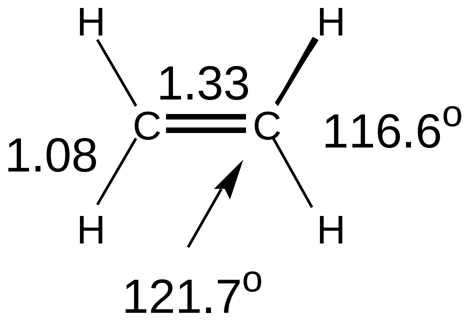
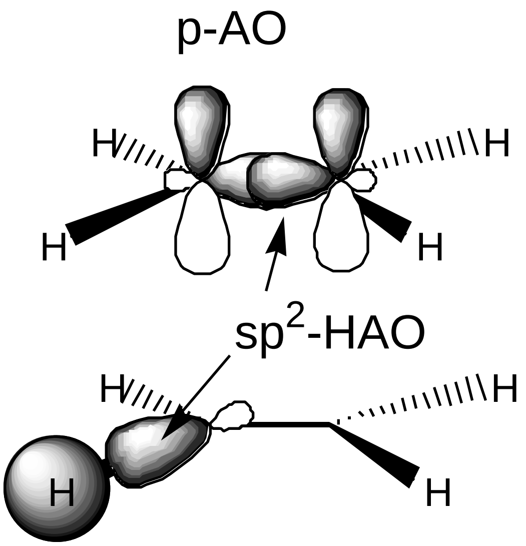
Alkenes aka Olefins: Structures, Properties & Uses

Bonding of Alkenes



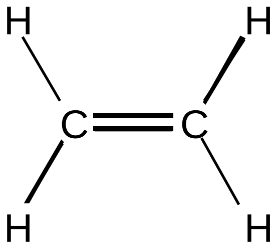


<u>σ-bond</u> results from overlap between two sp^2 AOs.
<u>π-bond</u> results from overlap between two p AOs.

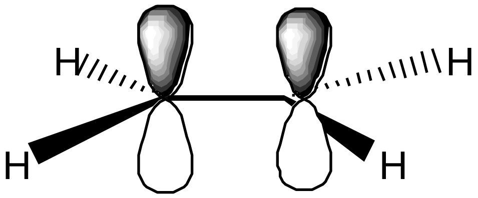
Note that the actual geometry is not exactly that predicted by the hybridization (H-C-H is 116.6° and H-C-C is 121.7°) but it is close. Remember C=C bond length.

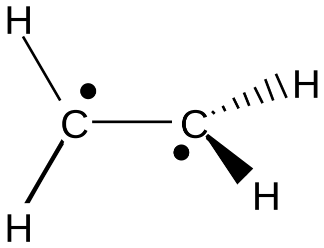
Bond Strength of Alkenes

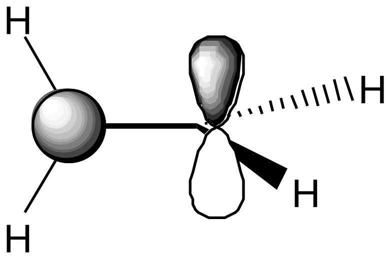
C-H bond strength is 107 kcal/mol
that is 9 kcal/mol more than the C-H in ethane.
C=C bond strength is 146 kcal/mol
that is 63 kcal/mol more than the C-C in ethane (83).



π-overlap







no π-overlap

The double bond strength is actually a bit less than the 63 kcal/mol. The C-C s-bond is stronger than the one ethane.

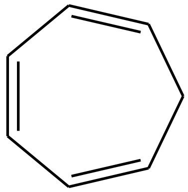
Moreover, the rotational barrier in poly-alkylsubstituted alkenes can be as low as 45 kcal/mol. The barrier can be further reduced by “push-pull” substituents.

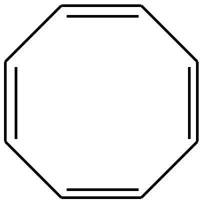
Nomenclature

Endings: **-ane** for the sat. alkanes
-ene for olefins
-ine or **-yne** for alkynes.

If there are several unsaturations, then use a prefix like di-, tri-, tetra-, ... in front of the characteristic ending.

