

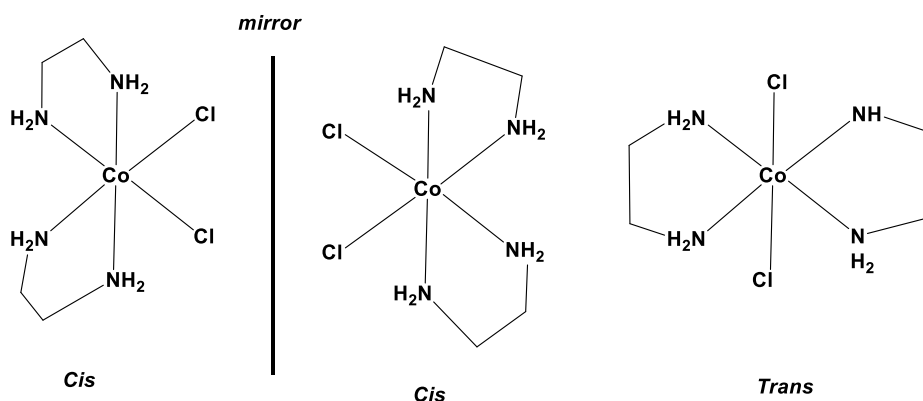
## Answer keys to CHM 113M: End-Sem Examination

1.

(a) Answer: **Cis and trans**; 2 GI are possible (1 mark)

**Cis** isomer shows optical isomerism (1 mark)

Structure drawing (2 mark)



(B).

Answer: For calculation

(3 Marks)

The CFSE for  $\text{Fe}^{2+}$  ( $d^6$  electronic configuration,  $e^3t_2^3$ ) in the tetrahedral field is:

$$[3 \times (-0.6) + 3 \times (0.4)]\Delta t = -0.6\Delta t = \mathbf{-0.27\Delta o} \quad (\Delta t = 4/9\Delta o)$$

$$\text{CFSE for } \text{Fe}^{2+} \text{ in octahedral field } (t_2g^4e_g^2) = [4 \times (-0.4) + 2 \times (0.6)]\Delta o = \mathbf{-0.4\Delta o}$$

CFSE for  $\text{Fe}^{3+}$  ( $d^5$ ) is = 0 in both tetrahedral or octahedral holes.

Thus,  $\text{Fe}^{2+}$  would occupy octahedral holes, and  $\text{Fe}^{3+}$  would go to tetrahedral sites.

This results in **inverse spinel structure**,  $\text{Fe}^{\text{III}}[\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}]\text{O}_4$

(1 Marks)

(C)

(1 + 1 Marks)

$$3 \text{ Ru}(0) = 3 \times 8 = 24 e^-$$

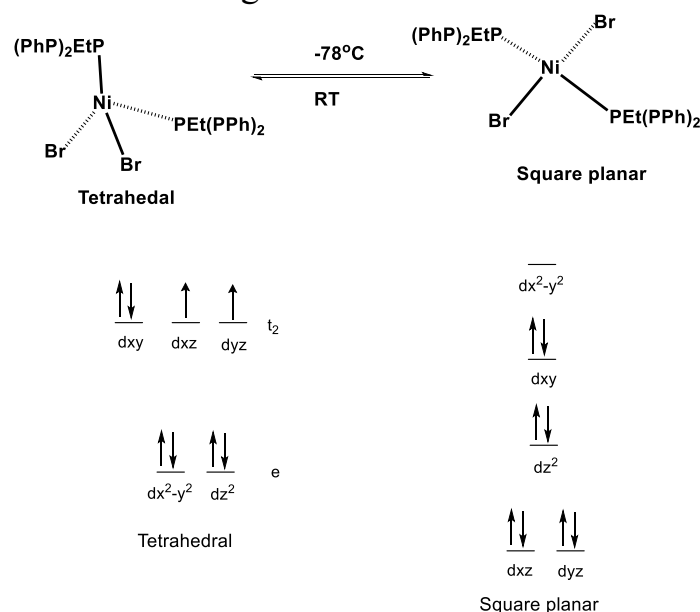
$$\text{No. of metal-metal bond is } = \frac{54-48}{2} = \mathbf{3}$$

$$\begin{array}{l} 12 \text{ CO} = 12 \times 2 = 24 e^- \\ \hline \text{Total} = 48 e^- \end{array}$$

