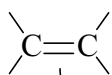


# Chapter 9

alkene ; functional group  $\Rightarrow$  double bond  $\left( \begin{array}{l} \text{rxns at double bond} \\ \text{rxns not at double bond} \\ \text{but at other positions} \end{array} \right.$



$\pi$  bond is weak, loosely held, exposed  $\Rightarrow$  reactive



p 319  $\Leftarrow$   $\left( \begin{array}{l} \text{electrophilic addition} \\ \text{free radical addition} \end{array} \right. \Leftarrow$  electron source

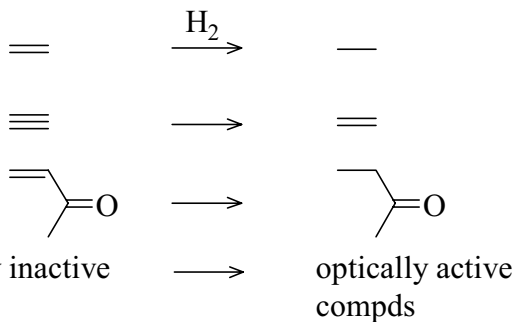


$\left( \begin{array}{l} \text{a } \pi \text{ bond is broken} \\ \text{two strong } \sigma \text{ bond are formed} \\ \text{a } \sigma \text{ bond is broken} \end{array} \right)$

## Hydrogenation

unsaturated  $\xrightarrow{\text{H}_2}$  saturated  
comps                      comps

ex)



<p>formed ; 2 C-H broken ; H-H &amp; <math>\pi</math> bond</p> <p><math>\Downarrow</math></p>	$\Leftarrow$	<p>quantitative analysis is possible</p>	$\Leftarrow$	<p><math>\left( \begin{array}{l} \text{Pt, Pd, Ni etc.} \\ \text{on supporter} \end{array} \right. \leftarrow</math> heterogeneous catalyst (two phases)</p> <p><math>\left( \begin{array}{l} \text{organic} \\ \text{complexes} \\ \text{of Rh, Ir etc} \end{array} \right. \leftarrow</math> homogeneous catalyst (one phase)</p>
---	--------------	--	--------------	---

heat is evolved ; heat of hydrogenation  
 ~ 30 Kcal/mole

↓

without catalysts, no rxn due to high  $E_a$

catalysts lower  $E_a$  to provide different mechanisms (Fig 9-2) ⇒

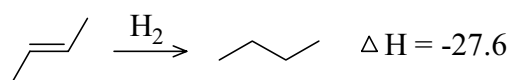
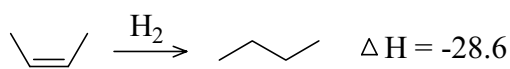
weaken  $\pi$  bond

break H-H bond

speed up  
dehydrogenation ←

also lower  $E_a$  of  
the reverse rxn

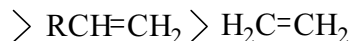
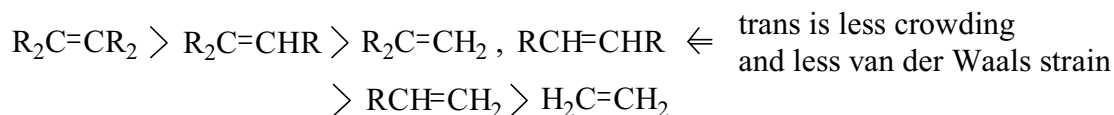
⇐



