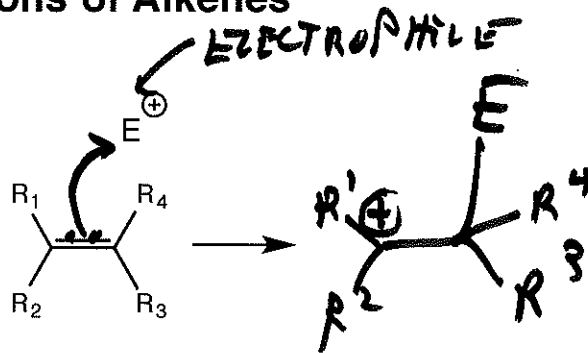
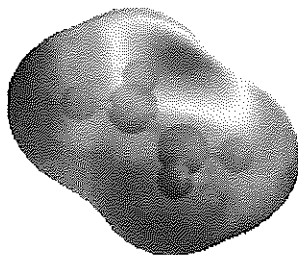
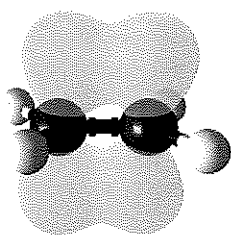


Chapter 9: Addition Reactions of Alkenes

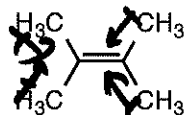
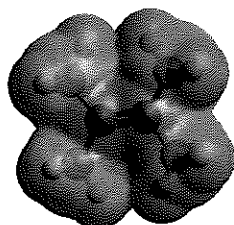
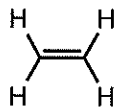
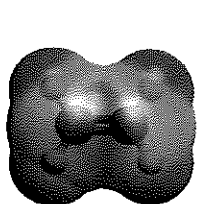
[Sections: 9.1-9.8]

Nature of the reactivity pi bond

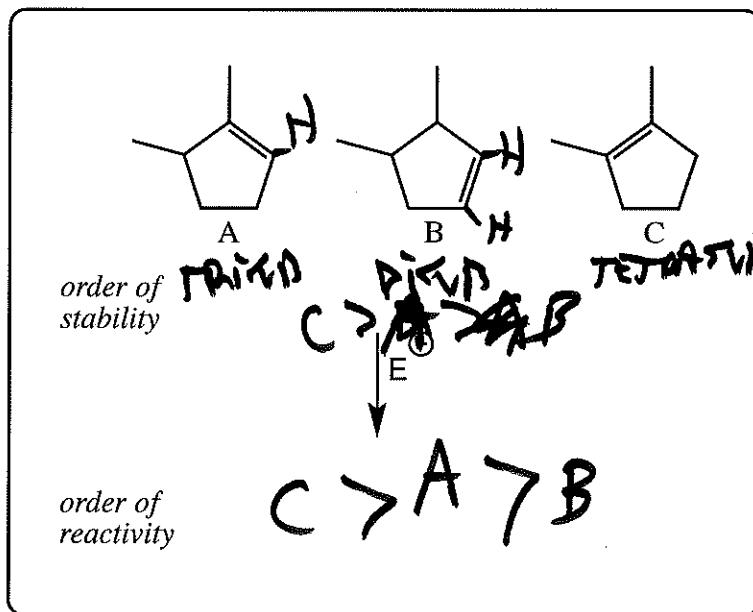
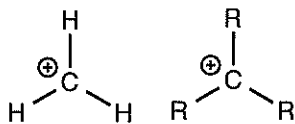


- pi (π) bond is weak (compared to sigma (σ) bond)
- clouds of electron density above and below the plane defined by the atoms of the molecule
- alkenes are electron-rich, and therefore good electron donors
- susceptible to reaction with electrophiles

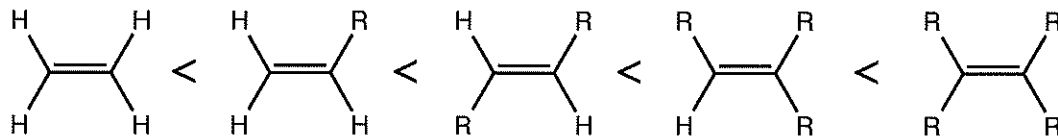
Relative reactivities of alkenes



flashback to carbocations:



