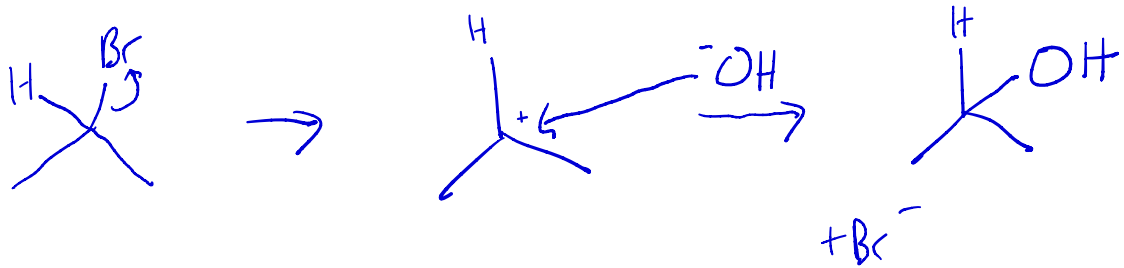
OCSP 2020 | Lecture #10

Today’s Agenda

- Introduce 2 important mechanisms: SN1 and SN2
- Discuss leaving group (LG) stability
- Discuss nucleophile stability

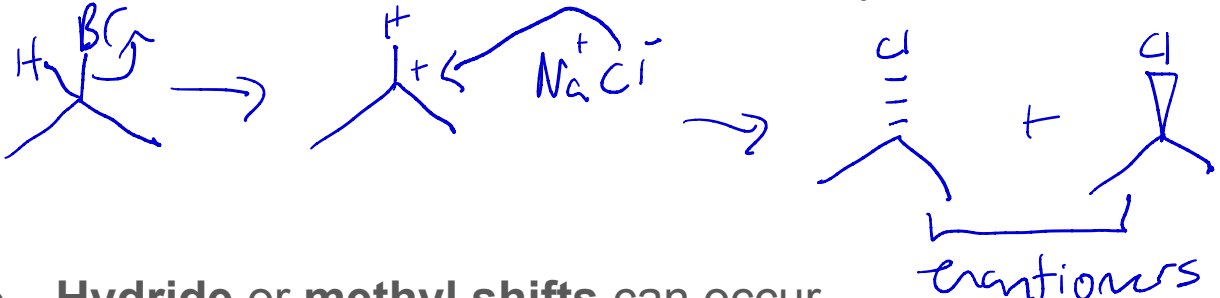
SN1 Reaction Mechanism



SN1 reaction characteristics

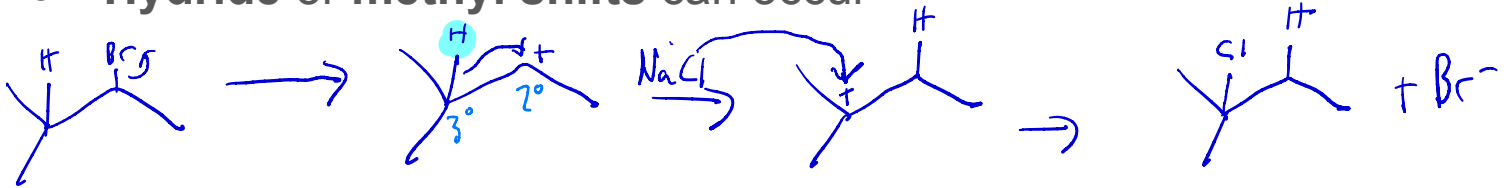
Nucleophilic Unimolecular Substitution

- Rate = K[alkyl] First order
- Rate determining step = formation of the **carbocation**
- Only occur on secondary or tertiary substrates
  - 3' > 2' > 1' > methyl
- Stereochemical outcome: **racemized** product



