Topics in the June 2007 Exam Paper for CHEM1611

Click on the links for resources on each topic.

2007-J-2:

- Assumed Knowledge
- Chemical Bonding

2007-J-3:

- The Shapes of Molecules
- Intermolecular forces
- Acids and Bases
- Assumed Knowledge

2007-J-4:

- Assumed Knowledge

2007-J-5:

- Introduction to Organic Chemistry

2007-J-6:

- Aromatic Hydrocarbons
- Organic Halogen Compounds
- Aldehydes and Ketones

2007-J-7:

- Heterocyclic Compounds

2007-J-8:

- Alkenes

2007-J-9:

- Introduction to Organic Chemistry
- Stereochemistry

2007-J-10:

- Aromatic Hydrocarbons

2007-J-11:

- Aromatic Hydrocarbons
- Aldehydes and Ketones

2007-J-12:

- Carbohydrates

2007-J-13:

- Amino Acids, Peptides and Proteins

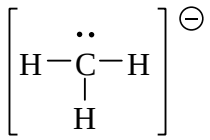
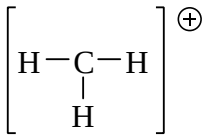
Marks 5

- Complete the following table. Give, as required, the formula, the systematic name, the oxidation number of the underlined atom and, where indicated, the number of *d* electrons for the element in this oxidation state.

Formula	Systematic name	Oxidation number	Number of *d* electrons
$\underline{C}O_2$	**carbon dioxide**	**+IV or +4**	**0**
$Na_2\underline{Cr}O_4$	**sodium chromate**	**+VI or +6**	**0**
$\underline{Fe}Cl_3 \cdot 3H_2O$	**iron(III) chloride-3-water (the non-IUPAC form "iron(III) chloride trihydrate" is also acceptable)**	**+III or +3**	**5**
K_2SO_4	potassium sulfate		

3

- Draw the Lewis structures, showing all valence electrons for the following species.

CH_3^-	CH_3^+
	

Indicate which of these species you expect will be more stable and explain why.

CH_3^- is more stable as it has a full octet of electrons

2

- Desferal is a siderophore-based drug that is used in humans to treat iron-overload. One molecule of Desferal (molecular formula: $C_{25}H_{48}O_8N_6$) can bind one Fe^{3+} ion. A patient with an iron-overload disease had an excess of 5.34×10^{-4} M Fe^{3+} in her bloodstream. Assuming the patient had a total blood volume of 4.84 L, what mass of Desferal would be required to complex all of the excess Fe^{3+}?

As one mole of Deferal will complex one mole of Fe^{3+}, the number of moles of Desferal required is:

number of moles = concentration × volume = $(5.34\times10^{-4}) \times 4.84 = 2.58\times10^{-3}$ M

The molar mass of $C_{25}H_{48}O_8N_6$ is:

(25 × 12.01 (C)) + (48 × 1.008 (H)) + (8 × 16.00 (O)) + (6 × 14.01 (N)) = 560.694

Hence, the mass required is:

mass = number of moles × molar mass = $(2.58 \times 10^{-3}) \times (560.694) = 1.45$ g

Answer: **1.45 g**

Marks

- Glycine, NH_2CH_2COOH, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4. **5**

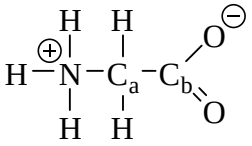
As pH = 7.4 is higher than the pK_a of the acid group, -COOH, it will exist primarily in its deprotonated, conjugate base form, $-COO^-$.

As pH = 7.4 is lower than the pK_a of the amino group, $-NH_2$, it will exist primarility in its protonated form, $-NH_3^+$.

Glycine will exist in the uncharged, zwitterionic form: $H_3\overset{\oplus}{N}-CH_2-COO^{\ominus}$

Describe the hybridisation of the two carbon atoms and the nitrogen atom in glycine and the geometry of the atoms surrounding these three atoms.

The structure is:



N has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.

C_a has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.

