

Today

Next Class

Chap 9 Substitution and Elimination

Sections 9.3 & 9.4
Factors that affect S_N2 and S_N1

Section 9.1
 S_N2 Introduction

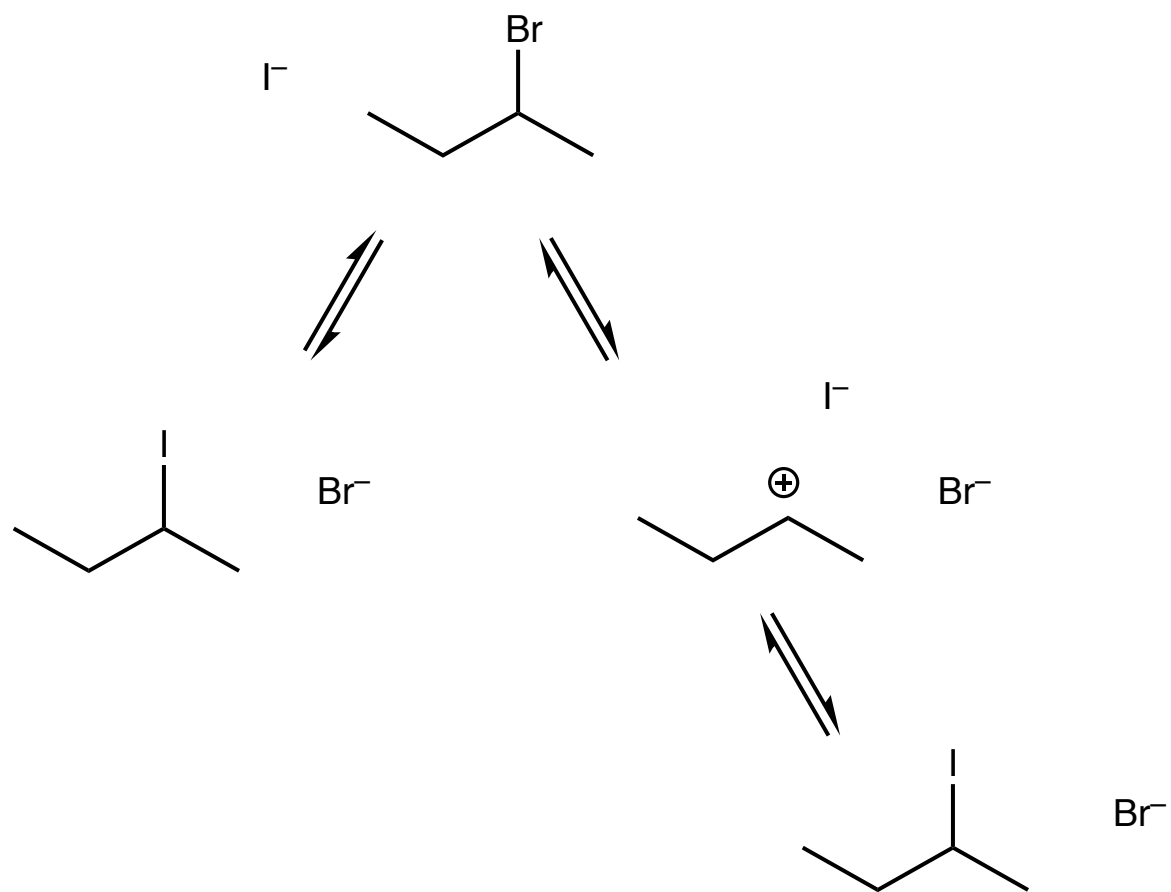
Section 9.5
Competition between S_N1 and S_N2

