	Marks
• Often pH is used to characterise acidic solutions. Give a brief definition of pH.	**5**

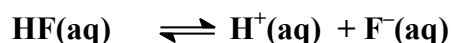> **pH is a measure of the $H^+(aq)$ ion concentration in a solution and is defined using the equation:**
>
> **pH = -log$_{10}$[H$^+$(aq)]**

Describe the difference between a strong acid and a weak acid.

> **A strong acid dissociates completely in water. For example:**
>
> **HCl(aq) → H$^+$(aq) + Cl$^-$(aq)**
>
> **A weak acid dissociated only slightly in water. For example:**
>
> **HF(aq) ⇌ H$^+$(aq) + F$^-$(aq)**
>
> **The pH of a solution of a strong acid depends on its concentration and a strong acid can give a high pH (corresponding to low [H$^+$(aq)]) if the acid is present in a low concentration.**

In general, can pH be used to define the strength of an acid? Explain your answer.

> **No.**
>
> **The pH of a solution of a strong acid depends on its concentration. Thus, the pH of a 0.1 M solution of HCl is 1.0 and the pH of a solution of 10^{-6} M HCl is 6.0.**
>
> **A low pH can arise from a solution of a strong acid or a more concentrated solution of a weak acid.**
>
> **A high pH can arise from a weak solution of a strong acid or from a stronger solution of a weak acid.**

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Rank H_2O(l), H_2S(aq) and HF(aq) in order of their Brønsted acid strengths. Explain your reasoning.

HF(aq) > H₂S(aq) > H₂O(l)

The H–F bond is more polar than H–O so is easier to break HF into H⁺ and F⁻ than to break H₂O into H⁺ and OH⁻. Hence HF is stronger acid than H₂O.

**S is much larger atom than O, so the H–S bond is much longer and weaker than H–O; hence H₂O is weaker acid than H₂S.**

HF is stronger than H₂S because the small F⁻ ion bonds more strongly to the water molecules than does the larger HS⁻ ion.

- Buffer systems are frequently used in chemistry. Briefly describe a buffer system and how it functions? Use equations where appropriate.
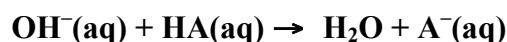
4

Buffer systems resist changes in pH. They consist of a weak acid (HA) and its conjugate base (A⁻) in high concentrations.

If H⁺ is added, it is consumed by the A⁻ ions:

 H⁺(aq) + A⁻(aq) → HA(aq)
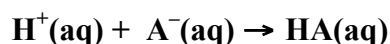
If OH⁻ is added, it is consumed by the acid present:

 OH⁻(aq) + HA(aq) → H₂O + A⁻(aq)

If the amount of H⁺ or OH⁻ added is too great, there may be insufficient HA or A⁻ present and so the buffer may not work.

What ratio of concentrations of acetic acid to sodium acetate would you require to prepare a buffer with pH = 4.00? The K_a of acetic acid is 1.8×10^{-5} M.

The pH of a buffer can be calculated using the Henderson-Hasselbalch equation can be used:

$$pH = pK_a + \log_{10}\left(\frac{[base]}{[acid]}\right)$$

For acetic acid, $pK_a = -\log_{10}K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$. Thus to achieve pH 4.00, the ratio of base to acid must be:

$$4.00 = 4.74 + \log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$\log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = -0.74 \quad \text{or} \quad \frac{[CH_3COOH]}{[CH_3COO^-]} = 5.6$$

Answer: **CH₃COOH : CH₃COO⁻ = 5.6**

**Marks
4**

- Barium sulfate is used as a contrast agent for X-ray images of intestines. What is the solubility product constant, K_{sp}, for $BaSO_4$, given that a maximum of 1.167×10^{-8} g will dissolve in 500 mL of water?

