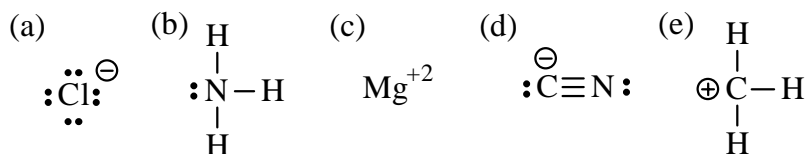


## Chapter 3

26. Which of the following are most likely to behave as electrophiles, and which as nucleophiles?

(a)  $\text{Cl}^-$ , (b)  $\text{NH}_3$ , (c)  $\text{Mg}^{+2}$ , (d)  $\text{CN}^-$ , (e)  $\text{CH}_3^+$

To see what we're dealing with it would be best to draw out complete Lewis structures —



For something to be an electrophile it must be able to function as a Lewis acid. For something to be a nucleophile it must be able to function as a Lewis base. A neutral molecule could be either a Lewis acid or base, but a negatively charged ion is more likely to be an electron donor (nucleophile) and a positively charged ion is more likely to be an electron acceptor (electrophile).

(a) Chloride ion can have more than eight electrons in its valence shell but it is happy with eight and doesn't struggle to exceed eight. On the other hand it is negatively charged and can share one of its pairs with another atom. Bottom line: nucleophile.

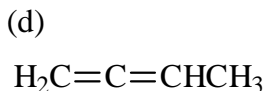
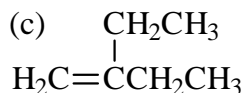
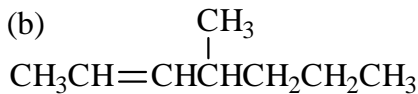
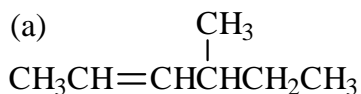
(b) The hydrogens and the nitrogen in ammonia cannot accept any more electrons, so this cannot be an electrophile. On the other hand, the N can donate its unshared pair of electrons to form a bond with another atom. Bottom line: nucleophile.

(c) Magnesium ion has no electrons in its valence shell, having lost the two it had when it was  $\text{Mg}^0$ . It is doubly positively charged and can accept electrons into its valence shell. Bottom line: electrophile.

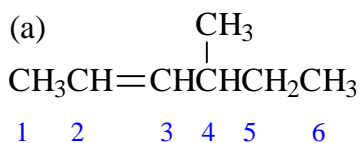
(d) If you didn't know  $\text{CN}^-$  had a triple bond between the C and the N, you know it now. The carbon is negatively charged and holds an unshared pair of electrons it could share with another atom. Bottom line: nucleophile.

(e) A carbocation. The carbon would like to complete its valence shell octet by snagging two electrons since it is seeing only 6 electrons at the moment. Bottom line: electrophile.

27. Give IUPAC names for the following alkenes.



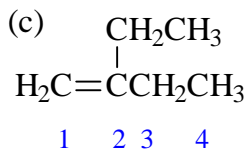
Solution:



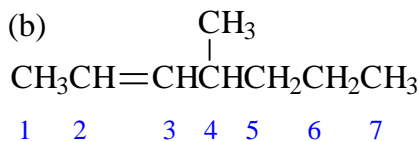
Select the longest chain containing the double bond and number it starting at the end closest to the double bond.

The parent name here is then 2-hexene, since the double bond is between C-2 and C-3.

There is a methyl group attached at C-4. So the complete name is 4-methyl-2-hexene.



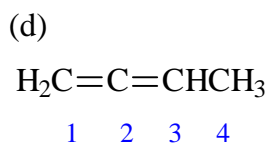
There are two 4-membered chains here, each containing the double bond. So, it doesn't matter which one we use as the parent, but we will again number from the end closest to the double bond: 2-ethyl-1-butene.



Select the longest chain containing the double bond and number it starting at the end closest to the double bond.

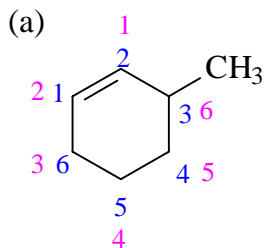
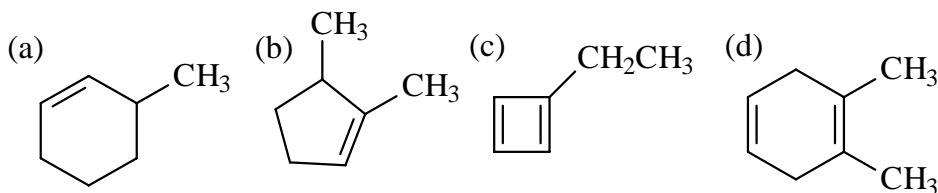
The parent name here is then 2-heptene, since the double bond is between C-2 and C-3.

There is a methyl group attached at C-4. So the complete name is 4-methyl-2-heptene.

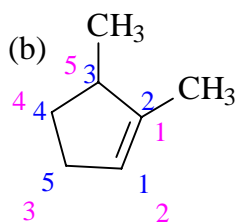


Since there are two double bonds in this molecule its suffix will be ...adiene instead of ...ene. The longest chain containing both double bonds has four carbons so the parent name is butadiene. The double bonds are located at carbons 1 and 2, so, 1,2-butadiene.

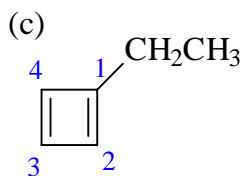
28. Name the following cycloalkenes by IUPAC rules.



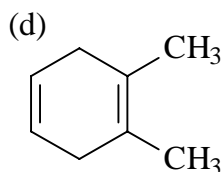
The double bond must be between C-1 and C-2 in the cyclohexene ring. This would appear to give us two options for numbering the ring: the one shown in blue and the one shown in magenta. However, the presence of the methyl group forces us to select the blue numbers since 3-methylcyclohexene provides a lower number than 6-methylcyclohexene.



Here again the double bond must be between C-1 and C-2 in the ring. In this case we use the magenta numbers so the name of the compound is 1,5-dimethylcyclopentene. The alternative numbers (blue) are not used because if they were the name would be 2,3-dimethylcyclopentene. This is not the correct name because 1 is smaller than 2. Note that it is *not* the *sum* of the numbers that must be smaller ( $2+3=5$ ,  $1+5=6$ ); it is the lowest number that must be smaller.

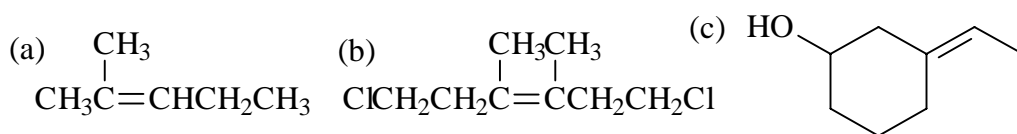


Here again the double bond must be between C-1 and C-2 in the ring. Giving the ethyl group as small a number as possible results in 1-ethyl-1,3-cyclobutadiene.



1,2-dimethyl-1,4-cyclohexadiene

32. Which of the following molecules show cis-trans isomerism?

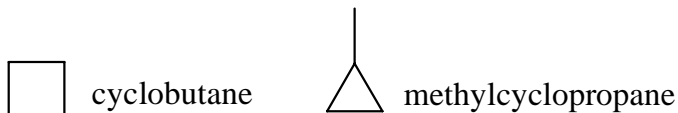
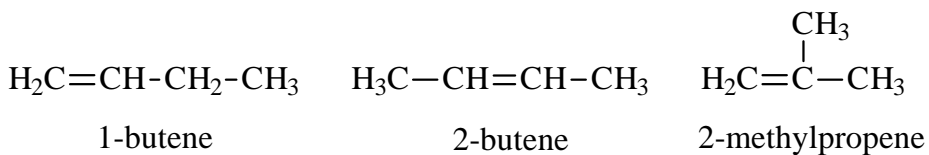


(a) No. The two methyl groups attached to the doubly-bonded carbon prevent this.

(b) Yes. Each of the doubly-bonded carbons has attached to it two different groups.

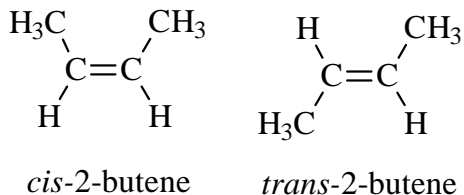
(c) Yes. At the right end of the double bond we have a hydrogen and methyl attached. At the left end we have the ring. If we traverse the ring in clockwise and then counterclockwise directions, we encounter the ring groups in different order. This is equivalent to two different groups being attached.

34. Neglecting cis-trans isomers, there are five substances with the formula  $\text{C}_4\text{H}_8$ . Draw and name them.



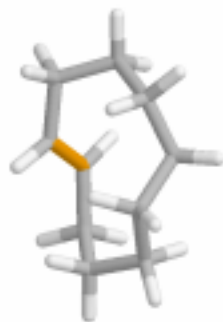
35. Which of the molecules you drew in problem 34 show cis-trans isomerism? Draw and name their cis-trans isomers.

2-Butene is the only compound capable of cis-trans isomerism.



37. How can you explain the fact that cyclohexene does not show cis-trans isomerism but cyclodecene does?

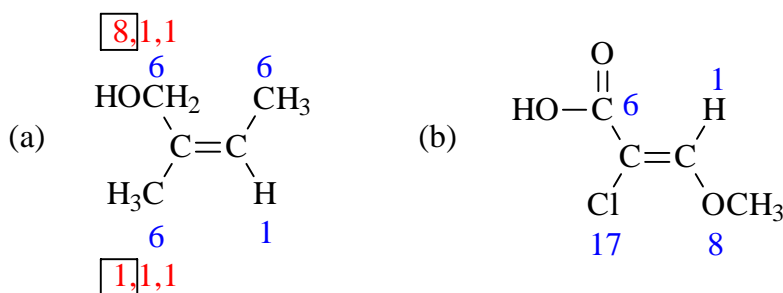
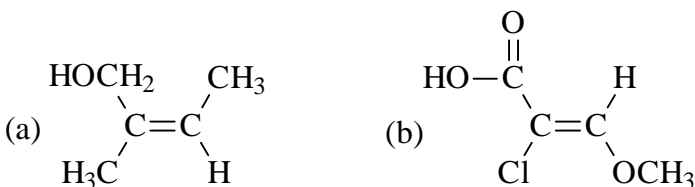
Cyclodecene is large enough to sustain the geometric requirements of a trans double bond. In other words the trans double bond will not cause enough angle strain in cyclodecene to prevent its existence. The same is not true for cyclohexene.



The molecular mechanics program that created the picture to the left will not allow me to create a *trans*-cyclohexene. It defaults to the *cis* version because the *trans* version is too strained.

*trans*-Cyclodecene. The *trans* double bond is highlighted on the left side of the molecule.

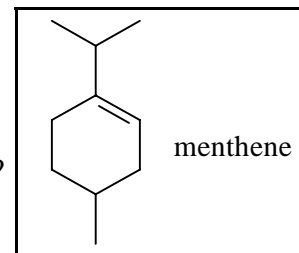
39. Assign E or Z configuration to the following alkenes.



(a) On the right side high priority goes to the methyl group because carbon (atomic number 6) is of higher priority than the other group, hydrogen (atomic number 1). On the left side, we cannot make a decision right away because it is carbon versus carbon, both atomic number 6. What we do in a case like this is write down the atomic numbers, in descending order, of the atoms that are attached to the equivalent atoms. Then we compare these numbers, starting with the first (highest) number in each group. In this instance the top group has an 8 and the bottom group has a 1. Since 8 is larger than 1, the top group is the one of high priority and the bottom group has the low priority. Note that we do not look at the numbers beyond the first point where we find a difference. Since the two high priority groups are on the same side of the double bond, this is a Z configuration.

(b) Since the high priority groups are on the same side of the double bond, this is a Z configuration.

41. Menthene, a hydrocarbon found in mint plants, has the IUPAC name 1-isopropyl-4-methylcyclohexene. What is the structure of menthene?



48. If a reaction has  $K_{eq} = 0.001$ , is it likely to be exothermic or endothermic? Explain.

When  $K_{eq} = 0.001$  about 0.1% of the material present is products and about 99.9% is reactants. Very little of the reactants have formed products because it is an uphill endeavor to do so. In other words, the products are higher in energy than the reactants, and, consequently, not much of the reactants will convert to products. If the products are higher in energy than the reactants energy must be provided from the surroundings (heat goes into the reaction mixture) for reaction to take place – this is known as endothermic.

50. If a reaction has  $\Delta H = 25$  kJ/mole, is it exothermic or endothermic? Is it likely to be fast or slow at room temperature? Explain.

If  $\Delta H = 25$  kJ/mole, the products are at higher energy than the reactants. So, for reaction to take place energy must be provided by the surroundings – this is endothermic. The rate of reaction depends on  $E_{act}$  not directly on  $\Delta H$ . However, it is true that if  $\Delta H$  is positive, then  $E_{act}$  must be *at least* as large as  $\Delta H$ . So  $E_{act}$  must be at least 25 kJ/mole and may be even larger.

Unfortunately, we are still in the dark since a reaction with  $E_{act} = 25$  kJ/mole could be fairly fast, while one that had a substantially larger  $E_{act}$  would be slow.

52. Draw a reaction energy diagram for a two-step reaction whose second step is faster than its first step.

See the diagram on page 99 in McMurry, “Fundamentals of Organic Chemistry,” 4<sup>th</sup> edition.

