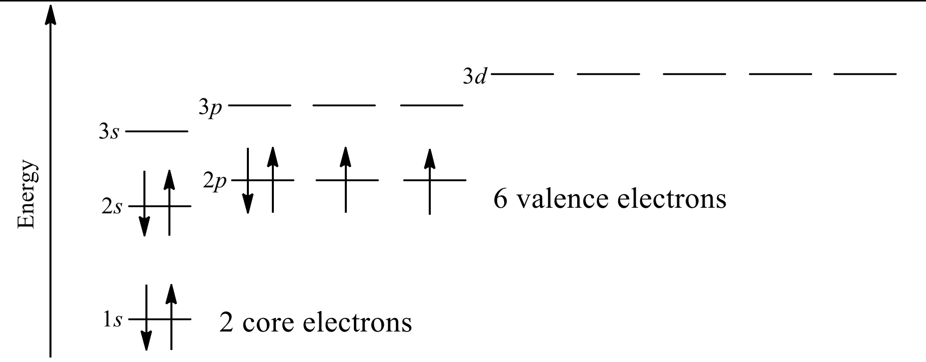
Marks 8

- What is the ground state electron configuration of oxygen?

1s^2 2s^2 2p^4

The following diagram represents the relative energies of the atomic orbitals in the first three shells. Using arrows to represent electrons, show the most stable electron arrangement of the oxygen atom. Label the core electrons and the valence electrons.



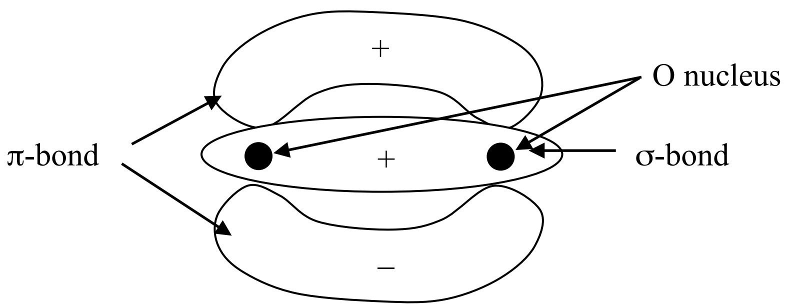
Briefly explain how your diagram illustrates the Pauli exclusion principle, Aufbau principle and Hund's rule.

Pauli exclusion principle: there's a maximum of 2 electrons in each orbital with opposite spins, ensuring that no two electrons have the same set of quantum numbers.

Aufbau principle: lowest energy orbitals fill first.

Hund's rule: electrons in degenerate orbitals (*i.e.* orbitals with same energy) have the maximum number of parallel spins to minimise electron / electron repulsion.

Draw an oxygen molecule showing the shapes of the σ-orbital and the π-orbital present.

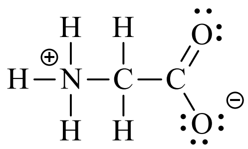


Oxygen and sulfur are both Group 16 elements with a valence of two. Oxygen is a diatomic molecule at room temperature, whilst the bonding in solid sulfur consists only of σ-bonds. Suggest reasons why, at room temperature, the O=O molecule is stable and the S=S molecule is not.

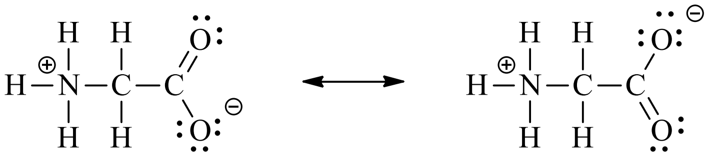
Sulfur would use 3*p* orbitals to form a π-bond. These orbitals are diffuse and overlap is poor and so it is more stable to use σ-bonds to 2 other atoms. Good overlap of the 2*p* orbitals in oxygen means that the π-bond is stable.

Marks 7

- 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 Lewis structure that indicates the charges on the molecule at the physiological pH of 7.4.



Use your structure to illustrate the concept of resonance.



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

N: *sp*^{3} hybridised; tetrahedral geometry

CH_2: *sp*^{3} hybridised; tetrahedral geometry

CO_2^-: *sp*^{2} hybridised; trigonal planar geometry

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

In its zwitterionic state, glycine has very strong electrostatic attractions (*i.e.* ionic bonds) between the NH_3^+ and CO_2^- groups giving it very high melting point.

