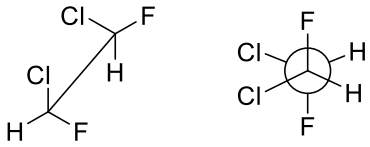
Department of Chemistry, IIT Bombay
Model Answer

CH 105: Organic Chemistry (End-Semester Examination)

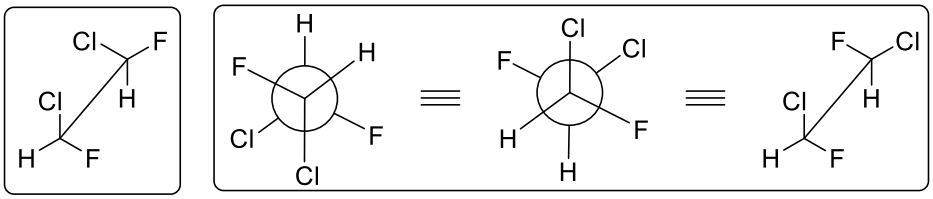
Marks: 25 Time: 2 hours November 26, 2022

1. Identify the following pairs as "Identical / Enantiomers / Diastereomers / Constitutional isomers". (2 marks)

a.

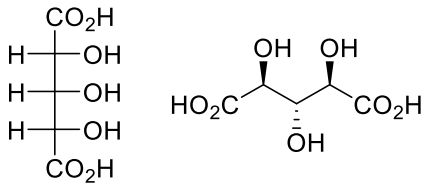


Ans.

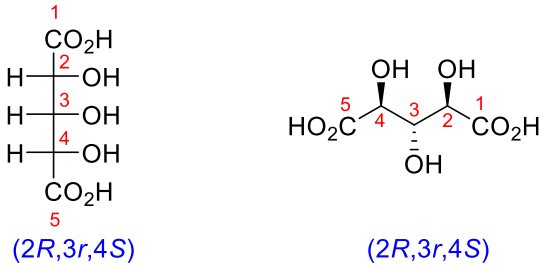


Diastereomers

b.

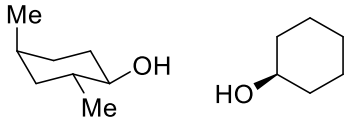


Ans.



Identical

2. Here is one stereoisomer of 2,4-dimethylcyclohexanol. Complete the structure on the right by introducing missing substituents of the given stereoisomer. (1 mark)

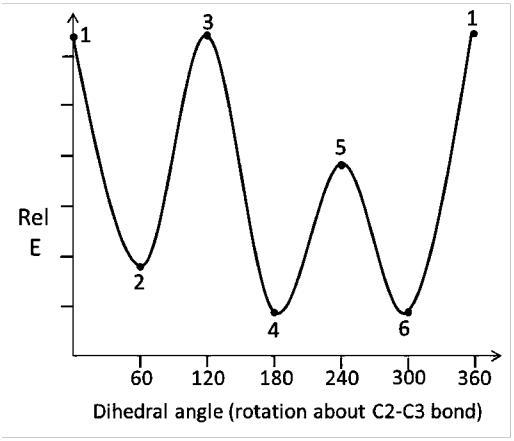


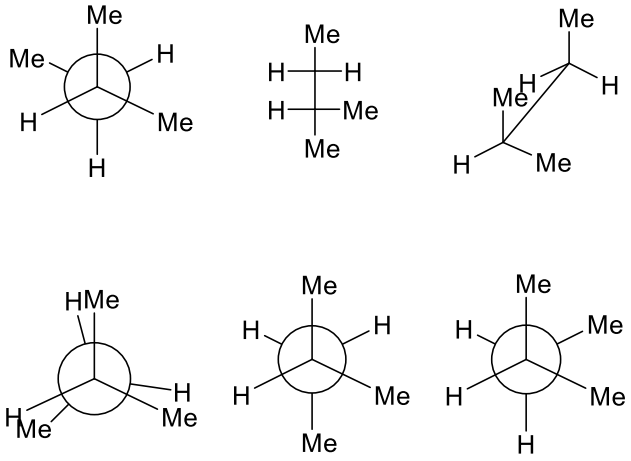
Ans.

