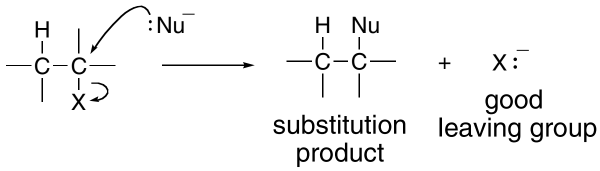
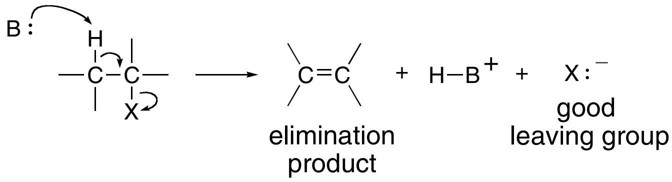
Chapter 8: Alkyl Halides and Elimination Reactions

♦ A comparison between nucleophilic substitution and β-elimination

Nucleophilic substitution—A nucleophile attacks a carbon atom (7.6).



β-Elimination—A base attacks a proton (8.1).

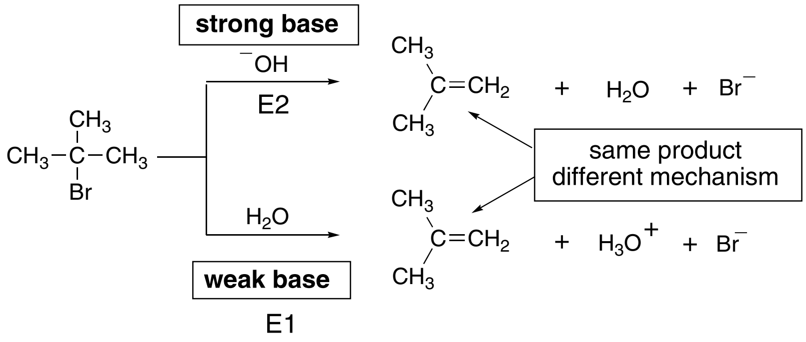


Similarities	Differences
• In both reactions RX acts as an electrophile, reacting with an electron-rich reagent. • Both reactions require a **good leaving group X:⁻** willing to accept the electron density in the C–X bond.	• In substitution, a nucleophile attacks a single carbon atom. • In elimination, a Brønsted–Lowry base removes a proton to form a π bond, and two carbons are involved in the reaction.

♦ The importance of the base in E2 and E1 reactions (8.9)

The strength of the base determines the mechanism of elimination.

- Strong bases favor E2 reactions.
- Weak bases favor E1 reactions.



♦ E1 and E2 mechanisms compared

	E2 mechanism	E1 mechanism
[1] Mechanism	• one step (8.4B)	• two steps (8.6B)
[2] Alkyl halide	• rate: $R_3CX > R_2CHX > RCH_2X$ (8.4C)	• rate: $R_3CX > R_2CHX > RCH_2X$ (8.6C)
[3] Rate equation	• rate = k[RX][B:] • second-order kinetics (8.4A)	• rate = k[RX] • first-order kinetics (8.6A)
[4] Stereochemistry	• anti periplanar arrangement of H and X (8.8)	• trigonal planar carbocation intermediate (8.6B)
[5] Base	• favored by strong bases (8.4B)	• favored by weak bases (8.6C)
[6] Leaving group	• better leaving group → faster reaction (8.4B)	• better leaving group → faster reaction (Table 8.4)
[7] Solvent	• favored by polar aprotic solvents (8.4B)	• favored by polar protic solvents (Table 8.4)
[8] Product	• more substituted alkene favored (Zaitsev rule, 8.5)	• more substituted alkene favored (Zaitsev rule, 8.6C)

♦ Summary chart on the four mechanisms: S_N1, S_N2, E1, or E2

Alkyl halide type	Conditions	Mechanism
1^o RCH_2X	strong nucleophile strong bulky base	**S_N2** **E2**
2^o R_2CHX	strong base and nucleophile strong bulky base weak base and nucleophile	**S_N2 + E2** **E2** **S_N1 + E1**
3^o R_3CX	weak base and nucleophile strong base	**S_N1 + E1** **E2**

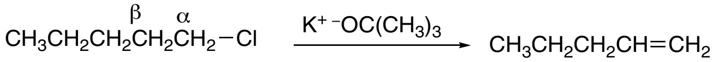
♦ Zaitsev rule

- β-Elimination affords the more stable product having the more substituted double bond.
- Zaitsev products predominate in E2 reactions except when a cyclohexane ring prevents trans diaxial arrangement.

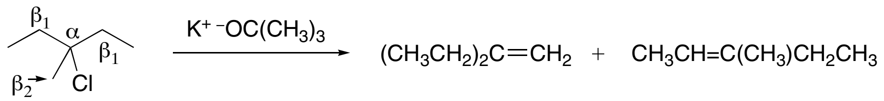
Chapter 8: Answers to Problems

8.1 • The carbon bonded to the leaving group is the **α carbon**. Any carbon bonded to it is a **β carbon**.

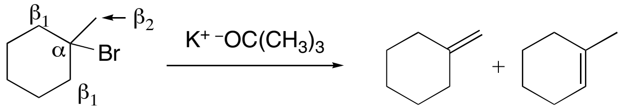
• **To draw the products of an elimination reaction:** Remove the leaving group from the α carbon and a H from the β carbon and form a π bond.

a. 

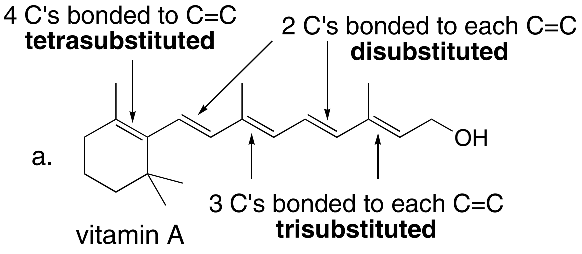
$CH_3CH_2CH_2\overset{\beta}{C}H_2\overset{\alpha}{C}H_2{-}Cl \xrightarrow{K^+\ ^-OC(CH_3)_3} CH_3CH_2CH_2CH{=}CH_2$

b. 

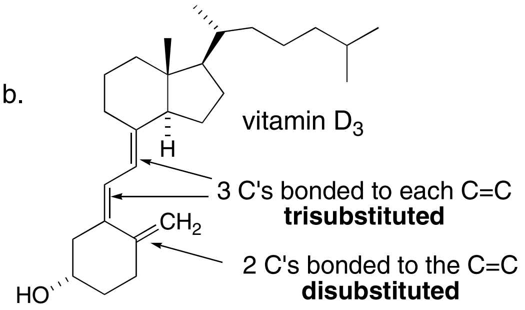
$(CH_3CH_2)_2C{=}CH_2 + CH_3CH{=}C(CH_3)CH_2CH_3$

c. 

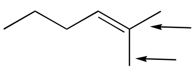
8.2 **Alkenes are classified by the number of carbon atoms bonded to the double bond.** A monosubstituted alkene has one carbon atom bonded to the double bond, a disubstituted alkene has two carbon atoms bonded to the double bond, etc.

a. 

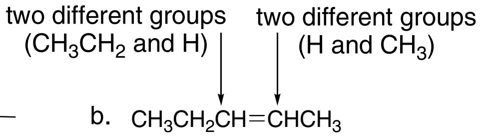
vitamin A

b. 

8.3 To have stereoisomers at a C=C, the two groups on each end of the double bond must be different from each other.

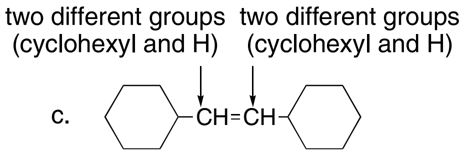
a. 

two CH3 groups
no stereoisomers
possible

b. 

$CH_3CH_2CH{=}CHCH_3$

stereoisomers possible

c. 

stereoisomers possible

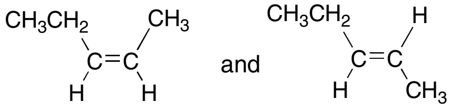
8.4 Two definitions:

- **Constitutional isomers** differ in the connectivity of the atoms.
- **Stereoisomers** differ only in the 3-D arrangement of atoms in space.

a.

different connectivity of atoms
constitutional isomers

c.

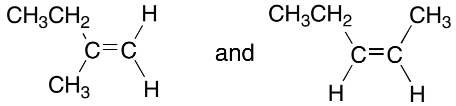


cis trans
different arrangement of atoms in space
stereoisomers

b.

trans trans
identical

d.

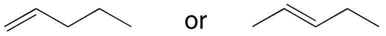


different connectivity of atoms
constitutional isomers

8.5 Two rules to predict the relative stability of alkenes:

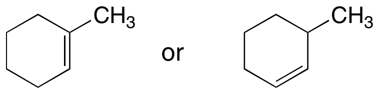
[1] Trans alkenes are generally more stable than cis alkenes.
[2] The stability of an alkene increases as the number of R groups on the C=C increases.

a.



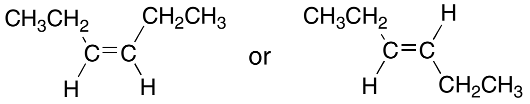
monosubstituted — disubstituted **more stable**

c.



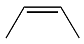
trisubstituted **more stable** — disubstituted

b.

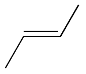


cis — trans **more stable**

8.6 Use the rules from Answer 8.5 to explain the energy differences.

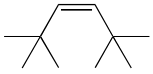


cis-2-butene

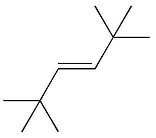


trans-2-butene

less steric interaction between smaller CH_3 groups
smaller energy difference



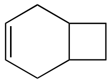
cis-2,2,5,5-tetramethyl-3-hexene



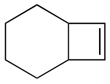
trans-2,2,5,5-tetramethyl-3-hexene

more steric interaction between larger *tert*-butyl groups in the cis isomer
larger difference in stability

8.7



A

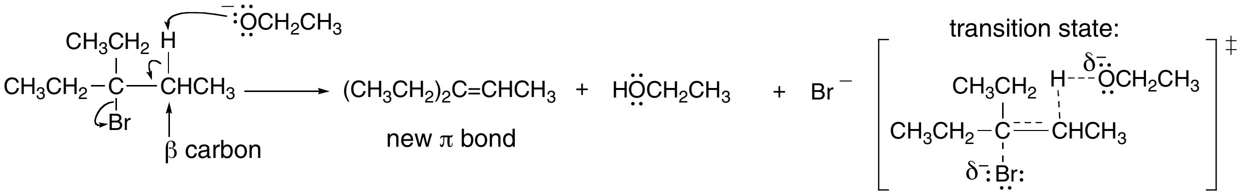


B

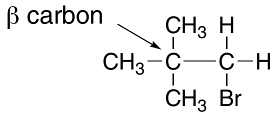
Alkene **A** is more stable than alkene **B** because the double bond in **A** is in a six-membered ring. The double bond in **B** is in a four-membered ring, which has considerable angle strain due to the small ring size.

8.8 In an E2 mechanism, four bonds are involved in the single step. Use curved arrows to show these simultaneous actions:

[1] The base attacks a hydrogen on a β carbon.
[2] A π bond forms.
[3] The leaving group comes off.

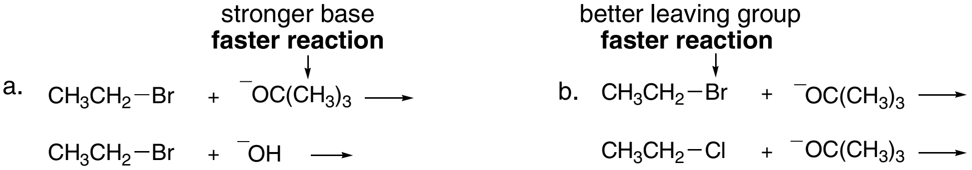


8.9 For E2 elimination to occur there must be at least one hydrogen on a β carbon.



no H's on β carbon
inert to E2 elimination

8.10 In both cases, the rate of elimination decreases.



a.
stronger base
faster reaction

CH_3CH_2-Br + $^{-}OC(CH_3)_3 \longrightarrow$

CH_3CH_2-Br + $^{-}OH \longrightarrow$

b.
better leaving group
faster reaction

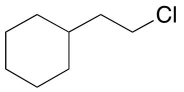
CH_3CH_2-Br + $^{-}OC(CH_3)_3 \longrightarrow$

CH_3CH_2-Cl + $^{-}OC(CH_3)_3 \longrightarrow$

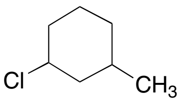
8.11 As the number of R groups on the carbon with the leaving group increases, the rate of an E2 reaction increases.

a. $(CH_3)_2CHCH_2CH_2CH_2Br$	$(CH_3)_2CHCH_2CH(Br)CH_3$	$(CH_3)_2C(Br)CH_2CH_2CH_3$
1° alkyl halide **least reactive**	2° alkyl halide **intermediate reactivity**	3° alkyl halide **most reactive**

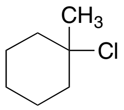
b.



