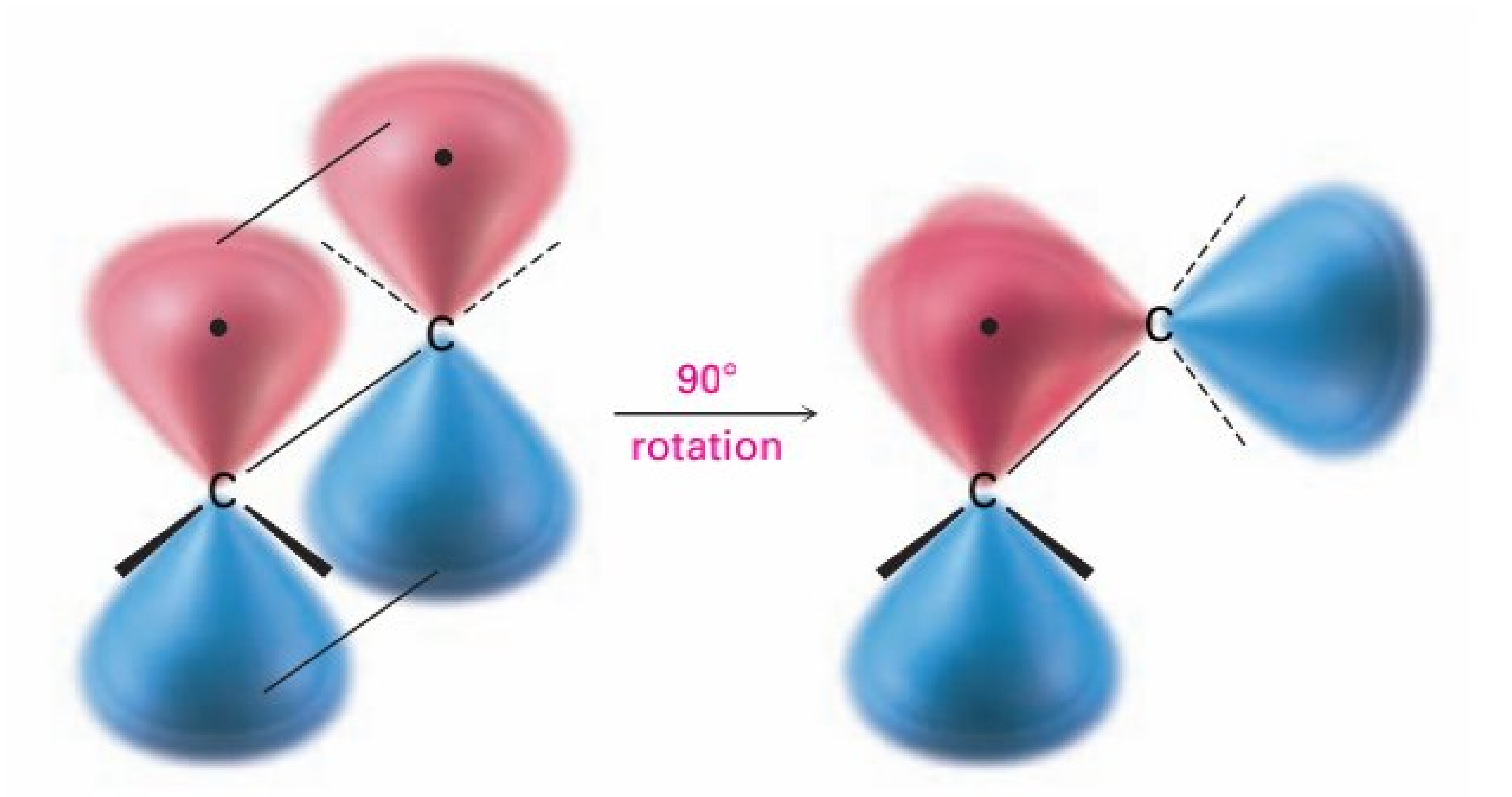
Problem 3.5 Change the following old names to new, post-1993 names, and draw the structure of each compound:

(a) 2,5,5-Trimethyl-2-hexene **(b)** 2,2-Dimethyl-3-hexyne
(c) 2-Methyl-2,5-heptadiene **(d)** 1-Methyl-1,3-cyclopentadiene

3.2 Electronic Structure of Alkenes

We saw in Section 1.8 that the carbon atoms in a double bond have three equivalent sp^2 hybrid orbitals, which lie in a plane at angles of 120° to one another. The fourth carbon orbital is an unhybridized p orbital perpendicular to the sp^2 plane. When two sp^2-hybridized carbon atoms approach each other, they form a σ bond by head-on overlap of sp^2 orbitals and a π bond by sideways overlap of p orbitals. The doubly bonded carbons and the four attached atoms lie in a plane, with bond angles of approximately 120° (Figure 3.1).

We also know from Section 2.5 that rotation can occur around single bonds and that open-chain alkanes like ethane and propane therefore have many rapidly interconverting conformations. The same is not true for double bonds, however. For rotation to take place around a double bond, the π part of the bond must break momentarily (Figure 3.1). Thus, the energy barrier to rotation around a double bond must be at least as great as the strength of the π bond itself, an estimated 350 kJ/mol (84 kcal/mol). Recall that the rotation barrier for a single bond is only about 12 kJ/mol.



π bond
(p orbitals are parallel)

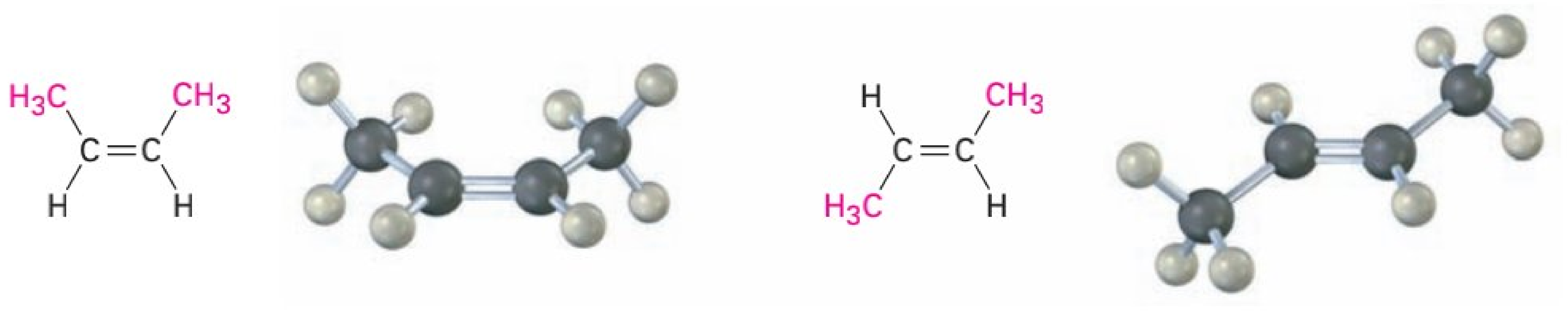
Broken π bond after rotation
(p orbitals are perpendicular)

Figure 3.1 The π bond must break momentarily for rotation around a carbon–carbon double bond to take place, requiring a large amount of energy.

3.3 Cis–Trans Isomers of Alkenes

The lack of rotation around carbon–carbon double bonds is of more than just theoretical interest; it also has chemical consequences. Imagine the situation for a disubstituted alkene such as but-2-ene. (*Disubstituted* means that two substituents other than hydrogen are bonded to the double-bond carbons.) The two methyl groups in but-2-ene can be either on the same side of the double bond or on opposite sides, a situation similar to that in substituted cycloalkanes (Section 2.8).

Because bond rotation can't occur, the two but-2-enes can't spontaneously interconvert and are different chemical compounds. As with disubstituted cycloalkanes, we call such compounds *cis–trans isomers.* The isomer with both substituents on the same side of the double bond is *cis*-but-2-ene, and the isomer with substituents on opposite sides is *trans*-but-2-ene (Figure 3.2).

