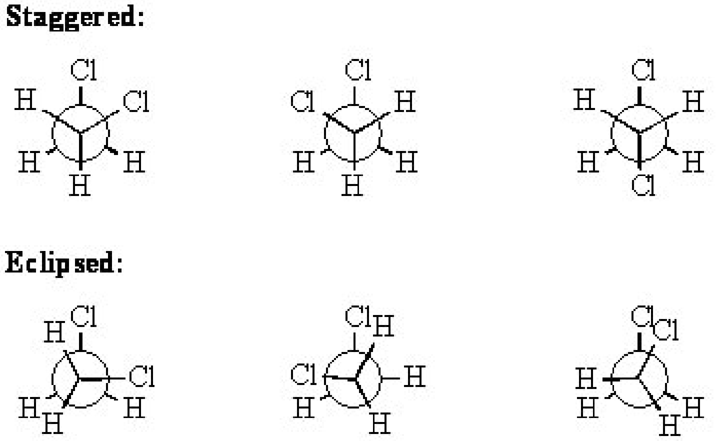
CHAPTER 16

Practice Exercises

16.1 Draw Newman projections for these staggered and three eclipsed conformations of 1, 2 - dichlorobutane as viewed downt he central C-C bond.



16.3 (a) The more stable conformation is the one with the t-b-tyl substituent equatorial and the methyl substituent axial.

(b) The more stable conformation is the one with both t-butyl subsittuents equatorial and the methyl substituent axial.

(c) The more stable conformation is the one with the two ADJACENT methyl substituents equatorial and the other methyl substituent axial.

16.5 (a) 2,2-dimethylpropane < 2-methylbutane < pentane

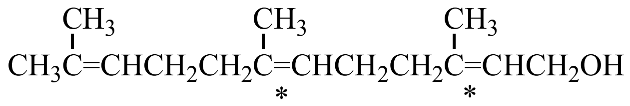
(bp 9.5 ˚C) (bp 28 ˚C) (bp 36 ˚C)

(b) 2,2,4-trimethylhexane < 3,3-dimethylheptane < nonane
(bp 112 ˚C) (bp 137 ˚C) (bp 151 ˚C)

16.7 (a) *cis*-4-methyl-2-pentene
(b) *trans*-2,2-dimethyl-3-hexane

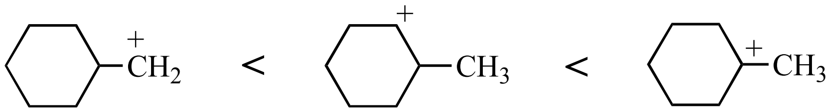
16.9 (a) 1-isopropyl-4-methyl-cyclohexene
(b) 4-methyleyelooctene
(c) 4-*tert*-butylcyclohexene

16.11 The given alcohol has two double bonds, indicated by an asterisk. The number of possible stereoisomers is 2^n, where n = the number of double bonds. Thus, there are 4 possible *cis-trans* isomers.

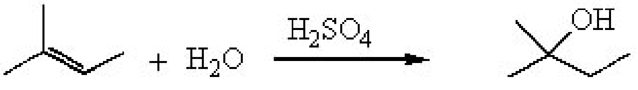


$$CH_3\overset{CH_3}{C}{=}CHCH_2CH_2\overset{CH_3}{\underset{*}{C}}{=}CHCH_2CH_2\overset{CH_3}{\underset{*}{C}}{=}CHCH_2OH$$

16.13 The order of increasing stability of carbocations is:
methyl < primary < secondary < tertiary

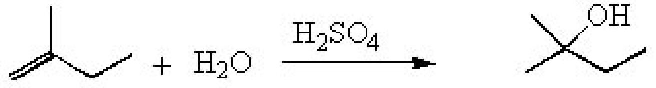


16.15 (a)



2-methyl-2-butanol

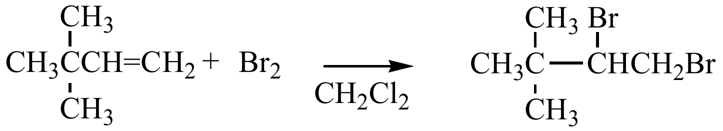
(b)



2-methyl-2-butanol

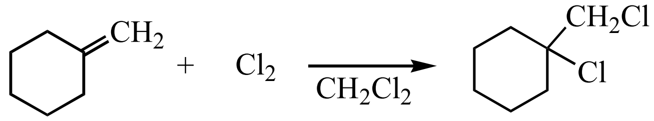
16.17

(a)

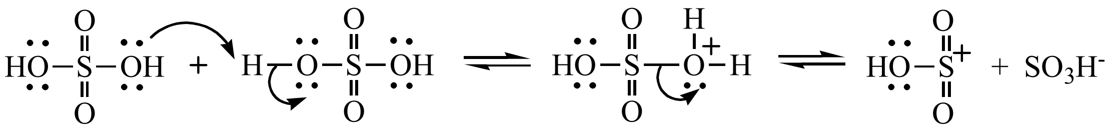


$$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH{=}CH_2 + Br_2 \xrightarrow[CH_2Cl_2]{} CH_3\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{Br}{C}HCH_2Br$$

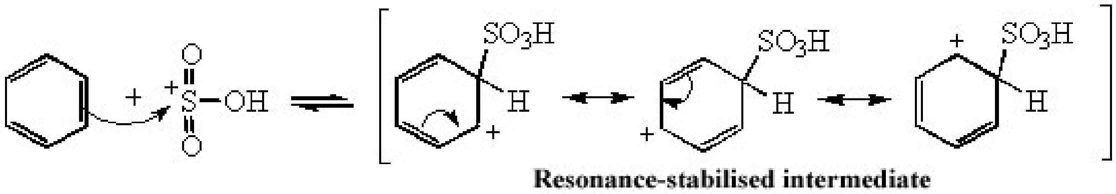
(b)



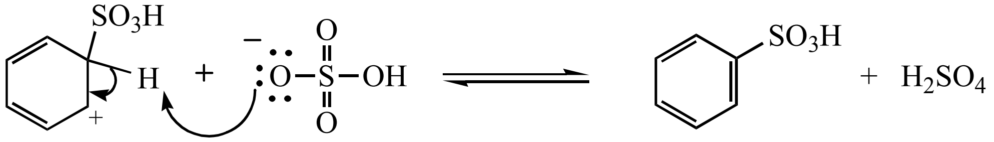
16.19 Step 1: Generation of the HSO_3^+ electrophile:



Step 2: Nucleophilic attack of benzene on HSO_3^+ electrophile:



Step 3: Loss of proton to regenerate aromatic ring (benzenesulfonic acid) and sulfuric acid:

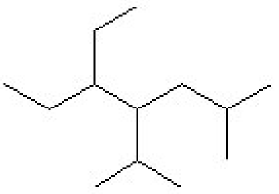


Review Questions

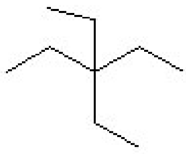
16.1 A hydrocarbon is a compound composed only of hydrogen and carbon atoms.