1° alkyl halide
least reactive



2° alkyl halide
intermediate reactivity



3° alkyl halide
most reactive

8.12 Use the following characteristics of an E2 reaction to answer the questions:

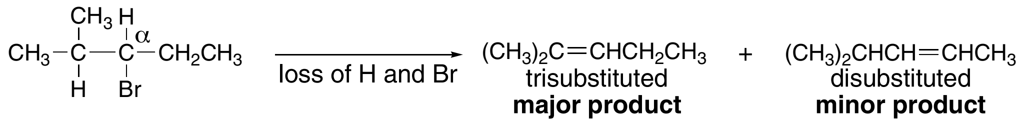
[1] E2 reactions are second order and one step.
[2] More substituted halides react faster.
[3] Reactions with strong bases or better leaving groups are faster.
[4] Reactions with polar aprotic solvents are faster.

Rate equation: rate = *k*[RX][Base]

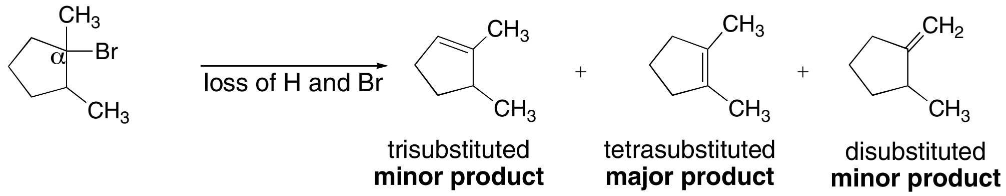
a. tripling the concentration of the alkyl halide = **rate triples**
b. halving the concentration of the base = **rate halved**
c. changing the solvent from CH_3OH to DMSO = **rate increases** (Polar aprotic solvent is better for E2.)
d. changing the leaving group from I^- to Br^- = **rate decreases** (I^- is a better leaving group.)
e. changing the base from ^-OH to H_2O = **rate decreases** (weaker base)
f. changing the alkyl halide from CH_3CH_2Br to $(CH_3)_2CHBr$ = **rate increases** (More substituted halide reacts faster.)

8.13 The Zaitsev rule states: In a β-elimination reaction, the major product has the more substituted double bond.

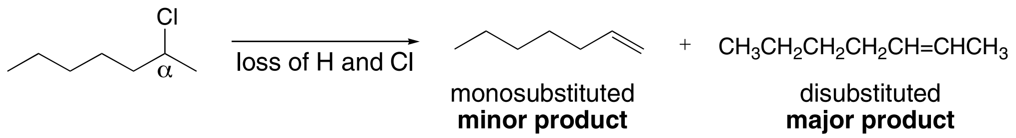
a.



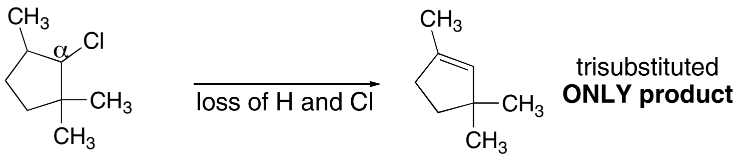
b.



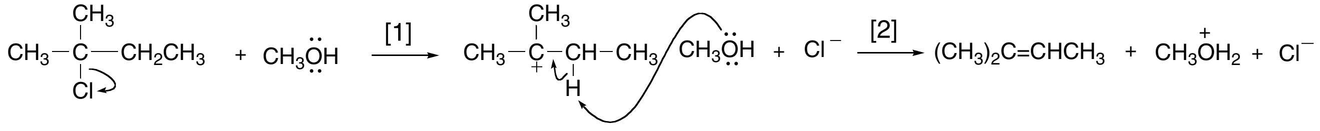
c.



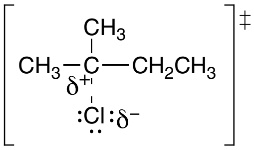
d.



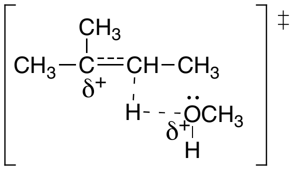
8.14 An E1 mechanism has two steps:
[1] The leaving group comes off, creating a carbocation.
[2] A base pulls off a proton from a β carbon, and a π bond forms.



transition state [1]:

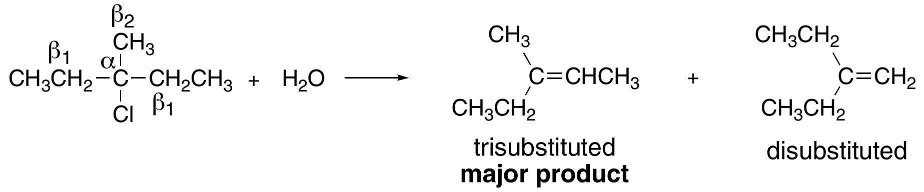


transition state [2]:

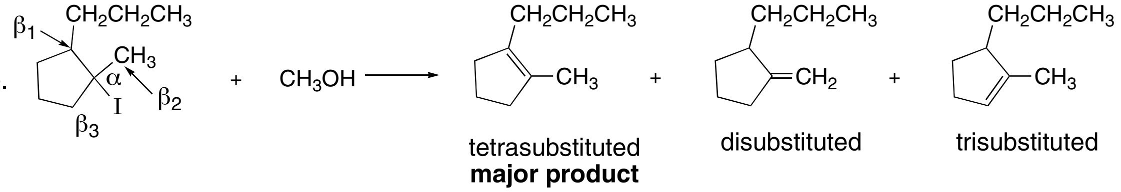


8.15 The Zaitsev rule states: In a β-elimination reaction, the major product has the more substituted double bond.

a.



b.



8.16 Use the following characteristics of an **E1 reaction** to answer the questions:

[1] E1 reactions are first order and two steps.
[2] More substituted halides react faster.
[3] Weaker bases are preferred.
[4] Reactions with better leaving groups are faster.
[5] Reactions in polar protic solvents are faster.

Rate equation: rate = *k*[RX]. The base doesn't affect rate.

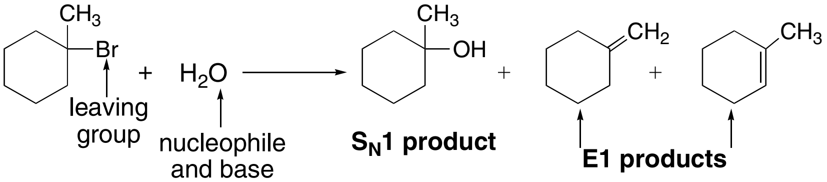
a. doubling the concentration of the alkyl halide = **rate doubles**
b. doubling the concentration of the base = **no change** (Base is not in the rate equation.)
c. changing the alkyl halide from $(CH_3)_3CBr$ to $CH_3CH_2CH_2Br$ = **rate decreases** (More substituted halides react faster.)
d. changing the leaving group from Cl^- to Br^- = **rate increases** (better leaving group)
e. changing the solvent from DMSO to CH_3OH = **rate increases** (Polar protic solvent favors E1.)

8.17 Both S_N1 and E1 reactions occur by forming a carbocation. To draw the products:

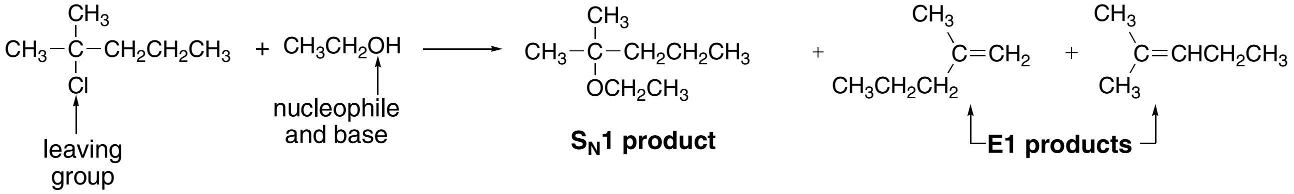
[1] **For the S_N1 reaction,** substitute the nucleophile for the leaving group.

[2] **For the E1 reaction**, remove a proton from a β carbon and create a new π bond.

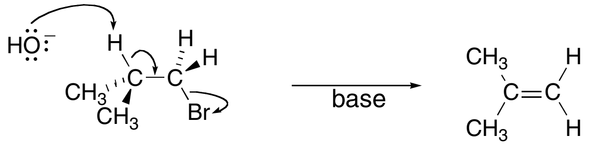
a.



b.

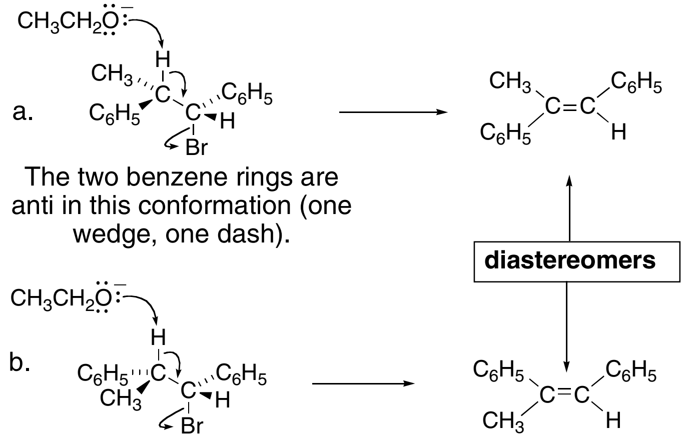


8.18 E2 reactions occur with anti periplanar geometry. **The anti periplanar arrangement uses a *staggered* conformation and has the H and X on *opposite sides* of the C–C bond.**



H and Br are on opposite sides =
anti periplanar

8.19 The E2 elimination reactions will occur in the anti periplanar orientation as drawn. To draw the product of elimination, maintain the orientation of the remaining groups around the C=C.



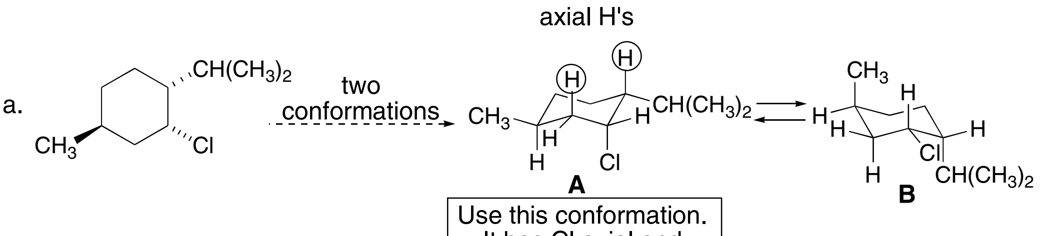
The two benzene rings are anti in this conformation (one wedge, one dash).

The two benzene rings remain on opposite sides of the newly formed C=C. This makes them **trans**.

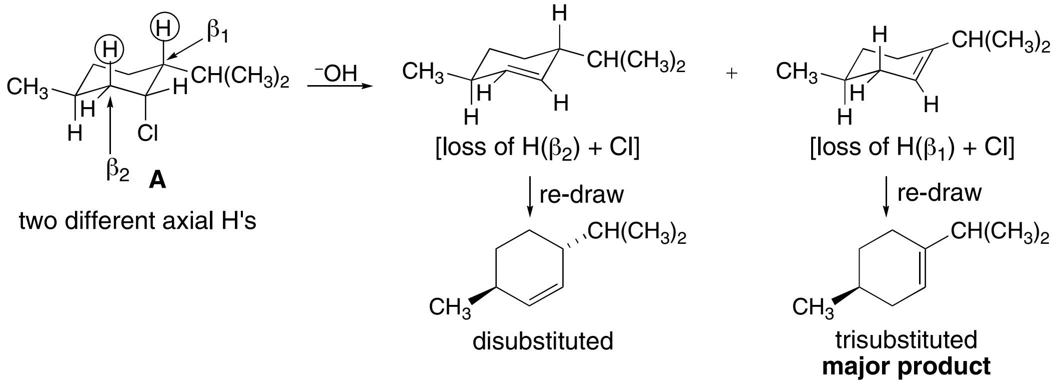
The two benzene rings are gauche in this conformation (both drawn on dashes, behind the plane).

The two benzene rings remain on the same side of the newly formed C=C. This makes them **cis**.

8.20 Note: The Zaitsev products predominate in E2 elimination *except* when substituents on a cyclohexane ring prevent a **trans diaxial** arrangement of H and X.



Use this conformation.
It has Cl axial and
two axial H's.



two different axial H's

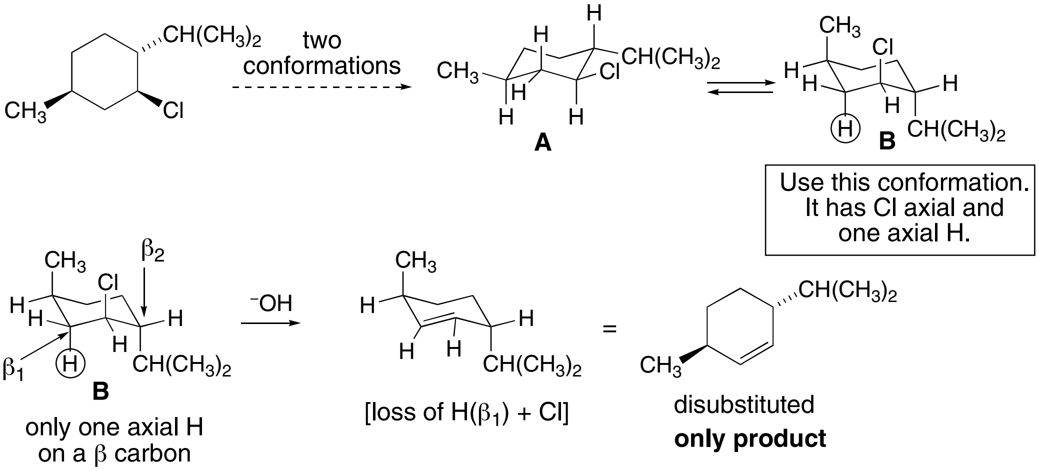
[loss of H(β2) + Cl]

[loss of H(β1) + Cl]

disubstituted

trisubstituted
major product

b.



