

Topics in the November 2014 Exam Paper for CHEM1902

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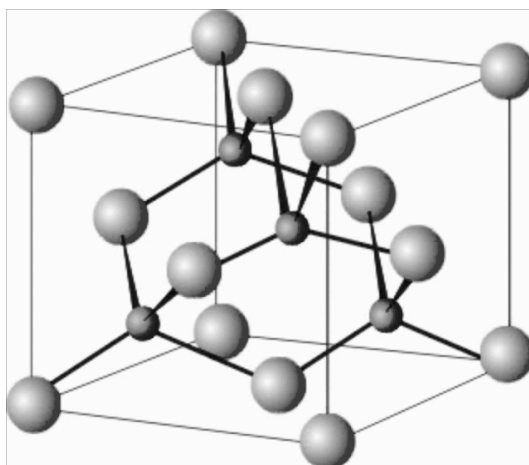
- [Aromatic Compounds](#)

2014-N-13:

- [Carboxylic Acids and Derivatives](#)

Marks
5

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

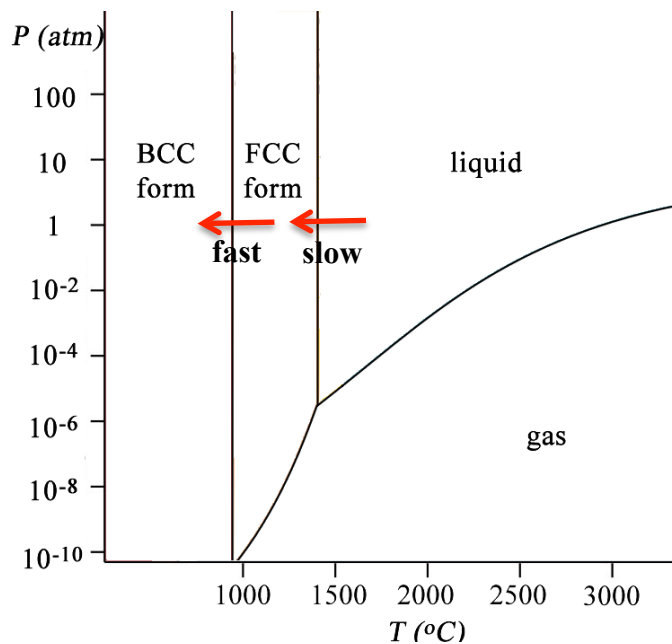
The cubic form of boron nitride is more thermally stable in air than diamond. Provide a reasonable explanation for this observation.

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.

A protective layer of B_2O_3 forms on the surface of BN in the presence of air. For diamond, gaseous CO_2 forms at high temperatures which leads to thermal degradation rather than protection.

Marks
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- 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 °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.

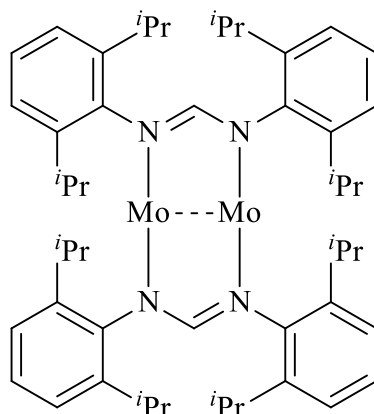
The line dividing the BCC and FCC forms is almost, but not quite vertical. Predict which way this line slopes and explain your answer.

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
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- In 2009, great excitement was generated amongst chemists worldwide with the report of a neutral Mo complex containing two bridging, anionic *N*-donor ligands. The structure of the complex is shown below. ^{*i*}Pr = isopropyl = $-\text{CH}(\text{CH}_3)_2$

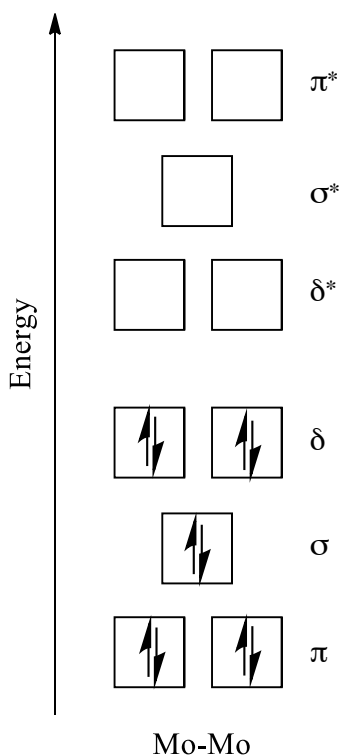


Name the complex by using standard IUPAC nomenclature. For simplicity, the name of the *N*-donor ligand (in its neutral form) can be shortened to “aminidate”.

bis(aminidato)dimolybdenum(I)

The Mo complex above possesses an extremely short Mo–Mo bond (202 pm), much shorter than the bonding distance between Mo atoms in Mo metal (273 pm)!