16.3 In saturated hydrocarbons, each carbon is bonded to four other atoms, either hydrogen or carbon atoms. Unsaturated hydrocarbons have carbon atoms that have a double or triple bond to another carbon atom.

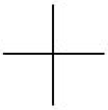
16.5 (a)



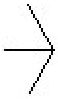
(b)



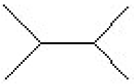
(c)



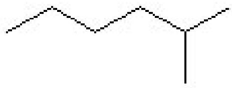
(d)



(e)



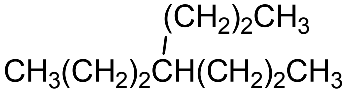
(f)



16.7

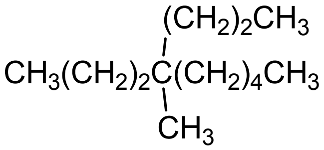
(a) $CH_3(CH_2)_4CH(CH_3)_2$

(b)



$CH_3(CH_2)_2CH((CH_2)_2CH_3)(CH_2)_2CH_3$

(c)



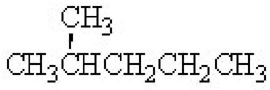
$CH_3(CH_2)_2C((CH_2)_2CH_3)(CH_3)(CH_2)_4CH_3$

16.9 (a) different compounds
(b) constitutional isomers
(c) constitutional isomers
(d) different compounds
(e) constitutional isomers
(f) constitutional isomers

16.11 (a) 2-methylpentane
(b) 2,5-dimethylhexane
(c) 3-ethyloctane
(d) 2,2,3-trimethylbutane
(e) isobutylcyclopentane
(f) 1-*tert*-butyl-2,4-dimethyl-cyclohexane

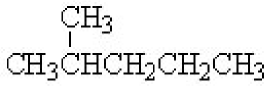
16.13 (a) 1,3-dimethylbutane — The longest chain is pentane.

The IUPAC name is 2-methylpentane.



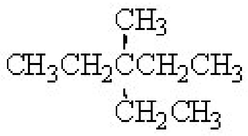
$CH_3CH(CH_3)CH_2CH_2CH_3$

(b) 4-methylpentane — The pentane chain is numbered incorrectly.
The IUPAC name is 2-methylpentane.



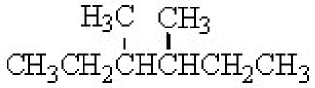
$CH_3CH(CH_3)CH_2CH_2CH_3$

(c) 2,2-diethylbutane — The longest chain in pentane.
The IUPAC name is 3-ethyl-3-methylpentane.



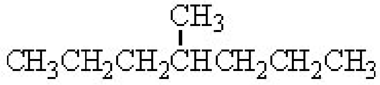
$CH_3CH_2C(CH_3)(CH_2CH_3)CH_2CH_3$

(d) 2-ethyl-3-methylpentane — The longest chain is hexane.
The IUPAC name is 3,4-dimethylhexane.



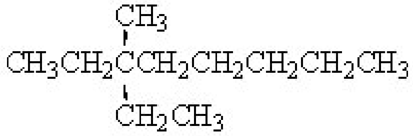
$CH_3CH_2\overset{H_3C}{\overset{|}{C}}H\overset{CH_3}{\overset{|}{C}}HCH_2CH_3$

(e) 2-propylpentane — The longest chain is heptane.
The IUPAC name is 4-methylheptane.



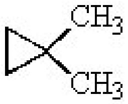
$CH_3CH_2CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$

(f) 2,2-diethylheptane — The longest chain is octane.
The IUPAC name is 3-ethyl-3-methyloctane.

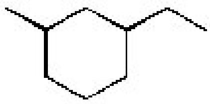


$CH_3CH_2\underset{CH_2CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2CH_2CH_2CH_2CH_3$

(g) 2,2-dimethylcyclopropane — The ring is numbered incorrectly.
The IUPAC name is 1,1-dimethylcyclopropane.

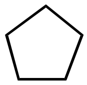


(h) 1-ethyl-5-methylcyclohexane — The ring is numbered incorrectly.
The IUPAC name is
1-ethyl-3-methylcyclohexane.

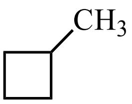


16.15 No, because alkanes do not have rings or C—C double bonds and so all conformations are usually interconvertable by rotation about a C—C single bond. However, there are some extremely crowded molecules which are locked into specific conformers. These are called ‘conformational isomers’ or ‘locked conformational isomers’ and are not correctly defined by *cis-trans* nomenclature.

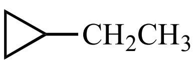
16.17 There are two enantiomers of the *trans*-1,2-dimethylcyclopropane..



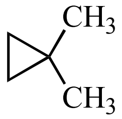
cyclopentane



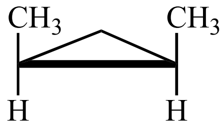
methylcyclobutane



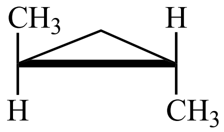
ethylcyclopropane



1,1-dimethylcyclopropane

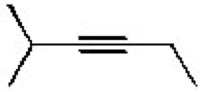


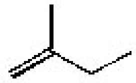
***cis*-1,2-dimethylcyclopropane**



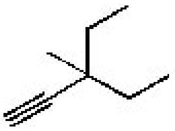
***trans*-1,2-dimethylcyclopropane**

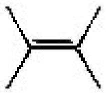
16.19 (a) *trans*-2-methylhex-3-ene (b) 2-methyl-3-hex-3-yne (c) 2-methylbut-1-ene

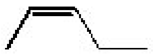




(d) 3-ethyl-3-methylpent-1-yne (e) 2,3-dimethylbut-2-ene (f) *cis*-pent-2-ene



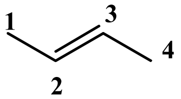




16.21 (a) 2-isobutylhept-1-ene
(b) 1,4,4-trimethylcyclopentene
(c) 1,3-cyclopentadiene
(d) 3,3-dimethylbut-1-yne
(e) 2,4-dimethylpent-2-ene
(f) oct-1-yne
(g) 2,2,5-dimethylhex-3-yne
(h) 3-methylpent-1-yne

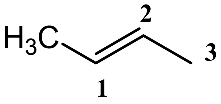
16.23 (a) 2,2-dimethylhex-3-yne
(b) oct-2,5-diyne
(c) 3,6-dimethylhept-2-ene-4-yne
(d) hept-1,4-diyne

16.25 (a) Correct name: but-2-ene.You must select the longest carbon chain containing the ‘ene’ functional group.



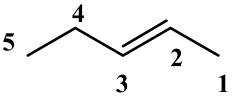
but-2-ene

Not:



1-methylpropene

(b) Correct name: pent-2-ene. You must number the chain to give the first carbon of the double bond the lowest possible number.



