Chapter 4

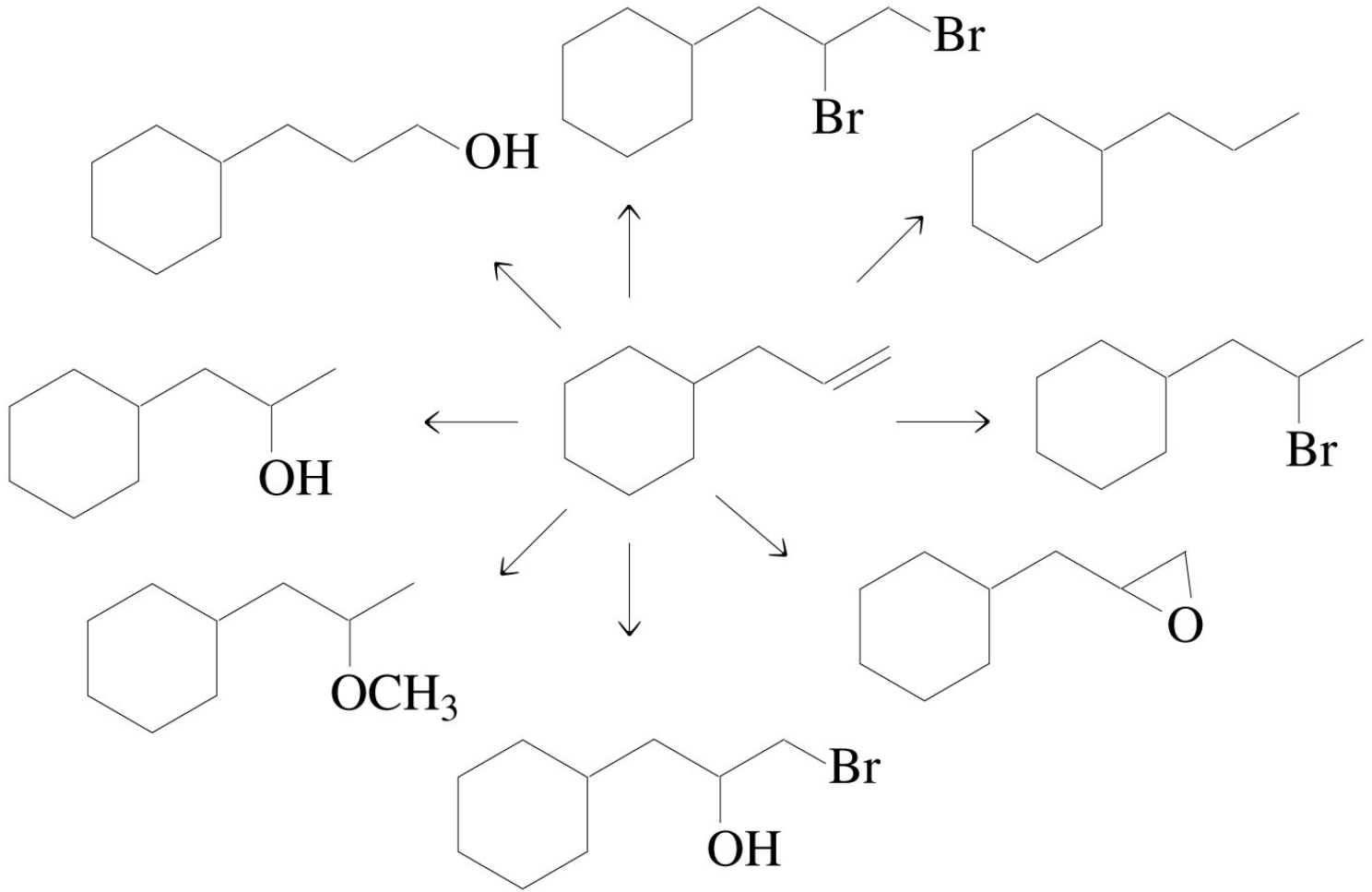
Reactions of alkenes

Addition reactions

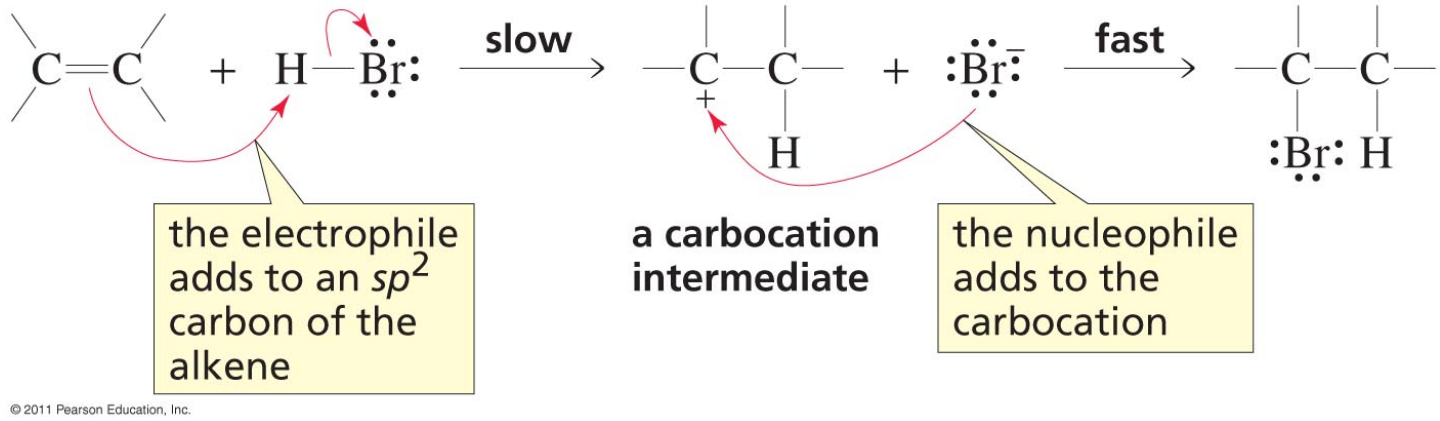
Carbocations

Selectivity of reactions

- Prob 47 p192. Give the reagents that would be required (including catalyst).



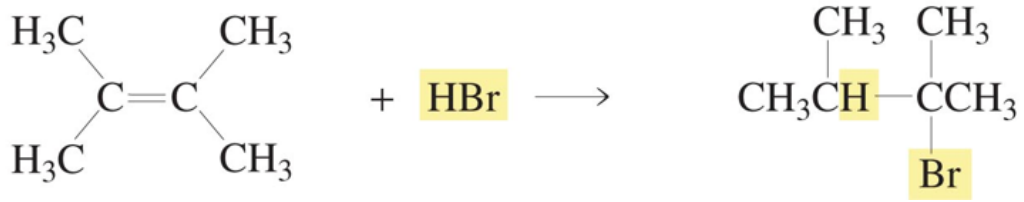
Electrophilic addition



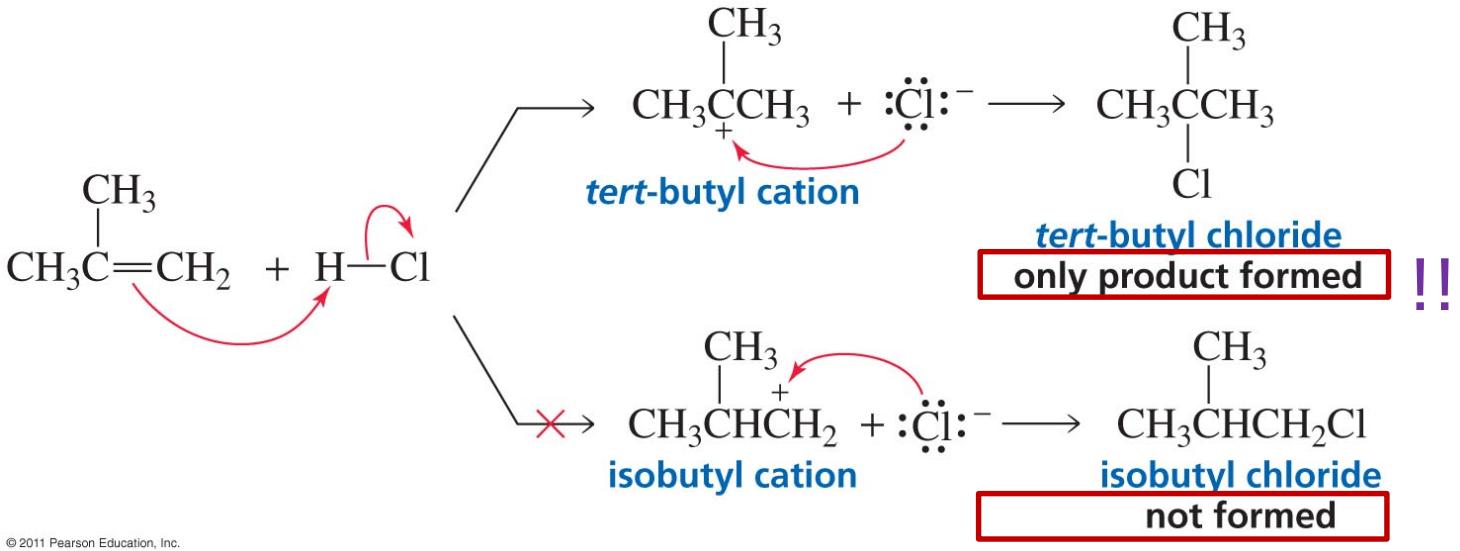
- addition of electrophile and then nucleophile to C=C
  - electrophile from E^+ $Nu:^-$ or $E^{\delta+}$–$Nu^{\delta-}$ or E-Nu
- (typically) 2-step reaction
  - 1st step ~ addition of E^+ to = ~ slow ~ RDS
    - C=C is a weak Nu ~ need strong E^+ like H^+
    - base destroys E^+ ~ run in acidic or neutral condition
  - 2nd step ~ addition of $Nu:^-$ to C^+ ~ fast

Addition of HX

- electrophilic addition of HF, HCl, HBr, or HI to =
  - E^+ is H^+ from $H^{\delta+}–X^{\delta-}$
- A symmetrical alkene gives one product.

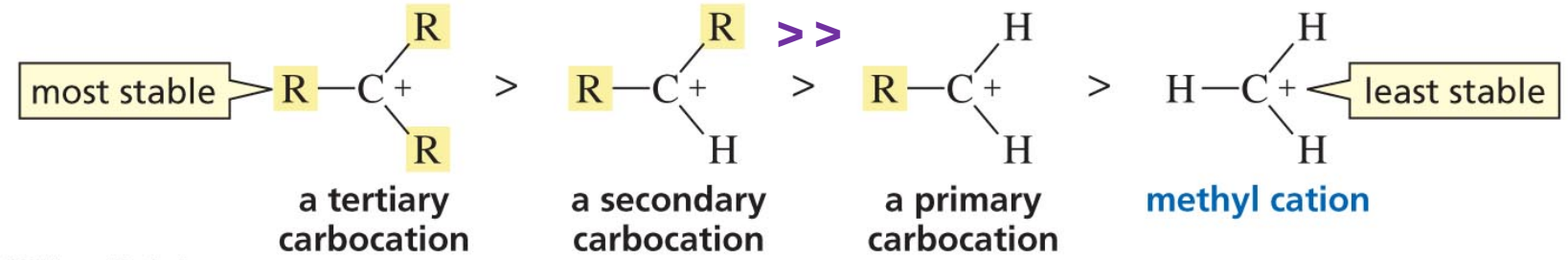


- unsymmetrical alkene?

