Topics in the November 2014 Exam Paper for CHEM1102

Click on the links for resources on each topic.

2014-N-2:

- Crystal Structures

2014-N-3:

- Physical States and Phase Diagrams
- Crystal Structures

2014-N-4:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-5:

- Weak Acids and Bases
- Calculations Involving pK_a

2014-N-6:

- Solubility Equilibrium

2014-N-7:

- Hydrolysis of Metal Ions
- Metals in Biology
- Coordination Chemistry

2014-N-8:

- Aldehydes and Ketones
- Alcohols
- Alkenes
- Alkynes
- Carboxylic Acids and Derivatives

2014-N-9:

- Stereochemistry
- Carboxylic Acids and Derivatives
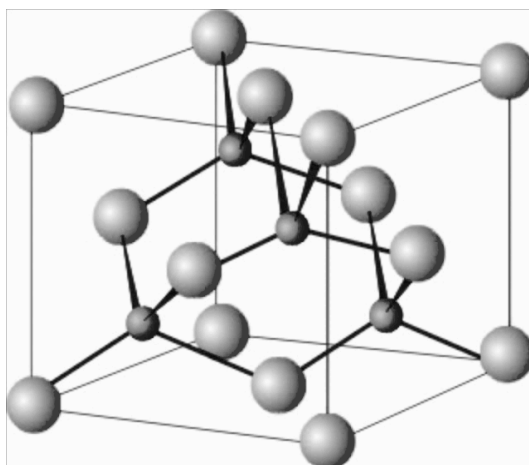- Amines

2014-N-10:

- Alcohols
- Stereochemistry

2014-N-11:

- Alkenes
- Alcohols
- Stereochemistry

2014-N-12:

- Synthetic Strategies

- The cubic form of boron nitride (borazon) is the second-hardest material after diamond and it crystallizes with the structure shown below. The large spheres represent the nitrogen atoms and the smaller spheres represent boron atoms.

From the unit-cell shown above, determine the empirical formula of boron nitride.

There are N atoms on the corners and on the faces of the unit cell:

- **There are 8 N atoms on the corners. These contribute 1/8 to the unit cell giving a total of 8 × 1/8 = 1 N atom.**
- **There are 6 N atoms on the faces. These contribute 1/2 to the unit cell giving a total of 6 × 1/2 = 3 N atoms.**
- **There are a total of 1 + 3 = 4 N atoms in the unit cell.**

There are B atoms inside the unit cell:

- **There are 4 B atoms completely inside the cell. These contribute only to this unit cell giving a total of 4 × 1 = 4 B atoms.**

The formula is therefore B_4N_4 which simplifies to BN.

Answer: **BN**

Determine the oxidation state of the boron atoms.

Nitrogen has an oxidation number of –III (or -3) to complete its octet. To ensure neutrality, boron must be +III (or +3).

Answer: **+III (or +3)**

ANSWER CONTINUES ON THE NEXT PAGE

The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

Boron and nitrogen have different electronegativities, with N more electronegative than B. This leads to partial δ+ and δ- charges on B and N respectively. These charges give the bonds partial ionic character and this acts to increase the strength of the bonds.

**Marks
5**

• A simplified phase diagram for iron is shown below, with the solid part divided into the body-centred cubic (BCC) and face-centred cubic (FCC) phases.
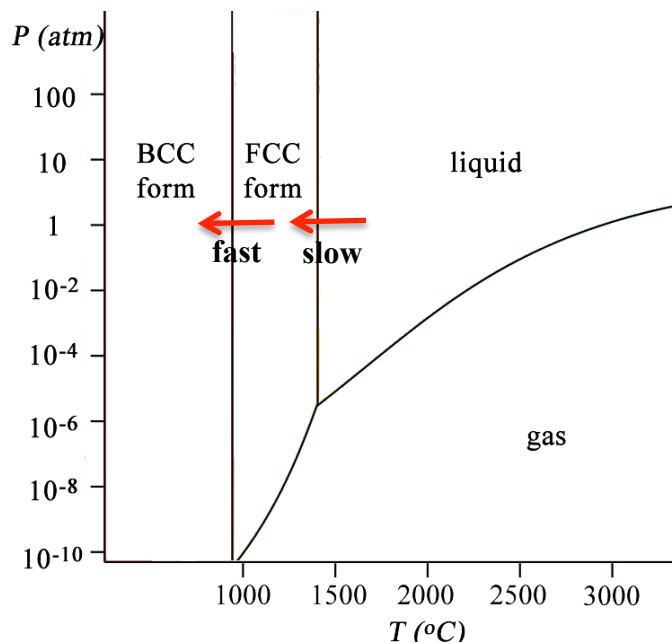
Which form of iron is stable at room temperature and pressure?

