



VOGEL's

TEXTBOOK OF PRACTICAL ORGANIC CHEMISTRY

FIFTH EDITION

Revised by former and current members of
The School of Chemistry,
Thames Polytechnic, London

Brian S. Furniss

Antony J. Hannaford

Peter W. G. Smith

Austin R. Tatchell



Copublished in the United States with
John Wiley & Sons, Inc., New York

Longman Scientific & Technical

Longman Group UK Limited
 Longman House, Burnt Mill, Harlow
 Essex CM20 2JE, England
 and Associated Companies throughout the world

Copublished in the United States with
 John Wiley & Sons, Inc., 605 Third Avenue, New York, NY 10158

© Longman Group UK Limited 1989

All rights reserved; no part of this publication
 may be reproduced, stored in a retrieval system,
 or transmitted in any form or by any means, electronic,
 mechanical, photocopying, recording, or otherwise,
 without either the prior written permission of the Publishers, or a
 licence permitting restricted copying in the United Kingdom issued by
 the Copyright Licensing Agency Ltd, 33–34 Alfred Place, London, WC1E 7DP.

First published 1948

New Impression with minor corrections, October 1948

Second Edition 1951

New Impression with addition of Chapter XII on Semimicro Technique 1954

Third Edition 1956

New Impression with corrections and additions 1957

New Impressions 1959, 1961, 1962, 1964, 1965, 1967

Fourth Edition 1978

Reprinted, with minor corrections 1979, 1981, 1984, 1986, 1987, 1988

Fifth Edition 1989

British Library Cataloguing in Publication Data

Vogel, Arthur Israel
 Vogel's textbook of practical organic chemistry –
 5th ed
 1. Organic chemistry. Laboratory techniques
 I. Title I. Furniss, B. S. (Brian Stanley), 1941 –
 547.0028
 ISBN 0-582-46236-3

Library of Congress Cataloging-in-Publication Data

Vogel, Arthur Israel.
 Vogel's Textbook of practical organic chemistry — 5th ed. / rev.
 by Brian S. Furniss ... [et al.]
 p. cm.
 Fourth ed. published in 1978 under title: Vogel's Textbook of
 practical organic chemistry, including qualitative organic analysis.
 Includes bibliographies and indexes.
 ISBN 0-470-21414-7
 1. Chemistry, Organic—Laboratory manuals. 2. Chemistry,
 Analytic—Qualitative. I. Furniss, Brian S. (Brian Stanley), 1941–
 II. Vogel, Arthur Israel. Vogel's Textbook of practical organic
 chemistry, including qualitative organic analysis. III. Title.
 QD261.V63 1989
 547—dc19

88-36786
 CIP

Set in 10/11 pt. Lasercomp Times New Roman

Filmset by Eta Services (Typesetters) Ltd, Beccles, Suffolk
 Printed in Great Britain
 by The Bath Press

CONTENTS

CHAPTER 1 ORGANIC SYNTHESIS	1
1.1 INTRODUCTION	1
1.2 STRUCTURE OF THE TARGET MOLECULE	2
1.3 REACTION MECHANISM AND THE METHODOLOGY OF SYNTHESIS	10
1.4 REACTION MECHANISM AND THE STRATEGY OF SYNTHESIS	17
1.5 CONCLUSION	23
REFERENCES	23
 CHAPTER 2 EXPERIMENTAL TECHNIQUES	 26
2.1 GENERAL INSTRUCTIONS FOR SAFE WORKING IN ORGANIC CHEMICAL LABORATORIES	26
2.2 PLANNING OF EXPERIMENTS AND RECORDING OF RESULTS	31
2.3 HAZARDS IN ORGANIC CHEMISTRY LABORATORIES	34
2.3.1 Introduction	34
2.3.2 Explosion and fire hazards	35
2.3.3 Reactive inorganic reagents	42
2.3.4 Hazards due to toxic chemicals	44
2.3.5 Electrical safety	51
2.3.6 Ultraviolet radiation	52
APPARATUS AND REACTION PROCEDURES	52
2.4 INTERCHANGEABLE GROUND GLASS JOINTS	52
2.5 TYPES OF GROUND GLASS JOINTS	55
2.6 CARE AND MAINTENANCE OF GROUND GLASS JOINTS	57
2.7 APPARATUS WITH INTERCHANGEABLE GROUND GLASS JOINTS SUITABLE FOR GENERAL USE IN PREPARATIVE ORGANIC CHEMISTRY	58
2.8 OTHER TYPES OF INTERCHANGEABLE JOINTS AND STOPCOCKS	63
2.9 THE USE OF CORKS AND RUBBER STOPPERS	64
2.10 CUTTING AND BENDING OF GLASS TUBING	65

