

Alkanes and Cycloalkanes; Conformational and Geometric Isomerism

Chapter Summary

Hydrocarbons contain only carbon and hydrogen atoms. **Alkanes** are acyclic **saturated hydrocarbons** (contain only single bonds); **cycloalkanes** are similar but have carbon rings.

Alkanes have the general molecular formula C_nH_{2n+2} . The first four members of this **homologous series** are **methane**, **ethane**, **propane**, and **butane**; each member differs from the next by a $-CH_2-$, or **methylene group**. The **IUPAC** (International Union of Pure and Applied Chemistry) nomenclature system is used worldwide to name organic compounds. The IUPAC rules for naming alkanes are described in Secs. 2.3–2.5. **Alkyl groups**, alkanes minus one hydrogen atom, are named similarly except that the *-ane* ending is changed to *-yl*. The letter **R** stands for any alkyl group.

The two main natural sources of alkanes are **natural gas** and **petroleum**. Alkanes are insoluble in and less dense than water. Their boiling points increase with molecular weight and, for isomers, decrease with chain branching.

Conformations are different structures that are interconvertible by rotation about single bonds. For ethane (and in general), the **staggered** conformation is more stable than the eclipsed conformation (Figure 2.5).

The prefix *cyclo-* is used to name cycloalkanes. **Cyclopropane** is planar, but larger carbon rings are puckered. **Cyclohexane** exists mainly in a **chair conformation** with all bonds on adjacent carbons staggered. One bond on each carbon is **axial** (perpendicular to the mean carbon plane); the other is **equatorial** (roughly in that plane). The conformations can be interconverted by "flipping" the ring, which requires only bond rotation and occurs rapidly at room temperature for cyclohexane. Ring substituents usually prefer the less crowded, equatorial position.

Stereoisomers have the same order of atom attachments but different arrangements of the atoms in space. *Cis-trans* isomerism is one kind of stereoisomerism. For example, two substituents on a cycloalkane can be on either the same (*cis*) or opposite (*trans*) sides of the mean ring plane. Stereoisomers can be divided into two groups, **conformational isomers** (interconvertible by bond rotation) and **configurational isomers** (not interconvertible by bond rotation). *Cis-trans* isomers belong to the latter class.

Alkanes are fuels; they burn in air if ignited. Complete combustion gives carbon dioxide and water; less complete combustion gives carbon monoxide or other less oxidized forms of carbon. Alkanes react with **halogens** (chlorine or bromine) in a reaction initiated by heat or light. One or more hydrogens can be replaced by halogens. This **substitution reaction** occurs by a **free-radical chain mechanism**.

Reaction Summary

Combustion

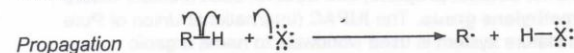
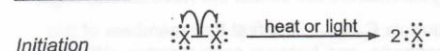


Halogenation (Substitution)



Mechanism Summary

Halogenation



Learning Objectives

1. Know the meaning of: saturated hydrocarbon, alkane, cycloalkane, homologous series, methylene group.
2. Know the meaning of: conformation, staggered, eclipsed, "dash-wedge" projection, Newman projection, "sawhorse" projection, rotational isomers, rotamers.
3. Know the meaning of: chair conformation of cyclohexane, equatorial, axial, geometric or *cis-trans* isomerism, conformational and configurational isomerism.
4. Know the meaning of: substitution reaction, halogenation, chlorination, bromination, free-radical chain reaction, chain initiation, propagation, termination, combustion.
5. Given the IUPAC name of an alkane or cycloalkane, or a halogen-substituted alkane or cycloalkane, draw its structural formula.
6. Given the structural formula of an alkane or cycloalkane or a halogenated derivative, write the correct IUPAC name.
7. Know the common names of the alkyl groups, cycloalkyl groups, methylene halides, and haloforms.
8. Tell whether two hydrogens in a particular structure are identical or different from one another by determining whether they give the same or different products by monosubstitution with some group X.

