

5.2: Geometric Isomers and E/Z Naming System

Geometric Isomers of Alkenes

In the discussions about 1,2-dimethylcyclohexane in **Chapter 4**, we have learned that there are two **geometric isomers** possible for that compound, that are **cis** and **trans**. The restricted C-C bond rotation of cyclic structure result in the *cis* or *trans* isomer of 1,2-dimethylcyclohexane. Restricted rotation also can be caused by a double bond, so geometric isomers apply to some alkenes as well.



Figure 5.2a Geometric isomers of disubstituted cycloalkanes

For the example of 2-butene, the condensed structural formula $\text{CH}_3\text{-CH=CH-CH}_3$ does not really represent the trigonal planar shape of the sp^2 carbons with double bonds. To show the shape explicitly, we need to draw the Kekulé structure that show all the bond angles. Then it will be noticed that there are two different shapes of 2-butene, with the CH_3 groups on either the same side or opposite side of the double bond.

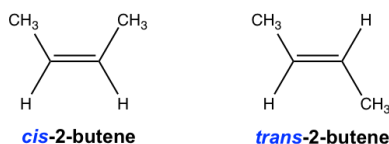
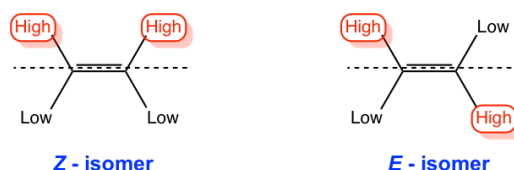


Figure 5.2b Geometric isomers of some alkenes

They are geometric isomers and can be labelled as **cis** or **trans** in a similar way as disubstituted cycloalkane. *Cis/trans* is the common designation for geometric isomers and might be ambiguous for some structures, here we will learn the IUPAC naming system for geometric isomers of alkene, that is the *E/Z* naming system.

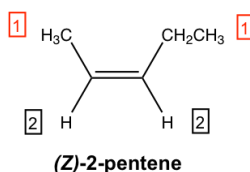
E/Z Naming System

To do the *E/Z* designation, at first, the groups connected on each sp^2 double bond carbon will be assigned the priority based on the atomic number (see following guidelines for details), then the isomer with same priority group on the same side of double bond is assigned as “**Z**”, and the isomer with the same priority group on the opposite side of double bond is called “**E**”. Both *E* and *Z* come from German, “**Zusammen**” means same side and “**Entgegen**” means opposite.



The guidelines for assigning group priority in E/Z naming system

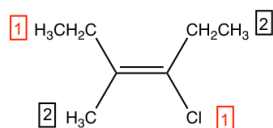
1. Priority is assigned based on the **atomic number** of the atoms bonded *directly* to the sp^2 double bond carbon, the larger the atomic number, the higher the priority (isotopes with higher mass number has higher priority). For example: $\text{S} > \text{O} > \text{N} > \text{C} > \text{H}$.



For the above structure of 2-pentene: on the left side sp^2 carbon, methyl group CH_3 is higher than hydrogen atom because $\text{C} > \text{H}$; on the right side sp^2 carbon, ethyl group CH_2CH_3 , is also higher than hydrogen. With higher priority group on both side of the double bond, this is the **Z** isomer, the complete name of the compound is **(Z)-2-pentene**.

The group with **higher** priority is labelled as **#1**, and the group with **lower** priority is labelled as **#2** in this book.

2. If the two groups bonded directly on an sp^2 carbon start with the same atom, means there is a tie from step 1, then we move on to the atoms that connected to the “tied” atom, priority increases as the atomic number of the next attached atom increases.



(E)-3-chloro-4-methyl-3-hexene

For the above structure, it is obvious that Cl is higher than C (C of CH_2CH_3 group) on the right side sp^2 carbon.

