Topics in the November 2012 Exam Paper for CHEM1002

Click on the links for resources on each topic.

2012-N-2:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-3:

- Weak Acids and Bases
- Calculations Involving pK_a

2012-N-4:

- Crystal Structures

2012-N-5:

- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

2012-N-6:

- Solubility Equilibrium

2012-N-7:

- Solubility Equilibrium

2012-N-8:

- Metal Complexes
- Metals in Biology
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2012-N-9:

- Alcohols
- Organic Halogen Compounds
- Carboxylic Acids and Derivatives

2012-N-10:

- Alkenes
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- Representations of Molecular Structure
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2012-N-12:

- Alkenes
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2012-N-13:

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2012-N-14:

- Synthetic Strategies
- Stereochemistry

Marks 6

- Solution A consists of a 0.050 M aqueous solution of benzoic acid, C_6H_5COOH, at 25 °C. Calculate the pH of Solution A. The pK_a of benzoic acid is 4.20.

As benzoic acid is a weak acid, $[H_3O^+]$ must be calculated using a reaction table:

	C_6H_5COOH	⇌	H^+	$C_6H_5COO^-$
initial	**0.050**		**0**	**0**
change	**-*x***		**+*x***	**+*x***
final	**0.050 –*x***		***x***	***x***

The equilibrium constant K_a is given by:

$$K_a = \frac{[H^+][C_6H_5COO^-]}{[C_6H_5COOH]} = \frac{x^2}{0.050 - x}$$

As pK_a = -log$_{10}K_a$, $K_a = 10^{-4.20}$ and is very small, 0.050 – x ~ 0.050 and hence:

$x^2 = 0.050 \times 10^{-4.2}$ **or** $x = 1.78 \times 10^{-3}$ M = $[H^+]$

Hence, the pH is given by:

pH = –log$_{10}[H^+]$ = –log$_{10}(1.78 \times 10^{-3})$ = 2.75

pH = **2.75**

What are the major species present in solution A?

K_a is very small and the equilibrium lies almost completely to the left. The major species present are water and the undissociated acid:
H_2O and C_6H_5COOH

Solution B consists of a 0.050 M aqueous solution of ammonia, NH_3, at 25 °C. Calculate the pH of Solution B. The pK_a of NH_4^+ is 9.24.

NH_3 is a weak base so $[OH^-]$ must be calculated by considering the equilibrium:

	NH_3	H_2O	⇌	NH_4^+	OH^-
initial	**0.050**	**large**		**0**	**0**
change	**-*y***	**negligible**		**+*y***	**+*y***
final	**0.050 – *y***	**large**		***y***	***y***

ANSWER CONTINUES ON THE NEXT PAGE

The equilibrium constant K_b is given by:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{y^2}{(0.050 - y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 - 9.24 = 4.76$

As $pK_b = 4.76$, $K_b = 10^{-4.76}$. K_b is very small so $0.050 - y \sim 0.050$ and hence:

$y^2 = 0.050 \times 10^{-4.76}$ **or** $y = 9.32 \times 10^{-4}$ M $= [OH^-]$

Hence, the pOH is given by:

$pOH = -\log_{10}[OH^-] = \log_{10}[9.32 \times 10^{-4}] = 3.03$

Finally, pH + pOH = 14.00 so

$pH = 14.00 - 3.03 = 10.97$

pH = **10.97**

What are the major species present in solution B?

K_b is very small and the equilibrium lies almost completely to the left. The major species present are water and the unprotonated weak base:

H_2O and NH_3

Marks
5

Write the equation for the reaction that occurs when benzoic acid reacts with ammonia?

$C_6H_5COOH(aq) + NH_3(aq) \rightarrow C_6H_5COO^-(aq) + NH_4^+(aq)$

Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

$$K = \frac{[C_6H_5COO^-(aq)][NH_4^+(aq)]}{[C_6H_5COOH(aq)][NH_3(aq)]}$$

What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia? Hint: multiply the above expression by $[H^+]/[H^+]$.

