

Topics in the November 2012 Exam Paper for CHEM1102

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- Aldehydes and Ketones
- Synthetic Strategies
- Organic Halogen Compounds

2012-N-14:

- Alkanes

2012-N-15:

- Alkenes
- Stereochemistry

- What is the pH of a 0.100 M solution of sodium acetate?
The pK_a of acetic acid is 4.76.

Marks
4

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

	$CH_3CO_2^-$	H_2O	\rightleftharpoons	CH_3COOH	OH^-
initial	0.100	large		0	0
change	-x	negligible		+x	+x
final	$0.100 - x$	large		x	x

The equilibrium constant K_b is given by:

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3CO_2^-]} = \frac{x^2}{(0.100 - x)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

$$pK_b = 14.00 - 4.76 = 9.24$$

As $pK_b = 9.24$, $K_b = 10^{-9.24}$. K_b is very small so $0.100 - x \sim 0.100$ and hence:

$$x^2 = 0.100 \times 10^{-9.24} \text{ or } x = 7.59 \times 10^{-6} \text{ M} = [OH^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-] = \log_{10}[7.59 \times 10^{-6}] = 5.12$$

Finally, $pH + pOH = 14.00$ so

$$pH = 14.00 - 5.12 = 8.88$$

$$pH = 8.88$$

ANSWER CONTINUES ON THE NEXT PAGE

What is the ratio of acetate ion to acetic acid in this solution?

From the Henderson–Hasselbalch equation,

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]}$$

At pH = 8.88,

$$8.88 = 4.76 + \log \frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]}$$

so

$$\frac{[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{COOH}]} = 10^{4.12} = 1.3 \times 10^4$$

Answer: 1.3×10^4

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- Citric acid, $\text{C}_6\text{H}_8\text{O}_7$, has three pK_a values: $\text{pK}_{a1} = 3.13$, $\text{pK}_{a2} = 4.76$ and $\text{pK}_{a3} = 6.40$. Explain, giving exact volumes and concentrations, how to make 1.0 L of a citrate-based buffer with pH 5.58.

Marks
4

The desired pH is equally close to pK_{a2} and pK_{a3} so the best buffer could use either of these equilibria. Using pK_{a3} corresponds to using the equilibrium:



Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = 6.40 + \log \frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]}$$

At pH = 5.58,

$$\log \frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = (5.58 - 6.40) = -0.82$$

$$\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = 0.15$$

As 1.0 L of the buffer is required,

$$\begin{aligned} [\text{Cit}^{3-}] &= n_{\text{Cit}^{3-}} / 1.0 \text{ M} \\ [\text{HCit}^{2-}] &= n_{\text{HCit}^{2-}} / 1.0 \text{ M} \end{aligned}$$

So,

$$\frac{[\text{Cit}^{3-}]}{[\text{HCit}^{2-}]} = \frac{n_{\text{Cit}^{3-}}}{n_{\text{HCit}^{2-}}} = 0.15$$

There are *many* ways to construct the buffer to achieve this ratio when the acid and base are mixed.

If the two solutions have the same initial concentrations, then the ratio of the *volumes* used is 0.15. The volumes add up to 1000 mL:

$$\text{volume of HCit}^{2-} = x \text{ L} \qquad \text{volume of Cit}^{3-} = 1.0 - x \text{ L}$$

So,

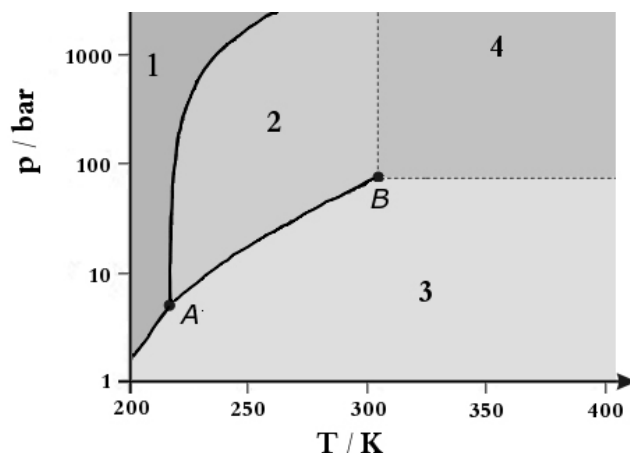
$$\frac{V_{\text{Cit}^{3-}}}{V_{\text{HCit}^{2-}}} = \frac{1.0 - x}{x} = 0.15$$

$$x = 0.87$$

Hence, 870 mL of HCit^{2-} and 130 mL of Cit^{3-} are used.