3. The energy diagram shows the relative energies of the conformations of 2-methylbutane produced during the rotation about the C2-C3 bond. (3 marks)

a. Match the structural representations provided to the appropriate points on the energy profile.

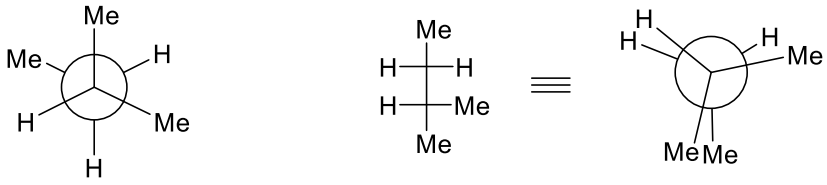
b. Calculate the energy difference between the conformations corresponding to the points 2 and 5.
(Given: Gauche interactions: Me/Me = 0.9 kcal mol^{-1}, Eclipsing interactions: Me/Me = 4.00 kcal mol^{-1}, Me/H = 1.3 kcal mol^{-1}, H/H = 1.0 kcal mol^{-1})





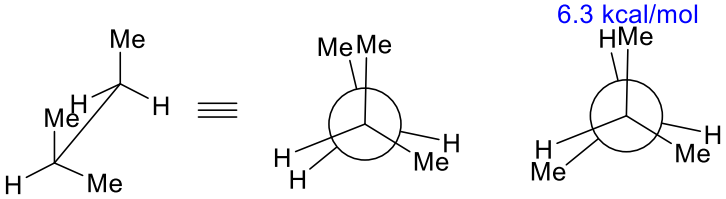
Ans.

a.



1 Gauche Interaction
0.9 kcal/mol

1 Me-Me Eclipsing Interaction
1 Me-H Eclipsing Interaction
1 H-H Eclipsing Interaction
6.3 kcal/mol



1 Me-Me Eclipsing Interaction
1 Me-H Eclipsing Interaction
1 H-H Eclipsing Interaction
6.3 kcal/mol

3 Me-H Eclipsing Interaction
3.9 kcal/mol

1 Gauche Interaction
0.9 kcal/mol

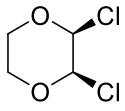
2 Gauche Interaction
1.8 kcal/mol

- 1 – C, 2 – F, 3 – B, 4 – E, 5 – D, 6 – A

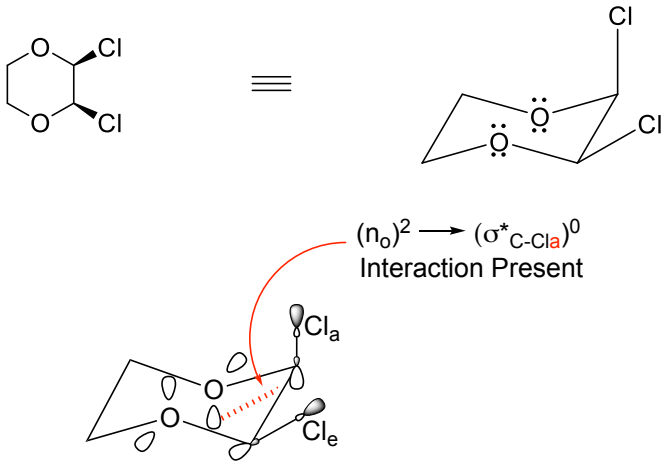
b.

- Energy difference = 3.9 – 1.8 = 2.1 kcal/mol

4. For *cis*-2,3-dichloro-1,4-dioxane (given below), two C−Cl bond distances are observed at 1.781 and 1.819 Å. Explain your observation very briefly (with the help of MO pictures!). (2 mark)

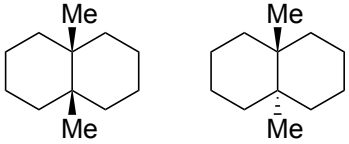


Ans.



