



Alkenes and Alkynes: The Nature of Organic Reactions

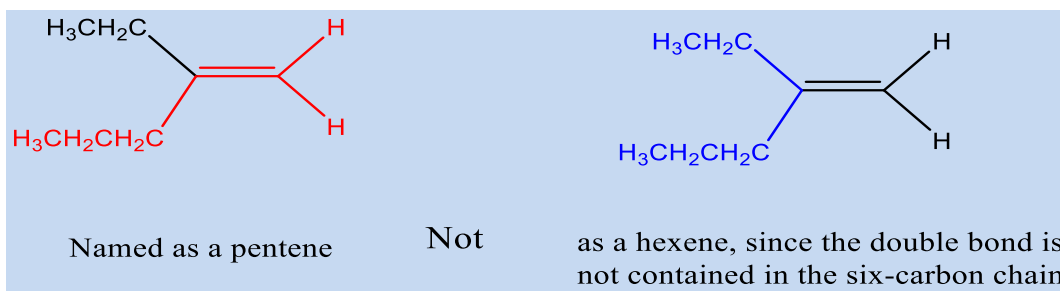
Alkenes, sometimes called *olefins*, are hydrocarbons that contain a carbon–carbon double bond, $C=C$, and **alkynes** are hydrocarbons that contain a carbon–carbon triple bond, $C\equiv C$.

Naming Alkenes and Alkynes

Alkenes are named using a series of rules similar to those for alkanes, with the suffix *-ene* used in place of *-ane*. There are three steps.

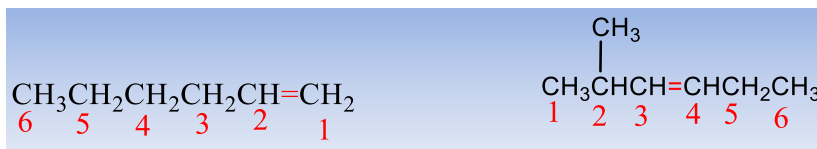
STEP 1 Name the parent hydrocarbon.

Find the longest carbon chain that contains the double bond, and name the compound using the suffix *-ene* in place of *-ane*.



STEP 2 Number the carbon atoms in the chain.

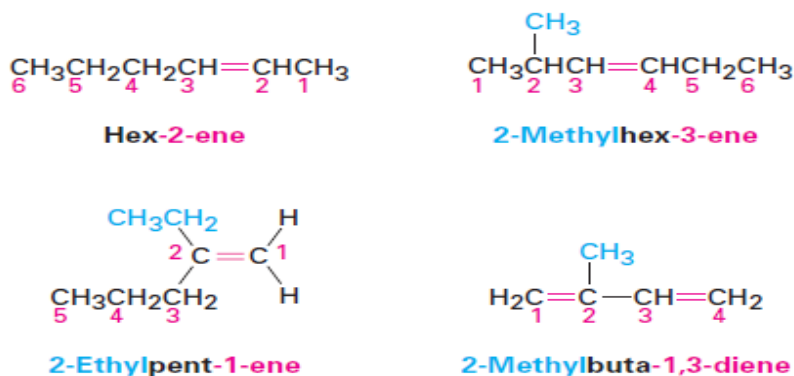
Begin numbering at the end nearer the double bond, or, if the double bond is equidistant from the two ends, begin at the end nearer the first branch point.



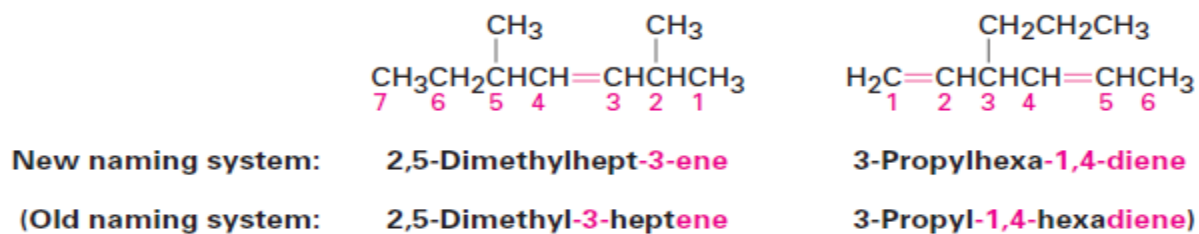


STEP 3 Write the full name.

If more than one double bond is present, give the position of each and use the appropriate multiplier suffix *-diene*, *-triene*, *-tetraene*, and so on.



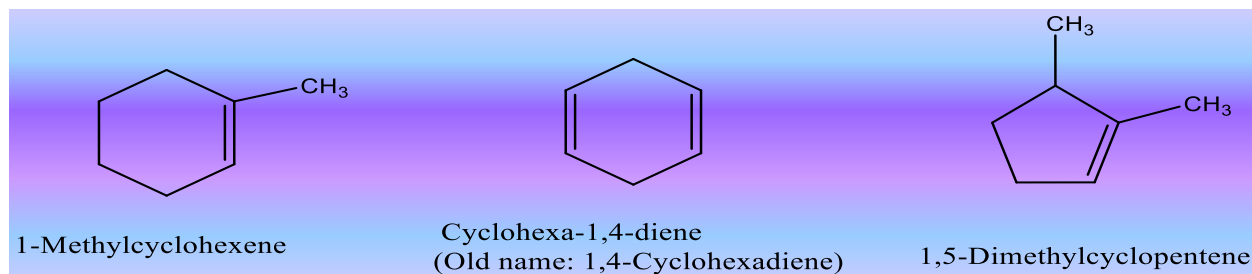
We should also note that IUPAC changed its naming rules in 1993. Prior to that time, the locant, or number locating the position of the double bond, was placed before the parent name rather than before the *-ene* suffix: 2-butene rather than but-2-ene, for instance.



Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkene so that the double bond is between C1 and C2 and the first substituent has as low a number as possible. Note that it's not necessary to specify the position of the double bond in the name because it's always between C1 and C2.



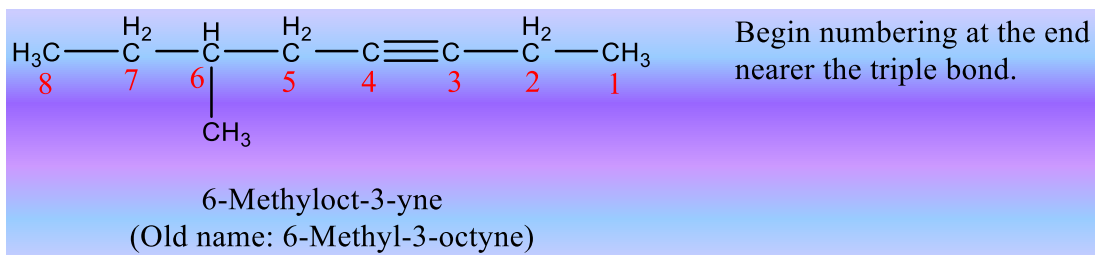
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Suzanne Jubere Abass



For historical reasons, there are a few alkenes whose names don't conform to the rules.

Common names of some alkenes		
Compound	Systematic name	Common name
$\text{CH}_2=\text{CH}_2$	Ethane	Ethelene
$\text{CH}_3\text{CH}=\text{CH}_2$	Propene	Propelene
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}=\text{CH}_2 \end{array}$	2- Methylpropene	Isobuyelene

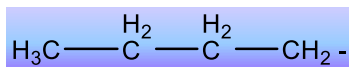
Alkynes are named in the same way as alkenes, with the suffix *-yne* used in place of *-ene*.



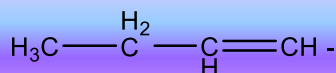
As with alkyl groups derived from alkanes, *alkenyl* and *alkynyl* groups are also possible.



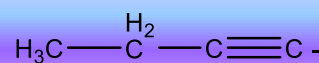
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Butyl
(an alkyl group)



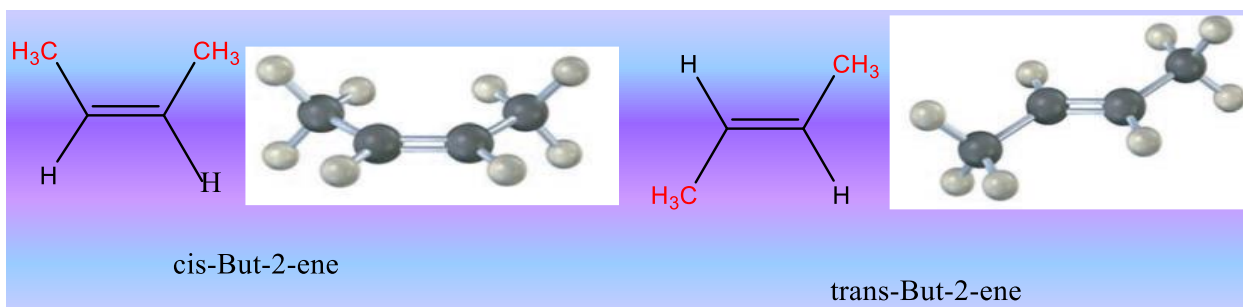
But-1-enyl
(a vinylic group)



But-1-ynyl
(an alkynyl group)

Cis – Trans Isomers of Alkenes

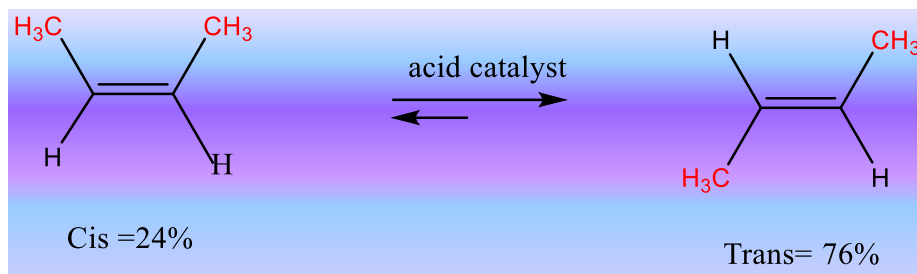
Imagine the situation for a disubstituted alkene such as but-2-ene. The two methyl groups in but-2-ene can be either on the same side of the double bond or on opposite sides, because bond rotation can't occur, the two but-2-enes can't spontaneously interconvert and are different chemical compounds, we 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*.



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.



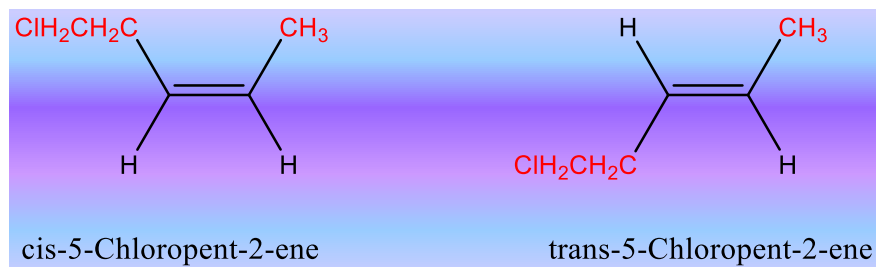
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Cis alkenes are less stable than their trans isomers because of steric (spatial) interference between the large substituents on the same side of the double bond. This is the same kind of interference, or *steric strain*.

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

Solution



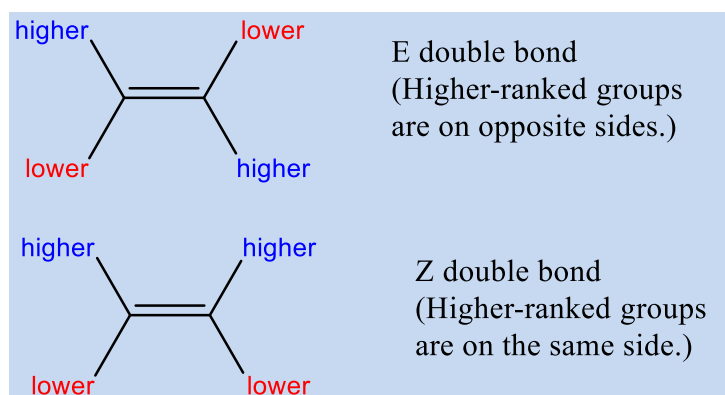
Sequence Rules: The *E,Z* Designation

The cis–trans naming system used in the previous section works only with disubstituted alkenes—compounds that have two substituents other than hydrogen on the double bond. With trisubstituted and tetrasubstituted alkenes, however, a more general method is needed for describing double-bond geometry.

According to the ***E,Z* system**, a set of *sequence rules* is used to rank the two substituent groups on each double-bond carbon. If the higher-ranked groups on each carbon are on opposite sides of the double bond, the alkene is said to have *E* stereochemistry, for the German *entgegen*, meaning “opposite.” If the higher-



ranked groups are on the same side, the alkene has *Z* stereochemistry, for the German *zusammen*, meaning “together.”



Called the *Cahn–Ingold–Prelog* rules after the chemists who proposed them, the sequence rules are as follows:

RULE 1 Considering the double-bond carbons separately, look at the atoms directly attached to each carbon and rank them according to atomic number.

The atom with the higher atomic number has the higher ranking, and the atom with the lower atomic number (usually hydrogen) has the lower ranking. Thus, the atoms commonly found attached to a double-bond carbon are assigned the following rankings.

Atomic number 35 17 16 15 8 7 6 1

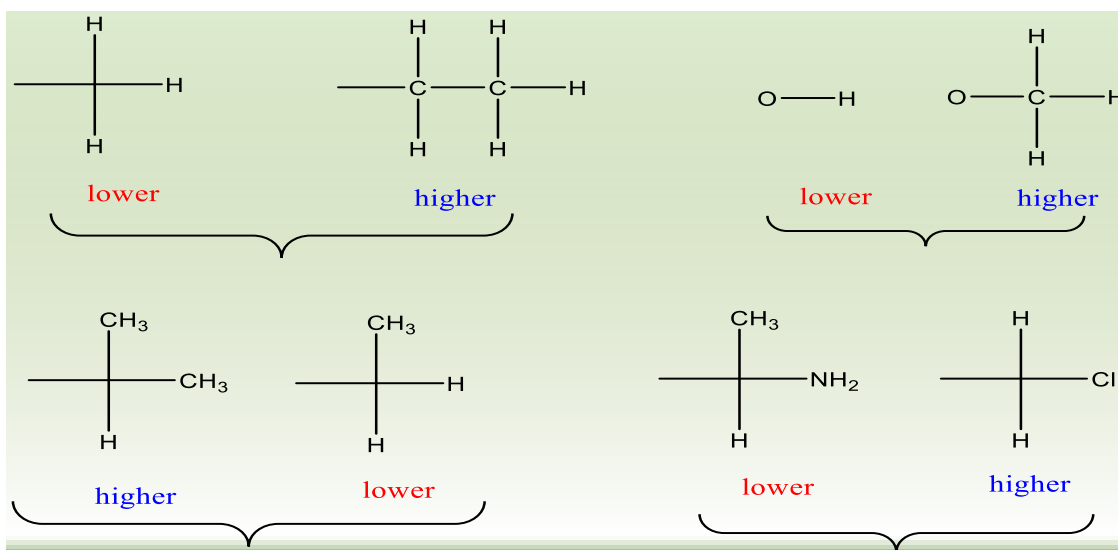
Higher ranking Br > Cl > S > P > O > N > C > H **Lower ranking**

Because chlorine has a higher atomic number than carbon, it ranks higher than a methyl (CH₃) group. Methyl ranks higher than hydrogen and so on.

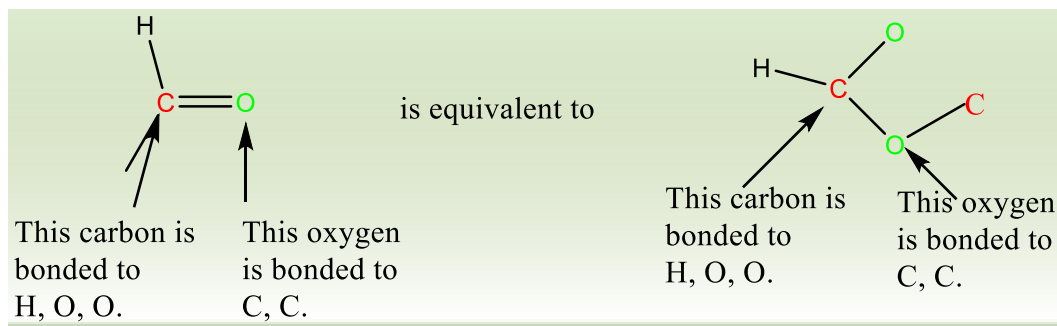


RULE 2 If a decision can't be reached by ranking the first atoms in the substituents, look at the second, third, or fourth atoms away from the double-bond carbons until the first difference is found.

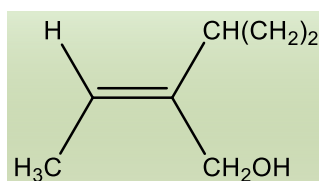
Thus, a $\text{-CH}_2\text{CH}_3$ substituent and a -CH_3 substituent are equivalent by rule 1 because both have carbon as the first atom. By rule 2, however, ethyl ranks higher than methyl because ethyl has a *carbon* as its highest *second* atom, while methyl has only hydrogen as its second atom. Look at the following examples to see how the rule works:



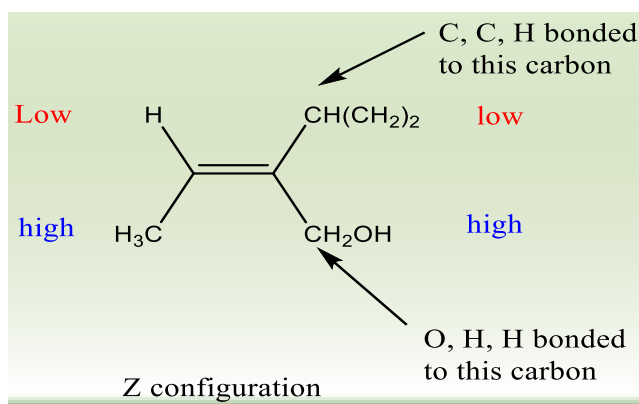
RULE 3 Multiple-bonded atoms are equivalent to the same number of single-bonded atoms. For example, an aldehyde substituent (-CH=O), which has a carbon atom *doubly* bonded to *one* oxygen, is equivalent to a substituent having a carbon atom *singly* bonded to *two* oxygens.



Example Assign *E* or *Z* stereochemistry to the double bond in the following compound.



Solution The left-hand carbon has two substituents, -H and -CH₃, of which -CH₃ ranks higher by rule 1. The right-hand carbon also has two substituents, -CH(CH₃)₂ and -CH₂OH, which are equivalent by rule 1. By rule 2, however, -CH₂OH ranks higher than -CH(CH₃)₂ because -CH₂OH has an *oxygen* as its highest second atom, whereas -CH(CH₃)₂ has *carbon* as its highest second atom. The two higher-ranked groups are on the same side of the double bond, so the compound has *Z* stereochemistry.

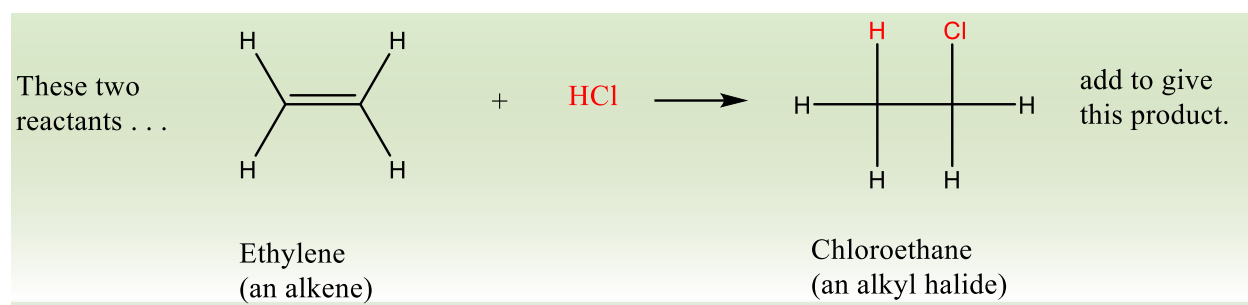




Kinds of Organic Reactions

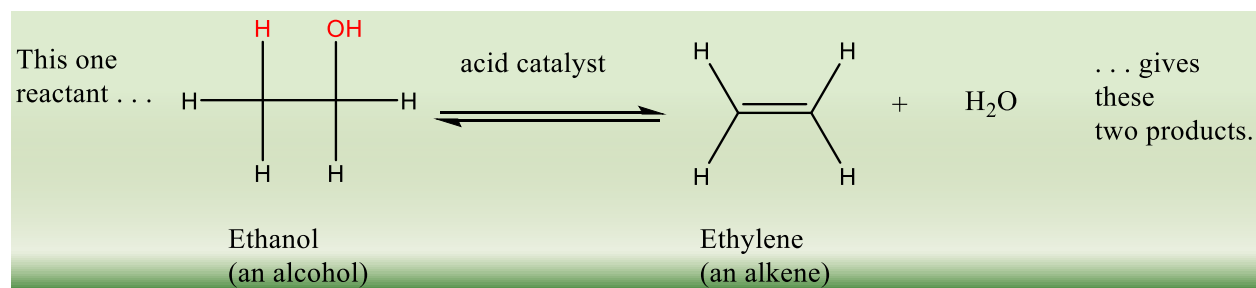
There are four particularly broad types of organic reactions: *additions*, *eliminations*, *substitutions*, and *rearrangements*.

• **Addition reactions** occur when two reactants add together to form a single new product with no atoms “left over.” An example that we’ll be studying soon is the reaction of an alkene with HCl to yield an alkyl chloride.



• **Elimination reactions** are, in a sense, the opposite of addition reactions.

They occur when a single organic reactant splits into two products, often with formation of a small molecule such as H₂O or HCl. An example is the acid-catalyzed reaction of an alcohol to yield water and an alkene.

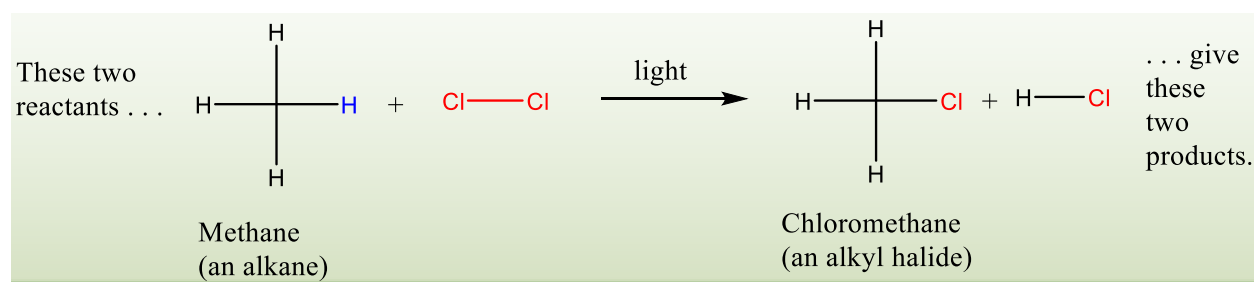




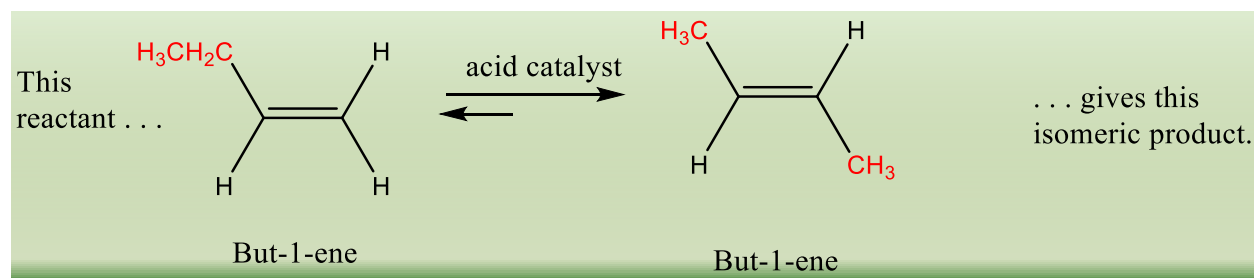
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- **Substitution reactions** occur when two reactants exchange parts to give two new products. An example that is the reaction of an alkane with Cl_2 in the presence of ultraviolet light to yield an alkyl chloride. A $-\text{Cl}$ group substitutes for the $-\text{H}$ group of the alkane, and two new products result.



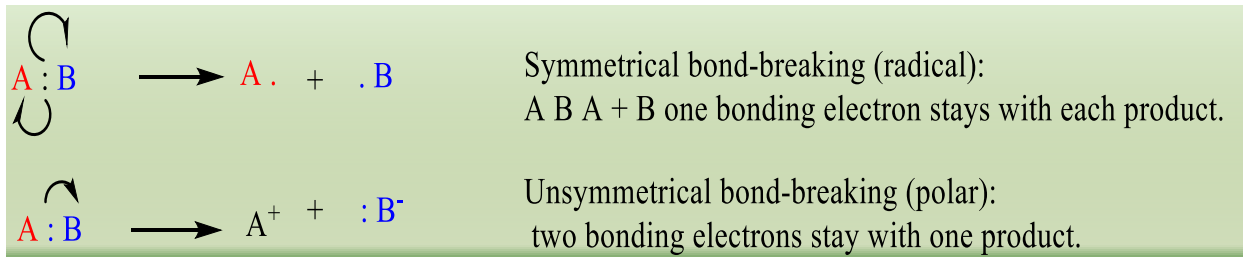
- **Rearrangement reactions** occur when a single organic reactant undergoes a reorganization of bonds and atoms to yield a single isomeric product. An example that we saw is the conversion of *cis*-but-2-ene into its isomer *trans*-but-2-ene by treatment with an acid catalyst.



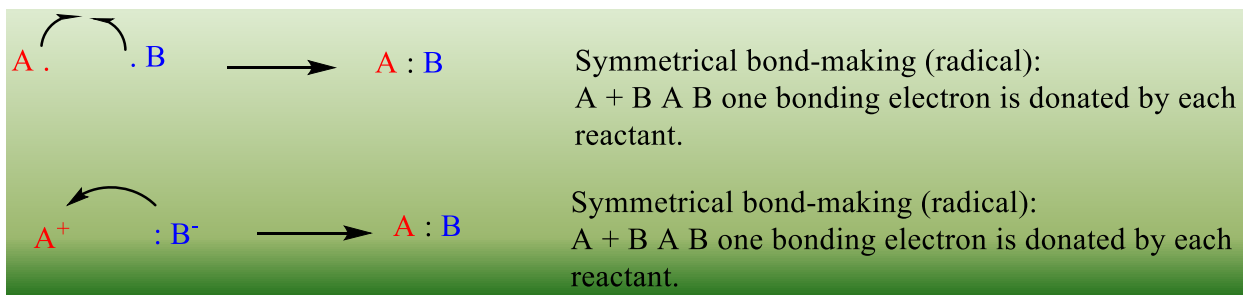


How Reactions Occur: Mechanisms

All chemical reactions involve bond-breaking in the reactant molecules and bond-making in the product molecules, which means that the electrons in those bonds must move about and reorganize. Fundamentally, a covalent two electron bond can break in two ways: a bond can break in an electronically *symmetrical* way so that one electron remains with each product fragment, or a bond can break in an electronically *unsymmetrical* way so that both electrons remain with one product fragment, leaving the other fragment with a vacant orbital. The symmetrical cleavage is said to be *homolytic*, and the unsymmetrical cleavage is said to be *heterolytic*.

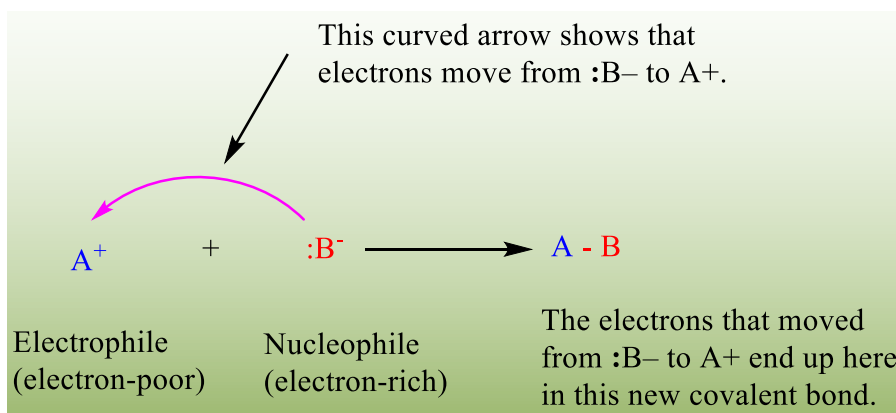


A bond can form in an electronically symmetrical way if one electron is donated to the new bond by each reactant or in an electronically unsymmetrical way if both bonding electrons are donated by one reactant.





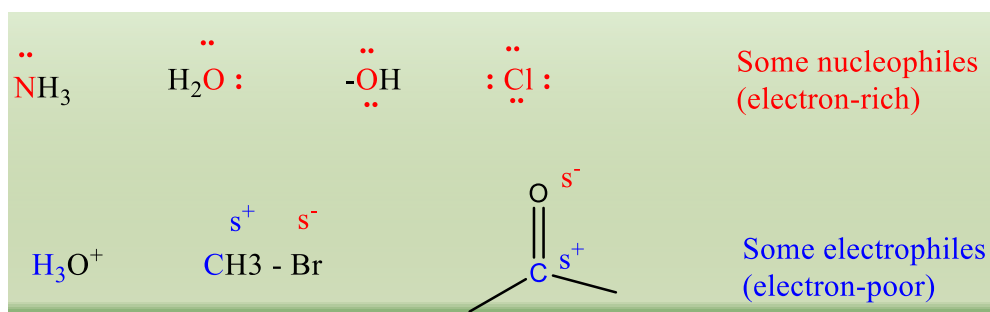
Processes that involve symmetrical bond-breaking and bond-making are called **radical reactions**. A **radical**, often called a *free radical*, is a neutral chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals. Chemists normally indicate the movement of an electron pair during a polar reaction by using a curved, full-headed arrow. A curved arrow shows where electrons move when reactant bonds are broken and product bonds are formed. It means that an electron pair moves *from* the atom (or bond) at the tail of the arrow *to* the atom at the head of the arrow during the reaction.



In referring to the electron-rich and electron-poor species involved in polar reactions, chemists use the words *nucleophile* and *electrophile*. A **nucleophile** is a substance that is “nucleus loving” and thus attracted to a positive charge. A nucleophile has a negatively polarized, electron-rich atom and can form a bond by donating an electron pair to a positively polarized, electron-poor atom. Nucleophiles can be either neutral or negatively charged and usually have lone-pairs of electrons: ammonia, water, hydroxide ion, and chloride ion are examples. An **electrophile**, by contrast, is “electron-loving.” An electrophile has a positively



polarized, electron-poor atom and can form a bond by accepting a pair of electrons from a nucleophile. Electrophiles can be either neutral or positively charged. Acids (H^+ donors), alkyl halides, and carbonyl compounds are examples.



If the definitions of nucleophiles and electrophiles sound similar to those given in for Lewis acids and Lewis bases, that's because there is indeed a correlation. Lewis bases are electron donors and behave as nucleophiles, whereas Lewis acids are electron acceptors and behave as electrophiles.

Example Which of the following species is likely to behave as a nucleophile and which as an electrophile?

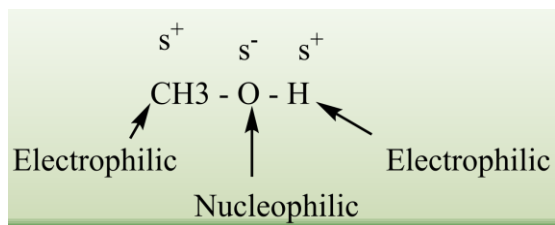
(a) NO_2^+ (b) CH_3O^- (c) CH_3OH

Solution

(a) NO_2^+ (nitronium ion) is likely to be an electrophile because it is positively charged.

(b) CH_3O^- (methoxide ion) is likely to be a nucleophile because it is negatively charged.

(c) CH_3OH (methyl alcohol) can be either a nucleophile, because it has two lone pairs of electrons on oxygen, or an electrophile, because it has polar C-O and O-H bonds.



Describing a Reaction: Catalysis

A **catalyst** is a substance that increases the rate of a chemical transformation by providing an alternative mechanism. The catalyst *does* take part in the reaction, but it is regenerated at some point and thus undergoes no net change. An example that we'll see in the next chapter, for instance, is the use of a metal catalyst such as palladium to effect the reaction of an alkene with H_2 gas and produce an alkane. In the absence of palladium, an alkene undergoes no reaction with H_2 gas even at high temperature, but in the presence of palladium, reaction occurs rapidly at room temperature. Called a *hydrogenation* reaction.

