

Contents to all Volumes

Volume E10 a

Introduction

A. Fluorinating Agents

Volume E10b/Part 1

B. Synthesis of Fluorinated Compounds

Volume E10b/Part 2

B. Synthesis of Fluorinated Compounds

C. Transformations of Fluorinated Compounds

Bibliography

Author Index

Subject Index

Volume E10c/Part 1

Methods Index

Volume E10c/Part 2

Methods Index

Table of Contents

Volume E10b/Part 2

3.	By Oxidation Reactions	1
	(O. PALETA)	
3.1.	Fluorinated Hydrocarbons	1
3.1.1.	Aliphatic and Alicyclic	1
3.1.1.1.	Alkanes and Cycloalkanes	1
3.1.1.2.	Alkenes and Cycloalkenes	5
3.1.1.3.	Dienes and Alkynes	23
3.1.2.	Aromatic	26
3.1.3.	Aryl-Aliphatic and Aryl-Alicyclic	30
3.2.	Oxygen Compounds	34
3.2.1.	Hydroxy Compounds	34
3.2.1.1.	Alcohols	34
3.2.1.1.1.	Primary Alcohols	34
3.2.1.1.2.	Secondary Alcohols	37
3.2.1.1.3.	Polyfunctional Alcohols	40
3.2.1.2.	Phenols	41
3.2.2.	Ethers and Furans	43
3.2.3.	Aldehydes, Ketones, Ketenes, and Carbohydrates	45
3.2.4.	Carboxylic Acids and Their Derivatives	49
3.3.	Nitrogen Compounds	52
3.3.1.	Amines	53
3.3.1.1.	Aliphatic and Alicyclic	53
3.3.1.2.	Aromatic and Monofunctional	54
3.3.1.3.	Aromatic and Polyfunctional	56
3.3.2.	Azomethines and Isocyanides	59
3.3.3.	Hydrazines, Hydrazones, and Azo Compounds	61
3.3.4.	Hydroxylamines, and Nitroso and Nitro Compounds	62
3.3.5.	Heterocyclic Compounds	65
3.3.5.1.	Alicyclic	65
3.3.5.2.	Aromatic	65
3.4.	Organoelement Compounds	68
3.4.1.	Boron and Phosphorus Compounds	68
3.4.2.	Sulfur and Selenium Compounds	70
3.4.2.1.	Oxidations Not Involving the Sulfur Atom	70
3.4.2.2.	Oxidations at the Sulfur Atom	71
3.4.2.3.	Oxidation of Selenium Compounds	78
3.4.3.	Iodine Compounds	79
3.5.	Steroid Compounds	80
4.	Preparation of Unsaturated Organo-Fluorine Compounds by Intra- molecular Dehydrohalogenation and Dehalogenation Reactions	90
4.1.	Dehydrohalogenation	90
	(A. YA. IL'CHENKO)	

