THE CATHOLIC UNIVERSITY OF EASTERN AFRICA

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MAIN EXAMINATION

JANUARY – APRIL 2020 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF NATURAL SCIENCE (CHEMISTRY)

REGULAR PROGRAMME

CHEM 303: PHYSICAL – ORGANIC CHEMISTRY

Date: APRIL 2020	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions	

1. (a) What do chemists mean by strain? [3 marks]

   (b) Use the table of group increments provided to calculate ΔH_f for cyclohexene in kcal/mole. [6 marks]

   (c) Given that the experimental value for ΔH_f = -1.20 kcal/mole, calculate the strain energy of cyclohexene. [4 marks]

   (d) Sketch a complete 360° torsional itinerary for butane for rotation about the C2–C3 bond which includes

   i. a graph of the change in energy with dihedral angle; [6 marks]

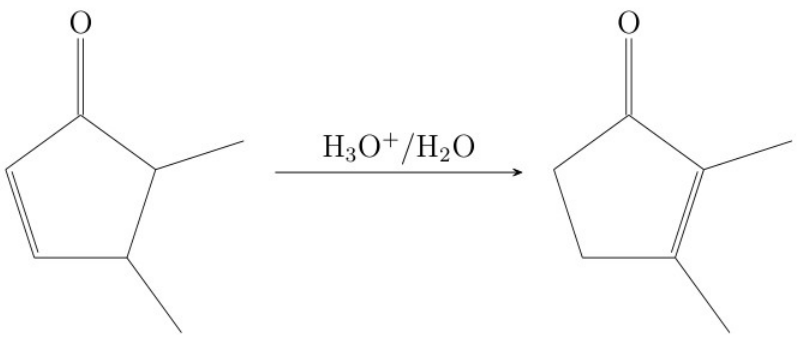
   ii. the four Newman projections giving both the two types of staggered forms and the two types of eclipsed forms and [5 marks]

   iii. the names for the two types of staggered forms. [2 marks]

   (e) Which staggered form is statistically favored? [2 marks]

   (f) Which has the higher strain energy? [2 marks]

2. Write a reasonable mechanism for the following transformation. Remember to draw all of the relevant lone pairs and show proper electron pushing for all the steps. [20 marks]



3. **N.B.:** The answers to this question, if you attempt it, are to be placed on the last page of this question paper and submitted with your exam booklet.

   (a) Copy the part of the Walsh diagram for pyramidal CH_3 found below on to the diagram at the end of this question paper and populate the orbitals for methyl radical. [6 marks]

4. Estimate $\Delta H^{\ominus}$ for each of the following conformational equilibria:

   (a) [7 marks]

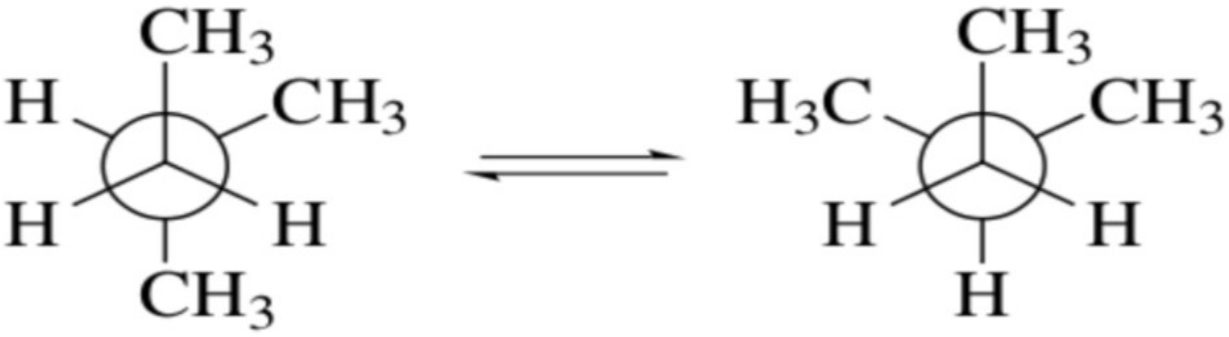


Figure 4

(b) [7 marks]

