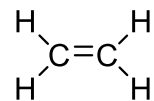# Structure and Synthesis of Alkenes

Alkenes (olefins) are hydrocarbons which have carbon–carbon double bonds.

A double bond is a σ bond and a π bond.

|	
Double bond B.D.E.	= 146 kcal/mol
σ bond B.D.E.	= 83 kcal/mol

Therefore π B.D.E. must = 63 kcal/mol.

A π bond is weaker than a σ bond.

π Bonds are *more reactive* than σ bonds, and π bonds are considered to be a functional group.

Structure of Alkenes

In ethene (ethylene) each carbon is bonded to 3 other atoms, with zero nonbonding electrons => sp^2 hybridization.
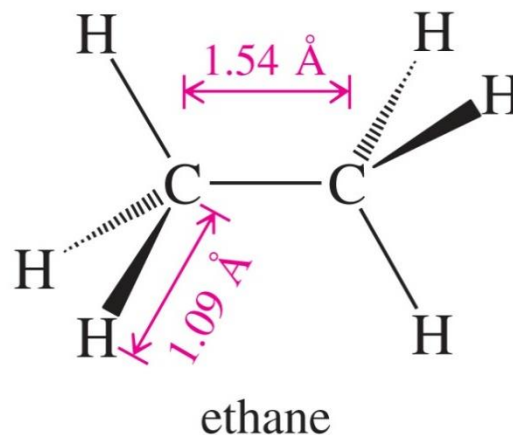

sigma bonding orbitals of ethylene
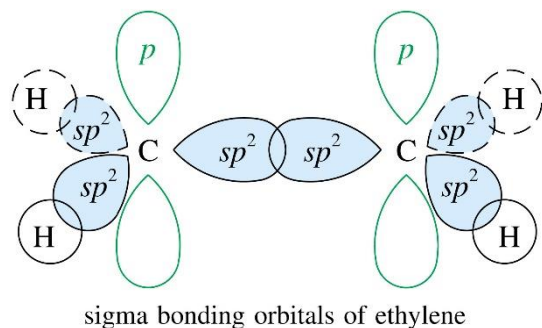
The C-H bonds are formed by overlap of sp^2 orbitals from the Carbon overlapping with 1s orbital from the Hydrogen.

(The C-H bonds in ethane are sp^3/1s overlapping orbitals. The ethene C-H bonds contain more s character than the ethane C-H bonds and are therefore *shorter* and *stronger*).

ethylene
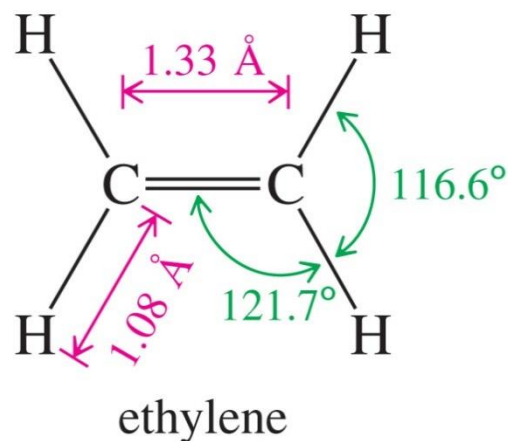
ethane

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sp^2 are 1/3 s, whereas sp^3 are 1/4 s in character (s orbitals are closer to the nucleus and lower in energy).

The carbon-carbon bond in ethene is shorter and stronger than in ethane partly because of the sp^2-sp^2 overlap being stronger than sp^3-sp^3, but especially because of the extra π bond in ethene.

Pi Bond

The unhybridized p orbitals on each carbon align parallel to form a π bond.
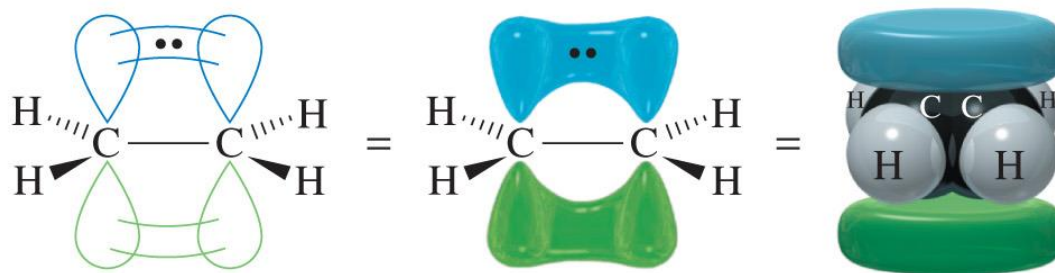
The π bond prevents rotation about the C=C bond because it would force the p orbitals into a non overlapping formation (i.e. break the π bond).