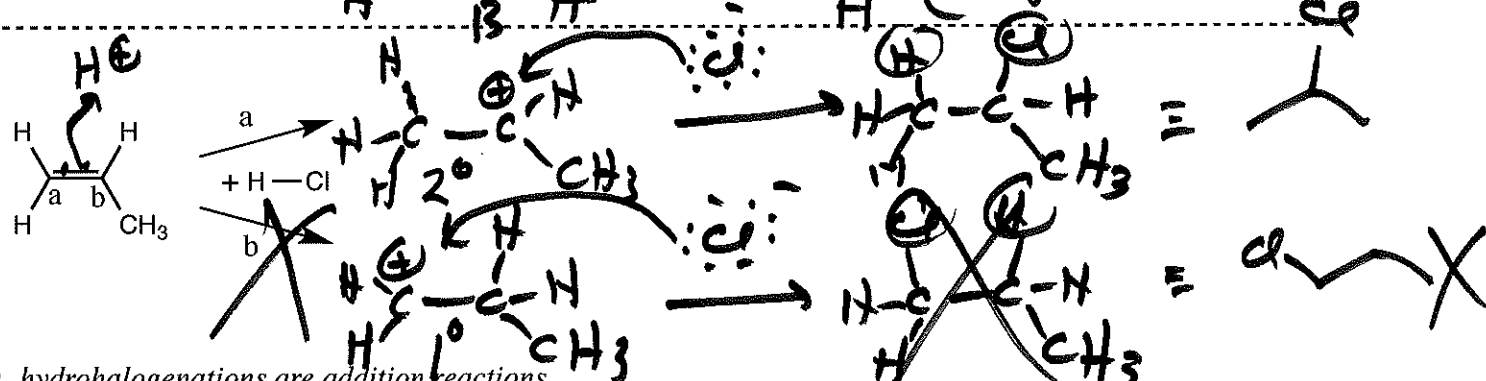
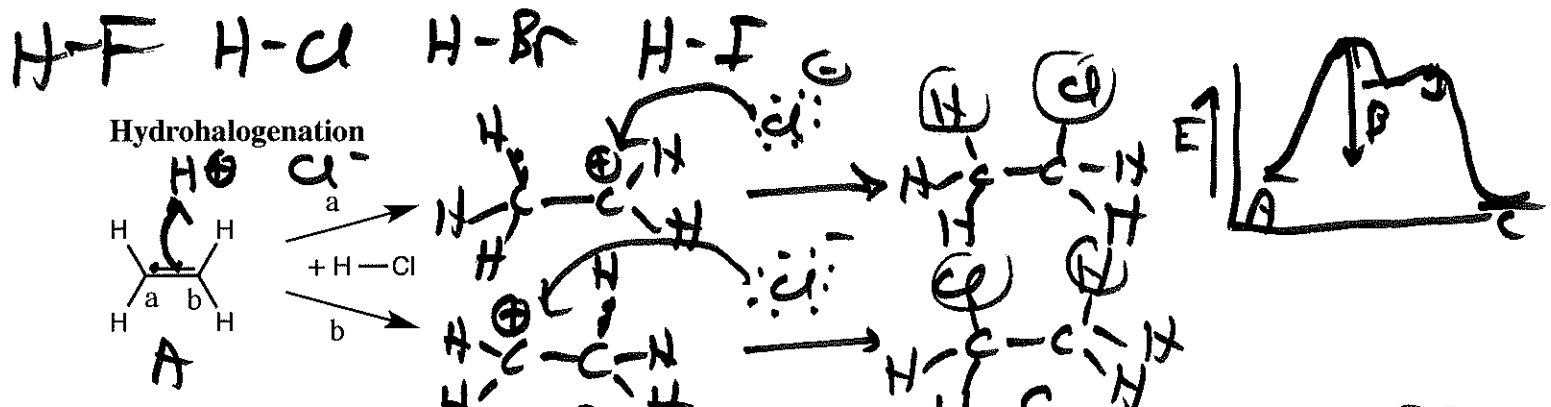
- electron density of the pi bond increases with increasing substitution about the double bond



