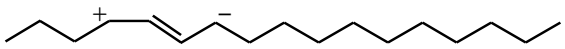
Answers to Puzzles of Chapter 8
Alkenes

8.1 (a) 2-pentene (b) 2-propen-1-ol (c) 1,4-pentadiene (d) (*Z*)-1-bromo-1-propene
(e) 1-methylcyclopentene

8.2 (a) vinyl bromide: CH_2=CHBr; allyl bromide: CH_2=CH-CH_2Br;
4-bromo-1-butene: CH_2=CH-CH_2-CH_2Br
(b) 4-bromo-1-butene because of greater size and dispersion forces.

8.3 An sp^3 orbital has more *p* character and is larger than an sp^2 orbital. Therefore, a C(sp^3)-H(1*s*) bond on ethane is longer than a C(sp^2)-H(1*s*) bond on ethene.

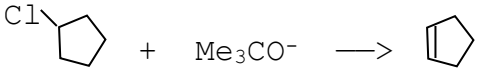
8.4 (a) 

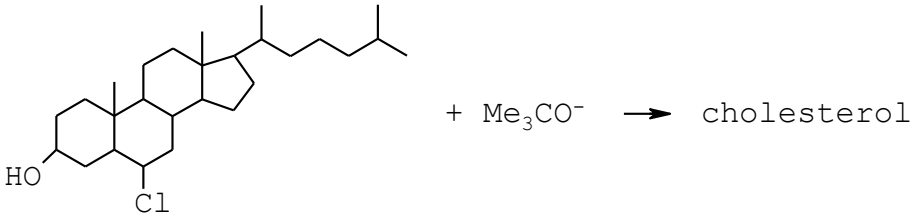
(b) Because of minor resonance forms, the C(4)-C(5) bond in this alkene is not a full double bond and is therefore longer than the full double bond in ethene.
(c) Because of minor resonance forms, the C(5)-C(6) bond in this alkene has some double bond character and is therefore shorter than the single carbon-carbon bond in ethane.

8.5 (a) no stereoisomers (b) *E* and *Z* stereoisomers (c) no stereoisomers
(d) no stereoisomers (ring strain prevents the *E* stereoisomer)

8.6 1-chlorobutane has the higher bp because it is larger with more dispersion forces and is polar with dipole-dipole forces. (The strength of the C=C double bond does not matter!)

8.7 (a) A saturated fat has a more regular crystal lattice
(b) A saturated fat has a higher melting point because its crystal lattice is more regular and stabler.
(c) Yes, because more *Z* double bonds lowers the melting point.

8.8 

8.9 

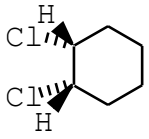
8.10 (a) Compare conjugate acids:

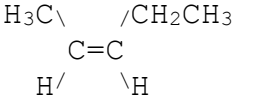
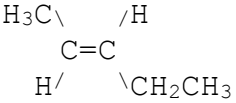
in stability: CH_3-$\overset{+}{C}H_2$ (1° C^+) < CH_3-CH_2-$\overset{+}{C}H$-CH_3 (2° C^+)

so in acidity: CH_3-$\overset{+}{C}H_2$ > CH_3-CH_2-$\overset{+}{C}H$-CH_3

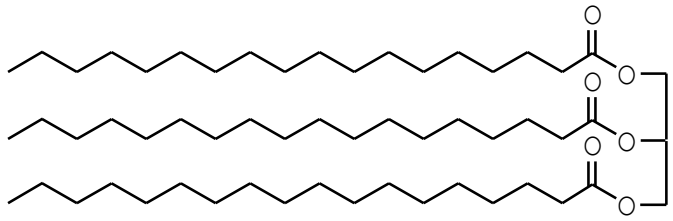
so in basicity: CH_2=CH_2 < (*Z*)-CH_3-CH=CH-CH_3

(b) in nucleophilicity: CH_2=CH_2 < (*Z*)-CH_3-CH=CH-CH_3 because they have similar softness, and so basicity determines relative nucleophilicity.

