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The Systematic Identification of Organic Compounds

Seventh Edition

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The Systematic Identification of Organic Compounds

7th Edition

Preface

This edition is dedicated to the memory of R.L. ("Ralph") Shriner. Ralph Shriner passed away on June 7, 1994 at the age of 94 while this edition was being prepared. He was the major force in the publication of the first (1935) and other early editions of this text. Organic chemistry had long been a daunting component of the chemistry curriculum and the idea of an advanced course built on the identification of unknown organic compounds (organic qualitative analysis, or "org qual") was identified as a way of providing students with a method of organizing their thoughts about this subject in a way that would lead to improved comprehension and an appreciation of systematic methods of characterization. Shriner, along with C.S. "Speed" Marvel, then at the University of Illinois, a major center of chemistry and research, already had prepared mimeographed notes to teach the "org qual" lab course. When Marvel said he could not participate in the preparation of a book, it was up to Shriner, assisted by R.C. ("Bob") Fuson (also at Illinois), to publish the text. David Curtin was brought on board to incorporate spectroscopic methods (in the 4th edition, 1956, which was the edition used by TCM when he took org qual at Syracuse University in 1960). Interestingly, spectroscopy in the 4th edition included only infrared and ultraviolet methods. NMR was incorporated into the 5th edition (1964). One of us (TCM) was brought in in 1980 to update spectroscopic methods (6th edition, 1980), as well as to revise the book as a whole, and Chris Hermann did the heavy work necessary to get this edition (the 7th) off the ground.

Ralph Shriner received a bachelors degree in chemical engineering from Washington University (St. Louis) in 1921, followed by a PhD from the University of Illinois (Champaign-Urbana, 1925) under the direction of Roger Adams. After a two-year post-doctoral position at the SUNY-College of Agriculture, he returned to join the faculty of the University of Illinois in 1927, and he taught there (including rising to professor and department chair) until he left for the University of Indiana in 1941 to be their depart-

ment chair. He left Indiana to assume the chair of the University of Iowa in 1963, upon his "retirement" in 1963, he became a visiting professor at Southern Methodist University, retiring from that position in 1978. Professor Shriner received the 1966 Flack Norris Award of the Northeastern Section of the American Chemical Society for teaching. He was one of the early participants in the establishment of "Organic Syntheses," a well-known series of books that has been an excellent source of tested, and thus reliable, synthetic procedures. He, and his wife Rachel, published a comprehensive text for Organic Synthesis entitled "Organic Synthesis, Collective Volumes I-V". A testament to Ralph Shriner's popularity and the effect that he had upon college chemistry is the fact that when the 6th edition of "The Systematic Identification of Organic Compounds" appeared, a number of unsolicited (and very insightful) reviews came from chemists in many locations, especially the midwest. Ralph Shriner was the coauthor of the other book and published in excess of 120 papers. He also held a number of leadership positions in the American Chemical Society. An important niche in Professor Shriner's activities was the thoroughness with which he approached chemical or "wet" tests. He would scrutinize any new procedure and test it on literally dozens of compounds, being very strongly of the opinion that the tests should work, and he did not want any test included in the text until it did work. A balky case had been the nitrogen test, which until the 6th edition was somewhat of a problem child. It was Ralph Shriner's efforts at SMU which led to the 6th edition to include a nitrogen test which has proved to be very reliable.

In the preparations of this 7th edition two major areas were addressed. First, it was clear that modernization was important, especially in areas such as spectroscopy. Since reviewers and users have requested flexibility, thus chemical and spectroscopic tests were separated in this edition. This allows users to choose how much and where IR vs. nuclear magnetic resonance, etc., should be used to teach this subject.

Chapter 1 continues to be an introduction including an updated description of the ever-important area of lab safety. Chapter 2 continues to be a survey of many of the following chapters; it is intended to give students an overview of how compound identification is carried out.

