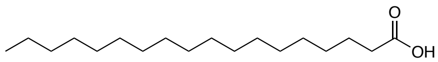
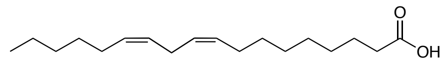
Chapter 6. Alkenes: Structure and Stability



Steric Acid (saturated fatty acid)



Linoleic Acid (unsaturated fatty acid)

Degrees of unsaturation

saturated hydrocarbon	C_nH_{2n+2}
cycloalkane (1 ring)	C_nH_{2n}
alkene (1 π-bond)	C_nH_{2n}
alkyne (2 π-bonds)	C_nH_{2n-2}

For each ring or π-bond, -2H from the formula of the saturated alkane

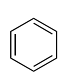
Degrees of unsaturation: # of rings and/or π-bonds in a molecule.
Information can be obtained from the molecular formula

Correction for other elements:

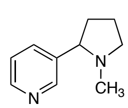
For Group VII elements (halogens):
subtract 1H from the H-deficiency for each halogen,
or add 1H to the molecular formula of each halogen

For Group VI elements (O and S)
No correction is needed

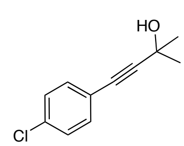
For Group V elements (N and P)
add 1H to the H-deficiency for each N or P
or subtract 1H from the molecular formula for each N or P



C_6H_6



$C_{10}H_{14}N_2$



$C_{11}H_{11}OCl$

Systematic Nomenclature (IUPAC System)

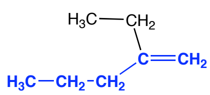
Prefix-Parent-Suffix

Naming Alkenes

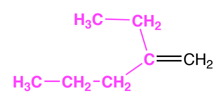
Suffix: -ene

Many of the same rules for alkanes apply to alkenes

1. Name the parent hydrocarbon by locating the longest carbon chain that contains the double bond and name it according to the number of carbons with the suffix -ene.



Parent = pentene



not hexene
(does not contain double bond)

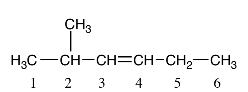
2a. Number the carbons of the parent chain so the double bond carbons have the lowest possible numbers.

$$H_3C-CH_2-CH_2-CH{=}CH-CH_3$$

6 5 4 3 2 1

2-hexene

b. If the double bond is equidistant from each end, number so the first substituent has the lowest number.



2-methyl-3-hexene

3. Write out the full name, numbering the substituents according to their position in the chain and list them in alphabetical order.

4. Indicate the double bond by the number of the first alkene carbon.

$H_3C-CH_2-CH_2-CH=CH-CH_3$

6 5 4 3 2 1

2-hexene

5. If more than one double bond is present, indicate their position by using the number of the first carbon of each double bond and use the suffix -diene (for 2 double bonds), -triene (for 3 double bonds), -tetraene (for 4 double bonds), etc.

$H_2C=CH-CH_2-CH=CH_2$

1 2 3 4 5

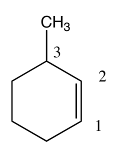
1,4-pentadiene

$H_2C=CH-CH=CH-CH_3$

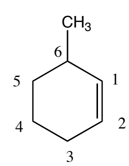
1 2 3 4 5

1,3-pentadiene

6a. Cycloalkenes are named in a similar way. Number the cycloalkene so the double bond carbons get numbers 1 and 2, and the first substituent is the lowest possible number.

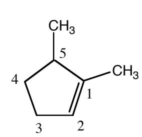


3-methylcyclohexene

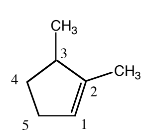


NOT
6-methylcyclohexene

b. If there is a substituent on one of the double bond carbons, it gets number 1.

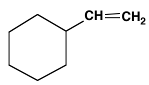


1,5-dimethylcyclopentene

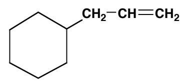


NOT
2,3-dimethylcyclopentene

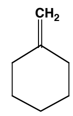
Alkenes as substituents:



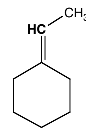
ethenyl or vinyl
(vinylcyclohexane)



2-propenyl or allyl
(allylcyclohexane)

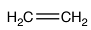


methylene
(methylenecyclohexane)

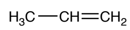


ethylidene
(ethylidenecyclohexane)

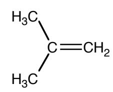
Non-IUPAC Alkenes (Table 6.1, pg. 194)



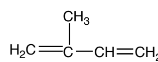
ethylene
(ethene)



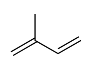
propylene
(propene)



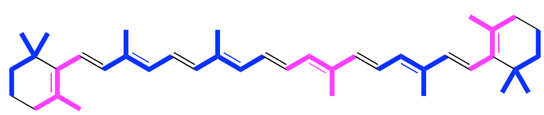
isobutylene
(2-methylpropene)