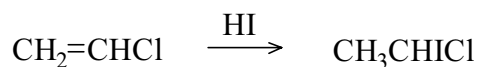
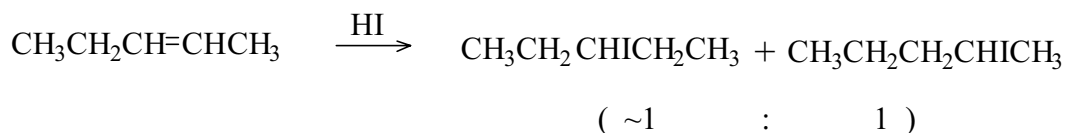
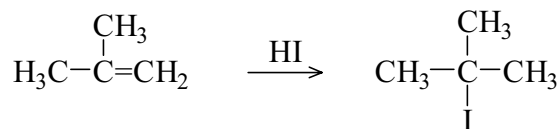
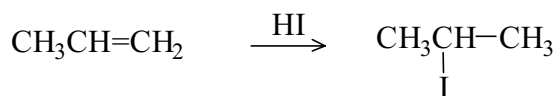
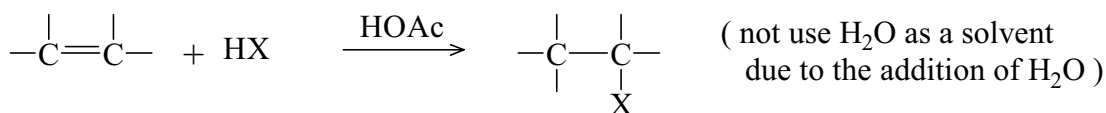
⇒ trans is more stable than  
cis by about 1Kcal

↓

p327



← more stable

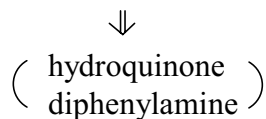


↓

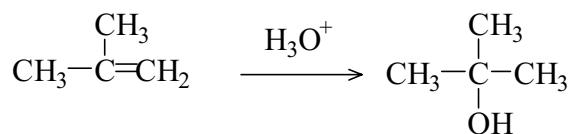
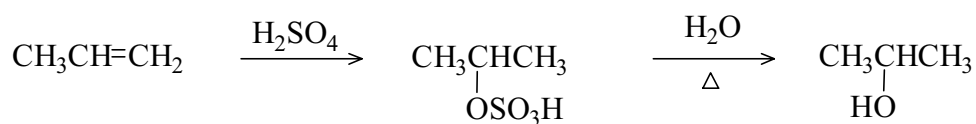
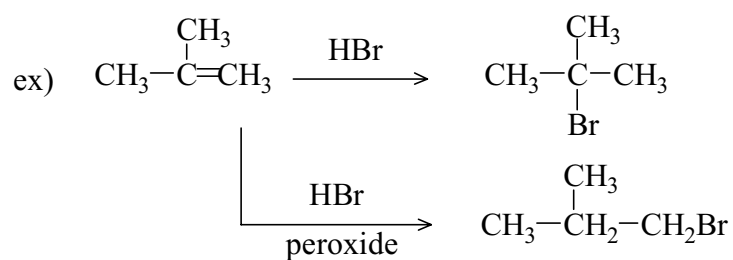
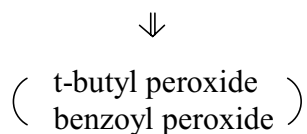
Markovnikov's rule ; H in HX attaches to the carbon having more H.

regioselective

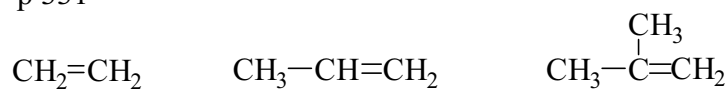
HBr addition ; normal condition (in the presence of inhibitor) → Markovnikov addition



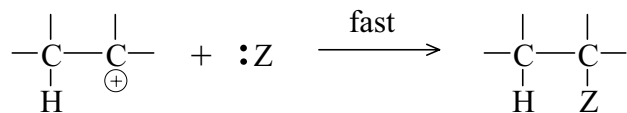
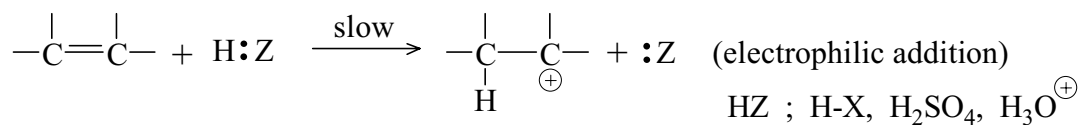
with peroxide → anti-Markovnikov addition