Multiplying the expression above by $[H^+] / [H^+]$ gives:

$$K = \frac{[C_6H_5COO^-(aq)][NH_4^+(aq)]}{[C_6H_5COOH(aq)][NH_3(aq)]} \cdot \frac{[H^+(aq)]}{[H^+(aq)]}$$

$$= \frac{[H^+(aq)][C_6H_5COO^-(aq)]}{[C_6H_5COOH(aq)]} \cdot \frac{[NH_4^+(aq)]}{[NH_3(aq)][H^+(aq)]}$$

$$= K_a \times \frac{K_b}{[H^+(aq)][OH^-(aq)]} = \frac{K_a \times K_b}{K_w}$$

$$= \frac{(10^{-4.20}) \times 10^{-4.76}}{(10^{-14})} = 1.1 \times 10^5$$

Answer: **1.1×10^5**

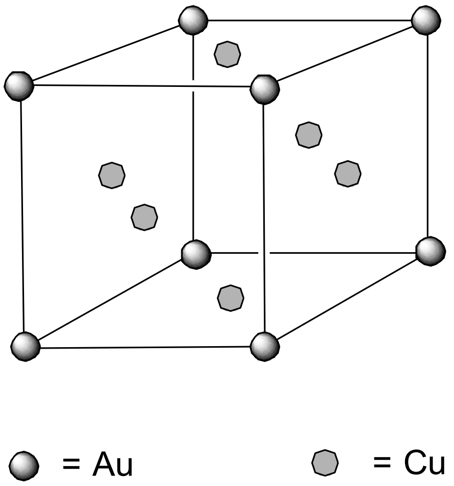
What are the major species in the solution that results from adding together equal amounts of solutions A and B?

The equilibrium strong favours products so the major species are:

$C_6H_5CO_2^-(aq)$, $NH_4^+(aq)$, $H_2O(l)$

Marks 6

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The length of the side of the cubic unit cell is 0.36 nm.



What is the chemical formula of the alloy?

There are 8 Au atoms and each is on a corner so contributes 1/8 to the unit cell:

total number of Au atoms = 8 × 1/8 = 1

There are 6 Cu atoms and each is on a face so contributes 1/2 to the unit cell.

total number of Cu atoms = 6 × 1/2 = 3

Answer: **$AuCu_3$ or Cu_3Au**

Pure gold is 24 carat, whilst gold alloys consisting of 75 % gold by weight are termed 18 carat gold. What carat gold is this alloy?

The molar mass of Cu_3Au is:

molar mass = (3 × 63.55 (Cu) + 196.97 (Au)) g mol^{-1} = 387.62 g mol^{-1}

The percentage gold is therefore:

percentage gold = 196.97 / 387.82 ×100% = 50%

As 100% gold is 24 carat and 75% gold is 18 carat, this corresponds to 12 carat.

Answer: **12 carat**

What is the volume (in cm^3) of the unit cell?

The length of the side of the unit cell is 0.36 nm. This corresponds to 0.36 × 10^{-9} m or 0.36 × 10^{-7} cm. As the unit cell is cubic, its volume, *V*, is given by:

$V = (0.36 \times 10^{-7})^3$ cm^3 = 4.7 × 10^{-23} cm^3

Answer: **4.7 × 10^{-23} cm^3**

ANSWER CONTINUES ON THE NEXT PAGE

What is the density (in g cm^{-3}) of the alloy?

