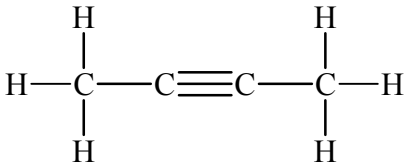
CHAPTER 18
ORGANIC CHEMISTRY I:
THE HYDROCARBONS

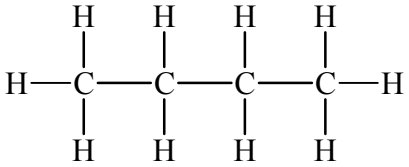
18.1

(a)



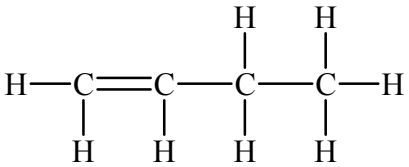
alkyne

(b)



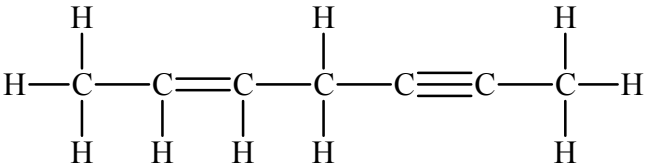
alkane

(c)



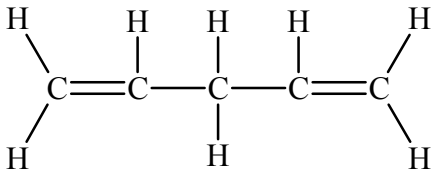
alkene

(d)



alkene and alkyne

(e)



alkene

18.3 (a) $(CH_3)_3CH$ or C_4H_{10}, alkane; (b) $C_6H_7CH_3$ or C_7H_{10} alkene; (c) C_6H_{12}, alkane; (d) C_6H_{12} alkane

18.5 (a) $C_{12}H_{26}$, alkane; (b) $C_{13}H_{20}$, alkene; (c) C_7H_{14}, alkane; (d) $C_{14}H_8$ aromatic hydrocarbon

18.7 (a) propane; (b) butane; (c) heptane; (d) decane

18.9 (a) methyl; (b) pentyl; (c) propyl; (d) hexyl

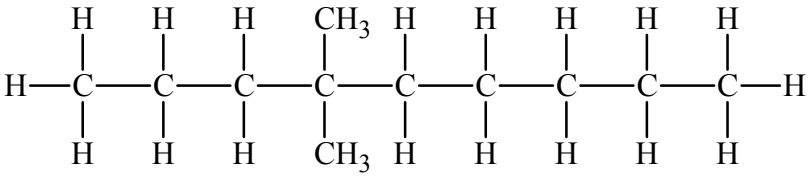
18.11 (a) propane; (b) ethane; (c) pentane; (d) 2,3-dimethylbutane

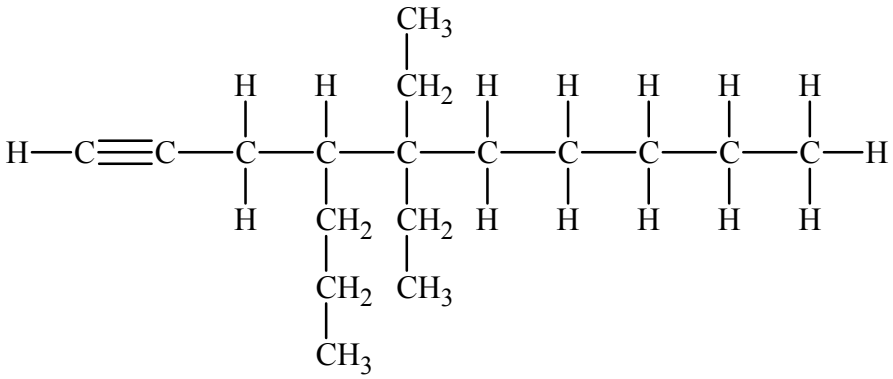
18.13 (a) 4-methyl-2-pentene; (b) 2,3-dimethyl-2-phenylpentane

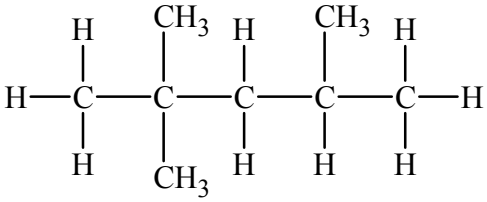
18.15 (a) $CH_2{=}CHCH(CH_3)CH_2CH_3$;
(b) $CH_3CH_2C(CH_3)_2CH(CH_2CH_3)(CH_2)_2CH_3$;
(c) $HC{\equiv}C(CH_2)_2C(CH_3)_3$; (d) $CH_3CH(CH_3)CH(CH_2CH_3)CH(CH_3)_2$