## 2. Answer:

(2+2 Marks)

The tetrahedral complex shows an electronic configuration of Ni(II),  $e^4 t_2^4$  with two unpaired electrons, thus paramagnetic in nature. All the electrons are paired in the square planar Ni(II) complex which is diamagnetic.



(B)

(1 Marks)

Answer:

(ii) < (i) < (iv) < (iii)

(C)

(1 + 1 + 1 + 1 Marks)

(i)

Compounds	Specify the origin of the color
I. $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$\text{Mn}^{2+}$ high-spin $d^5$ , spin, and Laporte-forbidden d-d transition
II. $[\text{CoCl}_4]^{2-}$	Tetrahedral structure, non-centrosymmetric molecule, Laporte selection rule not applicable, d-d transition
III. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Centrosymmetric compound, Laporte forbidden, spin-allowed allowed d-d transition
IV. $[\text{Cr}_2\text{O}_7]^{2-}$	$\text{Cr}^{6+}$ ( $d^0$ ) system, ligand (oxygen) to metal ( $\text{Cr}^{6+}$ ) charge-transfer transition (LMCT), Laporte and spin-allowed

(1 Marks)

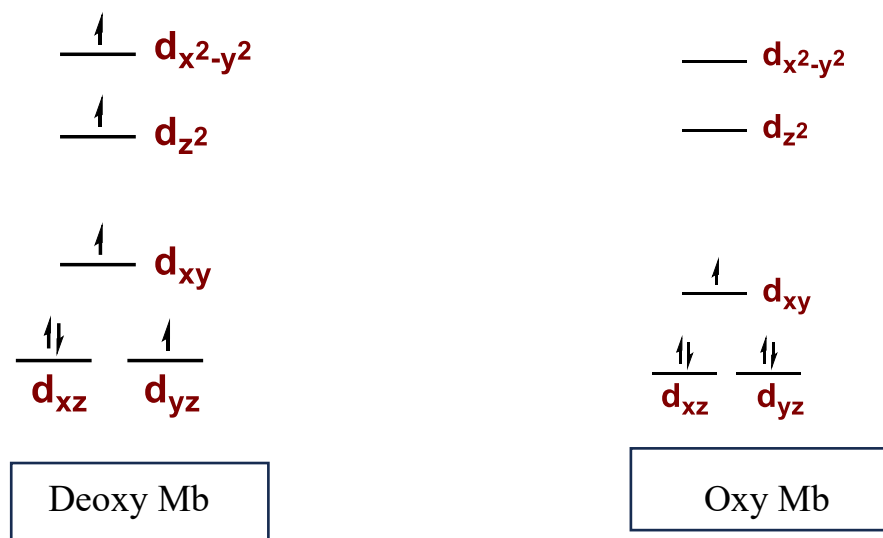
(ii) Answer:

(i) < (iii) < (ii) < (iv)

3. (A).