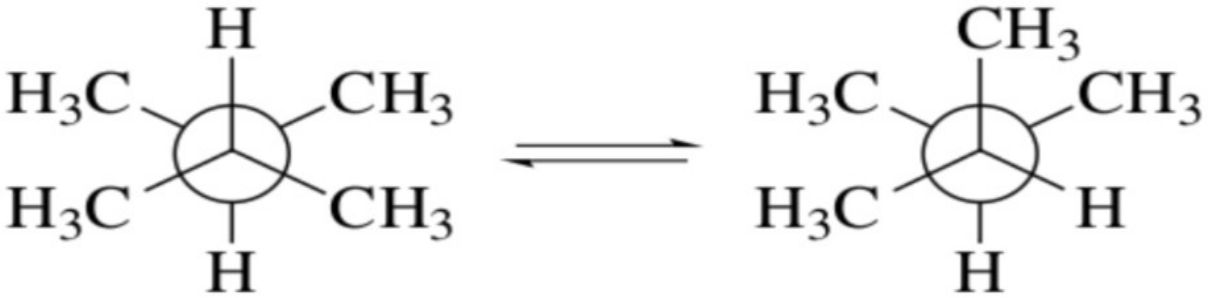


Figure 5

(c) [6 marks]

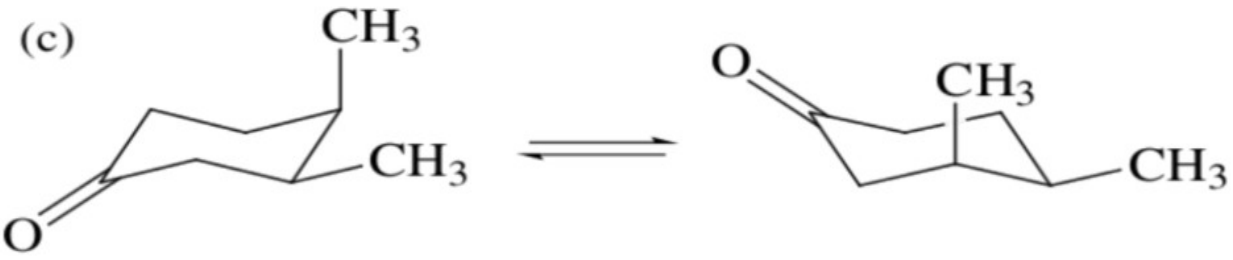


Figure 6

4. Estimate $\Delta H^{\ominus}$ for each of the following conformational equilibria:

(a) [7 marks]

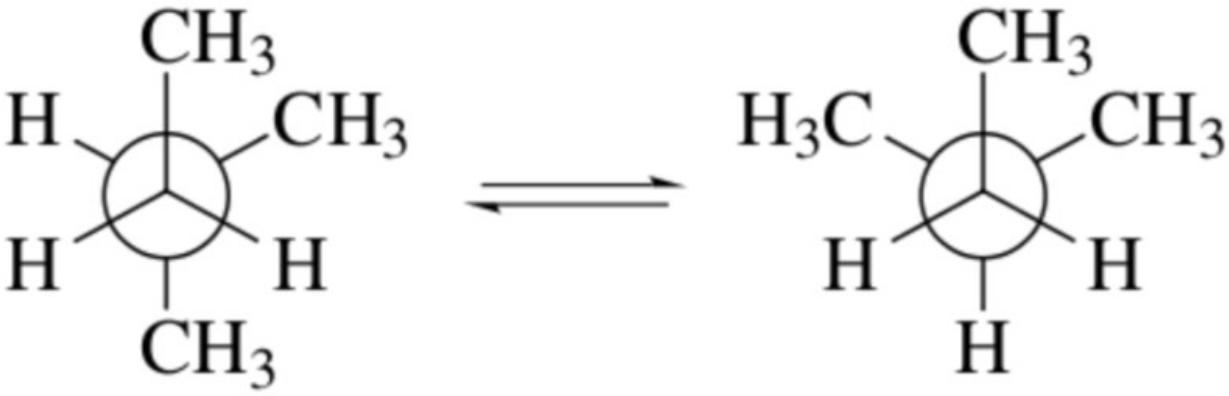


Figure 4

(b) [7 marks]

