OPERATIONAL ORGANIC CHEMISTRY

A Laboratory Course

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Allyn and Bacon, Inc. *Boston* *London* *Sydney* *Toronto*

To My Parents

Library of Congress Cataloging in Publication Data

Lehman, John W
Operational organic chemistry.

Bibliography: p.
Includes index.
1. Chemistry, Organic—Experiments. I. Title.
QD261.L39 547'.0028 80-28118
ISBN 0-205-07146-5

Printed in the United States of America.

10 9 8 7 6 5 4 3 85 84 83 82 81

Production editors: David Dahlbacka and Greg Giblin

Preface

This book began more than seven years ago as a modest collection of supplemental experiments for the organic chemistry laboratory course at Lake Superior State College. It has been expanded and improved considerably in the interim, and a year's respite from teaching in 1978–79 gave me the time and opportunity to complete the present manuscript. Throughout the development of the text I have been guided by certain personal convictions: (1) that an "operational" approach to the organic chemistry laboratory is superior to the more traditional "cookbook" approach; (2) that motivation is as important as ability in assuring a student's success in the laboratory; (3) that a solid and reasonably rigorous laboratory course can also be "fun" and can be taught without subjecting the student to too much unpleasantness; (4) that exploding costs necessitate the use of comparatively inexpensive chemicals and basic apparatus in the undergraduate laboratory; (5) that students should be made safety-conscious and aware of the potential impact of chemicals on the environment.

I have tried to emphasize throughout the book that a synthetic experiment, for example, is not a unique process requiring detailed step-by-step directions, but is rather a series of easily mastered experimental operations performed in sequence and adapted to the requirements of the preparation. This approach is exemplified by the detailed operation descriptives in Part V, and by extensive Methodology sections in each experiment which explain the experimental approach. Reactant quantities are given in moles or millimoles to promote the student's understanding and appreciation of reaction stoichiometry. A motivational component is furnished by the use of imaginary "situations" and considerable background information stressing the relevance of each experiment. This kind of material is particularly important for students in the life sciences and preprofessional fields, who are often turned off by the abstract nature of chemical reactions and mechanisms. When feasible, natural products are used because they often cost less, smell nicer, and are more pleasant to work with than their purely synthetic analogs. Although numerous experiments are designed to use gas chromatography and spectrometric methods, nearly all can be performed satisfactorily without the instruments by furnishing students with authentic spectra or chromatographic data. Magnetic stirring is suggested in a number of procedures, but is required for only one experiment utilizing phase-transfer catalysis; and all the basic operations can be performed using the glassware found in a typical 19/22 organic labkit. Safety is emphasized throughout the text, with special symbols to indicate chemical hazards and a summary of hazards and precautions in each experiment. Proper methods for handling chemicals are discussed, and the student is frequently reminded of the need to dispose of harmful chemicals safely.

Operational Organic Chemistry incorporates a wide variety of laboratory experiences to help maintain interest and avoid unnecessary repetition. This makes the book suitable for many different kinds of students and courses—it should be as useful for biology, pre-medical, pre-pharmacy, medical technology and other majors as it is for chemistry students. The main-sequence experiments in Part I are suitable for a short course in organic chemistry. A more rigorous general or majors course can be built around a core of main-sequence experiments with judicious selections from the supplementary experiments in Part II, along with some qualitative analysis experiments based on Part III and perhaps a few advanced projects from Part IV. Additional flexibility is provided by the Minilabs and the Experimental Variations section found in each experiment.

Many people have been involved in the preparation of this book and their contributions should be acknowledged. The manuscript in various stages of development was reviewed by Newton D. Werner (Cerritos College), Kurt C. Schreiber (Duquesne University), Bruce Jarvis (University of Maryland), Robert H. Feiertag (Ohio State University), James B. Ellern (University of Southern California), Fred M. Dewey (Metropolitan State College), H. Leroy Nyquist (California State University at Northridge), Gerald F. Koser (University of Akron), Constance Suffredini (University of California at Irvine), Hance H. Hamilton (Eastfield College), and Robert E. Kohrman (Central Michigan University). The reviewers provided many valuable suggestions which resulted in a number of changes and improvements. Thanks are due to my laboratory students at Lake Superior State College who have class-tested most of the procedures and suffered through a few of my less successful efforts during the long process of development. I would like to express my special appreciation to Professor David Todd of Worcester Polytechnic Institute who, with his graduate students, tested a dozen of the experiments in Part II; to George Sypniewski (Michigan Technological University), who supervised the class-testing of several experiments at L.S.S.C. during my absence; and to the following graduate and undergraduate students who lab-tested the remainder of the experiments: Mike Lingo (Central Michigan University), Edwin Tewes (Tufts University), Greg Bosch (Massachusetts Institute of Technology), Masayuki Nakajima (University of Massachusetts—Arlington) and Kunio Kano (University of Massachusetts—Boston). Acknowledgements are in order for the assistance provided by Professors Gerald D. Weatherby and Purna Chandra of Lake Superior State College, who read several experiments and offered helpful comments; to Professor Dagmar Ponzi, who provided laboratory space at M.I.T. for some of the lab testing; and to Linda Dicks, Deborah Morley, and other laboratory assistants at L.S.S.C., who checked some

