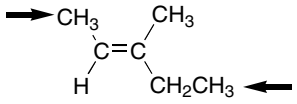
Chapter 10: Alkenes

♦ General facts about alkenes

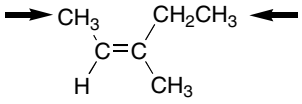
- Alkenes contain a carbon–carbon double bond consisting of a stronger σ bond and a weaker π bond. Each carbon is sp^2 hybridized and trigonal planar (10.1).
- Alkenes are named using the suffix ***-ene*** (10.3).
- Alkenes with different groups on each end of the double bond exist as a pair of diastereomers, identified by the prefixes *E* and *Z* (10.3B).

Two higher priority groups on **opposite** sides



***E* isomer**
(2*E*)-3-methyl-2-pentene

Two higher priority groups on the **same** side

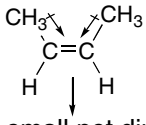


***Z* isomer**
(2*Z*)-3-methyl-2-pentene

- Alkenes have weak intermolecular forces, giving them low mp's and bp's, and making them water insoluble. A cis alkene is more polar than a trans alkene, giving it a slightly higher boiling point (10.4).

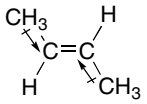
cis-2-butene

more polar isomer →



a small net dipole
higher bp

trans-2-butene



← **less polar isomer**

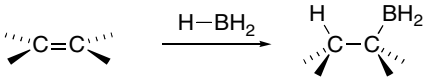
no net dipole
lower bp

- Since a π bond is electron rich and much weaker than a σ bond, alkenes undergo addition reactions with electrophiles (10.8).

♦ Stereochemistry of alkene addition reactions (10.8)

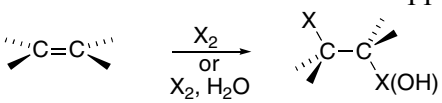
A reagent XY adds to a double bond in one of three different ways:

- **Syn addition**—X and Y add from the same side.



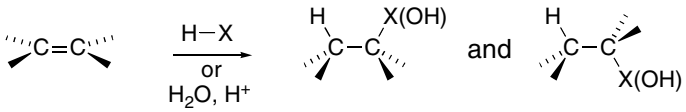
- Syn addition occurs in **hydroboration.**

- **Anti addition**—X and Y add from opposite sides.



- Anti addition occurs in **halogenation** and **halohydrin formation.**

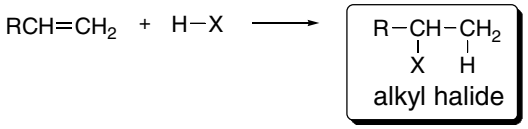
- **Both syn and anti addition** occur when carbocations are intermediates.



- Syn and anti addition occur in **hydrohalogenation** and **hydration.**

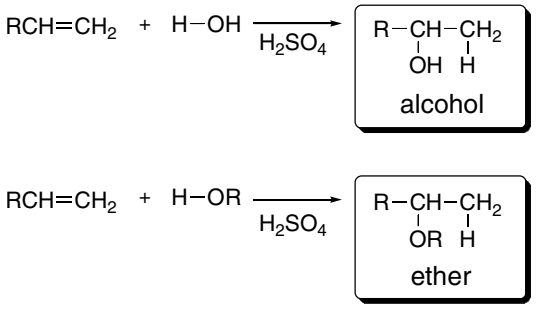
♦ Addition reactions of alkenes

[1] **Hydrohalogenation**—Addition of HX (X = Cl, Br, I) (10.9–10.11)



- The mechanism has two steps.
- Carbocations are formed as intermediates.
- Carbocation rearrangements are possible.
- Markovnikov's rule is followed. H bonds to the less substituted C to form the more stable carbocation.
- Syn and anti addition occur.

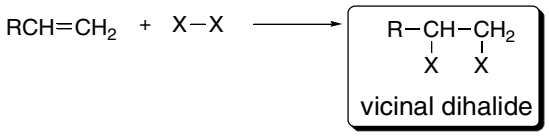
[2] **Hydration** and related reactions—Addition of H_2O or ROH (10.12)



For both reactions:

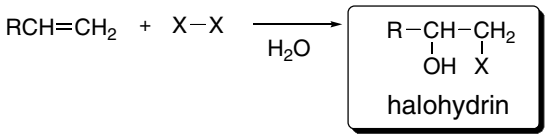
- The mechanism has three steps.
- Carbocations are formed as intermediates.
- Carbocation rearrangements are possible.
- Markovnikov's rule is followed. H bonds to the less substituted C to form the more stable carbocation.
- Syn and anti addition occur.

[3] **Halogenation**—Addition of X_2 (X = Cl or Br) (10.13–10.14)



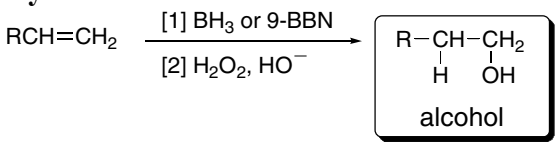
- The mechanism has two steps.
- Bridged halonium ions are formed as intermediates.
- No rearrangements occur.
- Anti addition occurs.

[4] **Halohydrin formation**—Addition of OH and X (X = Cl, Br) (10.15)



- The mechanism has three steps.
- Bridged halonium ions are formed as intermediates.
- No rearrangements occur.
- X bonds to the less substituted C.
- Anti addition occurs.
- NBS in DMSO and H_2O adds Br and OH in the same fashion.

[5] **Hydroboration–oxidation**—Addition of H_2O (10.16)

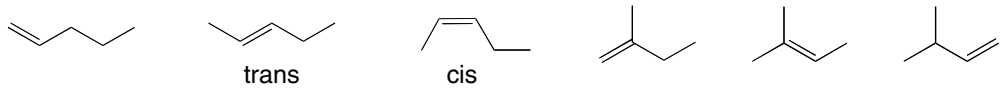


- Hydroboration has a one-step mechanism.
- No rearrangements occur.
- OH bonds to the less substituted C.
- Syn addition of H_2O results.

Chapter 10: Answers to Problems

10.1

Six alkenes of molecular formula C_5H_{10}:



trans cis

diastereomers

10.2 To determine the number of degrees of unsaturation:

[1] Calculate the maximum number of H's ($2n + 2$).
[2] Subtract the actual number of H's from the maximum number.
[3] Divide by two.

a. C_2H_2
[1] maximum number of H's = $2n + 2 = 2(2) + 2 = 6$
[2] subtract actual from maximum = $6 - 2 = 4$
[3] divide by two = 4/2 = **2 degrees of unsaturation**

b. C_6H_6
[1] maximum number of H's = $2n + 2 = 2(6) + 2 = 14$
[2] subtract actual from maximum = $14 - 6 = 8$
[3] divide by two = 8/2 = **4 degrees of unsaturation**

c. C_8H_{18}
[1] maximum number of H's = $2n + 2 = 2(8) + 2 = 18$
[2] subtract actual from maximum = $18 - 18 = 0$
[3] divide by two = 0/2 = **0 degrees of unsaturation**

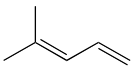
d. C_7H_8O
Ignore the O.
[1] maximum number of H's = $2n + 2 = 2(7) + 2 = 16$
[2] subtract actual from maximum = $16 - 8 = 8$
[3] divide by two = 8/2 = **4 degrees of unsaturation**

e. $C_7H_{11}Br$
Because of Br, add one more H (11 + 1 H = 12 H's).
[1] maximum number of H's = $2n + 2 = 2(7) + 2 = 16$
[2] subtract actual from maximum = $16 - 12 = 4$
[3] divide by two = 4/2 = **2 degrees of unsaturation**

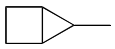
f. C_5H_9N
Because of N, subtract one H (9 – 1 H = 8 H's).
[1] maximum number of H's = $2n + 2 = 2(5) + 2 = 12$
[2] subtract actual from maximum = $12 - 8 = 4$
[3] divide by two = 4/2 = **2 degrees of unsaturation**

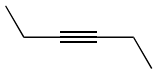
10.3

One possibility for C_6H_{10}:

a. a compound that has 2 π bonds 

b. a compound that has 1 ring and 1 π bond 

c. a compound with 2 rings 

d. a compound with 1 triple bond 

10.4 To name an alkene:

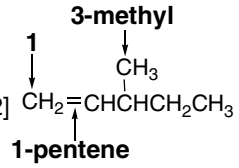
[1] Find the longest chain that contains the double bond. Change the ending from ***-ane*** to ***-ene***.
[2] Number the chain to give the double bond the lower number. The alkene is named by the first number.
[3] Apply all other rules of nomenclature.

To name a cycloalkene:

[1] When a double bond is located in a ring, it is always located between C1 and C2. Omit the "1" in the name. Change the ending from ***-ane*** to ***-ene***.
[2] Number the ring clockwise or counterclockwise to give the first substituent the lower number.
[3] Apply all other rules of nomenclature.

a. [1] $CH_2{=}CHCH(CH_3)CH_2CH_3$

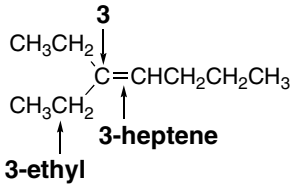
5 C chain with double bond
pentene

[2] 

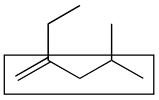
[3] **3-methyl-1-pentene**

b. [1] $(CH_3CH_2)_2C{=}CHCH_2CH_2CH_3$

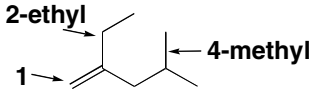
7 C chain with double bond
heptene

[2] 

[3] **3-ethyl-3-heptene**

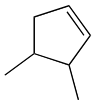
c. [1] 

5 C chain with double bond
pentene

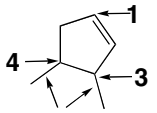
[2] 

1-pentene

[3] **2-ethyl-4-methyl-1-pentene**

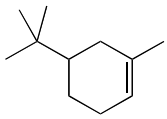
d. [1] 

5 C ring with a double bond
cyclopentene

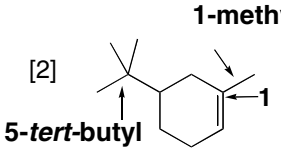
[2] 

3,4-dimethyl

[3] **3,4-dimethylcyclopentene**

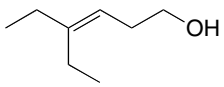
e. [1] 

6 C ring with a double bond
cyclohexene

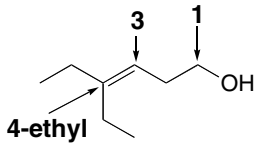
[2] 

[3] **5-*tert*-butyl-1-methylcyclohexene**

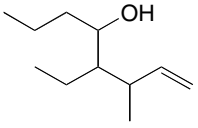
10.5 Use the rules from Answer 10.4 to name the compounds. Enols are named to give the OH the lower number. Compounds with two C=C's are named with the suffix ***-adiene***.

a. [1] 

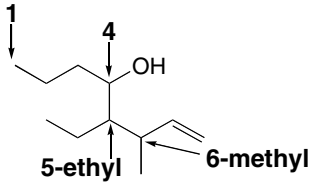
6 C chain with double bond
hexene

[2] 

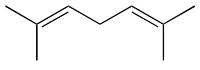
[3] **4-ethyl-3-hexen-1-ol**

b. [1] 

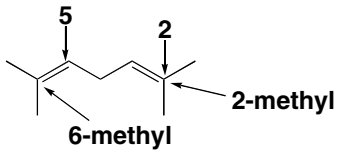
8 C chain with double bond
octene

[2] 

[3] **5-ethyl-6-methyl-7-octen-4-ol**

c. [1] 

7 C chain with two double bonds
heptadiene

[2] 

[3] **2,6-dimethyl-2,5-heptadiene**

10.6 To label an alkene as *E* or *Z*:

[1] **Assign priorities** to the two substituents ***on each end*** using the rules for *R*,*S* nomenclature.

[2] **Assign *E* or *Z*** depending on the location of the two higher priority groups.

- The ***E*** prefix is used when the two higher priority groups are on **opposite sides**.
- The ***Z*** prefix is used when the two higher priority groups are on the **same side** of the double bond.

a. **higher priority** → CH_3, Cl; H, Br ← **higher priority**

Two higher priority groups are on opposite sides: ***E* isomer.**

b. **higher priority** → CH_3CH_2, CH_2CH_3 ← **higher priority**

Two higher priority groups are on the same side: ***Z* isomer.**

c. **higher priority** → OCH_3; **higher priority** → C_6H_5; **higher priority**

kavain

In both double bonds, the two higher priority groups are on opposite sides: ***E* isomers.**

10.7 To name an alkene: First follow the rules from Answer 10.4. Then, when necessary, assign an *E* or *Z* prefix based on priority, as in 10.6.

a. [1] CH_3, $CH_2CH_2CH_3$; H, Br

6 C chain with double bond
hexene

[2] **2-hexene**; **higher priority** → CH_3, $CH_2CH_2CH_3$; H, Br ← **higher priority**

E alkene

3-bromo

[3] **(2*E*)-3-bromo-2-hexene**

b. [1] CH_3CH_2, $CH_2CH_2CH_2CH_2C(CH_3)_3$; H, CH_2CH_3

10 C chain with double bond
decene

[2] **3-decene**; **higher priority** → CH_3CH_2, $CH_2CH_2CH_2CH_2CCH_3$ ← **higher priority**; CH_3 ← **9,9-dimethyl**; CH_3 ← **9,9-dimethyl**; H, CH_2CH_3

Z alkene

4-ethyl

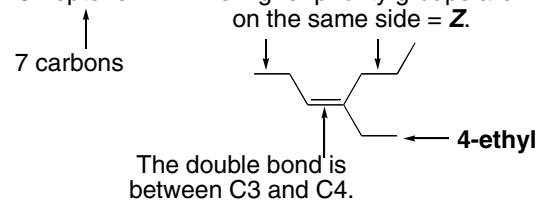
[3] **(3*Z*)-4-ethyl-9,9-dimethyl-3-decene**

10.8 To work backwards from a name to a structure:

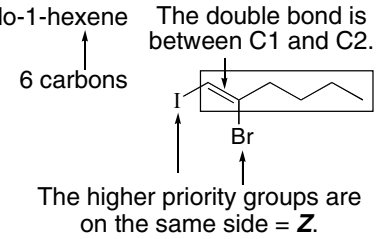
[1] Find the parent name and functional group and draw, remembering that the double bond is between C1 and C2 for cycloalkenes.

[2] Add the substituents to the appropriate carbons.

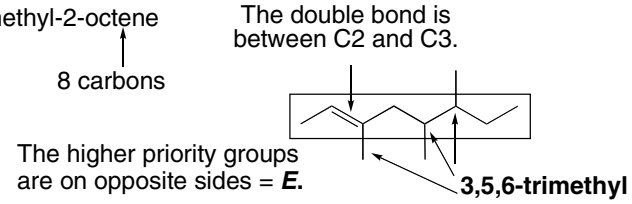
a. (3*Z*)-4-ethyl-3-heptene



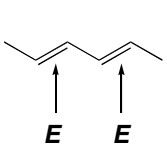
c. (1*Z*)-2-bromo-1-iodo-1-hexene



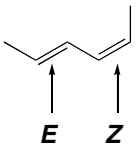
b. (2*E*)-3,5,6-trimethyl-2-octene



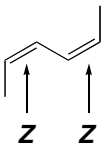
10.9 Draw all of the stereoisomers and then use the rules from Answer 10.6 to name each diene.