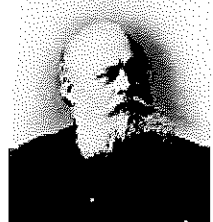
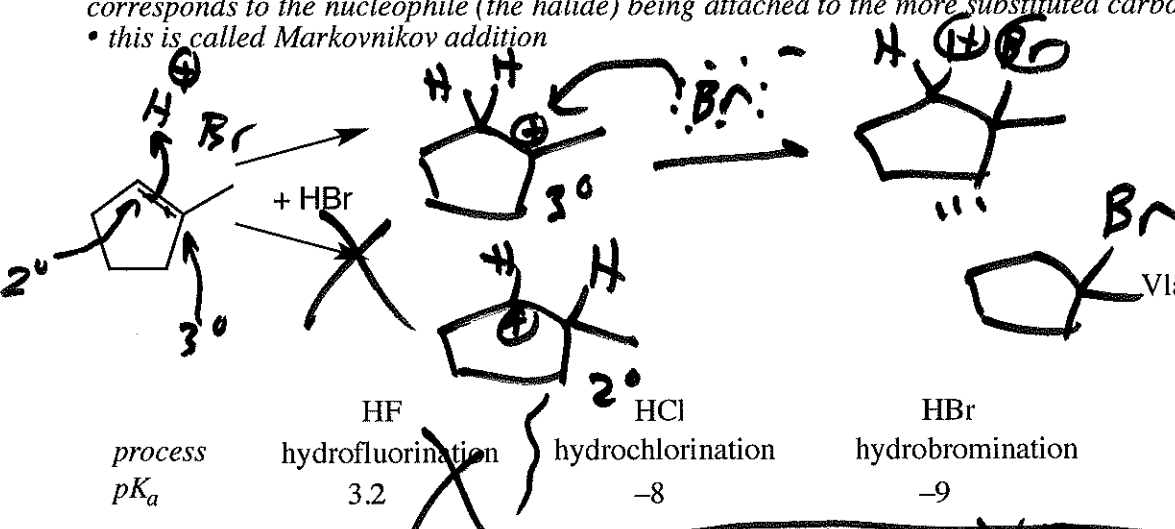
unsubstituted monosubstituted disubstituted trisubstituted tetrasubstituted

rate of reaction with electrophiles \rightarrow

- remember: earlier we determined that increasing substitution about the double bond increased stability!
- thus, if we have a set of isomeric alkenes, the most stable isomer is also be the most reactive towards electrophiles!



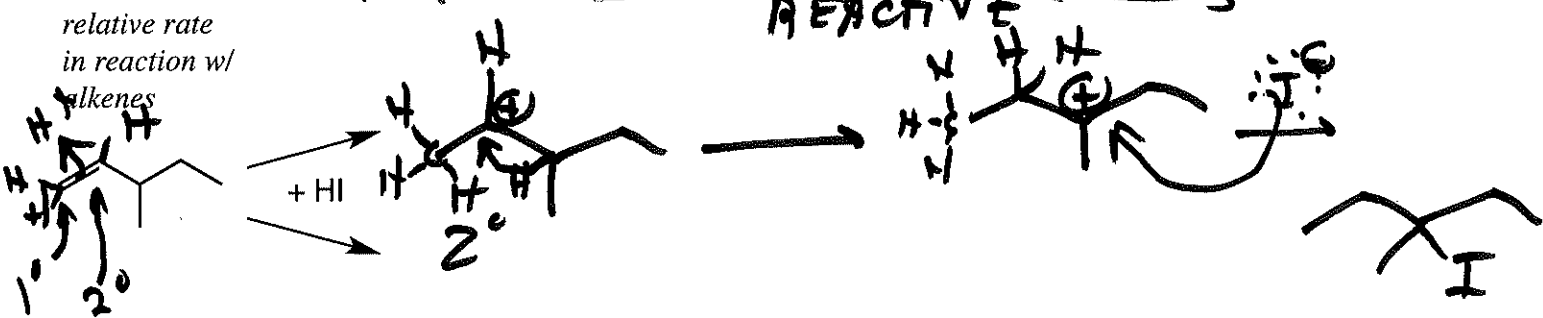
- hydrohalogenations are addition reactions
- generally exothermic since two sigma bonds are formed at the expense of a broken pi bond
- initial protonation favors formation of the more stable carbocation intermediate
- the carbocation intermediate is trapped by the halide nucleophile to form the final product
- since the most stable carbocation intermediate is the more substituted carbocation, the final product corresponds to the nucleophile (the halide) being attached to the more substituted carbon of the C=C bond
- this is called Markovnikov addition



Vladimir Markovnikov
1838-1904

process	hydrofluorination	hydrochlorination	hydrobromination	hydroiodination
pK_a	3.2	-8	-9	-10