- Propose a reasonable explanation for the very short Mo–Mo bond length in the complex by adding *d*-electrons into the (*partial*) MO scheme shown below.
- Determine the bond order for the metal-metal bond and re-draw the structure of the complex shown above indicating the actual bonding between the two Mo atoms.

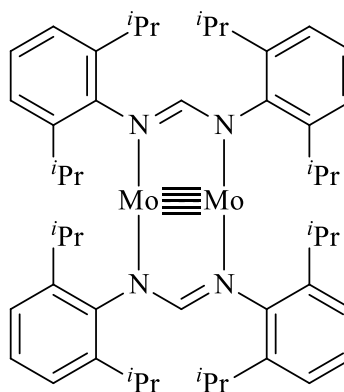


(b) Molybdenum is present as Mo(I): $4d^5$. The 2 Mo(I) contribute 10 electrons to the Mo-Mo bonding orbitals. This fills the bonding levels shown opposite:

$$\text{bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of antibonding electrons})$$

$$= \frac{1}{2} (10 - 0) = 5$$

There is a quintuple bond between the metal ions:



Marks
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Oxidation of the Mo complex by **two** electrons gives rise to a paramagnetic species in which the Mo–Mo distance increases significantly. Give a reasonable hypothesis for the bond-lengthening phenomenon.

If two electrons are removed, they will come from the bonding orbitals in 2014-N-4 and probably from the δ orbitals. As bonding electrons are removed, the Mo–Mo bond will be weakened. There will 8 bonding electrons remaining:

$$\begin{aligned}\text{bond order} &= \frac{1}{2} (\text{number of bonding electrons} - \\ &\quad \text{number of antibonding electrons}) \\ &= \frac{1}{2} (8 - 0) = 4\end{aligned}$$

As the bond is weaker, it is longer.

Determine the number of unpaired electrons in the oxidised Mo complex.

2 electrons remain in the δ orbitals. In accordance to Hund's rule, these occupy separate orbitals with spins parallel to minimise repulsion:



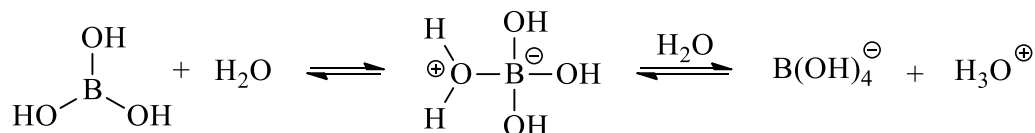
There are 2 unpaired electrons.

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks
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- Boric acid, B(OH)_3 , is a weak acid ($\text{p}K_a = 9.24$) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

The boron atom in B(OH)_3 is electron deficient: it has 6 rather than 8 electrons in its valence shell. It acts as a Lewis acid by readily accepting the lone pair from the oxygen in a water molecule to go from sp^2 to sp^3 hybridisation.



Solution A consists of a 0.60 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

As boric is a weak acid, $[\text{H}_3\text{O}^+]$ must be calculated using a reaction table (acid = B(OH)_3 and base = B(OH)_2^-)

	acid	H_2O	\rightleftharpoons	H_3O^+	base
initial	0.60	large		0	0
change	-x	negligible		+x	+x
final	$0.60 - x$	large		x	x

The equilibrium constant K_a is given by: $K_a = \frac{[\text{H}_3\text{O}^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.60 - x}$

As $\text{p}K_a = -\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.60 - x \sim 0.60$ and hence:

$$x^2 = 0.60 \times 10^{-9.24} \quad \text{or} \quad x = 1.86 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(1.86 \times 10^{-5}) = 4.73$$

$$\text{pH} = 4.73$$

At 25 °C, 1.00 L of Solution B consists of 112 g of NaB(OH)_4 dissolved in water. Calculate the pH of Solution B.

