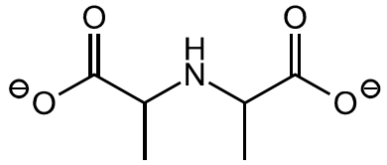
In an excess of NH_3, $CH_3CHCl COO^-$ undergoes a nucleophilic substitution reaction.

reaction 2 $CH_3CHCl COO^- + NH_3 \rightarrow CH_3CH(NH_2)COO^- + H^+ + Cl^-$

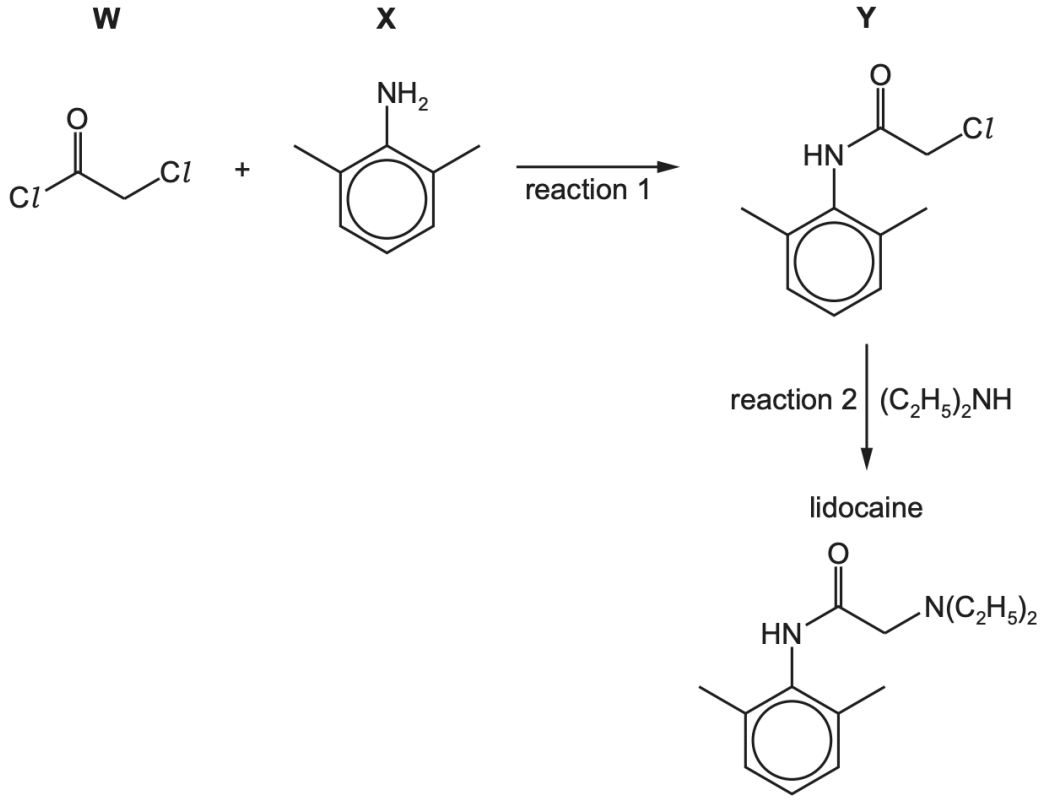
When an excess of $CH_3CHCl COO^-$ is used, further substitution reactions occur. One product has the formula $C_6H_9NO_4^{2-}$.

Suggest the structure of $C_6H_9NO_4^{2-}$.

Ans:



Lidocaine is used as an anaesthetic. A synthesis of lidocaine is shown in Fig. 6.1.

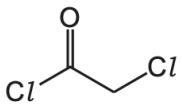


After W and X have reacted together, an excess of CH3COONa(aq) is added to the reaction mixture. Suggest why.

- to remove / neutralise excess H+ / acid produced
  OR to react with any acidic by-products / HCl / SO2
  OR to react with any unreacted W

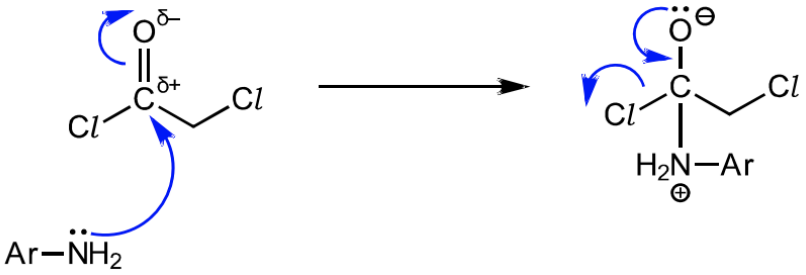
(c) The reaction of **W** with **X**, reaction 1, follows an addition–elimination mechanism.

