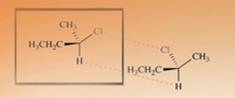
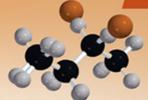
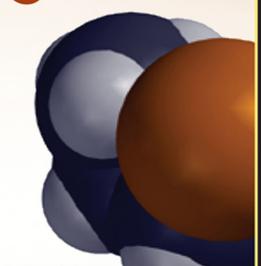
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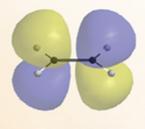


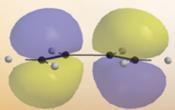
March's

Advanced Organic Chemistry



Reactions, Mechanisms, and Structure





Michael B. Smith





WILEY

MARCH'S ADVANCED ORGANIC CHEMISTRY

MARCH'S ADVANCED ORGANIC CHEMISTRY

REACTIONS, MECHANISMS, AND STRUCTURE

SEVENTH EDITION

Michael B. Smith Professor of Chemistry



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CONTENTS

PREFA	CE		xiii
COMM	ION AB	BREVIATIONS	xxi
BIOGE	RAPHIC	AL STATEMENT	XXV
PART :	I INTI	RODUCTION	1
1. Loca	alized Cl	nemical Bonding	3
1.A.	Covale	nt Bonding	3
	-	le Valence	6
	Hybrid		7
	Multipl		9
		lectron Spectroscopy	11
		nic Structures of Molecules negativity	14 15
		Moment	18
	-	ve and Field Effects	19
		Distances	21
1.K.	Bond A	angles	25
1.L.	Bond E	Energies	27
2. Delo	calized (Chemical Bonding	31
2.A.	Molecu	ılar Orbitals	32
2.B.	Bond E	Energies and Distances in Compounds Containing	
		lized Bonds	35
		iles that have Delocalized Bonds	37
		Conjugation	42
		lles of Resonance	43
		sonance Effect nhibition of Resonance and the Influences of Strain	45 46
		Bonding. Ylids	49
2.II. 2.I.	_		50
2.1.	2.I.i.	Six-Membered Rings	54
		Five, Seven, and Eight-Membered Rings	57
	2.I.ii.	Other Systems Containing Aromatic Sextets	62
2.J.		ant and Nonalternant Hydrocarbons	63
		•	

2.K.		Aromati	ic Systems with Electron Numbers other than Six	65
		2.K.i.	Systems of Two Electrons	66
		2.K.ii.	Systems of Four Electrons: Antiaromaticity	67
		2.K.iii.	Systems of Eight Electrons	71
		2.K.iv.	Systems of Ten Electrons	72
		2.K.v.	Systems of more than Ten Electrons: $4n + 2$ Electrons	74
		2.K.vi.	Systems of more than 10 Electrons: 4n Electrons	79
	2.L.	Other A	romatic Compounds	82
			onjugation	85
	2.N.	Tautome	erism	89
		2.N.i.	Keto-Enol Tautomerism	89
		2.N.ii.	Other Proton-Shift Tautomerism	92
3.	Bond	ding Weaker Than Covalent		96
	3.A.	Hydroge	en Bonding	96
	3.B.	π – π Inte	eractions	103
	3.C.	Addition	n Compounds	104
		3.C.i.	Electron Donor–Acceptor Complexes	104
			Crown Ether Complexes and Cryptates	108
			Inclusion Compounds	113
		3.C.iv.	Cyclodextrins	116
	3.D.	Catenan	nes and Rotaxanes	118
	3.E.	Cucurbi	t[n]Uril-Based Gyroscane	121
4. Stere		eochemistry and Conformation		122
	4.A.	Optical	Activity and Chirality	122
		4.A.i.	Dependence of Rotation on Conditions of Measurement	124
	4.B.	What Kinds of Molecules Display Optical Activity? The Fischer Projection		125
	4.C.			136
	4.D.	Absolut	e Configuration	137
		4.D.i.	The CAHN-INGOLD-PRELOG System	138
		4.D.ii.	Methods of Determining Configuration	141
	4.E.	The Cau	use of Optical Activity	145
	4.F.	Molecul	les with more than One Stereogenic Center	146
			etric Synthesis	149
			s of Resolution	154
	4.I.	Optical		160
	4.J.		as Isomerism	162
		4.J.i.	cis-trans Isomerism Resulting from Double Bonds	162
		4.J.ii.	cis-trans Isomerism of Monocyclic Compounds	165
		4.J.iii.	cis-trans Isomerism of Fused and Bridged Ring Systems	167
			Isomerism	168
			topic and Diastereotopic Atoms, Groups, and Faces	170
			pecific and Stereoselective Syntheses	173
	4.N.		national Analysis	173
		4.N.i.	Conformation in Open-Chain Systems	175

		CONTEN	ts vii
	4.N.ii.		180
		Conformation in Six-Membered Rings Containing Heteroatom Conformation in Other Rings	s 186 188
4.0			
	STRAIN	lar Mechanics	190 192
7.1.	4.P.i.		193
	4.P.ii.		193 199
	4.1.11. 4 Piii	Unsaturated Rings	201
	4.P.iv.	Strain Due to Unavoidable Crowding	204
5. Carl	ocations	s, Carbanions, Free Radicals, Carbenes, and Nitrenes	208
5.A.	Carboca	ations	208
	5.A.i.	Nomenclature	208
	5.A.ii.	Stability and Structure of Carbocations	209
	5.A.iii.	The Generation and Fate of Carbocations	218
5.B.	Carbani	ons	221
	5.B.i.	Stability and Structure	221
	5.B.ii.	The Structure of Organometallic Compounds	228
	5.B.iii.	The Generation and Fate of Carbanions	233
5.C.	Free Ra	dicals	234
	5.C.i.		234
	5.C.ii.		245
		Radical Ions	248
5.D.	Carbene		249
	5.D.i.	Stability and Structure	249
	5.D.ii.		253
5.E.	Nitrenes	S	257
6. Mec	hanisms	and Methods of Determining them	261
		f Mechanism	261
		f Reaction	262
		dynamic Requirements for Reaction	264
		Requirements for Reaction	266
6.E. 6.F.		dwin Rules for Ring Closure	270 271
		and Thermodynamic Control mmond Postulate	271
		copic Reversibility	273
6.I.	Marcus	±	273
6.J.		s of Determining Mechanisms	275
	6.J.i.	Identification of Products	275
	6.J.ii.	Determination of the Presence of an Intermediate	275
	6.J.iii.	The Study of Catalysis	277
	6.J.iv.	Isotopic Labeling	277
	6.J.v.	Stereochemical Evidence	278
	6.J.vi.	Kinetic Evidence	278
	6.J.vii.	Isotope Effects	285

viii CONTENTS

7.	Irrac	liation P	Processes in Organic Chemistry	289
	7.A.	Photoch	nemistry	289
		7.A.i.	Excited States and the Ground State	289
		7.A.ii.	Singlet and Triplet States: "Forbidden" Transitions	291
		7.A.iii.	Types of Excitation	292
		7.A.iv.	Nomenclature and Properties of Excited States	294
			Photolytic Cleavage	295
			The Fate of the Excited Molecule: Physical Processes	296
			The Fate of the Excited Molecule: Chemical Processes	301
			. The Determination of Photochemical Mechanisms	306
		Sonoche	· · · · · · · · · · · · · · · · · · ·	307
	7.C.	Microw	ave Chemistry	309
8.	Acid	s and Ba	ses	312
	8.A.	Brønste	d Theory	312
		8.A.i.	Brønsted Acids	313
		8.A.ii.	Brønsted Bases	320
	8.B.	The Me	chanism of Proton-Transfer Reactions	323
	8.C.	Measure	ements of Solvent Acidity	324
			d Base Catalysis	327
	8.E.	Lewis A	acids and Bases	330
		8.E.i.	Hard-Soft Acids-Bases	331
	8.F.	The Effe	ects of Structure on the Strengths of Acids and Bases	334
	8.G.	The Effe	ects of the Medium on Acid and Base Strength	343
9.	Effec	cts of Str	ucture and Medium on Reactivity	347
	9.A.	Resonar	nce and Field Effects	347
	9.B.	Steric E	ffects	349
	9.C.	Quantita	ative Treatments of the Effect of Structure on Reactivity	352
	9.D.	Effect o	f Medium on Reactivity and Rate	361
		9.D.i.	High Pressure	362
			Water and Other Non-Organic Solvents	363
			Ionic Solvents	364
		9.D.iv.	Solventless Reactions	366
P /	ART I	I INTI	RODUCTION	367
				207
10	_		bstitution, Nucleophilic and Organometallic	373
	10.A	. Mechan		373
		10.A.i.	21	374
			The S _N 1 Mechanism	379
			. Ion Pairs in the S _N 1 Mechanism	383
	10.5		Mixed $S_N 1$ and $S_N 2$ Mechanisms	387
	10.B	. SET Me	echanisms	389

