

Chapter 6 Alkenes and Alkynes

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Problems

Answers

Although **alkenes** and **alkynes** are both hydrocarbons which are composed of carbon and hydrogen atoms, they are different from alkanes in that the former has multiple bond(s). Alkenes have C-C double bond(s) and sometimes are called **olefins**. Ethylene is the simplest alkene. Alkynes have C-C triple bond(s). Acetylene is the simplest alkyne.

Contrary to alkanes, alkenes and alkynes are highly reactive. These react not only with such as halogens and hydrogen halides, but also with water under certain conditions. In this regard, a multiple bond may be regarded as a kind of a functional group. Compounds with multiple bond(s) form polymers by polymerization. Polyethylene and polypropylene, obtained by the polymerization of ethylene and propylene (propene), respectively, are most widely used polymers.

6.1 Properties and nomenclature of alkenes and alkynes

Alkenes are unsaturated chain hydrocarbons which contain one double bond. Their general formulas are C_nH_{2n} . Alkynes are unsaturated chain hydrocarbons which contain one triple bond. Their general formulas are C_nH_{2n-2} .

The physical properties of alkenes and alkynes are similar to those of alkanes. Thus, as the molecular weight increases, they change from gas to liquid *via* solid at normal temperature and pressure. They are hardly soluble in water, and dissolve in many organic compounds. Some alkenes are listed in Table 6.1.

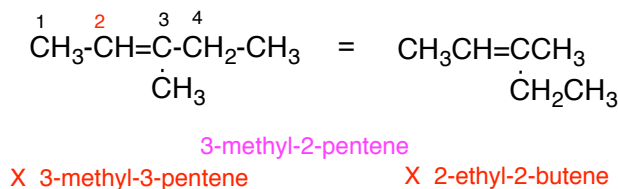
Table 6.1 Representative alkenes

name	molecular formula	simplified structural formula	m.p., (b.p) (°C)
ethene (ethylene)*	C_2H_4	$CH_2=CH_2$	-169.2, (-103.7)
propene (propylene*)	C_3H_6	$CH_3CH=CH_2$	-185.25, (-47.0)
1-butene	C_4H_8	$CH_3CH_2CH=CH_2$	-185.35, (-6.25)
<i>trans</i> -2-butene	C_4H_8	<i>trans</i> - $CH_3CH=CHCH_3$	-105.55, (0.88)
<i>cis</i> -2-butene	C_4H_8	<i>cis</i> - $CH_3CH=CHCH_3$	-138.91, (3.72)
2-methylpropene	C_4H_8	$(CH_3)_2CH=CH_2$	-140.35, (-6.90)
1-pentene	C_5H_{10}	$CH_3CH_2CH_2CH=CH_2$	-165.22, (29.968)
1,3-butadiene	C_4H_6	$CH_2=CH-CH=CH_2$	-108.915, (-4.413)

* Though both ethylene and propylene are common names, their use are admitted by IUPAC. The IUPAC names are ethene and propene, respectively.

The nomenclature of alkenes is similar to that of alkanes.

- 1: The longest chain containing the double bond is the main chain.
- 2: The end of the name of the corresponding alkane is changed from “ane” to “ene”.
- 3: The position of a double bond is indicated by the **locants** given to the double bond carbon atoms in main chain. The number of locants should be as small as possible. The locant of the double bond between C^1 and C^2 is 1.
- 4: The names of branched alkenes are given in a similar manner as those for branched alkanes.



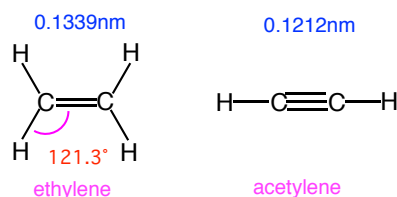
The nomenclature of alkynes is similar to that of alkenes except that the termination of the name of the corresponding alkene is changed from “ene” to “yne”.

6.2 Structure of alkenes and alkynes

(a) Bond length and bond angle

The carbon atoms of the double bond of ethylene are sp^2 hybridized, and these two carbon atoms and four hydrogen atoms form a planar skeleton. Ethylene is a planar molecule. The carbon atoms of

the triple bond of acetylene are sp hybridized, and these two carbon atoms and two hydrogen atoms form a linear skeleton. Acetylene is a linear molecule.



As was pointed out, the C-C-H angle is slightly larger than 120°. This is likely due to the repulsion between two hydrogen atoms located on the same side of the double bond. The C-C bond length decreases in the order C-C (0.154 nm) > C=C (0.1339 nm) > C≡C (0.1212 nm).

(b) Geometrical isomers of alkenes

As was described in Ch. 4.1, 2-butene has two isomers, one with two methyl groups on the other side of the double bond, *i.e.*, *trans* or *E* form, and the other with two methyl groups on the same side, *i.e.*, *cis* or *Z* form. These two molecules are **geometrical isomers** with the same molecular formula.

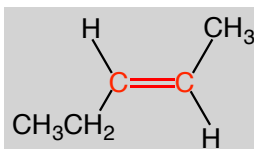
Exercise 6.1 Geometrical isomer

Name the following compound and draw the structure of its *trans* (*E*) isomer.

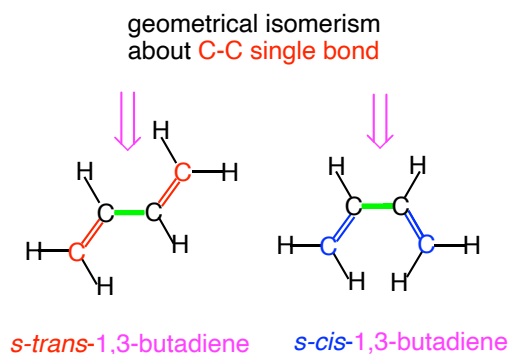


Answer

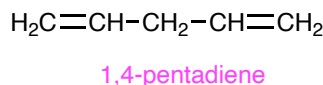
trans-2-pentene (*E*-2-pentene) (not *trans*-3-pentene)



1,3-Butadiene is a unique compound in that four carbon atoms are in a plane, and it has a pair of geometrical isomers about the C-C single bond (not about C-C double bond!), *i.e.*, *s-trans* and *s-cis* isomers.



1,3-Butadiene has a conjugate system, and hence its chemical property is different from those of non-conjugate compounds such as 1,4-pentadiene.



6.3 Reaction of alkenes

(a) Addition of halogens and hydrogen halides

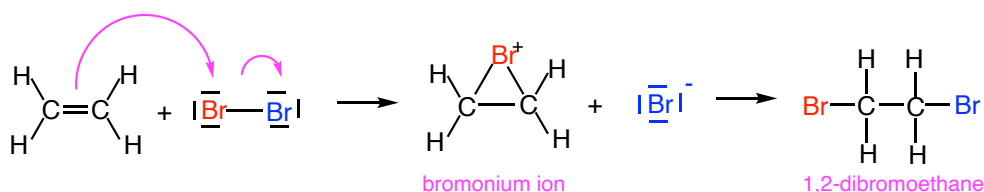
(1) Addition of halogens

The reactivity of alkenes and alkynes is higher than that of alkanes because of the unsaturated bonds with π electrons. This is particularly the case with addition reactions.

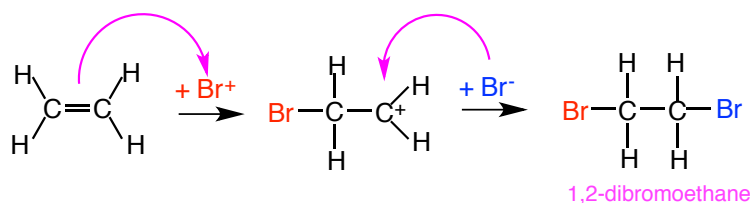
If ethylene (gas) is passed through bromine water, the color of bromine disappears. Such decolorization does not occur with ethane. This takes place because bromine adds (by the addition mechanism) to the double bond of ethylene to form colorless 1,2-dibromoethane.

Bromine is supposed to polarize as it approaches to ethylene. Then the π electron of alkene attacks the bromine atom which has a small amount of positive charge. As the result, the Br-Br bond is cleaved to yield **bromide ion** Br^- . The other species formed, Br^+ , is called **bromonium ion**.

As is indicated in the figure below, the positively charged bromine atom is bonded to two carbon atoms of ethylene to form a triangle structure. The structure is completely different from carbocations so far discussed.



Addition reactions between alkenes and bromine will be frequently discussed in this book. It is of no use writing the triangle structure repeatedly. Hereafter a simplified description will be used in this book in which bromine molecule is separated into Br^+ and Br^- , and the former reacts with the alkene to form a conventional carbocation intermediate. You should not forget, however, the real structure of the intermediate, a triangle structure.



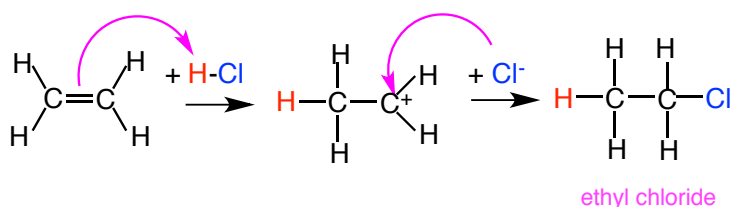
The second stage of the reaction is the process in which the bromide ion attacks carbocation to yield the neutral product.

The driving force of the reaction is the approach of π electrons to the bromine molecule and the result of the reaction is the addition of bromine. Hence this type of reaction is named **electrophilic addition**.

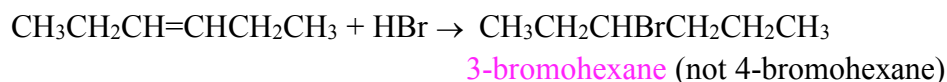
(2) Addition of hydrogen halides

The addition of hydrogen halides to alkenes exhibits the characteristics of electrophile addition more clearly. Let us discuss the addition of hydrogen chloride to ethylene as an example.

The 1st step of the reaction is the approach of π electrons to proton and subsequent formation of the carbocation intermediate. The 2nd step is the formation of a bond between chloride ion and carbocation intermediate to give the product, ethyl chloride. The process of the reaction is similar to that of the addition of bromine.

**Exercise 6.2** Addition of hydrogen halides

Draw the structure of the product of the addition between 3-hexene and hydrogen bromide and give a name to the product.

Answer**(3) Stereochemistry of addition reactions**

We simplified the course of addition of bromine to alkene as the attack of alkene to Br^+ to form the carbocation intermediate. When the bromide ion approaches to the carbocation formed, the energetically most favorable approach is the one from the other side of the newly bonded bromine atom. The reaction proceeds as depicted in Figure 6.1. Since Br^+ and Br^- approaches to ethylene assuming the *trans* relation each other with respect to the double bond, this type of addition is called the *trans (anti) addition*.

The *trans* addition is common to various addition reactions to alkenes. For instance, addition of hydrogen chloride to alkenes is also a typical *trans* addition.

Is there any method to confirm the addition of bromine to alkenes proceeds in fact *via* the *trans* addition? The product 1,2-dibromoethane is stereochemically similar to butane and the rotation about C-C bond of 1,2-dibromoethane is fast at room temperature. In other words, the *trans* geometry of two bromine atoms is not fixed. Hence it is impossible to prove the *trans* addition by observing the product. As you will learn later (Ch. 8.4), it is possible to prove experimentally the *trans* addition by investigating a reaction in which an asymmetric carbon atom (a carbon atom to which four different atoms or groups of atoms are bonded) is formed by the addition reaction.

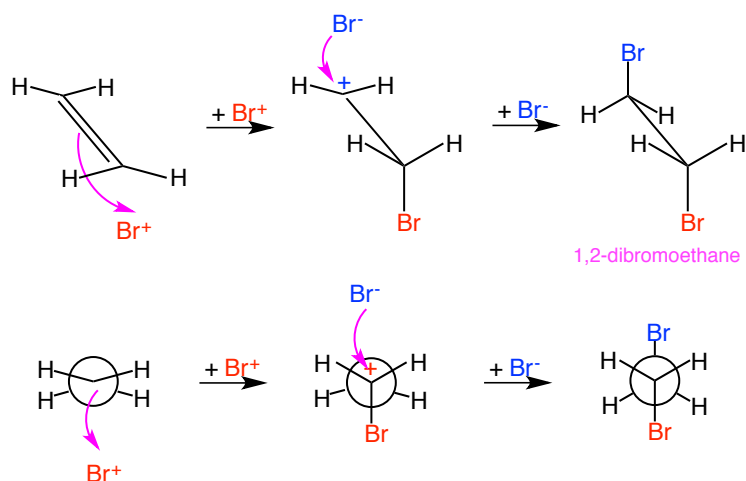
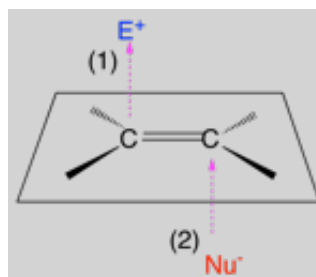


Figure 6.1 *Trans* addition to ethylene

Point: *Trans* addition

1st step: Alkenes approach to electrophilic reagents (E^+ , electrophilic portion).

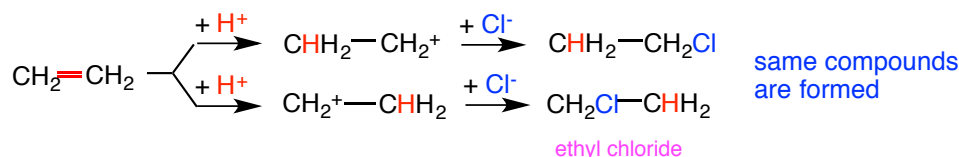
2nd step: Nucleophilic reagents (Nu^- , nucleophilic portion) approaches to the reaction intermediate



(b) Orientation of addition

(1) Addition to propene

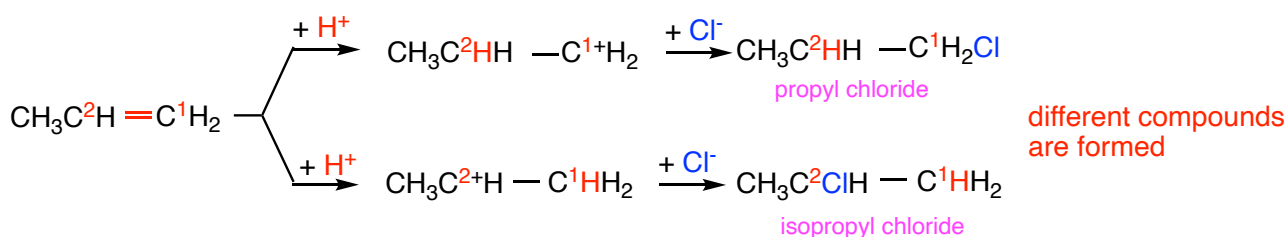
A problem remains when bromine or hydrogen chloride adds to ethylene. That is, which carbon atom is attacked by Br^+ or proton, or in other words, which carbon atom becomes positively charged. In the case of addition reaction of hydrogen chloride to ethylene, whether the proton attacks C^1 or C^2 will not make any difference in the products. Same products will be formed and it is impossible or useless to differentiate these two products.



Situation will be the same for alkenes symmetrical as regards the double bond, *i. e.*, such as 3-hexene. However, the situation will be different for alkenes asymmetrical as regard to the double bond such as propene. Of the two carbon atoms forming the double bond, which one will have positive charge, or in other words, which will make a bond with a halogen atom? The structure of the product will be changed depending on which is the case.

If the proton makes a bond with C^2 of propene, C^1 will have a positive charge, and consequently

Cl^- ion will make a bond with C^1 to give propyl chloride (1-chloropropane). On the other hand, if the proton makes a bond with C^1 of propene, C^2 will have a positive charge, and consequently Cl^- ion will make a bond with C^2 to give isopropyl chloride (2-chloropropane).

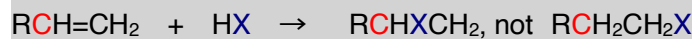


(2) Markovnikov's rule

In the middle of the 19th century, Russian chemist Vladimir Vasilevich Markovnikov (1838-1904) investigated a variety of reactions between asymmetrical alkenes with hydrogen halides. He reached a conclusion that one of the two possible products is predominantly formed and that there is some structural feature of the compounds predominantly formed. His conclusion was summarized as an empirical rule named Markovnikov's rule.

Point: Markovnikov's rule

When hydrogen halide adds to an asymmetric alkene, the halogen atom combines with the carbon atom most highly substituted by other carbon atom(s).



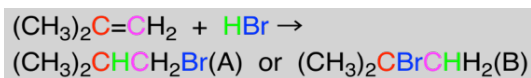
Let us apply Markovnikov's rule to propene. C^1 is not substituted by carbon atoms but C^2 is substituted by one carbon atom. According to Markovnikov's rule, isopropyl chloride (2-chloropropane) should be formed in which the chlorine atom is bonded to C^2 . This prediction was confirmed by experiments.

Exercise 6.3 Markovnikov's rule

Predict the product of the reaction between 2-methylpropene and hydrogen bromide.

Answer

According to Markovnikov's rule, the halogen atom should be bonded to the carbon atom to which two methyl groups are bonded. Thus, the main product is 2-bromol-2-methylpropane (B), but not (A). In fact, A is scarcely formed.



Markovnikov himself did not understand the theoretical ground of his empirical rule. Today it is possible to explain the reason in terms of electronic theory of organic chemistry.

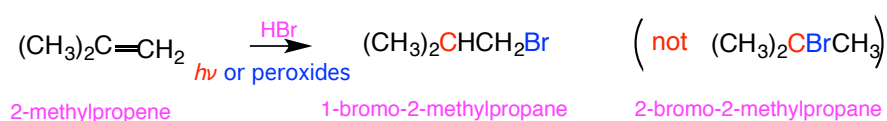
When hydrogen chloride adds to an alkene, the carbocation intermediate leading to propyl

chloride (1-chloropropane) is a primary carbocation, but the carbocation intermediate leading to isopropyl chloride (2-chloropropane) is a secondary carbocation, which is more stable than the primary one. Because of the difference in the stability of reaction intermediate, isopropyl chloride (2-chloropropane) is predominantly formed.

(3) Anti-Markovnikov's rule

Though empirical, the agreement between the prediction and the experimental result is very good for Markovnikov's rule. However, the addition reaction between alkenes and hydrogen halides in the presence of such peroxides as hydrogen peroxide H_2O_2 or benzoyl peroxide $(\text{C}_6\text{H}_5\text{COO})_2$, or under photoirradiation, the products are different from what is predicted by Markovnikov's rule.

For instance, the addition of hydrogen bromide to 2-methylpropene in the presence of peroxides gives the anti-Markovnikov product 1-bromo-2-methylpropane, but not 2-bromo-2-methylpropane.



This anomaly seems to make the generality of Markovnikov's rule suspicious. However, detailed analysis of the process of the reaction reveals that the reaction in the presence of peroxides (or irradiation of light) is different from the ionic reaction in a very important point. The process of the reaction is depicted in Figure 6.2.

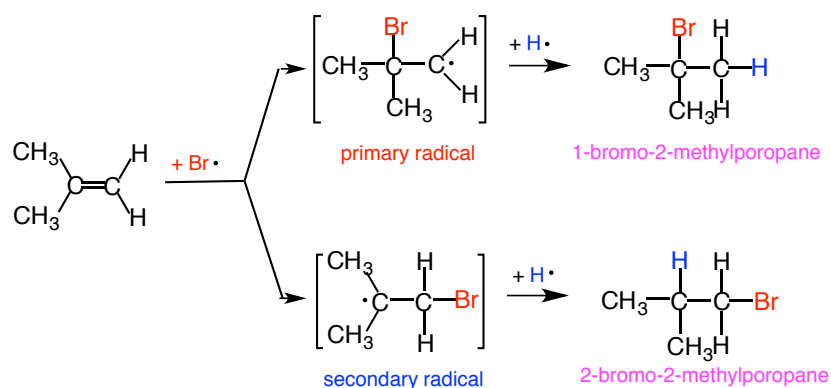


Figure 6.2 Addition of Br_2 to 2-methylpropene

- (1) In the presence of peroxides, hydrogen halides cleave to give radicals.
- (2) π electrons of alkenes initially attack bromine atom $\text{Br}\cdot$, not hydrogen atom $\text{H}\cdot$.
- (3) Hydrogen atom $\text{H}\cdot$ adds to the radical formed by the addition of bromine atom $\text{Br}\cdot$.

There are two possible sites for bromine to add, and the more stable secondary radical is predominantly formed. Hydrogen atom adds to this radical to give the anti-Markovnikov product.

The stability of radicals governs the course of the reaction, and the order of stability is

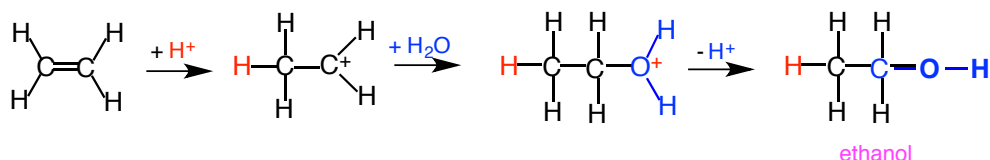


as is the case with stability of carbocation. Thus, what governs the orientation of the reaction is the stability of reaction intermediate regardless of the presence or absence of peroxides. In conclusion, the same rule applies to all types of additions.

(c) Other addition**(1) Addition of water**

In the presence of sulfuric acid, water adds by the addition mechanism to ethylene to give ethanol. The process of the reaction is similar to that of the addition of hydrogen halides. Proton is added to alkenes to give a carbocation intermediate.

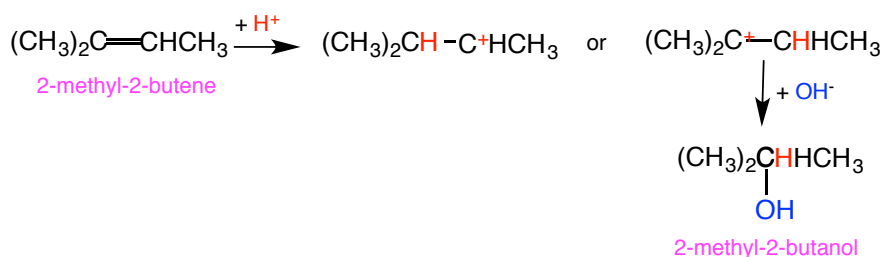
In an acidic condition, there is no hydroxide ion. Hence water behaves as the nucleophile to give a protonated alcohol. Proton is cleaved to give the final product ethanol.

**Exercise 6.4** Addition of water to alkenes

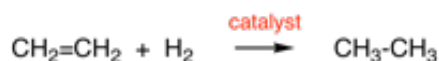
Draw the structure of an alcohol obtained by the addition of water to 2-methyl-2-butene.

Answer

Of the two possible carbocation intermediate, the latter is a tertiary cation and more stable. The alcohol obtained by the addition of water to this carbocation is 2-methyl-2-butanol.

**(2) Addition-of hydrogen (Reduction of alkenes)**

Addition of a hydrogen molecule to a double bond is a kind of reduction. In the presence of a catalyst, an addition of a hydrogen molecule to alkenes such as ethylene is called **catalytic reduction**. In most cases, platinum (as Pt_2O), nickel, or palladium are used as the catalyst.



The reaction takes place at the surface of the catalyst, and hence two hydrogen atoms adsorbed on the catalyst will add to alkenes from the same side since alkenes are also adsorbed on the catalyst.

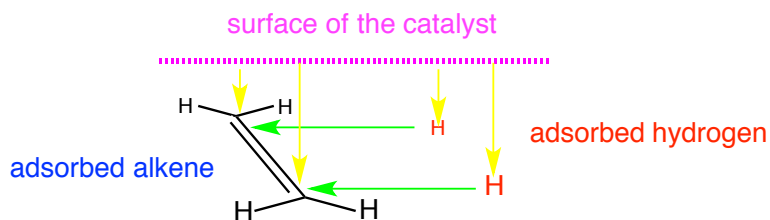
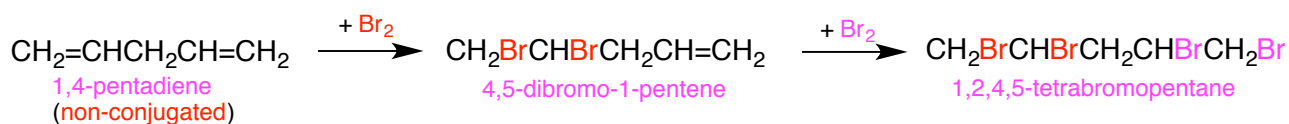


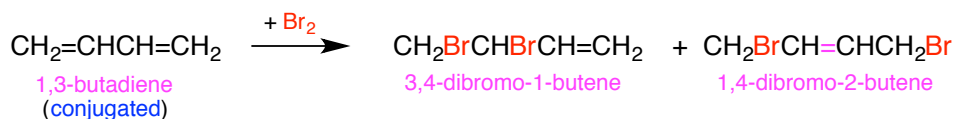
Figure 6.3 Schematic representation of catalytic hydrogenation

(d) Conjugate addition

If the addition between 1,4-pentadiene and a bromine molecule is carried out in 1:1 molar ratio, 4,5-dibromo-1-pentene is formed. If one mole of bromine is further added to this dibromoalkene, 1,2,4,5-tetrabromopentane is obtained. This type of reaction is common to all alkenes containing more than two unconjugated double bonds. Two double bonds behave completely independently.

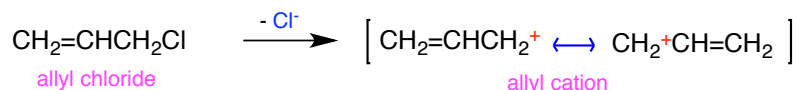


However, conjugated dienes in which two double bonds are conjugated (*i.e.*, connected by one single bond) behave in a different manner. When 1 mole of bromine is added to 1,3-butadiene, 1,4-dibromo-2-butene in addition to the expected 3,4-dibromo-1-butene, are formed.



The normal addition to double bonds is called **1,2-addition**, and the addition observed for the addition of butadiene, that is, an addition to the two termini of a conjugate system is called **1,4-addition** or **conjugate addition**.

Conjugate addition can be explained in terms of special stability of allyl cations containing a double bond formed in the 1st stage of the reaction. The simplest allyl type cation, an allyl cation, is generated when the chlorine atom is removed from allyl chloride $\text{CH}_2=\text{CHCH}_2\text{Cl}$. This cation is stabilized by the resonance between two resonance structures. Though formally it is a primary cation, its stability is equal to a secondary cation.



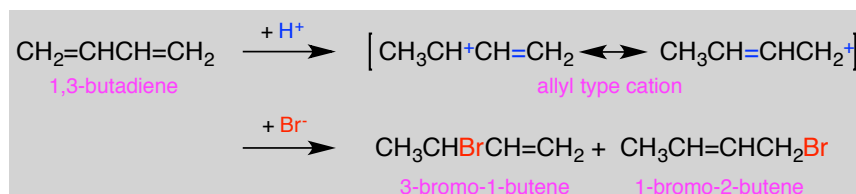
In the case of addition of bromine to 1,3-butadiene, the cation has two resonance formulas, and 1,2-adduct and 1,4 adduct are formed by the addition of bromide ion to each resonance formula. 1,4-Addition is common to addition reactions to a conjugate system, and sometimes, the 1,4-adduct is the main product.

**Exercise 6.5** Conjugate addition

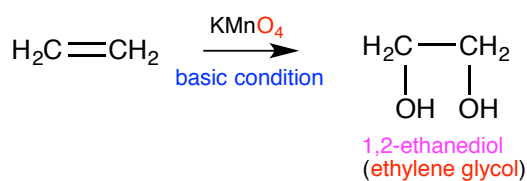
Draw the structure of compounds obtained when one mole of hydrogen bromide is added to 1,3-butadiene.

Answer

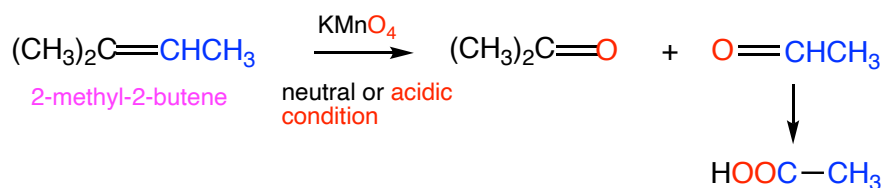
The first reagent to add to 1,3-butadiene is proton. Here again, an allyl type carbocation is formed, to which bromide ion is added.

**(e) Other reactions****(1) Oxidation of alkenes**

The double bond of alkenes is reactive, and is oxidized by standard oxidants such as potassium permanganate KMnO_4 . The process of the reaction may be various depending on the reaction conditions. When KMnO_4 is used as the oxidant under a relatively mild (basic) condition, a diol in which two hydroxy groups are attached is formed.



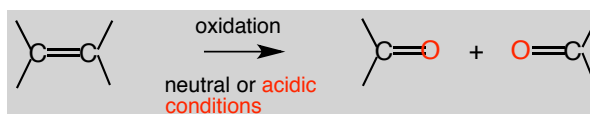
When the oxidation is carried out under a more vigorous condition (neutral or acidic), a cleavage of the double bond takes place and two carbonyl compounds or carboxylic acids are formed.



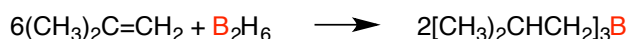
The above example can be explained as below. Acetone and acetaldehyde are formed by the cleavage of double bond, and the latter is further oxidized to acetic acid.

Point: Oxidation of alkenes

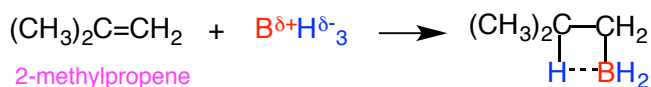
The result of oxidation is simplified as below. Suppose you cut the double bond with scissors, and paste an oxygen atom to each cut.

**(2) Hydroboration**

Boron is an electron-deficient metal and its hydride exists as diborane B_2H_6 rather than as borane BH_3 . If diborane is made to react with an alkene in a 6:1 molar ratio (3 mols of alkene and 1 mol of boron), trialkylborane is formed. The reaction of 2-methylpropene is shown as an example.

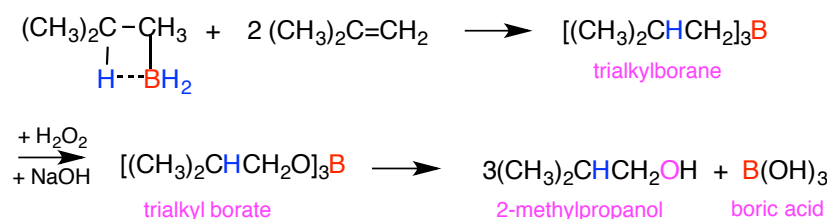


The 1st step of the reaction is addition of borane to the double bond.



For simplicity's sake, let us assume that alkenes react with BH_3 rather than B_2H_6 . The electrophilic part is B^+ (B is electron-deficient) and the nucleophilic part is H^- (hydride ion). If BH_3 attacks the terminal of the double bond of 2-methylpropene, a secondary carbocation is formed as an intermediate. If, on the other hand, BH_3 attacks the inner carbon atom of the double bond, a primary carbocation is formed. If Markovnikov's rule is applicable also in this case, the boron atom should attack the terminal carbon atom so that more stable secondary carbocation is formed.

The boron compound thus formed further reacts with two molecules of alkenes to give a trialkylborane. This compound is oxidized by hydrogen peroxide in a basic condition to give boric ester, which is hydrolyzed to alcohol and boric acid. This type of reaction is named **hydroboration**.



The alcohol obtained has an anti-Markovnikov orientation. Thus, it is possible to obtain alcohols with two different orientations by combined use of conventional addition of water and hydroboration.

(f) Diels-Alder reaction

1,3-Butadiene readily reacts with such alkenes as acrylonitrile which is substituted by electron-

withdrawing substituents to afford cyclic products (in the example below, 4-cyano-1-cyclohexene). This type of reaction is common to dienes which can have *s-cis* structures and named **Diels-Alder reaction** based on the name of the discoverers, Otto Paul Hermann Diels (1876–1954) and Kurt Alder (1902–1958) (Figure 6.4). Electron-deficient alkenes attacking dienes are named **dienophiles**.

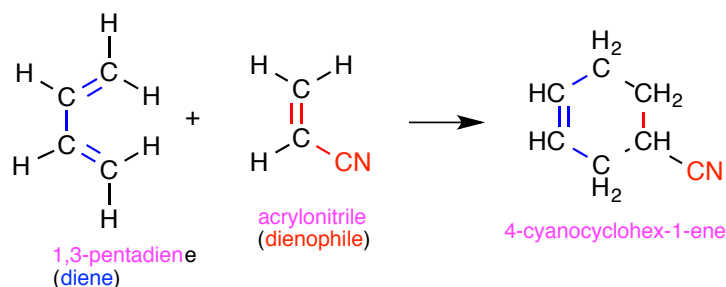
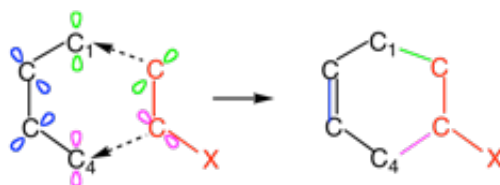


Figure 6.4 Diels-Alder reaction

This reaction is formally a 1,4-addition to a conjugate diene. Since cyclization takes place at the same time, the reaction is referred to as a **cycloaddition**.



Diels-Alder reaction does not belong to one of the categories of reactions so far discussed. This reaction is neither an ionic reaction nor a radical reaction. The driving force of the reaction is the overlap between the molecular orbitals (eclipses in the above figure) of dienes and dienophiles. This reaction is one of the reactions named **pericyclic reactions**. These reactions are also called **[4+2] addition** based on the number of carbon atoms involved. You are advised to consult with books devoted to this field if you want to study further.

Point: Diels-Alder reaction

A type of pericyclic reactions to afford cyclic compounds.

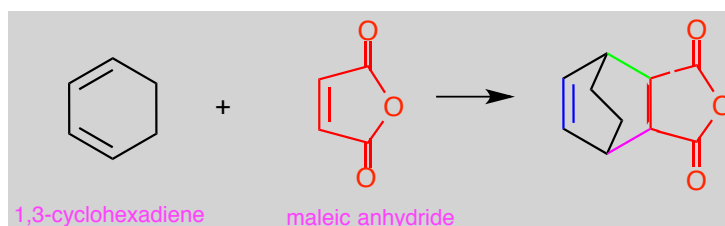
The driving force of the reaction is the overlap of molecular orbitals.

Exercise 6.6 Diels-Alder reaction

Draw the structure of the product of the reaction between 1,3-cyclohexadiene and maleic anhydride.

Answer

Since 1,3-cyclohexadiene is fixed into an *s-cis* configuration, it readily reacts with dienophiles. Furthermore, two electron withdrawing substituents are bonded to the double bonds of maleic anhydride. Hence it is a strong dienophile.



The detailed stereochemical structure of the product is beyond the scope of this book. For the time being, you are expected to be able to draw a planar structure. Since an additional cyclic structure is introduced into a cyclic compound, the product has two cyclic units. Hence these are named **bicyclic compounds**.

(g) Addition polymerization

In the presence of appropriate catalysts, ethylene and its derivatives in most cases readily react one after the other to add each other to form polymers with a high molecular weight. If the molecular weight is over 10,000, such a compound is usually named a polymeric compound or simply a **polymer**. Polyethylene made from ethylene may be regarded as a representative polymer. The molecule which is the repeating unit of a polymer is called a **monomer** (in the example below, ethylene).

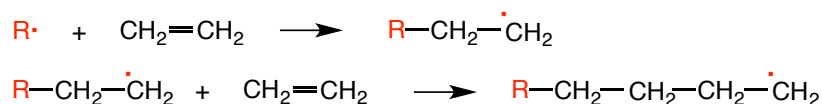
The reaction in which monomers react repeatedly to form a polymer is called **polymerization**. Since the polymerization of ethylene to polyethylene proceeds *via* addition mechanism, the whole process is named **addition polymerization**.

Monomers important in industry are vinyl compounds represented as $\text{CH}_2=\text{CHX}$. Table 6.2 lists important monomers and polymers obtained from these.

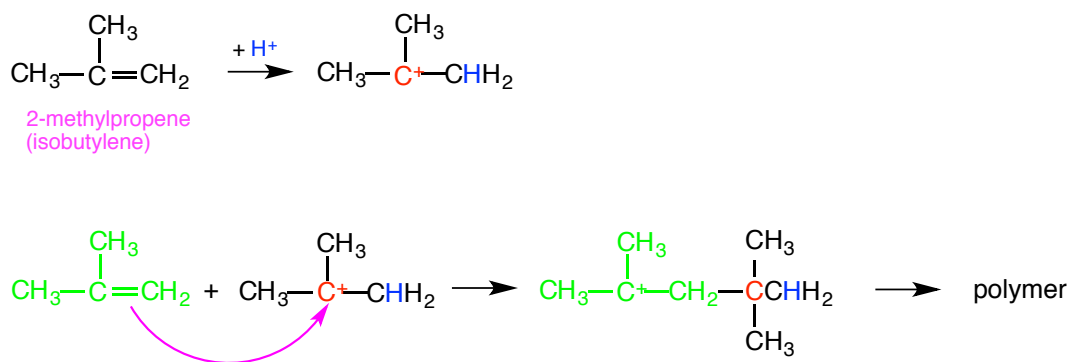
Table 6.2 Monomers and polymers of addition polymerization

monomer	formula	polymer	use
ethylene	$\text{CH}_2=\text{CH}_2$	polyethylene	bag, container, high frequency insulator
propene (propylene)	$\text{CH}_2=\text{CHCH}_3$	polypropylene	container, rope, fishing net, film
styrene	$\text{CH}_2=\text{CHC}_6\text{H}_5$	polystyrene	styrofoam
acrylonitrile	$\text{CH}_2=\text{CHCN}$	polyacrylonitrile	fiber, plastics
vinyl chloride	$\text{CH}_2=\text{CHCl}$	polyvinyl chloride	water pipe, building materials, electric tool, vinyl sheets
tetrafluoro- ethylene	$\text{CF}_2=\text{CF}_2$	polytetrafluoroethylene (Teflon)	cooking tool, scientific tool, insulator

If ethylene is caused to react at high temperature and high pressure, the reaction proceeds *via* radical mechanism. Usually an initiator which readily yields radicals is used. If the generated radical $R\cdot$ adds to ethylene, a radical $RCH_2CH_2\cdot$ is formed. This radical in turn adds to ethylene to lengthen the chain. Polymerization *via* radical mechanism is named **radical polymerization**.



Some polymerization proceeds *via* an ionic mechanism. Polymerization of 2-methylpropene (isobutylene) catalyzed by sulfuric acid is a typical cationic polymerization which proceeds *via* carbocation intermediate. The reaction proceeds as shown below.



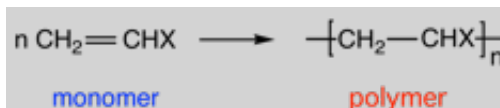
In the first stage, a proton from sulfuric acid adds to 2-methylpropene to form a stable tertiary carbocation, and in the second stage this carbocation reacts with a second 2-methylpropene to form a stable tertiary carbocation. By repeating this process, polyisobutylene will be formed.

If such species as alkaline metals are used as the initiator, carboanion or alkoxide anion will add to the monomer during the polymerization. Such polymerization is called **anionic polymerization**.

Point: Addition polymerization

Polymerization by addition:

Radical polymerization, ionic polymerization



6.4 Property and nomenclature of alkynes

The physical properties of alkynes are similar to those of alkenes. As their molecular weights increase, alkynes change from gases, *via* liquids, to solids at ambient temperature. These are hardly soluble in water, and readily soluble in organic solvents. In Table 6.3, representative alkynes are shown.

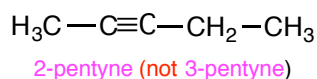
Table 6.3 Some alkynes

name	molecular formula	simple structural formula	m.p. (b.p.) (°C)
acetylene (ethyne)	C ₂ H ₂	CH≡CH	-81.8 (-83.6)
propyne	C ₃ H ₄	CH ₃ C≡CH	-102.7 (-23.22)
1-butyne	C ₄ H ₆	CH ₃ CH ₂ C≡CH	125.720 (8.07)
2-butyne	C ₄ H ₆	CH ₃ C≡CCH ₂	32.260 (26.99)

The rule of naming alkynes is much the same with that of naming alkenes.

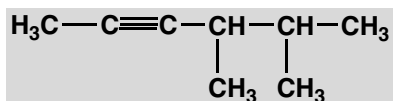
- 1: The longest chain containing a triple bond is chosen as the main chain and a name is given.
- 2: The ending of the name of the corresponding alkanes is changed to -yne.
- 3: The position of the triple bond is given by numbering the C-C bond of the main chain (locant). Care should be taken so that the number is as small as possible.

[Example]



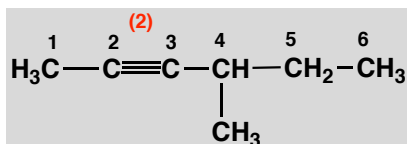
Exercise 6.7 Naming of alkynes

- (1) Draw the structural formula of 4-methyl-2-hexyne.
- (2) Name the following compound.



Answer

(1)

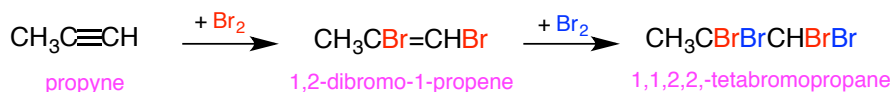


(2) 4,5-dimethyl-2-hexyne

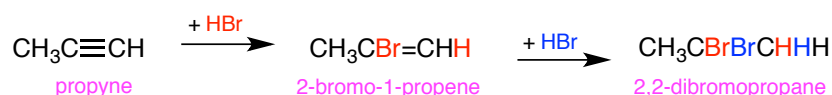
6.5 Reactions of alkynes

(a) Addition of halogens and hydrogen halides

The triple bond of alkynes shows the reactivity similar to that of the double bond of alkenes. For instance, 2 moles of bromine add to propyne. It is possible to stop the reaction when 1 mole of bromine is added if a proper reaction condition is chosen.

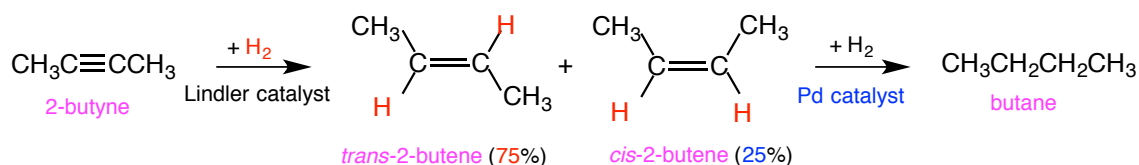


The addition of hydrogen halides follows the Markovnikov's law as is the case with alkenes.



(b) Addition of hydrogen

Addition of hydrogen in the presence of catalyst proceeds in a similar manner. If the reaction is terminated when 1 mole of hydrogen molecule is added, a mixture of *trans*- and *cis*-2-butene is obtained. By choosing an appropriate catalyst (*e.g.*, Lindler catalyst), it is possible to obtain *cis*-2-butene as the main product. Butane is obtained if 2 moles of hydrogen molecule are added.

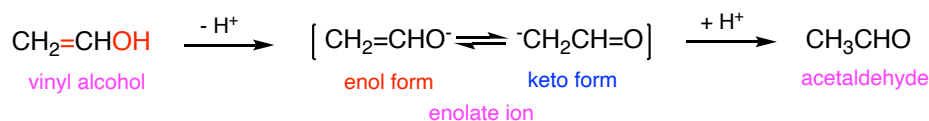


(c) Addition of water

If the addition of 1 mole of water to alkyne, acetylene as an example, proceeds in a manner similar to those of halogens or hydrogen halides, it is expected that vinyl alcohol will be formed. However, a rearrangement takes place to give acetaldehyde. In fact, this reaction was used for the industrial synthesis of acetaldehyde (Ch. 4.1). The mechanism of the reaction is readily understandable if you consider the stability of enolate anions.

Such species as vinyl alcohol in which a hydroxy group is bonded to a double bond are named **enols**. The hydrogen atom of the hydroxy group of an enol is readily cleaved as a proton. The remaining anion, *i.e.*, enolate anion is stabilized by the resonance similar to that in allyl cation.

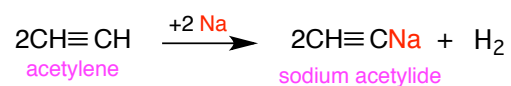
There are two resonance structures for enolate anion, one, enol type and the other, keto type. The proton can recombine to the carbon atom (of keto form) or the oxygen atom (of enol form). If combined with carbon, the proton will not readily leave as is the case with enol. This is the reason why vinyl alcohol is readily transformed into acetaldehyde.



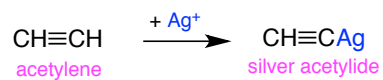
When a pair of isomers is in equilibrium, and is readily interchangeable, such pair is named **tautomeric isomer**, and this phenomenon **tautomerism**. The tautomerism between keto and enol forms is named **keto-enol tautomerism**.

(d) Formation of acetylides

The pK_a value of acetylenic proton is 25, which is 17 times larger than that of saturated hydrocarbons. This means that acetylene is more acidic as compared with saturated hydrocarbons and may be regarded as an extremely weak acid. Acetylene reacts with sodium to give sodium acetylide, and hydrogen is generated.

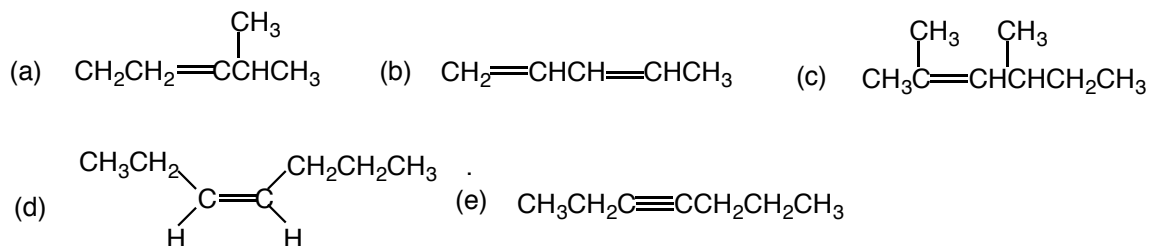


Acetylene and other alkynes with a terminal triple bond react with heavy metal ions such as Ag^+ or Cu^{2+} to form acetylides which are not soluble in water.



Problems**6.1**

Name the following alkenes or alkynes.

**6.2**

Draw the structural formula of the following alkenes or alkynes.

- (a) 2-methyl-2-heptene
 (b) 3-isopropyl-1-cyclopentene
 (c) *trans*-3-nonene
 (d) 3-ethyl-1-pentyne

6.3

Complete the following reaction formulas. When there are more than two products, write the main product only.

- (a) $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2 + \text{Br}_2 \rightarrow ?$
 (b) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \rightarrow ?$
 (c) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \rightarrow ?$ (in the presence of a peroxide)
 (d) $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2 + \text{H}_2\text{O} \rightarrow ?$ (acidified with sulfuric acid)

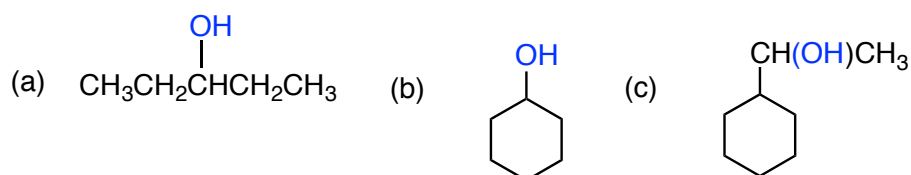
6.4

The following pairs of compounds have the same molecular weight. Suggest the chemical methods to differentiate the two compounds.

- (a) 1-hexene and cyclohexane
 (b) 1-pentyne and 1,3-pentadiene
 (c) cyclopentene and 1,3-pentadiene

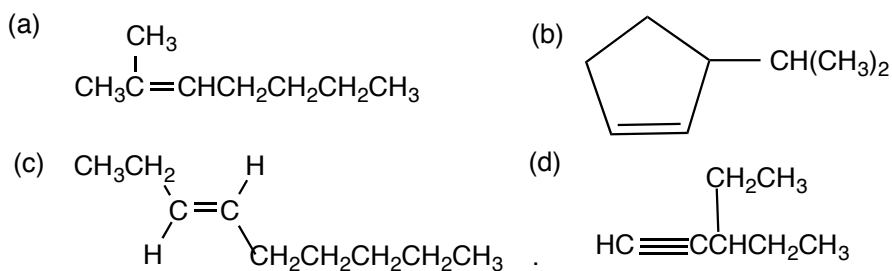
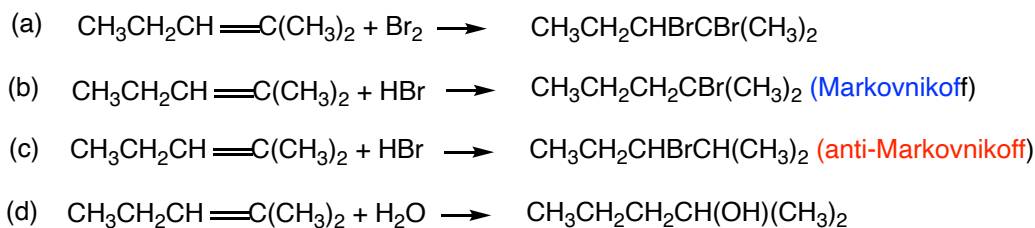
6.5

Suggest the structure of alkenes which can be used to obtain the following alcohols by the addition reaction of water.



Answers**6.1**

- (a) 4-methyl-2-pentene
 (b) 1,3-pentadiene
 (c) 2,4-dimethyl-2-hexene
 (d) *cis*-3-heptene
 (e) 3-heptyne

6.2**6.3****6.4**

- (a) Bromine adds to 1-hexene but not to cyclohexane.
 (b) 1-Pentyne can form acetylide but 1,3-pentadiene readily reacts with such dienophiles as acrylonitrile.
 (c) Same with (b).

6.5