Complete the mechanism for the reaction of **W** with **X**.
Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.
Use Ar–NH_2 to represent **X**.



Ar—NH_2

[4]



M1: curly arrow from **lone pair** on :NH_2 to carbonyl **C**$^{(\delta+)}$=O
M2: correct dipole on $^{\delta+}$C=O$^{\delta-}$ **AND** curly arrow from bond C=O to O$^{(\delta-)}$
M3: correct structure of the intermediate (inc. charges)
M4: curly arrow from lone pair on :O^- to C=O **AND** curly arrow from C—C*l* to C*l*

(d) The complex $[Cr(OCH_2CH_2NH_2)_3]^-$ is formed by reacting $Cr^{2+}(aq)$ with the conjugate base of 2-aminoethanol.

A synthesis of 2-aminoethanol is shown in Fig. 2.2.

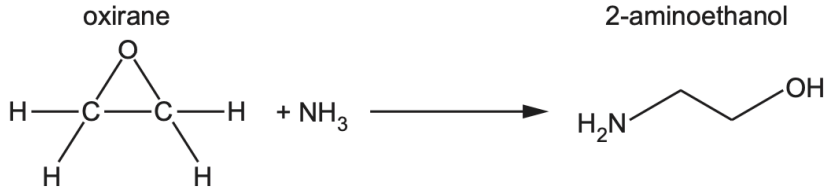
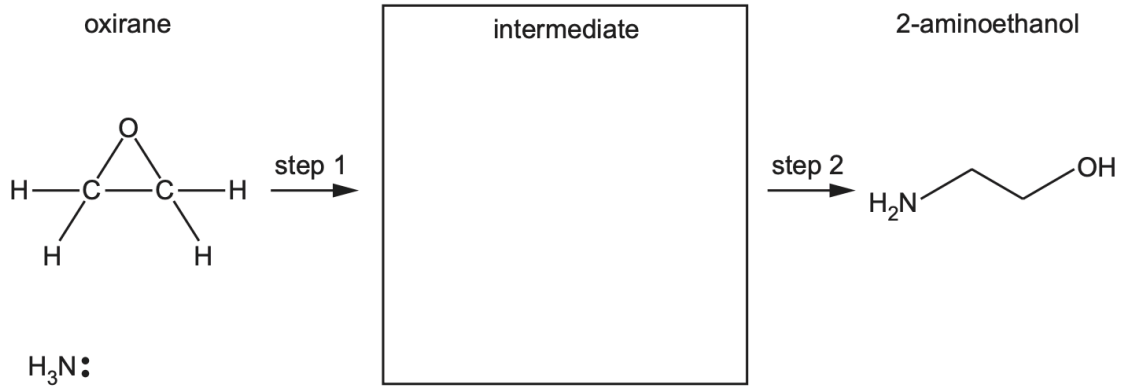


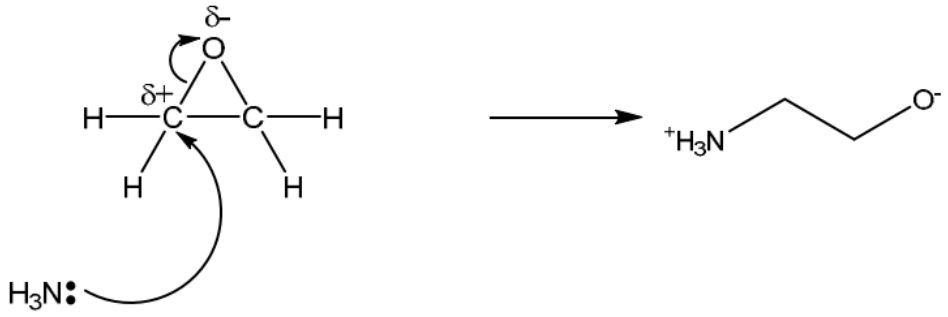
Fig. 2.2

(i) Suggest the mechanism for step 1 of the reaction of oxirane with ammonia in Fig. 2.3.