of the experimental procedures before they were used in the laboratory course.

Special thanks go to the administration and staff at Massachusetts Institute of Technology for granting me temporary faculty privileges, which greatly facilitated the library research that went into the preparation of the final manuscript; to Professor C. G. Swain, who sponsored my visit to M.I.T. and reviewed the kinetics experiments; and to the administration and staff of Lake Superior State College, which approved my leave of absence and generally supported my efforts. Finally I would like to express my appreciation to Kathy McCaskey, Barbara Vilenski, Deborah Brooks, and Deborah Hannon, who typed the various drafts of the manuscript; to James M. Smith, Greg Giblin, David Dahlbacka, Judy Fiske, Lorraine Perrotta, and other Allyn and Bacon personnel who furnished invaluable assistance during the manuscript preparation and other stages of publication; and to Larry Largray, who illustrated the book. Many other individuals provided help and moral support throughout the development and publication of this book, and their contributions are appreciated.

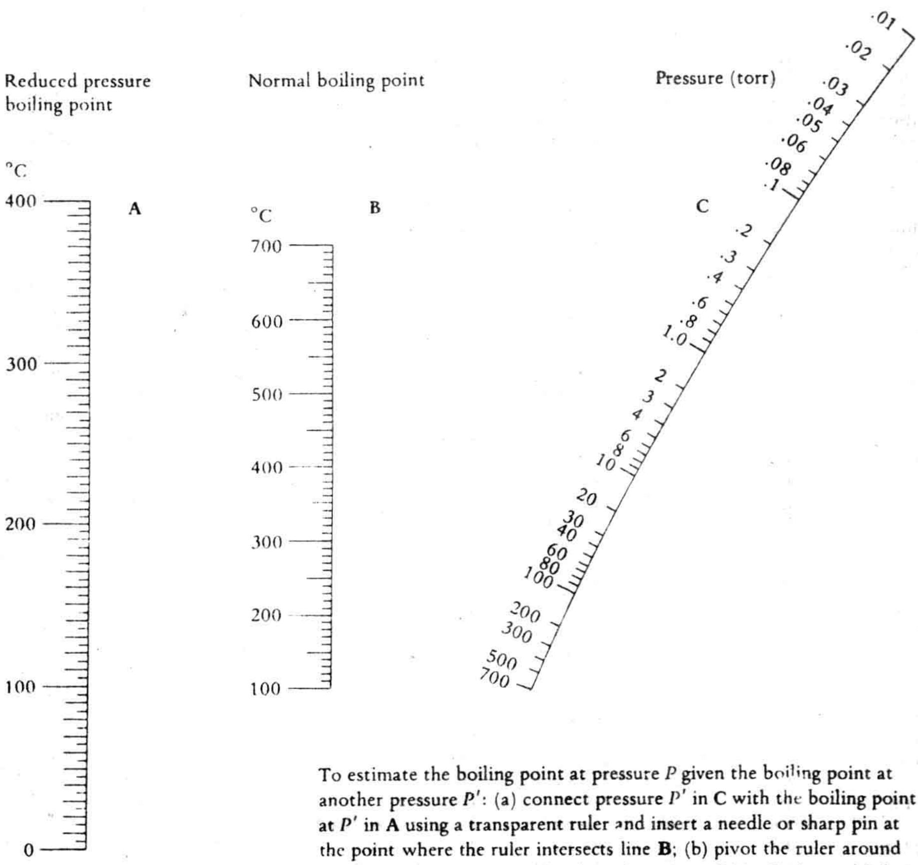
J. W. L.