			CONTENTS	ix
10.0	T	11 ·		201
10.C.		ghboring-Group Mechanism		391
	10.C.1.	Neighboring-Group Participation by π and σ Bonds:		204
10 D	TE1 C :	Nonclassical Carbocations		394
		Mechanism		408
10.E.	Rearrang	shilic Substitution at an Allylic Carbon: Allylic		409
10 F		whilic Substitution at an Aliphatic Trigonal Carbon:		409
10.1.		rahedral Mechanism		413
10.G	. Reactivi			417
	10.G.i.			417
	10.G.ii.			426
		The Effect of the Leaving Group		432
	10.G.iv.			435
	10.G.v.			442
		Influencing Reactivity by External Means		445
		. Ambident (Bidentant) Nucleophiles: Regioselectivity		446
	10.G.vii	i. Ambident Substrates		450
10.H	. Reaction	1S		451
		Oxygen Nucleophiles		451
		Attack by OR at an Alkyl Carbon		459
		Sulfur Nucleophiles		475
		Nitrogen Nucleophiles		481
		Halogen Nucleophiles		498
	10.H.V1.	Carbon Nucleophiles		510
11 Aro	matic Su	bstitution, Electrophilic		569
11.A	. Mechani			569
		The Arenium Ion Mechanism		570
		The S _E 1 Mechanism		576
11.B	Orientat	ion and Reactivity		576
	11.B.i.	Orientation and Reactivity in Monosubstituted		
		Benzene Rings		576
		The Ortho/Para Ratio		580
		Ipso Attack	-4:44	581
		Orientation in Benzene Rings with More Than One Subs Orientation in Other Ring Systems	stituent	583 584
11.0	11.B.v.			
	_	ative Treatments of Reactivity in the Substrate	ala ativity	586
11.D	Relation	itative Treatment of Reactivity of the Electrophile: The S	electivity	588
11 F		ect of the Leaving Group		591
	Reaction			591
21.11.	11.F.i.	Hydrogen as the Leaving Group in Simple		
	11.1.1.	Substitution Reactions		592
	11.F.ii.	Hydrogen as the Leaving Group in Rearrangement		2,2
		Reactions		635
	11.F.iii.	Other Leaving Groups		641

12. Aliphat and Or;		kenyl, and Alkynyl Substitution, Electrophilic	649
·			
12.A. Me			650
		Bimolecular Mechanisms: S _E 2 and S _E i	650
		The S _E 1 Mechanism	654
		Electrophilic Substitution Accompanied by Double-Bond Shifts	657
		Other Mechanisms	658
12.B. Re		•	658
12.C. Re			660
		Hydrogen as Leaving Group	660
		Metals as Leaving Groups	698
		Halogen as Leaving Group	713
		Carbon Leaving Groups	718
12.	.C.v.	Electrophilic Substitution at Nitrogen	727
13. Aromat	tic Sul	bstitution: Nucleophilic and Organometallic	732
13.A. Me	echani	sms	732
13.	.A.i.	The S _N Ar Mechanism	732
13.	.A.ii.	The S _N 1 Mechanism	735
		The Benzyne Mechanism	737
		The S _{RN} 1 Mechanism	739
13.	.A.v.	Other Mechanisms	740
13.B. Re		•	741
		The Effect of Substrate Structure	741
		The Effect of the Leaving Group	744
13.	.B.iii.	The Effect of the Attacking Nucleophile	745
13.C. Re	action	IS	745
13.	.C.i.	All Leaving Groups Except Hydrogen and N ₂ ⁺	746
		Hydrogen as Leaving Group	784
		Nitrogen as Leaving Group	788
13.	.C.iv.	Rearrangements	797
14. Substitu	ution]	Reactions: Radical	803
14.A. Me	echani	sms	803
14.	.A.i.	Radical Mechanisms in General	803
14.	.A.ii.	Free Radical Substitution Mechanisms	807
14	.A.iii.	Mechanisms at an Aromatic Substrate	809
14.	.A.iv.	Neighboring-Group Assistance in Free Radical Reactions	810
14.B. Re	activit	ty	812
	.B.i.	Reactivity for Aliphatic Substrates	812
		Reactivity at a Bridgehead	817
		Reactivity in Aromatic Substrates	818
		Reactivity in the Attacking Radical	819
14.	.B.v.	The Effect of Solvent on Reactivity	820

CONTENT	S XI
14.C. Reactions	821
14.C.i. Hydrogen as a Leaving Group	821
14.C.ii. N ₂ as Leaving Group	846
14.C.iii. Metals as Leaving Groups	849
14.C.iv. Halogen as Leaving Group	851
14.C.v. Sulfur as Leaving Group	851
14.C.vi. Carbon as Leaving Group	853
15. Addition to Carbon-Carbon Multiple Bonds	859
15.A. Mechanisms	859
15.A.i. Electrophilic Addition	859
15.A.ii. Nucleophilic Addition	865
15.A.iii. Free Radical Addition	867
15.A.iv. Cyclic Mechanisms	869
15.A.v. Addition to Conjugated Systems	869
15.B. Orientation and Reactivity	871
15.B.i. Reactivity	871
15.B.ii. Orientation	874
15.B.iii. Stereochemical Orientation	877
15.B.iv. Addition to Cyclopropane Rings	879
15.C. Reactions	881
15.C.i. Isomerization of Double and Triple Bonds	881
15.C.ii. Reactions in which Hydrogen Adds to One Side	883
15.C.iii. Reactions in which Hydrogen Adds to Neither Side	981
15.C.iv. Cycloaddition Reactions	1014
16. Addition to Carbon–Hetero Multiple Bonds	1067
16.A. Mechanism and Reactivity	1067
16.A.i. Nucleophilic Substitution at an Aliphatic Trigonal Carbon: The Tetrahedral Mechanism	1069
16.B. Reactions	1075
16.B.i. Reactions in which Hydrogen or a Metallic Ion Adds to the	1075
Heteroatom	1075
16.B.ii. Acyl Substitution Reactions	1189
16.B.iii. Reactions in which Carbon Adds to the Heteroatom	1239
16.B.iv. Addition to Isocyanides	1246
16.B.v. Nucleophilic Substitution at a Sulfonyl Sulfur Atom	1248
17. Eliminations	1253
17.A. Mechanisms and Orientation	1253
17.A.i. The E2 Mechanism	1254
17.A.ii. The E1 Mechanism	1261
17.A.iii. The E1cB Mechanism	1262
17.A.iv. The E1–E2–E1cB Spectrum	1267
17.A.v. The E2C Mechanism	1268
17 B. Regiochemistry of the Double Bond	1269

xii CONTENTS

17.C. Stered	ochemistry of the Double Bond	1273 1274
	. Effect of Substrate Structure	1274
	ii. Effect of the Attacking Base	1274
	iii. Effect of the Leaving Group	1276
	v. Effect of the Medium	1277
17.E. Mech	anisms and Orientation in Pyrolytic Eliminations	1278
17.E.i	. Mechanisms	1278
17.E.i	i. Orientation in Pyrolytic Eliminations	1281
17.E.i	ii. 1,4-Conjugate Eliminations	1282
17.F. React	ions	1282
17.F.i	Reactions in which $C=C$ and $C\equiv C$ Bonds are Formed	1282
17.F.i	i. Fragmentations	1307
17.F.i	ii. Reactions in which $C \equiv N$ or $C = N$ Bonds are Formed	1310
	v. Reactions in which C=O Bonds are Formed	1314
	Reactions in which N=N Bonds are Formed	1315
17.F.v	i. Extrusion Reactions	1316
18. Rearrange	ments	1321
18.A. Mech	anisms	1322
18.A.	. Nucleophilic Rearrangements	1322
18.A.i	i. The Actual Nature of the Migration	1324
	iii. Migratory Aptitudes	1328
18.A.	v. Memory Effects	1330
18.B. Longe	er Nucleophilic Rearrangements	1331
18.C. Free F	Radical Rearrangements	1333
	ne Rearrangements	1337
	ophilic Rearrangements	1337
18.F. React	ions	1337
18.F.i	1,2-Rearrangements	1338
18.F.i	i. Non-1,2 Rearrangements	1380
19. Oxidations	and Reductions	1433
19.A. Mech	anisms	1434
19.B. React	ions	1436
19.B.i	. Oxidations	1437
19.B.i	i. Reductions	1497
APPENDIX A	: THE LITERATURE OF ORGANIC CHEMISTRY	1569
APPENDIX B	: CLASSIFICATION OF REACTIONS BY TYPE OF COMPOUNDS SYNTHESIZED	1605
INDEXES		
AUTHOR I	NDEX	1631
SUBJECT INDEX		

This seventh edition of *March's Advanced Organic Chemistry* has been thoroughly updated to include new advances in areas of Organic chemistry published between 2005 and 2010. Every topic retained from the sixth edition has been brought up to date if there was activity in that area during that five year period. Changes also include a significant rewrite of most of the book. More than 5500 new references have been added for work published since 2005. As with the sixth edition, many older references were deleted to make room for new ones, and in cases where a series of papers by the same principal author were cited, all but the most recent were deleted. The older citations are usually found by referring to the more recent publication(s). Many of the figures relating to molecular orbitals dated to the 1960s. In all cases possible, they have been replaced by molecular orbitals drawings using Spartan software from Wavefunction, Inc. The fundamental structure of the seventh edition is essentially the same as that of all previous ones.