Marks
5

- The phase diagram of carbon dioxide is shown below.



Identify the four phases, shown as 1 - 4, in the phase diagram.

1	solid
2	liquid
3	gas
4	supercritical fluid

What names are given to the two points A and B?

A	triple point
B	critical point

What are the physical characteristics of carbon dioxide in phase 4?

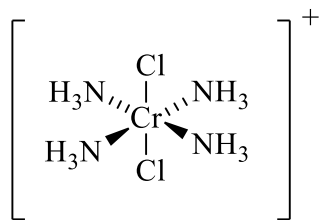
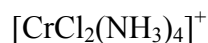
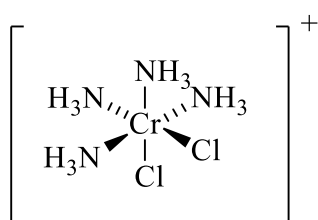
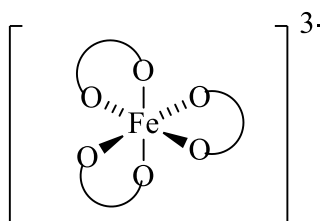
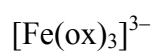
It has a viscosity similar to that of a liquid, but it can expand and contract like a gas filling its container. It is a good solvent.

Why is the line between phases 1 and 2 almost vertical at pressures below 100 bar?

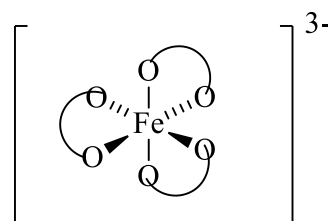
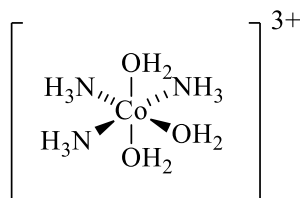
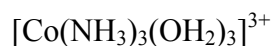
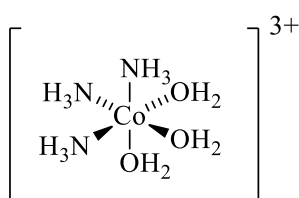
The density of liquid CO₂ and solid CO₂ are almost the same. Neither is easily compressed.

Marks
9

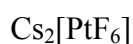
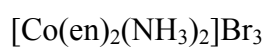
- The following three complex ions can all exhibit isomerism. Name the type of isomerism involved in each case and draw the structures of the isomeric pairs.
 ox = oxalate = $\text{C}_2\text{O}_4^{2-}$

*trans-* isomer*cis-* isomer
Geometrical isomerism


mirror


Optical isomerism
*mer-* isomerthe OH_2 ligands lie along a meridian*fac-* isomerthe OH_2 ligands define a face of an octahedron
Geometrical isomerism

- Give the systematic name of each of the following compounds.
 en = ethylenediamine = 1,2-diaminoethane = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$


caesium hexafluoridoplatinate(IV)

diamminebis(ethylenediamine)cobalt(III) bromide
3

Marks
3

- What are the structural differences between graphite and diamond and how do these differences impact on their physical properties? Mention at least three physical properties.

Diamond is a covalent network solid with each carbon bonded to 4 others in a tetrahedral arrangement. Graphite consists of sheets of sp^2 hybridised carbons, each bonded to 3 others in a trigonal planar arrangement.

Diamond is very hard as each atom is firmly bonded into its place in the crystal. Graphite is very soft and has a greasy feel as the sheets of carbon atoms are free to slide over one another.

Diamond is an insulator. Graphite can conduct a current in the plane of the sheets as the electrons in the unhybridised p orbitals are completely delocalised.

They have different appearances (diamond is colourless, graphite is black) due to their different electronic arrangements.

1

- Describe the periodic trends of **either** atomic radius **or** of ionisation energy. Explain the trend in the property selected.

Atomic radius:

Atomic radius decreases across a period and increases down a group. The numbers of protons and electrons increase as you move across a row. Electrons in s or p orbitals are not shielded from the increasing nuclear charge and hence the effective nuclear charge (Z_{eff}) is increasing. This results in smaller orbitals and decreasing atomic radius. At the end of the row, the next electron goes into an s orbital of greater n . This orbital is shielded by electrons in the lower energy orbitals and there is a consequent big drop in Z_{eff} . The atomic radius thus increases going down a group.