8.11 (a) A ≡ CH_3-CH_2CH_3 (b) B ≡ 

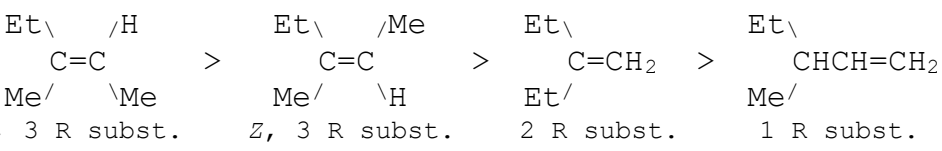
(c) **C** ≡ CH_2=$CHCH_2CH_2CH_3$ or  or 

(d) **D** ≡ cyclopentane

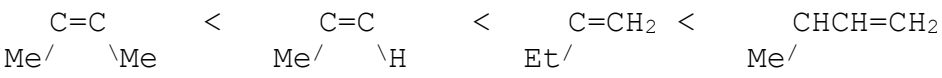
8.12 

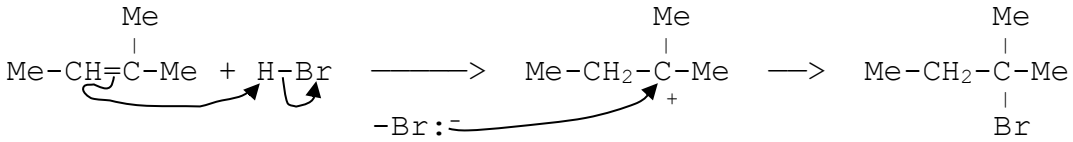
8.13 During hydrogenation one π bond (from C=C) and one σ bond (H-H) are lost, while two σ bonds (C-H) are gained. The net change is the loss of one π bond and a gain of one σ bond. Since σ bonds tend to be stronger than π bonds, it is not surprising that the reaction is exothermic.

8.14

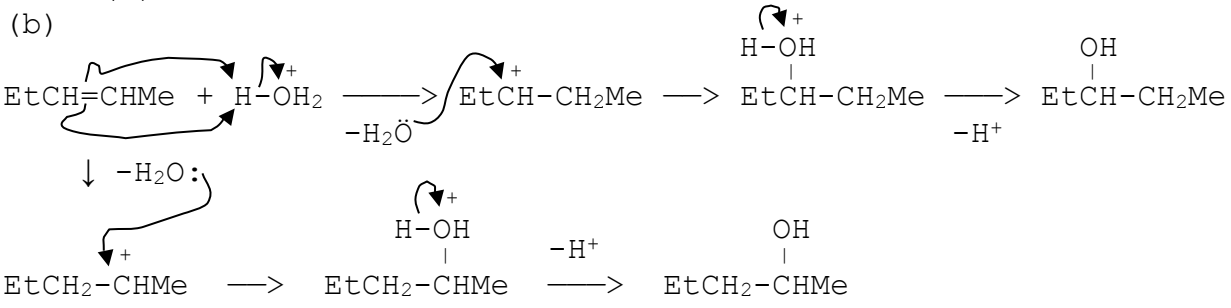
In stability: 

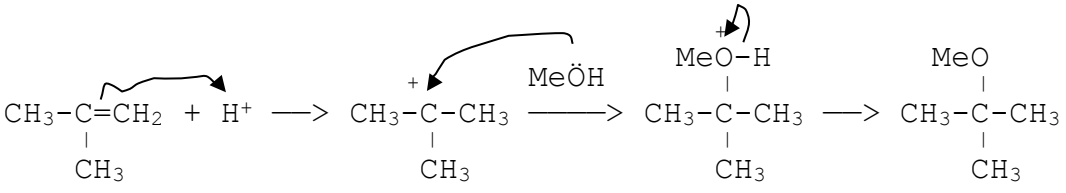
E, 3 R subst. *Z*, 3 R subst. 2 R subst. 1 R subst.