The formula mass of $BaSO_4$ is 137.34 (Ba) + 32.07 (S) + 4 × 16.00 = 233.41 g mol^{-1}. 1.167×10^{-8} g therefore corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{1.167 \times 10^{-8}}{233.41} = 5.000 \times 10^{-11}$$

Barium sulfate dissolves according to the equilibrium:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]$$
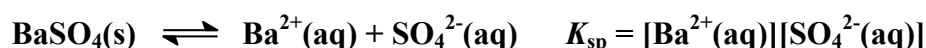
As 5.000×10^{-11} mol dissolves in 500 mL,

$$[Ba^{2+}(aq)] = [SO_4^{2-}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{5.000 \times 10^{-11}}{0.500} = 1.00 \times 10^{-10} \text{ M}$$

Hence,

$$K_{sp} = (1.00 \times 10^{-10}) \times (1.00 \times 10^{-10}) = 1.00 \times 10^{-20}$$

Answer: **1.00×10^{-20}**

What advantage would there be in administering $BaSO_4$ as a slurry that also contains 0.5 M Na_2SO_4?

As indicated by the very small solubility above, the equilibrium

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

lies far to the left. Adding more $SO_4^{2-}(aq)$ ions pushes it further to the left.

This acts to remove $Ba^{2+}(aq)$ ions from solution. This is advantageous as barium ions are highly toxic.
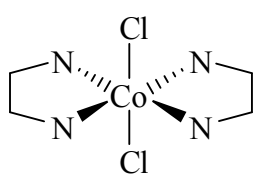
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.
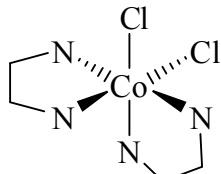
	Marks

• What is a chelate ligand?

4

A chelate is a ligand with more than one donor atom that can bond to the same metal ion.

Draw all possible isomers of $[CoCl_2(en)_2]$.   en = ethylenediamine = $NH_2CH_2CH_2NH_2$
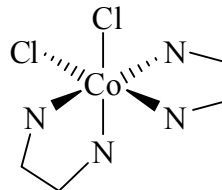
cis **and** *trans* **geometric isomers are possible. The** *cis***-isomer can exist as non-superimposable mirror images (enantiomers).**

trans-   *cis-*   *cis-*

• Explain briefly why the $[Fe(H_2O)_6]^{3+}$ cation has a K_a of 6×10^{-3} M, whilst the $[Fe(H_2O)_6]^{2+}$ cation has a K_a of 4×10^{-9} M.

2

The Fe^{3+} ion has a higher charge and is smaller than the Fe^{2+} ion – it has a higher charge density. The higher charge density withdraws electron density from the oxygen and leading to a more polarised O–H bonds that are more easily broken.

	Marks
• You may recall from a lecture demonstration or your laboratory work that solid CO_2 sublimes under ambient conditions while ice melts. Define the terms sublimation and melting.	**3**

> **Sublimation is a phase change from solid to gas without passing through the liquid phase.**
>
> **Melting is a phase change from solid to liquid.**

What is a triple point (*e.g.* in the phase diagram of CO_2 or H_2O)?

> **The triple point is the temperature and pressure at which all three phases (solid, liquid and gas) coexist in equilibrium.**

What does the different behaviour of ice and solid CO_2 indicate about the relative positions of their respective triple points?

> **The triple point of CO_2 is above ambient pressure.**
>
> **The triple point of H_2O is below ambient pressure.**

	Marks
• Carbon has a number of allotropes, the two major ones being graphite and diamond. The phase diagram of carbon shows that diamond is not the stable allotrope under normal conditions. Why then does diamond exist under normal conditions?	**1**

> **Graphite is more stable at room temperature and pressure. Diamond has a more compact structure than graphite and becomes more stable than graphite at very high pressures. Under very high pressures, graphite can be converted into diamond.**
>
> **When the pressure is released, the reverse process is favourable. However, the structural rearrangement required is considerable and the activation energy is very high. Thus, at low temperatures, the diamond → graphite conversion is extremely slow and diamonds can exist for many thousands of years.**

- Hydrogenation of nitric oxide to nitrogen and water is a potential means of reducing smog-forming NO_x gases:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
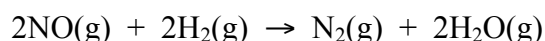
The initial rates of this reaction at constant temperature were determined at the following combination of initial pressures (P_0).

Run	P_0 (H_2) / kPa	P_0 (NO) / kPa	Rate / kPa s^{-1}
1	53.3	40.0	0.137
2	53.3	20.3	0.033
3	38.5	53.3	0.213
4	19.6	53.3	0.105

Derive an expression for the rate law for this reaction.