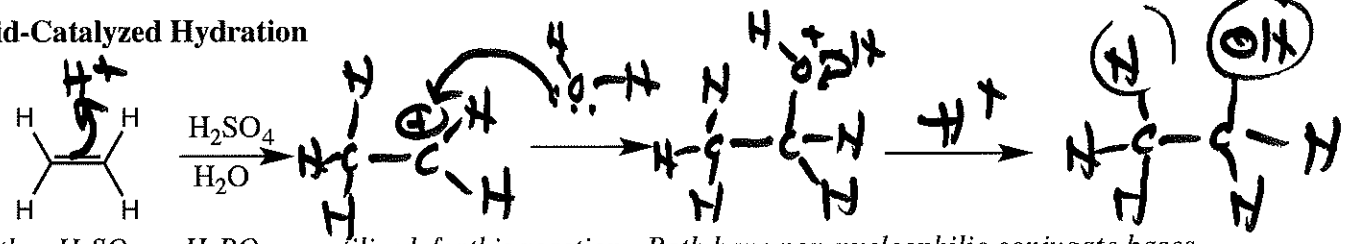
REACTIVE \rightarrow



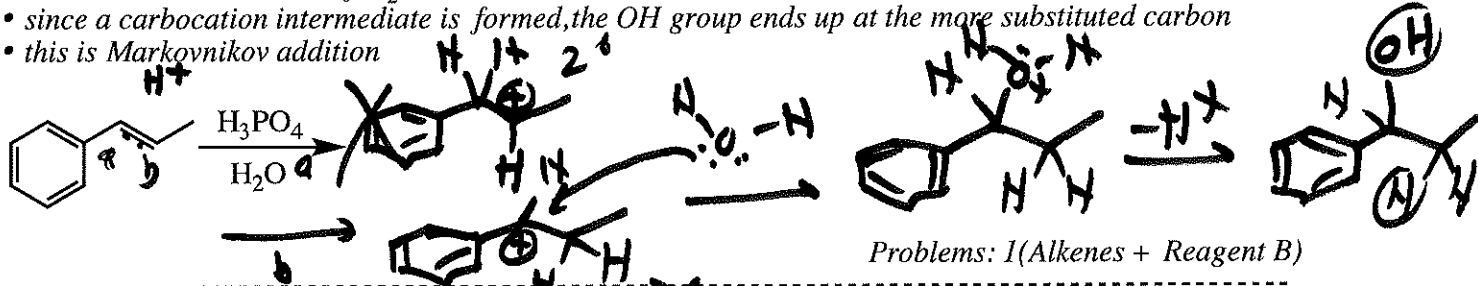
• as with ANY reaction that involves carbocation intermediates, be aware that rearrangements of the intermediate carbocations to more stable carbocations might occur!

HSO_4^- NUCLEOPHILIC

Acid-Catalyzed Hydration

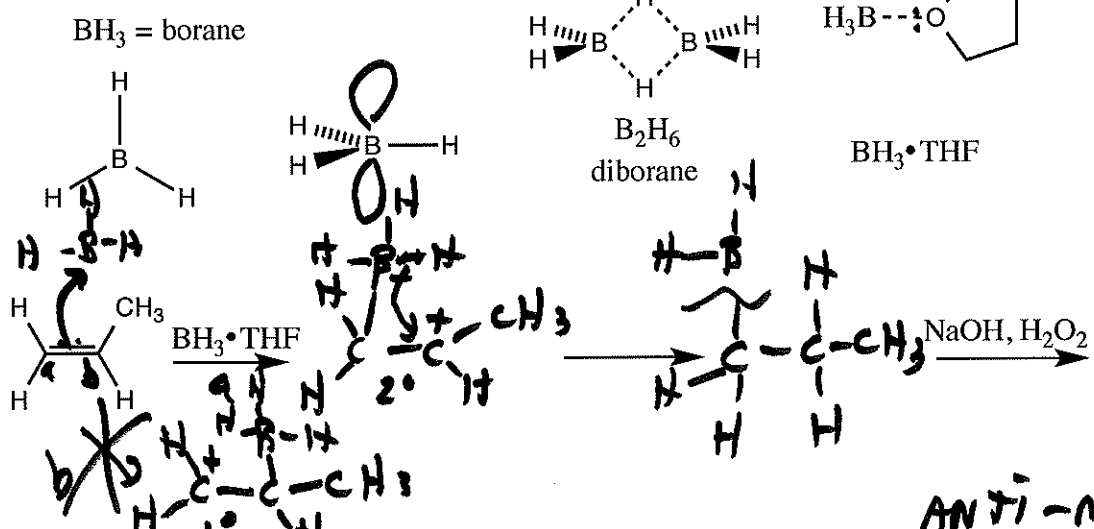


- either H_2SO_4 or H_3PO_4 are utilized for this reaction. Both have non-nucleophilic conjugate bases
- the net result is addition of H_2O across the double bond
- since a carbocation intermediate is formed, the OH group ends up at the more substituted carbon
- this is Markovnikov addition



