Brief contents 1: cycloadditions 2: sigmatropic and electrocyclic reactions 2: sigmatropic and electrocyclic reactions 3:50 Pericyclic reacti

	adical reactions 970
Abb	reviations xv Enot sened to the agreement of the sened to
	ace to the second edition xvii
Org	anic chemistry and this book xix
1	What is organic chemistry? 1
2	Organic structures 15
3	Determining organic structures 43
4	Structure of molecules 80
5	Organic reactions 107
6	Nucleophilic addition to the carbonyl group 125
7	Delocalization and conjugation 141
8	Acidity, basicity, and pK_a 163
9	Using organometallic reagents to make C—C bonds 182
10	Nucleophilic substitution at the carbonyl group 197
11	Nucleophilic substitution at C=0 with loss of carbonyl oxygen 222
12	Equilibria, rates, and mechanisms 240
13	¹ H NMR: Proton nuclear magnetic resonance 269
14	Stereochemistry 302
15	Nucleophilic substitution at saturated carbon 328
16	Conformational analysis 360
17	Elimination reactions 382
18	Review of spectroscopic methods 407
19	Electrophilic addition to alkenes 427
20	Formation and reactions of enols and enolates 449
21	Electrophilic aromatic substitution 471
22	Conjugate addition and nucleophilic aromatic substitution 498
23	Chemoselectivity and protecting groups 528
24	Regioselectivity 562
25	Alkylation of enolates 584
26	Reactions of enolates with carbonyl compounds: the aldol and Claisen reactions 614
27	Sulfur, silicon, and phosphorus in organic chemistry 656
28	Retrosynthetic analysis 694

Aromatic heterocycles 1: reactions

Aromatic heterocycles 2: synthesis

32 Stereoselectivity in cyclic molecules

Saturated heterocycles and stereoelectronics

825

30

33 Diastereoselectivity 852

BRIEF CONTENTS

33	Diastereoselectivity 852
34	Pericyclic reactions 1: cycloadditions 877
35	Pericyclic reactions 2: sigmatropic and electrocyclic reactions 909
36	Participation, rearrangement, and fragmentation 931
37	Radical reactions 970
38	Synthesis and reactions of carbenes 1003
39	Determining reaction mechanisms 1029
40	Organometallic chemistry 1069
41	Asymmetric synthesis 1102
42	Organic chemistry of life 1134
43	Organic chemistry today 1169
	4 Structure of molecules 80

10 Nucleophilic substitution at the earbonyl dropportuge

Figure acknowledgements 1182

Periodic table of the elements 1184

Index 1187

Contents

	notibution				
	eviations	XV	4	Structure of molecules	80
	ACGIOLES ALC LOUIS AND LOUIS AND LOS MICH SAS 216163A	xvii		Introduction	80
Orga	nic chemistry and this book	xix		Electrons occupy atomic orbitals	8:
				Molecular orbitals—diatomic molecules	88
	What is organic chemistry?	1		Bonds between different atoms	9!
-	Organic chemistry and you	201		Hybridization of atomic orbitals	99
	Organic compounds	2		Rotation and rigidity	10!
	Organic compounds Organic chemistry and industry	6		Conclusion	106
	Organic chemistry and the periodic table	11		Looking forward	106
	Organic chemistry and this book	13		Further reading	106
	Further reading	13		enormous coupling constants	
	Miscleophiles and leaving proups commission or word	357	5	Organic reactions	107
2	Organic structures	15		Chemical reactions	107
	Hydrocarbon frameworks and functional groups	16		Nucleophiles and electrophiles	111
	Drawing molecules	17		Curly arrows represent reaction mechanisms	116
	Hydrocarbon frameworks	22		Drawing your own mechanisms with curly arrows	120
	Functional groups	27		Further reading	124
	Carbon atoms carrying functional groups can be				
	classified by oxidation level	32	6	Nucleophilic addition to the	
	Naming compounds	33	183	carbonyl group	125
	What do chemists really call compounds?	36		Molecular orbitals explain the reactivity of the	
	How should you name compounds?	40		carbonyl group prison sales of zoillatemonages prizu	125
	Further reading	42		Attack of cyanide on aldehydes and ketones	127
	Conformation of the Hand of the House and the House of the Hand of			The angle of nucleophilic attack on aldehydes	
3	Determining organic structures	43		and ketones	129
	Introduction	43		Nucleophilic attack by 'hydride' on aldehydes	120
	Mass spectrometry	46		and ketones	130
	Mass spectrometry detects isotopes	48		Addition of organometallic reagents to aldehydes and ketones	132
	Atomic composition can be determined	381		Addition of water to aldehydes and ketones	133
	by high-resolution mass spectrometry	50		Hemiacetals from reaction of alcohols with aldehydes	444
	Nuclear magnetic resonance	52		and ketones	135
	Regions of the ¹³ C NMR spectrum	56		Ketones also form hemiacetals	137
	Different ways of describing chemical shift	57		Acid and base catalysis of hemiacetal and	
	A guided tour of the ¹³ C NMR spectra of some simple molecules	57		hydrate formation	137
	The ¹ H NMR spectrum	59		Bisulfite addition compounds	138
	Infrared spectra	63		Further reading	140
	Mass spectra, NMR, and IR combined make quick	05			
	identification possible	72	7	Delocalization and conjugation	141
	Double bond equivalents help in the search for a structure	74		Introduction	141
	Looking forward to Chapters 13 and 18	78		The structure of ethene (ethylene, CH ₂ =CH ₂)	142
	Further reading	78		Molecules with more than one C=C double bond	143