9. Know the relationship between boiling points of alkanes and (a) their molecular weights and (b) the extent of chain branching.
10. Write all steps in the free-radical chain reaction between a halogen and an alkane, and identify the initiation, propagation, and termination steps.
11. Write a balanced equation for the complete combustion of an alkane or cycloalkane.
12. Draw, using dash-wedge, sawhorse, or Newman projection formulas, the important conformations of ethane, propane, butane, and various halogenated derivatives of these alkanes.
13. Recognize, draw, and name *cis-trans* isomers of substituted cycloalkanes.
14. Draw the chair conformation of cyclohexane and show clearly the distinction between axial and equatorial bonds.
15. Identify the more stable conformation of a monosubstituted cyclohexane; also, identify substituents as axial or equatorial when the structure is "flipped" from one chair conformation to another.
16. Classify a pair of isomers as structural (constitutional) isomers or stereoisomers, and if the latter, as conformational or configurational (see Figure 2.8).

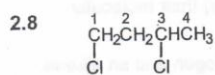
ANSWERS TO PROBLEMS

Problems Within the Chapter

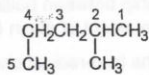
- 2.1 $C_{14}H_{30}$; use the formula C_nH_{2n+2} , where $n = 14$.
- 2.2 The formulas in parts b and d fit the general formula C_nH_{2n+2} and are alkanes. C_8H_{16} (part c) has two fewer hydrogens than called for by the alkane formula and must be either an alkene or a cycloalkane. C_7H_{18} (part a) is an impossible molecular formula; it has too many hydrogens for the number of carbons.
- 2.3
 - a. 2-methylbutane (number the longest chain from left to right)
 - b. 2-methylbutane (number the longest chain from right to left)
 The structures in parts a and b are identical, as the names show.
 - c. 2,2-dimethylpropane
- 2.4 Chlorofluoromethane; the substituents are alphabetized when more than one is present.
- 2.5

a. $CH_3CH_2CH_2Cl$	b. $(CH_3)_2CHI$	c. $(CH_3)_2CHCl$
d. $(CH_3)_3C-I$	e. $(CH_3)_2CHCH_2Br$	
f. RF; the letter R stands for any alkyl group		
- 2.6
 - a. 2-fluoropropane
 - b. 4-chloro-2,2-dimethylpentane (*not* 2-chloro-4,4-dimethylpentane, which has higher numbers for the substituents)
- 2.7

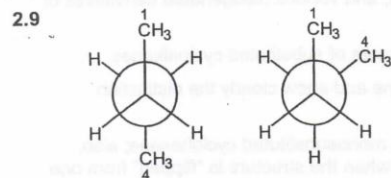
$$\begin{array}{c}
 CH_3 \\
 | \\
 CH_3CH_2CCH_2CH_3 \\
 | \\
 CH_3
 \end{array}$$



1,3-dichlorobutane



Correct name: 2-methylpentane; carbon-5 is not a substituent. It is part of the longest chain.

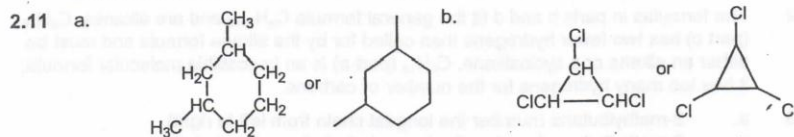


(anti)

(gauche)

Carbon-2 and carbon-3 in the chain each have two hydrogens and a methyl group attached. The staggered conformation at the left is the more stable. In the staggered conformation at the right, the two methyl substituents (large groups) come close to one another, a less stable arrangement than in the structure to the left. These conformations are referred to as *anti* and *gauche*, respectively.

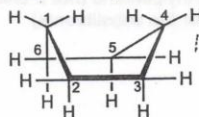
- 2.10 A cycloalkane has two fewer hydrogens than the corresponding alkane. Thus, the general formula for a cycloalkane is C_nH_{2n} .



