

Instructions for students

- Write your name and roll no. at the top of the first pages of all problems.
- This examination paper consists of 32 pages of problems including answer boxes.
- Total marks of INChO 2011 paper is 102 and the scores will be normalized to 100 marks. **
- You have 3 hours to complete all the problems.
- Request the supervisor to provide you with rough sheets for rough work.
- **Use only a pen to write the answers in the answer boxes. Anything written by a pencil will not be considered for assessment.**
- All answers must be written in the appropriate boxes. Anything written elsewhere will not be considered for assessment.
- For calculations, you must show the main steps.
- Use only a non-programmable scientific calculator.
- For objective type questions: Mark **X** in the correct box. Some of the objective questions may have more than one correct choice.
- Values of fundamental constants required for calculations are provided on page 2.
- A copy of the Periodic Table of the Elements is provided at the end of the paper.
- Do not leave the examination room until you are directed to do so.
- The question paper will be uploaded on the HBCSE website by 1st February 2011.

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Fundamental Constants

Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Electronic charge	$e = 1.602 \times 10^{-19} \text{ C}$
Molar gas constant	$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $= 8.314 \text{ K Pa} \cdot \text{dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$ $= 0.082 \text{ L} \cdot \text{atm K}^{-1} \text{ mol}^{-1}$
1 atomic mass unit (1u)	$= 931.5 \text{ MeV}/c^2$
1 eV	$= 1.602 \times 10^{-19} \text{ J}$
Rydberg constant	$R_H = 2.179 \times 10^{-18} \text{ J}$
Mass of electron	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Planck's constant	$h = 6.625 \times 10^{-34} \text{ Js}$
Speed of light	$c = 2.998 \times 10^8 \text{ ms}^{-1}$
Acceleration due to gravity	$g = 9.8 \text{ ms}^{-2}$
Density of mercury	$= 13.6 \times 10^3 \text{ kg m}^{-3}$
Faradays Constant	$= 96500 \text{ C}$

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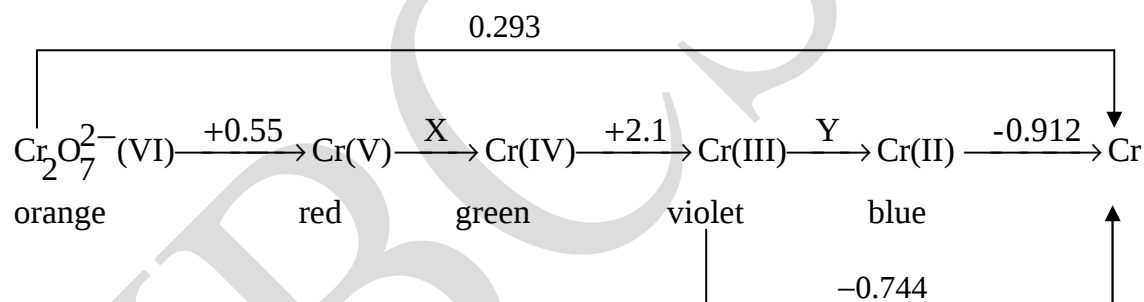
Roll No.

Problem 1

17 Marks

Chromium, the first element in Group 6 is a steely-gray, lustrous, hard metal. The name of this element is derived from the Greek word *chrōma* meaning colour because many of its compounds are intensely coloured. This element was discovered by Louis Nicolas Vauquelin in the mineral crocoite (lead chromate).

The diagram indicating the standard potential values connecting species of an element present in different oxidation states is known as Latimer diagram. In such a diagram, the most oxidized form of an element is represented at the extreme left, and in successive species the oxidation number of the element goes on decreasing from left to right. The numerical values of E° (volt) are written above the lines joining the successive species. Latimer diagram for chromium is presented below. (All data refer to pH = 1)



- 1.1 Calculate the values of X and Y in the above Latimer diagram.

(1.5 marks)

- 1.2 With appropriate calculations, show Cr (IV) disproportionate to Cr (III) and Cr (VI).

(2 marks)

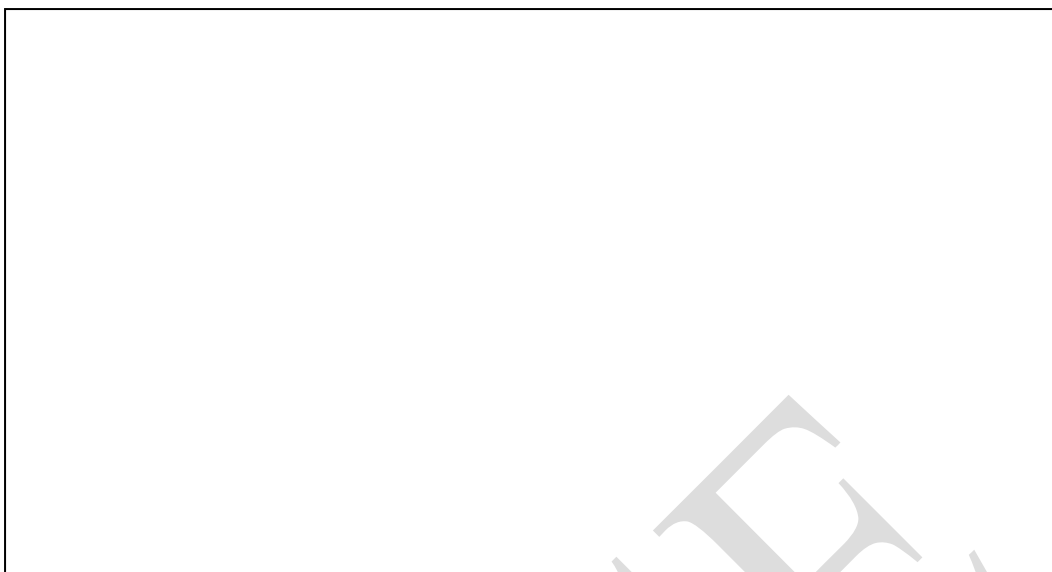
- 1.3 $[\text{Cr}_2\text{O}_7^{2-}]/[\text{Cr}^{3+}]$ system is used as an oxidising agent. Write the balanced chemical equation for this half cell reaction.

(0.5 mark)

- 1.4 Calculate the change in the potential of the above system, if the pH is changed from 1 to 3 ($T = 298 \text{ K}$) ($E^\circ(\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}) = 1.33 \text{ V}$). (Note: With change in pH in this range, assume that $[\text{Cr}_2\text{O}_7^{2-}]$ and $[\text{Cr}^{3+}]$ practically remain constant).