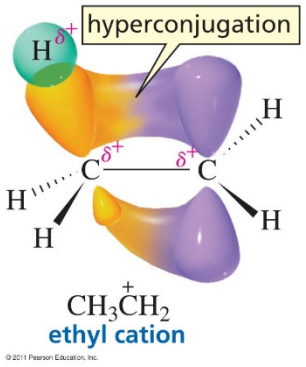


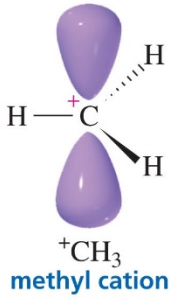
Stability of carbocation

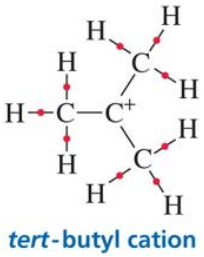
relative stabilities of carbocations

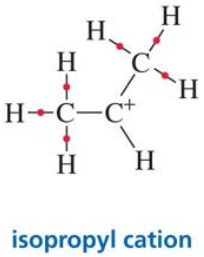


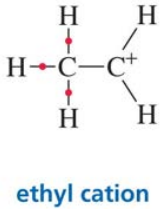
- due to charge dispersion by
  - inductive effect ~ e-donating R
  - hyperconjugation betw e in σ bond and empty p orbital





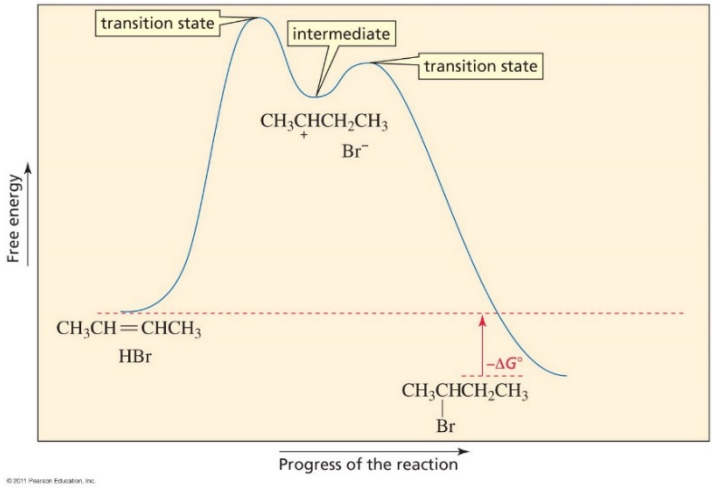


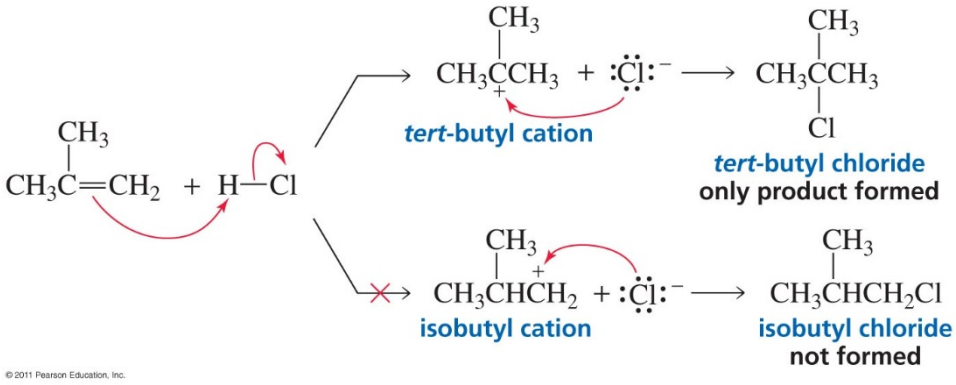


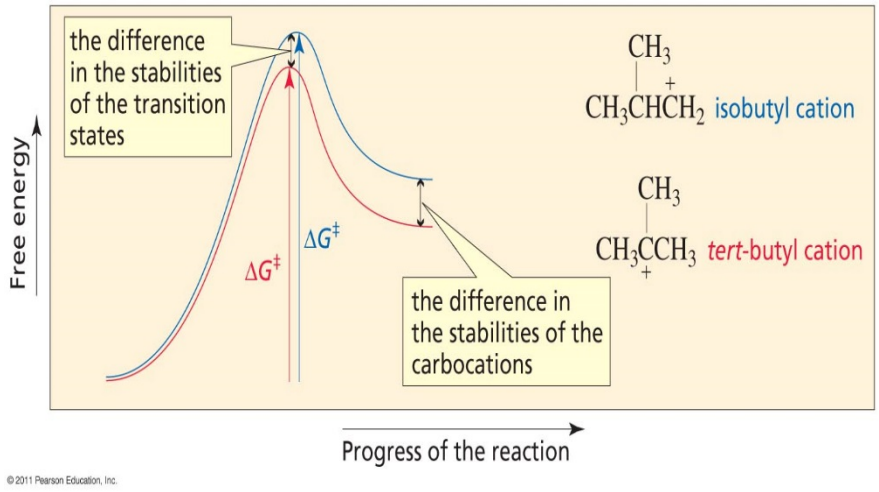


Regioselectivity

- The 1st step is the RDS, and the more stable carbocation intermediate is formed more rapidly. → regioselectivity



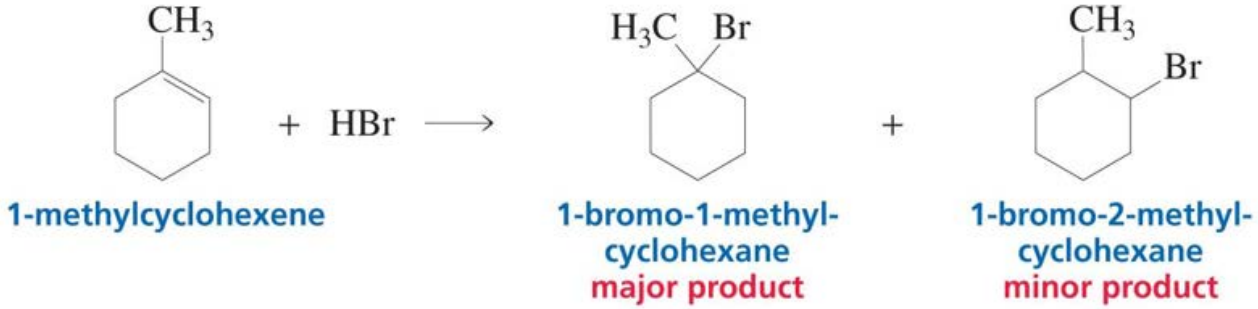




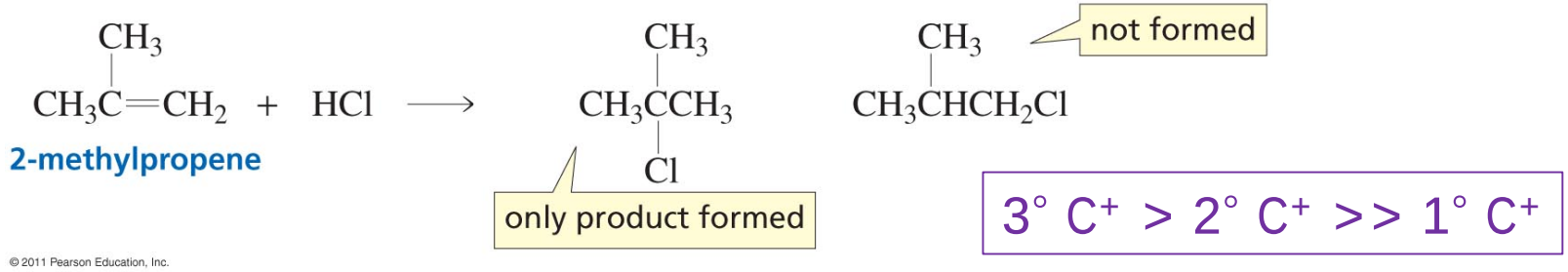
Hammond postulate:
"Structure of [TS]‡ is similar to that of the species of the similar energy."

- ✓ [TS]‡ resembles intermediate more than reactant.
- ✓ $\Delta G^‡$ for t-Bu cation is lower.

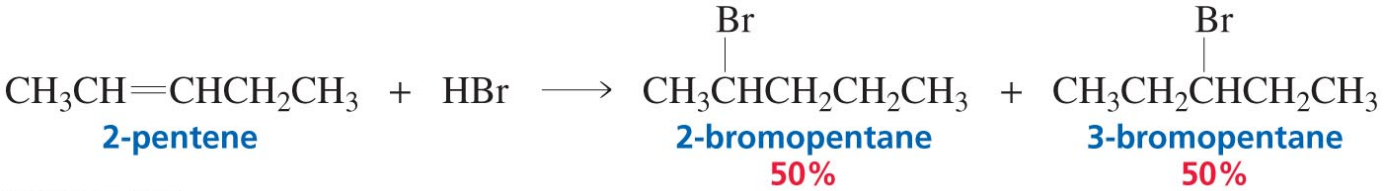
- regioselective



- completely regioselective ~ regiospecific



- not regioselective

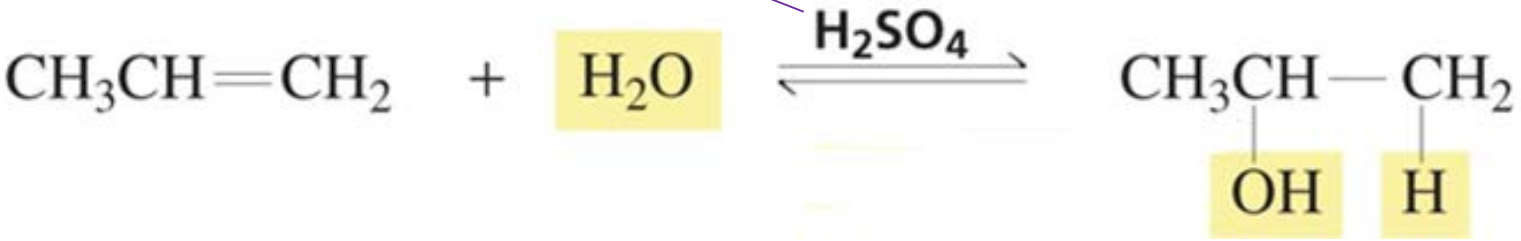


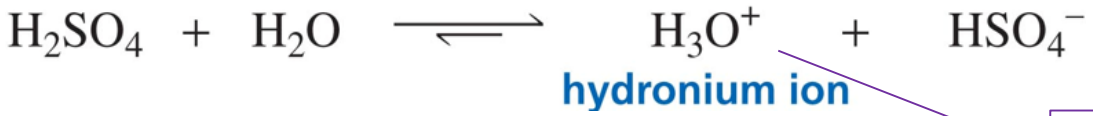
Markovnikov's rule

- Markovnikov in 1870
  - "In addition reactions of HX to alkenes, H bonds to C with more H."
- Restating
  - "In addition reactions to alkenes, E^+ adds so as to form more stable carbocation."

