

# Chemistry 210 -- Winter Semester 1997

## Chapter 11

### Alkenes aka Olefines

#### Nomenclature

Endings: *-ane* for the sat. alkanes, *-ene* for olefines, and *-ine* or *-yne* for alkynes.

If there are several unsaturations, then we use a prefix like di-, tri-, tetra-, ... in front of the characteristic ending. Examples: 1,3-butadiene and 1,3,5-hexatriene.

If there are other functional groups, then we use one ending for each. Examples: 3-buten-1-ol and 2-butenic acid.

The usual rules for numbering rings apply here as well.

#### Important Trivial Names of Alkenes

Ethylene	Ethene	30.5 billion lb/yr	Polyethylene, EtOH, ...
Propylene	Propene	14.9 bil. lb/yr	Polypropylene, PrOH, ...
Isobutylene	2-methylpropene		Polyisobutylene
Isoprene	2-methyl-1,3-butadiene		Rubber monomer

#### Important Trivial Names of Unsaturated Groups

$\text{H}_2\text{C}=\text{}$  is a *methylene* group. Example: Methylenecyclopropene.

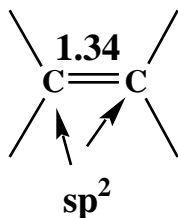
$\text{H}_2\text{C}=\text{CH}-$  is a *vinyl* group. Example: Vinylchloride

$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-$  is an *allyl* group. Example: Allyl alcohol.

#### Cis/Trans Isomerism in Alkenes

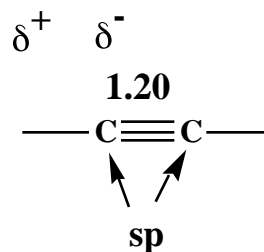
The alkenes do form geometrical isomers (*Cis/trans* or *E/Z*) and these stereochemical descriptors must be added in front of the name!

## Bonding



1 db in the plane that is perpendicular to the molecular plane.

**120 degree angles**



2 dbs that are in planes that are perpendicular with respect to each other.

**linear**

The triple bonded CC group has an EN comparable to Cl.

====> CH Polarity!

     bond results from overlap between two  $sp^2$  AOs.

     bond 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 length.

C-H Bond strength is 107 kcal/mol, that is 9 kcal/mol more than the C-H in ethane.

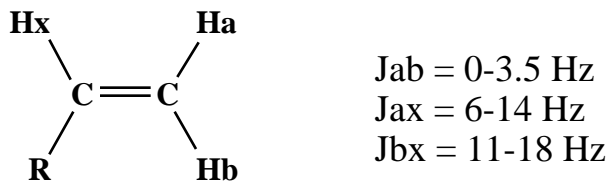
C=C Bond strength is 152 kcal/mol, that is 64 kcal/mol more than the C-C in ethane.

## Spectra

### NMR of Alkenes

**Chemical shift:** Very characteristic H signal at 4.7 - 5.3 ppm. Terminal “vinylic H” appear at 4.7 ppm, while the “vinylic H” in a 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.



*Each H signal appears as a doublet of doublets.*

### Infrared

Remember that we need a change in the dipole moment during the vibration otherwise there will be no intensity of the bands. 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 the CH stretches).

## Alkene Stability

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 from the same reason that the *trans* conformations are favored over the *cis* conformations: Steric interactions.

A more general measure for alkene stability is provided by **heats of hydrogenation**. For example: In the presence of Ni, Pd, or Pt *cis* and *trans* 2-butene will add hydrogen and turn into the same alkane. The reaction will be 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. The important result is that the *stability of alkenes increases with the number of alkyl substituents* attached to the double bond.

	H <sup>o</sup> (hydrog.)
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 bonds is delocalized into the \* MO.

## Preparations of Alkenes

### (a) Alkenes via Elimination from Alcohols and Alkyl Halides

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

*Eliminations from alkyl halides are base catalyzed (sodium alkoxides)*

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

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

*Secondary Alcohol.* No good as in the case of the primary alcohols.

*Secondary Halides.* Good reaction. Note that the secondary halides allow for regiochemistry (more substituted db formed) and stereochemistry (*trans* favored).

Example: 2-bromopentane with warm sodium ethoxide.

*Tertiary Alcohol.* Good via E1.

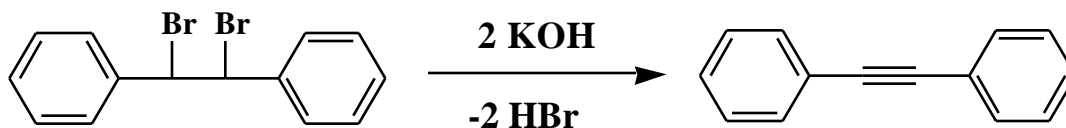
*Tertiary Halide.* Good via E2.

In both cases, 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.

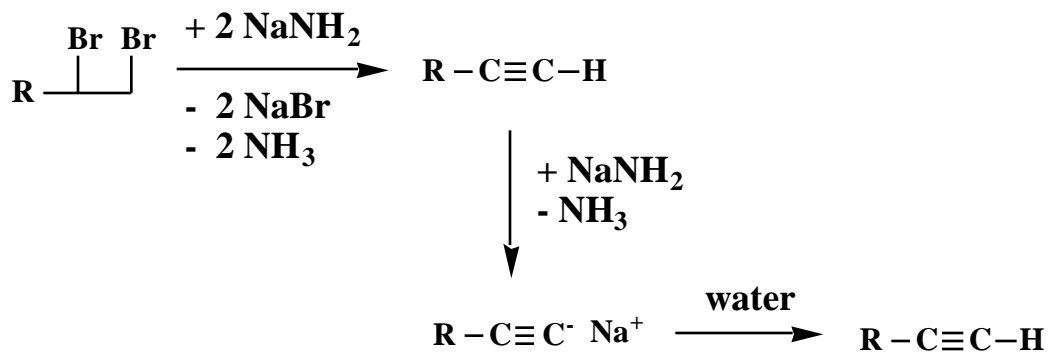
### (b) Alkynes *via* Double Elimination

1,2-dihalides can form alkynes by elimination of two HX under the influence of strong base (KOH in alcohol). Sequence: 1,2-dihalide  $\rightarrow$  vinylhalide  $\rightarrow$  acetylene.

Example 1: Nonterminal acetylene formation



Example 2: Terminal acetylene formation. The base makes the acetylide anion and the acetylene is reformed by hydrolysis.



### (c) Large Alkynes from Small Alkynes

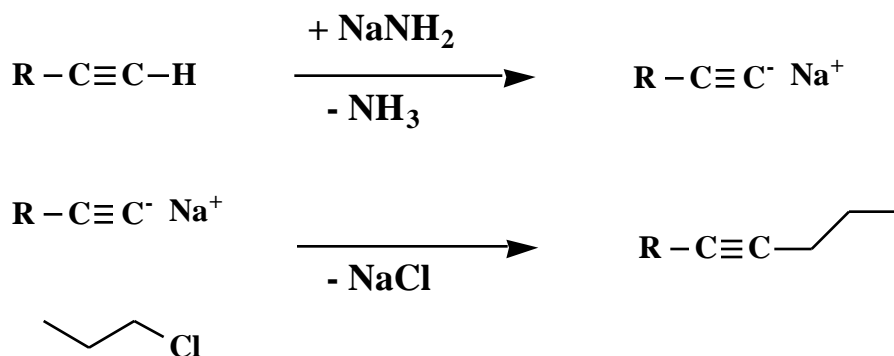
We use the property of alkynes to form acetylides. These acetylides are nucleophilic enough to undergo  $S_N2$  reactions with alkyl halides.