The goal, as in previous editions is to give equal weight to the three fundamental aspects of the study of organic chemistry: reactions, mechanisms, and structure. A student who has completed a course based on this book should be able to approach the literature directly, with a sound knowledge of modern organic chemistry. Major special areas of organic chemistry: terpenes, carbohydrates, proteins, many organometallic reagents, combinatorial chemistry, polymerization and electrochemical reactions, steroids, and so on, have been treated lightly or ignored completely. The use of this book in the first year of graduate study should help master the fundamentals. It is hoped that this book will lead a student to consult the many excellent books and review articles cited for various topics in order to understand the subject in more detail. Indeed, many of these topics are so vast, they cannot be explained completely in this book.

The organization is based on reaction types, and a relatively few principles suffice to explain nearly all of them despite the large number of organic reactions. Accordingly, the reactions-mechanisms section of this book (Part II) is divided into 10 chapters (10–19), each concerned with a different type of reaction. In the first part of each chapter, the appropriate basic mechanisms are discussed along with considerations of reactivity and orientation, while the second part consists of numbered sections devoted to individual reactions, where the scope and the mechanism of each reaction are discussed. Numbered sections are used for the reactions and are set in boldface. Since the methods for the preparation of individual classes of compounds (ketones, nitriles, etc.) are not treated all in one place, an updated and revised index has been provided (Appendix B) by use of which the synthesis of a given type of compound will be found. It is important to note that the numbers for each reaction in the 7th edition are *different* from editions 1–5 in many cases, but are the same as found in the 6th edition. For this reason, a correlation table is included at the end of this Preface that directly correlates the sections found in the 5th edition with the new ones in both the 6th and 7th editions.

The structure of organic compounds is discussed in Chapters 1–5 (Part I). This section provides a necessary background for understanding mechanisms and is also important in its own right. The discussion begins with chemical bonding (Chapt. 1) and ends with a chapter on stereochemistry (Chapt. 4). Two chapters follow (Chapt 6–7) on reaction mechanisms in general, one for ordinary reactions and the other for photochemical reactions. Part 1 concludes with two more chapters (Chapt 8 and 9) that give further background to the study of mechanisms.

The IUPAC names for many organic transformations are included, first introduced in the 3rd edition. Since then the rules have been broadened to cover additional cases; hence more such names are given in this edition. Furthermore, International Union of Pure and Applied Chemistry (IUPAC) has now published a system for designating reaction mechanisms, and some of the simpler designations are included.

Appendix A is devoted to the literature of organic chemistry.

In treating subjects as broad as structure, reactions, and mechanisms of organic chemistry, it is impossible to cover each topic in great depth, and this would not be desirable even if possible. This book is intended to point the reader to the primary literature of the areas it covers. To this end, there are >20,000 references to original papers. Secondary literature sources including reviews, books, and monographs have been included as well. Appendix A provides a brief introduction to using computer-based search engines (e.g., $Reaxys^{\text{(i)}}$ and $SciFinder^{\text{(i)}}$).

Although basically designed as a reference text for a one-year course on the graduate level, this book can also be used in advanced undergraduate courses, but only after completion of a one-year course in organic chemistry. A one year course in both inorganic and physical chemistry would be most helpful. It has been my experience that students who have completed the first-year courses often have a hazy recollection of the material and greatly profit from a representation of the material if it is easily accessible. The material in the first nine chapters, particularly Chapters 1, 2, 4, 6, and 8 may be helpful for reviewing such material when this book is used in connection with a course.

This book is probably most valuable as a reasonably up-to-date reference work. Students preparing for qualifying examinations and practicing organic chemists will find that Part II contains a survey of what is known about the mechanism and scope of a large number of reactions, arranged in an orderly manner based on reaction type and on which bonds are broken and formed.

For units of energy, IUPAC mandates joules, and many journals do use this unit exclusively. However, organic chemists who publish in United States journals commonly use calories. Virtually all energy values are presented in both calories and joules. Although IUPAC does not recommend angstrom units for bond distances, but rather picometers (pm), a vast number of bond distances published in the literature are in angstrom units, and this book therefore uses angstrom units.

I would like to acknowledge the contributions of those chemists cited and thanked by Professor March in the first-four editions, and those I thanked in the 5th and 6th editions. This book would not be possible without their contributions. For the 7th edition, I thank Lou Allinger for pointing out the deficiencies in the hyperconjugation section, and graciously helping me write the new section appearing in this new edition. I thank Warren Hehre for his invaluable help in calculating and presenting the molecular orbital drawings using Spartan. I also thank Adrian Shell (Elsevier) for facilitating the transfer of material relating to the program *Reaxys*, discussed in Appendix A. I thank the many people who have contributed comments or have pointed out errors in the 6th edition that were

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I encourage those who read and use the 7th edition to contact me directly with comments, errors, and with publications that might be appropriate for future editions. I hope that this new edition will due justice to the tradition that Professor March began with the first edition.

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MICHAEL B. SMITH *May*, 2012

Correlation Table 5th edition \rightarrow 7th edition Reactions

$\textbf{10-1} \rightarrow \textbf{10-1}$	$\textbf{10-18} \rightarrow \textbf{10-14}$	$\textbf{10-35} \rightarrow \textbf{16-68}$
$\textbf{10-2} \rightarrow \textbf{10-2}$	$\textbf{10-19} \rightarrow \textbf{10-15}$	$\textbf{10-36} \rightarrow \textbf{10-24}$
$\textbf{10-3} \rightarrow \textbf{10-3}$	$\textbf{10-20} \rightarrow \textbf{10-16}$	$\textbf{10-37} \rightarrow \textbf{10-25}$
$\textbf{10-4} \rightarrow \textbf{10-4}$	$\textbf{10-21} \rightarrow \textbf{16-61}$	$\textbf{10-38} \rightarrow \textbf{10-26}$
$\textbf{10-5} \rightarrow \textbf{10-5}$	$\textbf{10-22} \rightarrow \textbf{16-62}$	$\textbf{10-39} \rightarrow \textbf{16-69}$
$\textbf{10-6} \rightarrow \textbf{10-6}$	$\textbf{10-23} \rightarrow \textbf{16-63}$	$\textbf{10-40} \rightarrow \textbf{10-27}$
$\textbf{10-7} \rightarrow \textbf{10-7}$	$\textbf{10-24} \rightarrow \textbf{16-64}$	$\textbf{10-41} \rightarrow \textbf{10-28}$
$\textbf{10-8} \rightarrow \textbf{16-57}$	$\textbf{10-25} \rightarrow \textbf{16-65}$	$\textbf{10-42} \rightarrow \textbf{10-29}$
$\textbf{10-9} \rightarrow \textbf{16-58}$	$\textbf{10-26} \rightarrow \textbf{10-17}$	$\textbf{10-43} \rightarrow \textbf{10-30}$
$\textbf{10-10} \rightarrow \textbf{16-59}$	$\textbf{10-27} \rightarrow \textbf{10-18}$	$\textbf{10-44} \rightarrow \textbf{10-31}$
$\textbf{10-11} \rightarrow \textbf{16-60}$	$\textbf{10-28} \rightarrow \textbf{10-19}$	$\textbf{10-46} \rightarrow \textbf{10-32}$
$\textbf{10-12} \rightarrow \textbf{10-8}$	$\textbf{10-29} \rightarrow \textbf{16-66}$	$\textbf{10-47} \rightarrow \textbf{10-33}$
$\textbf{10-13} \rightarrow \textbf{10-9}$	$\textbf{10-30} \rightarrow \textbf{16-67}$	$\textbf{10-48} \rightarrow \textbf{16-70}$
$\textbf{10-14} \rightarrow \textbf{10-10}$	$\textbf{10-31} \rightarrow \textbf{10-20}$	$\textbf{10-49} \rightarrow \textbf{10-34}$
$\textbf{10-15} \rightarrow \textbf{10-11}$	$\textbf{10-32} \rightarrow \textbf{10-21}$	$\textbf{10-50} \rightarrow \textbf{10-35}$
$\textbf{10-16} \rightarrow \textbf{10-12}$	$\textbf{10-33} \rightarrow \textbf{10-22}$	$\textbf{10-51} \rightarrow \textbf{10-37}$
$\textbf{10-17} \rightarrow \textbf{10-13}$	$\textbf{10-34} \rightarrow \textbf{10-23}$	$\textbf{10-52} \rightarrow \textbf{10-38}$

