

TABLE OF CONTENTS

Chapter 1 - Theoretical Bases.....	1
Thierry Lepoint and Françoise Lepoint-Mullie	
1. Ultrasonic Waves	3
1.1. Frequency.....	3
1.2. Acoustic Intensity	4
1.3. Generation of Ultrasonic Pressure Waves.....	5
1.4. Propagation of Ultrasound.....	6
1.5. Attenuation	7
1.6. Radiation Pressure, Streaming, and Microstreaming.....	8
1.7. Spatial Distribution of the Sound Field	11
1.8. Measurements of Acoustic Intensity	12
1.8.1. The calorimetric method.....	13
1.8.2. The radiometric method.....	13
1.8.3. Measurements with hydrophones	14
2. Cavitation Inception, Nucleation.....	15
2.1. The Process of Nucleation.....	15
2.1.1. Statement of the problem.....	15
2.1.2. The crevice model	17
2.2. The Concept of Threshold.....	19
2.2.1. The Blake threshold.....	19
2.2.2. A word about the Minneart frequency.....	21
2.2.3. Rectified diffusion	21
2.2.4. Transient cavitation.....	24
3. Bubble Dynamics	25
3.1. Isolated Bubbles and Their Collapse	25
3.1.1. The Rayleigh-Plesset equation.....	25
3.1.2. Types of bubble behavior.....	28
3.2. Non-radial Oscillations (Rayleigh-Taylor instability).....	31
3.3. Bubbles Next to a Solid Wall: The Process of Erosion	32
3.3.1. Impact of liquid jets	33
3.3.2. Emission of shock waves.....	36
3.4. Forces on Bubbles in a Sound Field.....	36
3.4.1. Primary Bjerknes force.....	37
3.4.2. Secondary Bjerknes force.....	38

4. Bubbles as Acoustic Emitters.....	41
4.1. Elements of an Acoustic Spectrum.....	41
4.2. Chaotic Behavior, the Isolated Bubble	42
4.3. Bubble Cloud (The passage towards transient cavitation).....	44
5. How and Where Does the Chemical Activity of Cavitation Start?.....	45
6. Single Bubble Sonoluminescence and Sonochemistry	46
<i>Chapter 2 - Sonochemistry of Solutions.....</i>	51
Christian Pétrier and Jean-Louis Luche	
1. Sonochemical Reactivity	52
1.1. Sonochemical Switching.....	52
1.2. An Attempted Rational View on Sonochemical Reactions.....	52
1.3. Parameters Influencing the Sonochemical Reactivity.....	53
1.3.1. Frequency	53
1.3.2. Energy and temperature.....	54
1.4. The Site of the Sonolytic Reaction	57
1.4.1. Reactions in the gas phase inside the bubble.....	57
1.4.2. Reactions in the interfacial region	60
1.4.3. Reactions in the bulk liquid	62
2. Synthetic Applications.....	63
2.1. Processes Based on a Sonolytic Step.....	64
2.1.1. Sonolysis of the carbon-halogen bond	64
2.1.2. Sonolysis of the carbon-nitrogen bond	69
2.1.3. Sonolysis of hydrogen-element bonds.....	70
2.1.4. Sonolysis of transition metal complexes.....	74
2.1.5. Other sonolyses.....	77
2.2. Non-sonolytic Reactions.....	78
2.2.1. Additions with C-C bond formation	78
2.2.2. Formation and cleavage of carbon-heteroelement bonds.....	82
2.3. Substitutions.....	85
2.3.1. Substitutions leading to C-C bonds.....	86
2.3.2. Substitutions leading to carbon-heteroelement bonds.....	87
2.4. Redox Reactions.....	88
<i>Chapter 3 - Cycloadditions</i>	91
Houda Fillion and Jean-Louis Luche	
1. Sonochemical Cycloadditions	92
1.1. [2+2] Additions of Ketenes and Keteniminiums to Olefins.....	92
1.1.1. Cycloadditions of ketenes.....	92
1.1.2. Cycloadditions of keteniminiums.....	93
1.2. [3+2] Additions.....	94
1.2.1. Nitrones and nitrile oxides as 1,3-dipoles	94
1.2.2. Azides as 1,3-dipoles	96