Addition of water [hydration]

- H_2O is a too-weak acid to give electrophilic H^+ or $H^{\delta+}$
- need a catalyst

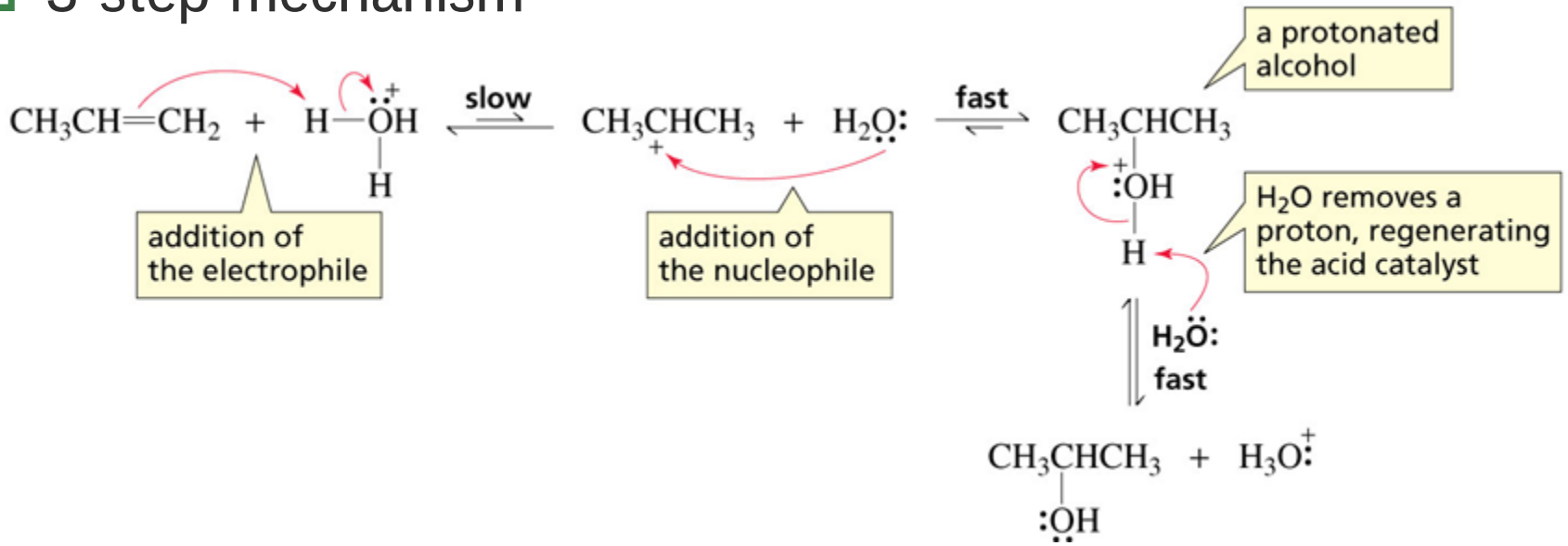




strong acid ~ gives H^+ as E^+

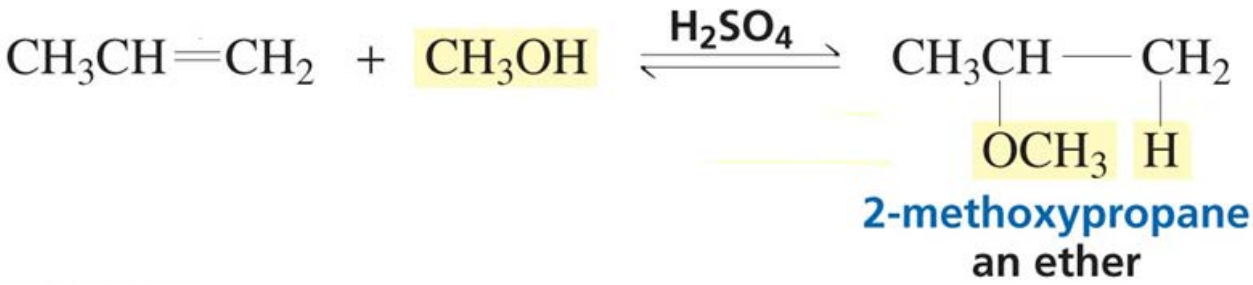
- a hydration [addition of water]
- an acid-catalyzed hydration
- Hydration of alkene gives alcohol.

- 3-step mechanism

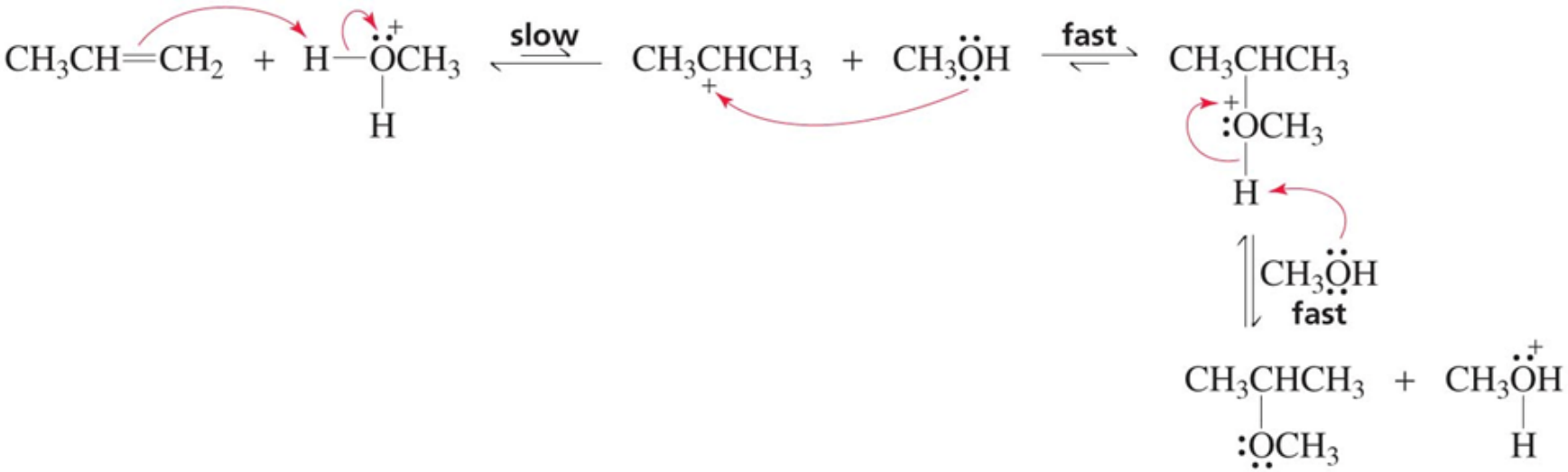


  - the first 2 steps the same to hydrohalogenation
    - obeying Markovnikov's rule
  - 3rd step ~ removal of H^+ ~ H^+ recovered
    - protonated alcohol [ROH_2^+] is a very strong acid ($pK_a < 0$)
  - HSO_4^- as the (competing) Nu:?
    - weaker (base) and smaller amount

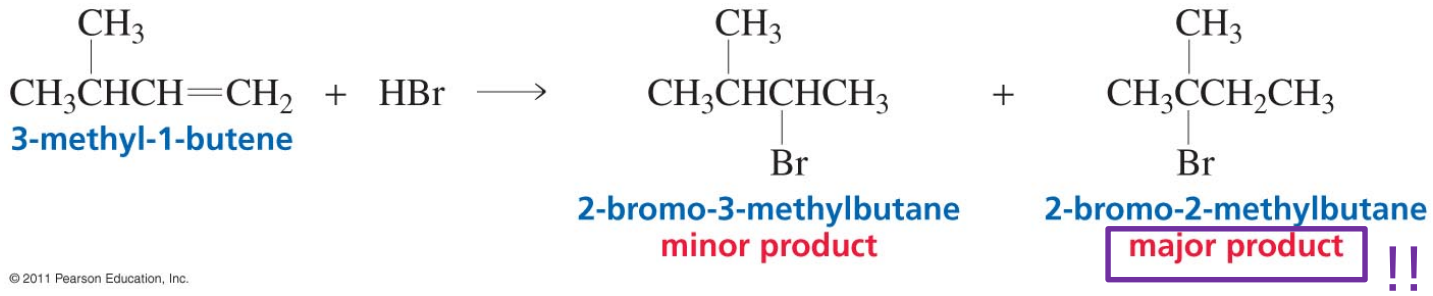
Addition of ROH



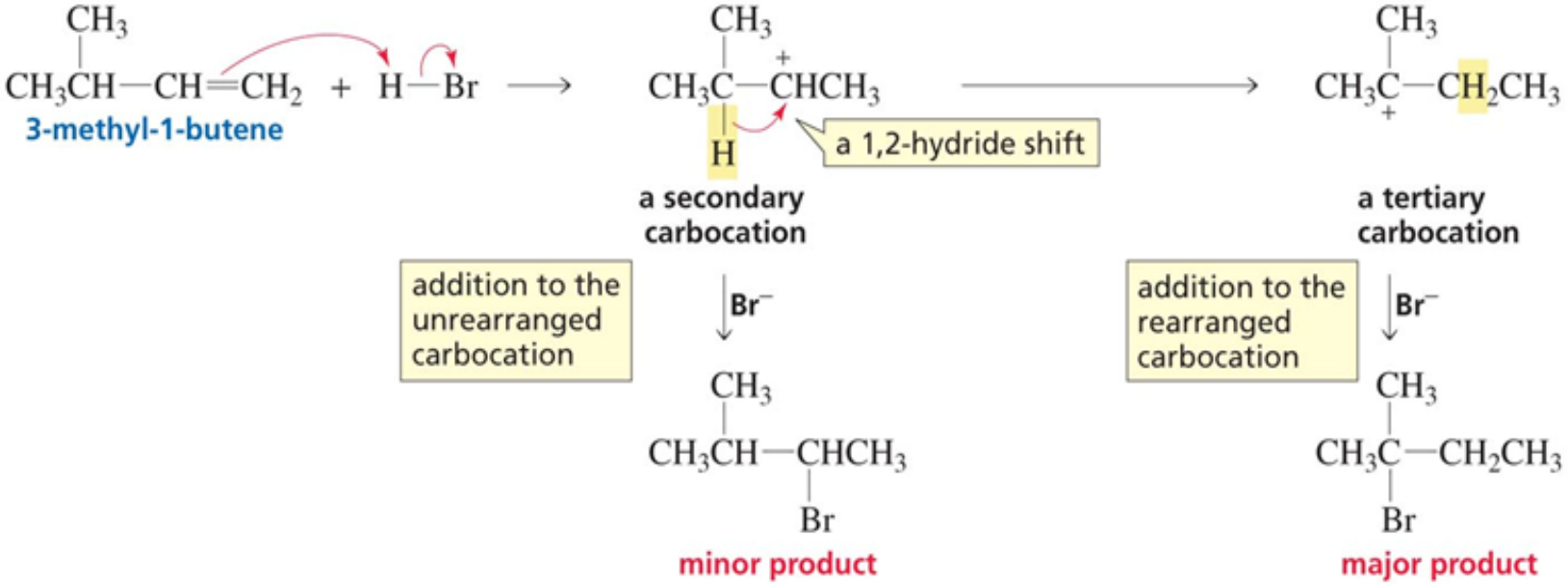
- acid-catalyzed addition of alcohol to alkene gives ether
- mechanism the same to hydration