Ionisation energy:

Ionisation energies increase across a row as the atoms become smaller. The smaller the atom, the more strongly the outer electrons are attracted to the nucleus and hence the higher the ionisation energy. Similarly, ionisation energies decrease down a group as the atoms become larger.

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Marks
2

- Order **either one** of the two following sets of oxides in terms of increasing acidity. Explain the reasons for your order.

1. HBrO_4 , H_3AsO_4 , H_2SeO_4 2. HClO_2 , HClO , HClO_4 , HClO_3 .**1. $\text{H}_3\text{AsO}_4 < \text{H}_2\text{SeO}_4 < \text{HBrO}_4$**

The acidic protons are all bonded to an O atom that in turn is bonded to the As, Se or Br. The more electronegative the central atom, the more electron density is drawn out of the O–H bond and the weaker this bond becomes. The weaker this bond, the stronger the acid. Acid strength therefore follows the electronegativity of the central atoms: $\text{Br} > \text{Se} > \text{As}$.

2. $\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4$

All are structurally $\text{H}-\text{O}-\text{Cl}(\text{O})_x$, where x is 0, 1, 2 or 3. Oxygen is a very electronegative atom and pulls electron density towards itself. The more O's bonded to the chlorine, the more pronounced this effect and the weaker the O–H bond becomes. The weaker this bond, the stronger the acid.

- A binary alloy has a face-centered cubic structure with atoms of element A in the faces and atoms of element B at the corners. What is the formula of the alloy? Explain your reasoning.

1

Atoms on the faces are shared between 2 cells: they contribute $\frac{1}{2}$ to each. There are 6 faces:

$$\text{number of A atoms} = 6 \times \frac{1}{2} = 3$$

Atoms on the corners are shared between 8 cells: they contribute $\frac{1}{8}$ to each. There are 8 corners:

$$\text{number of B atoms} = 8 \times \frac{1}{8} = 1$$

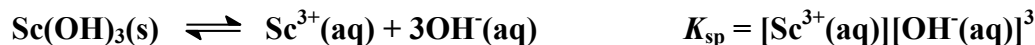
The stoichiometry is thus $\text{A} : \text{B} = 3 : 1$ so the formula is A_3B .

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- What is the solubility of scandium hydroxide, $\text{Sc}(\text{OH})_3$, ($K_{\text{sp}} = 2 \times 10^{-30}$) in water? Give your answer in g per 100 mL.

Marks
2

The dissolution reaction and solubility product are:



If S mol in one litre, $[\text{Sc}^{3+}(\text{aq})] = S$ M and $[\text{OH}^{-}(\text{aq})] = 3S$ M. Hence:

$$K_{\text{sp}} = (S)(3S)^3 = 27S^4 = 2 \times 10^{-30}$$

$$S = 1.6 \times 10^{-8} \text{ M}$$

This is the number of moles that dissolve in one litre. The number of moles that dissolve in 100 mL is therefore 1.6×10^{-9} mol.

The molar mass of $\text{Sc}(\text{OH})_3$ is:

$$\begin{aligned} \text{molar mass} &= (44.96 (\text{Sc}) + 3 \times 16.00 (\text{O}) + 3 \times 1.008 (\text{H})) \text{ g mol}^{-1} \\ &= 95.984 \text{ g mol}^{-1} \end{aligned}$$

The mass corresponding to 1.6×10^{-9} mol is therefore:

$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{molar mass} \\ &= (1.6 \times 10^{-9} \text{ mol}) \times (95.984 \text{ g mol}^{-1}) = 1.6 \times 10^{-7} \text{ g} \end{aligned}$$

The solubility is 1.6×10^{-7} g per 100 mL.

Answer: 1.6×10^{-7} g per 100 mL

- How does the interplay of ΔH and ΔS affect the spontaneity of the phase change between solid and liquid water?

4

$$\Delta G = \Delta H - T\Delta S$$

Any process is spontaneous if $\Delta G < 0$, i.e. if $T\Delta S > \Delta H$.

For the melting of ice, both ΔS and ΔH are positive, so this process is spontaneous at higher temperatures.

Conversely, for the freezing of water, both ΔS and ΔH are negative, so this process is spontaneous at lower temperatures.

- Consider the reaction $A(g) + B(g) + C(g) \rightarrow D(g)$ for which the following data were obtained at 25 °C.

