

Diels-Alder Reactions Worksheet

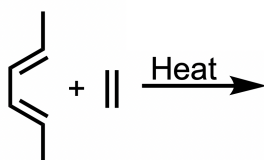
Warm-Up Questions:

Watch the [Khan Academy videos](#) on the Diels-Alder reaction.

- 1) Label the following substituents as either electron-withdrawing or electron-donating:
 - a) $-\text{COOH}$
 - b) $-\text{Me}$
 - c) $-\text{OH}$
 - d) $-\text{NO}_2$
- 2) To speed up a Diels-Alder reaction, what types of substituents should be placed on the diene and dienophile?

Example #1

Predict the product and arrow-pushing mechanism of the following Diels-Alder reaction.



Example #2:

Take screenshots of the HOMO of the diene and the LUMO of the dienophile. Where does the orbital overlap occur between the two reactants?

HOMO of Diene	LUMO of Dienophile

Example #3:

Using the AutoTS results, let's analyze the Diels-Alder reaction further. Answer the following questions:

- Take screenshots of the optimized geometries for the reactants, transition state structure, and products.
- List the C–C bond distances of each molecule using the Measure button in units of ångstroms.

Reactants	Transition State Structure	Products
Screenshot: 	Screenshot: 	Screenshot:

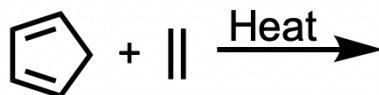
Bond distances:	Bond distances:	Bond distances:
-----------------	-----------------	-----------------

- c) Now let's analyze the transition state structure. Look at the animation of its vibration. What is the hybridization of the carbon atoms involved in the bond breaking and forming at the transition state? How does this differ from the reactants' starting geometry?
- d) Take a screenshot of the reaction energy diagram. Is the reaction exergonic or endergonic? What is the activation energy barrier in units of kcal/mol? Would the reaction speed up or slow down if the dienophile included an electron-withdrawing group such as an aldehyde?

Individual Exercise:

Part A:

For the following Diels-Alder reaction:



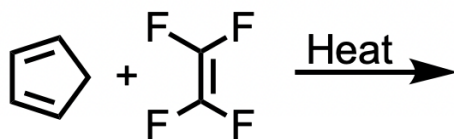
- 1) Label which reactant is the diene and which is the dienophile. Then, predict the product and draw the arrow-pushing mechanism.

- 2) Generate the HOMO and LUMO of the diene and dienophile. Take a screenshot and paste it below.

HOMO of Diene	LUMO of Dienophile

Part B:

For the following Diels-Alder reaction:



- 1) Label which reactant is the diene and which is the dienophile. Then, predict the product and draw the arrow-pushing mechanism.

- 2) Look at the pre-generated AutoTS results for this reaction. Take screenshots of the optimized geometries for the reactants, transition state structure, and products.

Reactants	Transition State Structure	Products
Screenshot:	Screenshot:	Screenshot:

-
- 3) Take a screenshot of the reaction energy diagram. Is the reaction exergonic or endergonic? What is the activation energy barrier in units of kcal/mol?

Part C:

Compare the two reactions from Part A and Part B. Which reaction do you expect to have a faster reaction rate and why?