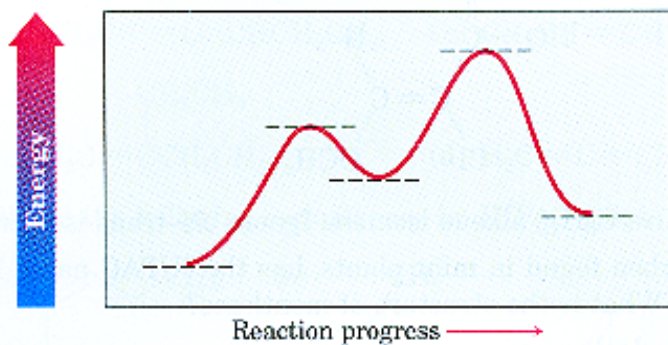
54. Describe the difference between a transition state and a reaction intermediate.

The transition state is an energy maximum in a reaction pathway. On one side, at lower energy, is a reactant, on the other side, again at lower energy, is a product.

A reaction intermediate is a molecule or ion that forms during the course of a reaction. It is product of the reactants that formed it, and it will be a reactant in a subsequent reaction that will lead to a product of some sort. It may be a stable or unstable species, but in either event it is at an energy minimum in the reaction pathway.

55. Consider the reaction energy diagram shown, and answer the following questions.

- Indicate the overall  $\Delta H$  for the reaction. Is it positive or negative?
- How many steps are involved in the reaction?
- Which step is faster?
- How many transition states are there? Label them.



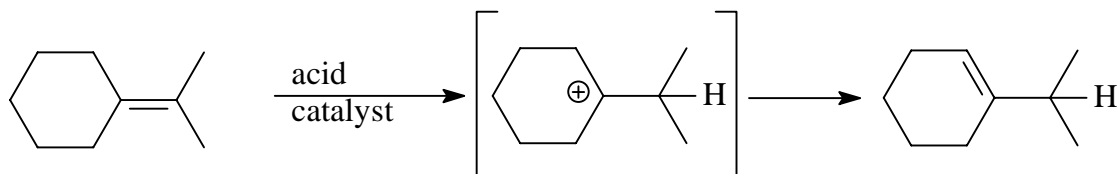
(a)  $\Delta H$  for the reaction is positive; the products are at a higher energy than reactants.

(b) Two steps. The first step is from reactants to intermediate. The second step is from intermediate to final product(s).

(c) The step with the smaller  $E_{act}$  would be faster. In this case both  $E_{act}$ s look about the same to me.

(d) There are two transition states. They are the maxima in the graph.

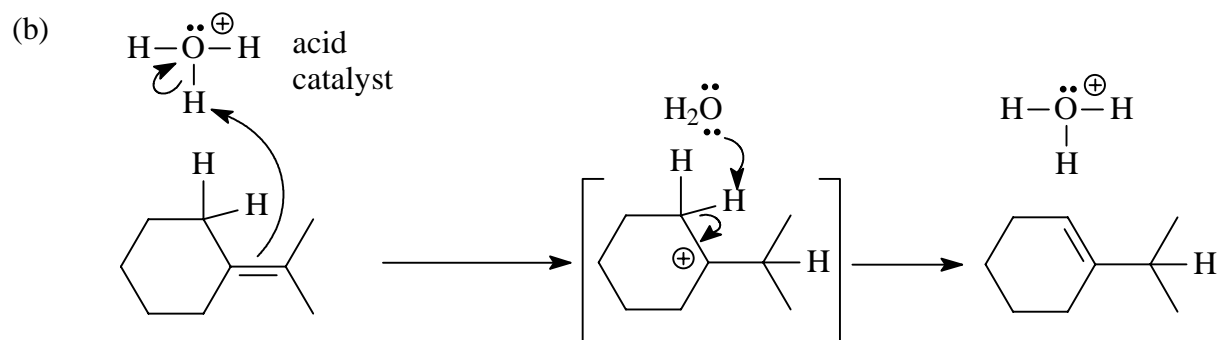
56. When isopropylidenecyclohexane is treated with strong acid at room temperature, isomerization occurs by the mechanism shown below to yield 1-isopropylcyclohexene.



At equilibrium, the product mixture contains about 30% isopropylidenecyclohexane and about 70% 1-isopropylcyclohexene.

- What kind of reaction is occurring? Is the mechanism polar or radical?
- Draw curved arrows to indicate electron flow in each step.
- Calculate  $K_{eq}$  for the reaction.

(a) The reaction type is a rearrangement. The product is a structural isomer of the reactant. The mechanism is evidently polar. We see a carbocation intermediate and the formation of this carbocation results from a Lowry-Bronsted acid base reaction.



(c)  $K_{\text{eq}} = \frac{[\text{product}]}{[\text{reactant}]} = \frac{[0.7]}{[0.3]} = 2.33$ . Note that we would usually use molar concentrations to do this calculation. However, in this case we do not have to because the reactant and product have the same molecular weight.