Atomic Masses and Numbers

Name	Symbol	Atomic number	Atomic mass	Name	Symbol	Atomic number	Atomic mass
Actinium	Ac	89	227.0278	Molybdenum	Mo	42	95.94
Aluminium	Al	13	26.98154	Neodymium	Nd	60	144.24
Americium	Am	95	(243)	Neon	Ne	10	20.179
Antimony	Sb	51	121.75	Neptunium	Np	93	237.0482
Argon	Ar	18	39.948	Nickel	Ni	28	58.70
Arsenic	As	33	74.9216	Niobium	Nb	41	92.9064
Astatine	At	85	(210)	Nitrogen	N	7	14.0067
Barium	Ba	56	137.33	Nobelium	No	102	(259)
Berkelium	Bk	97	(247)	Osmium	Os	76	190.2
Beryllium	Be	4	9.01218	Oxygen	O	8	15.9994
Bismuth	Bi	83	208.9804	Palladium	Pd	46	106.4
Boron	B	5	10.81	Phosphorus	P	15	30.97376
Bromine	Br	35	79.904	Platinum	Pt	78	195.09
Cadmium	Cd	48	112.41	Plutonium	Pu	94	(244)
Caesium	Cs	55	132.9054	Polonium	Po	84	(209)
Calcium	Ca	20	40.08	Potassium	K	19	39.0983
Californium	Cf	98	(251)	Praseodymium	Pr	59	140.9077
Carbon	C	6	12.011	Promethium	Pm	61	(145)
Cerium	Ce	58	140.12	Protactinium	Pa	91	231.0359
Chlorine	Cl	17	35.453	Radium	Ra	88	226.0254
Chromium	Cr	24	51.996	Radon	Rn	86	(222)
Cobalt	Co	27	58.9332	Rhenium	Re	75	186.207
Copper	Cu	29	63.546	Rhodium	Rh	45	102.9055
Curium	Cm	96	(247)	Rubidium	Rb	37	85.4678
Dysprosium	Dy	66	162.50	Ruthenium	Ru	44	101.07
Einsteinium	Es	99	(252)	Samarium	Sm	62	150.4
Erbium	Er	68	167.26	Scandium	Sc	21	44.9559
Europium	Eu	63	151.96	Selenium	Se	34	78.96
Fermium	Fm	100	(257)	Silicon	Si	14	28.0855
Fluorine	F	9	18.998403	Silver	Ag	47	107.868
Francium	Fr	87	(223)	Sodium	Na	11	22.98977
Gadolinium	Gd	64	157.25	Strontium	Sr	38	87.62
Gallium	Ga	31	69.72	Sulfur	S	16	32.06
Germanium	Ge	32	72.59	Tantalum	Ta	73	180.9479
Gold	Au	79	196.9665	Technetium	Tc	43	(98)
Hafnium	Hf	72	178.49	Tellurium	Te	52	127.60
Helium	He	2	4.00260	Terbium	Tb	65	158.9254
Holmium	Ho	67	164.9304	Thallium	Tl	81	204.37
Hydrogen	H	1	1.0079	Thorium	Th	90	232.0381
Indium	In	49	114.82	Thulium	Tm	69	168.9342
Iodine	I	53	126.9045	Tin	Sn	50	118.69
Iridium	Ir	77	192.22	Titanium	Ti	22	47.90
Iron	Fe	26	55.847	Tungsten (Wolfram)	W	74	183.85
Krypton	Kr	36	83.80	(Unnilhexium)	(Unh)	106	(263)
Lanthanum	La	57	138.9055	(Unnilpentium)	(Unp)	105	(262)
Lawrencium	Lr	103	(260)	(Unnilquadium)	(Unq)	104	(261)
Lead	Pb	82	207.2	Uranium	U	92	238.029
Lithium	Li	3	6.941	Vanadium	V	23	50.9415
Lutetium	Lu	71	174.967	Xenon	Xe	54	131.30
Magnesium	Mg	12	24.305	Ytterbium	Yb	70	173.04
Manganese	Mn	25	54.9380	Yttrium	Y	39	88.9059
Mendelevium	Md	101	(258)	Zinc	Zn	30	65.38
Mercury	Hg	80	200.59	Zirconium	Zr	40	91.22

SOURCE: Adapted from *Pure Appl. Chem.* **51,** 405 (1979). Values in parentheses are for nonnaturally occurring elements and are the mass numbers of the longest lived isotope of the element.