Use this conformation.
It has Cl axial and
one axial H.

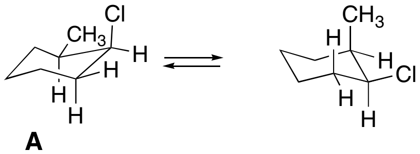
only one axial H
on a β carbon

[loss of H(β1) + Cl]

disubstituted
only product

8.21 Draw the chair conformations of *cis*-1-chloro-2-methylcyclohexane and its trans isomer. For E2 elimination reactions to occur, **there must be a H and X trans diaxial to each other.**

Two conformations of the cis isomer:

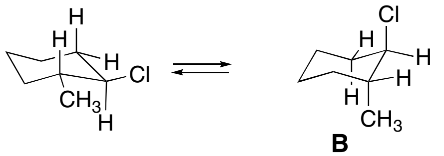


A

reacting conformation (axial Cl)

This reacting conformation has only one group axial, making it more stable and present in a higher concentration than **B**. This makes a **faster elimination reaction with the cis isomer.**

Two conformations of the trans isomer:



B

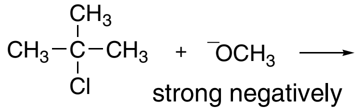
reacting conformation (axial Cl)

This conformation is less stable than **A**, since both CH_3 and Cl are axial. **This slows the rate of elimination from the trans isomer**.

8.22 E2 reactions are favored by strong negatively charged bases and occur with 1°, 2°, and 3° halides, with 3° being the most reactive.

E1 reactions are favored by weaker neutral bases and do not occur with 1° halides since they would have to form highly unstable carbocations.

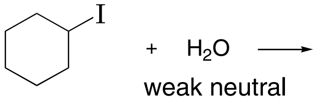
a.



$CH_3-C(CH_3)(Cl)-CH_3 + {}^-OCH_3 \longrightarrow$

strong negatively charged base
E2

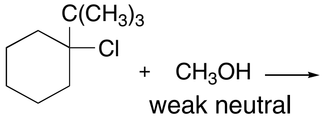
b.



$+ H_2O \longrightarrow$

weak neutral base
E1

c.



$+ CH_3OH \longrightarrow$

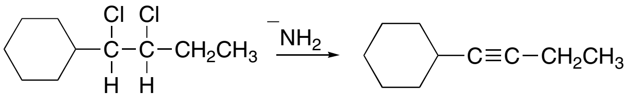
weak neutral base
E1

d. $CH_3CH_2Br + {}^-OC(CH_3)_3 \longrightarrow$

strong negatively charged base
E2

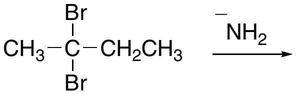
8.23 Draw the alkynes that result from removal of two equivalents of HX.

a.



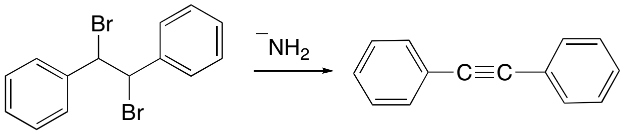
b. $CH_3CH_2CH_2CHCl_2 \xrightarrow[DMSO]{KOC(CH_3)_3} CH_3CH_2C\equiv CH$

c.



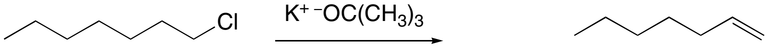
$CH_3-CBr_2-CH_2CH_3 \xrightarrow{{}^-NH_2} CH_3C\equiv CCH_3 + HC\equiv CCH_2CH_3$

d.



8.24

a.

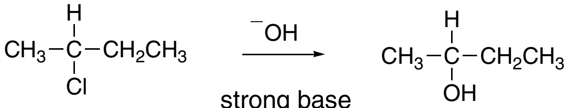


$\xrightarrow{K^+ {}^-OC(CH_3)_3}$

1° halide
S_N2 or E2

strong bulky base
E2

b.



$CH_3-CH(Cl)-CH_2CH_3 \xrightarrow{{}^-OH} CH_3-CH(OH)-CH_2CH_3 + CH_3-CH=CHCH_3 + CH_2=CH-CH_2CH_3$

2° halide
any mechanism

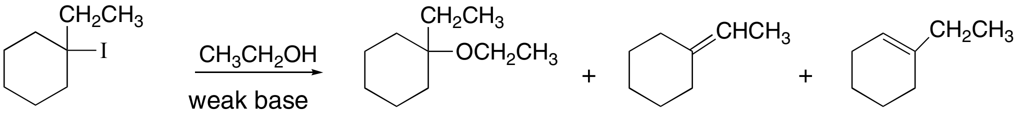
strong base
S_N2 and E2

S_N2 product

disubstituted
major E2 product

monosubstituted
minor E2 product

c.



3° halide
no S_N2

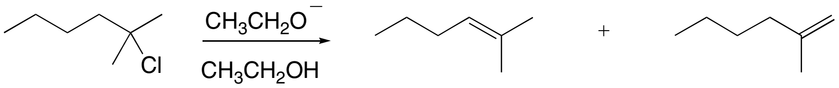
weak base
S_N1 and E1

S_N1 product

E1 product

E1 product

d.



strong base
$\xrightarrow[CH_3CH_2OH]{CH_3CH_2O^-}$

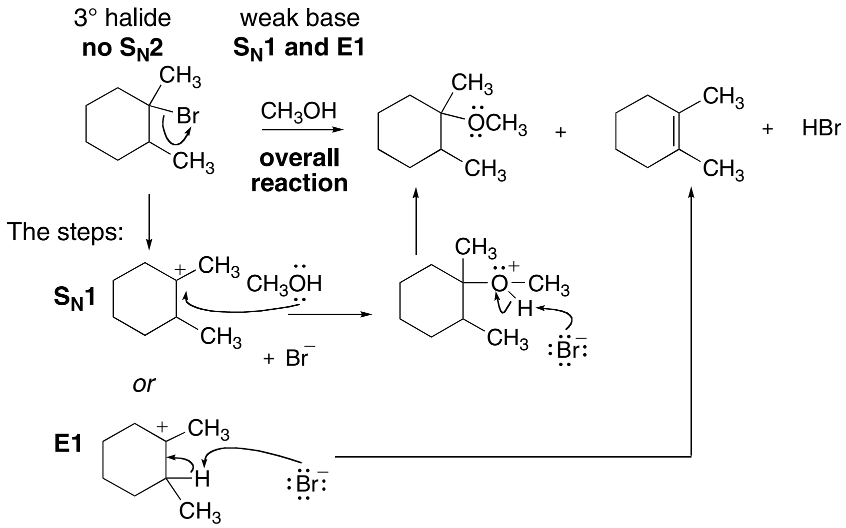
3° halide
no S_N2

E2

major E2 product

minor E2 product

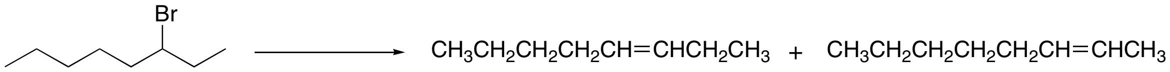
8.25


3° halide
no S_N2
weak base
S_N1 and E1
CH_3
Br
CH_3
CH_3OH
overall reaction
OCH_3
+
+ HBr
The steps:
S_N1
CH_3OH
+ Br^-
O–CH_3
H
Br^-
or
E1
H

8.26

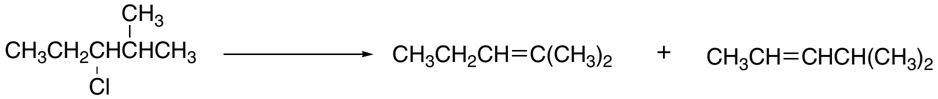
a. $CH_3CH_2CH_2CH_2CH_2CH_2Br \longrightarrow CH_3CH_2CH_2CH_2CH=CH_2$

b.



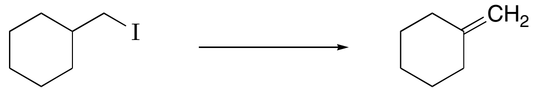
$\longrightarrow CH_3CH_2CH_2CH_2CH=CHCH_2CH_3 + CH_3CH_2CH_2CH_2CH_2CH=CHCH_3$

c.



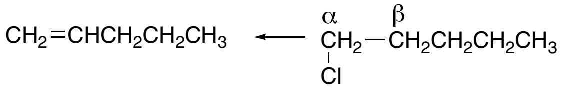
$CH_3CH_2\overset{CH_3}{\overset{|}{C}}H\underset{Cl}{\underset{|}{C}}HCH_3 \longrightarrow CH_3CH_2CH=C(CH_3)_2 + CH_3CH=CHCH(CH_3)_2$

d.



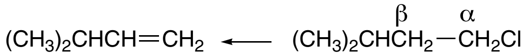
8.27 To give only one product in an elimination reaction, **the starting alkyl halide must have only one type of β carbon with H's.**

a.



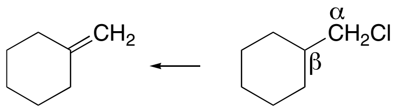
$CH_2=CHCH_2CH_2CH_3 \longleftarrow \underset{Cl}{\underset{|}{\overset{\alpha}{C}H_2}}-\overset{\beta}{C}H_2CH_2CH_2CH_3$

b.

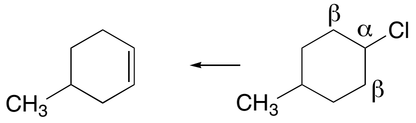


$(CH_3)_2CHCH=CH_2 \longleftarrow (CH_3)_2CH\overset{\beta}{C}H_2-\overset{\alpha}{C}H_2Cl$

c.

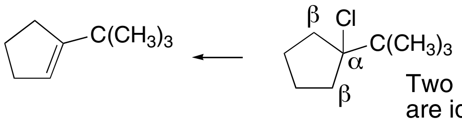


d.



Two β carbons are identical.

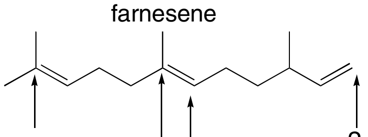
e.



Two β carbons are identical.

8.28 To have stereoisomers, the two groups on each end of the double bond must be different from each other.

a.

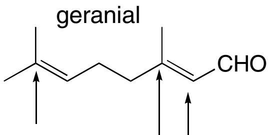


two methyl groups no stereoisomers

two different groups at each end **can have stereoisomers**

2 H's — no stereoisomers

b.

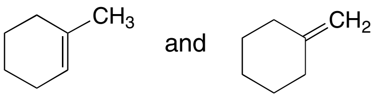


two methyl groups no stereoisomers

two different groups at each end **can have stereoisomers**

8.29 Use the definitions in Answer 8.4.

a.



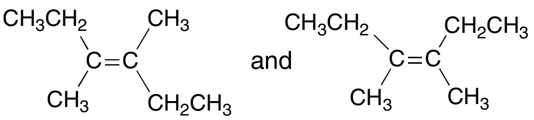
different connectivity
constitutional isomers

c.

trans trans and trans trans

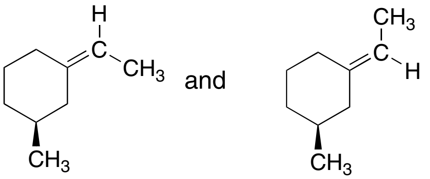
identical

b.



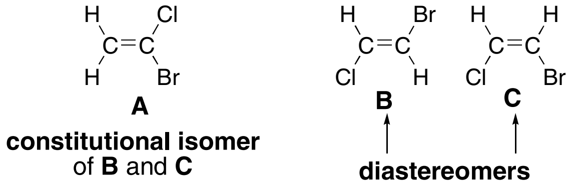
stereoisomers

d.