Marks
3

Experiment	Initial [A] (mol L ⁻¹)	Initial [B] (mol L ⁻¹)	Initial [C] (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
1	0.0500	0.0500	0.1000	6.25×10^{-3}
2	0.1000	0.0500	0.1000	1.25×10^{-2}
3	0.1000	0.1000	0.1000	5.00×10^{-2}
4	0.0500	0.0500	0.2000	6.25×10^{-3}

Write the rate law and calculate the value of the rate constant.

The general form of the rate equation for this reaction is:

$$\text{rate} = k[A]^a[B]^b[C]^c$$

Between experiments 1 and 2, [B] and [C] are constant. [A] is doubled. This leads to a doubling of the rate: the rate depends on [A]¹ so $a = 1$.

Between experiments 2 and 3, [A] and [C] are constant. [B] is doubled. This leads to the rate increasing by a factor of four: the rate depends on [B]² so $b = 2$.

Between experiments 1 and 4, [A] and [B] are constant. [C] is doubled but there is no change in the rate: the rate is independent of [C] so $c = 0$.

Hence, the rate law is:

$$\text{rate} = k[A][B]^2$$

The rate constant, k , can be calculated using the results of any of the experiments. Using experiment 1:

$$\text{rate} = k[0.0500 \text{ mol L}^{-1}][0.0500 \text{ mol L}^{-1}]^2 = 6.25 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

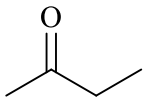
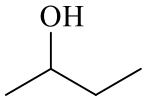
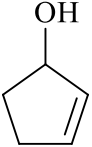
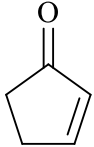
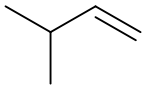
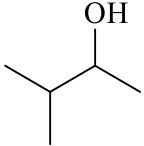
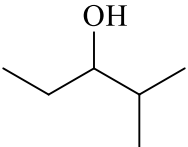
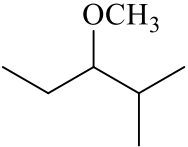
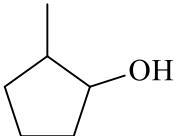
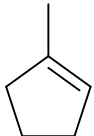
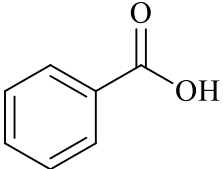
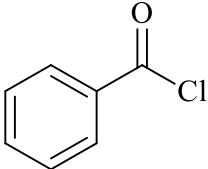
so

$$k = 50.0 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

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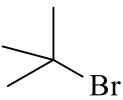
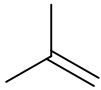
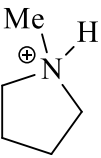
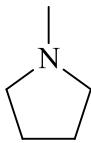
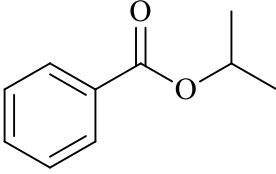
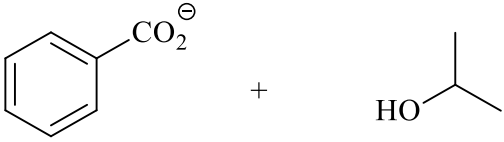
Marks
6

- Complete the following table.

STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	1. NaBH ₄ 2. H ⁺ / H ₂ O	
	Cr ₂ O ₇ ²⁻ / H ⁺	
	dilute H ₂ SO ₄	
	1. NaOH 2. CH ₃ Br	
	concentrated H ₂ SO ₄	
	SOCl ₂	

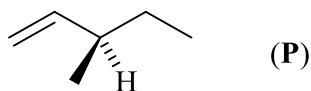
Marks
4

- Draw the structure of the organic product(s) formed when each of the following compounds is treated with 4 M sodium hydroxide. The first two reactions proceed at room temperature; the last one requires heating.

Compound	Organic Product(s)
	
	
	

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- Consider compound (**P**), whose structure is shown below.

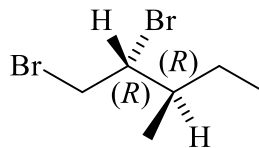
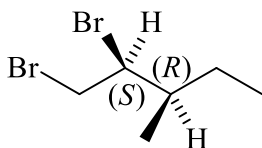


Marks
4

Give the full name of compound (**P**) that unambiguously describes its stereochemistry.

