

Topics in the November 2013 Exam Paper for CHEM1102

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- Carboxylic Acids and Derivatives

2013-N-14:

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- Aldehydes and Ketones

- The pK_a of formic acid, HCO_2H , is 3.77. What is the pH of a 0.20 M solution of formic acid?

Marks
7

As formic acid is a weak acid, $[\text{H}_3\text{O}^+]$ must be calculated using a reaction table:

| | HCO_2H | H_2O | \rightleftharpoons | H_3O^+ | HCO_2^- |
|---------|------------------------|----------------------|----------------------|------------------------|------------------|
| initial | 0.20 | large | | 0 | 0 |
| change | $-x$ | negligible | | $+x$ | $+x$ |
| final | $0.20 - x$ | large | | x | x |

The equilibrium constant K_a is given by:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = \frac{x^2}{0.20 - x}$$

As $pK_a = -\log_{10} K_a$, $K_a = 10^{-3.77}$ and is very small, $0.20 - x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-3.77} \quad \text{or} \quad x = 5.8 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(5.8 \times 10^{-3}) = 2.23$$

pH = 2.23

Give the equation for the reaction of formic acid with solid sodium hydroxide.



Calculate the ratio of formate ion / formic acid required to give a buffer of pH 4.00.

Using the Henderson-Hasselbalch equation,

$$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$4.00 = 3.77 + \log \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]}$$

$$\text{So, } \frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 10^{0.23} = 1.70$$

Answer: 1.70

ANSWER CONTINUES ON THE NEXT PAGE

What amount (in mol) of sodium hydroxide must be added to 100.0 mL of 0.20 M HCO_2H to prepare a solution buffered at pH 4.00?

If the concentration of OH^- which is added is x M then this will react with HCO_2H to produce HCO_2^- so that:

$$\begin{aligned} [\text{HCO}_2\text{H}] &= (0.20 - x) \text{ M and} \\ [\text{HCO}_2^-] &= x \text{ M} \end{aligned}$$

From above, if pH = 4.00, then $\frac{[\text{HCO}_2^-]}{[\text{HCO}_2\text{H}]} = 1.70$. Hence:

$$\frac{x}{0.20 - x} = 1.70 \quad \text{so } x = 0.13$$

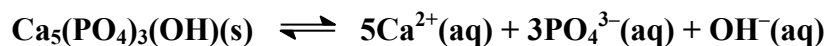
To achieve $[\text{OH}^-(\text{aq})] = 0.13 \text{ mol L}^{-1}$ in 100.0 mL, the number of moles of NaOH that must be added is:

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= 0.13 \text{ mol L}^{-1} \times 0.1000 \text{ L} = 0.013 \text{ mol} \end{aligned}$$

Answer: **0.013 mol**

- Give the equation for the dissolution of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, in water.

Marks
2



What is the formula for the solubility product constant for hydroxyapatite?

$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})]^5 [\text{PO}_4^{3-}(\text{aq})]^3 [\text{OH}^{-}(\text{aq})]$$

- Complete the following table.

6

| Formula | Geometry of complex | Ligand donor atom(s) |
|---|---------------------|----------------------|
| $[\text{Zn}(\text{OH})_4]^{2-}$ | tetrahedral | O |
| $[\text{CoCl}(\text{NH}_3)_5]\text{SO}_4$ | octahedral | Cl and N |
| $\text{K}_4[\text{Fe}(\text{CN})_6]$ | octahedral | C |
| $[\text{Ag}(\text{CN})_2]^{-}$ | linear | C |

Select any complex ion from the above table and state whether it is paramagnetic, diamagnetic or neither. Explain your reasoning.

