# PROBLEMS in

# ORGANIC CHEMISTRY

## A Functional Group Approach

by
RALPH DANIELS
and
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# PREFACE

The authors believe the introductory course in Organic Chemistry can be mastered most easily through an understanding of the concept of the functional group and the reaction type. For this reason the problems in this book are strongly oriented toward the chemical and physical properties of functional groups. For further emphasis there is presented in the introduction a list of common functional groups and common types of reactions.

The scope of the problems is that associated with a one year course in Organic Chemistry devoted to the fundamental concepts and theory as well as to the presentation of the chemical and physical properties of organic compounds. The material is presented from the integrated point of view—arenes are treated as a class of hydrocarbons and are introduced after alkynes.

Each functional group is treated in a separate chapter. Each chapter contains a section on the nomenclature related to that functional group. This is developed in considerable detail because frequently this aspect of organic chemistry is described to a limited extent in textbooks and in some instances, neglected entirely.

The section on nomenclature is followed by a chart or (charts) summarizing the important reactions of the functional group. A single, simple compound is used as an example and its transformations are presented in a manner which the authors believe highlight the reactions of the functional group as well as the class of compound produced.

The problems themselves appear after the summary chart and are grouped into the following categories.

(1) Theoretical considerations related to the functional group.
(2) Nomenclature.
(3) Reactions of the functional group.
(4) Syntheses of compounds containing the functional group.
(5) Distinguishing between compounds of similar structure but different functional groups.
(6) Separation by chemical means of compounds of similar structure.
(7) Determination of the structure of an unknown compound through degradative data.
(8) Uses of compounds having a given functional group.

In addition to chapters devoted to specific functional groups, there are chapters dealing with chemical bonding in organic compounds, geometrical isomerism, optical isomerism and a review chapter.

Throughout the book an attempt has been made to guide the student in solving problems in a meaningful and profitable manner. To this end the authors have developed certain forms for the presentation of the answers which are described when a new type of problem is first encountered.

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# FUNCTIONAL GROUPS AND TYPES OF REACTIONS

## I. *Definition of a "FUNCTIONAL GROUP"*

A FUNCTIONAL group is characteristic of a class of organic compounds and represents an atom or a unique combination of atoms which undergoes a reaction with a given reagent. During this reaction a new class of organic compounds is formed.

## II. *FUNCTIONAL GROUPS*

1. Acetal
2. Acetylide anion
3. Acid anhydride
4. Acid halide
5. Active methylene
6. Alcohol [state if 1°, 2°, or 3°]
7. Aldehyde
8. Alkene [if conjugated, state type]
9. Aliphatic group attached to an aromatic ring
10. Alkoxide anion
11. Alkyne
12. Amide
13. Amine [state if aliphatic or aromatic and if 1°, 2° or 3°]
14. Amine oxide
15. Ammonium cation
16. Arene
17. Azo
18. Azomethine
19. Azoxy
20. Carbanion [e.g. Grignard reagents, organometallo compounds]
21. Carboxylate anion
22. Carboxylic acid
23. Cycloalkane [state if 3- or 4-membered]
24. Diazonium cation
25. Disulfide
26. Epoxide
27. Ester
28. Ether
29. Halo [state if aliphatic, allylic, aromatic, benzyl or vinyl]
30. Hemiacetal
31. Hetereoaromatic
32. Hydrazine
33. Hydrazone
34. Hydroxylamine
35. Imide
36. Isocyanate
37. Isocyanide
38. Isothiocyanate
39. Ketal
40. Ketone
41. Mercaptal
42. Mercaptide anion
43. Mercaptol
44. Nitrate
45. Nitrile
46. Nitrite
47. Nitro
48. Nitroso [state if attached to C *or* N]
49. Oxime
50. Phenol
51. Phenoxide anion
52. Phosphate
53. Sulfate
54. Sulfide
55. Sulfonamide
56. Sulfonate anion
57. Sulfonate ester
58. Sulfone
59. Sulfonic acid
60. Sulfonyl halide
61. Sulfoxide
62. Thiol
63. Thiophenol
64. Thiophenoxide anion
65. Thiourea
66. Urea
67. Urethan [carbamate]

# CONTENTS

# Chapter 1

## INTRODUCTION

1. Define the following terms in words and give two *specific* examples of each:

   A. Electrovalent bond
   B. Nucleophilic reagent
   C. Polar bond
   D. Electrophilic reagent
   E. Covalent bond
   F. Dipole
   G. Coordinate covalent bond
   H. Non-polar solvent