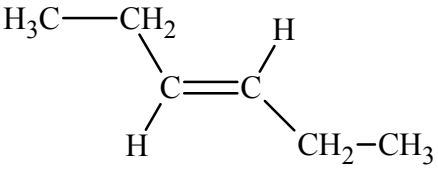
18.17

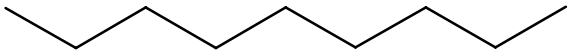
(a)



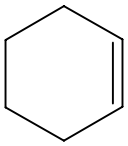
(b) 

(c) 

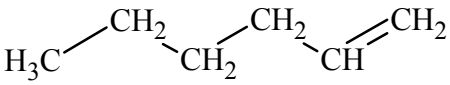
(d) 

18.19 (a) 

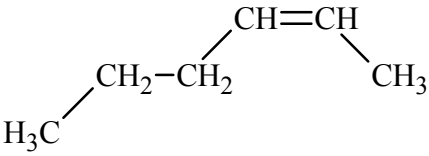
(b)

(c) 

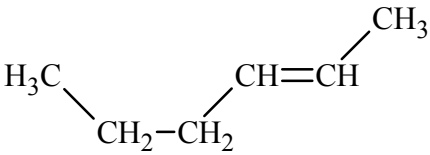
18.21 (a) hexenes:



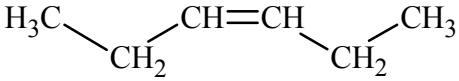
1-Hexene



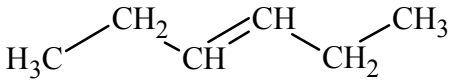
cis-2-Hexene



trans-2-Hexene

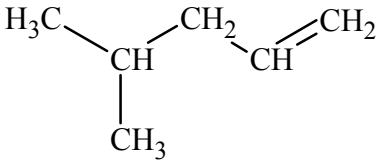


cis-3-Hexene

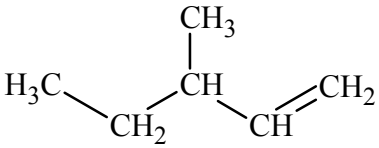


trans-3-Hexene

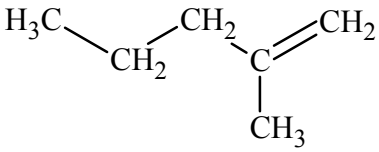
Pentenes:



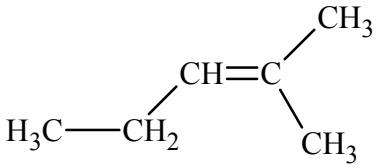
4-Methyl-1-pentene



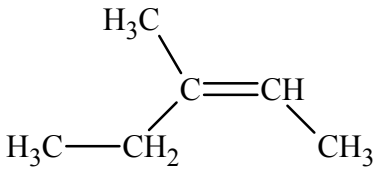
3-Methyl-1-pentene



2-Methyl-1-pentene

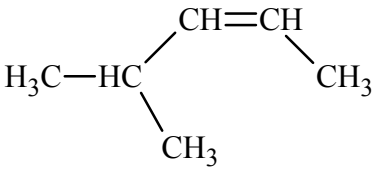


2-Methyl-2-pentene



cis-3-Methyl-2-pentene

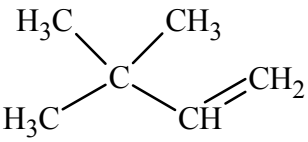
(+ trans isomer)



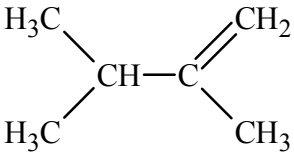
cis-4-Methyl-2-pentene

(+ trans isomer)

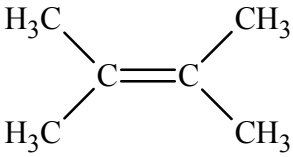
butanes:



3,3-Dimethyl-1-butene

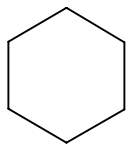


2,3-Dimethyl-1-butene

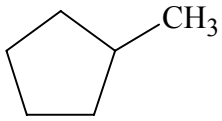


2,3-Dimethyl-2-butene

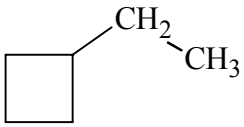
(b) cyclic molecules:



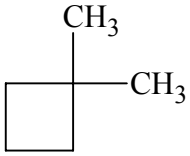
Cyclohexane



Methylcyclopentane

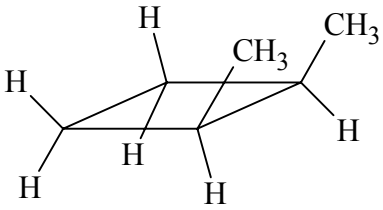


ethylcyclobutane

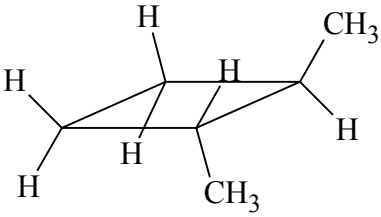


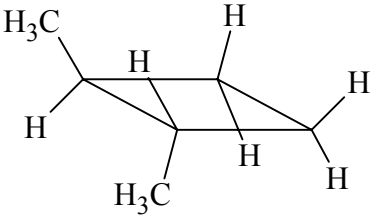
dimethylcyclobutane

The following structures are drawn to emphasize the stereochemistry



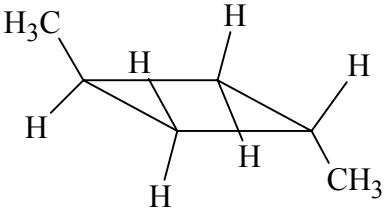
cis-1,2-Dimethylcyclobutane

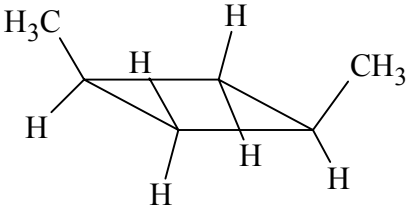




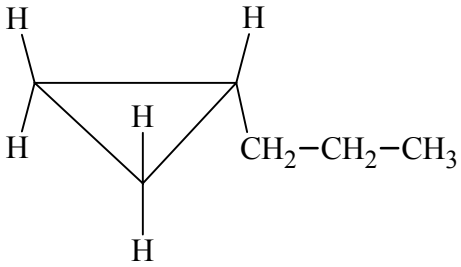
trans-1,2-Dimethylcyclobutane

(nonsuperimposable mirror images

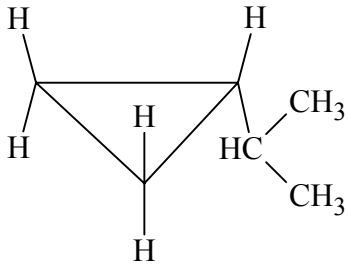




trans-1,3-Dimethylcyclobutane *cis*-1,3-Dimethylcyclobutane

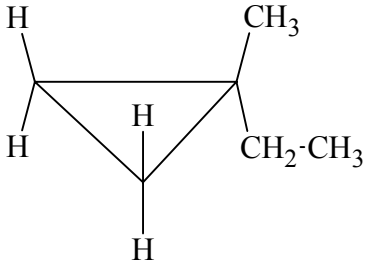


Propylcyclopropane

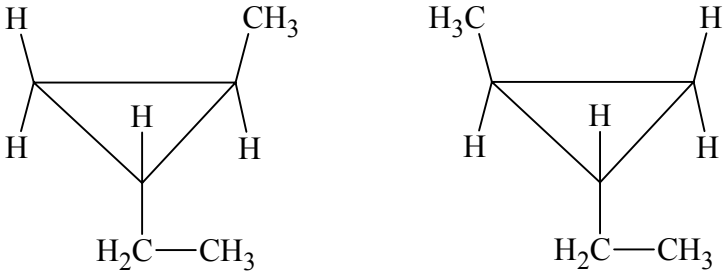


Isoropylcyclopropane

or 2-cyclopropylpropane

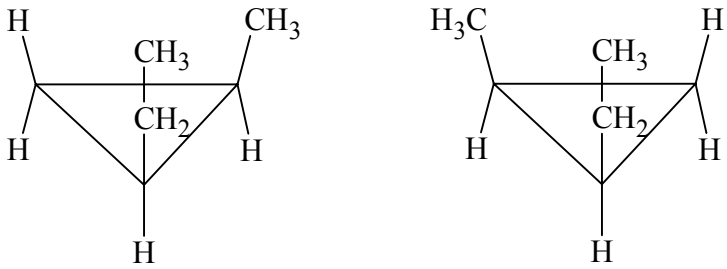


1-Ethyl-1-methylcyclopropane



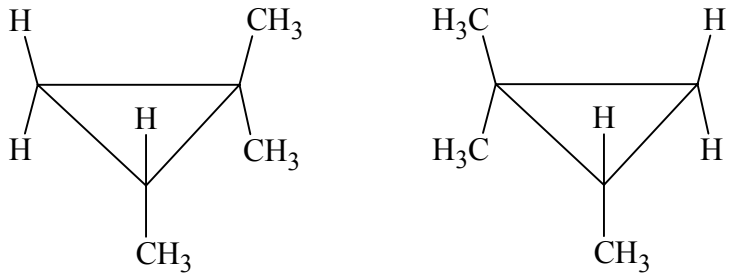
trans-1-Ethyl-2-methylcyclopropane

(nonsuperimposable mirror images)



cis-1-Ethyl-2-methylcyclopropane

(nonsuperimposable mirror images)



1,1,2-Trimethylcyclopropane

(nonsuperimposable mirror images)

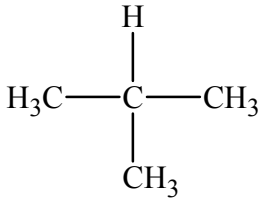
18.23 (a) Butane is C_4H_{10}, cyclobutane is C_4H_8. Because they have different formulas, they are not isomers.