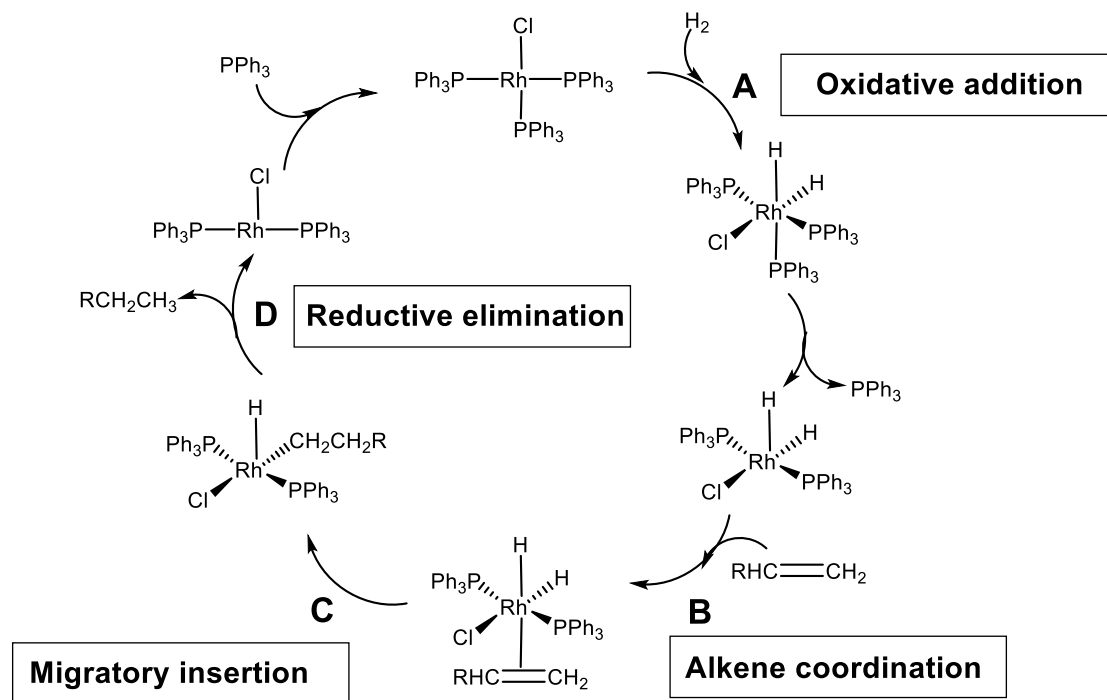
(3+1 Marks)

**Answer:** In deoxy Hb,  $\text{Fe}^{2+}$  is HS (four no. unpaired electrons). In oxy-Mb,  $\text{Fe}^{3+}$  is in LS, and due to antiferromagnetic coupling with  $\text{O}_2^-$ , it is diamagnetic.



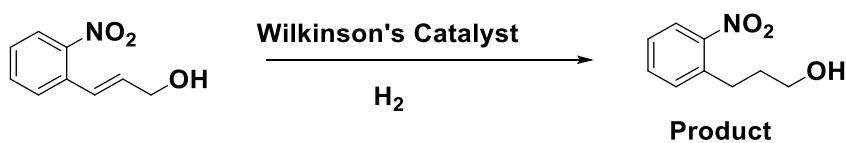
(B) Answer:

(1 + 1 + 1 + 1 Marks)

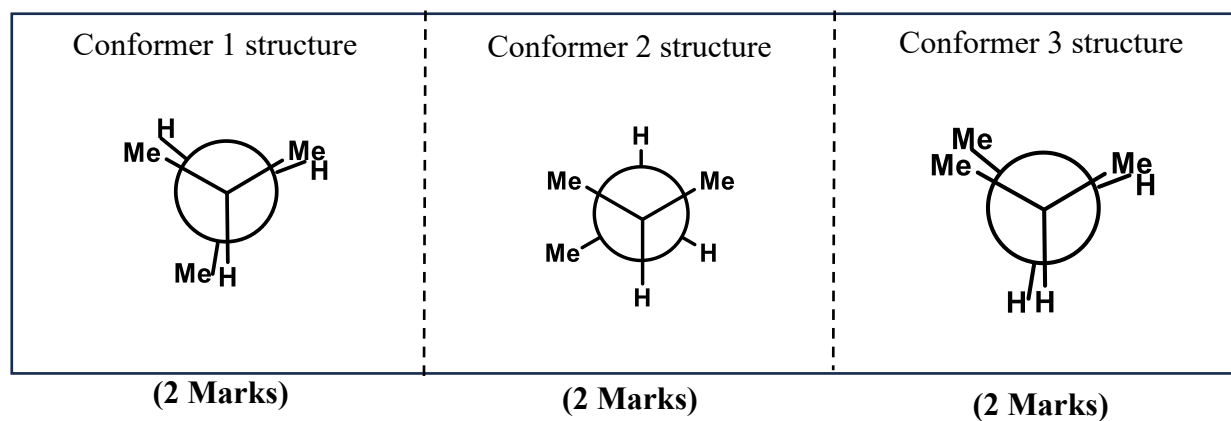


(C)

