

Ch 6

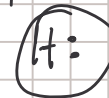
11/9/2005

Note Title

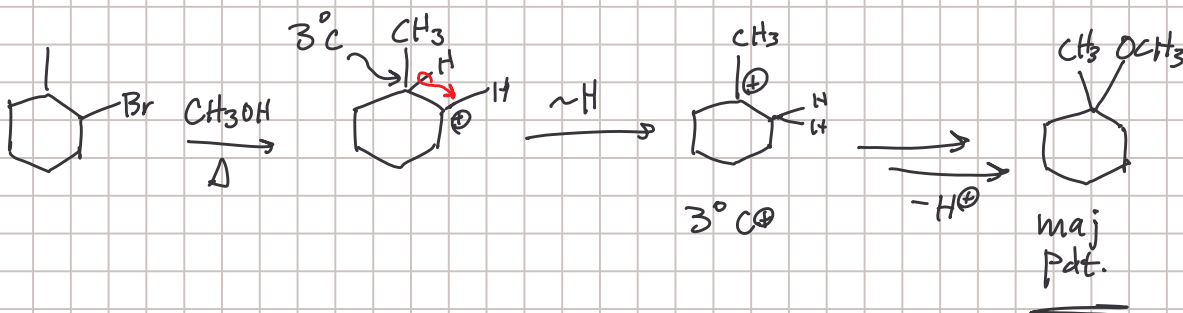
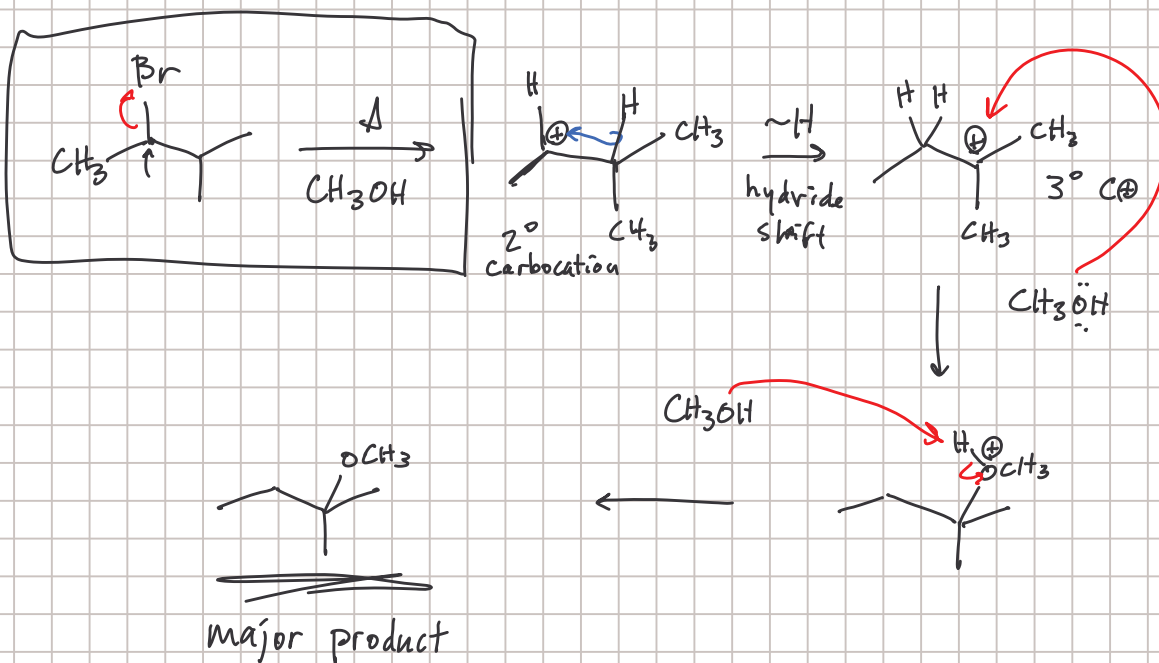
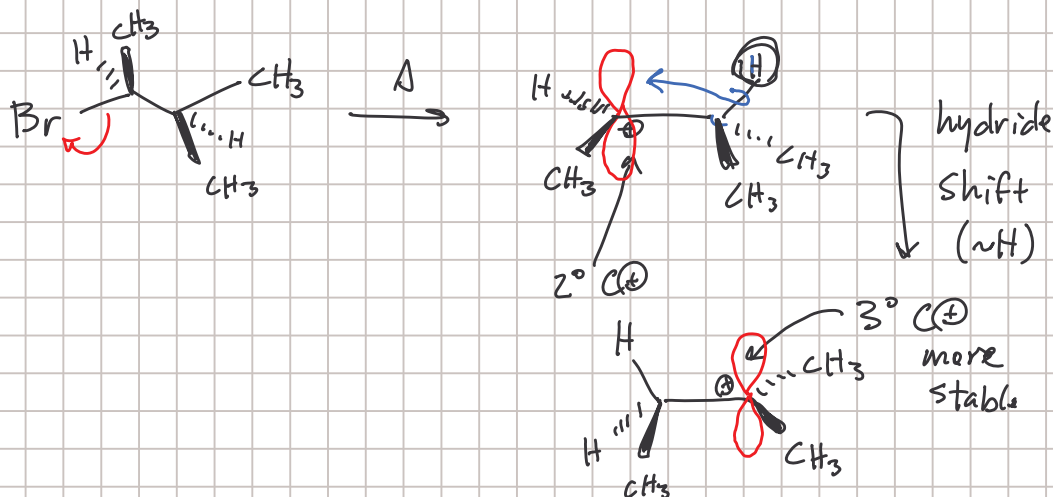
~~11/8/2005~~