Preliminary examination and determination of physical properties are the main topics of Chapter 3. Preliminary examination means observing the color, appearance, etc., of an unknown. The determination of the melting and boiling points is described in this chapter. Moreover, thin-layer chromatography (TLC) and gas chromatography (GC) are introduced in this chapter. TLC and GC are here as options that may be employed to determine the purity of a single unknown or the composition of a mixture. Use of chromatographic methods to separate mixtures is held until Chapter 10. Specialized methods of characterization are also covered in Chapter 3. These include specific gravity, refractive index, and optical rotation. It should be made clear that here, as well as elsewhere in this text, a number of techniques will be covered that may not be used in a given lab course but are merely providing choices, and the instructor must pave the way by guiding students to what is required and to what is optional.

The molecular formula of a compound is an important source of information, and this is the main topic of Chapter 4. The sodium fusion test has long been a way of determining whether a compound contains nitrogen, sulfur, or halogen. Since this test involves the remnants of sodium fusion into contact with water, it clearly has hazardous aspects and requires great care and explicit guidelines from instructors. Users are challenged to think long and hard as to whether this procedure is appropriate in their teaching situations. Alternatives include simply providing students with hetero atom content and using spectroscopic data as clues to atomic composition. We also describe combustion

and mass spectrometric approaches in this chapter. Actually conducting combustion analysis is an unlikely part of an organic qual course, but it is conceptually related, and we felt it is worthwhile for students to know about this research-related item. It is not uncommon for instructors to provide students with percent composition data as a source of clues to the identity of organic compounds.

Chapter 5 contains methods and theory of solubility classification. The fact that a compound is insoluble in water but soluble in a well-defined solution of base is a major clue in classification. The supposition that a compound is a carboxylic acid can be quickly checked by IR and the telltale broad O—H stretch linked to solubility classification clearly points to the carboxylic acid class of compound. Thus in this fashion solubility represents an important niche in the overall characterization of organic compounds.

As mentioned above, spectroscopic methods have been separated from chemical tests, and thus we provide spectrometric methods (IR, NMR, and UV) in Chapter 6. This of course required updating and certainly the greatest degree of development has been in the area of NMR. The expanded ability to use NMR to analyze organic compounds has been nothing short of incredible. The appearance of more common high fields (300 MHz seems to be very prevalent now), ever-expanding computer power, and the increasing ease of use of NMR software has made this area one of great activity. Special techniques such as 2D NMR are becoming more commonplace. The simple act of digitization of NMR results allows use of the “electronic superhighway” to do and teach organic chemistry. It is not uncommon now for students to be able to obtain their NMR results on a disk, and then to be able to expand signals, check integrations, etc., and finally to directly incorporate their results into a written report. IR has still has the important position of being a quick, reliable method of functional group identification. The major new development for IR is the area of Fourier transform IR (FT IR). While the basic information is essentially the same, the ability to obtain IR peak positions very accurately on very small amounts of compound, together with the power resulting from digitization of these results, is very meaningful.

Classification by chemical (or “wet”) tests is covered in Chapter 7. And covered is the operative word. We have added a number of pieces of information to provide the user with the widest possible scope of information. Again we do not expect all labs to use all tests. But we are confident that an extensive menu has been provided from which to choose. An important addition here is the inclusion of cleanup procedures for every chemical test. Waste disposal has become a great source of concern and indeed an expense that is competitive with and even greater than expenses associated with the purchase of chemicals and equipment. We have endeavored to treat this area in a comprehensive fashion.

The approach to Chapter 8 (Derivatives) is very similar to that of Chapter 7. Again we provide the user with a wide array of information. We do not expect all labs to use all derivative procedures. Additionally we have cleanup procedures for every derivative procedure.