cis   no overlap with the ends perpendicular   trans
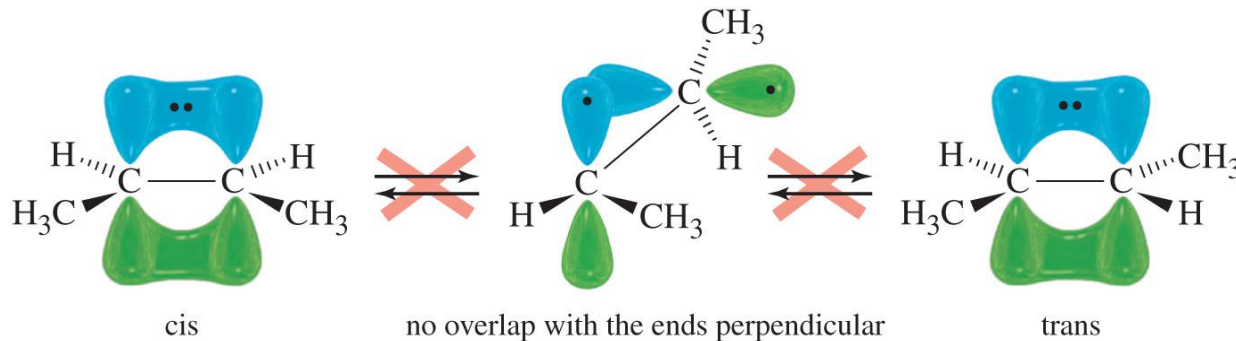
The π bond exists with half its electron density above the σ bond, and half below.
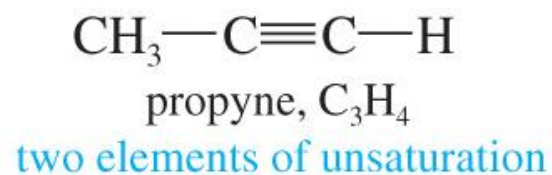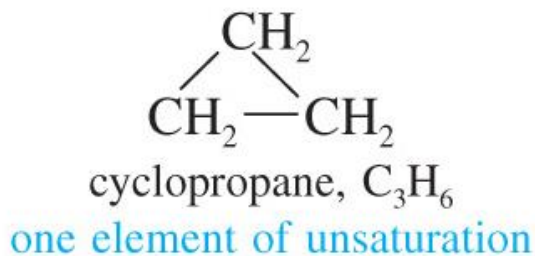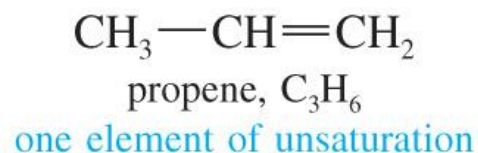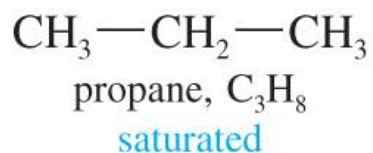
Elements of Unsaturation

Alkanes are said to be **saturated** since they have the maximum number of bonds to hydrogen.

An alkene is **unsaturated**.

Any π system or a ring system reduces the maximum number of hydrogens a molecule can have.

An **element of unsaturation** relates to <u>2</u> missing hydrogens from the saturated formula (C_nH_{2n+2}).

Consider alkanes, alkenes, alkynes and cycles:

$$CH_3-CH_2-CH_3$$
propane, C_3H_8
saturated

$$CH_3-CH=CH_2$$
propene, C_3H_6
one element of unsaturation

$$\begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ CH_2-CH_2 \end{array}$$
cyclopropane, C_3H_6
one element of unsaturation

$$CH_3-C\equiv C-H$$
propyne, C_3H_4
two elements of unsaturation

[*Heteroatom complications*
Heteroatoms are considered anything other than C or H.

Halogens
These simply substitute for hydrogens in the molecular formula.

Therefore just like C_2H_6 is saturated, so is $C_2H_4F_2$.

Oxygen
CH_3-CH_3 is saturated (C_2H_6)
CH_3-O-CH_3 is also saturated (C_2H_6O)

An oxygen can be added without requiring any additional hydrogens, so ignore the number of oxygens when calculating elements of Unsaturation.

Nitrogen
Nitrogen is trivalent, and when it replaces a C in a chain it requires only one hydrogen (-NH- vs. -CH_2-), so nitrogens count as half a carbon.

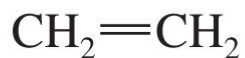*Thus C_4H_9N is equivalent to $C_{4.5}H_9$. (i.e. one element of Unsaturation).*]

Nomenclature of Alkenes

Simple alkenes are named like alkanes (root from the longest carbon chain), but the –**ane** suffix is replaced by-**ene**.

$$CH_2\!=\!CH_2 \qquad CH_2\!=\!CH\!-\!CH_3$$

IUPAC names:	ethene	propene	cyclohexene
Common names:	ethylene	propylene	

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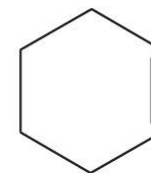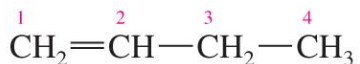
When the chain is longer than 3 carbons, number the atoms such that the *double bond* is given the lowest number (i.e. start at the end nearest the double bond).

$$\overset{1}{C}H_2\!=\!\overset{2}{C}H\!-\!\overset{3}{C}H_2\!-\!\overset{4}{C}H_3 \qquad \overset{1}{C}H_2\!=\!\overset{2}{C}H\!-\!\overset{3}{C}H_2\!-\!\overset{4}{C}H_2\!-\!\overset{5}{C}H_3$$

old IUPAC names:	1-butene	1-pentene
new IUPAC names:	but-1-ene	pent-1-ene

$$\overset{1}{C}H_3\!-\!\overset{2}{C}H\!=\!\overset{3}{C}H\!-\!\overset{4}{C}H_3 \qquad \overset{1}{C}H_3\!-\!\overset{2}{C}H\!=\!\overset{3}{C}H\!-\!\overset{4}{C}H_2\!-\!\overset{5}{C}H_3$$

old IUPAC names:	2-butene	2-pentene
new IUPAC names:	but-2-ene	pent-2-ene
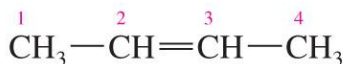
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Compounds with 2 double bonds are called *dienes*, 3 double bonds are *trienes*, etc.

$$\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH_2}$$

old IUPAC names: 1,3-butadiene
new IUPAC names: buta-1,3-diene

$$\overset{7}{CH_3}-\overset{6}{CH}=\overset{5}{CH}-\overset{4}{CH}=\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$$

1,3,5-heptatriene
hepta-1,3,5-triene
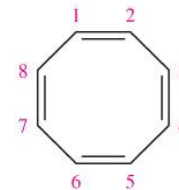
1,3,5,7-cyclooctatetraene
cycloocta-1,3,5,7-tetraene

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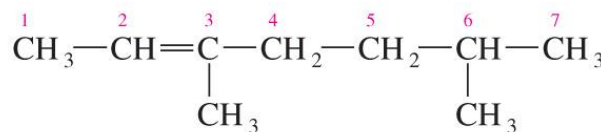For branches, each *alkyl* group is given a number, but the **double bond** is still given preference when numbering the chain.