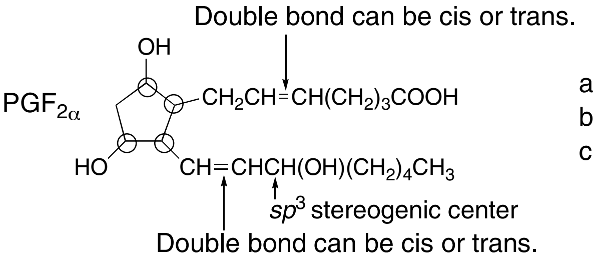


stereoisomers

8.30 There are three different isomers. Cis and trans isomers are diastereomers.

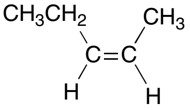
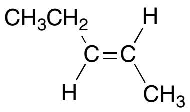


8.31



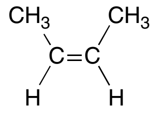
a. five *sp*^{3} stereogenic centers (four circled, one labeled)
b. Two double bonds can both be cis or trans.
c. 2^7 = 128 stereoisomers possible

8.32 Use the rules from Answer 8.5 to rank the alkenes.

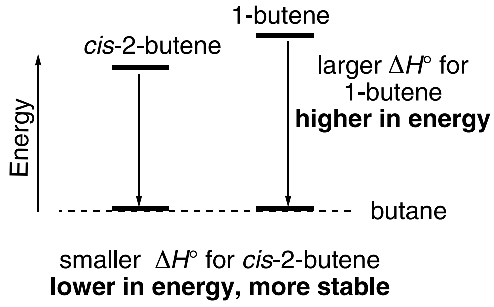
a.	$CH_2{=}CHCH_2CH_2CH_3$		
	monosubstituted	disubstituted cis	disubstituted trans
	least stable	**intermediate stability**	**most stable**
b.	$CH_2{=}CHCH(CH_3)_2$	$CH_2{=}C(CH_3)CH_2CH_3$	$(CH_3)_2C{=}CHCH_3$
	monosubstituted	disubstituted	trisubstituted
	least stable	**intermediate stability**	**most stable**

8.33 A larger negative value for Δ*H*° means the reaction is more exothermic. Since both 1-butene and *cis*-2-butene form the same product (butane), these data show that 1-butene was higher in energy to begin with, **since more energy is released in the hydrogenation reaction.**

$CH_2{=}CHCH_2CH_3 + H_2 \longrightarrow CH_3CH_2CH_2CH_3$ $\Delta H^\circ = -127$ kJ/mol
1-butene

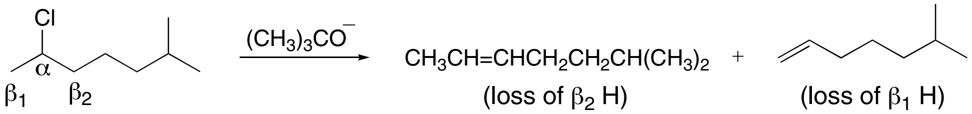

cis-2-butene

$+ H_2 \longrightarrow CH_3CH_2CH_2CH_3$ $\Delta H^\circ = -120$ kJ/mol



8.34

a.

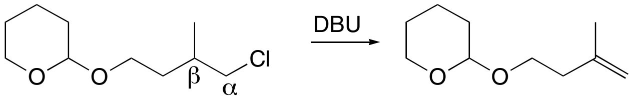


$CH_3CH{=}CHCH_2CH_2CH(CH_3)_2$ +

(loss of β_2 H)
major product
disubstituted

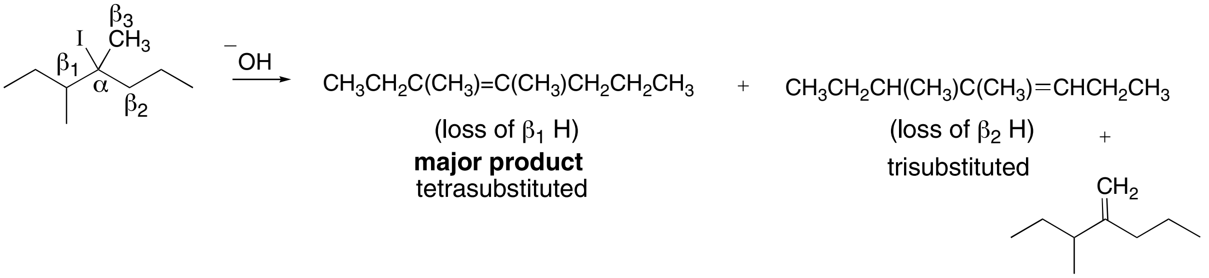
(loss of β_1 H)
monosubstituted

b.



only product

c.



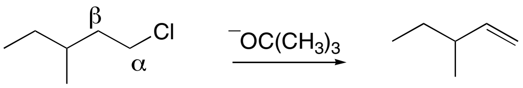
$CH_3CH_2C(CH_3){=}C(CH_3)CH_2CH_2CH_3$ + $CH_3CH_2CH(CH_3)C(CH_3){=}CHCH_2CH_3$ +

(loss of β_1 H)
major product
tetrasubstituted

(loss of β_2 H)
trisubstituted

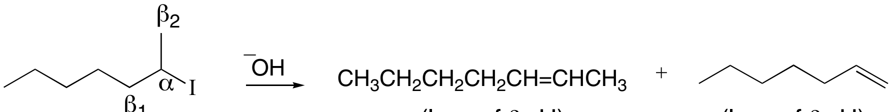
(loss of β_3 H)
disubstituted

d.



only product

e.

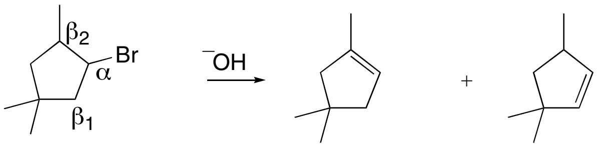


$CH_3CH_2CH_2CH_2CH{=}CHCH_3$

(loss of β_1 H)
major product
disubstituted

(loss of β_2 H)
monosubstituted

f.



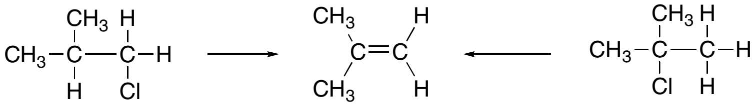
(loss of β_2 H)
major product
trisubstituted

(loss of β_1 H)
disubstituted

8.35 To give only one alkene as the product of elimination, the alkyl halide must have either:

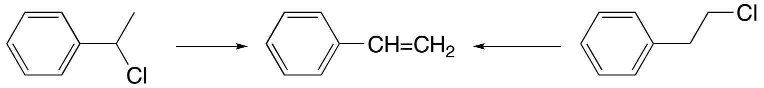
- only one β carbon with a hydrogen atom
- all identical β carbons so the resulting elimination products are identical

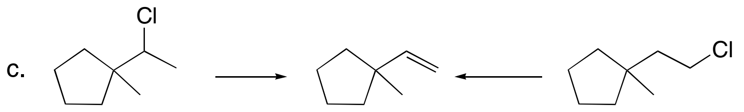
a.



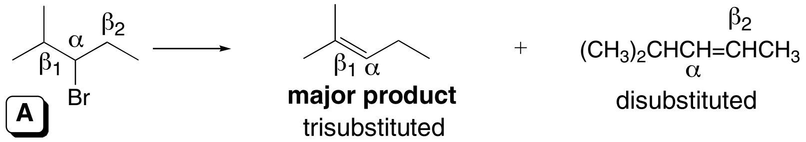
$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{Cl}{\overset{H}{C}}-H \longrightarrow (CH_3)_2C{=}CH_2 \longleftarrow CH_3-\underset{Cl}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-H$$

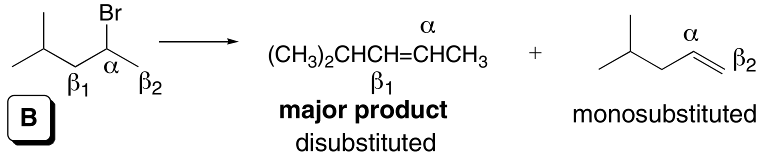
b.





8.36 Draw the products of the E2 reaction and compare the number of C's bonded to the C=C.

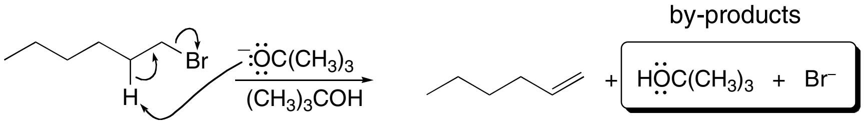




A yields a trisubstituted alkene as the major product and a disubstituted alkene as minor product. **B** yields a disubstituted alkene as the major product and a monosubstituted alkene as minor product. Since the major and minor products formed from **A** have more alkyl groups on the C=C (making them more stable) than those formed from **B**, **A** reacts faster in an elimination reaction.

8.37

a. Mechanism:



b. Rate = k[R–Br][$^-$OC(CH$_3$)$_3$]

[1] Solvent changed to DMF (polar aprotic) = **rate increases**

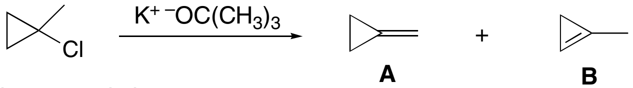
[2] [$^-$OC(CH$_3$)$_3$] decreased = **rate decreases**

[3] Base changed to $^-$OH = **rate decreases** (weaker base)

[4] Halide changed to 2° = **rate increases** (More substituted RX reacts faster.)

[5] Leaving group changed to I$^-$ = **rate increases** (better leaving group)

8.38

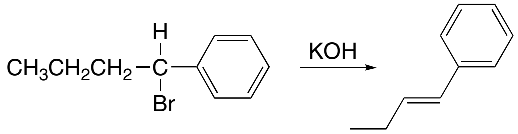


1-chloro-1-methyl-
cyclopropane

The dehydrohalogenation of an alkyl halide usually forms the more stable alkene. In this case **A** is more stable than **B** even though **A** contains a disubstituted C=C whereas **B** contains a trisubstituted C=C. The double bond in **B** is part of a three-membered ring, and is less stable than **A** because of severe angle strain around both C's of the double bond.

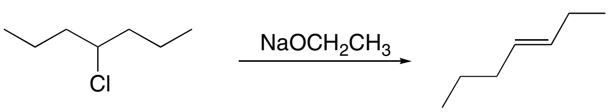
8.39

a.



trans isomer more stable
major product

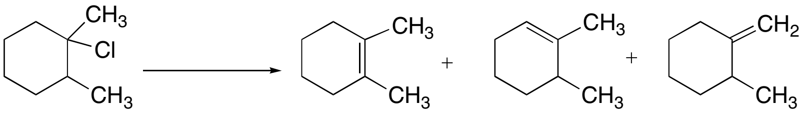
b.



trans isomer more stable
major product

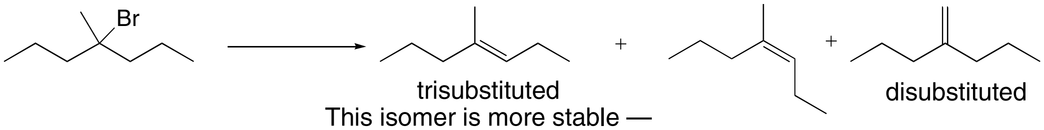
8.40

a.



tetrasubstituted **major product** · trisubstituted · disubstituted

b.

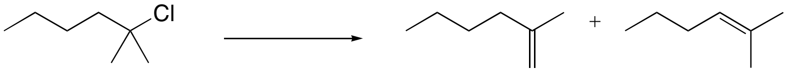


trisubstituted
This isomer is more stable —
large groups farther away.
major product

trisubstituted

disubstituted

c.

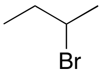


disubstituted

trisubstituted
major product

8.41 Use the rules from Answer 8.22.

a.

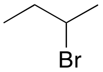


2° halide

$\xrightarrow[\text{strong base}]{^{-}OCH_3}$ **E2**

$CH_3CH{=}CHCH_3$ (cis and trans) + $CH_3CH_2CH{=}CH_2$

b.

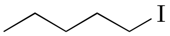


2° halide

$\xrightarrow[\text{weak base}]{CH_3OH}$ **E1**

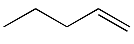
$CH_3CH{=}CHCH_3$ (cis and trans) + $CH_3CH_2CH{=}CH_2$

c.

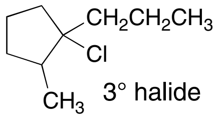


1° halide

$\xrightarrow[\text{strong base}]{^{-}OC(CH_3)_3}$ **E2**

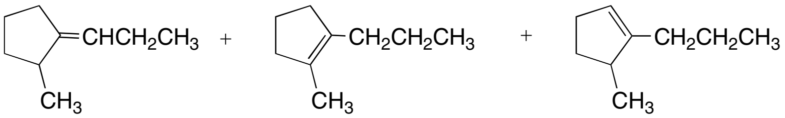


d.

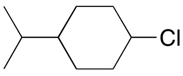


3° halide

$\xrightarrow[\text{weak base}]{H_2O}$ **E1**

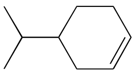


e.

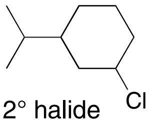


2° halide

$\xrightarrow[\text{strong base}]{^{-}OH}$ **E2**

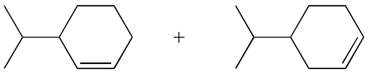


f.



