

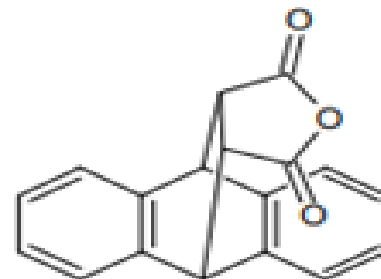


Salahaddin University – Erbil
College of Science
Chemistry Department

Practical Organic
chemistry 3rd Stage

Experiment (3):

The Diels-Alder Reaction of Anthracene with Maleic Anhydride

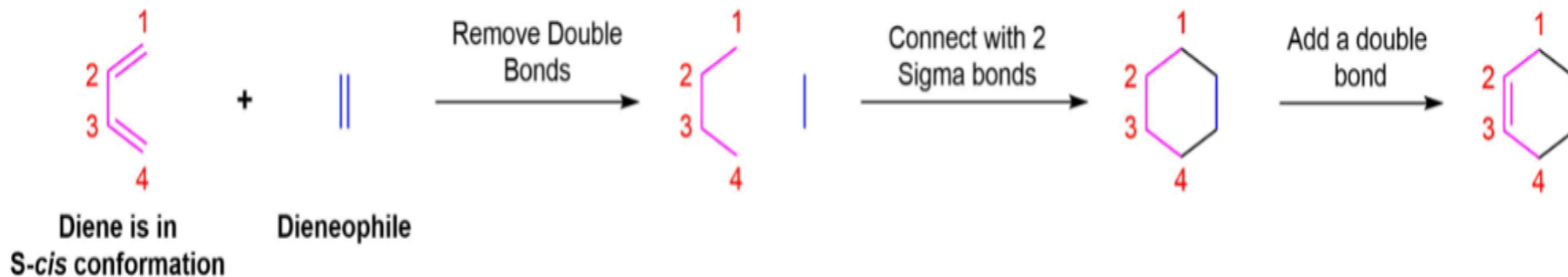
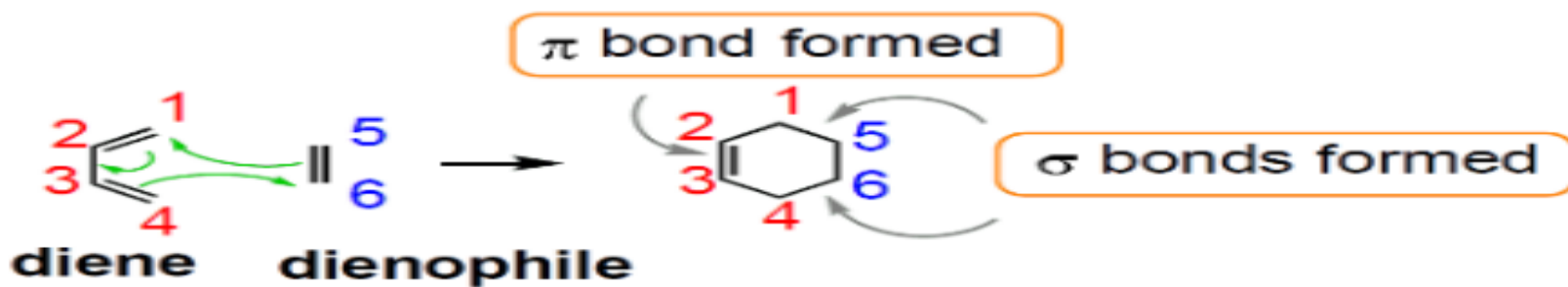