	The conjugation of two π bonds	146		And to conclude	220
	UV and visible spectra	148		Further reading	220
	The allyl system	150			
	Delocalization over three atoms is a common		11	Nucleophilic substitution at C=0 with loss	
	structural feature	154		of carbonyl oxygen	222
	Aromaticity	156		Introduction	222
	Further reading	162		Aldehydes can react with alcohols to form hemiacetals	223
na	39 Determination noncommental n	meg meg		Acetals are formed from aldehydes or ketones plus	
8	Acidity, basicity, and pK_a	163		alcohols in the presence of acid	224
	Organic compounds are more soluble in water as ions	163		Amines react with carbonyl compounds	229
	Acids, bases, and pK_a	165		Imines are the nitrogen analogues of	65 A
	Acidity	165		carbonyl compounds	230
	The definition of pK_a	168		Summary	238
	Constructing a pK_a scale	171		Further reading	239
	Nitrogen compounds as acids and bases	174	11101	Organic chemistry and moustry	
	Substituents affect the pK_a	175	[12]	Equilibria, rates, and mechanisms	240
	Carbon acids	176		How far and how fast?	240
	pK_a in action—the development of the			How to make the equilibrium favour the	
	drug cimetidine	178		product you want	244
	Lewis acids and bases	180		Entropy is important in determining	246
	Further reading	181		equilibrium constants	246
	Liebie de la constant interpresentation de la constant de la const			Equilibrium constants vary with temperature	248
9	Using organometallic reagents to make C—C bonds	100		Introducing kinetics: how to make reactions go faster and cleaner	250
		182		Rate equations	257
	Introduction	182		Catalysis in carbonyl substitution reactions	262
	Organometallic compounds contain a carbon—metal bond	102		Kinetic versus thermodynamic products	264
		183		Summary of mechanisms from Chapters 6–12	266
	Making organometallics	184		Further reading	267
	Using organometallics to make organic molecules Oxidation of alcohols	189		runtile reading	207
		194	13	¹ H NMR: Proton nuclear magnetic	
	Looking forward	196	EA	resonance	269
	Further reading	196		The differences between carbon and proton NMR	269
10	Nucleophilic substitution at the			Integration tells us the number of hydrogen atoms	203
10	carbonyl group	197		in each peak	270
	The product of nucleophilic addition to a carbonyl			Regions of the proton NMR spectrum	272
	group is not always a stable compound	197		Protons on saturated carbon atoms	272
	Carboxylic acid derivatives	198		The alkene region and the benzene region	277
	Why are the tetrahedral intermediates unstable?	200		The aldehyde region: unsaturated carbon bonded	
	Not all carboxylic acid derivatives are equally reactive	205		to oxygen	281
	Acid catalysts increase the reactivity			Protons on heteroatoms have more variable shifts	
	of a carbonyl group	207		than protons on carbon	282
	Acid chlorides can be made from carboxylic acids			Coupling in the proton NMR spectrum	285
	using SOCl ₂ or PCl ₅	214		To conclude	301
	Making other compounds by substitution reactions			Further reading	301
	of acid derivatives	216	72	identification possible	
	Making ketones from esters: the problem	216	14	Stereochemistry	302
	Making ketones from esters: the solution	218		Some compounds can exist as a pair of mirror-	
	To summarize	220		image forms	302