Zn^{2+} is d^{10} system. No unpaired electrons, therefore diamagnetic.

| | | | | |
|----|----|----|----|----|
| ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |
|----|----|----|----|----|

Co^{3+} is d^6 system. 2 paired electrons and 4 unpaired, therefore paramagnetic.

| | | | | |
|----|---|---|---|---|
| ↑↓ | ↑ | ↑ | ↑ | ↑ |
|----|---|---|---|---|

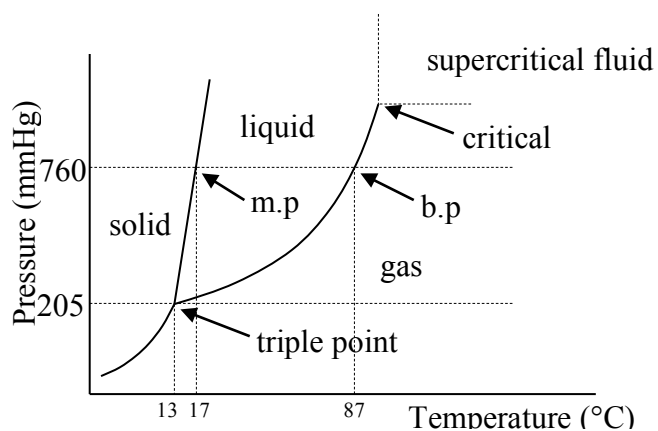
Fe^{2+} is d^6 system. 2 paired electrons and 4 unpaired, therefore paramagnetic.

| | | | | |
|----|---|---|---|---|
| ↑↓ | ↑ | ↑ | ↑ | ↑ |
|----|---|---|---|---|

Ag^{+} is d^{10} system. No unpaired electrons, therefore diamagnetic.

| | | | | |
|----|----|----|----|----|
| ↑↓ | ↑↓ | ↑↓ | ↑↓ | ↑↓ |
|----|----|----|----|----|

- A phase diagram of a pure compound has a triple point at 13 °C and 205 mmHg, a normal melting point at 17 °C, and a normal boiling point at 87 °C. Draw a phase diagram for this compound. Label all the different regions of the phase diagram.

Marks
7

Indicate whether each of the following statements regarding this compound is true or false.

The density of the solid is greater than that of the liquid.

True / False

If the pressure is reduced from 835 mmHg to 85 mmHg at a constant temperature of 11 °C, sublimation occurs.

True / False

At a constant pressure of 835 mmHg, evaporation occurs if the temperature is raised from 13 °C to 81 °C.

True / False

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

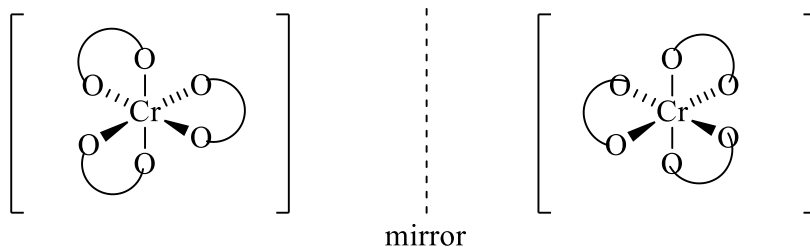
- Which of the following complexes is/are chiral? Explain your reasoning. Use diagrams where necessary.

Marks
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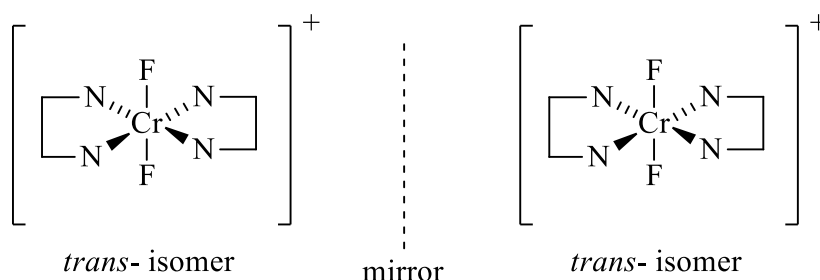
 acetylacetonate ion = $\text{CH}_3\text{COCHCOCH}_3^-$

