Alkanes are known by two or more names, common names and IUPAC names. [Sec. 2.6]
The two principal sources of alkanes are petroleum and natural gas. The components of petroleum are separated by a process called refining. [Sec. 2.7A]
Pyrolysis or cracking is an industrial method used to break large molecules into smaller and more useful molecules. [Sec. 2.7A]
The refined products of petroleum are called petrochemicals. [Sec. 2.7A]
Knocking is produced by a fuel with a low octane number rating. [Sec. 2.7B]
Methane is the major constituent of natural gas. [Sec. 2.7C]
The solubility of alkanes may be predicted by means of the "like dissolves like" rule. [Sec. 2.8A]
The physical properties of alkanes depend on chain length and degree of branching. [Sec. 2.8B]
A covalent bond can be broken during the course of an alkane reaction in either of two ways, homolytically or heterolytically. [Sec. 2.10]
Alkanes undergo two types of reactions, halogenation and combustion. [Sec. 2.11]
Halogenation proceeds via a free-radical chain mechanism: (a) $R{-}H + X\cdot \rightarrow R\cdot + HX$; (b) $R\cdot + X_2 \rightarrow RX + X\cdot$; back to (a). [Sec. 2.13]
Complete combustion of alkanes yields CO_2, H_2O, and heat. [Sec. 2.14]
Cycloalkanes are saturated hydrocarbons that exist in the form of a ring. [Sec. 2.15]
The lack of free rotation of singly bonded carbons in a ring gives rise to a kind of isomerism called geometric isomerism. [Sec. 2.16]
Geometric isomers in cycloalkanes can be formed by two substituents on the same side (*cis*) or opposite sides (*trans*) of the ring. [Sec. 2.16]

Key Terms

hydrocarbons
alkanes
conformation
conformer
homologous series
homolog
isomers
isomerism
structural (constitutional) isomers
primary (1°) carbons
secondary (2°) carbons
tertiary (3°) carbons
quaternary (4°) carbon
alkyl group, R
IUPAC system of nomenclature
common (trivial) names
octane number
free radical
carbocation
carbanion
halogenation
combustion
substitution reaction
reaction mechanism
free-radical chain mechanism
geometric isomerism
configuration

Exercises

Structure and Nomenclature of Alkanes and Cycloalkanes [Secs. 2.5, 2.6, 2.15, 2.16]

2.1 Write structural formulas for the following compounds.

(a) 3-Methylheptane
(b) 2,3-Dimethylpentane
(c) 2,3-Dimethyl-4-ethylhexane
(d) 2,3,5-Trimethylhexane
(e) 2-Chloro-3-methylpentane
(f) 2-Bromo-2,3-dichlorobutane
(g) 1,1,2,2-Tetrabromopropane
(h) Methylcyclobutane
(i) *trans*-1,2-Dibromocyclopentane
(j) *cis*-1-Chloro-2-ethylcyclopropane

2.2 Give IUPAC names for the following compounds.

(a) $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_2CH_2CH_3$

(b) $CH_3C(CH_3)_2CH_2CH(CH(CH_3)_2)CH_2CH_2CH_3$

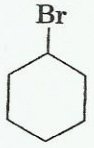
(c) $(CH_3)_3CCH_2CH_2CH_2C(CH_3)_3$

(d) CCl_3CH_3

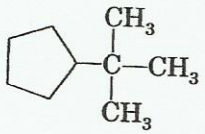
(e) $CHBr_2CHBr_2$

(f) CF_4

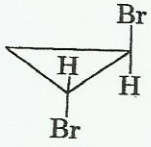
(g)



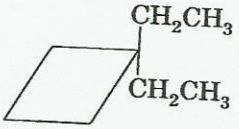
(h)



(i)



(j)



2.3 Write the structure for each of the incorrectly named compounds listed below. Explain why the given name is incorrect and give a correct name in each case.

(a) 3-Methylbutane
(b) 2-Ethylpropane
(c) 2,3-Dibromopropane
(d) *cis*-1,3-Dimethylcyclopropane
(e) 3,4-Dichloropentane
(f) 1,1,3-Trimethylbutane
(g) 2-Bromo-3-ethylbutane
(h) *trans*-1,6-Dimethylcyclohexane

Structural Isomerism and Geometric Isomerism [Secs. 2.3, 2.16]

2.4 Draw the indicated number of structural isomers of compounds for each molecular formula.

(a) C_3H_7Cl (two isomers)
(b) C_2H_7N (two isomers)
(c) C_3H_8O (three isomers)
(d) C_3H_9N (four isomers)
(e) C_4H_9Cl (four isomers)
(f) C_3H_6BrCl (five isomers)

2.5 There are seven isomeric dibromocyclohexanes, including *cis-trans* isomers, having molecular formula $C_6H_{10}Br_2$. Draw the structures of the seven compounds, using condensed formulas for the rings.