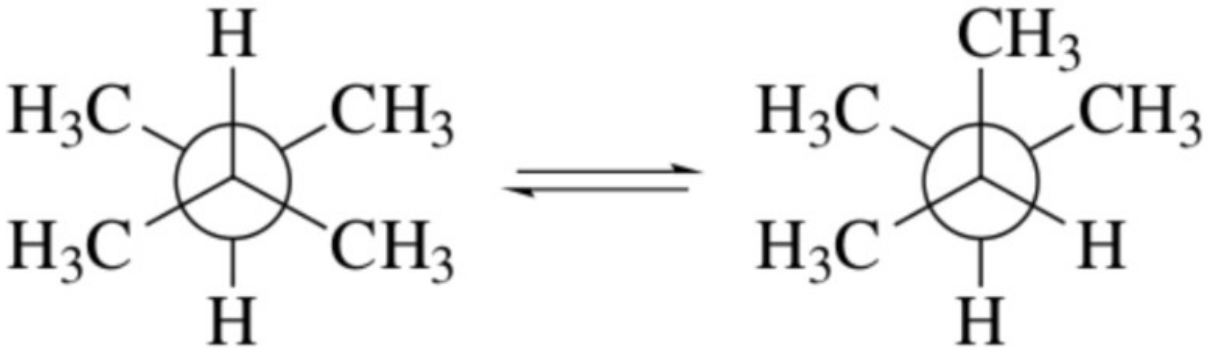


Figure 5

(c) [6 marks]

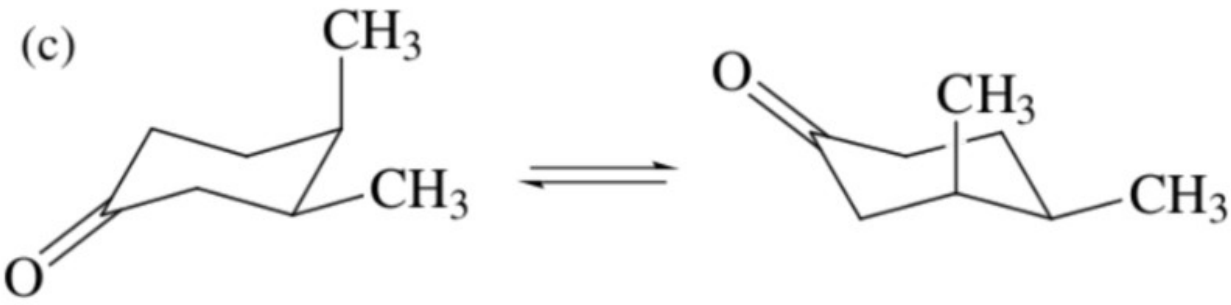
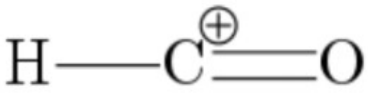


Figure 6

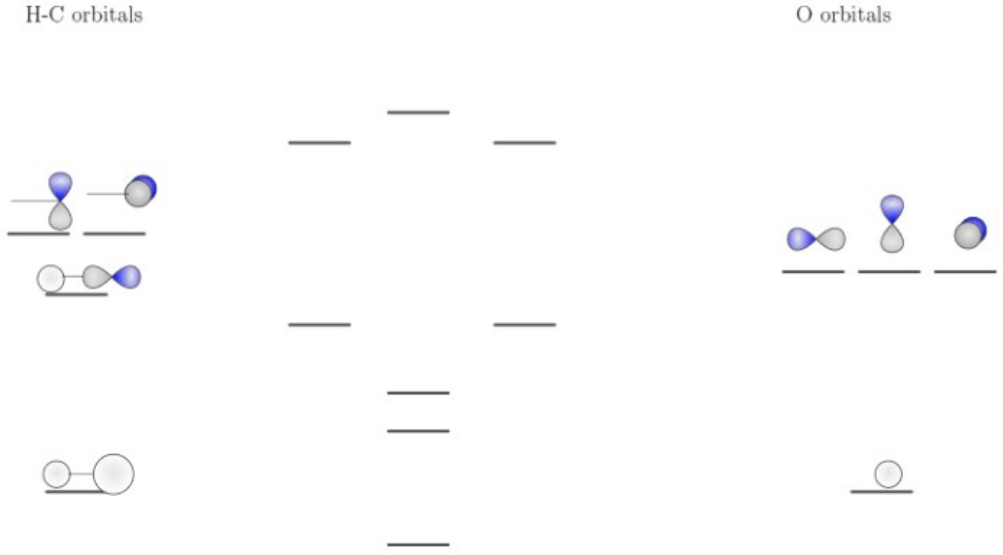
5. Bonding and Stability.

Acyl cations ($R-C^{+}=O$) are key intermediates in Friedel—Crafts acylation reactions. They are stabilized by the presence of oxygen and this can be demonstrated through either resonance or MO analysis.

(a) Consider the formyl cation, shown below. Show how it is stabilized, by drawing an additional resonance structure. [4 marks]



An orbital mixing diagram for the formyl cation, can be constructed starting with group orbitals for C-H and the O-atom. The molecular orbitals that are formed by combining the group orbitals are shown below.