Chapter 9 contains the ever-popular “road-map” problems. The idea is to simulate a lab experience by providing the student with a wide range of clues to the structures of organic unknowns. These include simple problems, as well as those which are more challenging. Moreover we have problems that are based solely on chemical tests, problems that rely heavily on spectrometric information (IR, NMR, mass spectrometry, etc.), and problems that integrate chemical and spectrometric methods. The chapter begins with an explanation of how to do problems. Successful completion of these problems requires knowledge of the chemical tests and derivatives (information from, respectively, Chapters 7 and 8), an understanding of the value of spectrometric methods described in Chapter 6,

and an appreciation of the melting point and boiling point tables for the various classes of organic compounds provided in the appendixes.

Techniques that serve to separate mixtures are described in Chapter 10. This includes extractions with aqueous acids and bases and chromatographic procedures. Chapter 11 is a description focused on literature methods useful for organic chemists. Here we have also included recent developments in electronic methods of searching, especially those provided by Chemical Abstracts.

We are grateful to the following chemists for contributing their time and ideas to this edition: Rogers Lambert (Radford University), C. F. H. Allen (Rochester Institute of Technology), William Bigler (Rochester Institute of Technology), William Closson (SUNY Albany), Louis Freidrich (University of Rochester), Robert E. Gilman, (Rochester Institute of Technology), Jack Kampmeier (University of Rochester), P. A. S. Smith (University of Michigan), David Strack (Waters Associates), Thomas P. Wallace (Rochester Institute of Technology), Casey Swallow (Merrimack College), Charles Garner (Baylor University), Clelia Mallory (University of Pennsylvania), David Minter (Texas Christian University), Francis Knowles (University of California-Davis), William Suggs (Brown University), and Walter Zajac (Villanova University). Christine Hermann owes a special debt of gratitude to her husband, Richard Hermann, for drawing all of the new original artwork and his patience during the preparation of this manuscript.

In summary, we hope that we have provided a book which is useful. We would appreciate receiving any input from users, from such relatively mundane items as correction of physical constants to broad recommendations we might use in future editions. Please feel free to inform us of anything you think might be of value to chemists at large.

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CHAPTER 1

Introduction

.1 SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS: THE NEED FOR ORGANIC QUALITATIVE ANALYSIS

The amount of information facing the student of organic chemistry is overwhelming. In roughly two dozen chapters of a standard organic text, the student encounters many chemical reactions. Literally millions of different organic compounds have been synthesized. Chemical companies sell thousands of compounds and industrial-scale production generates about 10,000 different compounds on various scales. And yet we maintain that characterization of organic compounds can be done by a handful of physical and chemical observations, if they are made in a systematic fashion. Aldrich Chemical Company lists about 9000 compounds. Many other chemical companies list only 100 to 1000 compounds. Industrially produced organic compounds number about 6000 to 10,000. Thus the list of more common and more readily available chemicals is much smaller than the millions that are possible.

In this text we have focused our attention on an even smaller list of compounds that can be used as “unknowns.” The melting point-boiling point tables give a very accurate idea of the focus of this book. Instructors using this book may very well use other references (CRC reference volumes,¹ the Aldrich Company catalog, etc.) for a more extensive list of possibilities for “unknown” compounds.

Organic chemists are often confronted with either of the following extreme situations:

1. Determination of the identity of a compound that has no prior history. This is often the case for a natural-products chemist who must study a very small amount of sample isolated from a plant or animal. A similar situation applies to the forensic chemist who analyzes very small samples related to a lawsuit or crime.

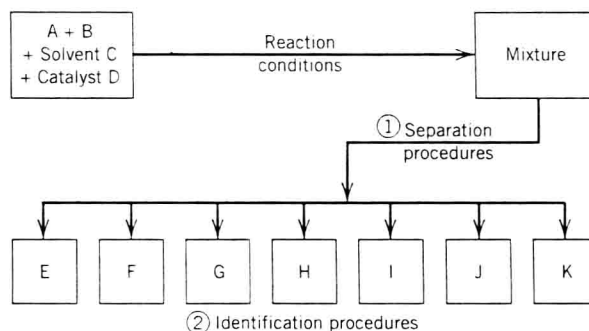
¹For example, *Handbook of Tables for Organic Compound Identification*, 3rd ed., edited by Z. Rappoport (CRC Press, Boca Raton, FL, 1967).