Do you expect glycine to be water soluble? Give a reason for your answer.

Yes. It is ionic so dissolves in the very polar solvent water.

Marks 5

- The autoionisation of water conforms to the following balanced equation:

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad \Delta H = 56.3 \text{ kJ mol}^{-1}$$

Is this an exothermic or endothermic reaction?

Endothermic (as Δ*H* is positive).

What will happen to the equilibrium if the temperature is raised?

The reaction will shift to the right. From le Chatelier's principle, the equilibrium will shift to reduce the effect of the change. As the forward reaction is endothermic, it is able to mitigate the increase in temperature by shifting forwards.

The equilibrium constant, K, for this reaction is 1.8×10^{-16} at 25 °C. Calculate ΔG.

Using $\Delta G = -RT\ln K$,

$$\Delta G = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times ((25 + 273) \text{ K}) \times 1.8 \times 10^{-16} = +89 \text{ kJ mol}^{-1}$$

Answer: **+89 kJ mol^{-1}**

Why is ΔG not equal to ΔH for this reaction?

By definition, $\Delta G = \Delta H - T\Delta S$. As the entropy change for the reaction and the temperature are not zero, so $\Delta G \neq \Delta H$.

The pH of pure water is 6.81 at 37 °C. Is water acidic, basic or neutral at this temperature? Explain.

Neutral. Pure water is neutral at all temperatures as the chemical equation always gives $[H_3O^+(aq)] = [OH^-(aq)]$. A pH value of 7.0 only corresponds to a neutral solution at 25 °C.

Marks
5

- The radioactive isotopes ^{131}I and ^{137}Cs have been detected in drinking water near the Japanese Fukushima nuclear reactor. They have half lives of 8 days and 30 years, respectively. What is the definition of half-life?

Half-life is the amount of time required for the amount (or activity) of a sample to decrease to half its initial value.

What percentage of both isotopes will still be detectable after 25 years?

The number of nuclei, N, decays with time, t, according to $\ln(N_0/N_t) = \lambda t$ where λ is the activity coefficient. This is related to the half life, $t_{1/2}$ by $\lambda = \ln 2/t_{1/2}$.

For ^{131}I, $t_{1/2}$ = 8 days = 8/365 years:

$\lambda = \ln 2 / (8/365)$ **years^{-1} = 32 years^{-1}**

When t = 25 years,

$\ln(N_0/N_t) = \lambda t$ **= (32 years^{-1})(25 years)**

$N_0/N_t = e^{790}$ **or** $N_t / N_o \approx 0$

N_t is very close to zero and effectively all of the ^{131}I has decayed.

For ^{137}Cs, $t_{1/2}$ = 30 years:

$\lambda = \ln 2 / (30)$ **years^{-1} = 0.023 years^{-1}**

When t = 25 years,

$\ln(N_0/N_t) = \lambda t$ **= (0.023 years^{-1})(25 years)**

$N_0/N_t = 1.8$ **or** $N_t / N_o = 0.56 = 56\%$

^{131}I: **0%**	^{137}Cs: **56%**

If you were exposed to equal concentrations of both isotopes for 1 hour, which isotope would do more damage? Explain.

^{131}I would do more damage.

It has the shorter half-life so undergoes more disintegrations and produces more radiation in a given time period.

Marks 5

- The concentration of a dissolved gas is related to its partial pressure by c = *k*p. What is the concentration of CO_2 dissolved in blood if the partial pressure of CO_2 in the lungs is 0.053 atm? The *k* for CO_2 is 0.034 mol L^{-1} atm^{-1}.

Using *c* = *k*p,

c = (0.034 mol L^{-1} atm^{-1})(0.053 atm) = 0.0018 mol L^{-1}

Answer: **0.0018 mol L^{-1}**

Calculate the pH of blood if all of this CO_2 reacted to give H_2CO_3.
The K_a of H_2CO_3 is 4.5 × 10^{-7}.