Include all relevant curly arrows, lone pairs of electrons, charges and partial charges.

Draw the structure of the organic intermediate.

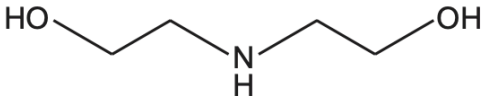




M1 two correct curly arrows
M2 correct dipole
M3 correct structure of intermediate

A small amount of by-product **E**, shown in Fig. 2.4, is produced during the reaction shown in Fig. 2.2.

E



Suggest how the formation of by-product E can be minimised.

- use an excess of ammonia OR limiting amount of oxirane.

Compound **F**, C_4H_9NO, can be formed from the reaction of by-product **E**, $C_4H_{11}NO_2$, with concentrated H_2SO_4.

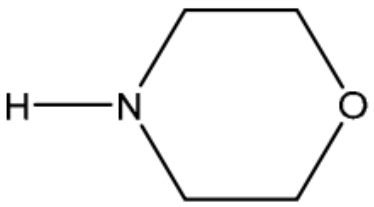
Compound **F** is a **saturated** and basic organic compound.

Suggest a structure for compound **F**. State the type of reaction undergone by **E** to form **F**.

F

type of reaction .....

[2]



M1

M2 elimination / dehydration / condensation

Explanation:

- First look at the difference between the 2 molecular formulae to get a hint.
- 2H atoms are removed, and 1 O atom is removed = H2O is removed!
- Hence, the reaction must be dehydration / elimination/ condensation.

- Now, when dehydration occurs, an alkene is usually formed. However, in this case the product formed is saturated.
- Hence, it must be a cyclic compound.
- So just join up both ends.
- Remember: The N will have H, but the H from the O atom will be removed. This is to satisfy their valencies (O=2, N=3)

State the hybridisation of the carbon atoms and the C–C–H bond angle in benzene, C6H6. Explain how orbital overlap leads to the formation of σ and π bonds in benzene.

- bond angle = 120° AND carbons are sp2
- σ bonds are formed by end-on-end / head on / head to head / linear overlap of orbitals
- π bonds are formed by sideways / lateral overlap of p orbitals

Ethanal, CH_3CHO, reacts with nitrogen dioxide, NO_2. The products of the first step of this reaction are a $CH_3\dot{C}=O$ radical and a molecule of nitrous acid, HNO_2.

$$CH_3CHO + NO_2 \rightarrow CH_3\dot{C}=O + HNO_2$$

(a) (i) Use **two** words to complete the sentence.

This reaction involves .... of the single covalent bond between a hydrogen atom and a carbon atom in CH_3CHO.

[1]

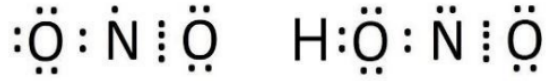
- The reaction forms a **radical** ($CH_3CO\bullet$).
- Radicals are produced by **homolytic** bond breaking, where each atom takes one electron.

(ii) The hydrogen atom mentioned in **(a)(i)** forms a covalent bond with one of the oxygen atoms of an NO_2 molecule. An NO_2 molecule has a single, unpaired electron on the nitrogen atom. All electrons are paired in an HNO_2 molecule.

Draw dot-and-cross diagrams of NO_2 and HNO_2 in the boxes. Show outer shell electrons only.

NO_2

HNO_2



For NO2

- Total number of valence electrons: 5 for N + 2 x 6 for O = 5+12 = 17
- Odd number, so there is the one unpaired electron on N.
- The N atom needs to have 5 electrons
- But, the N atom cannot have more than 8 electrons in its valence shell (because it is in the 2nd period) – expansion of octet can only occur from period 3 onwards (sulfur) have empty d-orbitals.
- Thus it has only 7, so one of the O–N bonds is single and one is double.

Use VSEPR theory to predict the bond angle at the N atom in an HNO2 molecule.

- Around the N atom, there are 3 pairs of electrons. Hence, 120˚.
- However, one of them is a lone pair.
- Hence, bond angle = 120 – 2.5 = 117.5˚

P, **Q**, **R**, **S**, **T**, **U**, and **V** are the seven structural isomers with molecular formula $C_5H_{10}O$ that have a carbonyl group.