There are two steps involved: (a) formation of the acetylide and (b) its reaction with an alkyl halide or (c) its reaction with a ketone (Grignard Reaction)

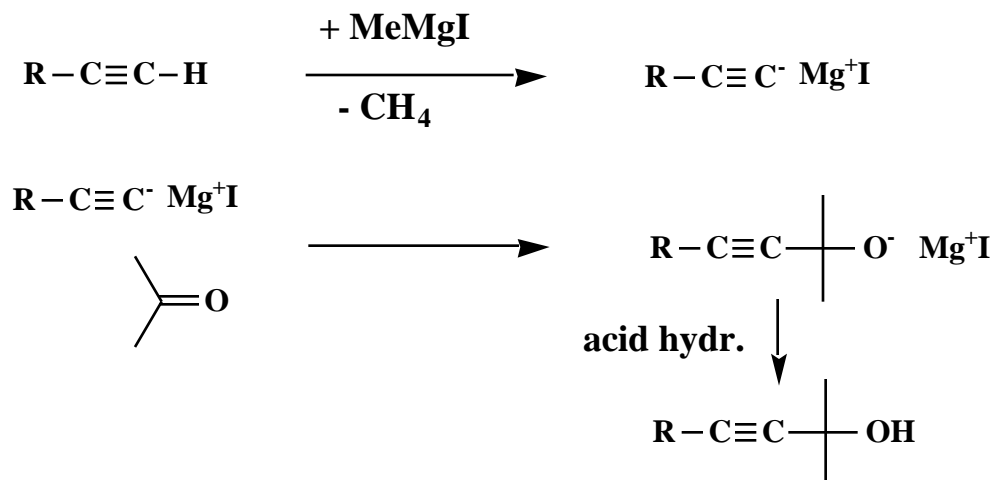
(a.1) Treat alkyne with strong base ( $\text{NaNH}_2$ ) to form the sodium acetylide.

(a.2) Treat alkyne with GR to form the acetylide Grignard reagent.

Example 1: Reaction with Alkyl Halide.



Example 2: Grignard Reaction.



## Alkene Electrophilic Addition Reactions

The greater part of the chemistry of these unsaturated hydrocarbons consists in the addition of X-Y molecules. All reactions are driven by the fact that the two newly formed bonds are stronger than the bond and the X-Y bond. Throughout the discussions of the addition reactions, pay attention to these few points:

- (1) Timing: Is the addition concerted or not. If not, what type of intermediate occurs.
- (2) Regiochemistry. If the alkene is asymmetric, which part of the reagent X-Y goes to goes to which C of the multiple bond?
- (3) Stereochemistry.  
Alkene formation: Chirality.  
Alkene formation: Geometrical isomer formation.

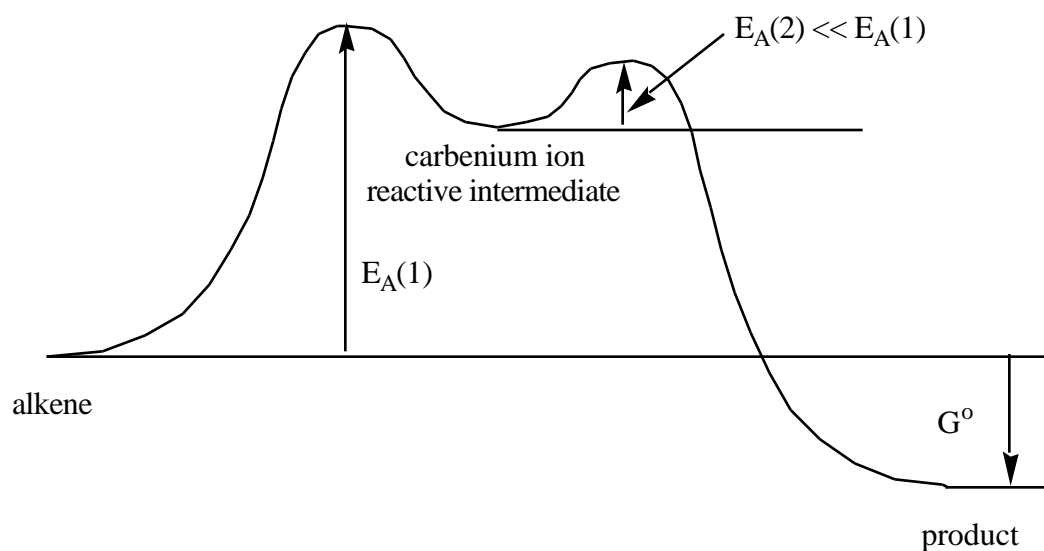


## HX Additions

HX gas is bubbled through a solution of the alkene to yield alkyl halides. The acid HX first protonates to yield a *carbenium ion* intermediate. Then, in the next step, the halide ion is added to that carbenium ion. The proton is an electrophile, so we call this an electrophilic addition reaction because the electrophile adds in the slow step.

### Potential Energy Diagram for the Addition Reaction

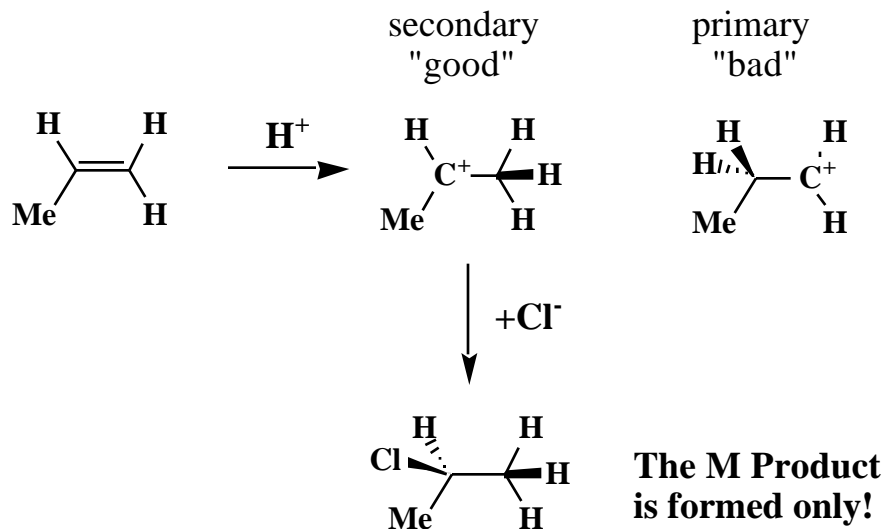
Electrophilic addition is a two-step process where the first step is the slow step.



## Regiochemistry

Markovnikov's Rule: The protonation occurs at that C of the unsymmetrical double bond that already has more Hs attached. **Hydrogen to hydrogen!** The reason for the M-rule is simple: You want to form the more stable, more substituted carbenium ion intermediate! This is all you need to know about the regiochemistry of the HX addition.

Example: HCl addition to propene.



A chiral C is formed in the process. This chiral C will be racemic because the intermediate is planar and can be attacked from either face with equal probability.

Anti-Markovnikov Rule: Obviously, if the HX is added with the opposite regiochemistry, that is, when hydrogen adds to the higher substituted site. This happens when the mechanism of the addition is not a polar mechanism but a radical mechanism instead. The important point to remember here is this:

- (a) Initiation: ROOR yields RO• radicals  
RO• radical reacts with HX to give ROH and X•
- (b) Propagation: step 1: X• adds to alkene *to give the more stable radical*  
step 2: the alkyl radical abstracts H from HX.
- (c) Termination: Any pair of radicals combines.