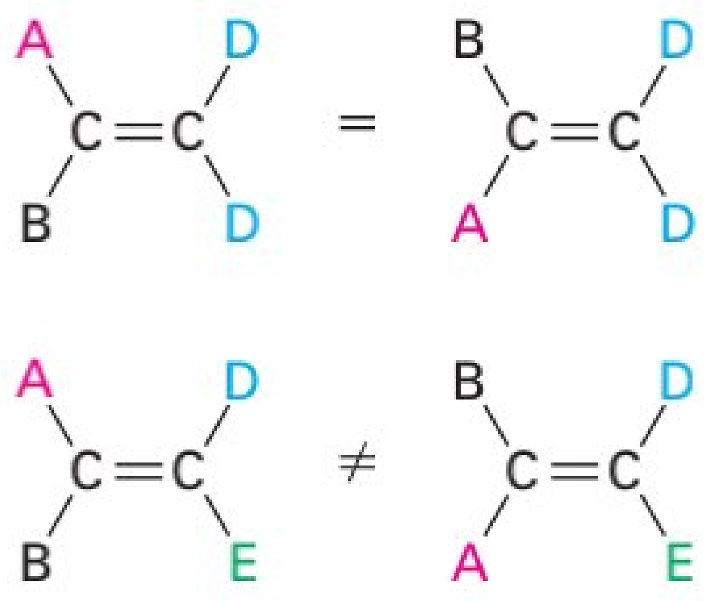


***cis*-But-2-ene**

***trans*-But-2-ene**

Figure 3.2 **Cis and trans isomers of but-2-ene. The cis isomer has the two methyl groups on the same side of the double bond, and the trans isomer has the methyl groups on opposite sides.**

Cis–trans isomerism is not limited to disubstituted alkenes. It occurs whenever each double-bond carbon is attached to two different groups. If one of the double-bond carbons is attached to two identical groups, however, then cis–trans isomerism is not possible (Figure 3.3).

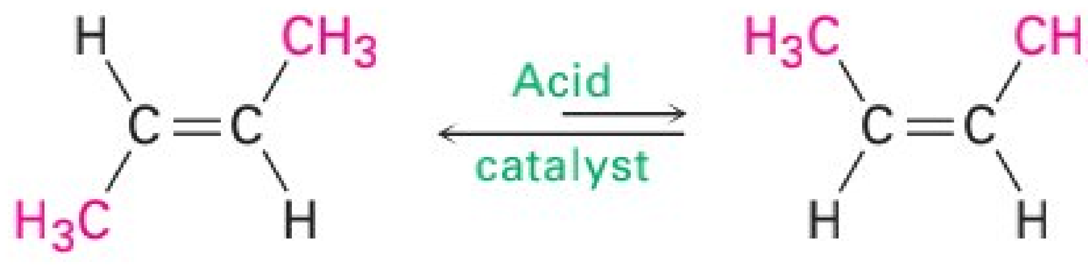


These two compounds are identical; they are not cis–trans isomers.

These two compounds are not identical; they are cis–trans isomers.

Figure 3.3 **The requirement for cis–trans isomerism in alkenes. Compounds that have one of their carbons bonded to two identical groups can't exist as cis–trans isomers. Only when both carbons are bonded to two different groups are cis–trans isomers possible.**

