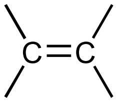
Elimination Reactions & Introduction to Alkenes - Chapter 7, part 2 (Klein)

Chapter Outline (Part 2)

I. Alkene structure & stability (7.6)
II. Alkene synthesis: E2 elimination (7.5, 7.7) ***SkillBuilders 7.3, 7.4, 7.5***
III. Alkene synthesis: E1 elimination (7.8)
  A) Dehydration of alcohols (7.10)
IV. Substitution vs. Elimination (7.9) ***SkillBuilder 7.7***
V. Synthesis strategies (7.11) ***SkillBuilder 7.8***

I. Alkene structure (review)

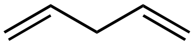
3-D sketch: *p* orbitals are orthogonal to sp^2 plane

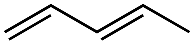


- π bonds are higher energy than σ bonds (more reactive, easier to break)
- π bonds are electron-rich (can react as a nucleophile or a base - see Chapter 8)

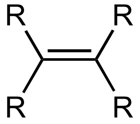
Alkene stability (7.6)

- conjugation increases stability (resonance)

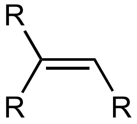




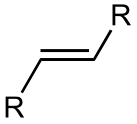
- increasing number of alkyl substituents increases stability

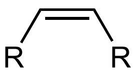


______substituted



______substituted





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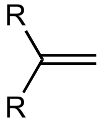
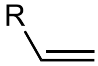




______substituted

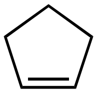
______substituted

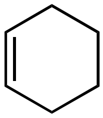
- trans is more stable than cis, except in rings

trans possible if ring is >7 carbons
Shown here is cyclooctene:

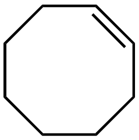
cis
(less stable)

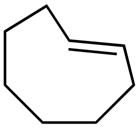
trans
(more stable)



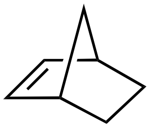


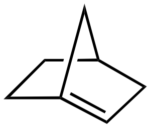
cis only



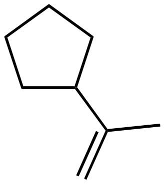


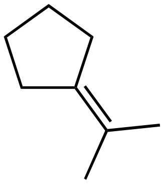
- FYI π bond is unstable at bridgehead carbons (Bredt's rule)

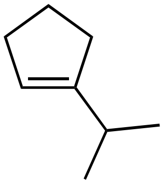




Example: Which alkene is most stable? Least stable?



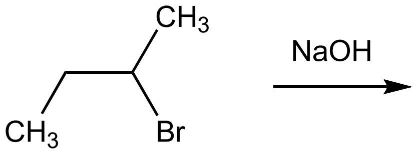




II. Alkene synthesis via E2 mechanism (7.5, 7.7) **Elimination Bimolecular**

- one-step mechanism
- needs strong base
- rate = *k* [RX] [base]

