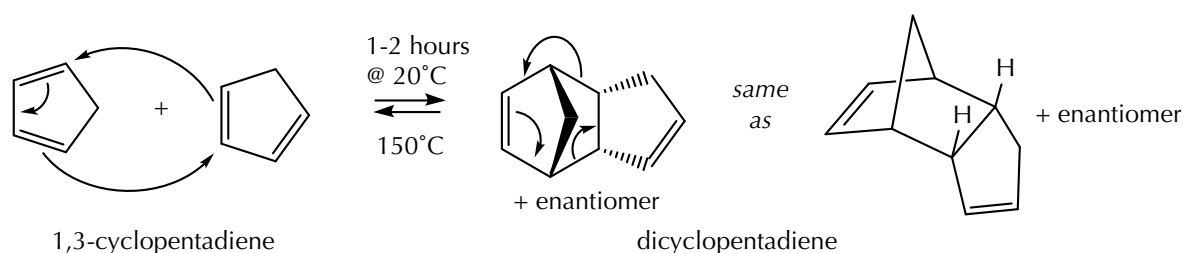


D. Retro Diels-Alder Reactions

In the earliest studies of the Diels-Alder reaction, one of the important observations was that the reaction was reversible. So, if the Diels-Alder reaction, in the forward direction, is called a cycloaddition, then the reverse reaction (the retro Diels-Alder reaction) is called a cycloreversion or sometimes a fragmentation reaction. The position of the equilibrium naturally depends on the relative stabilities of two sides of the reaction. For example, 1,3-cyclopentadiene, which has been used throughout the chapter as an excellent 100% *s-cis* diene, cannot be purchased as 1,3-cyclopentadiene because it undergoes a Diels-Alder reaction with itself in a matter of a few hours at room temperature to form its dimer, dicyclopentadiene (Figure 1550). At temperatures above 150°C, the retro Diels-Alder reaction takes place, which is called “cracking dicyclopentadiene,” and an experimentalist needs to use the resulting 1,3-cyclopentadiene right away, before it redimerizes.

Figure 1550

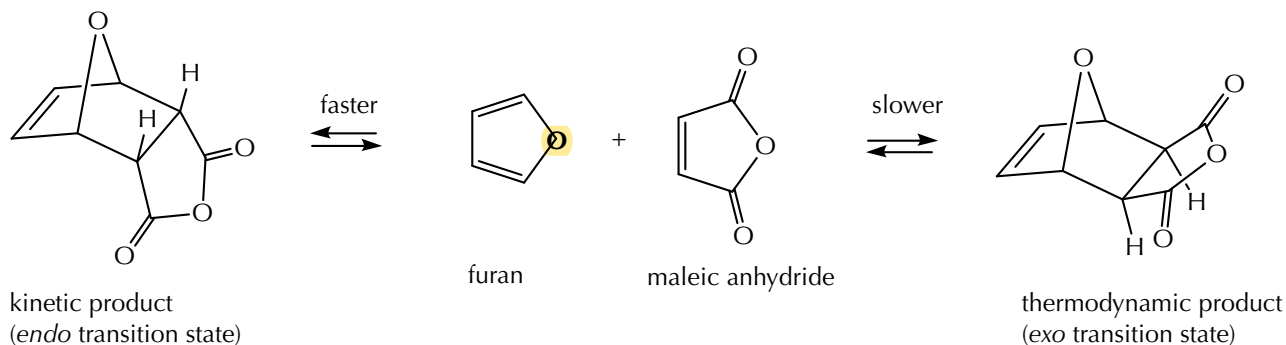
Dimerization of 1,3-cyclopentadiene and cracking dicyclopentadiene: the reversibility of Diels-Alder reaction.



The reversibility of the Diels-Alder reaction can affect the diastereoselectivity of the reaction. When furan and maleic anhydride react, the *endo* product forms about 500 times faster than the *exo* product, and this diastereoselectivity is attributed to the secondary orbital interactions. However, the rate of the retro Diels-Alder reaction is also high because of the relative steric hindrance of the *endo* product, and within minutes (at 40°C), the thermodynamically more stable *exo* product is formed and does not undergo a retro Diels-Alder reaction nearly as fast as the *endo* product (Figure 1551).

Figure 1551

Retro Diels-Alder reactions can affect the diastereoselectivity by creating equilibration between the *endo* and *exo* forms.



The retro Diels-Alder reaction can represent the favorable direction for the reaction, particularly if one or both products that form are aromatic. For example, the first bridged, bicyclic molecule shown in Figure 1552 undergoes an irreversible retro Diels-Alder reaction at about 60°C to release 1,4-cyclohexadiene and an aromatic benzene derivative. This strategy for preparing a double bond that might otherwise be quite reactive has been used often. In the second example, the nonaromatic product contains a ketene functional group ($R_2C=C=O$), which is formed in high yield at 140°C along with a completely unreactive aromatic byproduct.