

# **EXPERIMENT 2 (Organic Chemistry II) Pahlavan/Cherif**

## **Diels-Alder Reaction**

### **Preparation of ENDO-NORBORNENE-5,6-CIS-CARBOXYLIC ANHYDRIDE**



#### **Purpose**

- Study conjugated dienes
- Study diene and dienophile
- Study cycloaddition reaction

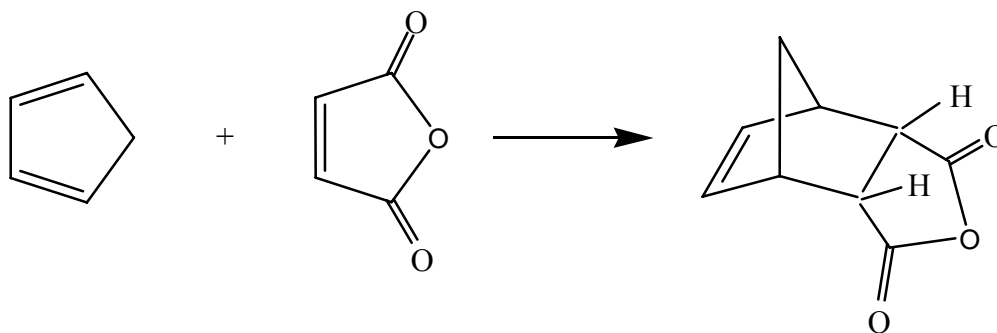
#### **Chemicals**

Maleic anhydride  
Ethyl acetate  
Cyclopentadiene  
Hexane ( OR Petroleum ether)

#### **Materials**

125 –ml Erlenmeyer flask  
400 – ml Beaker  
Hot water bath  
Ice bath  
Mel-temp  
Suction filtration funnel

#### **REACTION**



#### **Cyclopentadiene**

$C_5H_6$  M.W. = 66.10 g/mol  
B.P. = 41.5 – 42.0 °C  
M.P. = -85 °C  
Density = 0.80 g/ml (20-25 °C)

#### **Maleic anhydride**

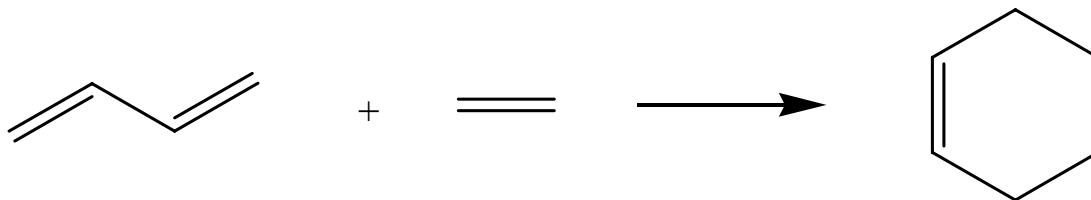
$C_4H_2O_3$  M.W. = 98.06 g/mol  
M.P. = 52.8 °C  
Cis- butanoic anhydride  
2,5- furandioic anhydride  
Toxic anhydride

#### **ENDO-Norbornen-5,6-cis-dicarboxylic anhydride**

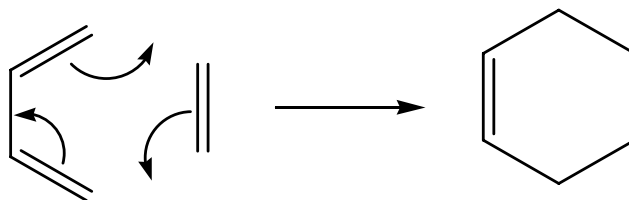
$C_9H_8O_3$  M.W. = 164.15 g/mol  
M.P. = 164 - 165 °C