The molar mass of NaB(OH)_3 is:

$$\begin{aligned} \text{molar mass} &= [22.99 (\text{Na}) + 10.81 (\text{B}) + 4 (16.00 (\text{O}) + 1.008 (\text{H}))] \text{ g mol}^{-1} \\ &= 101.83 \text{ g mol}^{-1} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

A mass of 112 g therefore corresponds to:

$$\text{number of moles} = \text{mass} / \text{molar mass} = 112 \text{ g} / (101.83 \text{ g mol}^{-1}) = 1.10 \text{ mol}$$

A 1.00 L solution contains this amount has a concentration of 1.10 M.

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

	base	H_2O	\rightleftharpoons	acid	OH^-
initial	1.10	large		0	0
change	-y	negligible		+y	+y
final	$1.10 - y$	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(1.10 - y)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00$$

$$\text{p}K_b = 14.00 - 9.24 = 4.76$$

As $\text{p}K_b = 4.76$, $K_b = 10^{-4.76}$. K_b is very small so $1.00 - y \sim 1.00$ and hence:

$$y^2 = 1.10 \times 10^{-4.76} \text{ or } y = 0.00437 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[0.00437] = 2.36$$

Finally, $\text{pH} + \text{pOH} = 14.00$ so

$$\text{pH} = 14.00 - 2.36 = 11.64$$

$$\text{pH} = 11.64$$

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a $\text{pH} = 9.24$.

The ratio of acid to conjugate base in the final needed can be calculated using the Henderson-Hasselbalch equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$:

$$9.24 = 9.24 + \log \frac{[\text{base}]}{[\text{acid}]} \text{ so } \frac{[\text{base}]}{[\text{acid}]} = 1.00 \text{ or } [\text{base}] = [\text{acid}]$$

ANSWER CONTINUES ON THE NEXT PAGE

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.00 L so:

$$V_a + V_b = 1.00 \text{ L}$$

Using $c_1V_1 = c_2V_2$, this mixing reduces the concentration of both:

$$\begin{array}{ll} \text{acid: } (0.60 \text{ M}) \times V_a = c_{\text{acid}} \times (1.0 \text{ L}) & \text{so } V_a = 1.67 \times c_{\text{acid}} \\ \text{base: } (1.10 \text{ M}) \times V_b = c_{\text{base}} \times (1.0 \text{ L}) & \text{so } V_b = 0.909 \times c_{\text{base}} \end{array}$$

Using the concentration ratio from the Henderson-Hasselbalch equation above, the ratio of the volumes needed is therefore:

$$V_b / V_a = (0.909 / 1.67) \times c_{\text{base}} / c_{\text{acid}} = (0.909 / 1.67) \times 1.00 = 0.545$$

or

$$V_b = 0.545 \times V_a$$

From above, $V_a + V_b = 1.00 \text{ L}$ so:

$$\begin{aligned} V_a + (0.545 \times V_a) &= 1.00 \text{ L} \\ 1.545 V_a &= 1.00 \text{ L} \\ V_a &= 0.647 \text{ L} \end{aligned}$$

Hence, $V_b = (1.00 - 0.647) \text{ L} = 0.35 \text{ L}$.

Answer: 650 mL of solution A and 350 mL of solution B

- At a certain temperature the following data were collected for the decomposition of HI.

Marks
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Experiment	Initial [HI] (mol L ⁻¹)	Initial rate of reaction (mol L ⁻¹ s ⁻¹)
1	1.0×10^{-2}	4.0×10^{-6}
2	2.0×10^{-2}	1.6×10^{-5}
3	3.0×10^{-2}	3.6×10^{-5}

Determine the rate law for the reaction.

Between experiment (1) and (2), the concentration of HI is doubled. This leads to the rate increasing by a factor of 4.

Between experiment (1) and (3), the concentration of HI is trebled. This leads the to rate increasing by a factor 9.

The rate is proportional to [HI]²:

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

What is the value of the rate constant for the decomposition of HI?