 ethylenediamine = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

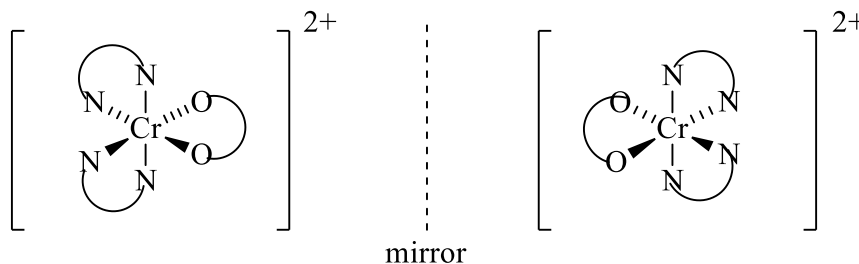
tris(acetylacetonato)chromium(III) is chiral – mirror images are non-superimposable



trans-bis(ethylenediamine)difluoridochromium(III) ion is not chiral – it is identical to its mirror image.



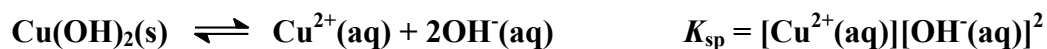
acetylacetonatobis(ethylenediamine)chromium(III) ion is chiral – mirror images are non-superimposable



- What is the solubility of $\text{Cu}(\text{OH})_2$ in mol L^{-1} ? $K_{\text{sp}}(\text{Cu}(\text{OH})_2)$ is 1.6×10^{-19} at 25°C .

Marks
7

The dissolution reaction and associated solubility product are:



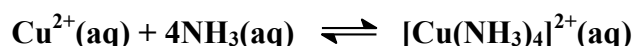
If x mol dissolve in one litre, $[\text{Cu}^{2+}(\text{aq})] = x \text{ M}$ and $[\text{OH}^{-}(\text{aq})] = 2x$. Hence:

$$K_{\text{sp}} = (x)(2x)^2 = 4x^3 = 1.6 \times 10^{-19}$$

$$x = 3.4 \times 10^{-7} \text{ M}$$

Answer: $3.4 \times 10^{-7} \text{ M}$

The overall formation constant for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 1.0×10^{13} . Write the equation for the reaction of Cu^{2+} ions with excess ammonia solution.



Calculate the value of the equilibrium constant for the following reaction.



This reaction can be considered to occur via (i) $\text{Cu}(\text{OH})_2$ dissolving followed by (ii) the $\text{Cu}^{2+}(\text{aq})$ ions that form being complexed by ammonia.

For the formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$, the equilibrium constant is:

$$K_{\text{stab}} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 1.0 \times 10^{13}$$

For the reaction of $\text{Cu}(\text{OH})_2(\text{s})$ with $\text{NH}_3(\text{aq})$, the equilibrium constant is:

$$K = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{OH}^{-}(\text{aq})]^2}{[\text{NH}_3]^4}$$

To obtain K , K_{sp} is multiplied by K_{stab} :

$$\begin{aligned} K &= K_{\text{sp}} \times K_{\text{stab}} \\ &= [\text{Cu}^{2+}(\text{aq})][\text{OH}^{-}(\text{aq})]^2 \times \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{OH}^{-}(\text{aq})]^2}{[\text{NH}_3]^4} \\ &= (1.6 \times 10^{-19}) \times (1.0 \times 10^{13}) = 1.6 \times 10^{-6} \end{aligned}$$

Answer: 1.6×10^{-6}

Would you expect $\text{Cu}(\text{OH})_2(\text{s})$ to dissolve in 1 M NH_3 solution? Briefly explain your answer.

No. Equilibrium constant K is very small so the reaction lies heavily in favour of reactants.