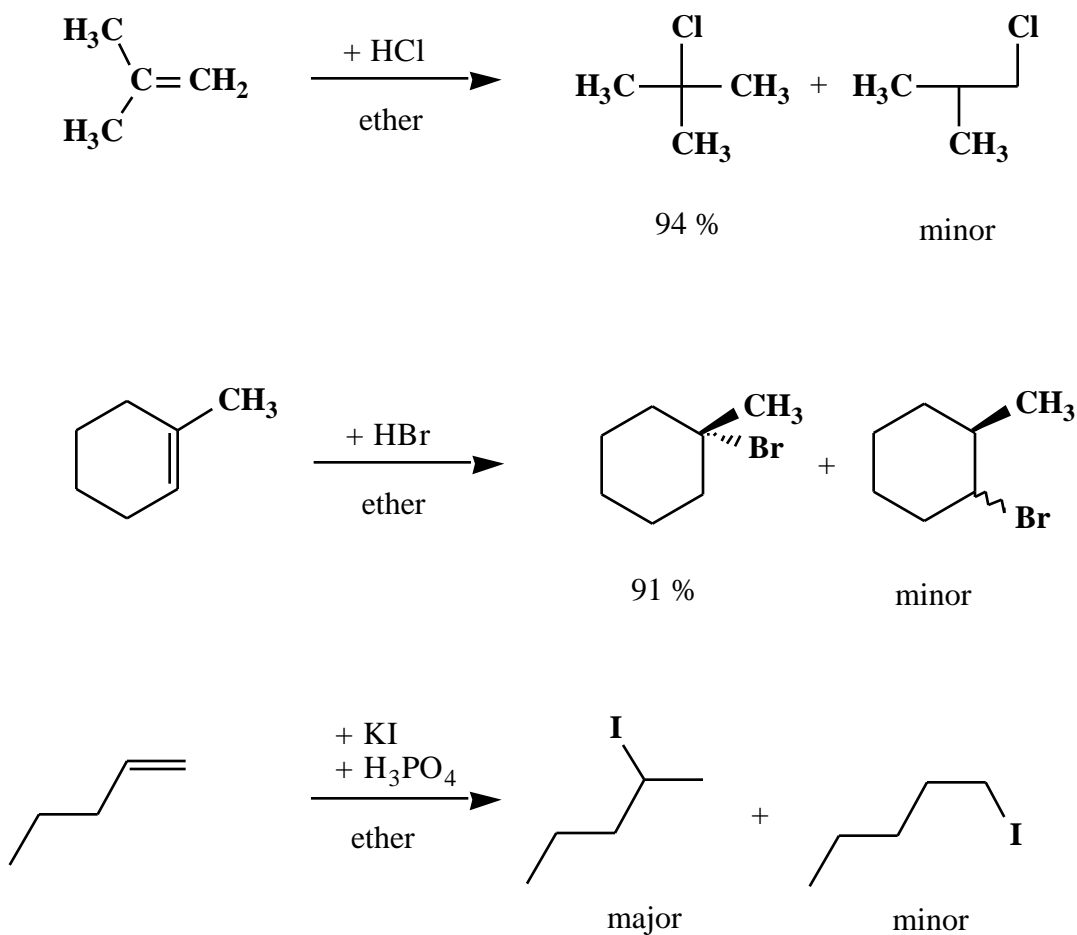
### **Regiochemistry of HX Addition**

Electrophilic addition via most stable carbenium ion gives Markovnikov Product

Radical addition via most stable radical gives Anti-Markovnikov Product

## Examples

Note the regiochemistry in each case. Note that HI additions usually are not done directly with HI but instead the HI is produced *in situ* from KI and H<sub>3</sub>PO<sub>4</sub>. The solvent is given either over or (more often) under the reaction arrow. Make sure you would be able to name all of the molecules in these examples.



## Addition Reactions of Alkenes

### 1,2- and 1,4-Additions of Dienes

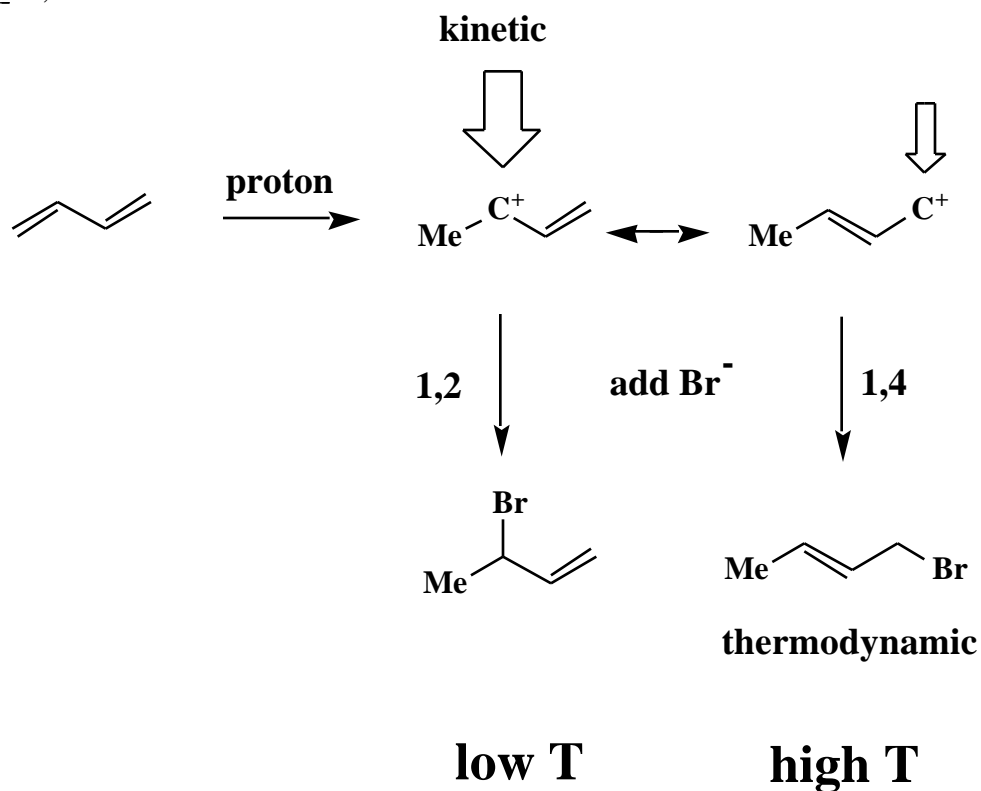
In the electrophilic additions to double bonds, we generate intermediate carbenium ions. If these carbenium ions are adjacent to another double bond, then we get allylic systems. These allylic system **can be attacked by a nucleophile at two places**. Thus, one can get two products in which the remaining double bond is at different places.

Which one of the products is preferred depends on the reaction conditions.

Low T  $\implies$  1,2 addition AND High T  $\implies$  1,4 addition

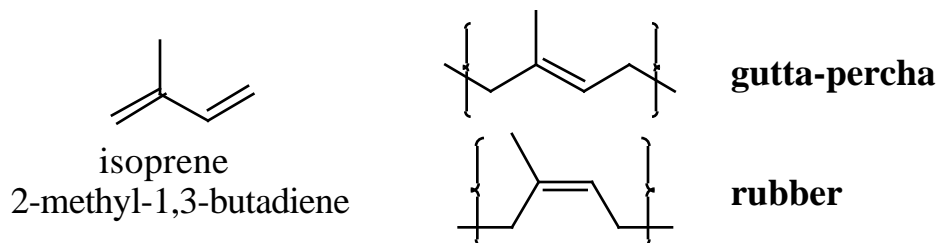
Traces of acid favor the 1,4 addition

Example 1: 1,3-butadiene and HBr.