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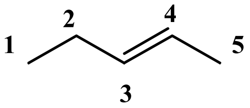
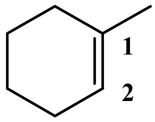
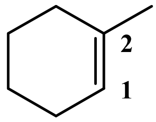


pent-2-ene **pent-3-ene**

(c) Correct name: 1-methylcyclohexene. By default, the first carbon of the double bond in a ring is given the number 1. In this case, this can also be the ring carbon with the methyl group attached.



Not:



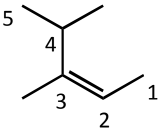
1-methylcyclohexene **2-methylcyclohexene**

(d) This name is not incorrect even though there is no indication of where the double bond is positioned. The indication of the two methyls on the third carbon means that the double bond is attached to the first carbon. Technically, the correct name is 3,3-dimethylpent-1-ene.

(e) Correct name: 4-hexyne. As with (b) the chain carbons are numbered to give the first carbon of the double bond the lowest possible number.

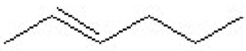
$$\overset{7}{C}H_3\overset{6}{C}H_2\overset{5}{C}H_2\overset{4}{C}\equiv\overset{3}{C}\overset{2}{C}H_2\overset{1}{C}H_3$$

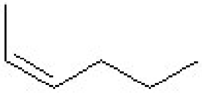
(f) Correct name: 2-isopropyl-2-butene. The longest chain containing the function group is a pentene.



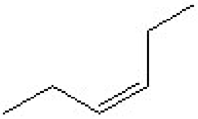
16.27 (a) No
(b) Yes
(c) Yes
(d) No
(e) Yes
(f) No

(b)

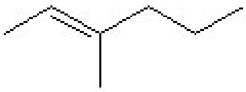


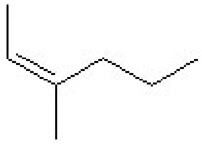


(c)



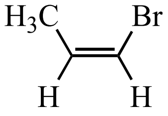
(e)



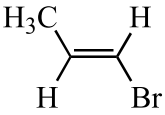


16.29 For alkenes to exist as a pair of *cis-trans* isomers, both carbons of the double bond must have two different substituents. Thus, only (b) and (d) can exist as a *cis* or *trans* isomer.

(b)

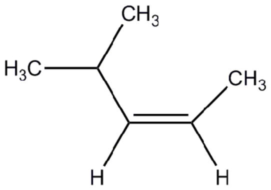


***cis*-bromoprop-1-ene**

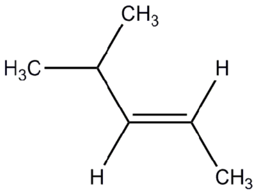


***trans*-bromoprop-1-ene**

(d)



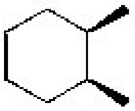
***cis*-4-methylpent-2-ene**



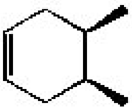
***trans*-4-methylpent-2-ene**

16.31Molecules (a) and (c) do not show *cis-trans* isomerism.

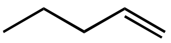
(b)



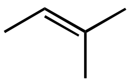
(d)



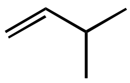
16.33 (a) Alkenes that do not show *cis-trans* isomerism are:



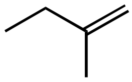
pent-1-ene



2-methylbut-2-ene

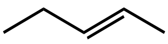


3-methylbut-1-ene

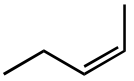


2-methylbut-1-ene

(b) Alkenes that do show *cis-trans* isomerism are:

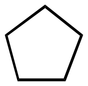


***trans*-pent-2-ene**

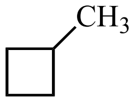


***cis*-pent-2-ene**

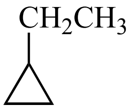
(c) Cycloalkanes that do not show *cis-trans* isomerism are:



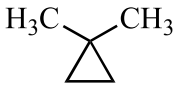
cyclopentane



methylcyclobutane

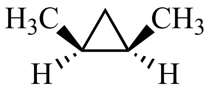


ethylcyclopropane

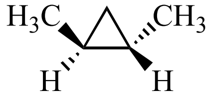


1,1-dimethyl cyclopropane

(d) Cycloalkanes that do show *cis-trans* isomerism are:

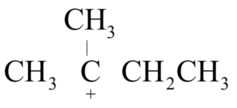


***cis*-1,2-dimethylcyclopropane**



***trans*-1,2-dimethylcyclopropane**

16.35 (a) $CH_3\overset{+}{C}HCH_3$ is more stable.



(b) $CH_3\underset{+}{\overset{\overset{CH_3}{|}}{C}}CH_2CH_3$ is more stable.

16.37

$$\mathbf{CH_3\overset{\overset{CH_3}{|}}{C}{=}CH_2 + 6O_2 \longrightarrow 4CO_2 + 4H_2O}$$

16.39

(a) $H_2C{=}CH_2 \xrightarrow[\textbf{Ni}]{\mathbf{H_2}} CH_3CH_3$

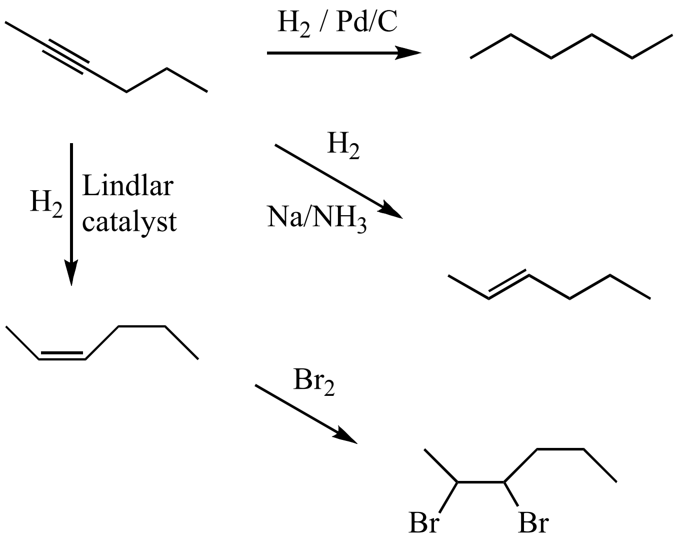
(b) $H_2C{=}CH_2 \xrightarrow[\mathbf{H_2SO_4}]{\mathbf{H_2O}} CH_3CH_2OH$

(c) $H_2C{=}CH_2 \xrightarrow{\textbf{HBr}} CH_3CH_2Br$

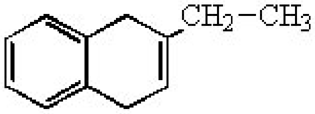
(d) $H_2C{=}CH_2 \xrightarrow{\mathbf{Br_2}} BrCH_2CH_2Br$