If [H_2CO_3(aq)] = 0.0018 mol L^{-1}, the pH can be calculated using the reaction table:

	H_2CO_3	H_2O	$\rightleftharpoons$	H_3O^+	HCO_3^-
initial	**0.0018**	**large**		**0**	**0**
change	**$-x$**	**negligible**		**$+x$**	**$+x$**
final	**$0.0018 - x$**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{x^2}{0.0018-x}$$

As K_a = 4.5 × 10^{-7} and is very small, $0.0018 - x \sim 0.0018$ and hence:

$x^2 = 0.0018 \times (4.5 \times 10^{-7})$ or $x = 2.8 \times 10^{-5}$ M = [H_3O^+]

Hence:

pH = $-\log_{10}$ [H_3O^+(aq)] = $-\log_{10}(2.8 \times 10^{-5})$ = 4.54

Answer: **4.54**

Hyperventilation results in a decrease in the partial pressure of CO_2 in the lungs. What effect will this have on the pH of the blood? Use a chemical equation to illustrate your answer.

If the CO_2 partial pressure decreases, the equilibrium below will shift to the left. This will decrease [H^+(aq)] and the pH will increase.

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

ANSWER CONTINUES ON THE NEXT PAGE

The pH of blood is maintained around 7.4 by the H_2CO_3 / HCO_3^- buffer system. Explain how a buffer works, illustrating your answer with chemical equations.

A buffer resists changes in pH. It contains substantial quantities of a weak acid and its conjugate base. In the H_2CO_3/HCO_3^- buffer, added acid is removed by the reaction:

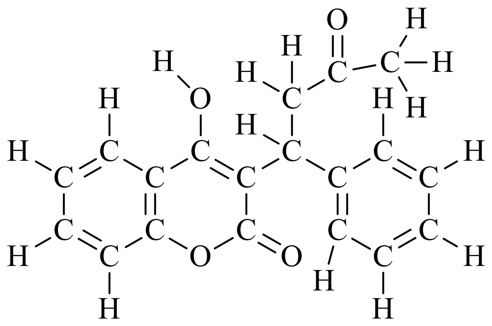
$$HCO_3^-(aq) + H^+(aq) \rightarrow H_2CO_3(aq)$$

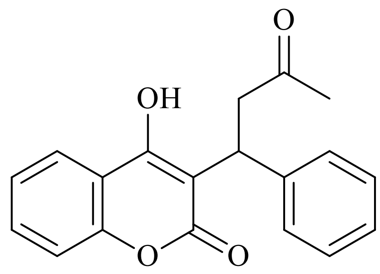
Added base is removed by the reaction:

$$H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O$$

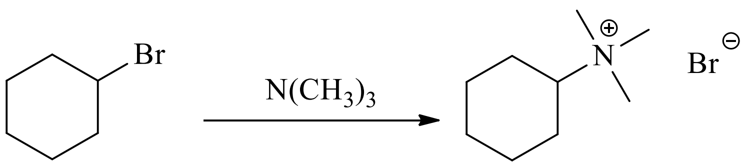
Marks

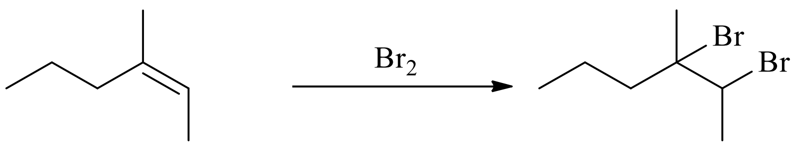
- A structural formula for Warfarin, an anticoagulant, showing all atoms and bonds is shown below. Draw a stick representation of the formula in the box provided. **1**

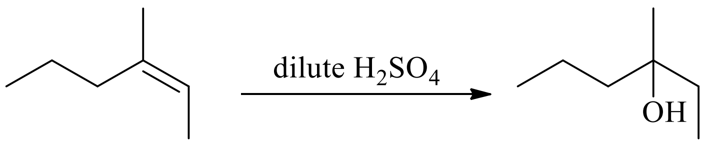


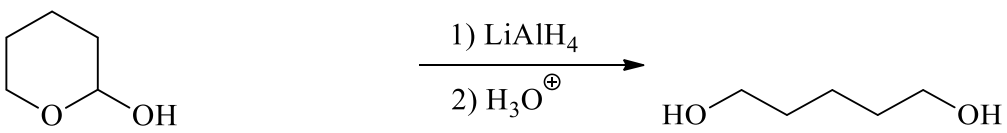


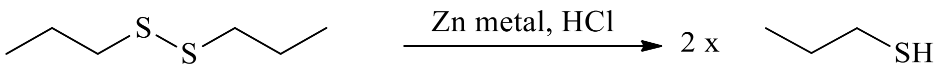
- Give the constitutional formula(s) of the major organic products formed in each of the following reactions: **5**





