The unique character of conjugated dienes manifests itself dramatically in the **Diels-Alder Cycloaddition Reaction**. A cycloaddition reaction is the concerted bonding together of two independent pi-electron systems to form a new ring of atoms. When this occurs, two pi-bonds are converted to two sigma-bonds, the simplest example being the hypothetical combination of two ethene molecules to give cyclobutane. This does not occur under normal conditions, but the cycloaddition of 1,3-butadiene to cyanoethene (acrylonitrile) does, and this is an example of the Diels-Alder reaction. The following diagram illustrates two cycloadditions, and introduces several terms that are useful in discussing reactions of this kind.

In the hypothetical ethylene dimerization on the left, each reactant molecule has a pi-bond (colored orange) occupied by two electrons. The cycloaddition converts these pi-bonds into new sigma-bonds (colored green), and this transformation is then designated a [2+2] cycloaddition, to enumerate the reactant pi-electrons that change their bonding location.

The Diels-Alder reaction is an important and widely used method for making six-membered rings, as shown on the right. The reactants used in such reactions are a conjugated diene, simply referred to as the **diene**, and a double or triple bond coreactant called the **dienophile**, because it combines with (has an affinity for) the diene. The Diels-Alder cycloaddition is classified as a [4+2] process because the diene has four pi-electrons that shift position in the reaction and the dienophile has two.

The Diels-Alder reaction is a single step process, so the diene component must adopt a cis-like conformation in order for the end carbon atoms (#1 & #4) to bond simultaneously to the dienophile. Such conformations are called **s-cis**, the s referring to the single bond connecting the two double bonds. The s-cis and s-trans conformers of 1,3-butadiene are shown in the preceding diagram. For many acyclic dienes the s-trans conformer is more stable than the s-cis conformer (due to steric crowding of the end groups), but the two are generally in rapid equilibrium, permitting the use of all but the most hindered dienes as reactants in Diels-Alder reactions. In its usual form, the diene component is electron rich, and the best dienophiles are electron poor due to electron withdrawing substituents such as CN, C=O & NO₂. The initial bonding interaction reflects this electron imbalance, with the two new sigma-bonds being formed simultaneously, but not necessarily at equal rates.

**Stereospecificity**

We noted earlier that addition reactions of alkenes often exhibited stereoselectivity, in that the reagent elements in some cases added syn and in other cases anti to the the plane of the double bond. Both reactants in the Diels-Alder reaction may demonstrate stereoisomerism, and when they do it is found that the relative configurations of the reactants are preserved in the product (the adduct). The following drawing illustrates this fact for the reaction of 1,3-butadiene with (E)-dicynoethene. The trans relationship of the cyano groups in the dienophile is preserved in the six-membered ring of the adduct. Likewise, if the terminal carbons of the diene bear substituents, their relative configuration will be retained in the adduct. Using the earlier terminology, we could say that bonding to both the diene and the dienophile is syn. An alternative description, however, refers to the planar nature of both reactants and terms the bonding in each case to be
**suprafacial** (i.e. to or from the same face of each plane). This stereospecificity also confirms the synchronous nature of the 1,4-bonding that takes place.

The essential characteristics of the Diels-Alder cycloaddition reaction may be summarized as follows:

i. The reaction always creates a new six-membered ring. When intramolecular, another ring may also be formed.

ii. The diene component must be able to assume a s-cis conformation.

iii. Electron withdrawing groups on the dienophile facilitate reaction.

iv. Electron donating groups on the diene facilitate reaction.

v. Steric hindrance at the bonding sites may inhibit or prevent reaction.

vi. The reaction is stereospecific with respect to substituent configuration in both the dienophile and the diene.

These features are illustrated by the following eight examples, one of which does not give a Diels-Alder cycloaddition. Try to predict the course of each reaction before checking the answers. The formation of a new six-membered ring should be apparent in every case where reaction occurs.

There is no reaction in example D because this diene cannot adopt a s-cis orientation. In examples B, C, F, G & H at least one of the reactants is cyclic so that the product has more than one ring, but the newly formed ring is always six-membered. In example B the the same cyclic compound acts as both the diene colored blue) and the dienophile (colored red). The adduct has three rings, two of which are the five-membered rings present in the reactant, and the third is the new six-membered ring (shaded light yellow). Example C has an alkyne as a dienophile (colored red), so the adduct retains a double bond at that location. This double bond could still serve as a dienophile, but in the present case the diene is sufficiently hindered to retard a second cycloaddition.
The quinone dienophile in reaction F has two dienophilic double bonds. However, the double bond with two methyl substituents is less reactive than the unsubstituted dienophile due in part to the electron donating properties of the methyl groups and in part to steric hindrance. The stereospecificity of the Diels-Alder reaction is demonstrated by examples A, E & H. In A & H the stereogenic centers lie on the dienophile, whereas in E these centers are on the diene. In all cases the configuration of the reactant is preserved in the adduct.

Exo and Endo Bicyclics

Cyclic dienes, such as those in examples B, C & G, give bridged bicyclic adducts for which an additional configurational feature must be designated. As shown in the following diagram, there are two possible configurations for compounds of this kind. If a substituent (colored magenta here) is oriented cis to the longest or more unsaturated bridge (colored blue here), it is said to be endo. When directed trans to the bridge it is exo. When the Diels-Alder reaction forms bridged bicyclic adducts and an unsaturated substituent is located on this bicyclic structure (as in B & G), the chief product is normally the endo isomer "Alder's Endo Rule". Example C does not merit such a nomenclature, since stereoisomeric orientations of the substituent are not possible.

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