THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS

A LABORATORY MANUAL

BY
RALPH L. SHRINER
Professor of Chemistry in Indiana University
AND
REYNOLD C. FUSON
Professor of Chemistry in the University of Illinois

SECOND EDITION

NEW YORK
JOHN WILEY & SONS, INC.
LONDON: CHAPMAN & HALL, LIMITED

8/42

PRINTED IN THE U. S. A.

THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS

PREFACE TO THE SECOND EDITION

The past five years have witnessed the development of many new and improved methods for the identification of organic compounds. There is evidence too of a more widespread appreciation of the peculiar value of identification courses in teaching. This revision has been prepared with the object of incorporating the developments along these two fronts.

From the pedagogical viewpoint, changes have been made primarily for clarification. To this end the original nine chapters have been revised and a new chapter has been created by placing the tables of compounds in a separate chapter. These tables have been arranged in alphabetical order. Many new compounds and a large number of new derivatives have been included. The discussion of methods for the preparation of derivatives and the laboratory procedures form another chapter. Here again the alphabetical order has been followed. This affords easy correlation of the discussion and procedures with the tables. This correlation has been further facilitated by improved indexing.

To the chapter on problems has been added a discussion of the modes of attack and the methods of reasoning involved in deducing structures from experimental observations. It shows the advantages gained by a systematic procedure as opposed to cut-and-try methods.

The new classification tests, procedures for the preparation of derivatives and special laboratory methods which appear in this edition have been subjected to thorough testing by use with classes. Many others have been cited.

The general scheme to be followed in the identification of unknown compounds has not been altered. It still requires the student to exercise his own judgment at every step in the process. Renewed emphasis has been placed on the idea that the primary purpose of courses in identification is to teach organic chemistry rather than merely to acquaint the student with a system of analysis.

R. L. S.
R. C. F.

URBANA, ILLINOIS
April, 1940

PREFACE TO THE FIRST EDITION

Laboratory courses designed to teach methods of identification of organic compounds have become increasingly popular during the past twenty-five years. Since the foundations in this field were laid by Mulliken, whose classic work, "The Identification of Pure Organic Compounds," was published in 1904, several other excellent treatises of the subject have appeared, and the teaching of systematic identification has become widespread.

The importance of this type of course in the training of the chemist is now universally recognized. The ability to identify compounds—valuable as it is to organic chemists—is, however, not the primary reason for the great popularity of laboratory courses in the subject. The great difference between this and other types of laboratory courses usually included in chemical curricula is that as yet no scheme has been devised which reduces this work to the mere following of directions. At every step in the identification of compounds by present methods the student is required to exercise his own judgment. The student's faculty for careful observation, his ability to make correct deductions from his observations and his originality in planning his work are at a premium in this type of course. From this point of view it is obvious that this sort of training is the best kind of experience for those preparing for research. In this work students not only become aware of the necessity for research but also are introduced to the methods which it involves.

A natural and important outgrowth of this interest in identification methods is the large amount of research which has been done recently in this field, particularly in connection with the preparation of derivatives suitable for characterization and identification work. A consequence of this is that the subject matter of these courses is in constant need of revision.

The present book is the outgrowth of several years of experience with the subject both on the pedagogical side and from the research point of view. Interest in this work at the University of Illinois was initiated by Professor C. G. Derick, who first gave a course of this sort in 1908. The course was subsequently developed by Professor Oliver Kamm, whose excellent textbook on the subject appeared in 1922. The laboratory exercises herein presented are those used at the present time at the University of Illinois in a one-semester course of two three-hour laboratory periods a week. The work is of such nature, however, that it can be readily adapted to longer or shorter terms by merely increasing or decreasing the number of unknown compounds assigned for identification. The course is designed for students who have had a year of organic chemistry.

In the preparation of the book, use has been made of many methods to be found in works of a similar nature. Chief among these are Mulliken's "The Identification of Pure Organic Compounds," Kamm's "Qualitative Organic Analysis," Clarke's "Handbook of Organic Analysis," Staudinger's "Introduction to Qualitative Organic Analysis," Porter, Stewart and Branch's "Methods of Organic Chemistry" and Bargellini's "Esercizi numerici di chimica organica." To the authors of these, grateful acknowledgment is hereby made. For many of the innovations contained in this book the authors are indebted to other teachers of the subject here and elsewhere. Throughout the preparation of the manuscript Professor C. S. Marvel has rendered constant and invaluable assistance. Professors John R. Johnson, A. W. Ingersoll, S. M. McElvain, G. H. Coleman, Wallace R. Brode, Ralph Connor and C. F. H. Allen have all contributed helpful suggestions which the authors gladly acknowledge. Finally, to the hundreds of students who have used these directions at the University of Illinois and who have been the final judges of the worth of the new features which appear in this book—to these, especial acknowledgment is made for indispensable assistance.