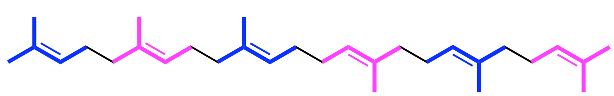
isoprene
(2-methyl-1,3-butadiene)



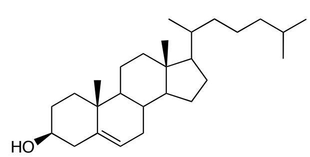
Isoprene (C_5)



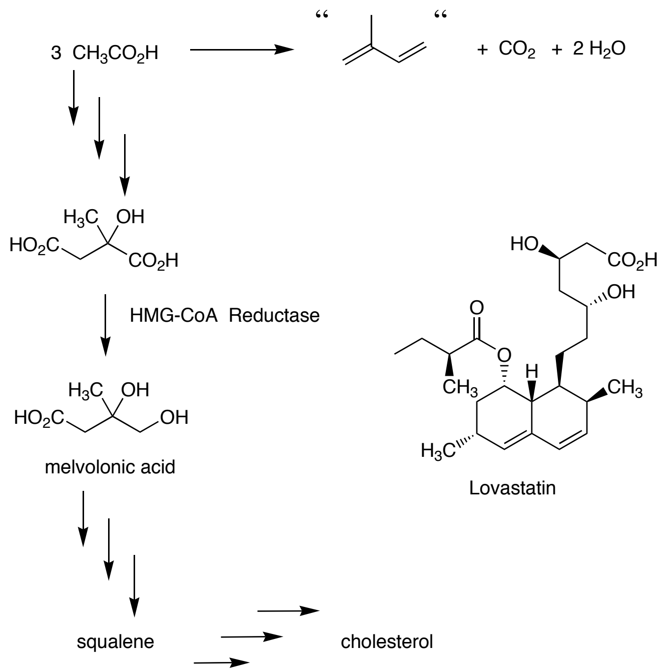
β-carotene (C_{40}, 8 isoprene units)



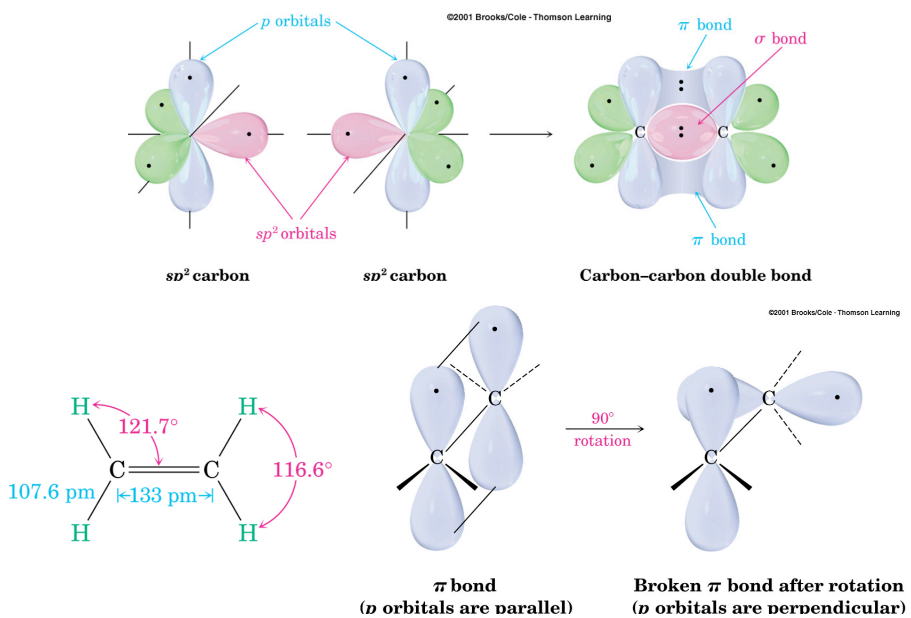
Squalene (C_{30}, 6 isoprene units)



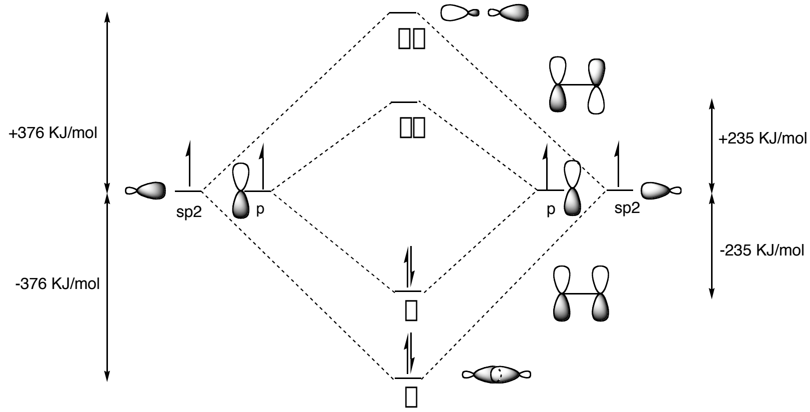
Cholesterol ($C_{27}H_{46}O$)



