4 NOMENCLATURE AND CONFORMATIONS OF ALKANES AND CYCLOALKANES

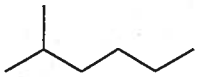
SOLUTIONS TO PROBLEMS

4.1



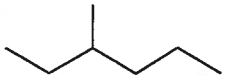
or

$CH_3(CH_2)_5CH_3$
Heptane



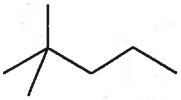
or

$(CH_3)_2CHCH_2CH_2CH_2CH_3$
2-Methylhexane



or

$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$
3-Methylhexane



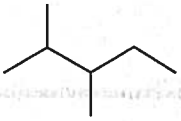
or

$(CH_3)_3CCH_2CH_2CH_3$
2,2-Dimethylpentane



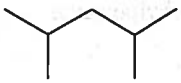
or

$(CH_3CH_2)_2C(CH_3)_2$
3,3-Dimethylpentane



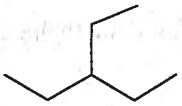
or

$(CH_3)_2CHCH(CH_3)CH_2CH_3$
2,3-Dimethylpentane



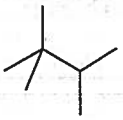
or

$(CH_3)_2CHCH_2CH(CH_3)_2$
2,4-Dimethylpentane



or

$(CH_3CH_2)_3CH$
3-Ethylpentane



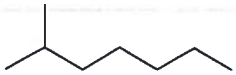
or

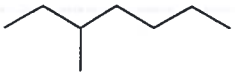
$(CH_3)_3CCH(CH_3)_2$
2,2,3-Trimethylbutane

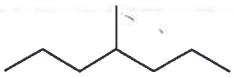
4.2 (d); it represents 3-methylpentane

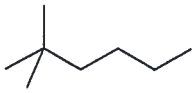
4.3 $CH_3CH_2CH_2CH_2CH_2CH_3$ hexane

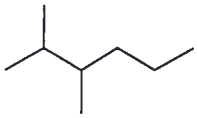
4.4 (a,b)

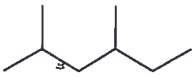

2-Methylheptane

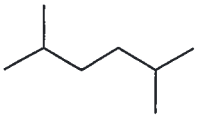

3-Methylheptane


4-Methylheptane

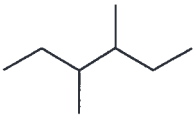

2,2-Dimethylhexane

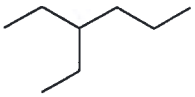

2,3-Dimethylhexane

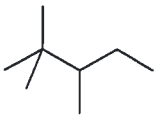

2,4-Dimethylhexane

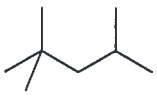

2,5-Dimethylhexane

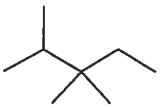

3,3-Dimethylhexane

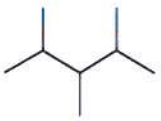

3,4-Dimethylhexane

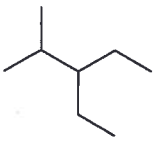

3-Ethylhexane


2,2,3-Trimethylpentane


2,2,4-Trimethylpentane


2,3,3-Trimethylpentane

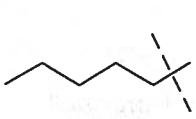

2,3,4-Trimethylpentane


3-Ethyl-2-methylpentane

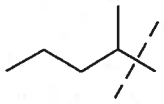

3-Ethyl-3-methylpentane


2,2,3,3-Tetramethylbutane

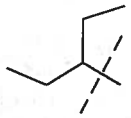
4.5 (a)



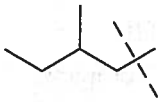
Pentyl



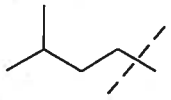
1-Methylbutyl



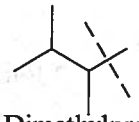
1-Ethylpropyl



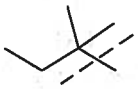
2-Methylbutyl



3-Methylbutyl



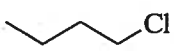
1,2-Dimethylpropyl



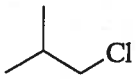
1,1-Dimethylpropyl

(b) See the answer to Review Problem 4.1 for the formulas and names of C_7H_{16} isomers.

