Overheads: - Outline

QUIZ # 1

Recap Wednesday: S_N2 Reactions

Leaving Groups:

Weaker base = better LG

$I^- > Br^- > Cl^- >> F^-$

Nucleophiles:

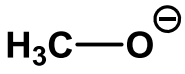
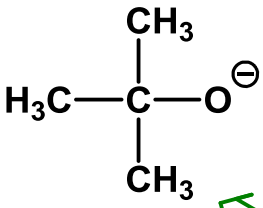
stronger base = better Nu^-

size matters

aprotic solvent

protic solvent (*eg* H_2O, CH_3OH)

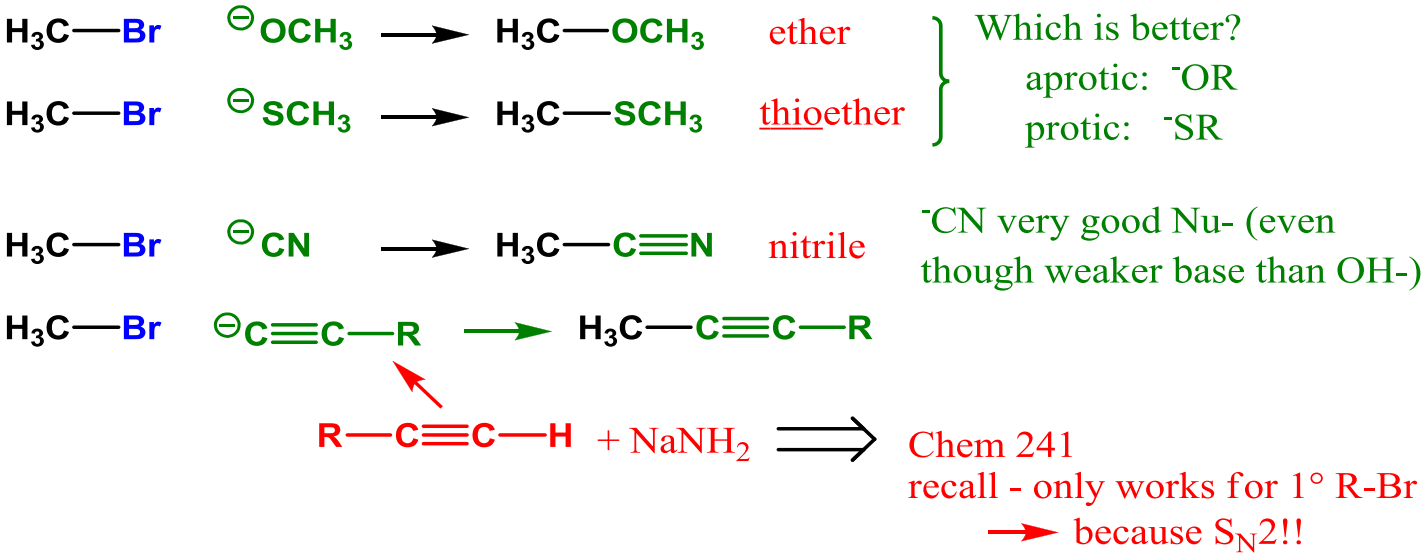
size trend reverses with H-bonding

Q:  *vs* 

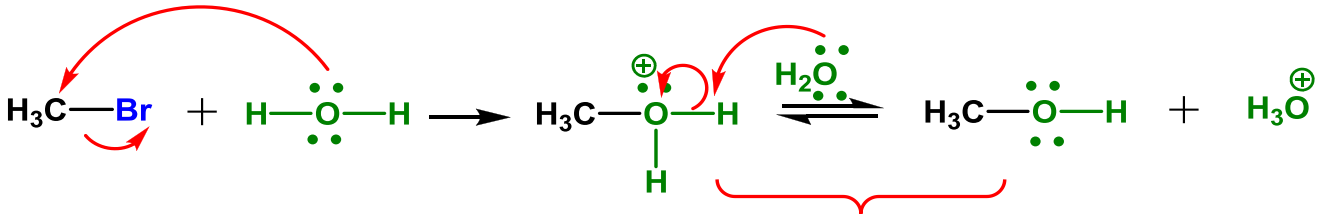
- similar base strength (*t*-BuO- slightly stronger)

too big! Good base, but very poor Nu^- (bulky base)

