

## 3 2-butene

### Aims

In this chapter you will learn *cis* and *trans* isomerism caused by restricted rotation about a double bond (that is, with higher energy barriers) by studying dichloroethylene, maleic acid and fumaric acid as examples. *Z*, *E* nomenclature will also be introduced for more complicated compounds in which *cis-trans* nomenclature is difficult to apply.

Furthermore, you will learn that the differentiation between geometrical isomerism and conformational isomerism should be discussed in terms of the amount of the barrier to rotation rather than the type of bond to be rotated.

The *s-trans* and *s-cis* isomerism in dienes will also be introduced.

### New terms and concepts

*cis-trans* isomerism  
geometrical isomerism  
*cis* isomer  
*trans* isomer  
*Z* configuration  
*E* configuration  
*s-trans* isomer  
*s-cis* isomer-

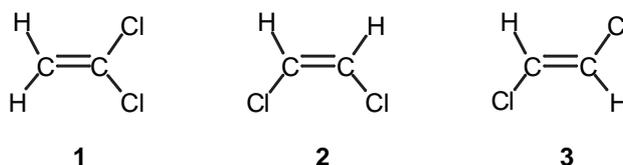
### Goal of this chapter

After you master this chapter successfully, you will be able to do the following:

- 1 to point out the presence of *trans* and *cis* isomers of compounds with a double bond, and distinguish these two isomers.
- 2 to expand the concept of *cis* and *trans* isomerism to compounds with a double bond other than the C=C bond.
- 3 to name complicated compounds by the *Z*, *E* nomenclature on the basis of the sequence rule.
- 4 to distinguish conformers of dienes.

### 3.1 *Cis-trans* isomerism

Of the various isomerisms, geometrical isomerism with a C=C double bond should be easy to understand. The three isomers of dichloroethylenes, **1**~**3** are a popular set of compounds to serve as an example. Though all of these are isomers, **1** and **2**, and **3** are structural isomers with different rational formulas. On the other hand, **2** and **3** are stereoisomers because they have common rational formula (ClCH=CHCl). There is a difference, however, in the arrangement of their atoms in space. For isomer **2**, the Cl ligands are on the same side of the plane constituted by the double bond, but these ligands are on opposite sides in the isomer **3**. Thus, these are the isomers with different configurations. The former is called a *cis* isomer, and the latter a *trans* isomer. This kind of stereoisomerism is called *cis-trans* isomerism or **geometrical isomerism**.



A pair of isomers which are stereoisomers but not enantiomers is called **diastereomers**. The *cis*

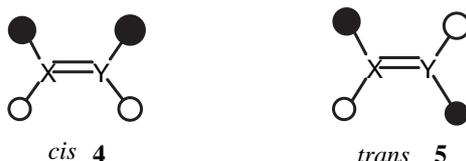
and *trans* isomers are not enantiomers, but diastereomers. The diastereomers in a pair are completely distinguishable by their different chemical and physical properties.

Since rotation about a double bond in contrast to a single bond, is prohibited by the overlap of p orbitals, geometrical isomers can usually be isolated because their chemical and physical properties are generally different to some extent. For example, the melting and boiling points of *trans*-1,2-dichloroethylene **3** is  $-50^{\circ}\text{C}$  and  $48.4^{\circ}\text{C}$  respectively, while those of *cis*-1,2-dichloroethylene **2** are  $-80.5^{\circ}\text{C}$  and  $60.3^{\circ}\text{C}$ , respectively. Their densities ( $\text{g cm}^{-3}$ ) are 1.259 for **3**, 1.265 for **2**. Thus, these two compounds possess different properties.