P $CH_3(CH_2)_3CHO$ **Q** $CH_3CH_2CH(CH_3)CHO$ **R** $(CH_3)_2CHCH_2CHO$

S $(CH_3)_3CCHO$ **T** $CH_3CH_2CH_2COCH_3$ **U** $CH_3CH_2COCH_2CH_3$

V $(CH_3)_2CHCOCH_3$

Identify the two compounds that give a positive result with alkaline I_2 (aq).

- T and V

Describe the observations when one of the compounds you have identified is treated with alkaline I_2 (aq) and give the structural formulae of the two carbon-containing products of this reaction.

- Yellow solid
- CHI3
- CH3CH2CH2COOH OR (CH3)2CHCOOH

Don't put COONa for these!

Asparagine and aspartic acid are two naturally occurring amino acids. Their structures and isoelectric points are shown in Table 8.1.

Table 8.1

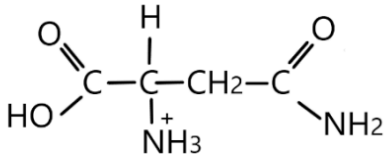
amino acid	structure	isoelectric point
asparagine	$HOOCCH(NH_2)CH_2CONH_2$	5.41
aspartic acid	$HOOCCH(NH_2)CH_2COOH$	2.77

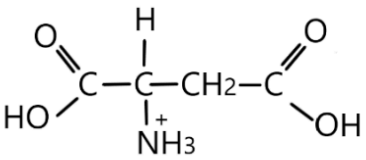
(b) Draw the structures of asparagine and aspartic acid at pH 2.

asparagine at pH 2

aspartic acid at pH 2

M1: $[HOOCCH(NH_3)CH_2CONH_2]^+$
M2: $[HOOCCH(NH_3)CH_2COOH]^+$





- In the first one, the amide stays an amide. You can't just acidify an amide.

Describe two similarities and one difference in the effect of 2 enantiomers on plane polarised light.

Similarities

- Both rotate the plane of plane polarised light
- By the same angle

Difference

- in opposite directions

Describe the bonding in benzene, C6H6.

Your answer should include:

• the hybridisation of the six carbon atoms

• the types of bond between the carbon atoms

• the orbitals that overlap to produce the bonds between the carbon atoms

• the type of bond between the carbon atoms and the hydrogen atoms

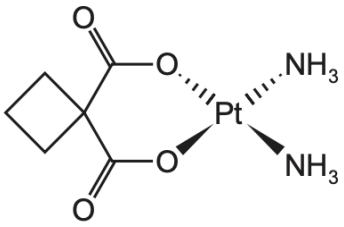
• the orbitals that overlap to produce the bonds between the carbon atoms and the hydrogen atoms.

- all C atoms are sp2 hybridised
- bonds between C atoms are and
- C–C bonds are formed by overlap of sp2 hybrid orbitals
- C–C bonds are formed by overlap of p orbitals
- bonds between C and H atoms are
- C–H bonds are formed by overlap of sp2 hybrid orbitals and s orbitals

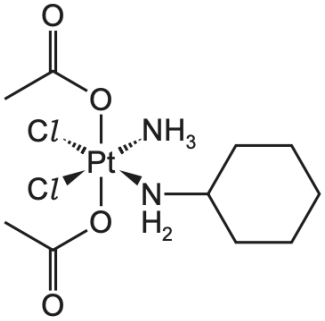
Describe the action of cisplatin as an anticancer drug.

- cisplatin can bond / bind with DNA / (nitrogenous) base A, T, C, G etc.
- which prevents replication (of the DNA / strand) OR prevents cell division / prevents mitosis OR prevents transcription (and formation of mRNA)

carboplatin



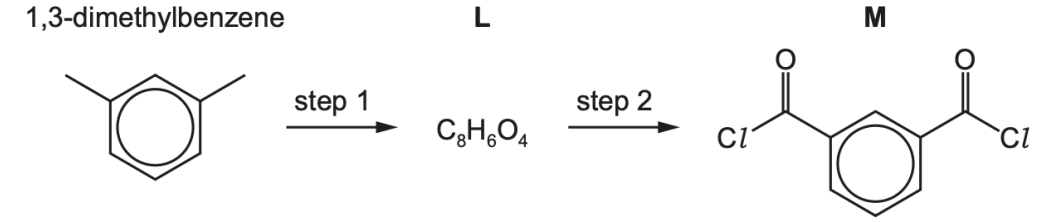
satraplatin



Suggest why carboplatin does not show cis-trans isomerism.