(e) $H_2C{=}CH_2 \xrightarrow{\textbf{HCl}} CH_3CH_2Cl$

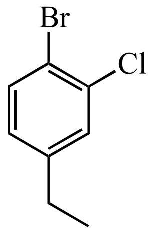
16.41



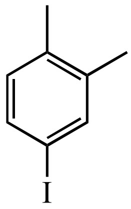
16.43



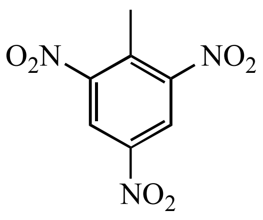
16.45 (a) 1-bromo-2-chloro-4-ethylbenzene



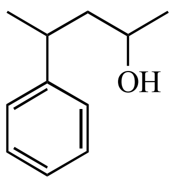
(b) 4-iodo-1,2-dimethylbenzene



(c) 2,4,6-trinitrotoluene

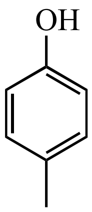


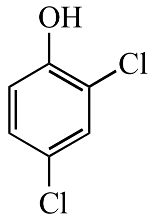
(d) 4-phenylpentan-2-ol



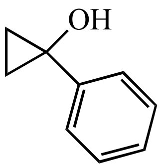
(e) *p*-cresol

(f) 2,4-dichlorophenol

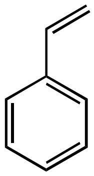




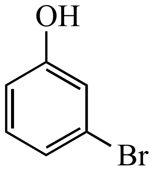
(g) 1-phenylcyclopropanol



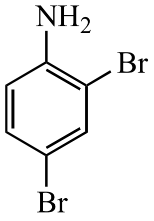
(h) styrene (phenylethene)



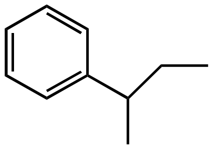
(i) *m*-bromophenol



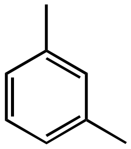
(j) 2,4-dibromoaniline



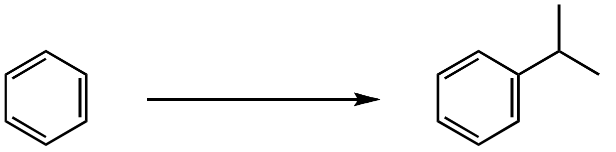
(k) isobutylbenzene



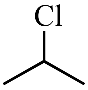
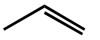
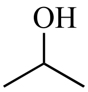
(l) *m*-xylene



16.47



isopropylbenzene

(1)  /$AlCl_3$ **(2)**  /H_2SO_4 **(3)**  /H_2SO_4

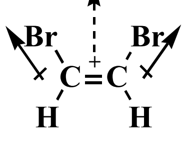
Review Problems

16.49 (1) Alkanes are less dense than water.
(2) As alkane molar mass increases, density increases.
(3) Constitutional isomers have similar densities.

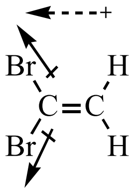
16.51 Boiling points of unbranched alkanes are related to their surface area: the larger the surface area, the greater the strength of the dispersion forces and the higher the boiling point. The relative increase in molecular size per CH_2 group is greatest between CH_4 and CH_3—CH_3 and becomes progressively smaller as molecular mass increases. Therefore, the increase in boiling point per CH_2 group is greatest between CH_4 and CH_3—CH_3, and becomes progressively smaller for the higher alkanes.

16.53 (a) No, alkanes are too non-polar to dissolve in a very polar solvent such as water.
(b) Yes, dodecane is non-polar and dissolves in a non-polar solvent such as hexane.
(c) Yes, alkanes burn when ignited in the presence of oxygen to produce water and carbon dioxide.
(d) It is a liquid. Alkanes containing 5 to 17 carbon atoms are colourless liquids.
(e) It is less dense than water. All liquid and solid alkanes are less dense than water (1.0 g/mL)

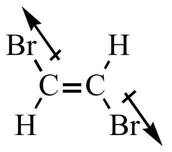
16.55 The three structures with molecular formula C2H2Br are 1,1-dibromoethane, *cis*-1,2-dibromoethane and *trans*-1,2-dibromoethane. The dipole moment of the C—Br bond is shown in the structures below by a solid arrow. *trans*-1,2-dibromoethane has no dipole moment because the two C—Br dipoles point in opposite directions and therefore cancel each other out. However, 1,1-dibromoethane and *cis*-1,2-dibromoethane both have a net dipole moment (in the direction shown by the dotted arrow) since the two C—Br dipoles do not point in opposite directions.



1,1-dibromoethane



cis-1,2-dibromoethane

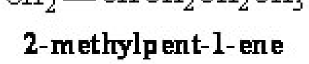


No dipole moment

trans-1,2-dibromoethane

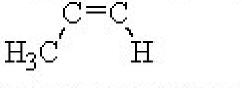
16.57

(a)

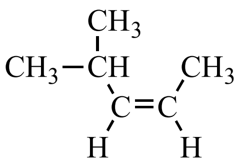


$$CH_2{=}\overset{CH_3}{\overset{|}{C}}HCH_2CH_2CH_3$$

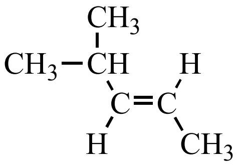
2-methylpent-1-ene



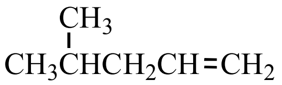
2-methylpent-2-ene



***cis*-4-methylpent-2-ene**



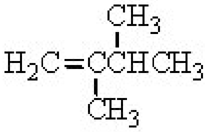
***trans*-4-methylpent-2-ene**



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH=CH_2$

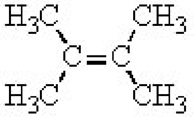
4-methylpent-1-ene

(b)



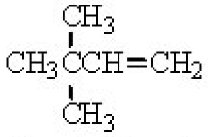
$H_2C=\underset{\underset{CH_3}{|}}{C}\overset{\overset{CH_3}{|}}{C}HCH_3$

2,3-dimethylbut-1-ene



2,3-dimethylbut-2-ene

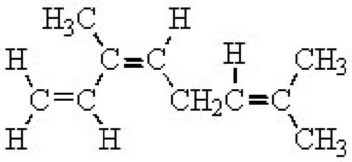
(c)



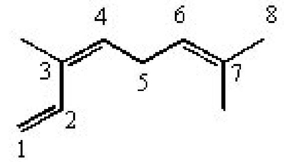
$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH=CH_2$