S_N1 rearrangements

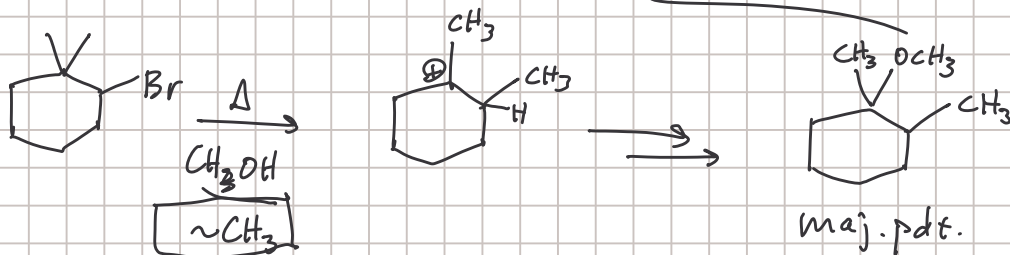
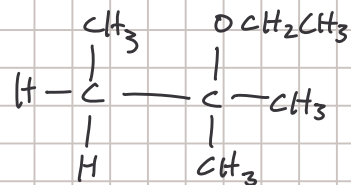
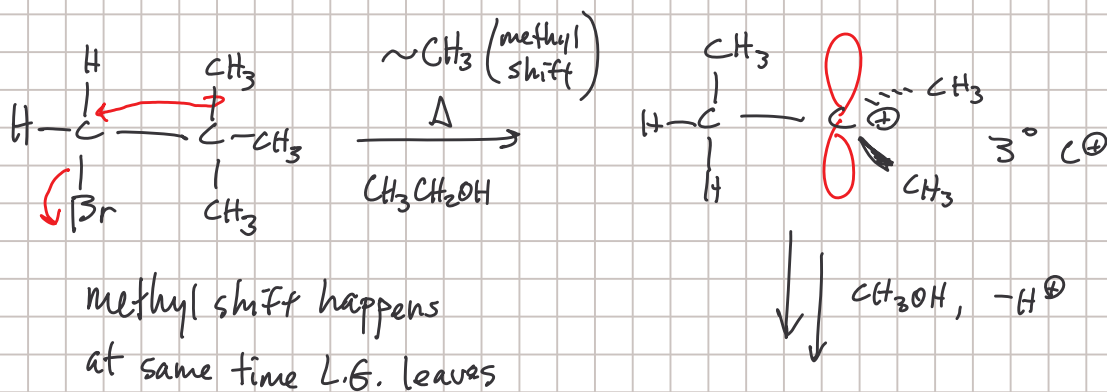
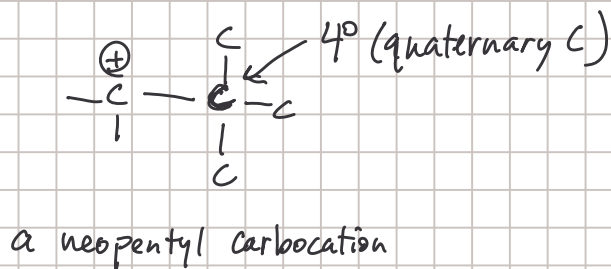
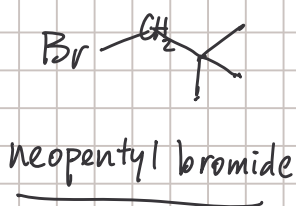
hydride