- the distance between two coordinating oxygens is too small to bond trans OR atoms in a bidentate ligand can only bond 90° not 180°

Compound **M** is made from 1,3-dimethylbenzene in a two-step synthesis.



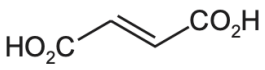
Suggest reactants and conditions for each step of this synthesis.

- Step 1: heat / reflux with acidified / alkaline KMnO4 (then acidify)
- Step 2: PCl5 OR SOCl2 OR (heat with) PCl3

REMEMBER!!
When drawing reaction mechanisms, the curly arrow goes from negative to positive region always!!!

Fumaric acid is a naturally occurring dicarboxylic acid.

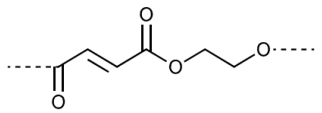
fumaric acid



Identify the products of the reaction between fumaric acid and an excess of hot, concentrated, acidified manganate(VII).

- CO2 and H2O

Draw the repeat unit of the polyester formed when fumaric acid reacts with ethane-1,2-diol, (CH2OH)2. The ester bond should be shown fully displayed.



M1: presence of an ester group from the diol and COOH **OR** presence of an ester group from the fumaric acid and OH
M2: rest of repeat unit including 'dangling' bonds

NOTE- don't forget that double bond from the fumaric acid!! In condensation polymerisation, there is no loss of double bonds! (only in addition)

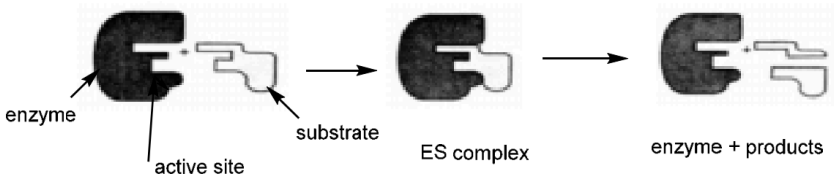
Explain why polyesters normally biodegrade more readily than polyalkenes.

- C—C bonds are non-polar / polyalkenes cannot be hydrolysed OR polyesters / they can be broken down by hydrolysis

The enzyme fumarase catalyses the reaction of fumarate ions, $C_4H_2O_4^{2-}$, with water to form malate ions, $C_4H_4O_5^{2-}$.

$$C_4H_2O_4^{2-} + H_2O \rightleftharpoons C_4H_4O_5^{2-}$$

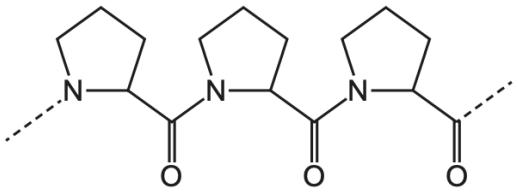
Describe, with the aid of a suitably labelled diagram, how an enzyme such as fumarase can catalyse a reaction.



M1: (can be in words or diagram) substrate shape is **complementary** to active site
M2: (can be in words or diagram) the substrate bind / bonds / fits (into the active site)
M3: (can be in words or diagram) products are released

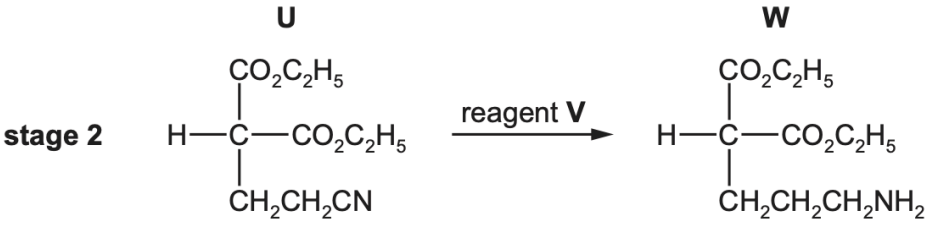
Proline is able to form a poly(proline) peptide chain.

A section of a poly(proline) chain is shown.



Suggest why the secondary structure of poly(proline) cannot be stabilised by hydrogen bonding.

- There is no H attached to the N



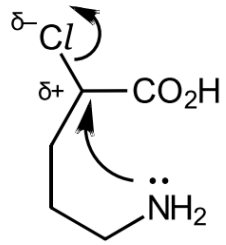
Suggest a suitable reagent V

- H2/ Ni OR H2/ Pt

NOTE- in this, LiAlH4 cannot be used, as it reduces esters.