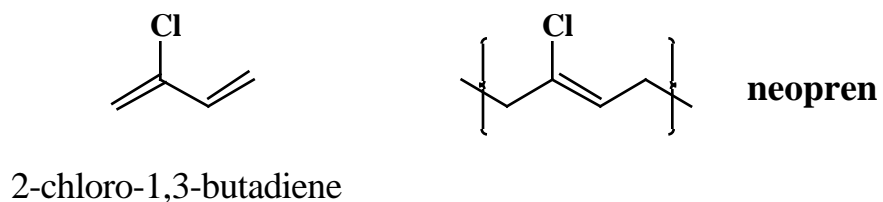


Example 2: Polyisoprene -- Electrophilic Polymerization

Catalytic (acid cat.) polymerization of isoprene leads to natural rubber. In rubber the remaining double bonds are all *cis*. If they are all *trans*, then the material is hard and called gutta-percha (golf ball coverings).



Example 3: Neopren -- all *trans* head-to-tail 1,4-polymer of 2-chloro-1,3-butadiene. This is synthetic rubber. There is a lot of history associated with this formula!



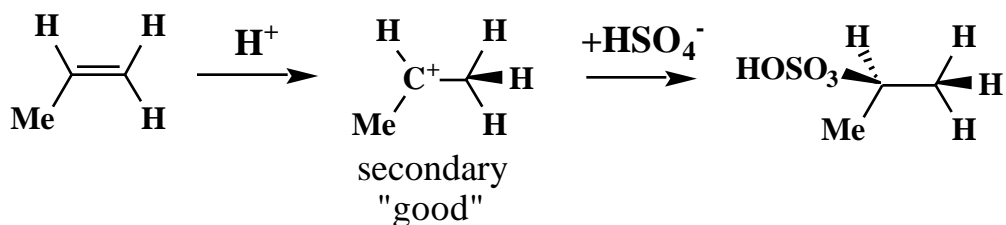
## H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O Additions

Same mechanism as discussed for the electrophilic HX addition.

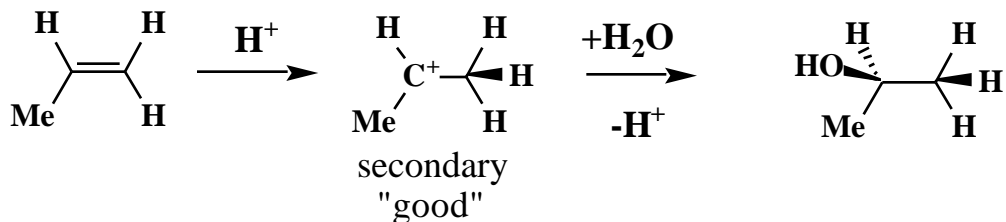
The addition of sulfuric acid to alkenes is a route to inorganic esters. These sulfates can then be used in S<sub>N</sub>2 reactions to form ethers and alcohols.

The hydration of alkenes yields alcohols. It is just the opposite of the formation of alkenes from alcohols. Which direction does go then? It depends on the experimental setup. If we take measures to get the water out of the reaction mixture, then we get the alkene and otherwise we get the alcohol.

Example 1: 2-propyl hydrogen sulfate



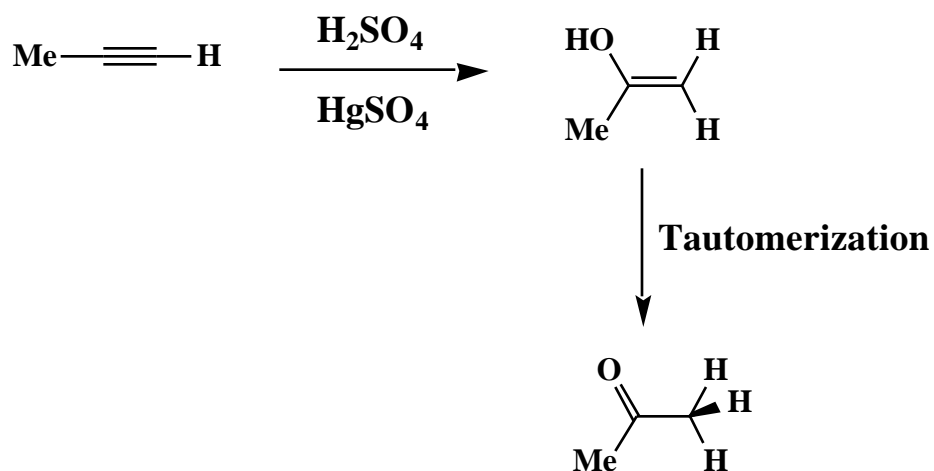
Example 2: 2-propanol



Example 3: 2 hexanone from the hydration of an alkyne

This is a bit more interesting because of tautomerism in the initial product. “Tautomerism” refers to isomers that differ in the position of one hydrogen. If we react an alkynes with aq. sulfuric acid, an acid catalyzed water addition occurs that yields the vinyl alcohol initially. Vinyl alcohols are called *enols*. A shift of an H gives the more stable ketone, a tautomer of the enol. Because of the ketone formation, there is no possibility to add another water!

Also very important is this: This reaction requires the presence of  $\text{HgSO}_4$  as a Lewis acid catalyst. ***This is a very important route to make ketones*** (what other ways are there to make ketones?)



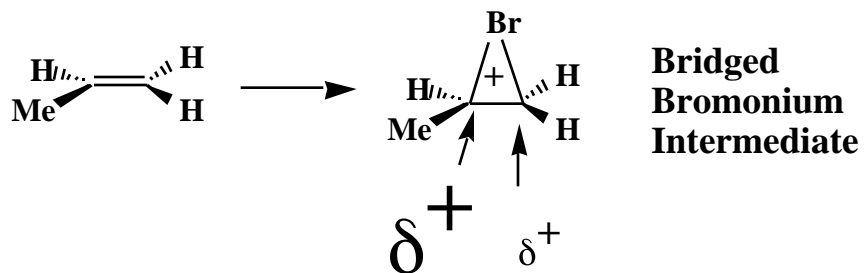


## Halogenation

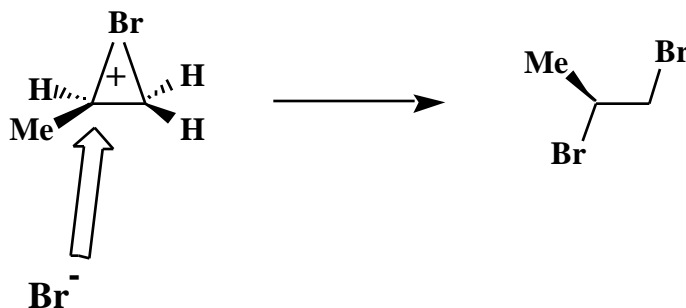
Only important for Br<sub>2</sub> and Cl<sub>2</sub>. For F<sub>2</sub>, the reaction is too exothermic (bumm!) and for I<sub>2</sub> is endothermic (no go). Mostly done with bromine.

Step 1: Autoionization. Br<sub>2</sub> undergoes heterolytic cleavage to Br<sup>+</sup> and Br<sup>-</sup>.

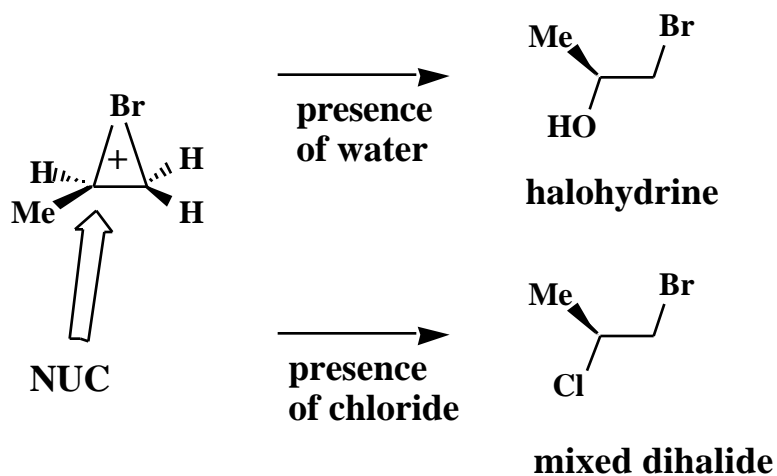
Step 2: Br<sup>+</sup> adds to form a cyclic bromonium ion.