1.3. The Diels-Alder Reaction.....	97
1.3.1. General aspects	97
1.3.2. The sonochemical Diels-Alder reaction.....	98
2. Final Remarks.....	105
 <i>Chapter 4 - Sonochemistry in Biphasic Systems</i>	107
André Loupy and Jean-Louis Luche	
1. Chemical Effects of Cavitation.....	108
1.1. Cavitation at Interfacial Boundaries.....	108
1.2. The Sonochemical Reactivity	109
1.3. Relationship of Sonochemistry with Tribiochemistry.....	110
1.4. The Sonochemical Activation of Solids	112
2. Synthetic Applications.....	113
2.1. Addition Reactions.....	114
2.1.1. Addition of radicals to olefins	114
2.1.2. Electrophilic additions to carbon-carbon multiple bonds.....	117
2.1.3. Nucleophilic additions to conjugated systems.....	120
2.1.4. Nucleophilic additions to carbon-heteroatom bonds	122
2.1.5. Acid-catalyzed additions.....	132
2.2. Eliminations.....	134
2.2.1. β -Eliminations.....	134
2.2.2. α -Eliminations.....	135
2.3. Alkylation and Acylation Reactions.....	137
2.3.1. Alkylation and acylation at a carbon atom.....	137
2.3.2. Alkylation and acylation at a nitrogen atom	139
2.3.3. Alkylation and acylation at an oxygen atom.....	142
2.3.4. Alkylation at sulfur atoms.....	143
2.4. Substitution	144
2.4.1. Nucleophilic substitutions.....	145
2.4.2. Aromatic substitutions.....	149
2.5. Reductions	151
2.6. Oxidations.....	153
2.6.1. Introduction of an oxygen atom	153
2.6.2. Oxidations without introduction of oxygen	158
2.7. Rearrangements	162
2.8. Access to Organoelement Compounds.....	163
2.8.1. Preparations of metal derivatives.....	163
2.8.2. Non-metal derivatives.....	165

Chapter 5 - Organometallic Sonochemistry.....	167
Pedro Cintas and Jean-Louis Luche	
1. Activation of Metals.....	168
1.1. Physical and Chemical Activation.....	169
1.1.1. Physical activation.....	169
1.1.2. Chemical activation.....	173
1.2. The Tribochemical Interpretation.....	174
2. Preparation of Active Metals.....	176
2.1. Direct Activation	176
2.2. Activation by Formation of Alloys	177
2.3. Reduction and Sonolysis of Metallic Derivatives.....	178
2.3.1. Reductions.....	178
2.3.2. Sonolyses.....	180
3. Organic Synthetic Reactions.....	181
3.1. Electron Transfers to Hydrocarbons	181
3.1.1. Aromatic radical anions.....	181
3.1.2. Radical anions from dienes.....	184
3.2. Electron Transfer to Unsaturated Groups	185
3.2.1. Reduction of carbon-carbon double bonds	185
3.2.2. Reduction of carbonyl groups.....	187
3.2.3. Miscellaneous.....	192
3.3. Electron Transfer to Single Bonds (except carbon-halogen bonds).....	194
3.3.1. Cleavage of the C-H bond.....	194
3.3.2. Reduction of carbon-carbon and carbon-heteroatom single bonds.....	195
3.3.3. Reduction of various bonds involving heteroatoms.....	198
3.4. Reduction of Carbon-Halogen Bonds.....	199
3.4.1. Formation of organoalkali and Grignard reagents.....	200
3.4.2. Transmetallation with sonochemically prepared organometallics.....	201
3.4.3. Direct access to organozinc reagents.....	203
3.4.4. Miscellaneous.....	205
3.5. Reactions Using <i>in situ</i> Generated Organometallics.....	206
3.5.1. Deprotonation by <i>in situ</i> generated organoalkali metal reagents	206
3.5.2. Wurtz- and Ullmann-type coupling reactions forming C-C bonds.....	207
3.5.3. The formation of carbon-heteroatom bonds	209
3.5.4. Coupling reactions of silicon, tin, and germanium compounds	209
3.5.5. Addition of organozinc reagents to multiple bonds.....	212
3.5.6. <i>In situ</i> preparation of dichloroketene	215
3.6. Additions of Organic Halides to Aldehydes and Ketones in the Presence of Metals	216
3.6.1. The Barbier reaction in the presence of lithium or magnesium.....	217
3.6.2. Barbier reactions in the presence of zinc.....	221
3.6.3. Extensions of the Barbier reaction. The use of aqueous media	223
3.6.4. Additions to trivalent functionalities.....	229
3.6.5. Reactions from α -halocarbonyl compounds.....	231