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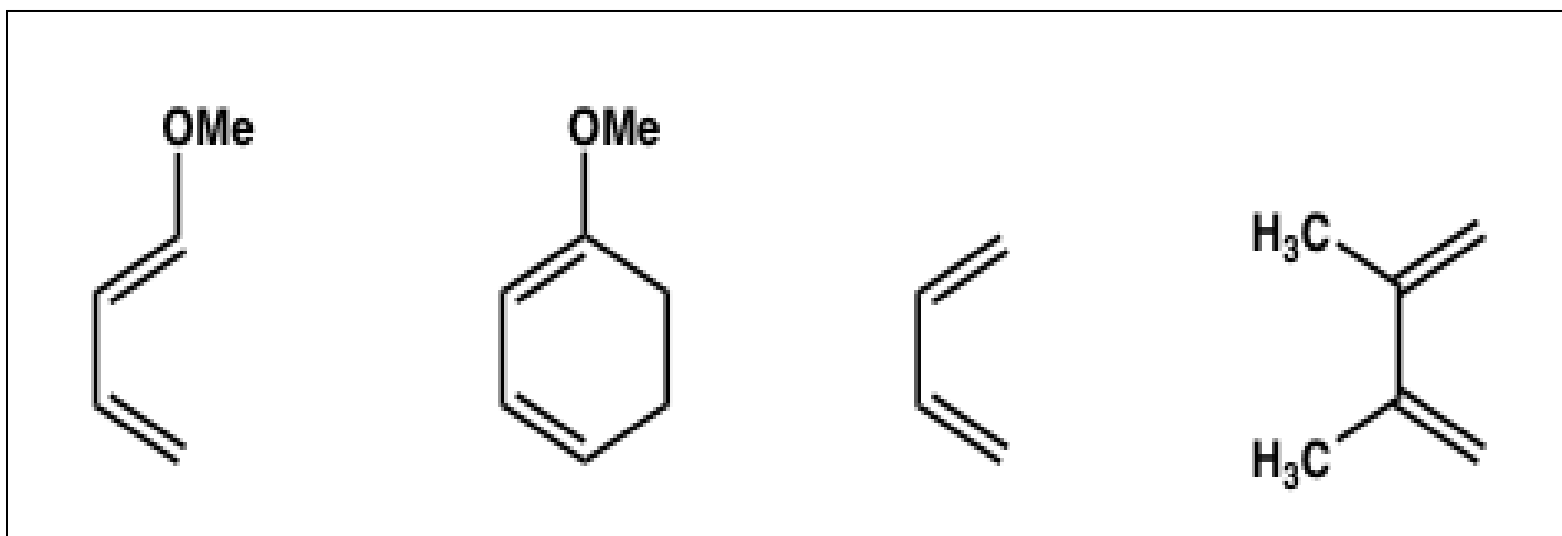
Prepared by Jala B. Ziwar

The **Diels-Alder reaction** is a method of producing cyclical organic compounds (a cycloaddition reaction), and is named for Otto Diels and Kurt Alder who in 1950 received the Nobel Prize for their experiments.

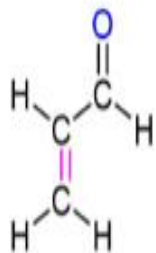
In all Diels-Alder reactions, three π bonds, two in a diene and one in a dienophile, reorganize to give a six-membered ring containing one π bond and two new sigma bonds.



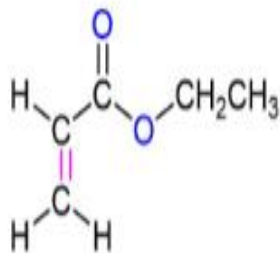
Diene: is the 4π –electron component. It is electron-rich, like a nucleophile in a Lewis acid-base reaction. Simple dienes like 1,3-butadiene are sufficiently electron-rich to react, but electron-releasing groups such as alkyl groups (-R) or alkoxy groups (-OR) enhance a diene's reactivity.



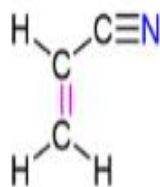
Dienophile is the 2 π –electron component called a "lover of dienes". Good dienophiles contain relatively electron-poor double bonds or triple bonds; at least one strongly electron-withdrawing group is needed.



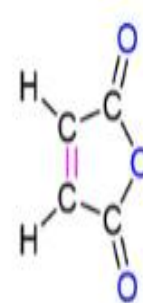
Prepenal
(Acrolein)



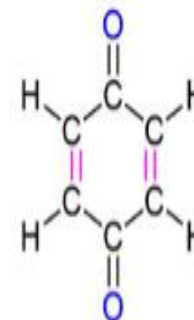
Ethyl propenoate
(Ethyl acrylate)



Propenenitrile
(Acrylonitrile)