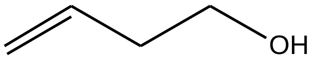
Examples: 1,3,5-cycloheptatriene and 1,3,5,7-cyclooctatetraene

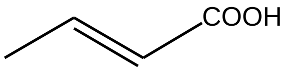




If there are other functional groups, use one ending for each.

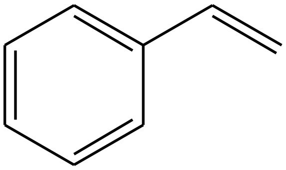
Examples: 3-buten-1-ol and 2-butenoic acid.





The “vinyl group” also is called “ethenyl” group.

Example: Styrene or ethenylbenzene



Important Trivial Names & Uses of Alkenes

Ethylene for ethene. **30.5 billion lb/yr.**

- Polymerize to polyethylene
- Oxidize to acetaldehyde and acetic acid
- Hydrolize to ethanol
- Epoxidise to ethyleneoxide and hydrolyze to glycol
- Convert to vinyl chloride and polymerize to PVC
- Convert to tetrafluoroethene and polymerize to Teflon

Propylene for propene. **14.9 bil. lb/yr**

- Polymerize to polypropylene
- Oxidize to acetone
- Hydrolize to isopropyl alcohol
- Epoxidise to propyleneoxide and hydrolyze to a glycol

Isobutylene for 2-methylpropene

- Used for polyisobutylene

Isoprene for 2-methyl-1,3-butadiene

- Used for synthetic rubber

Important Trivial Names of Unsaturated Groups

$H_2C=$ is a **methylene** group.

Example: Methylenecyclopropene.

$H_2C=CH-$ is a **vinyl** group.

Example: Vinylchloride

$H_2C=CH-CH_2-$ is an **allyl** group.

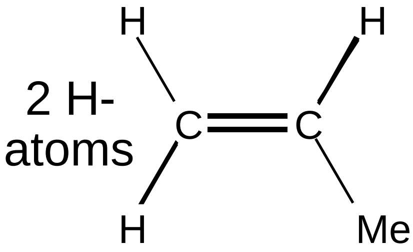
Example: Allylalcohol.

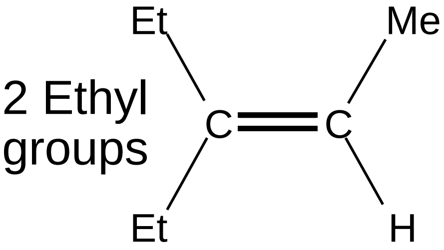
Stereoisomers of Alkenes

Geometrical isomerism, *cis/trans* isomerism, *E/Z*-isomerism.

Substituted alkenes can form diastereoisomers (non-superimposable and not mirror images).

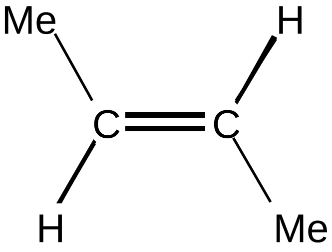
When: Whenever **both** alkene C-atoms have different substituents attached.