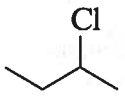
4.6 (a)



1-Chlorobutane



1-Chloro-2-methylpropane

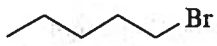


2-Chlorobutane

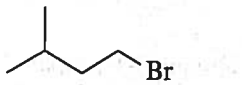


2-Chloro-2-methylpropane

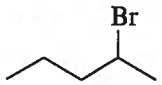
(b)



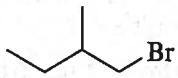
1-Bromopentane



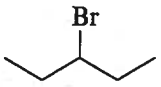
1-Bromo-3-methylbutane



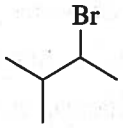
2-Bromopentane



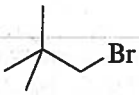
1-Bromo-2-methylbutane



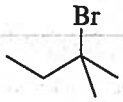
3-Bromopentane



2-Bromo-3-methylbutane

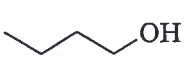


1-Bromo-2,2-dimethylpropane

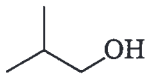


2-Bromo-2-methylbutane

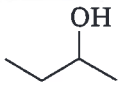
4.7 (a)



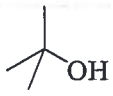
1-Butanol



2-Methyl-1-propanol

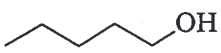


2-Butanol

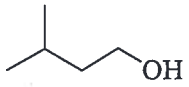


2-Methyl-2-propanol

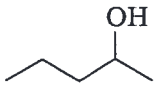
(b)



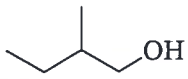
1-Pentanol



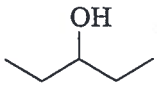
3-Methyl-1-butanol



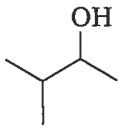
2-Pentanol



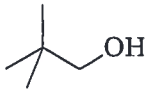
2-Methyl-1-butanol



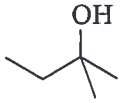
3-Pentanol



3-Methyl-2-butanol



2,2-Dimethyl-1-propanol



2-Methyl-2-butanol

4.8 (a) 1,1-Dimethylethylcyclopentane or *tert*-butylcyclopentane

(b) 1-Methyl-2-(2-methylpropyl)cyclohexane or 1-isobutyl-2-methylcyclohexane

(c) Butylcyclohexane

(d) 1-Chloro-2,4-dimethylcyclohexane

(e) 2-Chlorocyclopentanol

(f) 3-(1,1-Dimethylethyl)cyclohexanol or 3-*tert*-butylcyclohexanol

4.9 (a) 2-Chlorobicyclo[1.1.0]butane

(b) Bicyclo[3.2.1]octane

(c) Bicyclo[2.1.1]hexane

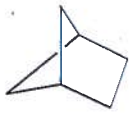
(d) 9-Chlorobicyclo[3.3.1]nonane

(e) 2-Methylbicyclo[2.2.2]octane

(f)

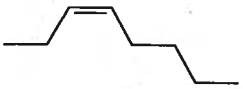
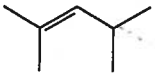


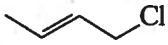
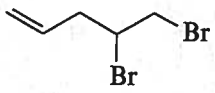
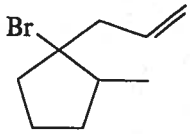
Bicyclo[3.1.0]hexane or

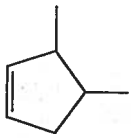
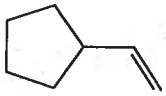
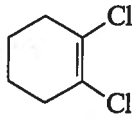


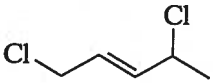
bicyclo[2.1.1]hexane

4.10 (a) *trans*-3-Heptene
(b) 2,5-Dimethyl-2-octene
(c) 4-Ethyl-2-methyl-l-hexene
(d) 3,5-Dimethylcyclohexene
(e) 4-Methyl-4-penten-2-ol
(f) 2-Chloro-3-methylcyclohex-3-en-1-ol