C_b has 3 bonds and no lone pairs: sp^2 with a trigonal planar arrangement.

Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

Glycine with a positively and a negatively charged end. There is therefore ionic bonding between the molecules leading to strong intermolecular forces.

- Many gases are available for use in compressed gas cylinders, in which they are stored at high pressures. Calculate the mass of oxygen gas that can be stored at 20 °C and 170 atm pressure in a cylinder with a volume of 60.0 L. **2**

Using the ideal gas law, PV = nRT, the number of moles that can be stored is:

$$\mathbf{n = \frac{PV}{RT} = \frac{(170)\times(60.0)}{(0.08206)\times(20+273)} = 424\,mol}$$

As the molar mass of O_2 is (2 × 16.00) = 32.00, this corresponds to a mass of:

mass = number of moles × molar mass = 424 × 32.00 = 13600 g = 13.6 kg

Answer: **13.6 kg**

- If 20.0 mL of a 0.100 M solution of sodium phosphate is mixed with 25.0 mL of a 0.200 M solution of zinc chloride, what mass of zinc phosphate will precipitate from the reaction?

Marks 6

25.0 mL of a 0.200 M solution of $ZnCl_2$ contains:

$$\mathbf{n(Zn^{2+}(aq)) = concentration \times volume = 0.200 \times \frac{25}{1000} = 0.00500\ mol}$$

20.0 mL of a 0.100 solution of Na_3PO_4 contains:

$$\mathbf{n(PO_4^{3-}) = 0.100 \times \frac{20}{1000} = 0.00200\ mol}$$

The ionic equation for the precipitation reaction is:

$$\mathbf{3Zn^{2+}(aq) + 2PO_4^{3-}(aq) \rightarrow Zn_3(PO_4)_2(s)}$$

As $n(Zn^{2+}(aq) > \frac{3}{2} \times n(PO_4^{3-}(aq))$, PO_4^{3-} which is the limiting reagent. The maximum amount of product depends on $n(PO_4^{3-})$. The amount of zinc phosphate formed is:

$$\mathbf{n(Zn_3(PO_4)_2(s) = ½ \times n(PO_4^{3-}(aq)) = ½ \times 0.00200 = 0.00100\ mol}$$

The formula mass of zinc phosphate is:

$$\mathbf{(3 \times 65.39\ (Zn)) + 2 \times (30.97\ (P) + 4 \times 16.00\ (O)) = 386.11}$$

The mass of this amount of zinc phosphate is therefore:

$$\mathbf{mass = number\ of\ moles \times formula\ mass = 0.00100 \times 386.11 = 0.386\ g}$$

Answer: **0.386 g**

ANSWER CONTINUES ON THE NEXT PAGE

What is the final concentration of zinc ions in solution after the above reaction?

The number of moles of $Zn^{2+}(aq)$ removed by precipitation = 3 × 0.00100 = 0.00300 mol. The amount remaining is therefore:

$n(Zn^{2+}(aq)) = 0.00500 - 0.00300 = 0.00200$ mol

The total volume of the solution after mixing is (20.0 + 25.0) = 45.0 mL so the concentration is:

$$[Zn^{2+}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.00200}{(45/1000)} = 0.0444\,M$$

Answer: **0.0444 M**

What is the final concentration of sodium ions in solution after the above reaction?

20.0 mL of a 0.100 solution of Na_3PO_4 contains:

$$n(Na^+) = 3 \times 0.100 \times \frac{20}{1000} = 0.00600 \text{ mol}$$

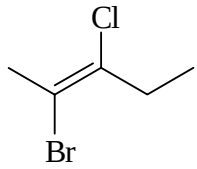
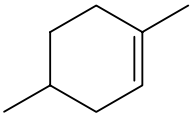
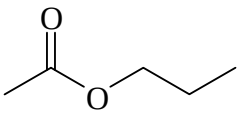
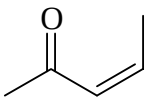
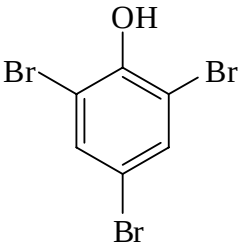
After mixing, this amount is contained in a volume of 45.0 mL so the concentration is:

$$[Na^+(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.00600}{(45/1000)} = 0.133\,M$$