Between Run 1 and 2, P_0 (H_2) is constant and P_0 (NO) is halved. This causes the rate to be reduced by a factor of four. The rate is second order with respect to NO.

Between Run 3 and 4, P_0 (H_2) is halved and P_0 (NO) is constant. This causes the rate to be reduced by a factor of two. The rate is first order with respect to H_2.

Overall,

$$\textbf{rate} = \textbf{\textit{k}} \times \textbf{\textit{P}}(\textbf{H}_2) \times \textbf{\textit{P}}^2(\textbf{NO})$$

Answer: **rate** = **k** × **P**(H_2) × **P^2**(NO)

Calculate the value of the rate constant.

Using Run 1, rate = 0.137 kPa s^{-1} when P(H_2) = 53.3 kPa and P(NO) = 40.0 kPa:

$$\textbf{0.137 kPa s}^{-1} = \textbf{\textit{k}} \times \textbf{53.3 kPa} \times (\textbf{40.0 kPa})^2$$

$$\textbf{\textit{k}} = \textbf{1.61} \times \textbf{10}^{-6} \textbf{ kPa}^{-2} \textbf{ s}^{-1}$$

Answer: **k = 1.61 × 10^{-6} kPa^{-2} s^{-1}**

What is the order of the reaction? | **1 (H_2) + 2 (NO) = 3 (third order)**

**Marks
3**

- Hemochromatosis or "iron overload" is a potentially fatal disorder in which excess iron is deposited in the bodily organs as insoluble hydrated iron(III) oxide. It can be treated by administration of desferioxamine B (*Desferal*), a natural substance isolated from fungi.
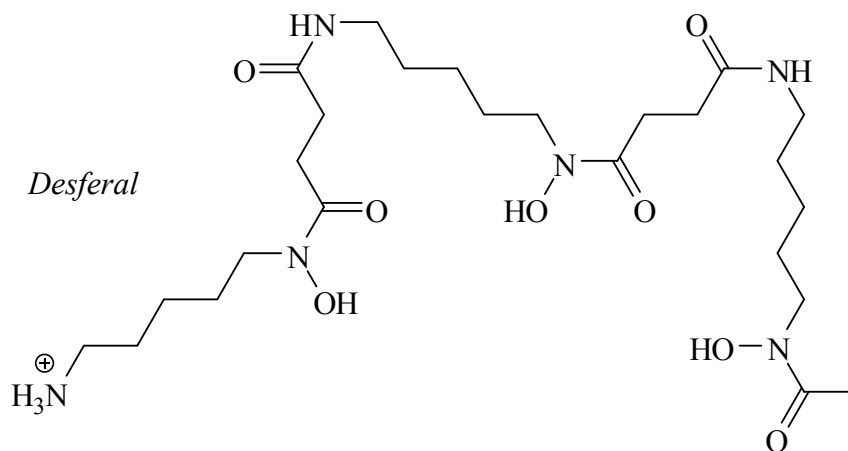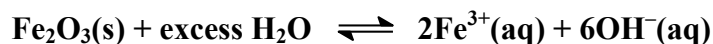

Desferal

Desferal is taken over 8-12 hour periods up to six times per week. A value of log K = 30.6 is associated with the following equilibrium:

$$Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \quad \text{where } LH_3^+ = Desferal$$
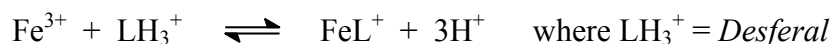
Briefly describe the chemical basis for the use of *Desferal* in iron overload therapy.

The solubility of Fe_2O_3 is *very* small - the equibrium for the reaction below lies far to the left:

$$Fe_2O_3(s) + \text{excess } H_2O \rightleftharpoons 2Fe^{3+}(aq) + 6OH^-(aq)$$

Complexation of Fe^{3+} ions with Desferal is very favourable – the equilibrium for the reaction below lies far to the right (as K for this reaction is $10^{30.6}$):

$$Fe^{3+} + LH_3^+ \rightleftharpoons FeL^+ + 3H^+ \quad \text{where } LH_3^+ = Desferal$$

The Desferal complexes all free Fe^{3+}(aq) ions, so more Fe_2O_3 must dissolve to re-establish the first equilibrium (le Chatelier's principle). Eventually all the Fe_2O_3 will dissolve.

