

Techniques and Experiments for Organic Chemistry

SIXTH EDITION

Addison Ault
Cornell College



University Science Books
Sausalito, California

Contents

Preface to the Sixth Edition	xix
Preface to the Fifth Edition	xxi

PART I Laboratory Operations

Preliminary Topics

1. Safety	3
1.1 Fire	4
1.2 Explosions	5
1.3 Poisoning	6
1.4 Cuts	7
1.5 Spills	7
1.6 Chemicals in the Eye	8
1.7 A Short List of Hazardous Materials and Some of Their Properties	8
2. Glassware Used in the Organic Chemistry Laboratory	16
3. Cleaning Up	21
3.1 Care of Ground-Glass-Jointed Glassware	22
3.2 Separatory Funnels and Glassware with Stopcocks	23
3.3 Drying of Glassware	23
4. Collection and Disposal of Waste	24
4.1 Solid Waste	24
4.2 Liquid Waste	25
4.3 General Instructions for Collection of Waste	25
5. The Laboratory Notebook	26
6. The Chemical Literature	31
6.1 Secondary Sources for Physical Properties of Organic Compounds	32
6.2 Secondary Sources for Methods of Preparation of Organic Compounds	35
6.3 Collections of Spectra	36
6.4 Miscellaneous	37

7. Tables	38
7.1 Solutions of Acids	39
7.2 Solutions of Bases	40
7.3 Molecular Weights and Molar Volumes of Acids	40
7.4 Molar Weights of Bases	41
7.5 Molecular Weights, Densities, and Molar Volumes of Selected Liquid Reagents	41
7.6 Periodic Table of the Elements	42

Separation of Substances; Purification of Substances

8. Filtration	44
8.1 Gravity Filtration	44
8.2 Micro-Scale Gravity Filtration	45
8.3 Vacuum or Suction Filtration	45
9. Recrystallization	48
9.1 Choice of Solvent	49
9.2 Dissolving the Sample	49
9.3 Decolorizing the Solution	50
9.4 Hot Filtration	50
9.5 Cooling for Crystallization	52
9.6 Cold Filtration	53
9.7 Washing the Crystals	53
9.8 Drying the Crystals	54
9.9 More Techniques of Crystallization	55
9.10 Micro-Scale Recrystallization	57
9.11 Selection of a Suitable Solvent	59
10. Distillation	62
10.1 Vapor Pressure	63
10.2 Distillation of a Pure Liquid	66
10.3 Miscible Pairs of Liquids	67
10.4 Fractional Distillation	70
10.5 Azeotropic Mixtures	72
10.6 Technique of Distillation	75
10.7 Small-Scale Distillation	77
11. Reduced-Pressure Distillation	80
11.1 Estimation of the Boiling Point at Reduced Pressure	81
11.2 Apparatus	82

11.3	Source of Vacuum	83
11.4	Pressure Measurement	84
11.5	Technique of Distillation Under Reduced Pressure	85
12.	Distillation of Mixtures of Two Immiscible Liquids; Steam Distillation	87
12.1	Theory of Steam Distillation	87
12.2	Technique of Steam Distillation	88
13.	Sublimation	90
13.1	Theory of Sublimation	90
13.2	Technique of Sublimation	91
14.	Extraction by Solvents	92
14.1	Theory of Extraction	92
14.2	Extraction of Acids and Bases	94
14.3	Technique of Extraction	97
14.4	Micro-Scale Extraction	101
15.	Chromatography	109
15.1	Theory of Column Chromatography	110
15.2	Technique of Column Chromatography	113
15.3	Theory of Thin-Layer Chromatography	116
15.4	Technique of Thin-Layer Chromatography	118
15.5	Theory of Paper Chromatography	120
15.6	Technique of Paper Chromatography	120
15.7	Theory of Vapor-Phase Chromatography	122
15.8	Technique of Vapor-Phase Chromatography	126
15.9	High-Pressure Liquid Chromatography	128
15.10	Batchwise Adsorption; Decolorization	129
16.	Removal of Water; Drying	129
16.1	Drying of Solids	130
16.2	Drying of Solutions	132
16.3	Drying of Solvents and Liquid Reagents	134

Determination of Physical Properties

17.	Boiling Point	138
17.1	Experimental Determination of Boiling Point	138
17.2	Boiling Point and Molecular Structure	141
17.3	Boiling Point and the Enthalpy and Entropy of Vaporization	144