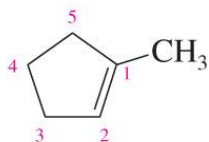$$\overset{4}{CH_3}-\overset{3}{CH}=\overset{2}{C}-\overset{1}{CH_3}$$
$$|$$
$$CH_3$$
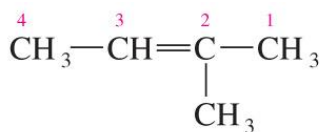
2-methyl-2-butene
2-methylbut-2-ene

$$\overset{4}{CH_3}-\overset{3}{CH}-\overset{2}{CH}=\overset{1}{CH_2}$$
$$|$$
$$CH_3$$
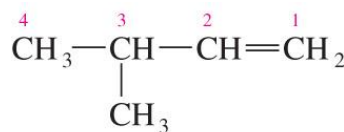
3-methyl-1-butene
3-methylbut-1-ene

$$\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{C}-\overset{4}{CH_2}-\overset{5}{CH_2}-\overset{6}{CH}-\overset{7}{CH_3}$$
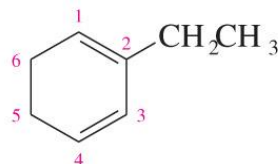$$|\qquad\qquad\qquad |$$
$$CH_3\qquad\qquad CH_3$$

3,6-dimethyl-2-heptene
3,6-dimethylhept-2-ene
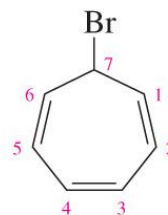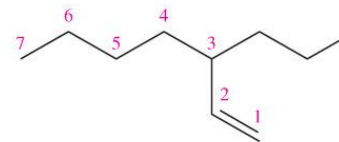

1-methylcyclopentene
1-methylcyclopentene
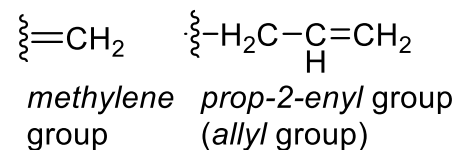

2-ethyl-1,3-cyclohexadiene
2-ethylcyclohexa-1,3-diene

7-bromo-1,3,5-cycloheptatriene
7-bromocyclohepta-1,3,5-triene

3-propyl-1-heptene
3-propylhept-1-ene

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When alkenes are *substituents*, they are termed *alkenyl* groups, and may be named systematically.

$\xi=CH_2$ $\xi-H_2C-\underset{H}{C}=CH_2$

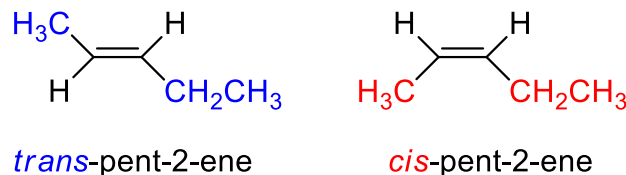*methylene*   *prop-2-enyl* group
group   (*allyl* group)

Geometric isomers

The *rigidity* of a π bond gives rise to geometric isomers.

When similar groups (not H's) are bound to the <u>same</u> side of the double bond the alkene is said to be *cis*.

When similar groups are bound to <u>opposite</u> sides of the double bond it is said to be *trans*.

$\underset{H}{\overset{H_3C}{\diagdown}}C=C\underset{CH_2CH_3}{\overset{H}{\diagup}}$ $\underset{H_3C}{\overset{H}{\diagdown}}C=C\underset{CH_2CH_3}{\overset{H}{\diagup}}$

trans-pent-2-ene   *cis*-pent-2-ene

Cycloalkenes must have 8 or more carbons before they are large enough to incorporate a *trans* double bond.
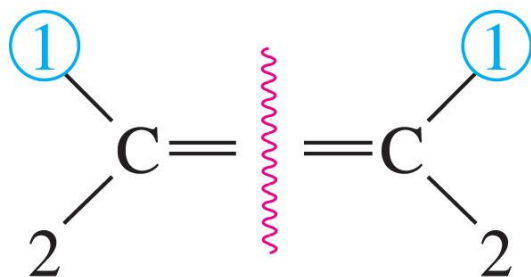
cyclohexene   *trans*-cyclodecene
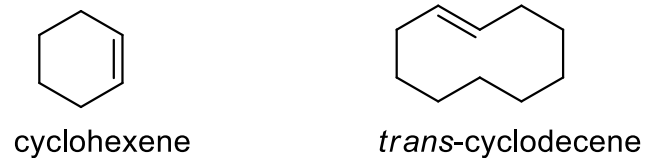
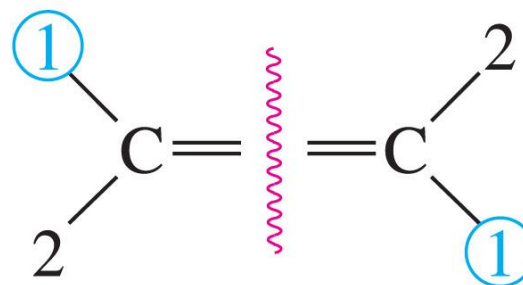Therefore cycloalkenes are deemed to be *cis* unless specified otherwise.

E-Z Nomenclature

The assignment of geometrical isomers as either E or Z follows on from the Cahn-Ingold-Prelog convention.