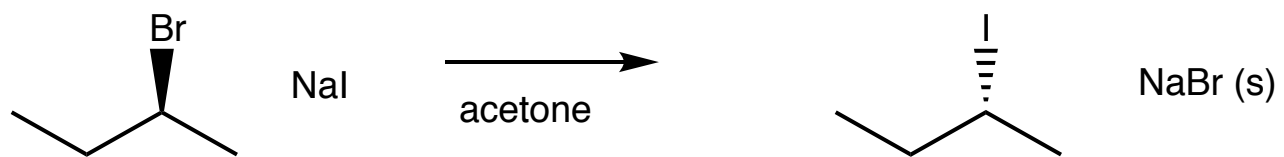
Section 9.3
 S_N1 Introduction

Section 9.6
Elimination Reactions

Sections 9.3 & 9.4
Factors that affect S_N2 and S_N1

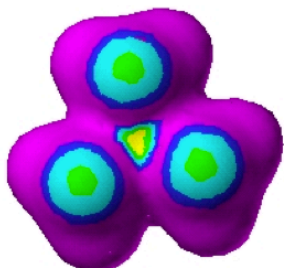
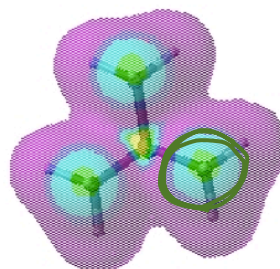
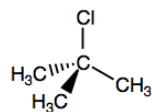
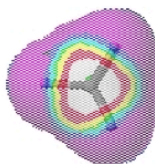
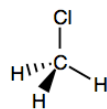
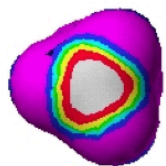
Review session in Wilson 134 and Zoom on 12/2 from 8:00 - 9:30





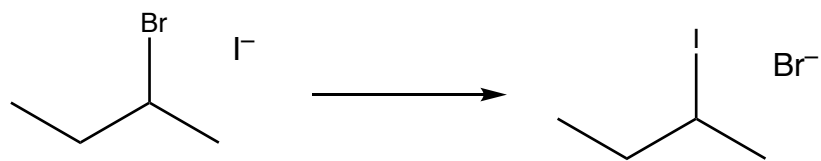
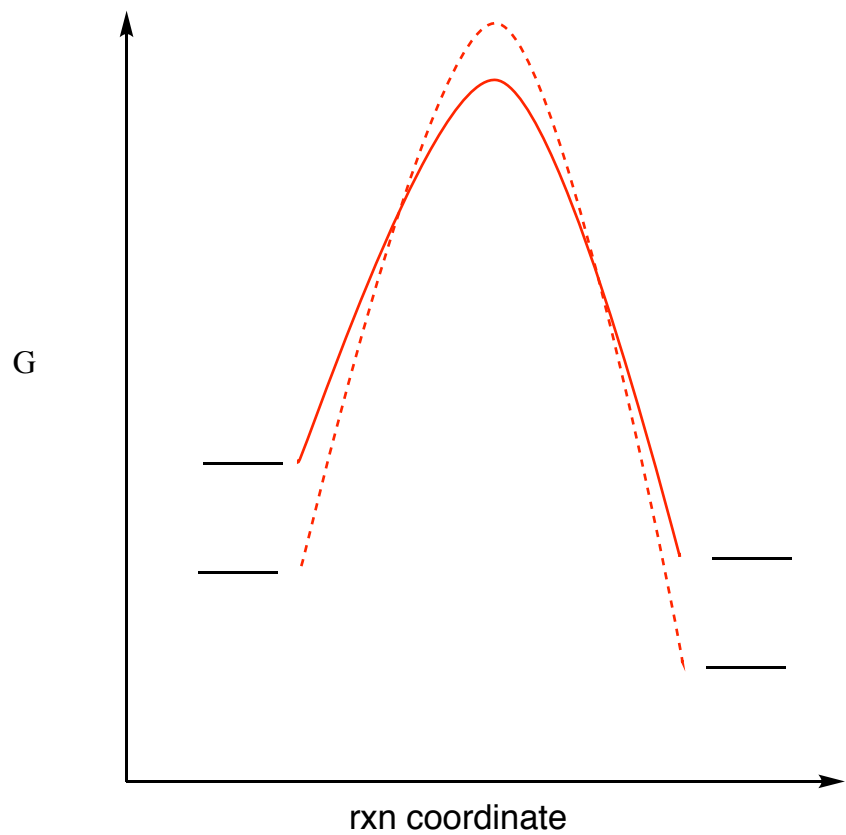
$$\text{rate} = k [\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}][\text{I}^-]$$