Step 3: Br<sup>-</sup> adds from the opposite side to give *trans* addition. The nucleophile cannot attack from the same side as the Br<sup>+</sup> because of the ring formation. The nucleophile will add to the more substituted carbon!



Alternative steps 3: Addition of some other nucleophile present. Again, the nucleophile will add to the more substituted carbon!



**Stereochemistry.** The additions always are *trans*. This also is called *anti* addition. If we do such a *trans* addition for a cyclohexene, then we will form two chiral carbons. If one *trans* addition leads to (R,R), then the other *trans* addition will lead to (S,S). That is, we will form enantiomers. Because of the *trans* addition, we will *not* form diastereoisomers. Make sure you get this! We'll talk about this in the review if you so desire.

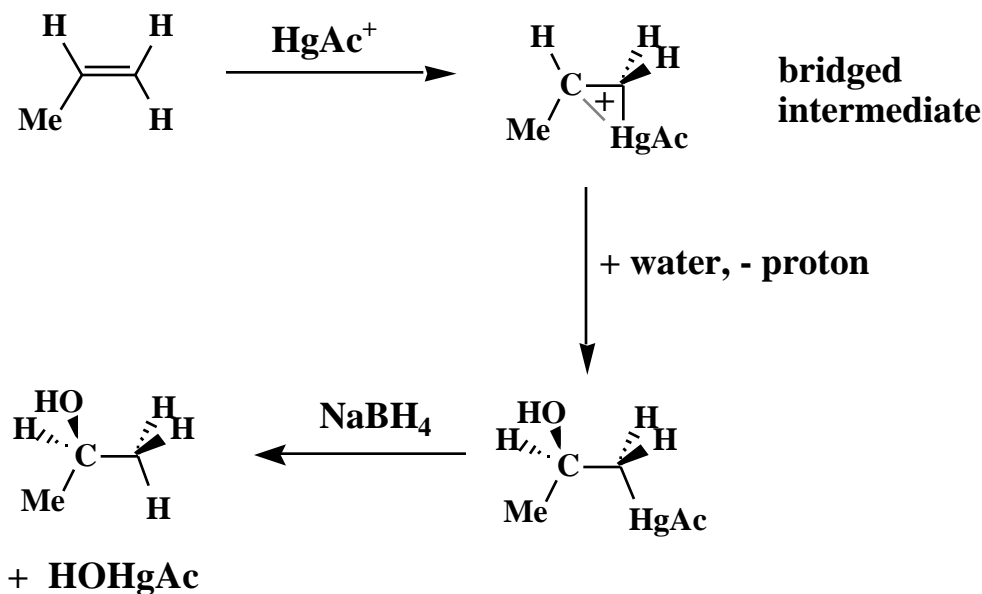
## Oxymercuration

Addition of mercuric acetate to alkenes yields oxymercured molecules which can be reduced with sodium borohydride to give the Markovnikov alcohol from the alkene.

This is another way of making alcohols from alkenes. There is one major advantage to do it this way: No rearrangements. Remember that the hydration involves a carbenium ion and this ion may undergo rearrangements to form more stable carbenium ions before the water is added. Oxymercuration shows no rearranged products.

### Mechanism

The reactive species is  $\text{HgAc}^+$  formed by loss of  $\text{Ac}^-$  from  $\text{HgAc}_2$ . The most important point is now, that the addition of  $\text{HgAc}^+$  to the alkene *does not give a carbenium ion but that instead a bridged, 3-membered ring cation is formed*, the mercurinium ion. In the event of rearrangement, this ring would have to be destroyed and that process requires too much energy. So, no rearrangement occurs. The bridged intermediate is then attacked by water, it loses a proton, and we get the oxymercured molecule. Reduction with  $\text{NaBH}_4$  follows.



Oxymercuration of 1-methylcyclopentene. The regiochemistry is Markovnikov and the stereochemistry is *anti* addition, that is, the OH and the introduced H (or D) will be in a trans relation with regard to each other.

## Hydroboration

Except for the radical HX addition, all of the reactions discussed so far lead to Markovnikov products. It would be good to also have a way to make the Anti-Markovnikov products in some way. The hydroboration is such a way to form AM-alcohols in excellent yields!

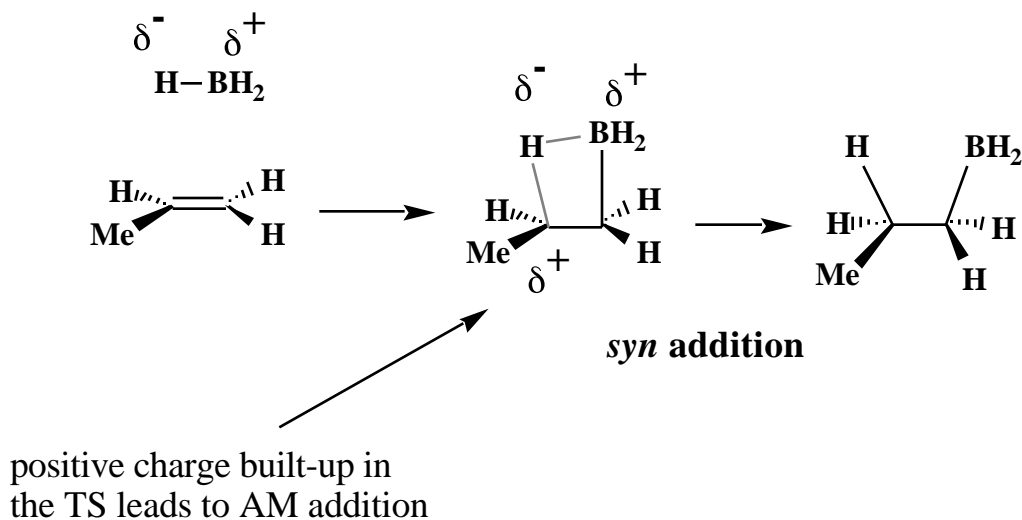
### Remember: Alkenes to Alcohols

- (1) HX addition to alkenes -- rearrangements possible -- M products
- (2) Oxymercuration -- no rearrangements -- M products
- (3) Hydroboration -- no rearrangements -- AM products

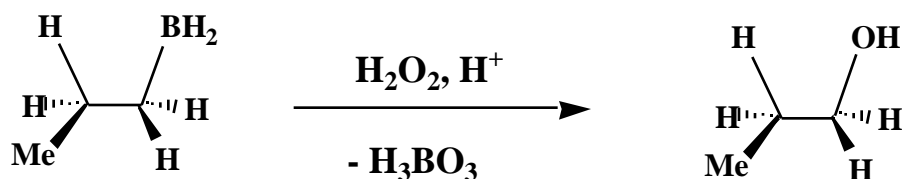
### Mechanism

The key here is with the polarity of the reagent  $\text{BH}_3$ , employed as the THF complex.  $\text{BH}_3$  has negatively polarized H and a positively polarized B. *The B is going to do the electrophilic attack here (!) and the H comes in as an anion -- not as a cation!* The rule that governs the regiochemistry is always the same: Make the more stable carbenium-type site in the TS (or intermediate). In this case, it is just that the B adds to the side that has more Hs already because that leads to the more stable carbenium-type TS. Then the H anion comes in to the site with fewer Hs.