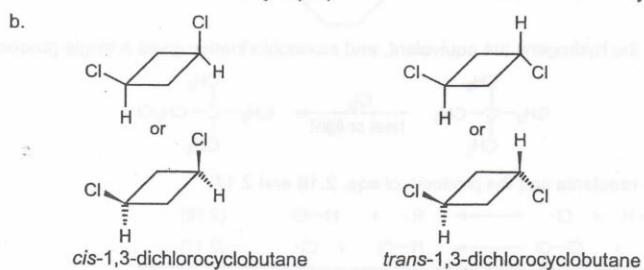
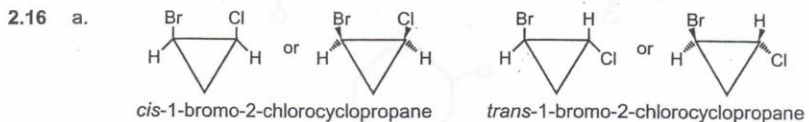
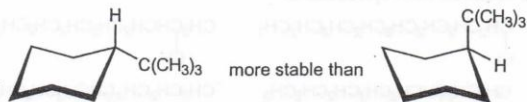
- 2.12 a. ethylcyclopentane
b. 1,1-dichlorocyclopropane
c. 1-bromo-3-methylcyclobutane

- 2.13 Since each ring carbon is tetrahedral, the H-C-H plane and the C-C-C plane at any ring carbon are mutually perpendicular.

- 2.14 If you sight down the bond joining carbon-2 and carbon-3, you will see that the substituents on these carbons are eclipsed. The same is true for the bond between carbon-5 and carbon-6. Also, two of the hydrogens on carbon-1 and carbon-4, the "inside" hydrogens, come quite close to one another. All these factors destabilize boat cyclohexane compared to chair cyclohexane.

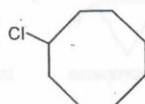
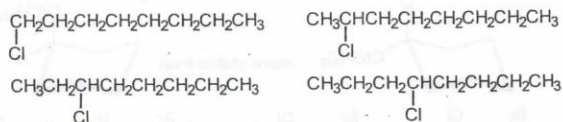


- 2.15 The *tert*-butyl group is much larger than a methyl group. Therefore, the conformational preference is essentially 100% for an equatorial *tert*-butyl group:

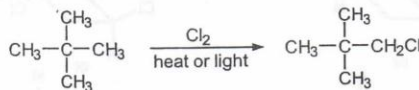


- 2.17 a. structural (constitutional) isomers
 b. configurational isomers (same bond pattern, but not interconvertible by σ -bond rotations)
 c. conformational isomers
- 2.18 a. Formaldehyde (two C–O bonds) is more highly oxidized than methanol (one C–O bond).
 b. The carbons in methanol (CH_3OH) and dimethyl ether (CH_3OCH_3) are equally oxidized. Each carbon has one C–O bond and three C–H bonds.
- 2.19 Follow eq. 2.12, but replace chloro with bromo:
- CH_3Br bromomethane (methyl bromide)
 CH_2Br_2 dibromomethane (methylene bromide)
 CHBr_3 tribromomethane (bromoform)
 CBr_4 tetrabromomethane (carbon tetrabromide)
- 2.20
- | | | |
|---|--|--|
| $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Br | $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_3$
Br | $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3$
Br |
| 1-bromopentane | 2-bromopentane | 3-bromopentane |

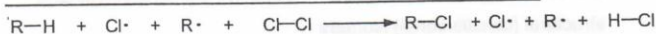
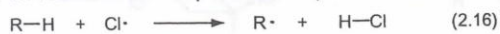
- 2.21 Four monochloro products can be obtained from octane, but only one monochloro product is obtained from cyclooctane.



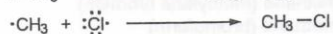
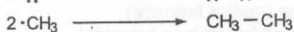
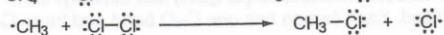
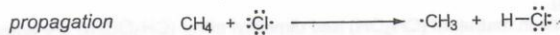
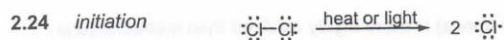
- 2.22 Yes. All the hydrogens are equivalent, and monochlorination gives a single product.



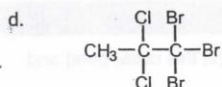
- 2.23 Add the reactants and the products of eqs. 2.16 and 2.17:



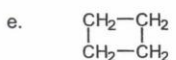
The intermediate radicals ($\text{R}\cdot$ and $\text{Cl}\cdot$) cancel and what is left is eq. 2.9:



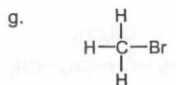
- 2.25 The second termination step in the answer to Problem 2.24 accounts for the formation of ethane in the chlorination of methane. Ethane can also be chlorinated, which explains the formation of small amounts of chloroethane in this reaction.