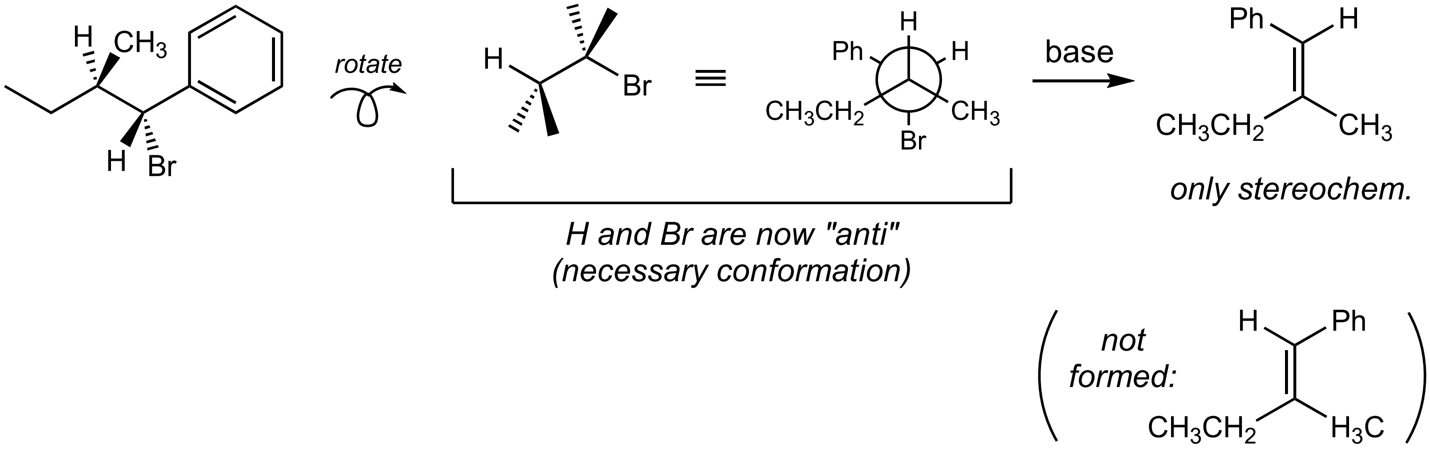
Example:



"eliminate" or lose β-hydrogen and LG (loss of HBr is called dehydrohalogenation)

Stereochemisty of E2 mechanism (7.7)

- β-hydrogen and LG must be anti-coplanar (180°) or anti-periplanar (close to 180°)
- E2 is called "anti elimination"

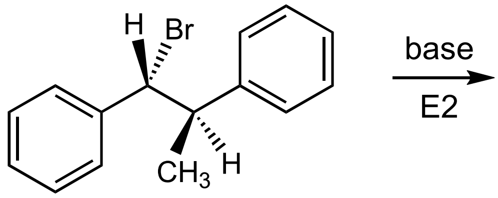


only stereochem.

H and Br are now "anti"
(necessary conformation)

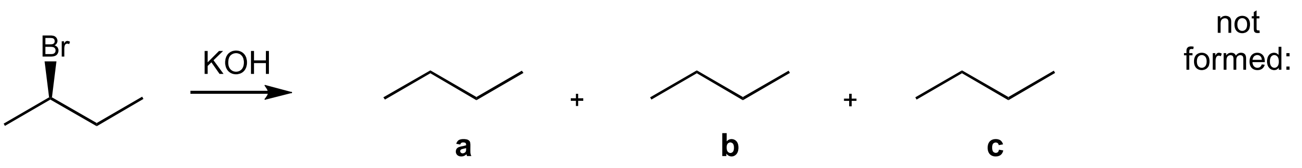
not formed:

Example:

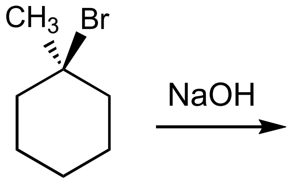


SkillBuilder 7.4

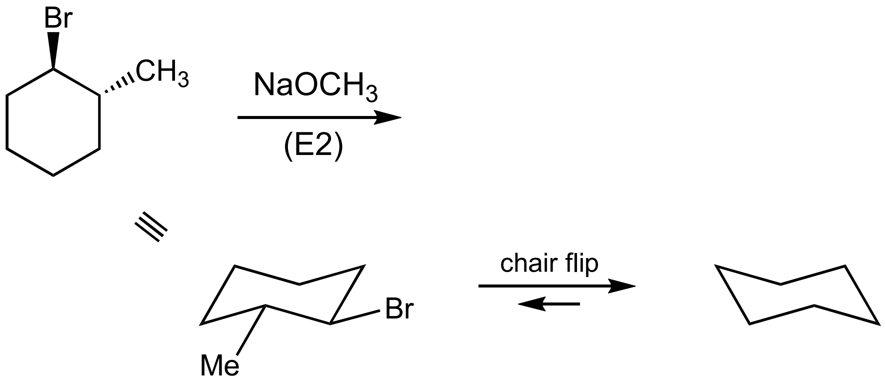
Regiochemistry of E2 mechanism (Zaitsev and Hofmann, 7.7)