From above, the mass of a mole of Cu_3Au is 387.62 g mol^{-1}. As this corresponds to Avogadro's number of formula units, the mass of the unit cell is:

mass of unit cell = (387.62 g mol^{-1}) / (6.022 × 10^{23} mol^{-1}) = 6.43673 × 10^{-22} g

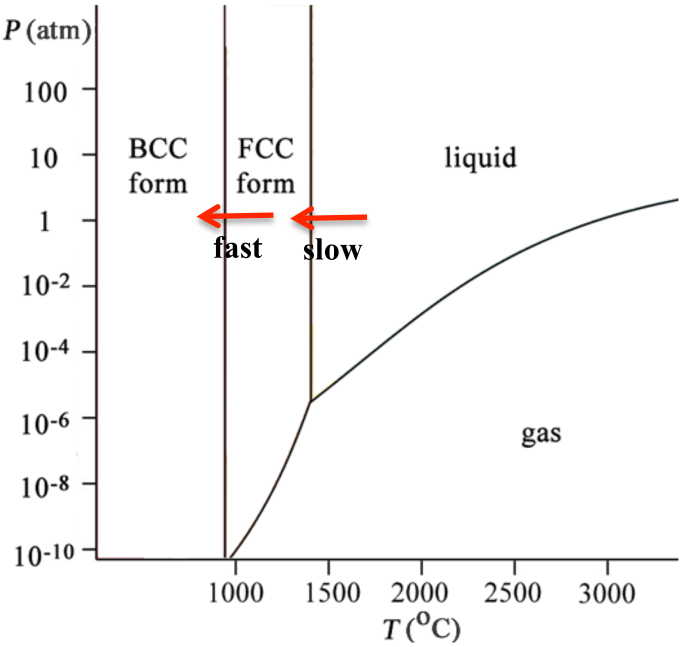
The density of the unit cell is therefore:

density = mass / volume
= (6.43673 × 10^{-22} g) / (4.7 × 10^{-23} cm^{3})
= 14 g cm^{-1}

Answer: **14 g cm^{-1}**

Marks 5

- A simplified phase diagram for iron is shown below.



Which form of iron is stable at room temperature and pressure? **BCC form**

If molten iron is cooled slowly to around 1200 °C and then cooled rapidly to room temperature, the FCC form is obtained. Draw arrows on the phase diagram to indicate this process and explain why it leads to the FCC form.

See diagram above.

The rapid cooling from 1200 to 25 °C does not allow time for the atoms in the FCC arrangement to reorganise themselves into the more stable BCC structure. The atoms have insufficient energy for the considerable re-arrangement of their positions to occur.

The line dividing the BCC and FCC forms is almost, but not quite vertical. Given that the FCC form is more efficiently packed, predict which way this line slopes. Explain your answer.

FCC is more efficiently packed so is more dense. Increasing the pressure favours the more dense form.

The BCC/FCC equilibrium line slopes to the *left* so that moving vertically (i.e. increasing pressure) at the BCC/FCC equilibrium leads to FCC.

Marks 6

- Explain what is meant by the "common ion effect".

The solubility of a salt is reduced by the presence of one of its constituent ions (the common ion) already in the solution. The presence of the common ion drives the equilibrium towards precipitation through Le Chatelier's principle.

Magnesium hydroxide is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp}.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

$$K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$$

What is the molar solubility of magnesium hydroxide in water? $K_{sp} = 7.1 \times 10^{-12}$

The molar solubility is the number of the moles that dissolve per litre. From the chemical equation, if *s* mol of the solid dissolves in a litre, then:

$[Mg^{2+}(aq)] = s$ **M and**
$[OH^-(aq)] = 2s$ **M**

Hence,

$$K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2 = (s)(2s)^2 = 4s^3 = 7.1 \times 10^{-12}$$

$$s = 1.2 \times 10^{-4}$$

Answer: **1.2×10^{-4} M**

What is the pH of a saturated solution of magnesium hydroxide in water?

From above,

$$[OH^-(aq)] = 2s \text{ M} = 2 \times (1.2 \times 10^{-4}) \text{ M} = 2.4 \times 10^{-4} \text{ M}$$

Hence,

$$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}(2.4 \times 10^{-4}) = 3.62$$

$$pH = 14.00 - pOH = 14.00 - 3.62 = 10.38$$

Answer: **10.38**

What is the molar solubility of magnesium hydroxide in a buffer solution at pH 9.24?

