

(4) Today

Sections 11.1 - 11.6: Substitution Reactions

Sections 10.5, 17.6: Alcohols in Nucleophilic Substitution Reactions

(6) Second Class from Today

Sections 11.7 - 11.11: Elimination Reactions

Section 17.6: Alcohols and Elimination Reactions

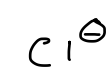
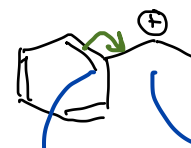
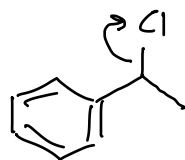
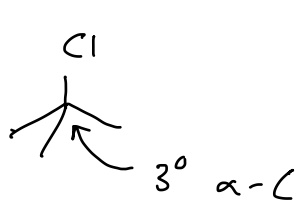
Next Class (5)

Sections 11.7 - 11.11: Elimination Reactions

Third Class from Today (7)

Chap 12: Mass Spectrometry and Infrared Spectroscopy

High degree of substitution on α-C or electron delocalization to promote C⁺ stability



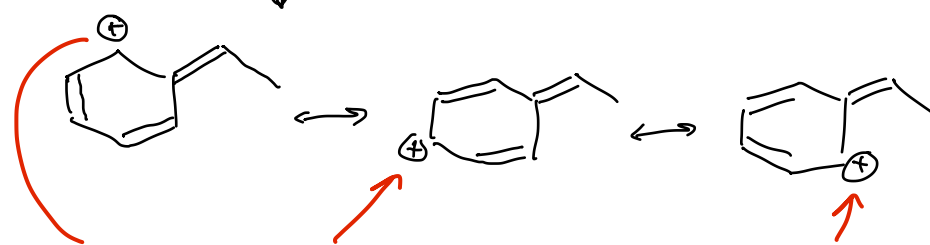
this C⁺ is an empty p orbital
π bonds are made from overlapping p orbital

Protic Solvents

stabilizes transition state
deactivates nucleophiles

Good Leaving Group

Leaving group has to leave...

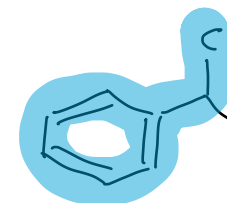
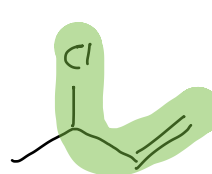


Nucleophiles do not attack here

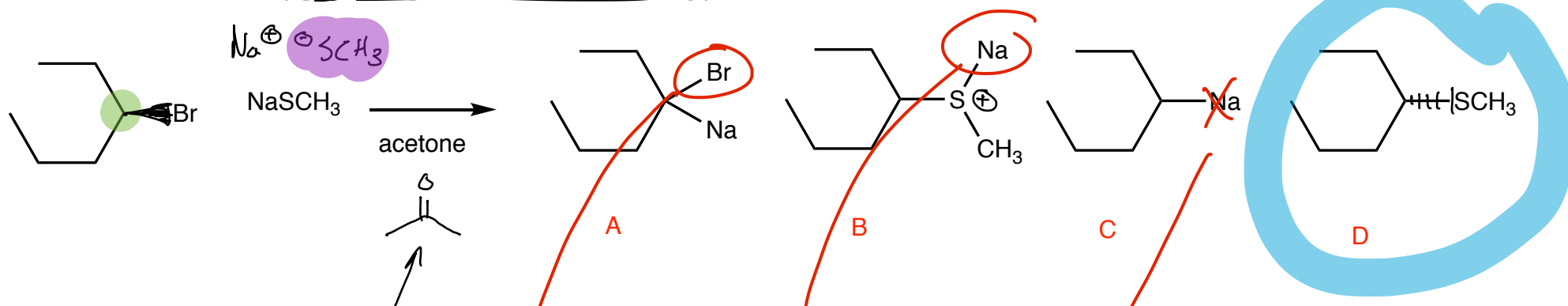
Weak Nucleophiles

Nucleophiles that wait around for the C⁺ to form.