C=C double bonds

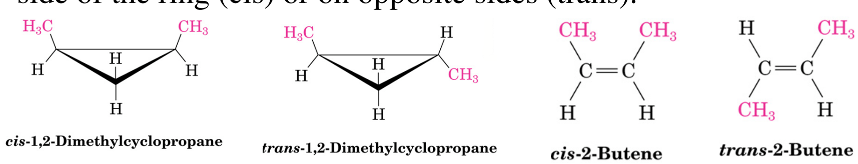


Molecular Orbitals of a Carbon-Carbon Double Bond

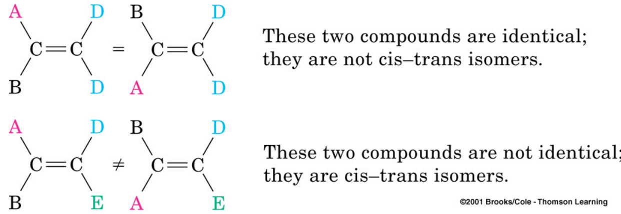


Alkenes Stereoisomers

recall cycloalkane stereoisomers: substituents are either on the same side of the ring (cis) or on opposite sides (trans).



Substituents on an alkene can also be either cis (on the same side of the double bond) or trans (on opposite sides of the double bond. Cis/trans isomers of alkenes are stereoisomers- they have the same connectivity but different three-dimensional arrangements of groups

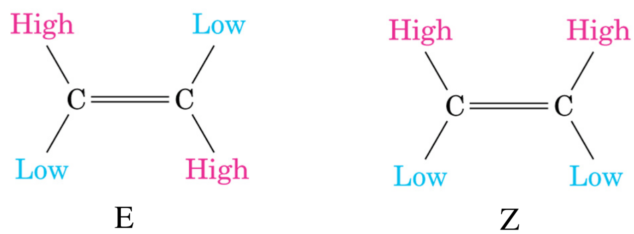


Designating Alkene Stereoisomers

The cis and trans becomes ambiguous when there are three or four substituents on the double bond.

E/Z System: For each carbon of the double bond, the groups are assign a priority (high or low) according to a system of rules. Thus, the high priority groups can be on the same side or on opposite side.

If the high priority groups are on opposite sides then the double bond is designated as E (entgegen- across)
If the high priority groups are on the same side then the double bond is designated as Z (zusammen- together)

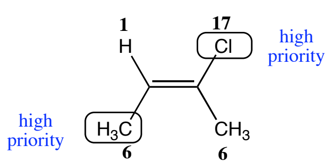


Assigning Group Priority: The Cahn, Ingold, Prelog Rules

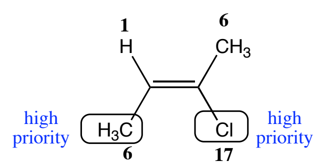
1. Look at the atoms directly attached to each carbon of the double bond. Rank them according to decreasing atomic number.

   priority of common atoms: I > Br > Cl > S > F > O > N > C > H

   If both high priority atoms are on the same side of the double bond it is designated **Z**. If the high priority atoms are on opposite sides of the double bond, it is designated as **E**.

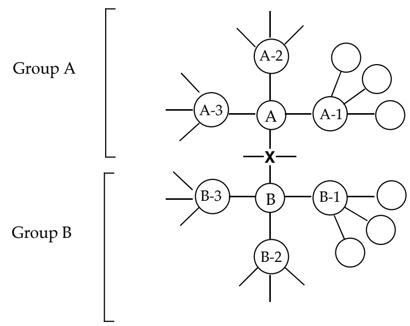


(E)-2-chloro-2-butene



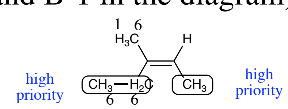
(Z)-2-chloro-2-butene

2.a. If the two atoms attached to the double bond carbon are identical (designated A and B below), look at all the atoms directly attached to the identical atoms in questions (designated A-1, A-2, A-3 and B-1, B-2, B-3). Assign priorities to all these atoms based on atomic number (1 is the highest priority, 3 the lowest).



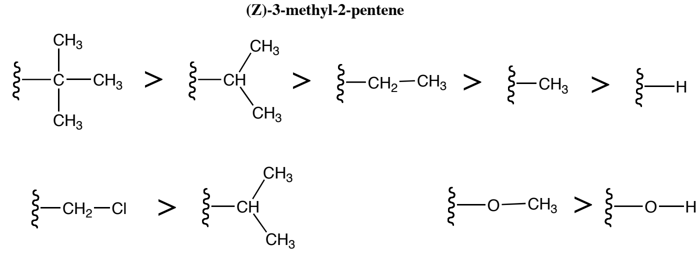
2b. Compare the highest priority atoms, i.e. compare A-1 with B-1. If A-1 is a higher priority atoms than B-1, then A is higher priority than B. If A-1 and B-1 are the same atom, then compare the second highest priority atoms directly bonded to A and B (A-2 with B-2); if A-2 is a higher priority atom than B-2, then A is higher priority than B. If A-2 and B-2 are identical atoms, compare A-3 with B-3.

c. If a difference still can not be found, move out to the next highest priority group (A-1 and B-1 in the diagram) and repeat the process.