R. L. S.
R. C. F.

URBANA, ILLINOIS
September, 1935

CONTENTS

CHAPTER I

INTRODUCTION

Organic compounds are so numerous and of such wide variety that the problem of identification assumes formidable proportions. For generations organic chemists have wrestled with the general problem, evolving ever more elaborate systems of dividing and subdividing the known compounds. Classifications have been made on the basis of elementary composition, melting points, boiling points, chemical reactions, color, solubility and many other properties.

The general method used in identifying an unknown compound has become traditional in its main aspects. Indeed, from the time of Liebig the procedure has invariably involved (*a*) measurement of certain physical constants, (*b*) quantitative analysis for the elements and (*c*) selected chemical tests, the three types of determinations being carried out in the order of mention.

The method herein set forth is designed for the identification of compounds which are known, that is, which have been previously characterized. The essential problem involved is to find in the literature a compound whose physical and chemical properties are identical with those possessed by the unknown compound whose identity is sought. The problem, therefore, resolves itself into two parts—a determination of certain of the properties of the unknown compound and a search of the literature for the description of a compound which has the properties observed in the laboratory.

As will appear in what follows, identification can usually be accomplished by reference to only a few of the characteristics of the compound in question. And nearly always the process may be facilitated by beginning the literature search before all the necessary experimental data have been accumulated. A knowledge of a small number of these will usually enable one to exclude from consideration all but a very few of the known compounds. A study of the descriptions given for these few remaining possibilities will then serve as a guide in the selection of other properties for determination and comparison.

A qualitative analysis of the compound for the elements is, of course, one of the first steps to be taken in the process of identification. The other readily determinable experimental data which are most useful in the literature search are the more common physical properties such as the melting point, the boiling point, the density and the solubility. In addition to a knowledge of the elements present in the compound and the above-mentioned properties of it, it is also necessary to know its behavior toward certain typical reagents. These reagents are so chosen as to enable one to use the results to allocate the compound to a certain homologous series or to a particular class of compounds.

The procedure in outline form is, therefore as follows:

A. Examination of the compound to be identified.
   1. Determination of the physical constants.
   2. Qualitative analysis for the elements.
   3. Study of solubility.
   4. Classification by reference to the behavior towards certain typical reagents.

B. A search of the literature referring to the class to which the unknown compound has been shown to belong.

C. Experimental work designed to furnish additional data which are necessary to complete the identification. This step usually consists in the preparation of one or more suitable derivatives of the unknown compound.

Before the identification of unknown compounds can be profitably undertaken it is necessary for the student to have some preliminary practice in the determination of solubilities and in the use of reagents in classifying compounds. These two assignments will, therefore, precede the examination of unknown compounds and will be taken up in the order of mention.

CHAPTER II

THE SOLUBILITY OF ORGANIC COMPOUNDS

The Solubility Classes

The division of organic compounds into large classes for the purpose of identification work may be effected on the basis of some common property such as volatility or solubility. Several writers, notably Kamm and Staudinger, have used solubility as a means of making such a classification. For this purpose water, ether, dilute acids, dilute alkalies and cold concentrated sulfuric acid have been most frequently employed as solvents. The classification scheme presented below is an extension of this idea and involves the use of the following solvents: water, ether, 5 per cent sodium hydroxide solution, 5 per cent hydrochloric acid, 5 per cent sodium bicarbonate solution, cold concentrated sulfuric acid and 85 per cent phosphoric acid.

The general scheme is shown in Fig. 1. Compounds are first divided into two great groups according to their solubilities in water. Each of these groups is then subdivided by the use of other solvents. The water-soluble compounds are divided into two classes—those soluble in ether (Class S_1) and those insoluble in ether (Class S_2).

By use of 5 per cent sodium hydroxide solution and 5 per cent hydrochloric acid, the compounds of the water-insoluble group are subdivided into three categories—acidic, basic and neutral compounds. The acidic compounds are separated into two classes by reference to their solubilities in sodium bicarbonate solution. Class A_1 includes those which are soluble and Class A_2 those which are insoluble in this reagent. The basic compounds are not further divided; they form Class B.

