## Topics in the June 2006 Exam Paper for CHEM1611

Click on the links for resources on each topic.

2006-J-2:

- Assumed Knowledge
- Atomic Structure
- Chemical Bonding

2006-J-3:

- Assumed Knowledge

2006-J-4:

- Chemical Bonding
- The Shapes of Molecules
- Intermolecular forces

2006-J-5:

- Acids and Bases

2006-J-6:

- Aromatic Hydrocarbons
- Alcohols, Phenols, Ethers and Thiols

2006-J-7:

- Introduction to Organic Chemistry
- Aldehydes and Ketones
- Spectroscopy
- Stereochemistry

2006-J-8:

- Alkenes
- Organic Halogen Compounds
- Alcohols, Phenols, Ethers and Thiols
- Amines
- Aromatic Hydrocarbons
- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2006-J-9:

- Aldehydes and Ketones
- Carboxylic Acids and Derivatives

2006-J-10:

- Carbohydrates

2006-J-11:

- Introduction to Organic Chemistry

2006-J-12:

- Amino Acids, Peptides and Proteins

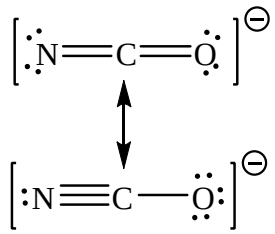
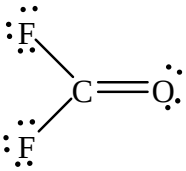
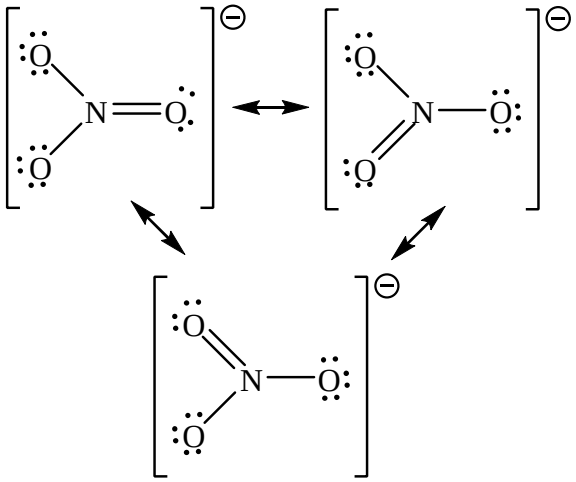
- Give the full electron configuration for the ground state K atom. **Marks 2**

**$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$**

What are the three quantum numbers that describe the orbital that contains the electron furthest from the nucleus in the K atom?

| | | |
|---|---|---|
| $n$ = **4** | $l$ = **0** | $m_l$ = **0** |

- Draw the Lewis structures, showing all valence electrons for the following species. Indicate which of the species have contributing resonance structures. **4**

| $NCO^-$ | $COF_2$ | $NO_3^-$ |
|---|---|---|
|  |  |  |
| Resonance: **<u>YES</u>** / NO | Resonance: YES / **<u>NO</u>** | Resonance: **<u>YES</u>** / NO |

- Human haemoglobin has a molar weight of $6.45 \times 10^4$ g mol$^{-1}$ and contains 3.46 g of iron per kg. Calculate the number of iron atoms in each molecule of haemoglobin. **3**

**A mole of haemoglobin has a mass of $6.45 \times 10^4$ g = 64.5 kg. As each kilogram contains 3.45 g of iron, a mole contains (64.5 × 3.45) = 223 g of iron.**

**The atomic mass of iron is 55.85 so this mass of iron corresponds to:**

$$\textbf{number of moles of iron} = \frac{\textbf{mass}}{\textbf{atomic mass}} = \frac{\textbf{223}}{\textbf{55.85}} = \textbf{3.98}$$

Answer:**4 iron atoms per molecule**

- If 50 mL of a 0.10 M solution of $AgNO_3$ is mixed with 50 mL of a 0.040 M solution of $BaCl_2$, what mass of AgCl(s) will precipitate from the reaction?