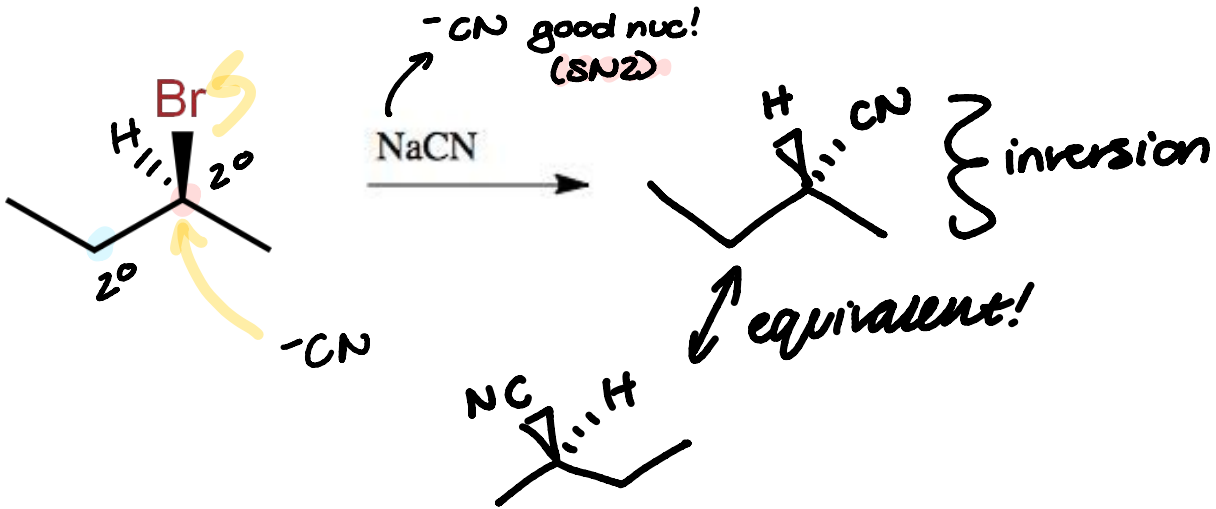
*note: this molecule isn't chiral! Just used as an example to show results if it were chiral

- **Hydride** or **methyl shifts** can occur

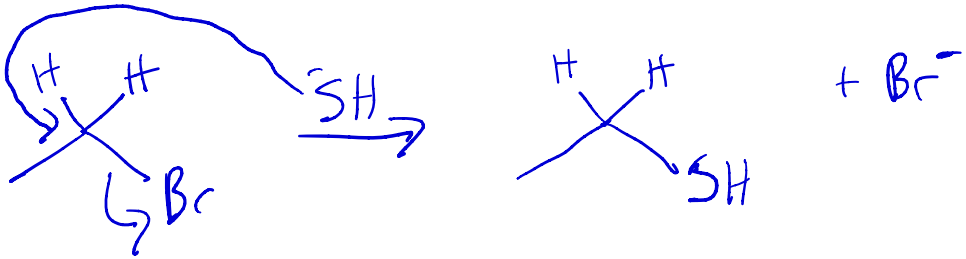


Practice!

- What are the products of this reaction?



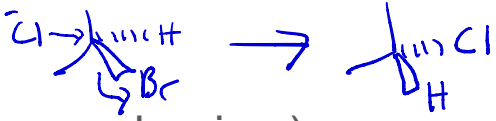
SN2 Reaction Mechanism



SN2 Reaction Characteristics

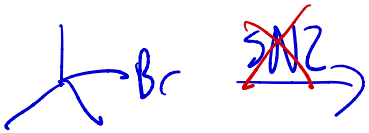
Nucleophilic Bimolecular substitution

- Rate = k[alkyl][Nu] → second order
- Rate determining step: interaction between alkyl (the substrate) and nucleophile
- **Inversion** of stereochemistry



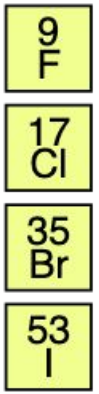
- **Concerted reaction** (one step mechanism)
- Can occur on methyl, primary and secondary substrates
  - Methyl > 1' > 2' > ~~3'~~

* again, this example molecule is NOT chiral. It was just used to show how the wedge & dash would switch



Leaving Group (LG) stability

- Best LG's = large molecules that are stable with a negative charge
- Most are weak bases (I^->Br^->Cl^-) -- larger/more polarizable is better
  - Some of the best LG have resonance (think **stability**)
- Not influenced by solvent
- **SN1** reactions especially need a good LG



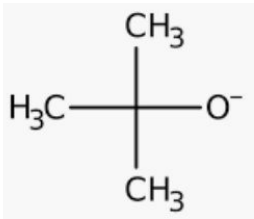
Nucleophiles

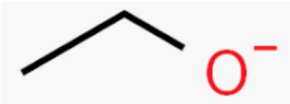
unstable

- **Order of best nucleophiles:**
  1. - on less electronegative atom $-CN$
  2. - on more electronegative atom $-OH$
  3. LP on less electronegative atom $:NH_3$
  4. LP on more electronegative atom $CH_3\ddot{O}H$
  5. Double/triple bond