S _N 2	S _N 1
Two molecules collide in a 1 step mechanism	Dissociation of one molecule controls the rate of a two step reaction
bimolecular rate determining step	unimolecular rate determining step
stereochemistry is inverted	stereochemistry is a mixture of inverted and retained (not inverted)
methyl, 1°, 2° α - C	3° alkyl 2° allylic/benzylic substrates
better the nucleophile the faster the reaction	the nucleophile is not involved in the rate determining step
good nucleophile	So so nucleophile
polar aprotic solvent	polar protic solvent



Reactions: S_N2 (ignoring stereochemistry)



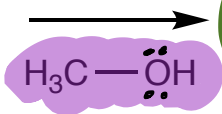
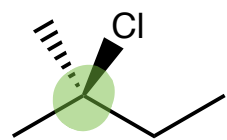
- Find α -C
- Find nucleophile do substitution

leaving group has to leave

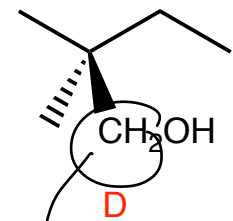
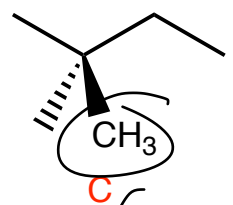
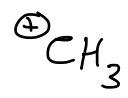
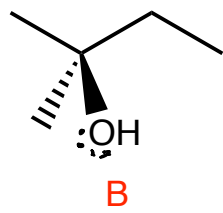
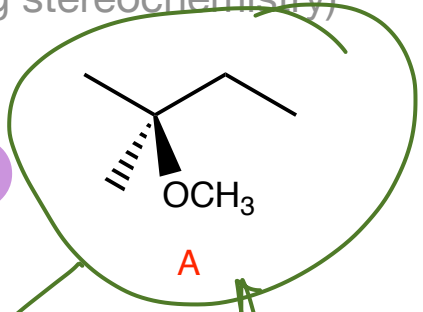
If sulfur gave away e^- density Na^+ wouldn't be attracted to it

Na^+ has no valence e^- 's so can't be nucleophile

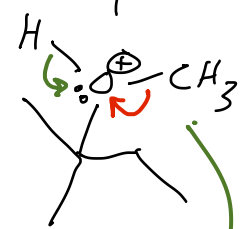
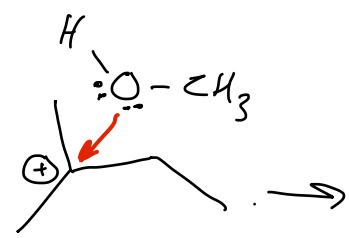
Reactions: S_N1 (not ignoring stereochemistry)



