Experiment 10. The Diels-Alder Reaction [see: Ege’s 18.4, pp 742-747]

Otto Diels and Kurt Alder (1950 Nobel Prize in Chemistry)

1,3-diene (or Diels-Alder diene) "electron-rich" partner
dienophile "electron-deficient" partner

Any structural changes that enhance these electronic characters result in the rate acceleration of the Diels-Alder reaction.

I. Diene Only the cisoid (or s-cis) form undergoes the Diels-Alder reaction [s: refers to the single bond between the two C=C’s]

- cyclopentadiene
- maleic anhydride

The two C=C bonds are cis.

One of the most reactive Diels-Alder dienes
One of the most reactive dienophiles

s-trans
stayer and more abundant

s-cis
the requisite conformer for the Diels-Alder reaction.

No Diels-Alder reactions are feasible with:

II. Dienophiles: More electron-deficient dienophiles undergo faster Diels-Alder Reactions.

X: electron-withdrawing groups such as -C=N, -NO₂, C(=O)-R (aldehyde/ketone), and -COOR (ester).

\[ \text{fastest Diels-Alder reactions} \]

X: electron-donating groups such as -OCH₃ and -NRR'

\[ \text{slower Diels-Alder reactions} \]
Question:

Which of the two C=C bonds is going to react with butadiene?

III. Stereochemistry of the Diels-Alder Reaction

“Diels-Alder reactions are one-step, concerted reactions.”

(1). Conservation of the stereochemistry.

a. cis-dienophile

b. cis-dienophile

c. trans-dienophile

(2). “endo”-selectivity

*Note:* Highly activated alkynes can serve as Diels-Alder dienophiles. The resulting products are 1,4-cyclohexadienes.
**Experiment 10**

0.20 g in 1 mL of ethyl acetaete then add 1 mL of 60-80 °C ligroin

maleic anhydride

add 0.2 mL of

room temperature (< 5 min)

endo-product

Cyclopentadiene: prepared by cracking dicyclopentadiene (see pp 592-595 of the textbook)