$\textbf{10-53} \rightarrow \textbf{10-39}$	$\textbf{10-101} \rightarrow \textbf{10-64}$	11-18 - deleted
$10-54 \rightarrow 10-40$	$10-102 \rightarrow 10-65$	$11-19 \rightarrow 11-19$
$10-55 \rightarrow 16-72$	$10-102 \rightarrow 10-05$ $10-103 \rightarrow 10-66$	$11-19 \rightarrow 11-19$ $11-20 \rightarrow 11-20$
$10-56 \rightarrow 16-72$ $10-56 \rightarrow 16-73$	$10\text{-}103 \rightarrow 10\text{-}60$ $10\text{-}104 \rightarrow 10\text{-}67$	$11-20 \rightarrow 11-20$ $11-21 \rightarrow 11-21$
$10\text{-}50 \rightarrow 10\text{-}75$ $10\text{-}57 \rightarrow 16\text{-}74$		
	$10-105 \rightarrow 10-68$	$11-22 \rightarrow 11-12$
$10-58 \rightarrow 16-75$	10-106 o 10-70	$11-23 \rightarrow 11-13$
$10-59 \rightarrow 16-76$	10-107 o 10-71	$11-24 \rightarrow 11-14$
$\textbf{10-60} \rightarrow \textbf{16-77}$	$\textbf{10-108} \rightarrow \textbf{10-72}$	$11-25 \rightarrow 11-22$
$\textbf{10-61} \rightarrow \textbf{10-41}$	$10\text{-}109 \rightarrow 10\text{-}73$	$11-26 \rightarrow 11-23$
$\textbf{10-62} \rightarrow \textbf{10-42}$	$\textbf{10-110} \rightarrow \textbf{10-74}$	$11\text{-}27 \rightarrow 11\text{-}24$
$\textbf{10-63} \rightarrow \textbf{10-36}$	$\textbf{10-111} \rightarrow \textbf{10-75}$	$11\text{-}28 \rightarrow 11\text{-}25$
$\textbf{10-64} \rightarrow \textbf{10-42}$	$\textbf{10-112} \rightarrow \textbf{10-76}$	$11\text{-}29 \rightarrow 11\text{-}26$
$10\text{-}65 \rightarrow 10\text{-}43$	$\textbf{10-113} \rightarrow \textbf{10-77}$	$\textbf{11-30} \rightarrow \textbf{11-27}$
$\textbf{10-66} \rightarrow \textbf{10-44}$	$\textbf{10-114} \rightarrow \textbf{16-81}$	$\textbf{11-31} \rightarrow \textbf{11-28}$
$\textbf{10-67} \rightarrow \textbf{10-45}$	$\textbf{10-115} \rightarrow \textbf{16-82}$	$\textbf{11-32} \rightarrow \textbf{11-29}$
$\textbf{10-68} \rightarrow \textbf{10-46}$	$\textbf{10-116} \rightarrow \textbf{16-83}$	$\textbf{11-33} \rightarrow \textbf{11-30}$
$\textbf{10-69} \rightarrow \textbf{10-47}$	$\textbf{10-117} \rightarrow \textbf{16-84}$	$\textbf{11-34} \rightarrow \textbf{11-31}$
$\textbf{10-70} \rightarrow \textbf{10-48}$	$\textbf{10-118} \rightarrow \textbf{16-85}$	$\textbf{11-35} \rightarrow \textbf{11-32}$
$\textbf{10-71} \rightarrow \textbf{10-49}$	$\textbf{10-119} \rightarrow \textbf{16-86}$	$\textbf{11-36} \rightarrow \textbf{11-33}$
$\textbf{10-72} \rightarrow \textbf{10-50}$	$\textbf{10-120} \rightarrow \textbf{16-87}$	$\textbf{11-37} \rightarrow \textbf{11-34}$
$\textbf{10-73} \rightarrow \textbf{10-51}$	$\textbf{10-121} \rightarrow \textbf{16-88}$	$\textbf{11-38} \rightarrow \textbf{11-35}$
$\textbf{10-74} \rightarrow \textbf{10-52}$	$\textbf{10-122} \rightarrow \textbf{16-89}$	$11\text{-}39 \rightarrow 11\text{-}36$
$\textbf{10-75} \rightarrow \textbf{10-53}$	$10-123 \rightarrow 16-90$	$11-40 \rightarrow 11-37$
$10\text{-}76 \rightarrow 10\text{-}54$	$10-124 \rightarrow 16-100$	$11-41 \rightarrow 11-38$
$10-70 \rightarrow 10-34$ $10-77 \rightarrow 16-79$	$10-125 \rightarrow 16-101$	$11-41 \rightarrow 11-30$ $11-42 \rightarrow 11-39$
$10-77 \rightarrow 10-79$ $10-78 \rightarrow 16-80$	$10\text{-}125 \rightarrow 10\text{-}101$ $10\text{-}126 \rightarrow 16\text{-}102$	$11-42 \rightarrow 11-39$ $11-43 \rightarrow 11-40$
$10-79 \rightarrow 10-80$ $10-79 \rightarrow 19-53$	$10\text{-}120 \rightarrow 10\text{-}102$ $10\text{-}127 \rightarrow 16\text{-}103$	$11-43 \rightarrow 11-40$ $11-44 \rightarrow 11-41$
		11-44 → 11-41
$10-80 \rightarrow 19-57$	$10-128 \rightarrow 16-104$	10.1 10.1
$10-81 \rightarrow 19-54$	$10\text{-}129 \rightarrow 16\text{-}105$	$12-1 \to 12-1$
$10-82 \rightarrow 19-58$		$12-2 \rightarrow 12-2$
$10-83 \rightarrow 19-66$	$11-1 \rightarrow 11-1$	$12\text{-}3 \rightarrow 12\text{-}3$
$10-84 \rightarrow 19-56$	$11-2 \rightarrow 11-2$	$12\text{-}4 \rightarrow 12\text{-}4$
$10\text{-}85 \rightarrow 19\text{-}35$	$11\text{-}3 \rightarrow 11\text{-}3$	$12\text{-}5 \rightarrow 12\text{-}5$
$\textbf{10-86} \rightarrow \textbf{19-59}$	$11\text{-}4 \rightarrow 11\text{-}4$	$\textbf{12-6} \rightarrow \textbf{12-6}$
$\textbf{10-87} \rightarrow \textbf{19-67}$	$11\text{-}5 \rightarrow 11\text{-}5$	$\textbf{12-7} \rightarrow \textbf{12-7}$
$\textbf{10-88} \rightarrow \textbf{19-70}$	$11\text{-}6 \rightarrow 11\text{-}6$	$\textbf{12-8} \rightarrow \textbf{12-8}$
$\textbf{10-89} \rightarrow \textbf{19-39}$	$\textbf{11-7} \rightarrow \textbf{11-7}$	$12-9 \rightarrow 12-10$
$\textbf{10-90} \rightarrow \textbf{19-40}$	$\textbf{11-8} \rightarrow \textbf{11-8}$	$\textbf{12-10} \rightarrow \textbf{12-11}$
$\textbf{10-91} \rightarrow \textbf{19-41}$	11-9	$\textbf{12-11} \rightarrow \textbf{12-12}$
$\textbf{10-92} \rightarrow \textbf{10-55}$	$\textbf{11-10} \rightarrow \textbf{11-9}$	$\textbf{12-12} \rightarrow \textbf{12-13}$
$\textbf{10-93} \rightarrow \textbf{10-56}$	$\textbf{11-11} \rightarrow \textbf{11-10}$	$\textbf{12-13} \rightarrow \textbf{12-14}$
$\textbf{10-94} \rightarrow \textbf{10-57}$	$\textbf{11-12} \rightarrow \textbf{11-11}$	$\textbf{12-14} \rightarrow \textbf{12-16}$
$\textbf{10-95} \rightarrow \textbf{10-58}$	$\textbf{11-13} \rightarrow \textbf{11-15}$	$\textbf{12-15} \rightarrow \textbf{12-18}$
$\textbf{10-96} \rightarrow \textbf{10-59}$	$\textbf{11-14} \rightarrow \textbf{11-17}$	$\textbf{12-16} \rightarrow \textbf{12-19}$
$\textbf{10-98} \rightarrow \textbf{10-61}$	$\textbf{11-15} \rightarrow \textbf{11-18}$	$\textbf{12-17} \rightarrow \textbf{12-20}$
$10-99 \rightarrow 10-63$	11-16 - deleted	$12-18 \rightarrow 10-69$
$10-100 \rightarrow 10-60$	11-17 - deleted	$12-19 \rightarrow 12-21$