Answer: **0.133 M**

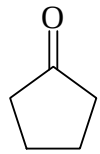
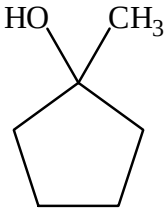
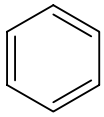
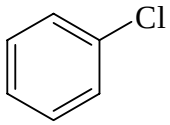
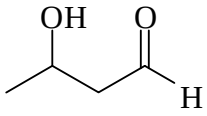
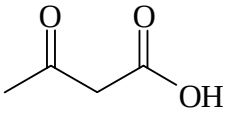
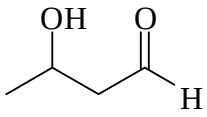
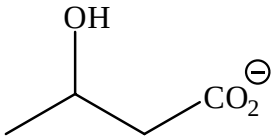
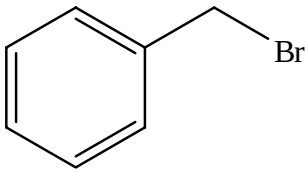
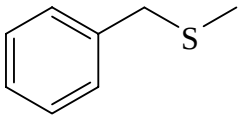
- Name the following compounds. Make sure you include stereochemical descriptors where appropriate.

Marks 5

	**(*E*)-2-bromo-3-chloro-2-pentene** **(*E* as the highest ranking substituents (Cl and Br) are on opposite sides of C=C bond)**
	**1,4-dimethylcyclohexene**
	**propyl acetate**
	**(*Z*)-3-penten-2-one** **(*Z* as highest ranking substituents (CH_3 and $COCH_3$) are on the same side of C=C bond)**
	**2,4,6-tribromophenol**

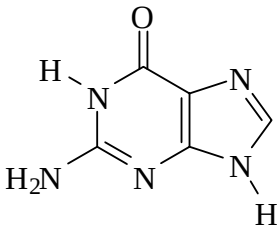
Marks 5

- Complete the following table.

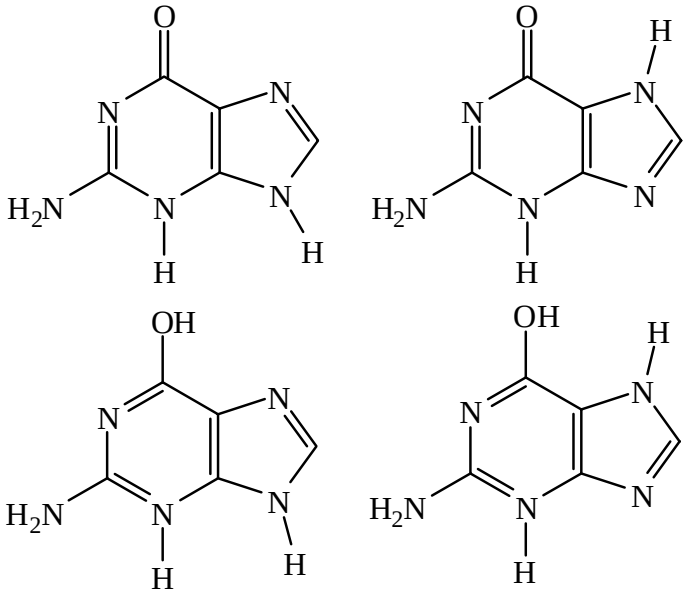
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	1. CH_3MgBr 2. $H^{\oplus}$ / H_2O	
	**$FeCl_3$ / Cl_2** **or** **$AlCl_3$ / Cl_2**	
	**$Cr_2O_7^{2-}$ / H^+**	
	$[Ag(NH_3)_2]^{\oplus}$ / $OH^{\ominus}$	
	$CH_3S^{\ominus}$ $Na^{\oplus}$	

- The nucleic base guanine is drawn below as a keto tautomer. Draw two other tautomers of guanine.

