

## Table of Contents

Preface .....	XIII
Abbreviations.....	XV
1. Abnormal Claisen rearrangement.....	1
2. Alder ene reaction.....	2
3. Allan–Robinson reaction .....	3
4. Alper carbonylation .....	5
5. Amadori glucosamine rearrangement.....	7
6. Angeli–Rimini hydroxamic acid synthesis .....	8
7. ANRORC mechanism .....	9
8. Arndt–Eistert homologation .....	10
9. Baeyer–Drewson indigo synthesis.....	11
10. Baeyer–Villiger oxidation .....	13
11. Baker–Venkataraman rearrangement .....	14
12. Bamberger rearrangement .....	15
13. Bamford–Stevens reaction.....	16
14. Bargellini reaction .....	17
15. Bartoli indole synthesis .....	18
16. Barton decarboxylation .....	20
17. Barton–McCombie deoxygenation.....	21
18. Barton nitrite photolysis .....	22
19. Baylis–Hillman reaction.....	23
20. Beckmann rearrangement .....	25
21. Beirut reaction .....	26
22. Benzilic acid rearrangement .....	28
23. Benzoin condensation.....	29
24. Bergman cyclization.....	30
25. Biginelli pyrimidone synthesis .....	31
26. Birch reduction .....	33
27. Bischler–Möhlau indole synthesis .....	35
28. Bischler–Napieralski reaction.....	36
29. Blaise reaction .....	37
30. Blanc chloromethylation reaction.....	38
31. Boekelheide reaction .....	39
32. Boger pyridine synthesis .....	40
33. Boord reaction .....	41
34. Borsche–Drechsel cyclization .....	42
35. Boulton–Katritzky rearrangement .....	43
36. Bouveault aldehyde synthesis.....	44
37. Bouveault–Blanc reduction .....	45
38. Boyland–Sims oxidation.....	46

39.	Bradsher reaction.....	48
40.	Brook rearrangement .....	49
41.	Brown hydroboration reaction.....	50
42.	Bucherer carbazole synthesis .....	51
43.	Bucherer reaction .....	52
44.	Bucherer–Bergs reaction .....	53
45.	Buchner–Curtius–Schlotterbeck reaction .....	54
46.	Buchner method of ring expansion.....	55
47.	Buchwald–Hartwig C–N bond and C–O bond formation reactions .....	56
48.	Burgess dehydrating reagent .....	57
49.	Cadiot–Chodkiewicz coupling .....	58
50.	Cannizzaro disproportionation reaction.....	59
51.	Carroll rearrangement.....	60
52.	Castro–Stephens coupling .....	61
53.	Chapman rearrangement.....	62
54.	Chichibabin amination reaction.....	63
55.	Chichibabin pyridine synthesis.....	64
56.	Chugaev reaction .....	66
57.	Ciamician–Dennsted rearrangement.....	67
58.	Claisen, Eschenmoser–Claisen, Johnson–Claisenand, and Ireland– Claisen rearrangements .....	68
59.	Clark–Eschweiler reductive alkylation of amines .....	70
60.	Combes quinoline synthesis .....	71
61.	Conrad–Lipach reaction .....	73
62.	Cope elimination reaction.....	74
63.	Cope, oxy-Cope, and anionic oxy-Cope rearrangements .....	75
64.	Corey–Chaykovsky epoxidation .....	77
65.	Corey–Fuchs reaction.....	78
66.	Corey–Bakshi–Shibata (CBS) reduction .....	79
67.	Corey–Kim oxidation .....	81
68.	Corey–Winter olefin synthesis .....	82
69.	Cornforth rearrangement .....	84
70.	Criegee glycol cleavage.....	85
71.	Criegee mechanism of ozonolysis .....	86
72.	Curtius rearrangement .....	87
73.	Dakin reaction .....	88
74.	Dakin–West reaction .....	89
75.	Danheiser annulation .....	90
76.	Darzens glycidic ester condensation.....	91
77.	Davis chiral oxaziridine reagent .....	92
78.	de Mayo reaction .....	93
79.	Demjanov rearrangement .....	95
80.	Dess–Martin periodinane oxidation.....	96
81.	Dieckmann condensation.....	97
82.	Diels–Alder reaction, reverse electronic demand Diels–Alder reaction, hetero-Diels–Alder reaction .....	98