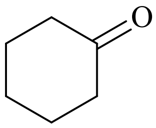
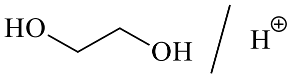
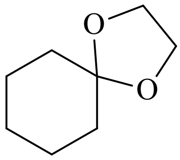
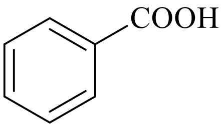
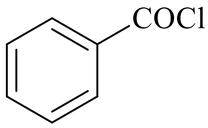
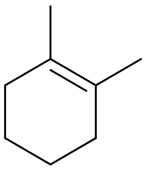
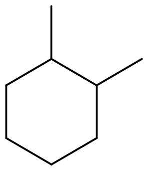
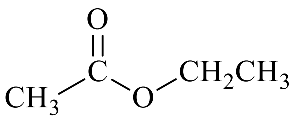
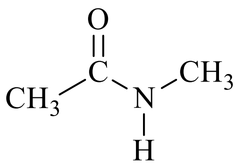






Marks 6

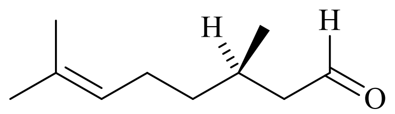
- Complete the following table.

Starting material	Reagent / Conditions	Major organic products(s)
		
	**$SOCl_2$**	
$CH_3CH_2COOCH_2CH_3$	2 M NaOH heat	$CH_3CH_2CO_2^{\ominus}$ + CH_3CH_2OH
	$H_2(g)$ Pd/C catalyst	
	NH_2CH_3	 + CH_3CH_2OH

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

Marks

- (+)-Citronellal is a widely occurring natural product present in citronella oil, lemon and lemon grass. It is used as a soap perfume and in insect repellents. **4**



citronellal

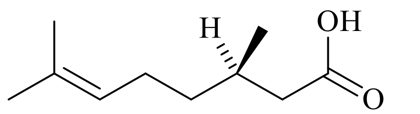
Give the molecular formula of citronellal. | **$C_{10}H_{18}O$**

Identify the functional groups present in citronellal.

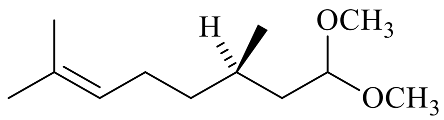
Aldehyde and alkene

Draw the constitutional formula of the product(s) formed when citronellal is treated with each of the following reagents.

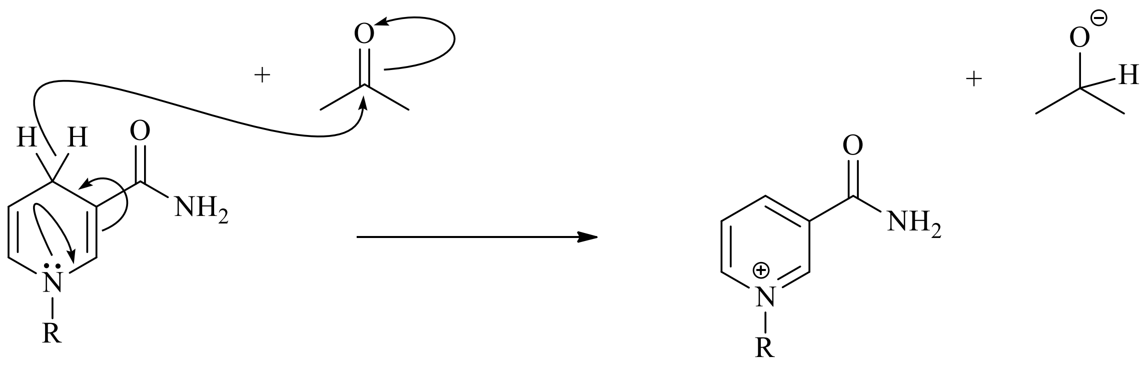
$Cr_2O_7^{2\ominus}$ / $H^{\oplus}$



excess CH_3OH / catalytic amount H_2SO_4



- NADH is the most important reducing agent in Nature. It is itself oxidised to NAD^+. Complete the scheme below by: **3**
  (a) drawing in curly arrows to show the movement of electrons during the first step in the reduction of acetone with NADH, and
  (b) drawing the structure of NAD^+.