## Introduction

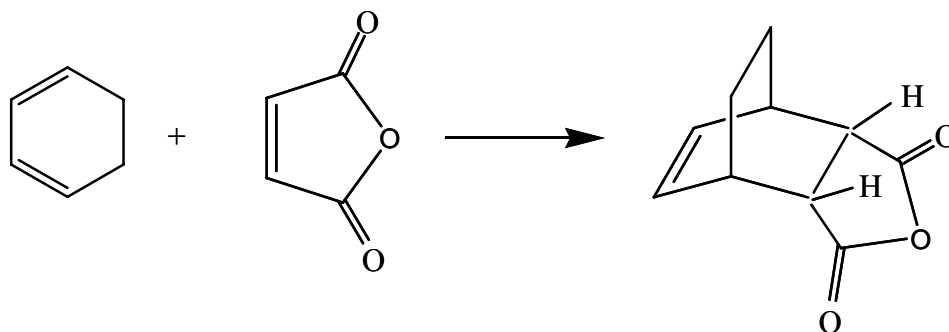
The Diels-Alder reaction is one of the most powerful tools used in the preparation of important organic molecules. When two carbon-carbon double bonds are positioned next to one another, a *conjugated diene* is formed. A **non-conjugated diene** is a molecule that has two olefins which are not next to each other. Conjugated dienes undergo a cycloaddition reaction (also called pericyclic addition) with certain double bonds to afford cyclohexenes and related compounds. The simplest Diels-Alder reaction is between 1,3-butadiene and ethylene:



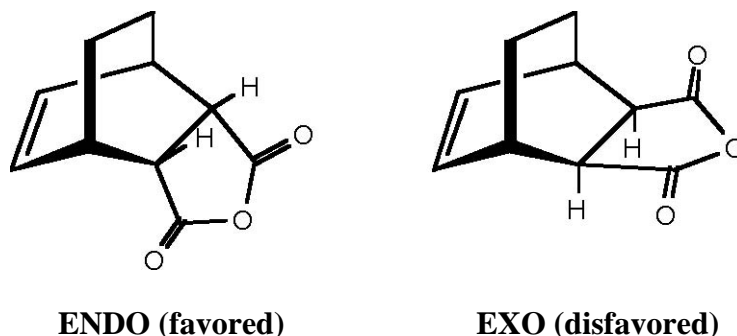
The formation of new carbon-carbon bonds is one of the most important aspects of synthetic organic chemistry. When a synthetic sequence calls for the formation of a ring of carbon atoms, this problem is compounded. Fortunately, the formation of six-membered carbon rings is much simpler than it would first appear. This reaction forms a six-membered ring from two pieces: a conjugated "**diene**" (which provides four of the ring atoms) and a "**dienophile**" (which provides two of the ring atoms). The main requirements for these species are that the *conjugated diene* must be somewhat **electron rich** (which is normally the case for dienes) and able to achieve the *s-cis* conformation, and that the "**dienophile**" have a two-atom  $\pi$  system that is relatively **electron poor**. The **mechanism** of the reaction begins with the diene assuming the higher energy, but more reactive, *cis* conformation. As the **diene** and the *dienophile* approach each other, the two terminal carbons of the diene meet the two carbons of the dienophile:



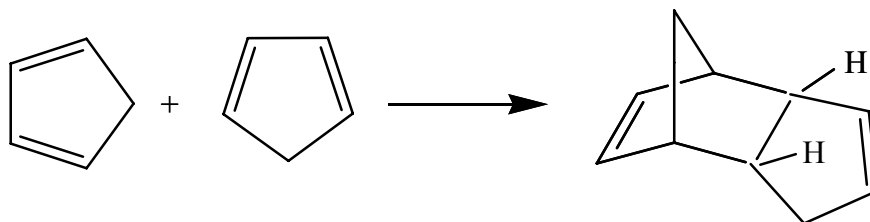
The Diels-Alder reaction is facilitated by the presence of electron donating groups (EDG) on the diene and by the presence of electron withdrawing groups (EWG) on the dienophile. For instance, **maleic anhydride** is a very good dienophile because it contains two highly electronwithdrawing carbonyl groups. In fact, maleic anhydride was one of the original dienophiles that Diels and Alder used in their studies. It will react with a variety of dienes to afford the corresponding cyclohexene system. The reaction of **maleic anhydride** and **cyclohexadiene** is shown as an example:



This example illustrates what is known as the **Endo Rule**. The addition of maleic anhydride to a diene yields entirely the **endo** product in which the bulkier parts of the dienophile are closer to the carbon-carbon double bond.