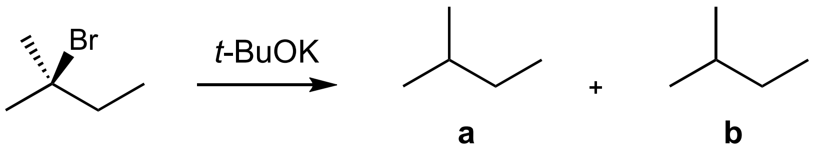
_____ is the major product because it is the most stable alkene (Zaitsev's Rule)



Effect of chair conformation on rate of E2 mechanism.

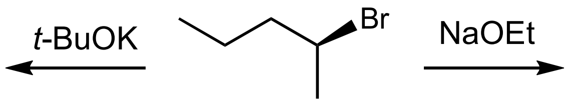


When a sterically hindered "bulky" base is used, then β-hydrogen on *less substituted* C is removed.



_____ is the major product because it is formed fastest (Hofmann's Rule)

Example: predict the major E2 elimination product for each reaction.



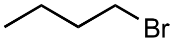
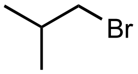
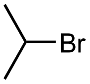
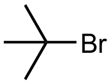
SkillBuilders 7.3, 7.5

S_N2 vs. E2 (see 7.9)

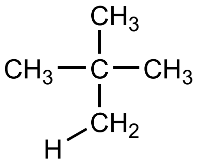
When do they compete? Reactions involving HO^- (hydroxide) or RO^- (alkoxide).

Compare rates:

$$R{-}Br \xrightarrow[EtOH]{EtONa}$$

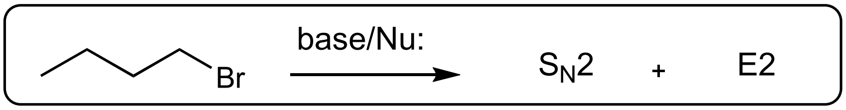
RBr	name	Type	% S_N2	% E2
CH_3Br				
				
				
				
				

Consider *t*-BuBr:

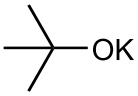


$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2-H}{C}}-CH_3$$

What if we vary base?



CH_3ONa



t-Butoxide is a very <u>bulky</u> base (also Et_3N, iPr_2NH, DBU, DBN)
- not good for S_N2
- classic E2 reaction conditions (gives Hofmann product if there is a choice)

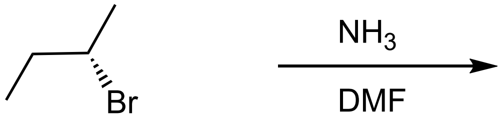
Addition of heat also favors elimination (T∆S becomes large)

Preference for E2 over S_N2 (by RX type):

E2 vs. S_N2: Predict the major product(s) expected for each of the following reactions. Remember to indicate stereochemistry, when appropriate. If no reaction is expected, write NR.

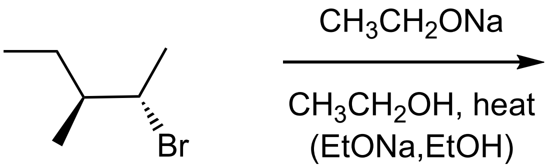
a) $CH_3OTs \xrightarrow[CH_3OH]{CH_3ONa}$

b)



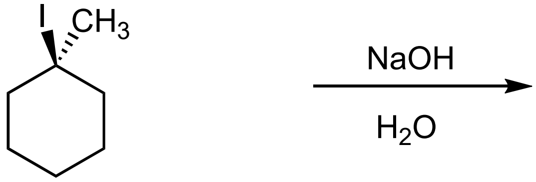
c)

d)