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 as a metastable phase.

The slow cooling leads to the most stable form at 1200 ^{o}C – the FCC form. Fast cooling to room temperature does not allow the atoms to re-arrange; they are stuck in the FCC form as considerable re-arrangement is needed to turn this in the BCC form.

The structure is stuck in the FCC arrangement even though BCC is more stable.

The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

BCC is less dense than FCC – the latter is a close packed structure so has the maximum possible density whereas the former is not closed packed.

Applying pressure will favour the more dense structure as it takes up less space. Increasing pressure therefore favours the FCC structure. The line between BCC and FCC has a negative slope (\\). If the system is on the line and the pressure is increased, the system moves into the FCC region.

**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	$\rightleftharpoons$	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:

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

Hence, the pH is given by:

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

pH = **2.75**

Other than water, 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: 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	$\rightleftharpoons$	NH_4^+	OH^-
initial	0.050	large		0	0
change	-y	negligible		+y	+y
final	0.050 – y	large		y	y

The equilibrium constant K_b is given by:

ANSWER CONTINUES ON THE NEXT PAGE

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

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**

Other than water, 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: NH_3

THIS QUESTION CONTINUES ON THE NEXT PAGE.

**Marks
5**

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

$C_6H_5COOH(aq) + NH_3(aq) \rightarrow C_6H_5COO^-(aq) + NH_4^+(aq)$
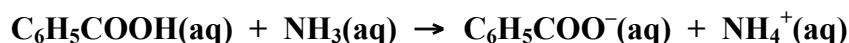
Write the expression for the equilibrium constant for the reaction of benzoic acid with ammonia?

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

What is the value of the equilibrium constant for the reaction of benzoic acid with ammonia?

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 dissolving equimolar amounts of benzoic acid and ammonia in water?

The equilibrium strong favours products so the major species are:

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

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

- The salt calcium oxalate, $CaC_2O_4 \cdot H_2O$, is sparingly soluble. Write down the chemical equation for its dissolution in water and the expression for K_{sp}.
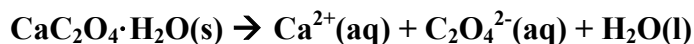
> $CaC_2O_4 \cdot H_2O(s) \rightarrow Ca^{2+}(aq) + C_2O_4^{2-}(aq) + H_2O(l)$
>
> $K_{sp} = [Ca^{2+}(aq)][C_2O_4^{2-}(aq)]$

What is the molar solubility of calcium oxalate? $K_{sp} = 2.3 \times 10^{-9}$

> **If x mol of the salt dissolves in one litre, then the molar solubility is x M. If x mol dissolves in one litre then $[Ca^{2+}(aq)] = x$ M and $[C_2O_4^{2-}(aq)] = x$ M.**
>
> $K_{sp} = [Ca^{2+}(aq)][C_2O_4^{2-}(aq)] = (x)(x) = x^2 = 2.3 \times 10^{-9}$
>
> $x = 4.8 \times 10^{-5}$ **mol L^{-1}**
>
> Answer: **4.8×10^{-5} mol L^{-1}**

If additional calcium oxalate is added to a saturated solution, what is the effect on $[Ca^{2+}(aq)]$?