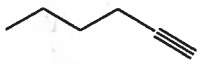
4.11 (a)  (b)  (c) 

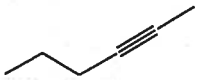
(d)  (e)  (f) 

(g)  (h)  (i) 

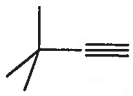
(j) 

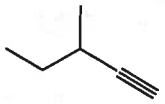
4.12

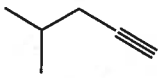

1-Hexyne


2-Hexyne


3-Hexyne

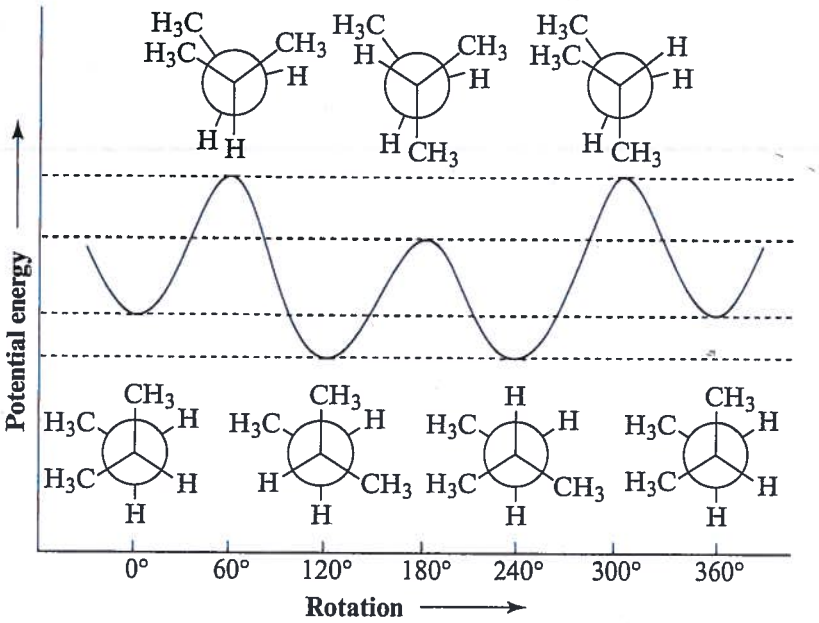

3,3-Dimethyl-1-butyne


3-Methyl-1-pentyne


4-Methyl-1-pentyne


4-Methyl-2-pentyne

4.13



4.14 $\log K_{eq} = \dfrac{\Delta G^\circ}{-2.303RT} = \dfrac{-7600\ \text{J}}{(-2.303)(8.314\ \text{J K}^{-1})(298\ \text{K})} = 1.32$

$K_{eq} = 21.38$

Let e = amount of equatorial form

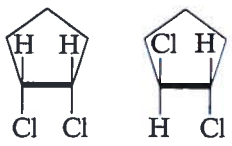
and a = amount of axial form

then, $K_{eq} = \dfrac{e}{a} = 21.38$

$e = 21.38a$

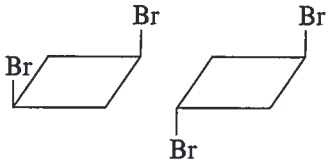
$\%\ e = \dfrac{21.38a}{a + 21.38a} \times 100 = 95.5\%$

4.15 (a)



(cis) (trans)

(b)



(cis) (trans)

(c) No

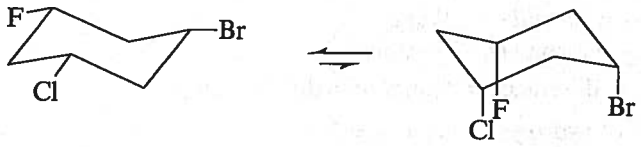
4.16 (a-d)