CONTENTS	ix
	IX

	Diastereoisomers are stereoisomers that are not enantiomers	211		Anion-stabilizing groups allow another	3 699
		311		mechanism—E1cB	399
	Chiral compounds with no stereogenic centres	319		To conclude easd one abos vd beavistes at noitestion.	404
	Axes and centres of symmetry Separating enantiomers is called resolution	320	457	Further reading beautiful seasons and in stalling and and an animal stalling as a	406
	Further reading	322		Available starting materials and to remain	
	ruitilei reading	327	[18]	Review of spectroscopic methods	407
15	Nucleophilic substitution at			There are three reasons for this chapter	407
19	saturated carbon	328		Spectroscopy and carbonyl chemistry	408
	Mechanisms for nucleophilic substitution	328		Acid derivatives are best distinguished by infrared	411
	How can we decide which mechanism (S _N 1 or S _N 2)	320		Small rings introduce strain inside the ring and	122
	will apply to a given organic compound?	332		higher's character outside it	412
	A closer look at the S _N 1 reaction	333		Simple calculations of C=0 stretching frequencies in IR spectra	413
	A closer look at the S _N 2 reaction	340		NMR spectra of alkynes and small rings	414
	Contrasts between S _N 1 and S _N 2	342		Proton NMR distinguishes axial and equatorial	72.5
	The leaving group in S _N 1 and S _N 2 reactions	347		protons in cyclohexanes	415
	The nucleophile in S _N 1 reactions	352		Interactions between different nuclei can give	
	The nucleophile in the S _N 2 reaction	353		enormous coupling constants	415
	Nucleophiles and leaving groups compared	357		Identifying products spectroscopically	418
	Looking forward: elimination and			Tables	422
	rearrangement reactions	358		Shifts in proton NMR are easier to calculate and	733
	Further reading	359		more informative than those in carbon NMR	425
				Further reading	426
16	Conformational analysis	360		Electron-withdrawing substituents give	
	Bond rotation allows chains of atoms to adopt	677	[19]	Electrophilic addition to alkenes	427
	a number of conformations	360		Alkenes react with bromine	427
	Conformation and configuration	361		Oxidation of alkenes to form epoxides	429
	Barriers to rotation	362		Electrophilic addition to unsymmetrical alkenes is	400
	Conformations of ethane	363		regioselective	433
	Conformations of propane	365		Electrophilic addition to dienes	435
	Conformations of butane	365		Unsymmetrical bromonium ions open regioselectively	436
	Ring strain	366		Electrophilic additions to alkenes can be stereospecific	439
	A closer look at cyclohexane	370		Adding two hydroxyl groups: dihydroxylation	442
	Substituted cyclohexanes	374		Breaking a double bond completely: periodate	256
	To conclude	381		cleavage and ozonolysis	443
	Further reading	381		Adding one hydroxyl group: how to add water	
	Ketone alkylation poses a problem in regioselectivity.	200		across a double bond	444
17	Elimination reactions	382		To concludea synopsis of electrophilic	760
	Substitution and elimination	382		addition reactions	447
	How the nucleophile affects elimination versus substitution	384		Further reading	447
	E1 and E2 mechanisms	386	20	Formation and reactions of enols	
	Substrate structure may allow E1	388		and enolates	449
	The role of the leaving group	390		Would you accept a mixture of compounds	
	E1 reactions can be stereoselective	391		as a pure substance?	449
	E2 eliminations have anti-periplanar			Tautomerism: formation of enols by proton transfer	450
	transition states	395		Why don't simple aldehydes and ketones exist	1//4
	The regioselectivity of E2 eliminations	398		as enols?	451