Marks 2

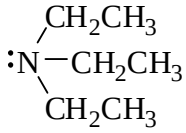


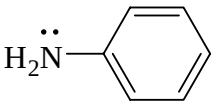
Tautomers include:



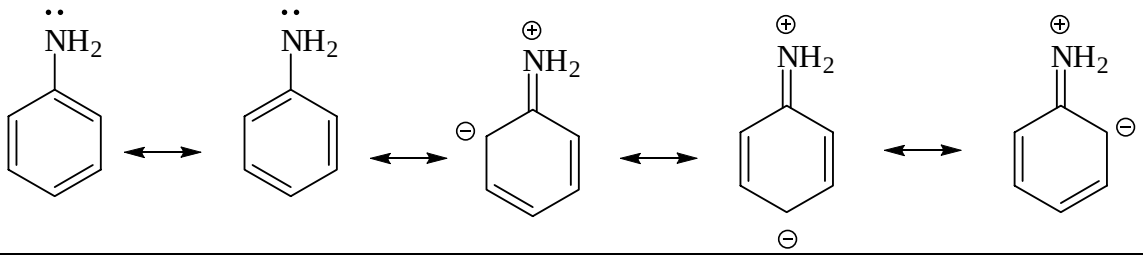
- The pK_b's of two nitrogen-containing compounds are given below. Explain the difference in basicity of these two compounds.