p 331



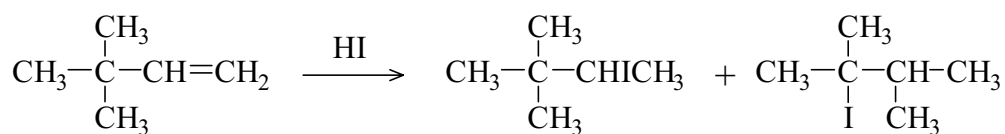
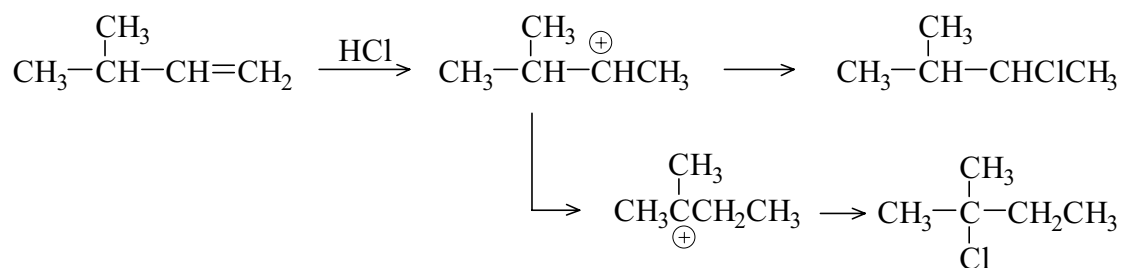
←  
require more concnd H<sub>2</sub>SO<sub>4</sub>



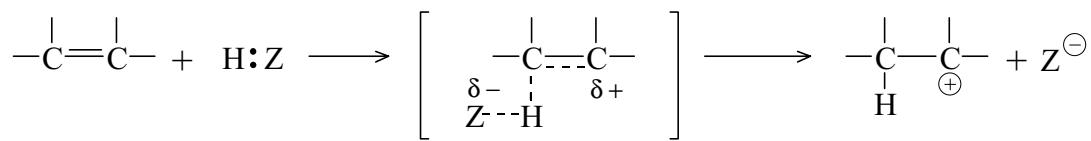
hydration rxn is reversible (p333)

Evidences for the mechanism

- 1) the rate depends on [alkene] and [HZ].
- 2) the rxn requires an acidic reagent.  
exception : H<sub>2</sub>O (requires strong acid)
- 3) rearrangement is possible



- 4) consistent with the orientation of addition  
the relative reactivities of alkenes



↓

more electron-releasing groups lower  $E_a$

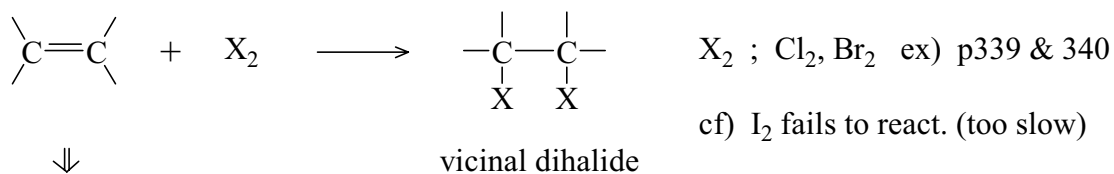
↓

more alkyl groups lower  $E_a$

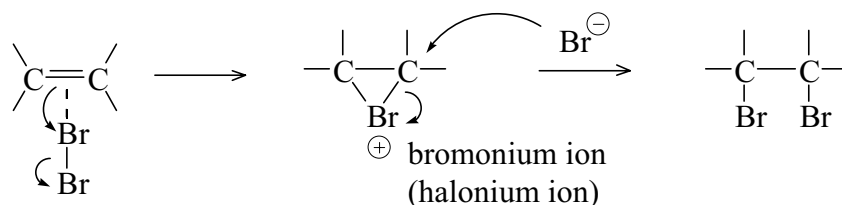
↓

explain orientation and reactivity ( Fig 9.4, p338)

ex)  $\text{CH}_2=\text{CH}_2$  is more reactive than  $\text{CH}_2=\text{CHCl}$



electrophilic addition

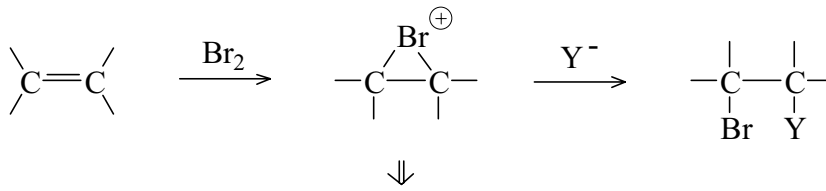


alkene ; base, nucleophile  
 $\text{Br}_2$  ; acid, electrophile

evidence ?