Carbocation rearrangement

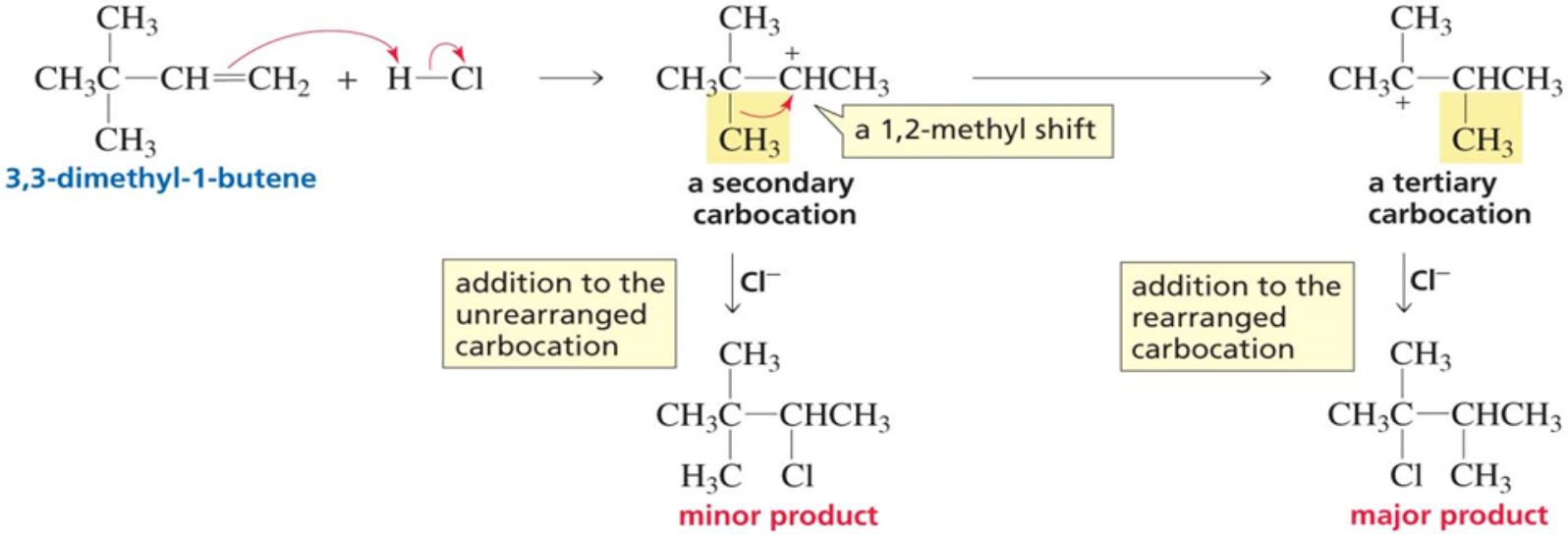


- rearrangement with 1,2-hydride [H:⁻] shift

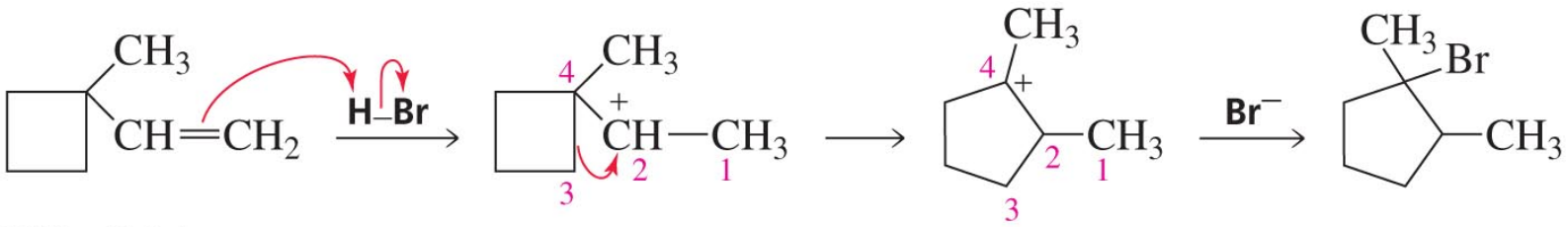


  - to form more stable carbocation

- rearrangement with 1,2-methyl shift

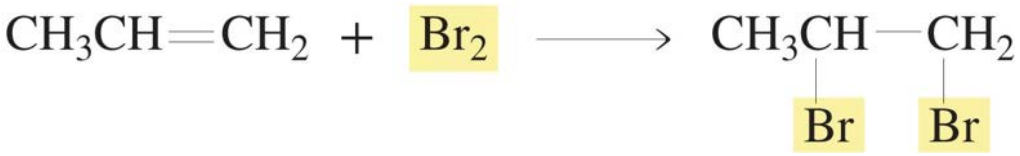


- rearrangement with ring expansion

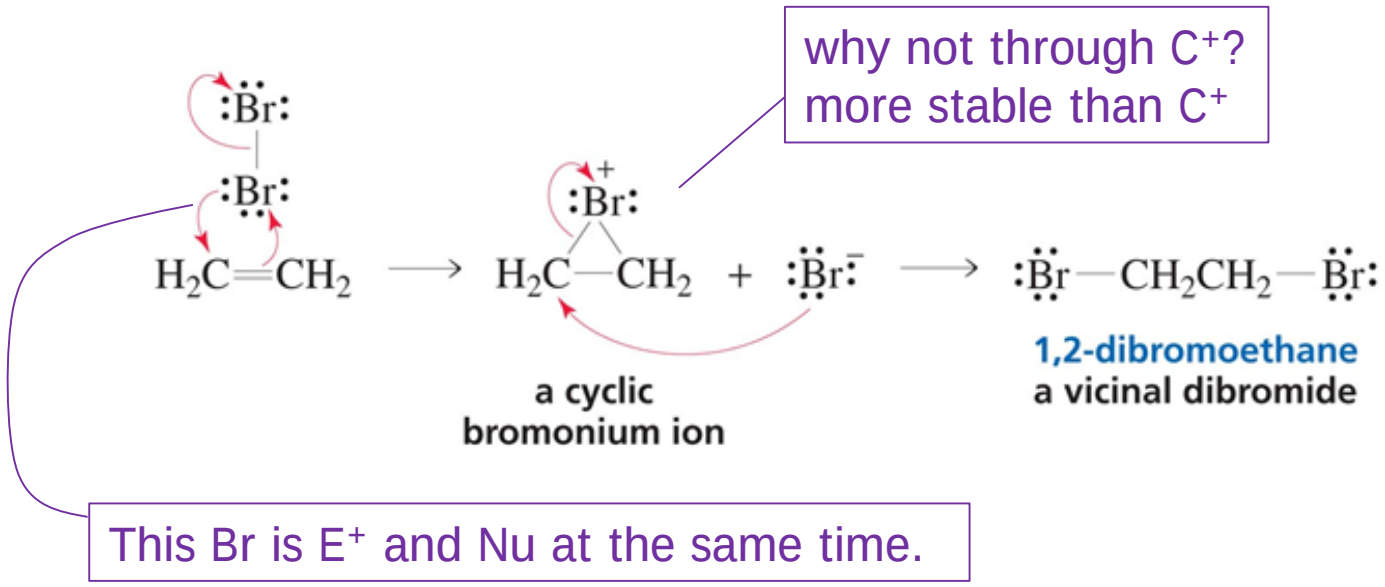


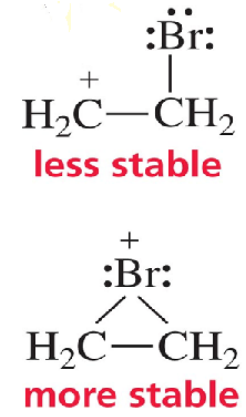
  - to form more stable C^+ and ring

Addition of X_2

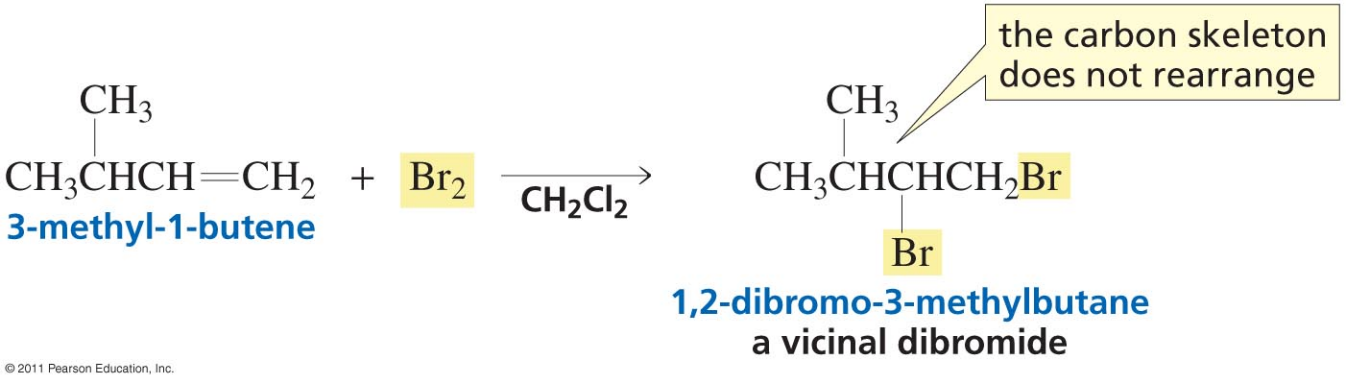


- addition of Cl_2 or Br_2 [chlorination, bromination]
  - in inert solvent like CH_2Cl_2 or $CHCl_3$
- mechanism ~ through cyclic intermediate

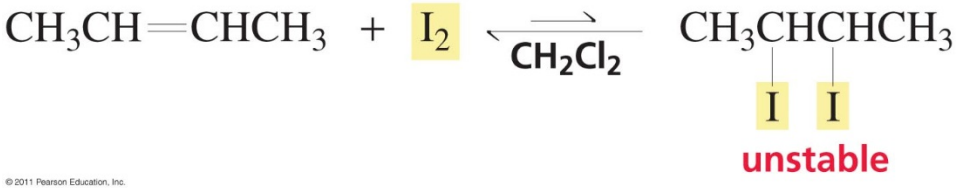




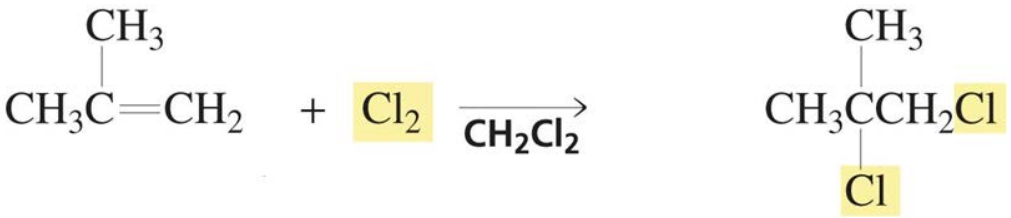
- How did they know that cyclic rather than C^+?
  - retrieving intermediate?
  - observing product



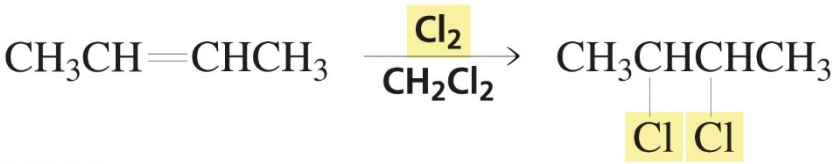
- addition of Cl_2 or Br_2; not F_2 or I_2
  - F_2 is too reactive [explosive]
  - I_2 is not reactive enough