CONTENTS

2.11 GENERAL LABORATORY APPARATUS	66
2.12 COOLING OF REACTION MIXTURES	70
2.13 HEATING OF REACTION MIXTURES	71
2.14 MECHANICAL AGITATION	73
2.15 TYPICAL ROUND GLASS JOINT ASSEMBLIES FOR STANDARD REACTION PROCEDURES	80
2.16 PRECAUTIONS FOR UNATTENDED REACTIONS	86
2.17 APPARATUS FOR SPECIAL REACTION TECHNIQUES	87
2.17.1 Catalytic hydrogenation	87
2.17.2 Reactions under pressure	97
2.17.3 Uncatalysed and catalysed vapour phase reactions	99
2.17.4 Ozonolysis	103
2.17.5 Organic photochemistry	106
2.17.6 Electrolytic (anodic) syntheses	115
2.17.7 Liquid ammonia techniques	116
2.17.8 Reactions involving air-sensitive compounds	120
ISOLATION AND PURIFICATION PROCESSES	131
2.18 GENERAL CONSIDERATIONS	131
2.19 FILTRATION TECHNIQUES	133
2.20 RECRYSTALLISATION TECHNIQUES	135
2.21 SUBLIMATION TECHNIQUES – FREEZE DRYING	153
2.22 SOLVENT EXTRACTION	156
2.23 DRYING OF LIQUIDS OR OF SOLUTIONS OF ORGANIC COMPOUNDS IN ORGANIC SOLVENTS	165
2.24 DISTILLATION AT ATMOSPHERIC PRESSURE	169
2.25 STEAM DISTILLATION	171
2.26 FRACTIONAL DISTILLATION AT ATMOSPHERIC PRESSURE	173
2.27 DISTILLATION UNDER DIMINISHED PRESSURE ('VACUUM' DISTILLATION)	181
2.28 HIGH VACUUM DISTILLATION – MOLECULAR DISTILLATION	186
2.29 VACUUM PUMPS	191
2.30 MANOMETERS, VACUUMSTATS, VACUUM GAUGES AND MANOSTATS	193
2.31 CHROMATOGRAPHY	197
2.32 STORAGE OF SAMPLES	234
DETERMINATION OF PHYSICAL CONSTANTS	236
2.33 MELTING POINT – MIXED MELTING POINTS	236
2.34 DETERMINATION OF BOILING POINT	241
2.35 DETERMINATION OF MOLECULAR WEIGHT	243
2.36 DETERMINATION OF OPTICAL ROTATORY POWER	244
2.37 DETERMINATION OF REFRACTIVE INDEX	249
REFERENCES	250

CONTENTS

CHAPTER 3 SPECTROSCOPIC METHODS AND THE INTERPRETATION OF SPECTRA	254
<i>Introduction</i>	254
<i>The electromagnetic spectrum</i>	255
3.1 INFRARED SPECTROSCOPY	256
<i>Instrumental features of infrared spectrophotometers</i>	258
<i>Determination of infrared spectra</i>	259
<i>Sample preparation</i>	260
<i>Features of an infrared spectrum</i>	268
<i>Interpretation of an infrared spectrum</i>	271
<i>Characteristic group frequencies</i>	273
3.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	316
<i>Features of the nuclear magnetic resonance spectrum</i>	319
<i>The chemical shift</i>	324
<i>Spin-spin splitting</i>	338
<i>Protons attached to heteroatoms</i>	348
<i>Simplification of ^1H spectra</i>	350
<i>Interpretation of the p.m.r. spectrum</i>	359
<i>Further information from ^{13}C-spectra</i>	360
3.3 MASS SPECTROMETRY	361
<i>The mass spectrum</i>	362
<i>Appearance of the mass spectrum</i>	372
<i>Interpretation of the mass spectrum</i>	373
<i>Mass spectra of classes of organic compounds</i>	373
3.4 ULTRAVIOLET-VISIBLE SPECTROSCOPY	383
<i>Instrumental features of ultraviolet-visible spectrophotometers</i>	384
<i>Determination of ultraviolet-visible spectra</i>	384
<i>Laws of light absorption</i>	385
<i>Solvents for ultraviolet spectroscopy</i>	386
<i>Solution preparation</i>	386
<i>Optical cells and their care</i>	387
<i>Features of an ultraviolet-visible spectrum</i>	388
REFERENCES	393
 CHAPTER 4 SOLVENTS AND REAGENTS	 395
4.1 THE PURIFICATION OF COMMON ORGANIC SOLVENTS	395
Saturated aliphatic hydrocarbons	397
Aromatic hydrocarbons	398
Halogenated hydrocarbons	399
Aliphatic alcohols	400
Ethers	404
Ketones	407
Esters	409