Examples of Nucleophiles:



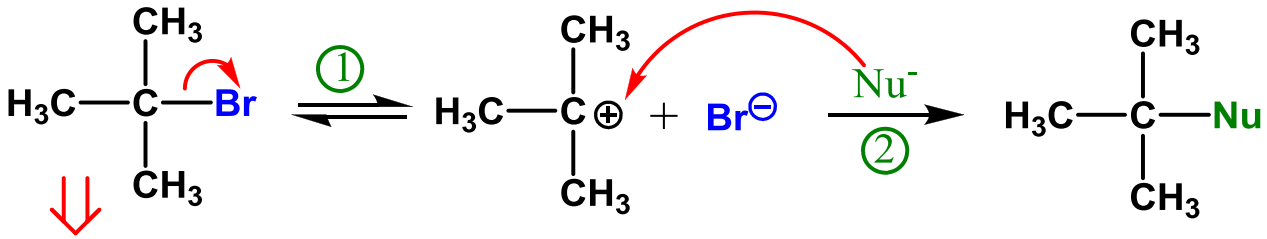
Neutral Nucleophiles:



need "extra" step to remove H^+ (fast eq'm)

same for: $H_3C-Br + NH_3 \rightarrow H_3C-\overset{H}{\underset{H}{N}}-H \xrightarrow{-H^+} H_3C-N-H$

S_N1 Reaction ⇨ Lab #2



No S_N2 (sterics)

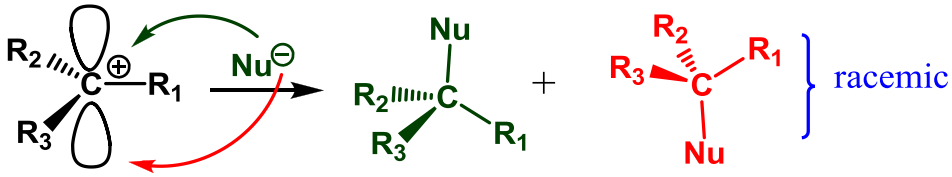
S_N1 - two steps
- first step is RDStep (C^+ form'n)

Compare to S_N2

1) Kinetics: only R-Br in RDStep, ∴ unimolecular (∴ S_N1)
rate = Δ[R-Br]/Δt = k[R-Br]
(if [Nu^-] ↑, rate does not ↑)

2) Stereochemistry: (S_N2 = inversion)

⇒ C^+ is flat, so Nu^- can add to either side



racemic

3) Effect of Substitution:
⇨ most stable C^+ formed fastest (TS ↓ , Ea ↓) (Same as Markovnikov!)

relative rates: ∴ 3° > 2° > > 1°
100,000 : 1 : 0 ⇐ No S_N1 - too unstable

Leaving Groups:
⇨ Need good LG to make C^+ (same trends as S_N2)

Nucleophiles:

⇨ Not in RDS ∴ do not affect rate

⇨ Can use lower concentration of weaker Nu^-

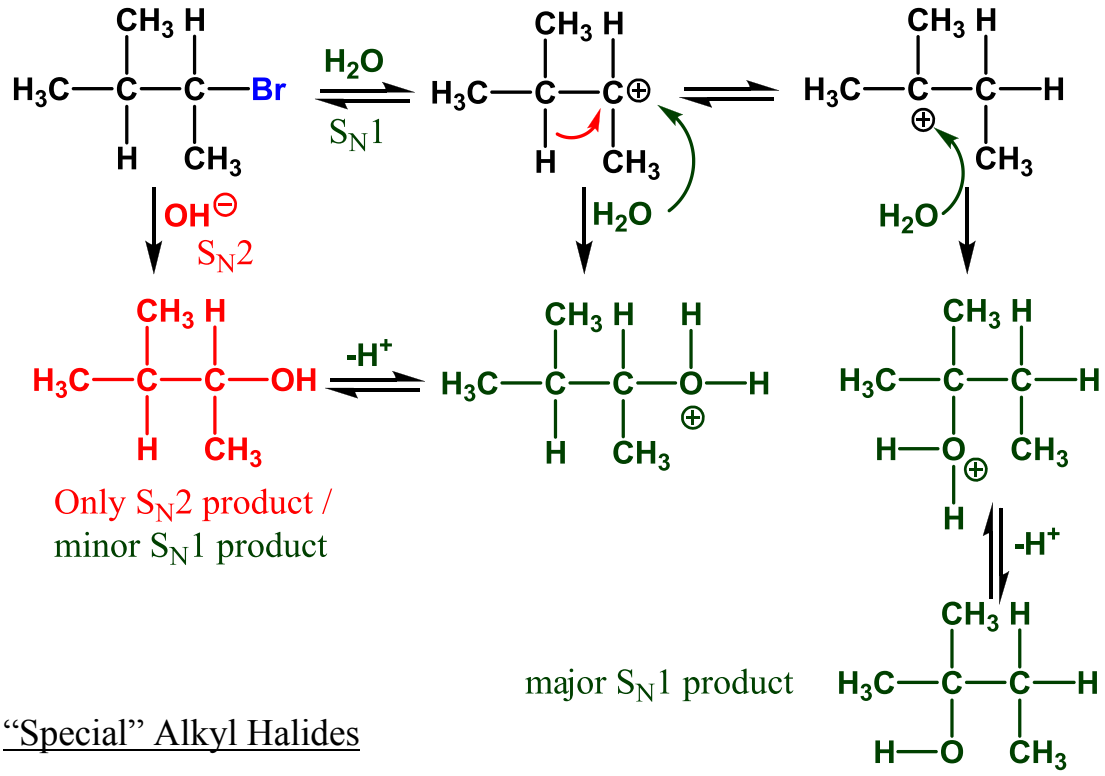
e.g. 

S_N2: Nu^- = OH-, high concentration helps (OH^- = strong base / Nu^-)

S_N1: Nu^- = H_2O (weaker base / Nu^-)

Added complication for S_N1

⇨ C^+ can rearrange

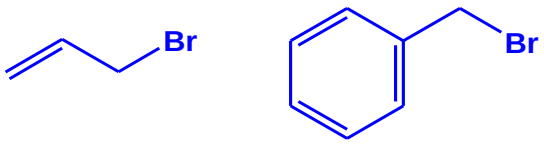


Only S_N2 product / minor S_N1 product

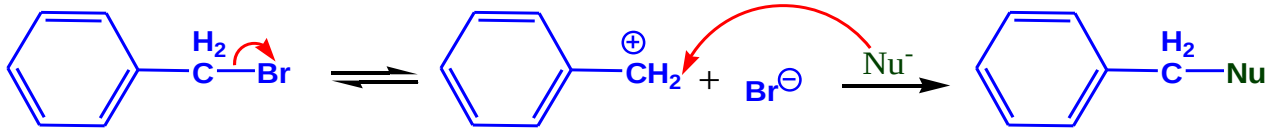
major S_N1 product

"Special" Alkyl Halides

1) Allylic & Benzylic Halides

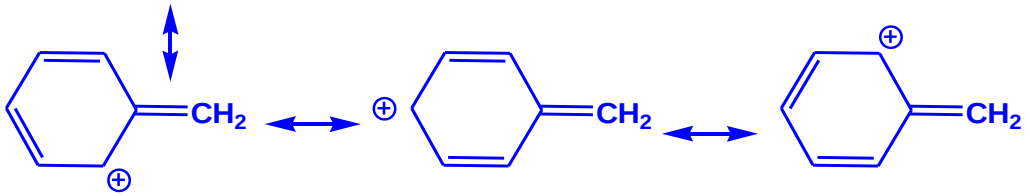


why special? Resonance!



1°, but can do S_N1

WHY???



Also makes S_N2 better (as long as not 3°):

- resonance stabilizes δ^+ in TS