**Marks
5**

- The structure of salbutamol, a drug used to treat bronchospasms, is given below.
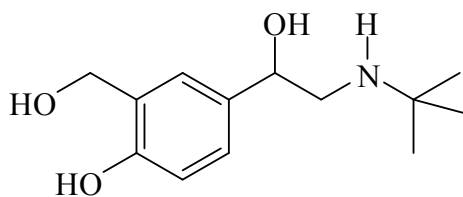
Give the molecular formula of salbutamol. | **$C_{13}H_{21}O_3N$**
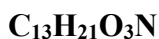
Calculate the *m/z* value for the major peak you would expect to see for the molecular ion in the high resolution mass spectrum.
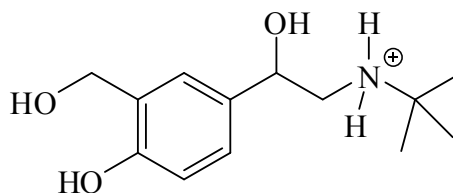[Atomic masses: $^1H = 1.0078$; $^{12}C = 12.0000$; $^{16}O = 15.9949$; $^{14}N = 14.0031$]

The molar mass of $C_{13}H_{21}O_3N$ is

13×12.0000 (C) $+ 21 \times 1.0078$ (H) $+ 3 \times 15.9949$ (O) $+ 1 \times 14.0031$ (N)

Answer: **239.1516**

Give the structure(s) of the major organic products formed when salbutamol is treated with the following reagents.

cold HCl (1 M)	
NaOH (1 M)	
$Cr_2O_7^{2-}$ / H^+	
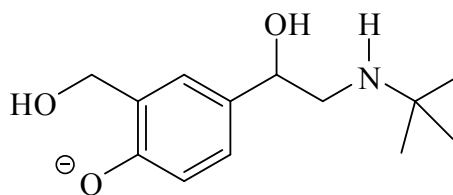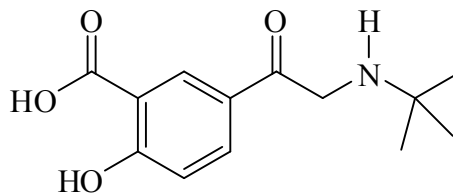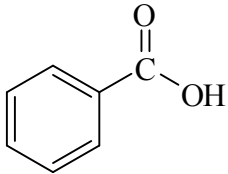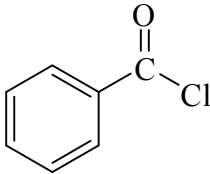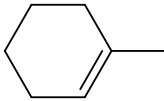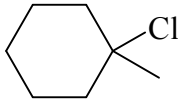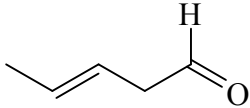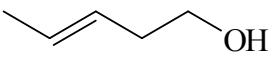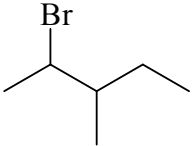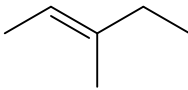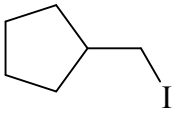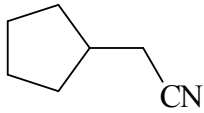
• Complete the following table.

Marks
5

Starting material	Reagents / Conditions	Major organic product(s)
(benzoic acid, Ph–C(=O)–OH)	**SOCl₂**	(benzoyl chloride, Ph–C(=O)–Cl)
(1-methylcyclohexene)	HCl	(1-chloro-1-methylcyclohexane)
(pent-3-enal, H–C(=O)–CH₂–CH=CH–CH₃)	1. NaBH₄ 2. H⁺/ H₂O	(pent-3-en-1-ol, HO–CH₂–CH₂–CH=CH–CH₃)
(2-bromo-3-methylpentane)	hot conc. KOH ethanol (solvent)	(3-methylpent-2-ene)
(iodomethylcyclopentane)	CN⁻	(cyclopentylacetonitrile)