Using experiment (1), [HI] = 1.0×10^{-2} mol L⁻¹ and rate = 4.0×10^{-6} mol L⁻¹ s⁻¹:

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

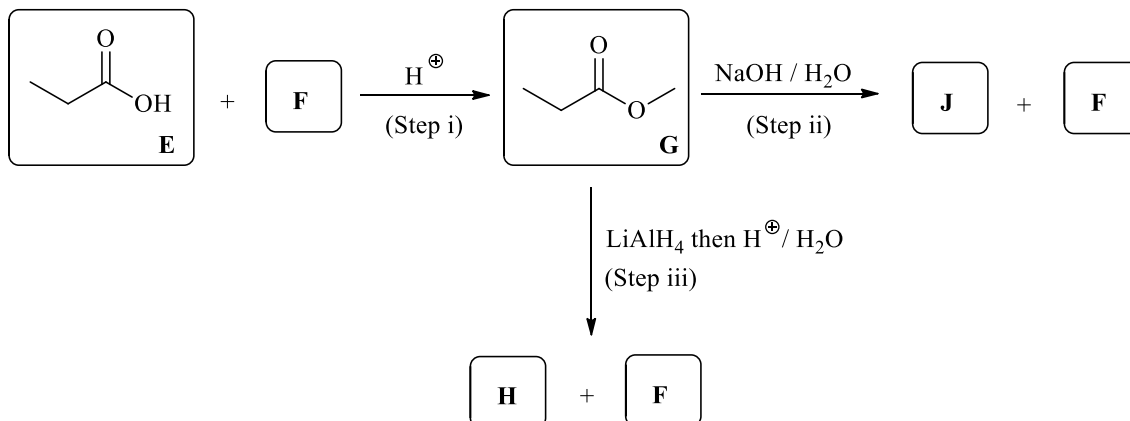
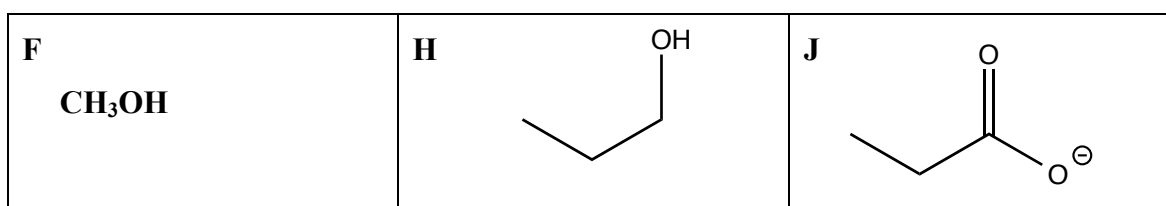
$$4.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} = (k) \times (1.0 \times 10^{-2} \text{ mol L}^{-1})^2$$

$$k = (4.0 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}) / (1.0 \times 10^{-2} \text{ mol L}^{-1})^2 = 4.0 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

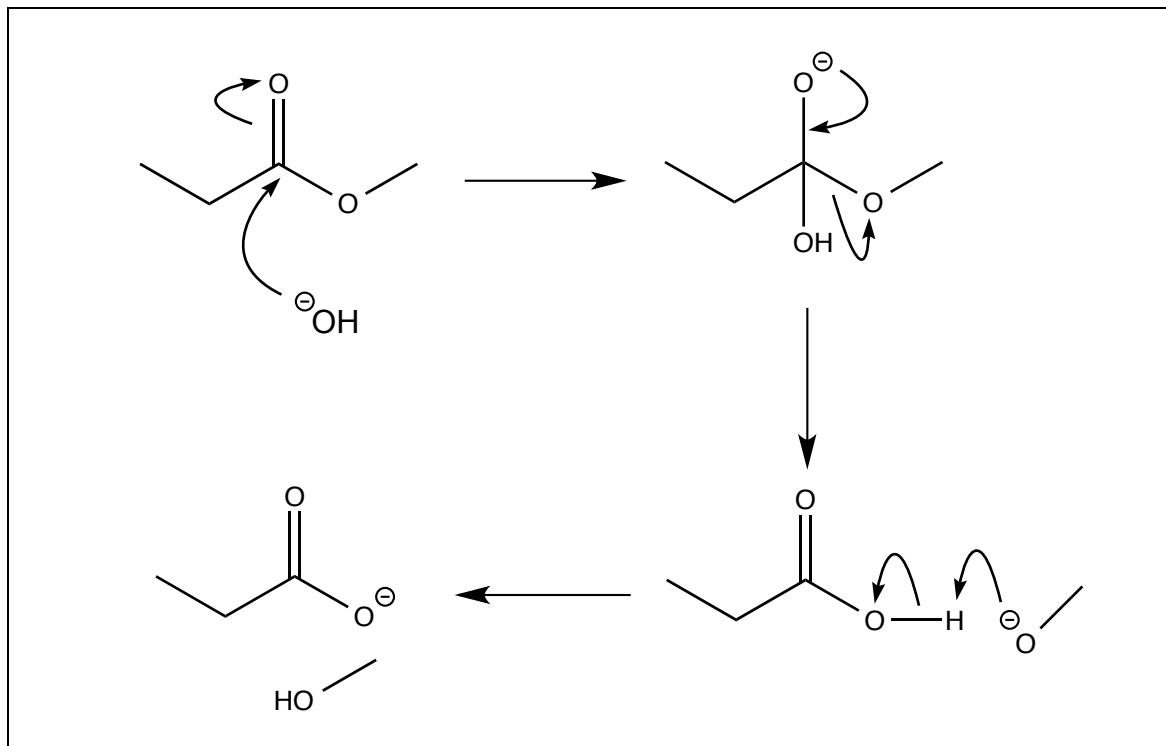
Answer: $4.0 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$