(b) Same formula, but different structures; therefore, they are structural isomers.

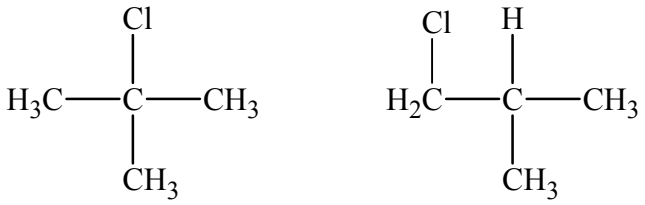
(c) Same formula (C_5H_{10}), same structure (bonding arrangement is the same), but different geometry; therefore, they are geometrical isomers.

(d) Not isomers, because only their positions in space are different and these positions can be interchanged. Same molecule.

18.25 (a)

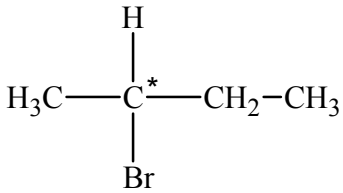


(b) If only two isomeric products are formed and they are both branched, then the only possibilities are

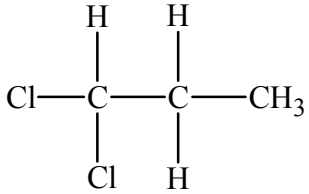


18.27 An * designates a chiral carbon.

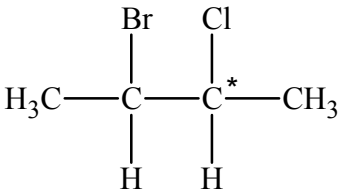
(a) optically active,



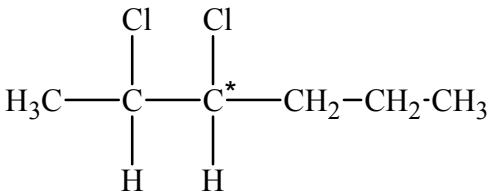
(b) not optically active,



(c) optically active,



(d) optically active,



18.29 The difference can be traced to the weaker London forces that exist in branched molecules. Atoms in neighboring branched molecules cannot lie as close together as they can in unbranched isomers.

18.31 The balanced equations are

$$C_3H_8(g) + 5\ O_2(g) \longrightarrow 3\ CO_2(g) + 4\ H_2O(l)$$

$$C_4H_{10}(g) + 13/2\ O_2(g) \longrightarrow 4\ CO_2(g) + 5\ H_2O(l)$$

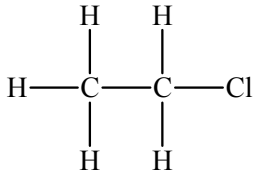
$$C_5H_{12}(g) + 8\ O_2(g) \longrightarrow 5\ CO_2(g) + 6\ H_2O(l)$$

The enthalpies of combustion that correspond to these reactions are listed in the Appendix:

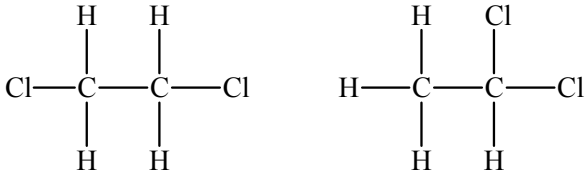
Compound	Enthalpy of combustion $kJ \cdot mol^{-1}$	Heat released per g $kJ \cdot g^{-1}$
Propane	−2220	50.3
Butane	−2878	49.5
Pentane	−3537	49.0

The molar enthalpy of combustion increases with molar mass as might be expected, because the number of moles of CO_2 and H_2O formed will increase as the number of carbon and hydrogen atoms in the compounds increases. The heat released per gram of these hydrocarbons is essentially the same because the H to C ratio is similar in the three hydrocarbons.

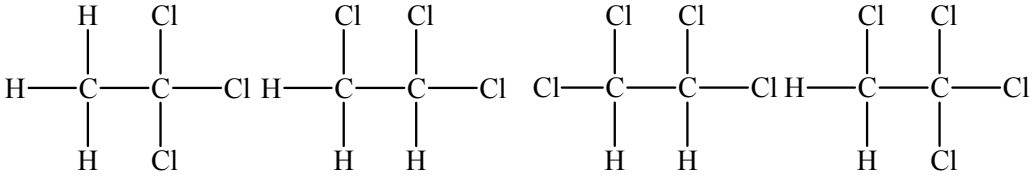
18.33 There are nine possible products:



one monochloro compound

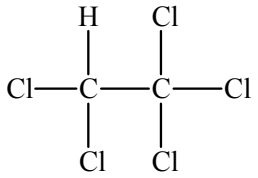


two dichloro compounds

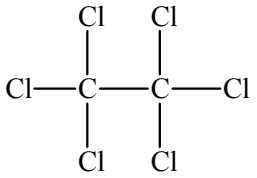


two trichloro compounds

two tetrachloro compounds



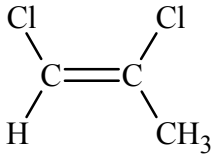
one pentachloro compound



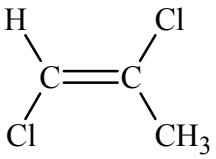
one hexachloro compound

None of these form optical isomers.