(vi) Complete the diagram to describe the reaction mechanism of the final stage. Draw curly arrows, ions and charges, partial charges and lone pairs of electrons, as appropriate.

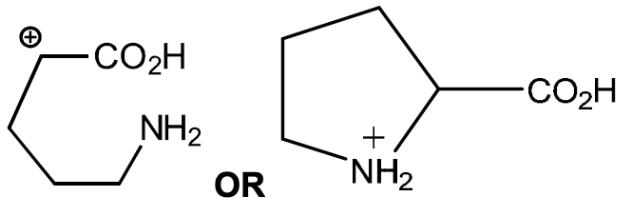
Draw the structure of any organic intermediate ion.



M1/2: All four correct:

- lone pair on NH_2
- curly arrow from N: to C of C—C*l*
- correct dipole on C—C*l*
- curly arrow from C—C*l* to C*l*

M3: intermediate =

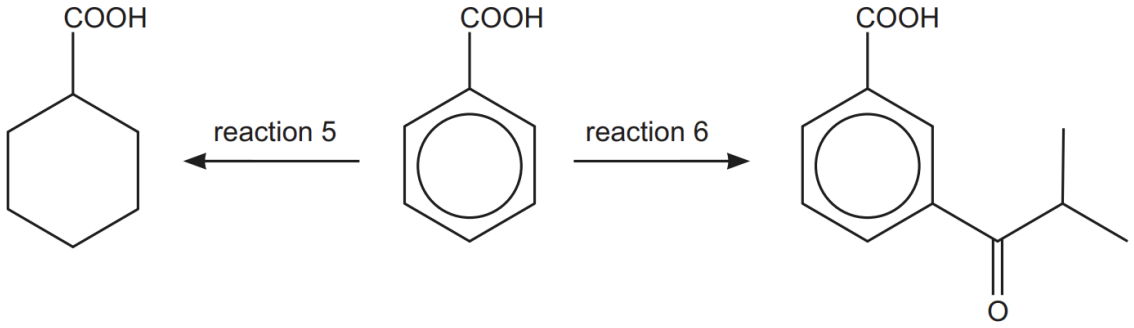


- Lone pair on N atom goes to delta +ve C atom.
- Electrons from C-Cl bond go to Cl, to form Cl- which is released.
- The Cl- then joins with the H+ that is released later to form HCl.
- Out of C and Cl, Cl is more electronegative. So when the bond breaks, the electron pair goes to Cl–. eq

Explain how the zwitterion of an amino acid forms.

- proton/ H+ transferred from carboxylic acid to amine.

(b) Fig. 5.1 shows two reactions of benzoic acid.



Suggest reagents and conditions for reaction 5 and for reaction 6 in Fig. 5.1.

- Reaction 5: Pt / Ni + H2 (+ heat)
- Reaction 6: (CH3)2CHCOCl + AlCl3 (+ heat)

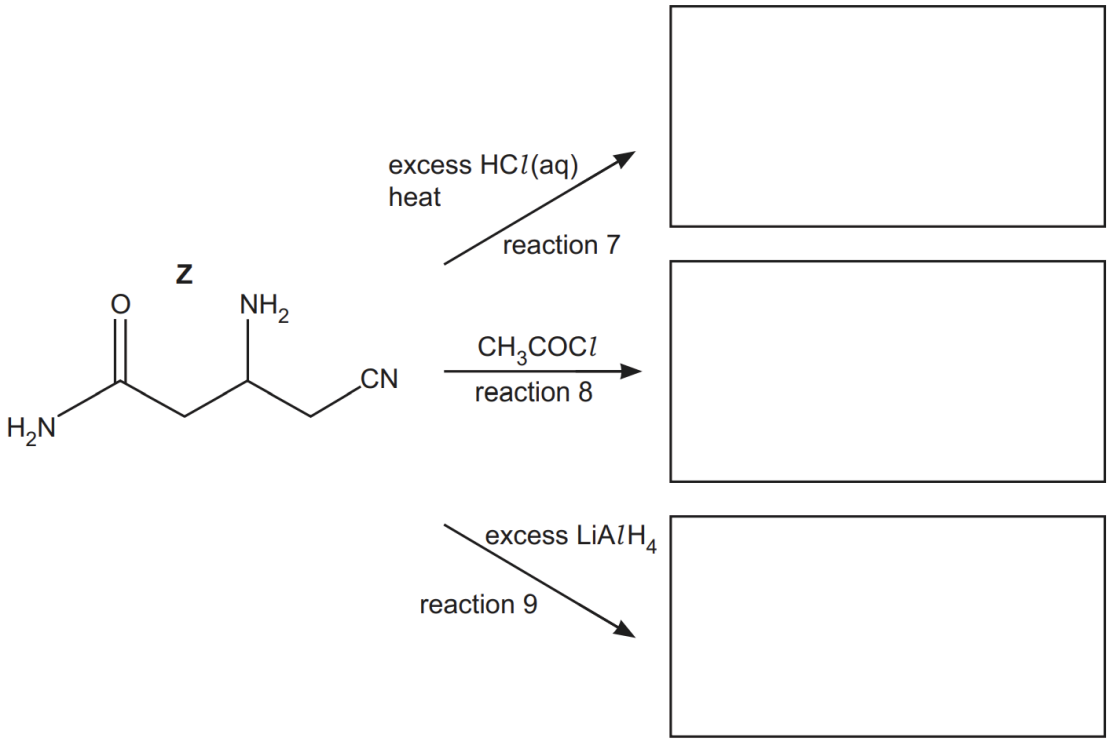
State the type of reaction for reaction 5 in Fig. 5.1.