Imagine the double bonds being split into two ends, and assign the priority of the substituents.
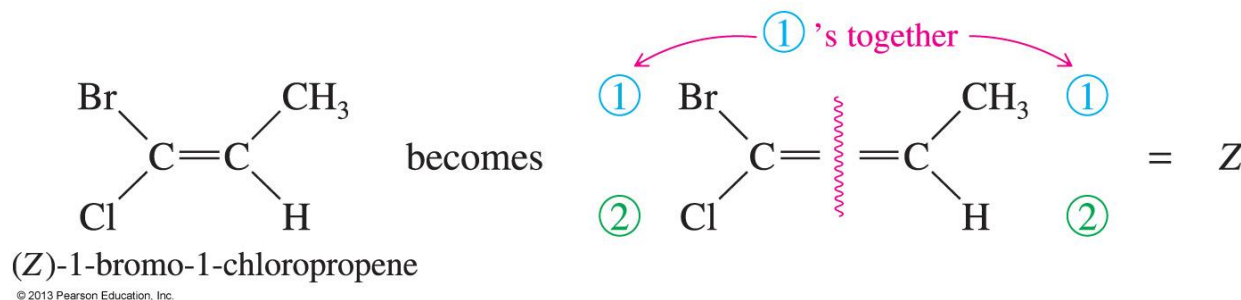

Zusammen   Entgegen

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If the two highest priority groups are on **opposite** sides of the double bond (*trans*) the isomer is assigned **E**.

If the two highest priority groups are on the **same** side of the double bond (*cis*) the isomer is assigned **Z**.

(Z)-1-bromo-1-chloropropene

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If there is more than one double bond, then the stereochemistry around each double bond must be specified.

Br

1   2   3   4   5   6   7   8

(3Z,5E)-3-bromoocta-3,5-diene
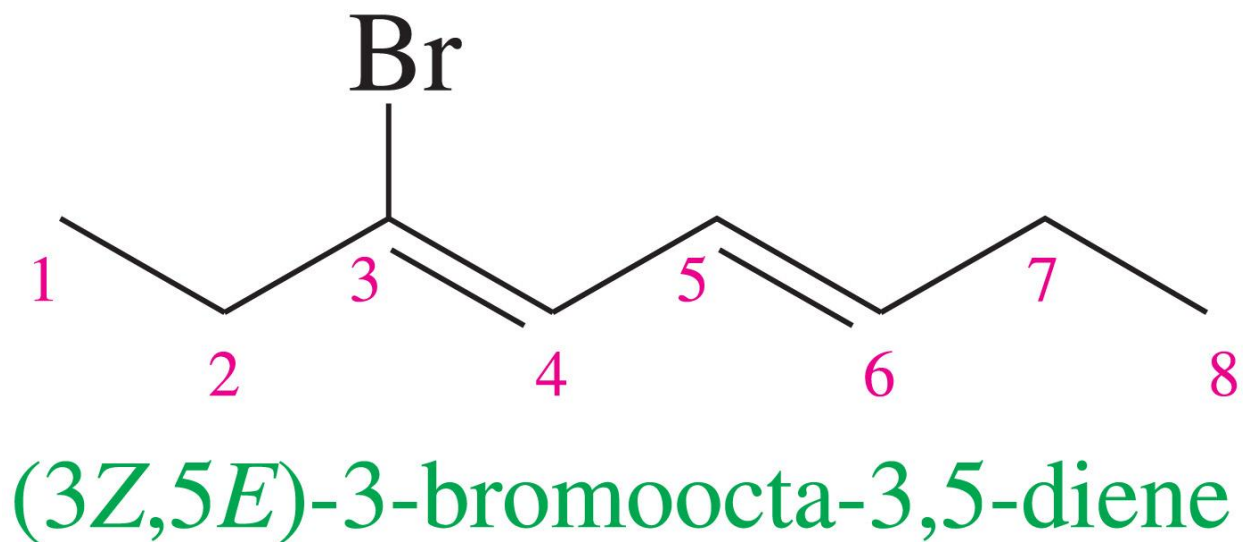
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Industrial Uses of Alkenes

Alkenes are useful intermediates in organic synthesis, but their main commercial use is as precursors (monomers) for polymers.


TFE → Polymerise → PTFE

Styrene → Polymerise → Polystyrene
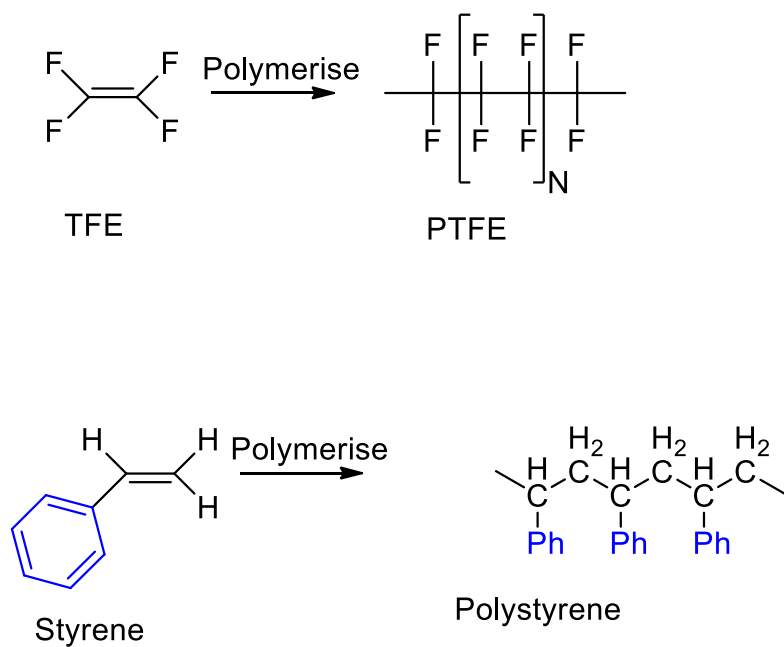
<u>Stability of Alkenes</u>

Alkenes are reduced to alkanes by the action of hydrogen gas in the presence of a catalyst.