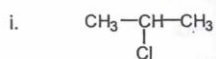
1,1,1-tribromo-2,2-dichloropropane (The placement of hyphens and commas important. Commas are used to separate numbers from numbers. Hyphens are used to separate numbers from letters. Also notice that "tribromo" comes before "dichloro" because prefixes are ignored when alphabetizing substituents.)



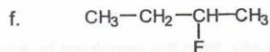
cyclobutane



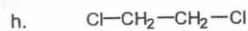
bromomethane



2-chloropropane



2-fluorobutane



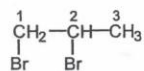
1,2-dichloroethane

2.28

	<u>Common</u>	<u>IUPAC</u>
a.	methyl bromide	bromomethane
b.	ethyl iodide	iodoethane
c.	methylene chloride (CH ₂ = methylene)	dichloromethane
d.	isopropyl iodide	2-iodopropane
e.	bromoform	tribromomethane
f.	<i>t</i> -butyl chloride	2-chloro-2-methylpropane
g.	<i>n</i> -propyl fluoride	1-fluoropropane

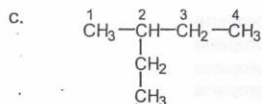
2.29

a. The numbering started at the wrong end. The name should be 1,2-dibromopropane.

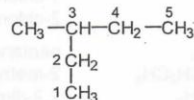


b. CH₃CH₂CH₂CH₂CH₃

The longest consecutive chain has five carbon atoms; the correct name is pentane.

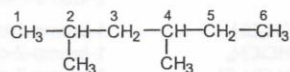


The longest chain was not selected when the compound was numbered. The correct numbering is

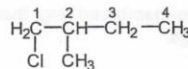


and the correct name is 3-methylpentane.

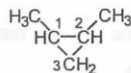
- d. The longest chain was not selected. The correct name is 2,4-dimethylhexane.



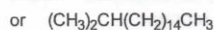
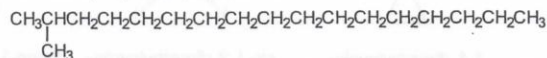
- e. The chain was numbered from the wrong end. The correct name is 1-chloro-2-methylbutane.



- f. The ring was numbered the wrong way to give the lowest substituent numbers. The correct name is 1,2-dimethylcyclopropane.



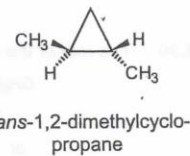
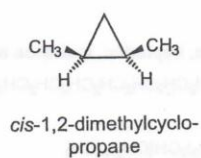
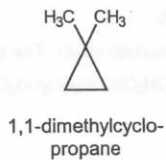
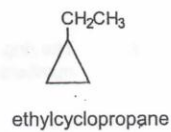
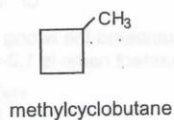
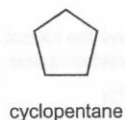
- 2.30 The root of the name, heptadec, indicates a 17-carbon chain. The correct formula is



- 2.31 Approach each problem systematically. Start with the longest possible carbon chain and shorten it one carbon at a time until no further isomers are possible. To conserve space, the formulas below are written in condensed form, but you should write them out as expanded formulas.

- a. $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$ butane
 $(\text{CH}_3)_3\text{CH}$ 2-methylpropane