**Marks 3**

**The precipitation reaction, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$, is a 1:1 reaction of $Ag^+(aq)$ and $Cl^-(aq)$ ions.**

$$\text{Number of moles of } Ag^+ = \text{concentration} \times \text{volume} = 0.10 \times \frac{50}{1000} = 0.0050 \text{ mol}$$

**As each mole of $BaCl_2(s)$ gives two moles of $Cl^-(aq)$:**

$$\text{Number of moles of } Cl^- = 2 \times 0.040 \times \frac{50}{1000} = 0.0040 \text{ mol}$$

**$Ag^+(aq)$ is present in excess so $Cl^-(aq)$ is the limiting reagent. Hence, 0.0040 mol of AgCl(s) will be formed.**

**The molar mass of AgCl(s) = (107.87 (Ag)) + (35.45 (Cl)) = 143.32.**

**The mass of AgCl(s) formed is:**

**mass = number of moles × molar mass = 0.0040 × 143.32 = 0.57 g**

Answer: **0.57 g**

What is the concentration of $NO_3^-$ ions in the final solution from the reaction above?

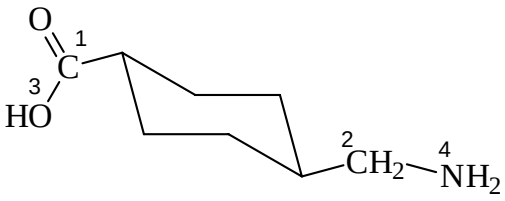
**The number of moles of $NO_3^-(aq)$ is 0.0050 mol. After mixing, the final solution has a volume of (50 + 50) = 100 mL. Hence, the concentration is:**

$$[NO_3^-] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.0050}{100/1000} = 0.050 \text{ M}$$

Answer: **0.050 M**

Marks

- Tranexamic acid, *trans*-(4-aminomethyl)cyclohexanecarboxylic acid, is used for the treatment of severe haemorrhage in patients with haemophilia.




**4**

Provide the requested information for each of the indicated atoms in tranexamic acid.

| Atom | Geometric arrangement of the electron pairs around the atom | Hybridisation of the atom | Geometry/shape of σ-bonding electron pairs around the atom |
|---|---|---|---|
| C-1 | **trigonal planar** | **$sp^2$** | **trigonal planar** |
| C-2 | **tetrahedral** | **$sp^3$** | **tetrahedral** |
| O-3 | **tetrahedral** | **$sp^3$** | **bent** |
| N-4 | **tetrahedral** | **$sp^3$** | **trigonal pyramidal** |

- Consider the boiling points of the compounds 1-propanol, 1-propanethiol and 1-propaneselenol shown in the table below?

**3**

| Compound | $CH_3CH_2CH_2OH$ | $CH_3CH_2CH_2SH$ | $CH_3CH_2CH_2SeH$ |
|---|---|---|---|
| Boiling point (° C) | 97.2 | 67.8 | 147.0 |

With reference to intermolecular forces, explain briefly why the boiling points increase in the order $CH_3CH_2CH_2SH < CH_3CH_2CH_2OH < CH_3CH_2CH_2SeH$.

**Polarisability of atoms increases as the size of the atoms increase. The greater the polarisability, the stronger the dispersion forces. On this basis, the expected boiling point order would be $C_3H_7OH < C_3H_7SH < C_3H_7SeH$.**

**$C_3H_7OH$ also has hydrogen bonding between the OH groups. H-bonding is a stronger intermolecular force than dispersion forces and this increases the boiling point of $C_3H_7OH$ to be above that of $C_3H_7SH$. The effect is not enough to push it above the boiling point of $C_3H_7SeH$.**

**Marks 5**

- Consider the following equation.

$$HBrO(aq) + NH_3(aq) \rightleftharpoons BrO^-(aq) + NH_4^+(aq)$$

Name all of the species in this equation.

| | |
|---|---|
| HBrO | **hypobromous acid** |
| $BrO^-$ | **hypobromite ion** |
| $NH_3$ | **ammonia** |
| $NH_4^+$ | **ammonium ion** |

Complete the following table by giving the correct p$K_a$ or p$K_b$ value where it can be calculated. Mark with a cross (✕) those cells for which insufficient data have been given to calculate a value.

| Species | HBrO | $NH_3$ | $BrO^-$ | $NH_4^+$ |
|---|---|---|---|---|
| p$K_a$ of acid | 8.64 | ✕ | ✕ | **9.24** |
| p$K_b$ of base | ✕ | 4.76 | **5.36** | ✕ |

Determine on which side (left or right hand side) the equilibrium for the reaction above will lie. Provide a brief rationale for your answer.