18. Melting Point	150
18.1 Experimental Determination of the Melting Point	150
18.2 The Melting Point as a Criterion of Purity	154
18.3 The Melting Point as a Means of Identification and Characterization	155
18.4 Mixture Melting Points	155
18.5 Melting Point and Molecular Structure	155
19. Density; Specific Gravity	159
19.1 Experimental Determination of the Density	159
19.2 Density and Molecular Structure	160
20. Index of Refraction	161
20.1 Experimental Determination of the Index of Refraction	161
20.2 Index of Refraction and Molecular Structure	162
21. Optical Activity	163
21.1 Experimental Determination of Optical Rotation	163
21.2 Optical Activity and Molecular Structure	166
22. Molecular Weight	168
22.1 Molecular Weight Determination by Mass Spectrometry	168
22.2 Molecular Weight Determination by Other Methods	169
23. Solubility	169
23.1 Solubility of Liquids in Liquids	170
23.2 Solubility of Solids in Liquids	174
23.3 Classification of Compounds by Solubility; Relationships Between Solubility and Molecular Structure	175
23.4 Techniques for Determination of Solubility	180
24. Infrared Absorption Spectrometry	182
24.1 Wavelength, Frequency, and Energy of Electromagnetic Radiation	183
24.2 Units of Light Absorption	183
24.3 Infrared Light Absorption and Molecular Structure	185
24.4 Interpretation of Infrared Spectra	186
24.5 Sample Preparation	191
25. Ultraviolet-Visible Absorption Spectrometry	201
25.1 Ultraviolet-Visible Light Absorption and Molecular Structure	202
25.2 Interpretation of Ultraviolet-Visible Spectra	203
25.3 Color and Molecular Structure	203
25.4 Sample Preparation	204

26. Nuclear Magnetic Resonance Spectrometry	207
26.1 Shielding; Chemical Shift	208
26.2 Splitting	211
26.3 The Integral	219
26.4 Nuclear Magnetic Resonance and Molecular Structure	220
26.5 Interpretation of NMR Spectra	222
26.6 Sample Preparation	226
27. Mass Spectrometry	231
27.1 Theory of Mass Spectrometry	231
27.2 Interpretation of Mass Spectra	234
27.3 High-Resolution Mass Spectrometry	236

Determination of Chemical Properties: Qualitative Organic Analysis

28. Qualitative Tests for the Elements	241
28.1 Ignition Test; Test for Metals	241
28.2 Beilstein Test; Test for Halogens (Except Fluorine)	242
28.3 Sodium Fusion Test; Test for Nitrogen, Sulfur, and the Halogens	242
29. Qualitative Characterization Tests: Tests for the Functional Groups	247
29.1 Detection of Ammonia from Ammonium Salts, Primary Amides, and Nitriles	249
29.2 Benzenesulfonyl Chloride (Hinsberg's Test)	250
29.3 Bromine in Carbon Tetrachloride	252
29.4 Chromic Anhydride	253
29.5 2,4-Dinitrophenylhydrazine	253
29.6 Ferric Chloride Solution	254
29.7 Ferric Hydroxamate Test	255
29.8 Hydrochloric Acid/Zinc Chloride Test (Lucas's Test)	258
29.9 Iodoform Test	258
29.10 Aqueous Potassium Permanganate Solution (Baeyer's Test)	260
29.11 Alcoholic Silver Nitrate Solution	261
29.12 Sodium Hydroxide Test	262
29.13 Sodium Iodide in Acetone	263
29.14 Tollen's Reagent: Silver-Ammonia Complex Ion	263