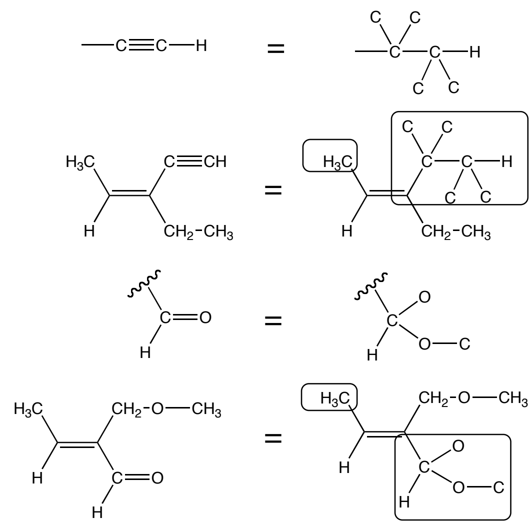


(Z)-3-methyl-2-pentene

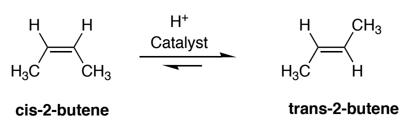
examples:



3. Multiple bonds are considered equivalent to the same number of single bonded atoms.



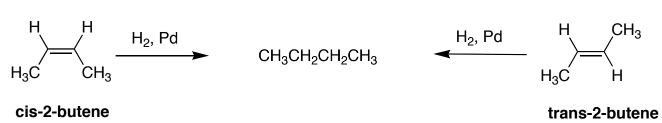
Alkene Stability:



at equilibrium, the ratio is 76% trans and 24% cis. $\Delta G°$ = -2.8 KJ/mol

$\Delta H°_{combustion}$: -2685.5 KJ/mol -2682.2 KJ/mol

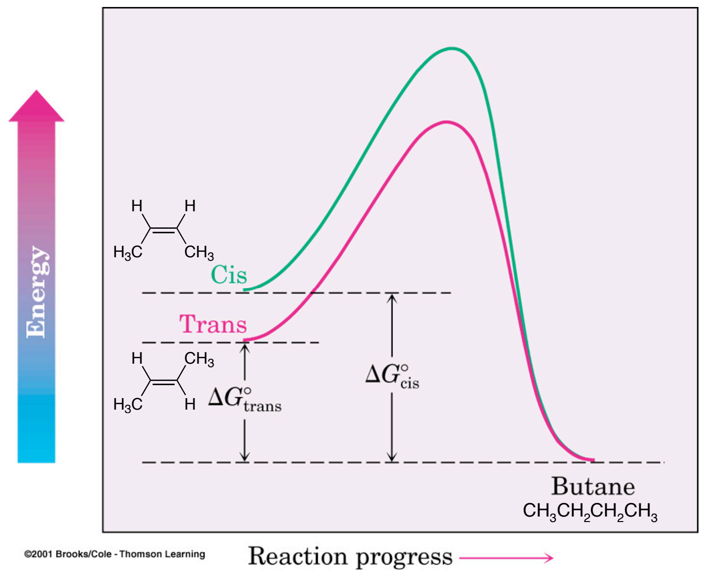
3.3 KJ/mol less energy is given off from trans isomer



$\Delta H°_{hydrogenation}$: -120 KJ/mol -115 KJ/mol

5 KJ/mol less energy is given off for trans isomer

The greater release of heat, the less stable the reactant.



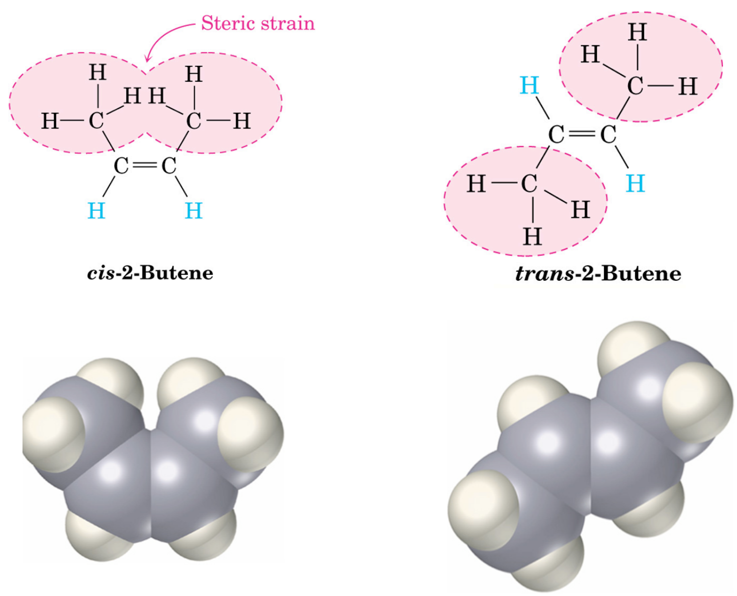
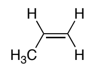
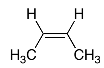
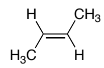
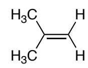
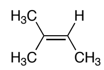
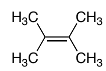
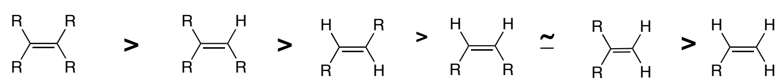