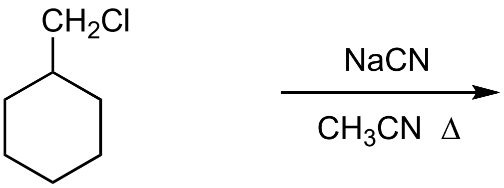


e)

f)

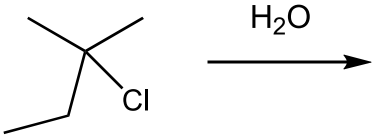


g)



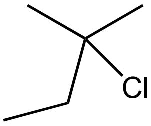
h)

III. Alkene synthesis via E1 mechanism (7.8) Elimination Unimolecular



E1 Mechanism: 2 steps, via carbocation

1) loss of LG



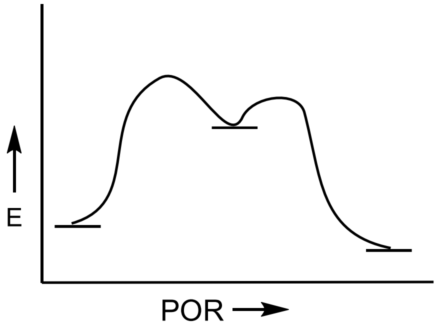
(same slow, rate-determining step as S_N1)

2) loss of β-H

(follows Zaitsev's rule - forms most substituted, most stable alkene)

E1 Kinetics Rate = *k*[RCl]

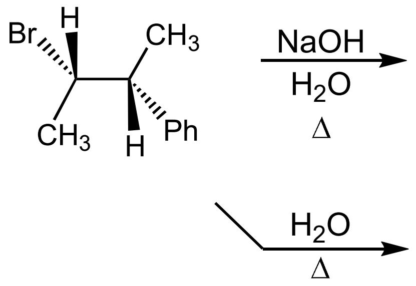
- unimolecular
- rate not dependent on [H_2O] so H_2O is not involved in rate-determining step
- a more stable carbocation will be formed faster (lower E_a) and gives faster E1/S_N1



Rate (by RX type)

allyl / benzyl / 3° > 2° >> 1° methyl

E1 Stereochemistry: via achiral carbocation intermediate so loss of stereochemistry



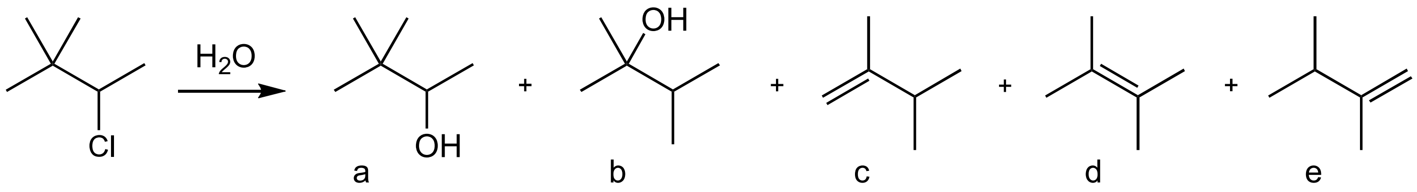
Carbocation Rearrangements (6.11)

Because of rearrangements, product mixtures are common for reactions involving carbocations.

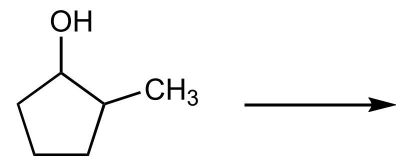
1) Of the elimination products shown below, which is expected to be major?

2) What mechanism accounts for the alcohol products? For the alkene products?

3) Provide detailed mechanisms to generate all products shown.

