

Chapter 9 Elimination Reactions

□ What to master

- ◆ Understanding [the E2 Mechanism, Its Stereochemistry, and When It Is Favored](#)
- ◆ Understanding [the E1 Mechanism, Its Stereochemistry, and When It Is Favored](#)
- ◆ [Using Zaitsev's Rule and Hofmann's Rule to Predict Elimination Products](#)
- ◆ Predicting the Products of Elimination Reactions
- ◆ Predicting the Major Reaction Pathway of Substitution and Elimination Reactions

Chapter 9 Elimination Reactions

□ 1,2-Elimination: β -elimination; [📖 313 bottom](#)

□ Bimolecular elimination reactions: E2, [📖 314](#)

◆ rate = $k[\text{EtO}^-][t\text{-BuBr}]$

◆ concerted TS: formation of a π -bond, [📖 314 bottom](#)

◆ kinetic isotope effect: $k_{\text{H}} / k_{\text{D}} > 2$; [📖 315 bottom](#)

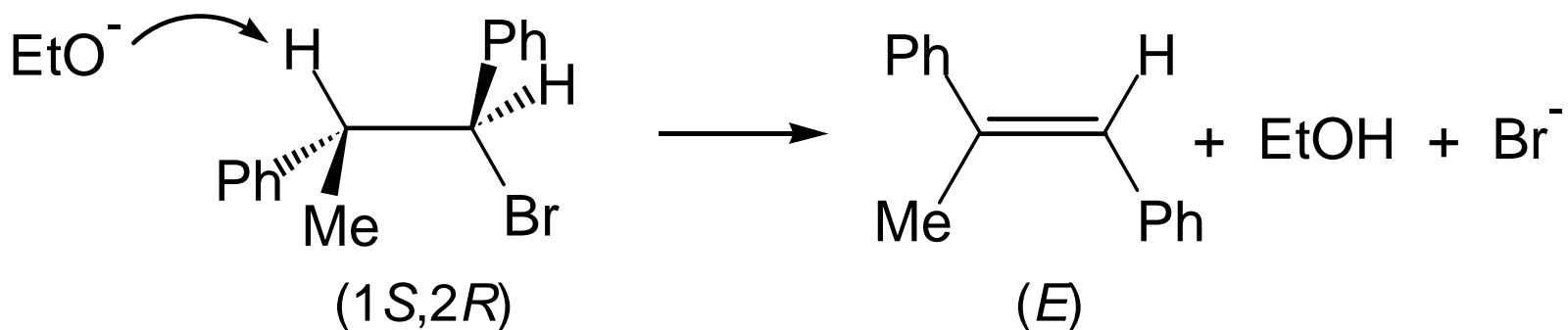
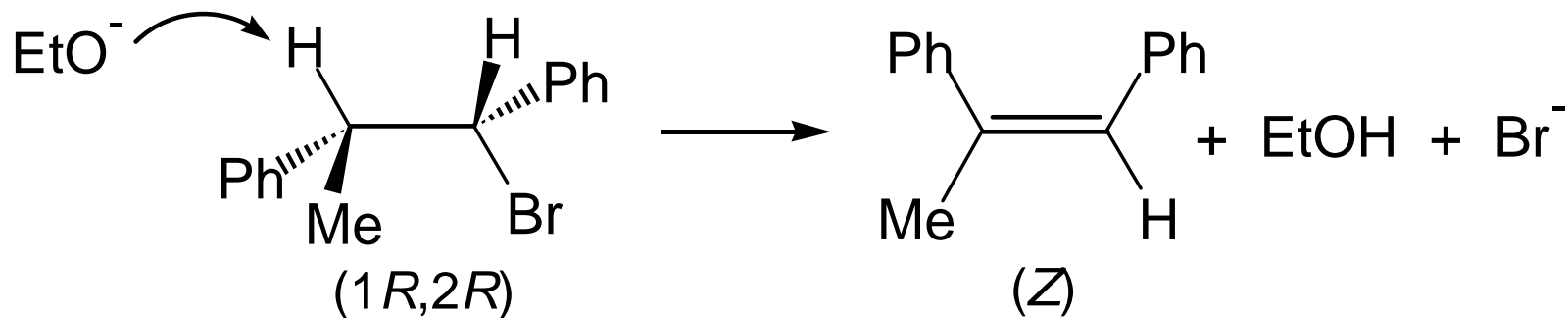
◆ stereoelectronic effect: syn-/anti-periplanar relationship

○ lower energy TS: anti; [📖 317 Figure 9.1](#) & [📖 318 top](#)