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2. The industrial chemist or college laboratory chemist who must analyze a sample that contains a major *expected* product and minor products, all of which could be expected from a given set of reagents and conditions. It is entirely possible that such a sample with a well-documented history will allow one to have a properly preconceived notion as to how the analysis should be conducted.

The theory and technique for identifying organic compounds constitute an essential introduction to research in organic chemistry. This study organizes the accumulated knowledge concerning physical properties, structures, and reactions of thousands of carbon compounds into a systematic, logical identification scheme. Although its initial aim is the characterization of previously known compounds, the scheme of attack constitutes the first stage in the elucidation of structure of newly prepared organic compounds.

If, for example, two known compounds A and B are dissolved in a solvent C, a catalyst D is added, and the whole subjected to proper reaction conditions of temperature and pressure, a mixture of new products plus unchanged starting materials results.



Immediately two problems arise:

1. What procedure shall be chosen to separate the mixture into its components?
2. How are the individual compounds (E through K) to be definitely characterized? Which ones are unchanged reactants? Which compounds have been described previously by other chemists? Finally, which products are new?

These two problems are intimately related. Separations of organic mixtures use both chemical and physical processes and are dependent on the structures of the constituents.

The present course of study centers attention on the systematic identification of individual compounds first. The specific steps are given in Chapter 2. Then the use of these principles for devising efficient procedures for the separation of mixtures is outlined in Chapter 10. The practical laboratory methods and discussion of principles for the steps in identification are given in Chapters 3 through 8.

In recent years the question of scale has become an issue. Scale has always been a focal point for qualitative analysis. The issue has been recognized at an even earlier point in the chemistry curriculum, and a very large number of colleges now incorporate some sort of microscale approach into their sophomore organic courses. (Here we loosely define microscale chemistry as the use of tens of milligrams of organic compound in a procedure, while macroscale reactions employ tens of grams.) Organic qualitative analysis has always been a test tube subject and thus should philosophically be in tune with the microscale revolution. We have left most of our experiments at the scale of the past editions of this text and thus many chemistry instructors may wish to scale down. We anticipate scaling down to 1/2, 1/5, or 1/10 of the cited amount should be very straightforward

in most cases, and thus scale is the option of the course coordinator. The only warning is that certain reactions (for example, conversion of a carboxylic acid to an amide or of an alcohol to a 3,5-dinitrobenzoate) are notoriously sensitive to the purity of the reagents. Thus a larger scale reaction is likely desirable here.

Cleanup and Waste Disposal

A related, and in some ways bigger, issue is that of waste disposal. The trend at most colleges in recent years is to have waste disposal done by a licensed company under contract with the college. Most instructors are not qualified to dispose of waste and thus they can only provide cleanup guidelines. We have attempted to prepare this edition with that in mind. It is usually the job of the instructor to provide containers for waste disposal (it is now very rare that a chemical can be washed down the sink). Waste disposal vessels are usually labeled as to their use such as solids vs. liquids and inorganic vs. organic compounds. In some cases a special vessel is provided for especially toxic wastes such as halogenated organic compounds. Moreover, there are usually special containers for glass (especially broken glass) objects. There may be places to recycle paper, and finally there are simple trash cans for garbage. Thus there is usually a classification decision for every act of discarding material. And most importantly the students should receive instructions from their lab instructor that are in accord with local regulations.

2 SUGGESTIONS TO STUDENTS AND INSTRUCTORS

Schedule. An exact time schedule applicable to all schools cannot be set because of the varied use of semester, quarter, trimester, and summer session terms of instruction. However, for a semester of 15 weeks, two 3-hr laboratory periods per week, plus one “lab lecture” per week works well. Modification can be made to adapt the course to individual schools.