> **A saturated solid has the maximum possible dissolution. Adding additional solid has no effect on the equilibrium and so no effect on $[Ca^{2+}(aq)]$.**

Following blood donation, a solution of sodium oxalate is added to remove $Ca^{2+}(aq)$ ions which cause the blood to clot. The concentration of $Ca^{2+}(aq)$ ions in blood is 9.7×10^{-5} g mL^{-1}. If 100.0 mL of 0.1550 M $Na_2C_2O_4$ is added to 100.0 mL of blood, what will be the concentration (in mol L^{-1}) of Ca^{2+} ions remaining in the blood?

> **The amount of Ca^{2+} present in 100.0 mL is 9.7×10^{-3} g. As its molar mass is 40.08 g mol^{-1}, this corresponds to:**
>
> **number of moles = mass / molar mass =**
> **= (9.7×10^{-3} g) / (40.08 g mol^{-1}) = 2.4×10^{-4} mol**
>
> **The number of moles of $C_2O_4^{2-}(aq)$ added is:**
>
> **number of moles = concentration × volume**
> **= (0.1550 mol L^{-1}) × (0.1000 L) = 0.01550 mol**
>
> **The amount of $C_2O_4^{2-}$ is *much* larger than the amount of Ca^{2+} present so precipitation of $CaC_2O_4.H_2O(s)$ does not reduce the $C_2O_4^{2-}$ significantly.**
>
> **When the oxalate is added to the blood, the total volume increases to (100.0 + 100.0) mL = 200.0 mL. The concentration of $C_2O_4^{2-}(aq)$ is now:**

ANSWER CONTINUES ON THE NEXT PAGE

concentration = number of moles / volume
= (0.01550 mol) / (0.2000 L) = 0.0775 mol L^{-1}

Using K_{sp} = [Ca^{2+}(aq)][C$_2$O$_4$$^{2-}$(aq)]:

[Ca^{2+}(aq)] = K_{sp} / [C$_2$O$_4$$^{2-}$(aq)] = (2.3 × 10^{-9} / 0.0775) M = 3.0 × 10^{-8} M

Answer: **3.0 × 10^{-8} M**

- The structure below represents the active site in carbonic anhydrase, which features a Zn^{2+} ion bonded to 3 histidine residues and a water molecule.
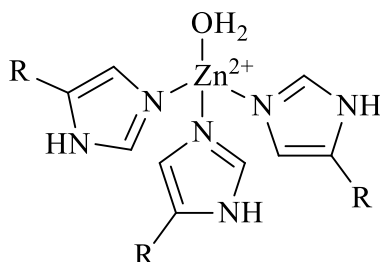
The pK_a of uncoordinated water is 15.7, but the pK_a of the water ligand in carbonic anhydrase is around 7. Suggest an explanation for this large change.

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, chemists often replace Zn^{2+} with Co^{2+}. Using the box notation to represent atomic orbitals, work out how many unpaired electrons are present in the Zn^{2+} and Co^{2+} ions.

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.

Suggest why it is useful to replace Zn^{2+} with Co^{2+} when studying the nature of the active site in carbonic anhydrase.

The ions have similar radii so the properties of natural carbonic anhydrase and the version with cobalt replacing zinc should have similar biological properties. The unpaired electrons on Co^{2+} however mean that it is paramagnetic and the magnetism can be used to study the active site.
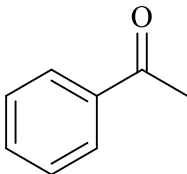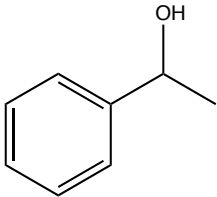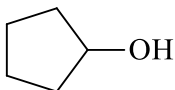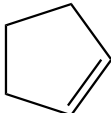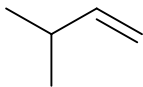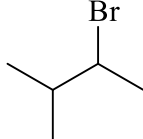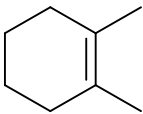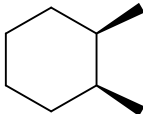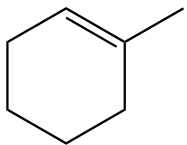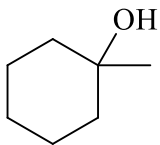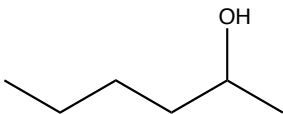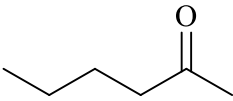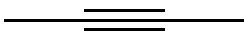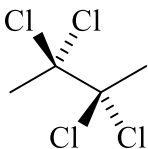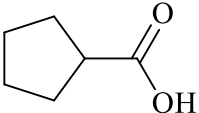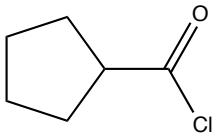
Suggest two differences in the chemistry of Zn^{2+} and Co^{2+} ions that may affect the reactivity of the cobalt-containing enzyme.