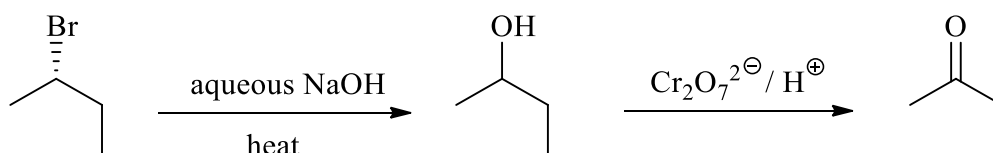
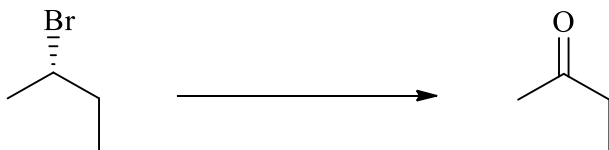
(R)-3-methyl-1-pentene

When compound (**P**) reacts with bromine (Br_2), two stereoisomers are formed. Draw the structure of both products and label all stereogenic centres appropriately.



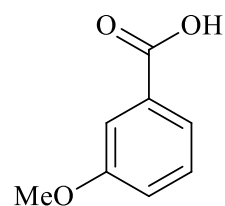
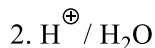
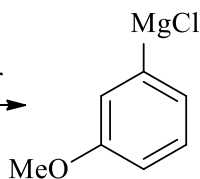
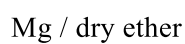
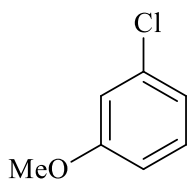
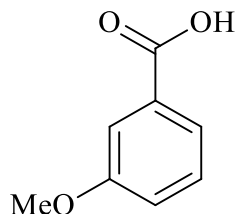
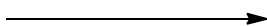
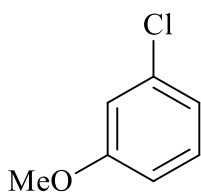
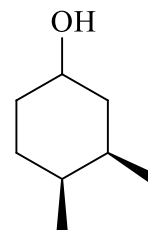
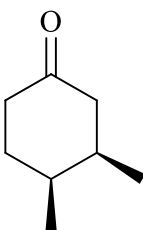
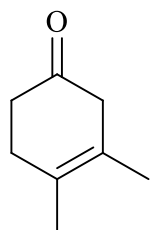
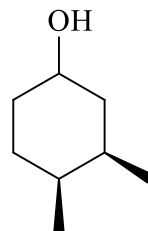
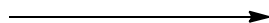
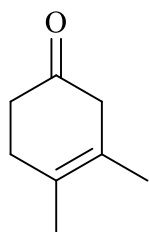
- Devise a synthesis of the following compound from the starting material indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.

