# Topics in the June 2012 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2012-J-2:

- Weak Acids and Bases
- Periodic Trends in Aqueous Oxide
- Metals in Biology
- Coordination Chemistry

2012-J-3:

- Metals in Biology
- Coordination Chemistry

2012-J-4:

- Weak Acids and Bases
- Calculations Involving p$K_a$

2012-J-5:

- Solubility Equilibrium

2012-J-6:

- Crystal Structures

2012-J-7:

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

2012-J-8:

- Kinetics
- Kinetics - Catalysis

2012-J-9:

- Representations of Molecular Structure
- Carboxylic Acids and Derivatives

2012-J-10:

- Alkenes
- Organic Halogen Compounds
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2012-J-11:

- Alkenes

2012-J-12:

- Stereochemistry
- Amines
- Carboxylic Acids and Derivatives

2012-J-13:

- Representations of Molecular Structure
- Alcohols
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2012-J-14:

- Synthetic Strategies

2012-J-15:

- Alkenes
- Stereochemistry

Marks

- Explain why $HClO_4$ is a stronger Brønsted acid than $HBrO_4$, but HCl is a weaker acid than HBr. **2**

**In Group 17 oxyacids, electron density is drawn away from the O atom as the electronegativity of the halogen increases. This in turn draws electron density away from the O–H bond and weakens it. The weaker the O–H bond, the stronger the acid. Cl is more electronegative than Br so $HOClO_3$ is stronger acid than $HOBrO_3$.**

**In binary acids such as HBr and HCl, the H–Br bond is longer than the H–Cl bond as Br is larger than Cl. The H–Br bond is therefore weaker than the H–Cl bond and HBr is thus a stronger acid than HCl.**

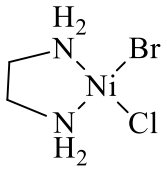
- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of $Cu^{2+}$. **2**

**$Cu^{2+}$ is $d^9$**  **is paramagnetic**

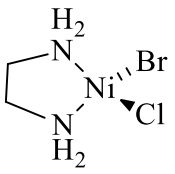
- Provide a systematic name for the complex [NiBrCl(en)] and draw both of its possible structures. (en = $NH_2CH_2CH_2NH_2$ = ethylenediamine = ethane-1,2-diamine) **4**

**Both of the following names are acceptable:**

- **bromidochlorido(ethylenediamine)nickel(II)**
- **bromidochlorido(ethane-1,2-diamine)nickel(II)**




square planar




tetrahedral

Is either complex chiral? Explain your reasoning.

**No. Both structures are superimposable on (*i.e.* identical to) their mirror images.**

**Marks 6**

- Complete the following table. (ox = oxalate = $C_2O_4^{2-}$)

| Formula | $Na[FeCl_4]$ | $[CrCN(NH_3)_5]Br_2$ | $K_3[VO_2(ox)_2]\cdot 3H_2O$ |
|---|---|---|---|
| Oxidation state of transition metal ion | **+III** | **+III** | **+V** |
| Coordination number of transition metal ion | **4** | **6** | **6** |
| Number of *d*-electrons in the transition metal ion | **5** | **3** | **0** |
| Species formed upon dissolving in water | **$Na^+(aq)$, $[FeCl_4]^-(aq)$** | **$[CrCN(NH_3)_5]^{2+}(aq)$, $Br^-(aq)$** | **$K^+(aq)$, $[VO_2(ox)_2]^{3-}(aq)$** |

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

Marks 8

- Solution A consists of a 1.00 M aqueous solution of HOCl at 25 °C. The p$K_a$ of HOCl is 7.54. Calculate the pH of Solution A.