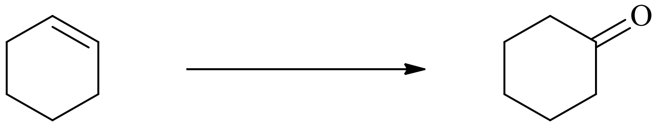


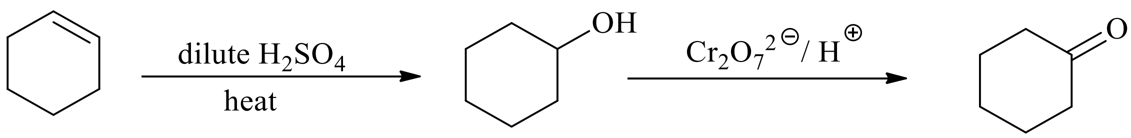
NADH

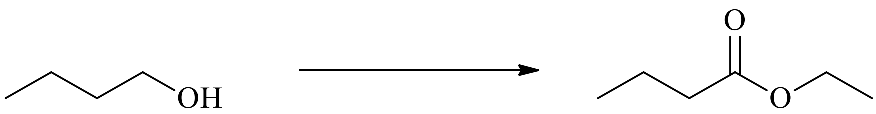
NAD^+

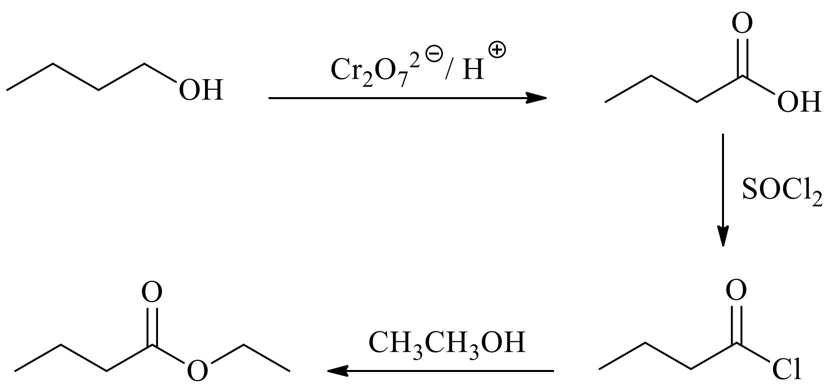
Marks
6

- Show clearly the reagents you would use to carry out the following chemical conversions. Note that more than one step is required and you should indicate all necessary steps and the constitutional formulas of any intermediate compounds.





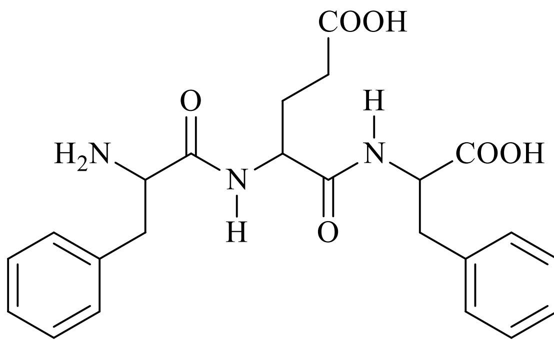




Marks
3

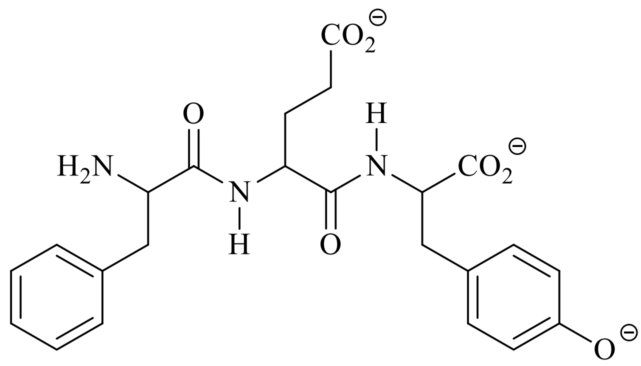
- Consider the tripeptide phenylalanylglutamyltyrosine (Phe-Glu-Tyr) (**F**), whose constitutional formula is shown below.