The problem of classifying neutral compounds is greatly simplified by making a separation on the basis not of solubility but of differences in elementary composition. Compounds containing

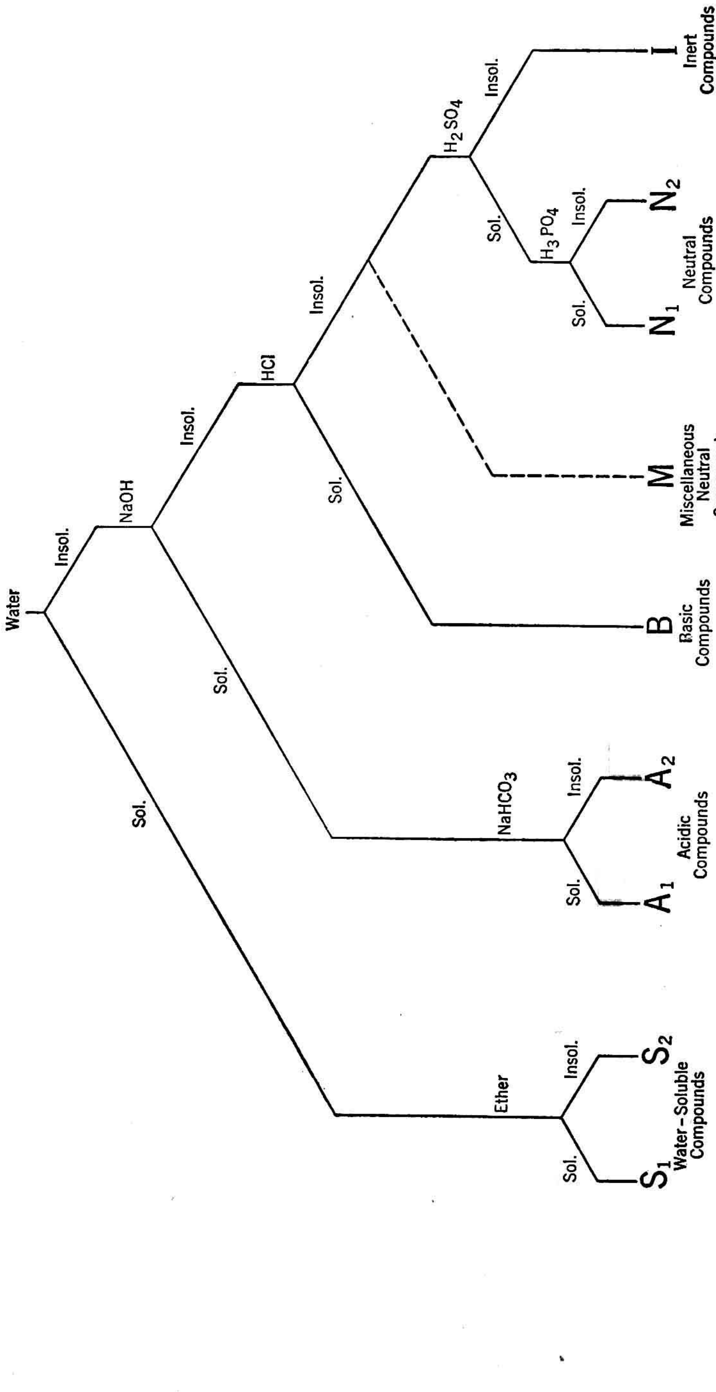

FIG. 1.—Division of Organic Compounds into Solubility Classes.

no elements other than carbon, hydrogen, oxygen and the halogens are placed in a separate division. This leaves a miscellaneous collection of compounds containing nitrogen, sulfur and other elèments of less common occurrence. These constitute Class M.

The remainder of the neutral compounds are subdivided by use of sulfuric acid. Those which are insoluble—the inert compounds—form Class I. The soluble compounds are further classified by reference to their solubilities in syrupy phosphoric acid and are put in Class N_1 or Class N_2, depending, respectively, on whether they are soluble or insoluble in this acid.

An examination of Fig. 1 shows that the solubility tests required in order to classify compounds of the various classes are as indicated in Table I.

TABLE I

Class	Water	Ether	NaOH	$NaHCO_3$	HCl	H_2SO_4	H_3PO_4
S_1	+ *	+					
S_2	+	−					
A_1	−		+ †	+			
A_2	−		+ †	−			
B	−		−		+		
M	−		−		−		
N_1	−		−		−	+	+
N_2	−		−		−	+	−
I	−		−		−	−	

* + Denotes solubility. − Denotes insolubility.