### S3.1 *cis-trans* isomerism (geometrical isomerism)

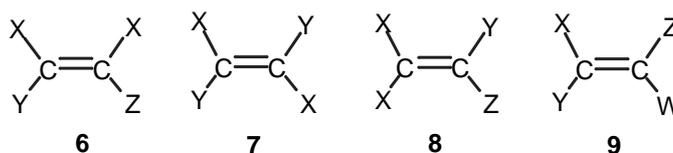
*cis* isomers: isomers with similar ligands on the same side of the double bond

*trans* isomers: isomers with similar ligands on the opposite side of the double bond



#### Q3.1

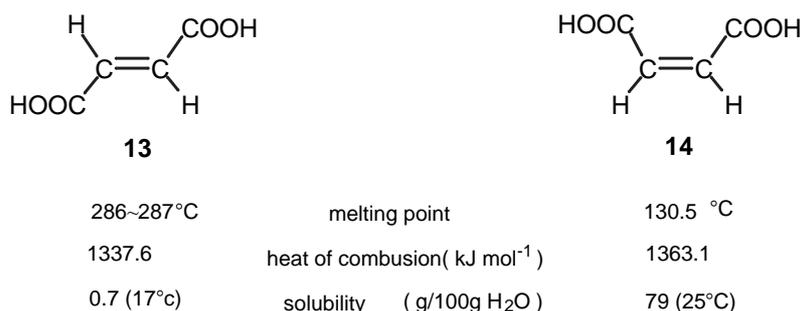
Which of the following compounds possess geometrical isomers? Distinguish whether the one you indicated is *trans* or *cis*. Write the structure of the compound with an opposite configuration.



□

#### Q3.2

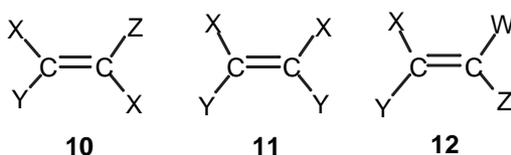
Fumaric acid and maleic acid are isomers with remarkably different physical properties (*e.g.*, melting point) as shown below. Interestingly, the heat of combustion of the *cis* isomer **14** is slightly higher than that of the *trans* isomer **13**. This is a general phenomenon among *cis* isomers. Why?



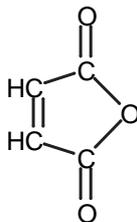
□

#### A3.1

- 6:** *cis* isomer, the opposite isomer is **10**
- 7:** *trans* isomer, the opposite isomer is **11**
- 8:** there is no geometrical isomer
- 9:** impossible to decide. the opposite isomer is **12**

**Q3.3**

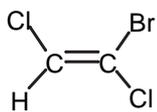
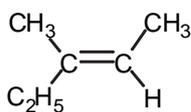
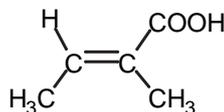
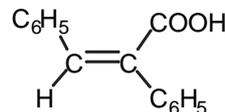
One of **13** or **14** is converted into maleic anhydride **15**, losing 1 mol of water, when heated to *ca.* 140°C. However, the other one shows no change when heated to the same temperature, and it is finally converted into **15** when heated to about 275°C. Explain this phenomenon, and identify whether **13** or **14** is converted to **15** more easily.

**15****A3.2**

The heat of combustion of **14** is higher than that of **13** because the energy contained in **14** should be larger than that in **13**. (the products of combustion are the same). This is due to the increased potential energies caused by the two bulky carbonyl groups nearby.

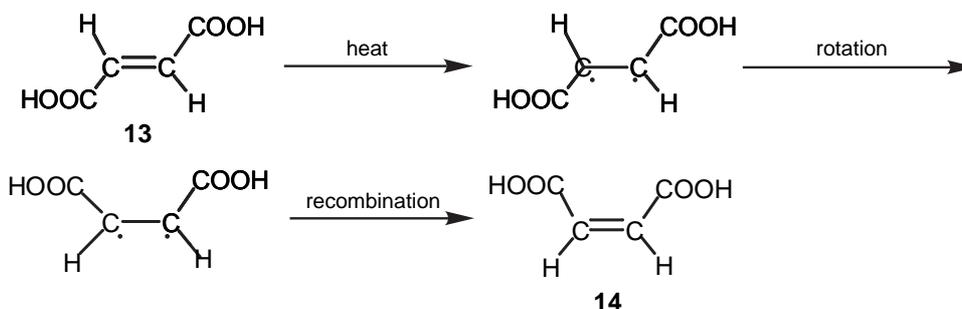
**Q3.4**

Are the following compounds *cis* or *trans*?