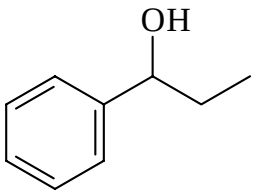
**The reaction is the sum of the acid-base equilibra for HBrO and $NH_3$:**

| | |
|---|---|
| **$HBrO(aq) \rightarrow H^+(aq) + BrO^-(aq)$** | **$K_a(HBrO) = 10^{-8.64}$** |
| **$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$** | **$K(NH_3) = \frac{1}{K_a(NH_4^+)} = 10^{+9.24}$** |
| **$HBrO(aq) + NH_3(aq) \rightarrow BrO^-(aq)$** | **$K = K_a(HBrO) \times K(NH_3)$** |

**Hence, $K = (10^{-8.64}) \times (10^{+9.24}) = 10^{+0.64} = 4.4$. As $K > 1$, the reaction favours products.**

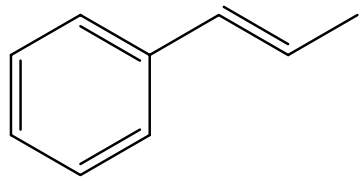
**Marks 6**

- 1-Phenyl-1-propanol (**J**) is treated with concentrated sulfuric acid to give a mixture of two alkenes (**K**) and (**L**). Alkenes (**K**) and (**L**) are diastereomers. Give the constitutional formulas for (**K**) and (**L**).

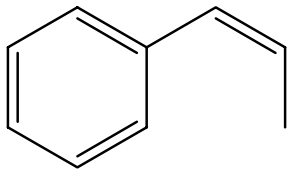



(**J**)

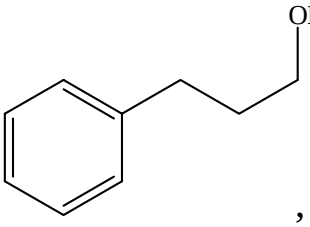
(**K**)



(**L**)



Give the structure of a constitutional isomer of (**J**).

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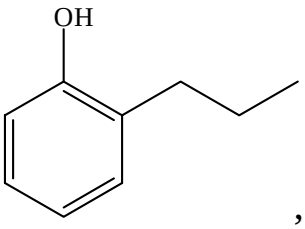


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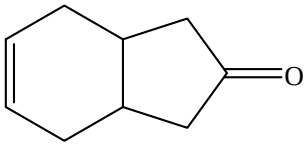
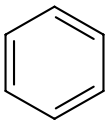
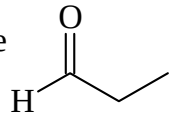
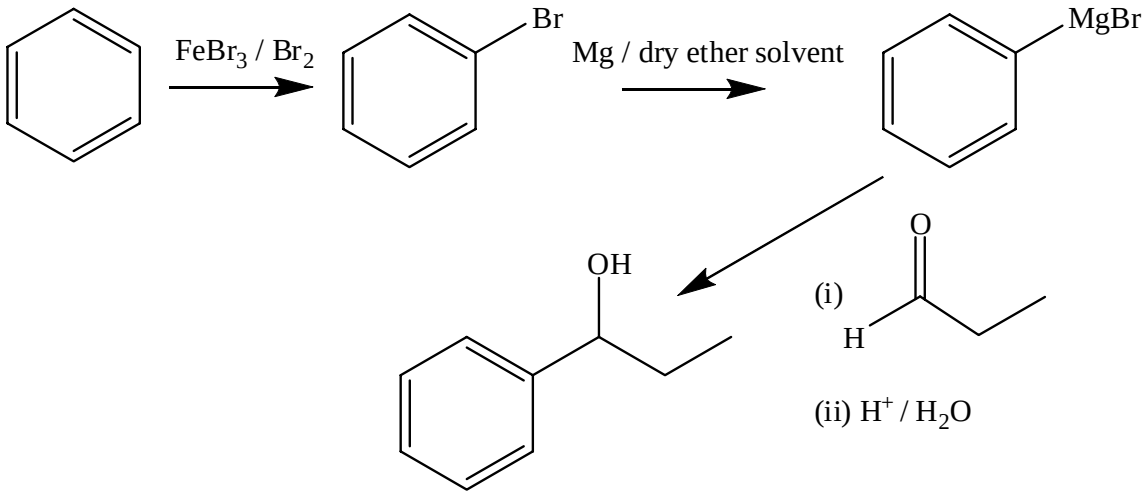