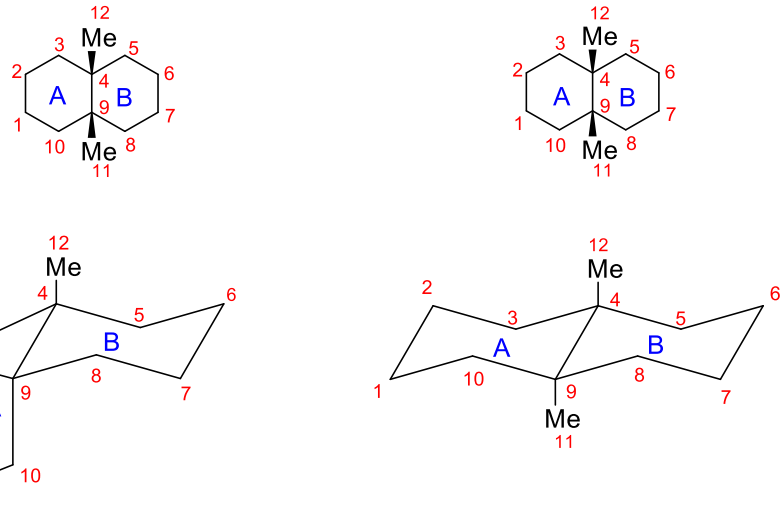
- $(n_o)^2 \longrightarrow (\sigma^*_{C\text{-}Cl_a})^0$ interaction is more favorable as both the orbitals are periplanar and hence can overlap readily. However, in other case, $(n_o)^2 \longrightarrow (\sigma^*_{C\text{-}Cl_e})^0$, both the orbitals are not periplanar and hence won't interact. Therefore, C-Cl_a bond (1.819 Å) is longer than C-Cl_e (1.781 Å).

5. Write the most stable conformer of the following molecules **M** and **N**. Calculate the gauche interactions in each and find the difference in their energy. (3 marks)
(Eclipsing interactions: H/H = 1 kcal/mol and H/Me = 1.3 kcal/mol, Me/Me = 4.00 kcal mol^{-1}; Me/Me gauche interaction = 0.9 kcal/mol)



M **N**

Ans.

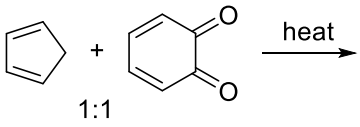


Ring A	Ring B	Ring A	Ring B
For Me_{11}:	For Me_{12}:	For Me_{11}:	For Me_{11}:
11-9-4-3	12-4-5-6	11-9-10-1	11-9-8-7
11-9-10-1	12-4-9-8	11-9-4-3	11-9-4-5
11-9-4-12	12-4-9-11	For Me_{12}:	For Me_{12}:
For C_5:	For C_{10}:	12-4-3-2	12-4-5-6
5-4-3-2	10-9-8-7	12-4-9-10	12-4-9-8
5-4-9-10	10-9-4-5		
Total Gauche Interaction = 8		Total Gauche Interaction = 8	

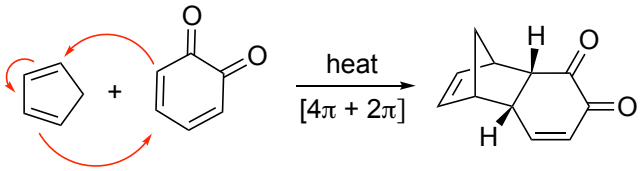
Energy difference in between M & N = 0 kcal/mol

6. Predict the **major** product formed in the following reactions. Indicate clearly the **regio- and stereochemistry**, wherever applicable. (3 marks)

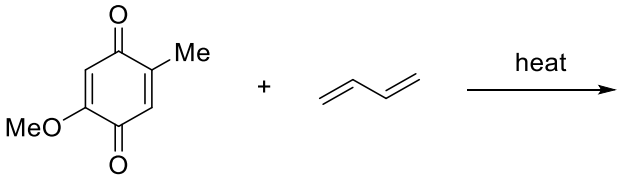
a.