Marks
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- Consider the following reaction sequences beginning with the carboxylic acid, **E**.

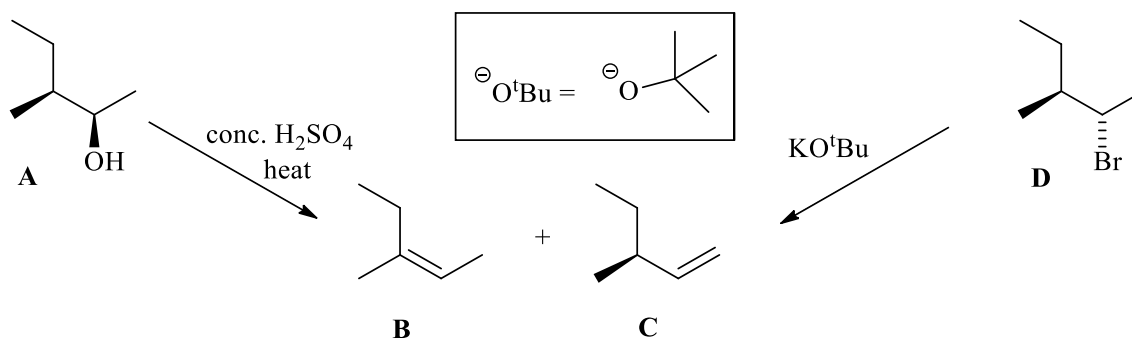
Name compounds **E** and **G**.**E: propionic acid****G: methyl propionate**Propose structures for compounds **F**, **H** and **J**.

Propose a mechanism for step (ii).

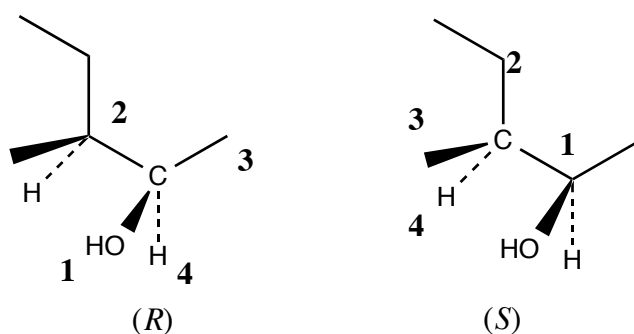


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7

- 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.



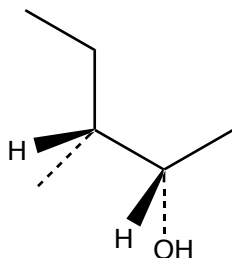
There are 2 chiral centres. On the diagram on the left, the priorities are as shown and are in an (*R*) configuration. On the diagram on the right, the priorities are in an (*S*) arrangement.

Name compound **B** fully.