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

	Marks

- A mixture of concentrated nitric and sulfuric acids generates the nitronium ion, NO_2^+. Benzene will react with such a mixture to give nitrobenzene.
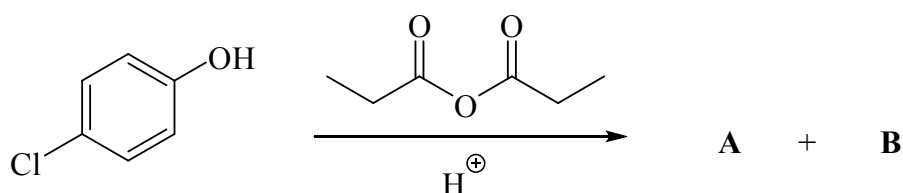

conc. HNO_3 / conc. H_2SO_4
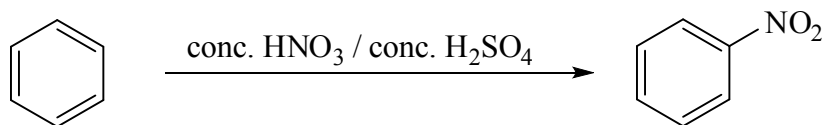
What 3-part name is given to the mechanism of this nitration reaction?
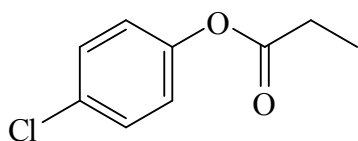
2

electrophilic aromatic substitution
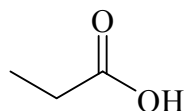
- Consider the reaction sequence below.

Draw the structures of products **A** and **B**.
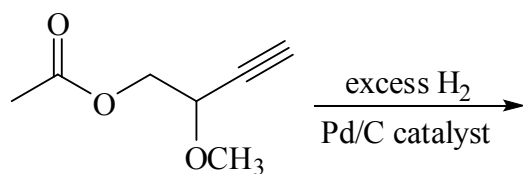
2

A

B

- Draw the structure of the product, **C,** from the following reaction.
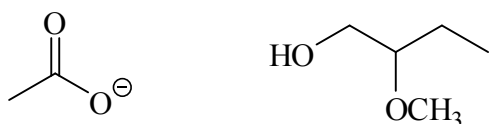
3