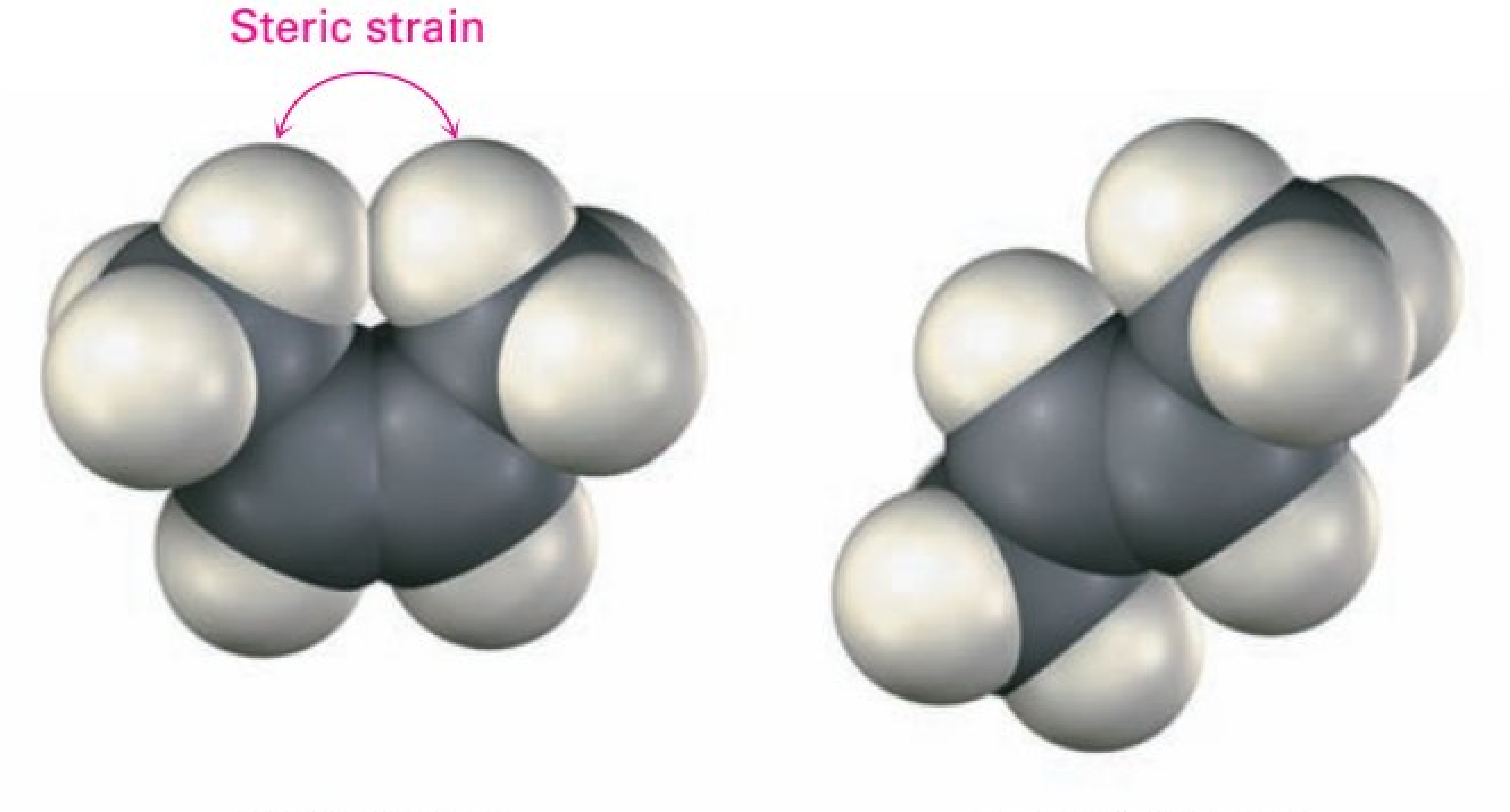
Although the interconversion of cis and trans alkene isomers doesn't occur spontaneously, it can be brought about by treating the alkene with a strong acid catalyst. If we do, in fact, interconvert *cis*-but-2-ene with *trans*-but-2-ene and allow them to reach equilibrium, we find that they aren't of equal stability. The trans isomer is more favored than the cis isomer by a ratio of 76 : 24.



Trans (76%)

Cis (24%)

Cis alkenes are less stable than their trans isomers because of steric (spatial) interference between the large substituents on the same side of the double bond. This is the same kind of interference, or *steric strain,* that we saw in the axial conformation of methylcyclohexane (Section 2.11).