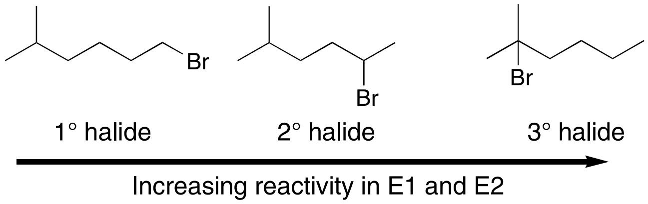
2° halide

$\xrightarrow[\text{strong base}]{^{-}OH}$ **E2**

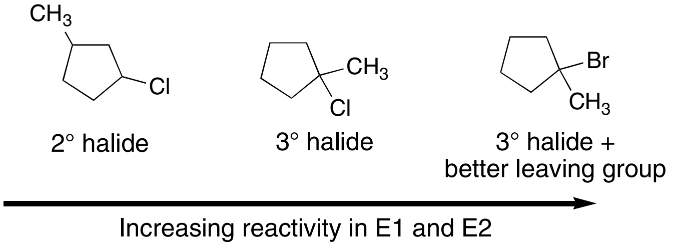


8.42 The order of reactivity is the same for both E2 and E1: 1° < 2° < 3°

a.

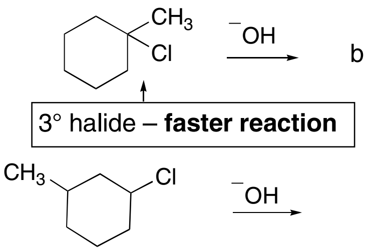


b.

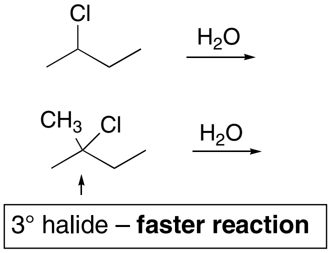


8.43

a.



b.



c.

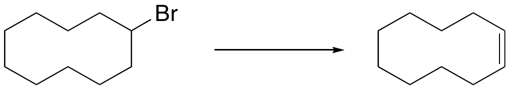
$$(CH_3)_3CCl \xrightarrow[H_2O]{^-OH}$$

$$(CH_3)_3CCl \xrightarrow[DMSO]{^-OH}$$

strong base – E2

polar aprotic solvent
faster reaction

8.44

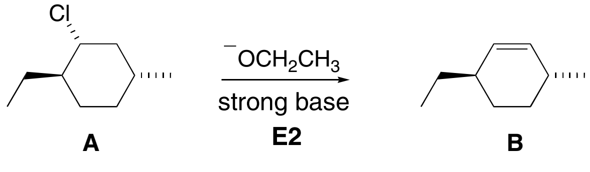


bromocyclodecane

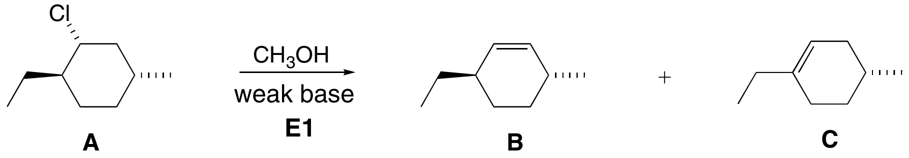
cis-cyclodecene

In a ten-membered ring, the cis isomer is more stable and, therefore, the preferred elimination product. The trans isomer is less stable because strain is introduced when two ends of the double bond are connected in a trans arrangement in this medium-sized ring.

8.45 With the strong base $^-OCH_2CH_3$, the mechanism is E2, whereas with dilute base, the mechanism is E1. E2 elimination proceeds with anti periplanar arrangement of H and X. In the E1 mechanism there is no requirement for elimination to proceed with anti periplanar geometry. In this case the major product is always the most stable, more substituted alkene. Thus, **C** is the major product under E1 conditions. (In Chapter 9, we will learn that additional elimination products may form in the E1 reaction due to carbocation rearrangement.)



Since this is an E2 mechanism, dehydrohalogenation needs an anti periplanar H to form the double bond. There is only one H trans to Cl, so the disubstituted alkene **B** must form.

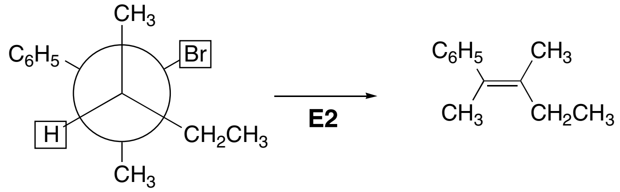


disubstituted alkene

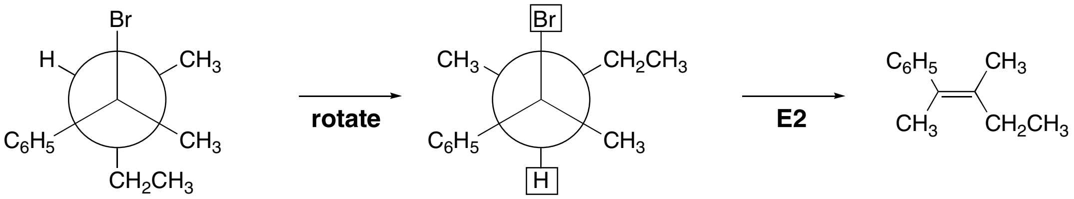
trisubstituted alkene
more stable

8.46 H and Br must be anti during the E2 elimination. Rotate if necessary to make them anti; then eliminate.

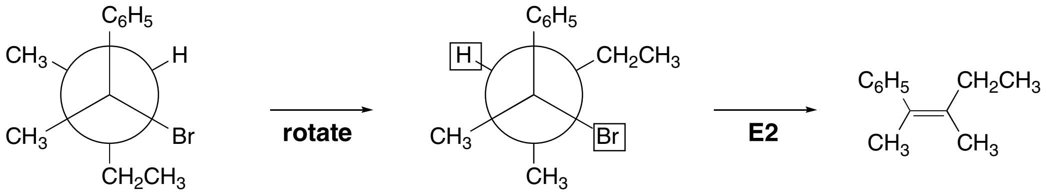
a.



b.

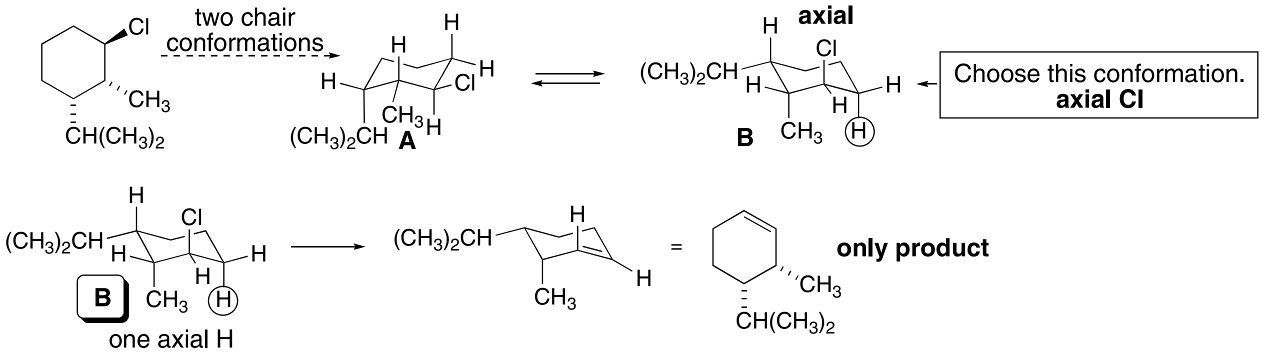


c.

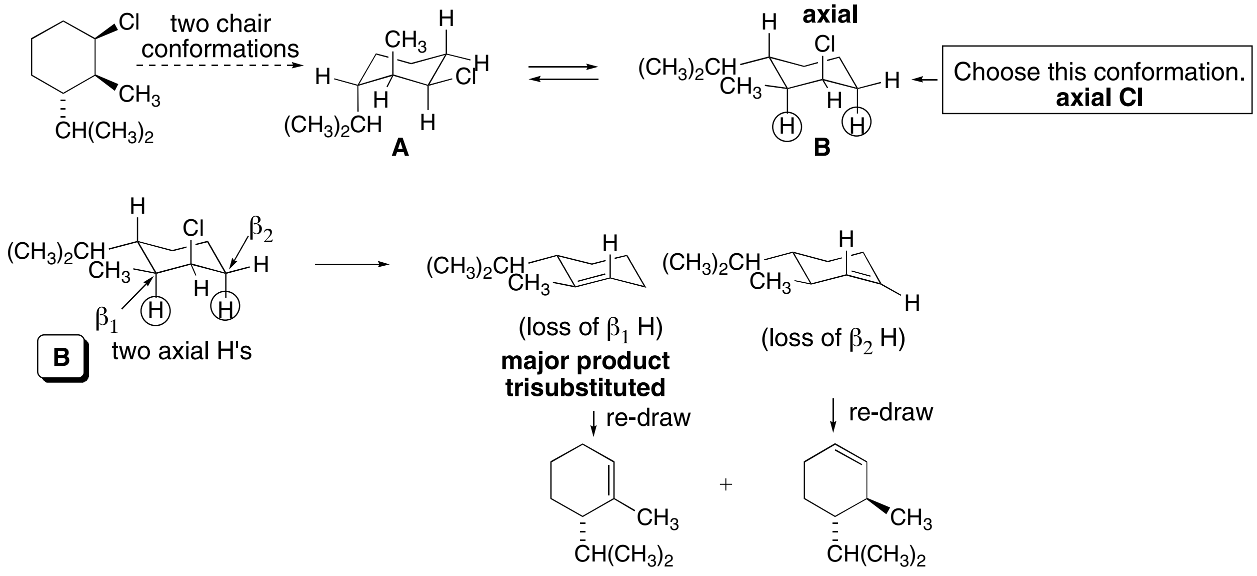


8.47

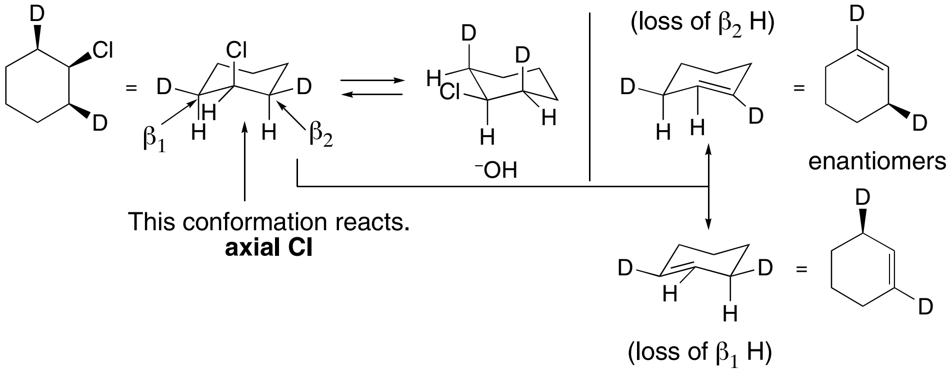
a.



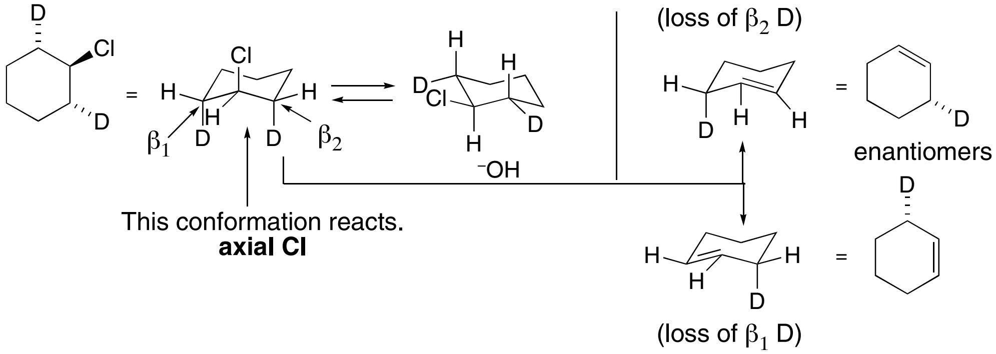
b.


Cl
CH3
CH(CH3)2
two chair conformations
A
axial
B
Choose this conformation.
axial Cl
(CH3)2CH
β2
β1
H
B
two axial H's
(loss of β1 H)
major product
trisubstituted
(loss of β2 H)
re-draw
re-draw
+

c.

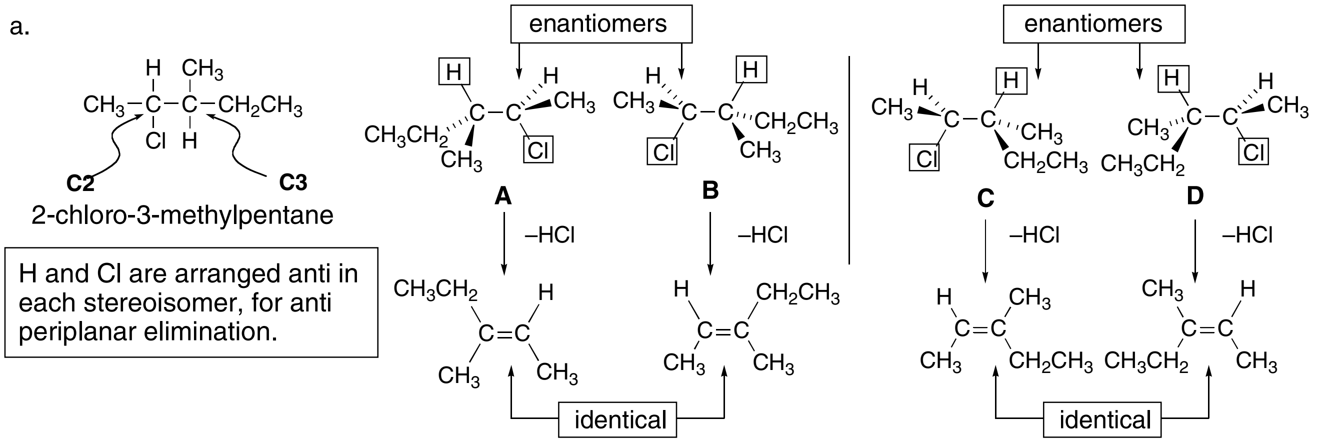

D
Cl
=
β1
β2
H
This conformation reacts.
axial Cl
-OH
(loss of β2 H)
enantiomers
(loss of β1 H)

d.


