	2.I. Aromaticity		54	
		2.I.i.	Six-Membered Rings	58
		2.I.ii.	Five-, Seven-, and Eight-Membered Rings	62
		2.I.iii.	Other Systems Containing Aromatic Sextets	67
	2.J.	Alternant	and Nonalternant Hydrocarbons	68
	2.K.	Aromatic	Systems with Electron Numbers Other Than Six	70
		2.K.i.	Systems of Two Electrons	72
		2.K.ii.	Systems of Four Electrons: Antiaromaticity	73
		2.K.iii.	Systems of Eight Electrons	76
		2.K.iv.	Systems of Ten Electrons	77
		2.K.v.	Systems of More than Ten Electrons: $4n + 2$ Electrons	80
		2.K.vi.	Systems of More Than Ten Electrons: 4n Electrons	85
	2.L.		omatic Compounds	89
		Hypercon		92
	2.N.	Tautomer		96
		2.N.i.	Keto–Enol Tautomerism	97
		2.N.ii.	Other Proton-Shift Tautomerism	100
3.	Bond	ing Weake	er Than Covalent	105
	3.A.	Hydrogen	Bonding	105
	3.B.	π–π Intera	•	113
	3.C.	Addition	Compounds	114
		3.C.i.	Electron Donor-Acceptor (EDA) Complexes	114
		3.C.ii.	Crown Ether Complexes and Cryptates	117
		3.C.iii.	Inclusion Compounds	122
		3.C.iv.	Cyclodextrins	125
	3.D.	Catenanes	s and Rotaxanes	127
	3.E.	Cucurbit[	n]Uril-Based Gyroscane	131
4.	Stere	ochemistry	y and Conformation	133
	4.A.	Optical A	ctivity and Chirality	133
	4.B.		nce of Rotation on Conditions of Measurement	135
	4.C.		ds of Molecules Display Optical Activity?	136
	4.D.		er Projection	147
	4.E.		Configuration	148
		4.E.i.	The Cahn-Ingold-Prelog System	150
		4.E.ii.	Methods Of Determining Configuration	152
	4.F.		e of Optical Activity	156
	4.G.		s with More Than One Stereogenic Center	157
	4.H. 4.I.	-	ric Synthesis of Resolution	161
	4.I. 4.J.	Optical P		166 173
	4.K.		s Isomerism	175
		4.K.i.	Cis-Trans Isomerism Resulting from Double Bonds	175
		4.K.ii.	Cis—Trans Isomerism of Monocyclic Compounds	179
		4.K.iii.	Cis—Trans Isomerism of Fused and Bridged Ring Systems	180

			CONTENT	s <b>vii</b>
	4.L.	Out-In Is		181
	4.M.		opic and Diastereotopic Atoms, Groups, and Faces	183
	4.N.		ecific and Stereoselective Syntheses	186
	4.0.		ational Analysis	187
		4.O.i.	Conformation in Open-Chain Systems	188
		4.O.ii.	Conformation in Six-Membered Rings	194
		4.O.iii.	Conformation in Six-Membered Rings Containing Heteroatoms	100
		4.O.iv.	Conformation in Other Rings	199 202
	4.P.		r Mechanics	204
	4.Q.	Strain	i Mechanics	204
	1.Q.	4.Q.i.	Strain in Small Rings	207
		4.Q.ii.	Strain in Other Rings	213
		4.Q.iii.	Unsaturated Rings	215
		4.Q.iv.	Strain Due to Unavoidable Crowding	218
5.	Carb	ocations, (	Carbanions, Free Radicals, Carbenes, and Nitrenes	223
	5.A.	Carbocati		224
	J.A.	5.A.i.	Nomenclature	224
		5.A.ii.	Stability and Structure of Carbocations	224
		5.A.iii.	The Generation And Fate Of Carbocations	234
	5.B.	Carbanio		237
	0.13.	5.B.i.	Stability and Structure	237
		5.B.ii.	The Structure Of Organometallic Compounds	244
		5.B.iii.	The Generation And Fate Of Carbanions	249
	5.C.	Free Radi		250
		5.C.i.	Stability and Structure	250
		5.C.ii.	The Generation and Fate of Free Radicals	261
		5.C.iii.	Radical Ions	265
	5.D.	Carbenes		266
		5.D.i.	Stability and Structure	266
		5.D.ii.	The Generation and Fate of Carbenes	269
		5.D.iii.	N-Heterocyclic Carbenes (NHCs)	274
	5.E.	Nitrenes		276
6.	Mech	nanisms an	nd Methods of Determining Them	279
	6.A.	Types of 1	Mechanism	279
	6.B.	Types of I		280
	6.C.		ynamic Requirements for Reaction	283
	6.D.	THE PERSON NAMED IN THE PERSON	equirements for Reaction	284
	6.E.	The Bald	win Rules for Ring Closure	288
	6.F.		nd Thermodynamic Control	290
	6.G.		mond Postulate	291
	6.H.	2000	pic Reversibility	291
	6.I.	Marcus T	neory	292