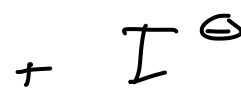
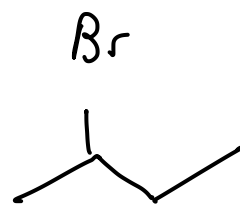
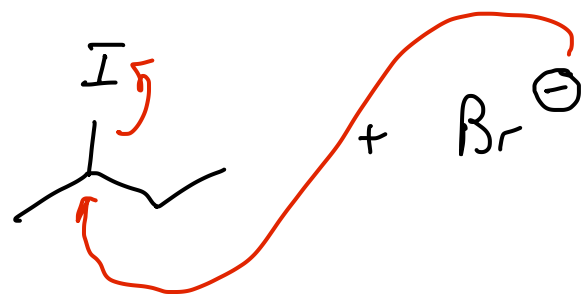
Substrate structure/degree of substitution, LG quality, solvent, Nu Quality



Factors affecting S_N2 (solvent)

Section 9.3





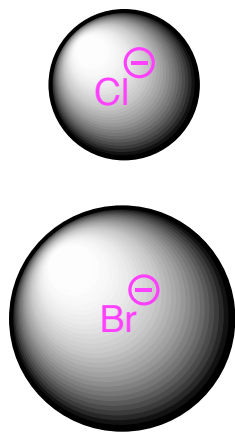
weaker base
 ↓
 as LG is favored

IF everything stays in soln, an equilibrium can result.
 Leaving group quality for S_N2 is important,
 because the LG has to get out of the
 way. The better the LG, the faster the
 S_N2 rxn will go.

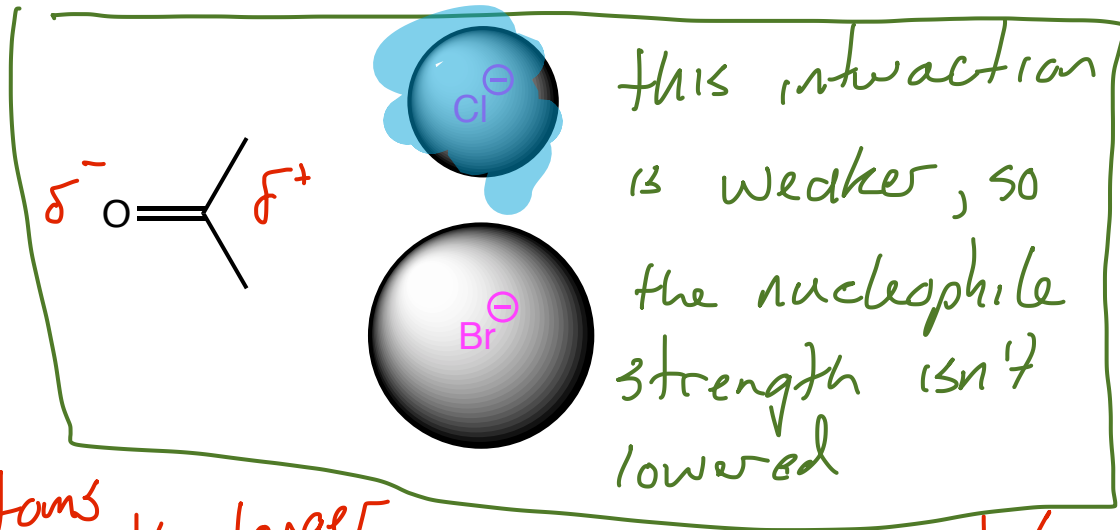
Leaving groups need to be stable once they leave.
 Weak bases are low E and make good LG.
 The weaker the base the better the LG.

Nu Quality and protic and aprotic solvents

dipole-ion interaction Section 9.3

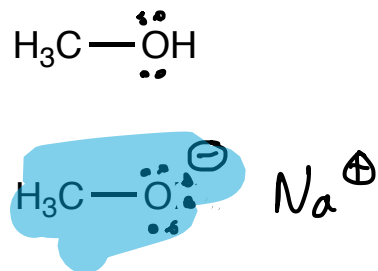
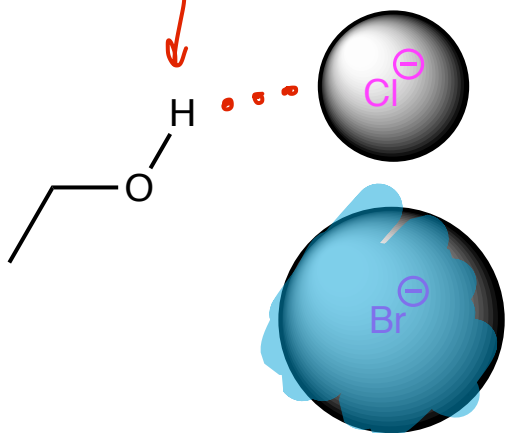


e^- rich nucleophiles



this interaction is weaker, so the nucleophile strength isn't lowered

protic H-bond donor interact with smaller atoms better than with larger atom



smaller nucleophiles can be distracted by H-bond donors

More e^- density should make for a better Nu unless... the nucleophile gets distracted... H atoms