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$\textbf{12-20} \rightarrow \textbf{12-22}$	$\textbf{13-14} \rightarrow \textbf{13-11}$	$14\text{-}37 \rightarrow 14\text{-}30$
$\textbf{12-21} \rightarrow \textbf{12-23}$	$\textbf{13-15} \rightarrow \textbf{13-17}$	$\textbf{14-38} \rightarrow \textbf{14-31}$
$12\text{-}22 \rightarrow 12\text{-}17$	$\textbf{13-16} \rightarrow \textbf{13-18}$	$\textbf{14-39} \rightarrow \textbf{14-32}$
$\textbf{12-23} \rightarrow \textbf{12-24}$	$\textbf{13-17} \rightarrow \textbf{13-20}$	
$\textbf{12-24} \rightarrow \textbf{12-25}$	$\textbf{13-18} \rightarrow \textbf{13-21}$	$\textbf{15-1} \rightarrow \textbf{15-1}$
$\textbf{12-25} \rightarrow \textbf{12-26}$	$\textbf{13-19} \rightarrow \textbf{13-22}$	$\textbf{15-2} \rightarrow \textbf{15-2}$
$\textbf{12-26} \rightarrow \textbf{12-27}$	$\textbf{13-20} \rightarrow \textbf{13-23}$	$\textbf{15-3} \rightarrow \textbf{15-3}$
$\textbf{12-27} \rightarrow \textbf{12-30}$	$\textbf{13-21} \rightarrow \textbf{13-30}$	$\textbf{15-4} \rightarrow \textbf{15-4}$
$\textbf{12-28} \rightarrow \textbf{12-31}$	$\textbf{13-22} \rightarrow \textbf{13-31}$	$\textbf{15-5} \rightarrow \textbf{15-5}$
$\textbf{12-29} \rightarrow \textbf{12-32}$	$\textbf{13-23} \rightarrow \textbf{13-32}$	$\textbf{15-6} \rightarrow \textbf{15-6}$
$\textbf{12-30} \rightarrow \textbf{12-33}$	$\textbf{13-24} \rightarrow \textbf{13-33}$	$\textbf{15-7} \rightarrow \textbf{15-7}$
$12\text{-}31 \rightarrow 12\text{-}34$		$\textbf{15-8} \rightarrow \textbf{15-8}$
$\textbf{12-32} \rightarrow \textbf{12-35}$	$\textbf{14-1} \rightarrow \textbf{14-1}$	$15-9 \rightarrow 15-9$
$\textbf{12-33} \rightarrow \textbf{12-36}$	$14\text{-}2 \rightarrow 14\text{-}3$	$\textbf{15-10} \rightarrow \textbf{15-10}$
$12\text{-}34 \rightarrow 12\text{-}37$	$14\text{-}3 \rightarrow 14\text{-}4$	$15-11 \rightarrow 15-11$
12-35 deleted	$14\text{-}4 \rightarrow 19\text{-}14$	$15-12 \rightarrow 15-12$
$12\text{-}36 \rightarrow 12\text{-}38$	$14-5 \rightarrow 14-5$	$15-13 \rightarrow 15-14$
$12-37 \rightarrow 12-39$	$14-6 \rightarrow 19-23$	$15 \cdot 14 \rightarrow 15 \cdot 13$
$12-38 \rightarrow 12-40$	$14-0 \rightarrow 19-23$ $14-7 \rightarrow 14-6$	$15-14 \rightarrow 15-15$ $15-15 \rightarrow 15-15$
$12-39 \rightarrow 12-40$ $12-39 \rightarrow 12-41$	$14-8 \rightarrow 14-7$	$15-16 \rightarrow 15-16$
$12-40 \rightarrow 12-42$	$14-9 \rightarrow 14-8$	$15-10 \rightarrow 15-10$ $15-17 \rightarrow 15-17$
$12-40 \rightarrow 12-42$ $12-41 \rightarrow 12-43$	$14-10 \rightarrow 14-9$ $14-10 \rightarrow 14-9$	$15-17 \rightarrow 15-17$ $15-18 \rightarrow 15-18$
$12-41 \rightarrow 12-43$ $12-42 \rightarrow 12-44$	$14-10 \rightarrow 14-9$ $14-11 \rightarrow 14-10$	$15-18 \rightarrow 15-18$ $15-19 \rightarrow 15-20$
$12\text{-}43 \rightarrow 12\text{-}45$ $12\text{-}43 \rightarrow 12\text{-}45$	$14-11 \rightarrow 14-10$ $14-12 \rightarrow 12-9$	$15-19 \rightarrow 15-20$ $15-20 \rightarrow 15-23$
$12-43 \rightarrow 12-43$ $12-44 \rightarrow 12-46$	$14-12 \rightarrow 12-9$ $14-13 \rightarrow 14-11$	$15-20 \rightarrow 15-23$ $15-21 \rightarrow 15-24$
$12\text{-}44 \rightarrow 12\text{-}40$ $12\text{-}45 \rightarrow 12\text{-}47$	$14-13 \rightarrow 14-11$ $14-14 \rightarrow 14-12$	
$12\text{-}45 \rightarrow 12\text{-}47$ $12\text{-}46 \rightarrow 12\text{-}48$	$14-14 \rightarrow 14-12$ $14-15 \rightarrow 14-14$	$15-22 \rightarrow 15-21$
$12\text{-}40 \rightarrow 12\text{-}48$ $12\text{-}47 \rightarrow 13\text{-}19$		$15-23 \rightarrow 15-22$
	14-16 o 14-16	$15-24 \rightarrow 15-25$
$12-48 \rightarrow 12-49$	$14-17 \rightarrow 13-27$	$15-25 \rightarrow 15-27$
$12-49 \rightarrow 12-50$	$14-18 \rightarrow 13-26$	$15-26 \rightarrow 15-28$
$12-50 \rightarrow 13-24$	$14-19 \rightarrow 13-10$	$15-27 \rightarrow 15-32$
$12-51 \rightarrow 12-51$	$14-20 \rightarrow 12-15$	$15-28 \rightarrow 15-33$
$12-52 \rightarrow 12-52$	$14-21 \rightarrow 14-17$	$15-29 \rightarrow 15-36$
$\textbf{12-53} \rightarrow \textbf{12-53}$	$14\text{-}22 \rightarrow 14\text{-}18$	$15\text{-}30 \rightarrow 15\text{-}35$
	$14\text{-}23 \rightarrow 14\text{-}19$	$15\text{-}31 \rightarrow 15\text{-}37$
$13-1 \rightarrow 13-1$	$14\text{-}24 \rightarrow 19\text{-}69$	$15\text{-}32 \rightarrow 15\text{-}34$
$13-2 \rightarrow 13-2$	$\mathbf{14\text{-}25} \rightarrow \mathbf{14\text{-}20}$	$\textbf{15-33} \rightarrow \textbf{15-38}$
$\textbf{13-3} \rightarrow \textbf{13-3}$	$\mathbf{14\text{-}26} \rightarrow \mathbf{14\text{-}21}$	$15-34 \to 15-19$
$13\text{-}4 \rightarrow 13\text{-}4$	$\mathbf{14\text{-}27} \rightarrow \mathbf{14\text{-}22}$	$15\text{-}35 \rightarrow 15\text{-}29$
$13-5 \rightarrow 13-5$	$\mathbf{14\text{-}28} \rightarrow \mathbf{13\text{-}28}$	$15\text{-}36 \rightarrow 15\text{-}30$
$\textbf{13-6} \rightarrow \textbf{13-6}$	$14\text{-}29 \rightarrow 13\text{-}25$	$15\text{-}37 \rightarrow 15\text{-}39$
$13-7 \rightarrow 13-7$	$\textbf{14-30} \rightarrow \textbf{14-23}$	$\textbf{15-38} \rightarrow \textbf{15-41}$
$13-8 \rightarrow 19-55$	$\textbf{14-31} \rightarrow \textbf{14-24}$	$15\text{-}39 \rightarrow 15\text{-}40$
13-9 deleted	$\mathbf{14\text{-}32} \rightarrow \mathbf{14\text{-}26}$	$\textbf{15-40} \rightarrow \textbf{15-42}$
$\textbf{13-10} \rightarrow \textbf{13-8}$	$\textbf{14-33} \rightarrow \textbf{14-25}$	$\textbf{15-41} \rightarrow \textbf{15-43}$
$\textbf{13-11} \rightarrow \textbf{13-9}$	$\textbf{14-34} \rightarrow \textbf{14-27}$	$\textbf{15-42} \rightarrow \textbf{15-44}$
$\textbf{13-12} \rightarrow \textbf{13-14}$	$\textbf{14-35} \rightarrow \textbf{14-28}$	$\textbf{15-43} \rightarrow \textbf{15-45}$
$\textbf{13-13} \rightarrow \textbf{13-15}$	$\textbf{14-36} \rightarrow \textbf{14-29}$	$\textbf{15-44} \rightarrow \textbf{15-46}$