(2 Mark)



4. (A) Answer:



(B) Answer:

(2 Marks)



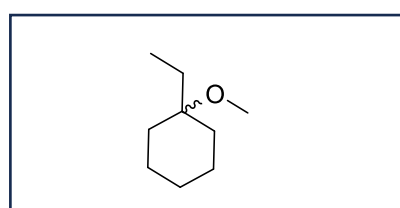
The energy of the molecule 3

=11 kJ/mol (CH<sub>3</sub>-CH<sub>3</sub> eclipsed) + 6 kJ/mol (CH<sub>3</sub>-H eclipsed) + 4 kJ/mol (H-H eclipsed)

=21 kJ/mol

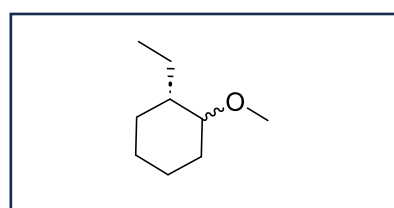
(C) Answer:

(2 Marks)



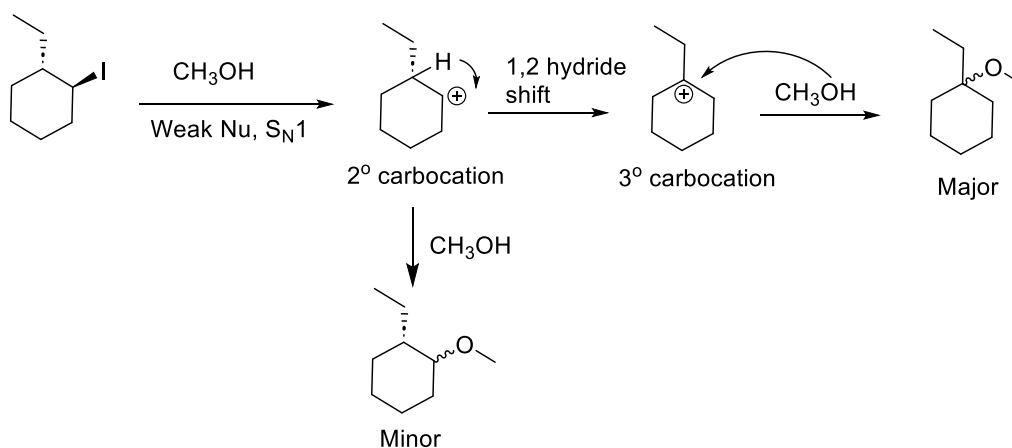
Major product

(1 mark)