S II

More e^- rich (more basic) nucleophile is
stronger nucleophile unless

The nucleophiles are different sizes
(different rows of P_n table) & the
solvent is protic

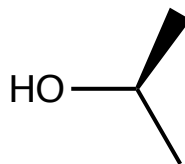
larger Nu will be the better Nu

Protic or Aprotic
OH's + NH's

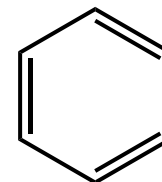
H-bond donor solvent is a protic solvent



protic



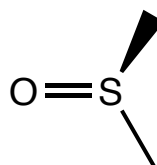
protic



aprotic



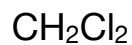
aprotic



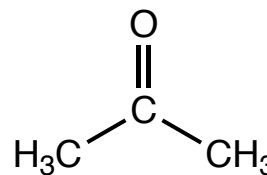
aprotic



aprotic



aprotic



aprotic

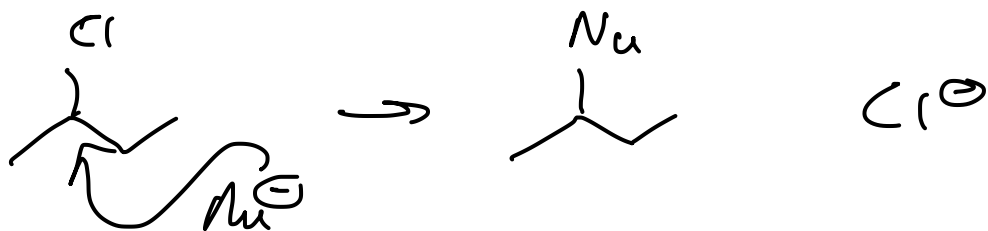
low degree of substitution on α-C

CH₃ > 1° >> 2° >>> 3° (can't do S_N2)

aprotic solvents so reactants & products aren't stabilized too much & the TS isn't destabilized

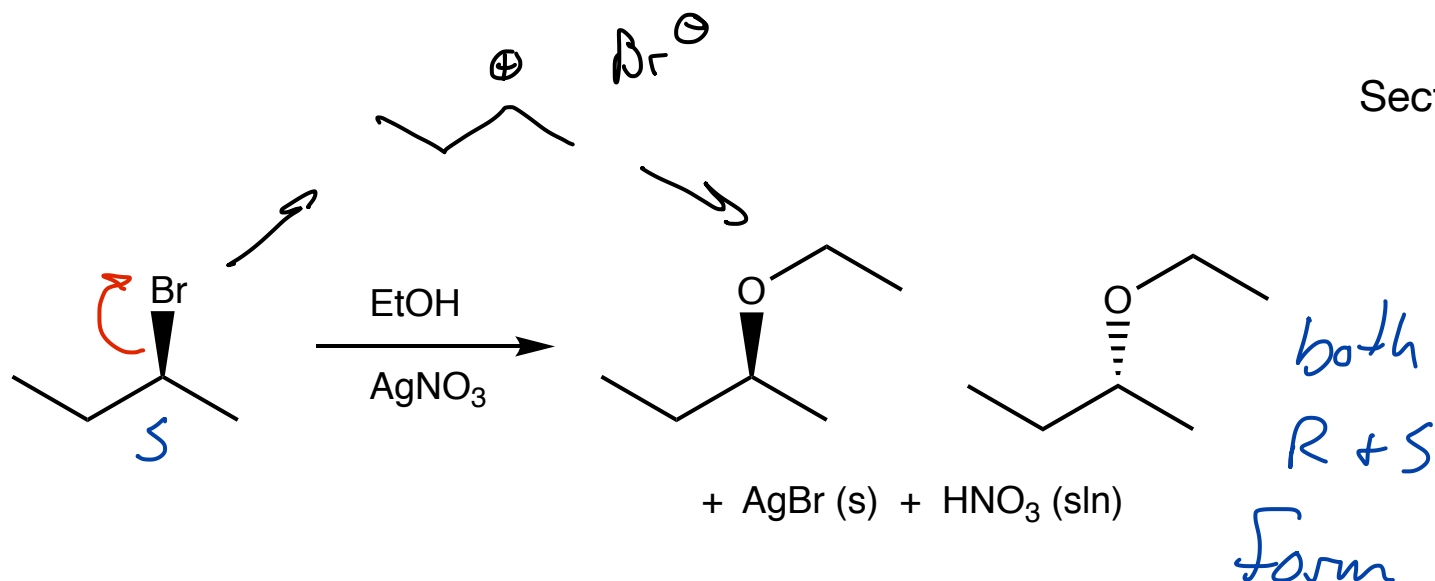
Good LG (weak bases)