**and many others**

Outline a reaction sequence that converts benzene into 1-phenyl-1-propanol (**J**) and that also uses propionaldehyde as a reactant somewhere in the sequence. Any solvents and inorganic reagents may be used. More than one step is required. Show clearly the reagents you would use and draw constitutional formulas for any intermediate compounds.

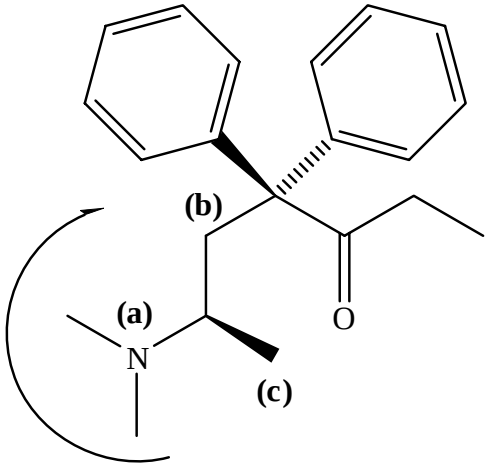
benzene 

propionaldehyde (propanal) 

**Marks 6**

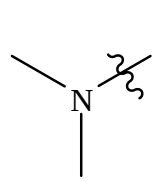
- A stick representation for the active enantiomer of methadone, an analgesic used as a maintenance drug in the treatment of heroin addiction, is shown below.

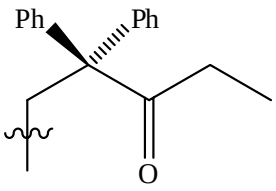


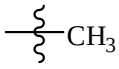

Give the molecular formula of methadone. **$C_{21}H_{27}NO$**

Methadone contains a stereogenic centre. List the substituents attached to this stereogenic centre in descending order of priority according to the sequence rules.

Highest priority Lowest priority





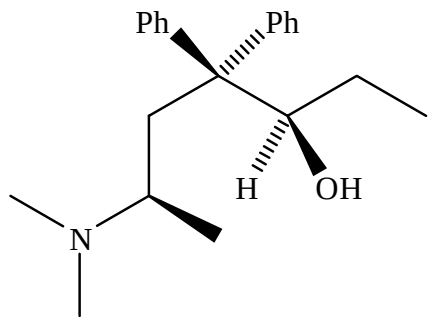
What is the stereochemistry at this stereocentre? Write (*R*) or (*S*). **(*R*)**

List the functional groups present in methadone.

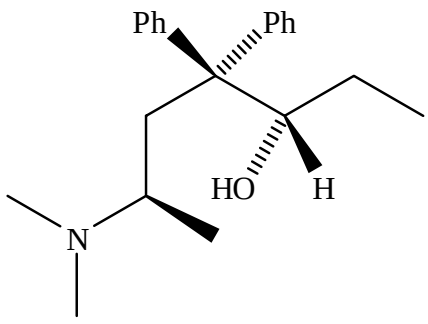
**tertiary amine, ketone, arene (aromatic ring)**

Treatment of methadone with $NaBH_4$ gives compounds (**X**) and (**Y**). Draw the structures of (**X**) and (**Y**).