(2*E*,4*E*)-2,4-hexadiene



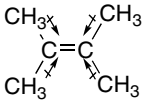
(2*E*,4*Z*)-2,4-hexadiene



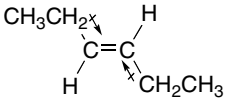
(2*Z*,4*Z*)-2,4-hexadiene

10.10 To rank the isomers by increasing boiling point:

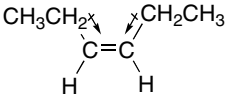
Look for polarity differences: *small net dipoles* make an alkene more polar, giving it a higher boiling point than an alkene with *no net dipole*. Cis isomers have a higher boiling point than their trans isomers.



All dipoles cancel.
smallest surface area
no net dipole
lowest bp

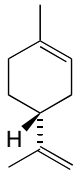


Two dipoles cancel.
no net dipole
trans isomer
intermediate bp

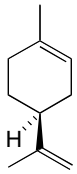


Two dipoles reinforce.
net dipole
cis isomer
highest bp

10.11 Recall from Section 5.13B that the odor of a molecule is determined more by shape than by functional groups. That is why the *R* and *S* isomers of limonene smell so differently.

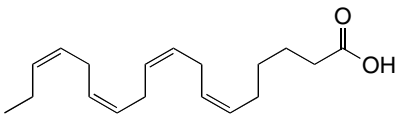


(*R*)-limonene

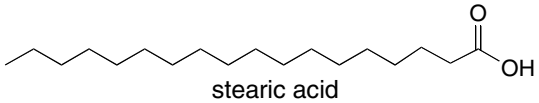


(*S*)-limonene

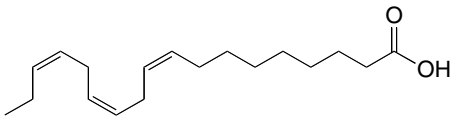
10.12 Increasing number of double bonds = decreasing melting point.



stearidonic acid
4 double bonds
lowest melting point

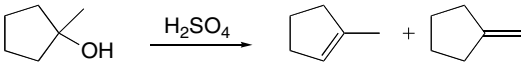


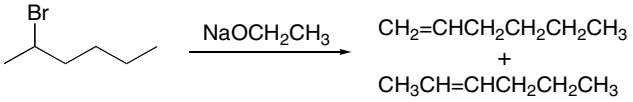
stearic acid
no double bonds
highest melting point



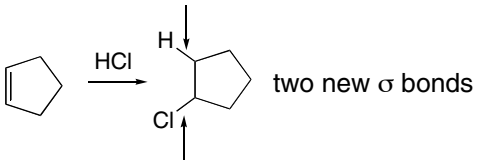
linolenic acid
3 double bonds
intermediate melting point

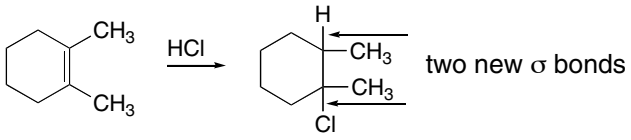
10.13

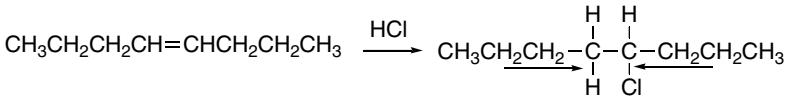
a. 

b. 

10.14 To draw the products of an addition reaction:
[1] Locate the two bonds that will be broken in the reaction. Always break the π bond.
[2] Draw the product by forming two new σ bonds.

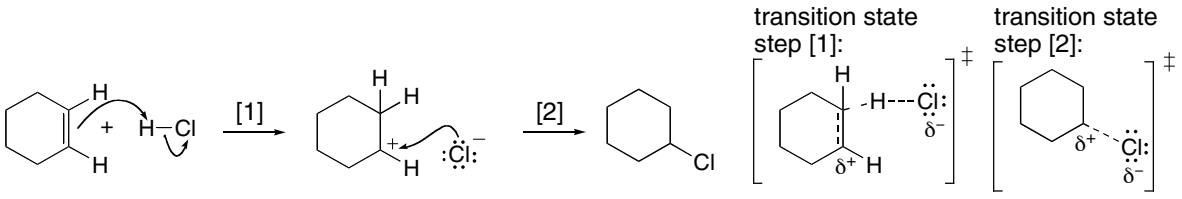
a. 

c. 

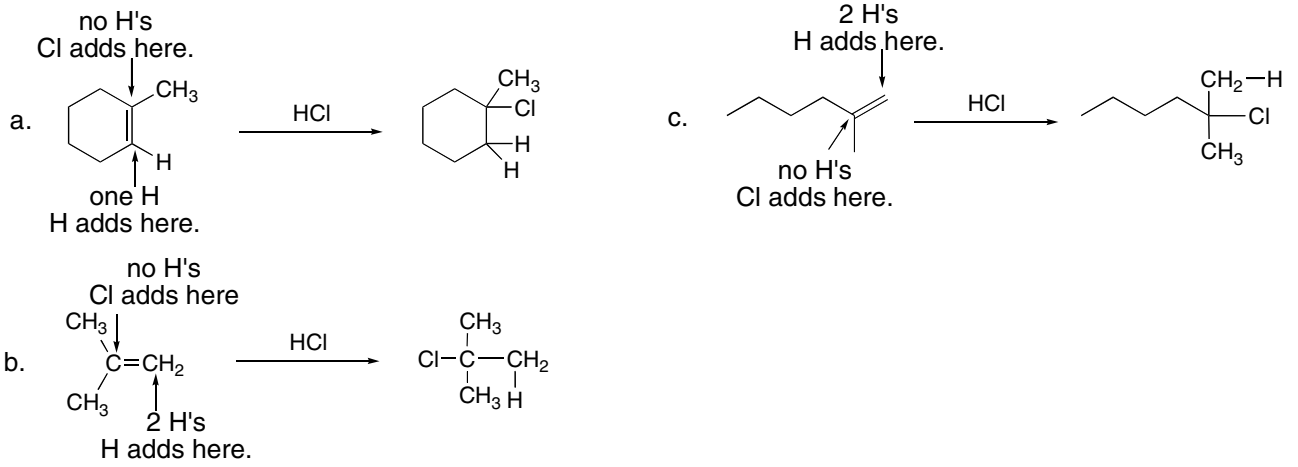
b. 

two new σ bonds

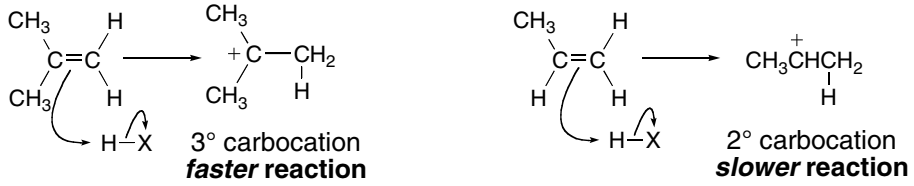
10.15 Addition reactions of HX occur in two steps:
[1] The double bond attacks the H atom of HX to form a carbocation.
[2] X^- attacks the carbocation to form a C–X bond.



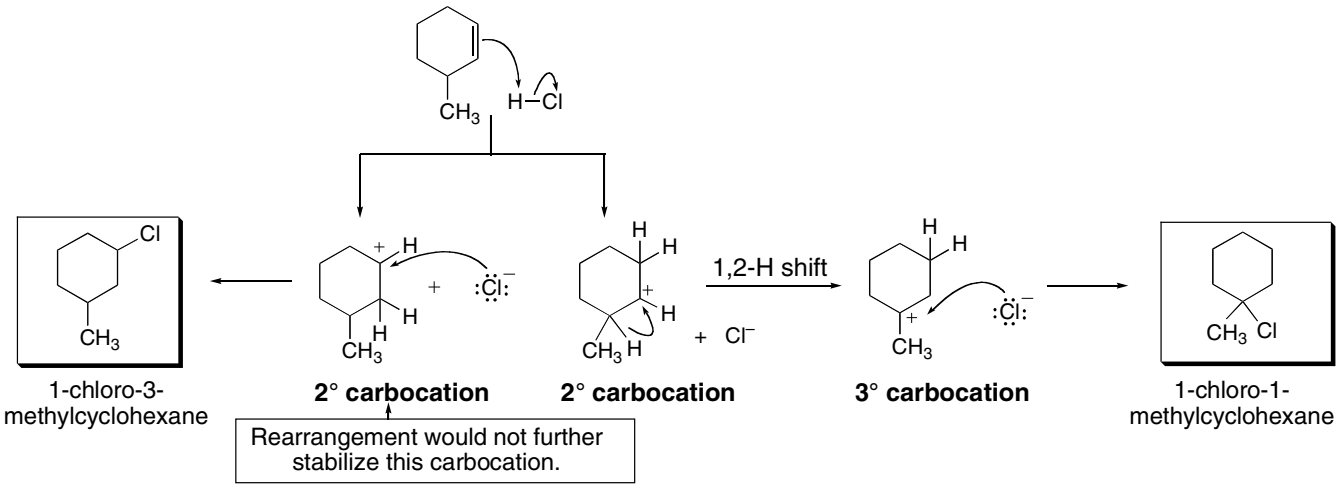
10.16 Addition to alkenes follows Markovnikov's rule: When HX adds to an unsymmetrical alkene, the H bonds to the C that has more H's to begin with.



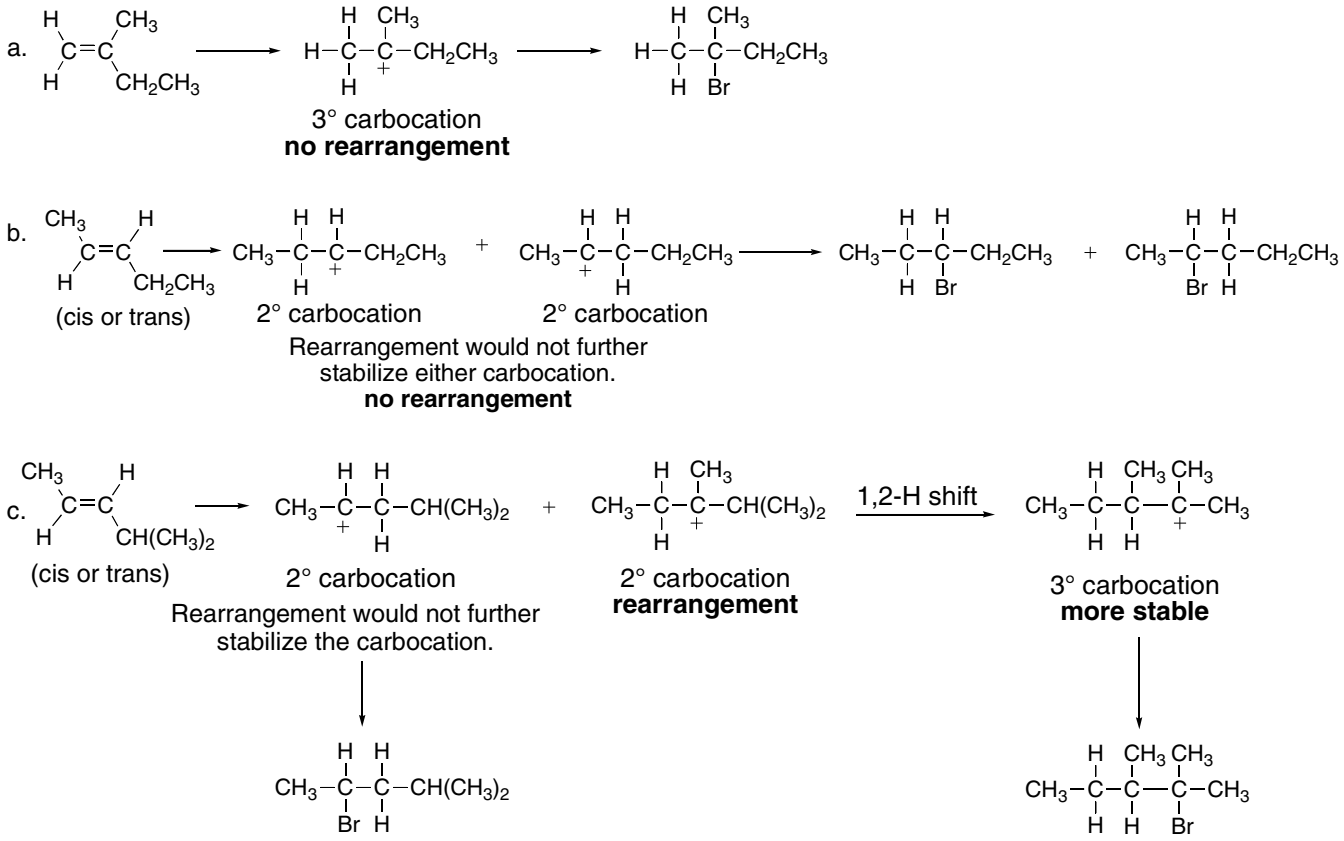
10.17 To determine which alkene will react faster, draw the carbocation that forms in the rate-determining step. The more stable, more substituted carbocation, the lower the E_a to form it and the faster the reaction.



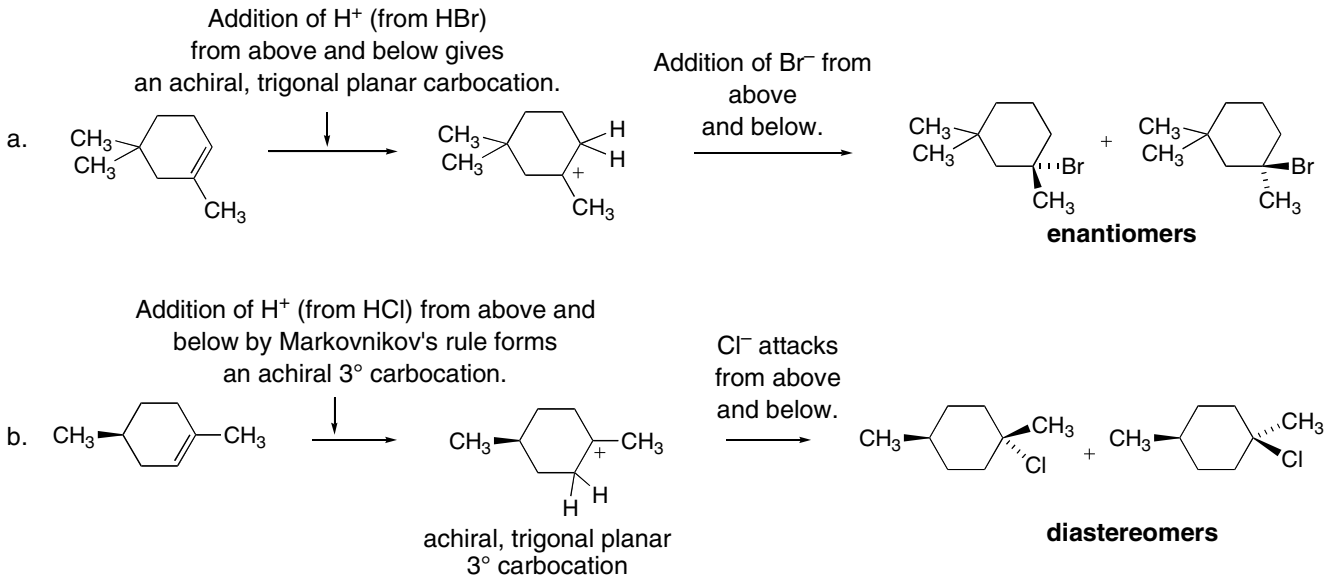
10.18 Look for rearrangements of a carbocation intermediate to explain these results.