REDUCED PRESSURE BOILING POINT ALIGNMENT CHART



To estimate the boiling point at pressure *P* given the boiling point at another pressure *P′*: (a) connect pressure *P′* in **C** with the boiling point at *P′* in **A** using a transparent ruler and insert a needle or sharp pin at the point where the ruler intersects line **B**; (b) pivot the ruler around the needle until it reaches the desired pressure (*P*) in **C**, then read the boiling point at *P* from **A**.

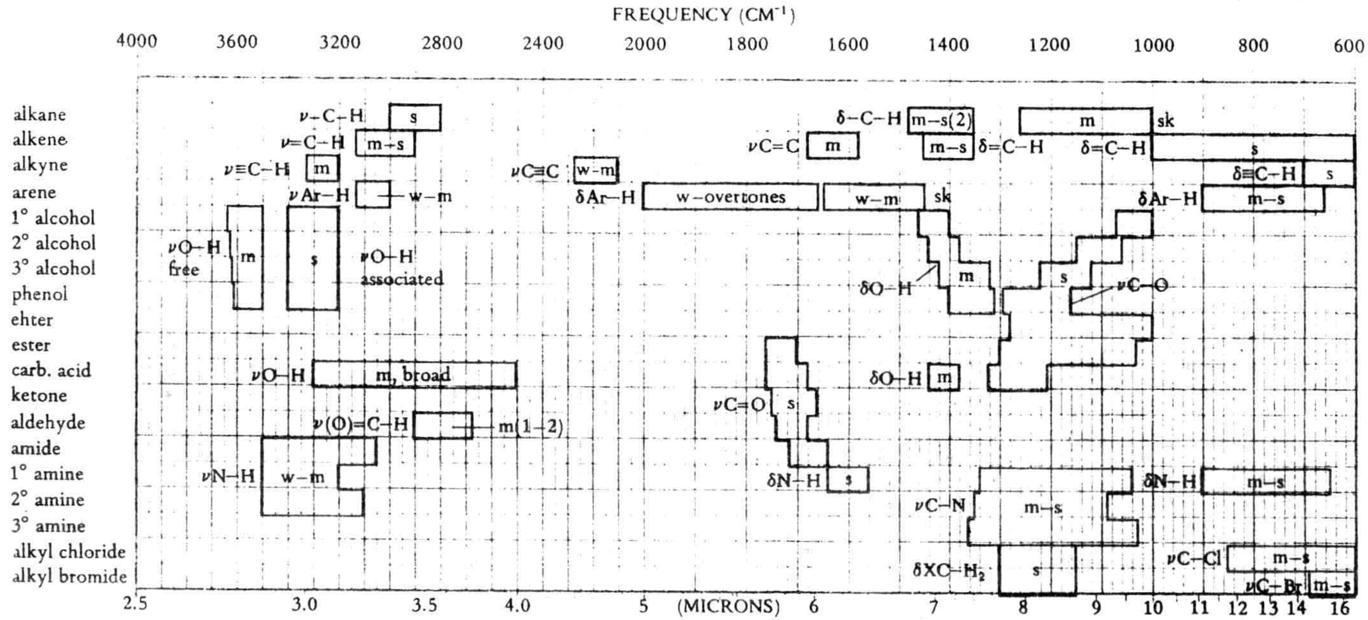
Example: the boiling point of dibutyl phthalate is reported to be 236° at 40 torr. Connecting these values in **A** and **C** causes the ruler to intersect line **B** at about 345° (which roughly equals the normal boiling point), and pivoting about that point to 10 torr on **C** yields a value (from **A**) of about 197° for the boiling point of dibutyl phthalate at 10 torr.