2. Write electronic structures for the following:

   A. Potassium fluoride
   B. Sodium chloride
   C. Ammonia
   D. Lithium hydroxide
   E. Aluminum bromide
   F. Ammonium sulfate
   G. Iodine monochloride
   H. Hydrogen chloride
   I. Sodium hydride
   J. Nitric acid
   K. Carbon dioxide
   L. Carbon monoxide
   M. Boron trifluoride
   N. Calcium carbonate

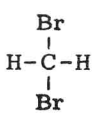
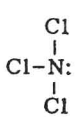
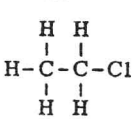
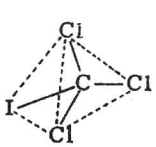
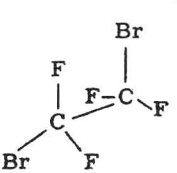
3. Arrange the following elements in order of increasing electronegativity:

   A. Nitrogen, oxygen, carbon, chlorine
   B. The halogens
   C. Selenium, sulfur, tellurium, oxygen
   D. Arsenic, nitrogen, phosphorus, bismuth, antimony.

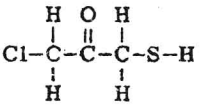
4. State which atom in the following compounds is the more electronegative:

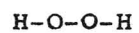
   A. Boron trifluoride
   B. Ammonia
   C. Carbon dioxide
   D. Water
   E. Iodine trichloride
   F. Nitrogen trichloride

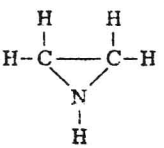
5. Which of the following molecules are polar? Why?

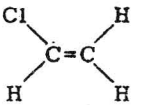
   A. 
   B. S=C=S
   C. 
   D. $CI_4$
   E. I-Cl
   F. 
   G. 
   H. 

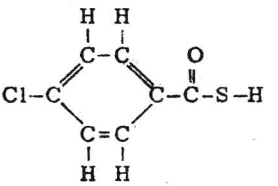
6. In the molecules below, indicate which *bonds* are *polar*.

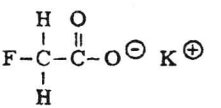
A. 

B. 

C. 

D. 

E. 

F. 

# Chapter 2

# ALKANES AND CYCLOALKANES

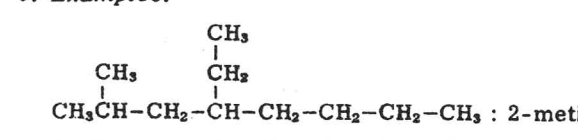
## NOMENCLATURE

A. *ALKANES* (systematic nomenclature): In all systematic notations a *STEM* name is assigned to a given number of carbon atoms. The rules for determining the number of carbon atoms to be included in the stem are given in the nomenclature for each class of organic compounds.

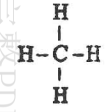
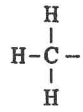
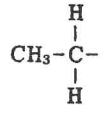
The stem names are given below together with the number of carbon atoms involved.

| Number of carbon atoms | STEM | Number of carbon atoms | STEM |
|---|---|---|---|
| 1 | METH | 7 | HEPT |
| 2 | ETH | 8 | OCT |
| 3 | PROP | 9 | NON |
| 4 | BUT | 10 | DEC |
| 5 | PENT | 11 | UNDEC |
| 6 | HEX | 12 | DODEC |

1. Select the *longest continuous chain* of carbon atoms in the molecule.
2. Number consecutively each carbon atom of this longest chain. Start with that end of the chain that assigns the *lower set of numbers* to the groups situated on the chain.
3. The identity and location of these groups situated on the chain are given by writing
   a. The number of the carbon atom to which it is attached, followed by
   b. The group name obtained by adding the letters YL to the stem name [see (5) below for a list of group names].
4. *NAME:* number of carbon atom to which first group is attached-the name of that group-number and name associated with second substituent-etc. STEM [associated with the longest chain determined in 1 and 2 above] ANE.
5. Names and structures of some alkanes and groups associated with a given number of carbon atoms [see table].
6. *Examples:*