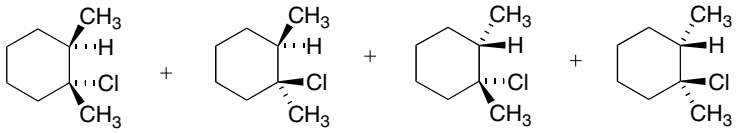
10.19 Addition of HX to alkenes involves formation of carbocation intermediates. Rearrangement of the carbocation will occur if it forms a more stable carbocation.



10.20 To draw the products, remember that addition of HX proceeds via a carbocation intermediate.

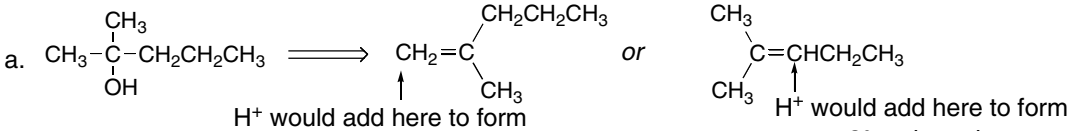


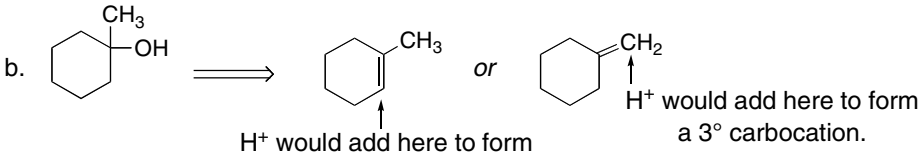
10.21 The product of syn addition will have H and Cl both up or down (both on wedges or both dashes), while the product of anti addition will have one up and one down (one wedge, one dash).

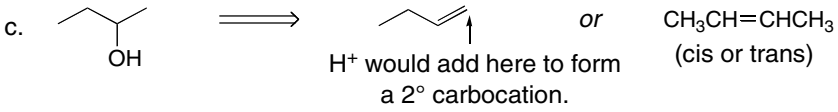


A syn addition **B** anti addition **C** anti addition **D** syn addition

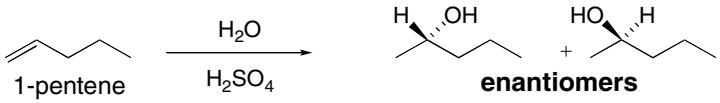
10.22

a. 

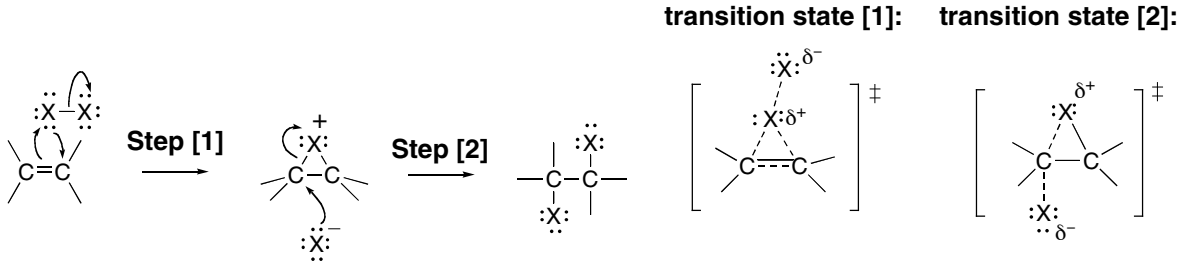
b. 

c. 

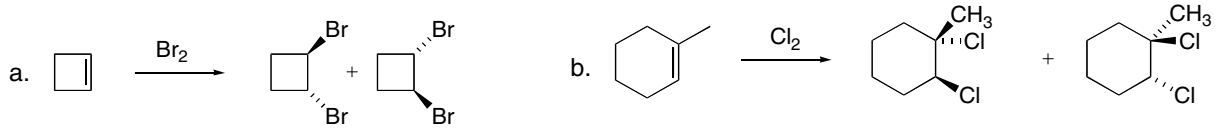
10.23



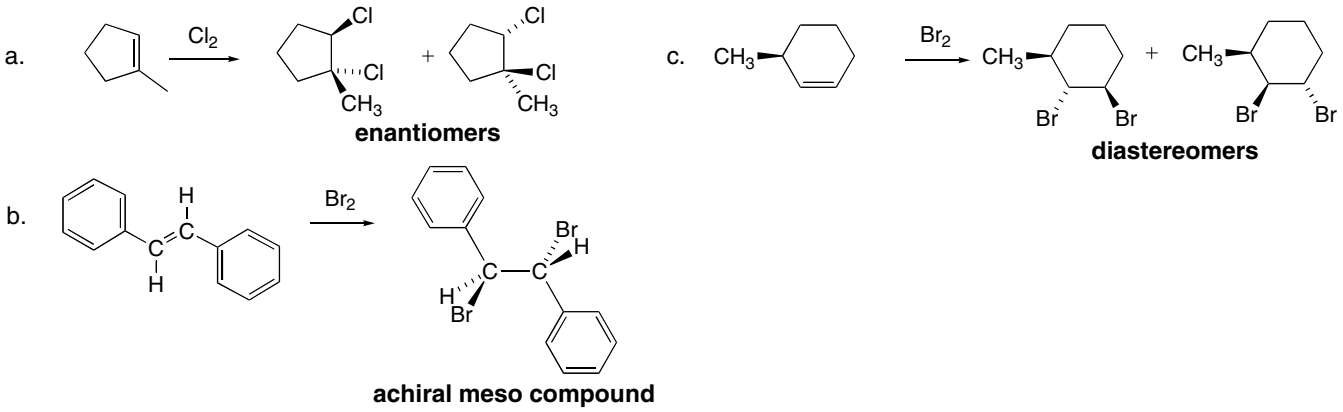
10.24 The two steps in the mechanism for the halogenation of an alkene are:
[1] Addition of X^+ to the alkene to form a bridged halonium ion
[2] Nucleophilic attack by X^-



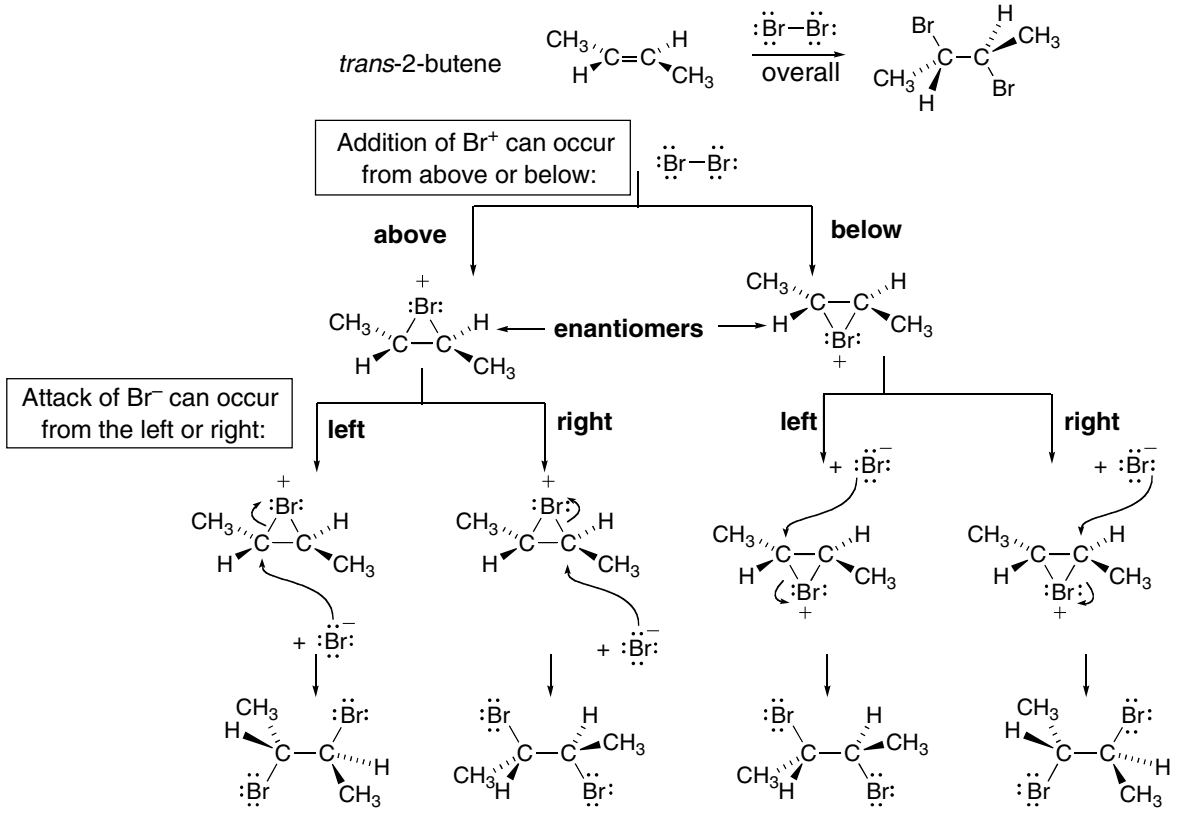
10.25 Halogenation of an alkene adds two elements of X in an anti fashion.



10.26 To draw the products of halogenation of an alkene, remember that the halogen adds to both ends of the double bond but only anti addition occurs.

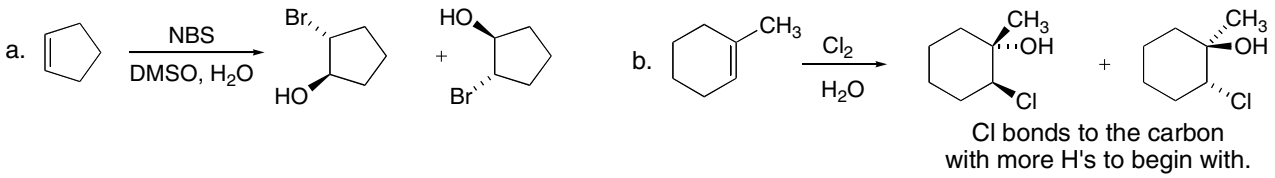


10.27 The two steps in the mechanism for the halogenation of an alkene are:
[1] Addition of X^+ to the alkene to form a bridged halonium ion
[2] Nucleophilic attack by X^-

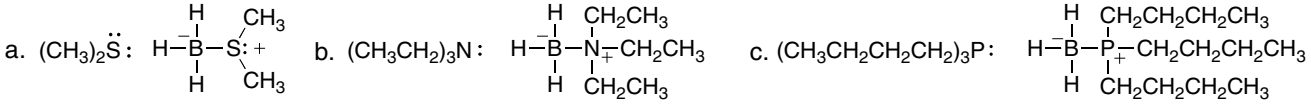


All four compounds are identical—an achiral meso compound.

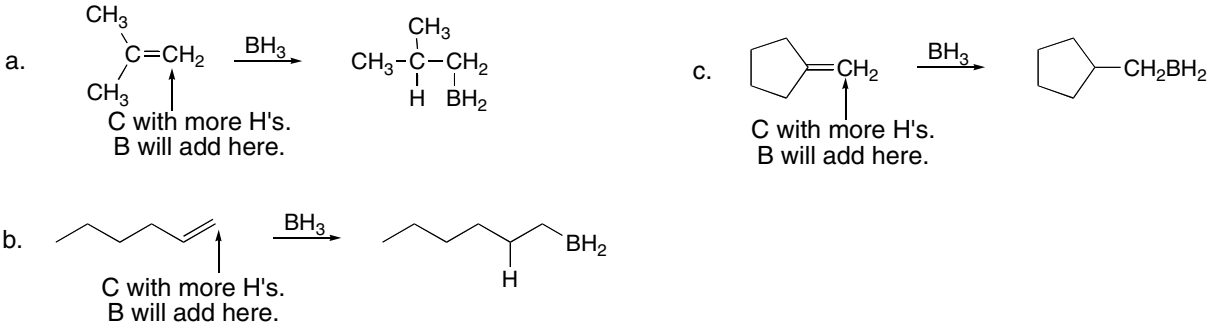
10.28 Halohydrin formation adds the elements of X and OH across the double bond in an anti fashion. The reaction is regioselective so X ends up on the carbon that had more H's to begin with.



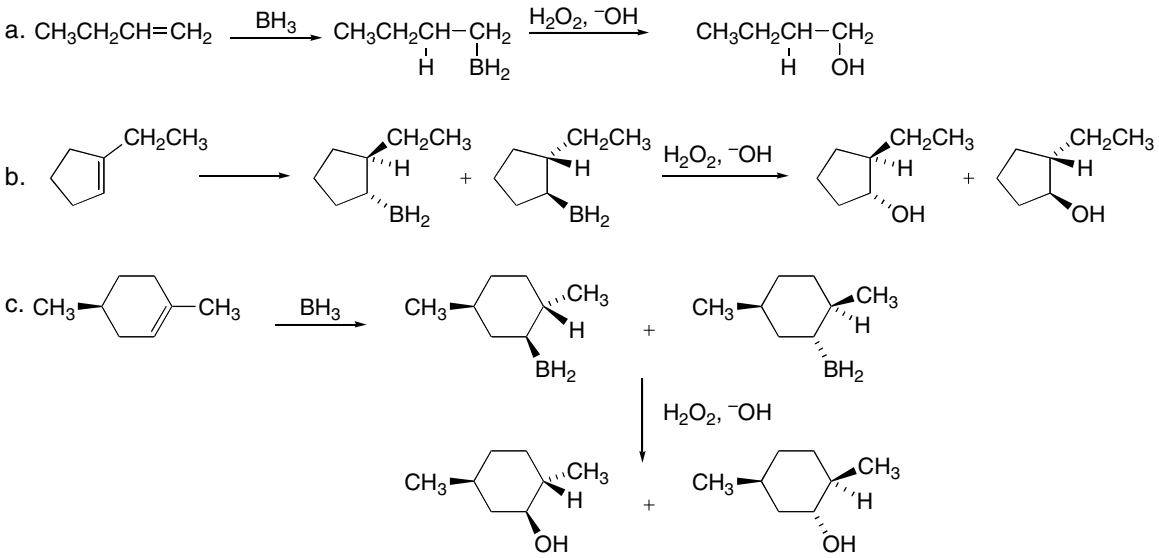
10.29



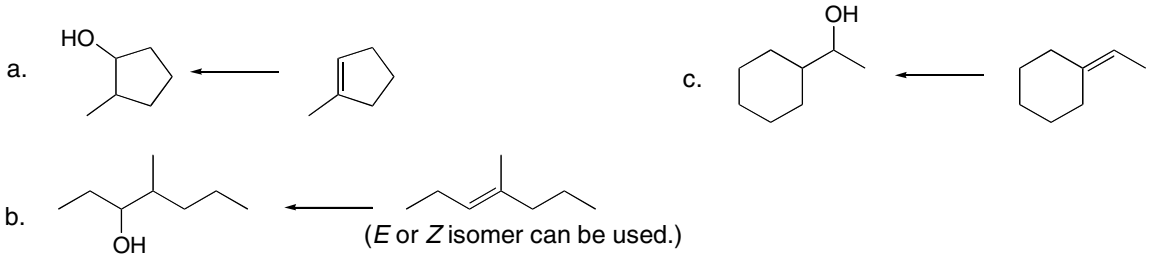
10.30 In hydroboration the boron atom is the electrophile and becomes bonded to the carbon atom that had more H's to begin with.