Marks 3

At pH 9.24,

pOH = 14.00 – 9.24 = 4.76

$[OH^-(aq)] = 10^{-pOH} = 10^{-4.76}$ M

From 2012-N-6, $K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$ so

$[Mg^{2+}(aq)] = K_{sp} / [OH^-(aq)]^2 = 7.1 \times 10^{-12} / (10^{-4.76})^2 = 0.024$ M

Answer: **0.024 M**

Do the relative solubilities of magnesium hydroxide in water and the buffer solution support the concept of the common ion effect? Explain your reasoning.

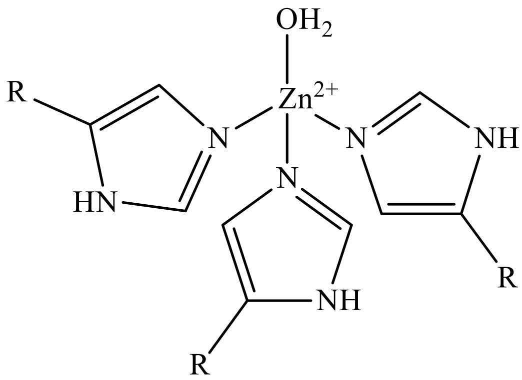
Yes. The $[OH^-(aq)]$ in the saturated $Mg(OH)_2$ solution is 2.4×10^{-4} M, higher than the $[OH^-(aq)]$ in the buffer solution which remains constant at $10^{-4.76}$ M, *i.e.* 1.7×10^{-5} M.

Normally the solubility of a solid decreases because of a high concentration of one of its ions. In this situation, the opposite is observed. Regardless of how much $Mg(OH)_2$ dissolves, the $[OH^-]$ remains below that seen in a saturated solution of $Mg(OH)_2$. Therefore the solubility of $Mg(OH)_2$ increases in this particular buffer.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
5

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to three histidine residues and a water molecule.



The pK_a of uncoordinated water is 15.7 but the pK_a of the water in carbonic anhydrase is around 7. Suggest an explanation for this large change.

The high charge on the Zn^{2+} ion draws electron density out of the O–H bonds in the water molecule. This weakens the O–H so the H^+ is more likely to leave.

The water in carbonic anhydrase is therefore more acidic, as shown by the large decrease in pK_a.

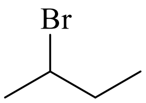
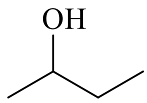
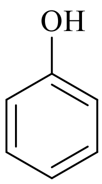
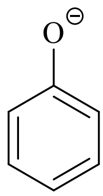
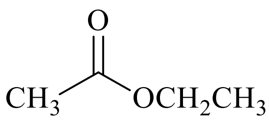
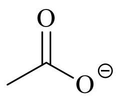
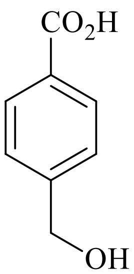
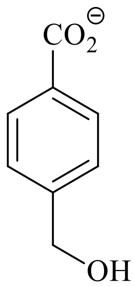
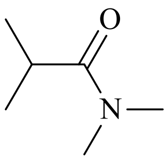
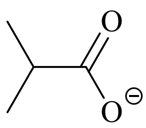
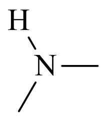
When studying zinc-containing metalloenzymes such as this, chemists often replace Zn^{2+} with Co^{2+} because of their different magnetic properties. Predict which of these species, if either, is attracted by a magnetic field. Explain your reasoning.

Zn^{2+}, $3d^{10}$	↑↓	↑↓	↑↓	↑↓	↑↓
Co^{2+}, $3d^{7}$	↑↓	↑↓	↑	↑	↑

Zn^{2+} has 0 unpaired *d* electrons, Co^{2+} has 3 unpaired *d* electrons. Co^{2+} is therefore paramagnetic and will be attracted by a magnetic field.

