Overheads: - Outline

Recap Monday: S_N2 Reactions

$$Nu^{\ominus} \quad R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}\overset{\delta^+ \ \delta^-}{-LG} \longrightarrow Nu-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}-R \ + \ LG^{\ominus}$$

$S_N\underline{2}$ = bimolecular / one step
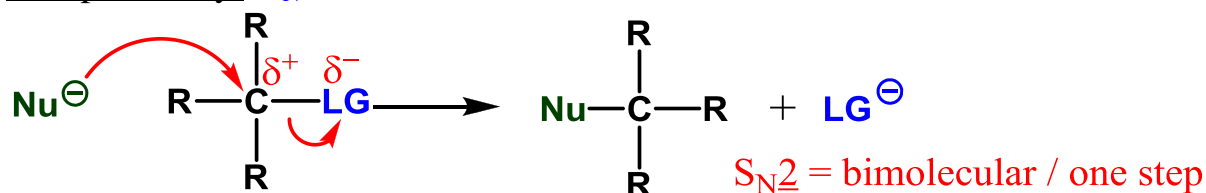
NOTE: "2" ≠ 2 steps! S_N2 = 1 step, S_N1 = 2 steps

Example: $$HO^{\ominus} \quad H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\overset{\delta^+ \ \delta^-}{-Br} \longrightarrow HO-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H \ + \ Br^{\ominus}$$

(one step ∴ no intermediates!)

TS: $$\left[HO\text{------}\overset{H}{\underset{H \ H}{C}}\text{------}Br \right]$$

Nu^- $1/2$ way in LG $1/2$ way gone
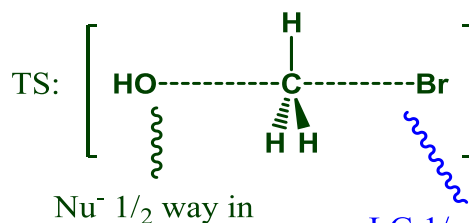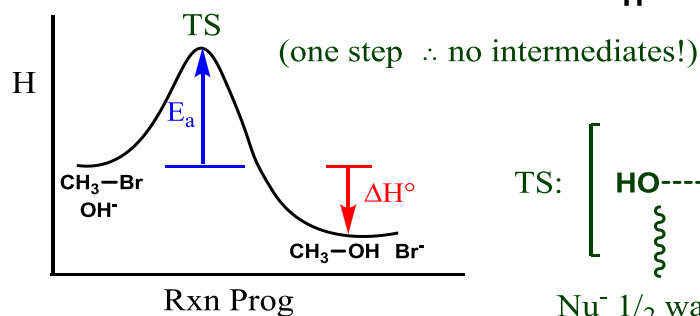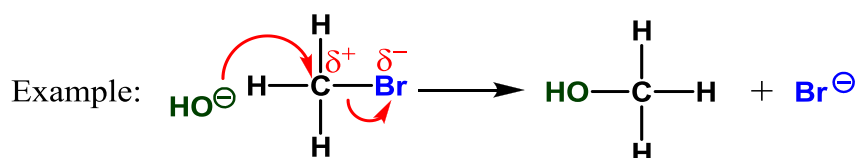
** The Nu- comes in from <u>behind</u> the LG to kick it out. *aka "back-side" attack*
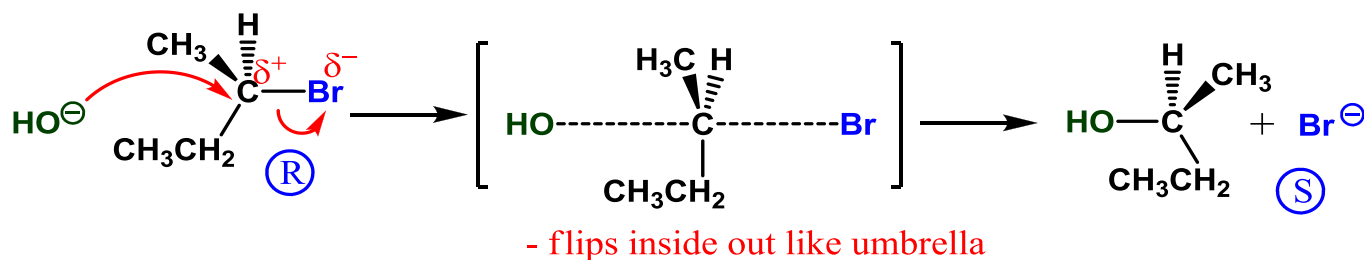
How do we know if a reaction was S_N2? (not S_N1)
1) <u>Kinetics</u>:   rate = $\Delta[R\text{-}Br]/\Delta t$ = $k[R\text{-}Br][OH^-]$
          (if double either conc., rate doubles)