3

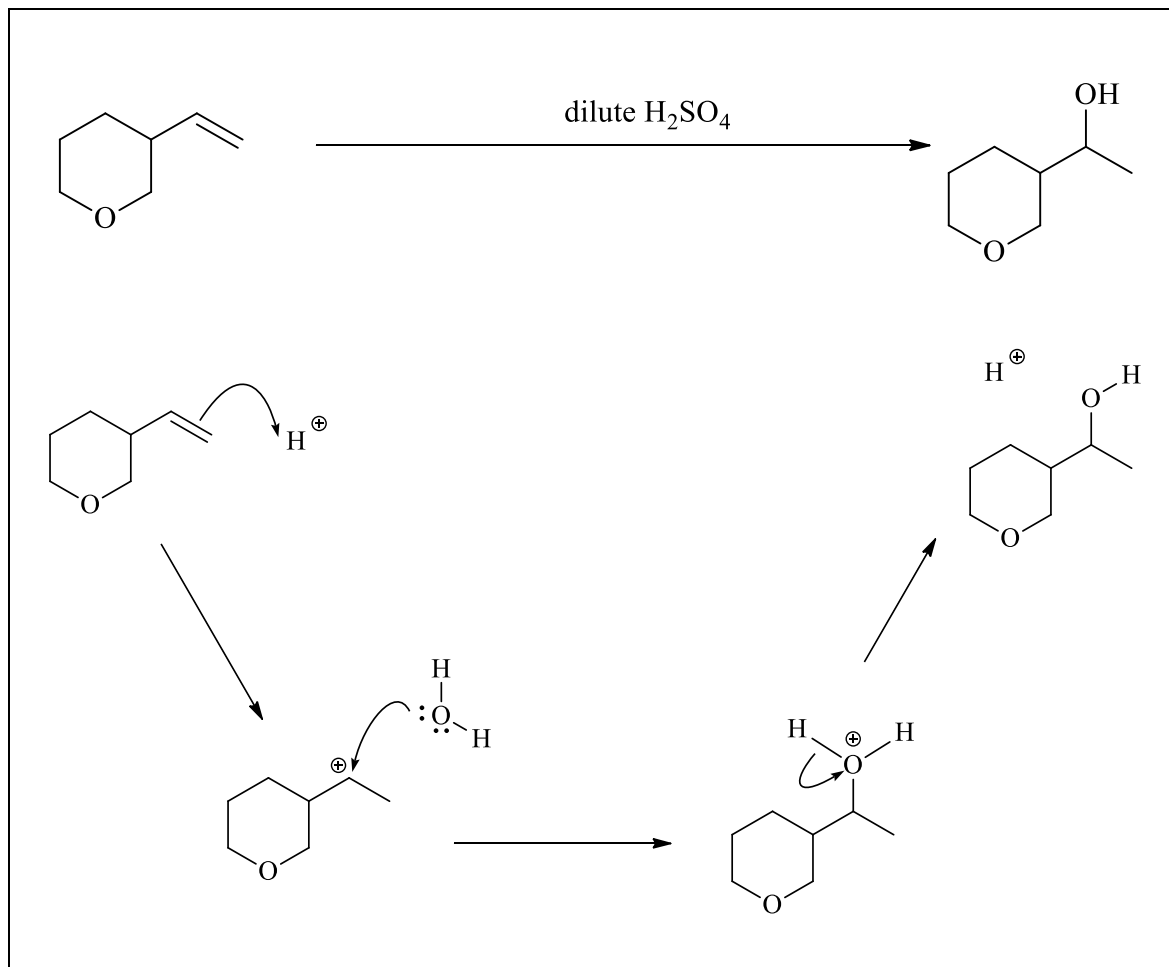


Marks
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- Devise a synthesis of the following compounds from the starting materials indicated. Note that more than one step will be required. Indicate all necessary reagents and the constitutional formulas of any intermediate compounds.



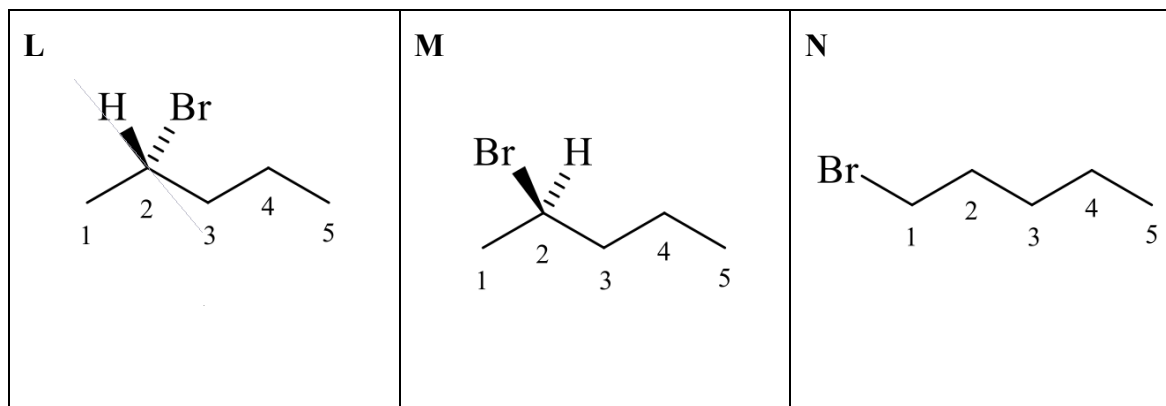
- Complete the mechanism for the following reaction. Give the structure of the carbocation intermediate and indicate (using curly arrows) all the bonding changes that occur.

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

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- When HBr reacts with 1-pentene, three products, **L**, **M** and **N**, are formed. **L** and **M** are enantiomers, whilst **L** and **N** (and **M** and **N**) are constitutional isomers. Give the structures of these products and explain how they form? Discuss the relative amounts of each product, paying attention to the regioselectivity and stereoselectivity of the reaction.

Hint: You need to discuss important aspects of the reaction mechanism, including the relative stabilities of any intermediates, but you do not need to give the full mechanism using curly arrows.



Electrophilic addition of H^+ to the double bond gives 2 possible carbocations.

The more stable carbocation leads to the major products **L and **M**, which are formed in equal amounts as attack by Br^- ion on the planar carbocation is equally likely from either top or bottom.**

The minor product, **N, comes from the less stable carbocation.**

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