Periodic Table of the Elements

PERIODS	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	O
	METALS												NONMETALS					
			TRANSITION METALS															
1	1 0079 **H** 1																1 0079 **H** 1	4 00260 **He** 2
2	6 94 **Li** 3	9 01218 **Be** 4											10 81 **B** 5	12 011 **C** 6	14 0067 **N** 7	15 9994 **O** 8	18 9984 **F** 9	20 179 **Ne** 10
3	22 9898 **Na** 11	24 305 **Mg** 12											26 9815 **Al** 13	28 086 **Si** 14	30 9738 **P** 15	32 06 **S** 16	35 453 **Cl** 17	39 948 **Ar** 18
4	39 098 **K** 19	40 08 **Ca** 20	44 9559 **Sc** 21	47 90 **Ti** 22	50 9414 **V** 23	51 996 **Cr** 24	54 9380 **Mn** 25	55 847 **Fe** 26	58 9332 **Co** 27	58 71 **Ni** 28	63 546 **Cu** 29	65 38 **Zn** 30	69 72 **Ga** 31	72 59 **Ge** 32	74 9216 **As** 33	78 96 **Se** 34	79 904 **Br** 35	83 80 **Kr** 36
5	85 4678 **Rb** 37	87 62 **Sr** 38	88 9059 **Y** 39	91 22 **Zr** 40	92 9064 **Nb** 41	95 94 **Mo** 42	98 9062 **Te** 43	101 07 **Ru** 44	102 9055 **Rh** 45	106 4 **Pd** 46	107 868 **Ag** 47	112 40 **Cd** 48	114 82 **In** 49	118 69 **Sn** 50	121 75 **Sb** 51	127 60 **Te** 52	126 9046 **I** 53	131 30 **Xe** 54
6	132 9054 **Cs** 55	137 34 **Ba** 56	57–71 *	178 49 **Hf** 72	180 9479 **Ta** 73	183 85 **W** 74	186 2 **Re** 75	190 2 **Os** 76	192 22 **Ir** 77	195 09 **Pt** 78	196 9665 **Au** 79	200 59 **Hg** 80	204 37 **Tl** 81	207 2 **Pb** 82	208 9804 **Bi** 83	(210) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	(223) **Fr** 87	(226 0254) **Ra** 88	89–103 †	(260) **Ku** 104	(260) **Ha** 105													

*** LANTHANIDE SERIES**	138 9055 **La** 57	140 12 **Ce** 58	140 9077 **Pr** 59	144 24 **Nd** 60	(145) **Pm** 61	150 4 **Sm** 62	151 96 **Eu** 63	157 25 **Gd** 64	158 9254 **Tb** 65	162 50 **Dy** 66	164 9304 **Ho** 67	167 26 **Er** 68	168 9342 **Tm** 69	173 04 **Yb** 70	174 97 **Lu** 71
† ACTINIDE SERIES	(227 **Ac** 89	232 0381 **Th** 90	231 0359 **Pa** 91	238 029 **U** 92	237 0482 **Np** 93	(242) **Pu** 94	(243) **Am** 95	(245) **Cm** 96	(245) **Bk** 97	(248) **Cf** 98	(253) **Es** 99	(254) **Fm** 100	(256) **Md** 101	(253) **No** 102	(257) **Lr** 103

INFRARED SPECTRUM-STRUCTURE CORRELATION CHART



ν = stretching vibration δ = bending vibration sk = skeletal vibrations
w = weak m = medium intensity s = strong

Contents

Washing and Drying Operations

Introduction and Advice for the Student

Purpose and Organization of the Textbook

As implied by the title, *Operational Organic Chemistry* stresses an operational approach to the laboratory practice of organic chemistry. Rather than viewing a given analysis or synthetic preparation as a unique process unrelated to any other, I have treated each experiment as a series of operations performed in a logical sequence to fulfill certain objectives. In turn, I have described each operation in sufficient depth to enable the student not only to master the basic manipulative techniques but also to improvise when necessary.

Perhaps even more important than providing a student with the *means* to complete an experiment successfully is to supply the *motivation* which will make him or her approach the experiment with anticipation (or at least without outright abhorrence) and thus learn from the experience. The motivational component is supplied by including enough background material to demonstrate the everyday relevance (and some of the fascination) of organic chemistry, and by providing "real-life" situations with each experiment.

Following the introduction and laboratory safety section, the textbook is divided into five parts. Part I contains enough experiments for a short course in organic chemistry and can give each student experience with nearly all of the operations described in Part V. The very fundamental operations, which will be practiced repeatedly throughout the course, are introduced in the first five experiments. These experiments are meant to perform the same function as the "techniques exercises" found in some laboratory textbooks, but without the concentrated, repetitive exposure to isolated techniques which many students find so tedious. Each operation is reinforced by later applications, often at a somewhat higher level of difficulty, so that mastery can be accomplished over a reasonable period of time. Experiment 6, which introduces some common functional groups, might be considered a "breather" in that it teaches no complicated operations and requires no special manipulative skills. The remaining experiments of Part I are keyed to topics covered in most organic chemistry lecture textbooks; they include more advanced operations as well as advanced applications of the basic ones.

Part II provides a large selection of experiments that can be incorporated into a full-year laboratory course in organic chemistry and/or substituted for some of the Part I experiments following Experiment 5. Although the general level of difficulty (with some exceptions) is higher than