**16****17****18****19****A3.3**

The one converted to **15** more easily is the *cis* isomer **14**. It is necessary for two carboxy (-COOH) groups close together to yield maleic anhydride by losing 1 mol of water from these two groups. **14** should be dehydrated more easily than **13**, because the two carboxy groups are on the same side of the double bond.

If the *trans* isomer **13** is to be converted to **15**, a cleavage of the double bond should occur to yield a single bond. The subsequent rotation by 180° and regeneration of a double bond takes place. Since the bond energy of a single bond and that of a double bond are different by 263 kJ mol<sup>-1</sup>, a considerable amount of energy is required for such a process.



### A3.4

**16** and **19** are *cis* isomers. **17** and **18** are *trans* isomers.

Since each of these compounds possess a pair of the same ligands on each of the two carbon atoms forming the double bonds, it seems easy to classify these compounds (as long as we follow the principle of Q3.1). However, some questions may arise regarding this classification. For example, according to the rule of nomenclature, **17** should be 3-methyl-2-pentene rather than 2-ethyl-2-butene. Clearly *trans* isomer if **17** should be considered a pentene. As another example of uncertainty, when **19** is regarded as a derivative of cinnamic acid  $C_6H_5CH=CHCOOH$ , it is *cis*. On the other hand, it should be classified as *trans* (the answer), if it is considered as a derivative of stilbene  $C_6H_5CH=CHC_6H_5$ . □

### 3.2 E, Z nomenclature

The *cis-trans* nomenclature involves some ambiguity as is shown in the examples given above. *Cis-trans* nomenclature is originally a trivial system that is useful when simple compounds are named. It is not useful, however, as a general nomenclature. Hence, a general nomenclature of geometrical isomers based on the sequence rule has been proposed. The procedure is as follows:

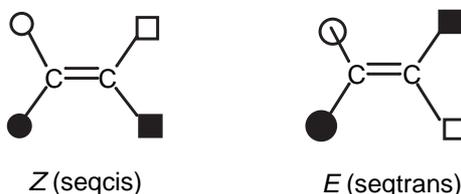
- 1) Determine the priority of two ligands (including a lone pair) bonded to each atom of the double bond based on the sequence rule.
- 2) Name the isomer, as indicated below, when the two ligands of higher priority are located on opposite sides of the double bond: *E* (abbreviation of *entgegen*) or seqtrans, and the same side of the double bond: *Z* (abbreviation of *zusammen*) or seqcis.

#### S3.2 E, Z nomenclature

*E* (or seqtrans): ligands with higher priority are placed on opposite sides of a double bond

*Z* (or seqcis): ligands with higher priority are placed on the same side of a double bond

(○ > ●, □ > ■)



Prefixes such as seqcis and seqtrans are equal to *cis* and *trans*, respectively, in the sequence rule (SEQUENCE rule). Symbols *Z* and *E* are, however, exclusively used today.

### Q3.5

Determine the priority of ligands on each carbon atom of **16-19** shown in Q3.4, and name each compound by the *E, Z* nomenclature. □

**Q3.6**

Draw the rational formula for each of the following compounds, and put a symbol  $\bigcirc$  on compounds with *cis-trans* isomerism.

- (a) 1-butene, (b) 2-butene, (c) 2-methyl-2-butene, (d) 1,2-dibromo-1-propene, (e) 1,3-dibromo-2-butene  $\square$

**A3.5**

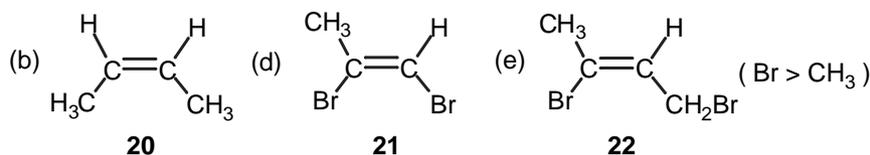
16: Br > Cl, Cl > H (Z), 17: C<sub>2</sub>H<sub>5</sub> > CH<sub>3</sub> (E), 18: COOH > CH<sub>3</sub> (E), 19: COOH > C<sub>6</sub>H<sub>5</sub> (Z)  $\square$

