

## Chem 343 – Organic Reactions

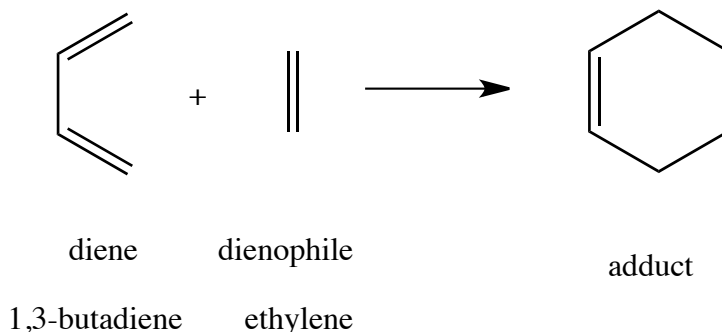
### Chapter 15

Prepared by José Laboy, MS

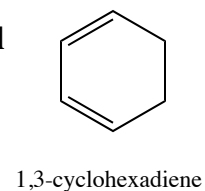
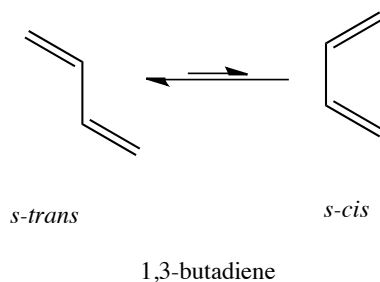
<http://www.chem.wisc.edu/areas/clc> (Resource page)

#### Diels-Alder #1: The Diels-Alder Reaction

#### 1,4-Cycloaddition Reactions of Conjugated Dienes (The Diels-Alder Reaction)

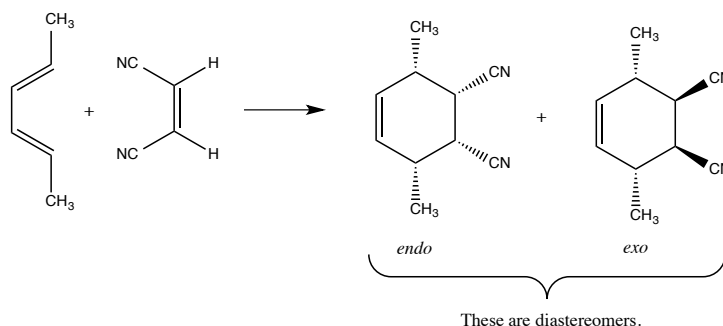


There are two components to the Diels-Alder reaction. Let's first address the conjugated diene, which has to attain the *s-cis* configuration if not in a ring structure (see equilibrium below). Ring structures are "fixed" with respect to rotation and therefore do not have equilibrium between configurations. An example of a conjugated diene ring is 1,3-cyclohexadiene. Consequently, cyclic conjugated dienes react faster than their linear counterparts.

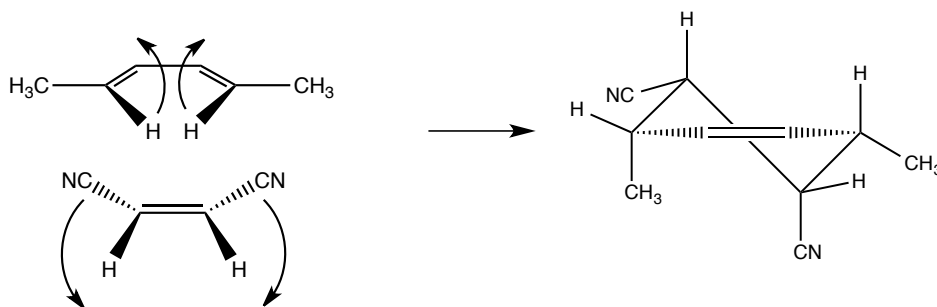


The other component of the reaction is a dienophile, which are molecular structures with at least one  $\pi$ -system to share. These can be alkenes, alkynes or even dienes.

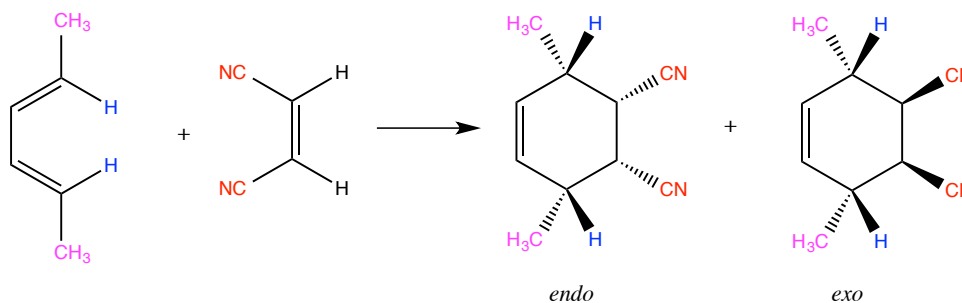
The reaction is concerted with a *syn* addition and occurs with retention of configuration of the dienophile. There are two diastereomeric products from this reaction (see below). One is called the *endo*-product and the other *exo*-product. The *endo*-product in most cases has the lowest energy transition state, therefore, formed in greater amount under kinetic control.



The illustration below shows the approach of the diene and dienophile to form the *endo*-product.



The adduct formed can be depicted in 2D by using the following illustration.



Molecular orbital (MO) theory gives a very nice explanation of the stereochemistry of the Diels-Alder reaction. If your lecturer provides such insight then use the following information.

Below are depicted side-by-side the MOs of each the diene and dienophile with their relative energies. The reaction occurs between the *HOMO* of the diene and the *LUMO* of the dienophile, which are close in energy. The interaction between these two MOs is a *syn* addition and concerted – illustrated below.