More stable because larger group is equatorial and so preferred at equilibrium

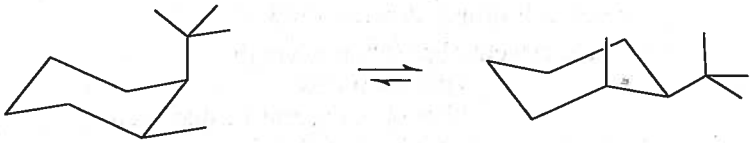
Less stable because larger group is axial

4.17



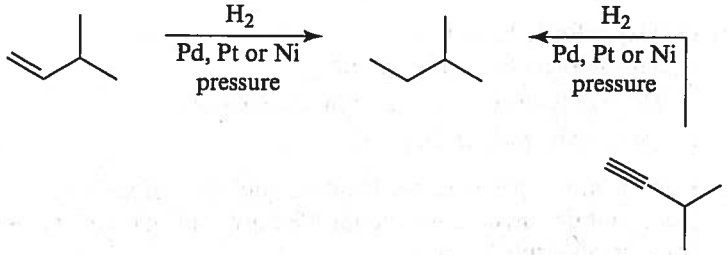
all equatorial (more stable) ⇌ all axial (less stable)

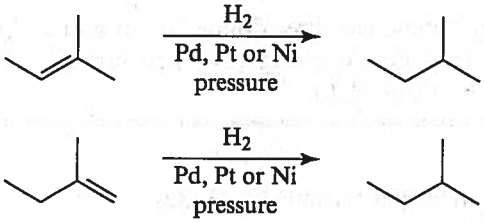
4.18 (a,b)



Less stable because the large *tert*-butyl group is axial (more potential energy) ⇌ More stable because the large *tert*-butyl group is equatorial (less potential energy)

4.19





4.20 (a) C_6H_{14} = formula of alkane
C_6H_{12} = formula of 2-hexene
H_2 = difference = 1 pair of hydrogen atoms
Index of hydrogen deficiency = 1

(b) C_6H_{14} = formula of alkane
C_6H_{12} = formula of methylcyclopentane
H_2 = difference = 1 pair of hydrogen atoms
Index of hydrogen deficiency = 1

(c) No, all isomers of C_6H_{12}, for example, have the same index of hydrogen deficiency.

(d) No

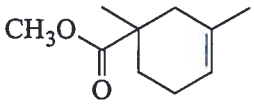
(e) C_6H_{14} = formula of alkane
$\underline{C_6H_{10}}$ = formula of 2-hexyne
H_4 = difference = 2 pairs of hydrogen atoms
Index of hydrogen deficiency = 2

(f) $C_{10}H_{22}$ (alkane)
$\underline{C_{10}H_{16}}$ (compound)
H_6 = difference = 3 pairs of hydrogen atoms
Index of hydrogen deficiency = 3
The structural possibilities are thus
3 double bonds
1 double bond and 1 triple bond
2 double bonds and 1 ring
1 double bond and 2 rings
3 rings
1 triple bond and 1 ring

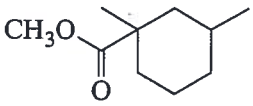
4.21 (a) $C_{15}H_{32}$ = formula of alkane
$\underline{C_{15}H_{24}}$ = formula of zingiberene
H_8 = difference = 4 pairs of hydrogen atoms
Index of hydrogen deficiency = 4

(b) Since 1 mol of zingiberene absorbs 3 mol of hydrogen, one molecule of zingiberene must contain three double bonds. (We are told that molecules of zingiberene do not contain any triple bonds.)

(c) If a molecule of zingiberene has three double bonds and an index of hydrogen deficiency equal to 4, it must have one ring. (The structural formula for zingiberene can be found in Review Problem 23.2.)