Good Nucleophiles e⁻ rich (and large if in a protic solvent)



Evidence for S_N1

Section 9.2



$$\text{rate} = -k [\text{CH}_3\text{CH}_2\text{CHBrCH}_3]$$

rate at which reactants are consumed only depends on conc of alkyl halide

3° α-C best at S_N1 > 2° α-C can do S_N1 >>> 1° α-C can't

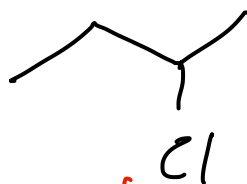


barely cloudy

1° C⁺ too unstable to form at 80°C

this is actually a slow S_N2

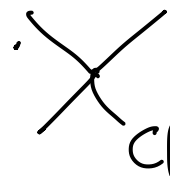
rxn 'cauz S_N1 isn't possible



E+OH

cloudy at 80°C

2° C⁺ harder to make

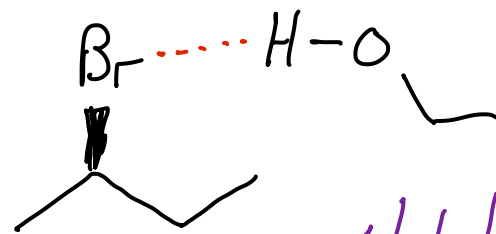
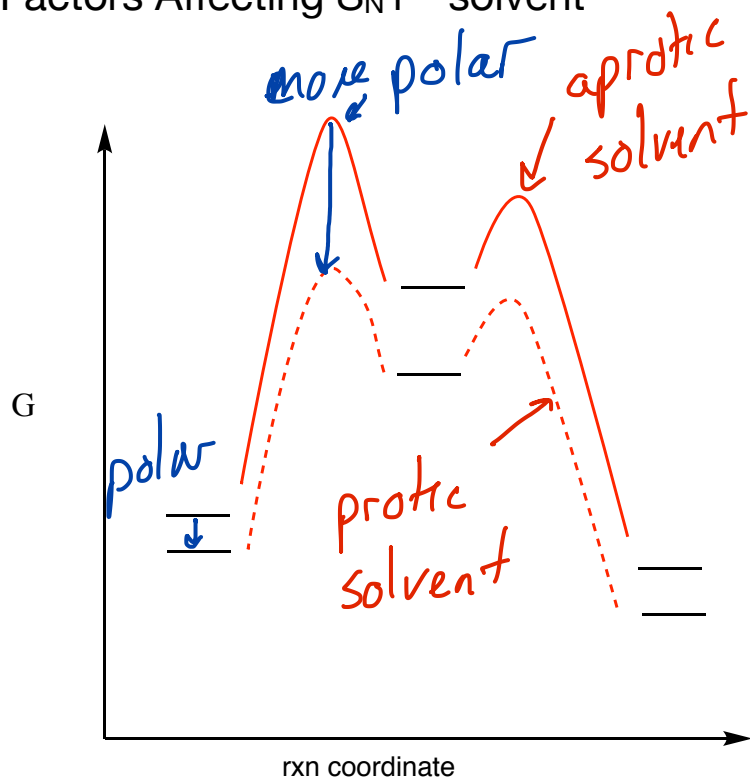


best rxn at RT

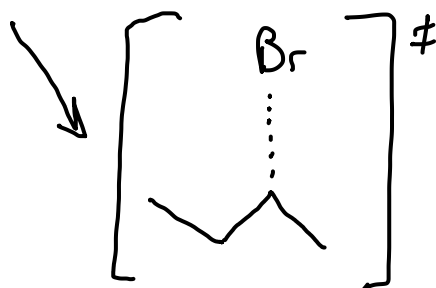
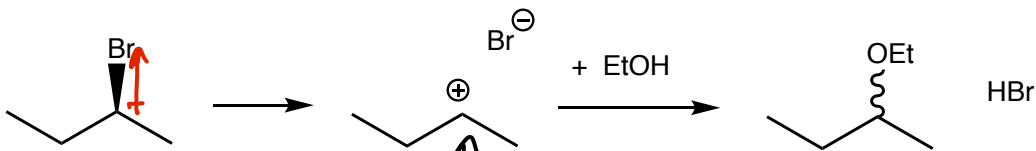
3° C⁺ are more stable