	Evidence for the equilibration of carbonyl			Diastereoisomers are stereoisomers that abulanoa oT	526
	compounds with enols	451		Further reading	527
	Enolization is catalysed by acids and bases	452	319		
	The intermediate in the base-catalysed reaction is an enolate ion	452	23	Chemoselectivity and protecting groups	528
				Selectivity	528
	Summary of types of enol and enolate Stable enols	454		Reducing agents	530
		456		Reduction of carbonyl groups	530
	Consequences of enolization	459		Hydrogen as a reducing agent: catalytic hydrogenation	534
	Reaction with enols or enolates as intermediates	460		Getting rid of functional groups	539
	Stable equivalents of enolate ions	465		Dissolving metal reductions	541
	Enol and enolate reactions at oxygen: preparation of enol ethers	467		Selectivity in oxidation reactions	544
	Reactions of enol ethers	468		Competing reactivity: choosing which group reacts	546
	To conclude	470	235	A survey of protecting groups	549
	Further reading	470		Further reading	561
	Turtifici readility per bris land separation and notors	4/0	3/4/2		
21	Electrophilic aromatic substitution	471	24	Regioselectivity	562
21		1/0		Introduction	562
	Introduction: enols and phenols	471		Regioselectivity in electrophilic aromatic substitution	563
	Benzene and its reactions with electrophiles	473		Electrophilic attack on alkenes	570
	Electrophilic substitution on phenols	479		Regioselectivity in radical reactions	571
	A nitrogen lone pair activates even more strongly	482		Nucleophilic attack on allylic compounds	574
	Alkyl benzenes also react at the <i>ortho</i> and	101		Electrophilic attack on conjugated dienes	579
	para positions Electron withdrawing substituents give	484		Conjugate addition	581
	Electron-withdrawing substituents give meta products	486		Regioselectivity in action	582
	Halogens show evidence of both electron withdrawal and donation	489		Further reading	583
	Two or more substituents may cooperate or compete	491	25	Alkylation of enolates	584
	Some problems and some opportunities	492	200	Carbonyl groups show diverse reactivity	584
	A closer look at Friedel—Crafts chemistry	492		Some important considerations that affect all alkylations	
	Exploiting the chemistry of the nitro group	494		Nitriles and nitroalkanes can be alkylated	585
	Summary	495		Choice of electrophile for alkylation	587
	Further reading	497		Lithium enolates of carbonyl compounds	587
	Nuclean indital weathwith returning tythroyd own pnibbA			Alkylations of lithium enolates	588
22	Conjugate addition and nucleophilic			Using specific enol equivalents to alkylate aldehydes	270
443	aromatic substitution	498		and ketones	591
	Alkenes conjugated with carbonyl groups	498		Alkylation of β-dicarbonyl compounds	595
	Conjugated alkenes can be electrophilic	499		Ketone alkylation poses a problem in regioselectivity	598
	Summary: factors controlling conjugate addition	509		Enones provide a solution to regioselectivity problems	601
	Extending the reaction to other electron-	303		Using Michael acceptors as electrophiles	605
	deficient alkenes	510		To conclude	612
	Conjugate substitution reactions	511		Further reading	613
	Nucleophilic epoxidation	513			
	Nucleophilic aromatic substitution	514	26	Reactions of enolates with carbonyl	
	The addition—elimination mechanism	515	UEC	compounds: the aldol and Claisen reactions	614
	The S _N 1 mechanism for nucleophilic aromatic			Introduction	614
	substitution: diazonium compounds	520		The aldol reaction	615
	The benzyne mechanism	523		Cross-condensations	618