$15\text{-}45 \rightarrow 15\text{-}47$	$\textbf{16-27} \rightarrow \textbf{16-24}$	$17\text{-}4 \rightarrow 17\text{-}5$
$\textbf{15-46} \rightarrow \textbf{15-48}$	$\textbf{16-28} \rightarrow \textbf{16-25}$	$\textbf{17-5} \rightarrow \textbf{17-6}$
$\textbf{15-47} \rightarrow \textbf{15-49}$	$\textbf{16-29} \rightarrow \textbf{16-26}$	$\textbf{17-6} \rightarrow \textbf{17-7}$
$\textbf{15-48} \rightarrow \textbf{15-50}$	$\textbf{16-30} \rightarrow \textbf{16-27}$	$\textbf{17-7} \rightarrow \textbf{17-8}$
$15-49 \rightarrow 15-62$	$16-31 \rightarrow 16-28$	$17-8 \rightarrow 17-9$
$15-50 \rightarrow 15-51$	$16-32 \rightarrow 16-29$	$17-9 \rightarrow 17-10$
$15-51 \rightarrow 15-52$	16-33 deleted	17-10 o 17-11
$15-52 \rightarrow 15-53$	combined	$17\text{-}11 \rightarrow 17\text{-}12$
$15\text{-}53 \rightarrow 15\text{-}54$	with 10-115	$17\text{-}12 \rightarrow 17\text{-}13$
$15\text{-}54 \rightarrow 15\text{-}55$	$16\text{-}34 \rightarrow 16\text{-}30$	$17-13 \to 17-14$
$15\text{-}55 \rightarrow 15\text{-}56$	$16\text{-}35 \rightarrow 16\text{-}31$	$\textbf{17-14} \rightarrow \textbf{17-15}$
$\textbf{15-56} \rightarrow \textbf{15-57}$	$\textbf{16-36} \rightarrow \textbf{16-32}$	$\textbf{17-15} \rightarrow \textbf{17-16}$
$15\text{-}57 \rightarrow 15\text{-}58$	$\textbf{16-37} \rightarrow \textbf{16-33}$	$\textbf{17-16} \rightarrow \textbf{17-17}$
$\textbf{15-58} \rightarrow \textbf{15-60}$	$\textbf{16-38} \rightarrow \textbf{16-34}$	$\textbf{17-17} \rightarrow \textbf{17-18}$
$15-59 \to 15-61$	$\textbf{16-39} \rightarrow \textbf{16-35}$	$17\text{-}18 \rightarrow 17\text{-}19$
$15-60 \to 15-59$	$16\text{-}40 \rightarrow 16\text{-}36$	$17-19 \rightarrow 17-3$
$15-61 \rightarrow 15-63$	$16-41 \rightarrow 16-38$	$17-20 \rightarrow 17-20$
$15-62 \rightarrow 15-64$	$16-42 \rightarrow 16-41$	$17-21 \rightarrow 17-21$
$15-63 \rightarrow 15-65$	$\textbf{16-43} \rightarrow \textbf{16-42}$	$17\text{-}22 \rightarrow 17\text{-}22$
$15\text{-}64 \rightarrow 15\text{-}66$	$\textbf{16-44} \rightarrow \textbf{16-39}$	$\textbf{17-23} \rightarrow \textbf{17-23}$
	$\textbf{16-45} \rightarrow \textbf{16-40}$	$\textbf{17-24} \rightarrow \textbf{17-24}$
$\textbf{16-1} \rightarrow \textbf{16-1}$	$\textbf{16-46} \rightarrow \textbf{16-43}$	$\textbf{17-25} \rightarrow \textbf{17-25}$
$\textbf{16-2} \rightarrow \textbf{16-2}$	$\textbf{16-47} \rightarrow \textbf{16-44}$	17-26 deleted
$\textbf{16-3} \rightarrow \textbf{16-3}$	$\textbf{16-48} \rightarrow \textbf{16-45}$	combined
$\textbf{16-4} \rightarrow \textbf{16-4}$	$\textbf{16-49} \rightarrow \textbf{16-50}$	with 17-25
$16-5 \rightarrow 16-5$	$16-50 \rightarrow 16-51$	$17\text{-}27 \rightarrow 17\text{-}26$
$16-6 \rightarrow 16-7$	$16-51 \rightarrow 16-52$	$17-28 \rightarrow 17-23$ $17-28 \rightarrow 17-27$
$16-7 \rightarrow 16-8$	$16-52 \rightarrow 16-53$	$17-29 \rightarrow 17-28$
$16-8 \rightarrow 16-9$	$16-53 \rightarrow 16-54$	$17-30 \to 17-29$
$\mathbf{16-9} \rightarrow \mathbf{16-10}$	$\textbf{16-54} \rightarrow \textbf{16-55}$	17-31 deleted
$\textbf{16-10} \rightarrow \textbf{16-11}$	$16\text{-}55 \rightarrow 16\text{-}56$	combined
$\textbf{16-11} \rightarrow \textbf{16-12}$	$\textbf{16-56} \rightarrow \textbf{16-91}$	with 17-30
$\textbf{16-12} \rightarrow \textbf{16-13}$	$\textbf{16-57} \rightarrow \textbf{16-6}$	$\textbf{17-32} \rightarrow \textbf{17-30}$
$\textbf{16-13} \rightarrow \textbf{16-18}$	$\textbf{16-58} \rightarrow \textbf{16-92}$	$\textbf{17-33} \rightarrow \textbf{17-31}$
$\textbf{16-14} \rightarrow \textbf{16-17}$	$\textbf{16-59} \rightarrow \textbf{16-93}$	$\textbf{17-34} \rightarrow \textbf{17-32}$
$\textbf{16-15} \rightarrow \textbf{16-19}$	$\textbf{16-60} \rightarrow \textbf{16-94}$	$\textbf{17-35} \rightarrow \textbf{17-33}$
16-16 o 16-20	$16-61 \rightarrow 16-46$	$17-36 \rightarrow 17-34$
$16 \cdot 17 \rightarrow 16 \cdot 21$	$16-62 \rightarrow 16-48$	$17-37 \rightarrow 17-35$
16-17 o 16-21 $16-18 o 16-22$	$16-63 \rightarrow 16-95$	
		$17-38 \rightarrow 17-36$
$16-19 \rightarrow 16-14$	$16-64 \rightarrow 16-96$	$17-39 \rightarrow 17-37$
$16-20 \to 16-15$	$16-65 \rightarrow 16-97$	$\textbf{17-40} \rightarrow \textbf{17-38}$
$\textbf{16-21} \rightarrow \textbf{16-16}$	$\textbf{16-66} \rightarrow \textbf{16-98}$	
$\textbf{16-22} \rightarrow \textbf{16-23}$	$\textbf{16-67} \rightarrow \textbf{16-99}$	$\textbf{18-1} \rightarrow \textbf{18-1}$
$\textbf{16-23} \rightarrow \textbf{19-36}$		$\textbf{18-2} \rightarrow \textbf{18-2}$
$\textbf{16-24} \rightarrow \textbf{19-42}$	$\textbf{17-1} \rightarrow \textbf{17-1}$	$\textbf{18-3} \rightarrow \textbf{18-3}$
$\textbf{16-25} \rightarrow \textbf{19-43}$	$\textbf{17-2} \rightarrow \textbf{17-2}$	$\textbf{18-4} \rightarrow \textbf{18-4}$
$16-26 \to 19-44$	$17\text{-}3 \rightarrow 17\text{-}4$	$\textbf{18-5} \rightarrow \textbf{18-5}$
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$\textbf{18-6} \rightarrow \textbf{18-6}$	$\textbf{18-43} \rightarrow \textbf{18-43}$	$\textbf{19-32} \rightarrow \textbf{19-34}$
$\textbf{18-7} \rightarrow \textbf{18-7}$	$\textbf{18-44} \rightarrow \textbf{18-44}$	$\textbf{19-33} \rightarrow \textbf{19-61}$
$\textbf{18-8} \rightarrow \textbf{18-8}$		$\textbf{19-34} \rightarrow \textbf{19-37}$
$\textbf{18-9} \rightarrow \textbf{18-9}$	$\textbf{19-1} \rightarrow \textbf{19-1}$	$19\text{-}35 \rightarrow 19\text{-}64$
$\mathbf{18-10} ightarrow \mathbf{18-10}$.	$\textbf{19-2} \rightarrow \textbf{19-2}$	$\textbf{19-36} \rightarrow \textbf{19-62}$
$\textbf{18-11} \rightarrow \textbf{18-11}$	$\textbf{19-3} \rightarrow \textbf{19-3}$	$\textbf{19-37} \rightarrow \textbf{19-63}$
$\textbf{18-12} \rightarrow \textbf{18-12}$	$\textbf{19-4} \rightarrow \textbf{19-4}$	$\textbf{19-38} \rightarrow \textbf{19-38}$
$\textbf{18-13} \rightarrow \textbf{18-13}$	$\textbf{19-5} \rightarrow \textbf{19-5}$	$\textbf{19-39} \rightarrow \textbf{19-65}$
$\textbf{18-14} \rightarrow \textbf{18-14}$	$\mathbf{19-6} \rightarrow \mathbf{19-6}$	19-40 deleted
$\textbf{18-15} \rightarrow \textbf{18-15}$	$\textbf{19-7} \rightarrow \textbf{19-7}$	incorporated
$\textbf{18-16} \rightarrow \textbf{18-16}$	$\textbf{19-8} \rightarrow \textbf{19-8}$	into 10-85
$\textbf{18-17} \rightarrow \textbf{18-17}$	$\textbf{19-9} \rightarrow \textbf{19-9}$	$\textbf{19-41} \rightarrow \textbf{19-45}$
$\textbf{18-18} \rightarrow \textbf{18-18}$	$\mathbf{19\text{-}10} \rightarrow \mathbf{19\text{-}10}$	$\textbf{19-42} \rightarrow \textbf{19-46}$
$\textbf{18-19} \rightarrow \textbf{18-19}$	$\textbf{19-11} \rightarrow \textbf{19-11}$	$\textbf{19-43} \rightarrow \textbf{19-47}$
$\textbf{18-20} \rightarrow \textbf{18-20}$	$\textbf{19-12} \rightarrow \textbf{19-12}$	$\textbf{19-44} \rightarrow \textbf{19-48}$
$\textbf{18-21} \rightarrow \textbf{18-21}$	$\textbf{19-13} \rightarrow \textbf{19-13}$	$\textbf{19-45} \rightarrow \textbf{19-50}$
$\textbf{18-22} \rightarrow \textbf{18-22}$	$\textbf{19-14} \rightarrow \textbf{19-17}$	$\textbf{19-46} \rightarrow \textbf{19-51}$
$\textbf{18-23} \rightarrow \textbf{18-23}$	$\mathbf{19\text{-}15} \rightarrow \mathbf{19\text{-}15}$	$\textbf{19-47} \rightarrow \textbf{19-71}$
$\textbf{18-24} \rightarrow \textbf{18-24}$	$\textbf{19-16} \rightarrow \textbf{19-18}$	$\textbf{19-48} \rightarrow \textbf{19-68}$
$\textbf{18-25} \rightarrow \textbf{18-25}$	19-17 deleted	$\textbf{19-49} \rightarrow \textbf{19-72}$
$\mathbf{18-26} \rightarrow \mathbf{18-26}$	incorporated	$\textbf{19-50} \rightarrow \textbf{19-60}$
$\textbf{18-27} \rightarrow \textbf{18-27}$	in 19-14	$\textbf{19-51} \rightarrow \textbf{19-49}$
$\textbf{18-28} \rightarrow \textbf{18-28}$	$\mathbf{19\text{-}18} \rightarrow \mathbf{19\text{-}19}$	$\textbf{19-52} \rightarrow \textbf{19-73}$
$\mathbf{18-29} \rightarrow \mathbf{18-29}$	$\mathbf{19-19} \rightarrow \mathbf{19-20}$	$\textbf{19-53} \rightarrow \textbf{19-74}$
$\textbf{18-30} \rightarrow \textbf{18-30}$	$\textbf{19-20} \rightarrow \textbf{19-21}$	$\textbf{19-54} \rightarrow \textbf{19-75}$
$\textbf{18-31} \rightarrow \textbf{18-31}$	$\textbf{19-21} \rightarrow \textbf{19-22}$	$\textbf{19-55} \rightarrow \textbf{19-76}$
$\textbf{18-32} \rightarrow \textbf{18-32}$	$\mathbf{19\text{-}22} \rightarrow \mathbf{19\text{-}25}$	$\textbf{19-56} \rightarrow \textbf{19-77}$
$\textbf{18-33} \rightarrow \textbf{18-33}$	$\textbf{19-23} \rightarrow \textbf{19-27}$	$\textbf{19-57} \rightarrow \textbf{19-78}$
$18\text{-}34 \rightarrow 18\text{-}34$	$\textbf{19-24} \rightarrow \textbf{19-28}$	$\textbf{19-58} \rightarrow \textbf{19-79}$
$18\text{-}35 \rightarrow 18\text{-}35$	$\mathbf{19\text{-}25} \rightarrow \mathbf{19\text{-}30}$	$\textbf{19-59} \rightarrow \textbf{19-80}$
$18\text{-}36 \rightarrow 18\text{-}36$	$\mathbf{19\text{-}26} \rightarrow \mathbf{19\text{-}26}$	$\textbf{19-60} \rightarrow \textbf{19-81}$
$\textbf{18-37} \rightarrow \textbf{18-37}$	$\mathbf{19\text{-}27} \rightarrow \mathbf{19\text{-}29}$	$\textbf{19-61} \rightarrow \textbf{19-82}$
$\textbf{18-38} \rightarrow \textbf{18-38}$	$\textbf{19-28} \rightarrow \textbf{19-31}$	$\textbf{19-62} \rightarrow \textbf{19-83}$
$18\text{-}39 \rightarrow 18\text{-}39$	$\textbf{19-29} \rightarrow \textbf{19-24}$	$\textbf{19-63} \rightarrow \textbf{19-84}$
$\textbf{18-40} \rightarrow \textbf{18-40}$	$\textbf{19-30} \rightarrow \textbf{19-32}$	
$\textbf{18-42} \rightarrow \textbf{18-42}$	$\textbf{19-31} \rightarrow \textbf{19-33}$	