(2 marks)

- 1.5 100 cm^3 of 0.1N potassium dichromate is titrated with 0.1N Fe(II) solution. Calculate the potential of the system when 100 cm^3 of 0.1N Fe(II) is added.
($\text{pH}=1$, $E^\circ = \text{Fe}^{3+}/\text{Fe}^{2+} = 0.77\text{V}$)



(2.5 marks)

In Chrome plating, a layer of chromium is electroplated on a metal object. In this process, chromium trioxide (CrO_3) is used as the source of chromium. In a typical setup, an electrolytic cell was filled with 150 L solution containing chromium trioxide (in this solution, chromium trioxide exists as chromic acid H_2CrO_4). The electrolysis was carried out for 8 hrs with a current of 2000A. The object that acted as cathode gained 350g of chromium at the end of 8 hrs. At cathode, in addition to deposition of chromium, another reaction involving liberation of a gas also took place. Hence, the efficiency for the electrodeposition of chromium was less than 100%.

- 1.6 Write balanced equation for the half cell reaction resulting in deposition of chromium at the cathode. Using this equation and the given data, calculate the percent efficiency for the electrodeposition of metallic chromium.

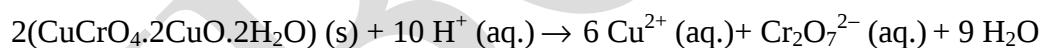


(2.5 marks)

- 1.7 Write balanced chemical equations for the half cell reactions involving liberation of gases at cathode and anode respectively. Using these equations, calculate the volume of the gases liberated at the cathode and the anode ($T = 298 \text{ K}$ and $P = 1.013 \times 10^5 \text{ N/m}^2$).

(3 marks)

- 1.8 An insecticide formulation contains copper (II) oleate $\text{Cu}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ (Molar mass = 626). A 9.9 g sample of the insecticide preparation was wet-ashed with a sulfuric-nitric acid mixture to destroy its organic components. The copper in the sample was then precipitated as the basic chromate, $\text{CuCrO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$, with an excess of potassium chromate. The solid was filtered, washed free of excess reagent, and then redissolved in acid:



Titration of the liberated dichromate required 15.7 mL of 0.232 M Fe^{2+} . Calculate the percentage of copper (II) oleate in the sample.



(3 marks)

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Problem 2

11 marks

Most elements form oxides and hydroxides with different characteristics. Often, regular periodic trends are observed in these oxides and hydroxides. Hydroxides of Na and Mg are distinctly alkaline, while oxides of N and S are distinctly acidic.

- 2.1 Identify the nature of the following oxides of Group 13 elements:- (strike off whichever is **not correct**)

B_2O_3	☐ acidic	☐ basic	☐ amphoteric	☐ neutral
Al_2O_3	☐ acidic	☐ basic	☐ amphoteric	☐ neutral
Tl_2O_3	☐ acidic	☐ basic	☐ amphoteric	☐ neutral

(1.5 marks)

Boron the first member of group 13, forms a hydride BH_3 . This hydride exists as a dimer (B_2H_6).

- 2.2 Draw the structure of B_2H_6 .



(0.5 mark)

The unusual bond present in B_2H_6 is a -

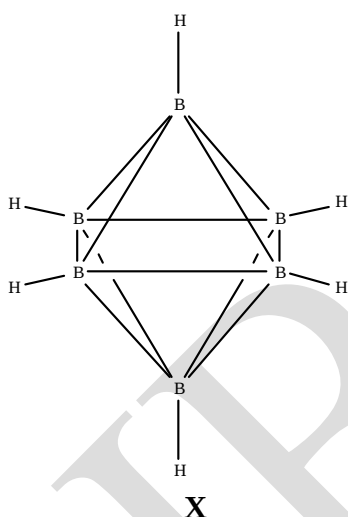
- | | | | |
|------------------------------|--------------------------|-------------------------------|--------------------------|
| a) Two centered $3e^-$ bond | ☐ | b) Three centered $2e^-$ bond | ☐ |
| c) Four centered $2e^-$ bond | ☐ | d) Four centered $4e^-$ bond | ☐ |

(0.5 mark)

- 2.3 Diborane reacts violently with water and releases hydrogen. Write a balanced equation of this reaction.

(1.5 marks)

A variety of polymeric boranes and anionic boron hydrides are formed. *Closo-boranes* are the compounds having formula $B_nH_n^{2-}$. They have closed regular polyhedral frameworks of boron atoms, with each boron bound to the neighbouring boron atoms and a terminal hydrogen atom. An example is $B_6H_6^{2-}$ which has the following structure (X).



A neutral *nido-borane* (Y) is formed by removing an apical Boron atom from X and adding the requisite number of hydrogens.

- 2.4 Draw the structure of Y.

(2 marks)

The corresponding *arachno-boranes* are formed by removal of two neighbouring apical boron atoms in **X**.

- 2.5 Write the general formula of *arachano-boranes*.

(0.5 mark)

- 2.6 Draw the structures of the possible *arachano-boranes* derived from **X**.

(2 marks)

Carboranes are neutral compounds which are formed by isoelectronic replacement of Boron by Carbon in boranes.

- 2.7 Write the molecular formula of a carborane (**Z**) obtained by replacing two Boron by carbon atoms in *closo-dodecaborane* anions.

(0.5 mark)

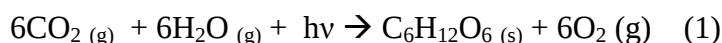
- 2.8 Draw the structures of all possible isomers of **Z** (show only boron-carbon framework).

(2 marks)

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Problem 3**18 Marks****Thermodynamics of a sustainable bio process**

- A. Photosynthesis is a bio process by which plants make energy rich molecules from low energy molecules with the help of energy from sun light. The photosynthesis of glucose can be represented as



The energy of one mole of a photon of wave length λ is known as one Einstein.

- 3.1 48 Einsteins of 650nm are absorbed by a plant for the production of 1 mole of glucose as given in (1). Calculate the % efficiency for the production of glucose by photosynthesis. The energy required for the formation of 1 mole of glucose is 2870 kJ.

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(1.5 marks)

- 3.2 On an average, solar radiation produces 7×10^{14} kg of glucose annually on earth. Calculate the annual decrease in the CO_2 level in the troposphere in ppm, due to photosynthesis. (1ppm = 1 g of CO_2 per 10^3 kg of air in troposphere). Assume that the total mass of air envelope surrounding the earth is 5.0×10^{15} kg and 80% of it is present in the troposphere.

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(1.5 marks)

- 3.3 Heats of combustion of graphite and hydrogen at 298K are $-393.5 \text{ kJmol}^{-1}$ and $-285.8 \text{ kJmol}^{-1}$ respectively. If on combustion 1 g of glucose releases 15.58 kJ of energy, calculate the heat of formation of glucose at 298K.

(1.5 marks)

Diabetic patients have to monitor their blood glucose level periodically. Home glucometer is an appliance used for this purpose. This device consists of a disposable test strip with carbon working electrodes and a reference electrode. The working electrode is covered with the enzyme glucose oxidase, which catalyses the reaction of glucose with dissolved oxygen.