Marks
5

- The following data were obtained for the iodide-catalysed decomposition of hydrogen peroxide, H_2O_2 .

| Experiment | $[\text{I}^-](\text{M})$ | $[\text{H}_2\text{O}_2](\text{M})$ | Initial rate(M s^{-1}) |
|------------|--------------------------|------------------------------------|-----------------------------------|
| 1 | 0.375 | 0 | 0 |
| 2 | 0.375 | 0.235 | 0.000324 |
| 3 | 0.375 | 0.470 | 0.000657 |
| 4 | 0.375 | 0.705 | 0.001024 |
| 5 | 0.375 | 0.940 | 0.001487 |
| 6 | 0 | 0.948 | 0 |
| 7 | 0.050 | 0.948 | 0.00045 |
| 8 | 0.100 | 0.948 | 0.00095 |
| 9 | 0.150 | 0.948 | 0.00140 |
| 10 | 0.200 | 0.948 | 0.00193 |

Determine the rate law from these data.

The rate law is of the form, $\text{rate} = k[\text{I}^-]^x[\text{H}_2\text{O}_2]^y$.

Between experiments 2 and 3, $[\text{I}^-]$ is unchanged. The increase in rate is due to the increase in $[\text{H}_2\text{O}_2]$:

$$\frac{\text{rate (3)}}{\text{rate (2)}} = \frac{k(0.375)^x(0.470)^y}{k(0.375)^x(0.235)^y} = \frac{(0.470)^y}{(0.235)^y} = \frac{0.000657}{0.000324} \quad \text{so } y = 1$$

Between experiments 7 and 8, $[\text{H}_2\text{O}_2]$ is unchanged. The increase in rate is due to the increase in $[\text{I}^-]$:

$$\frac{\text{rate (8)}}{\text{rate (7)}} = \frac{k(0.100)^x(0.948)^y}{k(0.050)^x(0.948)^y} = \frac{(0.100)^x}{(0.050)^x} = \frac{0.00095}{0.00045} \quad \text{so } x = 1$$

Hence,

$$\text{rate} = k[\text{I}^-][\text{H}_2\text{O}_2]$$

Use the data from Experiment 10 to calculate the rate constant for this reaction.

In experiment 10, $[\text{I}^-] = 0.200 \text{ M}$, $[\text{H}_2\text{O}_2] = 0.948 \text{ M}$ and $\text{rate} = 0.00193 \text{ M s}^{-1}$.
Hence:

$$k = \text{rate} / [\text{I}^-][\text{H}_2\text{O}_2] = (0.00193 \text{ M s}^{-1}) / (0.200 \text{ M} \times 0.948 \text{ M}) \\ = 0.0102 \text{ M}^{-1} \text{ s}^{-1}$$

$$k = 0.0102 \text{ M}^{-1} \text{ s}^{-1}$$

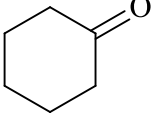
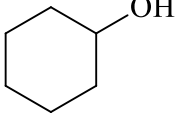

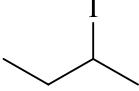
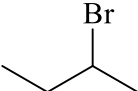

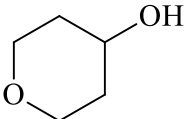
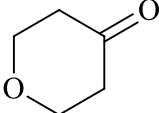
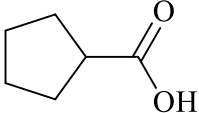
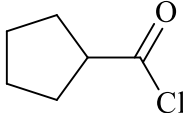
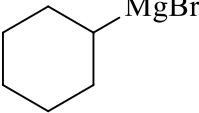
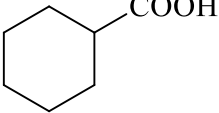
ANSWER CONTINUES ON THE NEXT PAGE

Iodide ion is used as a catalyst in this reaction. What is the role of a catalyst in a chemical reaction?