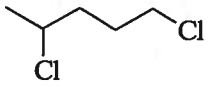
4.22  molecular formula $C_{10}H_{16}O_2$

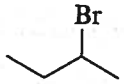
$C_{10}H_{22}$ = formula for alkane
$\underline{C_{10}H_{16}}$ = formula for unsaturated ester (ignoring oxygens)
H_6 = difference = 3 pairs of hydrogen atoms
IHD = 3

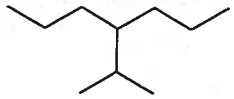
 molecular formula $C_{10}H_{18}O_2$

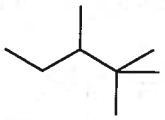
$C_{10}H_{22}$ = formula for alkane
$\underline{C_{10}H_{18}}$ = formula for hydrogenation product (ignoring oxygens)
H_4 = difference = 2 pairs of hydrogen atoms
IHD = 2

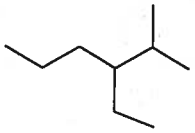
Nomenclature and Isomerism

4.23 (a) 

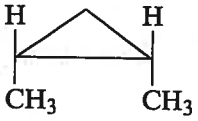
(b) 

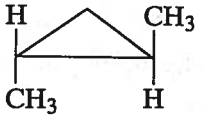
(c) 

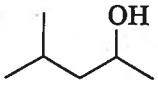
(d) 

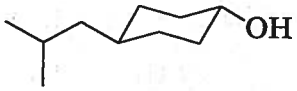
(e) 

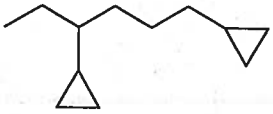
(f) 

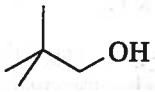
(g) 

(h) 

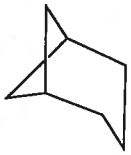
(i) 

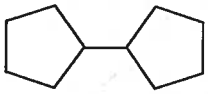
(j) 

(k) 

(l) 

(m)  or 

(n) 

(o) 

4.24 (a) 5-Ethyl-7-isopropyl-2,3-dimethyldecane

(b) 2,2,5-Trimethylhexane

(c) 4-Bromo-6-chloro-3-methyloctane

(d) 2-Methyl-1-butanol

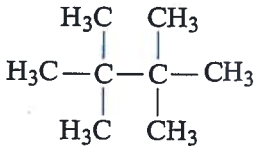
(e) 2-Bromobicyclo[3.3.1]nonane

(f) *trans*-1-Bromo-3-fluorocyclopentane

(g) 5,6-Dimethyl-2-heptane

(h) 7-Chlorobicyclo[2.2.1]heptane

4.25 The two secondary carbon atoms in *sec*-butyl alcohol are equivalent; however, there are three five-carbon alcohols (pentyl alcohols) that contain a secondary carbon atom.

4.26 (a) 

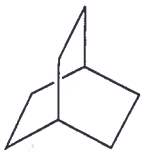
2,2,3,3-Tetramethylbutane

(b) 

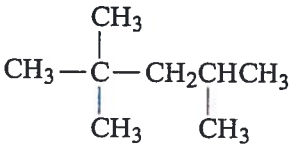
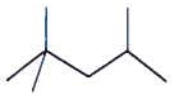
Cyclohexane

(c) 

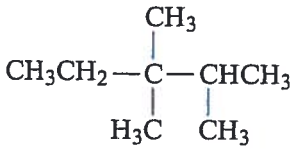
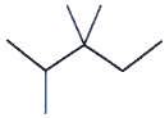
1,1-Dimethylcyclobutane

(d) 

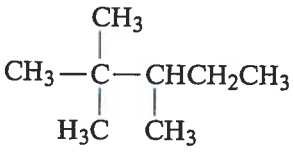
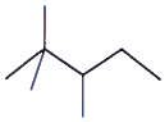
Bicyclo[2.2.2]octane

4.27  or 

2,2,4-trimethylpentane

 or 

2,3,3-trimethylpentane

 or 

2,2,3-trimethylpentane

4.28 

Cyclopentane



Methylcyclobutane



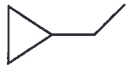
cis-1,2-Dimethylcyclopropane



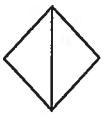
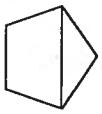
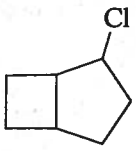
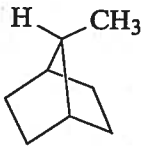
trans-1,2-Dimethylcyclopropane



1,1-Dimethylcyclopropane

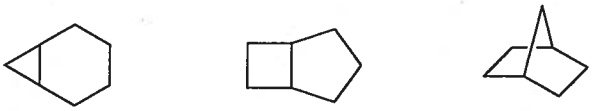


Ethylcyclopropane

4.29 (a)  (b)  (c)  (d) 

4.30 $S - A + 1 = N$
For cubane, $S = 12$ and $A = 8$. Thus $12 - 8 + 1 = N$; $N = 5$ rings in cubane.