Problems: 1 (Alkenes + Reagent B)

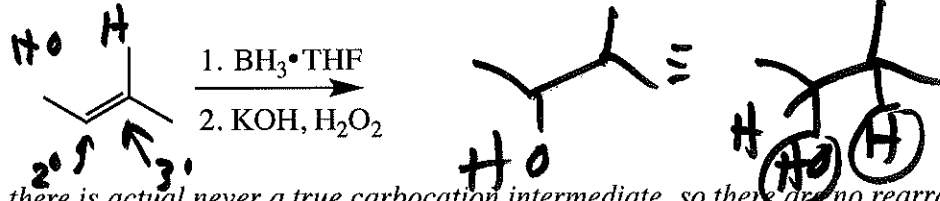
Hydration via Hydroboration



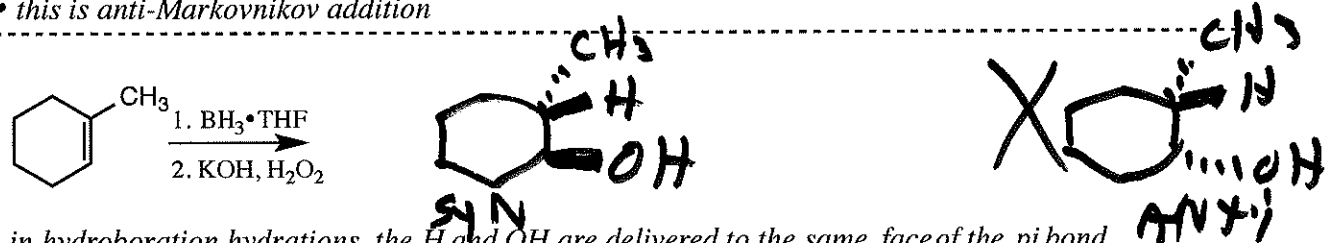
H.C. Brown
1912-2004
Nobel Prize 1979

ANTI-MARKOVNIKOV HYDRATION

Predict the major product(s) of the following reaction:



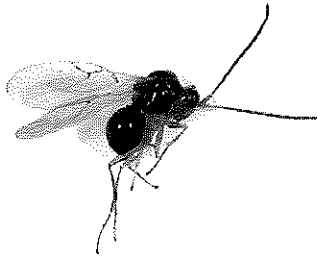
- there is actually never a true carbocation intermediate, so there are no rearrangements possible
- the net result is addition of H_2O across the double bond
- this is anti-Markovnikov addition



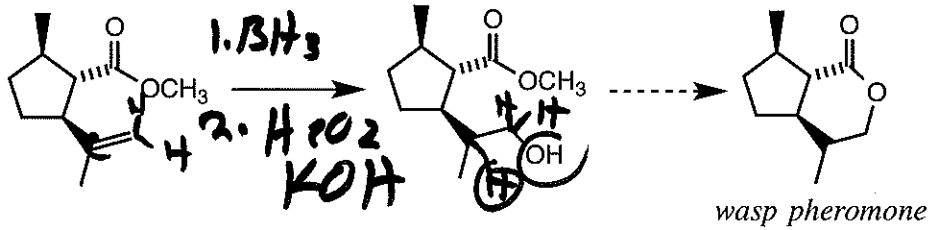
- in hydroboration hydrations, the H and OH are delivered to the same face of the pi bond
- addition to the same face of a pi bond is called "syn" addition
- this is considered to be a "stereospecific" reaction since a single stereoisomer results although two or more might be conceivably formed

Problems: 1 (Alkenes + Reagent C)

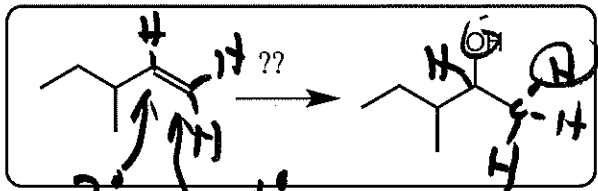
which reagent should be used for hydration?
 A) H^+ , H_2O
 B) BH_3 2) H_2O_2 , KOH
 C) who cares?