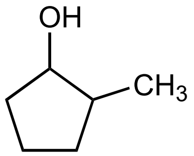


III A. Dehydration of Alcohols (7.10)

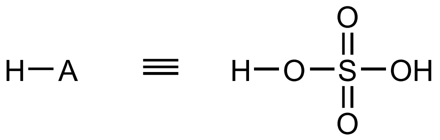


loss of ___________ = dehydration

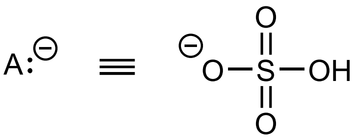
Mechanism? S_N1 S_N2 E1 E2



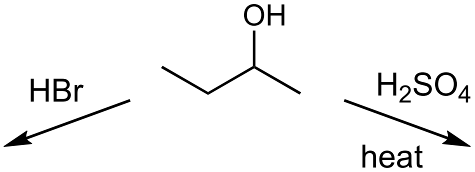
- produces most stable alkene possible (Zaitsev / Hofmann)
- carbocation can rearrange
- recall what is needed to make OH a good leaving group: __________________________



$$H-A \equiv H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$



$$A:^{\ominus} \equiv {}^{\ominus}O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OH$$



- strong / weak base
- non-nucleophilic, so no S_N1 competition
- A^- is like a spectator ion (N/R)

Start building up a set of flashcards to study CHM 3140 reactions and organize material (essential in Chapter 8!!). From any new reaction we learn in class, you can create **THREE** flashcards:

starting material $\xrightarrow{\text{reagent}}$ product

starting material $\xrightarrow{\text{reagent}}$?

predict the product

starting material $\xrightarrow{?}$ product

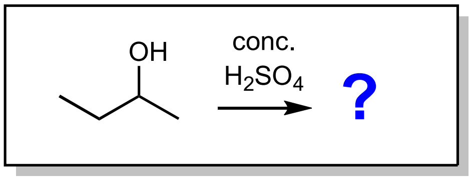
transform problem*

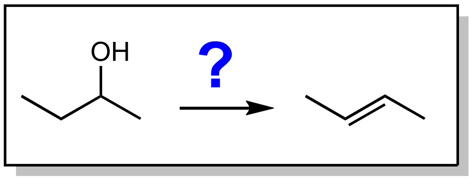
? $\xrightarrow{\text{reagent}}$ product

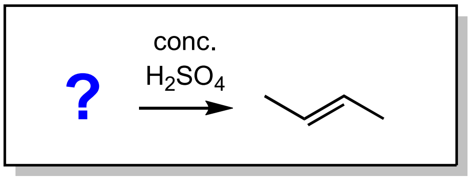
retrosynthesis*

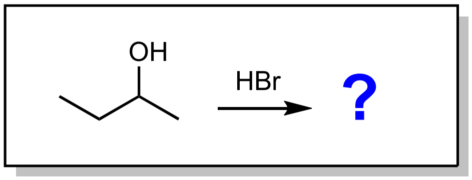
Useful for preparing for final, reviewing material in CHM 3150 and *planning a synthesis.

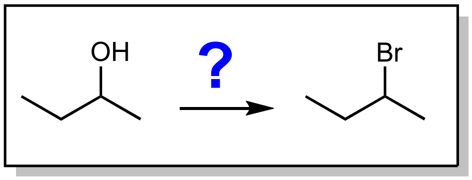
Sample Flashcards (Reactions of Alcohols)

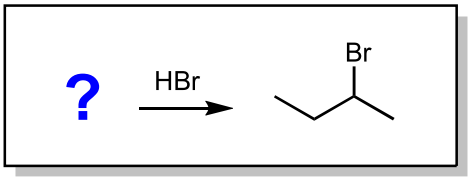












IV. Substitution vs. Elimination (7.9)

Bimolecular reactions (1-step mechanism)

S_N2 • requires good Nu: (X^-, NH_3, RNH_2, CN^-, N_3^-, RO^-, HO^-)

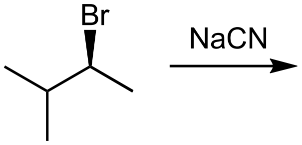
• steric hinderance slows S_N2: CH_3 (fastest) > 1° > 2° >> 3° (tertiary, slowest)