(b) Draw the scheme above on your answer sheet and use dotted lines to show which group orbitals combine to form the MO's. [8 marks]

(c) Place the appropriate number of valence electrons in the MO's. Label the π-MO's and use the number of occupied π MO's to explain that the MO's diagram confirms the Lewis structure of the resonance form you have drawn in part (a) [8 marks]

END

Reg No. _____ Booklet No. _____

Answer to Question 3 to be handed in with your exam booklet.

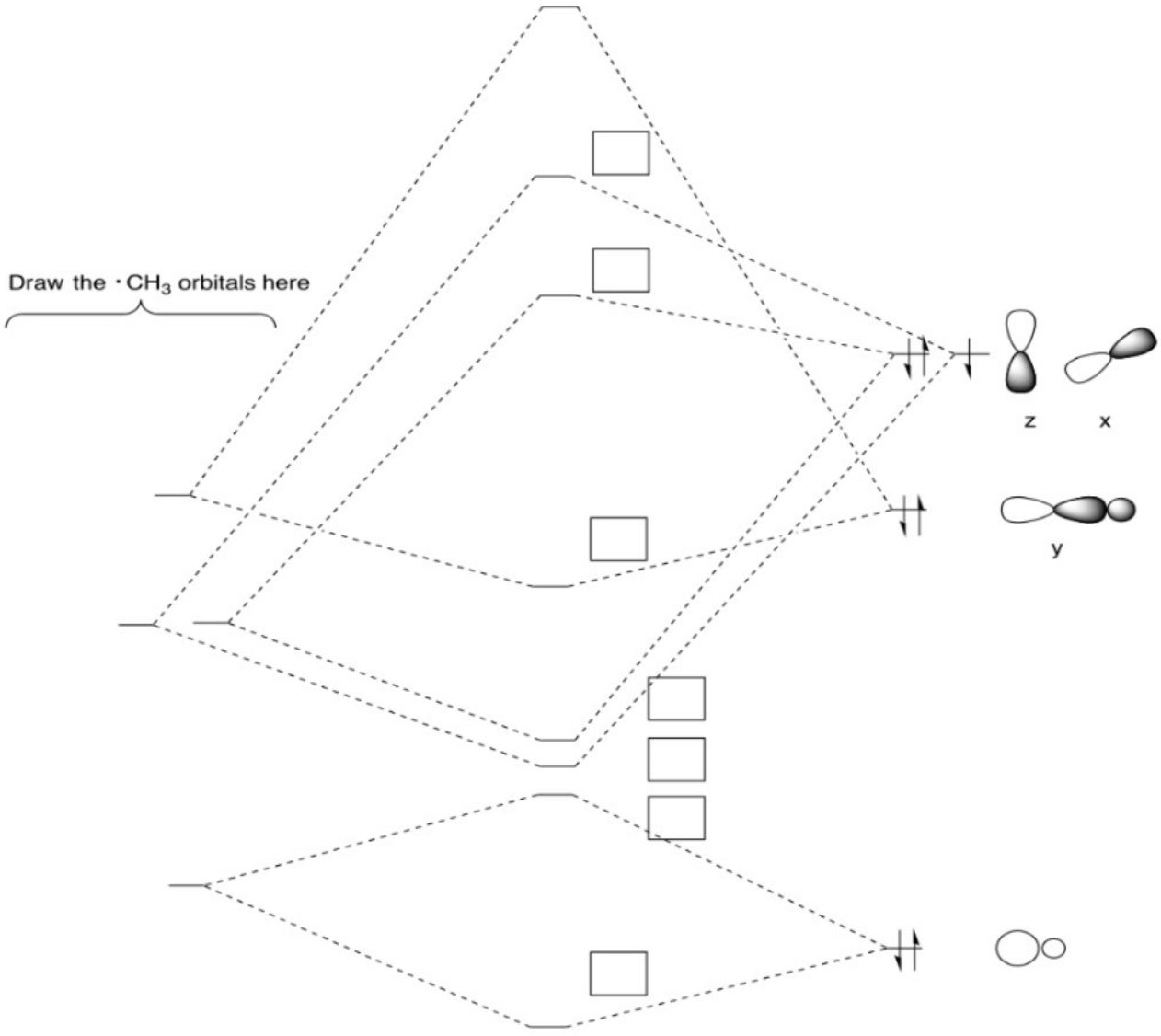


Figure 7: