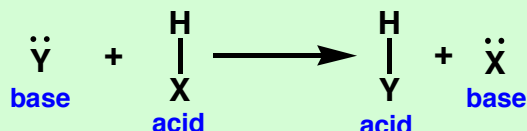


# Elimination Across $sp^3$ Carbons

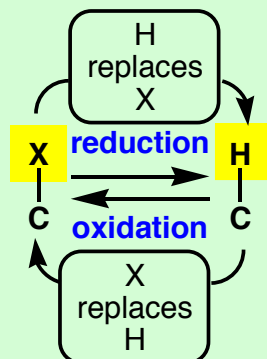
Next we examine a class of **elimination** reactions to produce carbon-carbon multiple bonds. We recently studied substitution reactions at  $sp^3$  carbon atoms. Elimination and substitution are **competing** reactions; some mechanisms of elimination and substitution have **common intermediates**.

## 1) Acid-Base - hydrogen swap

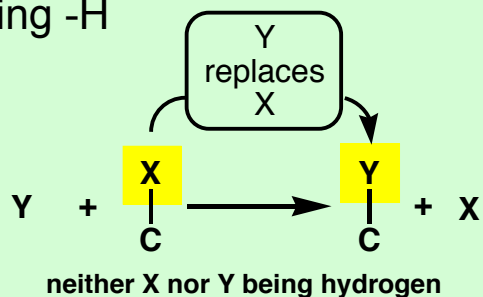


## 2 & 3) Oxidation & Reduction

change in the number of C-H bonds in relation to the number of C-X bonds

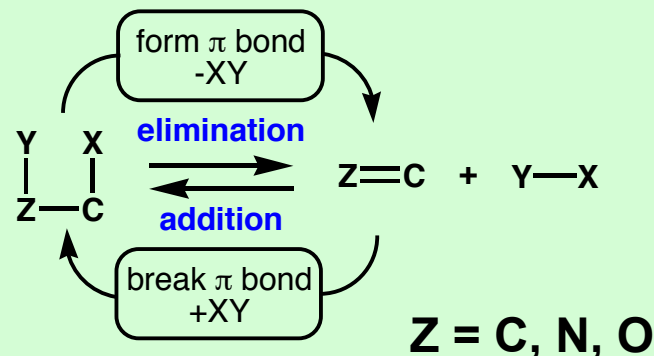


**4) Substitution** - replace C's substituent (-X) with another (-Y), neither being -H

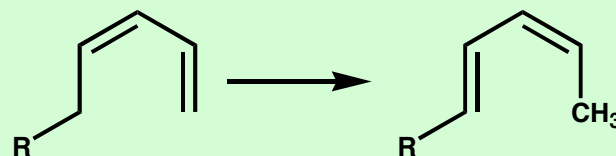


**5) Elimination** - loss of XY elements with concomitant pi bond formation

**6) Addition** - gain of XY elements with concomitant loss of pi bond



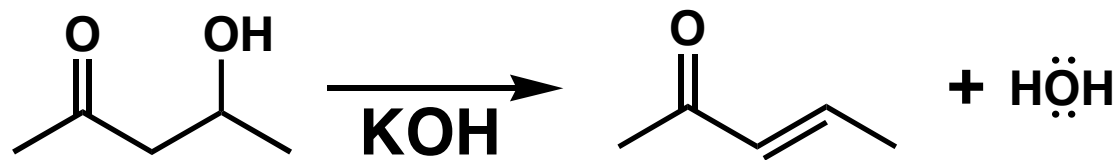
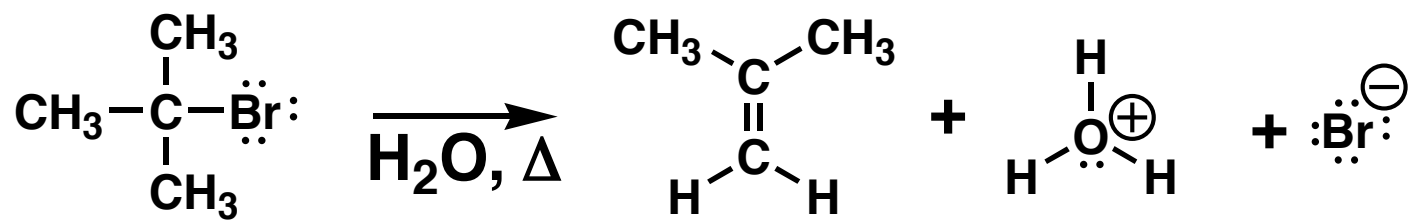
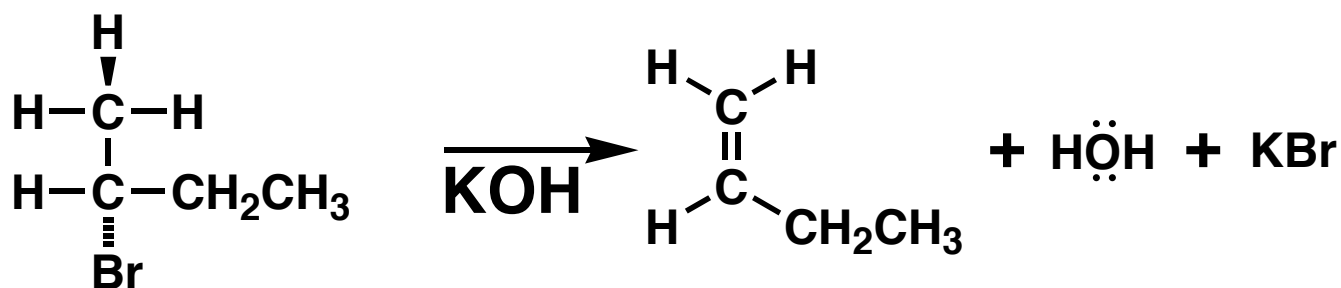
**7) Rearrangement** - isomerization process (no atoms lost or gained); results in new bonding connectivity (one of many examples shown as there is no generic representation).



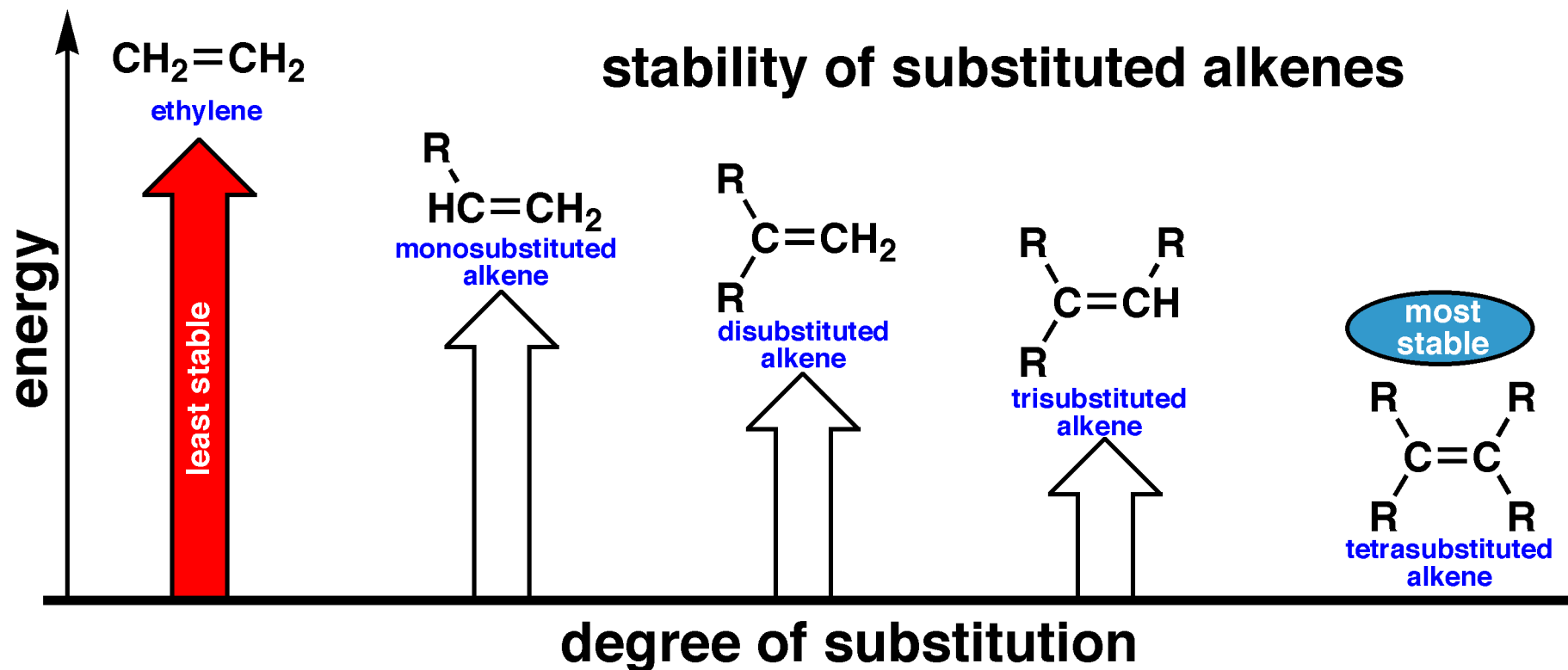
R stands for a generic "residue"