**As HOCl is a weak acid, [$H^+$(aq)] must be calculated by considering the equilibrium:**

| | HOCl(aq) | ⇌ | $OCl^-$(aq) | $H^+$(aq) |
|---|---|---|---|---|
| **initial** | **1.00** | | **0** | **0** |
| **change** | **-*x*** | | **+*x*** | **+*x*** |
| **final** | **1.00 – *x*** | | ***x*** | ***x*** |

**The equilibrium constant $K_a$ is given by:**

$$K_a = \frac{[OCl^-(aq)][H^+(aq)]}{[HOCl]} = \frac{x^2}{(1.00-x)}$$

**As p$K_a$ = 7.54, $K_a = 10^{-7.54}$. $K_a$ is very small so 1.00 – *x* ~ 1.00 and hence:**

$x^2 = 1.00 \times 10^{-7.54}$ **or** $x = 0.000170$ **M** $= [H^+(aq)]$

**Hence, the pH is given by:**

$$pH = -\log_{10}[H^+(aq)] = -\log_{10}[0.000170] = 3.77$$

pH = **3.77**

At 25 °C, 1.00 L of Solution B consists of 74.4 g of NaOCl dissolved in water. Calculate the pH of Solution B.

**The molar mass of NaOCl is:**

**molar mass = (22.99 (Na) + 16.00 (O) + 35.45 (Cl)) g mol$^{-1}$ = 74.44 g mol$^{-1}$**

**The number of moles present in 74.4 g is therefore:**

**number of moles = mass / molar mass = (74.4 g) / (74.44 g mol$^{-1}$) = 0.999 mol**

**If this is present in 1.00 L, then [$OCl^-$] = 0.999 M.**

**As it is a weak base, [$OH^-$] must be calculated by considering the equilibrium:**

| | $OCl^-$ | $H_2O$ | ⇌ | HOCl | $OH^-$ |
|---|---|---|---|---|---|
| **initial** | **0.999** | **large** | | **0** | **0** |
| **change** | ***-y*** | **negligible** | | ***+y*** | ***+y*** |
| **final** | **0.999 – *y*** | **large** | | ***y*** | ***y*** |

**ANSWER CONTINUES ON THE NEXT PAGE**

**The equilibrium constant $K_b$ is given by:**

$$K_b = \frac{[HOCl][OH^-]}{[OCl^-]} = \frac{y^2}{(0.999-y)}$$

**For an acid and its conjugate base:**

**$pK_a + pK_b = 14.00$**

**$pK_b = 14.00 - 7.54 = 6.46$**

**As $pK_b = 6.46$, $K_b = 10^{-6.46}$. $K_b$ is very small so $0.999 - y \sim 0.999$ and hence:**

**$y^2 = 0.999 \times 10^{-6.46}$ or $y = 0.000589$ M $= [OH^-]$**

**Hence, the pOH is given by:**

**$pOH = -\log_{10}[OH^-] = \log_{10}[0.000589] = 3.23$**

**Finally, pH + pOH = 14.00 so**

**$pH = 14.00 - 3.23 = 10.77$**

pH = **10.77**

Solution B (0.40 L) is poured into Solution A (0.60 L). What amount of NaOH (in mol) must be added to give a solution, after equilibration, with a pH of 8.20?

**The number of moles of HOCl in 0.60 L is:**

**number of moles = concentration × volume**
**$= (1.00 \text{ mol } L^{-1}) \times (0.60 \text{ L}) = 0.60$ mol**

**The number of moles of $OCl^-$ in 0.60 L is:**

**number of moles = concentration × volume**
**$= (0.999 \text{ mol } L^{-1}) \times (0.40 \text{ L}) = 0.40$ mol**

**The added NaOH will react with the HOCl to form more $OCl^-$:**

**$HOCl(aq) + OH^-(aq) \rightarrow OCl^-(aq) + H_2O(l)$**

**If $x$ mol of NaOH is added then this reaction will lead to:**

**number of moles of HOCl = $(0.60 - x)$ mol**
**number of moles of $OCl^-$ = $(0.40 + x)$ mol**

**ANSWER CONTINUES ON THE NEXT PAGE**

**The solution has a volume of 1.00 L so:**

**[HOCl] = (0.60 – $x$) M and [OCl$^-$] = (0.40 + $x$) M**

**Using the Henderson-Hasselbalch equation with pH = 8.20:**

$$\mathbf{pH = pK_a + \log\frac{[OCl^-(aq)]}{[HOCl(aq)]} = 7.54 + \log\frac{(0.40+x)}{(0.60-x)} = 8.20}$$