(**X**)




(**Y**)

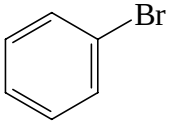
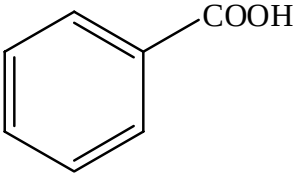
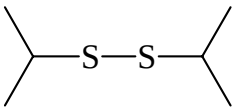
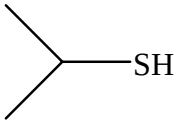
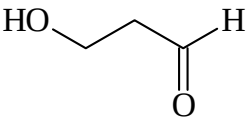
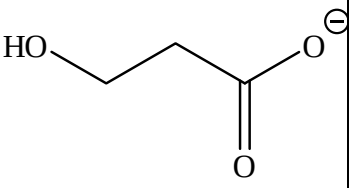
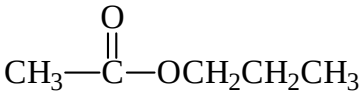
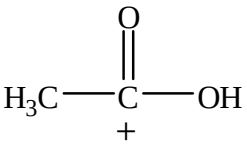
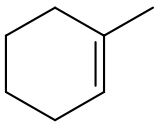
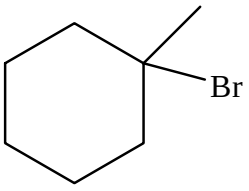
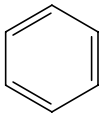
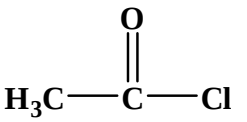
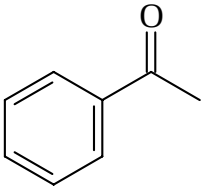
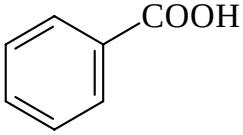
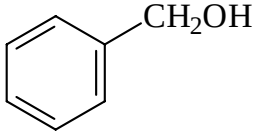



What is the stereochemical relationship between compounds (**X**) and (**Y**)?