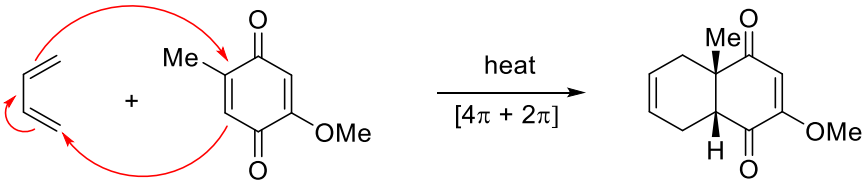
Ans.



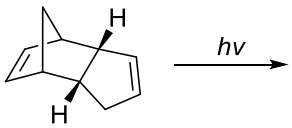
b.



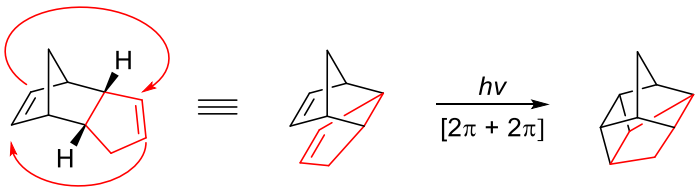
Ans.



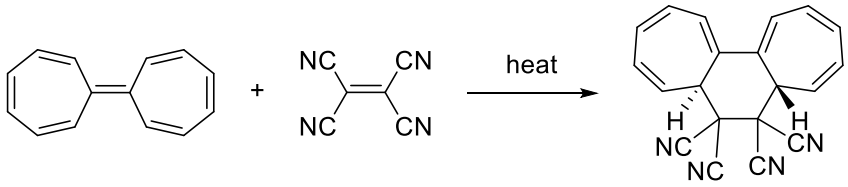
c.



Ans.



7. Consider the following reaction. (2 + 1 + 1 = 4 marks)



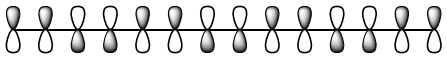
a. Draw the frontier orbitals (HOMO-LUMO) of reactants involved in the reaction (Treat the polyene as an equivalent to a linear system).

b. Predict whether the reaction is allowed or forbidden in a concerted manner under the reaction conditions indicated, according to FMO approach.

c. Classify the type of pericyclic reaction. {$n\pi$ electrocyclic (*con/dis*), cycloaddition [$n\pi_{a/s}+m\pi_{a/s}$] etc.}

Ans.

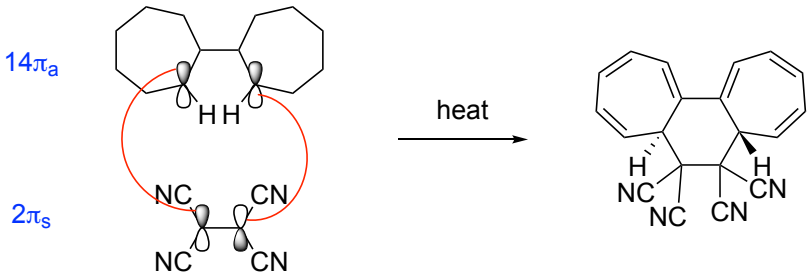
a.



14π e$^-$
HOMO = Ψ_7
Nodes = 6

2π e$^-$
LUMO = Ψ_2
Node = 1

b.



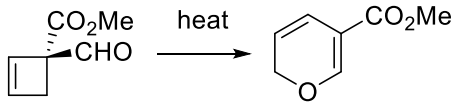
- This reaction is thermally allowed.

c.