The exothermicity of this reaction is called the heat of hydrogenation, and these values give information about the stability of the alkene.
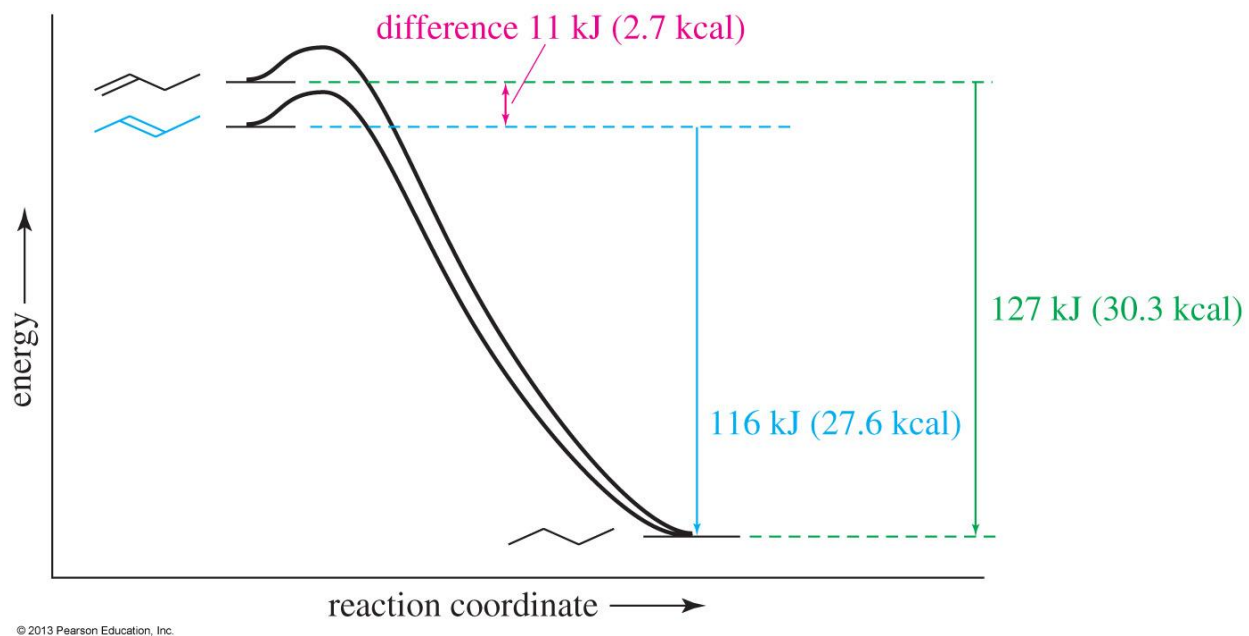
We observe that the data confirms the *Saytzeff rule*, that more highly substituted double bonds are more stable.

$$R_2C=CR_2 > R_2C=CRH > RHC=CHR \text{ and } R_2C=CH_2 > RCH=CH_2$$
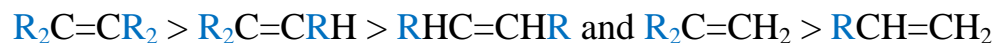
This is because the alkyl groups **stabilize** the double bond.
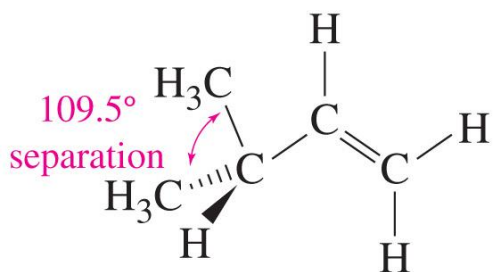
The stability arises from two factors:

1) the alkyl groups are electron donating (hyperconjugation) and so donate electron density into the π bond.
2) A double bond (sp^2) carbon separates bulky groups better than an sp^3 carbon, thus reducing steric congestion.
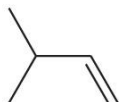
less substituted   more substituted
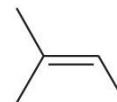
109.5°
separation

closer groups

120°
separation

wider separation
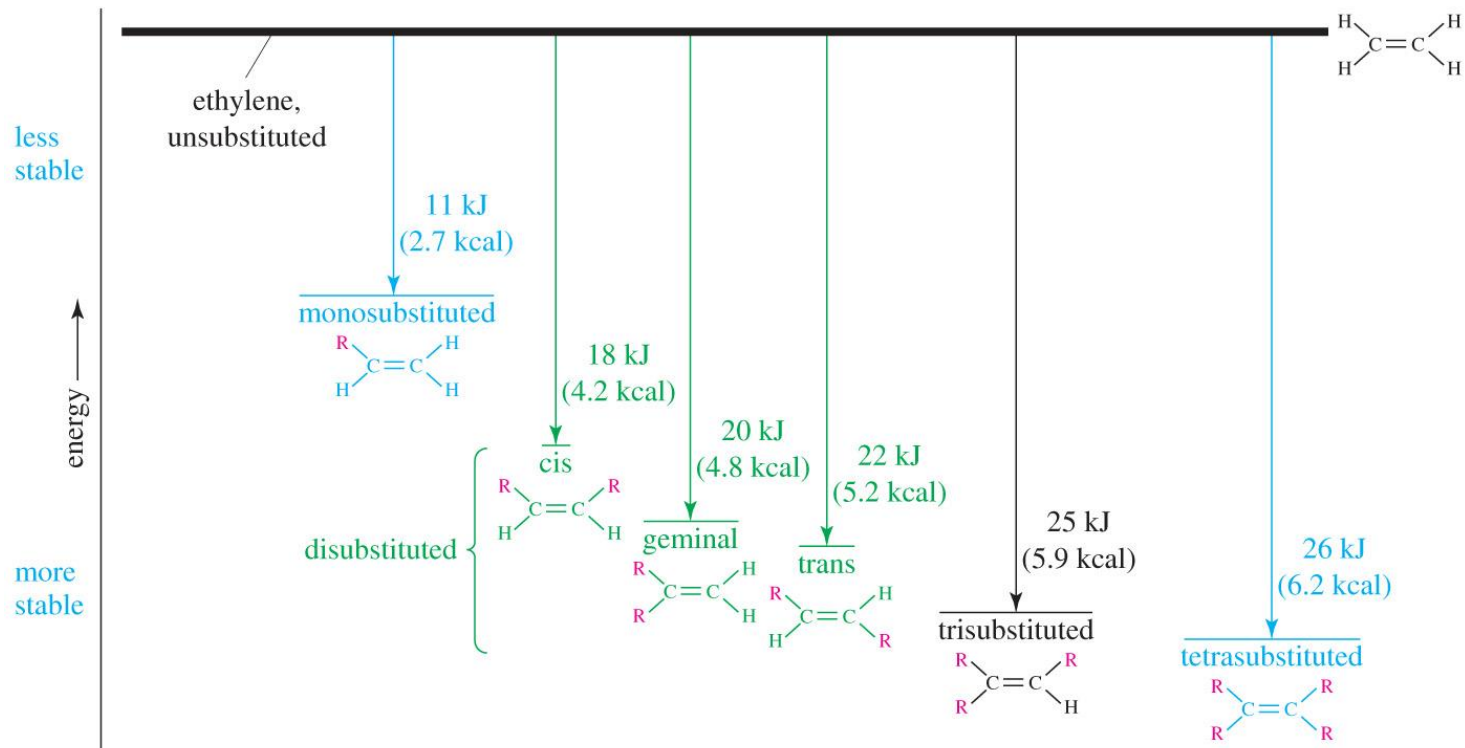
© 2013 Pearson Education, Inc.
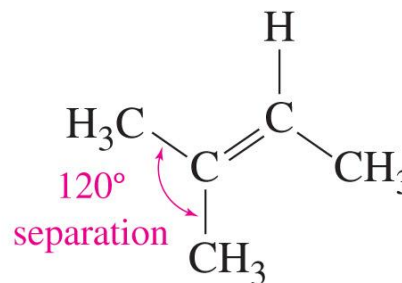
Energy differences in Alkenes