CONTENTS

Nitrogen-containing solvents	409
Sulphur-containing solvents	411
Phosphorus-containing solvents	412
4.2 THE PREPARATION AND PURIFICATION OF REAGENTS	413
REFERENCES	468
 CHAPTER 5 ALIPHATIC COMPOUNDS	 470
5.1 ALKANES	470
<i>Structure</i>	470
<i>Summary of preparative methods and of retrosynthetic strategies</i>	471
<i>Spectroscopic features</i>	472
5.1.1 The catalytic hydrogenation and chemical reduction of alkenes	472
5.1.2 The hydrolysis of alkylmagnesium halides and the hydrogenolysis of alkyl halides and of alkyl methane- or toluene- <i>p</i> -sulphonates	474
5.1.3 The reduction of aldehydes and ketones	476
5.1.4 Coupling reactions (a) using organometallic compounds, and (b) at the anode	477
5.2 ALKENES	484
<i>Structure</i>	484
<i>Summary of preparative methods and of retrosynthetic strategies</i>	485
<i>Spectroscopic features</i>	486
5.2.1 1,2-Elimination processes (β -elimination)	486
5.2.2 The partial hydrogenation of alkynes	493
5.2.3 Wittig and related reactions	495
5.2.4 Selected rearrangements of alkynes to allenes	504
5.3 ALKYNES	507
<i>Structure</i>	507
<i>Summary of preparative methods and of retrosynthetic strategies</i>	508
<i>Spectroscopic features</i>	508
5.3.1 The dehydrogenation of <i>vic</i> - and <i>gem</i> -dihalides	509
5.3.2 The oxidation of dihydrazones of 1,2-diketones	512
5.3.3 Alkylation of a terminal alkyne	513
5.3.4 Coupling reactions leading to diynes	515
5.4 ALIPHATIC ALCOHOLS	517
<i>Structure</i>	517
<i>Summary of preparative methods and of retrosynthetic strategies</i>	517
<i>Spectroscopic features</i>	519
5.4.1 The reduction of aldehydes, ketones and esters	519
5.4.2 The interaction of carbonyl-containing compounds with organometallic reagents	531
5.4.3 The hydroboration-oxidation of alkenes	542
5.4.4 The oxymercuration-demercuration of alkenes	545
5.4.5 The hydroxylation of alkenes	547
5.4.6 Methods for the protection of the hydroxyl group	550

CONTENTS

5.5 ALIPHATIC HALIDES	553
<i>Structure</i>	553
<i>Summary of preparative methods and of retrosynthetic strategies</i>	554
<i>Spectroscopic features</i>	554
5.5.1 Preparation of alkyl chlorides from alcohols	555
5.5.2 Preparation of alkyl bromides from alcohols	559
5.5.3 Preparation of alkyl iodides from alcohols	566
5.5.4 Displacement reactions involving a halogen atom	570
5.5.5 Displacement reactions involving a methanesulphonyloxy group	572
5.5.6 Displacement reactions involving the amino group	574
5.5.7 Addition of hydrogen halides or halogens to alkenes	574
5.5.8 The replacement of reactive allylic hydrogen atoms by bromine	577
5.6 ALIPHATIC ETHERS	579
<i>Structure</i>	579
<i>Summary of preparative methods and of retrosynthetic strategies</i>	580
<i>Spectroscopic features</i>	580
5.6.1 The formation of ethers from alcohols under acidic conditions	581
5.6.2 The interaction of an alcohol with a halogen compound under basic conditions	583
5.7 ALIPHATIC ALDEHYDES	585
<i>Structure</i>	585
<i>Summary of preparative methods and of retrosynthetic strategies</i>	585
<i>Spectroscopic features</i>	587
5.7.1 The controlled oxidation or dehydrogenation of primary alcohols	587
5.7.2 The oxidative cleavage of 1,2-diols	590
5.7.3 The ozonolysis of suitably substituted alkenes	592
5.7.4 The reduction of nitriles, carboxylic acids and carboxylic acid chlorides	594
5.7.5 Methods based upon alkyl halides	596
5.7.6 The hydrolysis and decarboxylation of α,β -epoxy esters (glycidic esters)	598
5.7.7 The oxidative hydrolysis of nitronate salts derived from primary nitroalkanes	599
5.7.8 Methods for the alkylation of the carbon chain	600
5.8 ALIPHATIC KETONES	604
<i>Structure</i>	604
<i>Summary of preparative methods and of retrosynthetic strategies</i>	605
<i>Spectroscopic features</i>	606
5.8.1 The oxidation of secondary alcohols	607
5.8.2 The hydration of alkynes	612
5.8.3 The thermal decarboxylation of acids over a metal oxide catalyst	612
5.8.4 The interaction of organometallic compounds with carboxylic acid chlorides and <i>N,N</i> -dimethylcarboxamides	616