CONTENTS	xi
----------	----

	Specific enol equivalents can be used to control	60.4		Functional group interconversion	699
	aldol reactions	624		Two-group disconnections are better than one-group	
	How to control aldol reactions of esters	631		disconnections	702
	How to control aldol reactions of aldehydes	632	200	C—C disconnections	706
	How to control aldol reactions of ketones	634		Available starting materials	711
	Intramolecular aldol reactions	636		Donor and acceptor synthons	712
	Acylation at carbon	640		Two-group C—C disconnections	712
	Crossed ester condensations	643		1,5-Related functional groups	719
	Summary of the preparation of keto-esters	989		'Natural reactivity' and 'umpolung'	719
	by the Claisen reaction	647		To conclude	722
	Controlling acylation with specific enol equivalents	648		Further reading belonged belonged belonged belonged belonged by the second belonged by the second belonged by the second belonged by the second by the secon	722
	Intramolecular crossed Claisen ester condensations	652	796	The Heck reactions of	
	Carbonyl chemistry—where next?	654	[29]	Aromatic heterocycles 1: reactions	723
	Further reading	654		Introduction	723
	ARRY 1809205 HUIT DUI anes and Dayues			Aromaticity survives when parts of benzene's ring	
27	Sulfur, silicon, and phosphorus in organic			are replaced by nitrogen atoms	724
010	chemistry	656		Pyridine is a very unreactive aromatic imine	725
	Useful main group elements	656		Six-membered aromatic heterocycles can have oxygen	1930
	Sulfur: an element of contradictions	656		in the ring	732
	Sulfur-stabilized anions	660		Five-membered aromatic heterocycles are good at electrophilic substitution	722
	Sulfonium salts	664			733
	Sulfonium ylids	665		Furan and thiophene are oxygen and sulfur analogues of pyrrole	735
	Silicon and carbon compared	668		More reactions of five-membered heterocycles	738
	Allyl silanes as nucleophiles	675		Five-membered rings with two or more nitrogen atoms	740
	The selective synthesis of alkenes	677		Benzo-fused heterocycles	745
	The properties of alkenes depend on their geometry	677		Putting more nitrogen atoms in a six-membered ring	748
	Exploiting cyclic compounds	678		Fusing rings to pyridines: quinolines and isoquinolines	749
	Equilibration of alkenes	679		Aromatic heterocycles can have many nitrogens	, 43
	E and Z alkenes can be made by stereoselective			but only one sulfur or oxygen in any ring	751
	addition to alkynes	681		There are thousands more heterocycles out there	753
	Predominantly E alkenes can be formed by			Which heterocyclic structures should you learn?	754
	stereoselective elimination reactions	684		Further reading	755
	The Julia olefination is regiospecific and connective	686		Diastereoselectivity anomaganist and property	
	Stereospecific eliminations can give pure single	1023	30	Aromatic heterocycles 2: synthesis	757
	isomers of alkenes	688	856	Thermodynamics is on our side	758
	Perhaps the most important way of making alkenes—the Wittig reaction	689		Disconnect the carbon—heteroatom bonds first	758
	To conclude			Pyrroles, thiophenes, and furans from 1,4-dicarbonyl	1134
		693		compounds	760
	Further reading	693		How to make pyridines: the Hantzsch pyridine synthesis	763
200	Controlling double bends using the agmentagon in refer			Pyrazoles and pyridazines from hydrazine and	
28	Retrosynthetic analysis	694		dicarbonyl compounds	767
	Creative chemistry	694		Pyrimidines can be made from 1,3-dicarbonyl	
	Retrosynthetic analysis: synthesis backwards	694		compounds and amidines	770
	Disconnections must correspond to known,			Unsymmetrical nucleophiles lead to selectivity questions	771
	reliable reactions	695		Isoxazoles are made from hydroxylamine or by	772
	Synthons are idealized reagents	695		cycloaddition Tetropoles and triangles are also made by gyaloodditions	774
	Multiple step syntheses: avoid chemoselectivity	1060		Tetrazoles and triazoles are also made by cycloadditions	775
	problems and a second vd more also be 8	698		The Fischer indole synthesis	175