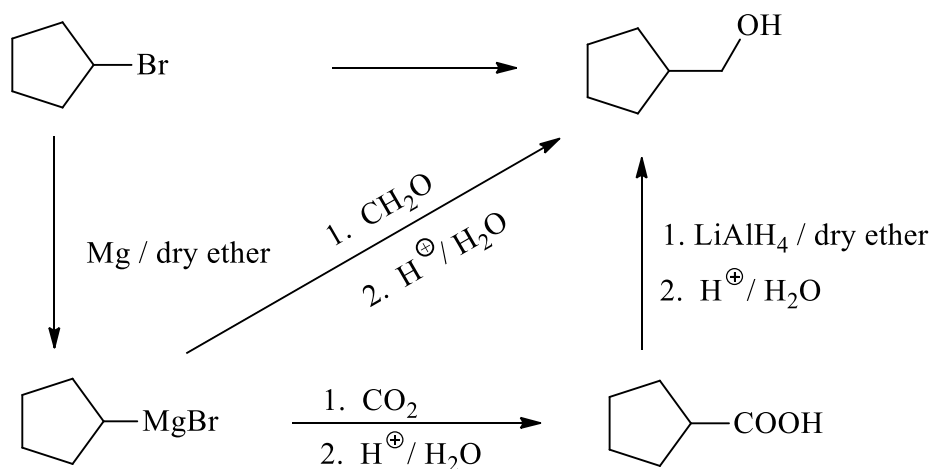
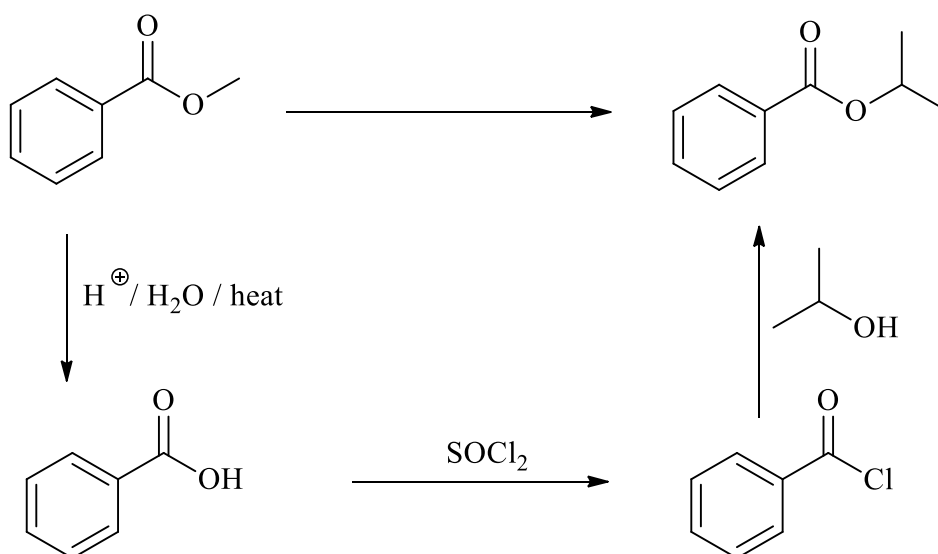
A catalyst provides a reaction pathway of lower activation energy and hence increases the rate of the reaction. It is unchanged at the end of the reaction and does not change the equilibrium position.

Marks
6

- Complete the following table.

| STARTING MATERIAL | REAGENTS/ CONDITIONS | CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S) |
|---|--|---|
|  | 1. LiAlH_4 in dry ether 2. $\text{H}^+ / \text{H}_2\text{O}$ |  |
|  | HI |  |
|  | hot conc. KOH in ethanol |  |
|  | $\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$ |  |
|  | SOCl_2 |  |
|  | 1. CO_2 2. $\text{H}^+ / \text{H}_2\text{O}$ |  |

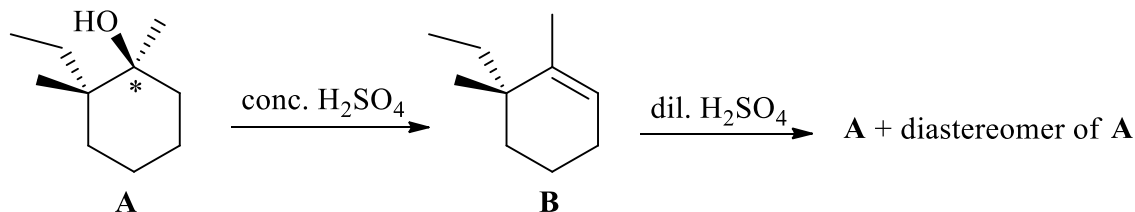
- Show clearly the reagents you would use to carry out the following chemical conversion. More than one step is required. Give the structures of any intermediate compounds formed.