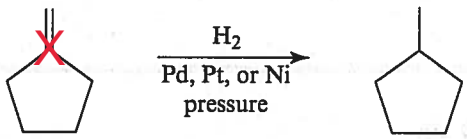
4.31 (a) 

(b) 

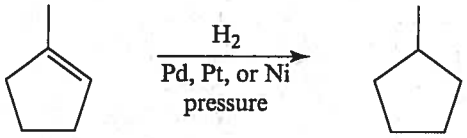
4.32 A homologous series is one in which each member of the series differs from the one preceding it by a constant amount, usually a CH_2 group. A homologous series of alkyl halides would be the following:

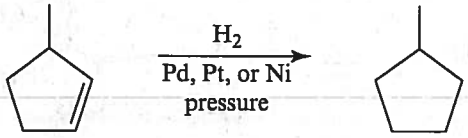
CH_3X
CH_3CH_2X
$CH_3(CH_2)_2X$
$CH_3(CH_2)_3X$
$CH_3(CH_2)_4X$
etc.

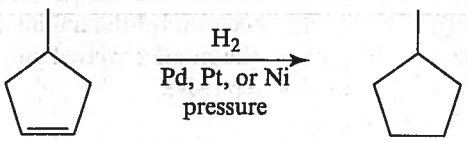
Hydrogenation

4.33 

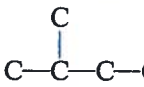
The double bond outside of the ring structure is not very stable. So, 3 alkenes transform into methylcyclohexane: 1-methylcyclohexene, 3-methylcyclohexene and 4-methylcyclohexene.



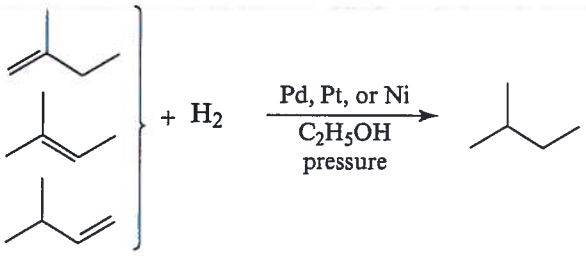




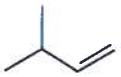
4.34 (a) Each of the desired alkenes must have the same carbon skeleton as 2-methylbutane,



C—C—C—C; they are therefore



(b)

