CATHOLIC JUNIOR COLLEGE
JC2 PRELIMINARY EXAMINATIONS
Higher 2

CHEMISTRY

9647/01

Paper 1 Multiple Choice

Wednesday 31 August 2016
1 hour

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.
Do not use staples, paper clips, glue or correction fluid.
Write your name and HT group on the Answer Sheet in the spaces provided.

There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.
Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.
Any rough working should be done in this booklet.
The use of an approved scientific calculator is expected, where appropriate.

WORKED SOLUTIONS

This document consists of **30** printed pages.

Section A

For each question there are ***four*** possible answers, ***A***, ***B***, ***C*** and ***D***. Choose the one you consider to be ***correct*** and record your choice in soft pencil on the ***separate Answer Sheet*** provided.

1 *Use of the Data Booklet is relevant to this question.*

Arsenic(III) sulfide, As_2S_3, is a bright yellow solid which has been used as a pigment in paintings.

When arsenic(III) sulfide is heated in air, it reacts with oxygen to give arsenic(III) oxide and sulfur(IV) oxide.

$$2As_2S_3 + 9O_2 \rightarrow 2As_2O_3 + 6SO_2$$

What would be the mass of arsenic(III) oxide produced if 550 dm^3 oxygen, measured at room temperature and pressure, reacted with arsenic(III) sulfide?

A 1010 g **B** 1070 g **C** 2010 g **D** 2160 g

Answer: A

Number of moles of $O_2 = \frac{550}{24} = 22.9$ mol

Since $9O_2 \equiv 2As_2O_3$

Number of moles of $As_2O_3 = \frac{22.9}{9} \times 2 = 5.09$ mol

M_r of $As_2O_3 = 74.9 \times 2 + 16.0 \times 3 = 197.8$

Mass of $As_2O_3 = 5.09 \times 197.8 = 1007$ g

2 Incomplete combustion of 20 cm^3 of a gaseous hydrocarbon gave carbon dioxide and carbon monoxide in a 6:1 ratio, as well as water vapour. It was found that the carbon dioxide took up a volume of 51.4 cm^3 whereas the water vapour took up a volume of 80 cm^3. All gas volumes are measured at the same temperature and pressure.

What is the molecular formula of the hydrocarbon?

A C_2H_4 **B** C_2H_6 **C** C_3H_6 **D** C_3H_8

Answer: D

$7C_xH_y + ?\ O_2 \rightarrow 6xCO_2 + xCO + \frac{7y}{2}H_2O$

Reduction of 80 cm^3 after passing through dehydrating agent

⇨ volume of water vapour was 80 cm^3

Reduction of 51.4 cm^3 after passing through KOH (aq)

⇨ volume of CO_2 was 51.4 cm^3

Mole ratio of $C_xH_y : CO_2 =$ $7 : 6x = 20 : 51.4$

$$\frac{6x}{7} = \frac{51.4}{20}$$

$$x = 2.99 \approx 3$$

Mole ratio of $C_xH_y : H_2O$ = $7 : \frac{7y}{2} = 20 : 80$

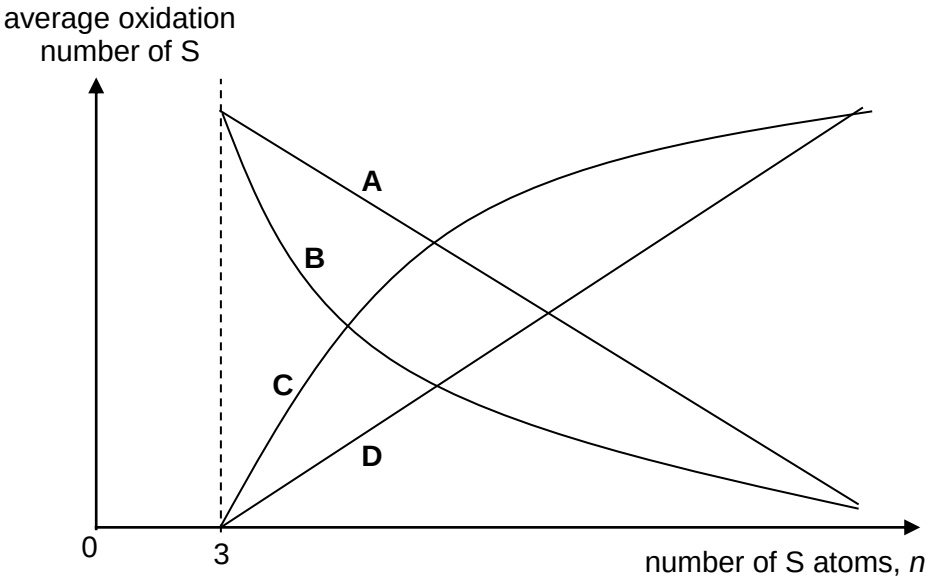
$$\frac{\frac{7y}{2}}{7} = 4$$

$$y = 8$$

Therefore, the molecular formula of the hydrocarbon is C_3H_8.

3 Polythionates are a series of sulfur-oxo anions with the general formula $S_nO_6^{2-}$, where $n > 2$. A simple example is tetrathionate ion, $S_4O_6^{2-}$.

Which of the following graphs best illustrates the variation in the average oxidation number of sulfur in $S_nO_6^{2-}$ with n?



Answer: B

Let the average oxidation number of S be y

For $S_nO_6^{2-}$, $-2 = 6(-2) + ny$

$$ny = +10$$

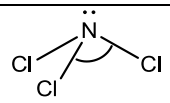
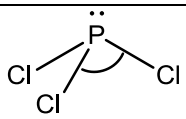
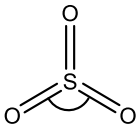
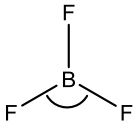
$$y = +\frac{10}{n}$$

Hence the graph is a hyperbolic graph starting from the point (3, +10/3), which corresponds to graph **B**.

4 Which of the following species has the smallest bond angle around the central atom?

A NCl_3 **B** PCl_3 **C** SO_3 **D** BF_3

Answer: B

	 3 bp, 1 lp 107°		 3 bp, 1 lp And P is less electronegative than N, so electron pairs less attracted to P, hence smallest bond angle, <107°		 3 bp, 0 lp 120°		 3 bp, 0 lp 120°

5 Which of the following shows the correct bonds present in solid CHI_3?

A Covalent bonds only
B Ionic bonds only
C Covalent bonds & temporary dipole-induced dipole forces of attraction
D Covalent bonds & permanent dipole-permanent dipole forces of attraction

Answer: D

CHI_3 (triiodomethane) is a simple covalent molecule which is polar, hence it contains covalent bonds between atoms and permanent dipole-permanent dipole forces of attraction between molecules.

6 Polymerisation is a process in which large number of small molecules (monomers) are joined together to form long–chain molecules.

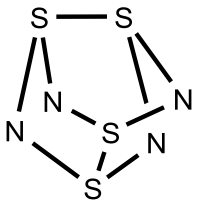
Considering that polymerisation is a spontaneous reaction, what are the correct signs of ΔS and ΔH for the process?

	ΔS	ΔH
A	–	–
B	–	+
C	+	–
D	+	+

Answer: A

ΔG = negative because it is a spontaneous reaction
ΔS = negative because the degree of disorderness decreases as polymerisation form orderly long-chain molecules.
Since $\Delta G = \Delta H - T\Delta S$, with ΔG = negative and $(-T\Delta S)$ = *positive*, ΔH has to be negative

7 S_4N_4 is a thermochromic solid which changes colour with temperature. S_4N_4 has a cage structure as shown in the diagram.



S_4N_4

Given the following data, what is the average bond energy of dissociation of S-N, in kJ mol^{-1}?

$\Delta H_f°$ (S_4N_4) = +460 kJ mol^{-1}

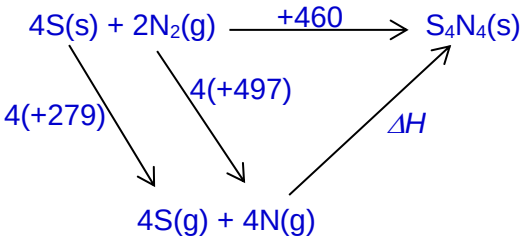
$\Delta H_{at}°$ (sulfur) = +279 kJ mol^{-1}

$\Delta H_{at}°$ (nitrogen) = +497 kJ mol^{-1}

(S-S) bond energy of dissociation in S_4N_4 = +204 kJ mol^{-1}

A +150 **B** +280 **C** +395 **D** +559

Answer: B



ΔH = -[4(+279) +4(497)] +460 = -2644 kJ mol^{-1}

Total Bond Energy = 2644 kJ mol^{-1} = 8 BE (S-N) + 2 BE (S-S)

8 BE (S -N) = 2644 – (2)(+204)

BE (S-N) = +279.5 = 280 kJ mol^{-1}

8 At 25 °C, a dented ping pong ball has an internal volume of 31.0 cm^3 and internal pressure of 110 kPa. It is then placed in a water bath maintained at 60 °C, which returned the ball to its original spherical shape with internal volume of 33.5 cm^3.