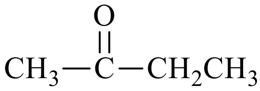
Marks 7

- A number of functional groups react with hydroxide ion. Complete the following table. NB: If there is no reaction, write "no reaction".

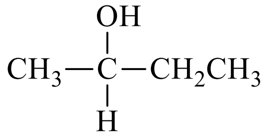
Starting Compound	Reaction Conditions	Organic Product(s)
	1 M aqueous NaOH	
	1 M aqueous NaOH	
	hot 4 M NaOH	 + $HOCH_2CH_3$
	1 M aqueous NaOH	
	hot 4 M NaOH prolonged heating	 + 

Marks
8

- Butanone is treated first with lithium aluminium hydride, $LiAlH_4$, in dry ether and then with aqueous acid to yield the alcohol, **A**.



butanone



A

State whether **A** is obtained as the (*R*)-enantiomer, the (*S*)-enantiomer or as a racemic mixture. Give a reason for your answer.

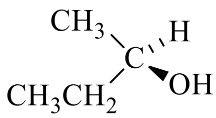
Racemic mixture. The geometry around the carbonyl group is trigonal planar, so the H^- nucleophile is equally likely to attack from either the top or bottom. This leads to equal amounts of the (*R*) and (*S*) enantiomers.

List below the substituents on the stereogenic (chiral) carbon atom in **A**, in descending order as determined by the sequence rule.

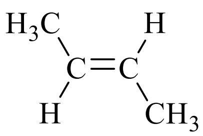
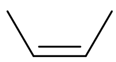
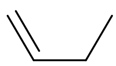
Highest priority Lowest priority

-OH	**$-CH_2CH_3$**	**$-CH_3$**	**-H**

Draw the stereoformula for the (*R*)-enantiomer with the lowest priority substituent at the back.

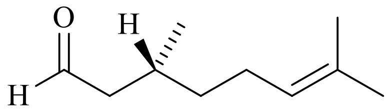


A is treated with concentrated sulfuric acid to give mainly the alkene **B** and two other alkenes **C** and **D**. Alkenes **B** and **C** are diastereomers, **B** and **D** (and **C** and **D**) are constitutional isomers. Give the structures for **C** and **D** and give systematic names for **B**, **C** and **D**.

B	**C**	**D**
		
Name: **(*E*)-2-butene**	Name: **(*Z*)-2-butene**	Name: **1-butene**

Marks 8

- The structure of (+)-citronellal, a widely occurring natural product, is shown below.



What is the molecular formula of (+)-citronellal?

$C_{10}H_{18}O$

Which of the following best describes (+)-citronellal?
achiral compound, racemic mixture,
(*R*)-enantiomer, or (*S*)-enantiomer

(*R*)

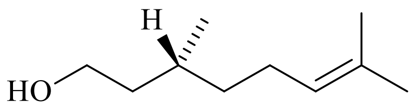
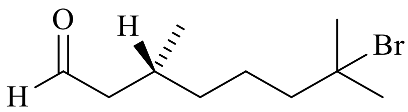
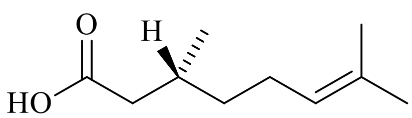
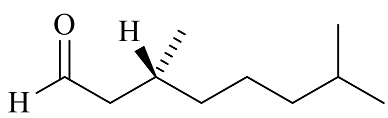
What functional groups are present in (+)-citronellal?

Aldehyde and alkene

Is it possible to obtain (*Z*) and (*E*) isomers of (+)-citronellal? Give a reason for your answer.