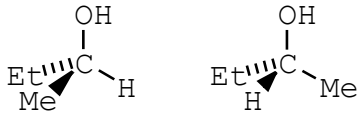
In enthalpy: 

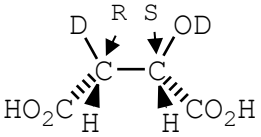
8.15 

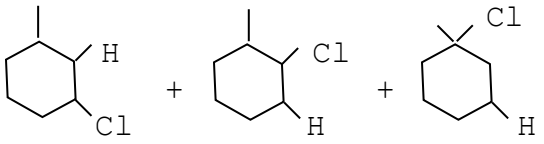
8.16 (a) 2

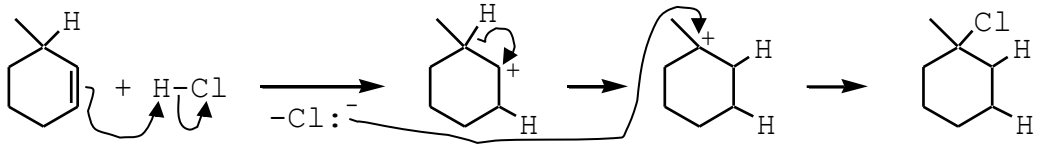
(b) 

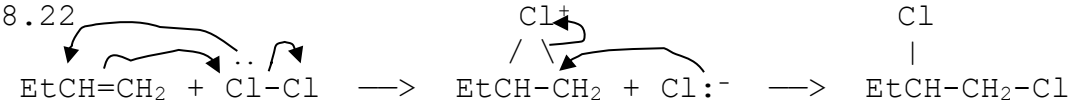
8.17 

8.18 

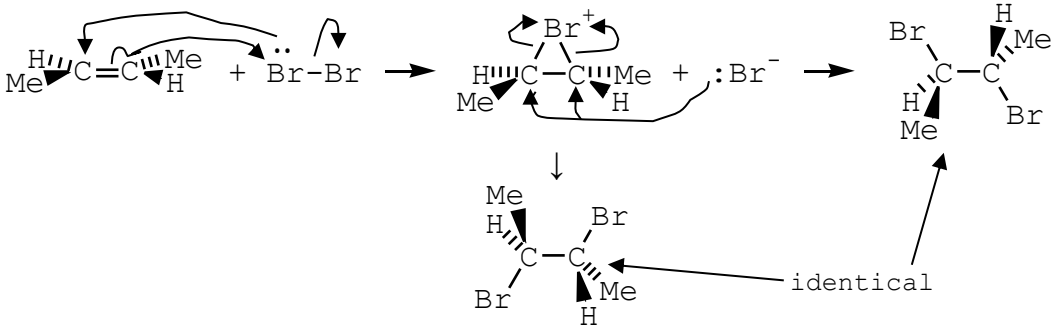
8.19 (a)  (b) anti

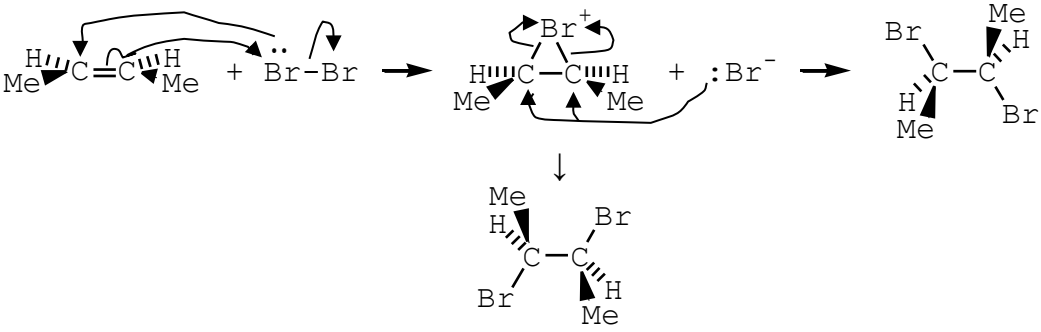
8.20 (a) 

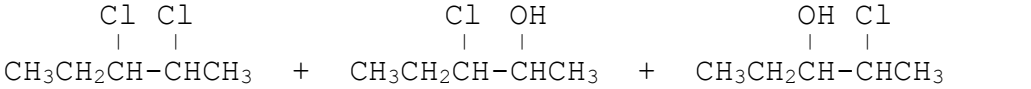
(b) 

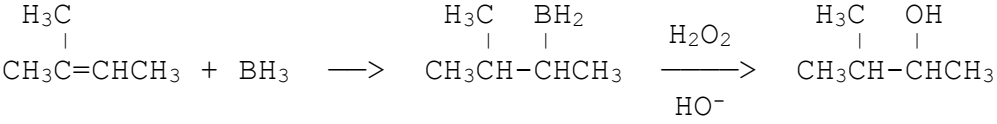
8.22 

8.23 (a) The initial brown color of Br_2 fades. (b) It has a ring instead of a π bond.