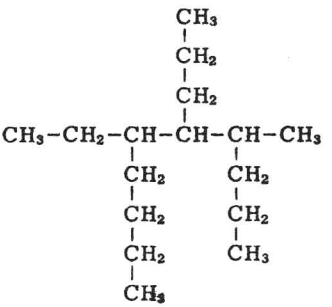


## NAMES AND STRUCTURES OF SOME ALKANES AND GROUPS ASSOCIATED WITH A GIVEN NUMBER OF CARBON ATOMS

| Structure of alkane | ALKANE [Stem+ANE] | Number of carbon atoms | ALKYL Group [Stem+YL] | Structure of Alkyl Group |
|---|---|---|---|---|
|  | METHANE | 1 | METHYL |  |
| $CH_3-CH_3$ | ETHANE | 2 | ETHYL |  |
| $CH_3-CH_2-CH_3$ | PROPANE | 3 | PROPYL | $CH_3-CH_2-CH_2-$ |
| $CH_3-CH_2-CH_2-CH_3$ | BUTANE | 4 | BUTYL | $CH_3-CH_2-CH_2-CH_2-$ |
| $CH_3-CH_2-CH_2-CH_2-CH_3$ | PENTANE | 5 | PENTYL | $CH_3-CH_2-CH_2-CH_2-CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_3$ | HEXANE | 6 | HEXYL | $CH_3CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ | HEPTANE | 7 | HEPTYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | OCTANE | 8 | OCTYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | NONANE | 9 | NONYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | DECANE | 10 | DECYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | UNDECANE | 11 | UNDECYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$ |
| $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$ | DODECANE | 12 | DODECYL | $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2-$ |

*NOTE* the longest chain has EIGHT carbon atoms. [There are 3 carbon, 6 carbon and 7 carbon chains] but rule 1 requires the selection of the longest chain].

*NOTE* that the numbering of the longest chain began with the left hand since the number assigned to the carbon atom holding the methyl group is 2 and that assigned to the carbon atom holding the ethyl group is 4. [The numbers assigned starting from the right end would be 7 and 5 respectively.

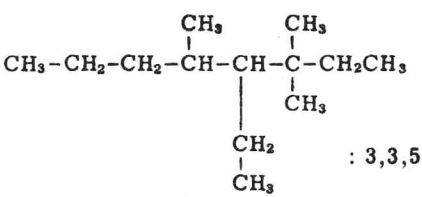


: 4-methyl-5-propyl-6-ethyldecane

*NOTE* that the longest continuous chain may not lie in a straight line but it is to be selected from among all of the chains apparent within the structure [There are 5 carbon, 6 carbon, 7 carbon, 8 carbon and 9 carbon chains].

7. Repeated groups: When a given group appears more than once, they are collected and recorded as follows
   a. Write consecutively the numbers of the carbon atoms to which the groups are attached.
   b. Then write POLYSTEMYL where "poly" is

| | |
|---|---|
| DI | if the group appears twice |
| TRI | if the group appears thrice |
| TETRA | if the group appears four times |
| PENTA | if the group appears five times |
| ETC. | |



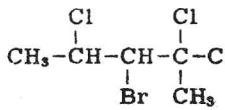
: 3,3,5-trimethyl-4-ethyloctane

*NOTE* that each of the methyl groups on carbon atom 3 is designated by a number in the name.

8. Halogen atoms are considered as HALO groups on the hydrocarbon chain:

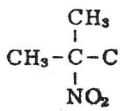
| Halogen | Name of Group | Formula |
|---|---|---|
| Fluorine | FLUORO | -F |
| Chlorine | CHLORO | -Cl |
| Bromine | BROMO | -Br |
| Iodine | IODO | -I |

*Examples:*



: 2,4-dichloro-3-bromo-2-methylpentane

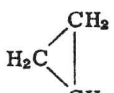
9. Similarly, the nitro group [$-NO_2$] is treated as a substituent on the hydrocarbon chain.



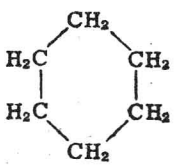
: 2-methyl-2-nitropropane

B. *CYCLOALKANES*

1. Unsubstituted rings are named by totaling the number of carbon atoms in the ring.
   NAME: CYCLOSTEM [determined in 1] ANE

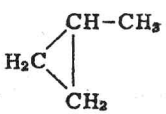


cyclopropane

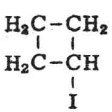


cyclohexane

2. Monosubstituted rings are named by writing
   a. The name of the group
   b. Then the name of the parent cycloalkane
   c. Examples

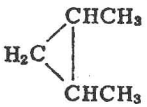


: methylcyclopropane

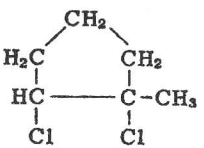


: iodocyclobutane

3. Polysubstituted rings are named by indicating the location of the groups by means of numbers. To do this:
   a. Start with a ring carbon atom that carries a group.
   b. Proceed to number the carbon atoms in the ring *consecutively*, clockwise or counterclockwise, so that the remaining groups are associated with carbon atoms with the lower set of numbers
   c. Of all the possible carbon atoms to use under *a*, choose the one that assigns the lowest set of numbers to the carbon atoms holding the groups.
   d. *NAME:* numbers and names of the groups [determined in a, b, and c] CYCLOSTEM [determined in b] ANE.