**They are diastereomers**

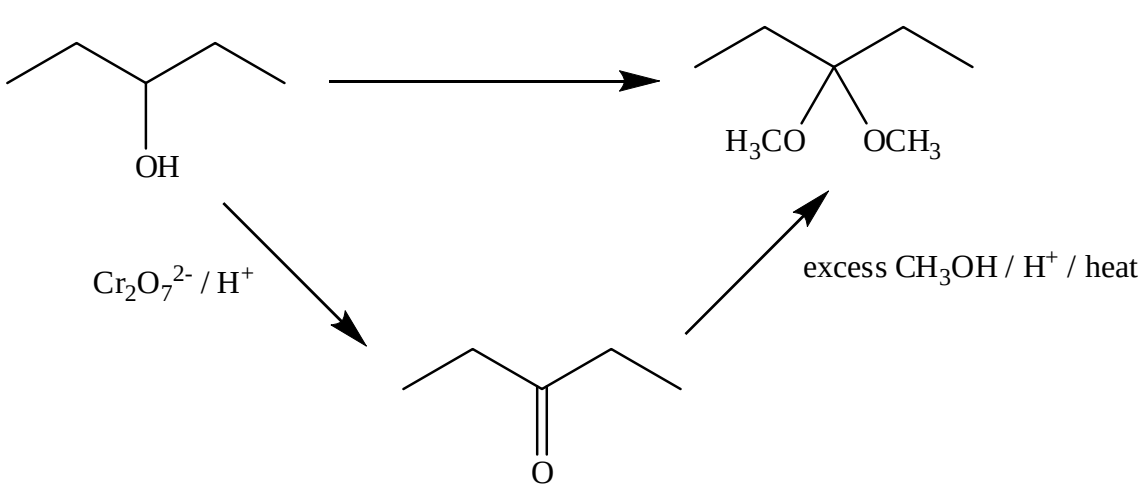
**Marks 9**

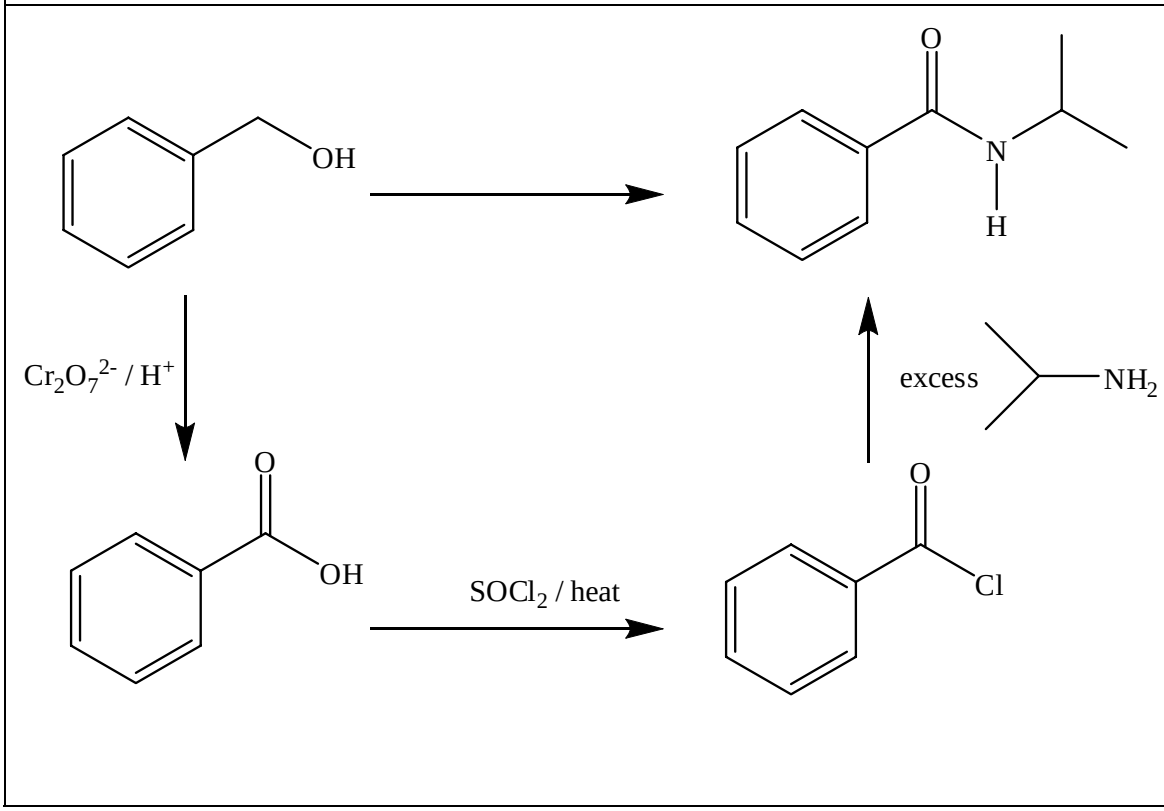
- Complete the following table.

| STARTING MATERIAL | REAGENTS/ CONDITIONS | CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S) |
|---|---|---|
| $CH_3CH_2CH_2Br$ | **$N(CH_3)_3$** | $Br^{\ominus}$ $^{\oplus}N(CH_3)_3$ with $CH_2CH_2CH_3$ |
|  | 1. Mg / dry ether<br>2. $CO_2$<br>3. $H^{\oplus}$ / $H_2O$ |  |
|  | $Zn / H^{\oplus}$ | 2  |
|  | $[Ag(NH_3)_2]^{\oplus}$ / $OH^{\ominus}$ |  |
|  | $H^{\oplus}$ / $H_2O$ / heat |  <br>+<br>$CH_3CH_2CH_2OH$ |
|  | $HBr / CCl_4$ (solvent) |  <br>(Markovnikov) |
|  |  **/ $AlCl_3$** |  |
|  | **(i) $LiAlH_4$, dry ether**<br>**(ii) $H^+$ / $H_2O$**<br>**($NaBH_4$ cannot be used in this reaction)** |  |

**Marks 8**

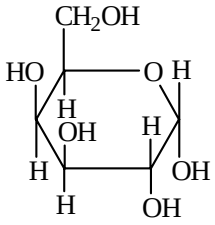
- Show clearly the reagents you would use to carry out the following chemical conversions. Draw constitutional formulas for any intermediate compounds. Note: More than one step is required in both cases.



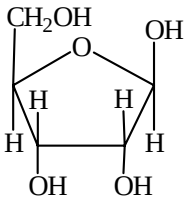



**Marks 7**

- Consider the following two monosaccharides **A** and **B**.