30. Characterization Through Formation of Derivatives	266
30.1 Benzoates, <i>p</i> -Nitrobenzoates, and 3,5-Dinitrobenzoates of Alcohols	272
30.2 Hydrogen 3-Nitrophthalates of Alcohols	273
30.3 Phenyl- and α -Naphthylurethans	274
30.4 Methone Derivations of Aldehydes	274
30.5 2,4-Dinitrophenylhydrazones	275
30.6 Semicarbazones	276
30.7 Oximes	276
30.8 Carboxylic Acids by Hydrolysis of Primary Amides and Nitriles	277
30.9 9-Acylamidoxanthenes from Amides	278
30.10 Hydrolysis of <i>N</i> -Substituted Amides	279
30.11 Substituted Acetamides from Amines	280
30.12 Substituted Benzamides from Amines	281
30.13 <i>p</i> -Toluenesulfonamides from Amines	282
30.14 Phenylthioureas and α -Naphthylthioureas	282
30.15 Picrates	283
30.16 Quaternary Ammonium Salts: Methiodides and <i>p</i> -Toluenesulfonates	285
30.17 Carboxylic Acid Amides	285
30.18 Anilides, <i>p</i> -Toluidides, and <i>p</i> -Bromoanilides of Carboxylic Acids	286
30.19 Phenacyl and Substituted Phenacyl Esters of Carboxylic Acids	287
30.20 <i>p</i> -Nitrobenzyl Esters of Carboxylic Acids	289
30.21 <i>N</i> -Benzylamides from Esters	290
30.22 3,5-Dinitrobenzoates from Esters	290
30.23 Hydrolysis of Esters	291
30.24 Bromination of Aromatic Ethers	292
30.25 <i>S</i> -Alkylthiuronium Picrates	293
30.26 <i>o</i> -Aroylbenzoic Acids from Aromatic Hydrocarbons	294
30.27 Aromatic Acids by Oxidation by Permanganate	295
30.28 Anilides, <i>p</i> -Toluidides, and α -Naphthalides from Alkyl Halides	295
30.29 2,4,7-Trinitrofluorenone Adducts of Aromatic Hydrocarbons	296
30.30 Bromination of Phenols	297
30.31 Aryloxyacetic Acids from Phenols	297

Apparatus and Techniques for Chemical Reactions

31. Assembling the Apparatus	299
32. Temperature Control	302
33. Methods of Heating and Cooling	305
33.1 Heating	305
33.2 Cooling	309
34. Stirring	310
35. Addition of Reagents	313
36. Control of Evolved Gases	315
37. Concentration; Evaporation	317
38. Use of an Inert Atmosphere	318
39. Working Up the Reaction; Isolation of the Product	319

PART II Experiments

Isolations and Purifications

E1	Isolation of Cholesterol from Gallstones	327
E2	Isolation of Lactose from Powdered Milk	329
E3	Isolation of Acetylsalicylic Acid from Aspirin Tablets	332
E4	Isolation of Ibuprofen from Ibuprofen Tablets	335
E5	Isolation of Caffeine from Tea and NoDoz	337
E6	Isolation of Piperine from Black Pepper	340
E7	Isolation of Trimyristin from Nutmeg	342
E8	Isolation of Clove Oil from Cloves	344
E9	Isolation of Eugenol from Clove Oil	346
E10	Isolation of (R)-(+)-Limonene from Grapefruit or Orange Peel	347
E11	Isolation of (R)-(-)-or (S)-(+)-Carvone from Oil of Spearmint or Oil of Caraway	350
E12	Resolution of α -Phenylethylamine by (R),(R)-(+)-Tartaric acid	355

Transformations

Isomerizations	363
E13 Adamantane from <i>endo</i> -Tetrahydrodicyclopentadiene via the Thiourea Clathrate	364
E14 <i>cis</i> -Dibenzoyl ethylene from <i>trans</i> -1,2-Dibenzoyl ethylene	367
Preparation of Cyclohexanol	371
E15 Cyclohexanol from Cyclohexene	371
E16 Cyclohexanol from Cyclohexanone	373
Reactions of Cyclohexanol	375
E17 Cyclohexene from Cyclohexanol	376
E18 Dehydration of 2-Methylcyclohexanol: A Variation	381
E19 Cyclohexyl Bromide from Cyclohexanol	384
E20 Cyclohexanone from Cyclohexanol	387
Addition of Dichlorocarbene to Alkenes by Phase Transfer Catalysis	389
E21 Addition of Dichlorocarbene to Cyclohexene	392
E22 Addition of Dichlorocarbene to Styrene: A Variation	394
E23 Addition of Dichlorocarbene to 1,5-Cyclooctadiene: Another Variation	395
Alkyl Halides from Alcohols	397
E24 Isoamyl Bromide from Isoamyl Alcohol	398
E25 <i>n</i> -Butyl Bromide from <i>n</i> -Butyl Alcohol: A Variation	402
E26 <i>tert</i> -Butyl Chloride from <i>tert</i> -Butyl Alcohol	403
E27 <i>tert</i> -Amyl Chloride from <i>tert</i> -Amyl Alcohol: A Variation	406
E28 Competitive Nucleophilic Substitution of Butyl Alcohols by Bromide and Chloride Ion	407
E29 Kinetics of the Hydrolysis of <i>tert</i> -Butyl Chloride	410