**Q3.7**

If the compounds in Q3.6 possess *cis-trans* isomers, write the structural formulas of its Z isomer.  $\square$

**A3.6**

- (a) CH<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, (b)  $\bigcirc$  CH<sub>3</sub>CH=CHCH<sub>3</sub>, (c) CH<sub>3</sub>CH=C(CH<sub>3</sub>)<sub>2</sub>, (d)  $\bigcirc$  CH<sub>3</sub>CBr=CHBr, (e)  $\bigcirc$  CH<sub>3</sub>CBr=CHCH<sub>2</sub>Br  $\square$

**A3.7** $\square$ **3.3 Configuration and conformation**

So far, the term conformers has been used to explain isomers related to rotation about the C-C single bond of ethane and butane derivatives and the term configuration to define some substituted methanes and ethylenes in the previous chapters. At first glance it seems straightforward to distinguish conformation and configuration. The stereoisomerism that is due to the rotation about a single bond is called conformation. Conformers are easily interconvertible and it is difficult to isolate the isomers. In contrast, when two compounds are different in their configurations, *e.g.*, a pair of enantiomers of bromochlorofluoromethane, or a pair of geometrical isomers such as maleic acid and fumaric acid, these are distinguishable compounds, and their isolation is possible.

However, if maleic acid can be converted into fumaric acid by heating, there remains some ambiguity in distinguishing conformational isomers and configurational isomers by the possibility of their interconversion. It would be more practical to classify them by the ease of interconverting them. A new nomenclature has been proposed where stereoisomers with a lower energy barrier to conversion are called **conformers** (conformational isomers), and those with a higher energy barrier are called **configurational isomers**. If the barrier to interconversion is above *ca.* 100 kJ mol<sup>-1</sup>, these are configurational isomers and if it is lower than 100 kJ mol<sup>-1</sup>, these are conformers.

**S3.3 Conformers and configurational isomers**

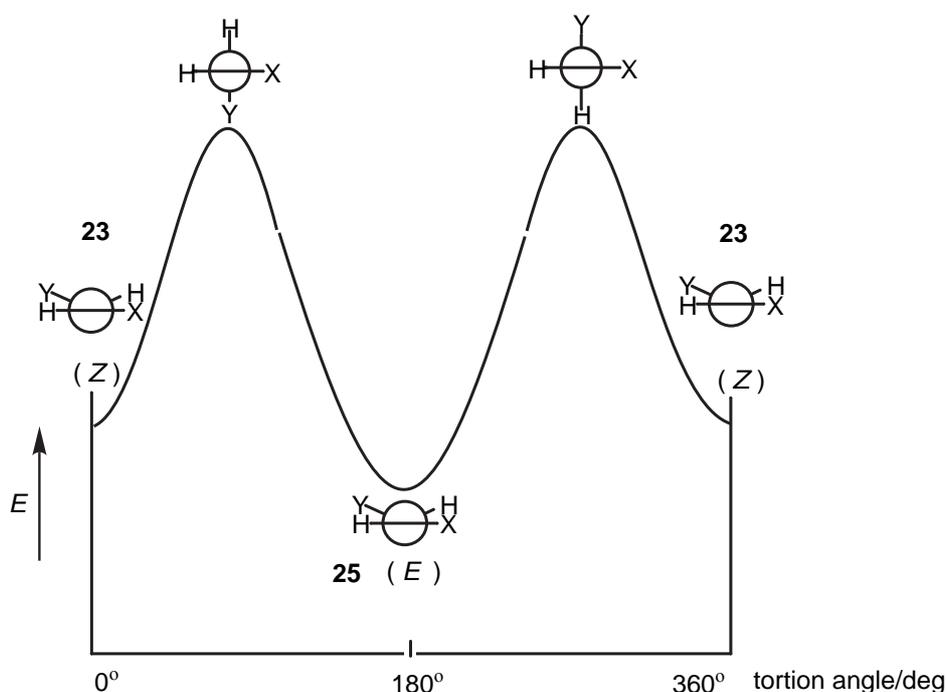
conformers: stereoisomers with energy barriers lower than *ca.* 100 kJ mol<sup>-1</sup>

configurational isomers: stereoisomers with energy barriers higher than *ca.* 100 kJ mol<sup>-1</sup>

It was previously explained that the rotation about a C=C double bond is prevented by the overlap of p-orbitals, and the rotation about a C-C single bond is relatively free. The rotation about a C=C double bond, however, can occur during a reaction; *e.g.*, when fumaric acid is converted into maleic acid by heating. Thus, the difference between rotation about a C-C bond and that about a

C=C bond might better be regarded as the difference in the energy required to achieve the transition state that is involved in the rotation.