Table 6.2 (pg 204). Heats of Hydrogenation of Some Alkenes
measure of alkene stability.

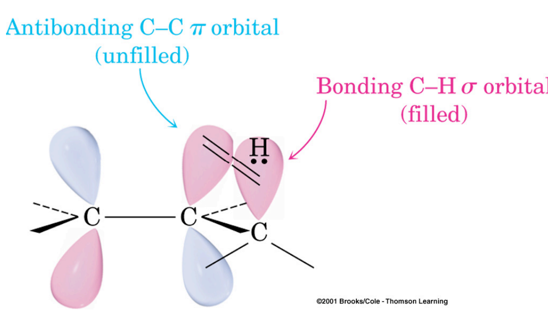
	Alkene	**$\Delta H°$ (KJ/mol)**
	$H_2C{=}CH_2$	-137
monosubstituted		-126
disubstituted		-120
		-115
		-119
trisubstituted		-113
tetrasubstituted		-111

tetrasubstituted > trisubstituted > disubstitutued > monosubstituted



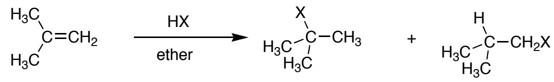
Trend: increased substitution decreases $\Delta H°_{hydrogenation}$. Increased substitution increases the alkene stability. More substituted alkenes are favored over less substituted alkenes

Hyperconjugation: stabilizing effect due to "<u>bonding</u>" interactions between a filled C-H orbital and a vacant neighboring orbital

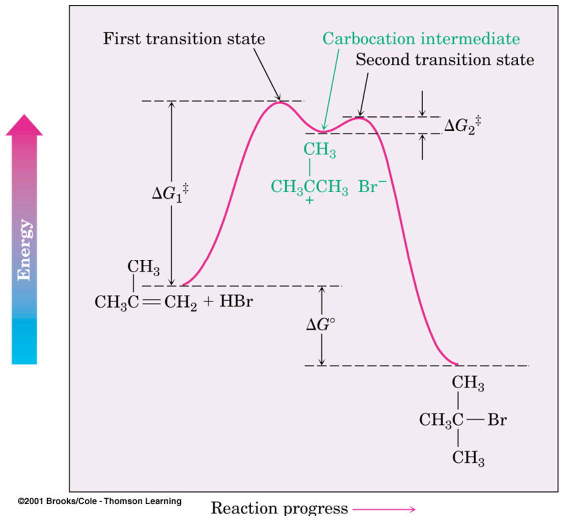


Increasing the substitution of an alkene, increases the number of possible hyperconjugation interactions

Electrophilic Addition of HX to Alkenes



none of this



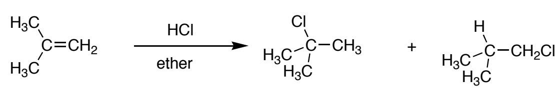
$\Delta G^\circ < 0$

$\Delta G^\ddagger$ for step one is large (slow)

$\Delta G^\ddagger$ for step two is small (fast)

READ: Writing Organic Reactions (pg 208)

Markovnikov's Rule: For the electrophilic addition of HX across a C=C bond, the H (of HX) will add to the carbon of the double bond with the most H's (the least substitutent carbon) and the X will add to the carbon of the double bond that has the most alkyl groups.



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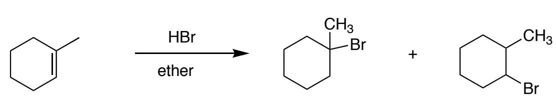
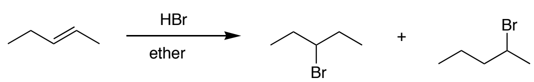