- 3.4 Write balanced equation for the reaction of glucose with O_2 in which O_2 is converted to H_2O_2 .

(0.5 mark)

The H_2O_2 generated is oxidized at the second working electrode generating a current, which is proportional to the glucose present in the sample. Typically, 5mmoles of glucose produces 2.5 mA current.

- 3.5 A weight lifter lifts a weight of 160kg through a height of 2.4m. Assuming all the energy required for this task is obtained by the combustion of glucose, calculate the change in the current produced by a sample of blood of the weight lifter. Same volume of blood (5mL) is tested both before and after lifting the weight and the total volume of blood in his body is 5L. (1 g of glucose releases 15.58 kJ of energy)

(1.5 marks)

Electrochemical oxidation of glucose to CO_2 and H_2O , which is the reverse of photosynthesis, is an important reaction and it can be used in the construction of a fuel cell. In a fuel cell, a working substance called fuel is electrochemically oxidised by O_2 . A fuel cell was devised with glucose under suitable pH conditions.

- 3.6 Write balanced equations for the half cell reactions corresponding to oxidation of glucose.

(1.5 marks)

- 3.7 Calculate the emf of this fuel cell at 25°C if ΔH° and ΔS° of photosynthesis are $2.82 \times 10^6 \text{ Jmol}^{-1}$ and -182 Jmol^{-1} respectively.

(1 mark)

- 3.8 Variation of emf of an electrochemical cell with temperature is known as the temperature coefficient of the cell. If $\delta(\Delta G / \delta T)_p = -\Delta S$, calculate the temperature coefficient of the glucose fuel cell at 25°C from the data given in 3.7.

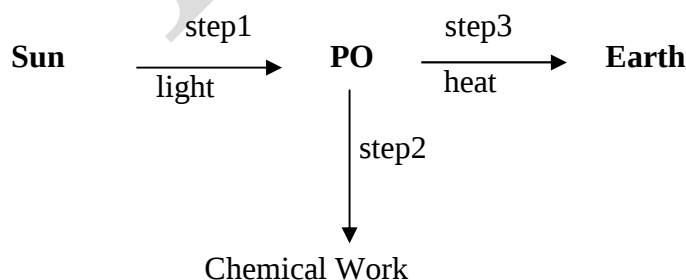
(1 mark)

- 3.9 A glucose fuel cell was designed to generate 4000Watts which was used to heat a room of 5m x 5m x 3m dimensions. The room is perfectly insulated and no heat flows out of the room. Calculate the time needed to increase the temperature of the room by 20°C, if the room was initially at 10°C and 1 atm. pressure. Assume that the air in the room behaves like an ideal gas and its molar heat capacity is 2.5R.

(2 marks)

- B. In photosynthesis, the Sun,(S) the Earth (E) and the Photosynthetic Organism (PO) can be considered as three different thermodynamic systems. The sun and the earth are at a constant temperature ($T_S = 5762K$; $T_E = 298.15K$) at constant pressure, volume and composition. The photosynthetic organism has a constant volume, temperature and pressure and $T_{PO} = T_E$.

The photosynthetic process is of three steps as shown



Scheme 1

- 3.10 Write the expressions for dU_S and dG_S for step1 in terms of T_S where U and G are internal energy and Gibbs free energy and S refers to the sun.

(1 mark)

Efficient plants need 60 photons to synthesize one glucose molecule.

- 3.11 Write the expression for the change in the internal energy of the sun $(\Delta U)_S$ and that of PO $(\Delta U)_{PO}$ in step (1) if the wave length of the absorbed photons is λ .

(1 mark)

- 3.12 What is the expression for the total entropy change of step 1, $(\Delta S)_{\text{step1}}$?

(1 mark)

In step (2), PO uses part of the energy absorbed in step (1) and transforms this into chemical energy in the synthesis of glucose. In this step PO does not exchange energy with its surroundings.

- 3.13 What is the total entropy change in step 2, $(\Delta S)_{\text{step2}}$ in terms of ΔG_{PO} ?

(1 mark)

In step (3), PO transmits to the earth the remaining energy that was not used in the synthesis of glucose.

3.14 Show that $\Delta S_{\text{step3}} = 0$



(1 mark)

T_S is very high and $1/T_S$ can be approximated to zero.

3.15 Under this condition, write the expression for the overall entropy change of Scheme 1.



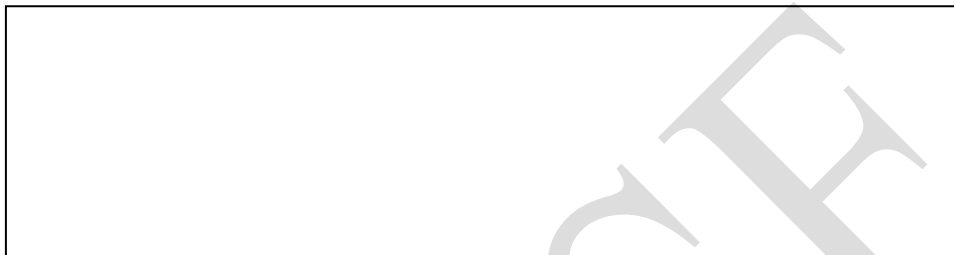
(1 mark)

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Problem 4**23 marks****Organosulphur Compounds**

Organosulphur reagents are useful in part due to the capacity of sulphur to utilize third shell orbitals for bonding besides its ability to occur in valence states higher than 2.

- 4.1 Draw the Lewis structure of thiosulphate ion ($\text{S}_2\text{O}_3^{2-}$).

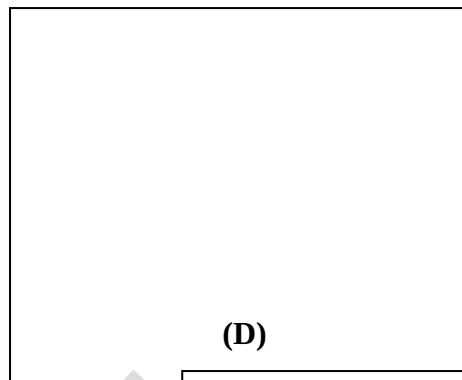
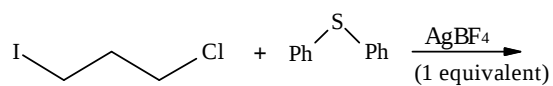
**(1 mark)**

- 4.2 Draw three non equivalent resonance structures of $\text{S}_2\text{O}_3^{2-}$.