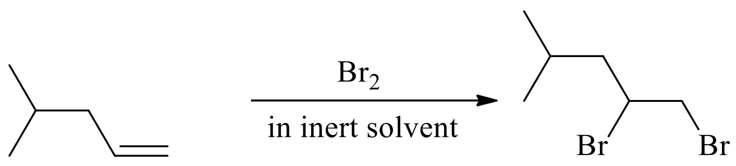
No. One end of the double bond has two identical groups (methyl) attached to it.

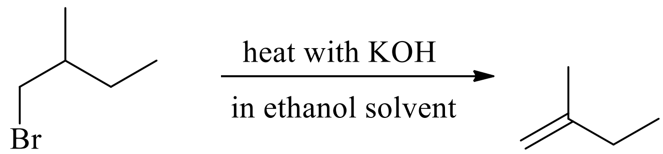
Give the constitutional formula of the organic product formed from (+)-citronellal in each of the following reactions.

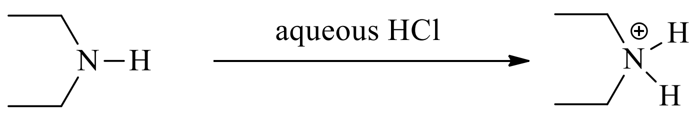
Reagents / Conditions	Constitutional Formula of Product
1. $LiAlH_4$ in dry ether (solvent) 2. H^+ / H_2O	
HBr in CCl_4 (solvent)	
$Na_2Cr_2O_7$ in aqueous acid	
H_2 / Pd-C catalyst	

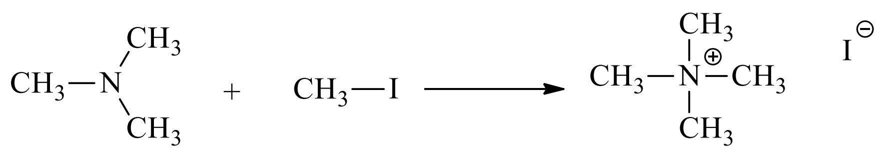
Marks
7

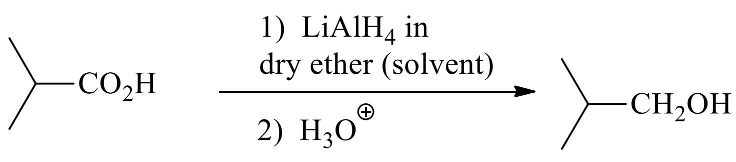
- Give the major organic product(s) from the following reactions. Pay particular attention to the stereochemistry and/or the correct ionic from where relevant.

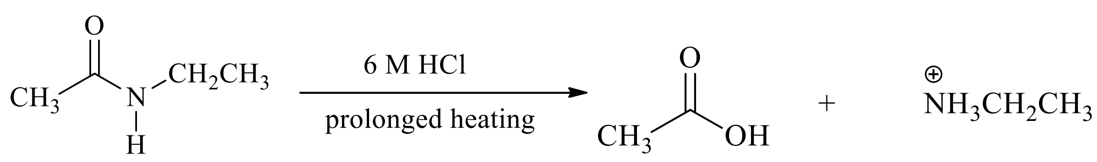






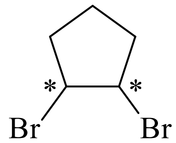






Marks 3

- 1,2-Dibromocyclopentane has two stereogenic carbon atoms, each marked with an asterisk (*) on the structure below.

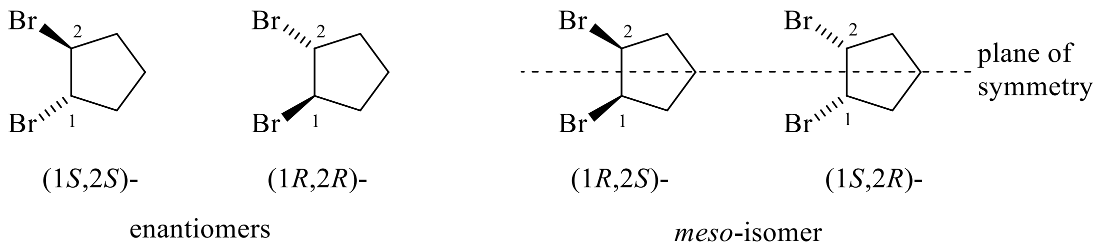


The maximum number of configurational stereoisomers is given by the formula 2^n, where n is the number of stereogenic centres.