- reduction/ hydrogenation

Describe the directing effect of the –CH2CH3 group. Explain your answer.

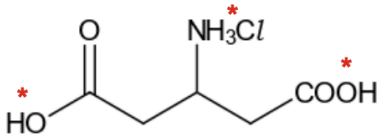
- CH2CH3 group directs to 2-, 4- and 6- positions AND due to being an electron donating group.

(b) **Z** can undergo different reactions, as shown in Fig. 6.1.

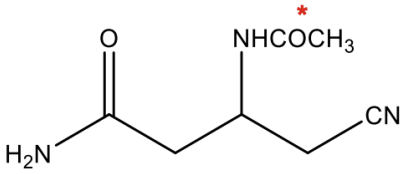


Draw the structures of the organic products of reactions 7, 8 and 9 in Fig. 6.1.

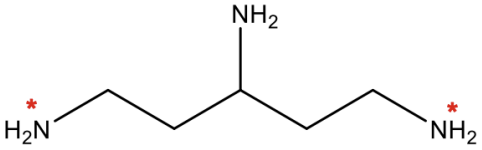
reaction 7



reaction 8



reaction 9

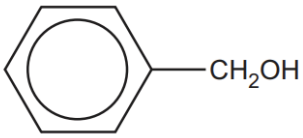


Name the two types of reaction occurring in reaction 7 in Fig. 6.1.

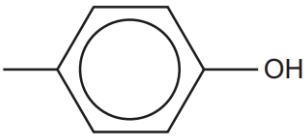
- acid-base / neutralisation AND hydrolysis

Phenylmethanol and 4-methylphenol are isomers.

phenylmethanol



4-methylphenol



(a) Complete Table 7.1 to show the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol, 4-methylphenol and water.

Explain your answer.

Table 7.1

	name of compound
most acidic ↓	
least acidic	

- (most acidic) benzoic acid
  4-methylphenol
  water
  (least acidic) phenylmethanol

- correct link of acidity to weakens O—H / H+ more easily lost / anion stabilised / conjugate base stabilised
- for benzoic acid: negative inductive effect of C=O / electronegative C=O / two electronegative O / –ve charge delocalised (across two O) / resonance in –COO–
- for 4-methylphenol: as lone pair on oxygen delocalised into the ring / system / delocalised system OR p orbital on oxygen overlaps with ring / system / delocalised system
- for phenylmethanol: positive inductive effect of alkyl group / R / CH2

Under certain conditions, ethane-1,2-diol, $HOCH_2CH_2OH$, reacts with propane-1,3-dioic acid, $HOOCCH_2COOH$, to form different organic products, as shown in Fig. 7.1.