Heats of hydrogenation also infer that *trans* isomers are more stable than *cis* isomers.

This seems correct since the bulky groups are further separated in space in a trans conformation.

Relative stabilities:

less stable

energy ⟶

more stable

ethylene, unsubstituted

11 kJ (2.7 kcal)

monosubstituted

18 kJ (4.2 kcal)

cis

disubstituted

20 kJ (4.8 kcal)

geminal

22 kJ (5.2 kcal)

trans

25 kJ (5.9 kcal)
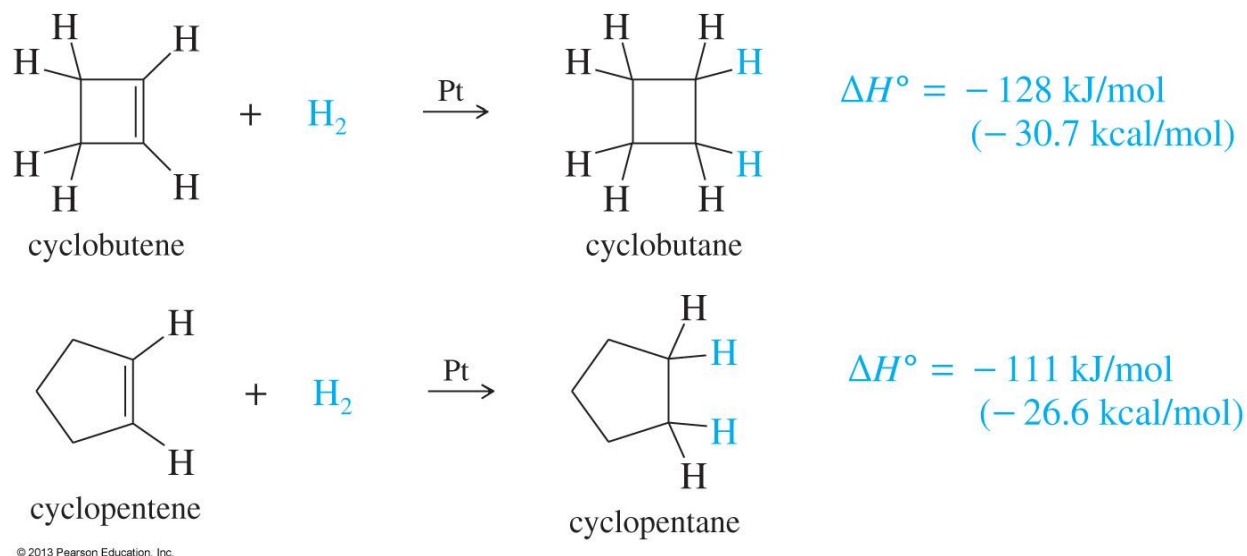
trisubstituted

26 kJ (6.2 kcal)

tetrasubstituted

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Cycloalkenes

The only difference in reactivity or energetics from acyclic systems occurs when there is significant ring strain in the cycloalkene.

Cyclopentene, -butene and even -propene exist, and these compounds have increasingly more reactive double bonds.

cyclobutene + H_2 $\xrightarrow{Pt}$ cyclobutane $\Delta H° = -128$ kJ/mol (-30.7 kcal/mol)

cyclopentene + H_2 $\xrightarrow{Pt}$ cyclopentane $\Delta H° = -111$ kJ/mol (-26.6 kcal/mol)

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Cyclobutene is about 4kcal/mol more strained than cyclopentene. (Smaller bond angles mean more deviation from 120º).

Bredt's Rule

We have already seen that cycloalkenes need *8 or more C atoms* to be large enough to accommodate a *trans* double bond.
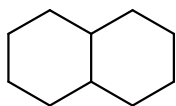
An extension of this is Bredt's rule which states:
A bridged bicyclic compound cannot have a double bond at a bridgehead position unless one of the rings contains at least eight carbon atoms.