Not in SN1/SN2

worse nucleophile: steric hindrance





- **SN2** reactions need a strong **nucleophile**
  a. For halogens: **solvent** determines whether a larger or small one is best
  b. Strong nucleophiles include: -OH, -SH, -CN
  c. Poor nucleophiles include: H_2O, CH_3OH
- **SN1** reactions often occur with a weaker nucleophile, such as H_2O

Don’t Confuse Nucleophiles & Bases

- **Nucleophilicity:** kinetic property, measure of reaction rate
  - Ask, “how quickly could this atom attack”?

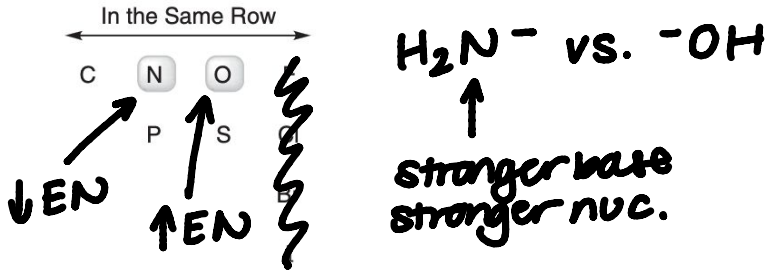
- **Basicity:** thermodynamic property, measure of pkb
  - Ask, “How stable is this atom with a negative charge?”
  - Remember, stable bases are weak bases

Bronsted Lowry
base ⇒ H+ acceptor

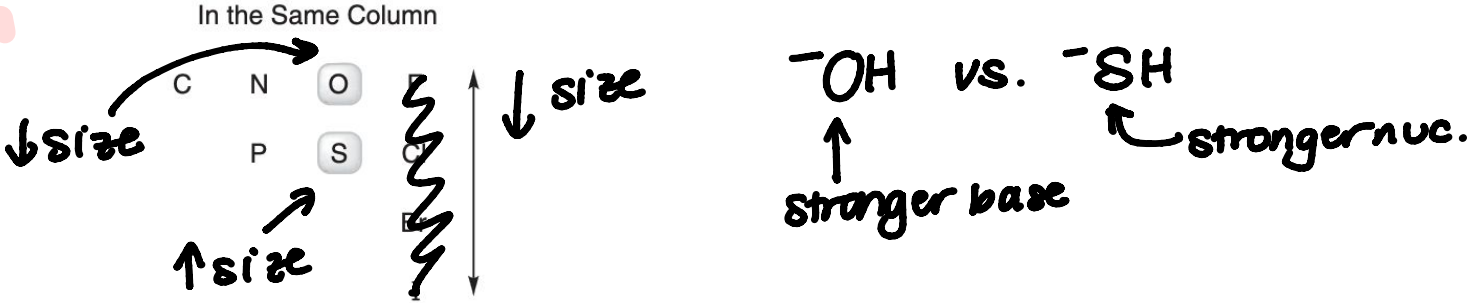
*weak base = stable with (-)
(less likely to
take H+)

Guidelines for Nucleophilicity and Basicity Trends

- Nucleophilicity and Basicity follow the **same** trend for atoms in the same row



- Nucleophilicity and Basicity follow the **opposite** trends for atoms in the same column



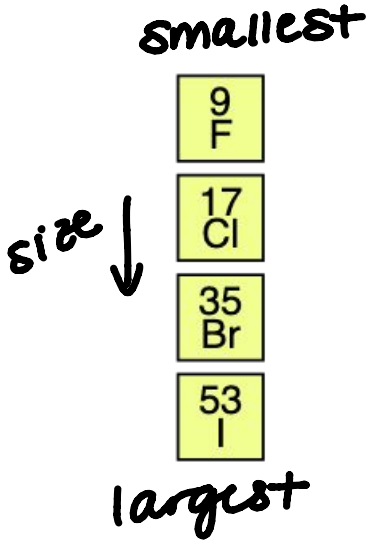
Practice!

- Which leaving group is the best?

