

Summary of S_N2, S_N1, E2 and E1 Reactions

Substrate (alkyl halide)

CH ₃ X	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{X} \\ \\ \text{R} \end{array}$
Methyl	1°	2°	3°
Gives S _N 2 reaction	S _N 2/ E2		S _N 1/ E1 or E2
	Gives mainly S _N 2, exception with a hindered strong base (e.g. (CH ₃) ₃ CO ⁻) and then gives mainly E2	Gives mainly S _N 2 with weak base/ strong nucleophile (e.g. I ⁻ , CN ⁻ , RCO ₂ ⁻) and mainly E2 with strong base (RO ⁻)	No S _N 2 In solvolysis gives S _N 1/ E1, and at lower temperature S _N 1 is favored. When a strong base is used E2 predominates
	Mixture of products		

Nucleophile/ Base

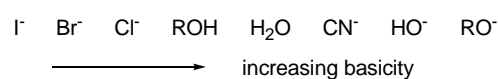
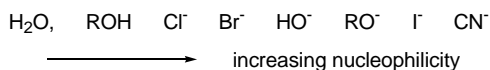
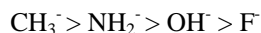
Strong nucleophile: S_N2

Weak nucleophile: S_N1

Strong base: E2

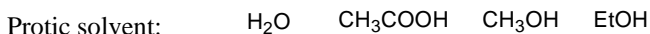
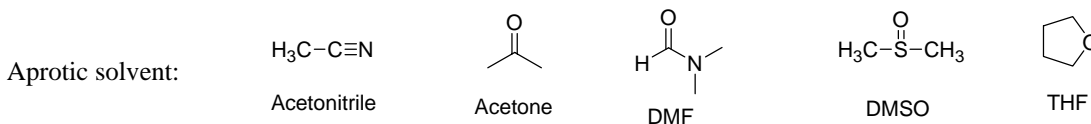
Weak base: E1

Like basicity, nucleophilicity increases from right to left within a period in periodic Table



Solvent

Polar aprotic solvent (no O-H or N-H) favors S_N2 reactions, whereas S_N1 reaction is favored by polar protic solvent.



Temperature

An increase in temperature increases the rates of both substitution and elimination reactions. However, an increase in temperature usually leads to a greater increase in elimination products.

S_N2 vs. S_N1

S_N2

- Methyl or primary (occasionally secondary)
- Strong nucleophile
- Polar aprotic solvent
- Rate = $k[\text{halide}][\text{Nuc}]$
- Inversion at chiral carbon
- No rearrangements

S_N1

- Tertiary
- Weak nucleophile (may also be solvent)
- Polar protic solvent, silver salts
- Rate = $k[\text{halide}]$
- Racemization of optically active compound
- Rearranged products

E2 vs. E1

E2

- Tertiary > Secondary
- Strong base required
- Solvent polarity not important
- Rate = $k[\text{halide}][\text{base}]$
- Zaitsev product (more substituted double bond), except when bulky base is used – Hofmann product (less substituted alkene)
- Coplanar leaving groups (usually anti)
- No rearrangements

E1

- Tertiary > Secondary
- Weak base
- Good ionizing solvent
- Rate = $k[\text{halide}]$
- Zaitsev product (more substituted alkene)
- No required geometry
- Rearranged products

Easy to Remember - Substitution or Elimination?

- Strength of the nucleophile determines order: Strong nucleophile, bimolecular, S_N2 or E2.
- Primary halide usually S_N2.
- Secondary halide mixtures of products are common.
- Tertiary halide mixture of S_N1, E1 or E2.
- High temperature favors elimination.
- Bulky bases favor elimination.
- Good nucleophiles, but weak bases, favor substitution.