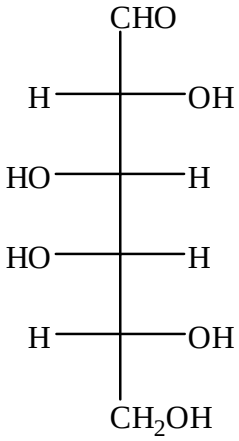

**A**: α-D-galactopyranose



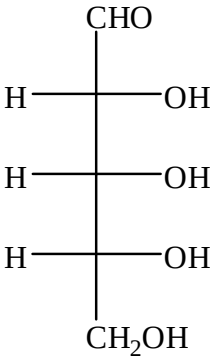

**B**: β-D-ribofuranose

Give the Fischer projections of the open chain form of **A** and **B**.

Fischer projection of D-galactose

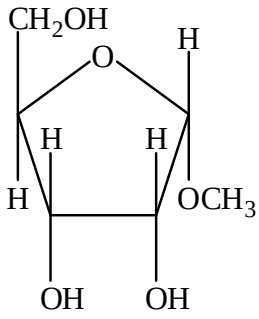



Fischer projection of D-ribose

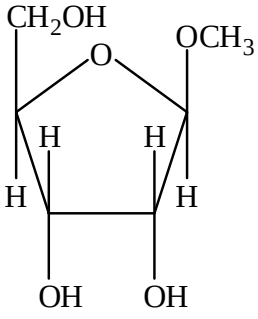



Give the products obtained when D-ribose is treated with the following reagents.

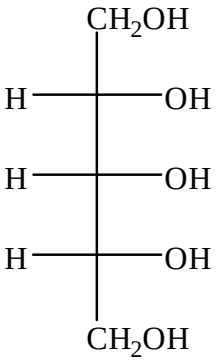
Acidified methanol



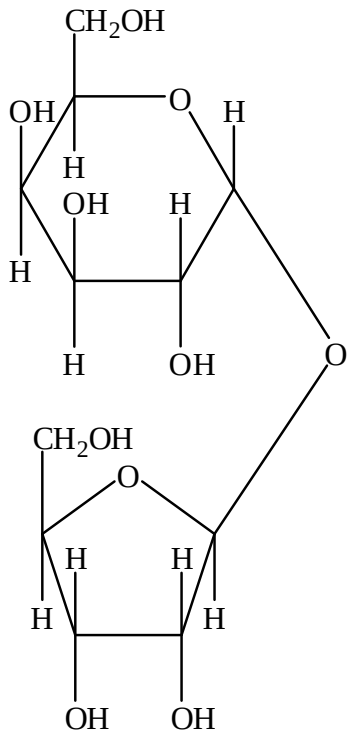

and




$NaBH_4$ in methanol solvent

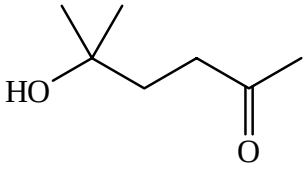
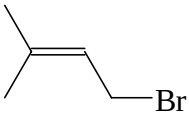


Draw the Haworth structure of a non-reducing disaccharide, which yields D-galactose and D-ribose on acid hydrolysis.



- Name the following compounds.

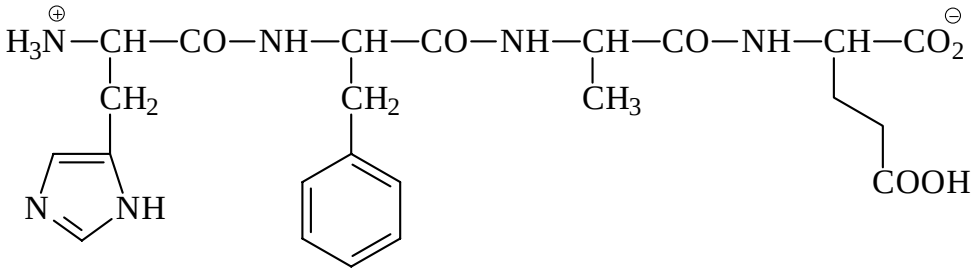
**Marks 2**

| | |
|---|---|
|   | **5-hydroxy-5-methyl-2-hexanone or**<br>**5-hydroxy-5-methylhexan-2-one** |
|   | **1-bromo-3-methyl-2-butene or**<br>**1-bromo-3-methylbut-2-ene** |