Assuming ideal gas behaviour, what is the pressure of air inside the ball at 60 °C in its original spherical shape?

A 101 kPa **B** 114 kPa **C** 122 kPa **D** 244 kPa

Answer: B

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

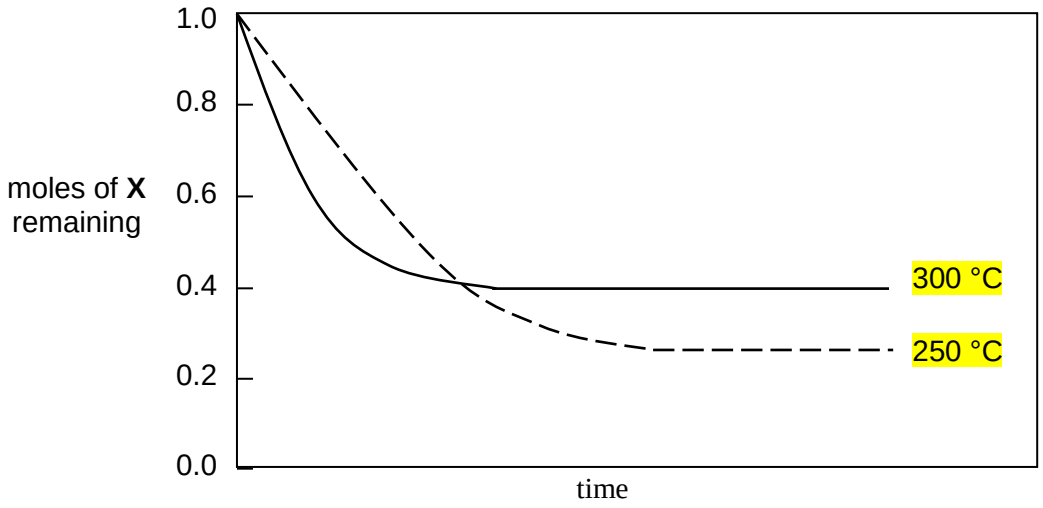
$\frac{(110)(31.0)}{(298)} = \frac{P_2(33.5)}{(333)}$

$p_2 = 113.7$ kPa

9 Gas **X** decomposes to two other gases, **Y** and **Z**, according to the following equation:

$$2\mathbf{X}(g) \rightleftharpoons 3\mathbf{Y}(g) + \mathbf{Z}(g)$$

The graph below shows the decomposition of 1.0 mol of pure gas **X** in the presence of a catalyst at various temperatures.



Which one of the following statements about the above system is **correct**?

A The decomposition of **X** is endothermic.
B The K_p of the system decreases with increasing temperature.
C The percentage decomposition of **X** is 40 % at 300 ^oC.
D The system becomes less disordered when it reaches equilibrium state.

Answer: B

A – As T increased, amount of **X** remaining at equilibrium increased. This shows that position of equilibrium shifts left, hence backward reaction is endothermic. Forward reaction is thus exothermic. ⇒ incorrect

B – Position of equilibrium shifts left with increasing T to favour endothermic reaction (since forward reaction is exothermic). Thus K_p will decrease with increasing T. ⇒ correct

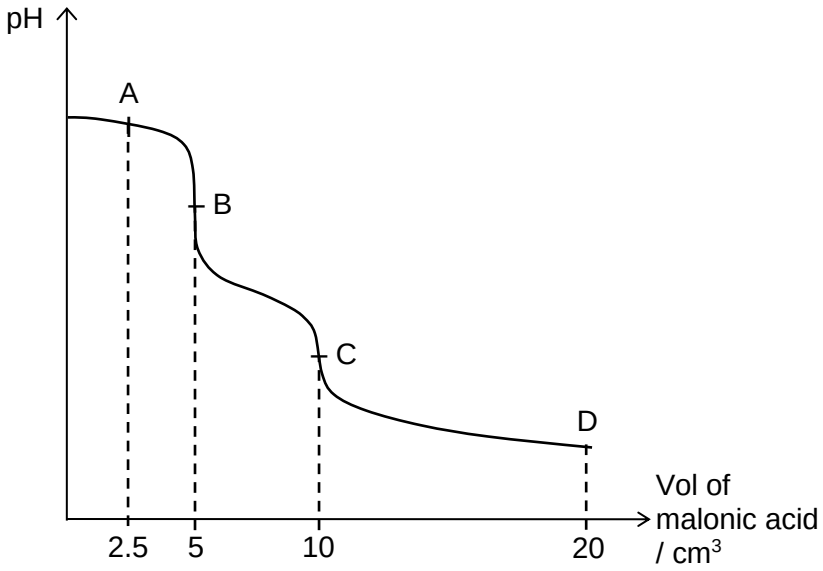
C – At 300 ^oC, amount of **X** remaining is 0.4 mol. Hence, percentage decomposition of **X** is 60 % instead of 40%. ⇒ incorrect

D – There is an increase in the number of moles of gaseous particles resulting in an increase in degree of randomness. ⇒ incorrect

10 Malonic acid, $HO_2CCH_2CO_2H$, is a weak dibasic acid.

Malonic acid is titrated against 20.0 cm^3 of sodium hydroxide of the same concentration, the following pH-volume curve is obtained.

At which point on the titration curve is the mixture **most** able to resist pH change upon addition of a small amount of aqueous acid or base?



Answer: D

A – NaOH will be present in excess. No buffer present.
B – NaOH still present in excess.
C – First equivalence point. $HO_2CHCHCO_2^-$ and water present.
D – Maximum buffering capacity where $HO_2CHCHCO_2^-$ (weak acid) and $^-O_2CHCHCO_2^-$ (salt) are present

11 The following is the reaction for compound **XY**,

$$\mathbf{XY}(g) \rightarrow \mathbf{X}(g) + \mathbf{Y}(g)$$

If the rate constant for the reaction is 5.78 x 10^{-3} s^{-1}, what is the time taken for the concentration of a sample of **XY** to decrease from 1.80 mol dm^{-3} to 0.225 mol dm^{-3}?

A 120 s **B** 240 s **C** 360 s **D** 480 s

Answer: C

$t_{1/2} = \frac{ln\,2}{k}$

$t_{1/2} = \frac{ln\,2}{(5.78 \times 10^{-3})}$

$t_{1/2} = 119.9s$

1.80 → 0.90 → 0.45 → 0.225

3 x 119.9 = 360s

12 The reaction between **C** and **D** is as follows:

$$\mathbf{C} + 2\mathbf{D} \rightarrow 2\mathbf{E}$$

In an experiment to investigate the effect of concentrations on the rate of reaction, the following results were obtained at constant temperature.

Experiment	[**C**] / mol dm^{-3}	[**D**] / mol dm^{-3}	Initial rate / mol $dm^{-3}s^{-1}$
1	1.0	1.0	0.0008
2	1.0	2.0	0.0016
3	1.0	3.0	x
4	2.0	2.0	0.0032

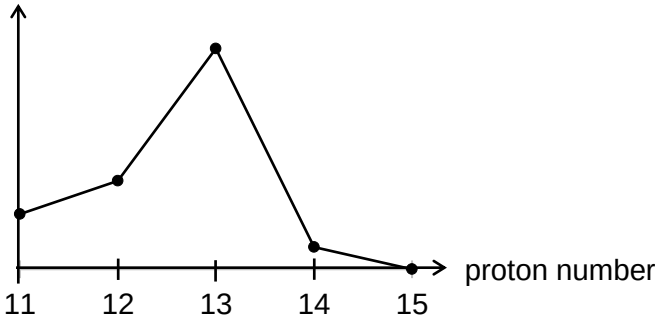
What is the value of x?

A 0.0008 **B** 0.0016 **C** 0.0024 **D** 0.0032

Answer: C

Comparing experiments 1 and 2, when [**D**] is doubled, rate doubles. Order of reaction wrt **D** is 1
Comparing experiments 2 and 4, when [**C**] is doubled, rate doubles. Order of reaction wrt **C** is 1.
Rate = k[**C**][**D**]
Comparing experiments 1 and 3, when [**D**] triples, rate should triple. Hence, value of **x** is 0.008 × 3 = 0.0024 mol dm^{-3} s^{-1}

13 The following graph shows how a property of the elements in Period 3, from Na to P, or their compounds, varies with proton number.



What property is shown by the graph?

A Melting point of element
B Melting point of oxide
C pH of aqueous chloride
D Conductivity of element

Answer: D

Electrical conductivity increases from Na to Al due to the increase in number of mobile delocalised electrons. Electrical conductivity then decrease to Si as Si is a semi-conductor and has poor conductivity under normal conditions. P does not conduct electricity as it neither have delocalised electrons nor mobile charge carriers.

14 Which of the following statements about calcium, strontium and barium is correct?

A The magnitude of the hydration energy of the M^{2+} ion increases from calcium to barium

B The energy required for the process M (g) $\rightarrow$ M^{2+} (g) + $2e^-$ increases from calcium to barium.

C The reducing power decreases from calcium to barium.