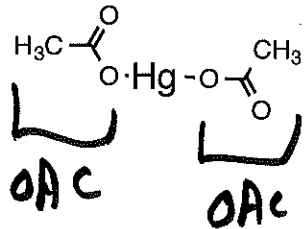
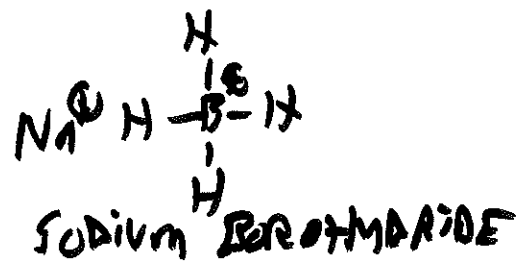
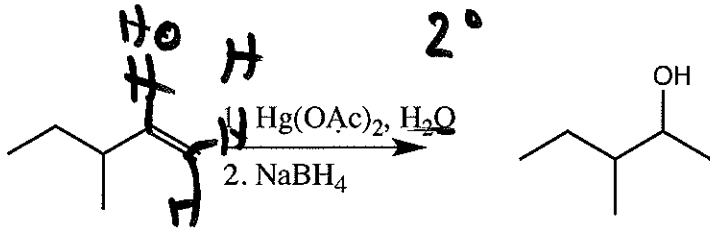
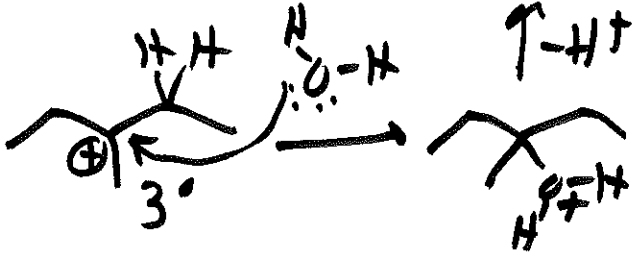
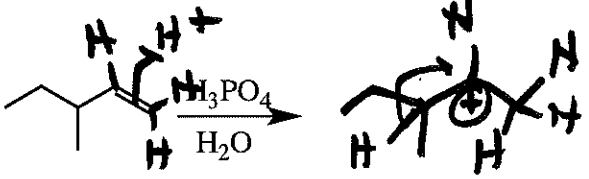
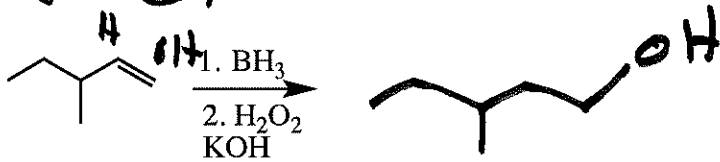
wasp *Alloxysta victrix*



Hydration via Oxymercuration

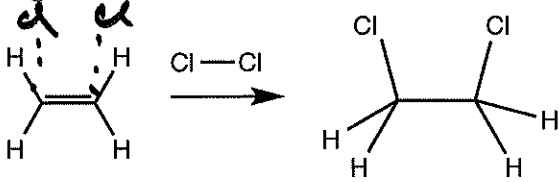


HYDRATION
 MARKOVNIKOV ADDITION

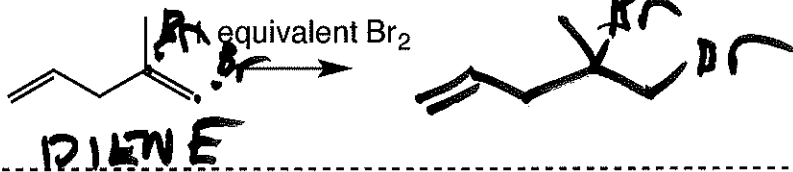
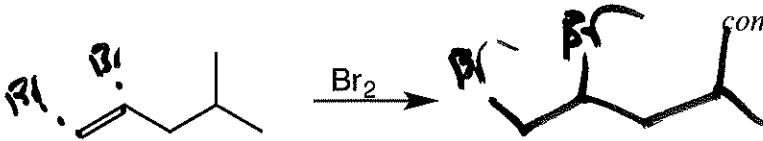


- process of oxymercuration
- two-step process
- result is Markovnikov hydration without possibility of rearrangement!