(**F**)

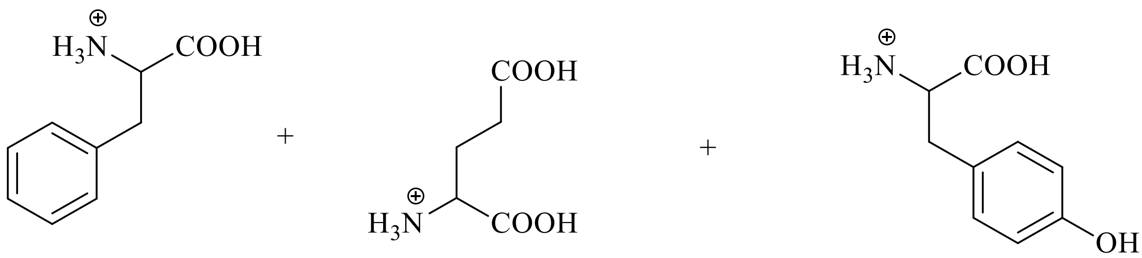


Draw the constitutional formula(s) of the product(s) obtained when the tripeptide (**F**) is subjected to the following conditions. Make sure you show the products in the appropriate ionic states.

cold 2 M NaOH

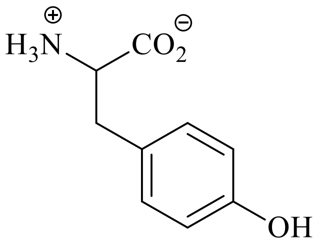


5 M HCl / heat



Marks 4

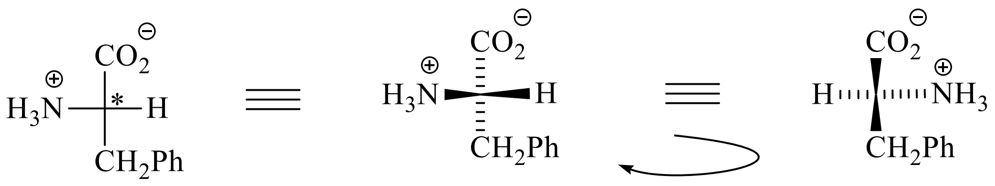
The pK_a values of tyrosine are pK_{a1} = 2.20 (α-COOH), pK_{a2} = 9.11 (α-$NH_3^{\oplus}$) and pK_{a3} = 10.07 (-$CH_2C_6H_4OH$). Draw the structure of the zwitterionic form of tyrosine.



At what pH will this be the predominant species in aqueous solution?

5.66 (halfway between pK_{a1} and pK_{a2})

The naturally occurring isomer of phenylalanine is (L)-phenylalanine. Draw the zwitterionic structure of (L)-phenylalanine and indicate the stereogenic centre with an asterisk (*). Determine whether this amino acid has the (*R*) or (*S*) configuration. Show your working.



Horizontal bonds in Fischer projections are out of the paper, vertical bonds are into the paper. Order of priority of substituents is NH_3^+ > CO_2^- > CH_2Ph > H. Reorient the molecule so that the lowest priority group (H) is at the back. Viewing down the C–H bond, the orientation of NH_3^+ → CO_2^- → CH_2Ph is anticlockwise. Therefore (L)-phenylalanine has (*S*) configuration.