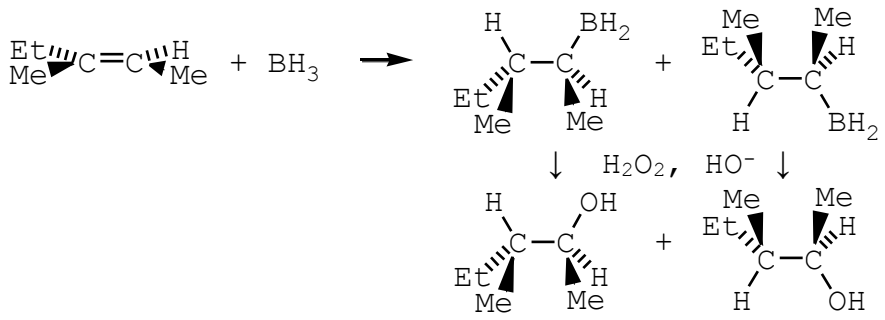
8.24 (a) 

(b) 

8.25 

8.26 

(b) $CH_3C(CH_3)=CHCH_3 + \text{aq. } H_2SO_4 \longrightarrow CH_3C(CH_3)(OH)-CH_2CH_3$

8.27 

8.28 (a) no redox (b) CH_3CH_2Cl

oxidized reduced; overall molecule is not reduced or oxidized

(c) $CH_2=CH_2$

oxidized; overall molecule is oxidized

(d) $HC\equiv CH$

reduced; overall molecule is reduced

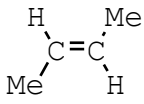
(e) $CH_3CH=O$

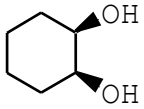
oxidized; overall molecule is oxidized

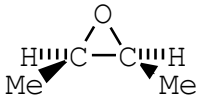
(f) no redox

(g) $CH_3CH=O$

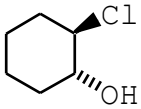
reduced; overall molecule is reduced

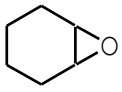
8.29 (a) A ≡ 

(b) B ≡ 

8.30 (a) A ≡ 

(b) B ≡ 

(c) C ≡ 

D ≡ 

8.31 (a) **A** ≡ $H_2C=O$ (b) **B** ≡ $Me_2C=O$ (c) **C** ≡ $O=CH(CH_2)_4CH=O$

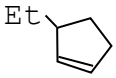
(d) **D** ≡ $O=CHCH_2CH=O$ (e) **E** ≡ $CH_3CH_2CH=O$, **F** ≡ $MeC(=O)Et$

(f) **G** ≡ 

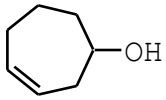
(g) **H** ≡ $MeCCH_2CH_2CH_2CH$ (=) $MeCCH_2CH_2CH_2CH$ or $MeCCH_2CH_2CH_2CH$ (=) $HCCH_2CH_2CH_2CMe$

8.32 $H_2C=O$, 2 $HCCH_2CH_2CCH_3$, $CH_3C(CH_2CH=O)CHCH_2CH_2CCH_3$

8.33 (a) e.g., 1-butene: $CH_2=CHCH_2CH_3$ (b) 6-bromo-2-hexene: $BrCH_2CH_2CH_2CH=CHCH_3$

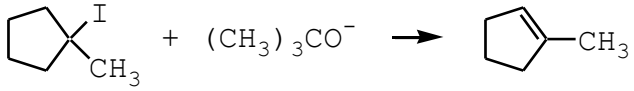
(c) 3-ethylcyclopentene: 

(d) 2-propen-1-ol: $CH_2=CH-CH_2OH$

(e) 3-cycloheptenol: 

8.34 (a) in bp: $CH_3-CH=CH_2 < HOCH_2-CH=CH_2$ because the 2nd chemical has H "bonds".
(b) in H_2O solubility: $CH_3-CH=CH_2 < HOCH_2-CH=CH_2$ because the 2nd chemical is polar.