D
Cl
=
β1
β2
H
This conformation reacts.
axial Cl
-OH
(loss of β2 D)
enantiomers
(loss of β1 D)

8.48

a.

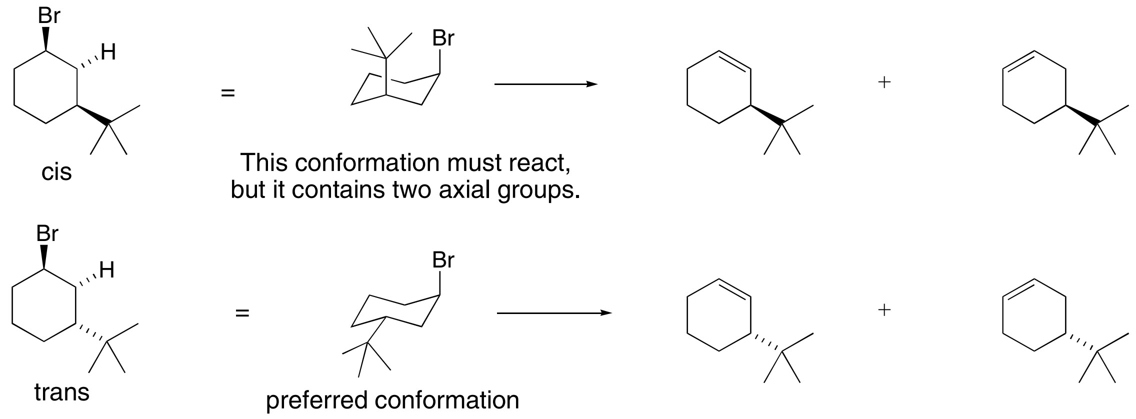


H and Cl are arranged anti in each stereoisomer, for anti periplanar elimination.

b. Two different alkenes are formed as products.

c. The products are diastereomers: Two enantiomers (**A** and **B**) give identical products. **A** and **B** are diastereomers of **C** and **D**. Each pair of enantiomers gives a single alkene. Thus diastereomers give diastereomeric products.

8.49 The trans isomer reacts faster. During elimination, Br must be axial to give trans diaxial elimination. In the trans isomer, the more stable conformation has the bulky *tert*-butyl group in the more roomy equatorial position. In the cis isomer, elimination can occur only when both the *tert*-butyl and Br groups are axial, a conformation that is not energetically favorable.

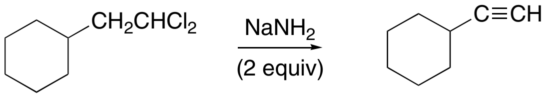


This conformation must react, but it contains two axial groups.

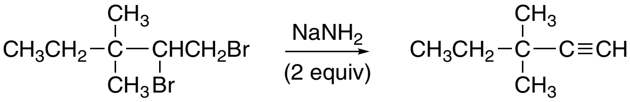
preferred conformation

8.50

a.

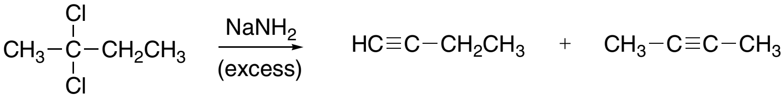


b.

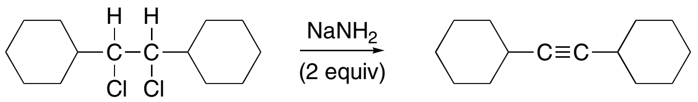


$$CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{C}HCH_2Br \xrightarrow[\text{(2 equiv)}]{NaNH_2} CH_3CH_2-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv CH$$

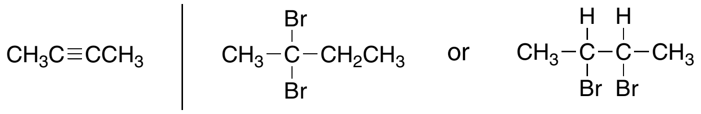
c.

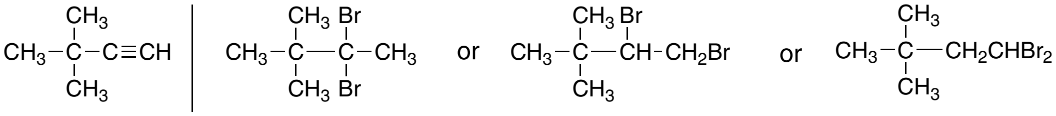


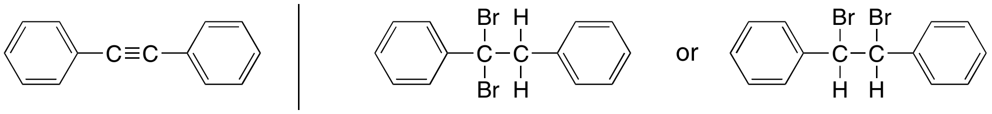
$$CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_2CH_3 \xrightarrow[\text{(excess)}]{NaNH_2} HC\equiv C-CH_2CH_3 \quad + \quad CH_3-C\equiv C-CH_3$$

d. 

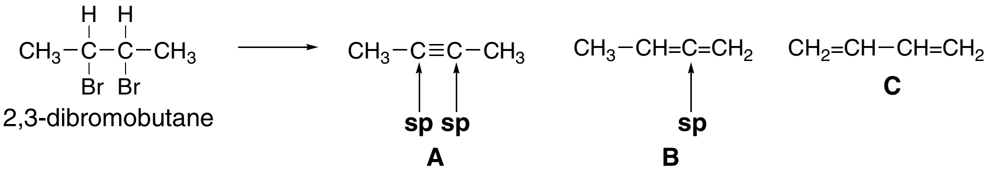
8.51

a. 
$CH_3C\equiv CCH_3$ | $CH_3-CBr_2-CH_2CH_3$ or $CH_3-CHBr-CHBr-CH_3$

b. 
$CH_3-C(CH_3)_2-C\equiv CH$ | $CH_3-C(CH_3)_2-CBr_2-CH_3$ or $CH_3-C(CH_3)_2-CHBr-CH_2Br$ or $CH_3-C(CH_3)_2-CH_2CHBr_2$

c. 

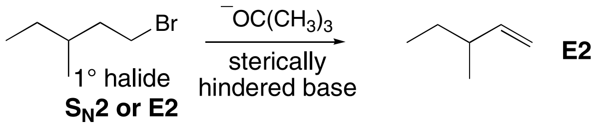
8.52

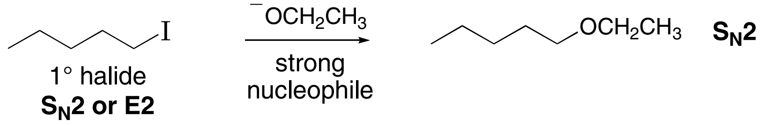

$CH_3-CHBr-CHBr-CH_3 \longrightarrow CH_3-C\equiv C-CH_3$ $CH_3-CH=C=CH_2$ $CH_2=CH-CH=CH_2$

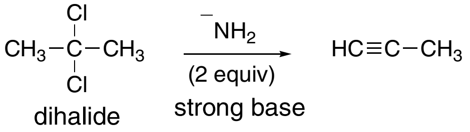
8.53 Use the "Summary chart on the four mechanisms: S_N1, S_N2, E1, or E2" on p. 8–2 to answer the questions.

a. Both S_N1 and E1 involve carbocation intermediates.
b. Both S_N1 and E1 have two steps.
c. S_N1, S_N2, E1, and E2 have increased reaction rates with better leaving groups.
d. Both S_N2 and E2 have increased rates when changing from CH_3OH (protic solvent) to $(CH_3)_2SO$ (aprotic solvent).
e. In S_N1 and E1 reactions, the rate depends on only the alkyl halide concentration.
f. Both S_N2 and E2 are concerted reactions.
g. CH_3CH_2Br and NaOH react by an S_N2 mechanism.
h. Racemization occurs in S_N1 reactions.
i. In S_N1, E1, and E2 mechanisms, 3° alkyl halides react faster than 1° or 2° halides.
j. E2 and S_N2 reactions follow second-order rate equations.

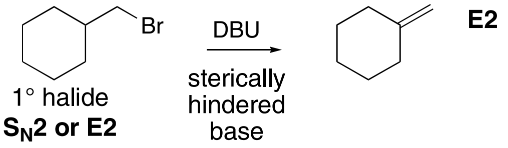
8.54

a. 

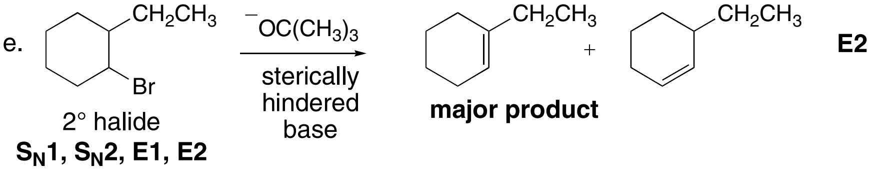
b. 

c. 
$CH_3-CCl_2-CH_3 \xrightarrow[\text{(2 equiv)}]{^{-}NH_2} HC\equiv C-CH_3$

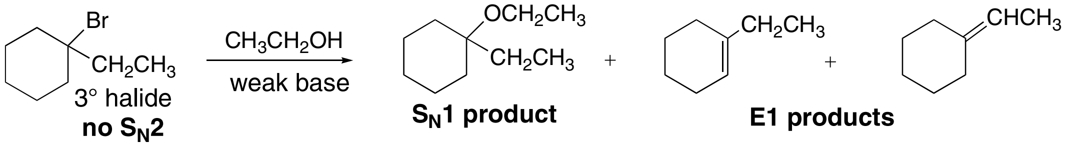
d.



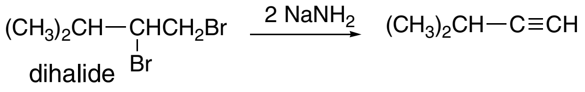
e.



f.



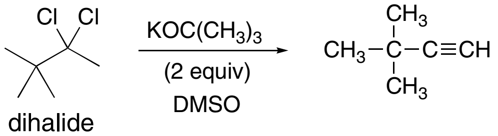
g.



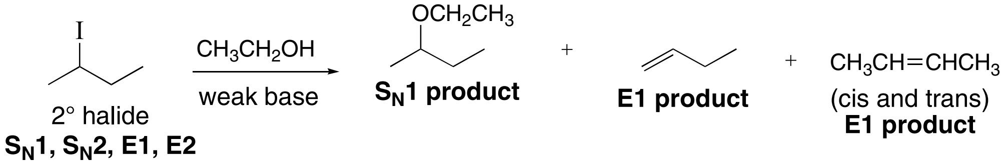
$(CH_3)_2CH-\underset{Br}{CH}CH_2Br \xrightarrow{2\ NaNH_2} (CH_3)_2CH-C\equiv CH$

dihalide

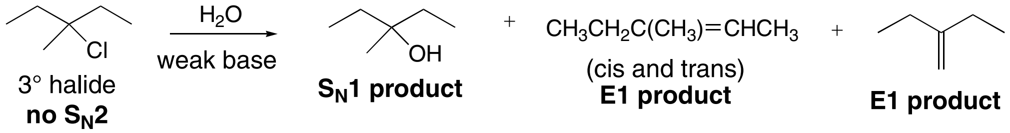
h.



i.



j.