$$\mathbf{\log\frac{(0.40+x)}{(0.60-x)} = 0.66 \quad or \quad \frac{(0.40+x)}{(0.60-x)} = 10^{0.66} = 4.57}$$

**Solving this gives $x$ = 0.42 mol.**

Answer: **0.42 mol**

Marks 5

- $BaSO_4$ is used as a contrast agent in medical imaging. It has a $K_{sp}$ of $1.1 \times 10^{-10}$. What is the molarity of $Ba^{2+}$ ions in a saturated aqueous solution of $BaSO_4$?

**The dissolution reaction is:**

$$\mathbf{BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)]}$$

**From the reaction, $[Ba^{2+}(aq)] = [SO_4^{2-}(aq)]$. Hence if $[Ba^{2+}(aq)] = S$:**

$$\mathbf{S^2 = K_{sp} = 1.1 \times 10^{-10}}$$
$$\mathbf{S = 1.0 \times 10^{-5}\ M}$$

Answer: **$1.0 \times 10^{-5}$ M**

What is the molar solubility of $BaSO_4$ in the presence of a 0.1 M solution of $Na_2SO_4$?

**The added $SO_4^{2-}$ will dominate over that produced in the dissolution reaction so $[SO_4^{2-}(aq)] = 0.1$ M. For the dissolution reaction to still be at equilibrium:**

$$\mathbf{K_{sp} = [Ba^{2+}(aq)][SO_4^{2-}(aq)] = 1.1 \times 10^{-10}}$$

**With $[SO_4^{2-}(aq)] = 0.1$ M,**

$$\mathbf{[Ba^{2+}(aq)] = K_{sp} / [SO_4^{2-}(aq)] = 1.1 \times 10^{-10} / 0.1\ M = 1 \times 10^{-9}\ M}$$

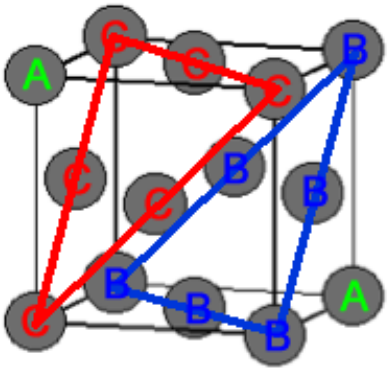
Answer: **$1 \times 10^{-9}$ M**

The lethal concentration of $Ba^{2+}$ in humans is about 60 mg $L^{-1}$ ($4 \times 10^{-4}$ M). Is there any advantage to administering $BaSO_4$ in the presence of 0.1 M $Na_2SO_4$ solution? Explain your reasoning.

**No. The lethal $[Ba^{2+}(aq)]$ is 40 times greater than the $[Ba^{2+}(aq)]$ in normal aqueous solution.**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