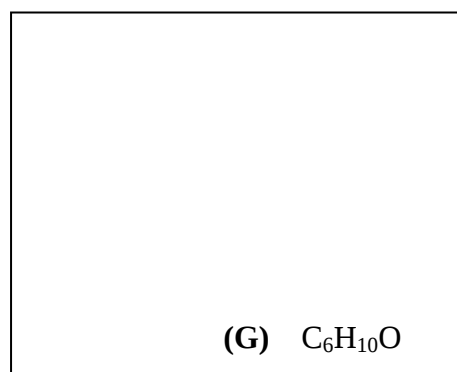
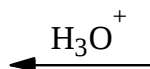
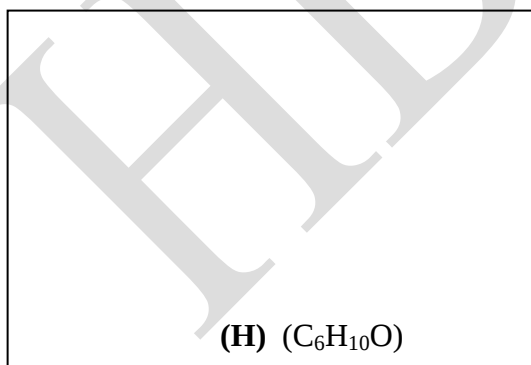
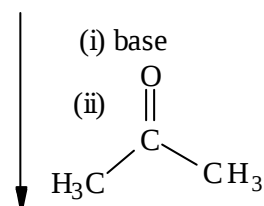
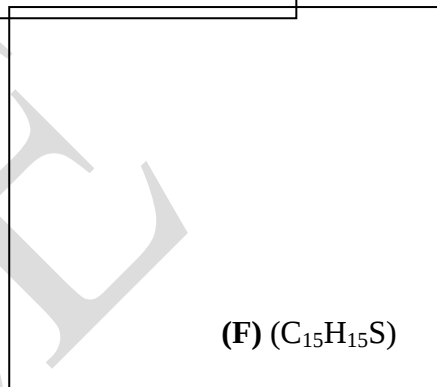
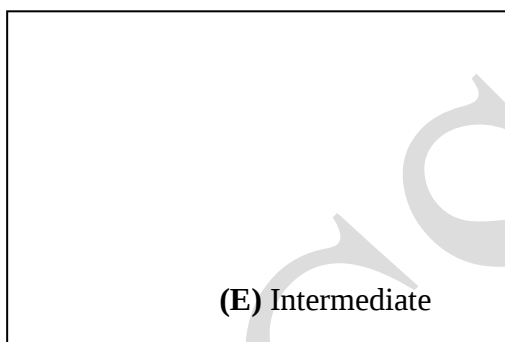
**(3 marks)**

Sulphur ylides are compounds in which positively charged sulphur is bonded to a negatively charged carbon atom (carbanion). Sulphur ylides are useful intermediates in synthesis.

- 4.3 Complete the following synthetic sequence. Product **H** gives a peak at 1740 cm^{-1} in the IR spectrum (Refer to Table 1 on page no. 22).

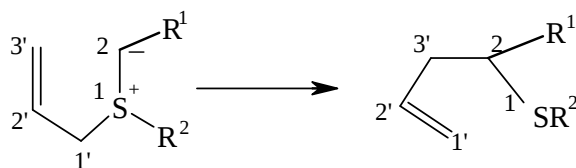


D NaH

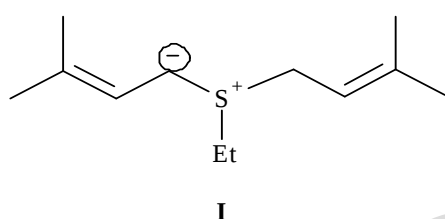


(6 marks)

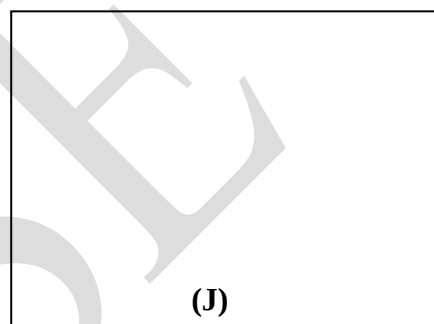
Sulphur ylides undergo rearrangements, when one of the substituents on the S atom is allylic. They are termed as [3,2] sigmatropic rearrangements (migration of σ bond) as the new σ bond is formed between 3' and 2 position as shown below:



- 4.4 Draw the structure of the product obtained from the [3,2] sigmatropic shift in the following ylide **I**.



[3,2]
sigmatropic
rearrangement



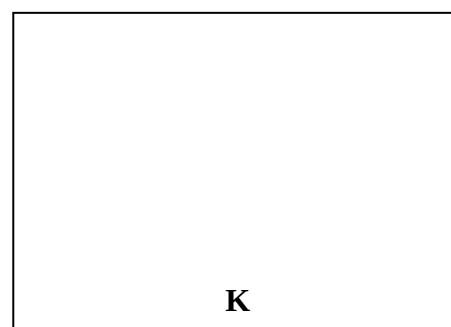
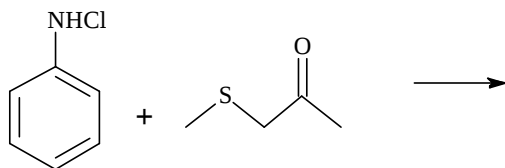
(1 mark)

- 4.5 What would be the structure of [1,2] sigmatropic shift in ylide **I**.

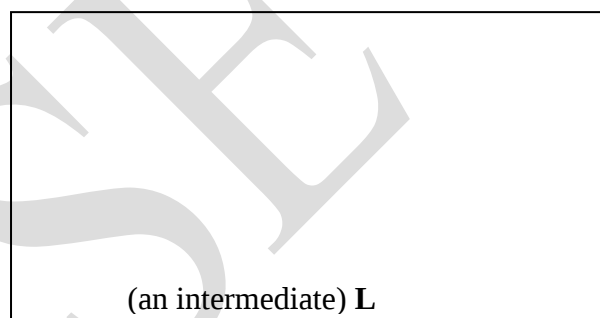
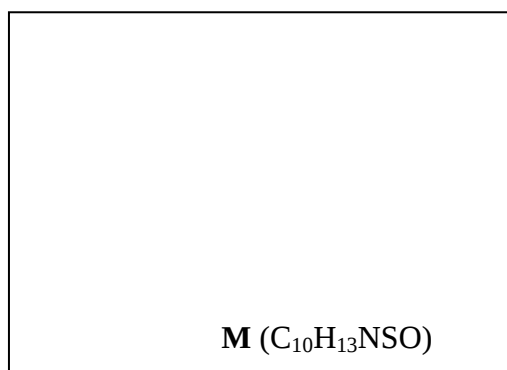


(1 mark)