18.35



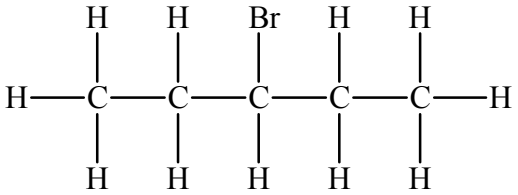
cis-1,2-Dichloropropene



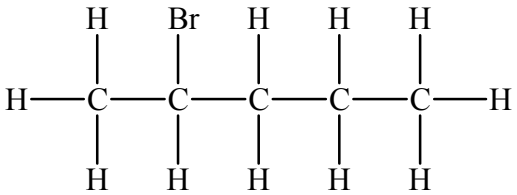
trans-1,2-Dichloropropene

cis-1,2-Dichloropropene is polar, although *trans*-1,2-Dichloropropene is slightly polar also.

18.37 (a)



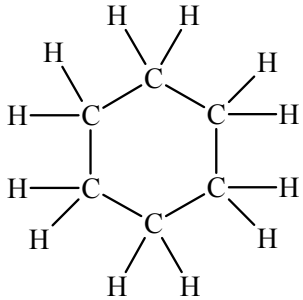
3-Bromopentane



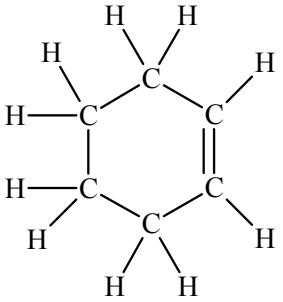
2-Bromopentane

(b) addition reaction

18.39 (a) $C_6H_{11}Br + NaOCH_2CH_3 \rightarrow C_6H_{10} + NaBr + HOCH_2CH_3$

(b) 

$+ \; NaOCH_2CH_3 \longrightarrow$



$+ \; NaBr \; + \; HOCH_2CH_3$

18.41 $C_2H_4 + X_2 \longrightarrow C_2H_4X_2$

We will break one X—X bond and form two C—X bonds.

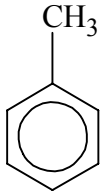
Using bond enthalpies:

Halogen	Cl	Br	I
X—X bond breakage $(kJ \cdot mol^{-1})$	+242	+193	+151
C—X bond formation $(kJ \cdot mol^{-1})$	$-2(338)$	$-2(276)$	$-2(238)$
Total $(kJ \cdot mol^{-1})$	-434	-359	-325

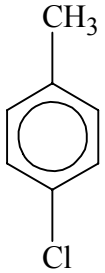
The reaction is less exothermic as the halogen becomes heavier. In general, the reactivity, and also the danger associated with use of the halogens in reactions, decreases as one descends the periodic table.

18.43 (a) 1-ethyl-3-methylbenzene; (b) pentamethylbenzene (1,2,3,4,5-pentamethylbenzene is also correct, but, because there is only one possible pentamethylbenzene, the use of the numbers is not necessary)

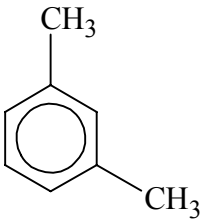
18.45 (a)



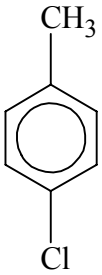
(b)



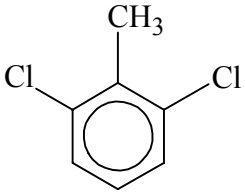
(c)



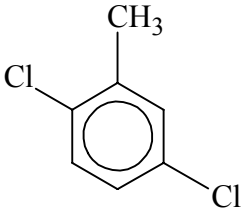
(d)