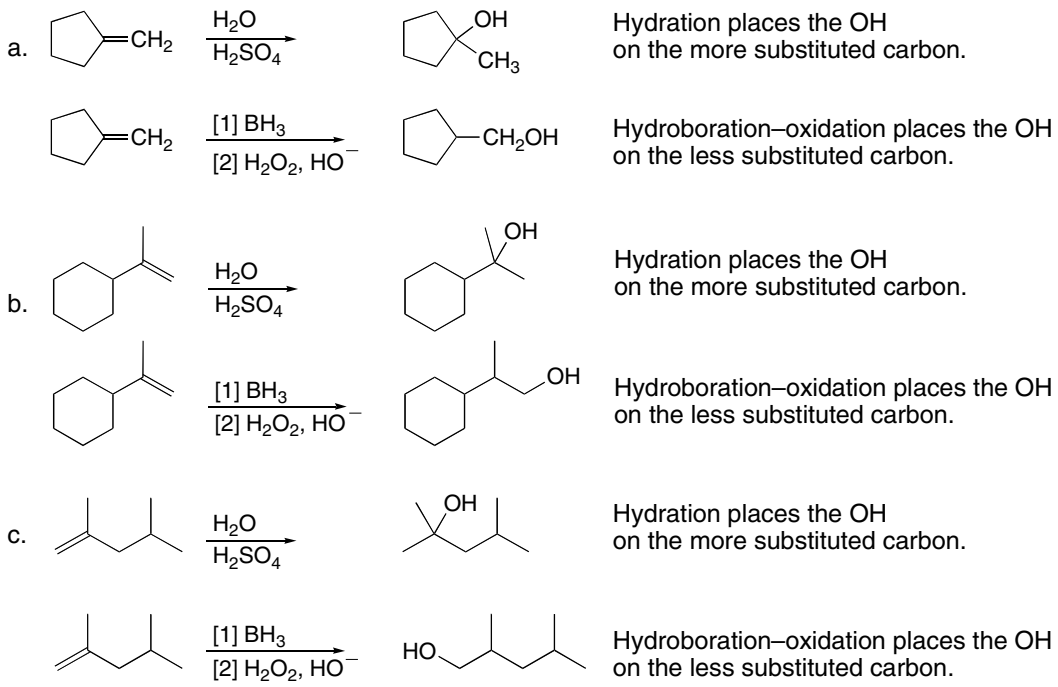
10.31 The hydroboration–oxidation reaction occurs in two steps:
[1] Syn addition of BH_3, with the boron on the less substituted carbon atom
[2] OH replaces the BH_2 with retention of configuration.



10.32 Remember that hydroboration results in addition of OH on the less substituted C.



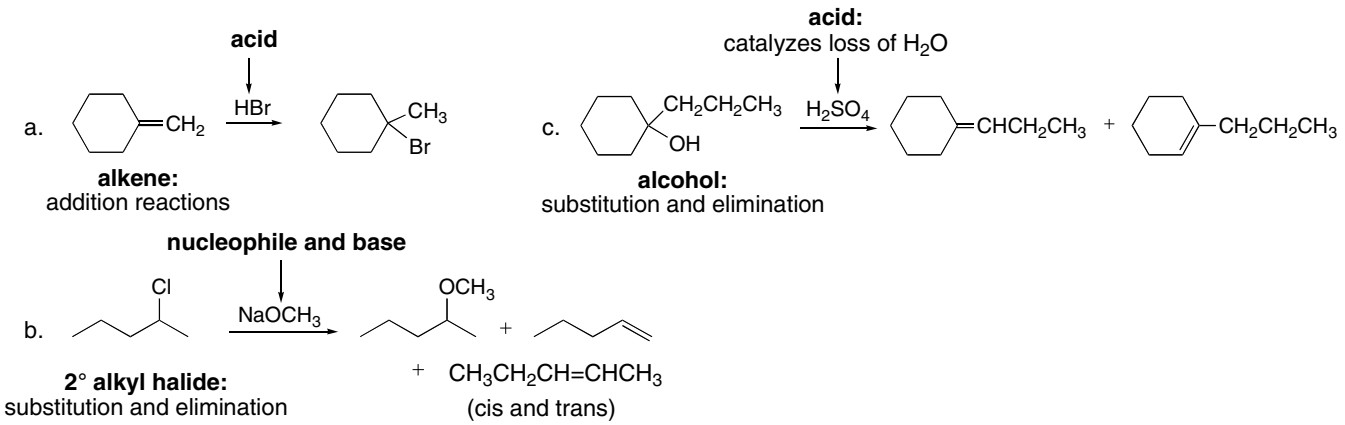
10.33



10.34 There are always two steps in this kind of question:

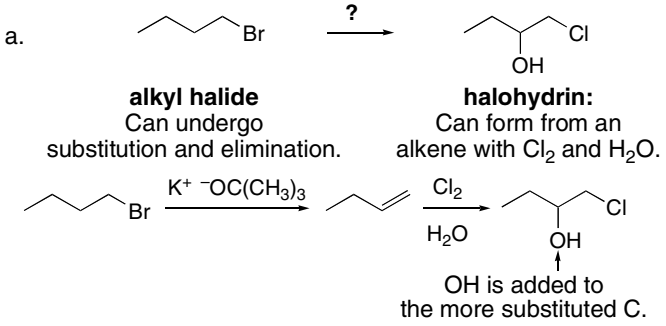
[1] **Identify the functional group and decide what types of reactions it undergoes** (for example, substitution, elimination, or addition).

[2] **Look at the reagent and determine if it is an electrophile, nucleophile, acid, or base.**

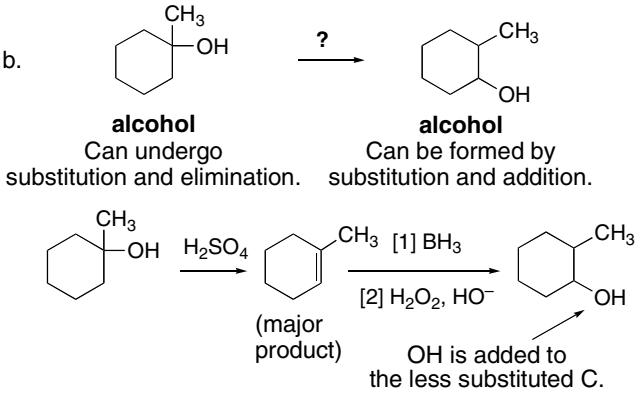


10.35 To devise a synthesis:
[1] Look at the starting material and decide what reactions it can undergo.
[2] Look at the product and decide what reactions could make it.

a.



b.



10.36 Use the directions from Answer 10.2 to calculate degrees of unsaturation.

a. C_3H_4
[1] maximum number of H's = $2n + 2 = 2(3) + 2 = 8$
[2] subtract actual from maximum = $8 - 4 = 4$
[3] divide by 2 = 4/2 = **2 degrees of unsaturation**

b. C_6H_8
[1] maximum number of H's = $2n + 2 = 2(6) + 2 = 14$
[2] subtract actual from maximum = $14 - 8 = 6$
[3] divide by 2 = 6/2 = **3 degrees of unsaturation**

c. $C_{40}H_{56}$
[1] maximum number of H's = $2n + 2 = 2(40) + 2 = 82$
[2] subtract actual from maximum = $82 - 56 = 26$
[3] divide by 2 = 26/2 = **13 degrees of unsaturation**

d. C_8H_8O
Ignore the O.
[1] maximum number of H's = $2n + 2 = 2(8) + 2 = 18$
[2] subtract actual from maximum = $18 - 8 = 10$
[3] divide by 2 = 10/2 = **5 degrees of unsaturation**

e. $C_{10}H_{16}O_2$
Ignore both O's.
[1] maximum number of H's = $2n + 2 = 2(10) + 2 = 22$
[2] subtract actual from maximum = $22 - 16 = 6$
[3] divide by 2 = 6/2 = **3 degrees of unsaturation**

f. C_8H_9Br
Because of Br, add one H (9 + 1 = 10 H's).
[1] maximum number of H's = $2n + 2 = 2(8) + 2 = 18$
[2] subtract actual from maximum = $18 - 10 = 8$
[3] divide by 2 = 8/2 = **4 degrees of unsaturation**

g. C_8H_9ClO
Ignore the O; count Cl as one more H (9 + 1 = 10 H's).
[1] maximum number of H's = $2n + 2 = 2(8) + 2 = 18$
[2] subtract actual from maximum = $18 - 10 = 8$
[3] divide by 2 = 8/2 = **4 degrees of unsaturation**

h. C_7H_9Br
Because of Br, add one H (9 + 1 = 10 H's).
[1] maximum number of H's = $2n + 2 = 2(7) + 2 = 16$
[2] subtract actual from maximum = $16 - 10 = 6$
[3] divide by 2 = 6/2 = **3 degrees of unsaturation**

i. $C_7H_{11}N$
Because of N, subtract one H (11 – 1 = 10 H's).
[1] maximum number of H's = $2n + 2 = 2(7) + 2 = 16$
[2] subtract actual from maximum = $16 - 10 = 6$
[3] divide by 2 = 6/2 = **3 degrees of unsaturation**

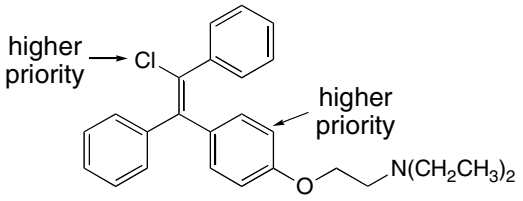
j. C_4H_8BrN
Because of Br, add one H, but subtract one for N
(8 + 1 – 1 = 8 H's).
[1] maximum number of H's = $2n + 2 = 2(4) + 2 = 10$
[2] subtract actual from maximum = $10 - 8 = 2$
[3] divide by 2 = 2/2 = **1 degree of unsaturation**

10.37 First determine the number of degrees of unsaturation in the compound. Then decide which combinations of rings and π bonds could exist.

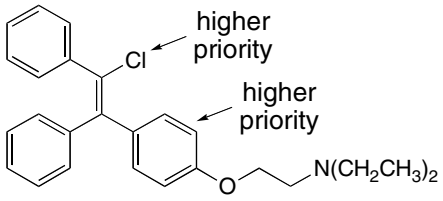
$C_{10}H_{14}$
[1] maximum number of H's = $2n + 2 = 2(10) + 2 = 22$
[2] subtract actual from maximum = $22 - 14 = 8$
[3] divide by two = 8/2 = **4 degrees of unsaturation**

possibilities:
4 π bonds
3 π bonds + 1 ring
2 π bonds + 2 rings
1 π bond + 3 rings
4 rings

10.38 The statement is incorrect because in naming isomers with more than two groups on a double bond, one must use an *E/Z* label, rather than a cis/trans label.



enclomiphene
***E* isomer**

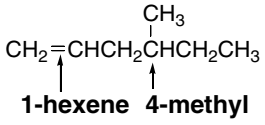


zuclomiphene
***Z* isomer**

10.39 Name the alkenes using the rules in Answers 10.4 and 10.6.

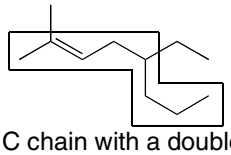
a. $CH_2{=}CHCH_2CH(CH_3)CH_2CH_3$

6 C chain with a double bond = **hexene**

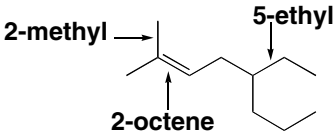


4-methyl-1-hexene

b.

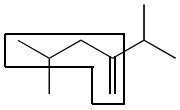


8 C chain with a double bond = **octene**

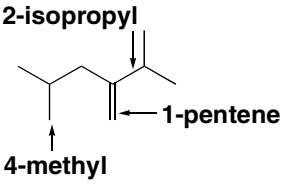


5-ethyl-2-methyl-2-octene

c.

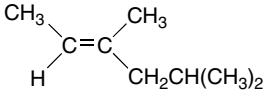


5 C chain with a double bond = **pentene**

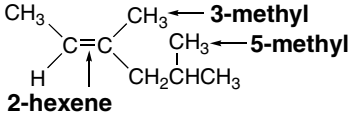


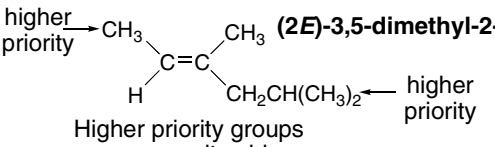
2-isopropyl-4-methyl-1-pentene

d.



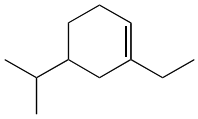
6 C chain with a double bond = **hexene**



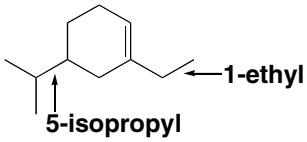


Higher priority groups are on opposite sides = ***E* alkene.**

e.

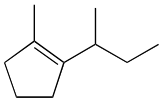


6 C ring with a double bond = **cyclohexene**

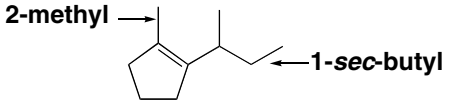


1-ethyl-5-isopropylcyclohexene

f.

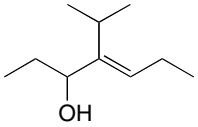


5 C ring with a double bond = **cyclopentene**

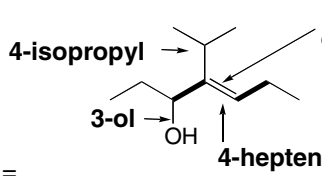


1-*sec*-butyl-2-methylcyclopentene

g.



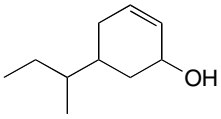
7 C chain with a double bond = **heptene**



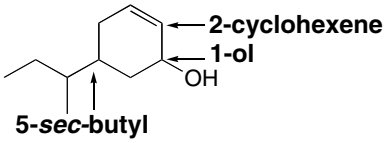
***E* double bond** (higher priority groups on opposite sides with bold bonds)

(4*E*)-4-isopropyl-4-hepten-3-ol

h.



6 C ring with a double bond = **cyclohexene**

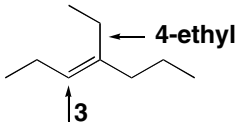


5-*sec*-butyl-2-cyclohexenol

10.40 Use the directions from Answer 10.8.

a. (3*E*)-4-ethyl-3-**heptene**

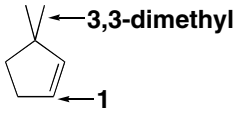
7 carbons



Higher priority groups on opposite sides = *E*.

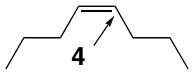
b. 3,3-dimethyl**cyclopentene**

5 carbon ring



c. *cis*-4-**octene**

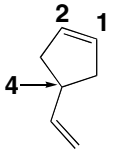
8 carbons



Higher priority groups on the same side = cis.

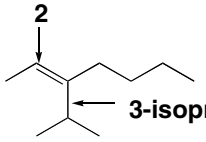
d. 4-vinyl**cyclopentene**

5 carbon ring



e. (2*Z*)-3-isopropyl-2-**heptene**

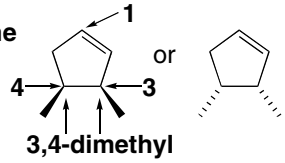
7 carbons



Higher priority groups on the same side = *Z*.