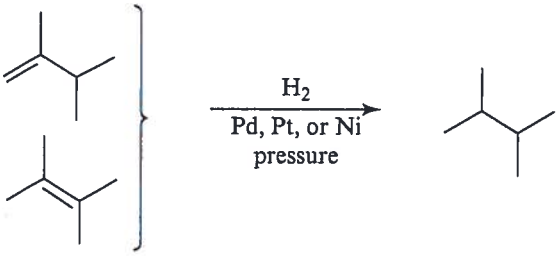


4.35



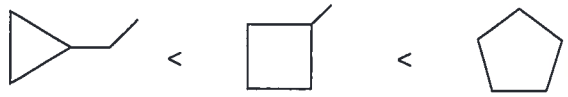
2,3-Dimethylbutane

From two alkenes



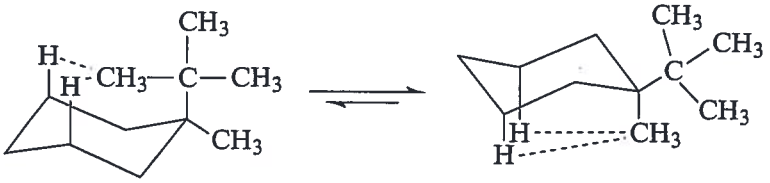
Conformations and Stability

4.36



Least stable — Most stable

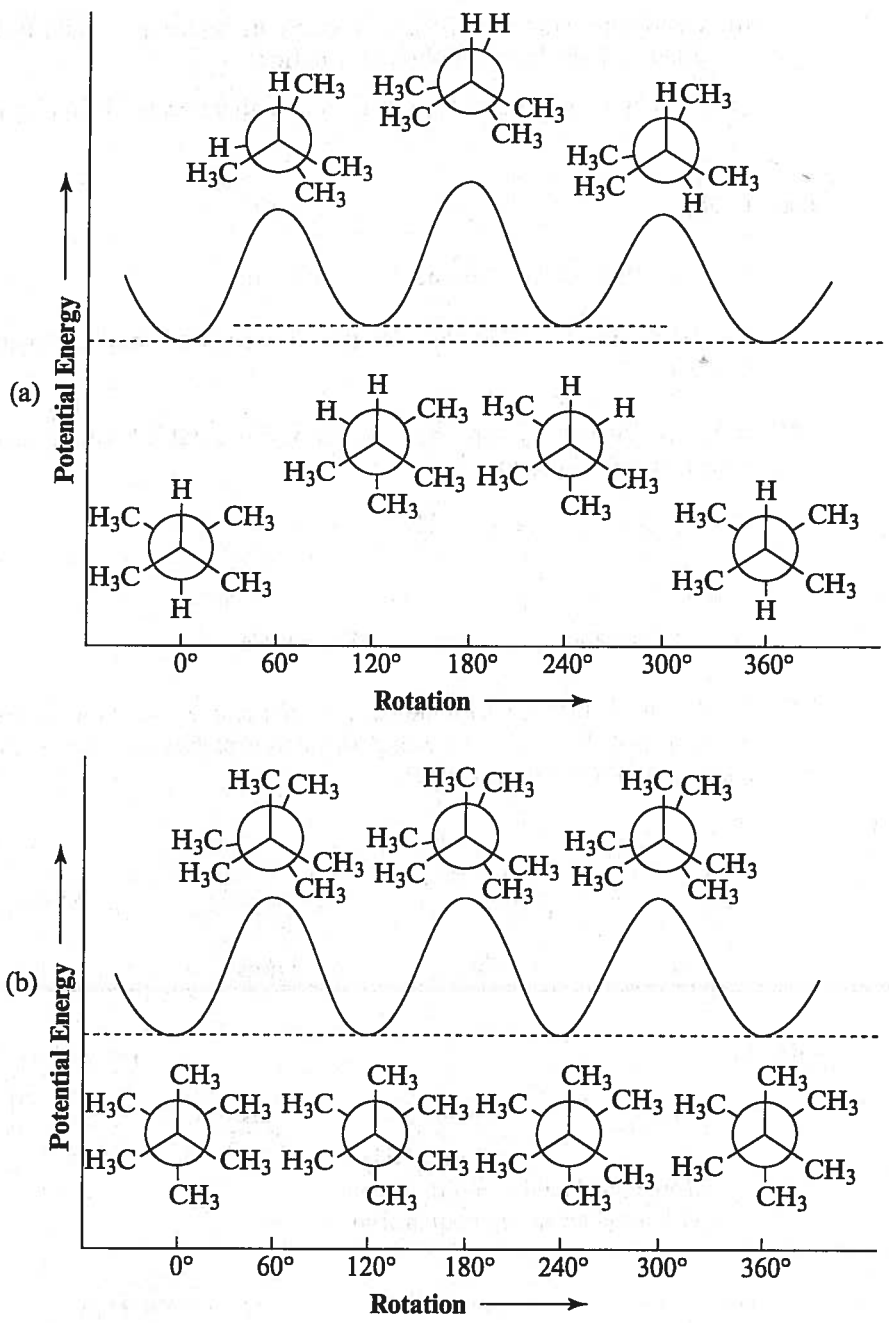
4.37



This conformation is *less stable* because 1,3-diaxial interactions with the large *tert*-butyl group cause considerable repulsion.