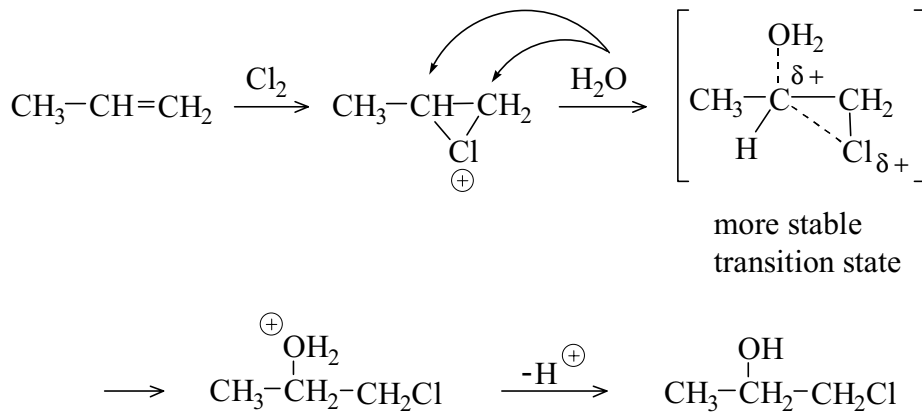
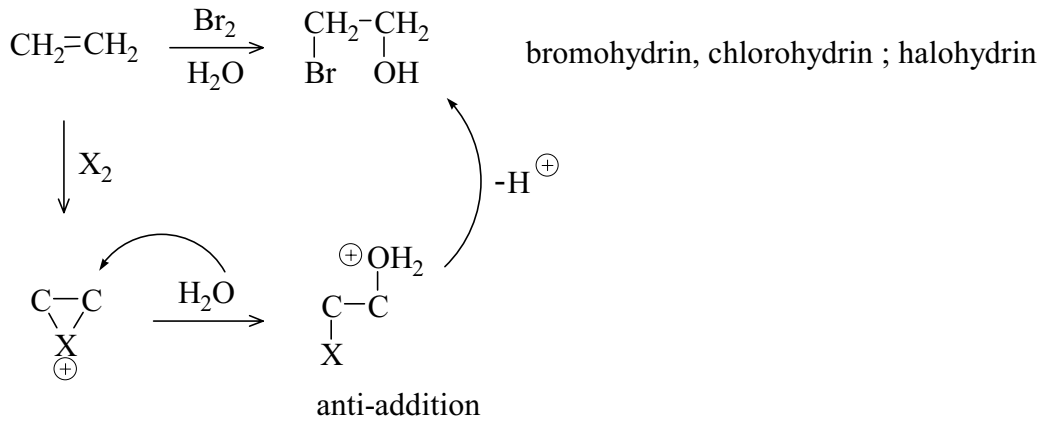
- the effect of the alkene structure on reactivity  
the more substituted alkene, the more reactive.  
electron-releasing substituents activate an alkene.  
electron-withdrawing substituents deactivate.