4.1.1.	Formation of Alkenes	90
4.1.2.	Formation of Allenes and Dienes	97
4.1.3.	Formation of Alkynes	99
4.1.4.	Formation of Cycloalkenes, Cycloalkadienes, and Benzenes	103
4.1.5.	Formation of Carboxylic Acid Derivatives	111
4.1.6.	Formation of Imines, Nitriles, and Azo Compounds	113
4.1.7.	Intramolecular Cyclization: Cycloalkanes and Heterocycles	114
4.1.8.	Formation of Unsaturated Heterocycles	120
4.2.	Dehalogenation	125
	(J. KVIČALA and O. PALETA)	
4.2.1.	Dehalogenation Agents and Methods	125
4.2.1.1.	Metals	125
4.2.1.2.	Organometallic Compounds and Metal Carbonyls	129
4.2.1.3.	Complex Hydrides	130
4.2.1.4.	Phosphorus Compounds	131
4.2.1.5.	Electrolysis	131
4.2.1.6.	Other Methods	132
4.2.2.	Selectivity	132
4.2.3.	Formation of Aliphatic Compounds	133
4.2.4.	Formation of Alicyclic Compounds	138
4.2.5.	Formation of Aromatic Compounds	141
4.2.6.	Formation of Aryl-Aliphatic Compounds	142
4.2.7.	Formation of Unsaturated Oxygen-Containing Compounds	147
4.2.8.	Formation of Unsaturated Nitrogen-Containing Compounds	149
4.2.9.	Formation of Unsaturated Organoelement Compounds	152
4.2.10.	Formation of Unsaturated Heterocyclic Compounds	155
5.	By Isomerization Reactions	162
	(O. PALETA and J. P. RICHMOND)	
5.1.	Isomerizations in Acyclic Systems	162
5.1.1.	Halogen Shift in Fluorohaloalkanes	162
5.1.2.	C=C Bond Migration	168
5.1.2.1.	Fluorohaloalkenes	168
5.1.2.2.	Perfluoroalkenes	170
5.1.2.3.	Perfluorodienes, Perfluoroallenes, and Perfluoroacetylenes	173
5.1.2.4.	Other Fluoroalkenes	176
5.1.3.	Carbon-Heteroatom Double Bond Migration	179
5.1.4.	1,2-Shifts and [2,3] Rearrangements	190
5.1.5.	[3,3] Sigmatropic Rearrangements	196
5.1.5.1.	Cope Rearrangement	197
5.1.5.2.	Aliphatic Claisen Rearrangements	198
5.1.5.3.	Johnson-Claisen Rearrangement	214
5.1.5.4.	Ireland-Claisen Rearrangement	218
5.1.5.5.	Reformatsky-Claisen Rearrangement	224
5.1.5.6.	Eschenmoser-Claisen and Ficini-Claisen Rearrangements	225
5.1.5.7.	Hetero-Claisen Rearrangements	228
5.2.	Isomerizations on Aromatic and Heteroaromatic Rings	232
5.3.	Isomerizations of Cyclic Systems	240
5.3.1.	Three-Membered Rings	240
5.3.1.1.	Cyclopropanes	240
5.3.1.2.	Heterocyclic Three-Membered Rings	246
5.3.2.	Four-Membered Rings	253

5.3.2.1.	Cyclobutenes	253
5.3.2.2.	Cyclobutanes	258
5.3.2.3.	Heterocyclic Four-Membered Rings	261
5.3.3.	Five-Membered Rings	263
5.3.3.1.	Cyclopentanes and Cyclopentenenes	263
5.3.3.2.	Heterocyclic Five-Membered Rings	264
5.3.4.	Six-Membered and Other Ring Systems	266
5.3.4.1.	Carbocyclic Six-Membered and Larger Rings	266
5.3.4.2.	Heterocyclic Six-Membered and Larger Rings	268
5.3.4.3.	Benzene/Dewar Benzene/Prismane/Benzvalene Valence Isomerization ..	269
5.3.4.4.	Heterocyclic Benzene/Dewar Benzene/Prismane/Benzvalene Valence Isomerization	272

6.	By Disproportionation Reactions	279
	(W. RUDOLPH and M. RIELAND)	
6.1.	Catalytic Disproportionation	280
6.1.1.	The Catalyst	280
6.1.2.	Disproportionation of Haloalkanes	281
6.1.2.1.	Chlorofluoromethanes	283
6.1.2.2.	Bromofluoromethanes	284
6.1.2.3.	Haloethanes	285
6.1.3.	Disproportionation of Haloalkenes	287
6.1.4.	Disproportionation of Perhalogenated Aromatic Compounds	290
6.2.	Thermal Disproportionation of Perhalogenated Aromatic Compounds ..	291

C. Transformations of Fluorinated Compounds **293**

1.	Bond Strengths and Reactivity in Organo-Fluorine Compounds	293
	(J. T. WELCH)	
1.1.	The Effect of Fluorine on Structure and Bonding	293
1.2.	The Effect of Fluorination on Acidity	294
1.3.	Steric Effects	296
1.4.	Carbocations	297
1.5.	Carbanions	298
1.6.	Free Radicals	299
1.7.	Carbenes	301