COMMON ABBREVIATIONS

Other, less common abbreviations are given in the text when the term is used.

Acetyl

acac Acetylacetonate (ligand)
AIBN Azobisisobutyronitrile

aq Aqueous

ARC Anion relay chemistry

Ax Axial

Ac

9-Borabicyclo[3.3.1]nonylboryl

9-BBN 9-Borabicyclo[3.3.1]nonane BDE Bond dissociation energy BER Borohydride exchange resin

BINAP (2R,3S)-2,2'-bis-(diphenylphosphino)-1,1'-binapthyl

BINOL 1,1'-Bi-2-naphthol BMS Borane methyl sulfide

Bn Benzyl —CH₂Ph

Boc tert-Butoxycarbonyl Ot-Bu

Bpy (Bipy) 2,2'-Bipyridyl

BSA *N-O-*Bis(trimethylsily)acetamide

Bu n-Butyl $-CH_2CH_2CH_3$

Bs Brosylate, *O*-(4-Bromophenyl) sulfenate

Bz Benzoyl

CAN Ceric ammonium nitrate $(NH_4)_2Ce(NO_3)_6$

cat Catalytic

Cbz N-Carbobenzyloxy CCH₂Ph

CD Circular dichroism

Chap Chapter(s)

Chirald (2S,3R)-(+)-4-dimethylamino-1,2-diphenyl-3-

methylbutan-2-ol

CIDNIP Chemically induced dynamic nuclear polarization

CIP Cahn-Ingold-Prelog

CNDO Complete Neglect of Differential Overlap

cod 1,5-Cyclooctadienyl (ligand)

xxii COMMON ABBREVIATIONS

FVP

GC

h **h**ν HF Flash vacuum pyrolysis

Gas chromatography Hour (hours) Irradiation with light

Hartree-Fock

xxii co	MMON ABBREVIATIONS	
cot	1,3,5-Cyclooctatrienyl (ligand)	
Ср	Cyclopentadienyl	
Op.	c) eropentuaterly:	
C		⊱ ⟨
Cy °C	Cyclohexyl	` 🔾
	Temperature in degrees Celcius	
3D	Three dimensional	
DABCO	1,4-Diazabicyclo[2.2.2]octane	Et NICE
DAST	Diethylammoniumsulfer trifluoride	Et ₂ NSF ₃
dba	Dibenzylidene acetone	
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene	
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene	CH N C N
DCC	1,3-Dicyclohexylcarbodiimide	c-C ₆ H ₁₁ -N=C=N- c -
DDO	22 D' 11 5 C I' 1 4 1 '	C_6H_{11}
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone	
DDT	1,1,1-Trichloro-2,2'-bis(<i>p</i> -chlorophenyl)ethane	IDI/CH CH)
DEA	Diethylamine	HN(CH ₂ CH ₃) ₂
DEAD	Diethylazodicarboxylate	$EtO_2C-N=NCO_2Et$
DHAD	Dihydroquinidine	
DHU	Dicyclohexylurea	
DIAD	Diisopropylazodicarboxylate	A CHOIL AIL
Dibal-H	Diisobutylaluminum hydride	$(Me_2CHCH_2)_2AlH$
DMA	Dimethylacetamide	
DMAP	4-Dimethylaminopyridine	M OCH CH OM
DME	Dimethoxyethane	MeOCH ₂ CH ₂ OMe
DMEAD	Di-2-methoxyethyl azodicarboxylate	
		O
DMF	<i>N,N'</i> -Dimethylformamide	H NMe
DMS	Dimethyl sulfide	11 111102
DMSO	Dimethyl sulfoxide (ligand)	
DNA	Deoxyribonucleic acid	
DOSY	Diffusion-ordered NMR Spectroscopy	
dppb	1,4-Bis-(Diphenylphosphino) butane	Ph ₂ P(CH ₂) ₄ PPh ₂
dppe	1,2-Bis-(Diphenylphosphino)ethane; see also Diphos	Ph ₂ PCH ₂ CH ₂ PPh ₂
dppf	Bis(Diphenylphosphino)ferrocene	1 11/21 C11/2C11/21 1 11/2
dpm	1,1-Bis(diphenylphosphino)methane	
dpm	1,3-Bis(Diphenylphosphino)propane	Ph ₂ P(CH ₂) ₃ PPh ₂
аррр е ⁻	Transfer of electrons	1 11/21 (C11/2)/31 1 11/2
% ee	% Enantiomeric excess	
EE	1-Ethoxyethoxy	EtO(Me)CH—
Et	Ethyl	-CH ₂ CH ₃
EDA	Electron donor–acceptor orbital	CITZCIT3
EDTA	Ethylenediaminetetraacetic acid	
Equiv	Equivalent(s)	
EPR	Electron paramagnetic resonance spectroscopy	
ESR	Electron spin resonance spectroscopy	
FMO	Frontier molecular orbital	
LMO	Elash an annua annualania	