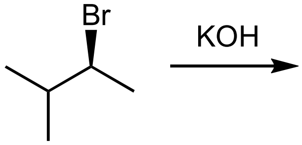
E2 • requires a strong base (RO^-, HO^-, NOT H_2O, ROH)

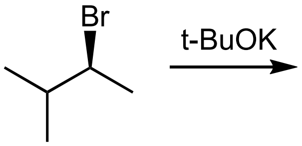
Unimolecular reactions (stepwise mechanism, via carbocation)

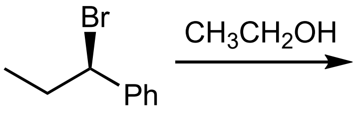
S_N1 and E1 • requires <u>NO</u> strong base/Nu: (usually H_2O, ROH – called solvolysis)

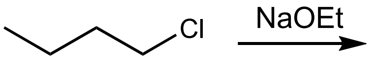
• more stable carbocation, faster reaction: benzyl/allyl, 3° > 2° >> 1°, methyl

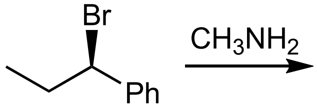
☐ 

☐ 

☐ 

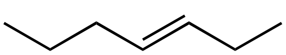
☐ 

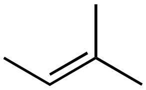
☐ 

☐ 

V. Synthesis strategies (7.11)

Provide suitable starting materials to synthesize the following target molecules (TM).





SkillBuilder 7.9

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

I. Review the pi (π) bond & Alkene stability (7.6)
  i) more alkyl groups, more stable
  ii) trans is more stable than cis (except in rings)
  iii) pi bond unstable at bridgehead carbon (Bredt's Rule)
  iv) alkene is more stable if conjugated with another pi bond (16.2)
II. Alkene synthesis: E2 mechanism (one-step) (7.5, 7.7) ***SkillBuilders 7.3, 7.4, 7.5***
  i) requires strong base (HO^-, RO^-, R_2N^-)
  ii) stereochemistry: anti-elimination of β-hydrogen and LG
  iii) regiochemistry: depends on base choice
    a. usually gives the most stable alkene (Zaitsev with NaOH, MeONa, EtONa)
    b. bulky base gives less substituted alkene (Hofmann with t-BuOK)
  iv) often in competition with S_N2 (E2 favored unless primary RX)
III. 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; E favored)
  iii) regiochemistry: gives the most stable alkene (Zaitsev)
  iv) usually in competition with S_N1 (E1 favored with heat)
  v) dehydration of alcohols (conc. H_3PO_4 or conc. H_2SO_4 + heat) (7.10)
IV. Predicting Products: Substitution vs. Elimination (7.9) ***SkillBuilder 7.7***
  i) Bimolecular (strong base/nu:): S_N2 vs. E2 (see below)
  ii) Unimolecular (carbocation): S_N1 vs. E1 (see below)
V. Synthesis Strategies (7.11) ***SkillBuilder 7.9***

Bimolecular reactions (1-step mechanism)

S_N2 • requires good Nu: (X^-, NH_3, RNH_2, CN^-, N_3^-, RO^-, HO^-)
• steric hinderance slows S_N2: CH_3 (fastest) > 1° > 2° >> 3° (tertiary, slowest)
E2 • requires a strong base (RO^-, HO^-, NOT H_2O, ROH)

Unimolecular reactions (stepwise mechanism, via carbocation)

S_N1 and E1 • requires <u>NO</u> strong base/Nu: (usually H_2O, ROH – called solvolysis)
• more stable carbocation, faster reaction: benzyl/allyl, 3° > 2° >> 1°, methyl

Alkyl Group (RX)	**S_N1, E1, E2**	**S_N2**
3° (tertiary)	common	rare
2° (secondary)	sometimes	sometimes
1° (primary)	rare	common
CH_3 (methyl)	rare	common