Writing organic reactions

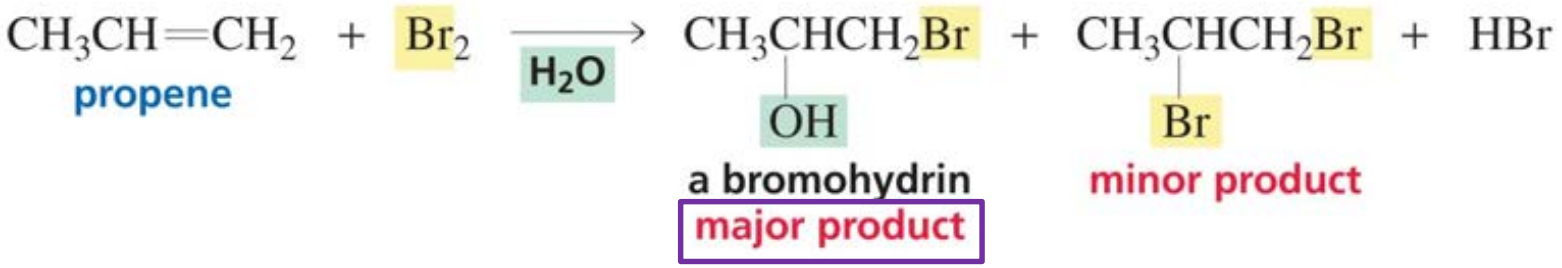


- reactants left, products right
- conditions above or below arrow
  - catalyst
  - solvent, temperature, heat [Δ]
- sometimes substrate (or organic comp'd) only on the left

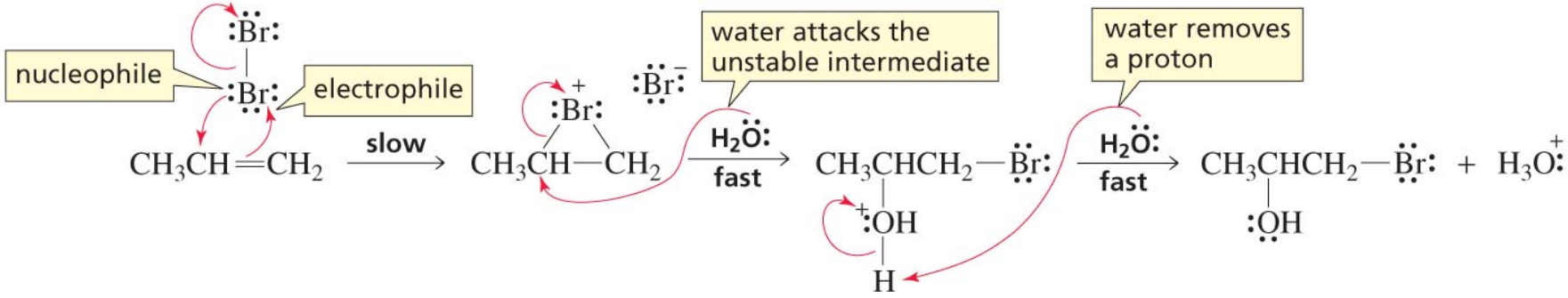


Halohydrin formation

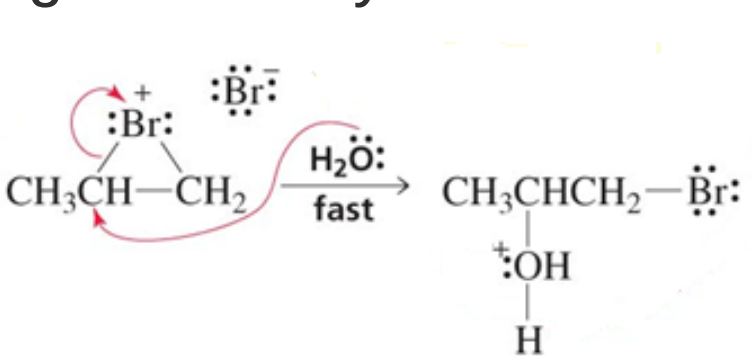
- reacting X_2 in H_2O

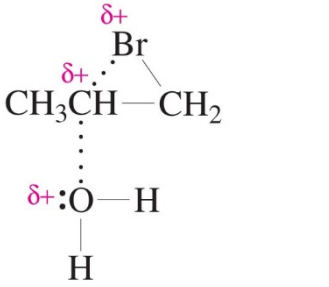


  - H_2O is Nu: awa solvent
    - Water is a nucleophilic solvent; CH_2Cl_2 is an inert solvent.
  - H_2O wins over $Br:^-$ as the Nu:
    - solvent ~ much larger # of molecules

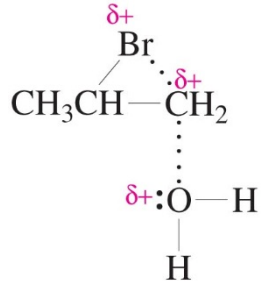


- regiochemistry



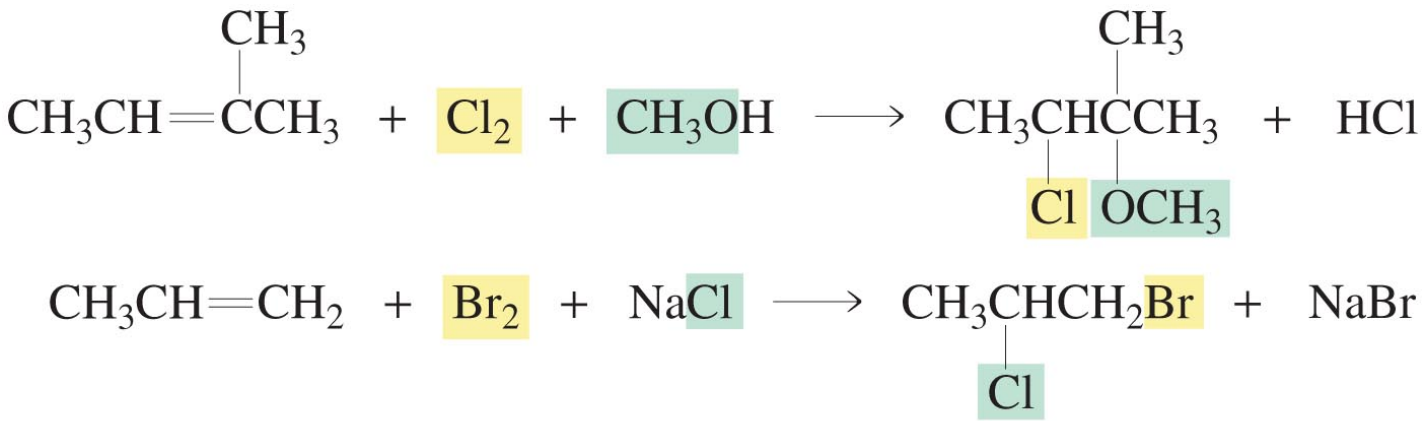


more stable transition state



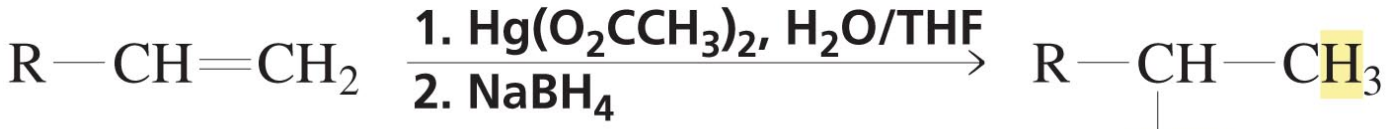
less stable transition state

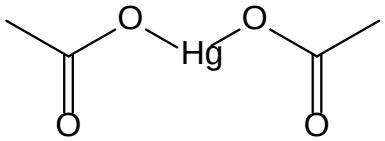
- other Nu's ~ when a larger amount than X_2 is used



Oxymercuration-reduction

- for alcohol synthesis
  - (acid-catalyzed) hydration of alkene
    - low yield, C^+ rearrangement
    - Still, industrial method
  - oxymercuration-reduction
    - high yield, no rearrangement
    - lab-preferred
- 1-pot 2-step reaction



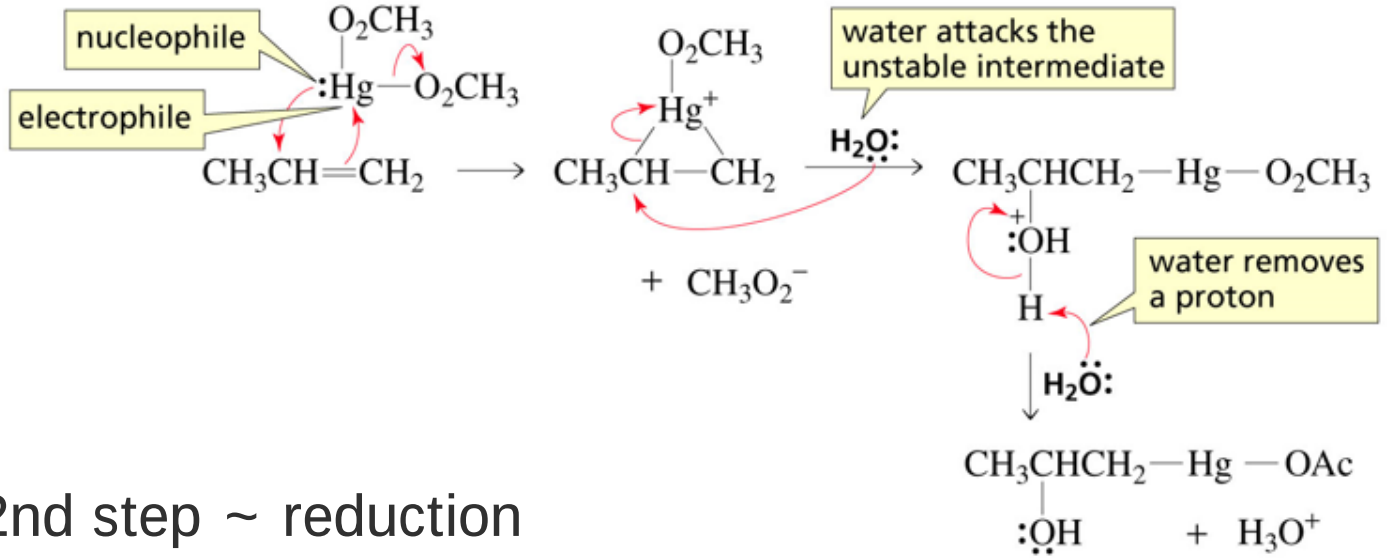


= $Hg(OC(O)CH_3)_2$ = $Hg(OAc)_2$

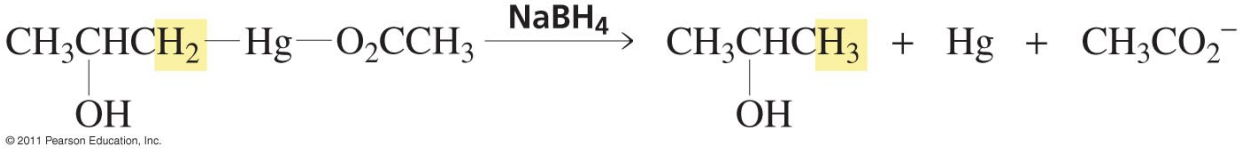
mercuric acetate

- mechanism
  - 1st step ~ same to X_2/H_2O

typo: O_2CH_3 should be $OC(O)CH_3$ or OAc



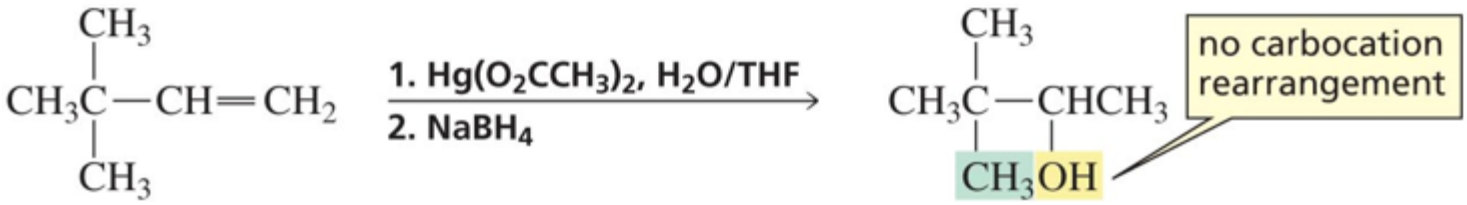
  - 2nd step ~ reduction



oxidation ~ adding C-O (C-N, C-X) bond and/or removing C-H bond
reduction ~ adding H and/or removing O (N, X)