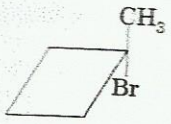
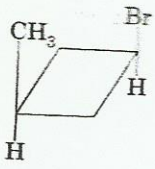
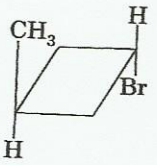
2.6 For each group of structures, identify the structural isomers, the geometric isomers, and the structures that represent the same compound.

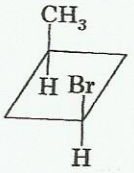
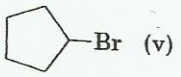
(a) $CH_3CH_2CH_2CH(CH_3)CH_3$ (i); $CH_2CH_2CH(CH_3)_2$ (ii); $CH_3CH(CH_2CH_3)CH_2$ (iii)

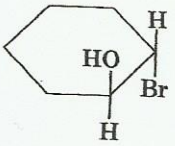
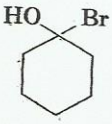
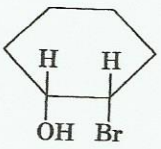
(b) $CH_2(CH_2)CH_2CH(CH_3)$ (i); $CH_2(CH_2)CH(CH_2CH_3)$ (ii); $CH_3CH(CH_2)CH_2CH_2$ (iii)

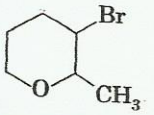
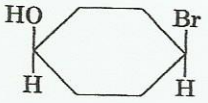
(c) $CH_3CH(Br)CH_2CH(CH_3)CH_3$ (i); $CH_3C(Br)CH_2CH_2CH_3$ (ii); $CH_3CH(CH_3)CH_2CHBrCH_3$ (iii);

$CH_3CH_2CH_2CH_2CH_2CH_2Br$ (iv)

(d)  (i);  (ii);  (iii);

 (iv);  (v)

(e)  (i);  (ii);  (iii);

 (iv);  (v)

2.7 Four possible isomers can be obtained upon monochlorination of 2,2,4-trimethylpentane. Draw partially condensed formulas for each of these compounds and name each isomer according to the IUPAC system.

Classes of Carbons and Hydrogens [Sec. 2.4]

2.8 How many 1°, 2°, 3°, and 4° carbons and hydrogens (if any) are there in 2,2,4-trimethylpentane (the alkane with an octane rating of 100)?

Physical Properties of Alkanes [Sec. 2.8]

2.9 Without referring to tables, arrange each series of compounds in order of increasing boiling point.

(a) *n*-Pentane; *n*-hexane, *n*-butane

(b) *n*-Hexane; *n*-pentane, 2-methylpentane

(c) *n*-Octane; 2,2,3-trimethylpentane, 2-methylheptane

Reactions of Alkanes and Cycloalkanes [Secs. 2.11–2.16]

2.10 Complete each of the following reactions by writing the structure of the product. If no reaction occurs, state so.

(a) $CH_3(CH_2)_3CH_3 \xrightarrow{\text{combustion}}$ **(b)**  $+ Cl_2 \xrightarrow[\text{heat}]{}$ **(c)**  $\xrightarrow{HCl}$

2.11 Draw structures for all possible monochlorinated and polychlorinated compounds that can be formed upon chlorination of ethane.

2.12 Bromination of ethane proceeds by the same mechanism as chlorination of ethane. Give the complete mechanism for the reaction, showing the initiation, propagation, and termination steps.

2.13 Isomeric compounds can sometimes be distinguished by observing the number of monochlorinated compounds that each one forms.

(a) If a compound forms three monochloro compounds, is it *n*-pentane or 2-methylbutane?

(b) If a compound forms three monochloro compounds, is it *n*-hexane or 2,3-dimethylbutane?

2.14 Draw structures, including *cis-trans* isomers, for all possible monobrominated compounds that can be formed upon bromination of methylcyclopentane.

2.15 In the chlorination of ethane, C_2H_6, the product we want is C_2H_5Cl. Which one of the following experimental conditions is likely to give the best yield of monochlorinated product? Explain why.

(a) $C_2H_6 + Cl_2 \xrightarrow[\text{uv light}]{}$ (b) $C_2H_6 + Cl_2 \xrightarrow[\text{dark, room temp}]{}$

(c) $C_2H_6 + Cl_2(\text{excess}) \xrightarrow[\text{uv light}]{}$ (d) $C_2H_6(\text{excess}) + Cl_2 \xrightarrow[\text{uv light}]{}$

2.16 In the monochlorination of ethane, trace amounts of chlorinated butanes are also found, suggesting that at some point in the reaction *n*-butane was formed. Refer to the mechanism of free-radical halogenation of alkanes in Section 2.13 and explain how *n*-butane could be formed during the chlorination of ethane.

2.17 The heat of combustion of a straight-chain alkane is 850 (±5) kcal/mole. Which alkane has undergone complete combustion?