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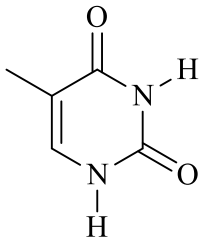
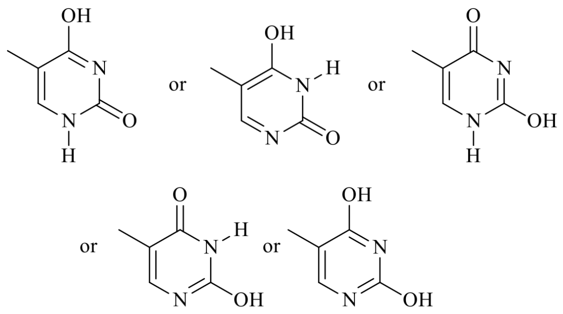
Marks

- Draw a tautomer of the structure of thymine, shown below. **1**

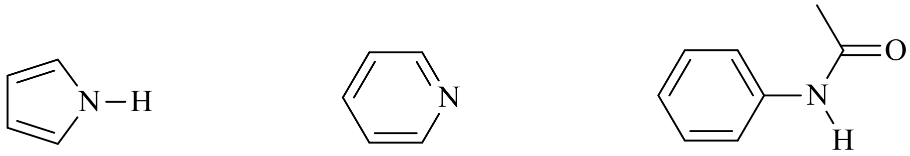
thymine



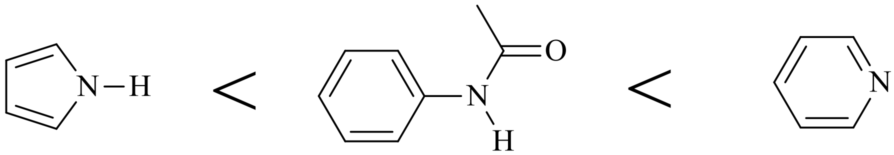
tautomer of thymine

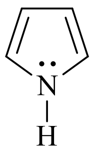


- Rank the following compounds in order of base strength and explain your reasoning. You may use diagrams to assist your explanation. **3**

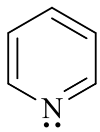


Order of base strength is:

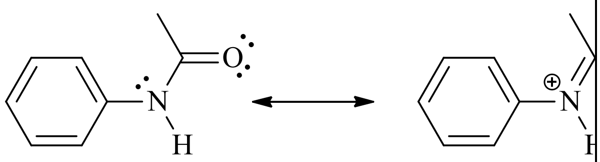




pyrrole
non-basic



pyridine
basic



N-phenylacetamide
essentially non-basic

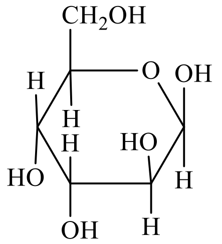
Pyridine is the most basic as the lone pair of electrons on nitrogen is available to bond with H^+.

Pyrrole is the least basic as the "lone pair" of electrons on nitrogen is part of the aromatic π-electron system and is delocalised around the ring. It is not available for bonding with H^+ ions.

N-Phenylacetamide is essentially non-basic as the lone pair of electrons is involved in resonance forms (including delocalisation of the positive charge into the aromatic ring, which is not shown).

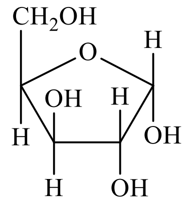
Marks
6

- Consider the following two monosaccharides, (**A**) and (**B**).



(**A**)

β-D-altropyranose

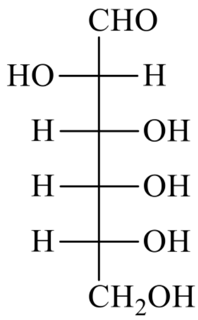


(**B**)

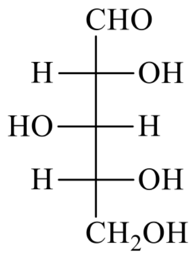
α-D-xylofuranose

Draw Fischer projections of the open chain forms of (**A**) and (**B**).

(**A**)

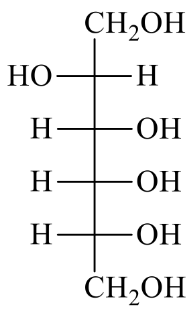


(**B**)



Draw the major organic product of the reaction of D-altropyranose with the following reagents.

1. $NaBH_4$ 2. $H^{\oplus}$ / H_2O



$[Ag(NH_3)_2]^{\oplus}$ / $OH^{\ominus}$