Factors Affecting S_N1 - solvent

Since the TS is more polar it is stabilized more by polar solvents than the reactants are. The activation energy goes down



The protic solvent is better at stabilizing the LG, and can help the LG leave.



the Br becomes more \ominus in TS
 the C is becoming more \oplus in TS
 the C + Br are farther away
 the dipole in the TS state is larger

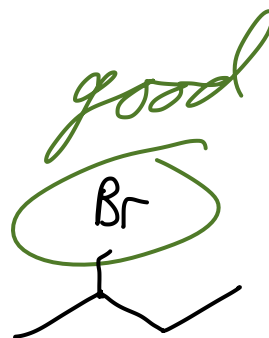
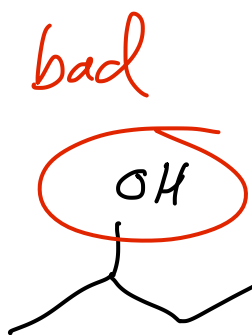
LG needs to be a good leaving group.

the better the LG the faster the rxn.

the LG must be stable, have low E , be a very weak base

Nu quality... since the Nu has to wait for the c^+ to form a weak Nu can still react to form our products

$-OH$ strong base



Br^- is a large atom

High substitution on the α -C
3° or 2° α -C

Good LG

Solvent polar protic solvents

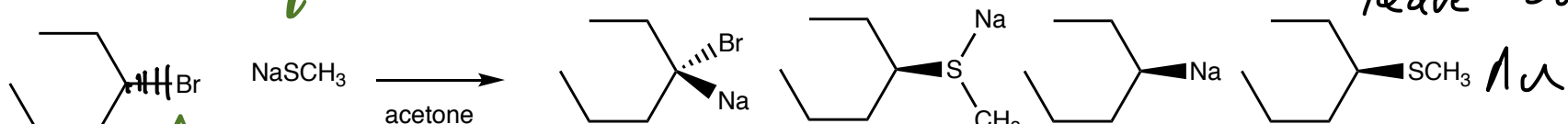
Competition	
S _N 2	S _N 1
Two molecules collide in a 1 step mechanism	Dissociation of one molecule controls the rate of a two step reaction
bimolecular rate determining step	unimolecular rate determining step
stereochemistry is inverted	stereochemistry is a mixture of inverted and retained (not inverted)
methyl, 1°, 2°	if the solvent is the nucleophile and the leaving group is a halogen only 3°
better the nucleophile the faster the reaction	the strength of nucleophile has no effect on the rate
good nucleophile	So so nucleophile
polar aprotic solvent	polar protic solvent

Why might we prefer S_N2 over S_N1... S_N1 uses C⁺ intermediates... rearrangements i, and no control of stereochem

Reactions

S_N2

good nucleophile. what do we know about Na in this compound? Na^+ $^-SCH_3$ no H-bond interaction to help LG leave so



A

B

C

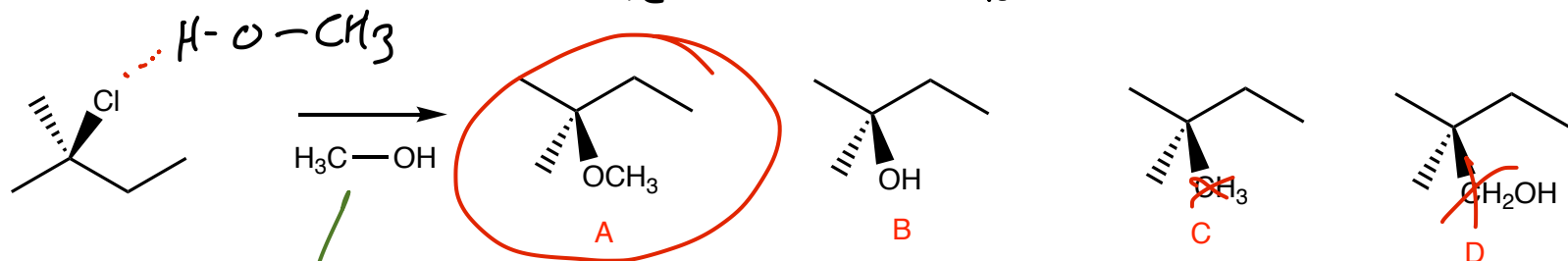
D

LG

aprotic solvent

must push LG off.