<i>Chapter 6 - Catalytic Reactions</i>	235
Vittorio Ragagni and Claudia L. Bianchi	
1. Specific Changes in the Activities of Catalysts Prepared under Sonication	236
1.1. Sonochemical Preparation of Ultrafine Particles.....	236
1.2. Sonochemical Synthesis of Amorphous Iron	239
1.3. Preparation of Very Active Metal Powders	240
1.4. Preparation of Supported Catalysts.....	241
2. Effect of Sonication on Heterogeneous Catalytic Reactions	246
2.1. Steps of a Catalytic Heterogeneous Reaction.....	246
2.1.1. How to individuate the different regimes.....	247
2.2. Cavitation Inside the Pores of a Catalyst	250
2.2.1. Relationship between frequency and resonant bubble radius.....	251
2.2.2. Consequences.....	252
2.3. Examples of Heterogeneous Reactions Using Solid Catalysts and Ultrasound.....	252
2.3.1. Reactions of industrial concern.....	253
2.3.2. Catalytic reactions in the laboratory.....	259
<i>Chapter 7 - Organic Sonoelectrochemistry</i>	263
David J. Walton and Timothy J. Mason	
1. Electrochemical Principles.....	264
1.1. The Electrochemical Cell	265
1.1.1. General considerations.....	265
1.1.2. Electrosynthesis, the divided cell.....	265
1.1.3. Electroanalysis.....	266
1.1.4. Experimental parameters affecting sonoelectrochemistry.....	266
1.1.5. Benefits of using ultrasound in electrochemistry	268
1.2. Procedural Aspects in Sonoelectrochemistry	268
2. Results.....	269
2.1. Electroanalytical Studies	269
2.1.1. Methodology	270
2.1.2. Hydrodynamics.....	271
2.1.3. Electrode fouling	273
2.1.4. Kinetic effects.....	274
2.1.5. Thermodynamics	275
2.1.6. Scale-up considerations	277
2.2. Sonoelectroorganic Synthesis	278
2.2.1. History	278
2.2.2. Electrooxidative syntheses.....	280
2.2.3. Electroreductive syntheses.....	287
2.2.4. Organometallic systems.....	291
2.2.5. Electroinitiated polymerizations.....	293
2.2.6. Sonoelectrochemiluminescence	297

Chapter 8 - Practical Considerations for Process Optimization 301**Timothy J. Mason and Eric Cordemans de Meulenaer**