:

viii	CONTENTS
------	----------

	6.J.	Methods of Determining Mechanis	sms	293
		6.J.i. Identification of Produc	ts	293
		6.J.ii. Determination of the Pr	esence of an Intermediate	294
		6.J.iii. The Study of Catalysis		295
		6.J.iv. Isotopic Labeling		296
		6.J.v. Stereochemical Evidence	e	296
		6.J.vi. Kinetic Evidence		291
		6.J.vii. Isotope Effects		304
	6.K.	Catalyst Development		308
7.	Irra	diation Processes and Techniques t	hat Influence Reactions in	
		anic Chemistry		313
	7.A.	Photochemistry		314
		<ol><li>7.A.i. Excited States and the C</li></ol>	round State	314
		7.A.ii. Singlet and Triplet State	s: "Forbidden" Transitions	316
		<ol><li>7.A.iii. Types of Excitation</li></ol>		317
		<ol><li>7.A.iv. Nomenclature and Prope</li></ol>	erties of Excited States	318
		<ol><li>7.A.v. Photolytic Cleavage</li></ol>		319
		7.A.vi. The Fate of the Excited	Molecule: Physical Processes	320
		7.A.vii. The Fate of the Excited	Molecule: Chemical Processes	325
		7.A.viii. The Determination of Pl	notochemical Mechanisms	330
	7.B.	Sonochemistry		331
	7.C.	Microwave Chemistry		334
	7.D.	Flow Chemistry		336
	7.E.	Mechanochemistry		338
8.	Acid	s and Bases		339
	8.A.	Brønsted Theory		339
		8.A.i. Brønsted Acids		340
		8.A.ii. Brønsted Bases		347
	8.B.	The Mechanism of Proton Transfer	Reactions	350
	8.C.	Measurements of Solvent Acidity		352
	8.D.	Acid and Base Catalysis		355
	8.E.	Lewis Acids and Bases		357
		8.E.i. Hard-Soft Acids-Bases		359
	8.F.	The Effects of Structure on the Stre	ngths of Acids and Bases	361
	8.G.	The Effects of the Medium on Acid		370
9.	Effec	ts of Structure and Medium on Re	activity	375
	9.A.	Resonance and Field Effects		375
	9.B.	Steric Effects		377
	9.C.	Quantitative Treatments of the Effe	ct of Structure on Reactivity	380
	9.D.	Effect of Medium on Reactivity and		
	9.E.	High Pressure		390
	9.F.	Water and Other Nonorganic Solver	nts	391
	9.D.	Effect of Medium on Reactivity and		390
	9.F.		nts	
				U / 1

			CONTE	NTS	ix
	9.G. 9.H.		aid Solvents as Reactions		393 395
PART II		INTROD	UCTION		397
10.	Aliph	atic Substi	itution, Nucleophilic and Organometallic		403
	10.A.	Mechanis	ms		404
		10.A.i.	The S <sub>N</sub> 2 Mechanism		404
		10.A.ii.	The S <sub>N</sub> 1 Mechanism		410
		10.A.iii.	Ion Pairs in the S <sub>N</sub> 1 Mechanism		414
		10.A.iv.	Mixed S <sub>N</sub> 1 and S <sub>N</sub> 2 Mechanisms		418
	10.B.	SET Mech	hanisms		420
	10.C.	The Neigh	nboring-Group Mechanism		422
		10.C.i.	Neighboring-Group Participation by $\pi$ and $\sigma$ Bonds:		
			Nonclassical Carbocations		425
	10.D.	The S <sub>N</sub> i M	Mechanism		440
	10.E.	Statement of the statem	ilic Substitution at an Allylic Carbon: Allylic		
	1572/120	Rearrange			441
	10.F.	The section of the second	ilic Substitution at an Aliphatic Trigonal Carbon: The		
	10 C		al Mechanism		445
	10.G.	Reactivity			449
		10.G.i.	The Effect of Substrate Structure		449
		10.G.ii. 10.G.iii.	The Effect of the Attacking Nucleophile		457
			The Effect of the Leaving Group The Effect of the Reaction Medium		469
		10.G.v.	Phase-Transfer Catalysis		474
		10.G.vi.	7		477
			Ambident (Bidentant) Nucleophiles: Regioselectivity		478
			Ambident Substrates		481
	10.H.	Reactions			483
		10.H.i.	Oxygen Nucleophiles		483
		10.H.ii.	Sulfur Nucleophiles		506
		10.H.iii.	Nitrogen Nucleophiles		512
		10.H.iv.	Halogen Nucleophiles		534
		10.H.v.	Carbon Nucleophiles		545
11.	Aron	atic Subst	itution, Electrophilic		607
	11.A.	Mechanis	ms		607
		11.A.i.	The Arenium Ion Mechanism		608
		11.A.ii.	The S <sub>E</sub> 1 Mechanism		613
	11.B.	Orientatio	on and Reactivity		614
		11.B.i.	Orientation and Reactivity in Monosubstituted Benzene		
			Rings		614
		11.B.ii.	The Ortho/Para Ratio		618
		11.B.iii.	Ipso Attack		620