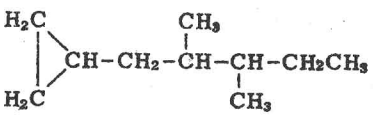


: 1,2-dimethylcyclopropane

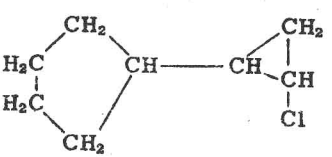


: 1-methyl-1,2-dichlorocyclopentane

4. The use of the cyclic system as a substituent. Frequently a structure cannot be named readily as a cycloalkane. In these cases it is possible to name the cyclic system as a group on an alkane chain. The group name is then : CYCLOSTEMYL.



: 1-cyclopropyl-2,3-dimethylpentane



: 1-chloro-2-cyclopentylcyclopropane

## PROBLEMS

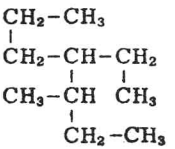
1. For the compounds below write
   (1) Empirical formulas
   (2) Molecular formulas
   (3) Structural formulas
   (4) Electronic formulas

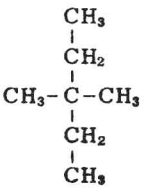
   A. Ethane
   B. Iodomethane
   C. Cyclopropane
   D. 1,3-Dichlorobutane

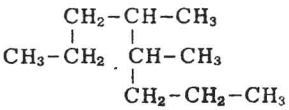
2. Draw the structures of the following compounds.

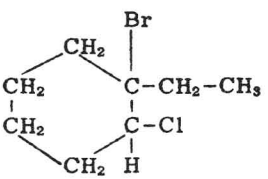
A. 1-Bromo-2-methyl-3-ethylcyclobutane
B. 4,6-Dimethyl-4,6-dipropylnonane
C. 2,3,4-Trichloro-3-methyl-4,5-diethyldecane
D. Isopentane
E. 3-Cyclopropylheptane
F. 2,3,4-Trimethyloctane
G. 1,3,3-Trimethyl-5-ethylcycloheptane
H. 4,4-Dipropylheptane
I. 1,1,1-Trifluoro-5-butylnonane
J. 6-Pentyldodecane
K. 2,4,5-Tribromo-2-methyl-4-propyloctane

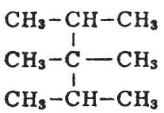
3. Name the following compounds by the I.U.C. method.

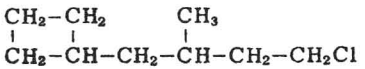
A. 

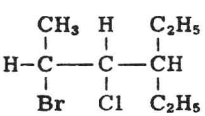
B. 

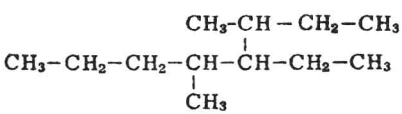
C. 

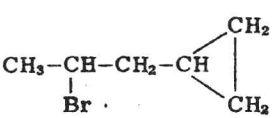
D. 

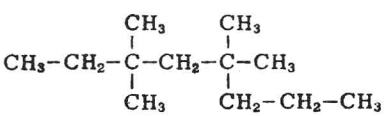
E. 

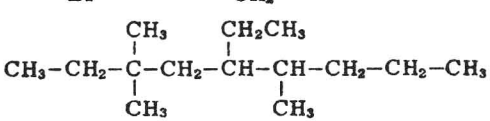
F. 

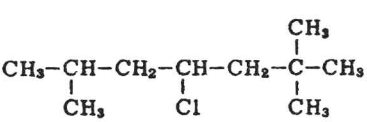
G. 

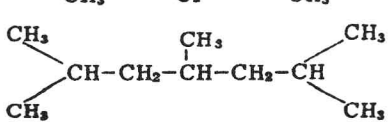
H. 