1. The Acoustical Parameters	302
1.1. Why Worry about Using Specific Frequencies?	302
1.2. Methods of Generating Ultrasound.....	303
1.2.1. Baths.....	304
1.2.2. Horn generators.....	305
1.2.3. The cup-horn set-up.....	309
1.2.4. Other types of equipment.....	311
1.2.5. High-frequency cells	312
1.3. How to Measure Ultrasonic Power	313
1.3.1. The calorimetric method.....	313
1.3.2. Chemical methods	313
1.4. The Mapping of Ultrasound Fields: Topology	314
2. How to Optimize the Sonochemical System	316
2.1. Methods of Enhancing Cavitation.....	317
2.1.1. Addition of solid aids to cavitation.....	317
2.1.2. Should a gas be entrained?.....	317
2.2. The Characteristics of the Reaction in Question.....	317
2.2.1. The physical state of the reaction	317
2.2.2. The mechanism	318
2.2.3. The optimization of power.....	319
2.2.4. Should continuous or pulsed conditions be used?.....	320
2.2.5. Temperature and pressure.....	321
2.2.6. Parameters related to the cavitation zone.....	321
3. Chemical and Mechanical Effects.....	324
4. The Use of Ultrasound in Combination with Other Techniques.....	325
5. Some Significant Industrial Examples.....	326
6. The 10 Commandments (and a Few More) for the Correct Use of Ultrasonic Equipment	327
6.1. General Rules	328
6.2. For Bath Systems	328
6.3. For Probe Systems.....	328
<i>Chapter 9 - Selected Experiments.....</i>	331

Edited by Jean-Louis Luche

1. Acyloins	
Reductive condensation of esters; Preparation of 1,2-bis(trimethylsilyloxy)cyclobutene J. Salaün	331
2. Aldehydes	
2.1. By a modified Bouveault reaction; Preparation of perfluoroheptanal A.O. Miller, D. Peters, C. Zur, M. Frank, and R. Miethchen	332

2.2. By conjugate addition on an α -enal;	
Cyclization of N-(4-iodo-1-oxo)-butyl-3-formyl-4-methyl-1,4-dihydropyridine	
S. Raussou, N. Urbain, P. Mangeney, and A. Alexakis.....	333
2.3. By oxidation of alcohols	
2.3.1. Furan-2,5-dicarbaldehyde from 5-hydroxymethyl-2-furfural	
L. Cottier, G. Descotes, J. Lewkowski, and R. Skowronski	333
2.3.2. 4-Nitrobenzaldehyde from 4-nitrobenzyl alcohol	
F.A. Luzzio and R.W. Fitch.....	334
2.3.3. Cinnamaldehyde from cinnamic alcohol	
B.H. Han.....	336
3. Alkanes	
3.1. Reduction of olefins; Hydrogenation of 4,4-dimethyl-cyclopent-2-en-1-one	
C. Pétrier and J.L. Luche	337
3.2. A new Clemmensen reduction;	
Preparation of 5α -androstan- 17β -ol from 5α -androstan- 17β -ol-3-one	
J.A.R. Salvador, M.L. Sá e Melo, and A.S. Campos Neves	337
4. Amides	
4.1. Masking of an amine with a Boc group;	
Preparation of the N^α -Boc derivative of L-diphenylalanine	
G. Chassaing and H. Josien	338
4.2. Alkylation at a nitrogen atom;	
Synthesis of 1(1-cyano-2,3,5-tri-O-benzoyl- β -D-ribofuranosyl)thymine	
A. Grouiller, G. R. Chen, V. Uteza, and G. Descotes.....	339
5. Amines	
5.1. Hydrogenolysis of hydrazines; General procedure	
A. Alexakis, N. Lensen, and P. Mangeney	340
5.2. Reduction of nitro groups; Aniline from nitrobenzene, iron, and hydrazine	
B.H. Han.....	340
6. Aryl Compounds	
Wurtz coupling; Biphenyl from bromobenzene	
G.J. Price and A.A. Clifton.....	341
7. Cyanides	
7.1. Acyl cyanides from acyl chlorides; Preparation of 4-methoxybenzoyl cyanide	
J. Ichihara and T. Ando	341
7.2. α -Functional nitriles from aldehydes	
7.2.1. Preparation of α -(N-methylamino)phenylacetonitrile	
J. Ichihara and T. Ando.....	342
7.2.2. Preparation of α -hydroxyphenylacetonitrile isobutyrate	
J. Ichihara and T. Ando.....	342
8. Cyclic Compounds	
8.1. Carbocyclization; Preparation of methyl (<i>E</i>)-1-indanylideneacetate	
Fen-Tair Luo	343
8.2. Heterocyclization; Sodium 2-triethylsilyl-1H-aziridine-2-carboxylate	
E. Lukevics and V. Dirnens.....	344