Recall:
Bicyclic means two rings.
Bridgehead carbon is part of both rings.
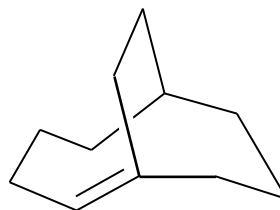
bicyclic
(fused)

bridged
bicyclic

A bridged bicyclic compound has at least one carbon in each the three links between the bridgehead atoms.

Bredt's rule
violation
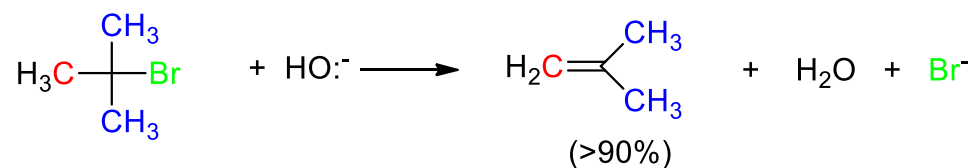
stable: trans in a
9 membered ring

Alkene Synthesis
Typically alkenes are produced by **elimination** reactions.

Recall the E2 elimination of H-X (dehydrohalogenation) can be an excellent synthetic method *if*:
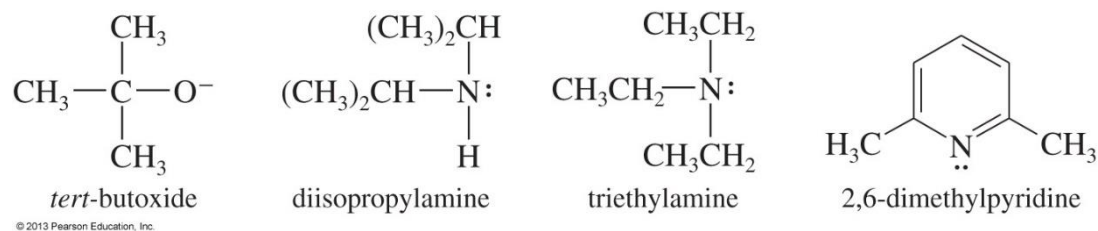the reactant is a poor S_N2 substrate, and a strong base is used.
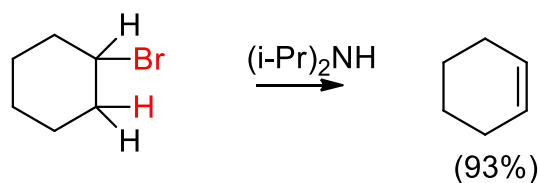
For example:

(>90%)

Use of a bulky base
A bulky base can further discourage undesired substitution reactions (i.e. a good base, poor nucleophile).

Common (bulky) bases:

tert-butoxide   diisopropylamine   triethylamine   2,6-dimethylpyridine

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E.g.

(i-Pr)$_2$NH

(93%)

Formation of Other Products

The Saytzeff rule predicts the major alkene product from an elimination to be the more **highly substituted** alkene.

Sometimes, strong, bulky bases can form products that are *not* Saytzeff products.

The proton which must be removed to give the more substituted alkene is often the more **sterically hindered** proton, and the bulky base would rather remove a more accessible proton, which leads to a less stable product.
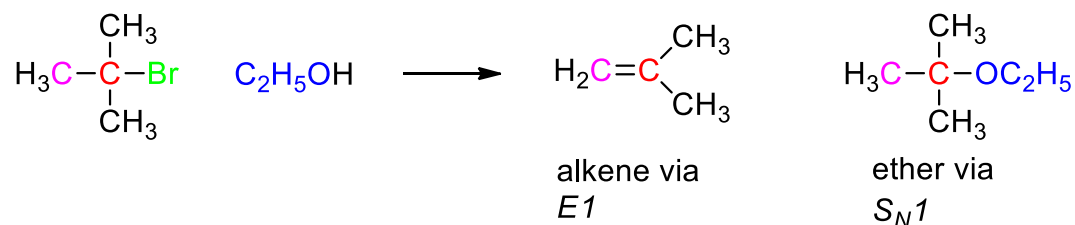
Such a product is a **Hofmann** product.
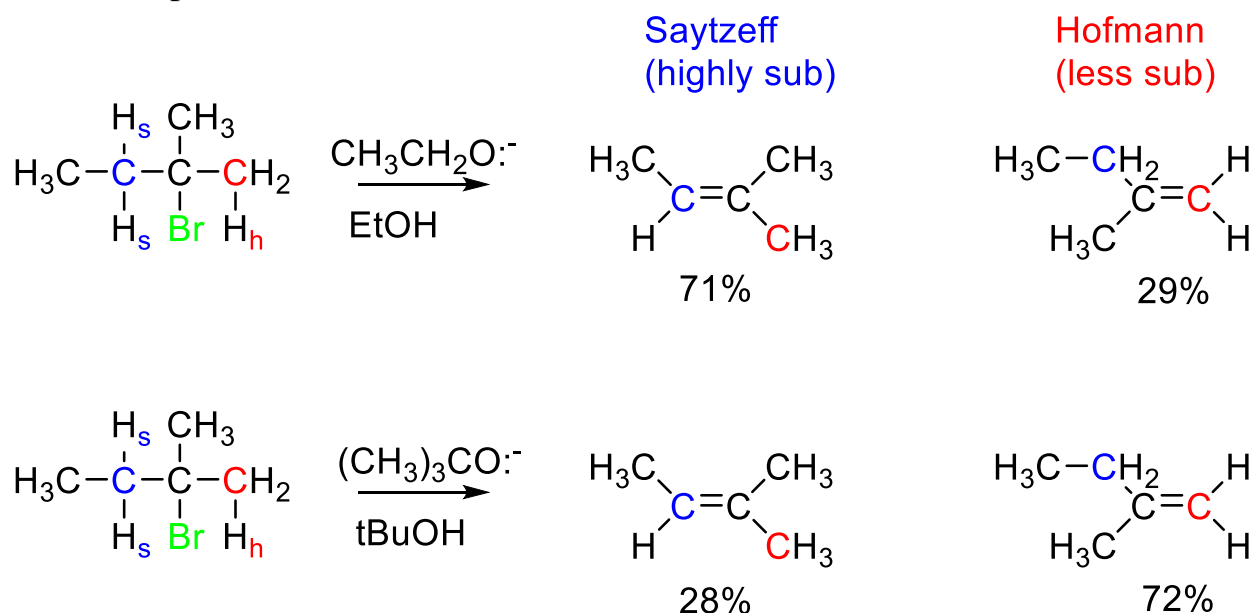
The bulky base (t-butoxide) gives more Hofmann than Saytzeff product.