		11.B.iv.	Orientation in Benzene Rings With More Than One	
			Substituent	621
		11.B.v.	Orientation in Other Ring Systems	622
		-	ive Treatments of Reactivity in the Substrate	624
	11.D.	~	tative Treatment of Reactivity of the Electrophile: The	(2)
	11.5		y Relationship	626
		Reaction:	ct of the Leaving Group	628 629
	11.r.			029
		11.F.i.	Hydrogen as the Leaving Group in Simple Substitution Reactions	629
		11.F.ii.	Hydrogen as the Leaving Group In Rearrangement	
			Reactions	675
		11.F.iii.	Other Leaving Groups	680
12.	_		nyl, and Alkynyl Substitution: Electrophilic and	
	Orga	nometalli	e	687
	12.A.	Mechanis	sms	687
		12.A.i.	Bimolecular Mechanisms. S <sub>E</sub> 2 and S <sub>E</sub> i	688
		12.A.ii.	The S <sub>E</sub> 1 Mechanism	691
		12.A.iii.	Electrophilic Substitution Accompanied by Double-Bond	
			Shifts	694
		12.A.iv.	Other Mechanisms	695
		Reactivit	•	695
	12.C.	Reactions		697
		12.C.i.	Hydrogen as Leaving Group	697
		12.C.ii.	Metals as Leaving Groups	733
		12.C.iii.	Halogen as Leaving Group	746
		12.C.iv.	Carbon Leaving Groups	751
		12.C.v.	Electrophilic Substitution At Nitrogen	760
13.	Arom	natic Subs	titution: Nucleophilic and Organometallic	767
	13.A.	Mechanis	sms	768
		13.A.i.	The S <sub>N</sub> Ar Mechanism	768
		13.A.ii.	The S <sub>N</sub> 1 Mechanism	771
		13.A.iii.	The Benzyne Mechanism	772
		13.A.iv.	The S <sub>RN</sub> 1 Mechanism	774
		13.A.v.	Other Mechanisms	776
	13.B.	Reactivit	y	776
		13.B.i.	The Effect of Substrate Structure	776
		13.B.ii.	The Effect of the Leaving Group	778
		13. <b>B</b> .iii.	The Effect of the Attacking Nucleophile	779
	13.C.	Reactions	S	779
		13.C.i.	All Leaving Groups Except Hydrogen And N2+	779
		13.C.ii.	Hydrogen as Leaving Group	823

