MTW 11/7/24

Haloalkanes + Nucleophiles / Bases

Substitution. Elimination.

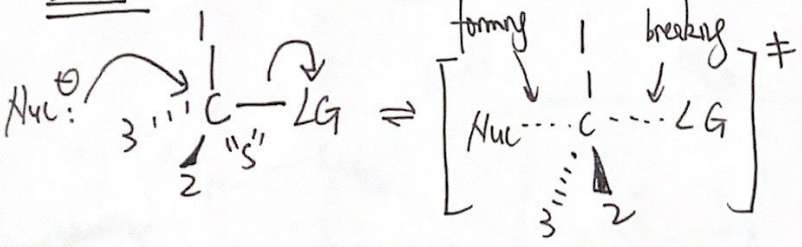
The Big picture: these rxns compete with each other.

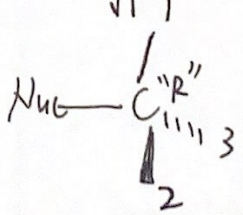
↳ Stronger bases favor <u>elimination</u>

↳ steric hindrance (greater sterics on Nu/Base and or on haloalkane) favors <u>elimination</u>

Substitution → swap a nucleophile with leaving group (LG)

<u>SN2</u>:





Invert the chiral center where Nuc added.

↓↓ are stable molecules when they leave.

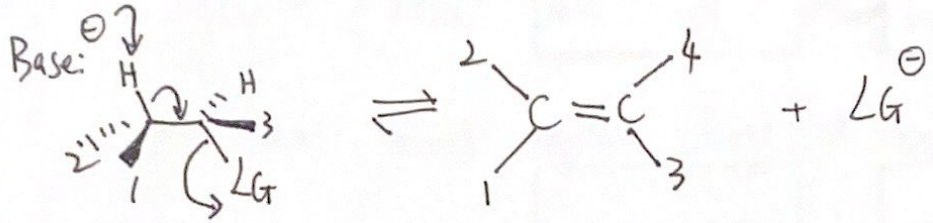
Better LG?

$HO^{\ominus}$ or H_2O: ✓

$Cl^{\ominus}$ vs $I^{\ominus}$ ✓

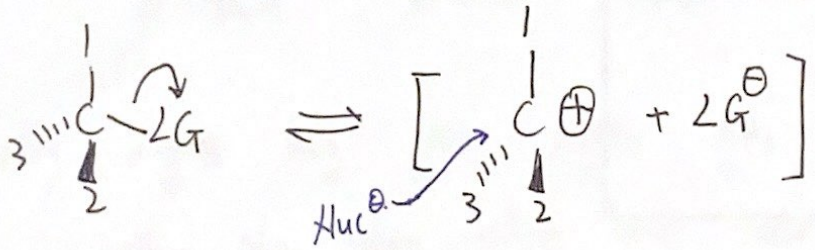
Elimination

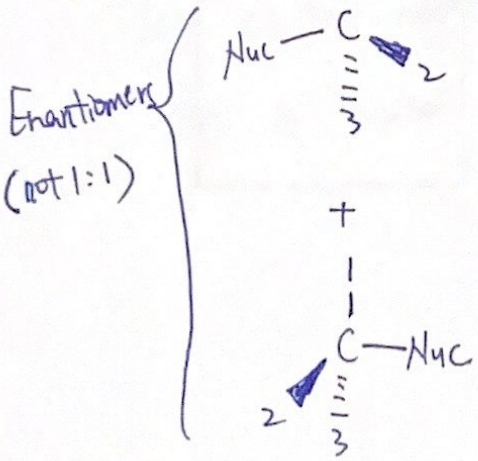
E2.



antiperiplanar

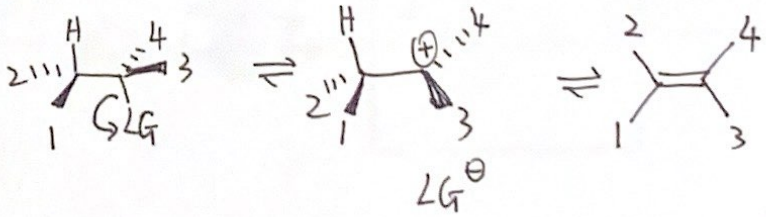
SN1 ~~E1~~





~~E2~~

E1



- favors to form the more stable Carbocation.
- Never going to form 1° or methyl Carbocation.