C

excess H_2
Pd/C catalyst
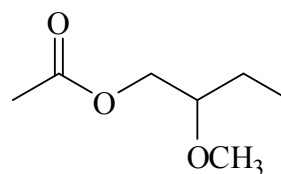
Product **C** undergoes hydrolysis when heated with 4 M NaOH. Give the structures of the products (in their correct ionic states) formed in this reaction.
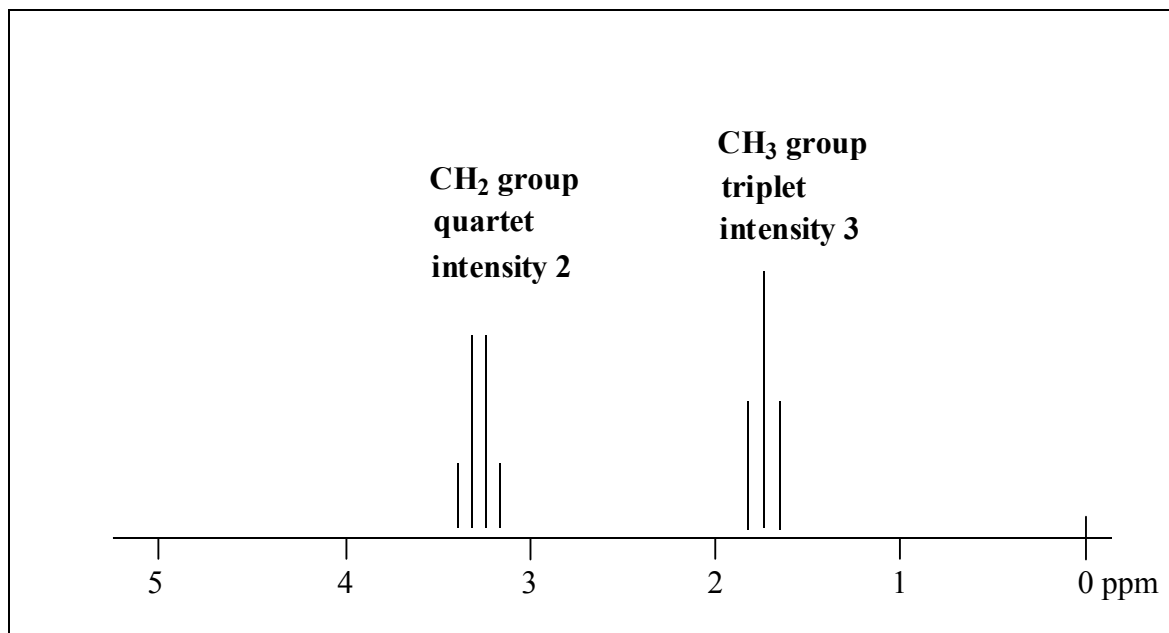
	Marks
• The incomplete proposed mechanism for the reaction of acetyl chloride with ammonia is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.	5
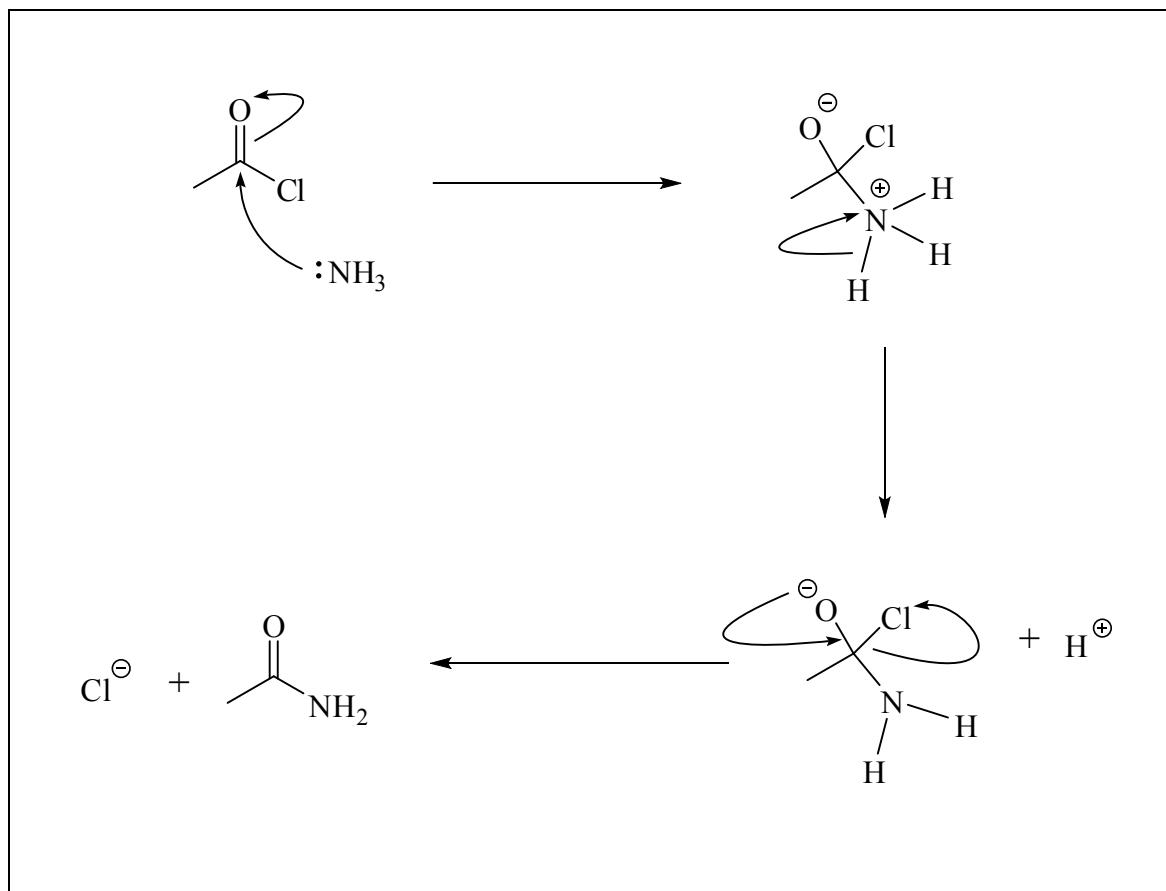
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

| |
|---|
| • Sketch the ^1H NMR spectrum of bromoethane, CH_3CH_2Br. The signals appear at 1.7 and 3.3 ppm. Clearly indicate the splitting patterns of both signals and show their relative intensities. |

Marks
5

CH$_2$ group
quartet
intensity 2

CH$_3$ group
triplet
intensity 3

5   4   3   2   1   0 ppm

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
6

- Devise a synthesis of 3-methylheptan-3-ol using the two starting materials shown. Show the structures of any intermediate products involved, as well as the reagents required for each step. More than one step is required.