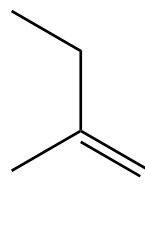
(Z)-3-methylpent-2-ene

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

enantiomer of **A**

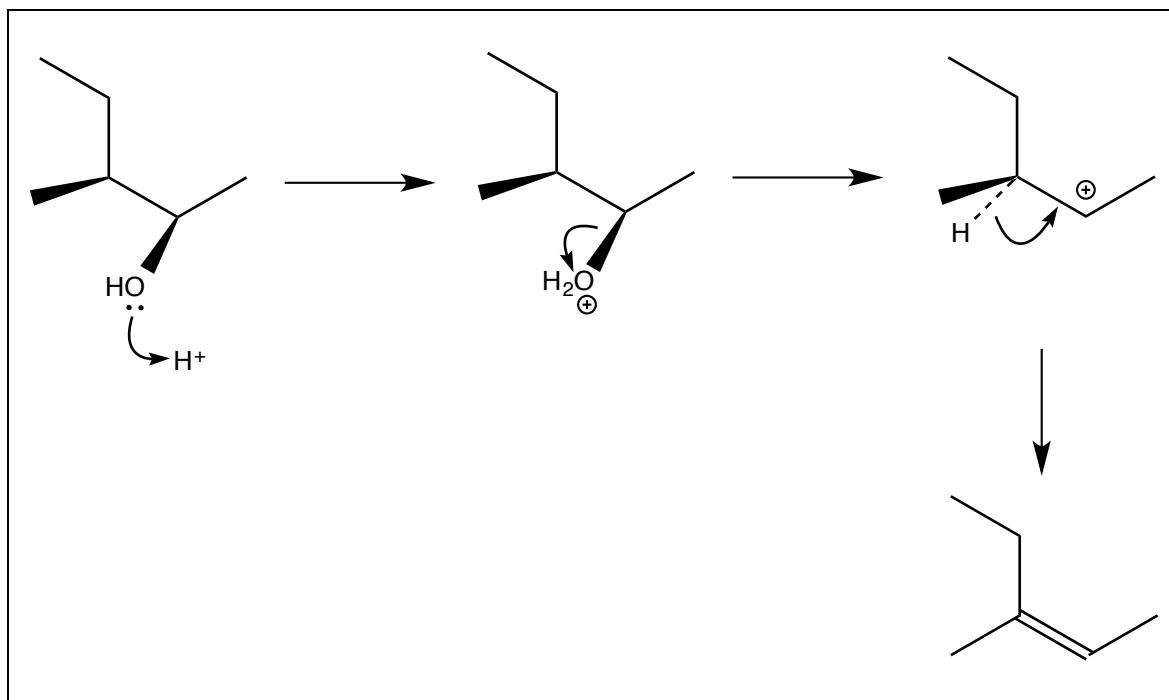


diastereoisomer of **B**



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



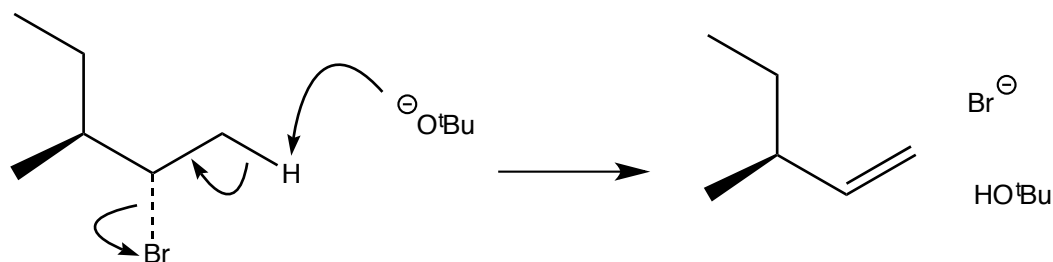
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Explain why compound **C** is the minor product of this reaction.

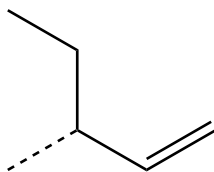
Marks
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C has the new C=C bond with fewer substituents. This is an example of Zaitsev's rule: the more substituted alkene is more thermodynamically stable.

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



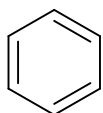
Compound **C** is the major product formed from **D** under these conditions. What would be the major product if the enantiomer of **D** were exposed to the same reaction conditions?



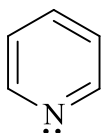
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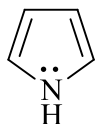
- Benzene, pyridine and pyrrole are all aromatic.



benzene



pyridine



pyrrole

cyclopentadiene
 $pK_a = 15$ cyclopentene
 $pK_a = 45$

What three criteria must be met for a compound to be aromatic?

- Cyclic and planar,**
- Each atom in the ring must have be sp^2 hybridised so that it has a p -orbital perpendicular to the ring and**
- The π system must have $4n+2$ electrons where n is any integer.**

Apply your previous answer to explain the following.

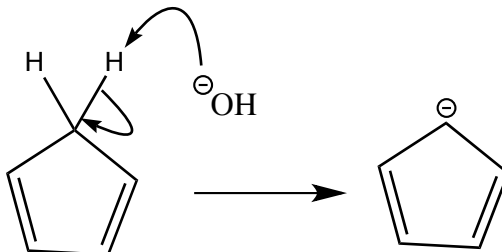
Pyridine is basic but pyrrole is not.