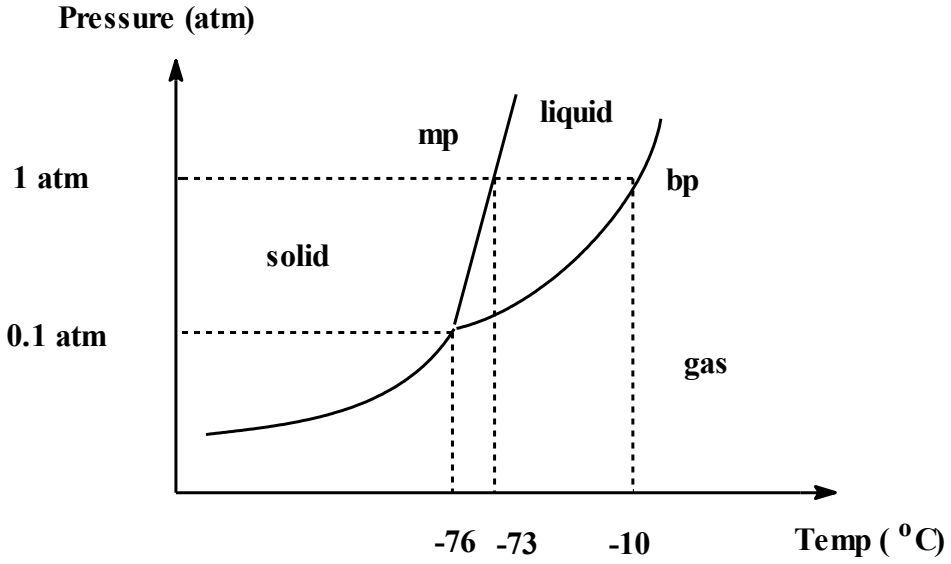
| | Marks |
|---|---|
| • A face centred cubic (FCC) unit cell has the maximum possible space filling of 74 %. Show the close packed layers, labelling them A, B and C, on the unit cell below. | **3** |




| | |
|---|---|
| How many atoms are in the unit cell? | **Atoms on corners: 8 × 1/8 = 1**<br>**Atoms on faces: 6 × 1/2 = 3**<br>**Total: 1 + 3 = 4** |

Marks 4

- The phase diagram for sulfur dioxide, $SO_2$, is shown below.




Io, the innermost of the four Galilean moons orbiting Jupiter, is the most geologically active body in the solar system. Its surface is covered with a frost of solid $SO_2$. The atmospheric pressure on Io is $10^{-7}$ atm and the surface temperature is between 90 and 110 K (–183 to –163 °C). As the temperature is raised on Io, does the $SO_2$ melt or sublime?

**It sublimes.**

Io has a hot molten magma core. What is the physical state of $SO_2$ several hundred metres below the surface of Io, where the temperature is –50 °C and the pressure rises to 1 atm?

**Liquid**

Is it possible to "ice skate" on a surface of solid $SO_2$? Explain your answer.

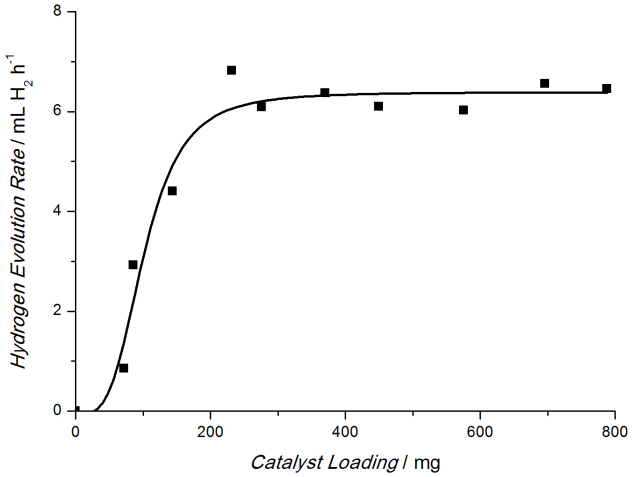
**No. The increase in pressure can never cause the solid to liquid phase change due to the slope of the solid/liquid equilibrium line.**

Marks
2

- When irradiated with visible light, CdS can catalyse the production of $H_2$ from water.

$$H_2O + \text{light} \xrightarrow{CdS} H_2 + \tfrac{1}{2}O_2$$

The rate of $H_2$ production from 80 mL of water at constant illumination varies with the amount of catalyst present (*i.e.* CdS loading) as shown below.