3

A  pK_b = 2.99

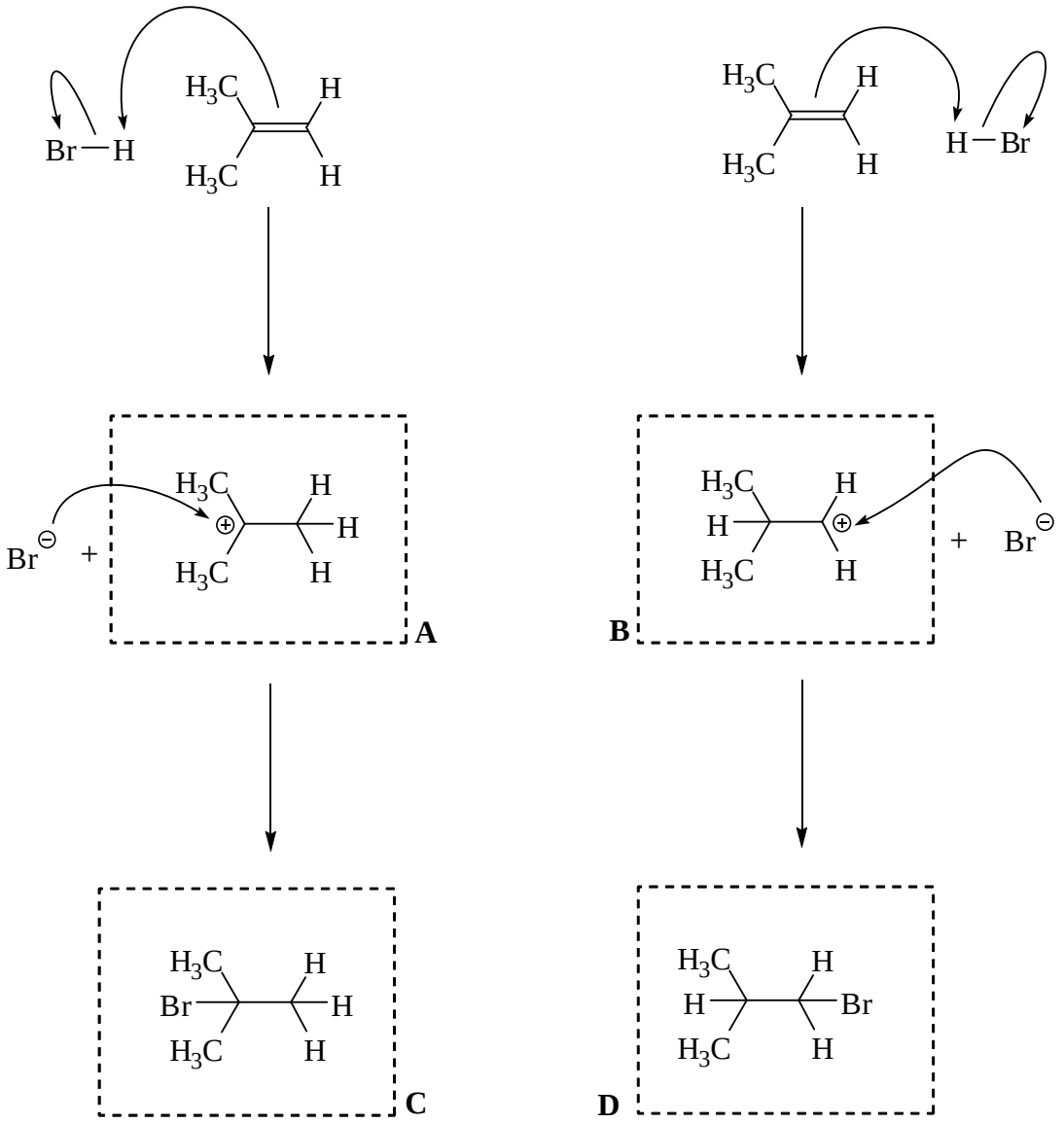
B  pK_b = 9.37

The pK_b of B is higher meaning that it is *less* basic. This is due to delocalization of the nitrogen lone pair onto the aromatic ring. This stabilization of the lone pair decreases its availability to donate to a proton.
The delocalization may be represented by resonance contributions of the form:



Marks 6

- When HBr adds to 2-methylpropene there are two possible products. Using the template below, draw the mechanism of this reaction to show the formation of both products, **C** and **D**. Use curly arrows to show the movement of electrons and draw the structures of the intermediates **A** and **B**.



Which product will be the major one? Explain why it will predominate.

C will be the major product as the carbocation intermediate along the path to its formation, A, is more stable than that, B, along the path to formation of D.

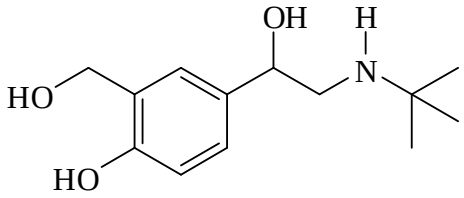
The tertiary carbocation A is more stable than the primary carbocation B.

This results in the Markovnikov addition product C as the major product.

What is the name given to this type of reaction?	**Electrophilic addition**

Marks 6

- Salbutamol is available under the trade name Ventolin® as a racemic mixture of compounds. A stick representation of the compound is shown below.



salbutamol

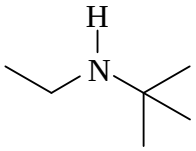
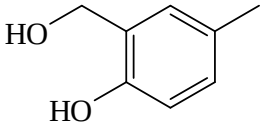
Give the molecular formula of salbutamol. **$C_{13}H_{21}O_3N$**

List the functional groups present in salbutamol.

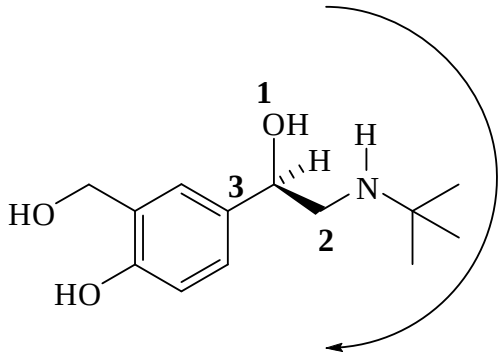
alcohol (primary and secondary), phenol, amine (secondary)

A competing manufacturer distributes a product, which contains only the (*R*)-enantiomer of salbutamol, under the trade name Xopenex®. On the structure above, mark the stereogenic centre with an asterisk (*).