⇒ Do kinetics <u>experiments</u> to see if rate depends on <u>both</u> (2nd order)   must be S_N2
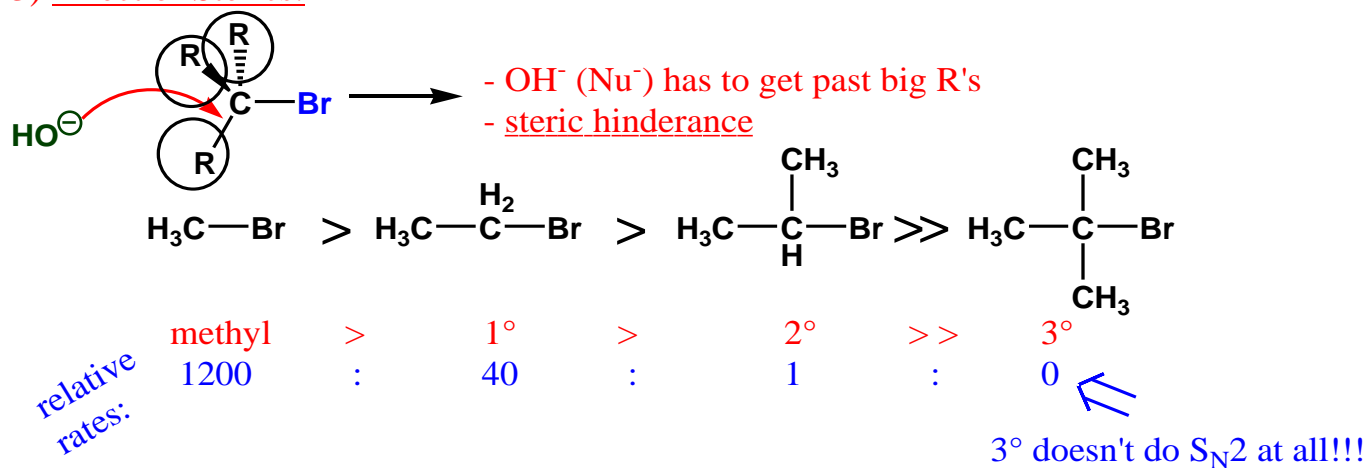
2) <u>Stereochemistry</u>:

- flips inside out like umbrella

⇒ stereochemistry is <u>inverted</u> (reverses)
        aka inversion of stereochemistry

$$\left.\begin{array}{c} R \longrightarrow S \\ S \longrightarrow R \end{array}\right\} \text{stereospecific reaction}$$

3) Effect of Sterics:

- OH⁻ (Nu⁻) has to get past big R's
- steric hinderance

H_3C—Br > H_3C—$\overset{H_2}{C}$—Br > H_3C—$\underset{H}{\overset{CH_3}{C}}$—$Br$ >> H_3C—$\underset{CH_3}{\overset{CH_3}{C}}$—$Br$

relative rates:	methyl	>	1°	>	2°	>>	3°
	1200	:	40	:	1	:	0

3° doesn't do S_N2 at all!!!

Leaving Groups: Halides = most common (others in Ch. 11)
⇒ anything that likes to leave! (with e⁻ pair)
⇒ X⁻ must be stable (X = Electronegative)

What makes a good LG?