D The reactivity of the elements with water increases from calcium to barium.

Answer: D

A – hydration energy $\propto \frac{charge}{size}$. Since size increases down the group, magnitude of hydration energy decreases.

B – IE decreases down the group as valence electrons are less strongly attracted to the metal nucleus.

C – Reducing power (or ease of being oxidised, ie. loss of electrons to form M^{2+}) increases down the group.

D – Reactivity does increase down the group, due to increased reducing power down the group.

15 When 1.0 g of each of the following Group II metals is added to cold water and any gas produced is collected at 25 °C and 1 atm, which sample will most likely produce the largest volume of gas?

A Mg **B** Ca **C** Sr **D** Ba

Answer: B

Group II metals react with cold water to form their hydroxides and hydrogen gas:

$$M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$$

A – No. of mol of Mg = $\frac{1.0}{24.3}$ = 0.0412 mol, but there will be almost no reaction in cold water due to insoluble $Mg(OH)_2$ layer preventing further reaction.

B – No. of mol of Ca = $\frac{1.0}{40.1}$ = 0.0250 mol, and although $Ca(OH)_2$ is only partially soluble, the reaction should go to completion. Largest amount (in moles) of gas produced, hence largest volume.

C – No. of mol of Sr = $\frac{1.0}{87.6}$ = 0.0114 mol (< 0.0250)

D – No. of mol of Ba = $\frac{1.0}{137}$ = 0.00730 mol (< 0.0250)

16 Which statement about the trends in the properties of the halogens is correct?

A The volatility of halogens increases down the group.
B The electronegativity of halogens increases down the group.
C The reactivity of halogens with hydrogen decreases down the group.
D The bond dissociation energy of halogens increases down the group.

Answer: C

A – Boiling point increases down the group (gas to solid), hence volatility decreases down the group.

B – Electronegativity decreases down the group as atomic radius increases.

C – Reactivity decreases down the group as strength of H-X bond decreases.

D – Bond dissociation energy decreases down the group, as size of atoms increase, reducing effectiveness of orbital overlap.

17 "Bromine tablets" are used as disinfectants. It is a source of HC*l*O(aq) and HBrO(aq), both of which are oxidising agents.

HBrO destroys bacteria, fungi and algae via its oxidising property in the process. HC*l*O is a stronger oxidising agent than HBrO and helps to sustain the effectiveness of the bromine tablets.

What is the likely role of HC*l*O in relation to HBrO?

A Oxidises Br^- to BrO^-
B Oxidises Br^- to Br_2
C Reduces BrO^- to Br^-
D Reduces BrO^- to Br_2

Answer: A

Oxidation state of Br in HBrO is +1. When HBrO destroys bacteria through its oxidising property, it gets reduced to Br^-. However, since HC*l*O is a stronger oxidising agent than HBrO, hence it will oxidise Br^- to BrO^-. This helps to sustain the effectiveness of the bromine tablets by regenerating BrO^-.

$ClO^- + 2H^+ + 2e^- \rightleftharpoons Cl^- + H_2O$ $\quad E^\ominus_1$
$BrO^- + 2H^+ + 2e^- \rightleftharpoons Br^- + H_2O$ $\quad E^\ominus_2$
$E^\ominus_1 > E^\ominus_2$

18 When drops of aqueous ammonia are added to a solution of $CuSO_4$, a pale blue precipitate is formed. This precipitate dissolved when excess aqueous ammonia is added, forming a deep blue solution. On addition of dilute hydrochloric acid, the pale blue precipitate is reformed.

Which process does **not** occur in the above?

A Dative bond formation
B Formation of a complex ion
C Precipitation of copper(II) hydroxide
D Reduction of copper(II) ions

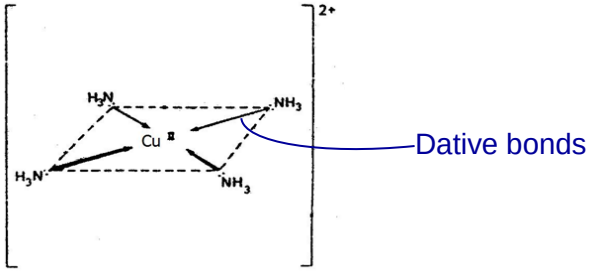
Answer: D

When a few drops of aqueous ammonia are added to solution of $CuSO_4$, the following reaction occurs and a pale blue ppt, $Cu(OH)_2$ is formed.

$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$

Upon addition of excess ammonia, the pale blue ppt dissolves. A complex, $Cu(NH_3)_4]^{2+}$ is formed.

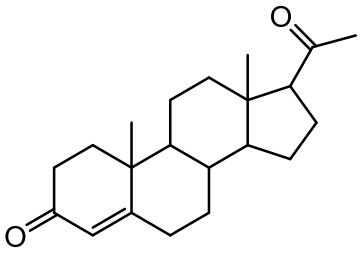
$Cu(OH)_2(s) + 4\ NH_3\ (aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq) + 2\ OH^-(aq)$ ----(1)



When **dilute** hydrochloric acid is added, it reacts with the ammonia ligands and causes equilibrium position (1) to shift to the left, forming back $Cu(OH)_2$, seen as the blue ppt.

Reduction of copper (II) ions does not occur.

19 Progesterone is an endogenous steroid involved in the menstrual cycle and pregnancy, of humans. It has the structure shown below.

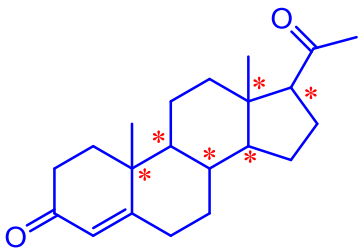


progesterone

How many chiral centers does progesterone contain?

A 2 **B** 4 **C** 6 **D** 8

Answer: C



6 chiral centers

20 *Use of the Data Booklet is relevant to this question.*

An organic compound **A** is commonly used in skin-care products. It has the following features.

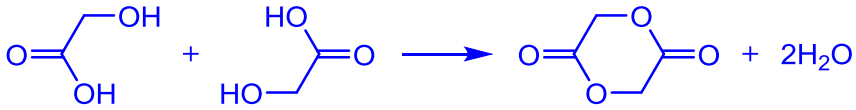
- It is a monobasic acid.
- One mole of compound **A** reacts with Na to give 1 mole of H_2 gas.
- It dimerises in the presence of hot concentrated H_2SO_4 to give an organic compound of relative molecular mass 116.

How many carbon atoms are in one molecule of this organic compound **A**?

A 1 **B** 2 **C** 3 **D** 4

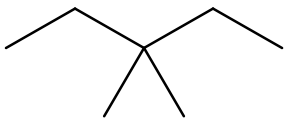
Answer: B

- It is monobasic. $\Rightarrow$ 1 $-CO_2H$ functional group present
- Since ROH + Na $\rightarrow$ ½ H_2 + RO^-Na^+ and 1 mol of **A** gives 1 mole of H_2 gas.
  $\Rightarrow$ 2 -OH functional groups present
- It dimerises in the presence of hot concentrated H_2SO_4 to give a compound of relative molecular mass 116. $\Rightarrow$ the acid has $–CO_2H$ group and –OH group. In the presence of H_2SO_4, esterification will occur. A cyclic product is formed.



Given the Mr, there are 4 carbons in the product, since product is formed from the dimersiation of compound A, thus compound A has 2 carbons.

21 3,3-dimethylpentane, C_7H_{16}, reacts with bromine to form monobromo compounds with molecular formula of $C_7H_{15}Br$.



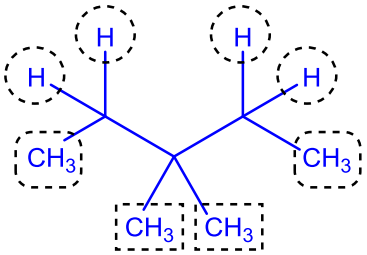
3,3-dimethylpentane

How many possible structural isomers, each with molecular formula $C_7H_{15}Br$, could be produced by 3,3-dimethylpentane?

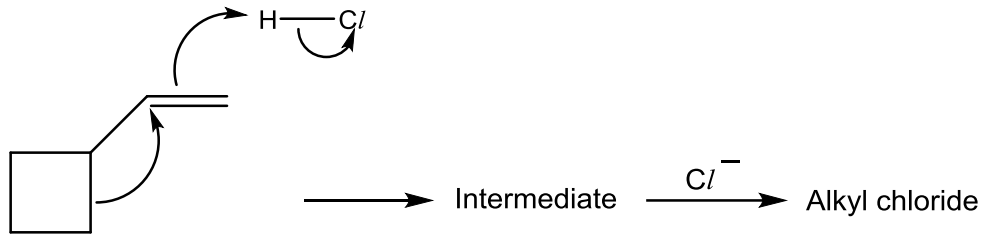
A 3 **B** 4 **C** 6 **D** 7

Answer: A

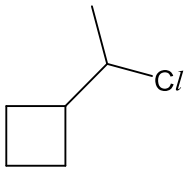
3,3-dimethylpentane undergoes free radical substitution in the presence of sunlight. There are 3 different sets of chemically equivalent hydrogen atoms that can be substituted to give 3 different monobromo products. Note that the molecule is symmetrical.