List the substituents attached to this stereogenic centre in descending order of priority according to the sequence rules by drawing them in the boxes below.

Highest priority			Lowest priority
-OH			-H

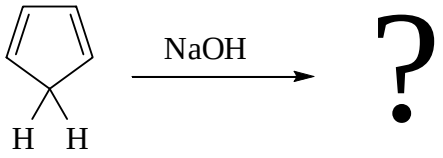
Draw the (*R*)-enantiomer of salbutamol.



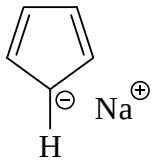
clockwise: 1-2-3

Marks 2

- Cyclopentadiene reacts with sodium hydroxide. Predict the structure of the product and explain its relative stability.

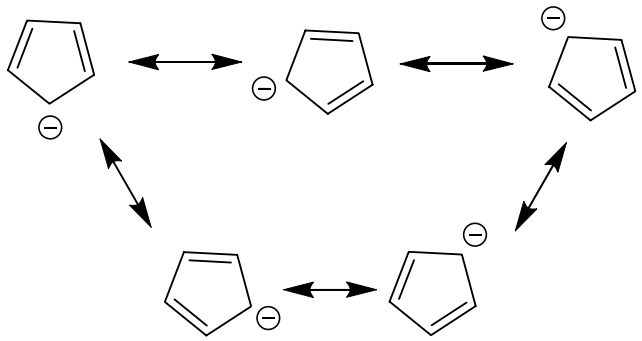


The product is the cyclopentadienyl anion.
This is an aromatic ring as it:



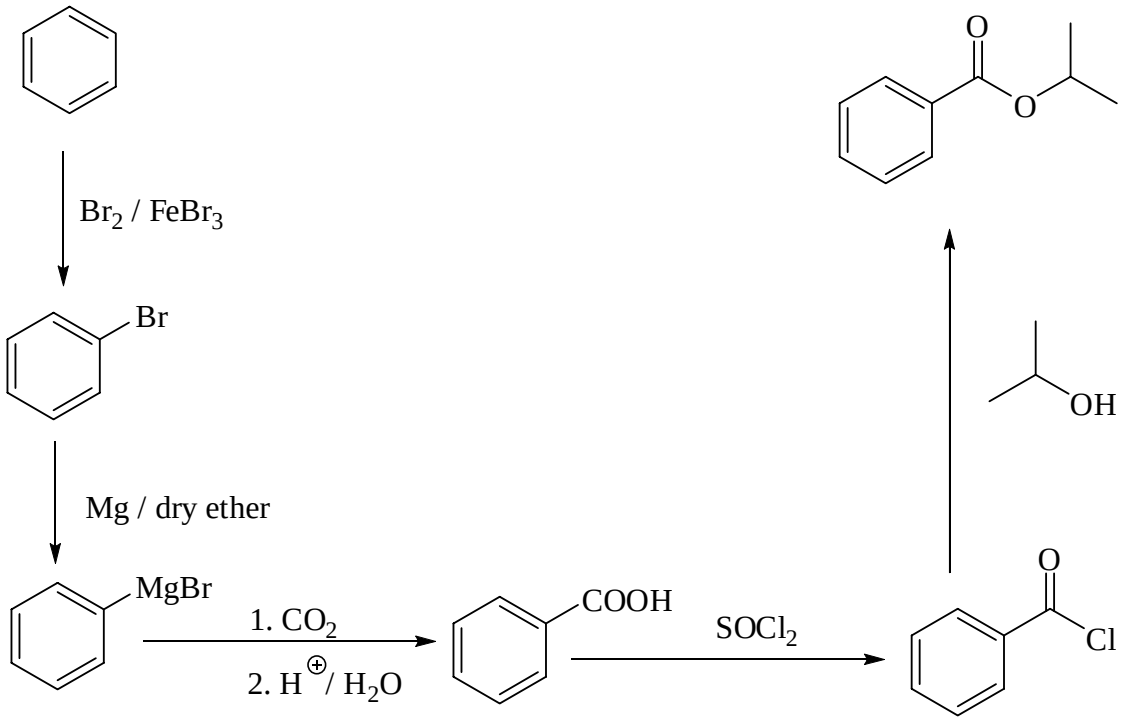
(i) flat
(ii) has 6π electrons (2 C=C bonds and a lone pair on the C^- atom) so satisfies Hückel's 4n+2 rule with n = 1
(iii) all C atoms are sp^2 hybridized.
(iv)