○ stereochemistry of alkenes: *E* / *Z*, [📖 318 Figure 9.2](#)

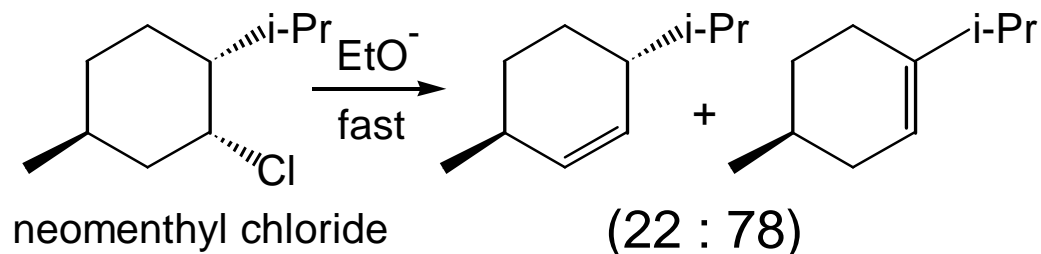
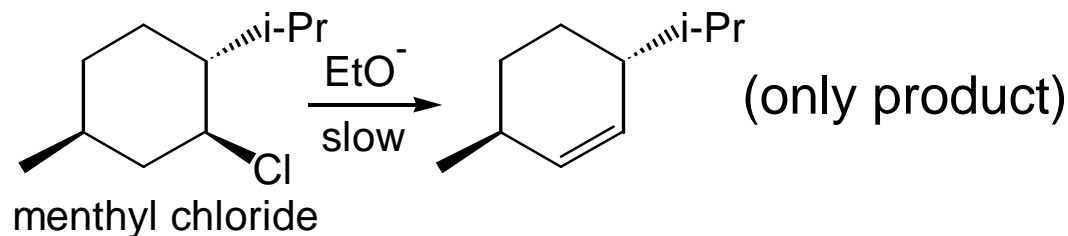
◆ *practice*: [📖 319 Practice 9.1](#) [📖 315-9, Problems 9.1-9.4](#)

Different alkenes from diastereomers: E2



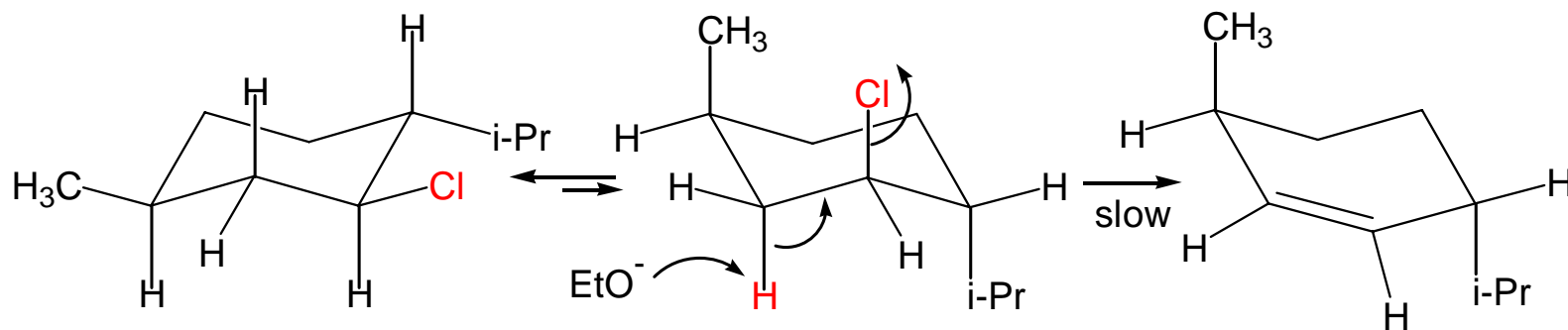
E2 Reactions (II)

- Cyclic compounds: depending on the rigidity
 - ◆ flexible rings: trans-diaxial (anti), [📖 321-2, Figure 9.4 & 9.5](#)
 - ◆ rigid rings: *syn*-E2 possible, [📖 320 bottom](#)
 - ◆ *practice*: [📖 322-3 Problems 9.5 & 9.6](#)