Why does the rate of $H_2$ production as a function of catalyst loading plateau?

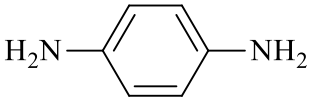
**Energy from light causes the water to split. The energy input is constant and this determines the maximum rate of reaction. (Essentially, light is the limiting reagent.)**

**Increasing the amount of catalyst increases the amount of light captured (0 - 200 catalyst loading), but cannot increase it above the amount being provided (plateau region).**

**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

**Marks 5**

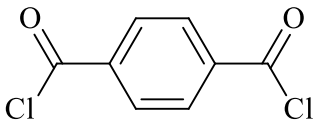
- Indicate the hybridisation of the carbon and nitrogen atoms in the diamine **P**.



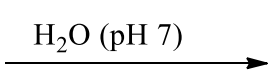
**P**

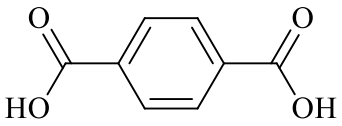
| | |
|---|---|
| N atoms: $sp^3$ | C atoms: $sp^2$ |

Draw the product of the reaction when diacyl chloride **Q** reacts with water.

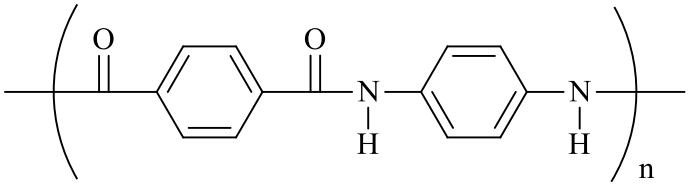


**Q**



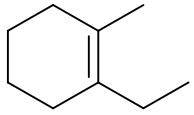
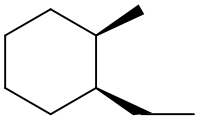
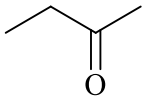
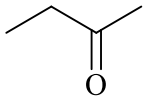
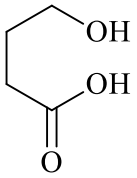
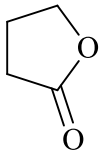
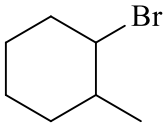
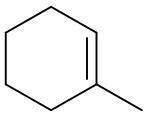
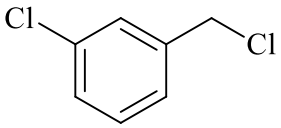
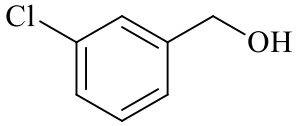
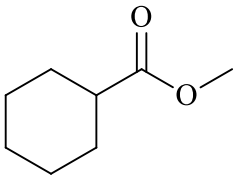
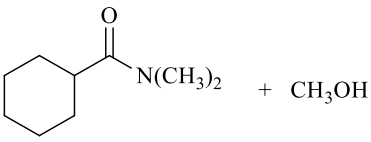
Kevlar (used in bullet-proof vests) is a polyamide polymer which is made from diacyl chloride building block **Q** and diamine building block **P**. Draw the repeating polymer unit formed in the reaction of **P** with **Q**.



**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

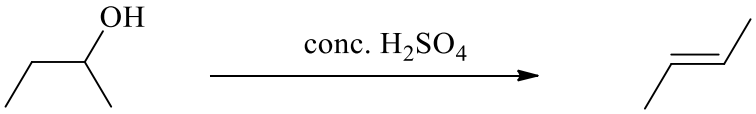
**Marks 7**

- Complete the following table. If there is no reaction, write "NR". Show any relevant stereochemistry.