XII CONTENTS

	Quinolines and isoquinolines	780		The Woodward–Hoffmann description of the	526
	More heteroatoms in fused rings mean more	704		Diels-Alder reaction Transing reactive intermediates by systemediates additions	892
	choice in synthesis	784		Trapping reactive intermediates by cycloadditions Other thermal cycloadditions	893
	Summary: the three major approaches to the synthesis of aromatic heterocycles	785		Other thermal cycloadditions Photochomical [2 + 2] cycloadditions	894 896
	Further reading	788		Photochemical [2 + 2] cycloadditions Thormal [2 + 2] cycloadditions	
		456		Thermal [2 + 2] cycloadditions Making five-membered rings: 1,3-dipolar	898
31	Saturated heterocycles and			cycloadditions	901
21	stereoelectronics	789		Two very important synthetic reactions: cycloaddition	
	Introduction	789		of alkenes with osmium tetroxide and with ozone	905
	Reactions of saturated heterocycles	790		Summary of cycloaddition reactions	907
	Conformation of saturated heterocycles	796		Further reading	908
	Making heterocycles: ring-closing reactions	805	654	Carbonyl chemistry—where next?	
	Ring size and NMR	814	35	Pericyclic reactions 2: sigmatropic and electrocyclic reactions	909
	Geminal (2J) coupling	817			
	Diastereotopic groups	820		Sigmatropic rearrangements	909
	To summarize	824		Orbital descriptions of [3,3]-sigmatropic rearrangements	912
	Further reading	824		The direction of [3,3]-sigmatropic rearrangements	913
	Devicence and its reactions with clicate philes on and of			[2,3]-Sigmatropic rearrangements	917
[32]	Stereoselectivity in cyclic molecules	825		[1,5]-Sigmatropic hydrogen shifts	919
	Introduction	825		Electrocyclic reactions	922
	Stereochemical control in six-membered rings	826		Further reading	930
	Reactions on small rings	832		Conjugate addition bersomos nodras bus nosilis	550
	Regiochemical control in cyclohexene epoxides	836	36	Participation, rearrangement, and	
	Stereoselectivity in bicyclic compounds	839	677	fragmentation and to also the service of the servic	931
	Fused bicyclic compounds	841		Neighbouring groups can accelerate	
	Spirocyclic compounds	846		substitution reactions	931
	Reactions with cyclic intermediates or cyclic			Rearrangements occur when a participating group	584
	transition states	847		ends up bonded to a different atom	937
	To summarize	851		Carbocations readily rearrange	940
	Further reading	851		The pinacol rearrangement	945
33	Diastereoselectivity	852		The dienone-phenol rearrangement	949
33				The benzilic acid rearrangement	950
	Looking back	852		The Favorskii rearrangement	950
	Prochirality	856		Migration to oxygen: the Baeyer–Villiger reaction	953
	Additions to carbonyl groups can be diastereoselective even without rings	858		The Beckmann rearrangement	958
	Stereoselective reactions of acyclic alkenes	865		Polarization of C—C bonds helps fragmentation	960
	Aldol reactions can be stereoselective	868		Fragmentations are controlled by stereochemistry	962
	Single enantiomers from diastereoselective reactions	871		Ring expansion by fragmentation Controlling double bands using fragmentation	963
	Looking forward	876		Controlling double bonds using fragmentation The synthesis of poetketones fragmentation	965
	Further reading	876		The synthesis of nootkatone: fragmentation showcase	966
	compounds and amidines routed and amidines			Looking forward	969
34	Pericyclic reactions 1: cycloadditions	877		Further reading	969
	A new sort of reaction	877		reliable reactions	
	General description of the Diels—Alder reaction	879	37	Radical reactions	970
	The frontier orbital description of cycloadditions	886		Radicals contain unpaired electrons	970
	Regioselectivity in Diels-Alder reactions	889		Radicals form by homolysis of weak bonds	971