# Elimination Across Carbon-Carbon Bonds: Three Examples



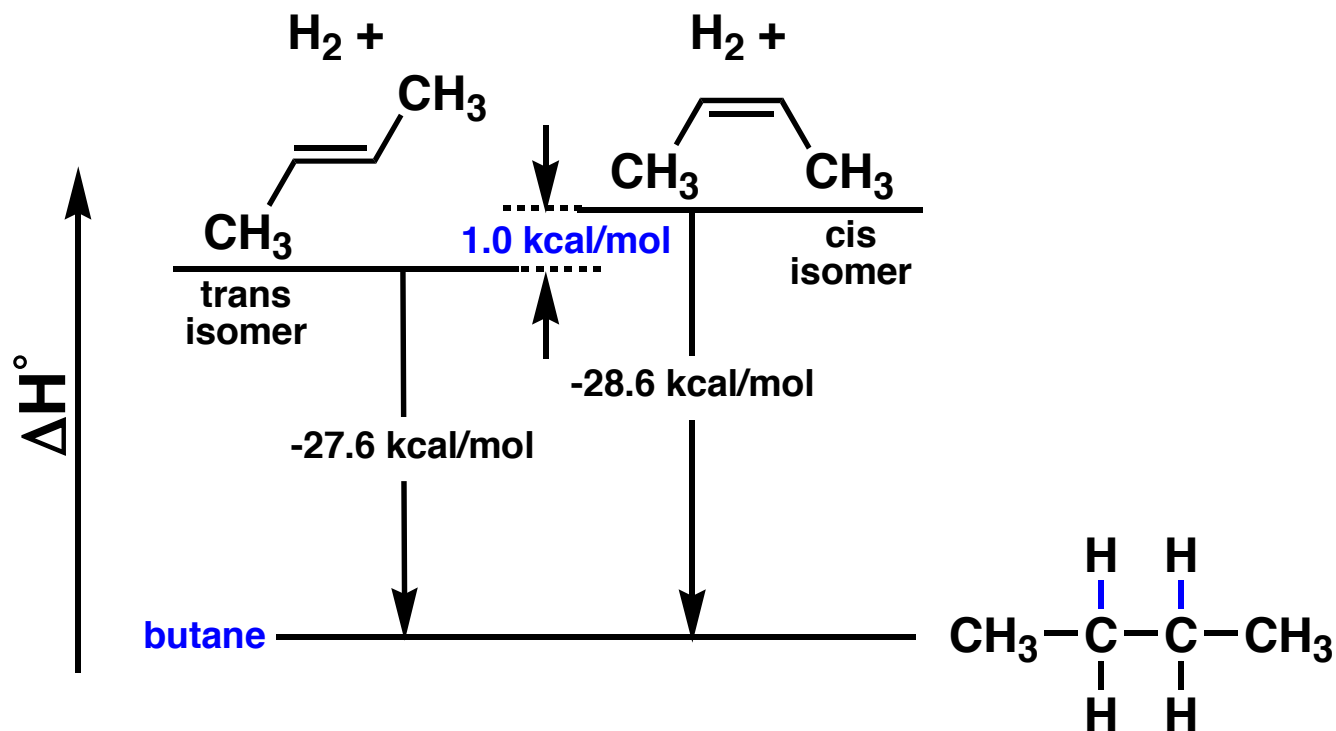
# The Relative Stability of Carbon-Carbon Double Bonds



**Alkenes** are hydrocarbons that contain the double bond functional group. Alkenes are also called **olefins** and they are said to be **unsaturated** compounds meaning that their carbon atoms do not have the maximum number of allowed substituents (4 for carbon). As explained on the following page, heats of hydrogenation can be used to determine stability for alkenes that differ by their degree of alkene substitution. **The general conclusion is that the more alkyl substituents that are bonded to  $sp^2$  carbons of an alkene, the more stable is the double bond.**

# Heats of Hydrogenation and an Experimental Determination of Alkene Stability

The addition of hydrogen to carbon-carbon double bond is known as hydrogenation. This **reduction** reaction transforms alkenes into alkanes. The conditions and mechanism of the reaction do not concern us at this time. We are going to use this reaction to experimentally determine the relative stability of alkenes.



The heat produced by a reaction is accurately measured by a calorimeter. Let's compare the hydrogenation of cis and trans 2-butene. Both reactions yield the same product, butane. The enthalpy change for the trans isomer is  $-27.6 \text{ kcal/mol}$  whereas for the cis isomer the enthalpy change is  $-28.6 \text{ kcal/mol}$ . Since both reactions yield the same product, we know that the energy difference comes from the difference of the starting alkenes. The diagram illustrates this result, and shows that the trans isomer is more stable than the cis isomer by about  $1.0 \text{ kcal/mol}$ . The origin of this stability difference is a steric interaction between the methyl groups. You can use MarvinSketch to convince yourself of the close proximity of the methyl groups in the cis isomer.