Marks
7

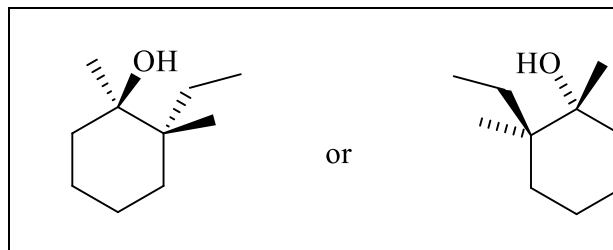
- Shown below is a reaction sequence beginning with the chiral alcohol, **A**.

Marks

7



Draw the enantiomer of **A**.



The specific optical rotation of **A** is +30. If equal amounts of **A** and its enantiomer are mixed, what is the optical rotation of the mixture?

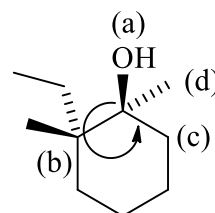
0°

Assign the stereochemistry of the atom in alcohol **A** indicated by the asterisk (*), showing how you arrived at your answer.

The order of priority is:

O > C(C,C,C) > C(C,H,H) > C(H,H,H)

With lowest priority (d) at back, the order of the groups goes anticlockwise as shown. Therefore the stereochemistry is (S).



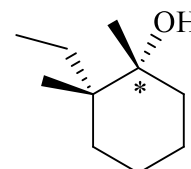
Alcohol **A** is dehydrated to give the alkene **B**. Is alkene **B** chiral? Why/why not?

The molecule is still chiral as the molecule still contains a stereogenic centre.

Alkene **B** is hydrated with dilute sulfuric acid, to give a sample that contains **A** and a diastereomer of **A**. Draw this diastereomer. In this sample, what do you expect to be the ratio of **A** and its diastereomer? Why?

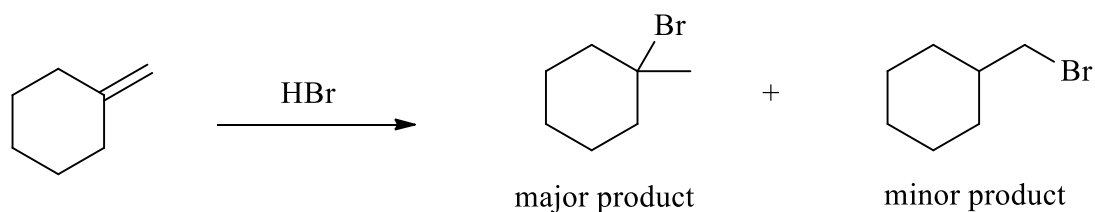
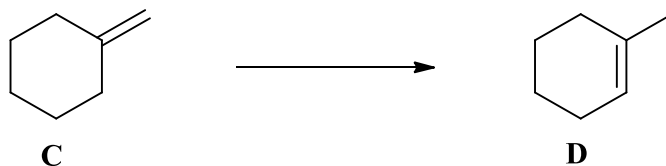
Ratio A : diastereomer is approximately 1 : 1.

The tertiary carbocation intermediate has trigonal planar geometry, so the attacking nucleophile (H₂O) is equally likely to attack from above or below the plane of the ring.