The N in pyridine contributes $1 e^-$ to π system which adds to the $5 e^-$ from the carbon atoms to give an aromatic electron count of 6. The lone pair on N is in an sp^2 hybrid, pointing out from the molecule and lying in the plane. It is not involved in the π system and is free to attach a proton. It is basic.

The N atom in pyrrole uses its 'lone pair' in the π system to add to the $4 e^-$ from the carbon atoms to give an aromatic electron count of 6. The 'lone pair' is in a p -orbital and is part of the π bonding. It is not available to attach a proton. It is not basic.

The pK_a of cyclopentadiene is much lower than that of cyclopentene.

Cyclopentadiene, C_5H_6 is not aromatic; there is a CH_2 group in the ring and it is not planar. Lose of a proton to give $C_5H_5^-$ however leads to a lone pair on one carbon atom. Adopting a planar geometry gives 6π electrons and an aromatic molecule

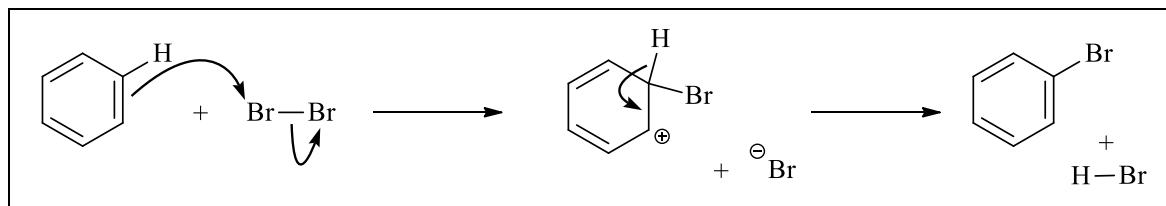


The analogous reaction for cyclopentene does not lead to an aromatic system as there are still CH_2 groups in the ring and it is not planar.

The additional aromatic stabilisation of the conjugate base of cyclopentadiene increases its acidity and lowers its pK_a .

Marks
9

- Benzene can undergo an S_EAr reaction with bromine, Br_2 , as shown below. Demonstrate your understanding of this reaction by adding curly arrows to complete the mechanism.



Explain what each part of the abbreviation S_EAr means.

S = substitution

E = electrophilic

Ar = aromatic

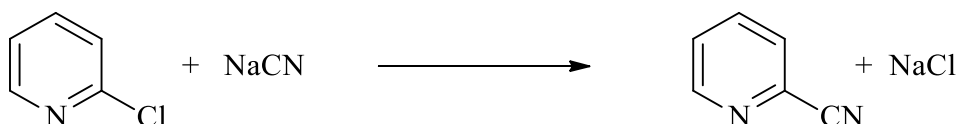
Identify one nucleophile and one electrophile in the scheme above.

nucleophile	electrophile
C=C in step (i). Br^- in step (ii)	Br_2 in step (i). Carbocation in step (ii).

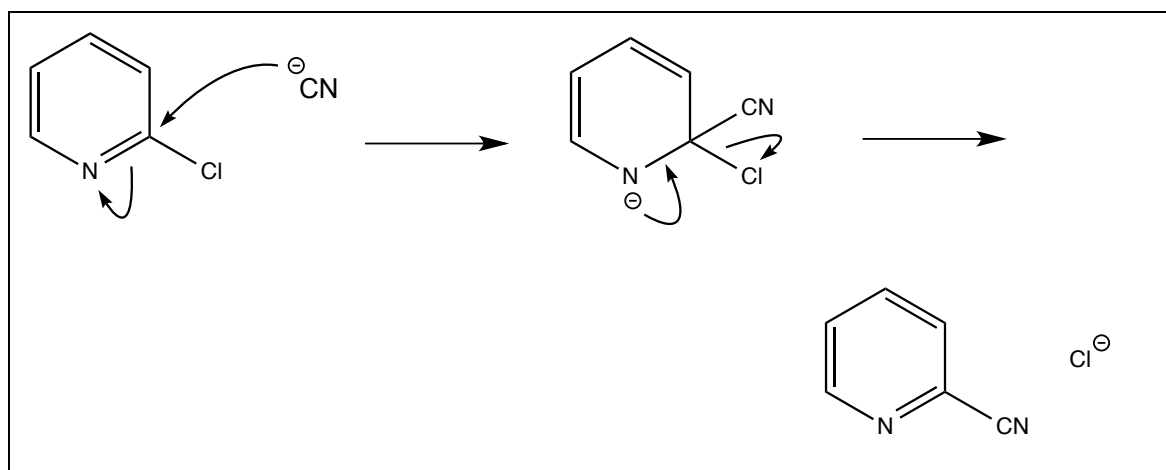
Iron(III) bromide, $FeBr_3$, is often added to the reaction shown above. Why?