83.	Dienone–phenol rearrangement.....	100
84.	Di- $\pi$ -methane rearrangement.....	101
85.	Doebner reaction .....	102
86.	Doebner–von Miller reaction.....	104
87.	Doering–LaFlamme allene synthesis.....	106
88.	Dornow–Wiehler isoxazole synthesis.....	107
89.	Dötz reaction .....	109
90.	Dutt–Wormall reaction.....	110
91.	Eschenmoser coupling reaction .....	111
92.	Eschenmoser–Tanabe fragmentation.....	112
93.	Étard reaction .....	113
94.	Evans aldol reaction .....	114
95.	Favorskii rearrangement and Quasi-Favorskii rearrangement.....	116
96.	Feist–Bénary furan synthesis.....	118
97.	Ferrier rearrangement .....	119
98.	Fischer–Hepp rearrangement.....	120
99.	Fischer indole synthesis.....	121
100.	Fischer–Speier esterification .....	122
101.	Fleming oxidation.....	123
102.	Forster reaction.....	125
103.	Frater–Seebach alkylation .....	127
104.	Friedel–Crafts reaction .....	128
105.	Friedländer synthesis .....	130
106.	Fries rearrangement .....	132
107.	Fritsch–Buttenberg–Wiechell rearrangement .....	133
108.	Fujimoto–Belleau reaction .....	134
109.	Fukuyama amine synthesis.....	135
110.	Gabriel synthesis .....	137
111.	Gassman indole synthesis.....	138
112.	Gattermann–Koch reaction.....	139
113.	Gewald aminothiophene synthesis .....	140
114.	Glaser coupling.....	142
115.	Gomberg–Bachmann reaction .....	143
116.	Gribble indole reduction.....	144
117.	Gribble reduction of diaryl ketones .....	145
118.	Grob fragmentation .....	146
119.	Guareschi–Thorpe condensation .....	148
120.	Hajos–Wiechert reaction .....	149
121.	Haller–Bauer reaction.....	151
122.	Hantzsch pyridine synthesis .....	152
123.	Hantzsch pyrrole synthesis .....	154
124.	Haworth reaction .....	155
125.	Hayashi rearrangement .....	156
126.	Heck reaction.....	158
127.	Hegedus indole synthesis.....	160
128.	Hell–Volhard–Zelinsky reaction .....	161

129.	Henry reaction (nitroaldol reaction) .....	162
130.	Herz reaction .....	163
131.	Heteroaryl Heck reaction.....	164
132.	Hiyama cross-coupling reaction .....	165
133.	Hodges–Vedejs metallation of oxazoles.....	167
134.	Hofmann rearrangement (Hofmann degradation reaction).....	168
135.	Hofmann–Löffler–Freitag reaction.....	169
136.	Hofmann–Martius reaction (Reilly–Hickinbottom rearrangement) .....	170
137.	Hooker oxidation .....	172
138.	Horner–Wadsworth–Emmons reaction .....	174
139.	Houben–Hoesch synthesis .....	176
140.	Hunsdiecker reaction .....	178
141.	Ing–Manske procedure .....	179
142.	Jacobsen–Katsuki epoxidation .....	180
143.	Jacobsen rearrangement.....	182
144.	Japp–Klingemann hydrazone synthesis.....	184
145.	Julia–Lythgoe olefination .....	185
146.	Kahne glycosidation .....	186
147.	Keck stereoselective allylation .....	188
148.	Keck macrolactonization .....	190
149.	Kemp elimination .....	192
150.	Kennedy oxidative cyclization .....	193
151.	Kharasch addition reaction .....	194
152.	Knoevenagel condensation.....	195
153.	Knorr pyrrole synthesis .....	197
154.	Koch carbonylation reaction (Koch–Haaf carbonylation reaction) .....	198
155.	Koenigs–Knorr glycosidation.....	200
156.	Kolbe–Schmitt reaction.....	201
157.	Kostanecki reaction .....	202
158.	Krapcho decarboxylation.....	204
159.	Kröhnke reaction (pyridine synthesis).....	205
160.	Kumada cross-coupling reaction .....	207
161.	Larock indole synthesis .....	209
162.	Lawesson’s reagent .....	210
163.	Leuckart–Wallach reaction.....	211
164.	Lieben haloform reaction .....	212
165.	Liebeskind–Srogl coupling.....	213
166.	Lossen rearrangement.....	214
167.	Luche reduction.....	215
168.	McFadyen–Stevens reduction .....	216
169.	McLafferty rearrangement.....	217
170.	McMurry coupling .....	218
171.	Madelung indole synthesis .....	219
172.	Mannich reaction .....	220
173.	Marshall boronate fragmentation.....	221
174.	Martin’s sulfurane dehydrating reagent.....	222