9.	Dibromocarbene	
	Preparation of 7,7-dibromobicyclo[4.1.0]heptane	
	Linxiao Xu and U.H. Brinker	344
10.	Dichloroketene	
	[2+2]-Cycloaddition of dichloroketene to olefins;	
	Preparation of 8,8-dichloro-1-methylbicyclo[4.2.0]octanone	
	J.P. Deprés	345
11.	Diorganozinc Reagents	
	Preparation of (4-methylphenyl)cyclohexylzinc	
	J.C. De Souza Barboza, C. Pétrier, and J.L. Luche	347
12.	Epoxides	
	From olefins; Preparation of methyl 9,10-epoxystearate	
	M.S.F. Lie Ken Jie, C.K. Lam, and P. Kalluri	348
13.	Esters	
13.1.	Amino acid esters via a homo-Reformatsky reaction;	
	Benzyl 2-(S)-(t-butoxycarbonyl)amino-4-oxo-4-phenylbutanoate	
	R.F.W. Jackson and A. Wood.....	348
13.2.	Aminophosphonic esters;	
	Diethyl 2-(N-methylamino)-2-(3-thienyl)methylphosphonate	
	J.L. Luche, C. Hubert, A. Muñoz, and B. Garrigues.....	350
13.3.	Dieckmann condensation of diesters;	
	Preparation of 2-carboethoxy-4,4-ethylenedioxycyclohexanone	
	and 2-carboethoxy-2-methyl-4,4-ethylenedioxycyclohexanone	
	P.R.R. Costa, L.C. Sequeira, and A.F. Neves.....	351
14.	Halides	
14.1.	Alkyl halides from thiohydroxamic esters; Preparation of 1-chloropentadecane	
	B.A. Kowalczyk, D.P. Bridon, and W.G. Dauben.....	353
14.2.	Fluoro compounds via the Baltz-Schiemann reaction; Preparation of fluorobenzene	
	A. Müller, U. Roth, S. Siegert, and R. Miethchen.....	354
14.3.	Fluoro compounds from alcohols; 4-Methoxybenzyl fluoride	
	D. Peters and R. Miethchen	354
14.4.	Bromide from a C-H bond;	
	Preparation of 2,3,5-tri-O-benzoyl-1-bromo-D-ribofuranosyl cyanide	
	G.R. Chen and G. Descotes	354
15.	Hydroxyl Compounds	
15.1.	Alcohol by reduction of an epoxide;	
	Selective reduction of 16 α ,17 α -epoxy-3 β ,21-dihydroxy pregn-5-en-20-one	
	M.J.S.M. Moreno, M.L. Sá e Melo, and A.S. Campos Neves	355
15.2.	Barbier reaction on carbonyl compounds;	
	Preparation of 5-chloro-1-phenyl-pentan-1-ol	
	J.L. Luche, J.C. De Souza Barboza, and C. Pétrier	356
15.3.	Phenols from phenyl silyl ethers;	
	Preparation of 3-[(<i>t</i> -butyldimethylsilyloxy)-methyl]phenol	
	J.S. Sawyer and E.A. Schmittling.....	357