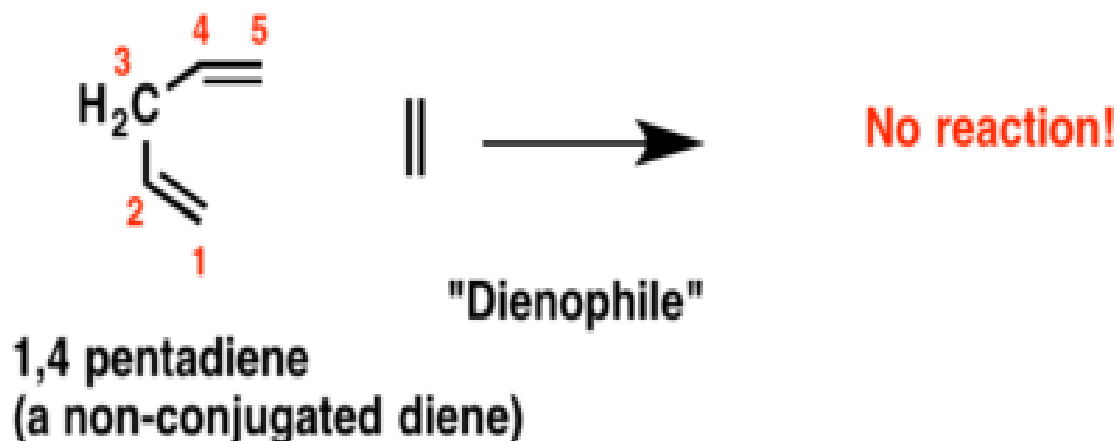
Maleic anhydride



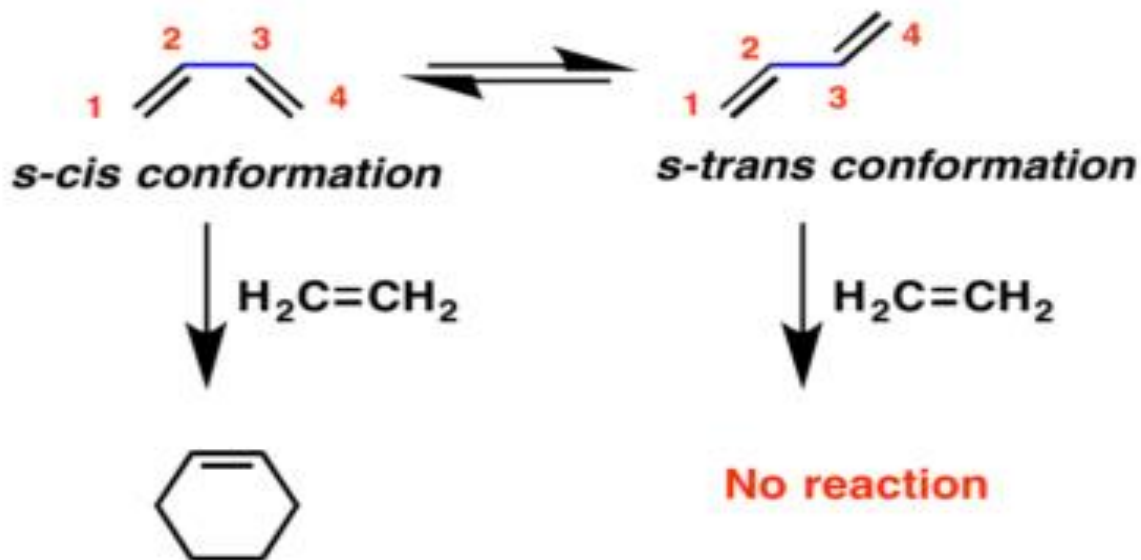
Benzoquinone

The diene must be conjugated to participate in a Diels-Alder reaction. No conjugation, no Diels-Alder. So while 1,3-butadiene readily undergoes the Diels-Alder reaction, 1,4-pentadiene (below) does not.

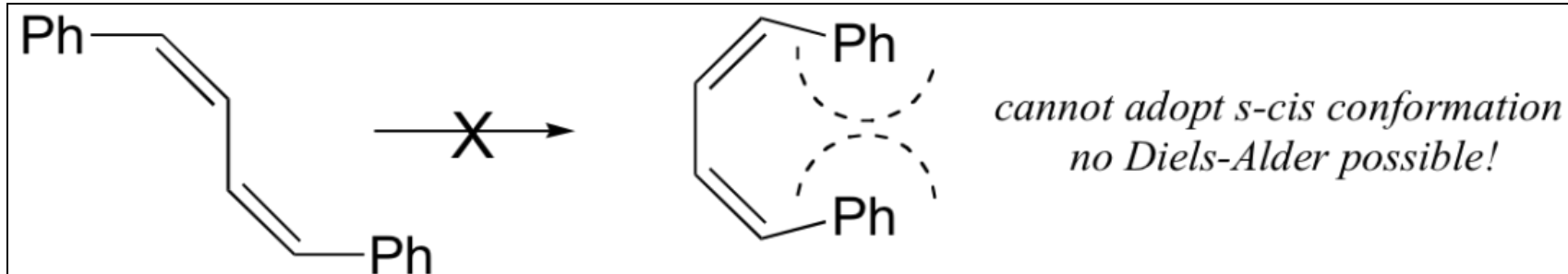
The diene must be conjugated in order for the Diels-Alder to occur:



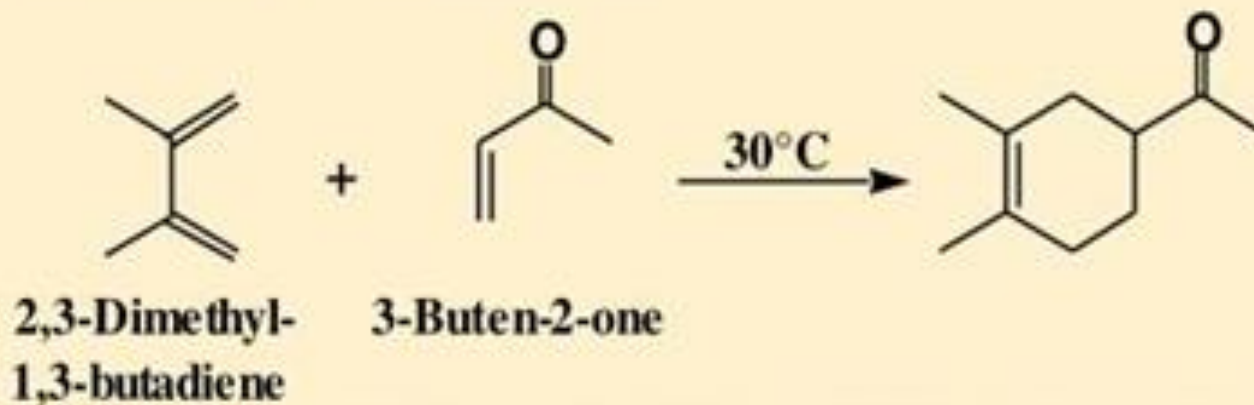
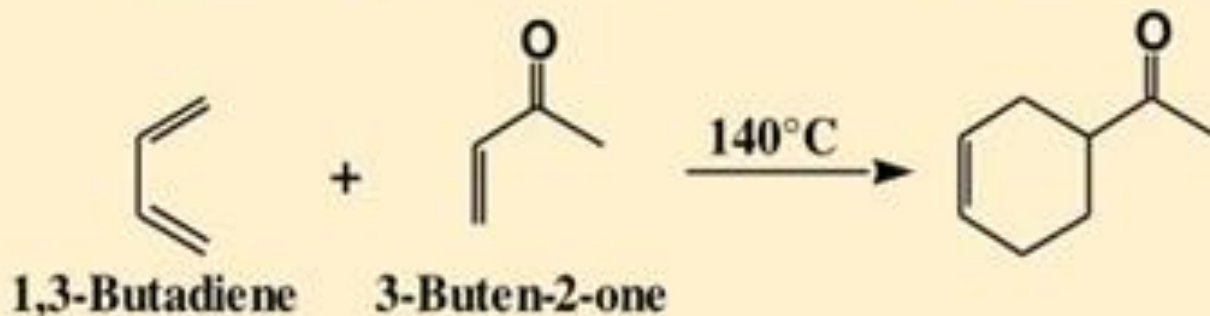
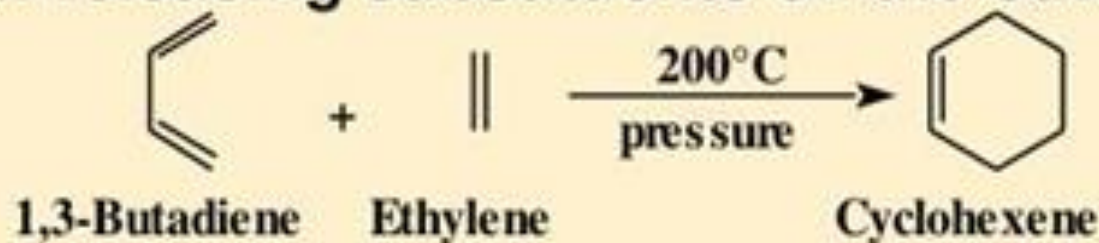
The diene must be in the *s-cis* conformation to participate in the Diels-Alder reaction



The *s-cis* conformation is higher in energy than the *s-trans* conformation, due to steric hindrance. For some dienes, extreme steric hindrance causes the *s-cis* conformation to be highly strained, and for this reason such dienes do not readily undergo Diels-Alder reactions.



Reaction is facilitated by a combination of electron-withdrawing substituents on one reactant and electron-releasing substituents on the other.