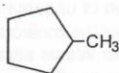
- b. $\text{CH}_3\text{CH}_2\text{CHF}_2$ 1,1-difluoropropane
 $\text{CH}_3\text{CHFCH}_2\text{F}$ 1,2-difluoropropane
 $\text{CH}_2\text{FCH}_2\text{CH}_2\text{F}$ 1,3-difluoropropane
 $\text{CH}_3\text{CF}_2\text{CH}_3$ 2,2-difluoropropane
- c. The two hydrogens can be on either the same or different carbon atoms:
 CH_2ClCF_3 2-chloro-1,1,1-trifluoroethane
 $\text{CH}_2\text{FCClF}_2$ 1-chloro-1,1,2-trifluoroethane
 CHClFCHF_2 2-chloro-1,1,2-trifluoroethane
- d. $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ pentane
 $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ 2-methylbutane
 $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_3$ 2,2-dimethylpropane
- e. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ 1-iodobutane
 $\text{CH}_3\text{CHICH}_2\text{CH}_3$ 2-iodobutane
 $(\text{CH}_3)_2\text{CHCH}_2\text{I}$ 1-iodo-2-methylpropane
 $(\text{CH}_3)_3\text{CI}$ 2-iodo-2-methylpropane
- f. $\text{CHBrClCH}_2\text{CH}_3$ 1-bromo-1-chloropropane
 $\text{CH}_2\text{BrCHClCH}_3$ 1-bromo-2-chloropropane
 $\text{CH}_2\text{BrCH}_2\text{CH}_2\text{Cl}$ 1-bromo-3-chloropropane
 $\text{CH}_2\text{ClCHBrCH}_3$ 2-bromo-1-chloropropane
 $\text{CH}_3\text{CBrClCH}_3$ 2-bromo-2-chloropropane
- 2.32 a. Start with a five-membered ring, then proceed to the four- and three-membered rings.



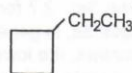
b.



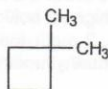
cyclohexane



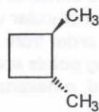
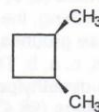
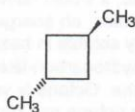
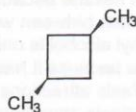
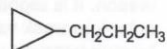
methylcyclopentane



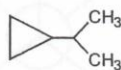
ethylcyclobutane



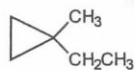
1,1-dimethylcyclobutane

*trans*-1,2-dimethylcyclobutane*cis*-1,2-dimethylcyclobutane*trans*-1,3-dimethylcyclobutane*cis*-1,3-dimethylcyclobutane

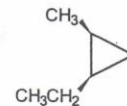
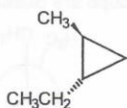
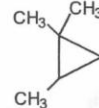
1-propylcyclopropane



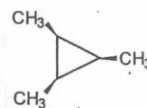
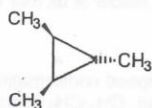
2-propylcyclopropane



1-ethyl-1-methylcyclopropane

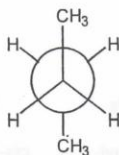
*cis*-1-ethyl-2-methylcyclopropane*trans*-1-ethyl-2-methylcyclopropane

1,1,2-trimethylcyclopropane

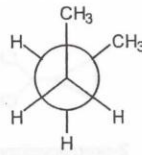
*cis,cis*-1,2,3-trimethylcyclopropane*cis,trans*-1,2,3-trimethylcyclopropane

2.33 A = methylcyclohexane and B = 2,2-dimethylbutane

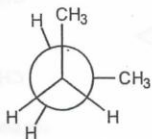
- 2.34 See Sec. 2.7 for a discussion of underlying principles. When comparing a series of alkanes, in general, the lower the molecular weight, the lower the intermolecular contact, the lower the van der Waals attractions, the less energy required to separate molecules from one another and the lower the boiling point. Thus, the hexane isomers (e and d) are expected to have lower boiling points than the heptane isomers (a, b, and c). Within a series of isomeric compounds, the greater the branching, the lower the intermolecular contact and the lower the boiling point. On these grounds, the expected order from the lowest to highest boiling point should be e, d, c, a, b. The actual boiling points are as follows: e, 2-methylpentane (60°C); c, 3,3-dimethylpentane (86°C); d, *n*-hexane (69°C); a, 2-methylhexane (90°C); b, *n*-heptane (98.4°C).
- 2.35 See Sec. 2.7 for a discussion of underlying principles. The expected order of solubility in hexane is b (water) less than c (methyl alcohol) less than a (octane). Water does not dissolve in hexane because, to do so, it would have to break up hydrogen bonding interactions between water molecules, an energetically unfavorable process. Methyl alcohol is only sparingly soluble in hexane for the same reason. It is slightly soluble because it has a small hydrocarbon-like portion that can enter into weak van der Waals attractions with hexane. Octane is very soluble with hexane because van der Waals attractions between octane and hexane and between octane and itself are nearly equal.
- 2.36 The four conformations are as follows:



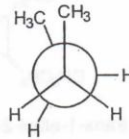
A: most stable staggered conformation



B: less stable staggered conformation (large groups are closer together)



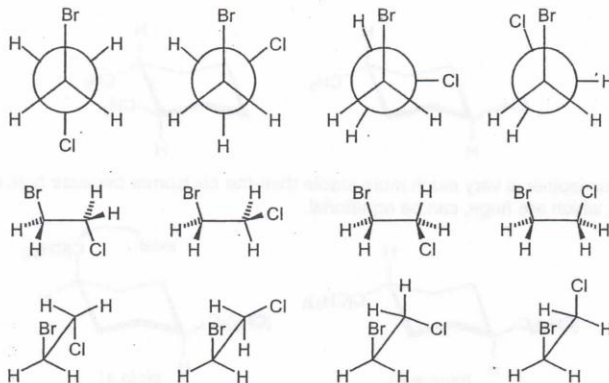
C: less stable than the staggered but more stable than the eclipsed conformation with two methyls eclipsed



D: least stable of all four conformations

Staggered conformations are more stable than eclipsed conformations. Therefore A and B are more stable than C or D. Within each pair, CH₃-CH₃ interactions (for methyls on adjacent carbons) are avoided because of the large size of these groups.

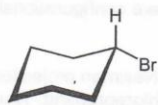
2.37



The stability decreases from left to right in each series of structures.

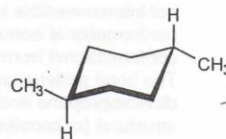
2.38

a.



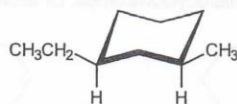
The bromo group is equatorial.

b.



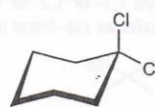
Both alkyl groups are equatorial and *trans*.

c.



Both alkyl groups are equatorial and *cis*.

d.

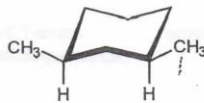


One chloro group is axial; one is equatorial.

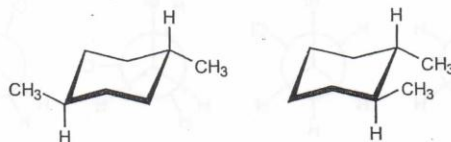
2.39 In each case, the formula at the left is named; the right-hand structure shows the other isomer.

a. *cis*-1,3-dichlorocyclohexaneb. *trans*-1-bromo-2-methylcyclohexane

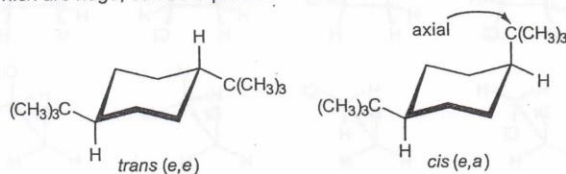
2.40 *cis*-1,3-Dimethylcyclohexane can exist in a conformation in which both methyl substituents are equatorial:



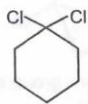
In the *trans* isomer, one methyl group must be axial. On the other hand, in 1,2- or 1,4-dimethylcyclohexane, only the *trans* isomer can have both methyls equatorial.



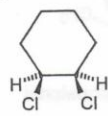
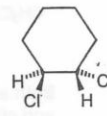
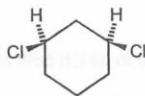
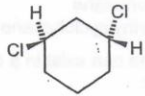
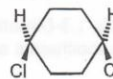
- 2.41 The *trans* isomer is very much more stable than the *cis* isomer because both *t*-butyl groups, which are *huge*, can be equatorial.