16. Ketones	
16.1. Oxidation of alcohols	
16.1.1. Preparation of 2-decanone	
J. Ichihara and T. Ando.....	358
16.1.2. Oxidation of cholesterol to cholest-4-ene-3,6-dione	
M.J.S. M. Moreno, M.L.Sá e Melo, and A. S. Campos Neves	358
16.1.3. Preparation of <i>dl</i> -camphor from <i>dl</i> - <i>endo</i> -borneol	
F.A. Luzzio and R.W. Fitch.....	360
16.2. From carboxylates via a Barbier reaction	
16.2.1. Preparation of 2-[5-(1-phenyl)-hydroxymethyl]-furanyl-phenylmethanone	
M.J. Aurell and J.L. Luche	361
16.2.2. Synthesis of (<i>Z</i>)-1-methoxytetracos-15-en-7-one	
L. Rodefeld and W. Tochtermann.....	361
16.3. Conjugate additions to electron-deficient olefins;	
Synthesis of vitamin D metabolites and analogues	
A. Mouríño, J. Pérez-Sestelo, and L.A. Sarandeses.....	363
17. Lactones	
17.1. The vinyl epoxide-iron carbonyl method; Preparation of	
1'-η1-2,4-η3-(1-oxy-carbonyl-1-spirocyclohexane-but-3-en-2-ylato)tricarbonyliron	
S.V. Ley.....	366
17.2. Annulation of olefins;	
Preparation of α-carbomethoxy-γ-lactone from dihydropyran	
A.-D'Annibale and C. Trogolo.....	367
18. Lithium Di-isopropylamide	
From diisopropylamine and <i>in situ</i> butyllithium	
J.L. Luche and J. Einhorn	368
19. Nitroxides	
Oxidation of a secondary amine;	
Preparation of 2,2,6,6-tetramethyl-4-stearoyloxy piperidin-1-oxyl	
V. Kaliska, S. Toma, and J. Lesko.....	369
20. Olefins	
Vinylsulfones by a Wittig-Horner reaction;	
Preparation of 2-(4-nitrophenyl)-propen-1-yl methyl sulfone	
H. El Fakih, F. Pautet, H. Fillion, and J.L. Luche.....	370
21. Phenylselenide Sodium Salt	
Preparation of (<i>Z</i>)-1-selenophenylhex-3-ene	
S.V. Ley.....	371
22. Pyrazolines	
A multistep synthesis involving 3 sonochemical steps;	
Preparation of methyl 9-(5-hexyl-1 <i>H</i> -pyrazol-3-yl)octanoate	
M.S.F. Lie Ken Jie, C.K. Lam, and P. Kalluri	373
23. Quinones	
Oxidation of ellipticine with Frémy's salt	
F. Pautet, P. Formisyn, and J. Bourgois	374

24. Sulfones	
Reductive bond cleavage of sulfolane with UDP; Preparation of butyl methyl sulfone	
Ta-shue Chou.....	375
<i>Conclusions - Sonochemistry : Quo Vadis?</i>	377
Michel Chanon and Jean-Louis Luche	
1. Heuristic Consequences of the Classification of Sonochemical Effects	377
1.1. A General Approach to Sonochemical Reactivity.....	378
1.1.1. Reactions related to class 1	378
1.1.2. Class 2 reactions.....	382
1.1.3. Class 3 reactions	383
2. Comparison of Sonochemistry with Other Specified Fields.	
Practical Consequences.....	384
2.1. Chemical Methods Based on the Direct Use of Electrons	384
2.1.1. Photochemistry, sonochemical consequences?	385
2.1.2. Radiochemistry.....	385
2.1.3. Electrochemistry, understanding the solid-liquid interface.....	386
2.1.4. Plasma chemistry	387
2.2. Methods Based on Thermal Activation.....	387
2.2.1. Piezochemistry.....	387
2.2.2. Flash thermolysis, subsonic normal beams.....	388
2.2.3. Chemistry in supercritical fluids.....	389
2.3. Mastering of Activation, Sonochemistry and Selectivities.....	390
3. Less Known Physical Phenomena Associated with Sonication	391
4. Final Remarks.....	392
<i>Author Index</i>	393
<i>Subject Index</i>	411