Br-
(2)

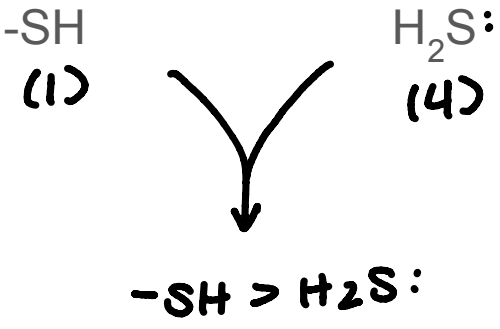
I-
(1)
↑
largest
most polarizable

F-
(3)



Practice!

- Rank the following nucleophiles from best to worst:

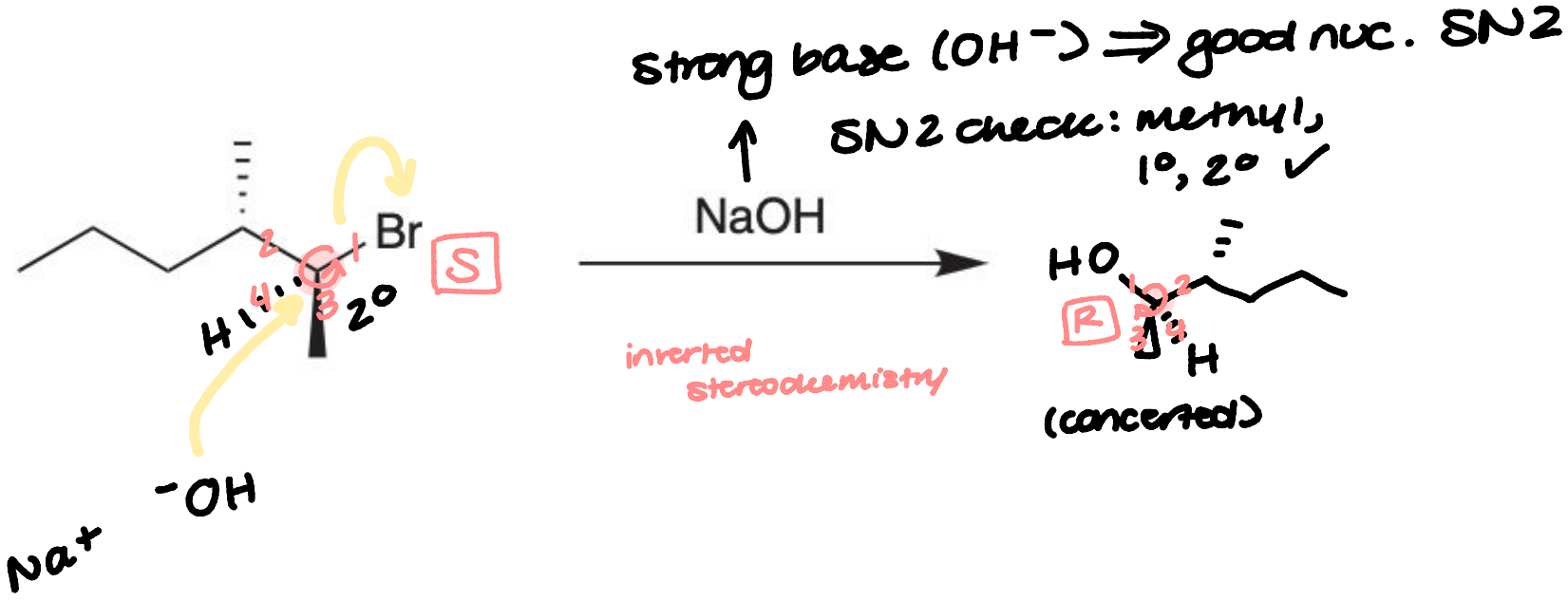


-OH (2) F- (3)