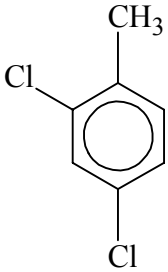
18.47



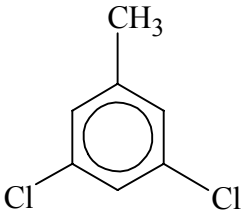
1,3-Dichloro-2-methylbenzene



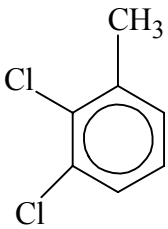
1,4-Dichloro-2-methylbenzene



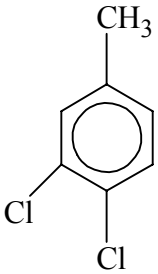
1,2-Dichloro-3-methylbenzene



1,3-Dichloro-5-methylbenzene



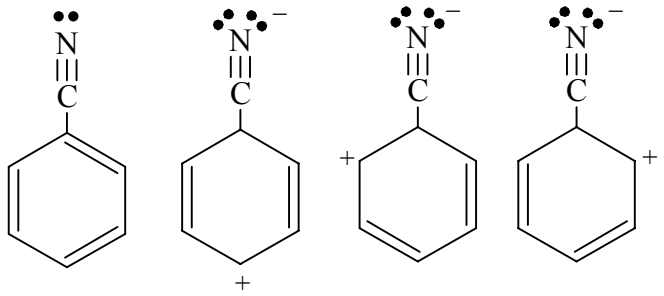
1,2-Dichloro-3-methylbenzene



1,2-Dichloro-4-methylbenzene

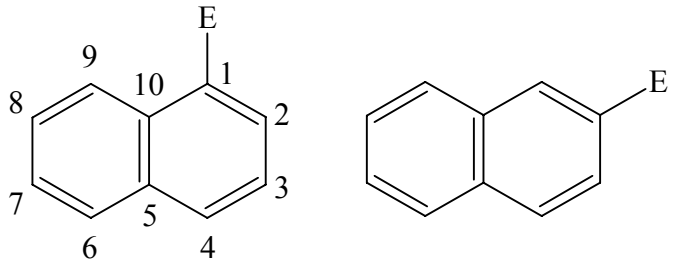
(b) All of these molecules are at least slightly polar.

18.49



Electrophiles tend to avoid the ortho and para positions that develop slight + charges in the resonance forms.

18.51 Two compounds can be produced. Resonance makes positions 1, 4, 6, and 9 equivalent. It also makes positions 2, 3, 7, and 8 equivalent. Positions 5 and 10 are equivalent but have no H atom.



18.53 These hydrocarbons are too volatile (they are all gases at room temperature) and would not remain in the liquid state.

18.55 Cracking is the process of breaking down hydrocarbons with many carbon atoms into smaller units, whereas alkylation is the process of combining smaller hydrocarbons into larger units. Both processes are carried out catalytically, and both are used to convert hydrocarbons into units having from 5 to 11 carbon atoms suitable for use in gasoline.

18.57 (a) 4 σ-type single bonds

(b) 2 σ-type single bonds and 1 double bond with a σ- and a π-bond

(c) 1 σ-type single bond and 1 triple bond with a σ-bond and 2 π-bonds

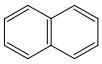
18.59 (a) substitution, $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

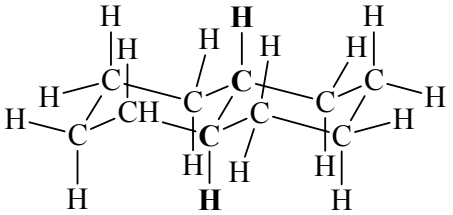
(b) addition $CH_2{=}CH_2 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$

18.61 Water is not used as the nonpolar reactants will not readily dissolve in a highly polar solvent like water. Also, the ethoxide ion reacts with water.

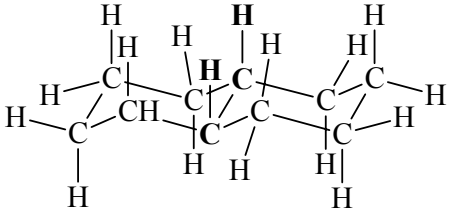
18.63 The double bond in alkenes makes them more rigid than alkanes. Some of the atoms of alkene molecules are locked into a planar arrangement by the π-bond; hence, they cannot roll up into a ball as compactly as alkanes can. Because they do not pack together as compactly as alkanes do, they have lower boiling and melting points.

18.65 (a) 2-methyl-1-propene, no geometrical isomers; (b) *cis*-3-methyl-2-pentene, *trans*-3-methyl-2-pentene; (c) 1-hexyne, no geometrical isomers; (d) 3-hexyne, no geometrical isomers; (e) 2-hexyne, no geometrical isomers.

18.67 (a) $C_{10}H_{18}$; (b) naphthalene,  , $C_{10}H_8$; (c) Yes. Cis and trans forms (relative to the C-C bond common to the two six-membered rings) are possible.

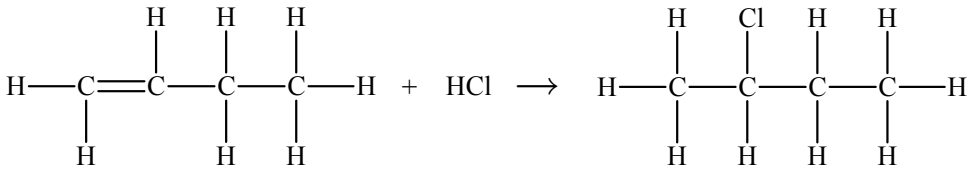


trans-Decalin



cis-Decalin

18.69



Bonds Broken: H-Cl, C=C

Bonds Formed: C-Cl, C-H, C-C

The reaction enthalpy will be equivalent to the enthalpy gained by the system in breaking bonds minus the enthalpy lost during bond formation:

$\Delta H_r = 431\ \text{kJ·mol}^{-1} + 612\ \text{kJ·mol}^{-1} - 338\ \text{kJ·mol}^{-1}$

$- 412\ \text{kJ·mol}^{-1} - 348\ \text{kJ·mol}^{-1}$

$= 55\ \text{kJ·mol}^{-1}$

18.71 $$\text{number of moles of H} = \left(\frac{4.48\ \text{g H}_2\text{O}}{18.02\ \text{g H}_2\text{O/mol H}_2\text{O}}\right)\left(\frac{2\ \text{mol H}}{1\ \text{mol H}_2\text{O}}\right) = 0.497\ \text{mol H}$$

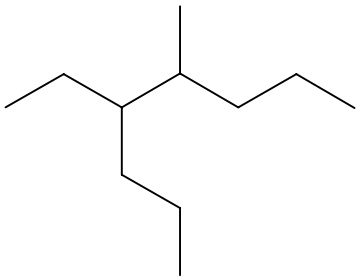
$$\text{number of moles of C} = \left(\frac{9.72\ \text{g CO}_2}{44.01\ \text{g CO}_2\text{/mol CO}_2}\right)\left(\frac{1\ \text{mol C}}{1\ \text{mol CO}_2}\right) = 0.221\ \text{mol C}$$

$$\frac{0.497\ \text{mol H}}{0.221\ \text{mol C}} = \frac{9\ \text{mol H}}{4\ \text{mol C}}$$

The empirical formula is C_4H_9; the molecular formula might be C_8H_{18}, which matches the formula for alkanes (C_nH_{2n+2}). It is not likely an alkene or alkyne, because there is no reasonable Lewis structure for a compound having the empirical formula C_4H_9 and multiple bonds.

18.73 (a) 4-methyl-3-propylheptane

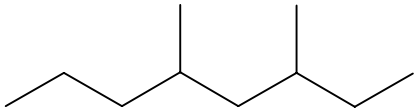
The longest chain has eight carbon atoms in it. The systematic name of the compound is 4-ethyl-5-methyloctane.



4-ethyl-5-methyloctane;

(b) 4,6-dimethyloctane

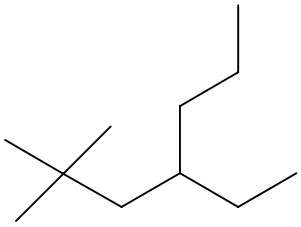
The compound name is almost correct, but the numbering scheme with the lowest numbers would be 3,5-dimethyloctane.



3,5-dimethyloctane;

(c) 2,2-dimethyl-4-propylhexane

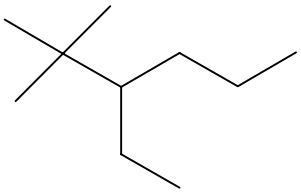
The longest carbon chain in the molecule is seven carbon atoms long. The systematic name is 2,2-dimethyl-4-propylheptane.



2,2-dimethyl-4-ethylheptane;

(d) 2,2-dimethyl-3-ethylhexane.

The name is essentially correct except that ethyl should be listed first The systematic name is 3-ethyl-2,2-dimethylhexane

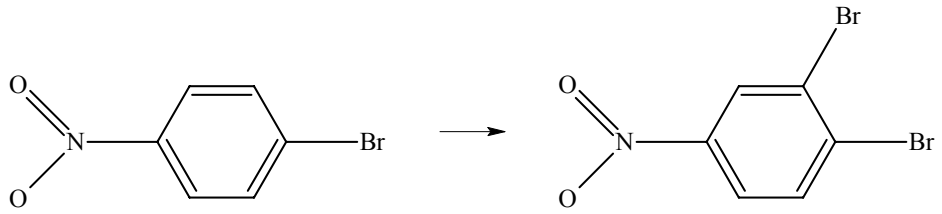


3-ethyl-2,2-dimethylhexane

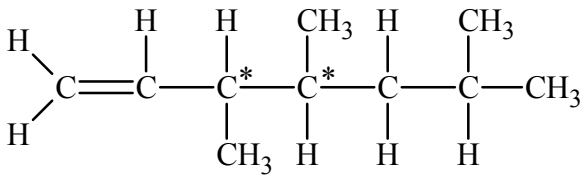
18.75 Bromine is an electrophile which will undergo an addition reaction with alkenes in the dark. The lack of a reaction in the dark with Br_2 indicates that the molecule is not an alkene. In the presence of light, bromine will undergo a substitution reaction with alkanes. Therefore, the molecule is most likely an alkane and the only alkane with the molecular formula C_3H_6 is cyclopropane.