① C⁺ next to 3° will undergo hydride shift



② neopentyl carbocations undergo methyl shift



Nuc:

S_N1
 strength
 unimportant
 (usu. weak)
 CH₃OH, CH₃CH₂OH
 common

S_N2
 must be strong!
 Br⁻, OH⁻, OCH₃, etc.

substrate: 3° > 2°
 (1° = mix. of rearrangements)

CH₃X > 1° > 2°
 (3° too hindered)

solvent: S_N1
 polar (usu. protic)
 solvent required
 H₂O, CH₃OH, CH₃CH₂OH

S_N2
 most work fine.

kinetics: rate = k [RX]
 1st-order
 unimolecular

rate = k [RX][Nuc]
 2nd order
 bimolecular

stereochem: racemization
 (mix. of retention & inversion)

Complete inversion

rearrangements: common

impossible (no C[⊕])

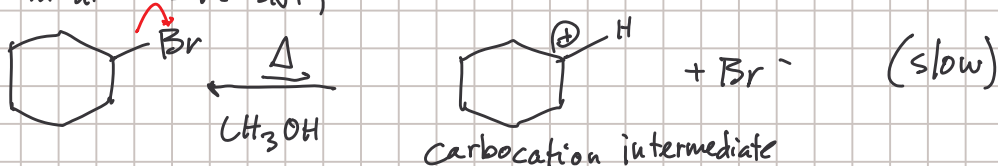
other: heat and/or
 AgNO₃ required
 for ionization

Eliminations - loss of 2 atoms/groups from substrate
 - new π bond formed

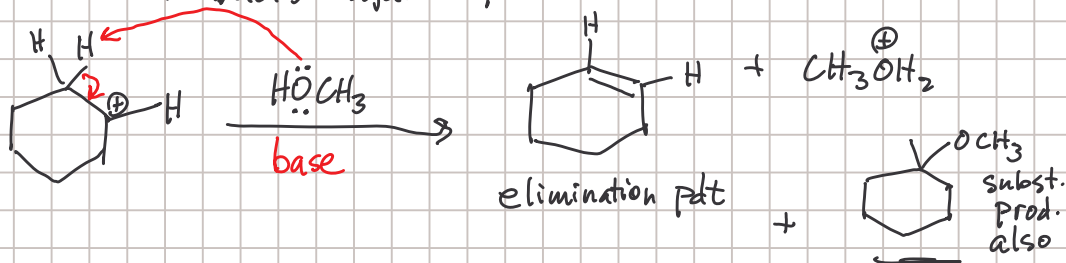
E1 1st-order elimination * usu. occurs in
 competition with S_N1

(S_N1 & E1 normally happen together)

① ionization (like S_N1)