		CONTENTS	s xi
	13.C.i 13.C.i		824 834
14.	Radical Rea	ctions	839
	14.A. Mecha	anisms	839
	14.A.i	. Radical Mechanisms in General	839
	14.A.i		844
	14.A.i	ii. Mechanisms at an Aromatic Substrate	845
	14.A.i	v. Neighboring-Group Assistance in Free-Radical Reactions	847
	14.B. Reacti	vity	848
	14.B.i	. Reactivity for Aliphatic Substrates	848
	14.B.i	i. Reactivity at a Bridgehead	853
	14.B.i		854
	14.B.i		855
	14.B.v	•	856
	14.C. Reacti	ons	856
	14.C.i	. Hydrogen as Leaving Group	856
	14.C.i	<b>C</b> 1	880
	14.C.i	E E I	883
	14.C.i	5 1	883
	14.C.	. Carbon as Leaving Group	885
15.	Addition to	Carbon–Carbon Multiple Bonds	891
	15.A. Mecha	anisms	892
	15.A.i	. Electrophilic Addition	892
	15.A.i	있다	895
	15.A.i		896
	15.A.i	8 PC	898
	15.A.	, , , , , , , , , , , , , , , , , , , ,	898
	15.B. Orient	ation and Reactivity	899
	15.B.i		899
	15.B.i		902
	15.B.i		904
	15.B.i		906
	15.C. Reacti		908
	15.C.i	어는 사람들은 사람들이 어려워 하게 되어 있다면 하는데 사람들이 아니는데 아이를 하는데 하는데 아이를 보고 있다면 하는데 얼마를 하는데 아이를 하는데 아이를 하는데 아	908
	15.C.i		910
	15.C.i	war - Salan dagwaan an an an an ar an	992 1027
	15.C.i	v. Cycloaddition Reactions	102/
16.	Addition to	Carbon-Heteroatom Multiple Bonds	1087
	16.A. Mecha	anism and Reactivity	1087
	16.A.i	. Nucleophilic Substitution at an Aliphatic Trigonal Carbon: The Tetrahedral Mechanism	1089

## xii CONTENTS

	16.B.	Reactions		1094
	10.2.	16.B.i.	Reactions in Which Hydrogen or a Metallic Ion Adds	
			to the Heteroatom	1095
		16.B.ii.	Acyl Substitution Reactions	1218
		16.B.iii.	Reactions in Which Carbon Adds to the Heteroatom	1257
		16.B.iv.	Addition to Isocyanides	1264
		16.B.v.	Nucleophilic Substitution at a Sulfonyl Sulfur Atom	1266
17.	Elimi	nation Rea	actions	1273
	17.A.	Mechanis	ms and Orientation	1273
		17.A.i.	The E2 Mechanism	1274
		17.A.ii.	The E1 Mechanism	1280
		17.A.iii.	The E1cB Mechanism	1281
		17.A.iv.	The E1-E2-E1cB Spectrum	1286
		17.A.v.	The E2C Mechanism	1287
	17.B.	Regiocher	mistry of the Double Bond	1288
			emistry of the Double Bond	1290
	17.D.	Reactivity	y	1291
		17.D.i.	Effect of Substrate Structure	1291
		17.D.ii.	Effect of the Attacking Base	1293
		17.D.iii.	Effect of the Leaving Group	1294
		17.D.iv.	Effect of the Medium	1294
	17.E.	Mechanis	sms and Orientation in Pyrolytic Eliminations	1295
		17.E.i.	Mechanisms	1295
		17.E.ii.	Orientation in Pyrolytic Eliminations	1298
		17.E.iii.	1,4 Conjugate Eliminations	1298
	17.F.	Reactions		1299
	17.12.	17.F.i.	Reactions in Which C=C and C≡C Bonds Are Formed	1299
		17.F.ii.	Fragmentations	1321
		17.F.iii.	Reactions in Which C≡N or C=N Bonds Are Formed	1325
		17.F.iv.	Reactions in Which C=O Bonds Are Formed	1328
		17.F.v.	Reactions in Which N=N Bonds Are Formed	1329
		17.F.vi.	Extrusion Reactions	1329
18.	Rear	rangemen	ts	1335
	18.A	Mechanis	sms	1336
	10.11	18.A.i.		1336
		18.A.ii.	The Actual Nature of the Migration	1337
		18.A.iii.		1340
		18.A.iv.	Memory Effects	1343
	18 D		Sucleophilic Rearrangements	1344
		•	lical Rearrangements	1345
			Rearrangements	1349
			hilic Rearrangements	1349
		Reaction	-	1350
			-	

				CONTENTS	xiii
		18.F.i. 18.F.ii.	1,2-Rearrangements Non 1,2-Rearrangements		1350 1389
19.	Oxida	itions an	d Reductions		1439
	19.A.	Mechani	isms		1440
	19.B.	Reaction	ns .		1442
		19.B.i.	Oxidations		1442
		19.B.ii.	Reductions		1510
APF	ENDI	XA: T	HE LITERATURE OF ORGANIC CHEMISTR	Y	1607
APF	PENDI		LASSIFICATION OF REACTIONS BY TYPE ( OMPOUNDS SYNTHESIZED	OF	1645
IND	EXES	E			
A	UTHO	R INDE	X		1669
-7/2		CT INDE			1917