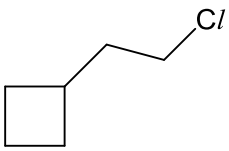
22 Vinylcyclobutane can react with HC*l* to give a rearranged alkyl chloride. With the aid of the flow of electrons represented by the curved arrows, what is the alkyl chloride product obtained?



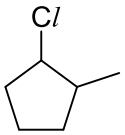
A



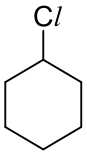
B



C

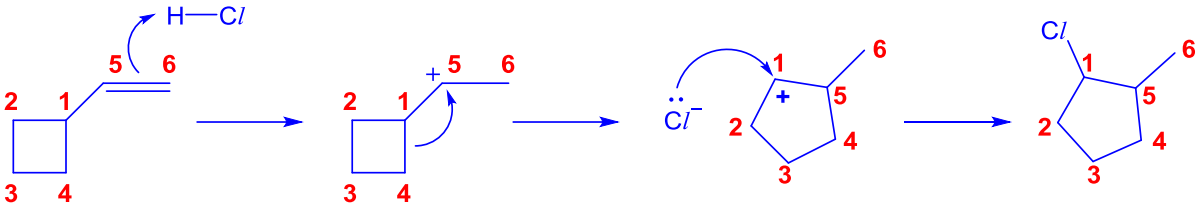


D



Answer: C

The diagram below shows the breakdown of the flow of electrons. However, the first 2 steps should be concerted.

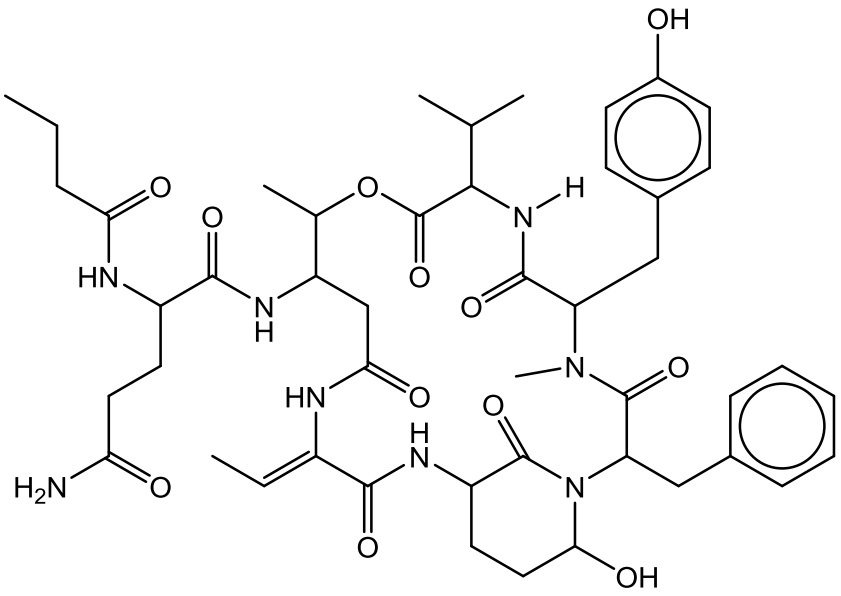


The alkene functional group will undergo electrophilic addition with HC*l*.
By following the arrow which represents the flow of electrons:

- the bond between C1 and C4 is broken
- a new bond is formed between C4 and C5
- C1 will be positively charged.
- A 5 membered-ring is formed.

Thus, the Cl^- will attack the carbocation on C1.

23 Yanucamide B can be extracted from a marine sponge and has the structure shown below.



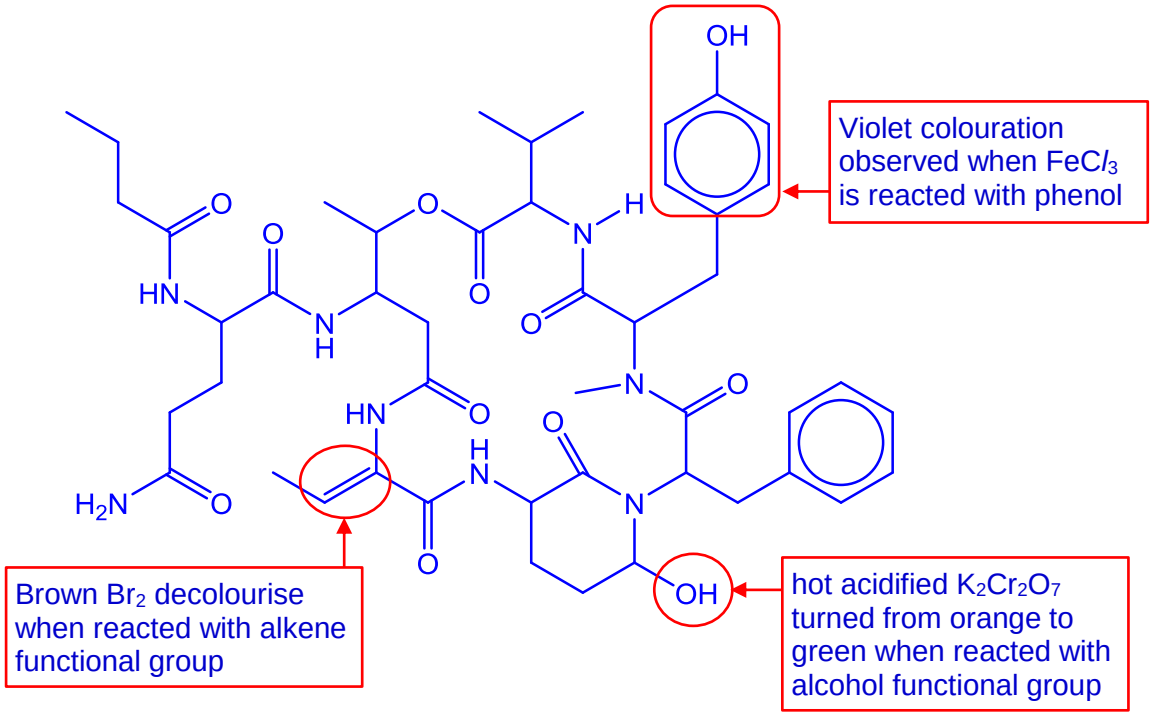
Yanucamide B

Which of the following set of reagents and conditions will not result in a colour change?

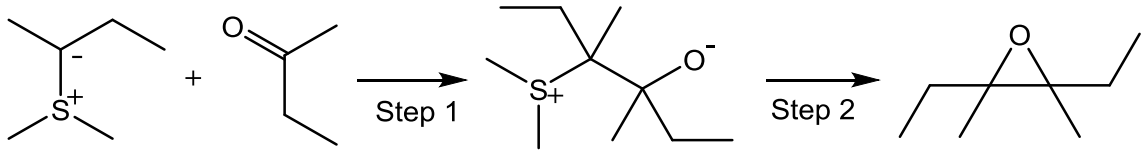
A Br_2 in CCl_4
B neutral $FeCl_3$(aq)
C $LiAlH_4$ in dry ether
D hot acidified $K_2Cr_2O_7$

Answer: C

$LiAlH_4$ react with Yanucamide B by reducing the amide and ester functional groups, however there is no colour change.

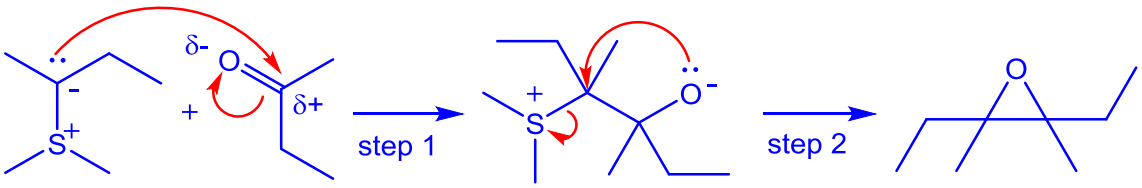


24 In the following sequence of reactions, what is the mechanism of step 1?

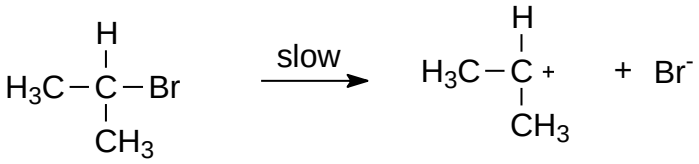


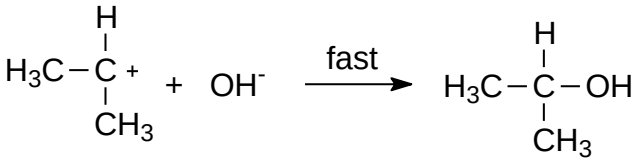
A Nucleophilic Addition
B Nucleophilic Substitution
C Electrophilic Addition
D Electrophilic Substitution

Answer: A



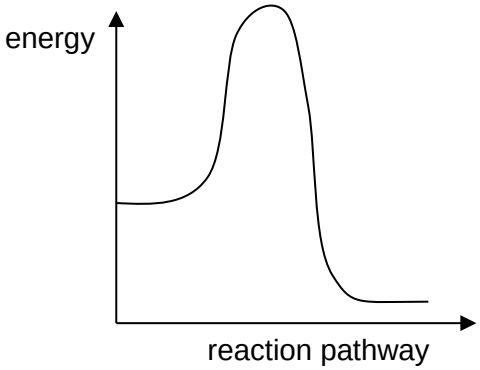
25 2–bromopropane undergoes nucleophilic substitution with aqueous NaOH via the following mechanism.