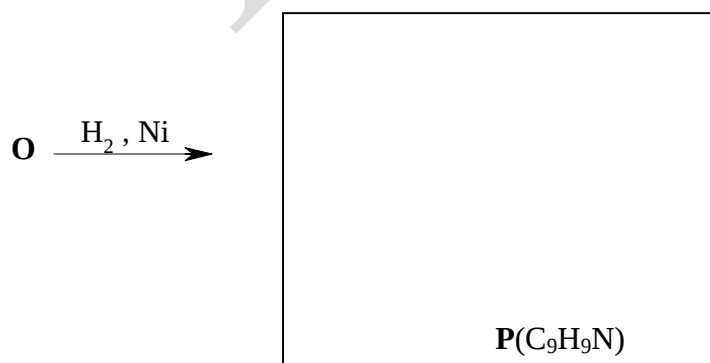
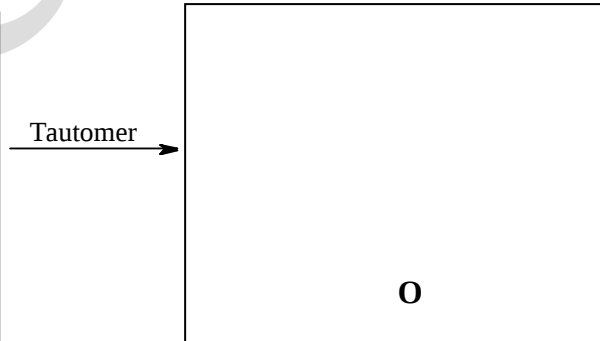
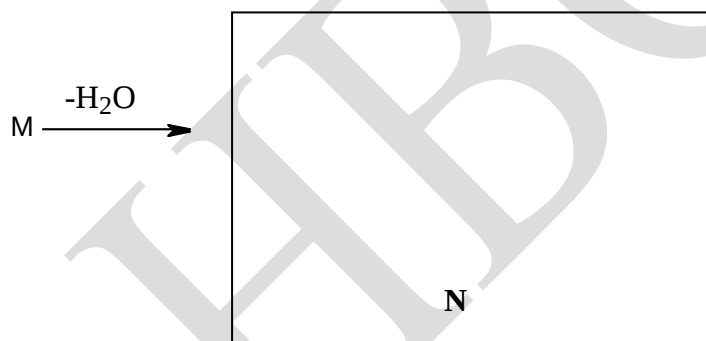
- 4.6 Organosulphur ylides find use as intermediates in the synthesis of compound **P** (C_9H_9N). Complete the following synthesis.



- i) Base (NEt_3),
ii) [3,2] sigmatropic rearrangement

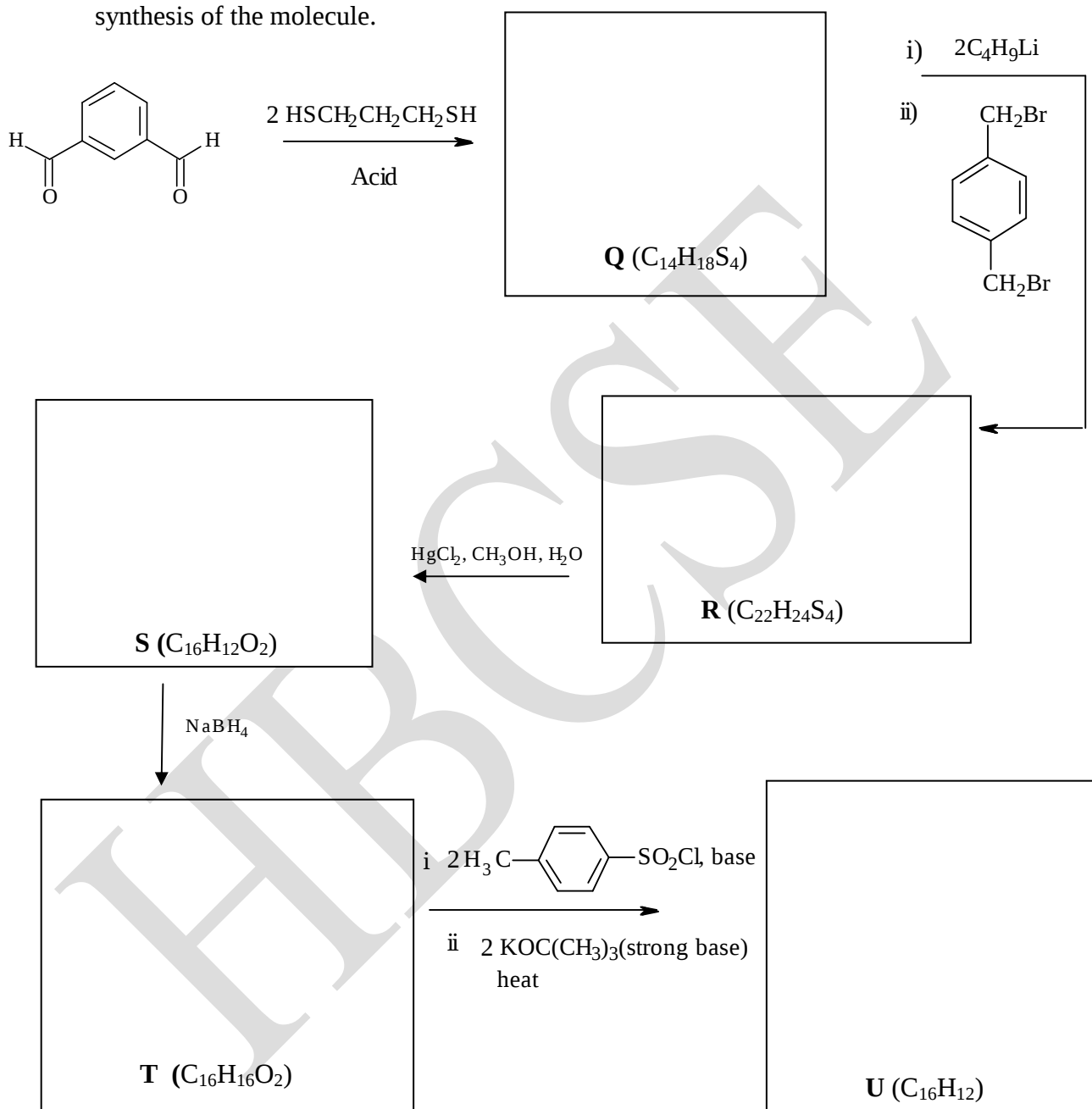


M gives a doublet at 3300 cm^{-1} in the IR spectra.
(Refer to IR table on Page 22)



(6 marks)

- 4.7 In the presence of certain substituents the polarity of carbonyl carbon is reversed. This reversal of polarity is called 'UMPOLUNG' and this is used to bring about synthesis of compounds which are otherwise difficult to synthesize. Complete the following synthesis of the molecule.