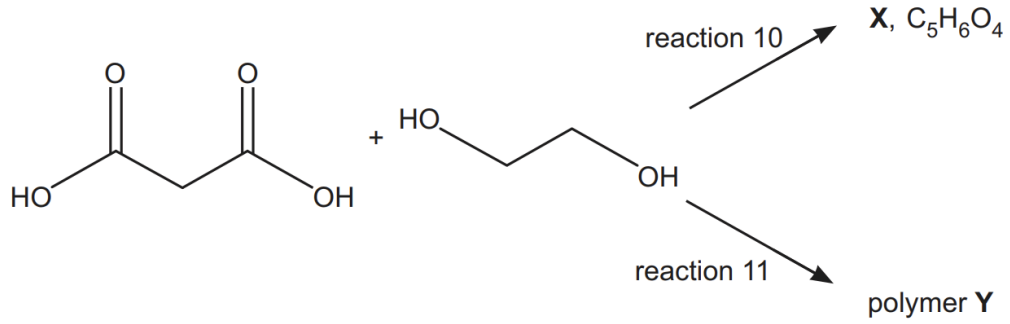
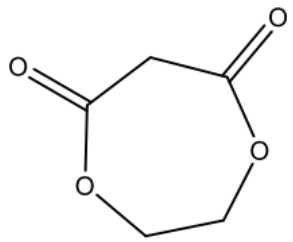


Fig. 7.1

(i) **X** does **not** react with Na metal.

Draw the structure of the organic product **X**, $C_5H_6O_4$, shown in Fig. 7.1.



Reactions 10 and 11 in Fig. 7.1 are different types of reaction. Name the type of reaction for reaction 10 and for reaction 11.

- Reaction 10: addition–elimination / condensation / esterification
- Reaction 11: addition–elimination / condensation (polymerisation) / esterification

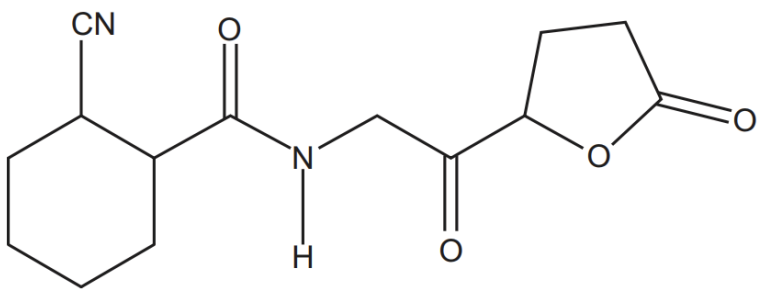
Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water. Explain your answer.

- chlorobenzene is less reactive than ethanoyl chloride.

- p orbital / lone pair on Cl / –Cl will overlap / delocalise into the ring OR C of COCl has most electron deficient OR has an electronegative oxygen atom / two electronegative atoms / electron withdrawing C=O group.
- due to partial double C–Cl bond OR C–Cl bond strengthened (more) / stronger bond between Cl and benzene / ring OR C–Cl weakened in ROCl.

The structure of compound **V** is shown.

V



Name all the functional groups in V.

- Nitrile, amide, ketone / carbonyl, ester

CAREFUL!! This compound doesn't contain any arenes!! Cyclic doesn't mean arene. Arene means benzene ring (hexagon with circle inside/ with double bonds inside).

Deduce the number of possible optical isomers for V.

- Eight

REMEMBER!! Number of optical isomers = 2^(number of chiral centres)!!

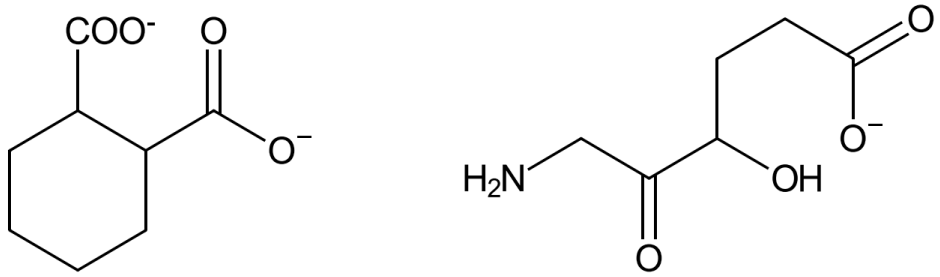
Suggest one reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer for use as a drug.

- No need to separate optical isomers.

(c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.



M1: amide bond hydrolysed and COO^- and NH_2 formed

M2: nitrile bond hydrolysed and COO^- formed

M3: ester bond hydrolysed and COO^- and OH formed

REMEMBER:

- Nitriles get hydrolysed to form carboxylic acid
- when OH is formed in alkaline hydrolysis, it does not become O– as alcohols do not react with hydroxides like NaOH.