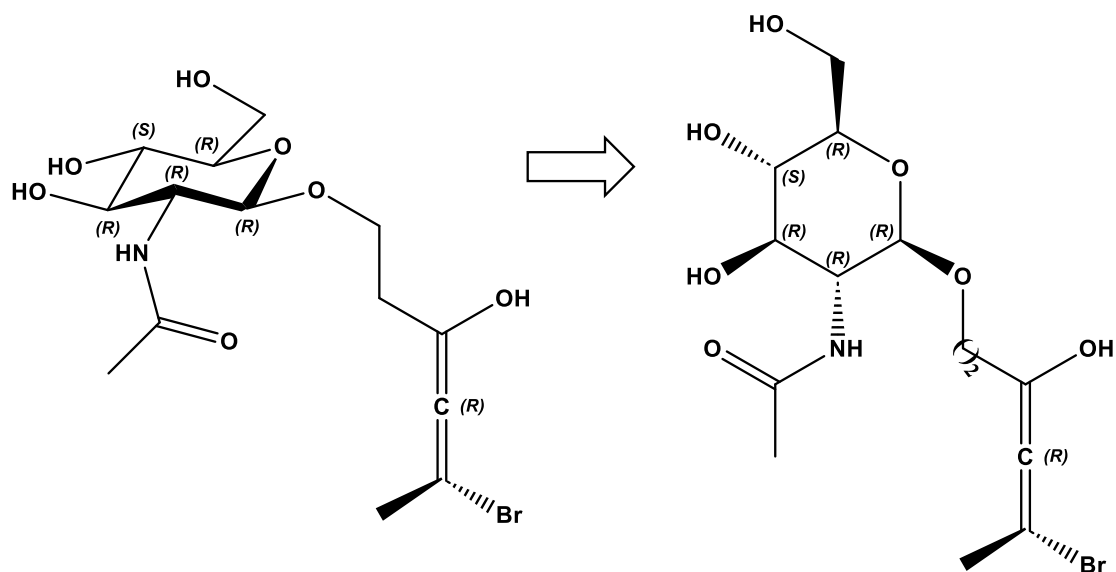
Minor product

(1 mark)



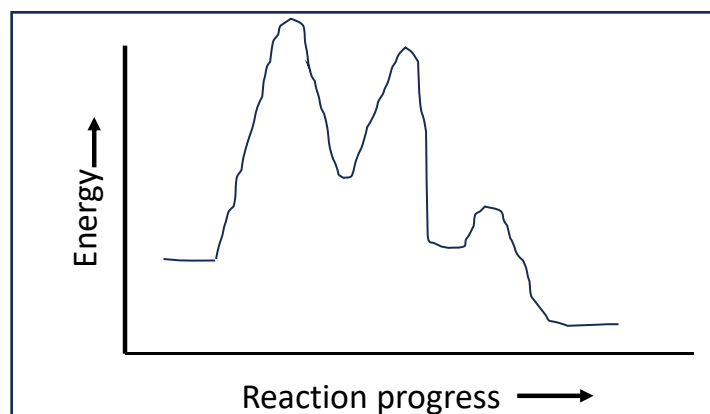
5. (A) Answer:

(6 Marks)



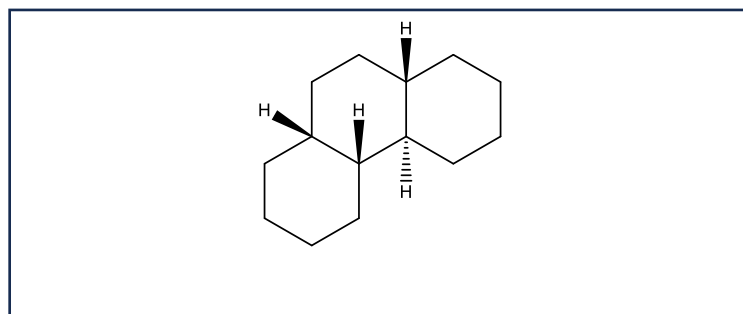
(B) Answer:

(2 Marks)



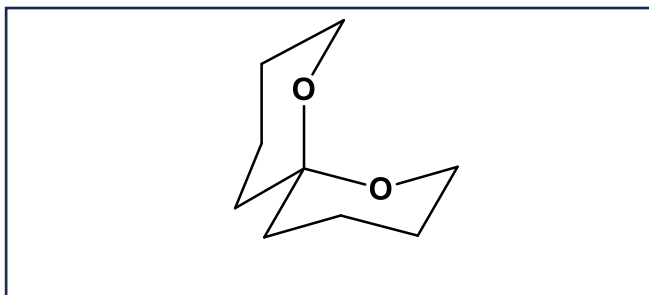
(C). Answer:

(2 Marks)



6. (A) Answer:

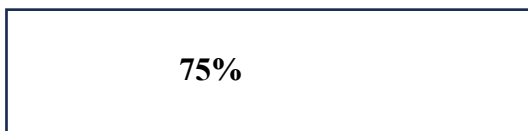
(4 Marks)



Both the oxygen is in axial position w.r.t. the neighbor ring, the structure is stabilized due to the anomeric effect.