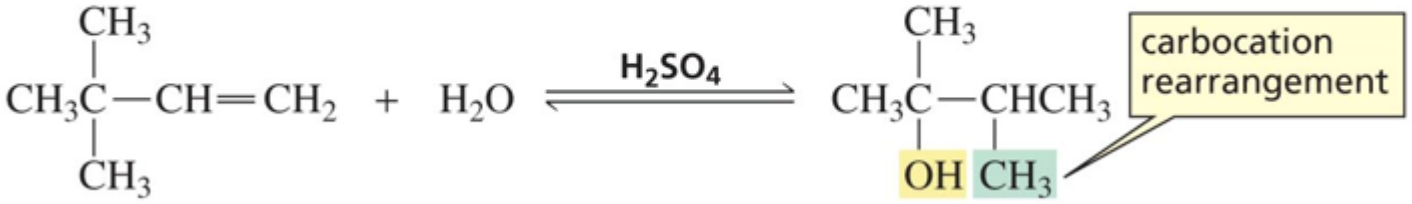
- gives the same product as hydration
  - Markovnikov alcohol

oxymercuration-reduction

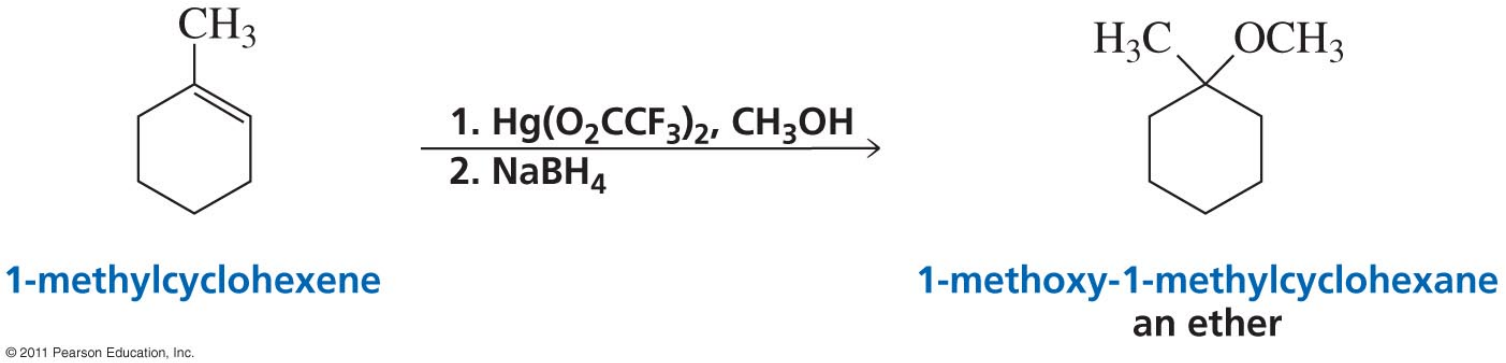


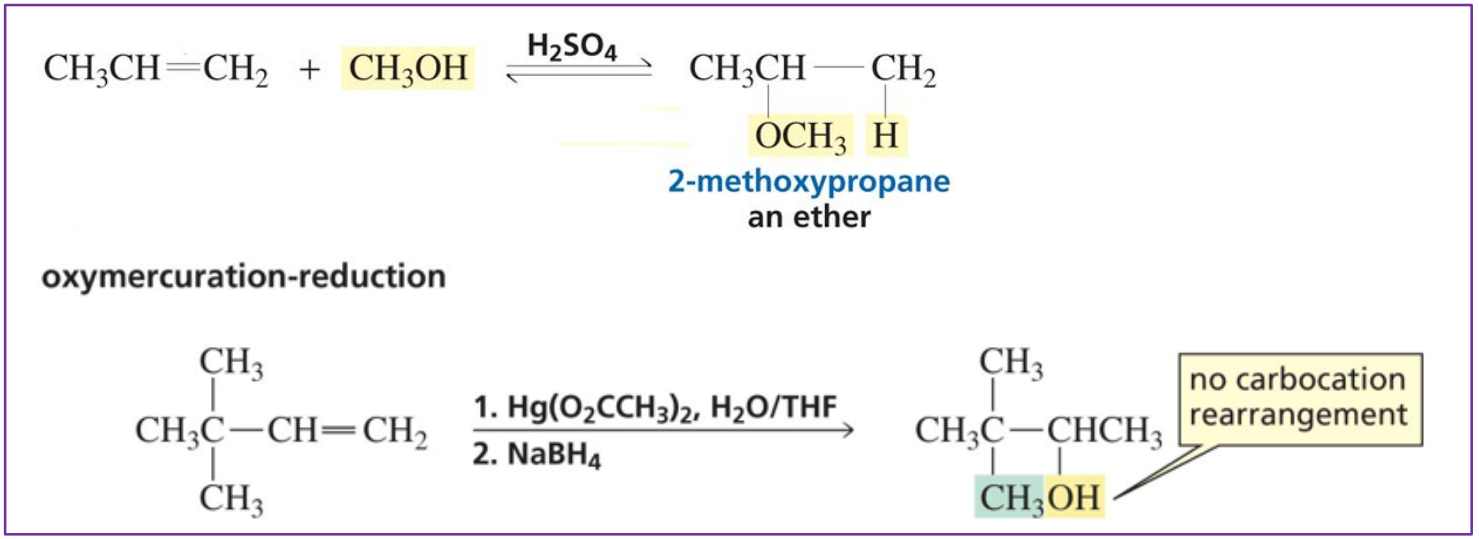
  - if C^+ rearrangement possible in hydration ~ different product

acid-catalyzed addition of water



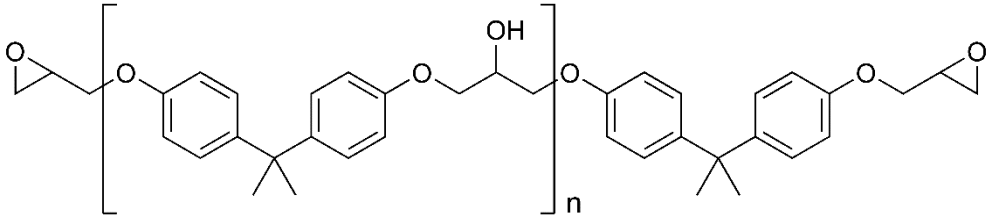
- alkoxymercuration-reduction
  - gives ether



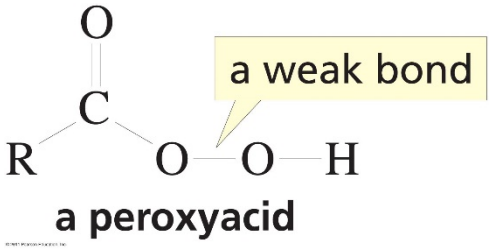


Addition of peroxyacid

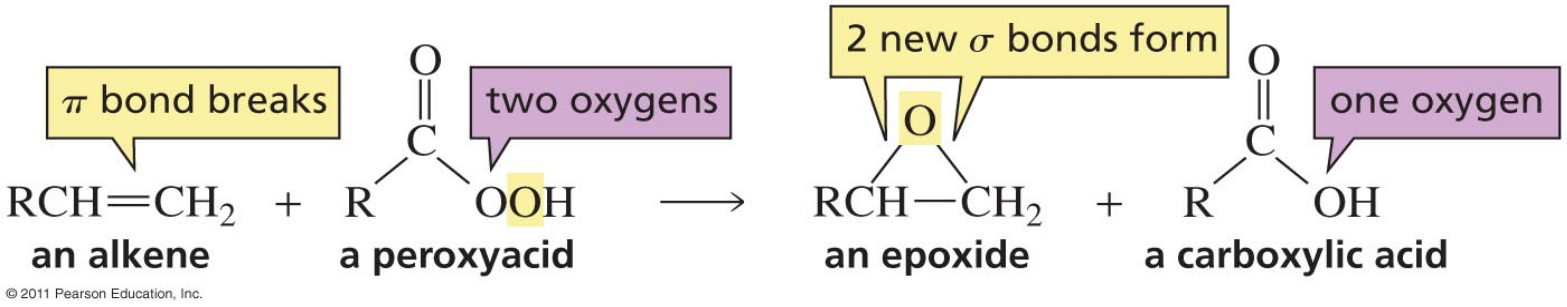
- to prepare epoxide ring
  - epoxide ~ 3-membered cyclic ether ~ reactive
  - 'epoxy' resin ~ cured



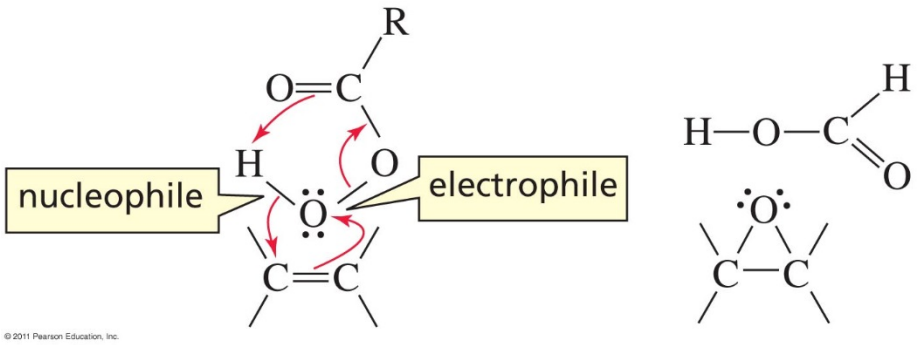
- peroxyacid [hydroperoxide]



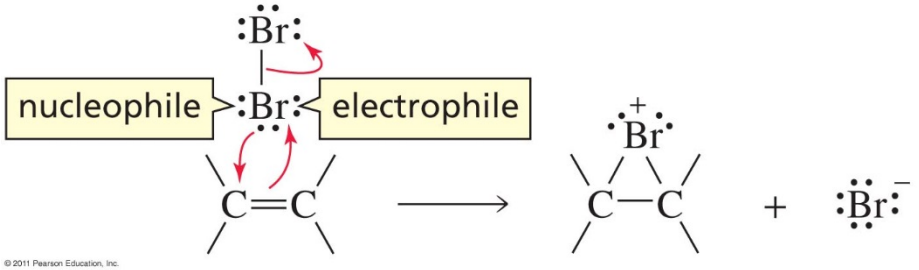
- addition of hydroperoxide

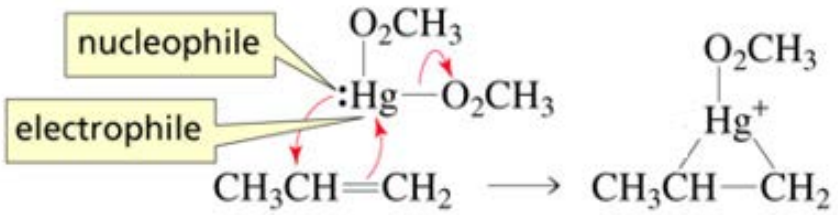


- mechanism ~ ‘concerted’