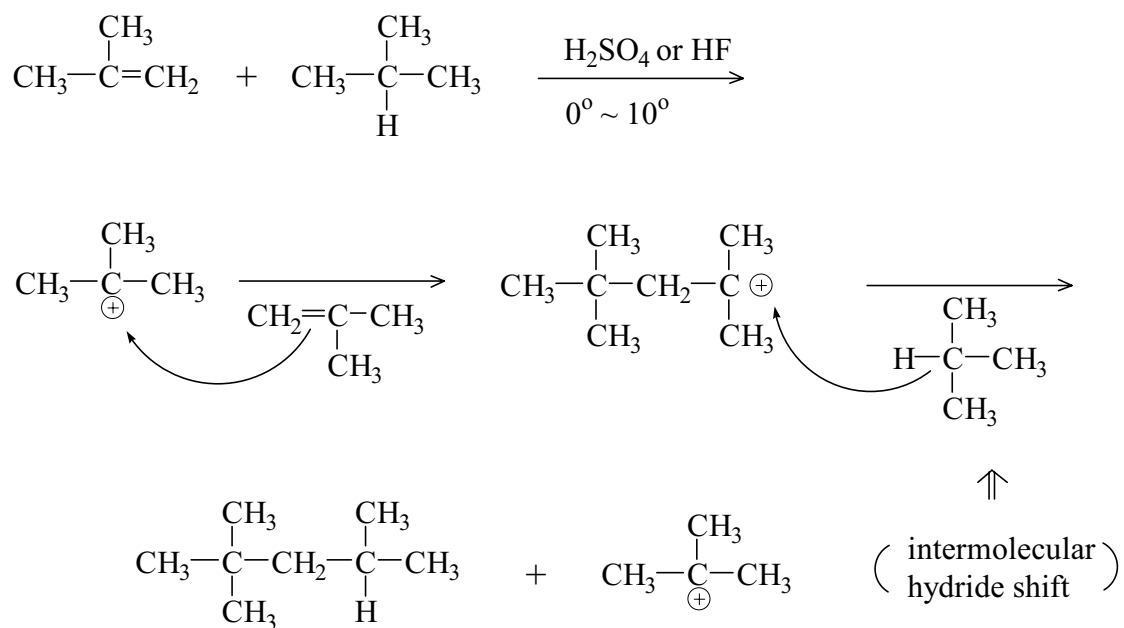
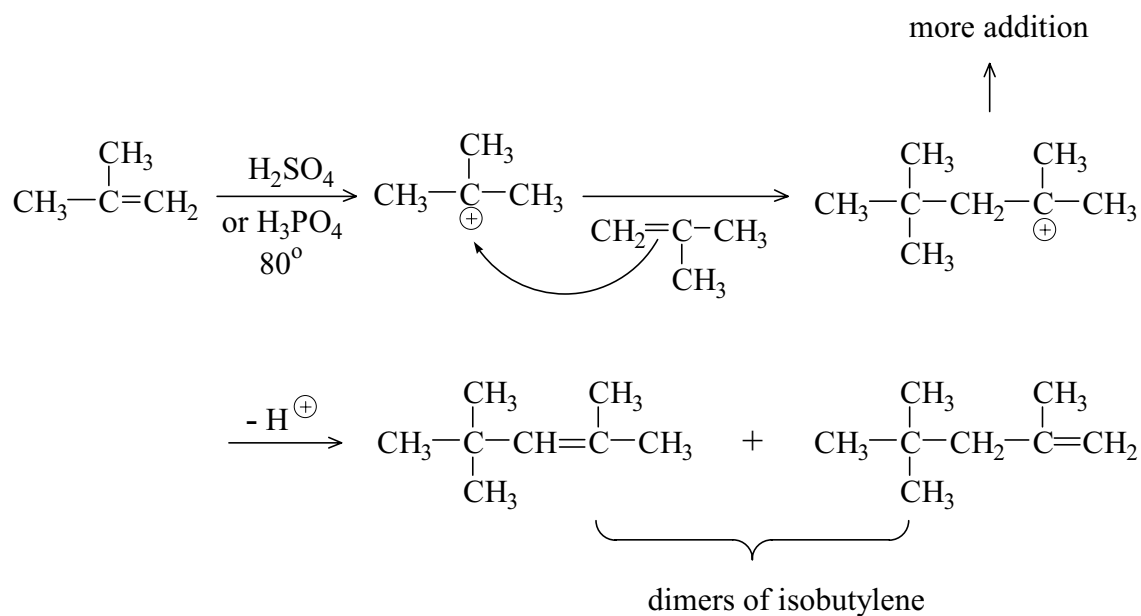
- the effect of the added nucleophiles on the products



how about open carbocation? (p342)