HMO Hückel molecular orbital

 $\begin{array}{lll} HMPA & Hexamethylphosphoramide & (Me_2N)_3P = O \\ HMPT & Hexamethylphosphorus triamide & (Me_2N)_3P \end{array}$

¹H NMR Proton nuclear magnetic resonance spectroscopy

HOMO Highest occupied molecular orbital HPLC High-performance liquid chromatography

HSAB Hard–Soft Acid–Base IBX o-Iodoxybenzoic acid

i-Pr Isopropyl —CH(Me)₂

IR Infrared spectroscopy

IUPAC International Union of Pure and Applied Chemistry

ISC Intersystem crossing

LCAO Linear combination of atomic orbitals LICA Lithium *N*-isopropyl-*N*-cyclohexylamide

(LIPCA)

LDA Lithium diisopropylamide $LiN(i-Pr)_2$ LHMDS Lithium hexamethyl disilazide $LiN(SiMe_3)_2$

LTMP Lithium 2,2,6,6-tetramethylpiperidide LUMO Lowest unoccupied molecular orbital Mcpba *m*-Chloroperoxybenzoic acid

Me Methyl $-CH_3$ or Me

MEM β-Methoxyethoxymethyl MeOCH $_2$ CH $_2$ OCH $_2$ -Mes Mesityl 2,4,6-tri-Me $_2$ CH $_2$

min minutes

MMPP Magnesium monoperoxyphthalate

MO Molecular Orbital

MOM Methoxymethyl MeOCH₂—
Ms Methanesulfonyl MeSO₂—

MTO Methyl trioxorhenium

NBS N-Bromosuccinimide

NCS N-Chlorosuccinimide

NHS N-Hydroxysuccinimide

NIS N-Iodosuccinimide

NMO N-Methylmorpholine N-oxide NMP N-Methylpyrrolidinone NMR Nuclear magnetic resonance

NOESY Nuclear overhauser effect spectroscopy

NOE Nuclear overhauser effect

Nu (Nuc) Nucleophile

OBs O-(4-Bromophenyl)sulfinate Oxone[®] 2 KHSO₅·KHSO₄·K₂SO₄

Polymeric backbone

PCC Pyridinium chlorochromate
PDC Pyridinium dichromate
PEG Polyethylene glycol
PES Photoelectron spectroscopy

Ph Phenyl PhH Benzene PhMe Toluene



XXIV COMMON ABBREVIATIONS

PIFA Phenyliodine (III)-bis-(trifluoroacetate)
PPHF Pyridinium poly(hydrogen fluoride)

PMHS Polymethylhydrosiloxane

Pr n-Propyl $-CH_2CH_2CH_3$

Pyridine

Quanti Quantitative yield

Red-Al [(MeOCH₂CH₂O)2AlH₂]Na ROESY Rotating-frame NOE spectroscopy

rt Room temperature

sBuLi sec-Butyllithium CH₃CH₂CH(Li)CH₃

s seconds

salen Bis (salicylidene) ethylenediamine

sc CO₂ supercritical CO₂
SCF self-consistant field
SDS Sodium dodecyl sulfate

Sec. Section(s)

SET Single electron transfer

Siamyl

Py

(Sia)₂BH Disiamylborane sec-Isoamyl SOMO Singly occupied molecular orbital

Tr Tritium

TBAF Tetrabutylammonium fluoride $n\text{-Bu}_4\text{N}^+\text{F}^$ t-Bu tert-Butyl —CMe₃

TEAB Tetraethylammonium bromide
TEBA Triethylbenzylammonium

TEBA Triethylbenzylammonium
TED Tetraethylenediamine

TEMPO 2,2,6,6-Tetramethylpiperidinyloxy free radical

TFA Trifluoroacetic acid (solvent) CF_3COOH tfa Trifluoroacetic acid (ligand) $(CF_3CO)_2O$

Tf (OTf) Triflate $-SO_2CF_3$ ($-OSO_2CF_3$)

 $Bn(Et_3)_3N^+$

Pr₄N⁺RuO₄⁻

THF Tetrahydrofuran (solvent)

THP Tetrahydropyran

TMEDA Tetramethylethylenediamine Me₂NCH₂CH₂NMe₂

TMS Trimethylsilyl or tetramethylsilane $-Si(CH_3)_3$ Tol Tolyl $4-(Me)C_6H_4$

TOSMIC Toluenesulfonylmethyl isocyanide TPAP Tetrapropylammonium perruthenate

TPP Triphenylphosphine (solvent)

tpp Triphenylphosphine (ligand) pPh₃

Ts(Tos) Tosyl = p-Toluenesulfonyl 4-(Me)C₆H₄SO₂

UV Ultraviolet spectroscopy VCD Vibrational circular dichroism

VDW van der Walls vis Visible

XPS X-ray photoelectron spectroscopy

BIOGRAPHICAL STATEMENT

Professor Michael B. Smith was born in Detroit, Michigan in 1946. In 1957, he and his family moved to Madison Heights, Virginia. After graduation from Amherst County high school, he entered Ferrum Jr. College and graduated with an A.A. Professor Smith transferred to Virginia Polytechnic Institute (Virginia Tech), where he did undergraduate research with Professor Harold Bell, and graduated with a B.S in chemistry in 1969. After working as an analytical chemist at the Newport News Shipbuilding and Dry Dock Co. (Tenneco) in Newport News, Virginia for three years, he began graduate studies at Purdue University under the mentorship of Professor Joseph Wolinsky. Professor Smith graduated with a Ph.D. in Organic chemistry in 1977. He spent one year as a faculty research associate at the Arizona State University in the Cancer Research Institute, directed by Professor George R. Pettit, and a second year doing postdoctoral work at the Massachusetts Institute of Technology under the mentorship of Professor Sidney Hecht. In 1979 he began his independent academic career, where he now holds the rank of full professor.

Professor Smith is the author of approximately 90 independent research articles, and 20 published books. The books include the 5th and 6th edition of *March's Advanced Organic Chemistry* (Wiley), volumes 6–12 of the *Compendium of Organic Synthetic Methods* (Wiley), *Organic Chemistry a Two Semester Course* (HarperCollins) into its 2nd edition, and *Organic Synthesis* (Elsevier) in its 3rd edition. A new undergraduate organic chemistry book, *Organic Chemistry: An Acid-Base Approach*, was published in 2011 by the CRC Press.

Professor Smith's current research involves the synthesis and structural verification of lipids obtained from the dental pathogen *Porphyromonas gingivalis*, which show inflammatory activity, induce bone degeneration and are involved in triggering multiple sclerosis. A main area of research is the synthesis of fluorescent dye-heterocyclic conjugates that target hypoxic cancerous tumors, allowing non-invasive fluorescence imaging in the near IR. The synthesis of anti-cancer alkaloids is also ongoing.

INTRODUCTION

This book contains 19 chapters. Chapters 1–9 may be thought of as an introduction to Part II. The first-five chapters deal with the structure of organic compounds. These chapters discuss the kinds of bonding important in organic chemistry, the fundamental principles of conformation and stereochemistry of organic molecules, and reactive intermediates in organic chemistry. Chapters 6–9 are concerned with general principles of mechanism in organic chemistry, including acids and bases, photochemistry, sonochemistry and microwave irradiation, and finally the relationship between structure and reactivity.

Chapters 10–19, which make up Part II, are directly concerned with the nature and the scope of organic reactions and their mechanisms.

March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, Seventh Edition. Michael B. Smith.

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