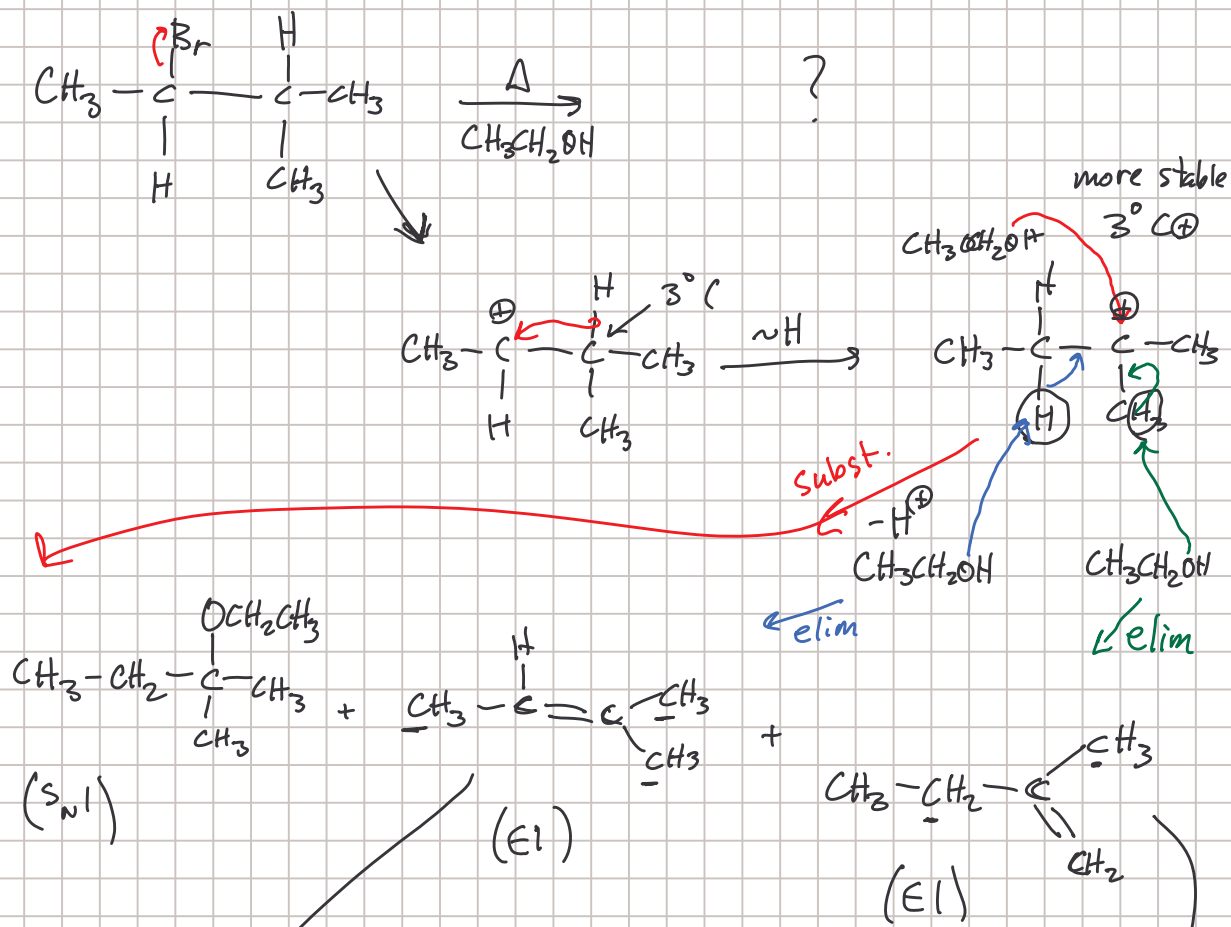


② Solvent abstracts adjacent proton to make π bond



S_N1 : Solvent = nucleophile (attacks C^+)

$E1$: Solvent = base (attacks H)



In eliminations, the highest-substituted double bond is favored.

(#C attached to $C=C$)

trisubstituted favored over disubst.