3,3-dimethylbut-1-ene

16.59

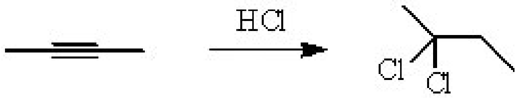


or

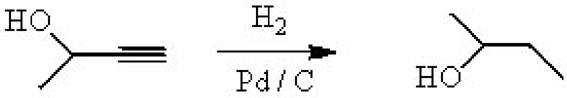


(3*Z*)-3,7-dimethylocta-1,3,6-triene

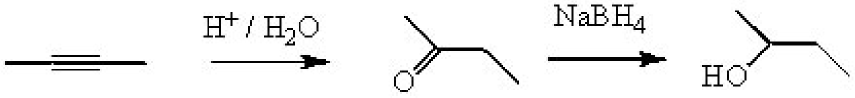
16.61 (a) 2,2-dichlorobutane



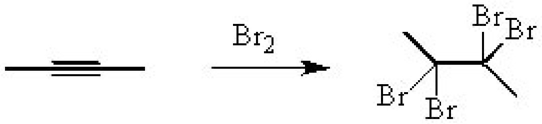
(b) butan-2-ol



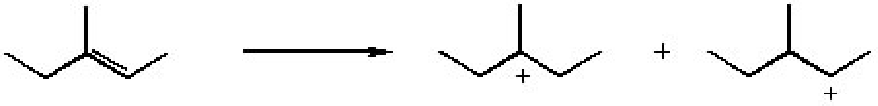
OR



(c) 2,2,3,3-tetrabromobutane



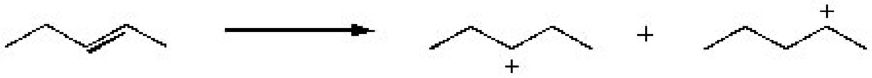
16.63 (a)



3° carbocation formed more readily

2° carbocation

(b)

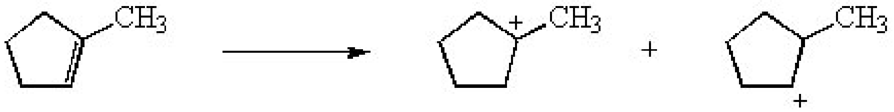


2° carbocation

2° carbocation

Both carbocations are of equal stability and formed at approximately equal rates.

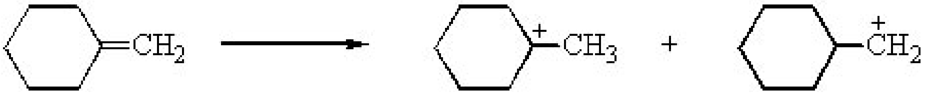
(c)



3° carbocation formed more readily

2° carbocation

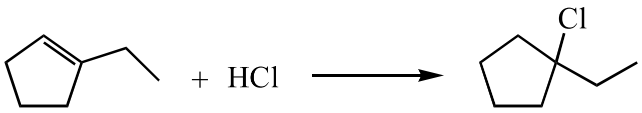
(d)

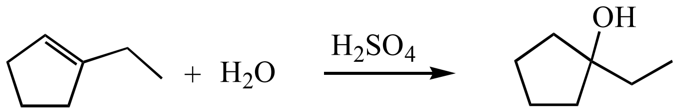


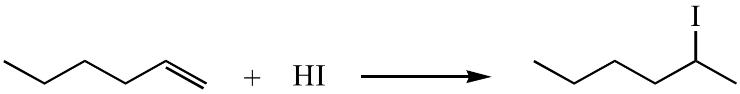
3° carbocation formed more readily

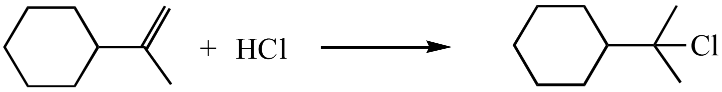
1° carbocation

16.65

(a)


(b)


(c)


(d)


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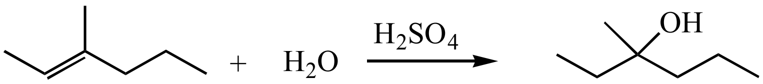

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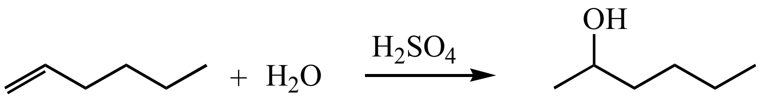
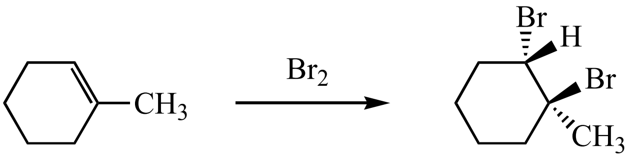


16.67 Halogens undergo anti addition to alkenes. In cycloalkenes, anti addition results in *trans* dihalides.

(a)


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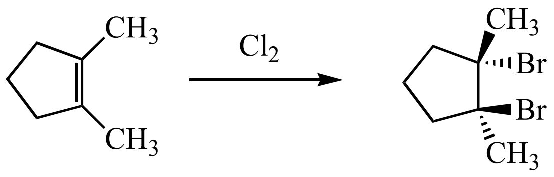
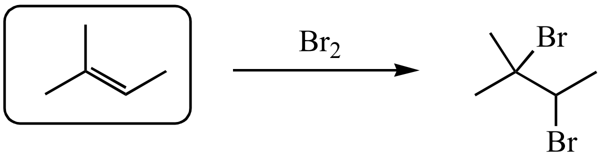
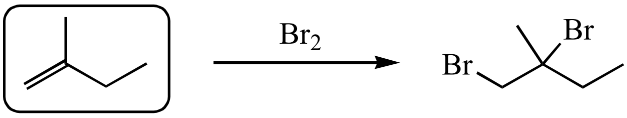
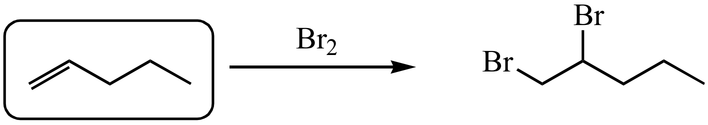


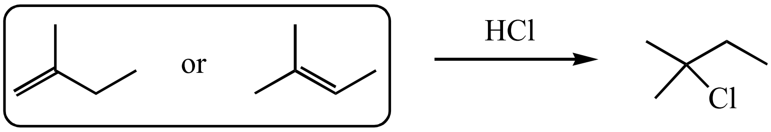
16.69

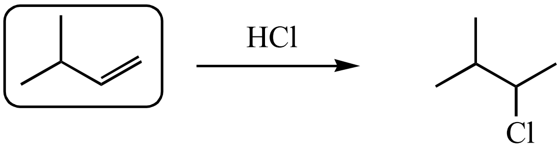
(a) 

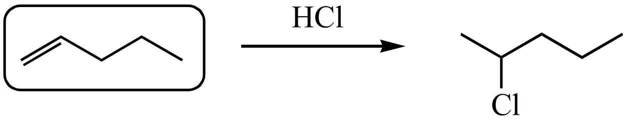
(b) 