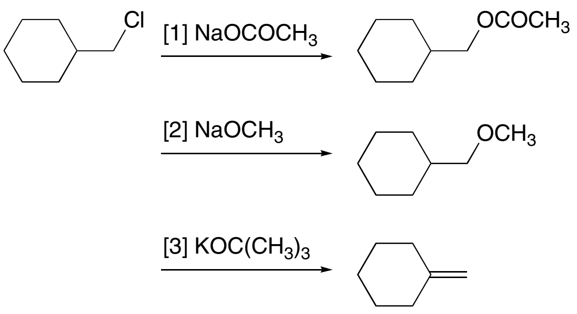
8.55 [1] $NaOCOCH_3$ is a good nucleophile and weak base, and substitution is favored. [3] $KOC(CH_3)_3$ is a strong, bulky base that reacts by E2 elimination when there is a β hydrogen in the alkyl halide.

a. $CH_3Cl \xrightarrow{[1]\ NaOCOCH_3} CH_3OCOCH_3$

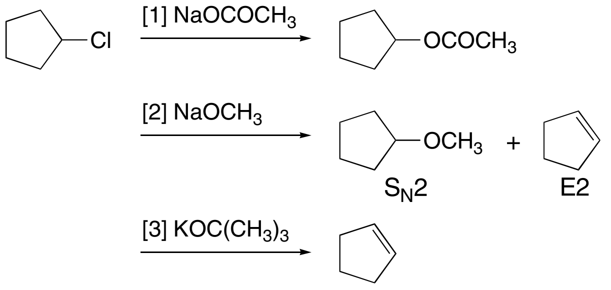
$\xrightarrow{[2]\ NaOCH_3} CH_3OCH_3$

$\xrightarrow{[3]\ KOC(CH_3)_3} CH_3OC(CH_3)_3$

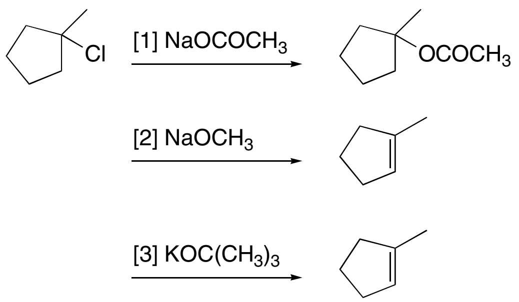
b.



c.

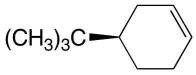


d.

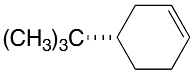


8.56

a. two enantiomers:

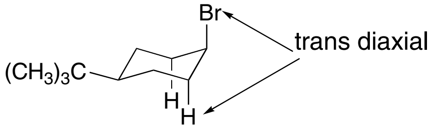


A

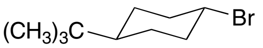


B

b. The bulky *tert*-butyl group anchors the cyclohexane ring and occupies the more roomy equatorial position. The cis isomer has the Br atom axial, while the trans isomer has the Br atom equatorial. For dehydrohalogenation to occur on a halo cyclohexane, the halogen must be axial to afford trans diaxial elimination of H and X. The cis isomer readily reacts since the Br atom is axial. The only way for the trans isomer to react is for the six-membered ring to flip into a highly unstable conformation having both $(CH_3)_3C$ and Br axial. Thus, the trans isomer reacts much more slowly.



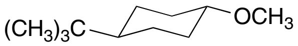
cis-1-bromo-4-*tert*-butylcyclohexane



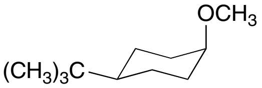
trans-1-bromo-4-*tert*-butylcyclohexane

c. two products:

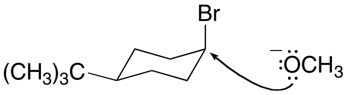
C =



D =

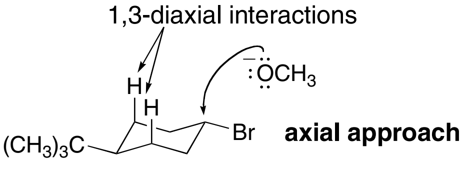


d. *cis*-1-Bromo-4-*tert*-butylcyclohexane reacts faster. With the strong nucleophile $^-OCH_3$, backside attack occurs by an S_N2 reaction, and with the cis isomer, the nucleophile can approach from the equatorial direction, avoiding 1,3-diaxial interactions.



equatorial approach preferred

cis-1-bromo-4-*tert*-butylcyclohexane

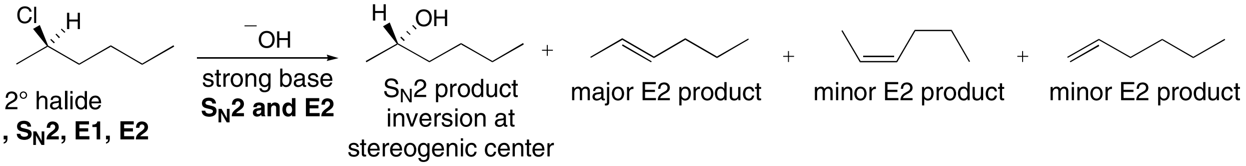


trans-1-bromo-4-*tert*-butylcyclohexane

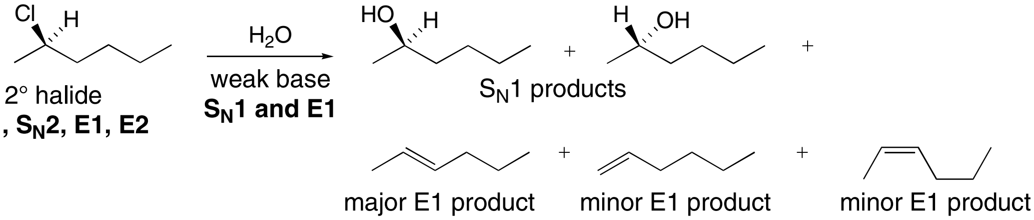
e. The bulky base $^-OC(CH_3)_3$ favors elimination by an E2 mechanism, affording a mixture of two enantiomers **A** and **B**. The strong nucleophile $^-OCH_3$ favors nucleophilic substitution by an S_N2 mechanism. Inversion of configuration results from backside attack of the nucleophile.

8.57

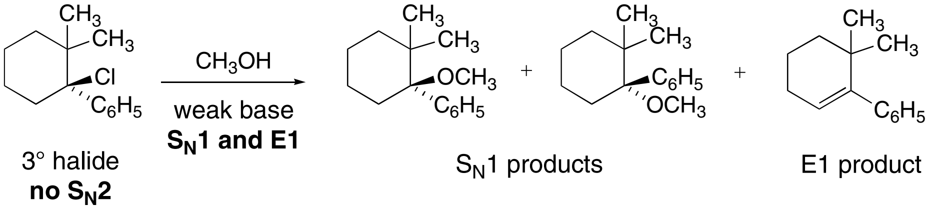
a.



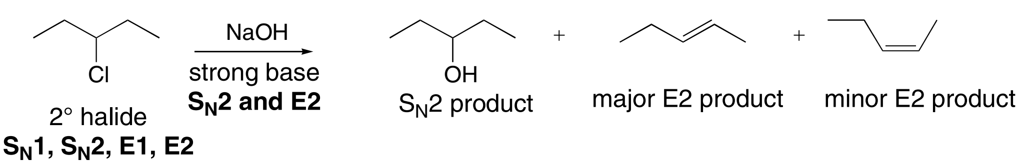
b.



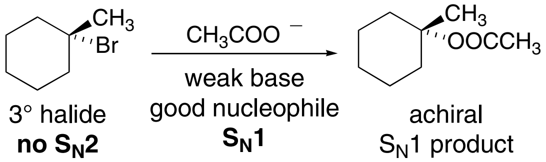
c.



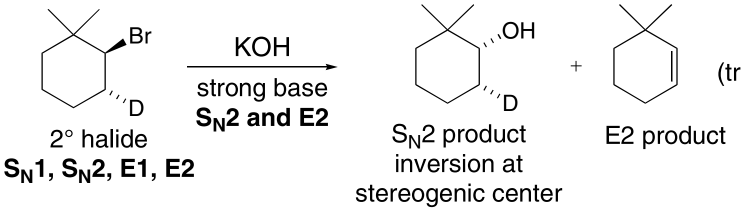
d.



e.



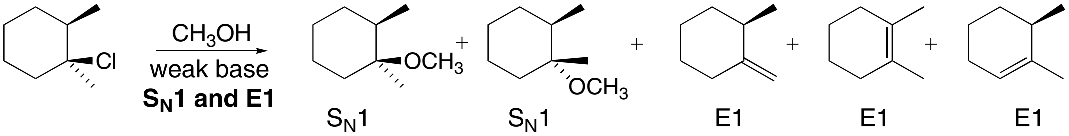
f.



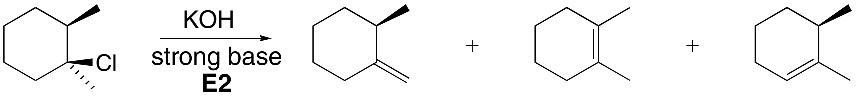
(trans diaxial elimination of D, Br)

8.58

a.

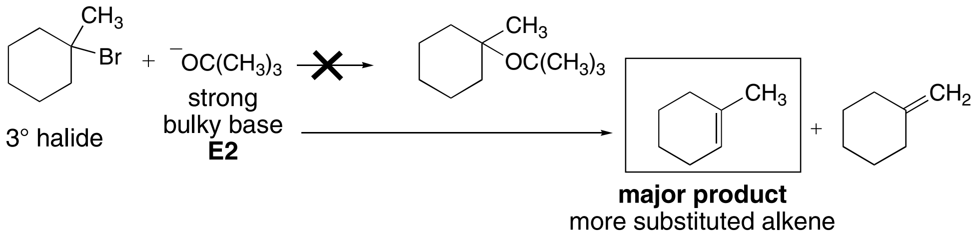


b.



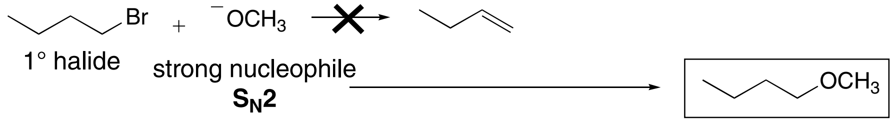
8.59

a.



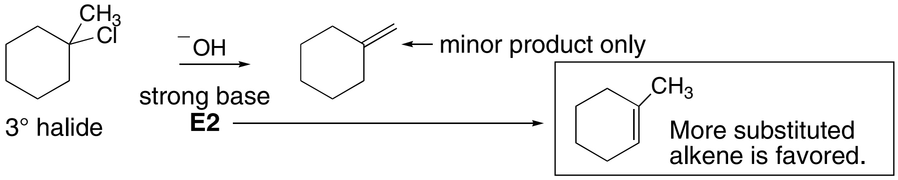
No substitution occurs with a strong bulky base and a 3° RX. The C with the leaving group is too crowded for an S_N2 substitution to occur. Elimination occurs instead by an E2 mechanism.

b.

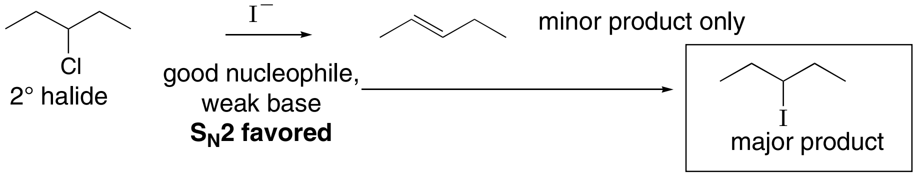


All elimination reactions are slow with 1° halides.
The strong nucleophile reacts by an S_N2 mechanism instead.

c.



d.

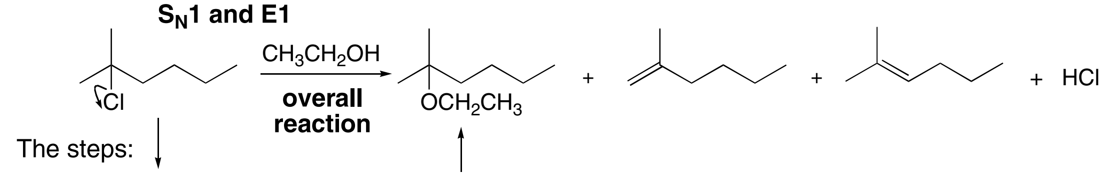


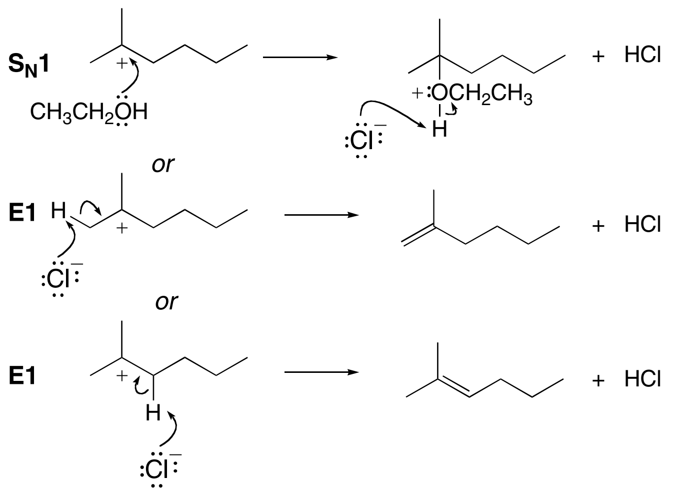
The 2° halide can react by an E2 or S_N2 reaction with a negatively charged nucleophile or base. Since I^- is a weak base, substitution by an S_N2 mechanism is favored.

8.60

a.