† If a compound contains nitrogen its solubility in hydrochloric acid should also be tested to see whether or not it is amphoteric. If it is soluble in hydrochloric acid much can be gained by placing it in class A_1(B) or A_2(B).

From the foregoing table it will be apparent that in identifying a compound we gain an enormous advantage by first assigning it to one of the nine solubility classes. This will be made clearer if we now consider each class separately.

Class S_1: Compounds soluble in water and in ether. In this class are found almost all compounds of low molecular weight except (*a*) low-molecular-weight hydrocarbons and their halogen derivatives—these fall in Class I; and (*b*) low-molecular-weight compounds which are strongly polar—these belong in Class S_2.

Class S_2: Compounds soluble in water and insoluble in ether. Salts of all kinds (provided, of course, that they are soluble in water), many polyhydroxy compounds, polybasic acids, hydroxy acids, amino acids, as well as some amides, amines and sulfur derivatives are in this class. In many cases benzene may be profitably substituted for ether in order to decide between Classes S_1 and S_2.

Class A_1: Compounds insoluble in water and soluble in both sodium hydroxide solution and in sodium bicarbonate solution. Acids and a few negatively substituted phenols such as picric acid and *s*-tribromophenol make up this class.

Class A_2: Compounds insoluble in water and in sodium bicarbonate solution and soluble in sodium hydroxide solution. Weakly acidic compounds belong in this class. Oximes, imides, amino acids, sulfonamides of primary amines, primary and secondary nitro compounds, enols, phenols and certain mercaptans make up this class.

Class B: Compounds insoluble in water and in alkali but soluble in dilute hydrochloric acid. Amines make up this class. Diaryl- and triarylamines are exceptions, being insoluble in 5 per cent hydrochloric acid. Amphoteric compounds are classed as A_1(B) or A_2(B).

Class M: Neutral compounds which are insoluble in water and which contain elements other than carbon, hydrogen, oxygen and the halogens. Nitro compounds, amides, negatively substituted amines, nitriles, azo compounds, hydrazo compounds, sulfones, sulfonyl derivatives of secondary amines, mercaptans, thio ethers and many less commonly occurring types of compounds are classified in the miscellaneous group.

Class N_1: Neutral compounds which are insoluble in water and soluble in both sulfuric and phosphoric acids. Those alcohols, aldehydes, methyl ketones, alicyclic ketones and esters which have fewer than nine carbon atoms fall in this class.

Class N_2: Neutral compounds which are insoluble in water and in syrupy phosphoric acid and soluble in sulfuric acid. All aldehydes, alcohols, ketones and esters, containing more than nine carbon atoms, quinones, ethers and unsaturated hydrocarbons are the principal types of compounds of this class. Anhydrides, lactones and acetals may be found here as well as in Classes S_1 and N_1.

Class I: Compounds which are insoluble in water and which dissolve in none of the reaction solvents. Saturated aliphatic hydrocarbons, aromatic hydrocarbons, and halogen derivatives of these constitute the inert class.

Laboratory Exercises in Solubility

In this work a compound will be said to be soluble in a given solvent if 0.2 cc. (0.1 g. of a solid compound) of the solute dissolves in 3 cc. of the solvent at room temperature. The solubility determinations will be carried out according to the following directions.

Place 0.2 cc. (0.1 g. of a solid) of the compound in a test tube and add in portions 3 cc. of solvent. Shake vigorously after the addition of each portion of solvent, being careful to keep the mixture at room temperature.

Solids should be finely powdered to increase the rate of solution. If the solid appears to be insoluble in water or ether it is sometimes advisable to heat the mixture gently. If solution is effected in this way the liquid is again cooled to room temperature and is shaken to prevent supersaturation. It is always well in such cases to "seed" the cooled solution by adding a crystal of the solid. Especial care should be taken in weighing the sample used; it should weigh 0.10 g. within 0.01 g.

Liquids are most conveniently handled by means of a graduated pipet which permits accurate measurement of the amount added.

When the solubility in acid or alkali is being determined heat should not be applied since it might cause hydrolysis to occur. If the mixture is shaken thoroughly the time required for solution to take place should not be more than one or two minutes.

In the case of reaction solvents it is frequently more expeditious and more economical to place the 3 cc. of solvent in the test tube and to add the solute portion-wise. Thus for compounds which are very insoluble this fact may be established by use of only a very little of the substance, and the amount will not need to be weighed or measured. In general, where rough tests of solubility are adequate for the purpose in view, the prescribed procedure may be