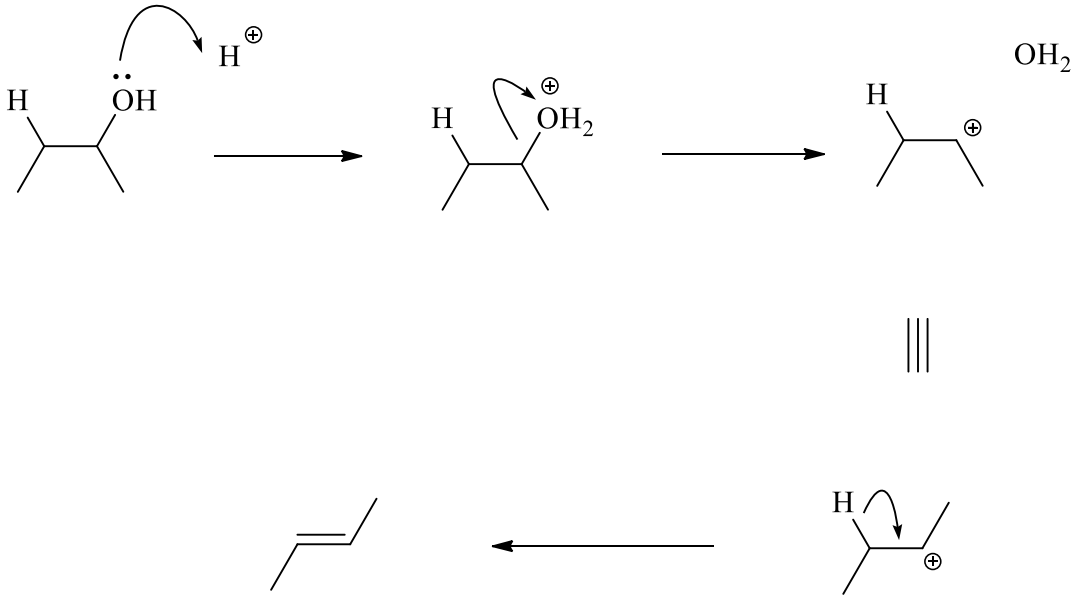
| STARTING MATERIAL | REAGENTS/ CONDITIONS | CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S) |
|---|---|---|
|  | $H_2$, Pd/C |  |
|  | $Cr_2O_7^{2-}$ / $H^+$ |  |
|  | $H^+$ catalyst / heat |  |
|  | conc. KOH in ethanol solvent |  |
|  | hot aqueous NaOH |  |
|  | $(CH_3)_2NH$ / heat |  |

**Marks 7**

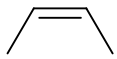
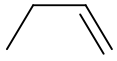
- Consider the following dehydration reaction.




Use curly arrows to show the mechanism of this reaction.

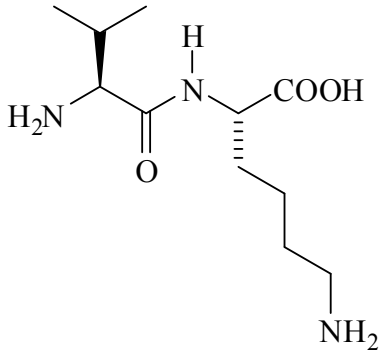



Two minor products are also formed in this reaction. They both have the same molecular formula as the product above. Draw their structures and name them.

| Structure | Name |
|---|---|
|  | **(*Z*)-2-butene** |
|  | **1-butene** |

**Marks 6**

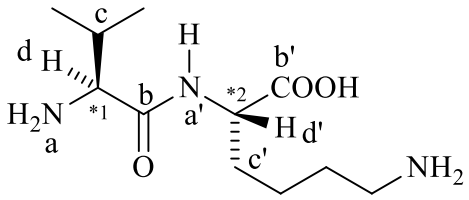
- Consider the following molecule (**M**) isolated from a natural source.



(**M**)

Indicate on the above structure all stereogenic centres in molecule (**M**).
Use numbered asterisks (∗1, ∗2, *etc*.).