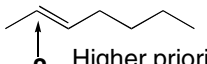
f. *cis*-3,4-dimethyl**cyclopentene**

5 carbon ring



g. *trans*-2-**heptene**

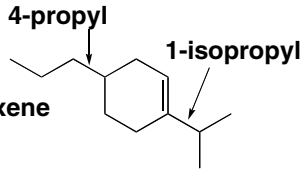
7 carbons



Higher priority groups on opposite sides = trans.

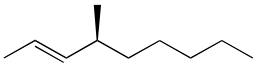
h. 1-isopropyl-4-propyl**cyclohexene**

6 carbon ring

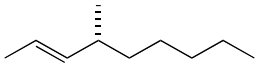


10.41

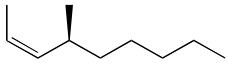
a.



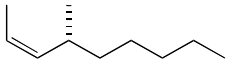
(2*E*,4*S*)-4-methyl-2-nonene **A**



(2*E*,4*R*)-4-methyl-2-nonene **B**



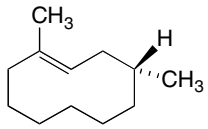
(2*Z*,4*S*)-4-methyl-2-nonene **C**



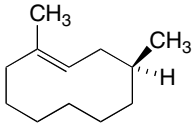
(2*Z*,4*R*)-4-methyl-2-nonene **D**

b. **A** and **B** are enantiomers. **C** and **D** are enantiomers.
c. Pairs of diastereomers: **A** and **C**, **A** and **D**, **B** and **C**, **B** and **D**.

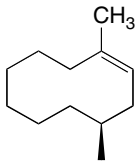
10.42

a. 

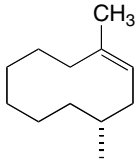
(1*E*,4*R*)-1,4-dimethylcyclodecene

b. 

(1*E*,4*S*)-1,4-dimethylcyclodecene
enantiomer

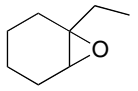
c. 

(1*Z*,4*S*)-1,4-dimethylcyclodecene
diastereomer

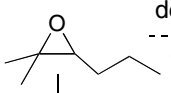


(1*Z*,4*R*)-1,4-dimethylcyclodecene
diastereomer

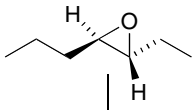
10.43 Name the alkene from which the epoxide can be derived and add the word *oxide*.

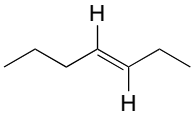
a. 

derived from
1-ethyl
6 carbon ring
cyclohexene
1-ethylcyclohexene
1-ethylcyclohexene oxide

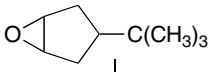
b. 

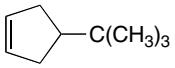
derived from
2-methyl
6 carbon chain
hexene
2-methyl-2-hexene
2-methyl-2-hexene oxide

c. 

derived from


7 carbon chain
heptene
(3*E*)- 3-heptene
or
***trans*-3-heptene**
(3*E*)- 3-heptene oxide
or
***trans*-3-heptene oxide**

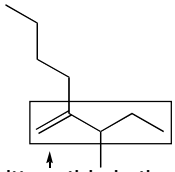
d. 

derived from


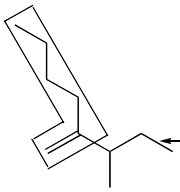
5 carbon ring
cyclopentene
4-*tert*-butylcyclopentene
4-*tert*-butylcyclopentene oxide

10.44

a. 2-butyl-3-methyl-1-pentene

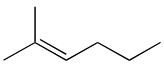


As written, this is the parent chain, but there is another longer chain containing the double bond.



new name:
2-*sec*-butyl-1-hexene

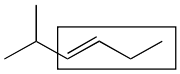
b. (*Z*)-2-methyl-2-hexene



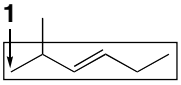
new name:
2-methyl-2-hexene

Two groups on one end of the C=C are the same (2 CH_3's), so no *E* and *Z* isomers are possible.

c. (*E*)-1-isopropyl-1-butene

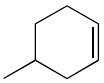


As written, this is the parent chain, but there is another longer chain containing the double bond.

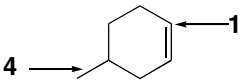


new name:
(3*E*)-2-methyl-3-hexene

d. 5-methylcyclohexene

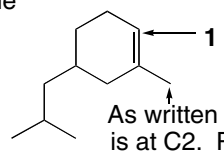


As written the methyl is at C5. Re-number to put it at C4.

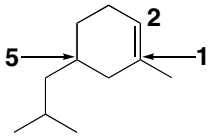


new name:
4-methylcyclohexene

e. 4-isobutyl-2-methylcylohexene

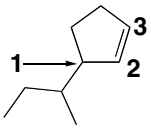


As written this methyl is at C2. Re-number to put it at C1.

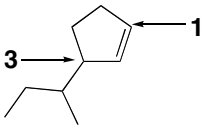


new name:
5-isobutyl-1-methylcyclohexene

f. 1-*sec*-butyl-2-cyclopentene

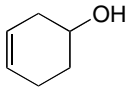


This has the double bond between C2 and C3. Cycloalkenes must have the double bond between C1 and C2. Re-number.

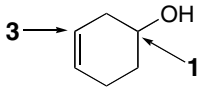


new name:
3-*sec*-butylcyclopentene

g. 1-cyclohexen-4-ol

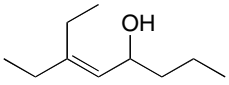


The numbering is incorrect. When a compound contains both a double bond and an OH group, number the C skeleton to give the OH group the lower number.

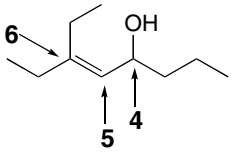


3-cyclohexenol (The "1" can be omitted.)

h. 3-ethyl-3-octen-5-ol



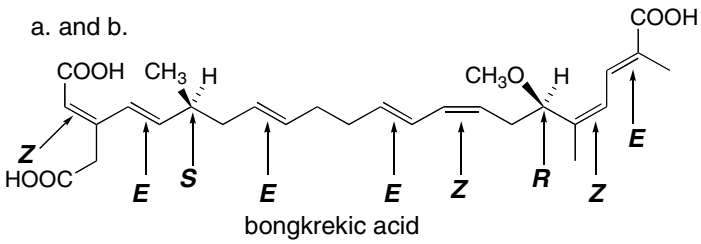
The numbering is incorrect. When a compound contains both a double bond and an OH group, number the C skeleton to give the OH group the lower number.



6-ethyl-5-octen-4-ol

10.45

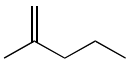
a. and b.

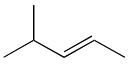


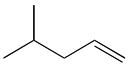
bongkrekic acid

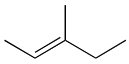
c. Since there are 7 double bonds and 2 tetrahedral stereogenic centers, $2^9 = 512$ possible stereoisomers.

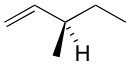
10.46

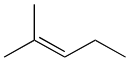

2-methyl-1-pentene


(2*E*)-4-methyl-2-pentene

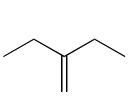

4-methyl-1-pentene

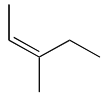

(2*E*)-3-methyl-2-pentene

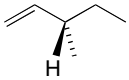

(3*R*)-3-methyl-1-pentene


2-methyl-2-pentene

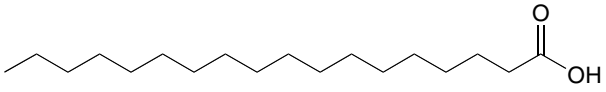

(2*Z*)-4-methyl-2-pentene


2-ethyl-1-butene

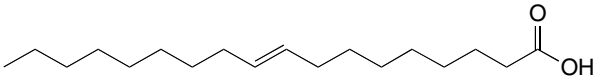

(2*Z*)-3-methyl-2-pentene


(3*S*)-3-methyl-1-pentene

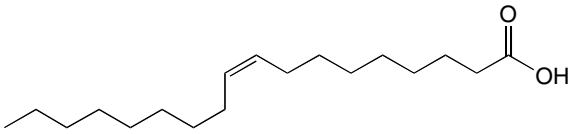
10.47


stearic acid

hIghest melting point
no double bonds

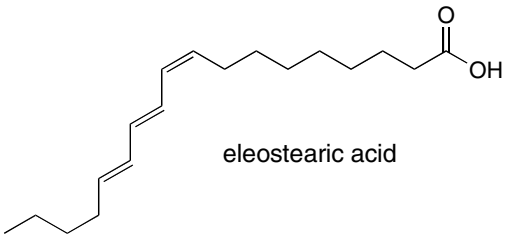

elaidic acid

intermediate melting point
one *E* double bond

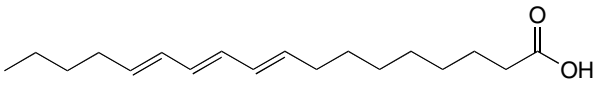

oleic acid

lowest melting point
one *Z* double bond

10.48

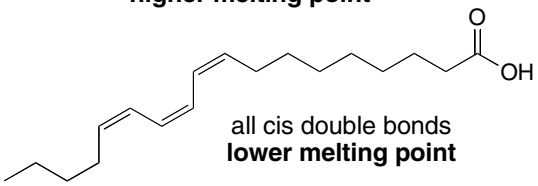

eleostearic acid

a.



all trans double bonds
higher melting point

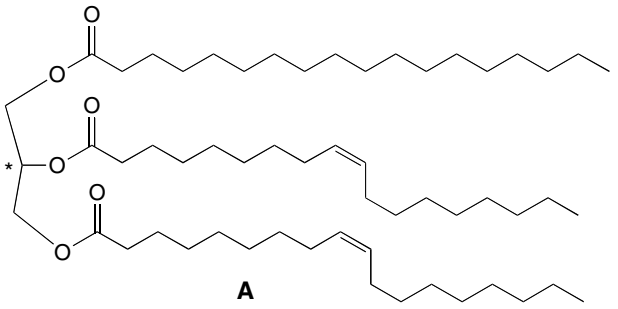
b.



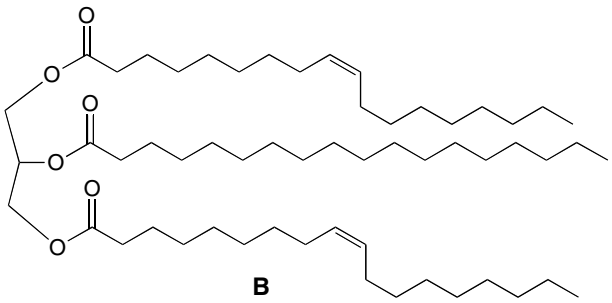
all cis double bonds
lower melting point

10.49

a.



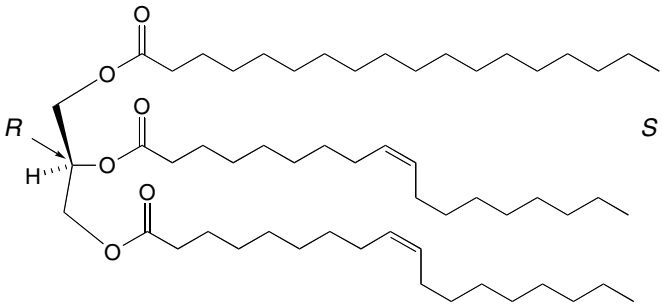
A

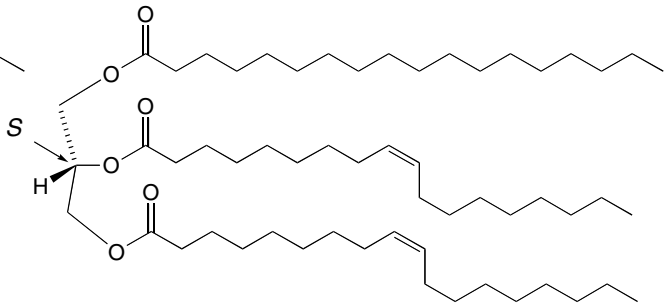


B

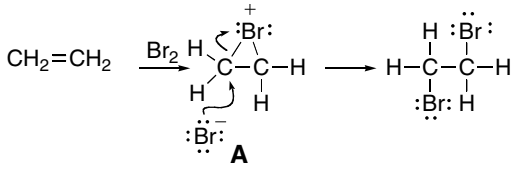
A has one tetrahedral stereogenic center, labeled with an asterisk [*].

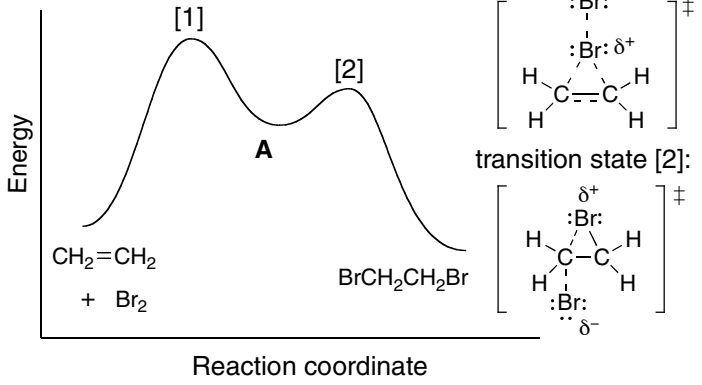
b.





10.50





10.51 The more negative the $\Delta H°$, the larger the K_{eq} assuming entropy changes are comparable. Calculate the $\Delta H°$ for each reaction and compare.