$Cr_2O_7{}^{2\ominus}/\ H^{\oplus}$

Mg / dry ether

1.　MgBr

2. $H^{\oplus}/\ H_2O$

OH
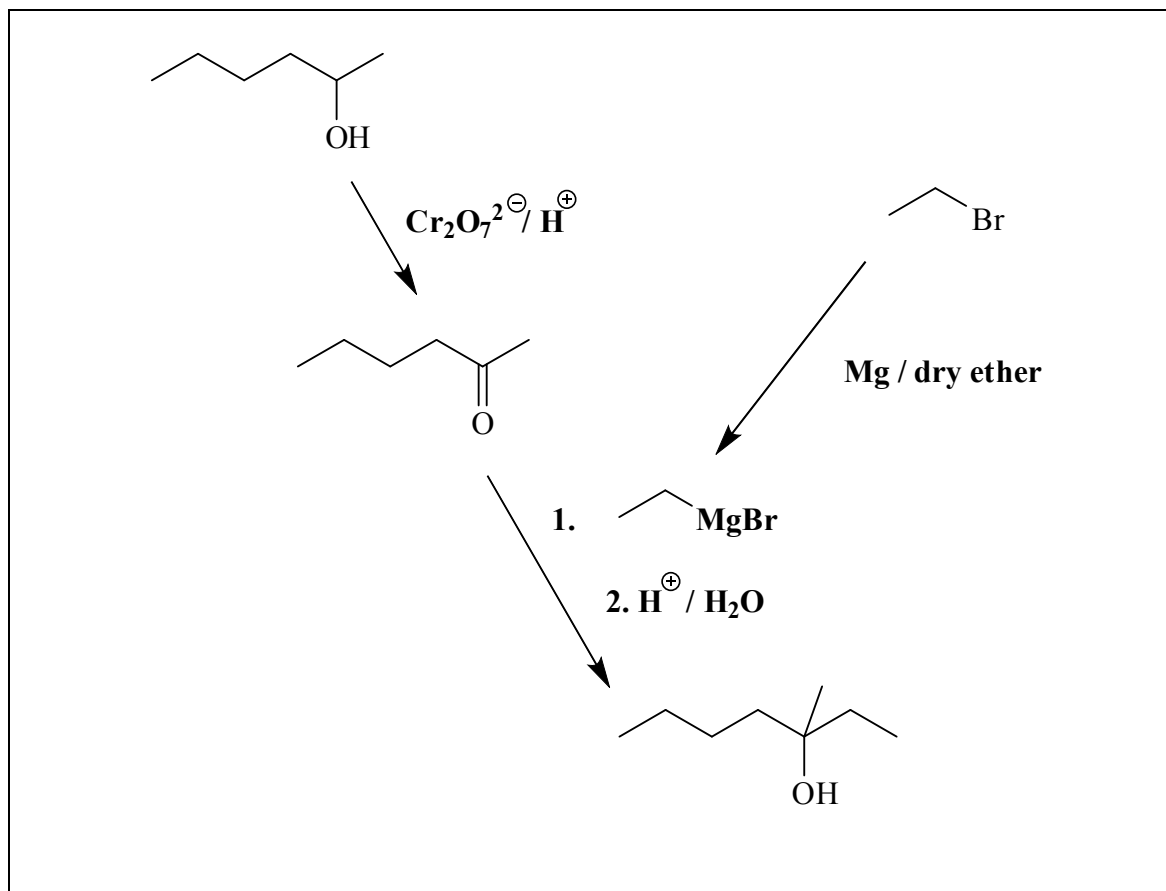
| Would the product be isolated as a racemic mixture or a single enantiomer or is the product achiral? | **racemic mixture** |