CONTENTS	xiii

	Most radicals are extremely reactive	974	1169	Summary of methods for the investigation	
	How to analyse the structure of radicals: electron	Periodic		of mechanism	106
	spin resonance	975		Further reading	106
	Radical stability	977	0111	hemistry vs viruses in a secure control of	
	How do radicals react?	980	[40]	Organometallic chemistry	106
	Radical-radical reactions	980		Transition metals extend the range of	
	Radical chain reactions	984		organic reactions	106
	Chlorination of alkanes	986		The 18 electron rule	107
	Allylic bromination	989		Bonding and reactions in transition metal complexes	107
AE	Reversing the selectivity: radical substitution of Br by H	990		Palladium is the most widely used metal in homogeneous catalysis	107
	Carbon—carbon bond formation with radicals	992		The Heck reaction couples together an organic	
	The reactivity pattern of radicals is quite different			halide or triflate and an alkene	107
	from that of polar reagents	997		Cross-coupling of organometallics and halides	108
	Alkyl radicals from boranes and oxygen	998		Allylic electrophiles are activated by palladium(0)	108
	Intramolecular radical reactions are more efficient	000		Palladium-catalysed amination of aromatic rings	109
	than intermolecular ones	999		Alkenes coordinated to palladium(II) are attacked	
	Looking forward	1002		by nucleophiles	109
	Further reading	1002		Palladium catalysis in the total synthesis of a natural alkaloid	109
38	Synthesis and reactions of carbenes	1003		An overview of some other transition metals	109
	Diazomethane makes methyl esters from			Further reading	110
	carboxylic acids	1003			
	Photolysis of diazomethane produces a carbene	1005	41	Asymmetric synthesis	110
	How do we know that carbenes exist?	1006	H	Nature is asymmetric	110
	Ways to make carbenes	1006		The chiral pool: Nature's chiral centres	110
	Carbenes can be divided into two types	1010		'off the shelf'	110
	How do carbenes react?	1013		Resolution can be used to separate enantiomers	110
	Carbenes react with alkenes to give	, , ,		Chiral auxiliaries	110
	cyclopropanes	1013		Chiral reagents	111.
	Insertion into C–H bonds	1018		Asymmetric catalysis	111
	Rearrangement reactions	1020		Asymmetric formation of carbon–carbon bonds	112
	Nitrenes are the nitrogen analogues of carbenes	1022		Asymmetric aldol reactions	1129
	Alkene metathesis	1023		Enzymes as catalysts	113
	Summary	1027		Further reading	113
	Further reading	1027			
	1.8-Piazabicyclof5.4-Olundec-7-en		42	Organic chemistry of life	1134
39	Determining reaction mechanisms	1029	12		
0307	There are mechanisms and there are mechanisms			Primary metabolism	1134
	Determining reaction mechanisms: the	1029		Life begins with nucleic acids	113!
	Cannizzaro reaction	1031		Proteins are made of amino acids	1139
	Be sure of the structure of the product	1035		Sugars—just energy sources?	1142
	Systematic structural variation	1040		Lipids Lipids	1147
	The Hammett relationship	1040		Mechanisms in biological chemistry	1149
	Other kinetic evidence for reaction mechanisms	1050		Natural products	1156
	Acid and base catalysis	1050		Fatty acids and other polyketides are made from	110
	The detection of intermediates			Torpopos are volatile constituents of plants	1161
		1060		Terpenes are volatile constituents of plants	1164
	Stereochemistry and mechanism	1063		Further reading	1167

XIV CONTENTS

43	Organic chemistry today	1169		acknowledgements	1182
1001	Science advances through interaction		Perioc	lic table of the elements	1184
	between disciplines	1169	Index		1187
	Chemistry vs viruses	1170			
	The future of organic chemistry	1179		Photochemical 2 + 2 cycloaddiffbsen zlapibar ob wol-	
	Further reading	1181			
	organic reactions				
	The 18 electron rulebns and but better bette				
	Allylic electrophiles are activated by palladium(Q)				
				Intramolecular radical reactions are more efficient upon	A STATE OF
				Orbital descriptions of [3,3]-signorgiuseloment mant	
				Looking forward biswiot priziool	
				The cirection of 13.31-sigmatropic reamaged begins in 19.31-sigmatropic reamaged begi	
	Natidire is asymmetric			How do we know that carbenes exist?	
	The chiral pool: Nature's chiral centres				
	Asymmetric catalysis				
	Asymmetric formation of carbon-carbon bonds:				
	Asymmetric aldol reactions - vivity alaconatic aldol reactions				
	Further reading				
	Single enaminomers fraggical against 18 95 95 97 548 97057				
				Controlling doubed bombins the characters of nootkatone: fragmenting the synthesis of nootkatone: fragment the synthesis of nootkatone: fragment the synthesis of nootkatone.	
	Sugars—just energy sources? Lipids			showcase sure of the product and the spiral entitle of the product.	
				The Hammett relationship	
	Fatty acids and other polyketides are made from VPI acetyl Coarses related and in northernal section of the General section continues acetyl Coarses replied and in northernal sections.			Radical reactions sizylates each bna bioA	

0001 Radicals contain unpaire@etabbementni to noitseteb eril 970