***cis*-But-2-ene** ***trans*-But-2-ene**

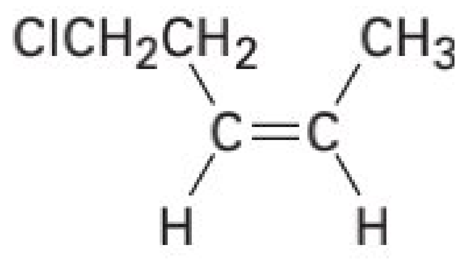
Worked Example 3.2

Drawing Cis and Trans Alkene Isomers

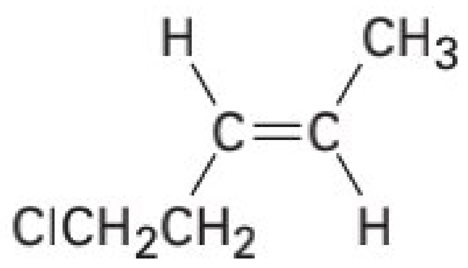
Draw the cis and trans isomers of 5-chloropent-2-ene.

Strategy First, draw the molecule without indicating isomers to see the overall structure: $ClCH_2CH_2CH{=}CHCH_3$. Then locate the two substituent groups on the same side of the double bond for the cis isomer and on opposite sides for the trans isomer.

Solution



***cis*-5-Chloropent-2-ene**



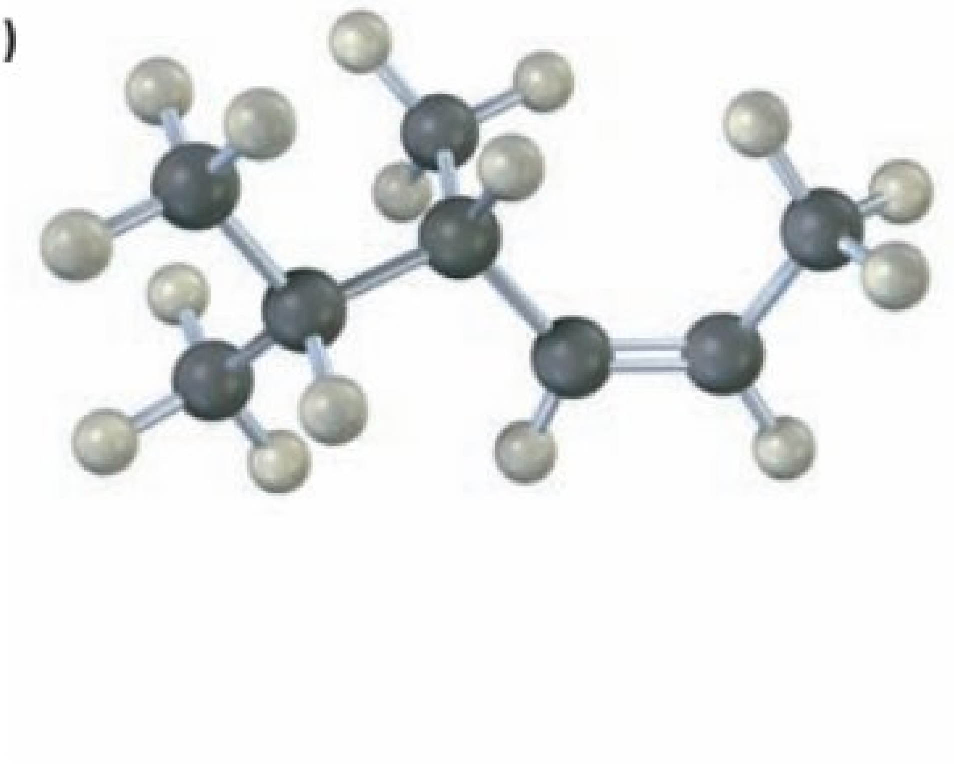
***trans*-5-Chloropent-2-ene**

Problem 3.6 Which of the following compounds can exist as cis–trans isomers? Draw each cis–trans pair.

(a) $CH_3CH{=}CH_2$
(b) $(CH_3)_2C{=}CHCH_3$
(c) $ClCH{=}CHCl$
(d) $CH_3CH_2CH{=}CHCH_3$
(e) $CH_3CH_2CH{=}C(Br)CH_3$
(f) 3-Methylhept-3-ene

Problem 3.7 Name the following alkenes, including the cis or trans designation:

(a)



(b)