Nucleophiles.

Strong Nuc : $Br^{\ominus}$ $I^{\ominus}$ $R-S^{\ominus}$ $H-S^{\ominus}$ $N\equiv C^{\ominus}$ $H_3^{\ominus}$

$RC\equiv C^{\ominus}$ $R-O^{\ominus}$ $^{\ominus}OH$ strong base.

All have formal negative charge. → excess of $e^{\ominus}$s

Not all of them are strong base → depend on conj. acid strength

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- Weak Nuc are weak bases as well. → Neutral "O" atom

  $R-CO_2H$ $R-O-H$ H_2O

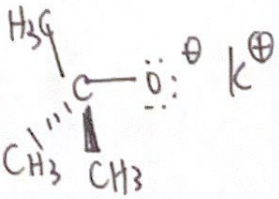
- Why $\underset{=}{R-S-H}$ $\underset{=}{R_2S}$ $\underset{=}{NH_3}$ $\underset{=}{RNH_2}$ $\underset{=}{NR_3}$ medium Nuc. and are better Nuc than those having neutral O atom?

  Less electron negative elements are better Nuc in neutral form. (willing to donate / share $e^{\ominus}$)

  C **N** O F
  S

Role of sterics:

Nuc / Base



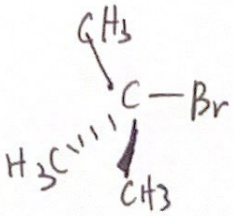
$tBuO^{\ominus}K^{\oplus}$

Not a Nuc, b/c too steric hindered.

It's only a base.

No SN2.

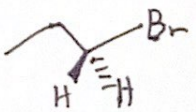
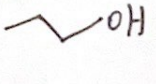
Halo alkane.



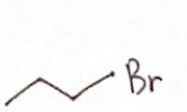
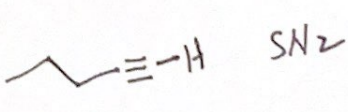
3°

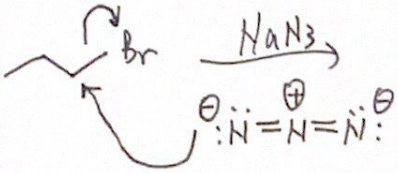
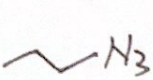
No SN2 rxn possible.

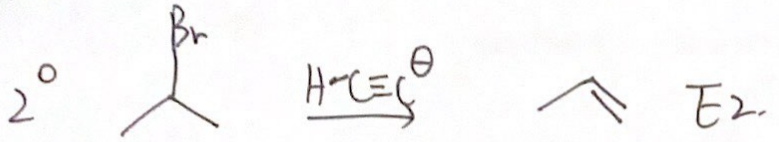
1°  $\xrightarrow{KOtBu}$  E2

 $\xrightarrow{NaOH}$  SN2

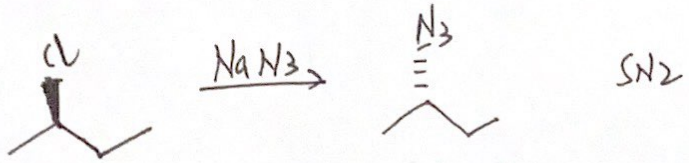
 $\xrightarrow{NaI}$  SN2

 $\xrightarrow{H-C\equiv C^{\ominus}\ Na^{\oplus}}$  SN2

 $\xrightarrow{NaN_3}$  SN2.



more hindered than 1°



Inversion