(c) 

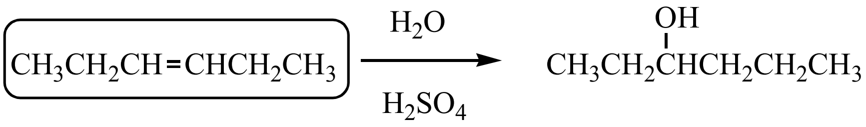
16.71

(a) 

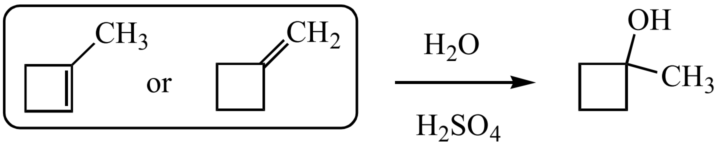
(b) 

(c) 

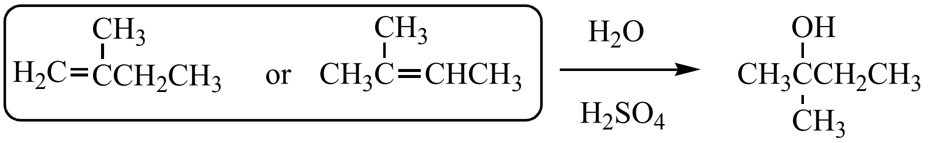
16.73

(a) 

$$\boxed{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow[H_2SO_4]{H_2O} CH_3CH_2\overset{OH}{C}HCH_2CH_2CH_3$$

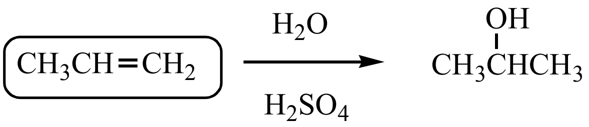
(b) 

(c)



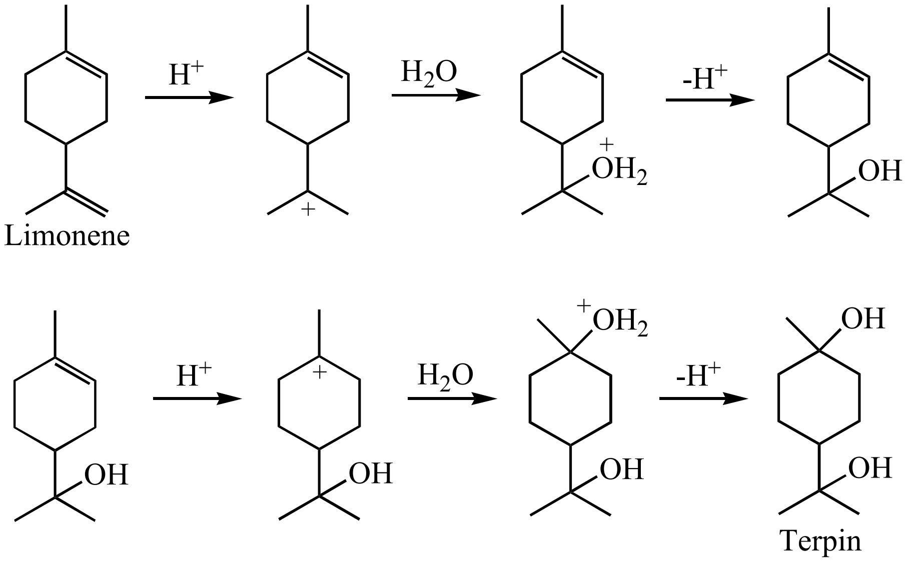
$$\boxed{H_2C{=}\overset{CH_3}{C}CH_2CH_3 \quad \text{or} \quad CH_3\overset{CH_3}{C}{=}CHCH_3} \xrightarrow[H_2SO_4]{H_2O} CH_3\underset{CH_3}{\overset{OH}{C}}CH_2CH_3$$

(d)

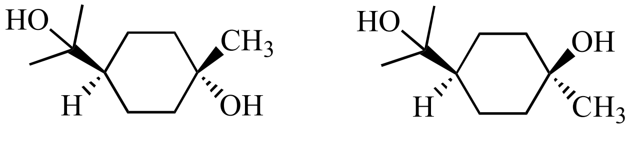


$$\boxed{CH_3CH{=}CH_2} \xrightarrow[H_2SO_4]{H_2O} CH_3\overset{OH}{C}HCH_3$$

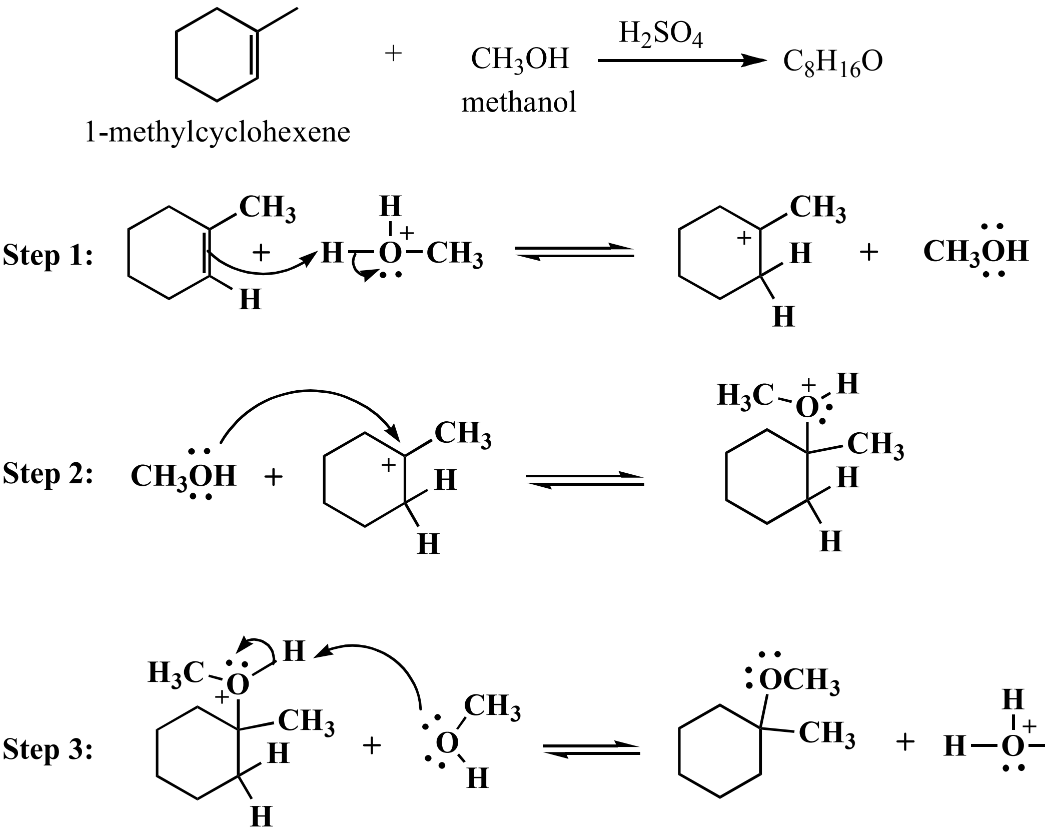
16.75 (a) Add water to each double bond by regioselective protonation of the double bond to form a 3° carbocation (Markovnikov's rule). Reaction of each carbocation with water and the loss of a proton yields terpin. Note that the reactions do not necessarily proceed in the order shown. Both carbon-carbon double bonds react at similar rates because in each case, a tertiary carbocation is formed.