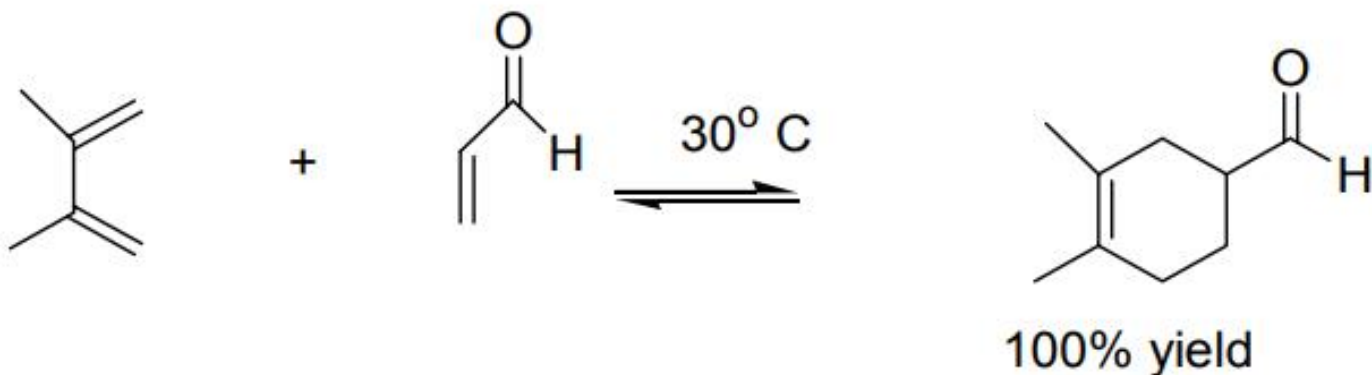
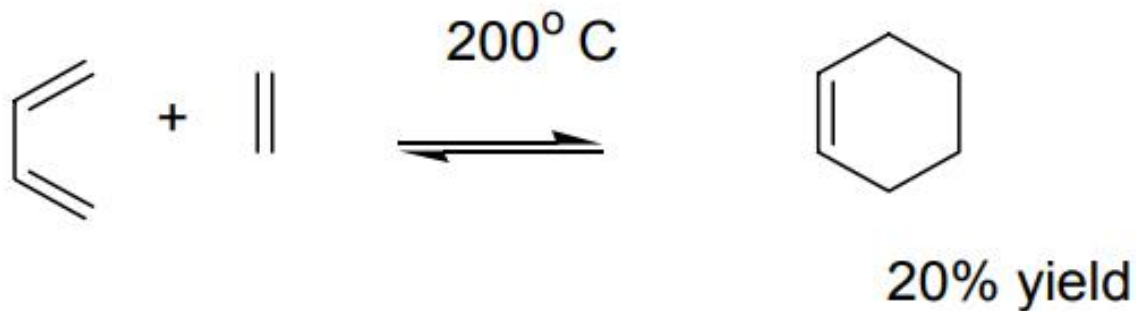
**Electron-Releasing
Groups**

- **CH₃**, alkyl groups
- **OR** (ether)
- **OOCR** (ester)

**Electron-Withdrawing
Groups**

- **CHO** (aldehyde, ketone)
- **COOH** (carboxyl)
- **COOR** (ester)
- **NO₂** (nitro)
- **C≡N** (cyano)