Solvent is the nucleophile



2-2
nucleophile substitution

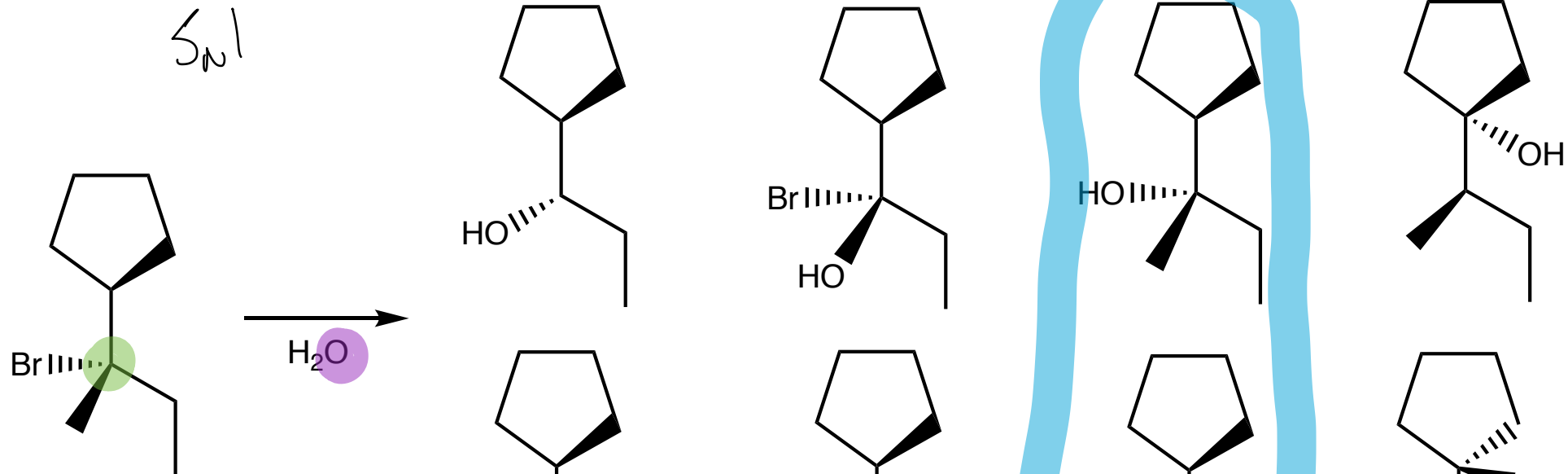


where did the H⁺ go? H⁺ easy to transfer to CH₃OH

methyl c⁺... NO methyl react with solvent... less likely, not as ⊕ as H

where did the H go?
C had not e⁻ to donate... all e⁻'s were in σ-bonds

Reactions: S_N? (not ignoring stereochemistry)



analyze α-C

3° α-C

analyze solvent

protic

nucleophile

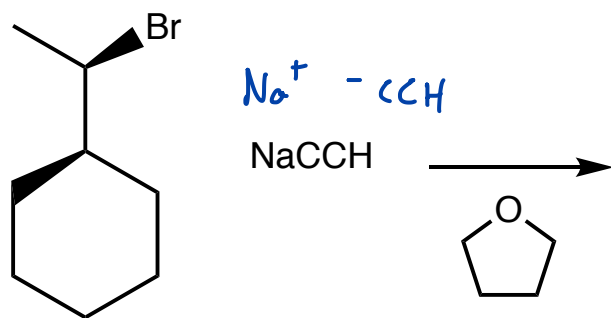
A
CH₂ was lost

B
leaving group never left

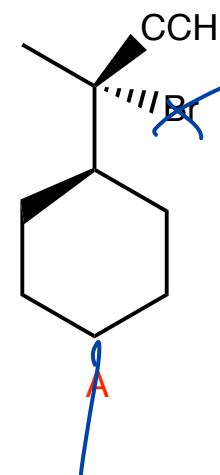
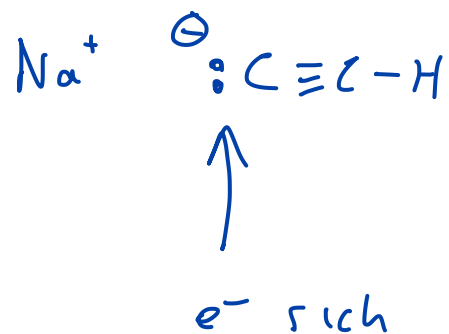
C
H⁺ went to a solvent molecule
all because 3° c⁺ on chiral C

D
rearrangement from 3° c⁺ to 3° c⁺ is unlikely

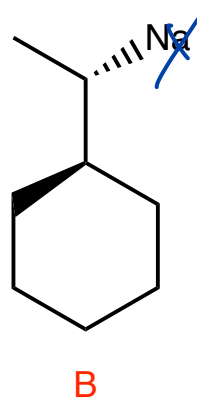
Reactions: S_N2 (not ignoring stereochemistry)



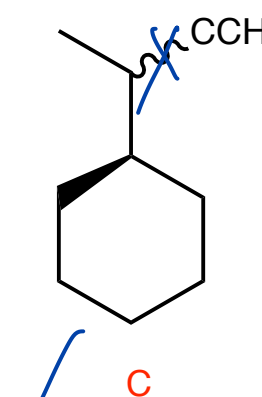
$\alpha-C$ 2° so-so
 solvent aprotic
 nucleophile very σ rich