I. 

K. 

J. 

L. 

M. 

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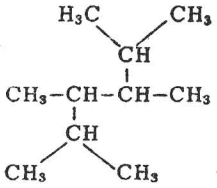

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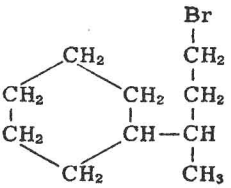

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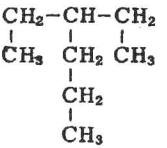

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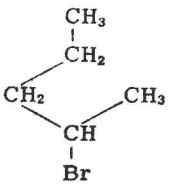

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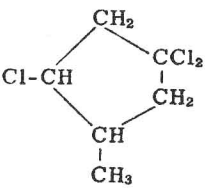

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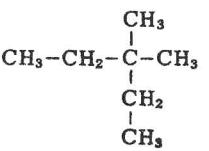

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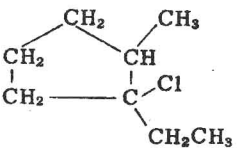

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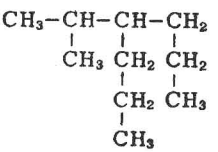

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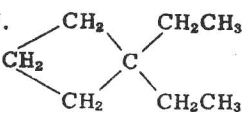

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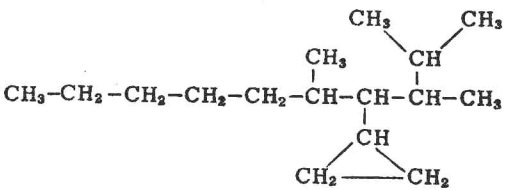

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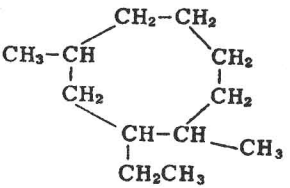

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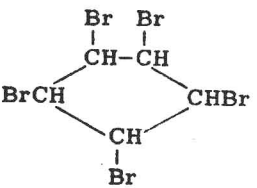

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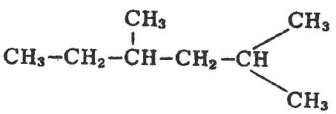


4. Complete the following equations by recording the required information. This is to be done by drawing a table identical to that shown in the example.

*NOTES:* (a) Occasionally, a given reaction cannot be classified easily into one of the reaction types given on page viii.
(b) You may not be able to name all of the compounds given below.

*EXAMPLE:* Cyclobutane + hydrogen bromide

*ANSWER:*

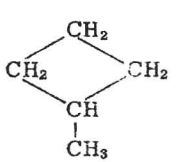
| Reactants | Reagents | Products | |
|---|---|---|---|
| $CH_2—CH_2$<br>$\vert \quad \vert$<br>$CH_2—CH_2$ | HBr → | $CH_3CH_2CH_2CH_2Br$ | *Group (s) reacting:* Four-membered cycloalkane |
| | | | *Group (s) formed:* Aliphatic halo |
| *Name:* Cyclobutane | | *Name:* 1-Bromobutane | *Reaction type:* Electrophilic addition |

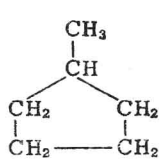
A. Cyclopropane + chlorine
B. Cyclobutane + hydrogen chloride
C. Cyclopentane + hydrogen bromide
D. Methylcyclobutane + bromine
E. 2-Cyclopropylpropane + aq. potassium permanganate
F. Cyclobutane + conc. sulfuric acid
G. 1,2,3-Trimethylcyclopropane + hydrogen [Pt catalyst]
H. 1-Methyl-2,3-dibromocyclohexane + chlorine
I. Cyclopropylmagnesium bromide + water
J. Cyclopropane + conc. sulfuric acid
K. Iodocyclobutane + magnesium [dry ether]
L. Methylcyclopropane + potassium permanganate

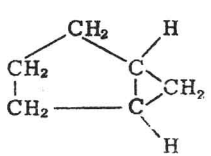
5. In a manner identical to question 4, answer the following question.

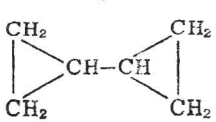
The compounds shown below are treated independently with the following reagents:

(1) Chlorine gas
(2) Hydrogen bromide
(3) Hydrogen [Pt catalyst]
(4) conc. Sulfuric acid.

A. 

B. 

C. 

D. 

E.