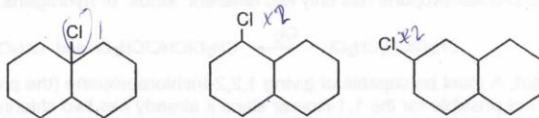
- 2.42 a. All pairs have the same bond patterns and are stereoisomers. Since they are *not* interconvertible by σ -bond rotations, they are configurational isomers.
 b. conformational isomers
 c. conformational isomers
 d. The bond patterns are *not* the same; the first Newman projection is for 1,1-dichloropropane and the second is for 1,2-dichloropropane. Thus, these are structural (or constitutional) isomers.
 e. The structures are *identical* (both represent 2-methylpentane) and are not isomers at all.
- 2.43 We can have 1,1- or 1,2- or 1,3- or 1,4-dichlorocyclohexanes. Of these, the last three can exist as *cis-trans* isomers.



1,1-dichlorocyclohexane

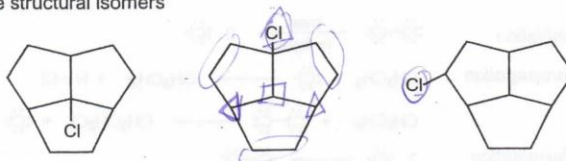
*cis*-1,2-dichlorocyclohexane*trans*-1,2-dichlorocyclohexane*cis*-1,3-dichlorocyclohexane*trans*-1,3-dichlorocyclohexane*cis*-1,4-dichlorocyclohexane*trans*-1,4-dichlorocyclohexane

- 2.44 a. Three monochlorinated structural isomers are possible.

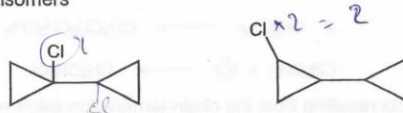


Several stereoisomers (not shown here) are possible for each structural isomer.

- b. Three structural isomers

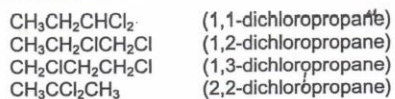


- c. Two structural isomers

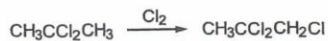


- 2.45 a. $\text{CH}_3\text{CH}_2\text{CH}_3 + 5\text{O}_2 \longrightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$
 b. $\text{CH}_3(\text{CH}_2)_3\text{CH}_3 + 8\text{O}_2 \longrightarrow 5\text{CO}_2 + 6\text{H}_2\text{O}$
 c. $2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + 13\text{O}_2 \longrightarrow 8\text{CO}_2 + 10\text{H}_2\text{O}$
- 2.46 a. $\text{CH}_3\text{CH}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow[\text{or light}]{\text{heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}(\text{Cl})\text{CH}_3 + \text{HCl}$
 1-chloropropane 2-chloropropane
- b. + $\text{Br}_2 \xrightarrow[\text{or light}]{\text{heat}}$ + HBr
 bromocyclopentane
- c. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + 10\text{Cl}_2 \xrightarrow[\text{or light}]{\text{heat}} \text{CCl}_3\text{CCl}_2\text{CCl}_2\text{CCl}_3 + 10\text{HCl}$
 decachlorobutane

- 2.47 The four possible structures are



Only the last structure has all hydrogens equivalent and can give only one trichloro compound. This structure must, therefore, be C:

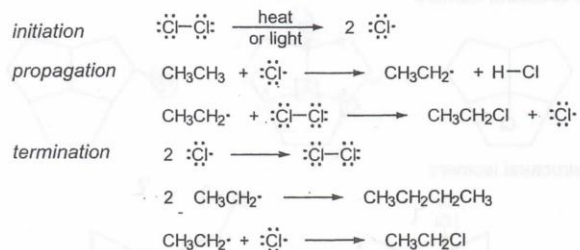


1,3-Dichloropropane has only two different "kinds" of hydrogens. It must be D:



Next, A must be capable of giving 1,2,2-trichloropropane (the product from C). This is not possible for the 1,1-isomer since it already has two chlorines on carbon-1. Therefore, A must be 1,2-dichloropropane; it can give the 1,2,2-trichloro product (as well as 1,1,2- and 1,2,3-). By elimination, B is $\text{CH}_3\text{CH}_2\text{CHCl}_2$.

2.48 The equations follow the same pattern as in eqs. 2.16 through 2.21.



By-products resulting from the chain-termination steps would be butane and any chlorination products derived from it.