175.	Masamune–Roush conditions .....	223
176.	Meerwein arylation .....	225
177.	Meerwein–Ponndorf–Verley reduction .....	226
178.	Meinwald rearrangement .....	227
179.	Meisenheimer complex .....	228
180.	Meisenheimer rearrangement .....	230
181.	Meyer–Schuster rearrangement .....	231
182.	Michael addition .....	232
183.	Michaelis–Arbuzov phosphonate synthesis .....	233
184.	Midland reduction .....	234
185.	Miller–Snyder aryl cyanide synthesis .....	235
186.	Mislow–Evans rearrangement .....	237
187.	Mitsunobu reaction .....	238
188.	Miyaura boration reaction .....	239
189.	Moffatt oxidation .....	240
190.	Morgan–Walls reaction (Pictet–Hubert reaction) .....	241
191.	Mori–Ban indole synthesis .....	242
192.	Morin rearrangement .....	244
193.	Mukaiyama aldol reaction .....	246
194.	Mukaiyama esterification .....	247
195.	Myers–Saito cyclization .....	249
196.	Nametkin rearrangement (retropinacol rearrangement) .....	250
197.	Nazarov cyclization .....	251
198.	Neber rearrangement .....	252
199.	Nef reaction .....	253
200.	Negishi cross-coupling reaction .....	254
201.	Nenitzescu indole synthesis .....	255
202.	Nicholas reaction .....	257
203.	Noyori asymmetric hydrogenation .....	258
204.	Nozaki–Hiyama–Kishi reaction .....	260
205.	Oppenauer oxidation .....	261
206.	Orton rearrangement .....	262
207.	Overman rearrangement .....	264
208.	Paal–Knorr furan synthesis .....	265
209.	Paal–Knorr pyrrole synthesis .....	266
210.	Parham cyclization .....	267
211.	Passerini reaction .....	269
212.	Paterno–Büchi reaction .....	270
213.	Pauson–Khand cyclopentenone synthesis .....	271
214.	Payne rearrangement .....	273
215.	Pechmann condensation (coumarin synthesis) .....	274
216.	Pechmann pyrazole synthesis .....	275
217.	Perkin reaction (cinnamic acid synthesis) .....	276
218.	Perkow vinyl phosphate synthesis .....	278
219.	Peterson olefination .....	279
220.	Pfau–Plattner azulene synthesis .....	280