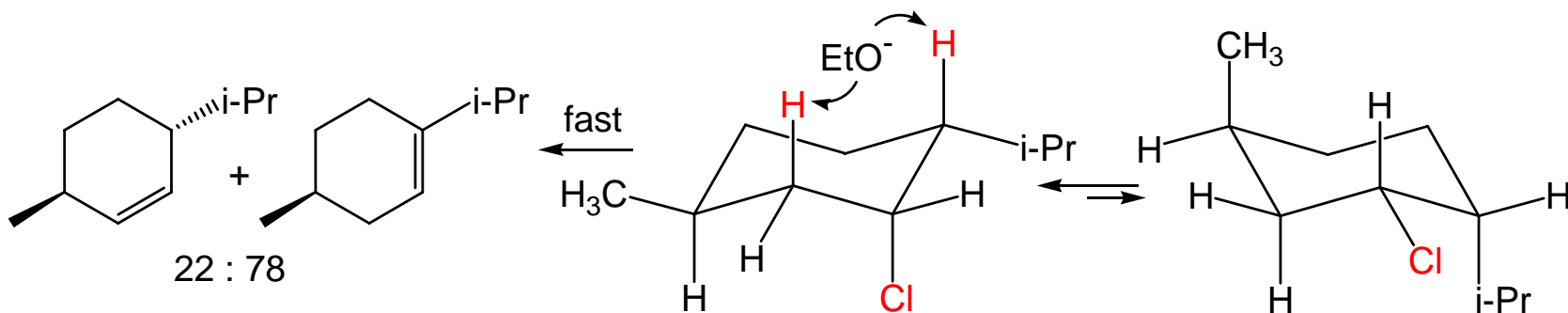


E2 reactions in cyclic compounds

□ menthyl chloride



□ neomenthyl chloride



E2 Reactions (III)

- Regiochemistry/regioselectivity: [📖 322](#) & [📖 324 top](#)
 - ◆ Zaitsev's rule: 'more substituted alkenes favored',
 - stability of alkenes: hyperconjugation effect, [📖 324 middle](#)
 - product development control: [📖 325 Figure 9.6](#)
 - *practice*: [📖 325 Practice 9.2](#) & [📖 326, Problems 9.7 & 9.8](#)
 - ◆ Hofmann's rule: 'less substituted alkenes favored', [📖 326](#)
 - (kinetic) acidity (a poor leaving group) & steric effect: [📖 328 mid](#)
 - ◆ conjugated alkenes preferred: more stable, [📖 328 bottom](#)
 - ◆ *practice*: [📖 327 Practice 9.3](#), [📖 327-9 Problems 9.9 & 9.10](#)

Unimolecular Elimination Reactions (E1)

- Rate = $k[t\text{-BuBr}]$: weak base; [📖 329 bottom](#)
 - ◆ stepwise mechanism: carbocation; [📖 330 Figure 9.7](#)
 - ◆ higher energy path than S_N1 : [📖 330 Figure 9.7](#)
 - ◆ regiochemistry: Zaitsev's product, [📖 331 bottom](#)
 - no *trans*-diaxial requirement: [📖 332 top](#) (*cf.* [📖 321](#))
 - ◆ *practice*: [📖 332 Practice 9.4](#), [📖 331-3, Problems 9.11. 9.12 & 9.13](#)
- E1cb mechanism: [📖 333 Focus On](#)
 - ◆ more stable alkenes: major; [📖 334 top](#)

Elimination vs Substitution (Conditions)

- S_N2 / $E2$ over S_N1 ($E1$): a good Nu or base
 - ◆ steric hindrance favors elimination: [📖 335 middle](#)
 - ◆ stronger Nu (stronger base) favors elimination: [📖 336 top](#)
 - ◆ higher temperature favors elimination: [📖 336 middle](#)
- S_N1 ($E1$) over S_N2 / $E2$: weak bases & in polar solvents
 - ◆ carbocation intermediates: $3^\circ/2^\circ$ substrates in polar solvents
 - ◆ S_N1 is always accompanied by $E1$: [📖 330](#) & [📖 331](#)

Elimination vs Substitution (Substrate)

- Primary carbons (**except allylic/benzylic**): mostly S_N2
 - ◆ E2: with bulky bases, [📖 337 top](#) [CH₃L: always S_N2]
- Secondary carbons: depending on the conditions
 - ◆ S_N2: small, good & weakly basic Nu (AcO⁻, CN⁻, RS⁻)
 - ◆ E2: strong & bulky base ([RO⁻](#), [t-BuO⁻](#))
 - ◆ S_N1: weakly basic polar solvent (solvolysis), [📖 337 bottom](#)
- Tertiary carbons: E2 with a strong base, [📖 338 top](#)
 - ◆ S_N1 in weakly basic polar solvent without a base (**no S_N2**)
 - ◆ *practice*: [📖 338 Practice 9.5](#), [📖 338-9 Problems 9.15 & 9.16](#)