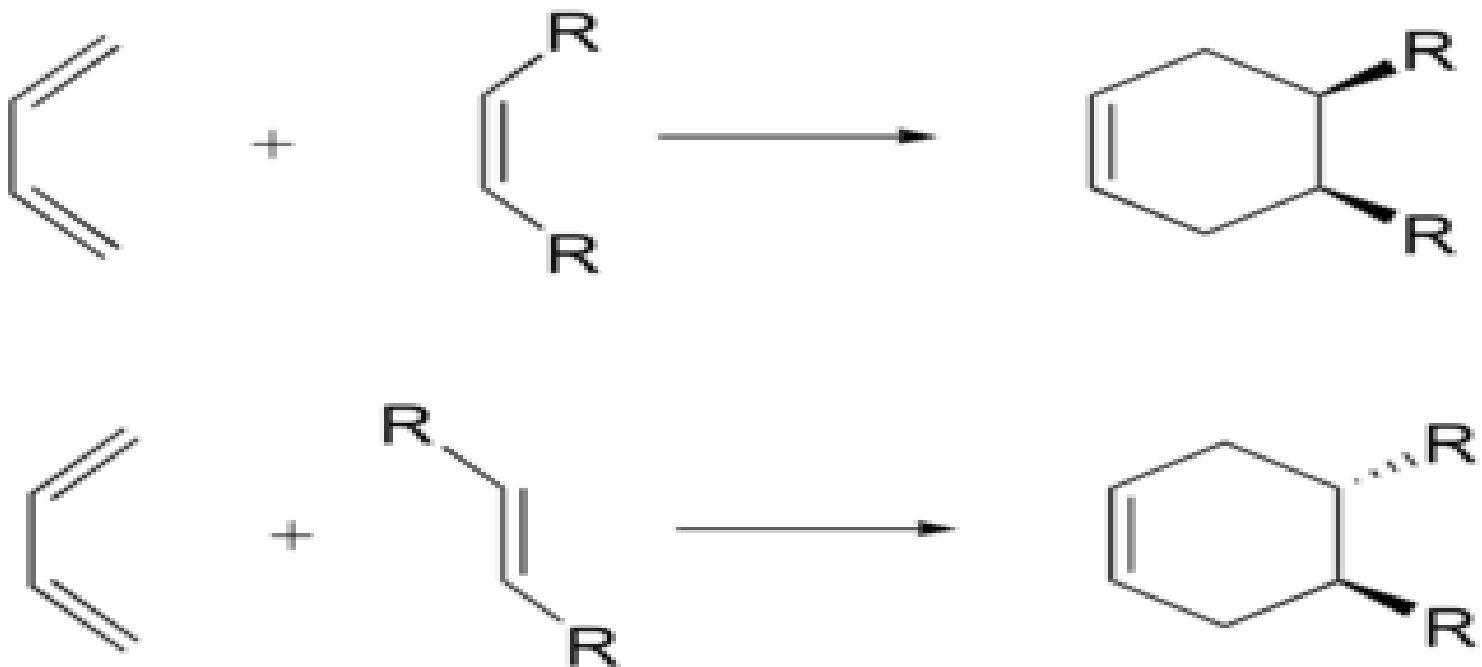
Examples of Dienes and Dienophiles



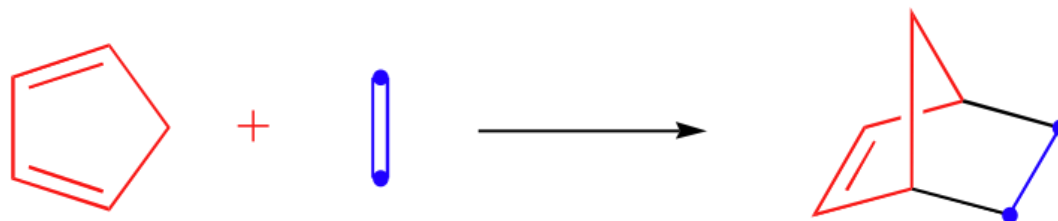
OR>> Employ electron withdrawing groups on dienes and electron donating groups on dienophile

The Diels-Alder reaction is enormously useful for synthetic organic chemists, not only because ring-forming reactions are useful in general but also because in many cases two new stereocenters are formed, and the reaction is inherently **stereospecific**.

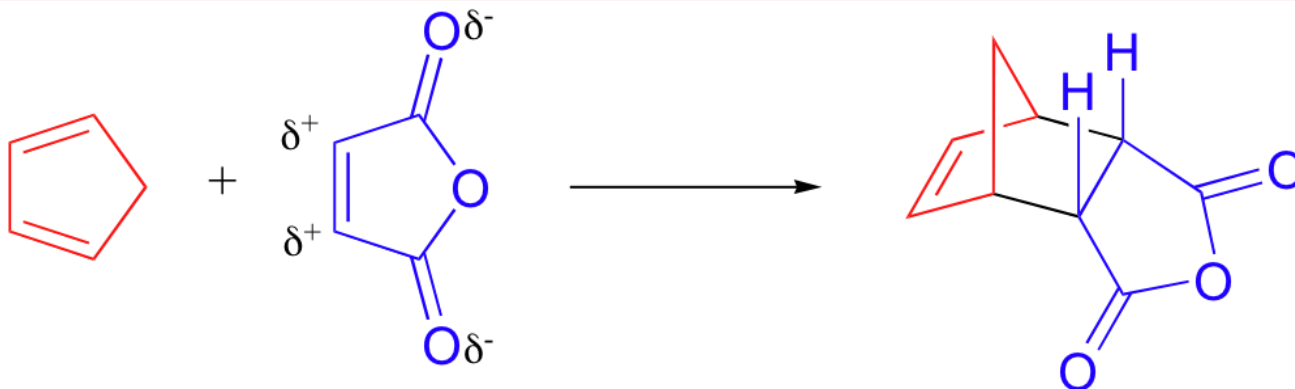
A *cis* dienophile will generate a ring with *cis* substitution, while a *trans* dienophile will generate a ring with *trans* substitution:



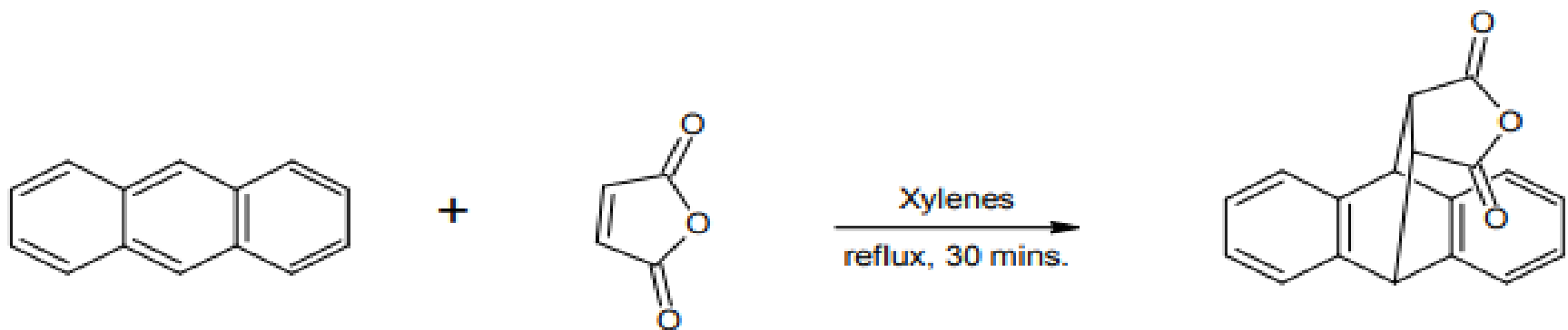
Cyclic dienes, on the other hand, which are 'locked' in the s-cis conformation are especially reactive. The result of a Diels-Alder reaction involving a cyclic diene is a **bicyclic** structure:



The rate at which a Diels-Alder reaction takes place depends on **electronic** as well as **steric** factors. A particularly rapid Diels-Alder reaction takes place between cyclopentadiene and maleic anhydride.



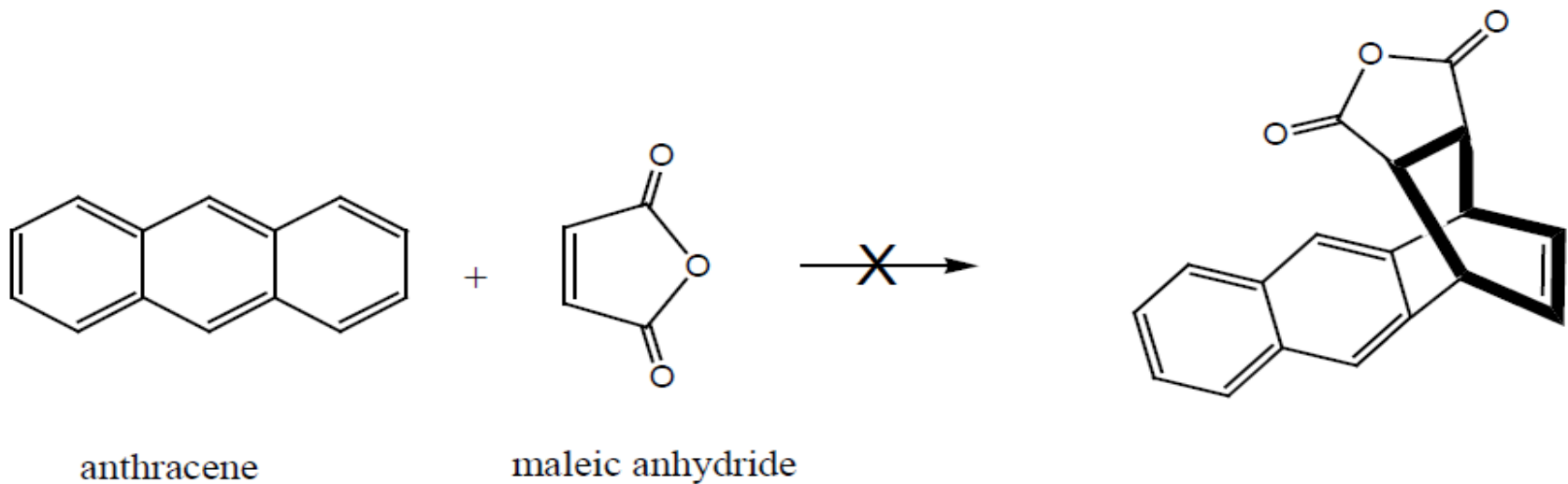
The purpose of this experiment is to form 9,10-dihydroanthracene-9,10- α,β -succinic anhydride by way of a Diels Alder reaction between anthracene and maleic anhydride, as shown in the reaction below. Anthracene acts as the diene and maleic anhydride functions as the dienophile. Xylene (dimethylbenzene) is used as a high boiling temperature solvent so that the reaction will proceed quickly .