It is a catalyst. Br_2 attaches weakly to it causing the non-polar Br-Br bond to become polarised with a partial positive charge on one end. This makes it more electrophilic.

2-Chloropyridine can undergo the following reaction with sodium cyanide.



This reaction also proceeds via a two-step mechanism and an ionic (*i.e.* charged) intermediate. Apply your understanding of organic reactions to propose a mechanism for this reaction.



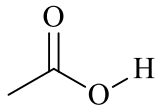
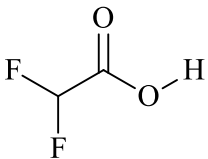
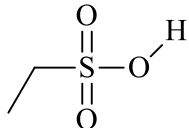
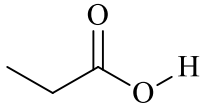
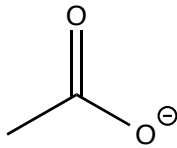
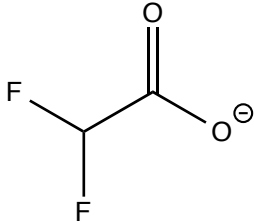
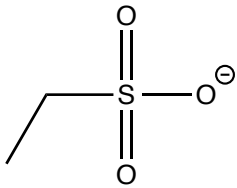
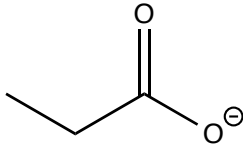
ANSWER CONTINUES ON THE NEXT PAGE

If the reaction of benzene shown above is S_EAr , how would you classify this reaction of chloropyridine?

S_NAr (nucleophilic)

Marks
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- Draw the conjugate bases for the following acids.

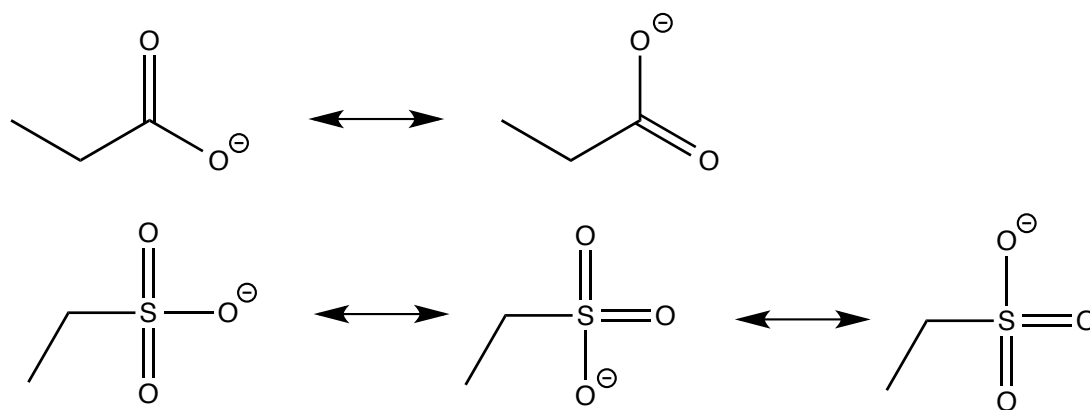
S	T	U	V
			
Conjugate base of S	Conjugate base of T	Conjugate base of U	Conjugate base of V
			

Which of **S** and **T** is the stronger acid? Give a reason for your answer.

T will be a stronger acid. In acting as an acid, the conjugate base will be formed. The conjugate base of T is more stable than that of S as the electronegative fluorine atoms will withdraw electron density from the negatively charged O atom.

Which of **U** and **V** is the stronger acid? Give a reason for your answer.

U is a stronger acid than V because the conjugate base is more stable. Both are stabilised by resonance which acts to delocalise the negative charge over the electronegative O atoms present:



For the conjugate base of U, the negative charge is delocalised over 3 O atoms. For the conjugate base of V, the negative charge is only delocalised over 2 O atoms