This conformation is *more stable* because 1,3-diaxial interactions with the smaller methyl group are less repulsive.

4.38



4.39 (a) Pentane would boil higher because its chain is unbranched. Chain-branching lowers the boiling point.

(b) Heptane would boil higher because it has the larger molecular weight and would, because of its larger surface area, have larger van der Waals attractions.

(c) 2-Chloropropane because it is more polar and because it has a larger molecular weight.

(d) 1-Propanol would boil higher because its molecules would be associated with each other through hydrogen-bond formation.

(e) Propanone (CH_3COCH_3) would boil higher because its molecules are more polar.

4.40 C_4H_6



Bicyclo[1.1.0]butane



1-Butyne

The IR stretch at ~2250 cm^{-1} for the alkyne C≡C bond distinguishes these two compounds.

4.41 *trans*-1,2-Dimethylcyclopropane would be more stable because there is less crowding between its methyl groups.

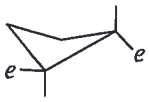


Less stable

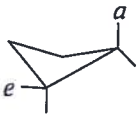


More stable

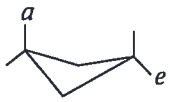
4.42 For 1,2-disubstituted cyclobutanes, the trans isomer is *e,e*; the cis isomer is *a,e*, and so the less stable of the two. For 1,3-disubstituted cyclobutanes, the cis isomer is *e,e* and more stable than the *a,e* trans isomer.



Trans



Cis



Trans

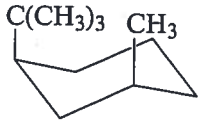


Cis

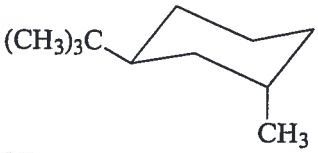
4.43 (a)



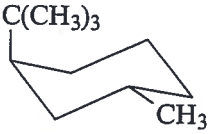
More stable conformation because both alkyl groups are equatorial



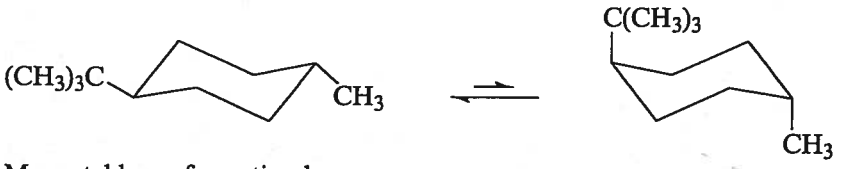
(b)



More stable because larger group is equatorial



(c)



More stable conformation because both alkyl groups are equatorial

(d)

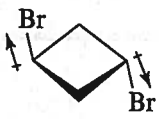


More stable because larger group is equatorial

4.44 Certainly it is expected that the alkyl groups would prefer the equatorial disposition in a case such as this, and indeed this is true in the case of *all-trans*-1,2,3,4,5,6-hexaethylcyclohexane, which does have all ethyl groups equatorial.

Apparently, the torsional and steric effects resulting from equatorial isopropyl groups destabilize the all-equatorial conformation to a greater degree than axial isopropyl groups destabilize the all-axial conformation. The fully axial structure assigned on the basis of X-ray studies is also supported by calculations.

4.45 If the cyclobutane ring were planar, the C—Br bond moments would exactly cancel in the trans isomer. The fact that *trans*-1,3-dibromocyclobutane has a dipole moment shows the ring is not planar.



Planar form
$\mu = 0$ D



Bent form
$\mu \neq 0$ D

Synthesis

4.46 (a) H_2; Pd, Pt, or Ni catalyst, pressure

(b) H_2; Pd, Pt, or Ni catalyst, pressure

(c) Predicted IR absorption frequencies for reactants in parts (a) and (b) are the following:

(1) *trans*-5-Methyl-2-hexene has an absorption at approximately 964 cm^{-1}, characteristic of C—H bending in a trans-substituted alkene.

(2) The alkene double bond of the reactant is predicted to have a stretching absorption between 1580 and 1680 cm^{-1}.