18.77 The NO_2 group is a meta-directing group and the Br atom is an ortho, para-directing group. Because the position para to Br is already substituted with the NO_2 group, further bromination will not occur there. The resonance forms show that the bromine atom will activate the position ortho to it as expected. The NO_2 group will deactivate the group ortho to itself, thus in essence enhancing the reactivity of the position meta to the

NO_2 group. This position is ortho to the Br atom, so the effects of the Br and NO_2 groups reinforce each other. Bromination is thus expected to occur as shown:

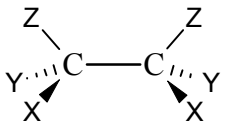


18.79 (a) and (b)



(c) No, there are no cis/trans isomers for this molecule.

18.81 If the molecule contains two carbon centers that have four different substituents attached but are arranged such that they are mirror images of one another within the molecule, the molecule will not be optically active. Such an example is shown below in general for a 1,2-X-1,2-Y-1,2-Z substituted ethane. Many other examples are possible, the only criterion being that the carbon atoms that have four substituents must have a mirror image carbon center within the molecule.



18.83 For a molecule such as 1,2-dichloro-4-diethylbenzene, $C_6H_3C_{l2}(CH_2CH_3)$, 175.04 u, it is relatively easy to lose heavy atoms such as chlorine and groups of atoms such as methyl and ethyl fragments. Molecules can also lose hydrogen atoms. In mass spectrometry, *P* is used to represent the *parent ion*, which is the ion formed from the molecule without fragmentation. Fragments are then represented as $P - x$, where x is the

particular fragment lost from the parent ion to give the observed mass. Because the mass spectrum will measure the masses of individual molecules, the mass of carbon used will be 12.00 u (by definition) because the large majority of the molecules will have all ^{12}C. The mass of H is 1.0078 u. Some representative peaks that may be present are listed below.

Fragment formula	Relation to parent ion	Mass, u
$C_6H_3{}^{35}Cl_2(CH_2CH_3)$	*P*	174.00
$C_6H_3{}^{35}Cl^{37}Cl(CH_2CH_3)$	*P*	176.00
$C_6H_3{}^{37}Cl_2(CH_2CH_3)$	*P*	177.99
$C_6H_3{}^{35}Cl(CH_2CH_3)$	*P*-Cl	139.03
$C_6H_3{}^{37}Cl(CH_2CH_3)$	*P*-Cl	141.03
$C_6H_3{}^{35}Cl_2(CH_2)$	*P*-CH_3	158.98
$C_6H_3{}^{35}Cl^{37}Cl(CH_2)$	*P*-CH_3	160.97
$C_6H_3{}^{37}Cl_2(CH_2)$	*P*-CH_3	162.97
$C_6H_3{}^{35}Cl_2$	*P*-CH_2CH_3	144.96
$C_6H_3{}^{35}Cl^{37}Cl$	*P*-CH_2CH_3	146.96
$C_6H_3{}^{37}Cl_2$	*P*-CH_2CH_3	148.96
$C_6H_3{}^{35}Cl$	*P*-CH_2CH_3-Cl	109.99
$C_6H_3{}^{37}Cl$	*P*-CH_2CH_3-Cl	111.99
Etc.		

18.85 The presence of one bromine atom will produce in the ions that contain Br companion peaks that are separated by 2 u. Any fragment that contains Br will show this "doublet" in which the peaks are nearly but not exactly equal in intensity. Thus, seeing a mass spectrum of a compound that is known to have Br or that was involved in a reaction in which Br could have been added or substituted with such doublets, is almost a sure sign that Br is present in the compound. It is also fairly easy to detect Br atoms in the mass spectrum at 79 and 81 u, confirming their presence. If more than one Br atom is present, then a more complicated pattern is observed for the presence of the two isotopes. The possible combinations for a molecule of unknown formula with two Br atoms is $^{79}Br^{79}Br$, $^{79}Br^{81}Br$, $^{81}Br^{79}Br$, and $^{81}Br^{81}Br$. Thus, a set of three peaks (the two possibilities $^{79}Br^{81}Br$ and $^{81}Br^{79}Br$ have identical masses) will be

generated that differ in mass by two units. The center peak, which is produced by the $^{79}Br^{81}Br$ and $^{81}Br^{79}Br$ combinations, will have twice the intensity of the outer two peaks, because statistically there are twice as many combinations that produce this mass. All modern mass spectrometers have spectral simulation programs that can readily calculate and print our the relative isotopic distribution pattern expected for any compound formulation, so that it is possible to easily match the expected pattern for a particular ion with the experimental result.

18.87 C_8H_{10} will have an absorption maximum at a longer wavelength. Molecular orbital theory predicts that in conjugated hydrocarbons (molecules which contain a chain of carbon atoms with alternating single and double bonds) electrons become delocalized and are free to move up and down the chain of carbon atoms. Such electrons may be described using the one dimensional "particle in a box" model introduced in Chapter 1. According to this model, as the box to which electrons are confined lengthens, the quantized energy states available to the electrons get closer together. As a result, the energy needed to excite an electron from the ground state to the next higher state is lower for electrons confined to longer boxes. Therefore, lower energy photons, i.e. photons with longer wavelengths, will be absorbed by the C_8H_{10} molecule because it provides a longer "box" than C_6H_8.