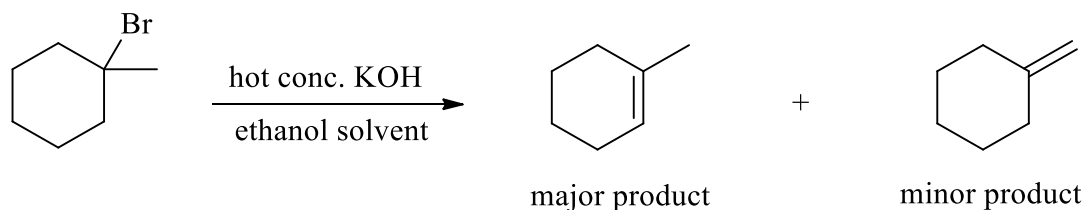


Marks
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- Devise a way to convert alkene **C** to alkene **D** using hydrogen bromide (HBr) as one of the reagents. Provide any other reagents you might need. If any of the steps you use could form two products, explain whether there is any selectivity and why.

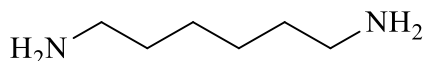
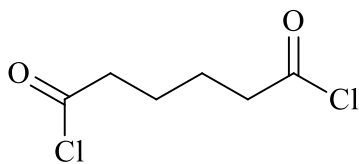


Electrophilic addition follows Markovnikov's rule. There are two possible intermediates, a primary and a tertiary carbocation. The tertiary is more stable so is formed preferentially.

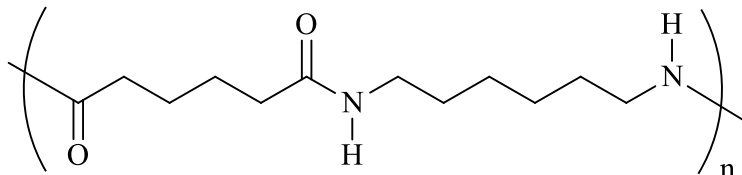


Base catalysed elimination of HBr follows Saytzev's rule – the more highly substituted product will predominate.

- The polymer Nylon 66 can be made by mixing the following two reagents.

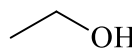
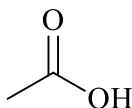
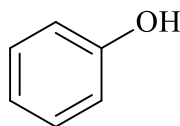


Draw the structure of Nylon 66.

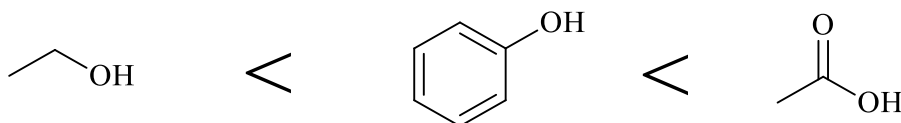


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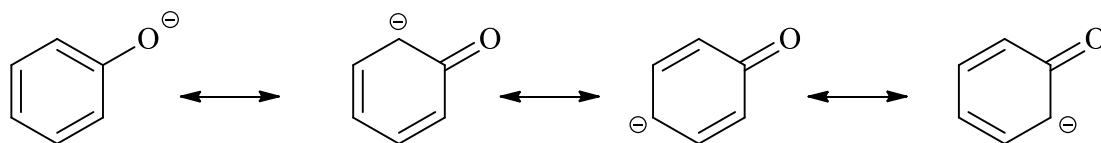
- Consider the three compounds shown below.



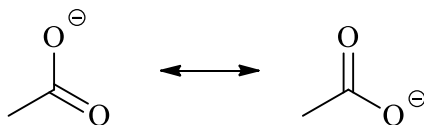
Arrange these compounds in order of increasing acidity. Explain your reasoning.



Ethanol is the weakest acid as its conjugate base is not resonance stabilised. Phenol is a stronger acid as its conjugate base is resonance stabilised – the negative charge can be delocalised into the aromatic ring as shown below.