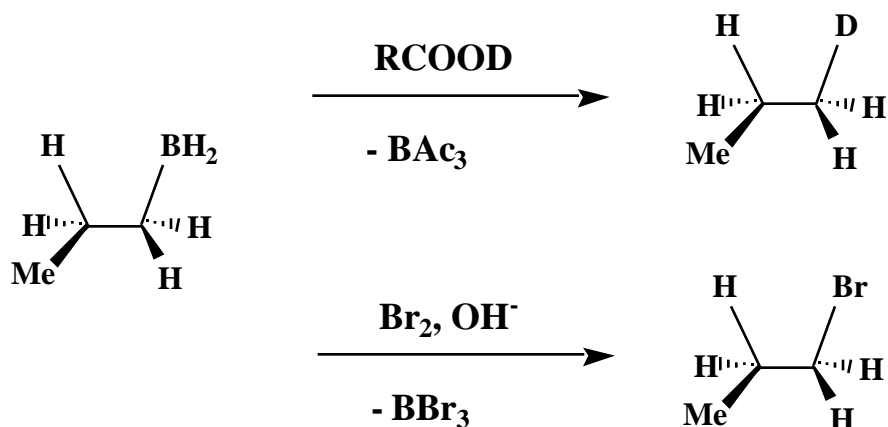
The CH and CB bond formations occur via a 4-membered ring TS. That is, both H and  $\text{BH}_2$  will attack the db from the same side. This is an important feature: H and  $\text{BH}_2$  will always be placed *cis* with regard to each other.



Once we have formed the alkyl borane, we treat it with hydrogenperoxide/acid to get the alcohol. The borane is turned into boronic acid in the process. *This process occurs with retention of configuration at the C-B carbon.* This is the most usual second step and the boration together with this oxidation is the hydroboration.



The alkyl boranes can also do other reactions. Reactions with acid and with halogen are shown. The first one is a good way to put a D label in place.



Finally, all of the reactions were written with the alkyl boranes R-BH<sub>2</sub>. This was done for simplicity only. In reality, BH<sub>3</sub> will react with three alkenes to form BR<sub>3</sub> and all of the subsequent reactions occur then three times for each BR<sub>3</sub>. So instead of the alkylboranes formed, we really do form trialkylboranes.

## Hydrogenation -- Catalytic H<sub>2</sub> Additions

The metal catalyst serves to cleave the H<sub>2</sub> homolytically. H radicals are the reactive species that add to the surface coordinated alkene/alkyne. Hydrogenations with solid metal catalysts are *heterogeneous* reactions (draw cartoons of surface reaction). Hydrogenations with dissolved metal catalysts are *homogeneous* reactions.

***Stereochemistry of heterogeneous reaction.*** The two Hs most usually add from the same side - *cis* or *syn* addition. This matters (a) in the reduction of alkynes to alkenes (gives *cis* and not the thermodynamically more stable *trans* alkene), (b) in the reduction of cycloalkenes to a,e-cycloalkanes, and (c) if we add Hs to tetrasubstituted alkane that get two chiral centers from the hydrogenation.

(a) ***Typical catalysts are Pt and Pd.*** Cheaper metals also can be used but they usually require higher reaction T and p. Unless special precautions are taken, all unsaturations will be removed -- complete hydrogenation. The Adams catalyst PtO<sub>2</sub> forms Pt in situ. Pd is used as palladium black Pd/C, Pd surface on graphite.

alkene ==> alkane

alkyne ==> alkane

aldehyde/ketone ==> primary/secondary alcohols

nitriles ==> primary amines

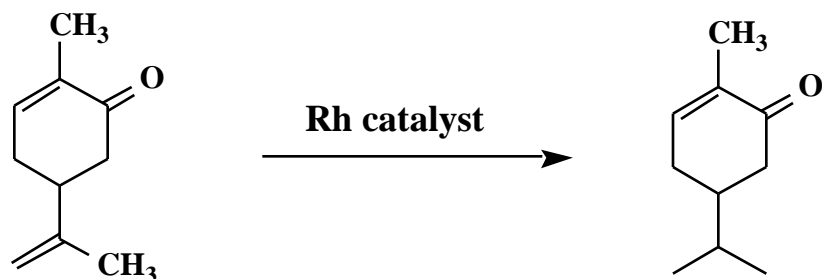
aromatics ==> cycloalkanes

(b) ***Poisoned Catalysts.*** Such catalysts can be used to reduce alkynes to alkenes without further reduction to the alkane. They consist of a metal catalyst and some added compound. The add-ons are things like quinoline or BaSO<sub>4</sub>.

(c) ***Oil and Fat Hardening.*** Vegetable oils are liquids (oils!) and that is so because they have many unsaturations in the hydrocarbons of the acids (of the glycerine triester). So, partial hydrogenation reduces the number of these unsaturations and we get margarine (butter is better).

Example: Linoleic acid - C18 piece: all *cis* H<sub>3</sub>C-(CH<sub>2</sub>)<sub>4</sub>-CH=CH-CH<sub>2</sub>-CH=CH-(CH<sub>2</sub>)<sub>7</sub>-COOR - is reduced with H<sub>2</sub> at Pd/C catalyst to stearic acid.

(c) **Homogeneous Hydrogenation with  $(Ph_3P)_3RhCl$ .** The alkene coordinates to the metal and so does the  $H_2$ . The nice thing about these homogeneous catalysts is that the less hindered db will be reduced preferentially. Here is an example:



Another advantage of these complexes relates to chiral induction. The phosphines can be made chiral and with such catalysts the hydrogenation can be carried out stereospecifically.

Note also that the carbonyl group was not reduced under these conditions. This is actually one of the excellent features of the catalytic hydrogenation in general: It is quite selective for double bonds and does not reduce polar multiple bonds.

Example 1: Unsaturated Ketone. 2-cyclohexenone to cyclohexanone

Example 2: Unsaturated Ester. Methyl 3-phenylpropenoate to methyl 3-phenylpropanoate

Example 3: Unsaturated Nitrile. Cyclohexylideneacetonitrile to cyclohexylacetonitrile.

## Oxidation of Alkenes

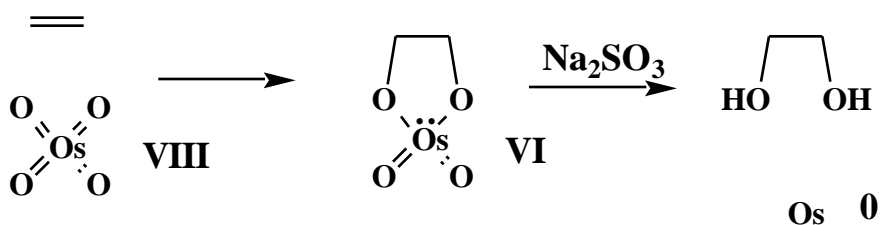
Many possible products depending on reactions conditions.

WITHOUT CC CLEAVAGE: Epoxides Diols (aka glycols) Methyl Ketones

WITH CC CLEAVAGE: Aldehydes Ketones Acids

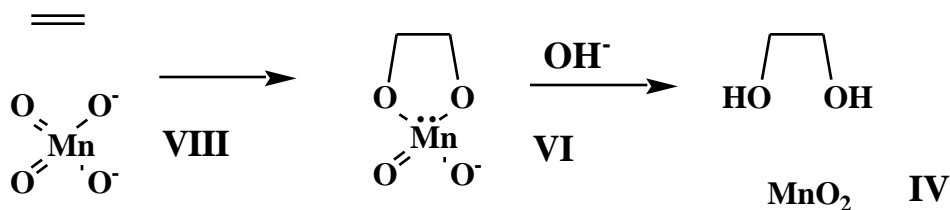
### (a) Diol Formation with $\text{OsO}_4$ .