ORDER OF NUC:
(1) – on ↓EN
(2) – on ↑EN
(3) LP on ↓EN } uncharged
(4) LP on ↑EN

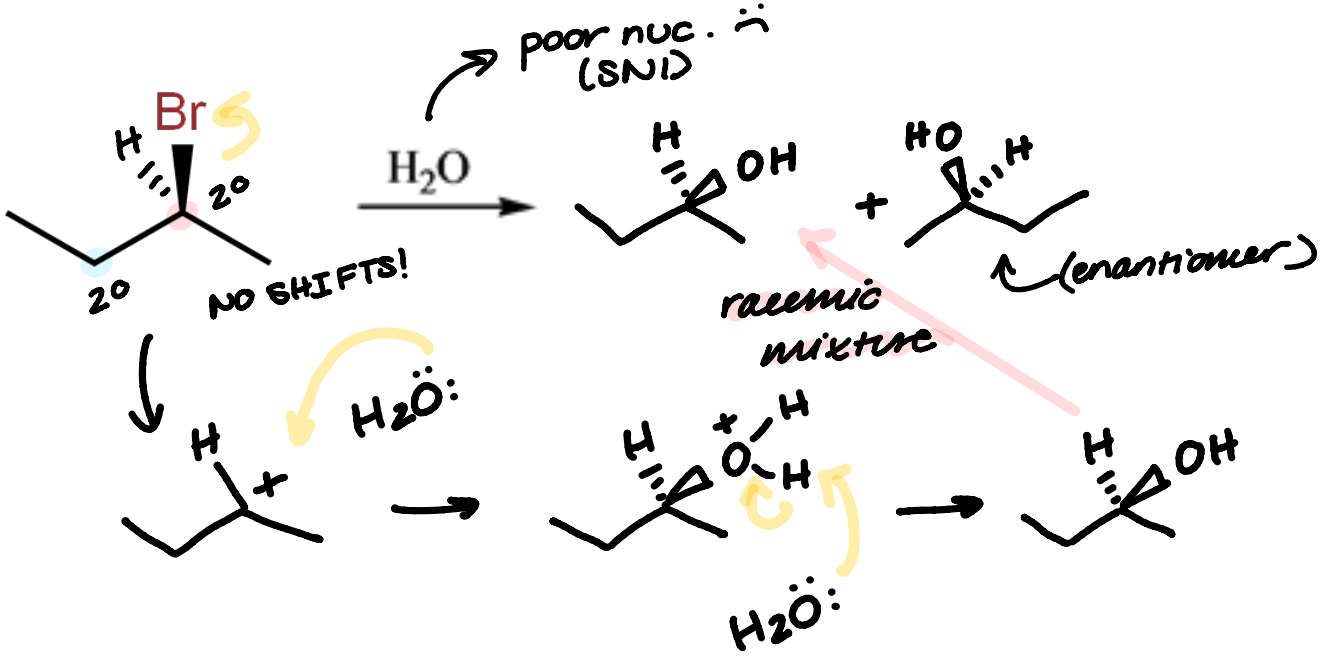
Practice!

- Based on the nucleophile present, would an SN1 or SN2 reaction occur?



Practice!

- What are the products of this reaction?



Practice!

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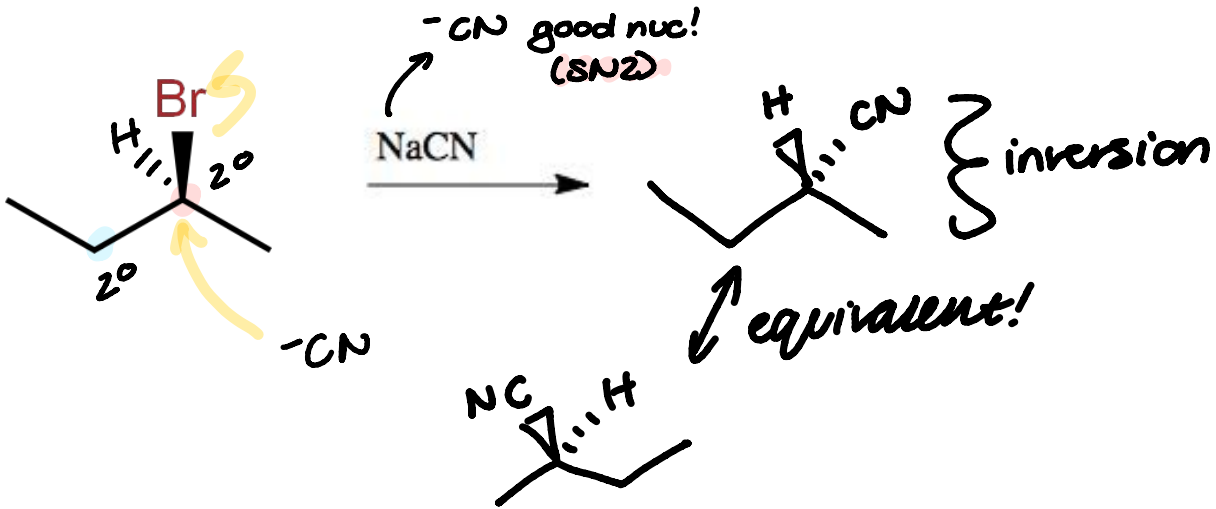

Practice!

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