Halogenation

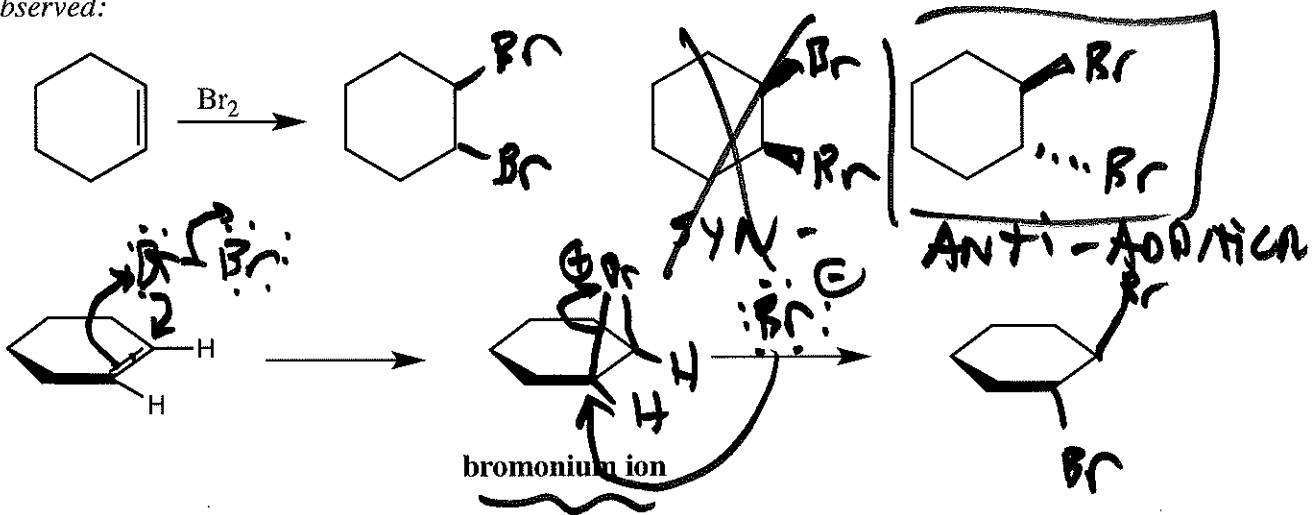


- halogenations are addition reactions
- generally exothermic since two fairly strong C-X bonds are formed at the expense of a broken pi bond and a weak X-X bond
- Br₂ and Cl₂ engage in reactivity. F₂ is TOO reactive and I₂ is too unreactive
- NOTE: HX reactions and X₂ reactions are completely different!



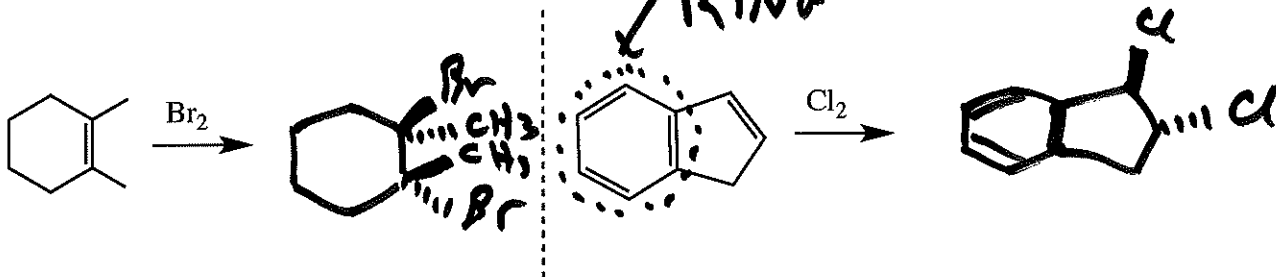
• DISUB MORE REACTIVE THAN MONOSUB

Observed:

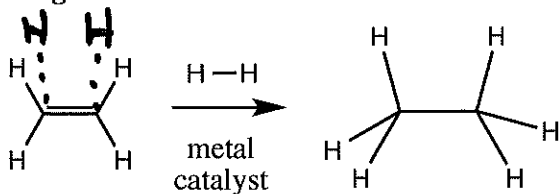


- bromonium ions are very strained intermediates due to angle strain and the fact that a positive charge is forced onto an electronegative atom
- bromonium ions are very reactive and seek to eliminate the characteristics that contribute to the strain
- reaction with Br⁻ to form the 1,2-dibromide relieves these sources of strain
- the net result is addition of the two bromine atoms onto either face of the original pi bond
- such addition is referred to as "anti" addition
- the reaction is therefore stereospecific