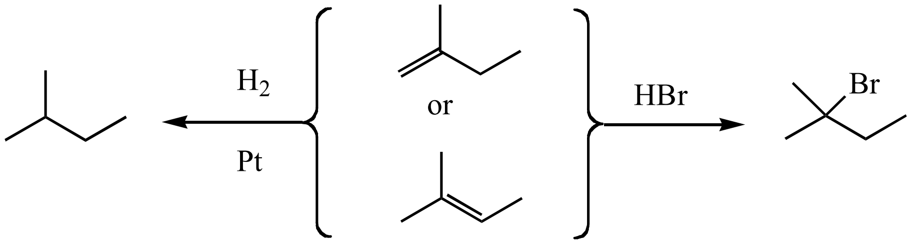
(b) Two *cis-trans* isomers are possible:



16.77 The mechanism for this reaction is similar to that proposed in problem 16.77 except for a different starting alkene.

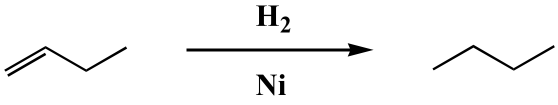


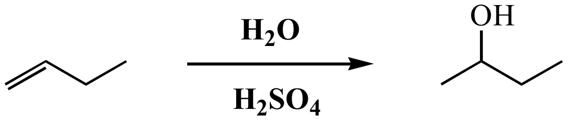
16.79 The key to solving the problem is recognising that the skeleton of the alkenes must be the same with only the position of the double bond being different.

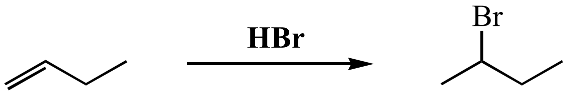


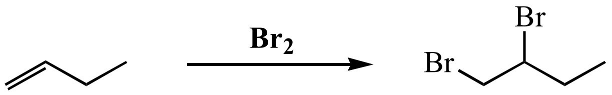
Structures A and B

16.81

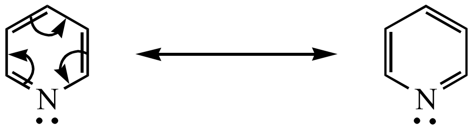
(a) 

(b) 

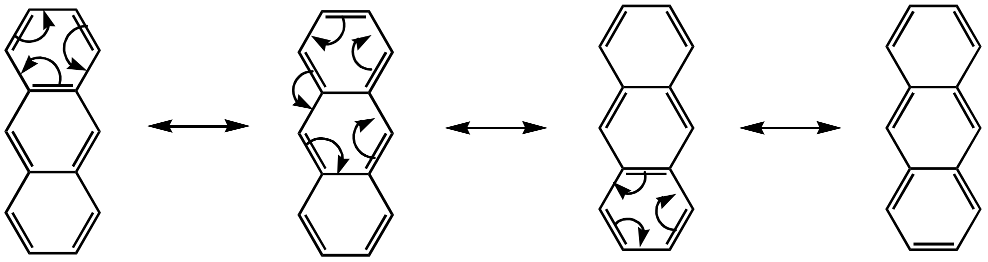
(c) 

(d) 

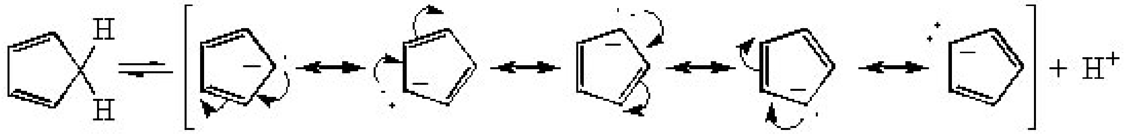
16.83 Resonance accounts for the two equivalent structures of benzene:



16.85 Resonance accounts for the four equivalent structures of anthracene:

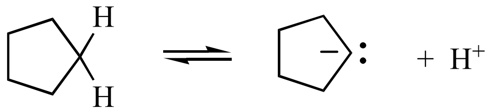


16.87 Cyclopentadiene:



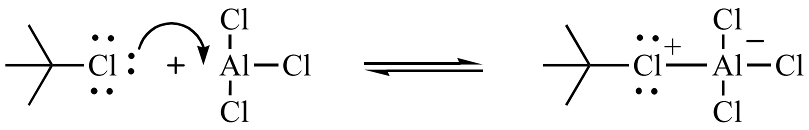
resonance stabilised cyclopentadienyl anion

Cyclopentane:

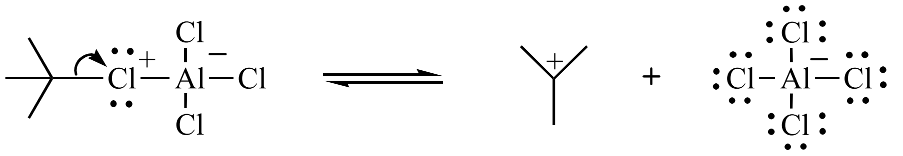


The conjugate base of cyclopentadiene is a highly stable six π electron aromatic anion with five resonance structures delocalising the negative charge over five different carbons. The cyclopentyl anion, a conjugate base of cyclopentane, has the negative charge on one carbon, making it a much stronger conjugate base than the resonance stabilised aromatic cyclopentadienyl anion. As a negatively charged conjugate base becomes more stable though delocalisation and resonance, its base strength becomes weaker. (Acid strengths are inversely proportional to their conjugate base strengths.)