Isoamyl Acetate: A Component of the Alarm Pheromone of the Honey Bee	417
E30 Isoamyl Acetate from Isoamyl Bromide and Potassium Acetate	421
E31 Isoamyl Acetate from Isoamyl Alcohol and Acetic Acid; The Fischer Estrification	424
Liquid Crystals	427
E32 Cholesteryl Benzoate from Cholesterol	428
Acetylation of Glucose	431
E33 α -D-Glucose Pentaacetate from Glucose	433
E34 β -D-Glucose Pentaacetate from Glucose	433
E35 Acetylation of Glucose in <i>N</i> -Methylimidazole: A Variation	434
E36 Preparation of Methyl Benzoate, Oil of Niobe	436
The Grignard Reaction	439
E37 Aliphatic Alcohols: Preparation by Grignard Synthesis	440
Preparation of Triphenylmethanol	444
E38 Preparation of Triphenylmethanol from Benzophenone	446
E39 Preparation of Triphenylmethanol from Methyl Benzoate	448
E40 Preparation of Triphenylmethanol from Dimethyl Carbonate	451
E41 Preparation of Aniline from Nitrobenzene	454
Preparation of Amides	456
E42 Acetanilide from Aniline	457
E43 <i>N,N</i> -Diethyl- <i>m</i> -Toluamide from <i>m</i> -Toluic Acid; A Mosquito Repellant: "Off"	461
Electrophilic Substitution Reactions of Benzene Derivatives	463
E44 Methyl <i>m</i> -Nitrobenzoate from Methyl Benzoate	464
E45 <i>p</i> -Bromoacetanilide from Acetanilide	466
E46 2,4-Dinitrobromobenzene from Bromobenzene	469

Nucleophilic Aromatic Substitution Reactions of 2,4-Dinitrobromobenzene	472
E47 2,4-Dinitroaniline	473
E48 2,4-Dinitrophenylhydrazine	474
E49 2,4-Dinitrodiphenylamine	475
E50 2,4-Dinitrophenylpiperidine	477
E51 4-Substituted 2,4-Dinitrophenylanilines: A Variation	478
Diazonium Salts of Aromatic Amines	480
E52 Benzenediazonium Chloride from Aniline	481
E53 <i>p</i> -Nitrobenzenediazonium Sulfate from <i>p</i> -Nitroaniline	482
Replacement Reactions of Diazonium Salts	482
E54 Chlorobenzene from Benzenediazonium Chloride	483
Reactions of Vanillin	485
E55 Acetylvainillin from Vanillin	486
E56 5-Bromovanillin from Vanillin	487
E57 5-Nitrovanillin from Vanillin	489
E58 Vanillin Oxime from Vanillin	490
E59 Vanillin Semicarbazone from Vanillin	491
E60 Vanillyl Alcohol from Vanillin	493
E61 Vanillideneacetone from Vanillin	494
Synthesis of Dyes	498
E62 Benzenediazonium Chloride and β -Naphthol: 1-Phenylazo-2-Naphthol (Sudan I)	499
E63 <i>p</i> -Nitrobenzenediazonium Sulfate and Phenol: (4-nitrobenzeneazo)-phenol	502
E64 <i>p</i> -Nitrobenzenediazonium Sulfate and β -Naphthol: 1-(<i>p</i> -nitrophenylazo)-2-naphthol (Para Red; American Flag Red)	503
E65 <i>p</i> -Nitrobenzenediazonium Sulfate and Dimethylaniline: (4-nitrobenzeneazo)-<i>N,N</i>-Dimethylaniline	505
The Diels-Alder Reaction	507
E66 Butadiene (from 3-Sulfolene) and Maleic Anhydride	508
E67 Cyclopentadiene and Maleic Anhydride	510
E68 Furan and Maleic Anhydride	514
E69 α -Phellandrene and Maleic Anhydride	515

