

Organic Chemistry I, CHM 3140, Dr. Laurie S. Starkey, Cal Poly Pomona
Elimination Reactions & Alkenes Summary (Klein Chapter 7, Part 2)

- I. Review the pi (π) bond and Nomenclature of alkenes and alkynes (8.3, 9.2)
- II. Alkene stability (7.6)
 - i) more alkyl groups, more stable
 - ii) trans is more stable than cis (except in small rings)
 - iii) pi bond unstable at bridgehead carbon (Bredt's Rule)
 - iv) alkene is more stable if conjugated with another pi bond (16.2)
- III. Alkene synthesis: E2 mechanism (one-step) (7.5, 7.7)
 - i) requires strong base (HO^- , RO^- , R_2N^-)
 - ii) stereochemistry: *anti*-elimination of β -hydrogen and LG
 - iii) regiochemistry: depends on base choice
 - i) usually gives the most stable alkene (Zaitsev with NaOH, MeONa, EtONa)
 - ii) bulky base gives less substituted alkene (Hofmann with *t*-BuOK)
 - iv) often in competition with $\text{S}_{\text{N}}2$ (E2 favored unless primary RX)
- IV. Alkene synthesis: E1 mechanism (7.8)
 - i) two steps, via carbocation (rearrangement can occur)
 - ii) proceeds with loss of stereochemistry (both E and Z alkenes formed)
 - iii) regiochemistry: gives the most stable alkene (Zaitsev)
 - iv) usually in competition with $\text{S}_{\text{N}}1$ (E1 favored with heat)
 - v) dehydration of alcohols (H_3PO_4 or H_2SO_4 + heat) (7.10)
- V. Predicting Products: Substitution vs. Elimination (7.9)
 - i) Bimolecular (strong base/nu.): $\text{S}_{\text{N}}2$ vs. E2 (see below)
 - ii) Unimolecular (carbocation): $\text{S}_{\text{N}}1$ vs. E1 (see below)
- VI. Synthesis Strategies (7.11)
 - i) Retrosynthesis of substitution products and alkenes

Summary of Substitution & Elimination Reactions

Alkyl Group (RX)	$\text{S}_{\text{N}}1$, E1, E2	$\text{S}_{\text{N}}2$
3° (tertiary)	common	rare
2° (secondary)	sometimes	sometimes
1° (primary)	rare	common
CH_3 (methyl)	never	common

Bimolecular reactions (1-step mechanism)

- $\text{S}_{\text{N}}2$
- requires good Nu: (X^- , NR_3 , CN^- , N_3^- , RO^- , HO^-)
 - steric hinderance slows $\text{S}_{\text{N}}2$: CH_3 (fastest) > 1° > 2° >> 3° (tertiary, slowest)
- E2
- requires a strong base (RO^- , HO^- , **NOT** H_2O , ROH)
 - regiochemistry governed by bulkiness of base used

Unimolecular reactions (stepwise mechanism, via carbocation)

- $\text{S}_{\text{N}}1$
- requires no strong base/Nu: (usually H_2O , ROH "solvolysis")
- E1
- more stable carbocation, faster reaction
benzyl/allyl, 3° > 2° >> 1°, methyl
 - racemization occurs, due to achiral intermediate