⇒ the easier it is to break C-LG bond, the better the LG (*ie* weaker bond)

which is
strongest
bond?

C—F shortest/strongest
C—Cl
C—Br
C—I longest/weakest
I big, so poor overlap

weaker bond / better LG

$I^{\ominus}$ > $Br^{\ominus}$ > $Cl^{\ominus}$ >> $F^{\ominus}$

relative rates: 30,000 : 10,000 : 200 :   1

F⁻ not great LG, rarely used

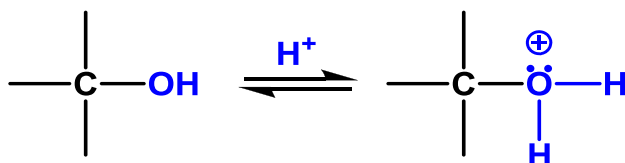**General Rule:** <u>Weaker base</u> = better LG
↳ worse e⁻ donor ∴ doesn't want to give back e⁻

* if base is stronger than F⁻, very bad LG!
e.g. OH⁻ stronger base ∴ terrible LG

but: —$\underset{|}{\overset{|}{C}}$—$OH$ $\underset{\longleftarrow}{\overset{H^+}{\longrightarrow}}$ —$\underset{|}{\overset{|}{C}}$—$\overset{\oplus}{\underset{H}{O}}$—$H$

H_2O = good LG (weak base)
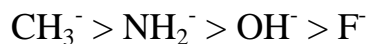⟹ Ch. 11 <u>and</u> Lab#2!!

<u>Nucleophiles:</u>
- love H^+ / δ^+ ≡ base
- must have lone pair of e^- to donate
- can be anionic ($H\text{-}\ddot{\text{O}}\text{:}^-$) or neutral ($H_2\ddot{\text{O}}\text{:}$)

<u>General Rule:</u> stronger base = better Nu^-
- opposite of LG ⇨ makes sense: Nu^- in / LG out!

$OH^- > H_2O$ ⇨ stronger base ⇨ anions generally better Nu^-

$CH_3^- > NH_2^- > OH^- > F^-$ acidity increases → (for HA)
⟵   ∴ basicity increases ⟵ (for A^-)
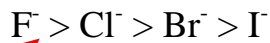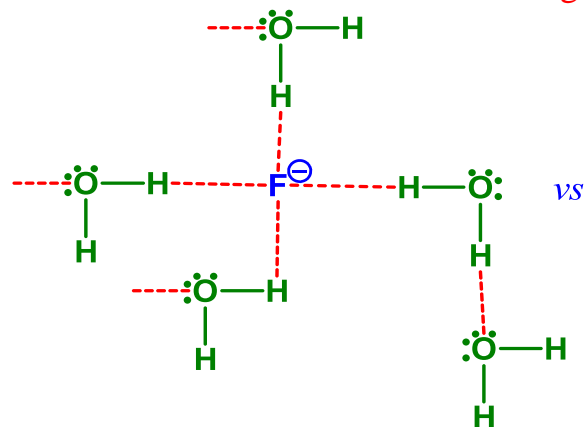
$F^- > Cl^- > Br^- > I^-$ F^- stronger base
⟵   (<u>AND</u> I^- bigger ∴ more steric hinderance)

true in <u>aprotic</u> solvent (no OH or NH); *e.g.* acetone or ether
BUT, in <u>protic</u> solvent, trend reversed
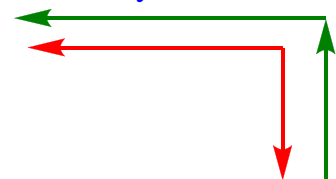   ↳   H-bonding increases <u>size</u> of Nu^-

vs

→ F^- H-bonds more than $Cl^- > Br^- > I^-$

∴ get big shell of H_2O's

→ F^- <u>very</u> big   ∴ steric hinderance ↑

<u>Summary of Nu^- trends:</u> (periodic table)

aprotic solvent (Nu^- = stronger base)

protic solvent (*eg* H_2O, CH_3OH)
           size trend reverses with H-bonding