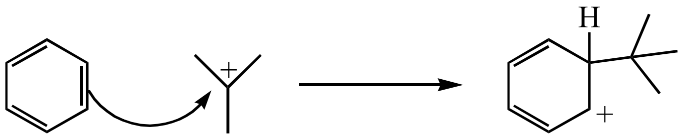
16.89 Step 1: Formation of Lewis acid-Lewis base complex:



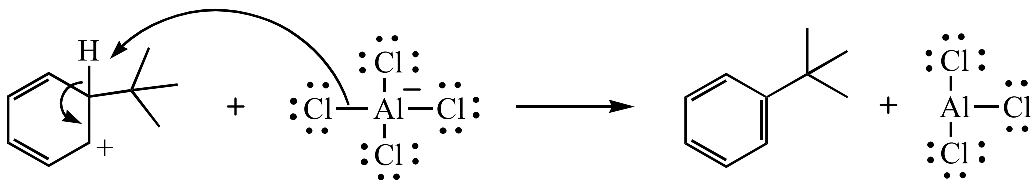
Step 2: Formation of the *tert*-butyl cation:



Step 3: Electrophilic attack on the benzene ring to form a resonance-stabilised carbocation intermediate with three resonance structures:

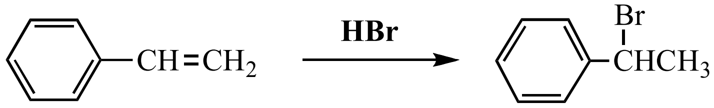


Step 4: Proton transfer to regenerate the aromatic ring:



16.91

(a)



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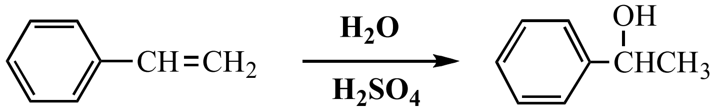
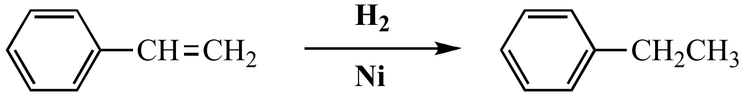


(c)

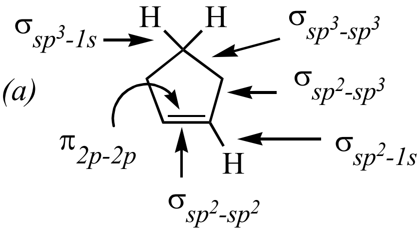


Additional Exercises

16.93 Both carbons in ethane have four electron pairs (all bonding pairs) surrounding each carbon atom. A tetrahedral arrangement of bonding pairs with bond angles of 109.5° minimises electron pair repulsions. In ethene, both carbons have three regions of electron density surrounding each carbon atom. A trigonal planar arrangement of three regions of electron density with bond angles of 120° minimises repulsions.

16.95

(a)



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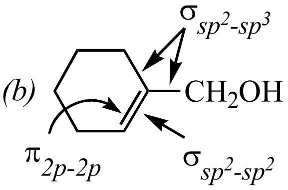

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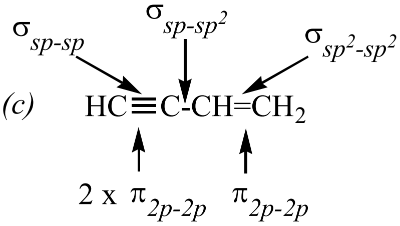
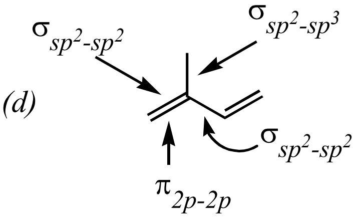
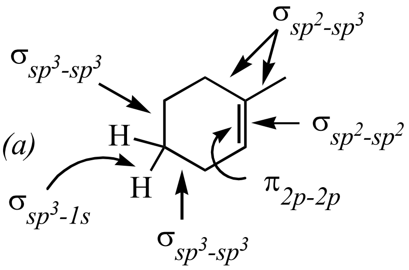


(d)



16.97

(a)



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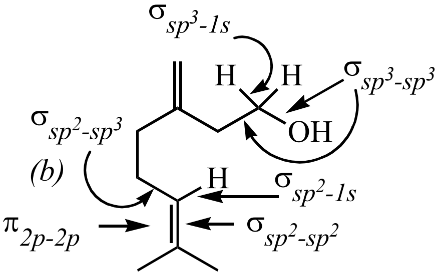

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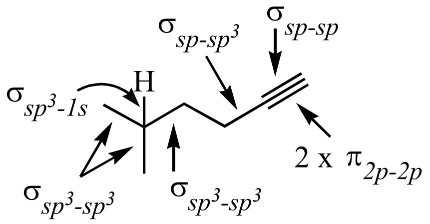

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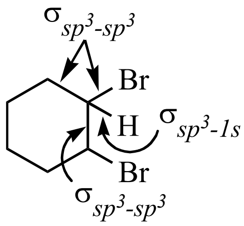
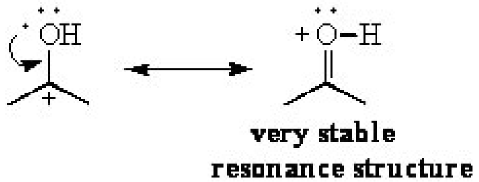
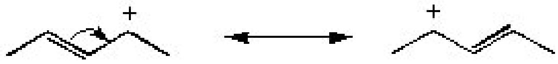


16.99 (a) The positive charge is delocalised over carbon and oxygen atoms via two resonance structures. The resonance structure on the right is especially stable because both these atoms have filled octets:

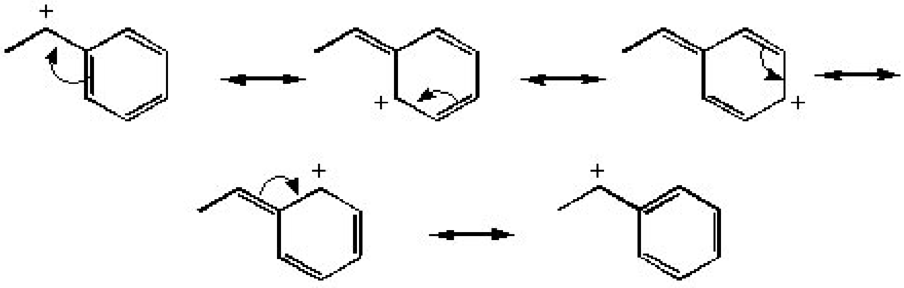
.



(b) The positive charge is delocalised between two carbon atoms via two equivalent resonance structures:

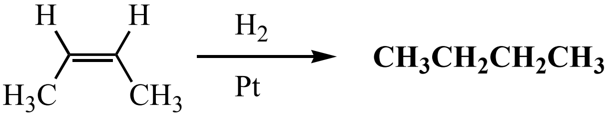


(c) The positive charge is delocalised over four carbon atoms via five resonance structures:

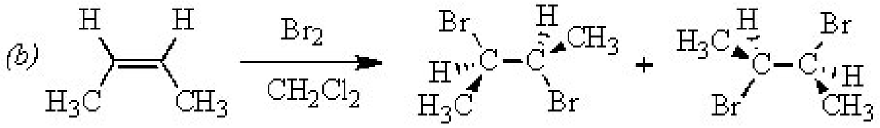


16.101

(a)



Same molecule results from either top or bottom attack



Two different molecules are formed which are non-superimposable and are mirror images of each other and are therefore enantiomers.