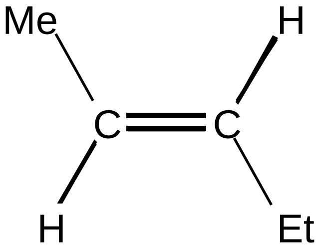




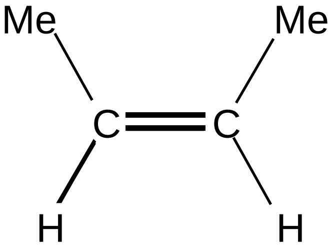
Cis/Trans Nomenclature

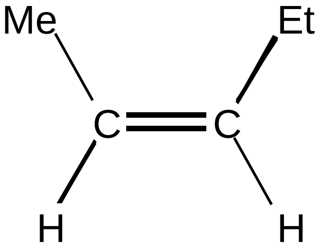
Trans





Cis

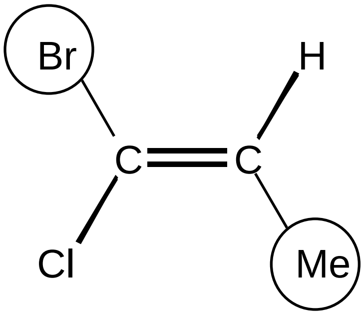


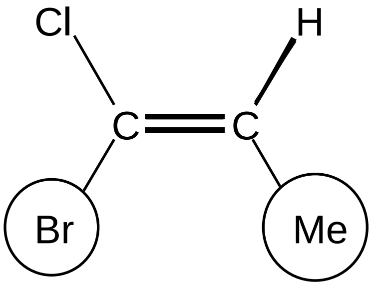


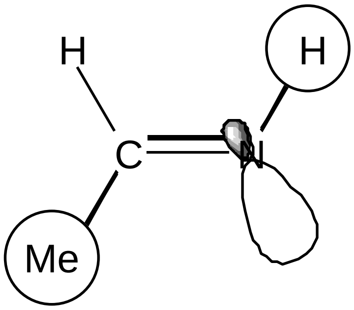
E/Z Nomenclature

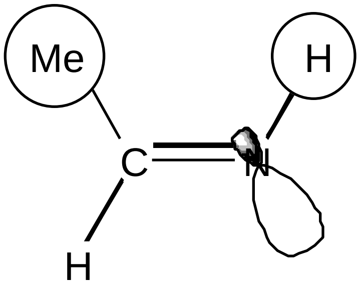
The *cis-trans* nomenclature works only as long as there is only one non-H group on each alkene-carbon. The more modern and general nomenclature is the *E/Z* nomenclature which is based on the Cahn-Ingold-Prelog rules.

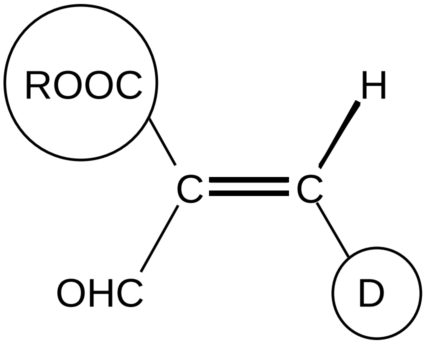
Establish priorities for each of the two methylene groups.
If the high priority substituents are on the same side, then the alkene is *Z* (zusammen = together)
If the high priority substituents are on opposite sides, then the alkene is *E* (entgegen = opposite)