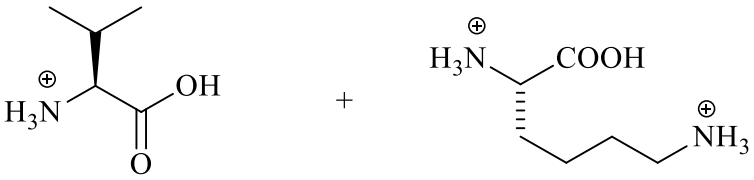
Select one of these stereogenic centres and determine its absolute configuration.
Show your working.



**Around C*1, the priority of the groups are a > b > c > d. Looking down the C-H bond the groups a → b → c go anticlockwise. Therefore configuration is (*S*)-.**

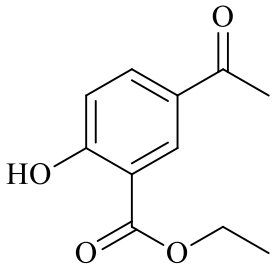
**Around C*2, the priority of the groups are a' > b' > c' > d'. Looking down the C-H bond (i.e. from behind the plane of the paper) the groups a' → b' → c' go anticlockwise. Therefore configuration is (*S*)-.**

Give the products when molecule (**M**) is hydrolysed by heating it with 6 M HCl.
Make sure you show the products in their correct ionisation states.



**Marks 3**

- Compound **T** is a precursor in the synthesis of the asthma drug salbutamol.

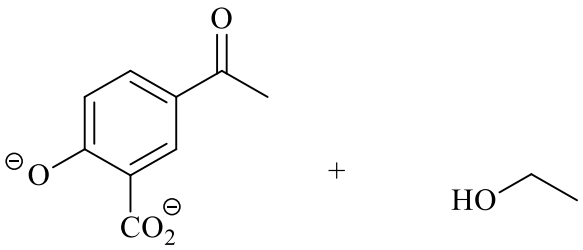


**T**

Give the molecular formula of compound **T**.