CONTENTS

5.8.5	The hydrolysis and decarboxylation of β -keto esters and the hydrolysis of β -diketones	619
5.8.6	The acid-catalysed rearrangement of 1,2-diols	623
5.8.7	The oxidative hydrolysis of nitronate salts from secondary nitroalkanes	623
5.8.8	Methods for the protection of the carbonyl group in aldehydes and ketones	623
5.9	DICARBONYL COMPOUNDS	626
	<i>Structure</i>	626
5.9.1	1,2-Dicarbonyl compounds	627
5.9.2	1,3-Dicarbonyl compounds	632
5.9.3	1,4-Dicarbonyl compounds	635
5.10	CARBOHYDRATES	637
	<i>Structure</i>	637
5.10.1	Carbohydrate interconversions	642
5.10.2	Carbohydrate interconversions	644
5.10.3	Carbohydrate interconversions	651
5.10.4	Carbohydrate interconversions	658
5.10.5	Carbohydrate interconversions	660
5.11	ALIPHATIC CARBOXYLIC ACIDS	664
	<i>Structure</i>	664
	<i>Summary of preparative methods and of retrosynthetic strategies</i>	664
	<i>Spectroscopic features</i>	666
5.11.1	Oxidative methods	667
5.11.2	Hydrolysis of alkyl cyanides	671
5.11.3	Carboxylation of Grignard reagents	673
5.11.4	The Arndt-Eistert method	675
5.11.5	Electrolytic (anodic) coupling	677
5.11.6	Methods utilising diethyl malonate	680
5.11.7	The synthesis of optically active carboxylic acids	687
5.11.8	Methods for the protection of the carboxyl group	690
5.12	CARBOXYLIC ACID DERIVATIVES	691
	<i>Structure</i>	691
	<i>Summary of retrosynthetic strategies</i>	692
	<i>Spectroscopic features</i>	692
5.12.1	Acyl halides	692
5.12.2	Acid anhydrides	693
5.12.3	Esters	695
5.12.4	Acid amides	708
5.13	ALIPHATIC NITRILES	710
	<i>Summary of preparative methods and of retrosynthetic strategies</i>	710
	<i>Spectroscopic features</i>	711
5.13.1	Displacement with cyanide ion on an alkyl halide	711
5.13.2	Displacement with cyanide ion on an arylsulphonylhydrazone	712
5.13.3	Dehydration of amides and aldoximes	715

CONTENTS

5.13.4	Cyanoethylation procedures and the α -alkylation of nitriles 717	
5.14	SUBSTITUTED CARBOXYLIC ACIDS AND THEIR DERIVATIVES	719
	<i>Structure</i> 719	
	<i>Spectroscopic features</i> 720	
5.14.1	Halogeno acids 720	
5.14.2	Hydroxy acids and lactones 725	
5.14.3	Keto acids and esters 735	
5.14.4	Amino acids and peptides 746	
5.15	NITROALKANES	763
	<i>Structure</i> 763	
	<i>Summary of preparative methods and of retrosynthetic strategies</i> 764	
	<i>Spectroscopic features</i> 764	
5.15.1	The displacement of a halogen by a nitrite ion in an alkyl halide 764	
5.15.2	The oxidation of oximes and amines 765	
5.15.3	C-Alkylation of nitroalkanes and other homologation procedures 768	
5.16	ALIPHATIC AMINES	769
	<i>Structure</i> 769	
	<i>Summary of preparative methods and of retrosynthetic strategies</i> 770	
	<i>Spectroscopic features</i> 771	
5.16.1	The reduction of alkyl azides, alkyl cyanides and amides 771	
5.16.2	The reduction of nitro compounds and oximes 774	
5.16.3	The reductive alkylation of ammonia or amines 776	
5.16.4	The alkylation of ammonia and its derivatives 779	
5.16.5	Imine and enamine formation 782	
5.16.6	Molecular rearrangements of the Hofmann type 783	
5.16.7	Methods for the protection of the amino and imino groups 784	
5.17	ALIPHATIC SULPHUR COMPOUNDS	786
	<i>Structure</i> 786	
	<i>Spectroscopic features</i> 787	
5.17.1	Thiols and thioacetals 787	
5.17.2	Dialkyl sulphides (thioethers) and trialkylsulphonium salts 789	
5.17.3	Sulphoxides and sulphones 791	
5.17.4	O,S-Dialkyl dithiocarbonates (xanthate esters) 792	
5.18	UNSATURATED COMPOUNDS	794
5.18.1	Unsaturated alcohols 794	
5.18.2	Unsaturated carbonyl compounds 798	
5.18.3	Unsaturated acids and esters 820	
5.19	RESOLUTION OF RACEMATES	809
	REFERENCES	816