(B) Answer:

(4 Marks)



Enantiomeric excess =  $(20/40) \times 100\% = 50\%$ . i.e. one of the isomers is present in 50% excess.

Here observed specific rotation is  $-20^\circ$ , and the *S* isomer is present in excess.

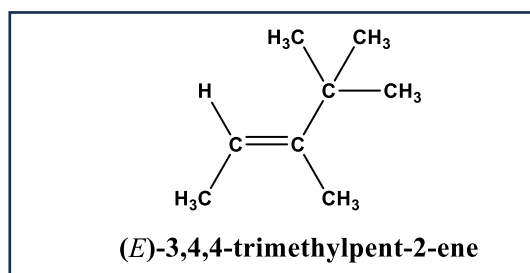
The remaining 50 % is an equal mixture of *R* and *S* (i.e., 25% *R* and 25% *S*)

So total content of *R* in the mixture is 25 %

The total content of *S* in the mixture is  $50 + 25\% = 75\%$

(C)

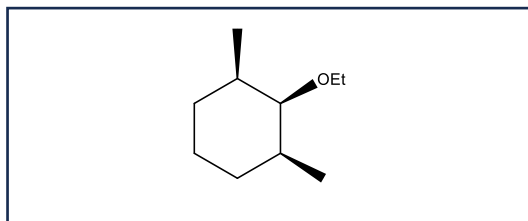
(2 Marks)



Alkane stability  $E > Z$

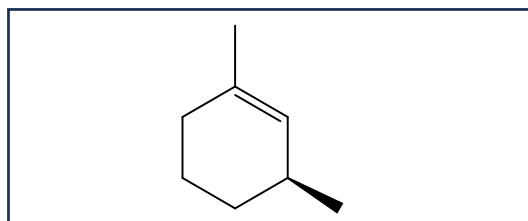
7. (A)

(4 Marks)



(2 marks)

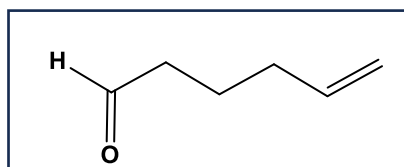
No,  $\beta$  hydrogen in the *trans* (*anti-periplanar*) position w.r.t. leaving group, Br. Thus, only  $S_N2$ .



(2 marks)

Only one,  $\beta$  hydrogen in the *trans* (*anti-periplanar*) position w.r.t. leaving group, Br. The elimination ( $E2$ ) leads to the formation of the major product.

(B) Answer:



(2 Marks)

(C) Answer:

(4 Marks)

Axial content is

2.787

%

'A' value indicates the preference of equatorial conformer over axial, the change in Gibbs free energy ( $\Delta G$ ) between the two conformers.

$$\Delta G = -RT \ln K_{eq}$$

$\Delta G$  is the change in Gibbs free energy, R is the universal gas constant, T is the absolute temperature (in Kelvin), Here,  $T=298K$ ,  $R= 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $\Delta G= 8.8 \text{ kJ.mol}^{-1}$

$$\Delta G = -RT \ln K_{eq}$$

$$8.8 \text{ kJmol}^{-1} = - (8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times (298 \text{ K}) \times \ln (K_{eq})$$

$$\ln (K_{eq}) = -3.552$$

$$K_{eq} = 0.02867$$

$$K_{eq} = [\text{axial}]/[\text{equatorial}]$$

$$\% \text{ axial} = \{ \text{axial} / (\text{axial} + \text{equatorial}) \} \times 100$$

$$= \text{axial} / \{ \text{axial} (1 + 1/K_{eq}) \} \times 100$$

$$= 1 / (1 + 34.8797) \times 100$$

$$= 2.787$$