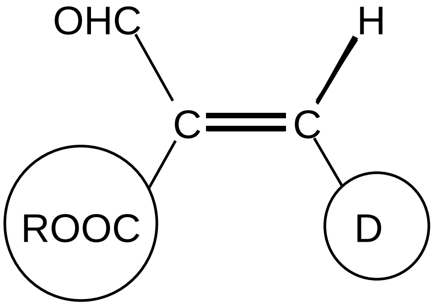


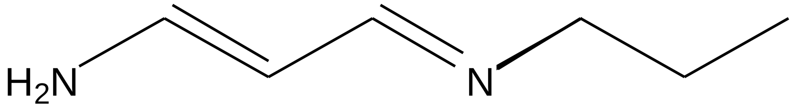


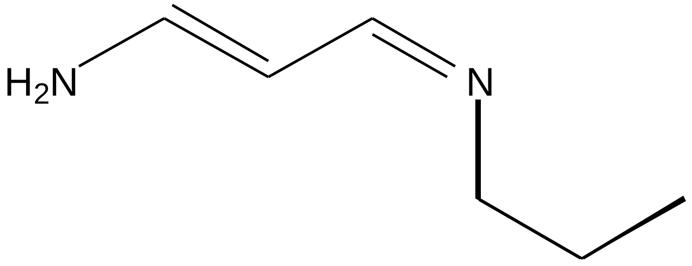


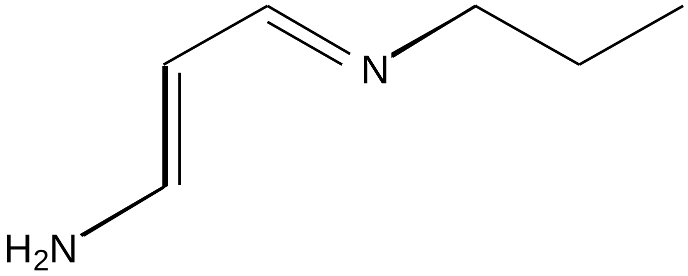



ROOC
H
C
C
OHC
D


OHC
H
C
C
ROOC
D


H2N
N


H2N
N

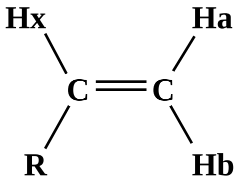

N
H2N

Spectra

NMR of Alkenes

Chemical shift: Characteristic H signal at 4.7 - 5.3 ppm. Terminal “vinylic H” appear at 4.7 ppm, while the “vinylic H” in nonterminal position occurs at higher chemical shift.

Spin-Spin Coupling: The couplings can be rather complex as there are several magnetically not equivalent Hs in these alkenes with comparable chemical shifts. There are two types of coupling: (a) vicinal and (b) geminal (coupling between different Hs attached to the same C) coupling.



Jab = 0-3.5 Hz
Jax = 6-14 Hz
Jbx = 11-18 Hz

Each H signal appears as a dublet of dublets.

IR-Spectra of Alkenes

Remember that a change in the dipole moment during the vibration is required for a band to have intensity. Thus: Only polar CC multiple bonds will show up in the IR.

IR of alkenes

(a) medium C=C band around 1600-1700 1/cm.

(b) medium =C-H band above 3000 1/cm (above CH stretches).

Alkene Stability - Principle

Direct Measurement of Equilibria

Relative stabilities of isomeric alkenes can be measured in some cases directly from their equilibrium concentrations. For example: *Cis* and *trans* 2-butene at equilibrium will have 76 % *trans* and 24 % *cis*. This translates into an energy difference of 0.66 kcal/mol in favor of the *trans* isomer. The *trans* isomer is favored for steric interactions.

Heats of Hydrogenation

A more general measure for alkene stability is provided by **heats of hydrogenation**. In the presence of Ni, Pd, or Pt *cis* and *trans* 2-butene will add hydrogen and turn into **the same alkane**. The reaction is exothermic for both but it will be more exothermic for the less stable alkene (the *cis* alkene). **The lower the heat of hydrogenation, the more stable is the alkene**.

Many heats of hydrogenation were measured and tabulated. It is found that the **stability of alkenes increases with the number of alkyl substituents** attached to the double bond.

<u>Example:</u> Butenes

Heat of hydrogenation of 1-butene: -30.3 kcal/mol

Heat of hydrogenation of *cis*-2-butene: -28.6 kcal/mol

Heat of hydrohenation of *trans*-2-butene: -27.6 kcal/mol

Alkene Stability and Degree of Substitution

	ΔH° (hydrogenation)
ethene	32.8
Monosubstituted	30.1 - 30.3
Disubstituted	27.6 - 28.6
Trisubstituted	26.9
Tetrasubstituted	26.6

One possible explanation for this effect is **hyperconjugation**. It is thought that electron density associated with C-H σ-bonds is delocalized into the π* MO.

Alkene Stability and *cis-trans* Isomers

Trans isomers are more stable than *cis* isomers. Sterics.

	ΔH°(hydrogenation)
Cis 2-butene	28.6
Trans 2-butene	27.6
Cis 2-pentene	28.6
Trans 2-pentene	27.6

Alkene Stability: Geminal vs Vicinal Isomers

Vicinal isomers are more stable than *geminal* isomers. Sterics.

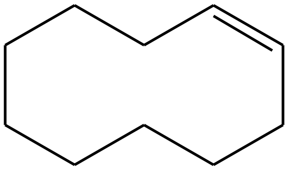
	ΔH°(hydrogenation)
2-methylpropene	28.0
Trans 2-butene	27.6
2,3-dimethyl-1-butene	28.0
Trans 2-pentene	27.6

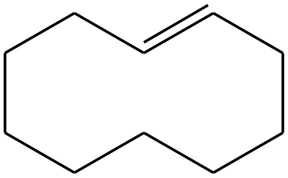
Stability of Cycloalkenes

	ΔH° (hydrogenation)
cyclobutene	30.7
only about 4 kcal/mol ring strain	
cyclopentene	26.6
a normal disubstituted alkene	