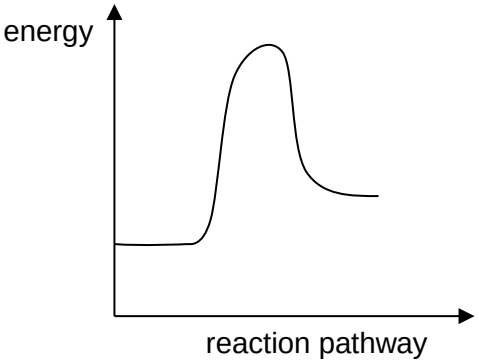


Which of the reaction pathway diagram fits the above mechanism?

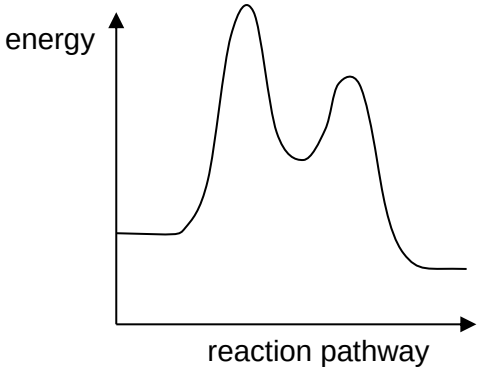
A



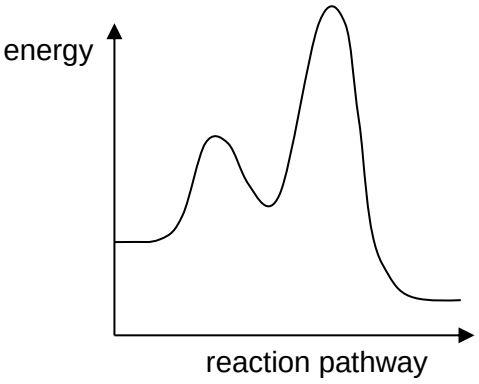
B



C

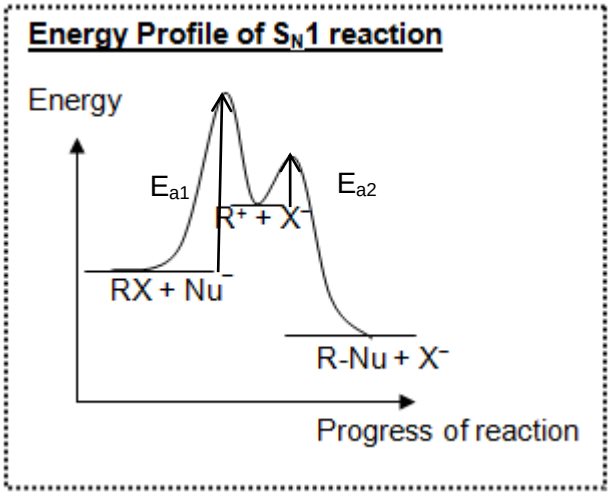


D



Answer: C

Since this is a 2-step reaction mechanism and a carbocation intermediate is formed, reaction proceeds via an S_N1 mechanism, where the slow step of the mechanism is unimolecular. The energy profile of a S_N1 reaction is as shown below.



Step 1 is the slow, rate-determining step, thus it would have the largest activation energy. $E_{a1} > E_{a2}$. Thus, option C is the answer.

26 Compound **X**, C_4H_9Br, undergoes the following reactions:

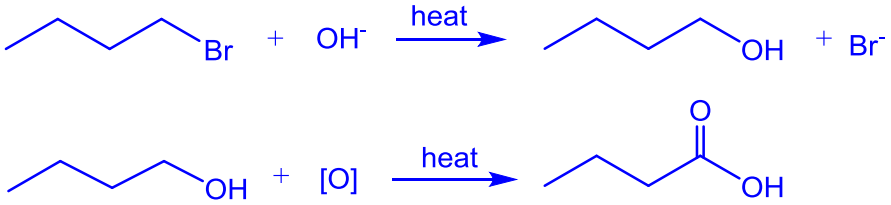
$$\underset{\textbf{X}}{C_4H_9Br} \xrightarrow[\text{heat under reflux}]{\text{NaOH(aq)}} C_4H_{10}O \xrightarrow[\text{heat under reflux}]{Cr_2O_7^{2-}(aq)/H^+(aq)} C_4H_8O \text{ only}$$

What is **X** likely to be?

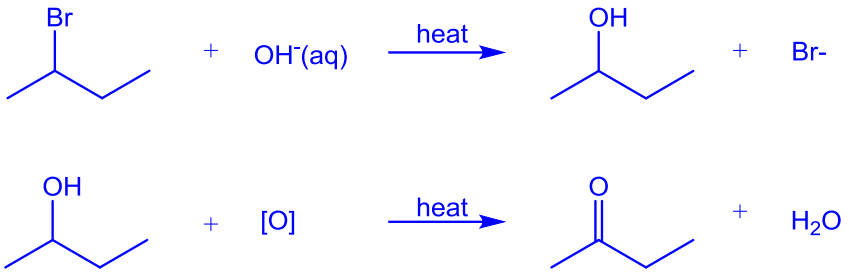
A 1-bromobutane
B 2-bromobutane
C 1-bromo-2-methylpropane
D 2-bromo-2-methylpropane

Answer: B

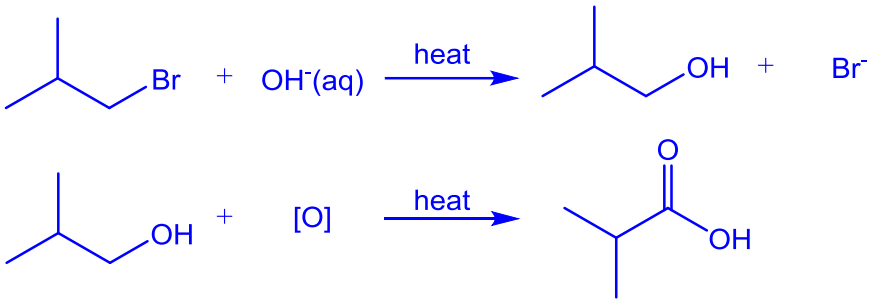
A – incorrect as reaction of 1-bromobutane (primary RX) will produce primary alcohol of substitution and in turn, result in carboxylic acid as the final product, having molecular formula, $C_4H_8O_2$.



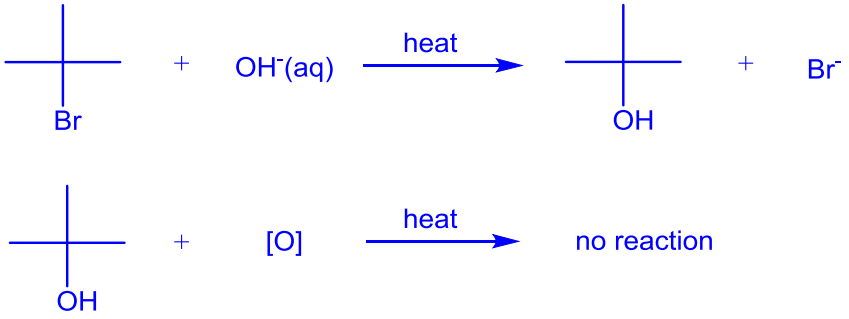
B – correct as substitution of 2-hydroxybutane (secondary RX) gives butan-2-ol (secondary alcohol) which in turn undergoes oxidation to yield butanone with molecular formula C_4H_8O.



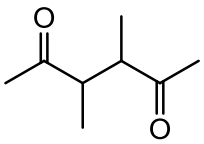
C – incorrect as reaction of 1-bromo-2-methylpropane (primary RX) will produce primary alcohol of substitution and in turn, result in carboxylic acid of molecular formula of $C_4H_8O_2$.



D – incorrect as 2-bromo-2-methylpropane (tertiary RX) undergoes substitution to give a tertiary alcohol. Tertiary alcohols do not undergo oxidation reactions. Molecular formula of tert-butanol is C_4H_9O.



27 Compound **X** shown below is an intermediate used to generate pyrroles which are essential to the production of many different chemicals in the pharmaceutical industry.



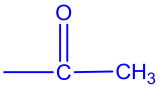
Compound **X**

Which sentence is correct for compound **X**?