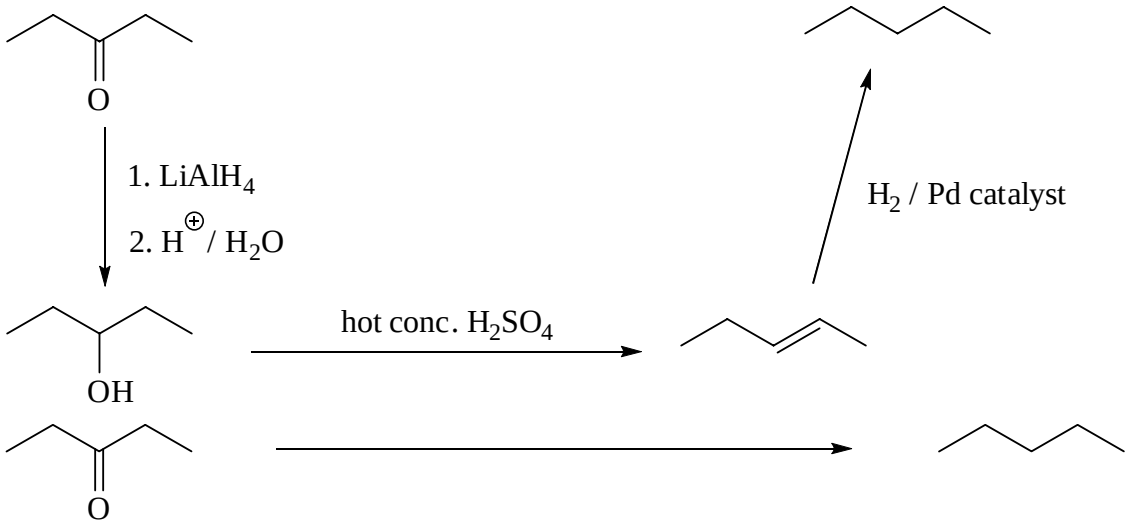
The negative charge is delocalized around the ring as shown in the resonance forms below:



Marks 8

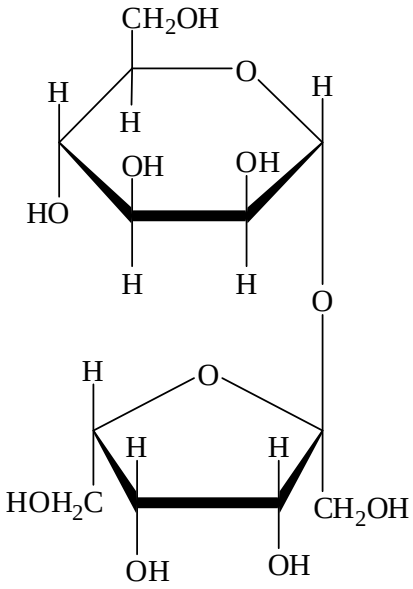
- Show clearly the reagents you would use to carry out the following chemical conversions. Draw constitutional formulas for any intermediate compounds. Note: More than one step is required in both cases.