Cis-trans Isomers in Cycloalkenes

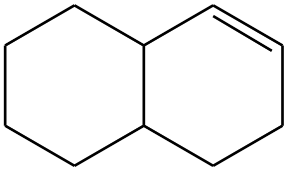
The larger cycloalkenes can form cis-trans isomers. The first cycloalkenes that forms stable *cis* and *trans* isomers is cyclooctene. The structures of these molecules can be found in the visualization center. Cyclodecene and larger cycloalkenes can easily incorporate *cis* or *trans* double bonds.

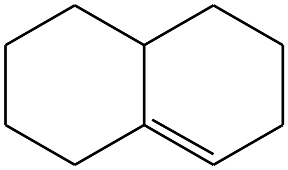




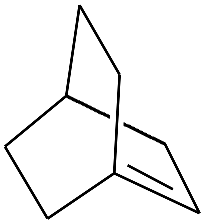
Bicyclic Alkenes

Bredt's rule: A bridged bicyclic compound cannot have a double bond unless the rings contain at least 8 C-atoms.

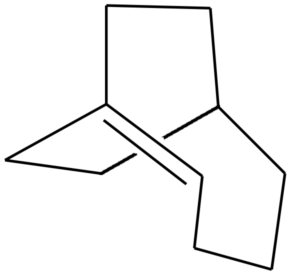




Bredt's rule does not apply. Not bridged!



Bredt's rule does apply. Ring too small.



Bredt's rule does apply. Ring size is 8.

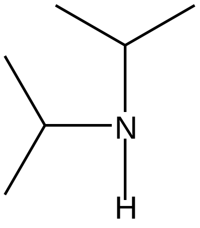
Preparations of Alkenes

Elimination from Alkyl Halides - Dehydrohalogenation

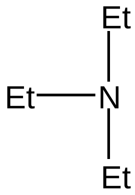
Eliminations from **alkyl halides** are base catalyzed (NaOR)

Primary Halide. Competition by S_N2 is reduced by using large alkoxides (e.g. *tert*-butoxide) and this works well via E2.

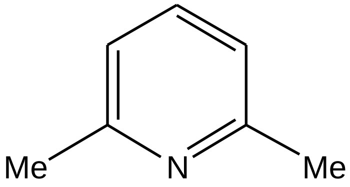
Secondary Halides. Good reaction. Use large base to discourage nucleophilic substitution! Aside from the bulky alkoxides, **bulky amines** also can be used.



Diisopropylamine



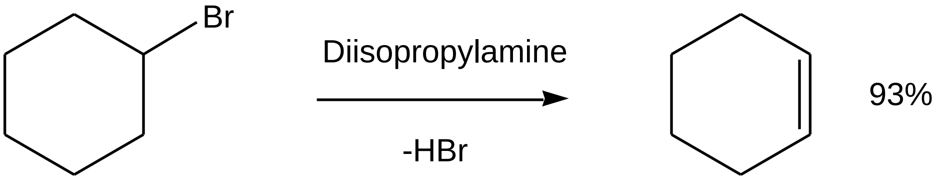
Triethyamine
TEA



2,6-dimethylpyridine

Secondary halides allow for regiochemistry (more substituted db formed, Saytzeff) and stereochemistry (*trans* favored).

<u>Example 1:</u> Cyclohexene Formation



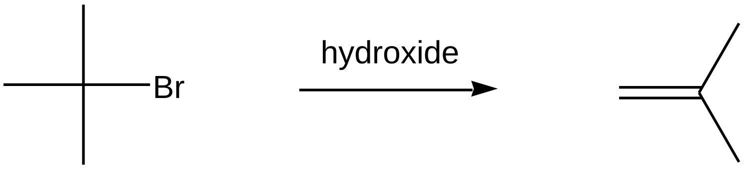
Tertiary Halide. Good via E2.

Regiochemistry and stereochemistry become issues. Usually all three R groups attached to the head C need to be the same otherwise a bad mixture of regioisomers is formed.