$CH_2{=}CH_2 + HI \longrightarrow CH_3CH_2{-}I$

[1] Bonds broken

	$\Delta H°$ (kJ/mol)
C–C π bond	+ 267
H—I	+ 297
Total	+ 564 kJ/mol

[2] Bonds formed

	$\Delta H°$ (kJ/mol)
$CH_2ICH_2{-}H$	– 410
C—I	– 222
Total	– 632 kJ/mol

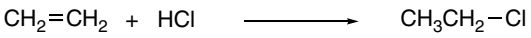
[3] Overall $\Delta H°$ =

sum in Step [1] + sum in Step [2]

+ 564 kJ/mol

– 632 kJ/mol

– 68 kJ/mol



[1] Bonds broken

	ΔH^o (kJ/mol)
C–C π bond	+ 267
H–Cl	+ 431
Total	+ 698 kJ/mol

[2] Bonds formed

	ΔH^o (kJ/mol)
CH_2ClCH_2-H	– 410
C–Cl	– 339
Total	– 749 kJ/mol

[3] Overall ΔH^o =

sum in Step [1] + sum in Step [2]

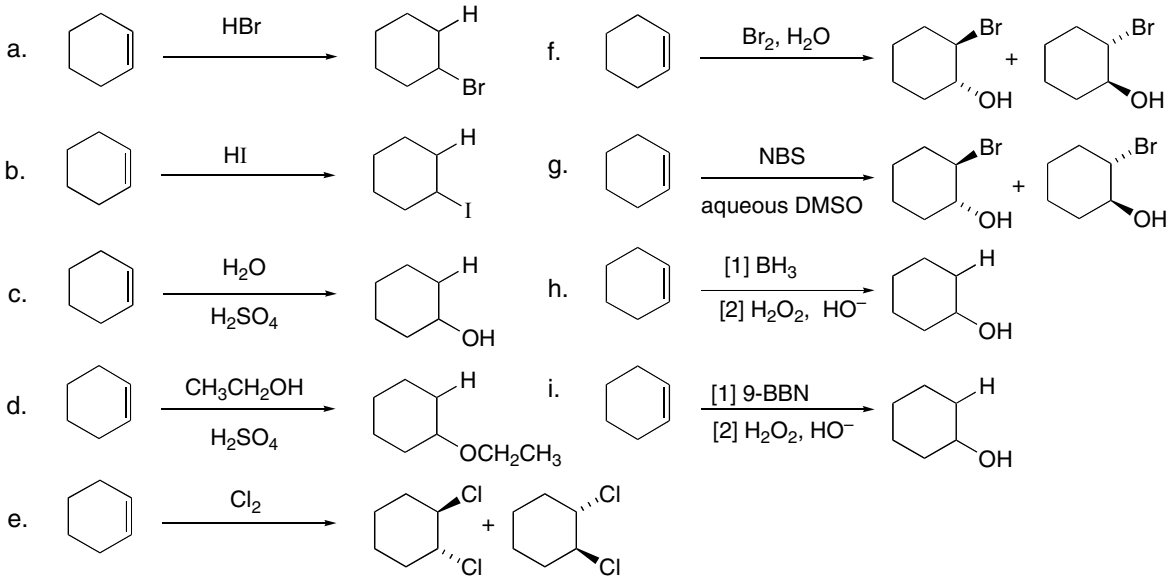
+ 698 kJ/mol

– 749 kJ/mol

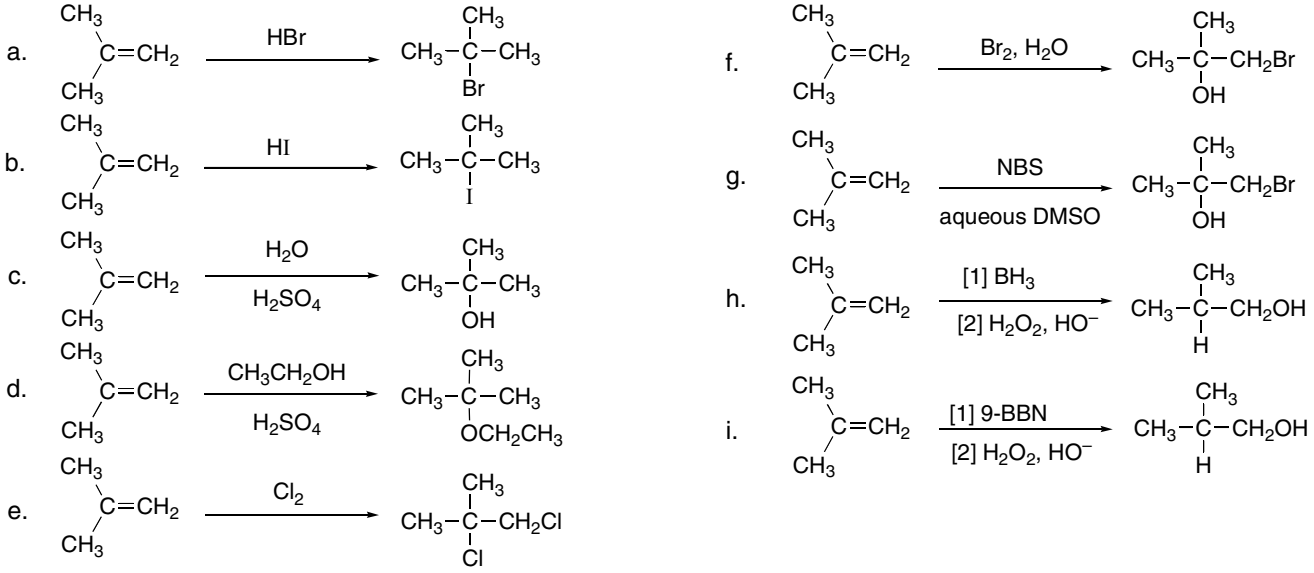
– 51 kJ/mol

Compare the $\Delta H°$:
Addition of HI: **–68 kJ/mol** more negative $\Delta H°$, larger K_{eq}.
Addition of HCl: **–51 kJ/mol**

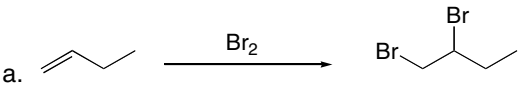
10.52



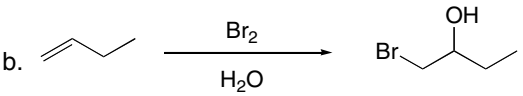
10.53



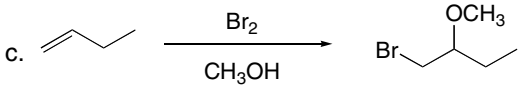
10.54

a. 

Halogenation

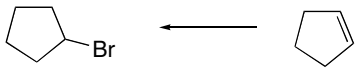
b. 

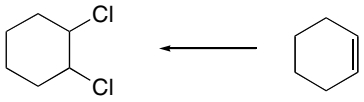
Halohydrin formation: Br adds to the C that had more H's to begin with.

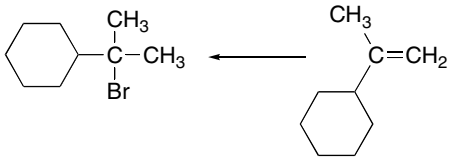
c. 

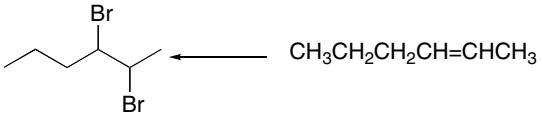
Same as halohydrin formation, except CH_3OH in place of H_2O.

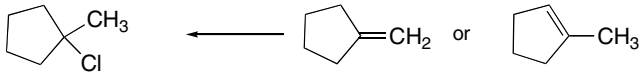
10.55

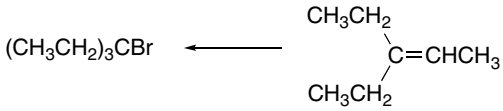
a. 

b. 

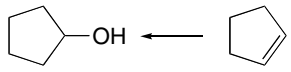
c. 

d. 

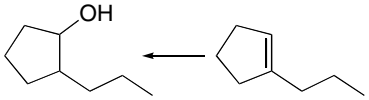
e. 

f. 

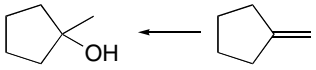
10.56 Hydroboration–oxidation results in addition of an OH group on the less substituted carbon, whereas acid-catalyzed addition of H_2O results in the addition of an OH group on the more substituted carbon.

a. 

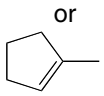
hydroboration–oxidation and acid-catalyzed addition

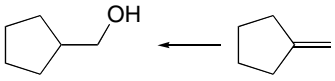
b. 

hydroboration–oxidation

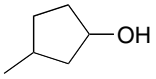
c. 

acid-catalyzed addition

or 

d. 

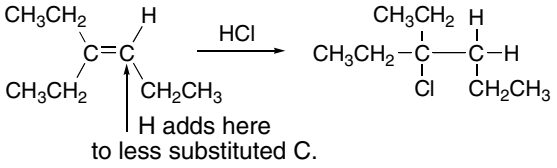
hydroboration–oxidation

e. 

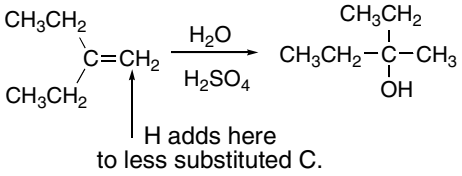
Both methods would give product mixtures.

10.57

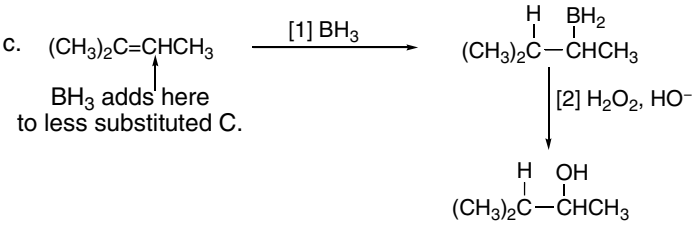
a. $(CH_3CH_2)_2C{=}CHCH_2CH_3$



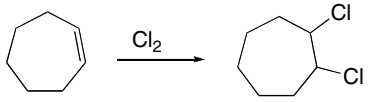
b. $(CH_3CH_2)_2C{=}CH_2$



c. $(CH_3)_2C{=}CHCH_3$



d.



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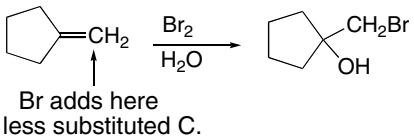

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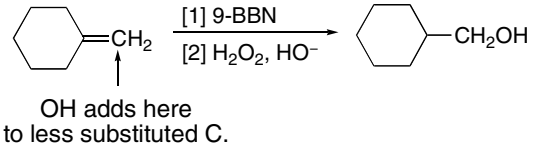
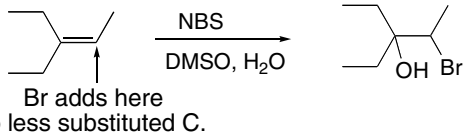
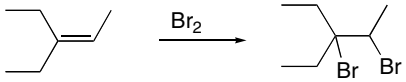


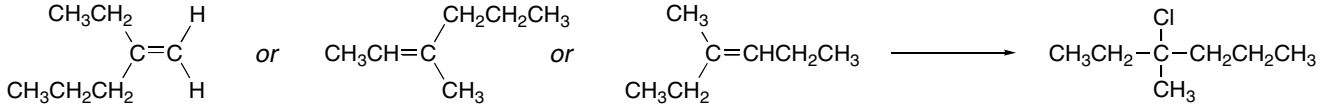
g.



h.

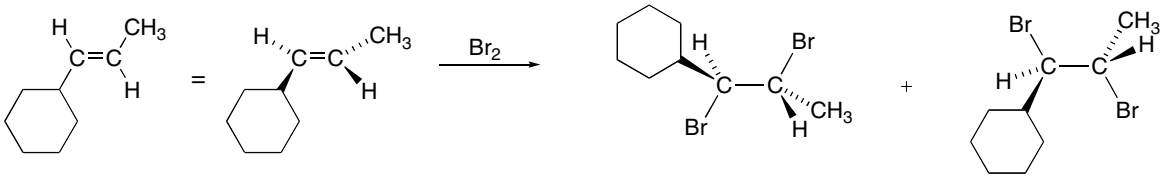


10.58

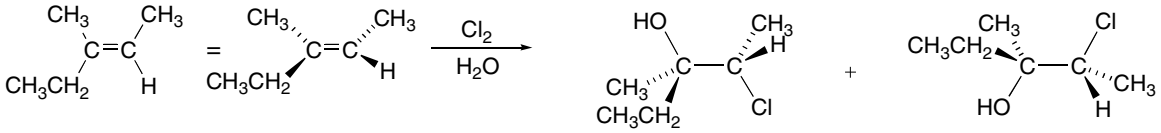


10.59

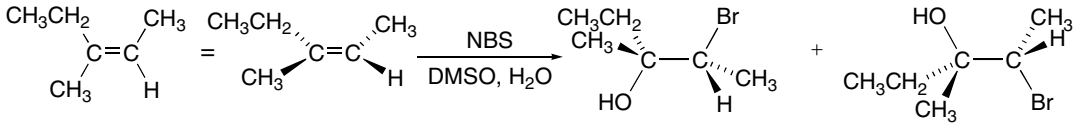
a.



b.

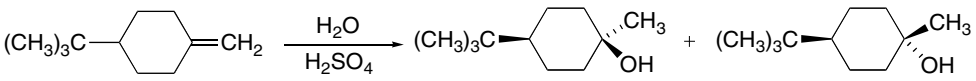


c.



10.60

a.



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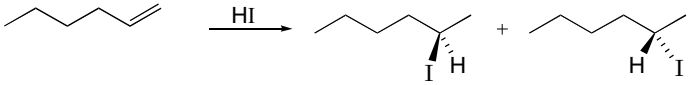
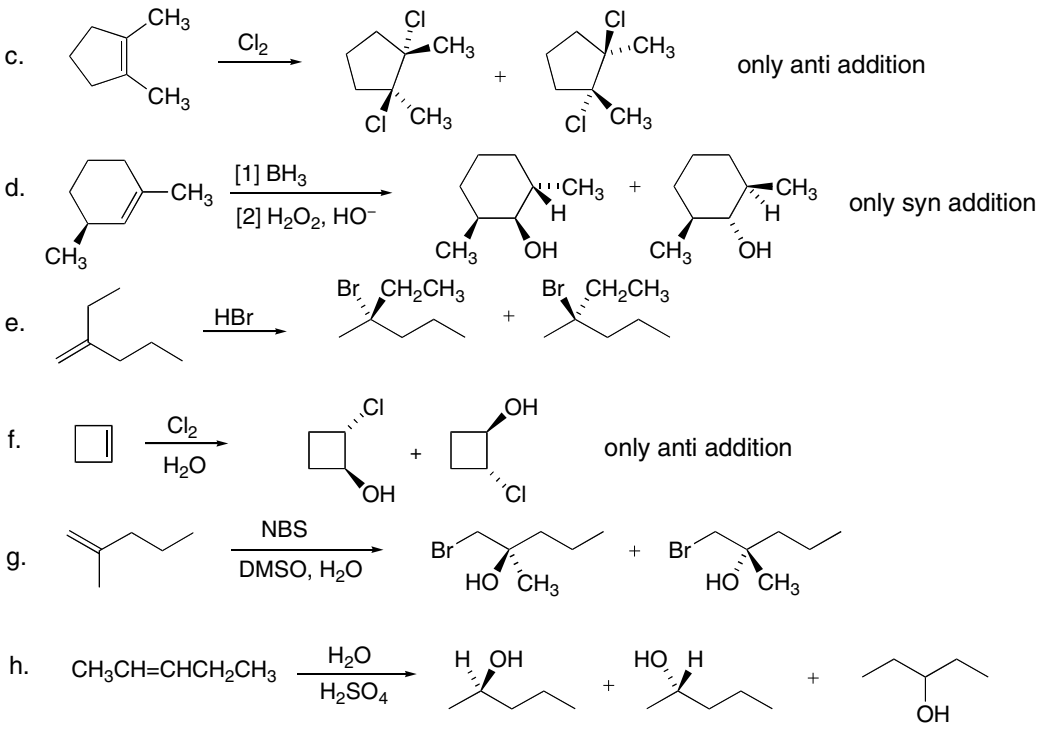
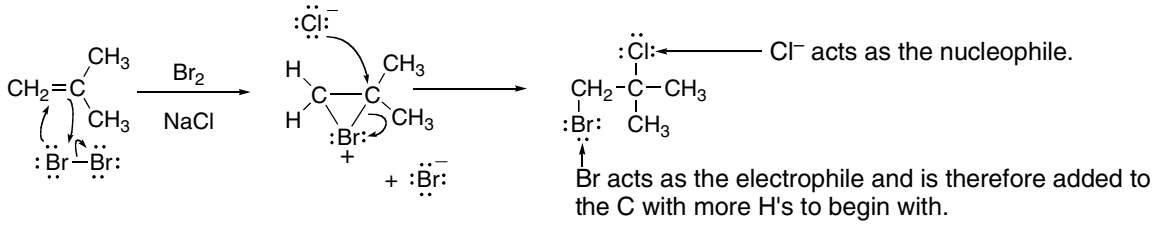
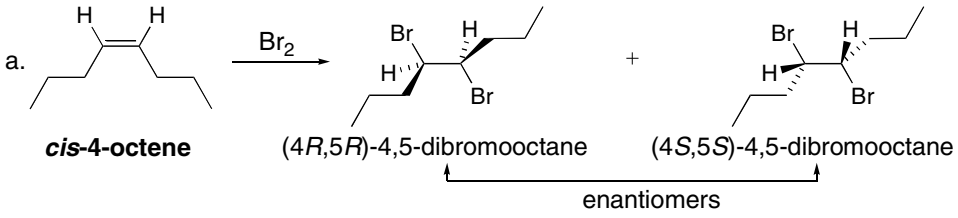