Dehydrohalogenation by the E1 route

This normally requires a good ionizing solvent, a secondary or tertiary alkyl halide and a weak nucleophile and base.

$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br \quad C_2H_5OH \longrightarrow H_2C=C\underset{CH_3}{\overset{CH_3}{<}} \qquad H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OC_2H_5$$

alkene via *E1*   ether via *S_N1*

Typically the E1 elimination is accompanied by S_N1 substitution. The mixture of products is **undesirable** for a synthetic route.

Reduction of Vicinal Dibromides

The action of iodide ion on vicinal dibromides to produce alkenes is an *elimination*, a *reduction* and a *dehalogenation* reaction. (The same reaction can be achieved through the action of zinc metal in acetic acid).

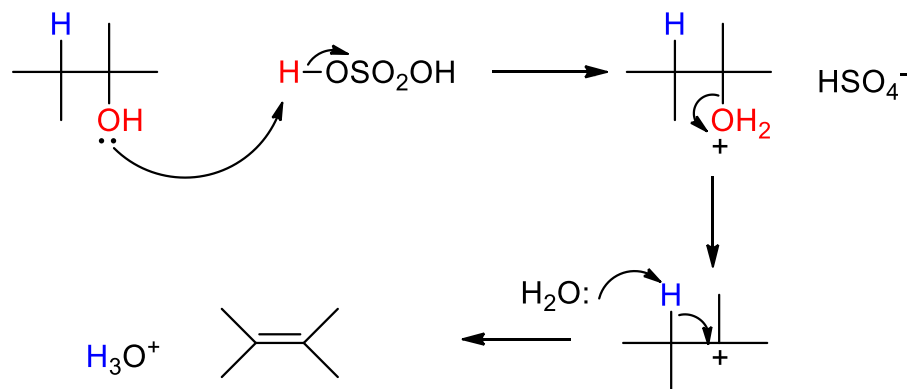The reaction prefers to go through the anti-coplanar T.S.
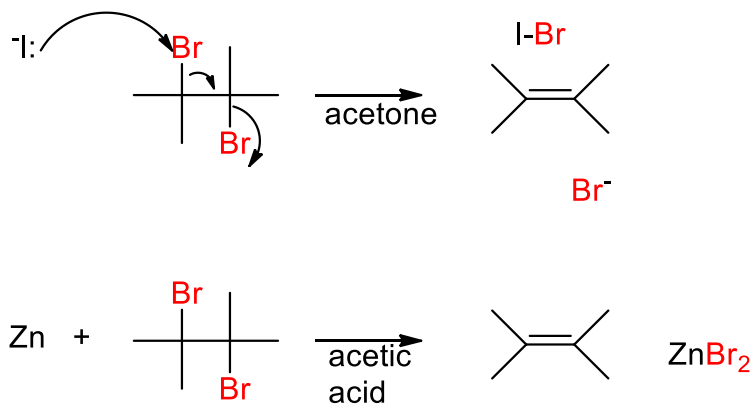
Alcohol Dehydration

The dehydration (removal of water) of alcohols is a good synthetic route to alkenes.
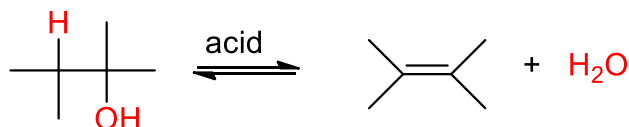
Normally strong acids like sulfuric or phosphoric acids are used.

The mechanism of dehydration is similar to the E1 mechanism.

The hydroxy group is <u>not</u> a good leaving group, but under acidic conditions it will protonate, and the $-OH_2^+$ group is a good leaving group.
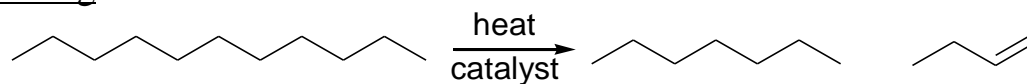
The ionization generates a molecule of water and a cation, which then easily deprotonates to give the alkene.

The intermediate cation can undergo rearrangements, and strong acid is often used to promote such reactions.
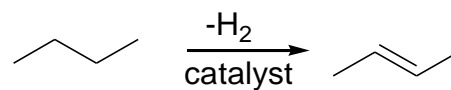
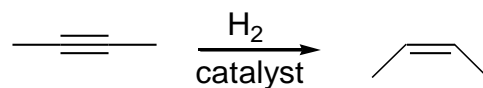## Other Syntheses of alkenes
These will be covered later in more detail:

Thermal Cracking

$$\text{(long chain alkane)} \xrightarrow[\text{catalyst}]{\text{heat}} \text{(heptane chain)} + \text{(alkene)}$$

Dehydrogenation of Alkanes

$$\text{(butane)} \xrightarrow[\text{catalyst}]{-H_2} \text{(butene)}$$

Hydrogenation of Alkynes

$$\text{(alkyne)} \xrightarrow[\text{catalyst}]{H_2} \text{(cis-alkene)}$$

Wittig Reaction

$$\underset{R'}{\overset{R}{>}}\!\!=\!\!O \;+\; PPh_3\!=\!CHR'' \longrightarrow \underset{R'}{\overset{R}{>}}\!\!=\!\!CHR'' \;+\; Ph_3P\!=\!O$$