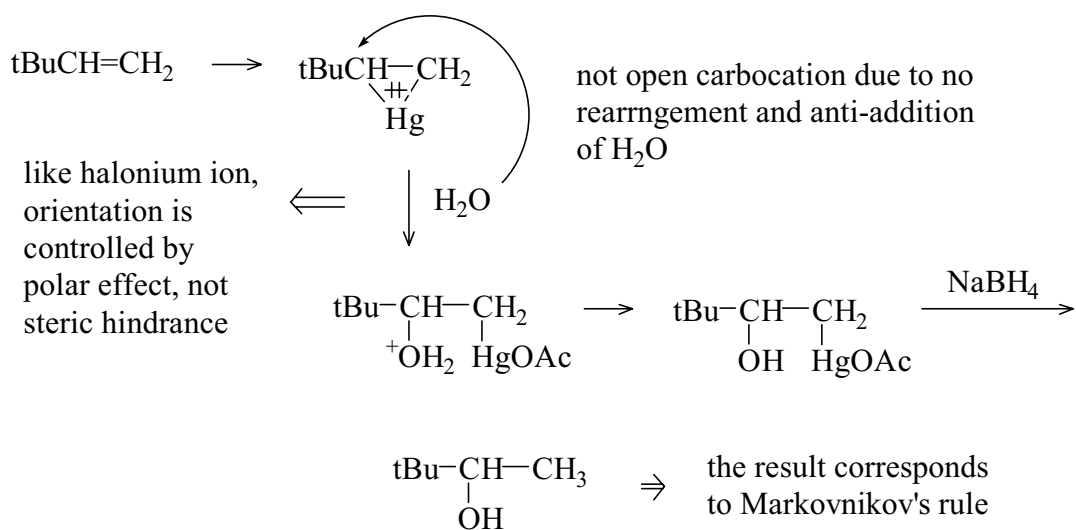
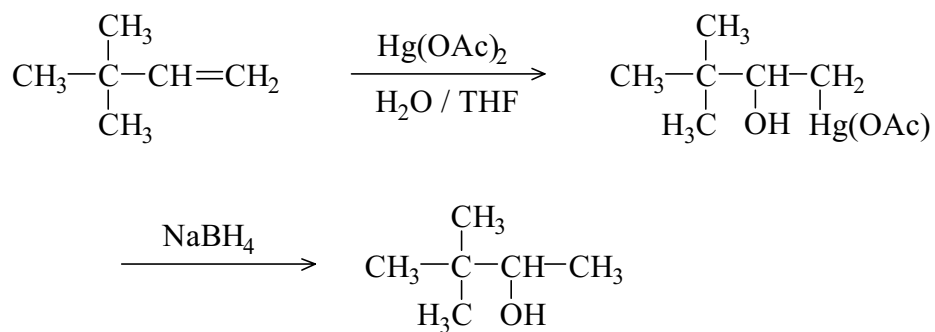
cyclic form from stereochemistry