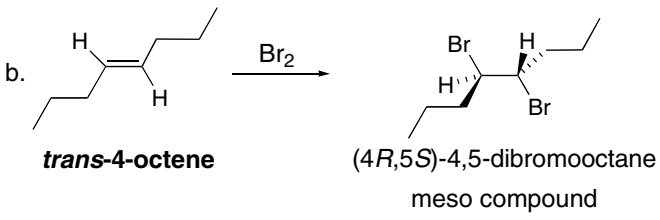


10.61

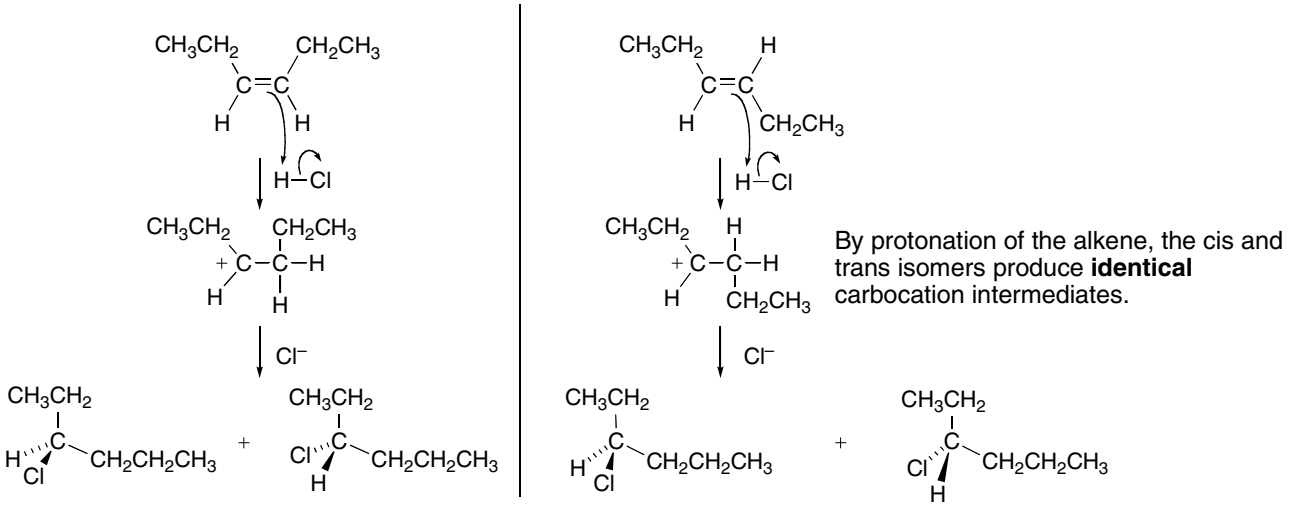


10.62 Draw each reaction. (a) The cis isomer of 4-octene gives two enantiomers on addition of Br_2. (b) The trans isomer gives a meso compound.





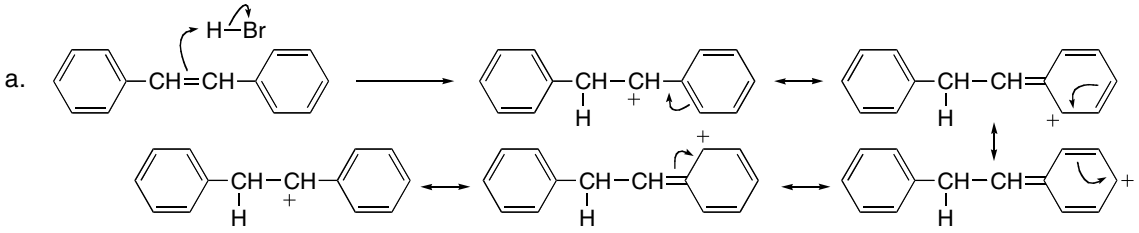
10.63



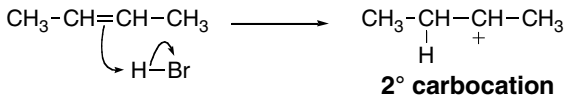
Both *cis*- and *trans*-3-hexene give the same racemic mixture of products, so the reaction is not stereospecific.

10.64 The alkene that forms the more stable carbocation reacts faster, according to the Hammond postulate.

a.

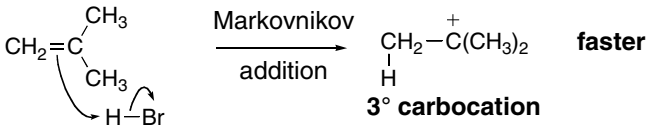


This 2° carbocation is resonance stabilized, making it more stable, so the starting alkene reacts **faster** with HBr.



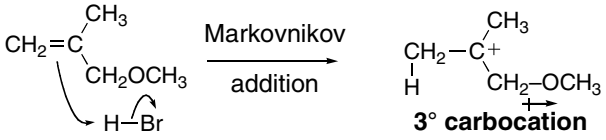
2° carbocation
no resonance stabilization

b.



faster

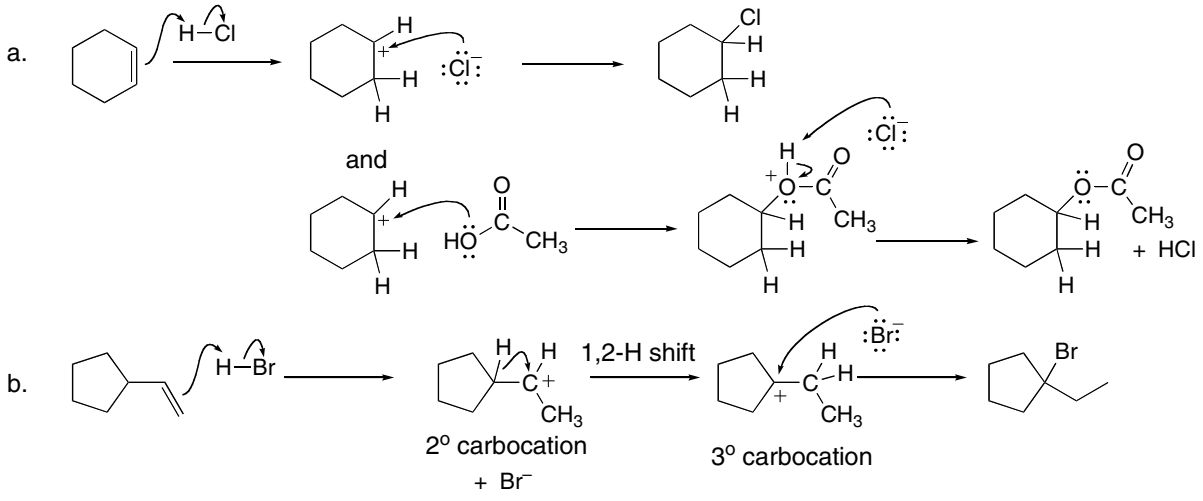
3° carbocation



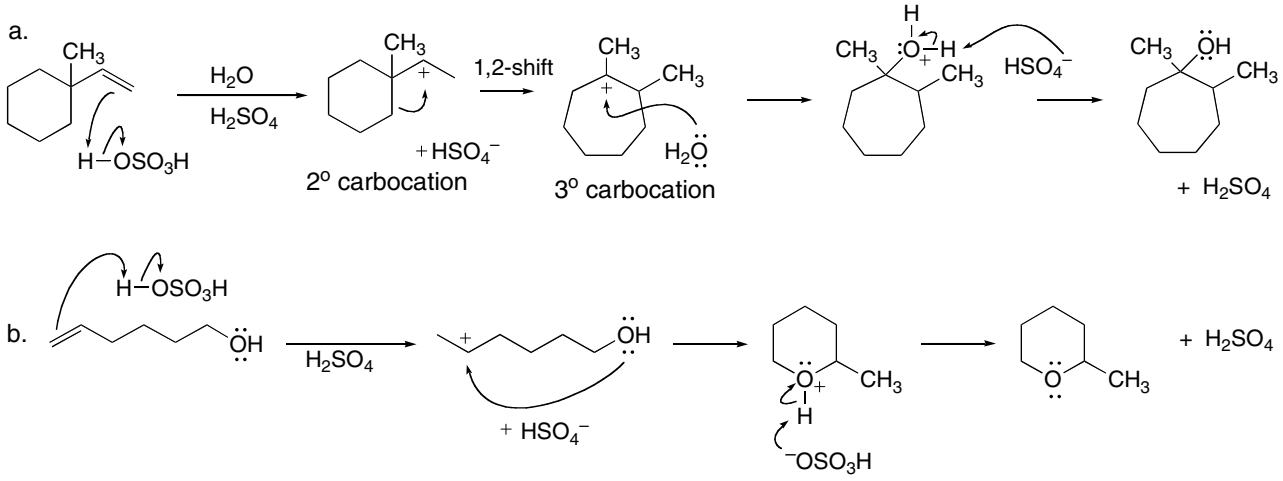
3° carbocation

This carbocation is still 3°, but the nearby electronegative O atom withdraws electron density from the carbocation, destabilizing it. Thus, the reaction to form this carbocation occurs more slowly.

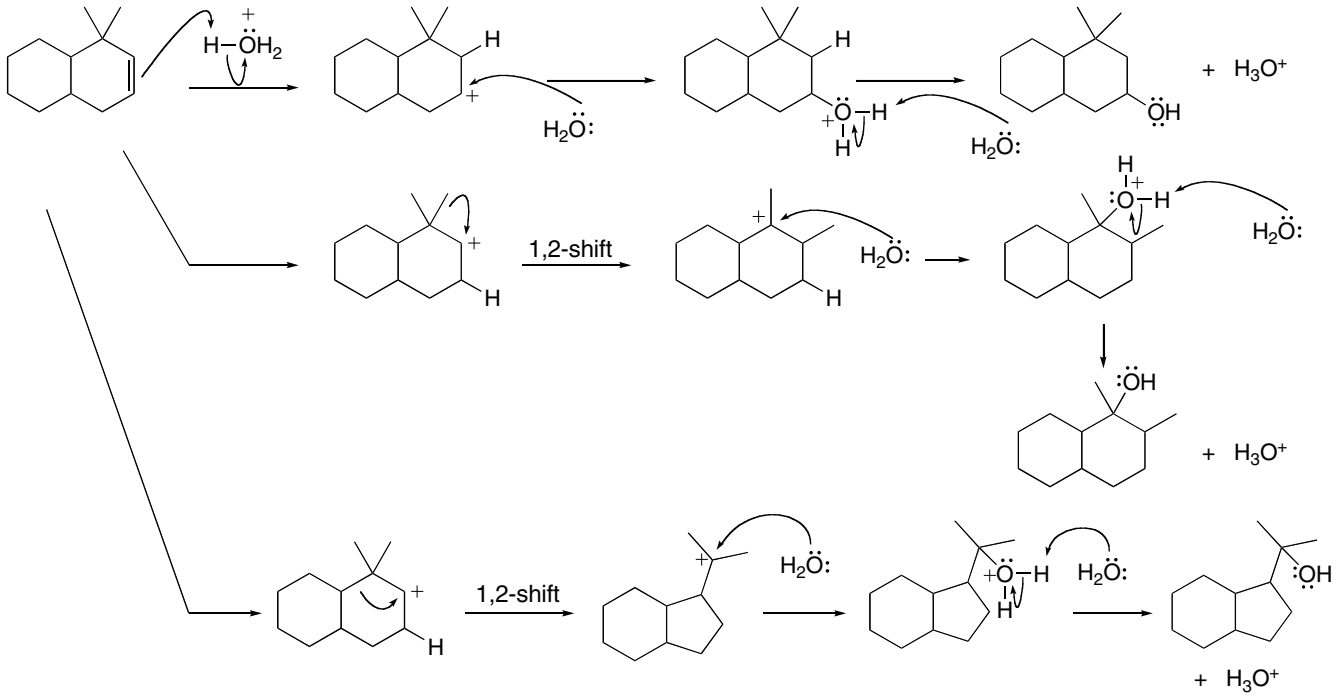
10.65


a.
H–Cl
:Cl:⁻
and
HO
CH3
+ HCl
b.
H–Br
1,2-H shift
:Br:⁻
Br
2° carbocation
+ Br⁻
3° carbocation

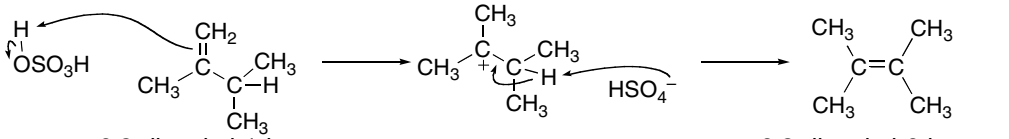
10.66


a.
CH3
H2O
H2SO4
H–OSO3H
+ HSO4⁻
2° carbocation
1,2-shift
3° carbocation
H2O
HSO4⁻
+ H2SO4
b.
H–OSO3H
OH
H2SO4
+ HSO4⁻
⁻OSO3H
+ H2SO4

10.67

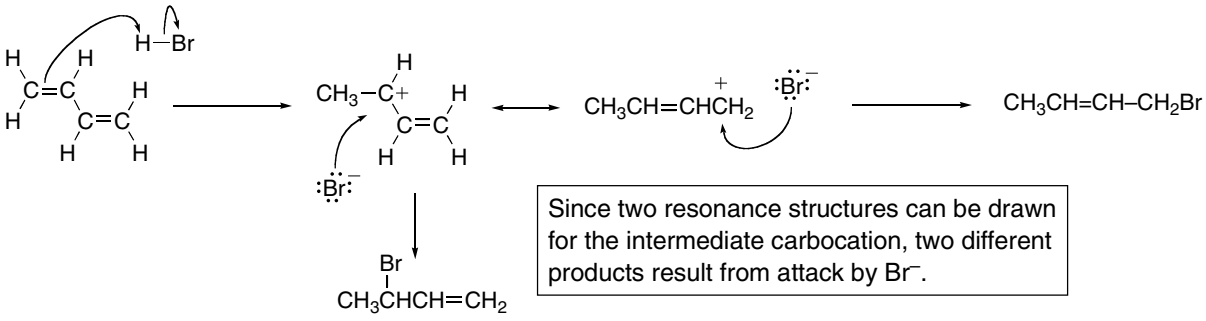


10.68 The isomerization reaction occurs by protonation and deprotonation.



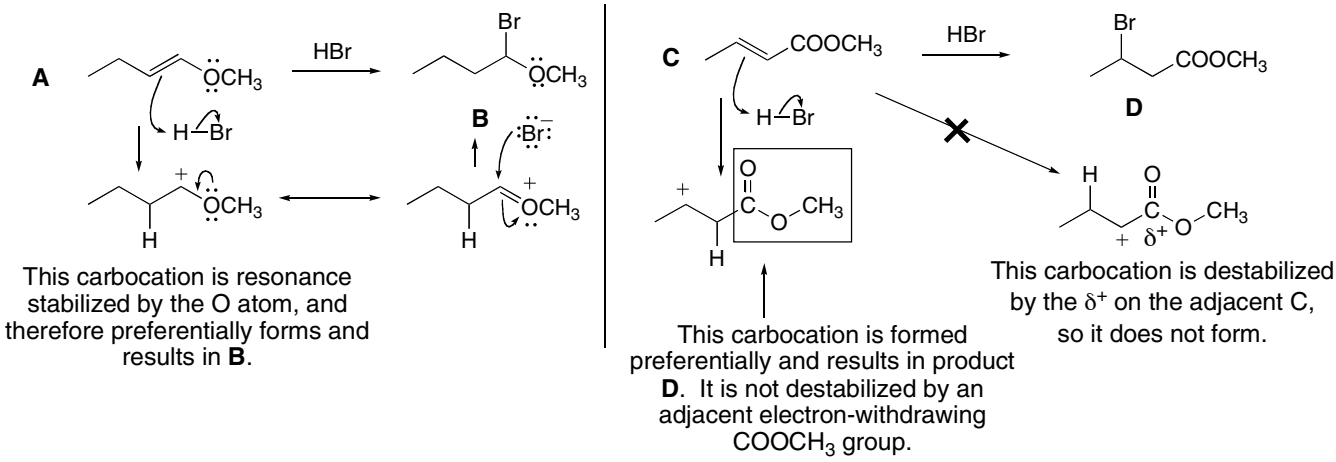
2,3-dimethyl-1-butene 2,3-dimethyl-2-butene