Zinc only forms +2 ions but cobalt forms +2 and +3. The cobalt-containing enzyme may be susceptible to oxidation.

Zn^{2+} tends to form 4-coordinate tetrahedral complexes but Co^{2+} is slightly larger and often forms 6-coordinate octahedral complexes. The metal ion may change its coordination by bonding extra ligands.
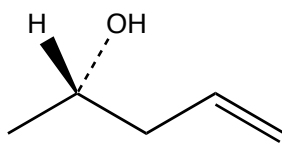
**Marks
8**

- Complete the following table.

STARTING MATERIAL	REAGENTS/CONDITIONS	THE MAJOR ORGANIC PRODUCT(S)
	1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O	
—OH	hot concentrated H_2SO_4	
	HBr	Br
	H2 / Pd / catalyst	
	dilute aqueous H_2SO_4	OH
OH	$Cr_2O_7{}^{2\ominus}$ / $H^{\oplus}$	
	2 equivalents of Cl_2	Cl Cl / Cl Cl
O / OH	$SOCl_2$	O / Cl

• Draw the structure of (*S*)-pent-4-en-2-ol.

When (*S*)-pent-4-en-2-ol reacts with bromine, Br$_2$, two stereoisomers are formed. Draw the structure of both products.
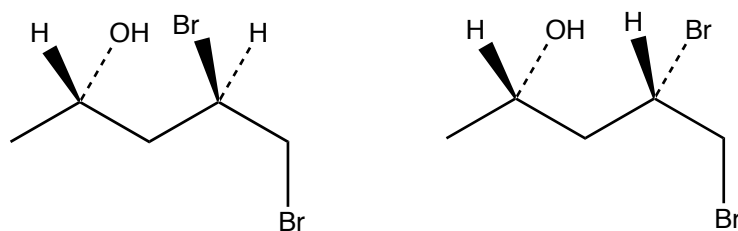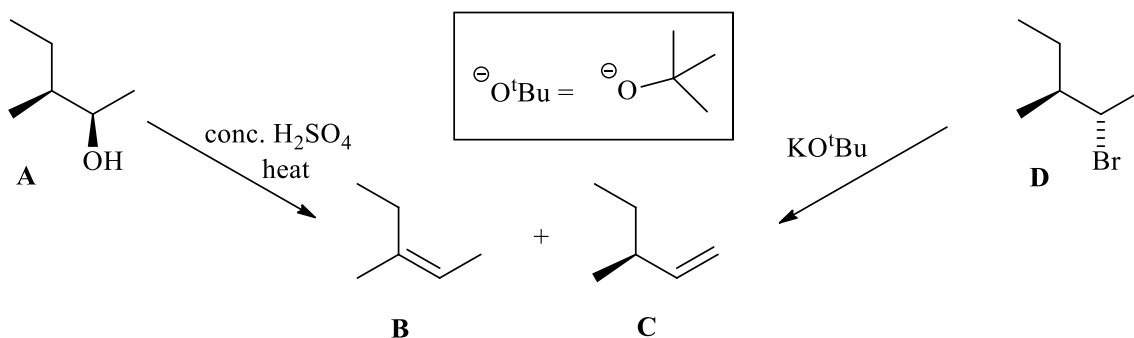