Lecture Material. The experiments and procedures (Chapters 7 and 8), and instructions for use of infrared and of nuclear magnetic resonance spectroscopy (Chapter 6) have been described such that students can study them as their work progresses. The first lecture should describe the course overview as outlined in Chapter 2. It is clearly not necessary to lecture on all the specific “recipes” listed in Chapters 7 and 8, although an introduction to some of the more commonly used tests is useful.

After the first one or two unknowns have been completed, it will be valuable to work some of the problems of Chapter 9 in class and discuss structure correlation with chemical reactions and spectral data.

Laboratory Work—Unknowns. By use of spectroscopic data and chemical reactions it is possible for students to work out six to eight single compounds and two mixtures (containing two or three components each) in a 15-week semester.

To get a rapid start and illustrate the systematic scheme, it may be useful to give a titratable acid to each student for a first unknown. The student is told that the substance is titratable and that he or she is to get the elemental analysis, melting or boiling point, and neutralization equivalent and to calculate the possible molecular weights.² Then, if

²Alternatively, the student can be given a compound with mass spectral data or elemental analyses (% C, H, N, O, ...).

the unknown contains halogen or nitrogen, the student is to select and try three or four (but no more) classification tests. Next, a list of possible compounds with derivatives is prepared by consulting the table of acids (pp. 565–575). One derivative is made and turned in with the report (see pp. 22–23). This first unknown should be completed in two 3-hour laboratory periods.

Since many schools run organic qualitative analysis in a lab course connected to the second semester (or last term) of the traditional sophomore course, the decision about how to order the functional groups possible for the unknown may very well depend upon the order of coverage of these groups in the lecture course.

The other unknowns should be selected so as to provide experience with compounds containing a wide variety of functional groups.

It is often desirable to check the student's progress after the preliminary tests, solubility classification, and elemental analyses have been completed. This checking procedure is highly recommended for the first one or two unknowns for each student.

Purity of Unknowns. Although every effort is made to provide samples of compounds with a high degree of purity, students and instructors should recognize that many organic compounds decompose or react with oxygen, moisture, or carbon dioxide when stored for a considerable time. Such samples will have wide melting or boiling point ranges, frequently lower than the literature values. Hence, for each unknown the student should make a preliminary report of the observed value for melting or boiling point. The instructor should verify these data and if necessary tell the student to purify the sample by recrystallization or distillation and to repeat the determination of the physical constant in question. This avoids waste of time and frustration from conflicting data. (Read also pp. 37–50.)

Amounts of Unknowns. As a general guide, the following amounts are suggested:

Unknown No. 1, a titratable acid, 4 g of a solid or 10 mL of a liquid

Unknown No. 2, 3 g of a solid or 8 mL of a liquid

Unknown No. 3, 2 g of a solid or 5 mL of a liquid

Unknown No. 4, 1 g of a solid or 5 mL of a liquid

Mixtures should contain 4–5 g of each component. *Note:* If repurification of a sample is required, an additional amount should be furnished to the student.

The amounts listed above are essentially macroscale unknowns; use of analytical techniques and instrumentation such as thin-layer chromatography and gas chromatography may very well allow sample sizes of unknowns to be ca. 20% of that listed above. *In such cases, that is, for microscale samples, it is imperative that chemical test and derivatization procedures described in Chapters 7 and 8 be scaled down correspondingly.*

Toward the end of the term, when the student's laboratory technique has been perfected and facility in interpreting reactions has been obtained, it is possible to work with still smaller samples of compounds by using smaller amounts of reagents in the classification tests and by using a smaller scale in the derivatization procedure.

Timesaving Hints. It is important to plan laboratory work in advance. This can be done by getting the elemental analyses, physical constants, solubility behavior, and infrared and NMR spectra on several unknowns during one laboratory period. This information should be carefully recorded in the notebook and then reviewed (along with the discussion in each of these steps) the evening before the next laboratory period. A list of