**$C_{11}H_{12}O_4$**

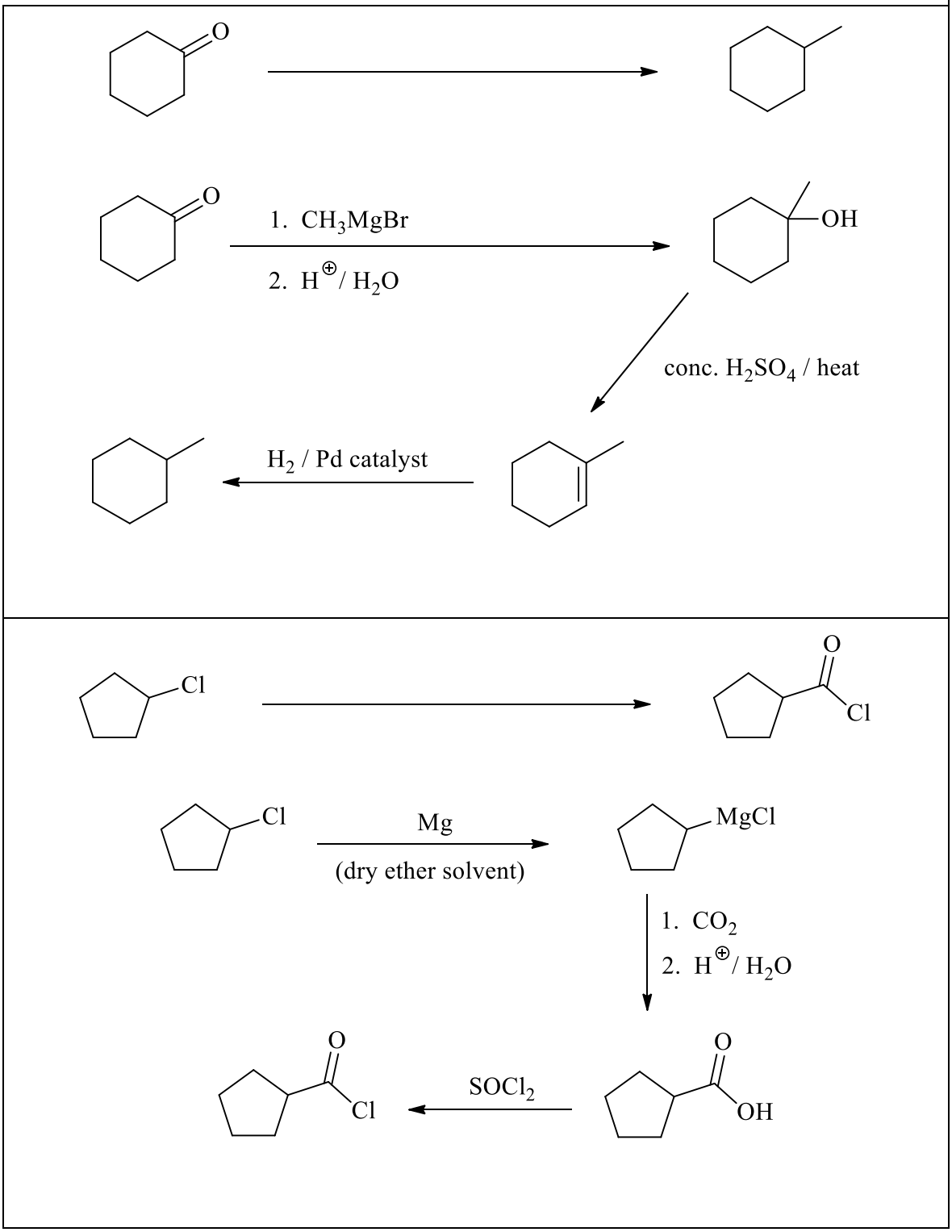
Give the structure(s) of all organic products formed when compound **T** is heated with 4 M NaOH.



**THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.**

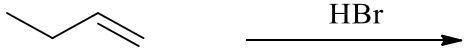
**Marks 5**

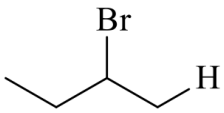
- Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.



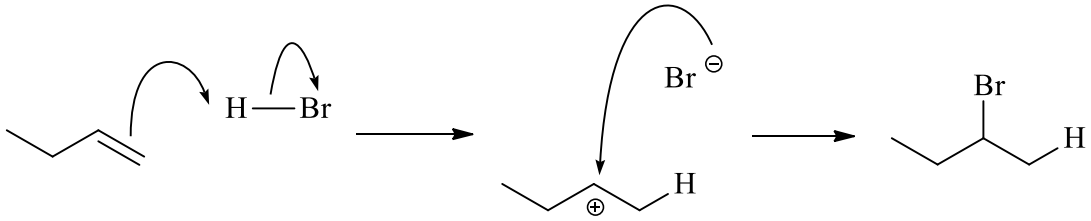
**Marks 6**

- Give the major product from the following reaction.



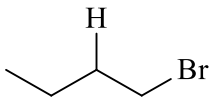

Show the mechanism of the reaction. Make sure you show structural formulas for all relevant intermediate species and the final product, as well as using curly arrows to indicate the movement of electrons (*i.e.* the breaking and formation of bonds).




What is the appropriate stereochemical descriptor for the major product of this reaction? Give a reason for your answer.

**Racemic mixture. The carbon where the Br is attached has 4 different groups around it, so is stereogenic. The carbocation from which it forms is planar and so attack by the $Br^-$ is equally likely from either the top or bottom side. This results in equal amounts of both enantiomers being formed.**

Give the structure of the minor product of this reaction and explain why very little of it forms.




**This product is derived from the primary carbocation intermediate. Secondary carbocations are more stable than primary carbocations, so little of this product forms.**