

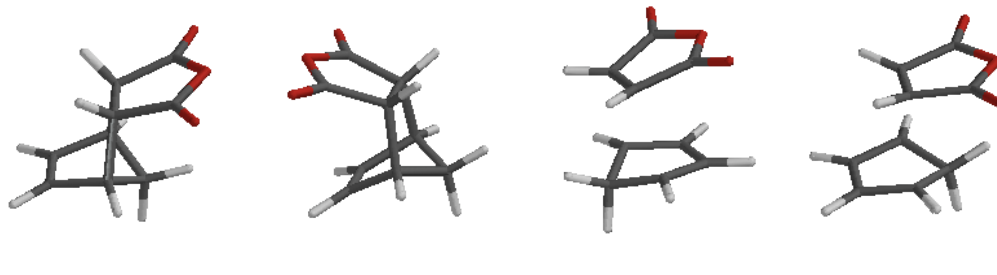
Molecular Modeling: Diels Alder Reactions (II)

This experiment relates molecular modeling to actual in-lab results. Modeling software such as WebMO can be used to build structures of reactants, transition state complexes, intermediates and products, but WebMO, which is free, unfortunately lacks the necessary computational engine to process the transition state models. Gaussian, a commercial modeling software that is used by other WebMO consortium members has the necessary engines, but it has an annual subscription fee of >\$2,000/yr. So, instead of building the molecules, we will apply modeling data that was generated using Spartan's computational engines. The data is archived on the *Molecular Modeling Workbook's* CD that is available from Dr. R.

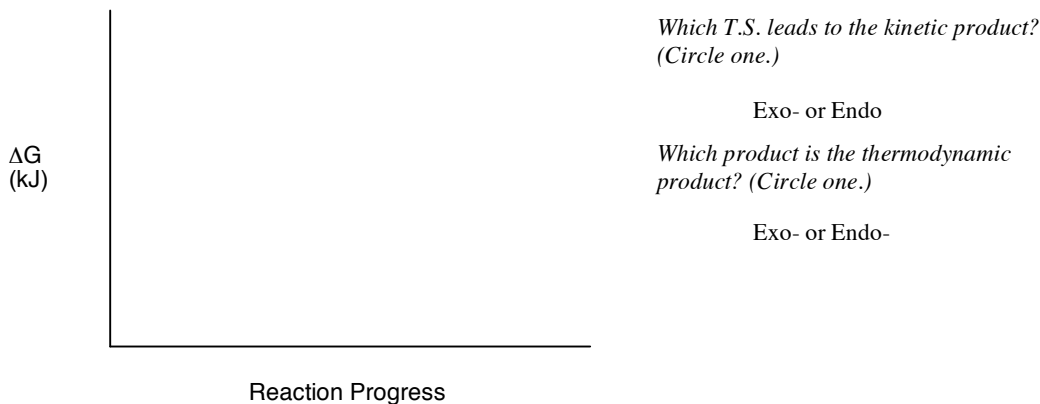
Working with a partner, obtain a *Molecular Modeling Workbook* CD; using either a PC or Mac open Spartan View and folder 15-11A. Complete the following table for cyclopentadiene and maleic anhydride (use four decimal places for *au* Energy values, (1 *au* = 2625.5 kJ/mol)). Answer the questions that follow. Refer to the University of Saskatchewan publication; complete the work-up of your reaction of maleic anhydride and furan. Identify your reaction product from the reaction as exo- or endo- from its melting point. Answer all of the accompanying questions.

	Energy (<i>au</i>)	E _(Normalized) (<i>au</i>)	E _(Normalized) (kJ)
Reactants	-566.8205	0	
A) endo- T.S.			
B) exo- T.S.			
C) endo-product			
D) exo-product			

1. Match the following structures from the CD with the correct letter from the table above.



2. Normalize the values in column #1 of the table, i.e. subtract -566.8205 from each value and record in column #2. (The reactants will be equal to zero.) Then convert to kJ ($1 \text{ au} = 2625.5 \text{ kJ/mol}$); record in the third column and plot a Reaction Coordinate-Energy Diagram below that includes the two transition states and the two products.



3. A former DVC student, who was inspired by this experiment to transfer to the University of Saskatchewan, repeated the maleic anhydride-cyclopentadiene reaction. She obtained a solid product and when she took the melting point it strangely looked like the solid almost instantly turned to a liquid and then vaporized at $162-163^\circ\text{C}$. Which product did she obtain: exo-5-norbornene-2,3-dicarboxylic anhydride, CAS # [2746-19-2] or endo-5-norbornene-2,3-dicarboxylic anhydride [129-64-6]. Was the product the kinetic or thermodynamic product?

Circle one: Kinetic or Thermodynamic.

4. Recrystallize your reaction product and record its melting point. (m.p. _____ $^\circ\text{C}$)
5. Which product did you obtain the exo- or endo-? _____ (It should be opposite of the cyclopentadiene product.)
6. Is your product the thermodynamic or kinetic product?

Circle one: Kinetic or Thermodynamic.

7. Your diene includes an oxygen and cyclopentadiene does not. Draw a resonance structure for furan. Furan has electron delocalization similar to benzene. Use this phenomena to explain why the product formed in your experiment does not form when oxygen is absent in the diene.