(5 marks)

Table 1: Important IR bands

Functional Group	Frequency (cm^{-1})
$-\text{NH}_2$ (doublet)	3400 – 3200
O – H	3600 – 3200
$\equiv \text{C} - \text{H}$	3340 – 3250
$= \text{C} - \text{H}$	3095 – 3075
$-\text{C} - \text{H}$	3000 – 2840
$-\text{C} = \text{O}$	1765 – 1650
$-\text{C} = \text{C}$	1650 – 1635
$\text{C} - \text{O}$	1310 – 1000

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Problem 5**17 marks****A. Chemistry of Main Group Elements**

Shapes of molecules containing a central p-block atom tend to be controlled by the number of electrons in the valence shell of the central atom. The valence shell electron pair repulsion model (VSEPR) provides a simple approach for predicting the shapes of such species.

- 5.1 a) Draw the Lewis structure of ClF_3 on the basis of VSEPR.

**(0.5 mark)**

- b) Lone pairs of electrons in the valence shell of the central atom in a molecule can occupy different positions. Draw all the possible structure/s of ClF_3 .

**(1 mark)**

- c) State the most stable shape that is predicted by the VSEPR model.

**(0.5 mark)**

5.2 Shape of triatomic molecules like SO_2 [$\text{O}=\text{S}=\text{O}$] can be explained on the basis of hybridization.

a) Give box structure diagrams of S atom in the ground, excited and hybridized states.

(2 marks)

b) Draw the shape of SO_2 molecule

(0.5 mark)

c) Do the electron pairs involved in π -bonds affect the shape of the molecule?

Yes

☐

No

☐

(0.5 mark)

A number of compounds of p-block elements are routinely used as reducing or oxidizing agents. Compounds of the last two elements of Group 14 (C group), Sn and Pb, are both oxidizing and reducing agents. Sn^{2+} compounds like SnO and SnCl_2 are well known reducing agents, while PbO_2 acts as an oxidizing agent.

5.3 i) Based on the above observations mark the correct statement

a) Sn^{2+} is more stable than Sn^{4+}

☐

b) Sn^{4+} is more stable than Sn^{2+}

☐

c) Pb^{2+} is more stable than Pb^{4+}

☐

d) Pb^{4+} is more stable than Pb^{2+}

☐

(1 mark)

- (0.5 mark)**

- $$\text{MnCl}_2 + \text{NaBiO}_3 \rightarrow \text{NaCl} + \quad +$$

(2 marks)

- 5.4** Complexes of iron exist with different numbers of unpaired electrons. For the given complexes, write the number of unpaired electrons and state whether they are high spin or low spin species.

Complex	No of unpaired electrons	Spin state
$[\text{Fe}(\text{CN})_6]^{4-}$		
$[\text{Fe}(\text{CN})_6]^{3-}$		
$[\text{FeCl}_4]^-$		
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$		

(4 marks)

- 5.5** The oxygen taken during respiration in human beings is carried through the blood stream with the help of haemoglobin. The latter is a tetramer containing four heme (iron-porphyrin) units. The oxidation state of iron in deoxyhaemoglobin is +2 and it is a high spin paramagnetic species. On binding with oxygen, the iron in haemoglobin changes its coordination sphere from 5 to 6. This results in the change in magnetic property. The value of magnetic moment in each unit of oxyhaemoglobin is

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(0.5 mark)

5.6 i) $[\text{IrCl}_6]^{2-}$ is a low spin octahedral complex, this is because

a) the central metal ion is in higher oxidation state.

☐

b) Ir belongs to third transition series.

☐

c) Cl^- , despite being a weak ligand, in this case acts as a strong ligand.

☐

d) it is a complex anion with -2 charge.

☐

(1 mark)

ii) Draw a simple labeled crystal field splitting diagram for $[\text{IrCl}_6]^{2-}$ showing distribution of electrons in the split d-orbitals.



(1 mark)

The f-block elements, lanthanides and actinides, are characterized by gradual filling of the 4f and 5f sub-shell respectively.

5.7 The most common oxidation state of lanthanides is 3+. This oxidation state of lanthanide ions arises due to the loss of two 6s electrons and one 5d electron in 4f/5d orbital. Besides 3+, some lanthanides like Ce, Sm and Eu also show other oxidation states.

Give the chemical equations for the general reactions of lanthanides (Ln) with i) water and ii) acid, and of cerium (Ce) with iii) oxygen and iv) fluorine.



(2 marks)

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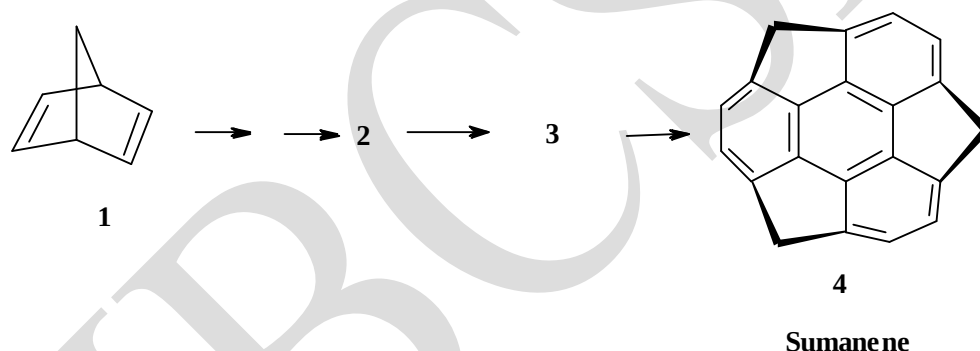
Problem 6

16 Marks

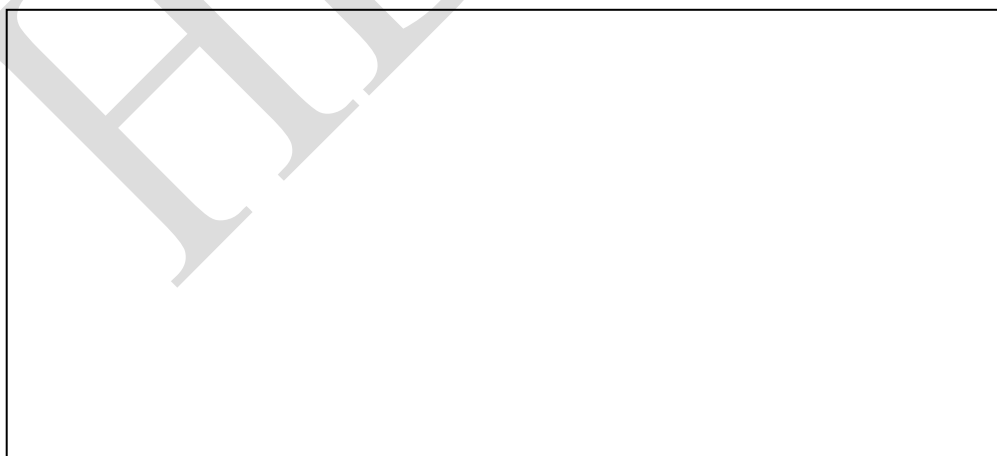
Chemistry of unusual organic compounds

Organic chemists have synthesized many compounds having unusual properties. Compounds having molecules which are apparently highly strained have also been synthesized in the laboratory. Many times the compounds have been named by chemists, taking into account the resemblance of the molecules with well known objects around us like basketane, pagodane, penguinone, garudane.

Sumanene (**4**), (Sanskrit *suman* = flower) is one such compound, whose molecule has a flower like shape. Synthesis of **4** starts with a simple bicyclic compound norbornadiene (**1**). **Conceptual trimerization** of **1** yields the crucial intermediate **2** ($C_{21}H_{18}$).



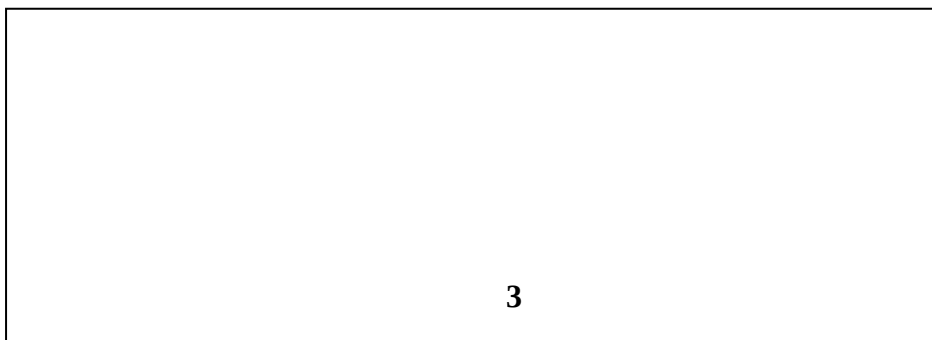
6.1 Draw the structure of two possible stereoisomers of **2**.



(1.5 marks)

2 undergoes a rearrangement in the presence of a Ru-catalyst to form a precursor **3** of sumanene. **3** on oxidation with a suitable reagent gives **4**.

6.2 Draw the structure of 3.



(1 mark)

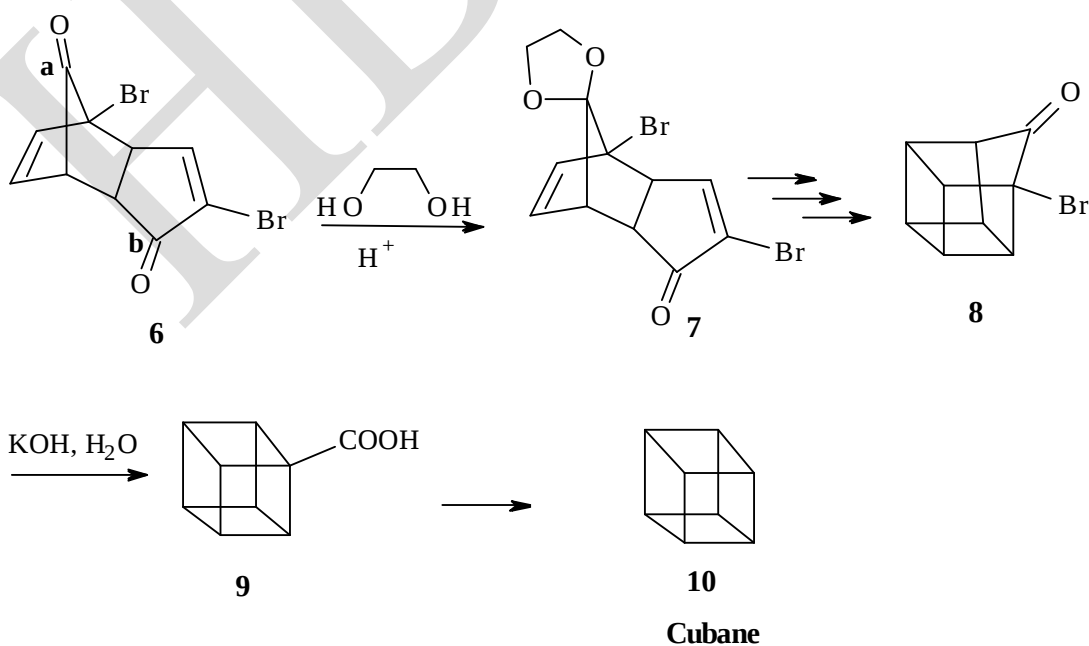
4 on oxidation with alkaline KMnO_4 gives 5.

6.3 Draw the structure of 5 ($\text{C}_{21}\text{H}_6\text{O}_3$).



(1 mark)

Cubane (**10**) is another interesting strained molecule. It is prepared through a reaction sequence with following intermediates.



6.4 The reaction of ethylene glycol with **6** takes place selectively on carbonyl group (**a**) as

(i) carbonyl group (**b**) has conjugated double bond ☐

(ii) carbonyl group (**a**) is sterically less hindered ☐

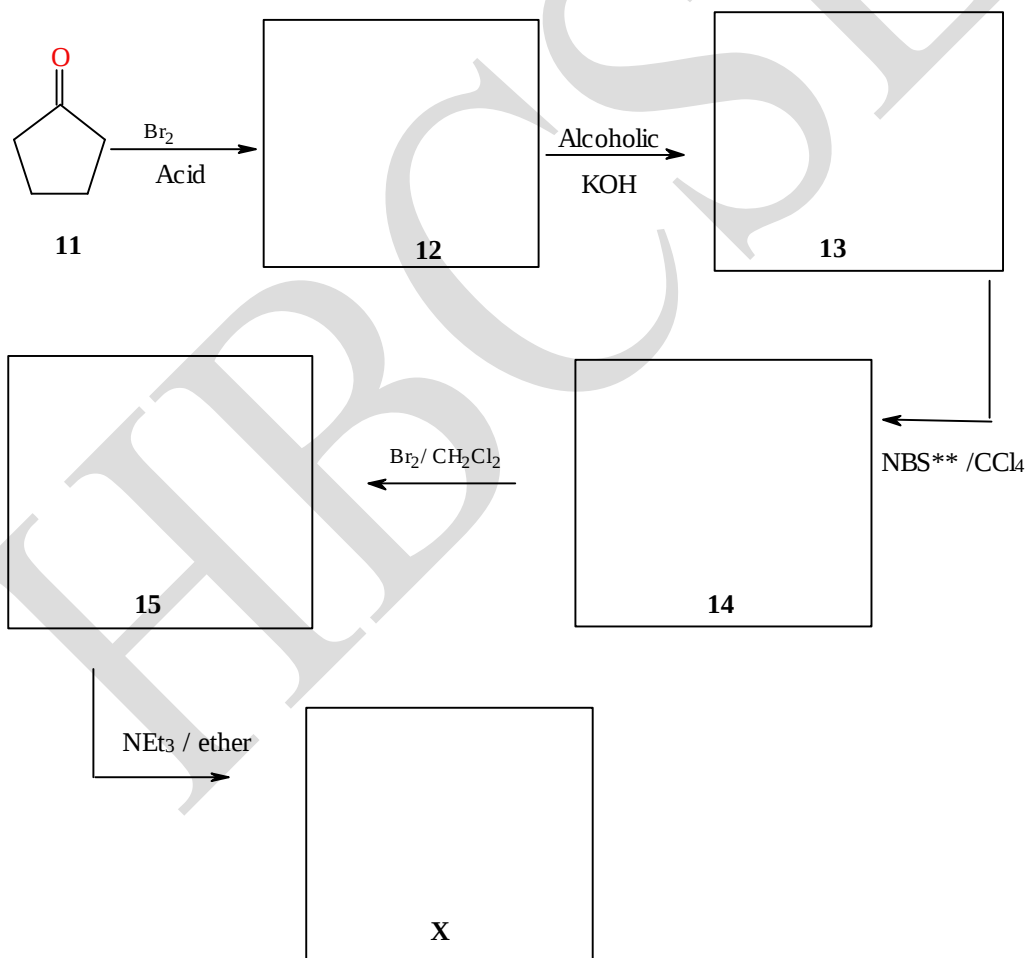
(iii) carbonyl group (**b**) is sterically less hindered ☐

(iv) the double bond adjacent to carbonyl group (**a**) assists the reaction ☐

(1 mark)

6 is obtained by dimerization of **X** through Diels – Alder reaction. **X** is obtained from cyclopentanone (**11**) as shown below.

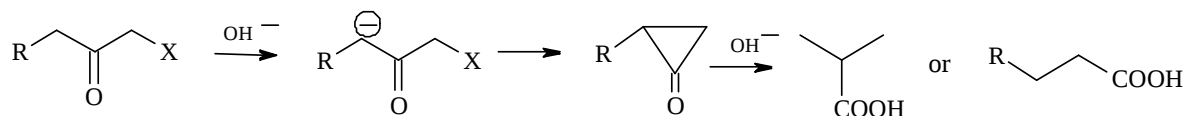
6.5 Draw the structures of the intermediates (**12-15**) and **X**.



** NBS is a reagent used to selectively brominate the allylic carbon.

(3.5 marks)

Favorskii rearrangement is a base catalysed reaction of α -haloketone to a carboxylic acid as shown below:



In the cubane synthesis conversion of **8** $\rightarrow$ **9** involves a Favorskii rearrangement.

6.6 Draw the structure of the neutral intermediate formed in the conversion of **8** $\rightarrow$ **9**.



(1 mark)

Cubane on chlorination gives dichlorocubane.

6.7 Draw the structures of all isomeric dichlorocubanes.



(1.5 marks)

6.8 Cubane is a _____

(i) tetracyclic compound

☐

(ii) pentacyclic compound

☐

(iii) hexacyclic compound

☐

(iv) octacyclic compound

☐

(1 mark)

Like cubane, propellane (C_5H_6) is another fascinating strained molecule, which can be synthesized from a carbene intermediate.

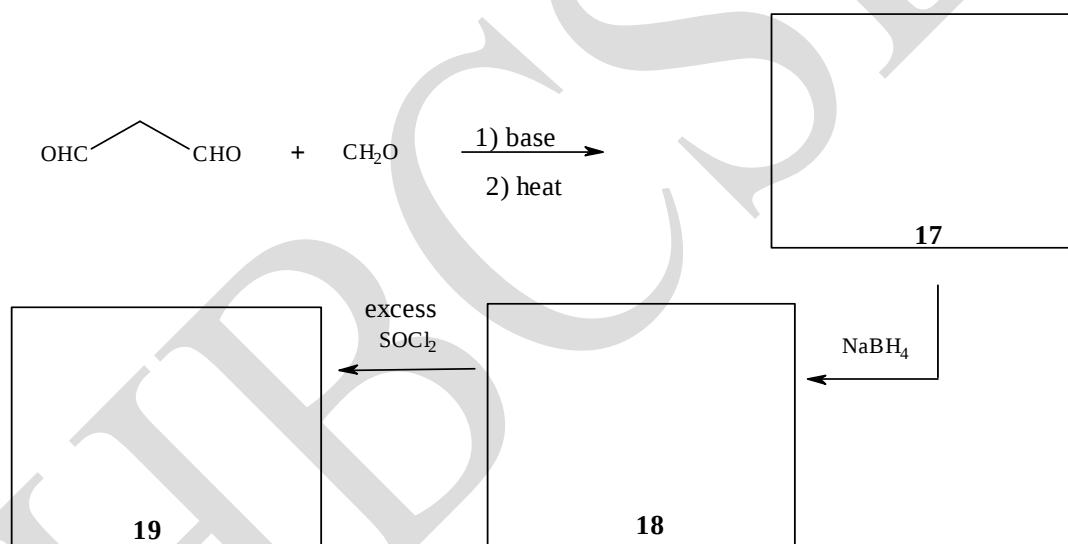
Haloforms, which contain acidic hydrogen, on heating with an alkali form an intermediate belonging to the class of carbenes. A carbene contains divalent carbon with a lone pair of electrons.

- 6.9 Write a balanced reaction of bromoform with NaOH to form carbene (16).



(1 mark)

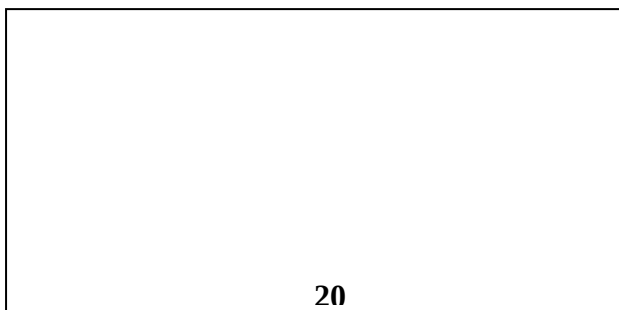
- 6.10 An interesting intermediate (19) in the synthesis of propellane is prepared by the following route. Identify the intermediates 17 -19.



(1.5 marks)

Carbenes add across $C=C$ to form cyclopropanes. Carbene **16** reacts with **19** to form **20**.

6.11 Draw the structure of **20**.



(1 mark)

20 on treatment with a strong base (CH_3Li) undergoes dehalogenation to give propellane.

6.12 Draw the structure of propellane.



(1 mark)