• Draw the structure of the organic product(s) formed when each of the following compounds is treated with 4 M sodium hydroxide. The first reaction requires heating.
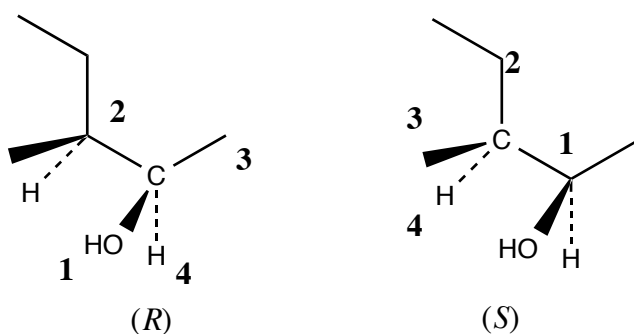
3

Compound	Organic products

Marks
7

- The elimination of H_2O from alcohol **A** can form the isomeric alkenes **B** and **C**. Elimination of HBr from the alkyl halide **D** can generate the same two alkenes.

Assign the absolute configuration of alcohol **A**. Show your working.


(R) (S)

There are 2 chiral centres. On the diagram on the left, the priorities are as shown and are in an (R) configuration. On the diagram on the right, the priorities are in an (S) arrangement.
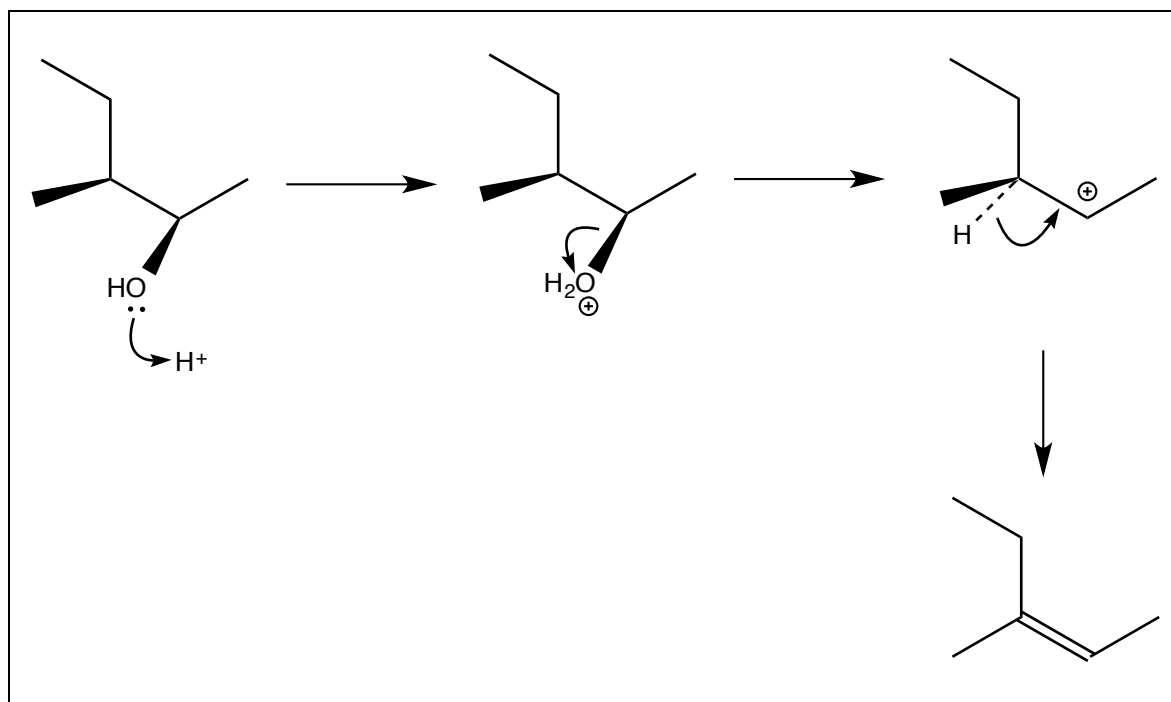
Name compound **B** fully.