**Note** - One important aspect of this experiment is that the cyclopentadiene must be freshly distilled within one day before the reaction is carried out. Why? *The cyclopentadiene undergoes dimerization at 25°C to produce dicyclopentadiene, using the Diels-Alder reaction, where one cyclopentadiene molecule acts as diene and the other cyclopentadiene molecule acts as dienophile.*



### **Instructor Procedure**

You will prepare your own cyclopentadiene using a fractional distillation setup (*in the hood*). The reflux column will be another condenser column (or you can use a fractional distillation column) using air to cool, if compressed air is available. Collect the cyclopentadiene into a receiver flask cooled to 0°C using an ice-water bath. Assemble a fractional distillation setup as used previously in lab, or as described above. This apparatus will use a 100-mL round-bottom distilling flask and a 50-mL round-bottom receiving flask. Place the receiving flask in a beaker filled with crushed ice and a little water so that the volatile product, cyclopentadiene, will be cooled to about 0°C, which prevents formation of the dicyclopentadiene.

Place about 30 mL of technical-grade dicyclopentadiene (about 85% pure) in your distillation flask, add several boiling stones, and attach the flask to your fractional distillation setup. Turn on the condenser water and heat the dicyclopentadiene until it refluxes briskly. The monomeric cyclopentadiene should start to distill within a few minutes. Continue to heat the dimer reagent to promote fairly rapid distillation, but do not allow the distillation temperature to exceed about 65 °C, which is slightly above the boiling point of cyclopentadiene (40-42 °C). It will take at least 30-40 minutes to collect the 12-mL sample of cyclopentadiene which is needed for the reaction.

When the cyclopentadiene has been collected, stop the distillation and discard the unused residue from the reaction flask, into the liquid waste container (boiling stones go into solid waste). If the cyclopentadiene is cloudy as a result of moisture condensing in the receiver, add a few pieces of anhydrous calcium chloride (chunks or balls), or you may use anhydrous magnesium sulfate. Decant the dry cyclopentadiene from the drying agent for use in the experimental protocol described by instructor.

## Safety Note

**Cyclopentadiene** (and its dimer, dicyclopentadiene) is an irritant, flammable, has an unpleasant odor and is harmful if inhaled — avoid breathing its vapors. No flames will be allowed in the lab. Wear gloves while handling these chemicals. *Dispense and use these chemicals in the hood to minimize inhalation hazards.* **Maleic anhydride** is corrosive and toxic--wear gloves while handling it. Be sure to wash your gloves and your hands after handling it. **Ethyl acetate** is a flammable liquid and an irritant. No flames allowed, and wear gloves while handling solvents if possible, and avoid inhaling their vapors.

## Student Procedure

Place 2 g of maleic anhydride in a 125- ml Erlenmeyer flask and dissolve it in 7.5 ml of ethyl acetate by warming on the steam bath (hot water bath).

Obtain 2 ml (40 drops) of cyclopentadiene in a 10 ml graduated cylinder from your instructor and add this to the **cold maleic anhydride** solution. Add 7.5 ml of hexane or (petroleum ether), and then cool the solution in an ice bath. Swirl the solution to effect mixing, replace it in the ice bath and wait until the product crystallizes from the solution. Once the product crystallizes, heat the mixture in hot water bath to redissolve the solid, and allow it to recool to induce recrystallization in the same container. Collect the product by suction filtration, and record the melting point of the dry crystals, weight, the percentage yield, and, if requested by your instructor, determine the IR spectrum(if available). Dispose of the filtrate in the organic waste container. Wrap the solid product in a paper with your name(s) and return to your instructor.