Now, let us examine the twist angle-energy diagram of rotation about the double bond. We shall follow the process of rotation starting from *E* isomer **25**, via *Z* isomer **23**, to **25**, the initial structure. The energy of the molecule will become maximal when the two p planes of each carbon atoms become orthogonal. In this state, the C=C bond is completely cleaved into a single bond, and the *E* isomer **25** ( $\theta = 180^\circ$ ), which is in the state of second energy minimum, was obtained by a rotation of the single bond. This minimum is usually lower than that of the *Z* isomer. The diagram from  $\theta = 180^\circ$  to  $\theta = 360^\circ$  is similar to the first half of the diagram.



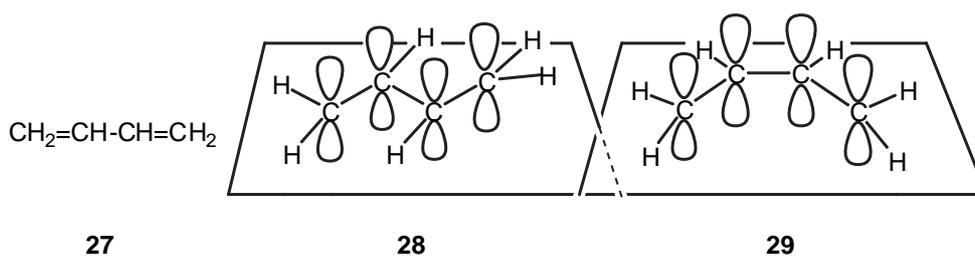
**Figure 3.1** Torsion angle--energy profiles of isomerization between geometrical isomers

### Q3.8

Give names to the following conformers **24** and **26** based on the nomenclature presented in S2.5. □

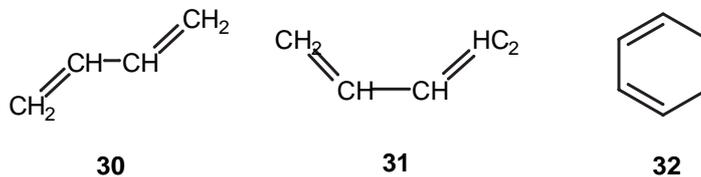
### 3.4 Conformational analysis of butadiene

Butadiene **27** is a molecule consisted of four successively bonded  $sp^2$  carbon atoms. When the structure is presented in the usual manner, as **27**, it seems as if there are two independent double bonds.



Now we draw the structure of butadiene in which the overlap of p orbitals are emphasized.

Since the maximum overlap, hence, the maximum stabilization, is obtained when adjacent p orbitals are parallel, there should be two stereoisomers of butadiene, **28** and **29**. If p orbitals are omitted, **28** and **29** will be represented simply as **30** and **31**, respectively. The two double bonds are placed in *trans* position for the central single bond in **30**, and *cis* in **31**. Hence these are called the *s-trans* and *s-cis* isomers, respectively. The prefix *s* means the single bond. The *s-cis* isomer is rare except for a fixed ring structure like cyclohexadiene **32**, since *s-trans* isomer has much less steric hindrance.

**A3.8**

**24**: +*sc*/*ac*; for **24**, clockwise rotation is required to put X upon Y. **26**: -*sc*/*ac*.

**Q3.9**

The *s-trans* and *s-cis* isomers are conformers to each other, but not geometrical isomers. Explain.

**Q3.10**

Draw the Newman projection of **30** and **31** by using the central C-C bond as the axis. Define the stereochemistry of these compounds.

**A3.9**

The *s-trans* and *s-cis* isomers are interconvertible by a rotation about the single bond but not about the double bond.

**A3.10**