  - ‘concerted’ mechanism we have seen

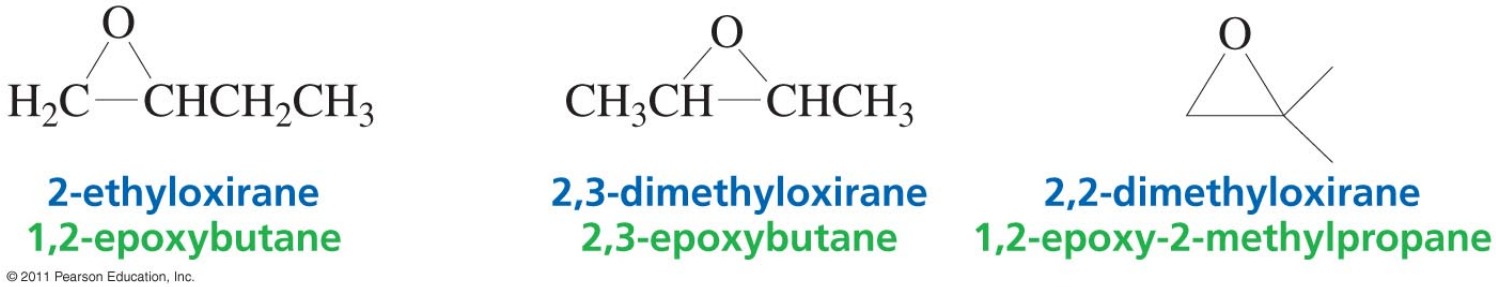




- nomenclature of epoxide ring
  - common name ~ ‘oxide’

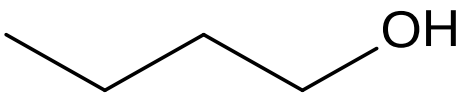
    - -ide for anion?
      - -OCH_3 methoxy; $CH_3CH_2O^-$ ~ ethoxide

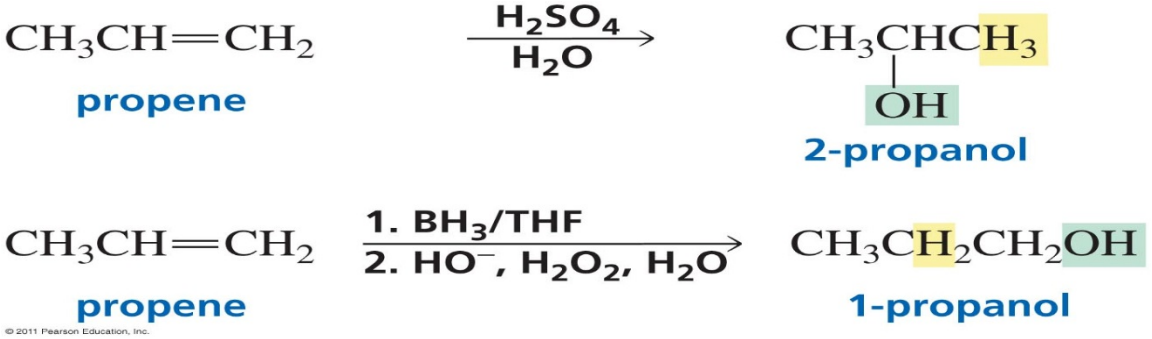
  - IUPAC name ~ ‘oxirane’ or ‘epoxy-’



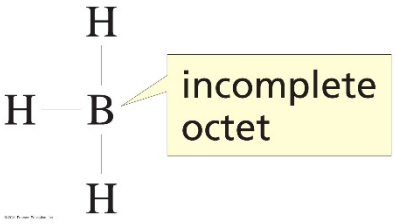
Hydroboration-oxidation

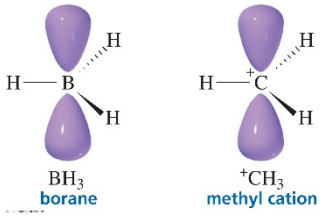
- gives 'anti-Markovnikov alcohol'
  - 'terminal' or primary alcohol
  - Hydration or oxymercuration-reduction gives not.



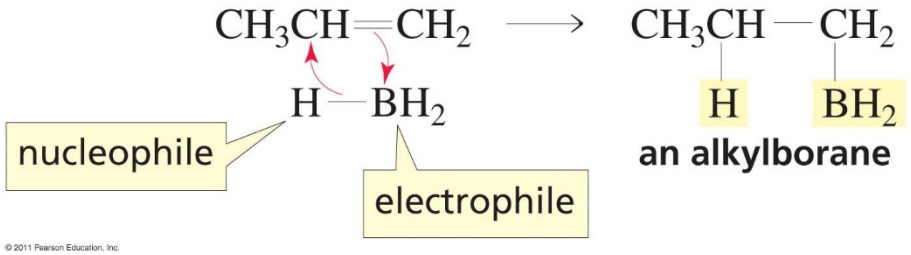


- borane, BH_3
  - Lewis acid ~ with empty orbital ~ E^+



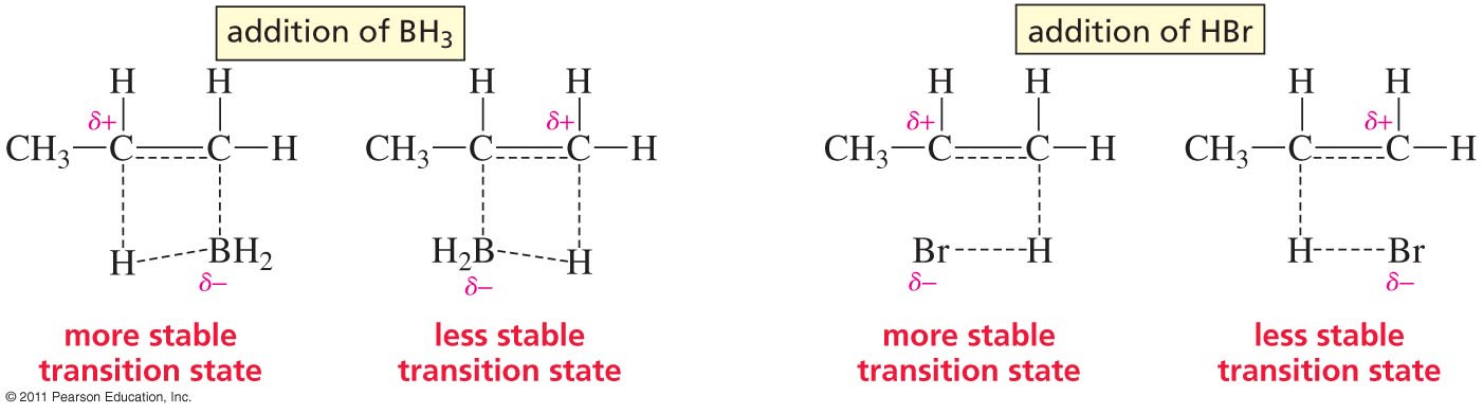


- mechanism: 1st step (actually, 1-1)



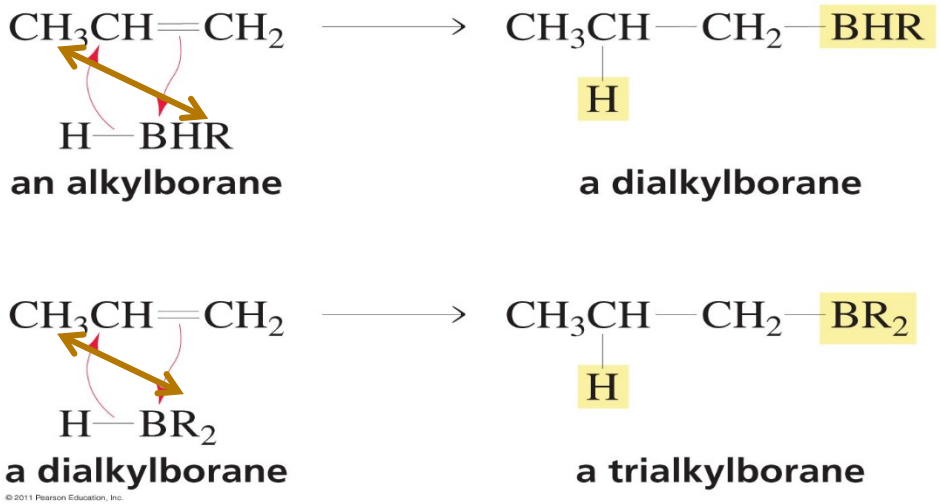
- why B on less-substituted C?

Explanation based on EN:
B(2.0)-H(2.1) → $B^{\delta+}$ is E^{+}
not quite correct



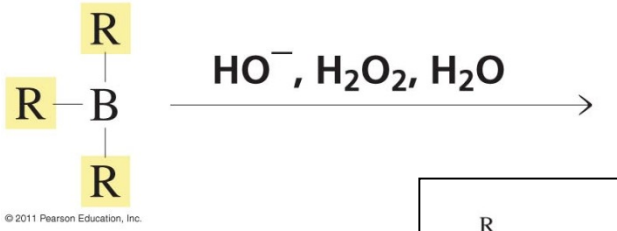
- through 4-center TS‡ not thru C^{+} ~ to explain the result
- actually, obeys (re-stated) Markovnikov's rule

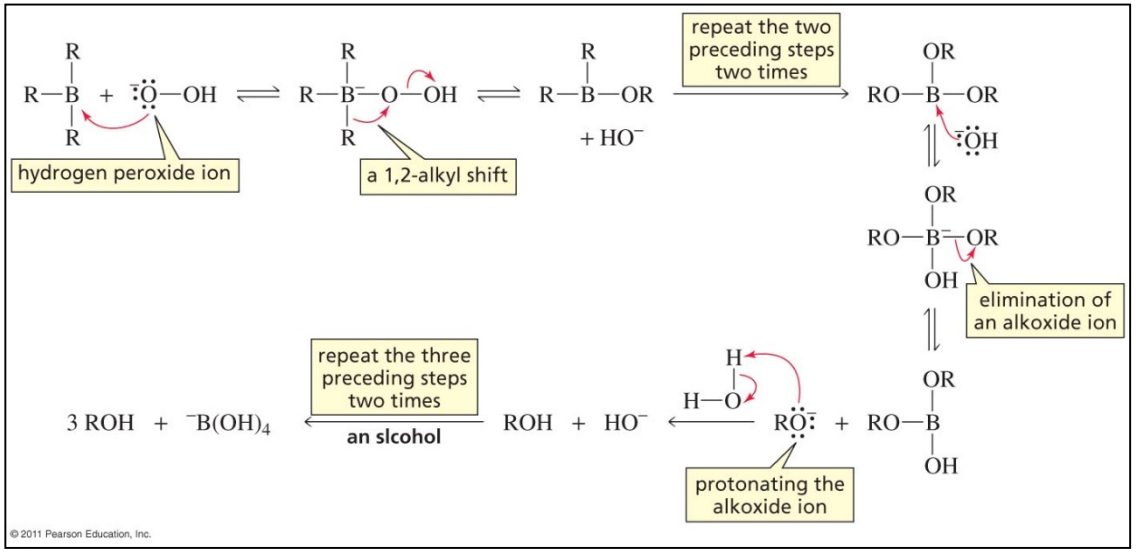
- mechanism: step 1-2 (and 1-3)
  - addition of alkyl borane RBH_2 (and dialkyl borane R_2BH)