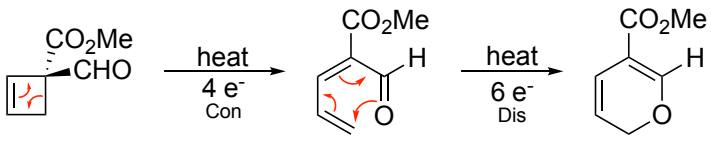
- Cycloaddition [$14\pi_a+2\pi_s$]

8. Write a reasonable mechanism for the following reactions. Indicate the stereochemistry of the products and reaction intermediates in each case. Your mechanism should give proper description of the pericyclic processes involved. (2 x 3 = 6 marks)

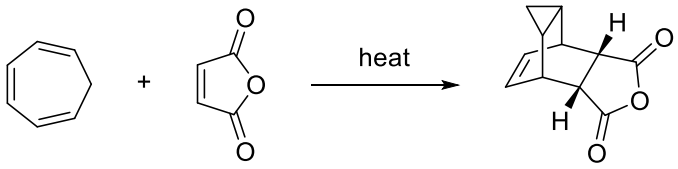
a.



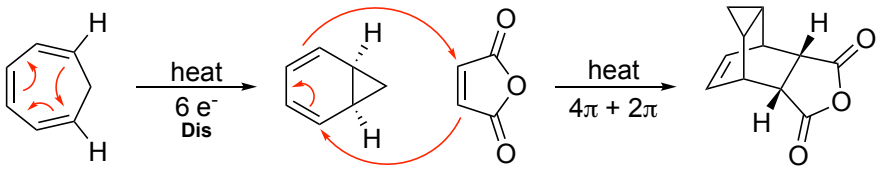
Ans.



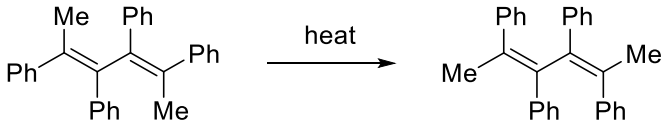
b.



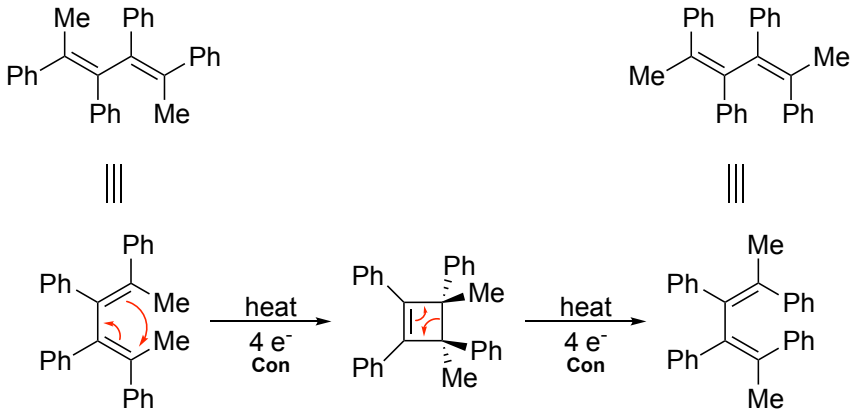
Ans.



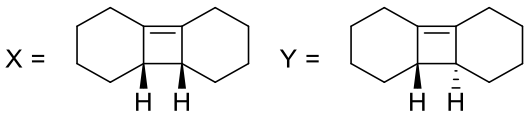
c.



Ans.



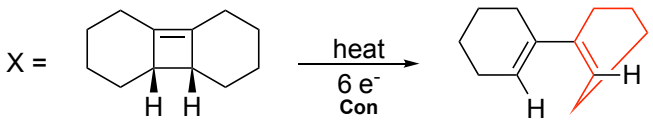
9. In the following pair of compounds which one will react faster in the given reaction? (1 mark)



for thermal ring opening reaction.

Ans.

- Y will react faster.



Trans double bond is not geometrically favourable in cyclohexene