H-bond interaction encourages LG to leave so S_N1 is favored



A

B

C

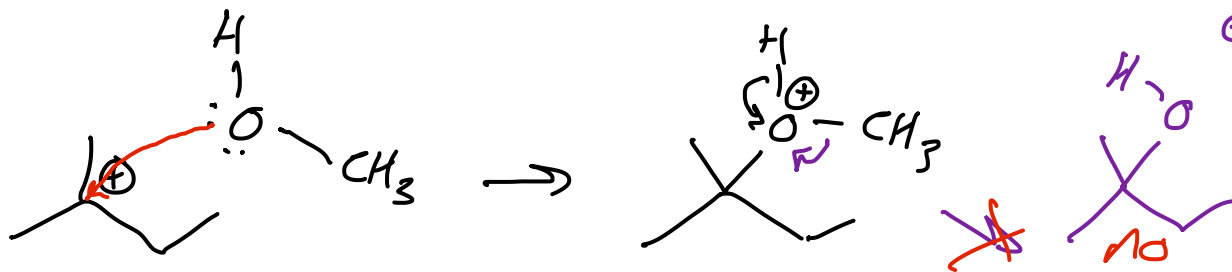
D

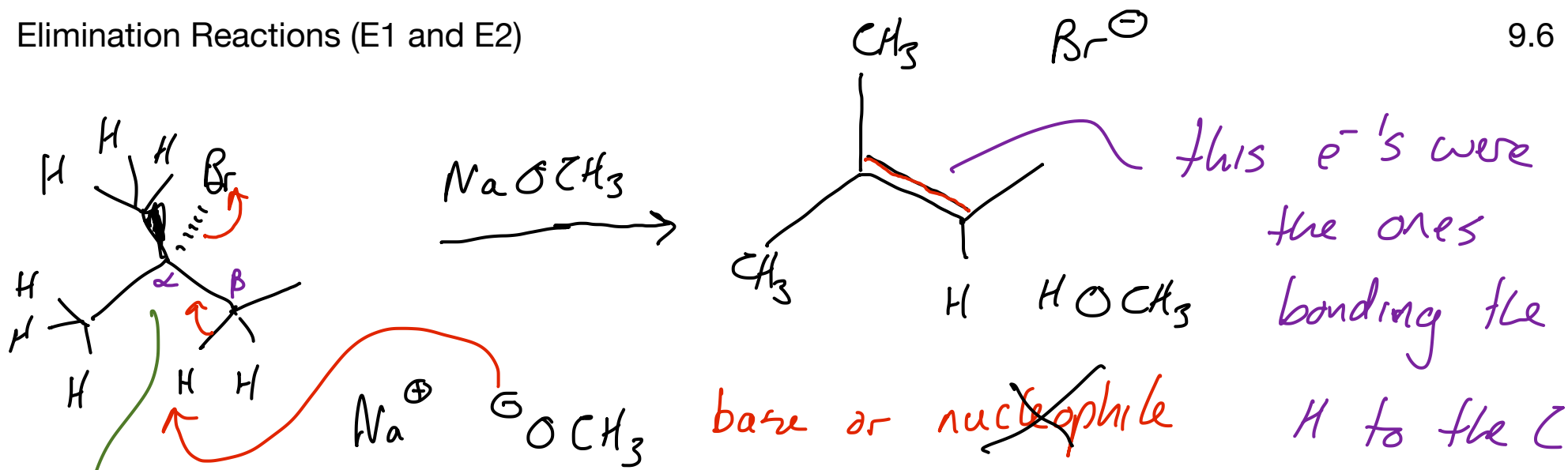
too unstable

$^+CH_3$

$3^\circ \alpha-C$

protic





Elimination reactions can be bimolecular
 base (OCH_3^-) grabs a $\beta\text{-H}$, e^- 's that used to hold βH in place fall in form a π bond and push the LG off.

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