

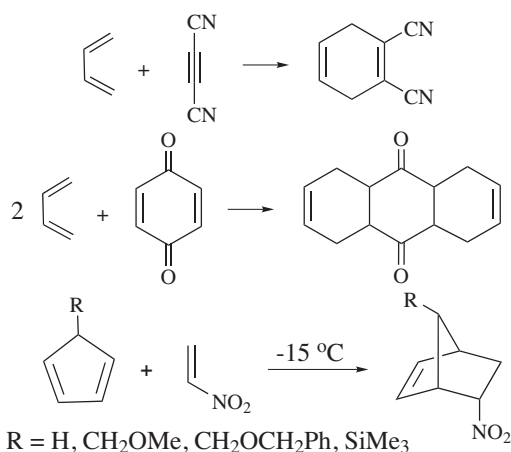
## Diels-Alder Reaction

K. Sarath D. Perera

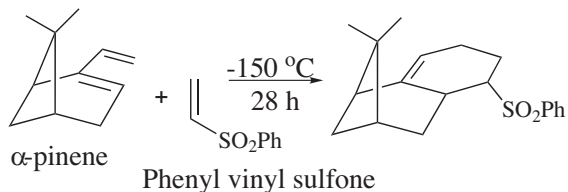
Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Diels-Alder (D-A) reaction is a  $(4\pi+2\pi)$  **cycloaddition** reaction. It is used to generate **six-membered rings** by combining two  $\pi$ -systems. The key components of this reaction are a **conjugated diene** (an alkene with two  $\pi$ -bonds) and a **dienophile** (simple alkene or alkyne). During this **concerted** reaction, two new sigma bonds are formed and change of two  $\pi$ -bonds into sigma bonds takes place.

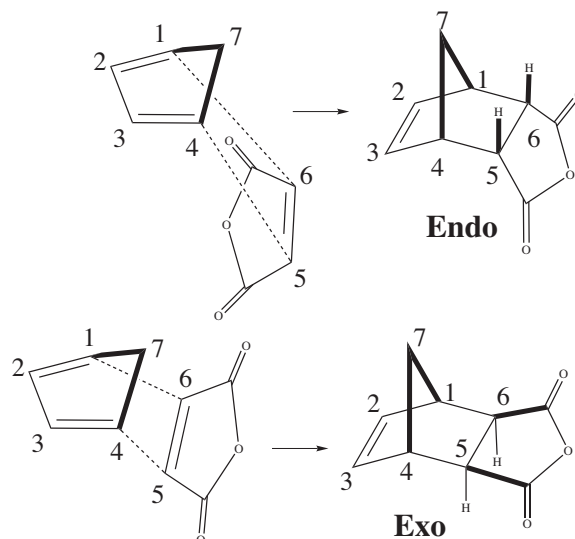
The D-A reaction is a **pericyclic reaction** (1,4-addition). Some examples are given below.



In the following D-A reaction, vinyl sulfone acts as a dienophile. Sulfone ( $-\text{SO}_2\text{Ph}$ ) is a powerful electron withdrawing group.



The products of a Diels-Alder reaction can be either **exo** or **endo** as shown below.

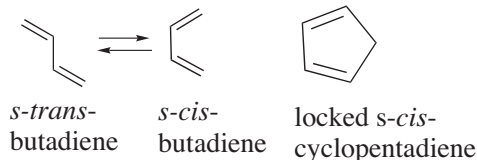


At high temperature, the *exo*-product is formed and at low temperature, the *endo*-product is formed. In the *exo*-product the bulky group is situated away from the double bond. The *endo*-product is kinetically favored due to secondary orbital interaction.

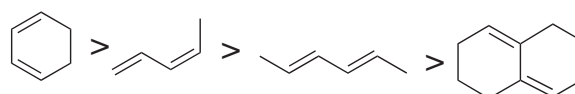
## Features of the Diels-Alder reaction

1. The conjugated diene must be in the **cisoid** configuration.

Cyclic dienes react faster than acyclic dienes as acyclic dienes have to be rotated about the single bond to achieve the cisoid configuration. D-A reaction takes place if the diene forms *s-cis* configuration.

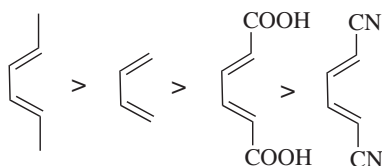


Reactivity of dienes increases as follows.



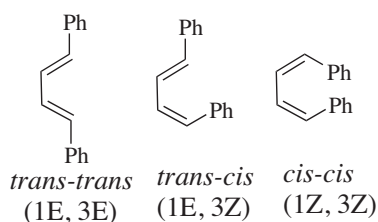
2. The electron-donating groups of the diene enhance the rate of the reaction.

Reactivity of dienes increases as follows.

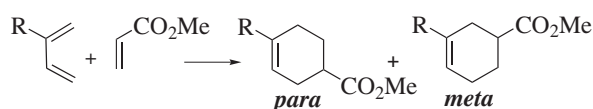


3. This reaction is sensitive to steric factors; thus, it is regioselective.

From the three isomers of 1,4-diphenyl butadiene, only the *trans-trans* (1E,3E) isomer undergoes this reaction.



*Ortho* or *para* substitution is favored over *meta*. The regioselectivity can be predicted by identifying most stable diradical "intermediate". Observations made on Diels-Alder reactions between butadiene system and methyl acrylate are given Table 1.

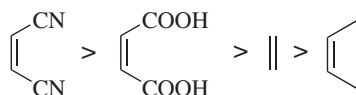


**Table 1:** % Yield and *para/meta* ratio of the above reaction

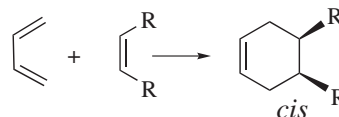
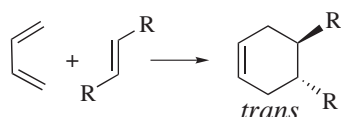
| R               | Yield % | <i>para:meta</i> ratio |
|-----------------|---------|------------------------|
| EtO             | 50      | 100 : 0                |
| Me              | 54      | 5.4 : 1                |
| Pr <sup>i</sup> | 65      | 3 : 1                  |

4. The electron-withdrawing groups of the dienophile increase the reaction rate.

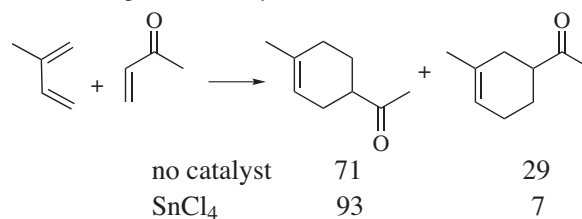
Reactivity of dienophiles increases as follows.



5. The addition of a *cis*-dienophile gives the *cis*-product, whilst the *trans*-alkene adds on anti-fashion to give the *trans*-product.



6. The reaction can be catalyzed by Lewis acids (such as  $\text{BF}_3$ ,  $\text{SnCl}_4$ ,  $\text{AlCl}_3$ ) and they increase the stereo- and regio-selectivity.



### Problems

1. Predict the products of the following reactions.