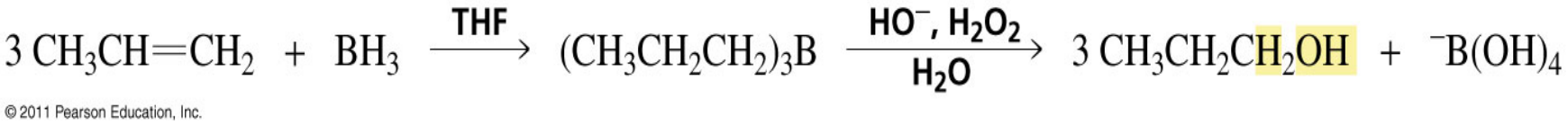
  - 2nd reason for 'anti-Markovnikov addition' ~ steric hindrance
  - Why B on less-substituted C?
    - (1) more stable C^+-like $TS^‡$ (2) steric hindrance
    - (0) BH_3 is a Lewis acid (accepting e on B)

- mechanism: 2nd step ~ trialky borane to (three) alcohols





- general:



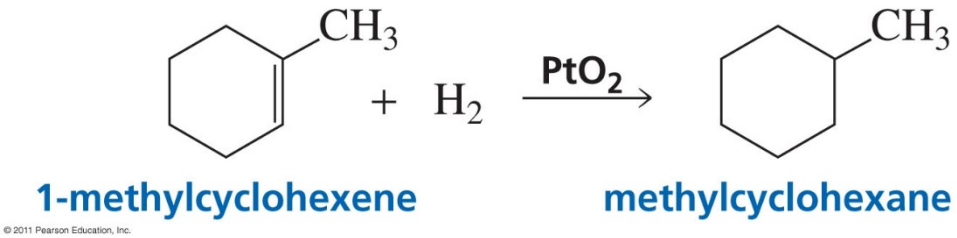
Addition of H_2 [hydrogenation]

- catalytic addition of H_2 to = → saturation
  - need catalyst ← strong H-H

$$CH_3CH{=}CHCH_3 + H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_3$$

2-butene → butane

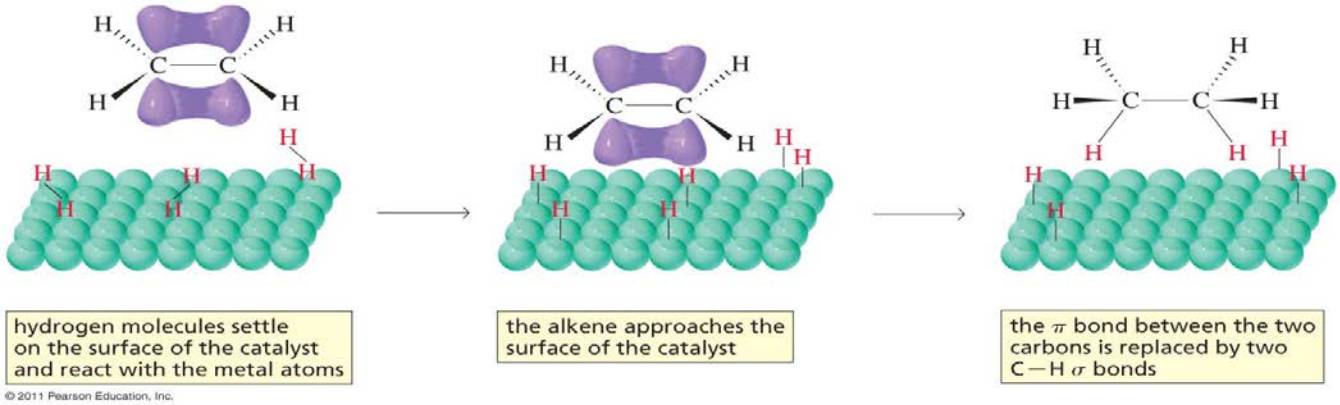
'palladium on carbon (black)'



1-methylcyclohexene → methylcyclohexane

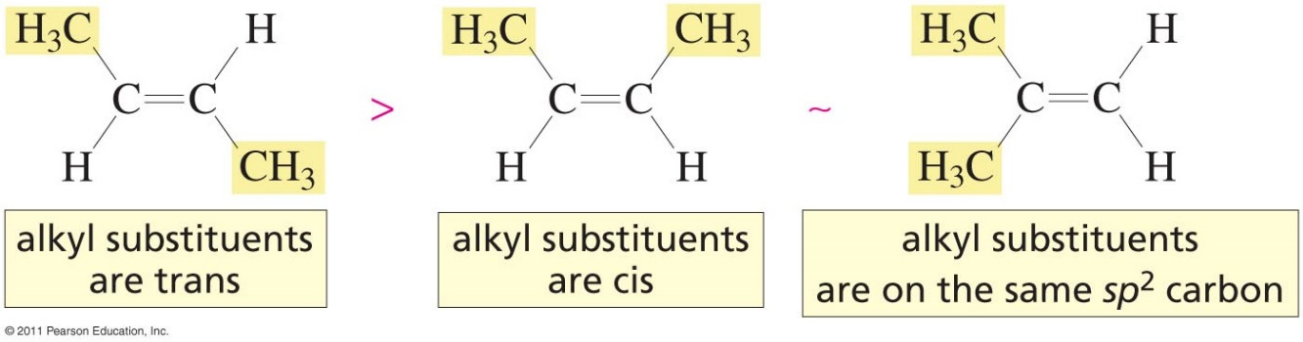
'Adams catalyst'

- mechanism ~ not understood ~ possibly radical

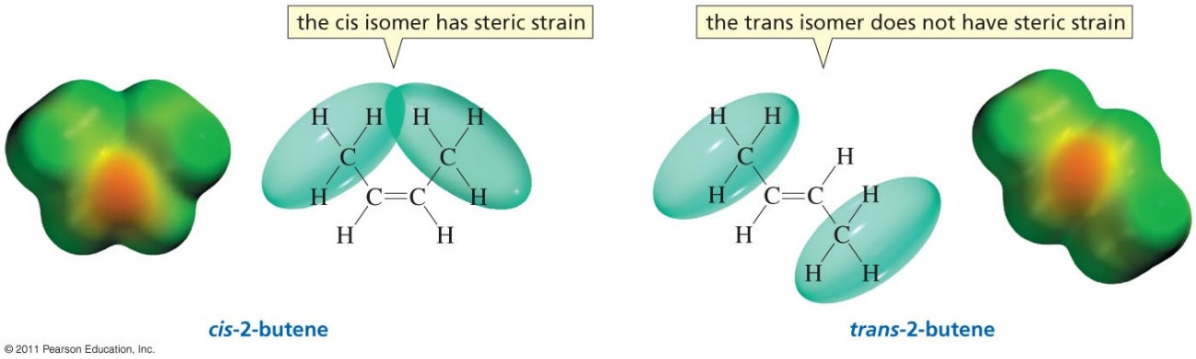


(Relative) stability of alkenes

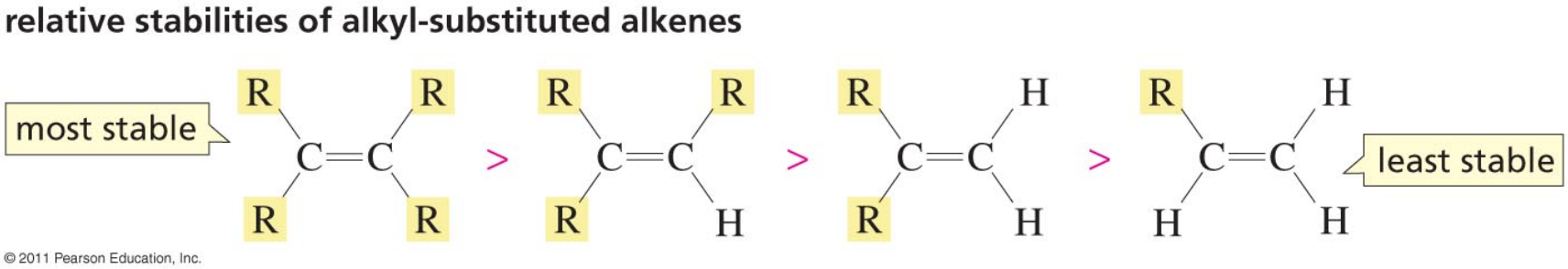
- trans-disubstituted alkenes is more stable than cis-

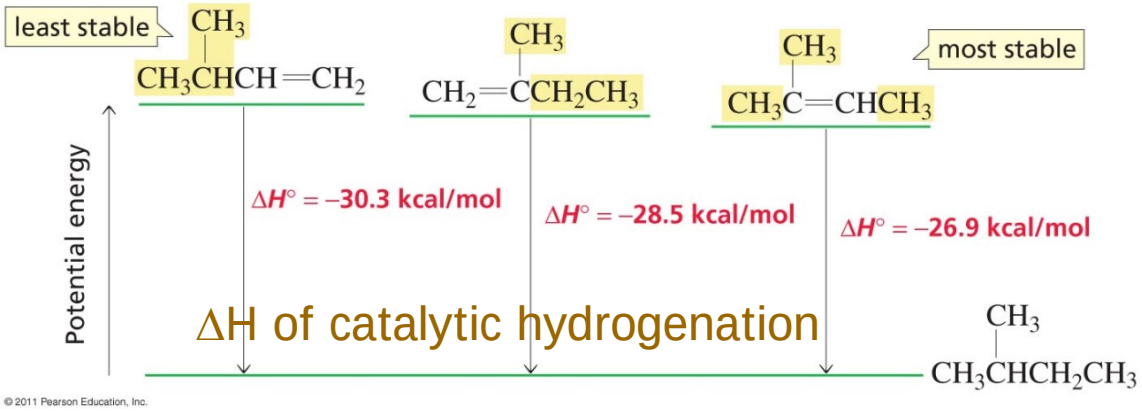


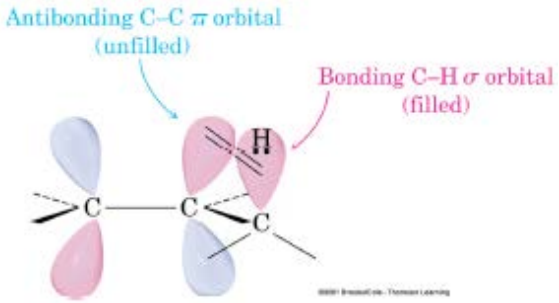
- steric hindrance



- More substituted alkene is more stable.

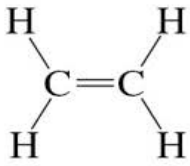
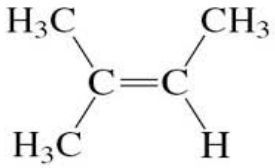
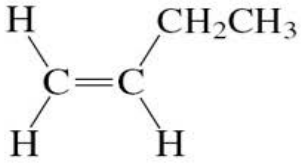
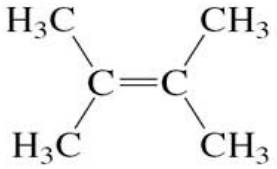
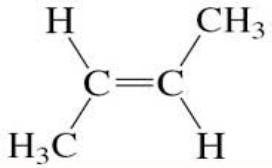






  - difference not huge
    - hyperconjugation ~ effect not as large as in C^+
    - steric hindrance

- stability and reactivity
  - relative reactivity to Br_2 addition

Alkene	Relative Rate	Alkene	Relative Rate
	1		1×10^5
	1×10^2		2×10^6
	2×10^3		

  - high nucleophilicity
  - higher hyperconjugation effect for C^+

학봉 김성일이 스승 퇴계 이황에게 공부하는 방법을 묻자, 이렇게 답했다.

"학문은 그저 익숙하도록 읽는 것뿐이다. 글의 뜻을 알았다 한들, 익숙하지 못하면 금방 잊어버리게 되어 마음에 간직할 수 없을 것이다.
반드시 배우고 난 뒤에 익숙해질 때까지 공부를 해야 마음에 간직할 수 있으며, 또 흠씬 젖어드는 맛도 느낄 수 있을 것이다."