8.35 (a) $CH_3-CH_2-CH_2-CH_2-Cl + (CH_3)_3CO^- \longrightarrow CH_3-CH_2-CH=CH_2$
(b) $CH_3-CHBr-CH_2-CH_3 + (CH_3)_3CO^- \longrightarrow CH_3-CH=CH-CH_3$ (+ 1-butene)

(c) 

(d) 

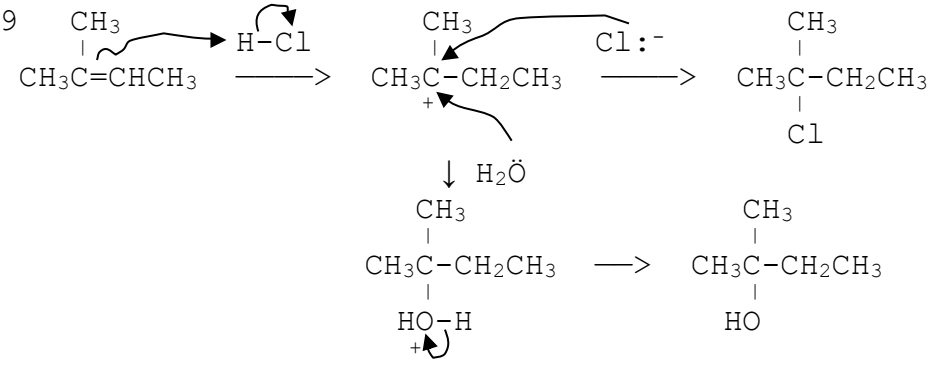
8.36 To increase its surface area, so that more catalyst is exposed to other reactants.

8.37 (a) $CH_2=C(CH_3)-CH_2-CH_3$ (A) or $CH_3-C(CH_3)=CH-CH_3$ (B) or $CH_3-CH(CH_3)-CH=CH_2$ (C)

(b) C would yield the most energy because its C=C has the fewest (1) C substituents.
(c) B would yield the least energy because its C=C has the most (3) C substituents.

8.38 (a) e.g., $CH_3-CH=CH-CH_2-CH_3 + HI \longrightarrow CH_3-CH_2-CHI-CH_2-CH_3 + CH_3-CHI-CH_2-CH_2-CH_3$

(b) This example does not violate Markovnikov's rule because both doubly bonded Cs of the alkene have the same number of Hs (and give equally stable 2° carbocations).

8.39 

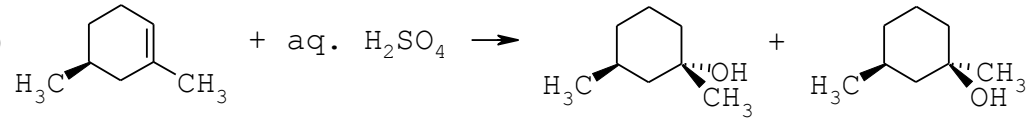
8.40 (a) $F_3C-CH=CH-CH_3 + H_3O^+ \longrightarrow$ $F_3C-\overset{\delta+}{C}H-CH_2-CH_3$ (none) or $F_3C-\overset{\delta+}{C}H_2-CH-CH_3$

$\downarrow H_2O$
$\downarrow -H^+$

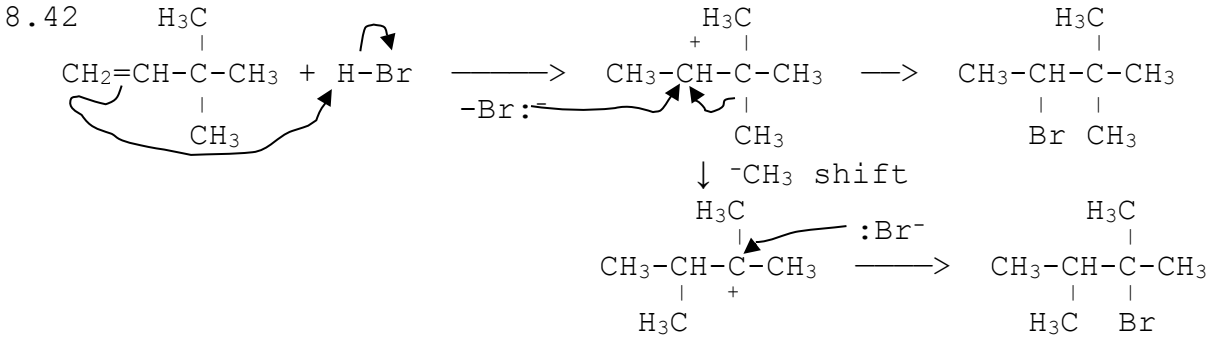
$F_3C-CH_2-CH(OH)-CH_3$

The Fs create a δ+, which destabilizes the 1st C^+ more than the 2nd C^+, whose + is more distant.