The Wittig Reaction	517
E70 The Preparation of <i>trans</i> -Stilbene	519
E71 Preparation of <i>trans,trans</i> -1,4-Diphenylbutadiene: A Variation	524
Analgesics: Aspirin, Phenacetin, and Tylenol	527
E72 Acetylsalicylic Acid from Salicylic Acid: Preparation of Aspirin	527
E73 <i>p</i> -Acetamidophenol from <i>p</i> -Aminophenol: Preparation of Tylenol	529
E74 <i>p</i> -Ethoxyacetanilide from <i>p</i> -Ethoxyaniline: Preparation of Phenacetin	531
E75 <i>p</i> -Ethoxyacetanilide from <i>p</i> -Acetamidophenol: Another Preparation of Phenacetin	535
Nitration of Phenacetin	536
E76 2-Nitrophenacetin from Phenacetin	536
Esterification of Salicylic Acid	538
E77 Preparation of Methyl Salicylate: Oil of Wintergreen	538
Coconut Aldehyde; γ-Nonanolactone	540
E78 3-Nonenoic Acid from Heptaldehyde and Malonic Acid	541
E79 Coconut Aldehyde from 3-Nonenoic Acid	543
Catalysis by Thiamine	546
E80 Thiamine-Catalyzed Formation of Benzoin from Benzaldehyde	546
A Model for the Reducing Agent NADH	552
E81 1-Benzylnicotinamide Chloride from Nicotinamide	554
E82 1-Benzyl-dihydronicotinamide from 1-Benzylnicotinamide Chloride	556
E83 Reduction of Malachite Green by 1-Benzyl- dihydronicotinamide	557
Two Thermochronic Compounds	559
E84 Dixanthylene from Xanthone	560
E85 Dianthroquinone from Anthrone via 9-Bromoanthrone	561

A Photochromic Compound: 2-(2,4-Dinitrobenzyl)pyridine	564
E86 A Photochromic Compound: 2-(2,4-Dinitrobenzyl)pyridine	564
E87 A Chemiluminescent Compound: Luminol	567

Synthetic Sequences: Experiments that Use a Sequence of Reactions

Steroid Transformations	578
E88 Cholesterol Dibromide from Cholesterol	580
E89 5 α ,6 β -Dibromocholestane-3-one from Cholesterol Dibromide	582
E90 Δ^5 -Cholestene-3-one from 5 α ,6 β -Dibromocholestane-3-one	583
E91 Δ^4 -Cholestene-3-one from Δ^5 -Cholestene-3-one	587

Tetraphenylcyclopentadienone: A Purple Compound	589
E92 Benzoin from Benzaldehyde	591
E93 Benzil from Benzoin	592
E94 Dibenzylketone from Phenylacetic Acid	593
E95 Tetraphenylcyclopentadienone from Benzil and Dibenzyl Ketone	595

Sulfanilamide	597
E96 <i>p</i> -Acetamidobenzenesulfonyl Chloride from Acetanilide	602
E97 <i>p</i> -Acetamidobenzenesulfonamide from <i>p</i> -Acetamidobenzenesulfonyl Chloride	604
E98 Sulfanilamide from <i>p</i> -Acetamidobenzenesulfonamide	605

A Bootstrap Synthesis: <i>p</i>-Phenetidine from <i>p</i>-Phenetidine	607
E99 Ethyldioxyazobenzene from <i>p</i> -Phenetidine	608
E100 Diethyldioxyazobenzene from Ethyldioxyazobenzene	610
E101 <i>p</i> -Phenetidine from Diethyldioxyazobenzene	611

1-Bromo-3-Chloro-5-iodobenzene	615
E102 2-Chloro-4-Bromoacetanilide from 4-Bromoacetanilide	617
E103 2-Chloro-4-Bromoaniline from 2-Chloro-4-Bromoacetanilide	620
E104 2-Chloro-4-Bromo-6-iodoaniline from 2-Chloro-4-Bromoaniline	622
E105 1-Bromo-3-chloro-5-Iodobenzene from 2-Chloro-4-bromo-6-iodoaniline	624
 MOED: A Merocyanine Dye	627
E106 1,4-Dimethylpyridinium Iodide from 4-Methylpyridine and Methyl Iodide	629
E107 Preparation of 4-(<i>p</i> -Hydroxystyryl)-1-Methylpyridinium Iodide from 1-4-Dimethylpyridinium Iodide and <i>p</i> -Hydroxybenzaldehyde	630
E108 1-Methyl-4[(Oxocyclohexadienylidene) -Ethylidene]-1,4-Dihydropyridine (MOED) from 4-(<i>p</i> -Hydroxystyryl)-1-Methyl- pyridinium Iodide	632
 Appendix	635
 Chemical Substance Index	647
 General Subject Index	655