Anthracene

Maleic anhydride

*9,10-dihydroanthracene-
-9,10- α,β -succinic anhydride*

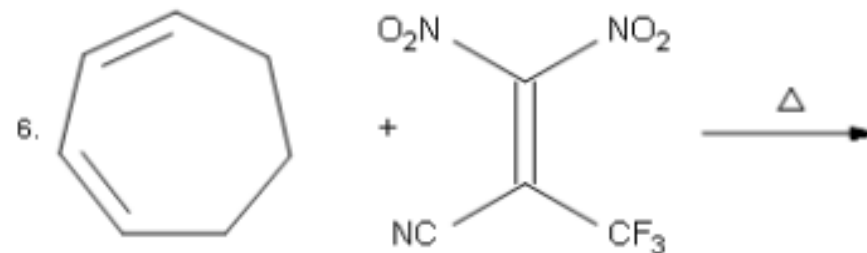
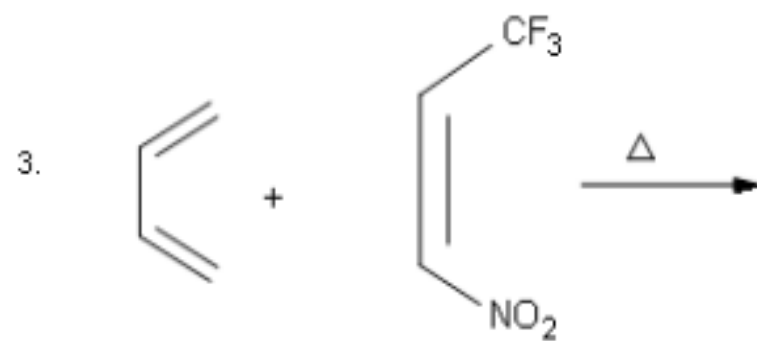
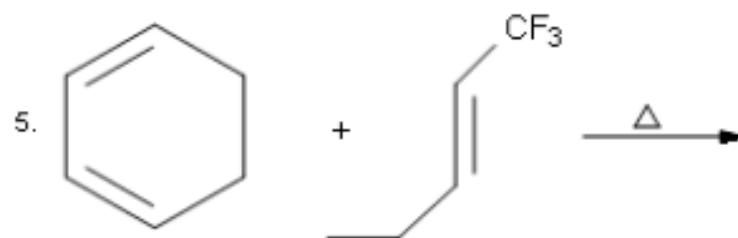
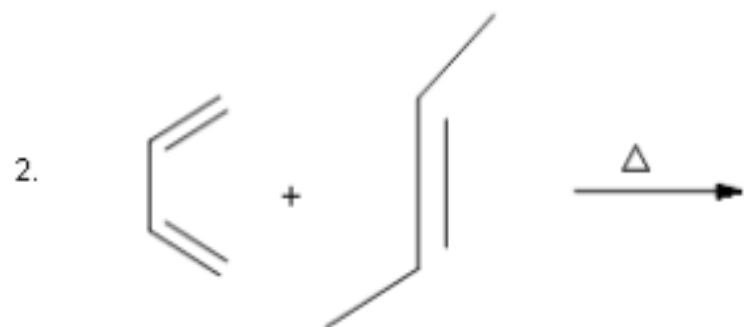


This reaction, shown above, does not occur to any significant extent, because the product formed has less aromatic stabilization. Testing has shown that products with two separate benzene rings are more stable than structures with a naphthalene component.

Procedure:

- 1- Weigh anthracene (0.5 gr.) and maleic anhydride (0.25 gr.).
- 2- Place weighed reagents in flask; add xylene (6 ml).
- 3- Assemble a reflux apparatus.
- 4- Heat anthracene and maleic anhydride at reflux for 30 min.
- 5- Cool the reaction mixture in an ice bath (5 min).
- 6- Use vacuum filtration to collect crude product.
- 7- Dry and weigh the product on a watch glass.

Problem



Draw the product for the following Diels-Alder reactions.