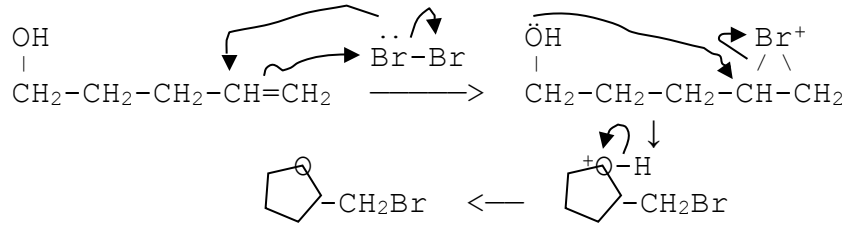
(b) This reaction violates Markovnikov's rule, which predicts the formation of both isomers.

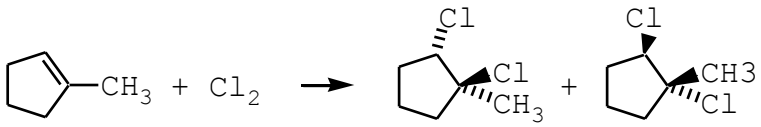
8.41 (a) 

(b) The 2 stereoisomer products are diastereomers because only 1 of 2 chiral atoms is inverted.

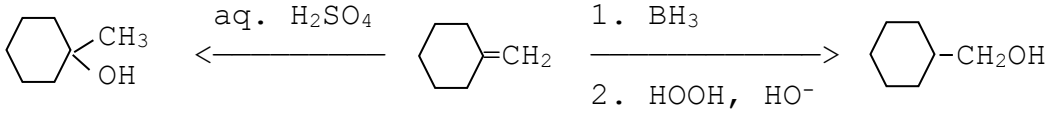
8.42 

8.43 C_5H_9BrO: (2 x 5 + 2 - (9 + 1))/2 = 1 π bond or ring.
Here there is 1 ring because the reactant's π bond has reacted.

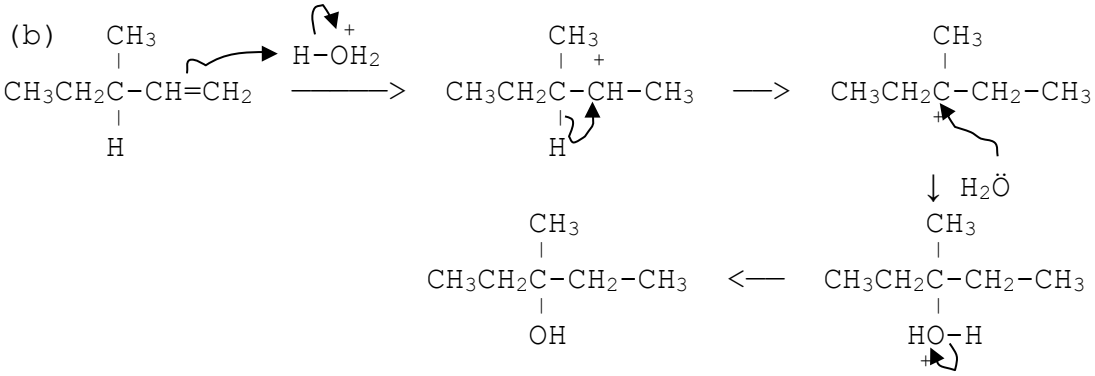


8.44 (a) 

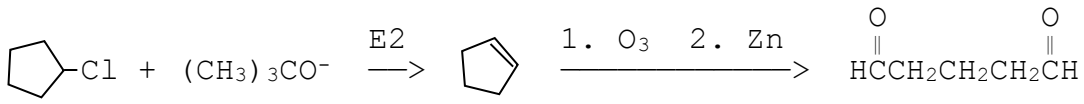
(b) The two products are enantiomers.