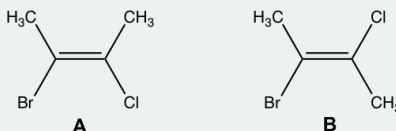
On the left side sp^2 carbon, we need to compare between methyl CH_3 group and ethyl CH_2CH_3 group. Both groups has carbon atom attached directly on the sp^2 carbon, that is a tie. In CH_3 group, the carbon atom is bonded to **H, H, H**; while in CH_2CH_3 group, the carbon atom is bonded with **H, H, C**. So ethyl CH_2CH_3 is higher than methyl CH_3 (see **Note** below). With higher priority group on opposite side of the double bond, this is the *E* isomer, the complete name of the compound is: **(E)-3-chloro-4-methyl-3-hexene**.

Note #1: For this round of comparison between **H, H, H** and **H, H, C**, compare the single atom with the greatest number in one group *verse* the single atom with the greatest number in the other group. So **H** in one group *verse* **C** in the other group, since $C > H$, therefore CH_2CH_3 is higher than CH_3 . Remember do **not** add the atomic numbers. For example, if one group has **C, C, C**, and the other group has **C, O, H**, then the C, O, H side is higher because O is higher than C.

Note #2: The above compound is *cis*-isomer if using the *cis/trans* naming system (both ethyl group are on the same side of double bond), but is *E*-isomer for E/Z system. So the *cis/trans* and E/Z are two different naming systems, don't always match.

3. Repeat step 2 if necessary, until the priority is assigned.

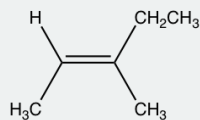
Examples: What is the correct structural formula of (Z)-2-bromo-3-chloro-2-butene?



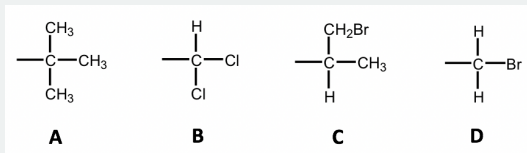
The answer is B.

Examples: Draw the structure of (Z)-3-methyl-2-pentene

Answer



Examples: Order the following groups based on priority.



Approach:

1st round: C, C, C, C (tie);

2nd round:

A: C bonded to C, C, C; (3rd)

B: C bonded to H, Cl, Cl; (Cl is the 2nd high)

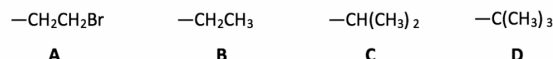
C: C bonded to H, C, C; (4th)

D: C bonded to H, H, Br (Br is the highest)

Solution: C < A < B < D

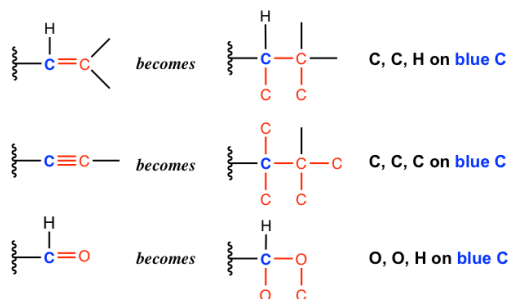
Exercises 5.1

Order the following groups based on decreasing priority for E/Z naming purpose.

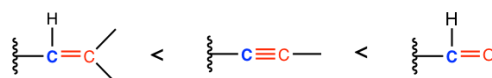


Answers to Practice Questions Chapter 5

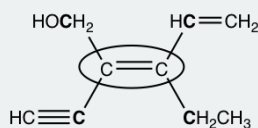
4. When multiple bond is part of the group, the multiple bond is treated as if it was *singly* bonded to multiple of those atoms. Specifically:



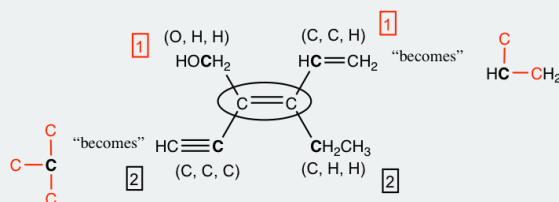
For these three groups involve multiple bonds, they all start with the carbon atom (the carbon atom highlighted in blue color), and we should compare the group of atoms that connected on the blue carbon by converting the multiple bond to “multiple single bonds”, as shown above. So, if we compare the order of these three groups, it is:



E/ZAssign of the double bond.Examples: circled



Thinking:



The answer is: Z-isomer.

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