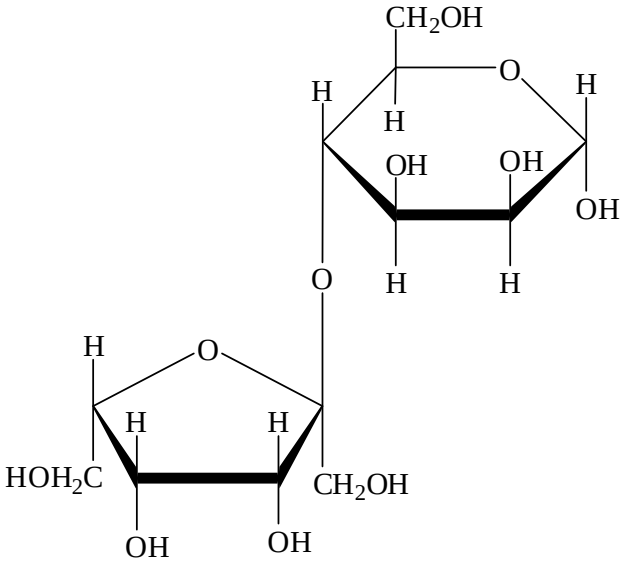


Marks 6

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



A

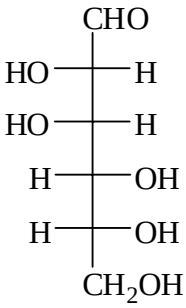
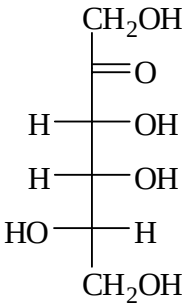


B

Classify each disaccharide as "reducing" or "not reducing".

A: **not reducing (no hemiacetal)**	**B**: **reducing (hemiacetal present)**

Both these disaccharides hydrolyse to give tagatose and mannose. Mannose is an aldohexose. Draw the Fischer projections of the open chain forms of mannose and tagatose.

Fischer projection of mannose	Fischer projection of tagatose
	

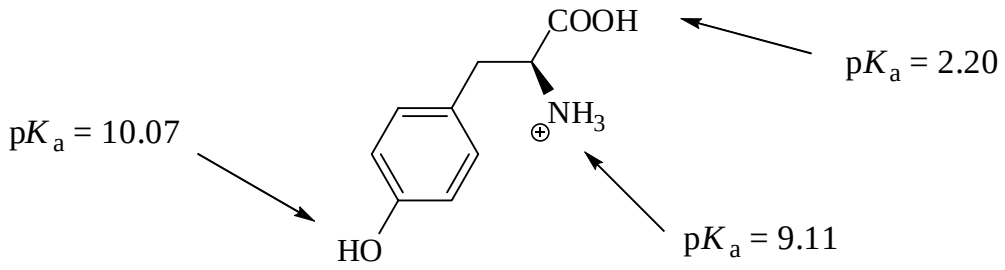
Mannose is classified as an aldohexose. What classification is given to tagatose?

ketohexose

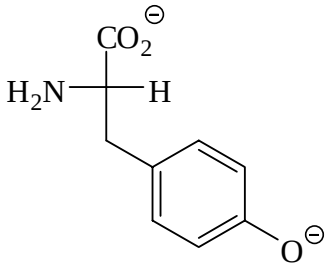
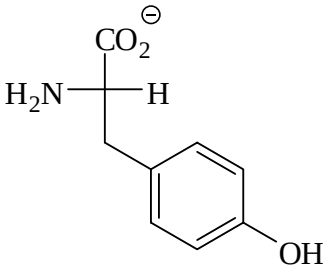
Specify the above mannose as D-mannose or L-mannose.	**D-mannose**
Specify the above tagatose as D-tagatose or L-tagatose.	**L-tagatose**

Marks 6

- The structure of L-tyrosine in 1 M HCl is drawn below. The pK_a for each acidic group is indicated on the diagram.



Draw Fischer projections of the predominant species present in a solution of tyrosine at pH 11.0 and pH 9.6. Indicate the overall charge of these species.

Fischer projection of tyrosine at pH 11.0	Fischer projection of tyrosine at pH 9.6
	
Overall charge: **-2**	Overall charge: **-1**

What is the isoelectric point (pI) of tyrosine? **½ (9.11 + 2.20) = 5.66**

Draw the predominant species of tyrosine at the isoelectric point.

Fischer projection of tyrosine at its isoelectric point.