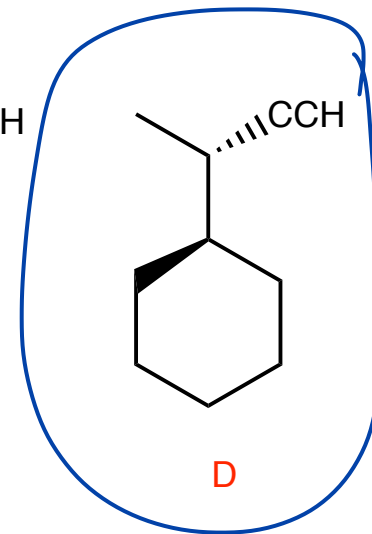
LG
 didn't
 L



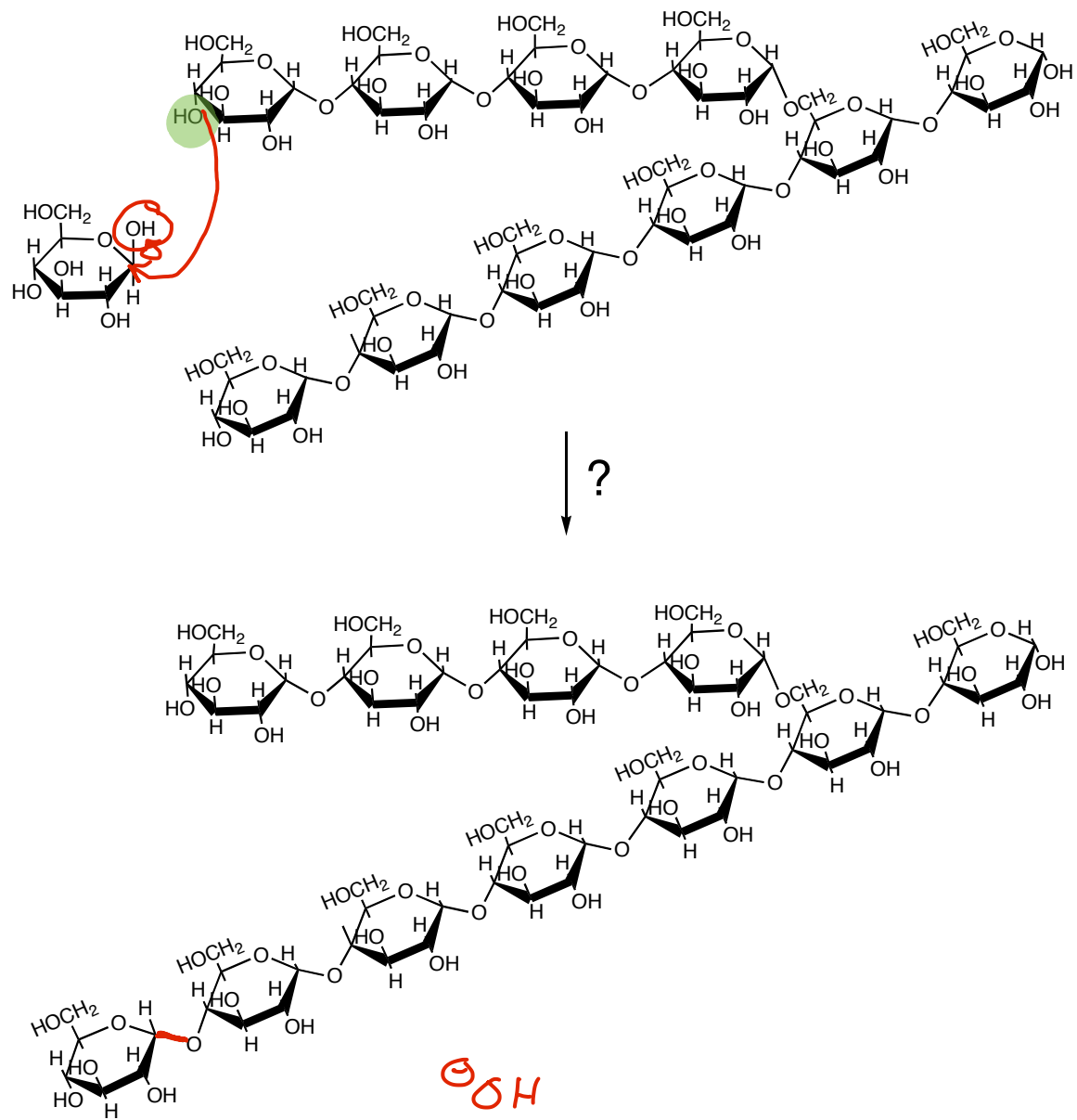
Na^+
 no
 valence e^-
 not
 nucleophilic



S_N2
 occurs
 with
 inversion -
 only 1 stereoisomer
 forms



Why?



Biochemical Conversion of a Bad Hydroxyl Leaving Group to a Good Phosphate Leaving Group