$\text{OsO}_4$  osmium tetroxide (toxic, expensive) followed by reduction of the cyclic product with sodium sulfite,  $\text{Na}_2\text{SO}_3$ , or sodium hydrogensulfite,  $\text{NaHSO}_3$ .



### b) Cold, alkaline, aq. solution of Permanganate. $\text{KMnO}_4 / \text{NaOH}$

This is very much similar to (a). This is the **Baeyer test** for unsaturation. Start with purple solution (permanganate) and get a brown precipitate of “brown stone” ( $\text{MnO}_2$ ).



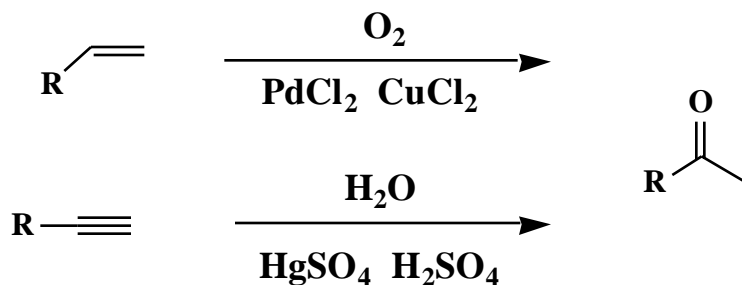
### (c) Epoxide Formation.

$\text{H}_2\text{O}_2$  and carboxylic acid or peroxy-carboxylic acids (MCPBA is meta-chloroperbenzoic acid) react with alkenes to form epoxides. **The very important thing to realize here is this:** Once you open up an epoxide to form a diol with  $\text{KOH}$  or such, you will form the *trans* diol (!) whereas the oxidations (a) and (b) give the *cis* diol.

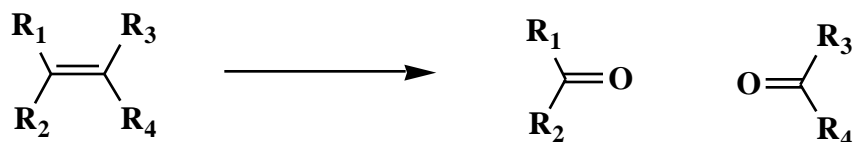


(d) Methyl Ketones from Terminal Alkenes.

Oxidation of terminal alkenes with  $\text{PdCl}_2$  in the presence of  $\text{CuCl}_2$  gives methyl ketones. Note that this is an alternative reaction to the hydration of the terminal alkynes.



(e) Hot Permanganate Oxidation.

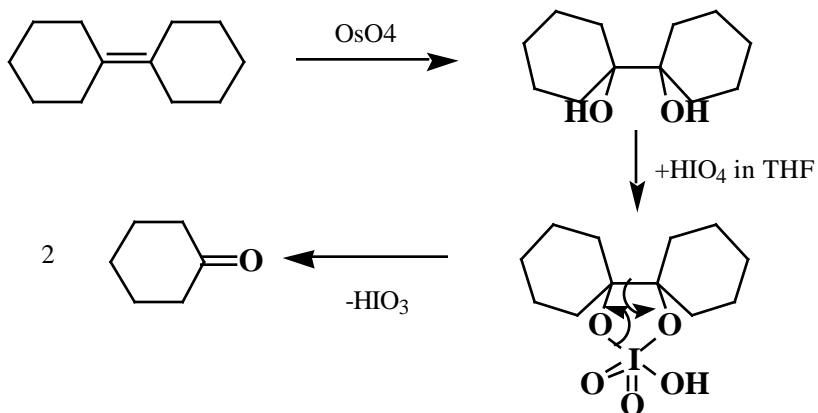


Depending on the nature of the R groups, we get aldehydes and/or ketones or both.

If aldehydes are formed, then these may be oxidized further to the acids. If formaldehyde is formed, then this will be oxidized to  $\text{CO}_2$  (via formic acid and carbonic acid).

(f) Oxidative Cleavage of 1,2-Diols

Alkenes can be oxidized with cleavage directly using hot permanganate (above) or ozone (below). In addition, there is an alternative route that works very well, namely the sequence of (1) forming the 1,2-diol with  $\text{OsO}_4$  and (2) cleavage of the diol with  $\text{HIO}_4$  in THF. There is a cyclic periodo intermediate involved.



### g) Ozonolysis

**Ozone Depletion.** The periodic increase of the sun activity, increased vulcanic activity, and a general alteration of the stratospheric climate have been suggested as possible natural causes. Other hypotheses link the ozone depletion to anthropogeneous causes and, specifically, to organic halogen compounds that form free chlorine radicals. Chlorine, hydroxy radical, and nitroso radical are well known to destroy ozone *via* catalytic cycle. However, the magnitude of the ozone depletion cannot be accounted for by these catalytic cycle alone. Three hypotheses have been suggested to explain the increase of the chlorine concentration.

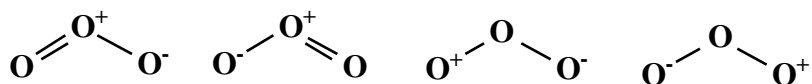
Hypothesis I: Solomon *et al.* (*Nature* **1986**, 321, 755) suggested that  $\text{ClONO}_2$  reacts in a surface catalyzed (clouds) dark reaction with HCl.

Hypothesis II: McElroy *et al.* (*Nature* **1986**, 321, 759) suggested an ozone decomposition cycle based on Cl and ClO which is made more effective by participation of BrO radicals.

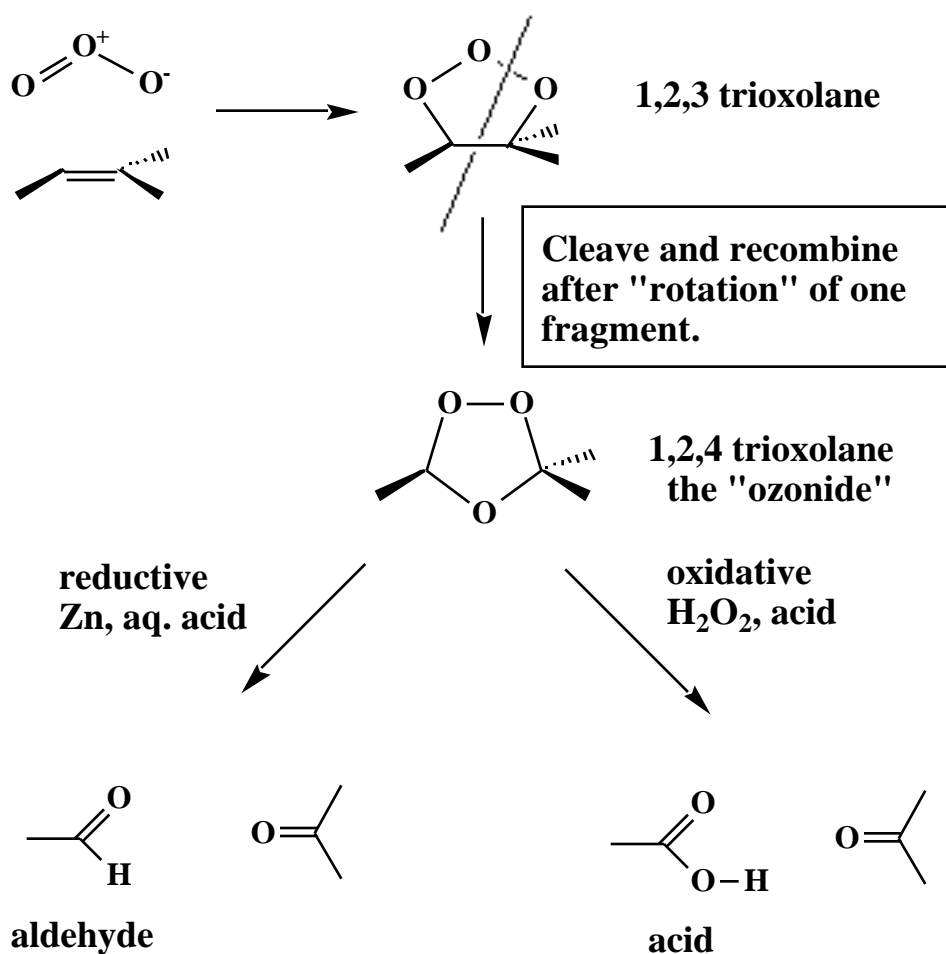
Hypothesis III: Molina *et al.* (*J. Phys. Chem.* **1987**, 91, 433) have suggested that  $\text{Cl}_2\text{O}_2$  has to be considered as a possible source of reactive chlorine.