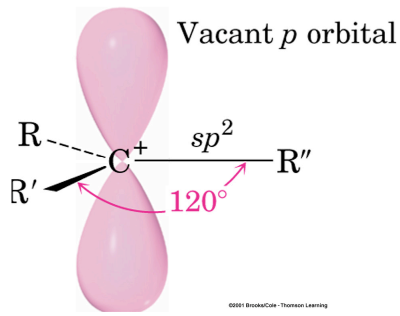
none of this



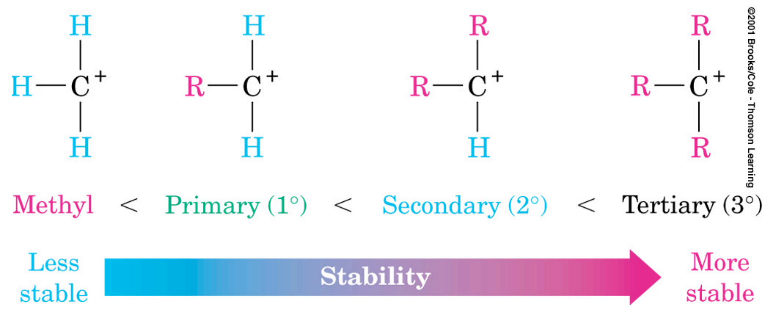
both products observed

Markovnikov's rule can be explained by the comparing the stability of the intermediate carbocations

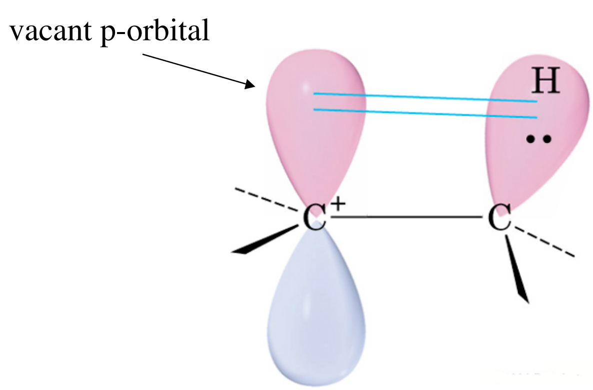
Carbocation Structure and Stability



Carbocations are sp2 Hybridized and have a trigonal planar geometry



Hyperconjugation stabilizes carbocations. Thus, more substituted carbocations are more stable.



The C-H □-bond on the neighboring carbon lines up with the vacant p-orbital and can donate electron density to the carbon cation. This is a “bonding” interaction and is stabilizing. The more hyperconjugation that are possible, the more stable the carbocation

Inductive Effects (section 2.1): shifting of electrons in a σ-bond in response to the electronegativity of a nearby atom (or group).

Carbon is a good electron donor. Substitution can also stabilize carbocations by donating electron density through the σ-bond.

3°: three alkyl groups donating electrons

2°: two alkyl groups donating electrons

1°: one alkyl group donating electrons

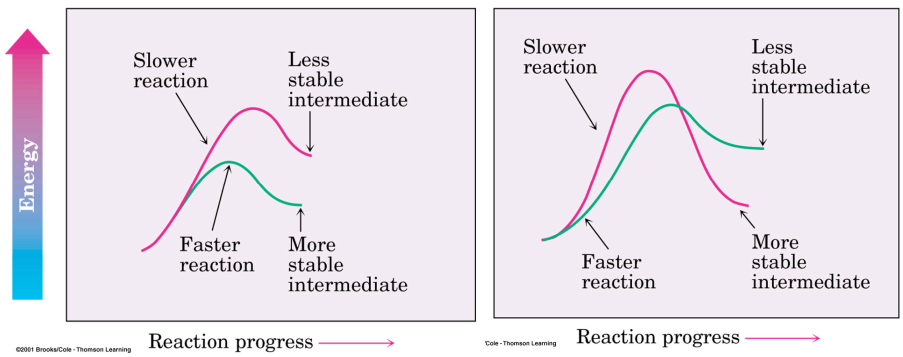
Methyl: no alkyl groups donating electrons

For the electrophilic addition of HX to an unsymmetrically substituted alkene:

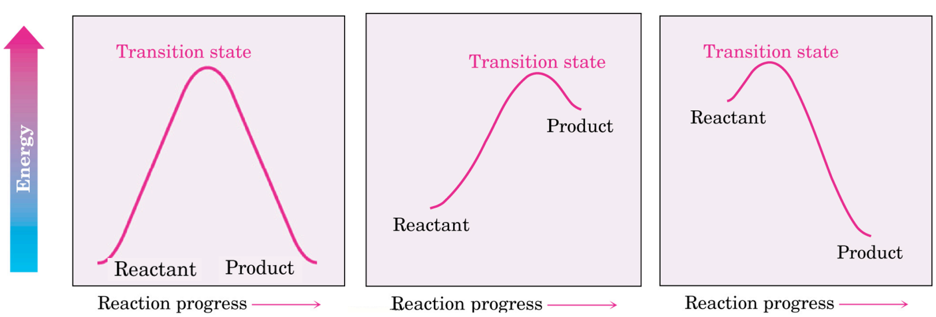
- The more highly substituted carbocation intermediate is formed.
- More highly substituted carbocations are more stable than less substituted carbocations. (hyperconjugation)
- The more highly substituted carbocation is formed faster than less substituted carbocation. Once formed, the more highly substituted carbocation goes on to the final product more rapidly as well.