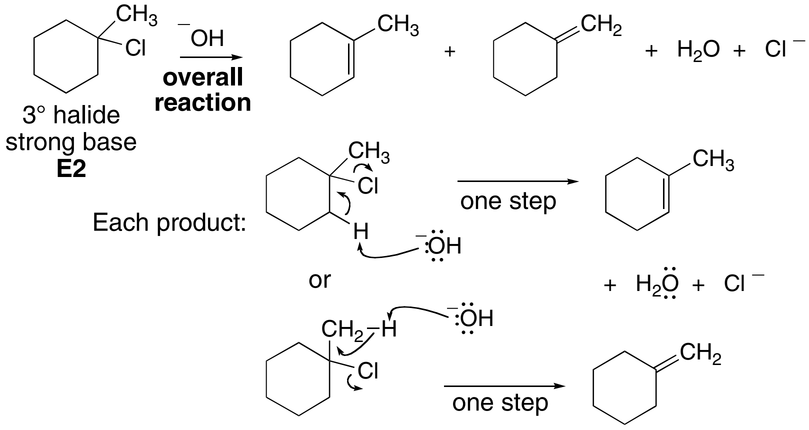
3° halide, weak base:
S_N1 and E1





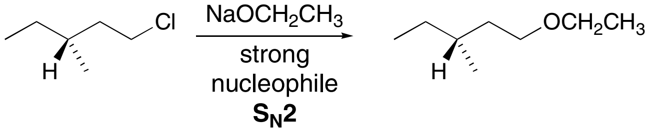
Any base (such as CH_3CH_2OH or Cl^-) can be used to remove a proton to form an alkene. If Cl^- is used, HCl is formed as a reaction by-product. If CH_3CH_2OH is used, $(CH_3CH_2OH_2)^+$ is formed instead.

b.

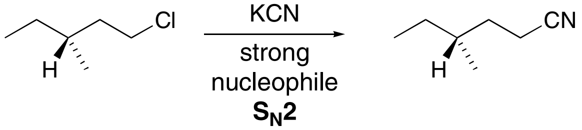


8.61 Draw the products of each reaction with the 1° alkyl halide.

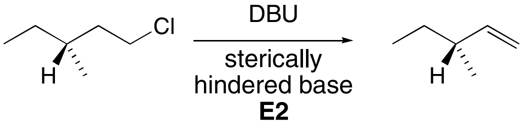
a.



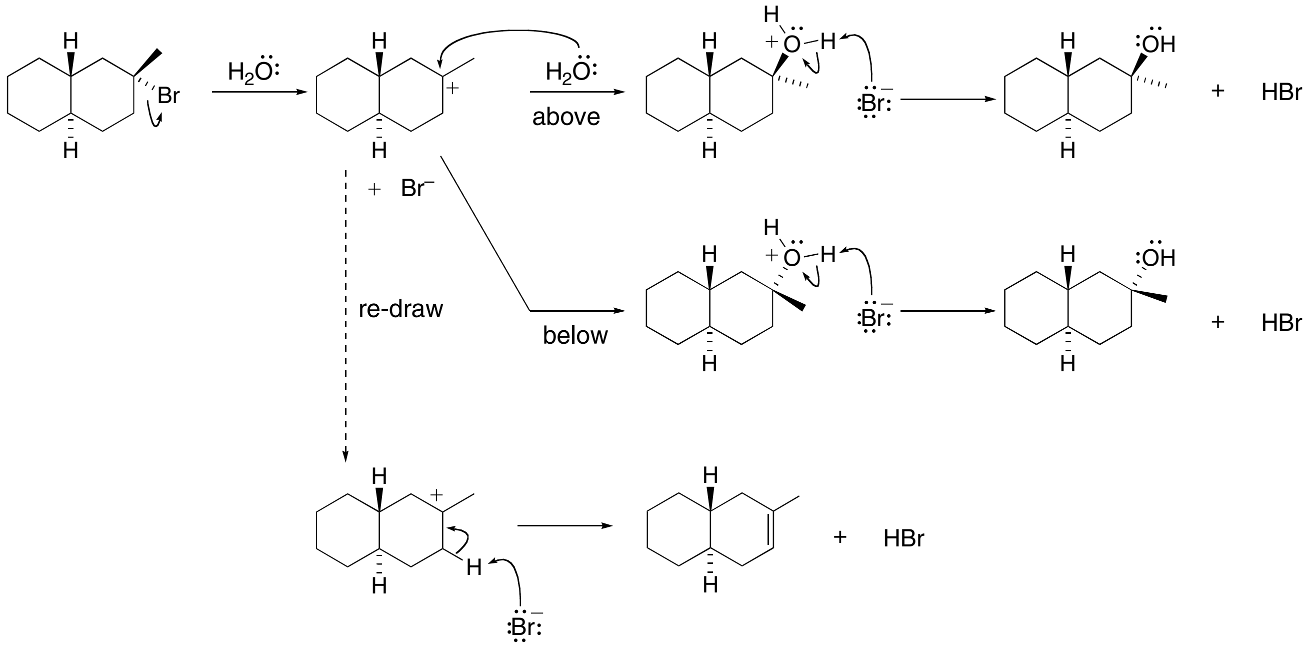
b.



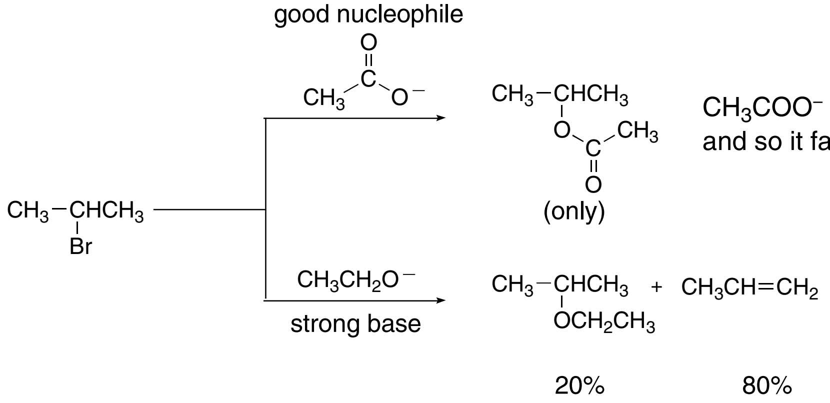
c.



8.62



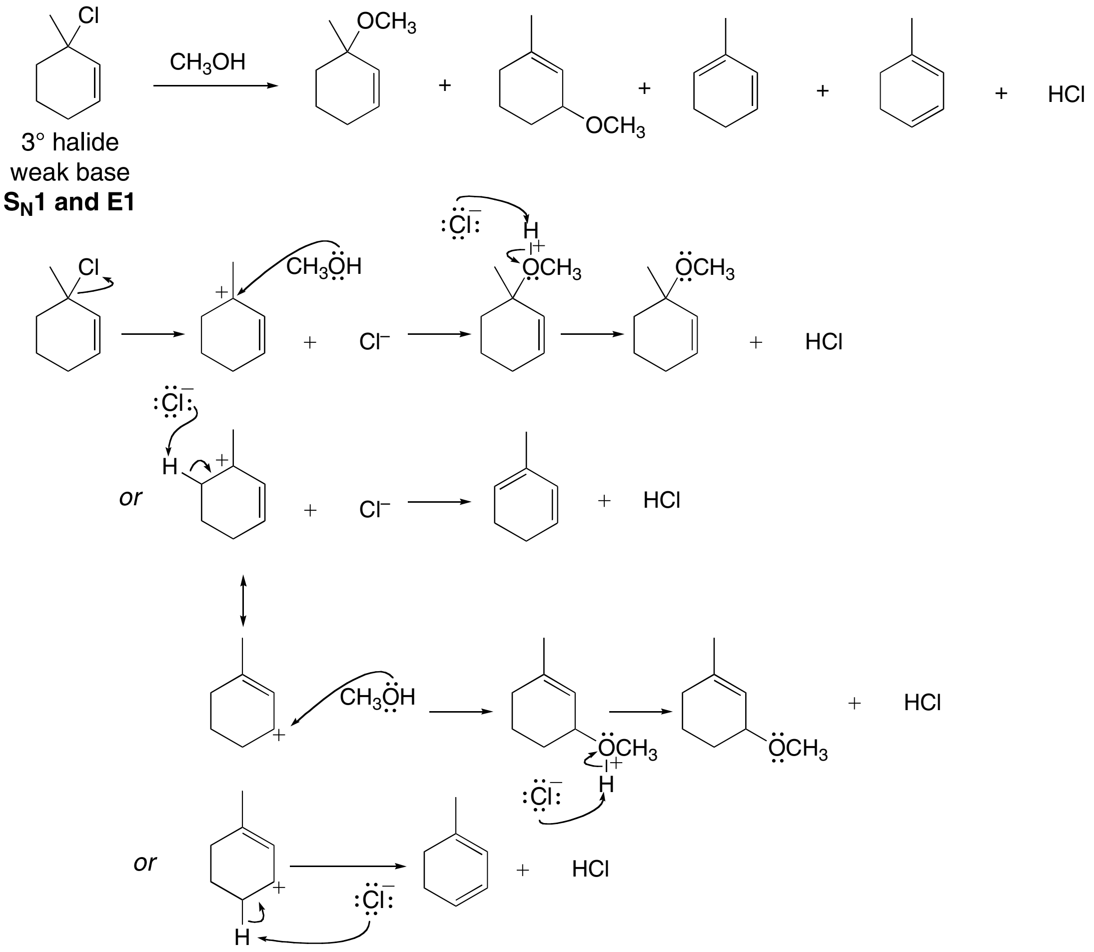
8.63



CH_3COO^- is a good nucleophile and a weak base and so it favors substitution by S_N2.

The strong base gives both S_N2 and E2 products, but since the 2° RX is somewhat hindered to substitution, the E2 product is favored.

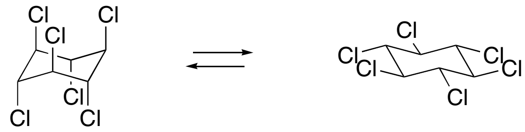
8.64



3° halide
weak base
S_N1 and E1

8.65 E2 elimination needs a leaving group and a hydrogen in the **trans diaxial** position.

Two different conformations:



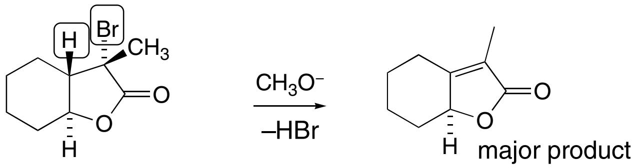
This conformation has Cl's axial, but no H's axial.

This conformation has no Cl's axial.

For elimination to occur, a cyclohexane must have a H and Cl in the trans diaxial arrangement. Neither conformation of this isomer has both atoms—H and Cl—axial; thus, this isomer only slowly loses HCl by elimination.

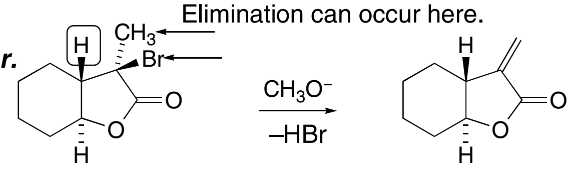
8.66

H and Br are ***anti periplanar.***
Elimination can occur.



major product

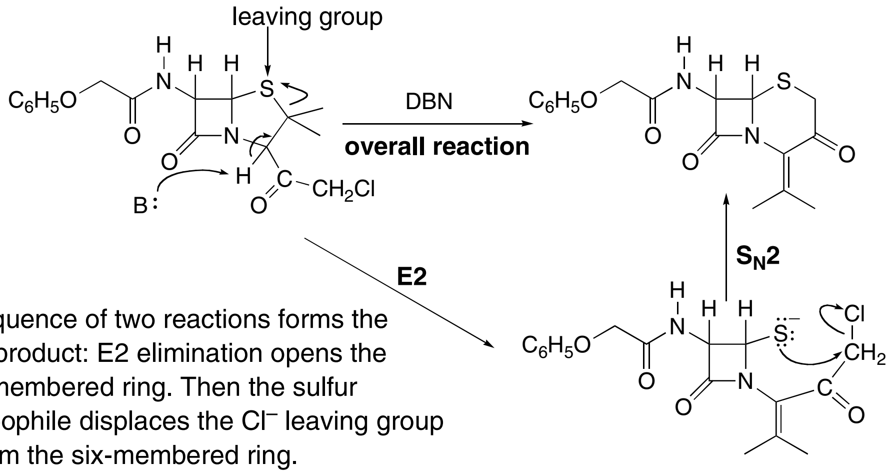
H (in the ring) and Br are **NOT *anti periplanar.***
Elimination can**not** occur using this H.
Instead elimination must occur with the
H on the CH_3 group.



Elimination can occur here.

Elimination cannot occur in the ring
because the required anti periplanar geometry is not present.

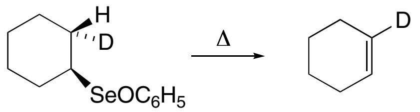
8.67



A sequence of two reactions forms the final product: E2 elimination opens the five-membered ring. Then the sulfur nucleophile displaces the Cl^- leaving group to form the six-membered ring.

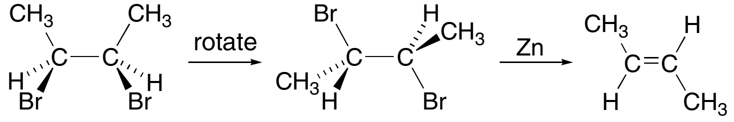
8.68

a.



$SeOC_6H_5$ and H are on the
same side of the ring.
syn elimination

b.



Both Br atoms are on the opposite
sides of the C–C bond.
anti elimination