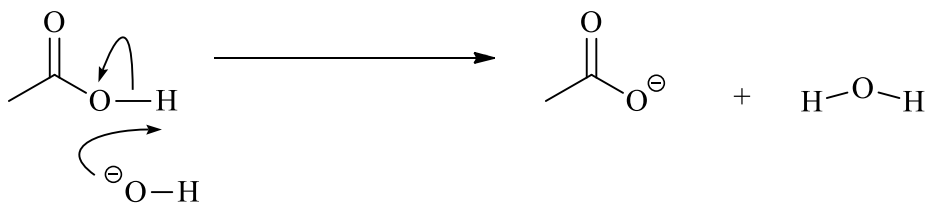
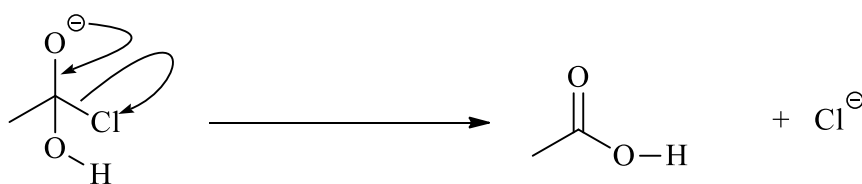
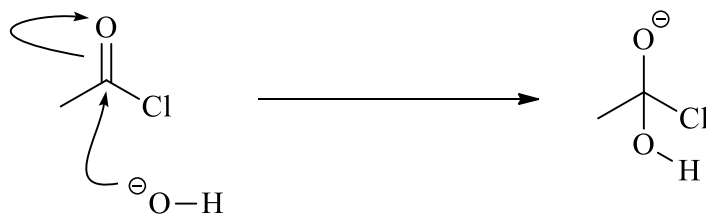
There is even greater resonance stabilisation for the acetate ion (the conjugate base of acetic acid), as the negative charge is delocalised onto the electronegative oxygen atoms (as opposed to the carbon atoms in the case of phenol).



3

Marks
3

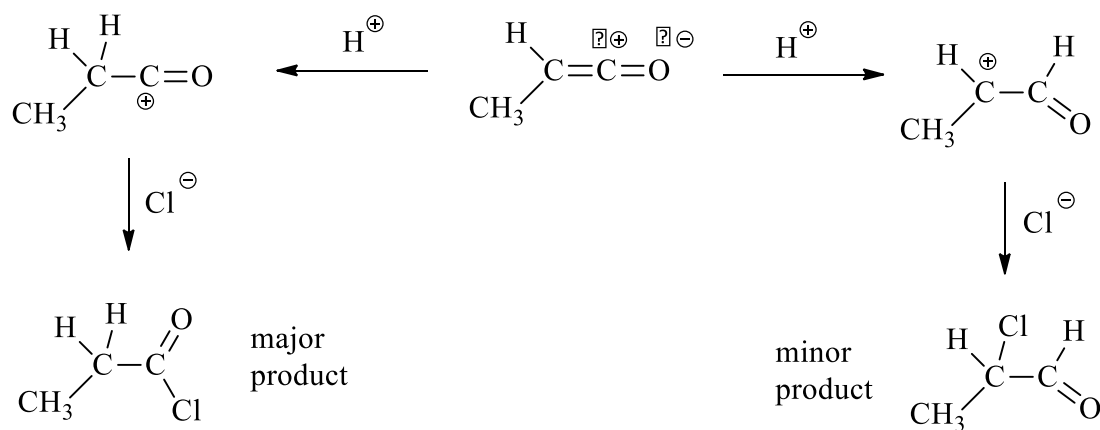
- The incomplete mechanism for the reaction of acetyl chloride with hydroxide ions is shown below. The reaction occurs in three steps. In each step complete the mechanism by adding curly arrows to indicate the bond changes taking place.



- Hydrogen chloride, HCl, reacts with the compound $\text{CH}_3\text{CH}=\text{C}=\text{O}$ in an electrophilic addition reaction. Use your knowledge of the mechanism of electrophilic addition to a $\text{C}=\text{C}$ double bond to predict the major product of this reaction. Explain your reasoning.

Marks
2

Electrophilic addition of H^+ to the $\text{C}=\text{C}$ double bond gives 2 possible carbocations. Due to polarisation, the carbon of the carbonyl $\text{C}=\text{O}$ double bond has a partial positive charge. The H^+ electrophile will not attack that carbon (like charges repel), so the carbocation on the left in the scheme below is formed preferentially. This carbocation then leads to the acid chloride as the major product.



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