8.45 

8.46 (a) 3-methyl-1-pentene

(b) 

8.47



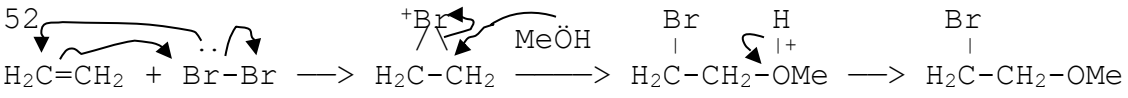
8.48 (a) Cl_2, H_2O (b) 1. BH_3 2. HOOH, HO^- (c) $KMnO_4$, HO^- (d) 1. O_3 2. Zn (e) $-CO_3H$ (f) 1. HBr 2. Et_3CO^-

8.49 (a) CH_3-CHOH-CH_3 (b) CH_3-CHBr-CH_2OH (c) CH_3-HC-CH_2 (O) (d) no rx. (e) CH_3-CHOH-CH_3 (f) CH_3-CHOH-CH_2OH (g) no rx. (h) CH_3-CHBr-CH_2Br (i) no rx. (j) CH_3-CH_2-CH_2OH (k) CH_3-CHCl-CH_3 (l) CH_3-CH=O + O=CH_2 (m) CH_3-CH_2-CH_3 (n) no rx.

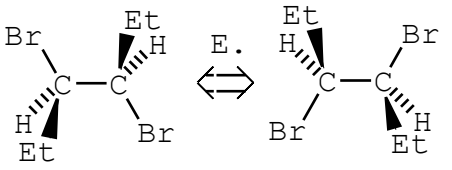
8.50 Use Pt, Pd, or Ni without H_2. A catalyst should work in either direction.

8.51 No reaction because CH_3-CH_3 has no base atom to protonate.

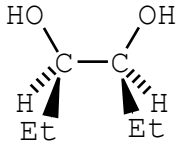
8.52



8.53 (a)

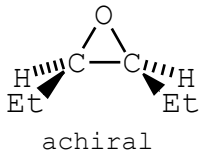


(b)



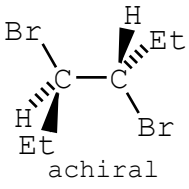
achiral

(c)



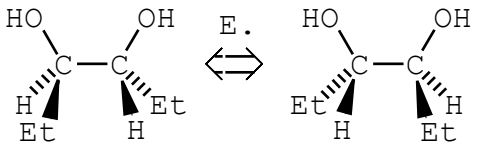
achiral

8.54 (a)

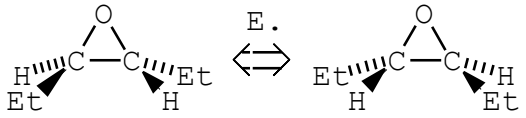


achiral

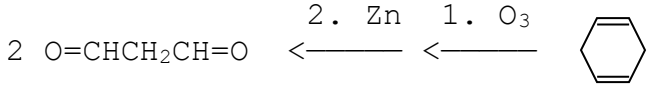
(b)



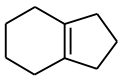
(c)



8.55



8.56



8.57 (a) the same equation: $C_6H_{12} + 9\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$
(b) Giving more energy while forming the same products, 1-hexene has more enthalpy. This results from its C-C π bond, weaker than any C-C σ bond in cyclohexane.

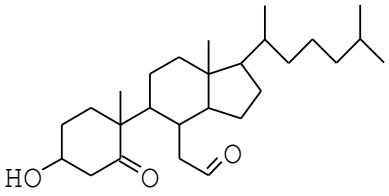
8.58 (a) the same equation: $2\ C_3H_6 + 9\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$
(b) Giving more energy while forming the same products, cyclopropane has more enthalpy. This

results from its very strained C-C σ bonds.

8.59 (a) in heat emitted: 1-butene > (*Z*)-2-butene > (*E*)-2-butene because 1-butene has the least hyperconjugation, and the Z stereoisomer has more steric repulsion than the E stereoisomer.
(b) Same answer as in part a, because the 3 isomers have the same molecular mass.

8.60 syn addition (the Cl & F_3CO are added to the same side of the C=C)

8.61



10/06