

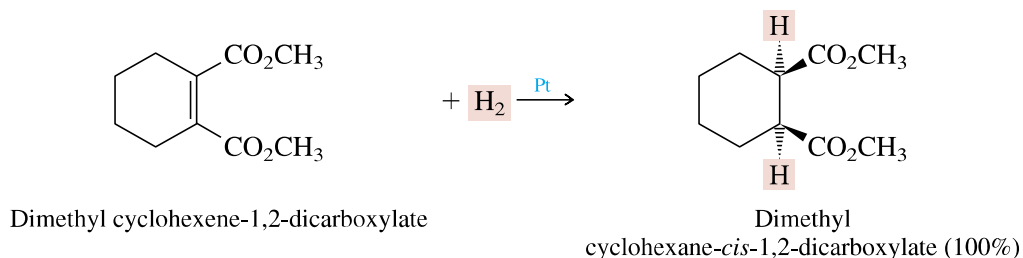
Ethylene, which has no alkyl substituents to stabilize its double bond, has the highest heat of hydrogenation. Alkenes that are similar in structure to one another have similar heats of hydrogenation. For example, the heats of hydrogenation of the monosubstituted (terminal) alkenes propene, 1-butene, and 1-hexene are almost identical. *Cis*-disubstituted alkenes have lower heats of hydrogenation than monosubstituted alkenes but higher heats of hydrogenation than their more stable *trans* stereoisomers. Alkenes with trisubstituted double bonds have lower heats of hydrogenation than disubstituted alkenes, and tetrasubstituted alkenes have the lowest heats of hydrogenation.

PROBLEM 6.2 Match each alkene of Problem 6.1 with its correct heat of hydrogenation.

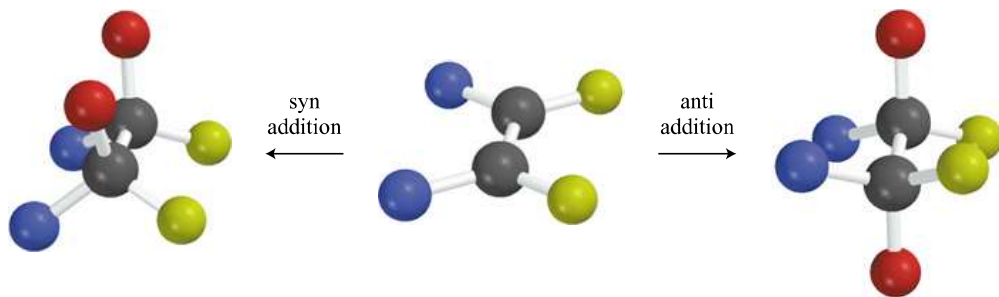
Heats of hydrogenation in kJ/mol (kcal/mol): 112 (26.7); 118 (28.2); 126 (30.2)

6.3 STEREOCHEMISTRY OF ALKENE HYDROGENATION

In the mechanism for alkene hydrogenation shown in Figure 6.1, hydrogen atoms are transferred from the catalyst's surface to the alkene. Although the two hydrogens are not transferred simultaneously, it happens that both add to the same face of the double bond, as the following example illustrates.



The term **syn addition** describes the stereochemistry of reactions such as catalytic hydrogenation in which two atoms or groups add to the *same face* of a double bond. When atoms or groups add to *opposite faces* of the double bond, the process is called **anti addition**.



Stereoselectivity was defined and introduced in connection with the formation of stereoisomeric alkenes in elimination reactions (Section 5.11).

A second stereochemical aspect of alkene hydrogenation concerns its **stereoselectivity**. A reaction in which a single starting material can give two or more stereoisomeric products but yields one of them in greater amounts than the other (or even to the exclusion of the other) is said to be **stereoselective**. The catalytic hydrogenation of α -pinene (a constituent of turpentine) is an example of a stereoselective reaction. Syn addition of

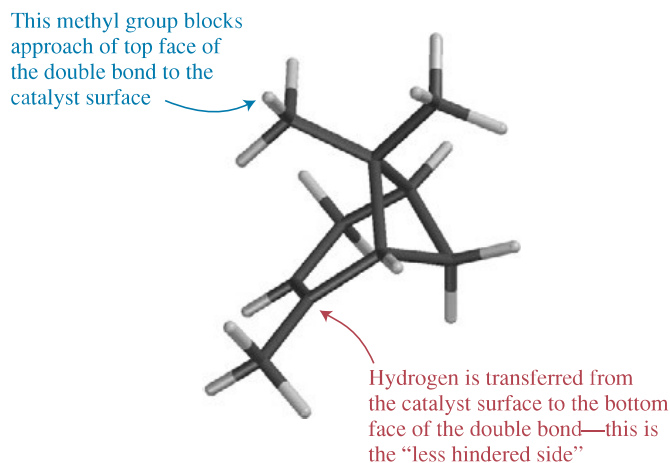
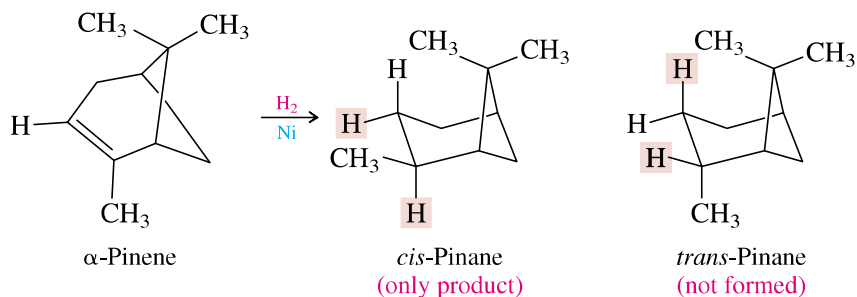


FIGURE 6.3 The methyl group that lies over the double bond of α -pinene shields one face of it, preventing a close approach to the surface of the catalyst. Hydrogenation of α -pinene occurs preferentially from the bottom face of the double bond.

hydrogen can in principle lead to either *cis*-pinane or *trans*-pinane, depending on which face of the double bond accepts the hydrogen atoms (shown in red in the equation).



cis-Pinane and *trans*-pinane are common names that denote the relationship between the pair of methyl groups on the bridge and the third methyl group.

In practice, hydrogenation of α -pinene is observed to be 100% stereoselective. The only product obtained is *cis*-pinane. None of the stereoisomeric *trans*-pinane is formed.

The stereoselectivity of this reaction depends on how the alkene approaches the catalyst surface. As the molecular model in Figure 6.3 shows, one of the methyl groups on the bridge carbon lies directly over the double bond and blocks that face from easy access to the catalyst. The bottom face of the double bond is more exposed, and both hydrogens are transferred from the catalyst surface to that face.

Reactions such as catalytic hydrogenation that take place at the “less hindered” side of a reactant are common in organic chemistry and are examples of steric effects on *reactivity*. We have previously seen steric effects on *structure* and *stability* in the case of *cis* and *trans* stereoisomers and in the preference for equatorial substituents on cyclohexane rings.

6.4 ELECTROPHILIC ADDITION OF HYDROGEN HALIDES TO ALKENES

In many addition reactions the attacking reagent, unlike H_2 , is a polar molecule. Hydrogen halides are among the simplest examples of polar substances that add to alkenes.