Back to earth. What does Ozone do to alkenes? Here we go:

### Ozone



The *Criegee mechanism* for the ozonolysis is shown. (i) 1,2,3-trioxolane formation (ii) cleavage as indicated by dashed line (iii) recombination to form 1,2,4-trioxolane (iv) oxidative (K and acid) or reductive (A/K) work-up.



## Carbene Additions -- Cyclopropane Synthesis

Carbenes are compounds of the type  $CR_2$ . Yes, just two groups attached to C and C has a lone pair. R groups can be H, alkyl, aryl, halogens, etc. This is exciting stuff, but we'll be looking only at the most simple case: The parent carbene  $CH_2$ .

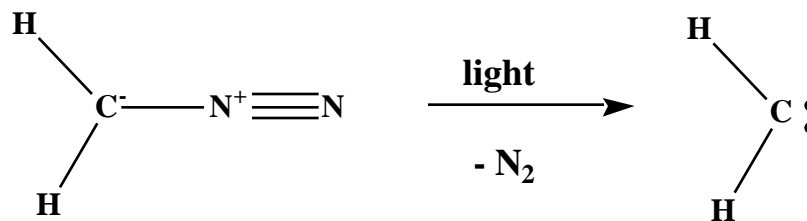
### Structure of Carbenes

They can be either bent with an  $sp^2$  carbon or they can be close to linear (close to  $sp$  hybridization). Note that the book says linear, but recent research shows these species to be not quite linear. The difference between the two is with the electron configuration.

bent	linear
Singlet Carbene	Triplet Carbene
2 paired electrons	2 unpaired electrons
in a C-AO	in two p C-AOs

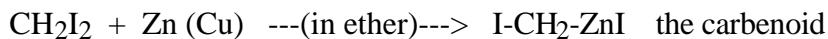
### Preparation of Singlet Carbene

(a) Photolysis of diazomethane,  $CH_2N_2$ . How do we get diazomethane? Let's not bother, we'll buy it.



(b) Alpha-Elimination from  $CHCl_3$ . This is the way the dichlorocarbene was made first. HCl elimination *from the same C* with strong base KOH yields  $CCl_2$ . Bent structure.

(c) Simmons Smith preparation of carbenoids. Excellent. Carbenoid because there is no free real carbene, but the reagent reacts just like a free carbene. Diiodides are reacted with Zn in the presence of Cu in ether.



## Reactions of Carbenes

They add to alkenes to form cyclopropanes. This is the best way to make three-membered rings! The stereochemistry always involves *cis* addition of course (how could one molecule possibly add from two sides?) and this *cis* addition can occur from either side. So, we'll form always one pair of enantiomers but not the diastereoisomers thereof. Meso forms are possible. Use the following three examples to review the stereochemistry of rings (yes, this is an order! [well meant though]).

Example 1: Addition of carbene to Z and E 2-pentene.

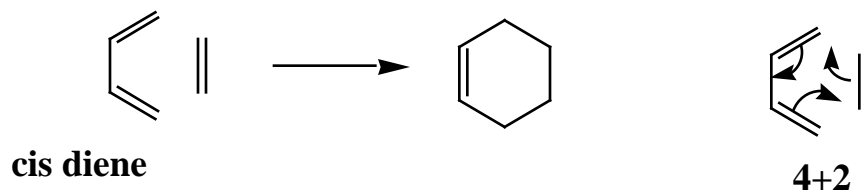
Example 2: Addition of carbene to Z and E 2-butene.

Example 3: Addition of carbene to propene.

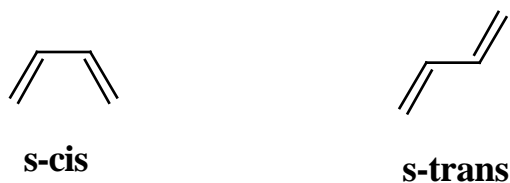
## Diels Alder Reaction

Nobel Prize winning (1950) method for the construction of 6-membered rings:

*Diene and alkene form a cyclohexene.*



It is important for this reaction that the diene is in the “s-cis” conformation as opposed to the more stable “s-trans” conformation. These names describe the relative positions of the dbcs with regard to the central single bond (single bond ==> s-)



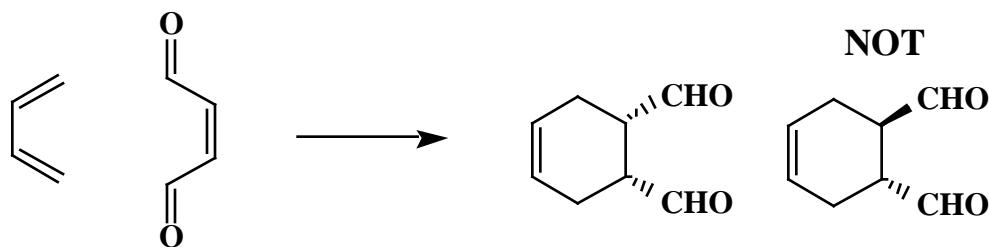
Two good rules are:

- (1) The diene wants to be electron-rich (alkyl substituents help)
- (2) The ene wants to be electron-poor (electron withdrawing groups attached)

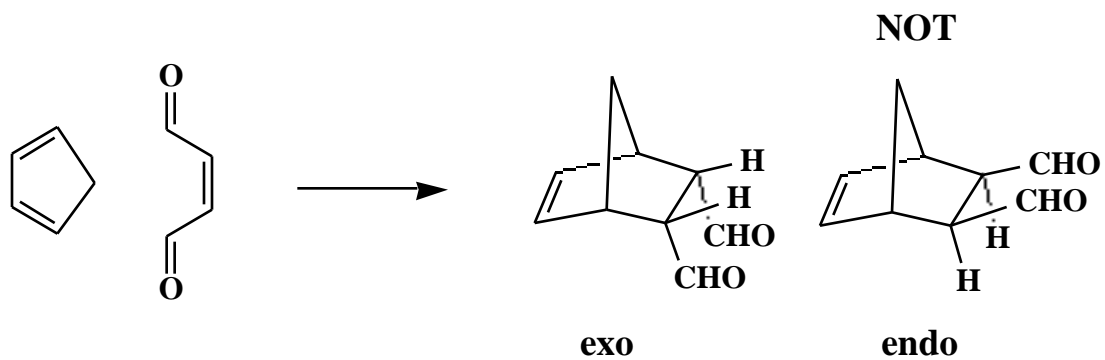
**Stereochemistry** (very briefly)

- (1) The bonds to the “ene” are formed in a *cis* fashion!
- (2) The large polar groups attached to the ene end up in the exo position (“under the diene”) and not in the endo position (away from the diene)

Example 1: Showing the *cis* addition



Example 2: Showing exo preference in case of cyclic dienes



Example 3: Further typical examples.