221.	Pfitzinger quinoline synthesis.....	281
222.	Pictet–Gams isoquinoline synthesis .....	282
223.	Pictet–Spengler isoquinoline synthesis .....	283
224.	Pinacol rearrangement .....	284
225.	Pinner synthesis.....	285
226.	Polonovski reaction .....	286
227.	Polonovski–Potier rearrangement.....	288
228.	Pomeranz–Fritsch reaction .....	289
229.	Prévost <i>trans</i> -dihydroxylation .....	291
230.	Prilezhaev reaction .....	292
231.	Prins reaction.....	293
232.	Pschorr ring closure.....	294
233.	Pummerer rearrangement .....	296
234.	Ramberg–Bäcklund olefin synthesis .....	297
235.	Reformatsky reaction .....	298
236.	Regitz diazo synthesis .....	299
237.	Reimer–Tiemann reaction .....	301
238.	Reissert reaction (aldehyde synthesis).....	303
239.	Riley oxidation (selenium dioxide oxidation) .....	305
240.	Ring-closing metathesis (RCM) using Grubbs and Schrock catalysts ..	306
241.	Ritter reaction.....	308
242.	Robinson annulation.....	309
243.	Robinson–Schöpf reaction.....	310
244.	Roush allylboronate reagent.....	312
245.	Rubottom oxidation .....	313
246.	Rupe rearrangement .....	314
247.	Rychnovsky polyol synthesis .....	315
248.	Sakurai allylation reaction (Hosomi–Sakurai reaction).....	317
249.	Sandmeyer reaction .....	319
250.	Sarett oxidation .....	320
251.	Schiemann reaction (Balz–Schiemann reaction).....	321
252.	Schlosser modification of the Wittig reaction .....	322
253.	Schmidt reaction.....	323
254.	Schmidt’s trichloroacetimidate glycosidation reaction.....	324
255.	Scholl reaction.....	326
256.	Schöpf reaction.....	328
257.	Schotten–Baumann reaction .....	329
258.	Shapiro reaction.....	330
259.	Sharpless asymmetric aminohydroxylation.....	331
260.	Sharpless asymmetric epoxidation .....	333
261.	Sharpless dihydroxylation .....	335
262.	Shi asymmetric epoxidation .....	338
263.	Simmons–Smith reaction .....	340
264.	Simonini reaction .....	341
265.	Simonis chromone cyclization .....	342
266.	Skraup quinoline synthesis.....	344

267.	Smiles rearrangement .....	346
268.	Sommelet reaction .....	347
269.	Sommelet–Hauser (ammonium ylide) rearrangement .....	349
270.	Sonogashira reaction .....	350
271.	Staudinger reaction .....	352
272.	Stetter reaction (Michael–Stetter reaction).....	353
273.	Stevens rearrangement.....	355
274.	Stieglitz rearrangement.....	357
275.	Still–Gennari phosphonate reaction.....	358
276.	Stille coupling.....	359
277.	Stille–Kelly reaction .....	360
278.	Stobbe condensation .....	362
279.	Stollé synthesis .....	363
280.	Stork enamine reaction .....	364
281.	Strecker amino acid synthesis.....	365
282.	Suzuki coupling .....	367
283.	Swern oxidation.....	358
284.	Tamao–Kumada oxidation .....	370
285.	Tebbe olefination (Petasis alkenylation) .....	371
286.	Thorpe–Ziegler reaction .....	372
287.	Tiemann rearrangement.....	373
288.	Tiffeneau–Demjanov rearrangement.....	374
289.	Tishchenko reaction.....	375
290.	Tollens reaction .....	376
291.	Tsuji–Trost allylation .....	377
292.	Ueno–Stork cyclization .....	378
293.	Ugi reaction .....	379
294.	Ullmann reaction .....	380
295.	Vilsmeier–Haack reaction .....	381
296.	von Braun reaction .....	383
297.	von Richter reaction .....	384
298.	Wacker oxidation.....	385
299.	Wagner–Meerwein rearrangement .....	386
300.	Wallach rearrangement.....	387
301.	Weinreb amide.....	388
302.	Weiss reaction .....	389
303.	Wharton oxygen transposition reaction .....	391
304.	Willgerodt–Kindler reaction.....	392
305.	Wittig reaction .....	396
306.	[1,2]-Wittig rearrangement.....	397
307.	[2,3]-Wittig rearrangement.....	398
308.	Wohl–Ziegler reaction.....	399
309.	Wolff rearrangement .....	400
310.	Wolff–Kishner reduction.....	401
311.	Woodward <i>cis</i> -dihydroxylation .....	402
312.	Yamada coupling reagent .....	403