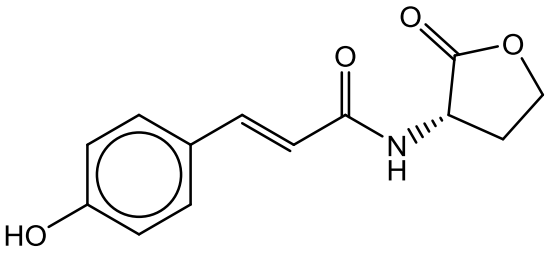
A It gives a silver mirror with Tollens' reagent.
B It decolourises acidified potassium manganate(VII).
C It does not give an orange precipitate with 2,4-dinitrophenylhydrazine.
D It gives yellow precipitate with alkaline aqueous iodine.

Answer: D

Compound **X** is a diketone.
Option A is incorrect since there is no aldehyde functional group in compound X and thus cannot give a silver mirror with Tollens' reagent.
Option B is incorrect since ketone cannot undergo further oxidation.
Option C is incorrect as ketone can undergo condensation with 2,4-DNPH to give an orange precipitate.

Option D is correct since it has  group and thus able to give a yellow precipitate with alkaline aqueous iodine.

28 4-coumaroyl-HSL is a new type of bacterial, quorum sensing signal compound. When one mole of 4-coumaroyl-HSL is heated under reflux with NaOH(aq) until no further reaction occurs, how many moles of NaOH will react?



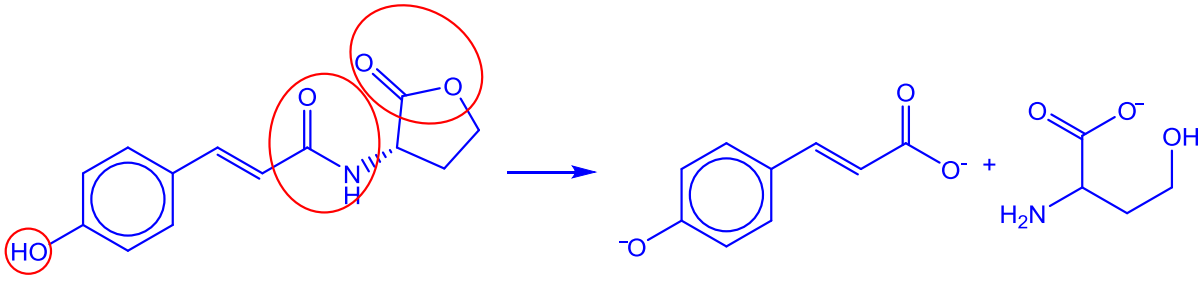
4-coumaroyl-HSL

A 1 **B** 2 **C** 3 **D** 4

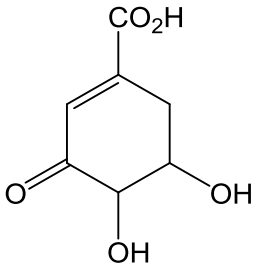
Answer: C

Phenol, amide and ester can undergo reaction with NaOH. Alcohol is neutral and will not undergo reaction with NaOH.

Functional group	**Type of reaction**	**Equation**
Phenol	Acid-base reaction	$RC_6H_4OH + NaOH \rightarrow RC_6H_4O^- + H_2O$
Amide	Basic hydrolysis	$RCONHR' + OH^- \rightarrow RCOO^- + R'NH_2$
Ester	Basic hydrolysis	$RCOOR' + OH^- \rightarrow RCOO^- + R'OH$

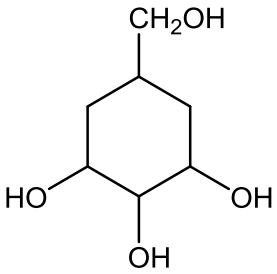


29 Shikimic acid is found in star anise. The following compound **Y**, is the intermediate that can be used to form shikimic acid. When $LiAlH_4$ is added to compound **Y**, what is the product obtained?

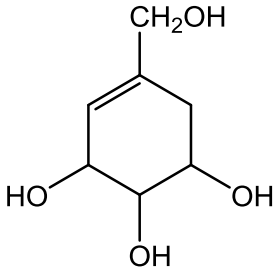


Compound **Y**

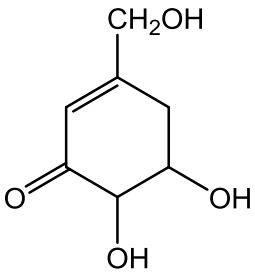
A



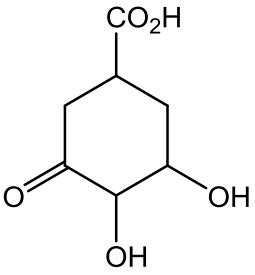
B



C



D



Answer: B

$LiAlH_4$ is a reducing agent that can reduce carboxylic acid and ketone to primary and secondary alcohols respectively. However, it cannot reduce alkene.

30 Consider the following compounds below:

I $C_6H_5NH_2$ **II** CH_3CONH_2 **III** $CH_3CH_2NH_2$ **IV** $(CH_2CH_3)_2NH$

Which of the following shows the correct order of decreasing pK_b values for the above compounds?

A **II**, **III**, **I**, **IV**
B **II**, **I**, **III**, **IV**
C **III**, **IV**, **I**, **II**
D **IV**, **III**, **I**, **II**

Answer: B

The stronger the base, the lower the pK_b value. Basicity depends on the availability of lone pair of electrons on N atom to attract a proton.

II is an amide which is neutral so it would have the highest pK_b value.

I is the weakest base as the lone pair of electrons on N is delocalised into the benzene ring thus making the lone pair of electrons on N atom less available to attract a proton.

III is a stronger base than **I** due to the presence of an electron-donating ethyl group that increases the availability of lone pair of electrons on N atom to attract a proton.

IV is the most basic as it has 2 electron-donating ethyl groups which increase the availability of lone pair of electrons on N atom to attract a proton to a larger extent.

Section B

For each of the questions in this section, one or more of the three numbered statements **1** to **3** may be correct.

Decide whether each of the statements is or is not correct (you may find it helpful to put a tick against the statements that you consider to be correct).

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

No other combination of statements is used as a correct response.

31 *Use of the Data Booklet is relevant to this question.*

Which of the following species has the electronic configuration of [Ar] $3d^5\ 4s^1$?

1 Cr
2 Mn^+
3 Fe^{2+}

Answer: B (1 and 2 only)

1 – Cr: [Ar] $3d^5\ 4s^1 \Rightarrow$ correct
2 – Mn: [Ar] $3d^5\ 4s^2$
Thus Mn^+: [Ar] $3d^5\ 4s^1 \Rightarrow$ correct
3 – Fe: [Ar] $3d^6\ 4s^2$
Thus Fe^{2+}: [Ar] $3d^6 \Rightarrow$ incorrect

32 The value of the ionic product of water, K_w, varies with temperature.

temperature / ^oC	K_w / $mol^2\ dm^{-6}$
25	1.0×10^{-14}
62	1.0×10^{-13}

Which of the following statement is correct?

1 The ionic dissociation of water is an endothermic process.
2 Water is a neutral liquid at 62 $^\circ$C.
3 pH < 7 at 62 $^\circ$C.

Answer: A (1, 2 and 3)

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

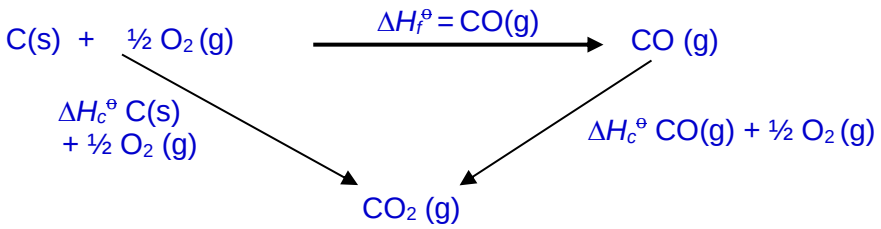
$$K_w = [H^+(aq)]\,[OH^-(aq)]$$

1 – When temperature increases, K_w increases. Position of equilibrium shifts to the right. Therefore the forward reaction is endothermic.
2 – $[H^+] = [OH^-]$ as water dissociates to the same extent.
3 – Since water is neutral, $[H^+] = [OH^-] = (1.0 \times 10^{-13})^{1/2} = 3.16 \times 10^{-7}$ mol dm^{-3}
pH = –log $(3.16 \times 10^{-7}) = 6.5 < 7$

33 Which of the following has the same value as the standard enthalpy change of formation, $\Delta H_f^{\ominus}$, of carbon monoxide?

1 $\Delta H_{combustion}^{\ominus}$ (C) − $\Delta H_{combustion}^{\ominus}$ (CO)
2 $\Delta H_f^{\ominus}$ (CO_2) − $\Delta H_{combustion}^{\ominus}$ (CO)
3 ½ $\Delta H_f^{\ominus}$(CO_2)

Answer: B (1 & 2 only)



$\Delta H_f^{\ominus}$ CO(g) = $\Delta H^{\ominus}_{combustion}$(C) − $\Delta H^{\ominus}_{combustion}$(CO)

$\Delta H_f^{\ominus}$ CO(g) = $\Delta H^{\ominus}_{formation}$($CO_2$) − $\Delta H^{\ominus}_{combustion}$(CO)

Note:

The **standard enthalpy change of combustion** of a compound is defined as the enthalpy change when 1 mol of the substance is burnt completely in oxygen under standard conditions of 298 K and 1 atm.