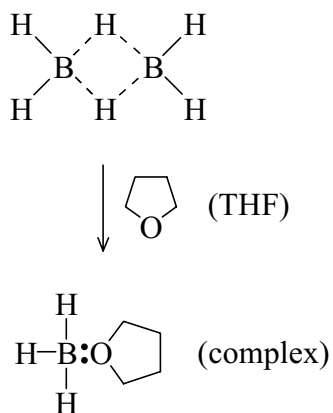


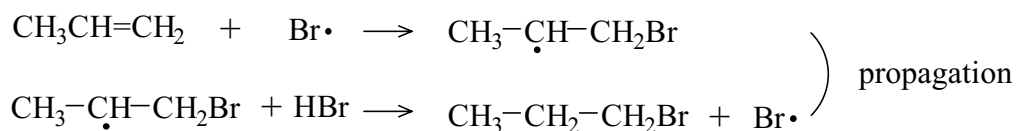
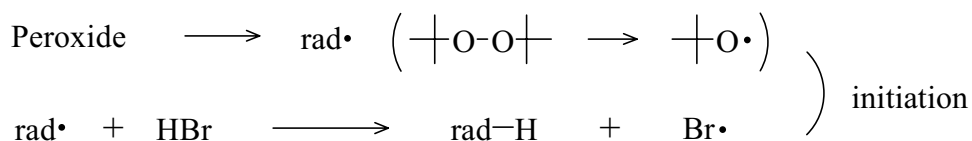
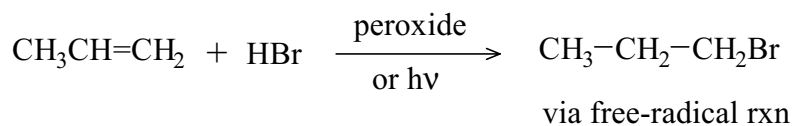
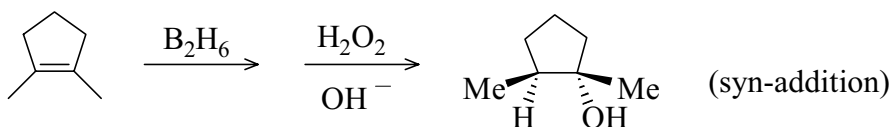
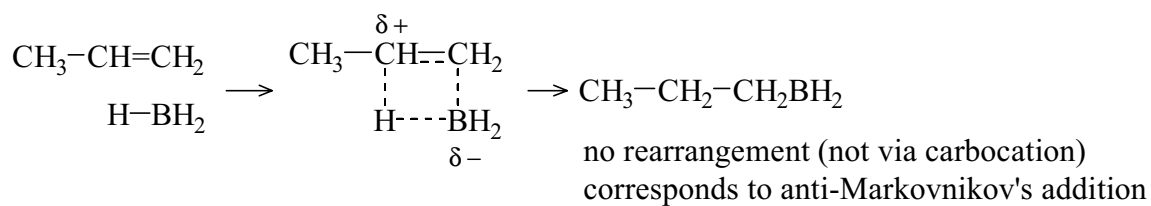
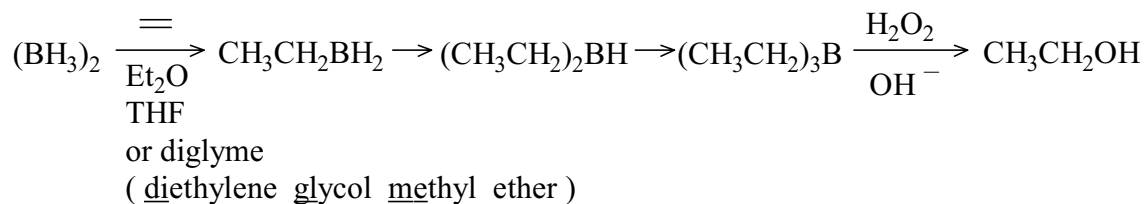
## Carbocation

- 1) combine with Nu
- 2) rearrange to a more stable carbocation
- 3) eliminate a H to form an alkene
- 4) add to an alkene
- 5) abstract a hydride from an alkane

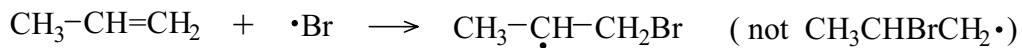


borane ( $\text{BH}_3$ ) exists as dimer  $\Rightarrow$  diborane ( $\text{B}_2\text{H}_6$ )

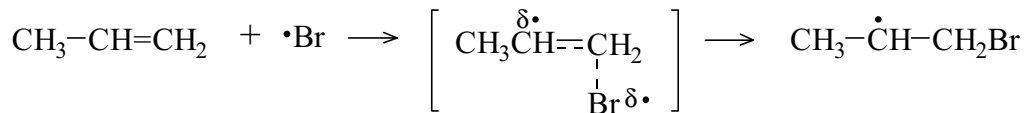




evidence ; a small amount of peroxide or hv  
 a small amount of inhibitor  
 ESR

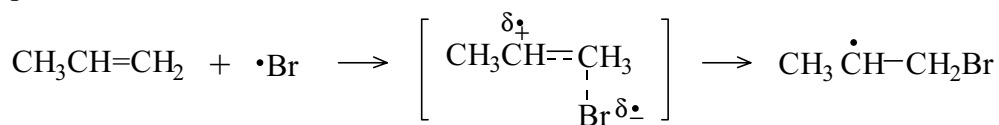


1) radical stability



more stable  
transition state

2) polar effect



carry a partial  
carbocation character

3) steric effect

the addition to C-1 is less hindered than the addition to C-2

↓

less crowded transition state

which one is more important? ⇒ it depends on the rxn

⇓

ex) conjugated system ) radical stability  
styrene

How about for HBr?

↓

three factors may work  
similarly.

⇐

•CBr<sub>3</sub> → steric effect

•CF<sub>3</sub> → polar effect

( carbocation mechanism ; H<sup>+</sup> is added first (electrophilic) ) ⇒ orientation is reversed  
 ( free radical mechanism ; Br• is added first )