# EXPERIMENT 2 (Organic Chemistry II)

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## The Diels-Alder Reaction

### Preparation of ENDO-NORBORNENE-5, 6-CIS-CARBOXYLIC ANHYDRIDE

#### REPORT FORM

Name \_\_\_\_\_

Instructor \_\_\_\_\_

Date \_\_\_\_\_

#### Calculation

a) Cyclopentadiene (M.W. = 66.10 g/mol) \_\_\_\_\_ g \_\_\_\_\_ mol  
(calculation)

b) Maleic anhydride (M.W. = 98.06 g/mol) \_\_\_\_\_ g \_\_\_\_\_ mol  
(calculation)

c) The limiting reagent ( smaller moles reagent) is \_\_\_\_\_

d) Theoretical yield of product (M.W. = 164.16 g/mol) \_\_\_\_\_ mol  
(calculation)

\_\_\_\_\_ g

e) Actual yield of product (collected solid product) \_\_\_\_\_ g

f) Percentage Yield (% Recovery) \_\_\_\_\_ %

g) Observed melting point range of product \_\_\_\_\_ °C

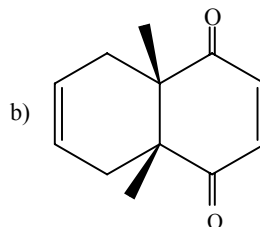
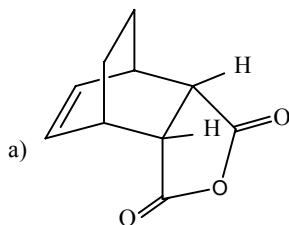
h) Literature melting point range of product \_\_\_\_\_ °C

# Pre-Laboratory Questions–EXP 2    Name:

**Due before lab begins. Answer in space provided.**

1. Define the terms diene and dienophile as they apply to the Diels-Alder reaction.
2. How many new bonds, and of what type ( $\sigma$  or  $\pi$ ), are created in a Diels-Alder reaction?
3. What is the structure of the dicyclopentadiene?

4. What diene and what dienophile could be used to prepare each of the following?



5. How is the “exo” and “endo” of a bridged bicyclic compound defined?

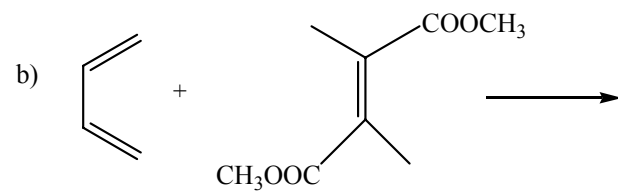
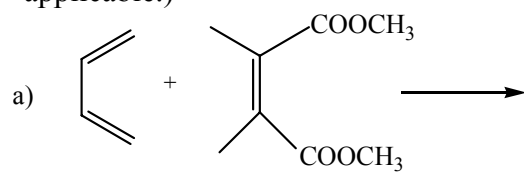
6. Why cannot cyclopentadiene be purchased directly from a commercial supplier?

# Post-Laboratory Questions–EXP 2    Name:

Due after completing the lab.

1. Write an equation for the Diels – Alder reaction of cyclopentadiene and 1,4-benzoquinone.
2. Draw the structures for the “endo” and “exo” products from the reaction of cyclopentadiene with maleic anhydride.

3. What are the products of the following Diels –Alder reactions? (Show the stereochemistry where applicable.)



4. The Diel- Alder reaction is said to be “stereospecific.” What does that mean in terms of product in each reaction in part a .
5. In this experiment you will react cyclopentadiene (the diene) with maleic anhydride (the dienophile) to produce the bicyclic compound, endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride. The endo-adduct is formed exclusively. Why?