$\Delta H^{\ominus}_{combustion}$(C) : C(s) + O_2(g) → CO_2(g)

$\Delta H^{\ominus}_{combustion}$(CO) : CO(g) + ½$O_2$(g) → CO_2(g)

The **standard enthalpy change of formation** of a compound is defined as the enthalpy change when 1 mol of the substance is formed from its elements under standard conditions of 298 K and 1 atm. (Elements must be in most stable physical form).

$\Delta H_f^{\ominus}$ (CO_2(g)) : C(s) + O_2(g) → CO_2(g)

Thus, $\Delta H_{combustion}$(C) and $\Delta H_{formation}$(CO_2(g)) are the same.

34 *Use of the Data booklet is relevant to this question.*

In the Daniell cell, copper and zinc electrodes are immersed in a solution of copper(II) sulfate and zinc sulfate respectively.

The two half-equations for a Daniell cell are given below

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$$

Which statements about this cell are correct when it is used?

1 The electron flow from the zinc electrode to the copper electrode in the external circuit.
2 The overall cell reaction is $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$.
3 The cell potential is +1.10V.

Answer: A (1, 2 and 3)

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\ominus = +0.34\ V$$

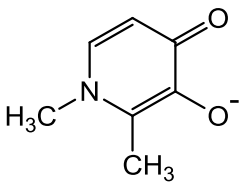
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad E^\ominus = -0.76\ V$$

Since $E^\ominus_{(Cu2+/Cu)}$ is more positive than $E^\ominus_{(Zn2+/Zn)}$, thus reduction occurs at copper electrode (cathode) whereas oxidation occurs at zinc electrode (anode).

Overall equation: $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
$E_{cell}^\ominus = E_{red}^\ominus - E_{oxd}^\ominus = 0.34 - (-0.76) = +1.10\ V$

Hence, all the options are correct.
Option 1 is correct as electron always flow from the anode to cathode.
Option 2 is correct since $E_{cell}^\ominus$ is positive, thus reaction is feasible.
Option 3 is correct as shown in the calculation above.

35 A neutral, red complex, Fe**A**$_3$, is formed when a bidentate ligand **A** is added to an aqueous solution of Fe^{3+} ions.



A

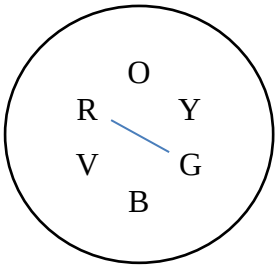
Which of the following statement is correct?

1 The complex has a coordination number of 3.
2 The complex absorbs radiation in the blue-green region of the visible spectrum.
3 The complex has a smaller energy gap between d-orbitals compared to yellow $[Fe(H_2O)_6]^{3+}$.

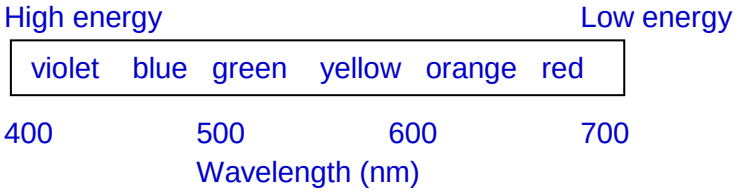
Answer: C (2 & 3 only)

1 – **A** is bidentate, as the complex formed is neutral, hence there must be 3 ligands forming 2 coordinate bonds each to balance out the Fe^{3+}, forming an octahedral complex (coordination number 6).

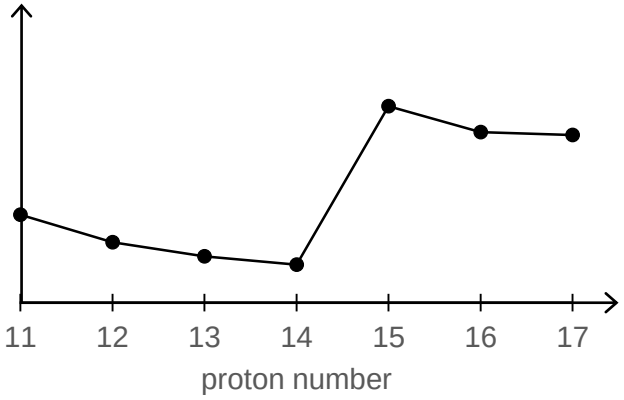
2 – The colour of the complex is the complementary colour to the wavelengths absorbed.



3 – As seen from the colours, the red complex is due to blue-green light being absorbed, with a lower wavelength or higher energy than the violet light that is absorbed to give yellow $[Fe(H_2O)_6]^{3+}$, hence the energy of the light absorbed is lower in the red complex, which corresponds to a smaller energy gap.



36 The graph shows how a property from Na to C*l* in Period 3 varies with proton number.



What is this property?

1 Ionic radius
2 First ionisation energy
3 Electronegativity

Answer: D (1 only)

1 – For each **isoelectronic series**, as we go across a period, nuclear charge increases. The electrons are pulled closer to the nucleus so the ionic radius decreases. Thus, the cationic radius decreases from $Na^+ > Mg^{2+} > Al^{3+} > Si^{4+}$ and anionic radius decreases from $P^{3-} > S^{2-} > Cl^-$
The anions are much larger than the cations because anions have one more filled electron shell, hence there is a larger shielding effect resulting weaker attraction of the outermost electrons from the nucleus.

2 – Ionisation energy generally increases across a period due to the increase in nuclear charge and a decrease in atomic radii.

3 – Recall the definition of electronegativity. Electronegativity is a measure of the ability of an atom in a covalent bond to attract the bonding electrons.
Electronegativity **increases** across the period. From Na to Cl, atomic radius **decreases** and the nucleus has **more attraction** to bonding electrons.

37 Williamson synthesis is one of the better methods to prepare ethers, R-O-R'. It involves a S_N2 displacement of halide ion in halogenoalkane (R'X) by an alkoxide ion nucleophile (RO^-) as shown.

$$R\text{-}O^- + R'\text{-}X \rightarrow \underset{\text{ether}}{R\text{-}O\text{-}R'} + X^-$$

Which of the following statements are true?

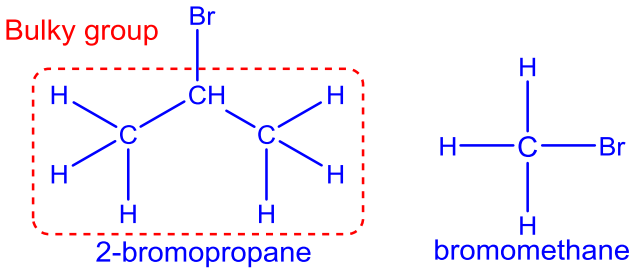
1 The rate equation involved is rate=k[RO^-][R'X]
2 The reaction involving bromomethane will be faster compared to chloromethane.
3 The reaction involving 2-bromopropane will be faster compared to bromomethane.

Answer: B (1 & 2 only)

1 – Correct as a S_N2 mechanism consist both halogenoalkan and alkoxide ions present in the rate-determining step of the mechanism.

2 – Correct since C-Br bond is longer than C-C*l* bond, thus C-Br bond (240 kJ mol^{-1})is weaker than C-C*l* (340 kJ mol^{-1})and more easily broken, thus the reaction involving bromoethane will be faster.

3 – Incorrect since presence of 2 bulky methyl groups in 2-bromopropane hinders approach (steric hindrance) of the nucleophile to the halogenoalkane, making bond formation difficult. Hence, the reaction involving 2-bromopropane should be slower than bromomethane.



38 Cars are fitted with a catalytic converter. What reactions typically occur in a catalytic converter?

1 $2NO + 2CO \rightarrow N_2 + 2CO_2$

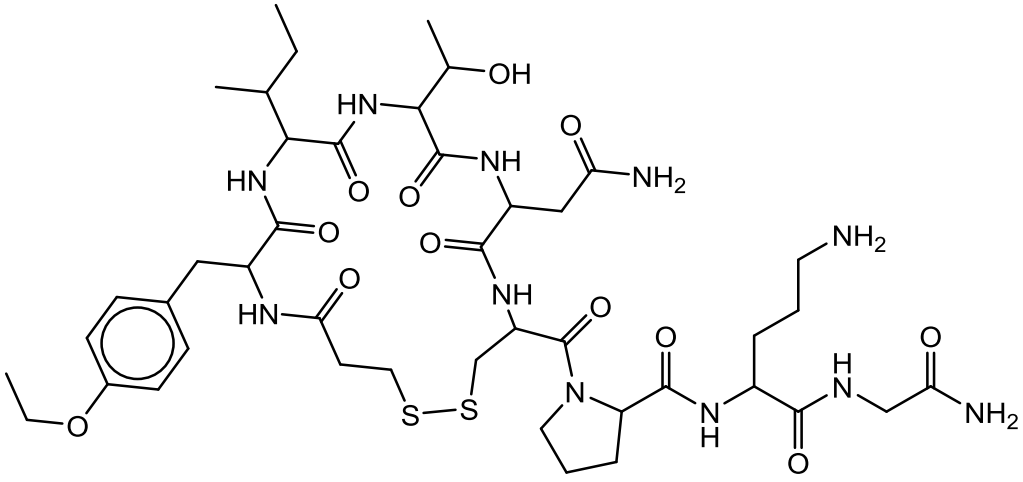
2 $C_xH_y + (\frac{x}{2} + \frac{y}{4})\ O_2 \rightarrow xCO + (\frac{y}{2})H_2O$

3 $CO_2 + NO \rightarrow CO + NO_2$

Answer: D (1 only)

Catalytic converters are used to remove pollutants such as CO, NO_x and unburnt hydrocarbons to form less harmful CO_2, N_2 and H_2O. Thus, options 2 and 3 are incorrect as CO and NO_2 should not be formed.

39 Atosiban, a protein, is used as an intravenous medication as a birth labour repressant to halt premature labour.

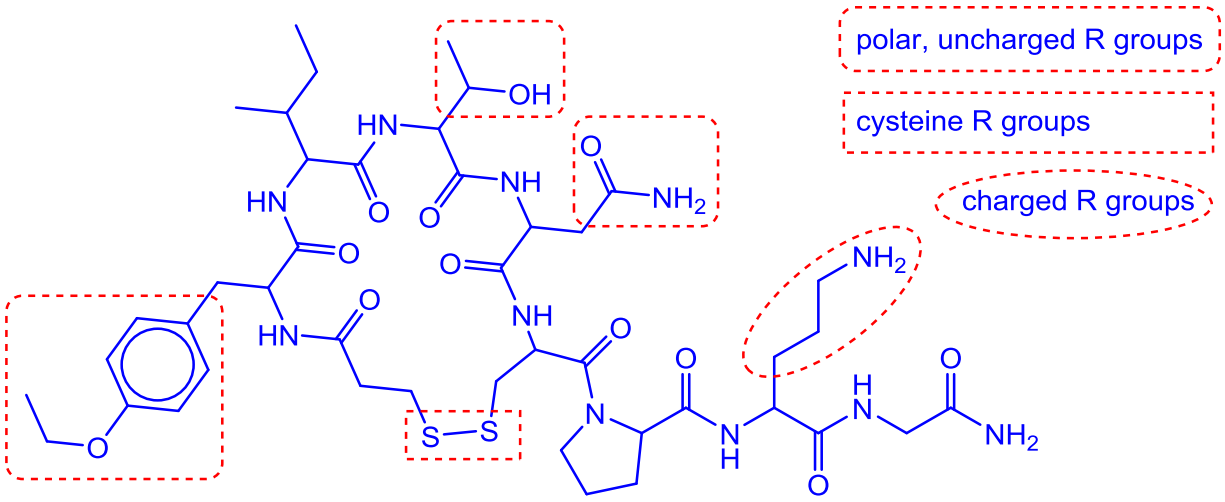


Atosiban

Which of the following R group interactions in the protein are possible?

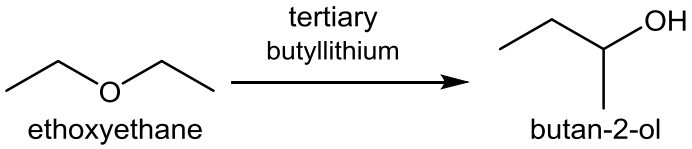
1 Hydrogen bond
2 Disulfide bond
3 Ionic bond

Answer: B (1 and 2)



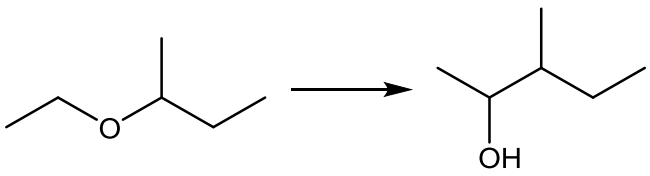
1 – Correct as a there are polar uncharged R groups which can forming hydrogen bonding.
2 – Correct since there is a S-S bond in the protein.
3 – Incorrect since there is only 1 charged R group present in the protein (a positively charged $–CH_2CH_2CH_2NH_3^+$ group). For ionic bonding to form, there must be at least 2 charged R groups and each of **opposite** charge.

40 The isomerisation of ethoxyethane to produce the corresponding alcohol is shown below.

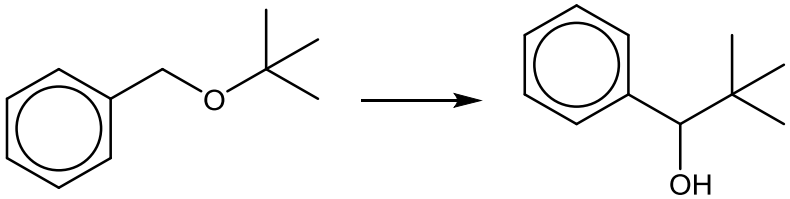


Which of the following shows the correct product formed under the same conditions?

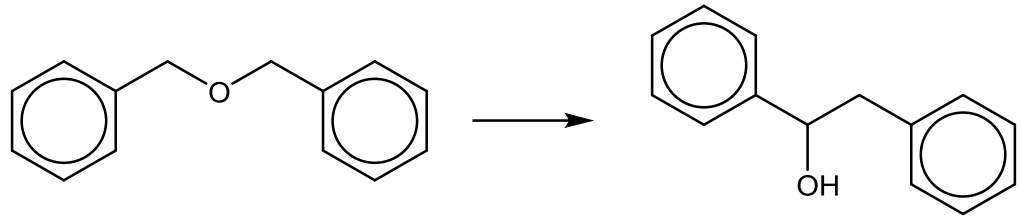
1



2

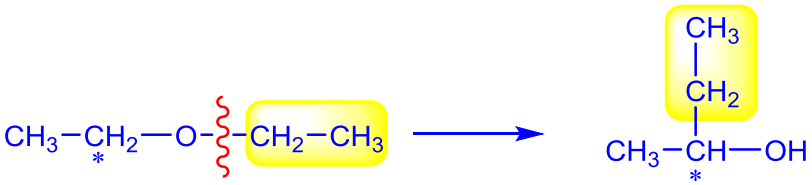


3



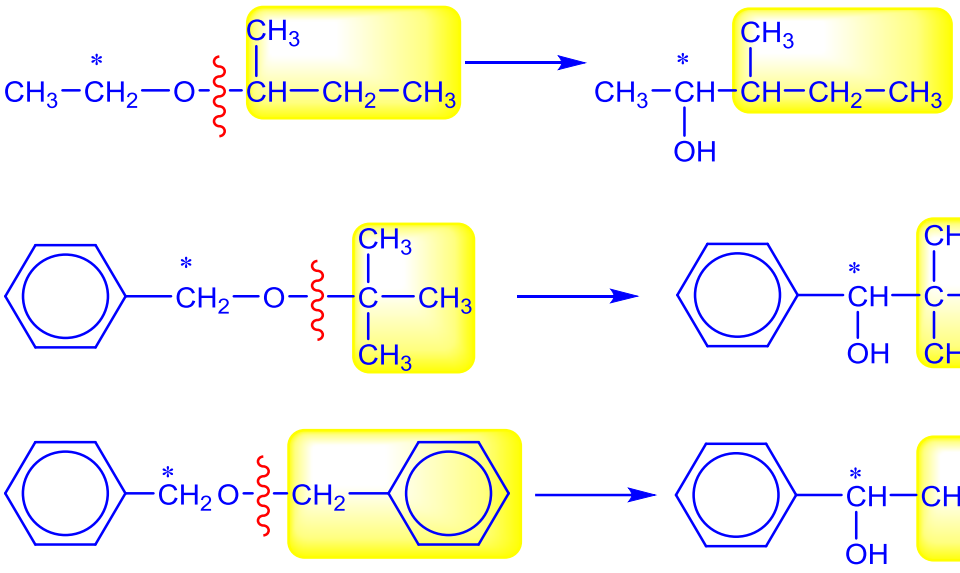
Answer: A (1, 2 and 3)

According to the scheme given,



The ethyl group next to the O is shifted to the C*.

Thus, following this pattern,



1	**A**	11	**C**	21	**A**	31	**B**
2	**D**	12	**C**	22	**C**	32	**A**
3	**B**	13	**D**	23	**C**	33	**B**
4	**B**	14	**D**	24	**A**	34	**A**
5	**D**	15	**B**	25	**C**	35	**C**
6	**A**	16	**C**	26	**B**	36	**D**
7	**B**	17	**A**	27	**D**	37	**B**
8	**B**	18	**D**	28	**C**	38	**D**
9	**B**	19	**C**	29	**B**	39	**B**
10	**D**	20	**B**	30	**B**	40	**A**