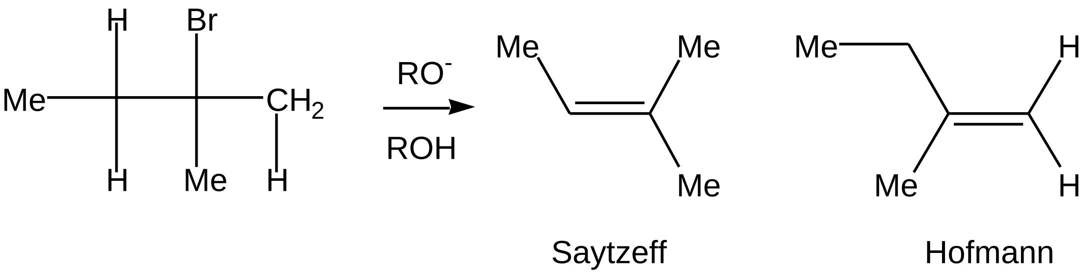
Stereochemistry favors *trans* in all cases.

<u>Example 1:</u> Isobutene from *tert*. Butyl Bromide

No regiochemical options. No stereochemical options.



<u>Example 2:</u> 2-bromo-2-methylbutane with warm sodium ethoxide or warm sodium *tert*.-butoxide.



71%	Ethoxide	29%
28%	*Tert.* Butoxide	72%

Elimination from Alcohols - Dehydration

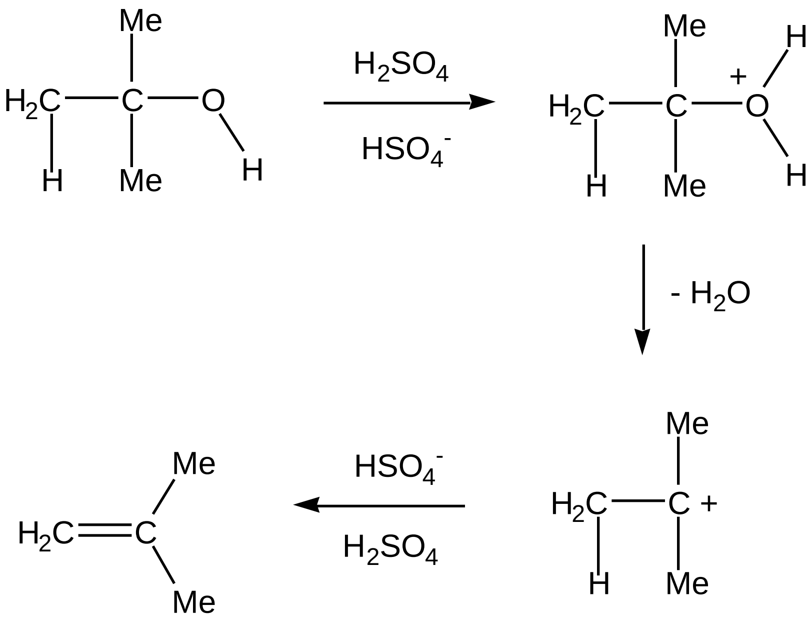
Eliminations from **alcohols** are acid catalyzed (H_2SO_4 cc)

Primary Alcohol. Unimolecular. Primary carbenium ion intermediate may isomerize. Bad.

Secondary Alcohol. As with primary alcohols, not good.

Tertiary Alcohol. Good via E1. The acid protonates the alcohol and the leaving group is water. The cation then is deprotonated.