(Z)-3-methylpent-2-ene

A diastereoisomer of **B** is also formed in these reactions. Draw the enantiomer of **A** and the diastereoisomer of **B**.

enantiomer of **A**	diastereoisomer of **B**
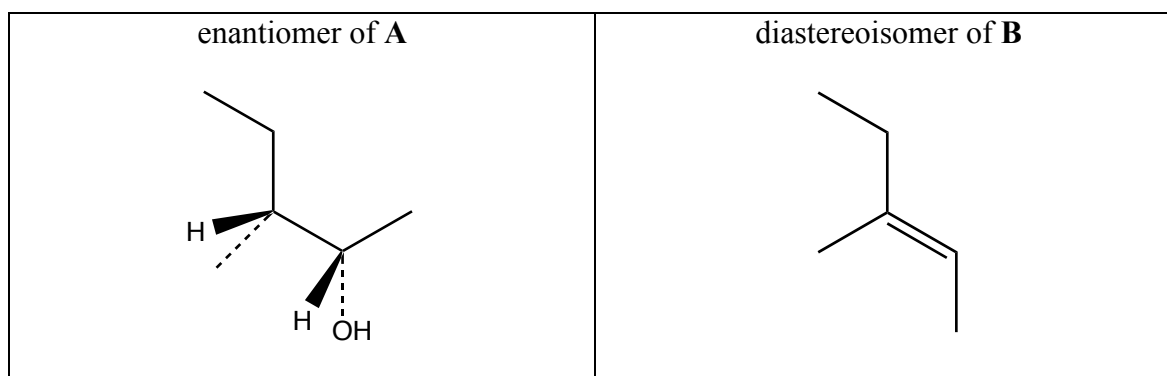
ANSWERS CONTINUES ON THE NEXT PAGE

Propose a mechanism for the formation of **B** from **A** under the conditions shown. Use curly arrows and draw the structures of any intermediates.


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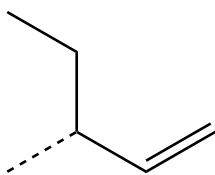|	Marks
Explain why compound **C** is the minor product of this reaction.	**4**

C has the new C=C bond with fewer substituents. This is an example of Zeitsev's rule: the more substituted alkene is more thermodynamically stable.

Propose a mechanism for the formation of **C** from **D** under the conditions shown. Use curly arrows and draw the structures of any intermediates.
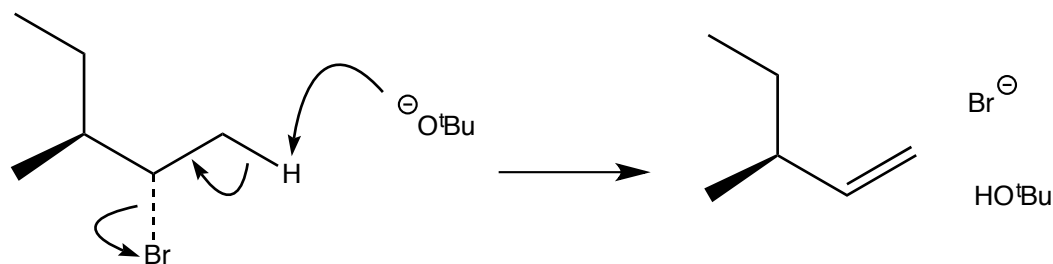
Compound **C** is the major product formed from **D** under these conditions. What would be the major product if the enantiomer of **D** were exposed to the same reaction conditions?


THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
8

- Propene can be converted into 1,2-dimethyl-1-phenylpropene using a sequence of 6 reactions. Demonstrate your knowledge of Grignard reactions by suggesting a plausible sequence. Make sure you draw the correct structure for each intemediate product and clearly indicate the reagent(s) required for each reaction. The following list of suggested reagents is sufficient to accomplish all necessary reactions, but you may use other reagents if you wish. One of the intermediates is shown for you.

Suggested reagents:
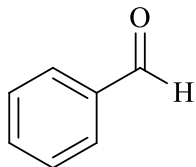
HBr   dilute HCl $K_2Cr_2O_7 / H^{\oplus}$

conc. HCl   Mg CH_3MgBr