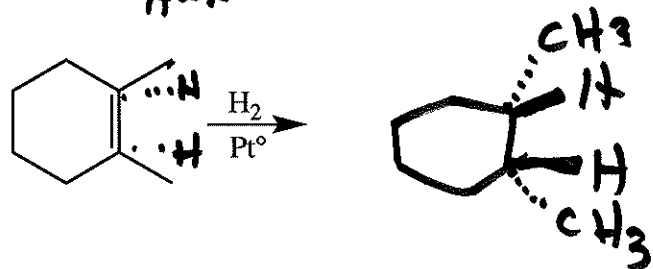
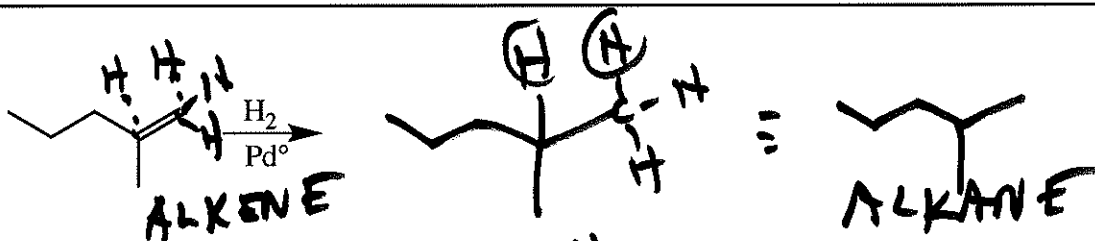
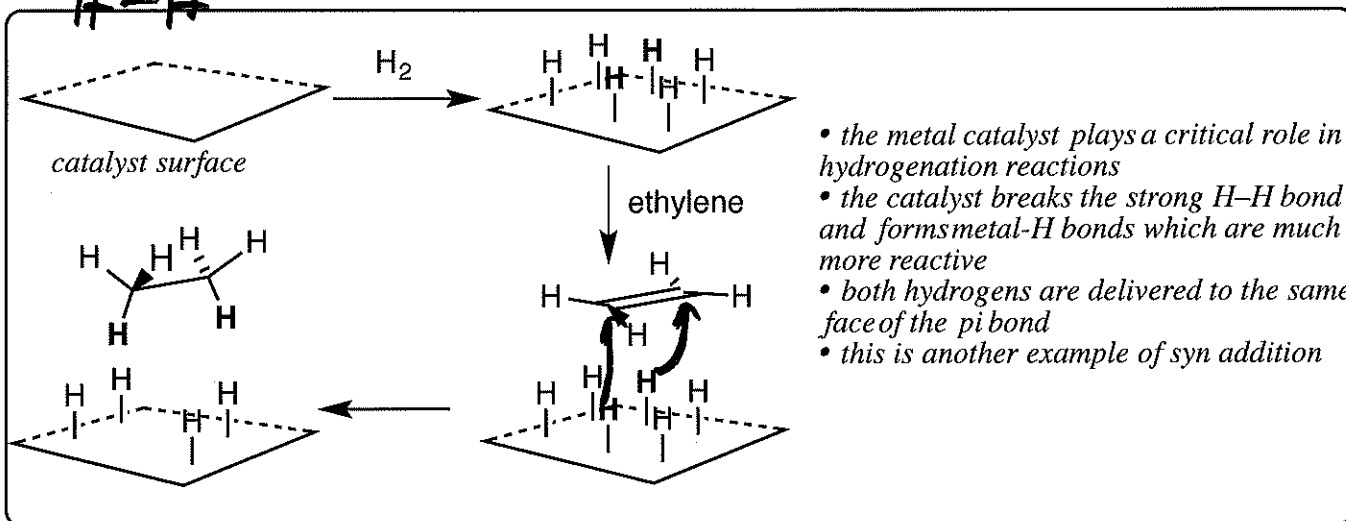
BENZENE RING = UNREACTIVE



Hydrogenation



- hydrogenations are addition reactions
- strongly exothermic since two strong CH sigma bonds are formed at the expense of a broken pi bond
- no reaction occurs in the absence of a suitable catalyst!
- the typical catalysts are Pd° , Pt° , Rh° or Ni°



- hydrogenations are stereospecific