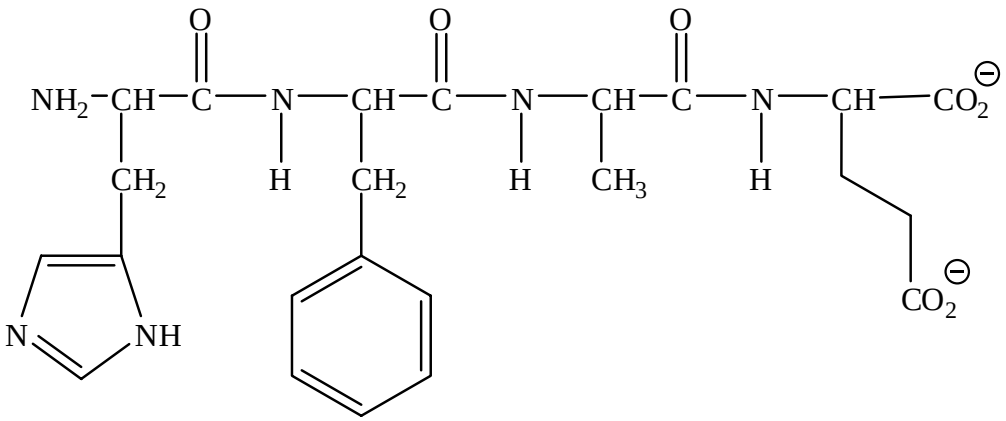
**Marks 10**

- The structure of the naturally occurring tetrapeptide His-Phe-Ala-Glu, **A**, is shown below as the zwitterion.

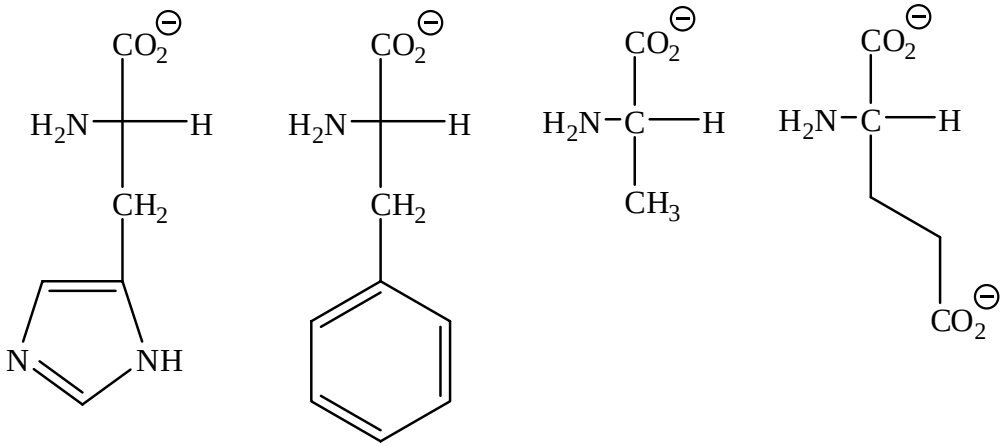
**A**



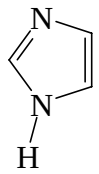
Give the product(s) obtained when **A** is treated with cold 1 M NaOH solution.

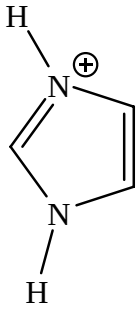


Give the Fischer projections of the four L-amino acids in their correct ionic states obtained from the vigorous basic hydrolysis (6 M KOH) of **A**.



The heterocycle present in the sidechain of histidine is imidazole, whose structure is shown on the right. Give the structure of the product formed when imidazole is treated with HCl. State, giving reasons, whether the product is aromatic.





**The product is aromatic as all ring atoms are $sp^2$ hybridised and there are 6 π electrons (4 in π bonds and 2 from the neutral N atom).**

**This agrees with the Hückel rule, which requires (4n+2) electrons in the π system for aromaticity.**

What is the major species present when histidine is dissolved in water at pH 1. The p$K_a$ values of histidine are 1.82 (-COOH), 9.17 (-$NH_3^{\oplus}$) and 6.04 (sidechain).