313.	Yamaguchi esterification.....	404
314.	Zaitsev elimination.....	406
315.	Zinin benzidine rearrangement (semidine rearrangement).....	407
Subject Index .....		409



## Preface

*What's in a name? That which we call a rose by any other name would smell as sweet.*<sup>a</sup> On the other hand, *name reactions* in organic chemistry and the corresponding mechanisms are nevertheless fascinating for their far-reaching utility as well as their insight into organic reactions. Furthermore, understanding their mechanisms greatly enhances our ability to solve more complex chemical problems. As a matter of fact, some name reactions are the direct result of better understanding of the mechanisms, as exemplified by the Barton–McCombie reaction.<sup>b</sup> In addition, our knowledge of how reactions work can shed light on side reactions and by-products, or when a reaction does not give the “desired” product, the mechanism may provide clues to where the reaction has gone awry.

I started collecting named and unnamed organic reactions and their mechanisms while I was a graduate student. It occurred to me that many of my fellow practitioners are doing exactly the same, and that these efforts could be made easier through a monograph tabulating interesting and useful mechanisms of name reactions. To this end, I have updated my collection with many *contemporary* name reactions and added more recent references, especially up-to-date review articles. In reflecting the advent of asymmetric synthesis, relevant name reactions in this field have been included to the repertoire. Since the step-by-step mechanisms delineated within are mostly self-explanatory, detailed verbal explanations are not offered, although some important jargons entailing the types of transformations are highlighted. For some reactions, short descriptions are given as mnemonics rather than accurate definitions. With regard to the references, the first one is generally the original article, whereas the rest are articles and review articles. Readers interested in in-depth coverage of name reactions are encouraged to follow up with the references as well as the following five books covering the relevant topic:

1. Mundy, B. R.; Eller, M. G. *Name Reactions and Reagents in Organic Synthesis* John–Wiley & Sons, New York, **1988**.
2. Hassner, A.; Stumer, C. *Organic Synthesis Based on Named and Unnamed Reactions* Pergamon, **1994**.
3. Laue, L.; Plagens, A. *Named Organic Reactions* John–Wiley & Sons, New York, **1999**.
4. “Organic Name Reactions” section, *The Merck Index* (13<sup>th</sup> edition), **2001**.
5. Smith, M. B.; March, J. “Advanced Organic Chemistry” (5<sup>th</sup> edition), Wiley, New York, **2001**.

I would like to express my grateful thanks to Dr. Brian J. Myers of Wayne State University, Profs. Jeffrey N. Johnston of Indiana University and Christian M. Rojas of Bernard College, who read the manuscript and offered many invaluable comments and suggestions. Special thanks are due to Profs. Gordon W. Gribble of Dartmouth College, Louis S. Hegedus of Colorado State University, and Thomas R. Hoye of University of Minnesota for their critique of the drafts. In addi-

tion, I am very much indebted to Nadia M. Ahmad, John (Jack) Hodges, Michael D. Kaufman, Peter L. Toogood, and Kim E. Werner for proofreading the manuscript. Any remaining errors are, of course, solely my own. I am also grateful to Ms. Ann Smith of Merck & Co., Inc. for her helpful communications and discussions. Last but not the least, I wish to thank my wife, Sherry Chun-hua Cai, for her understanding and support throughout the entire project.

Jack Li  
Ann Arbor, Michigan  
November, 2001

### References

- a. William Shakespeare, "*Romeo and Juliet*" Act II, Scene ii, **1594–1595**.
- b. Derek H. R. Barton, "*Some Recollections of Gap Jumping*" American Chemical Society, Washington, DC, **1991**.

Name Reactions

A Collection of Detailed Reaction Mechanisms

Li, J.J.

2002, XVIII, 417 p. 1 illus., Hardcover

ISBN: 978-3-540-43024-7