Example: Isobutene from *tert*.-butyl alcohol

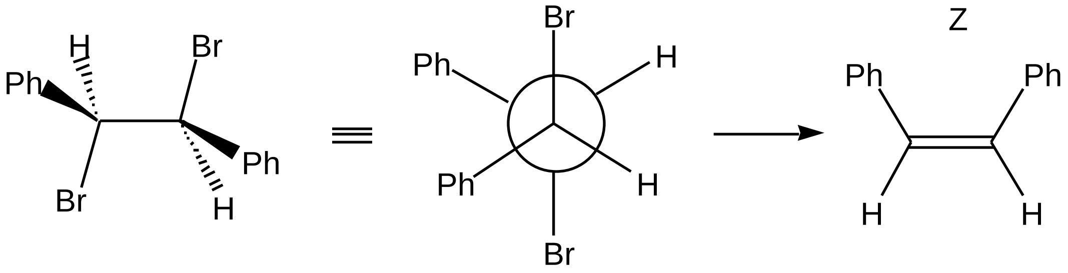


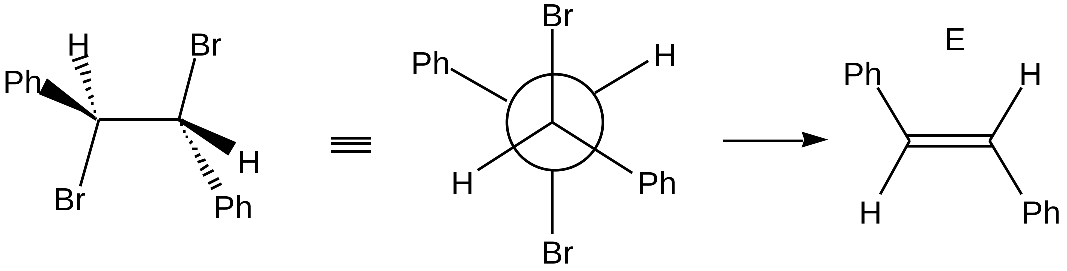
Elimination from Vicinal Dibromides - Dehalogenation

NaI in acetone: Binds Br_2 as IBr & NaBr

Zn in acetic acid: Binds Br_2 as $ZnBr_2$

The NaI reaction proceeds with a well-defined stereochemistry: Antiperiplanar elimination is preferred. Consider the reactions the diastereoisomeric dibromides to form **stilbene**.

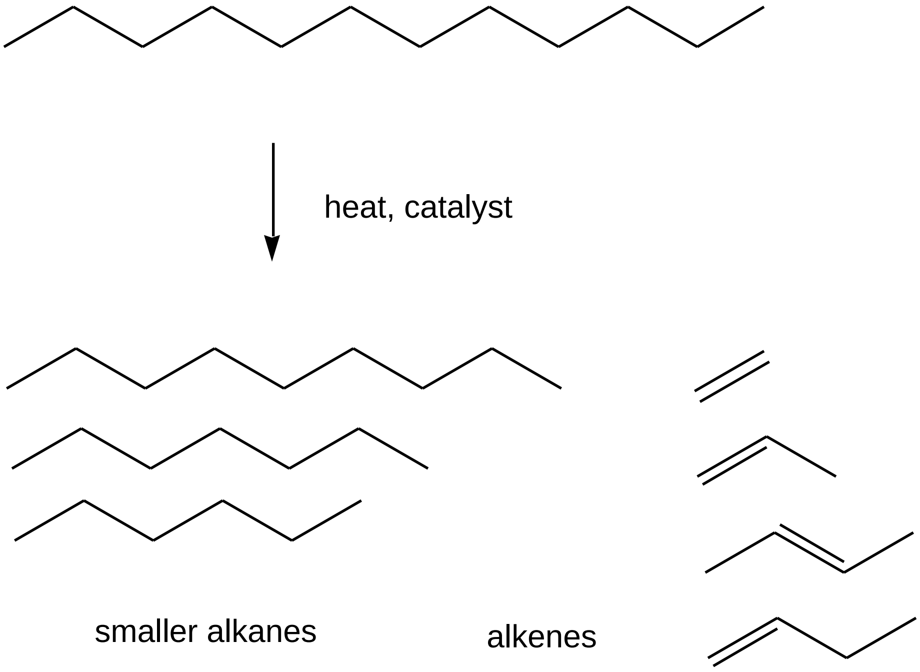




Alkenes from Alkanes - Industrial Cracking

See News Item to Chapter 7!

Alkanes are broken down to form smaller alkanes and very short alkenes (ethene, propene, butene). The reaction is endothermic and requires heat. The reaction is best done with a catalyst - **catalytic cracking**. The catalysts are **zeolites**, minerals that contain **silicates** and **aluminates**. Porous materials.



Thermal cracking is a **radical reaction**. A C-C bond breaks in the alkane. The radicals abstract H-atoms from other alkanes. The alkyl radicals undergo fragmentation.