The rate of a reaction is dependent upon $\Delta G^{\ddagger}$
There is no formal relationship between $\Delta G^{\ddagger}$ and $\Delta G°$
What is the structure of a transition state?
How can the structures of the reactants and products affect $\Delta G^{\ddagger}$

Hammond Postulate: provides an intuitive relationship between rate ($\Delta G^{\ddagger}$) and product stability ($\Delta G°$).



The Hammond Postulate: The structure of the transition state more closely resembles the nearest stable species (i.e., the reactant, intermediate or product)



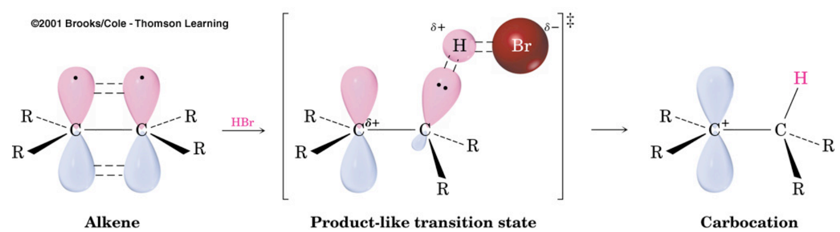
$\Delta G° = 0$	$\Delta G° > 0$	$\Delta G° < 0$
TS is halfway between reactant and products on the reaction coordinate	**TS lies closer to the products than the reactants on the reaction coordinate**	**TS lies closer to the reactants than the products on the reaction coordinate**

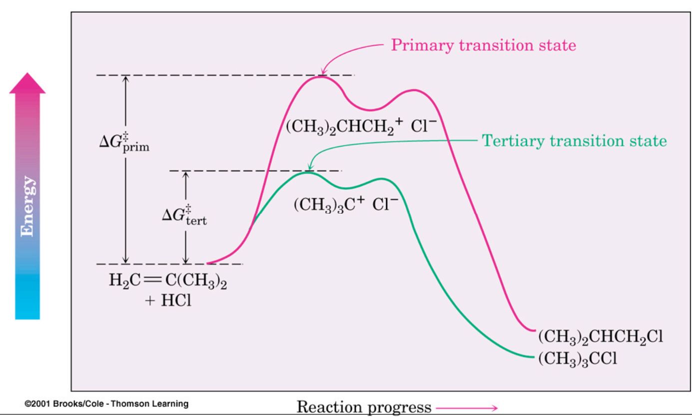
The Hammond Postulate: The structure of the transition state more closely resembles the nearest stable species (i.e., the reactant, intermediate or product).

For an endergonic reaction ($\Delta G^\circ > 0$), the TS is nearer to the products. The structure of the TS resembles that of the products. Therefore, things that stabilize the product will also stabilize the TS leading to those products.

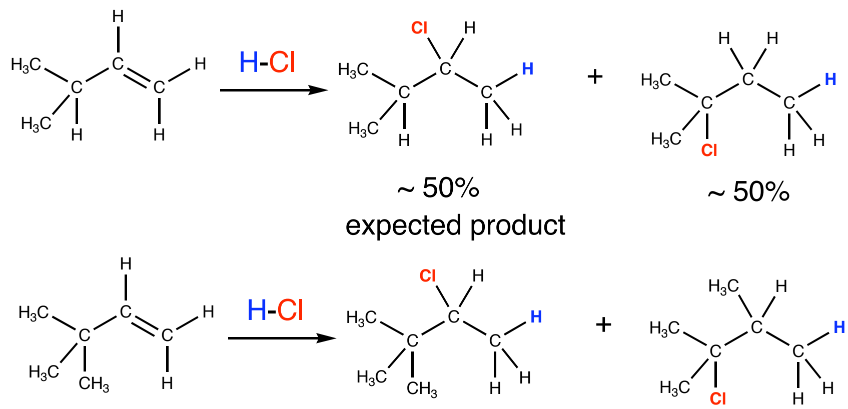
For an exergonic reaction ($\Delta G^\circ < 0$), the TS is nearer to the reactants. The structure of the TS resembles that of the reactants.

For the electrophilic addition of HX to alkenes:



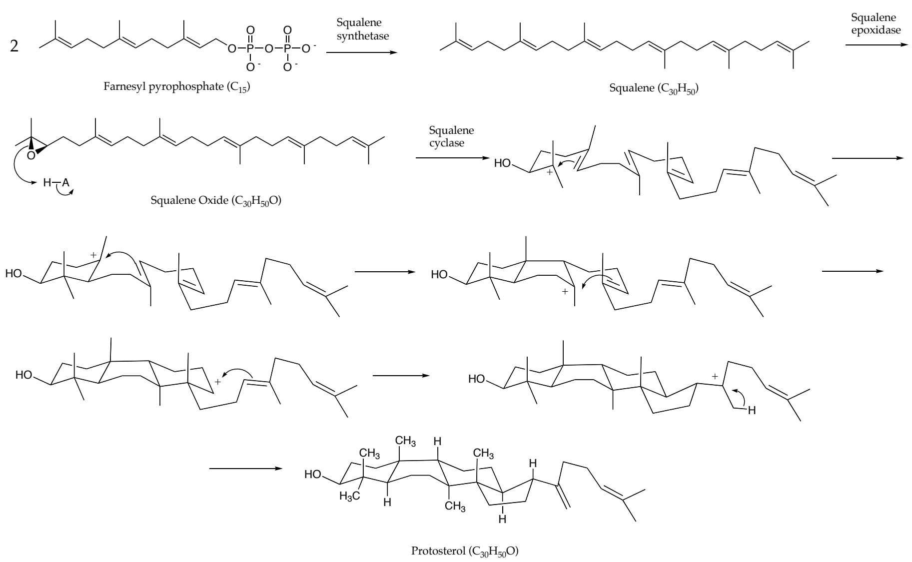


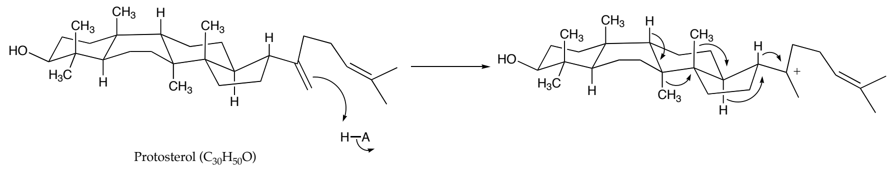
Carbocation Rearrangments: In reactions involving carbocation intermediates, the carbocation may sometimes rearrange if a more stable carbocation can be formed by the rearrangement. These involve hydride and methyl shifts.



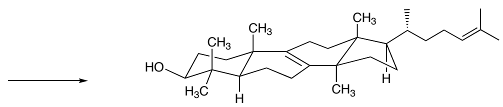
Note that the shifting atom or group moves with its electron pair.
A MORE STABLE CARBOCATION IS FORMED.

Steroid Biosynthesis: Polyene Cyclizations

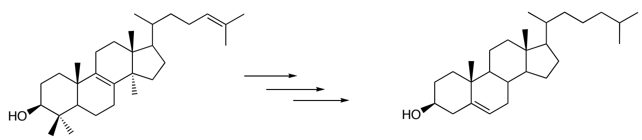




Protosterol ($C_{30}H_{50}O$)



Lanosterol ($C_{30}H_{50}O$)



Lanosterol ($C_{30}H_{50}O$) Cholesterol ($C_{27}H_{46}O$)

Oxidative Stress- a free radical chain process

Cellular respiration

$$O_2 \xrightarrow{4\,e^{\bullet -},\,4H^+} 2\,H_2O$$

Reactive Oxygen Species (ROS)

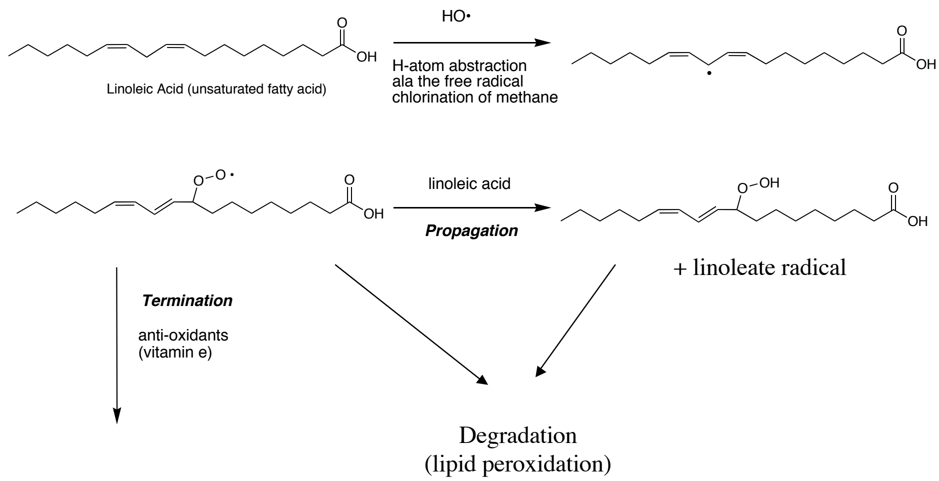
$O_2^{\bullet -}$	H_2O_2	$HO\bullet$
Superoxide: one-electron reduction of O_2	hydrogen peroxide	hydroxyl radical

$$O_2^{\bullet -} + \text{Fe (III)} \longrightarrow \text{Fe (II)} + O_2$$

$$\text{Fe (II)} + H_2O_2 \longrightarrow HO\bullet + HO^- + \text{Fe(III)}$$

$$O_2^{\bullet -} + \bullet NO \longrightarrow ONO_2^- \xrightarrow{H^+} ONO_2H \longrightarrow NO_2\bullet + HO\bullet$$

•NO: nitric oxide; ONO_2^-: peroxynitrate; ONO_2H: peroxynitrous acid



Linked to DNA damage, protein damage,
neurodegenerative disease, diabetes, cardiovascular disease