1,2-Dibromocyclopentane has only three configurational stereoisomeric forms, not four. Explain briefly why this is the case. Include drawings of the relevant stereoformulas in your answer.

There are 4 possibilities: (1*R*,2*R*)-, (1*S*,2*S*)-, (1*R*,2*S*)- and (1*S*,2*R*)-.

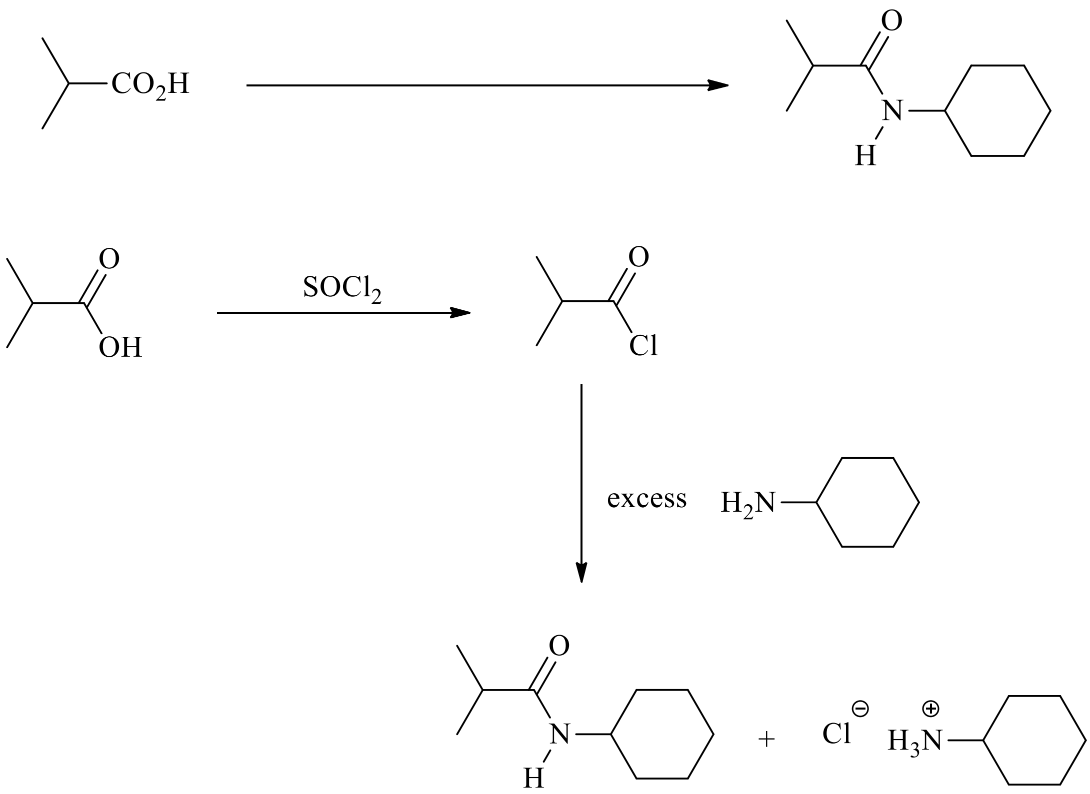
The first two of these are enantiomers. The last two are the same compound, a *meso*- isomer.



Marks

- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structure of any intermediate compounds formed. You have a supply of cyclohexylamine available.

3



- Convert the following structure into a Fischer projection.

3