10.69

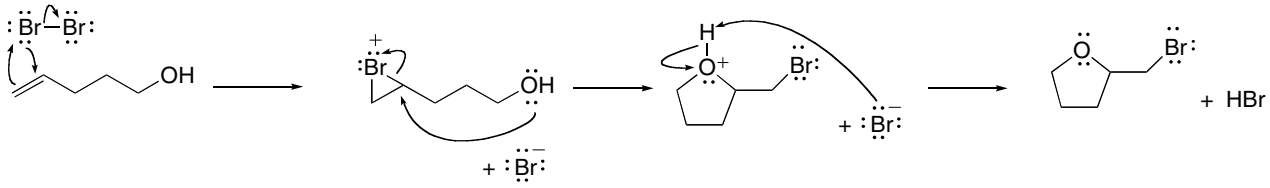


Since two resonance structures can be drawn for the intermediate carbocation, two different products result from attack by Br^-.

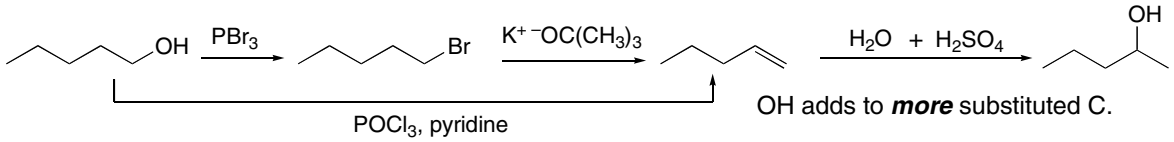
10.70

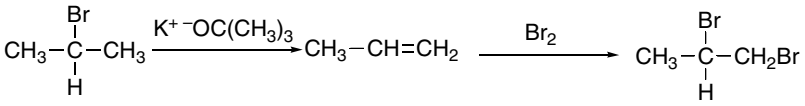


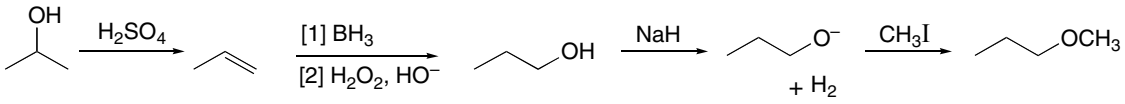
10.71

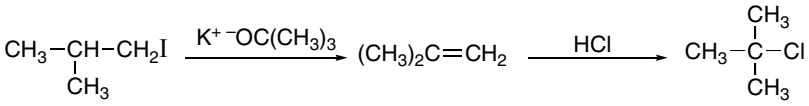


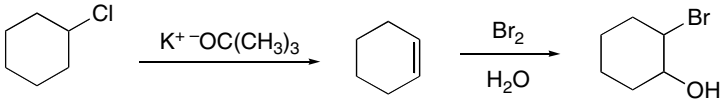
10.72

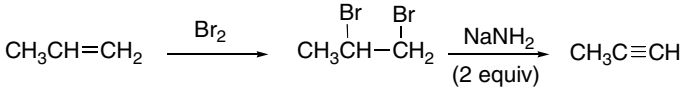
a. 

b. 

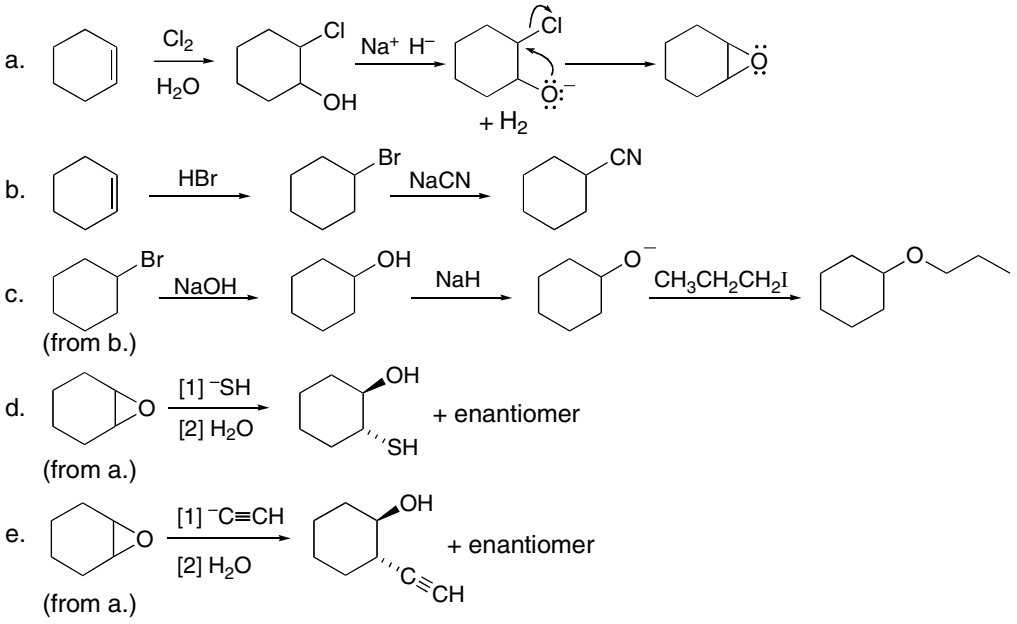
c. 

d. 

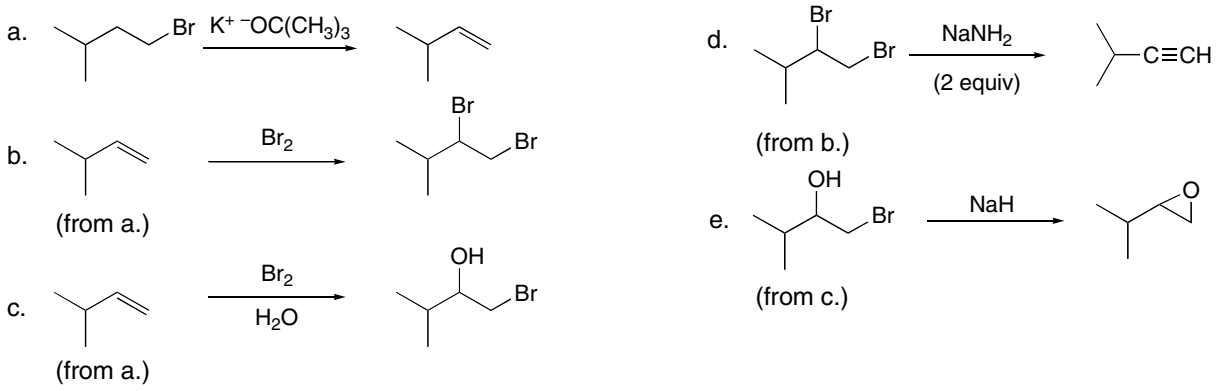
e. 

f. 

10.73



10.74



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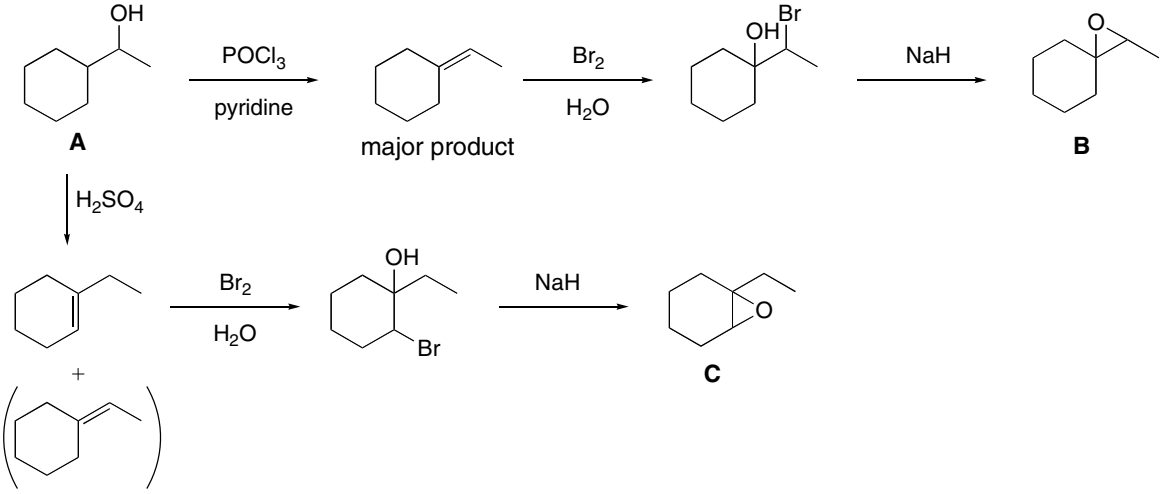
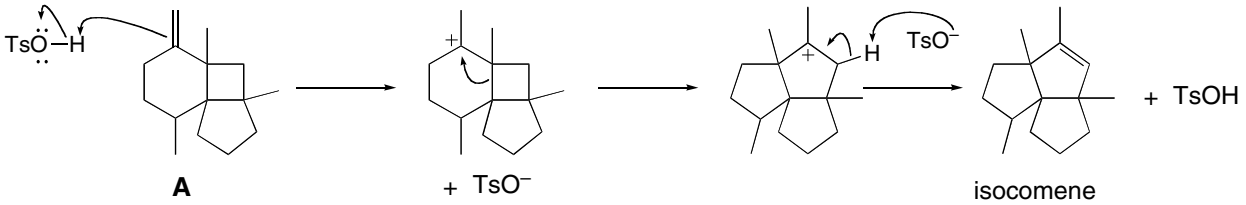


10.76



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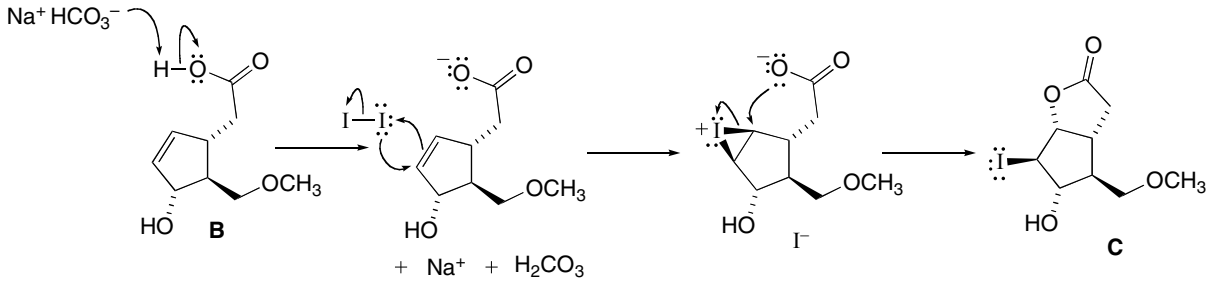

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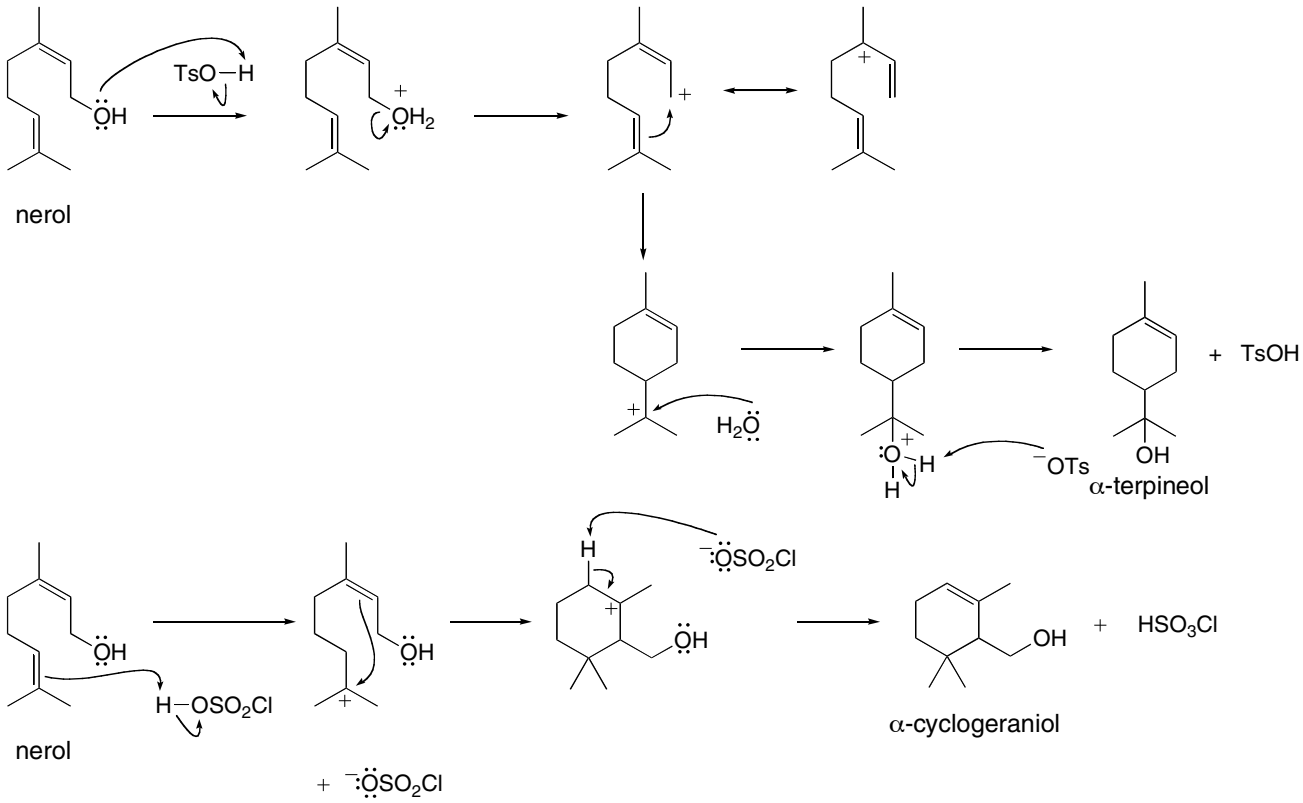

10.79