2.	Replacement of Fluorine by Hydrogen	306
	(O. PALETA)	
2.1.	Reactivity of C-F Bonds in Compounds	308
2.1.1.	Fluorinated Hydrocarbons	308
2.1.1.1.	Aliphatic and Alicyclic	309
2.1.1.2.	Aromatic	314
2.1.1.3.	Aryl-Aliphatic	316
2.1.2.	Oxygen Compounds	324
2.1.2.1.	Hydroxy Compounds and Ethers	324
2.1.2.2.	Ketones, Sugars, Diketones, and Quinones	325
2.1.2.3.	Carboxylic Acids and Their Derivatives	328
2.1.3.	Nitrogen Compounds	334
2.1.3.1.	Aliphatic, Alicyclic, Aromatic, Benzoaliphatic, and Aryl-Aliphatic ...	334

2.1.3.2.	Heterocyclic Compounds	337
2.1.4.	<i>N</i> -Fluoro Compounds	339
2.1.5.	Organoelement Compounds	340
3.	Loss of Fluorine To Form C=C Bonds	345
	(D. PETERS and R. MIETHCHEN)	
3.1.	Elimination of Hydrogen Fluoride	345
3.1.1.	By Thermolysis	345
3.1.2.	By Basic Reagents	346
3.1.2.1.	From Aliphatic and Aryl-Substituted Aliphatic Compounds	346
3.1.2.2.	From Cycloaliphatic Compounds	359
3.1.3.	By Other Reagents	362
3.2.	Elimination of Fluorine	363
3.2.1.	By Thermolysis	363
3.2.2.	By Other Reagents	366
3.3.	Simultaneous Elimination of Fluorine and Other Halogens	371
3.3.1.	By Metals	371
3.3.2.	By Other Reagents	376
4.	Replacement of Fluorine To Form C—O Bonds	382
	(A. YA. IL'CHENKO)	
4.1.	Replacement of Fluorine by Hydroxy Groups	382
4.1.1.	Hydrolysis of Fluorine Bonded to Aliphatic Compounds	382
4.1.2.	Hydrolysis of Fluorine Bonded to Aromatic Compounds	386
4.1.3.	Hydrolysis of Fluorine Bonded to Heterocyclic Compounds	389
4.2.	Replacement of Fluorine by Alkoxy and Aryloxy Groups	391
4.2.1.	In Aliphatic Compounds	391
4.2.2.	In Aromatic Compounds	395
4.2.3.	In Heterocyclic Compounds	405
4.3.	Elimination of Fluorine To Form Cyclic Compounds with an Incorporated Oxygen	410
4.4.	Hydrolysis of Difluoromethyl Groups To Form Aldehydes	412
4.5.	Hydrolysis of Difluoromethylene Groups To Form Carbonyl Compounds	412
4.6.	Hydrolysis of Trifluoromethyl Groups To Form Carboxy Groups	418
4.6.1.	Acidic Hydrolysis	418
4.6.2.	Basic Hydrolysis	419
5.	Elimination of Fluorine To Form C—S Bonds	426
	(ST. RÜDIGER)	
5.1.	Elimination of Fluorine Bonded to Aliphatic or Arylaliphatic Compounds	426
5.2.	Elimination of Fluorine Bonded to Aromatic Compounds	428
5.2.1.	Monofluoro and Difluoro Aromatic Compounds	428
5.2.2.	Polyfluoro Aromatic Compounds	433
5.2.2.1.	Partial Substitution of Fluorine	433
5.2.2.2.	Complete Elimination of Fluorine	439
5.3.	Elimination of Fluorine Bonded to Heterocyclic Compounds	443
5.3.1.	Nitrogen-Containing Monocyclic Systems	443
5.3.2.	Polycyclic Systems	446

6.	Elimination of Fluorine To Form C–N Bonds	449
	(J. PODLECH)	
6.1.	Elimination of Nonaromatically Bonded Fluorine	449
6.1.1.	At sp^3 -Bonded Fluorine	449
6.1.2.	At sp^2 -Bonded Fluorine	452
6.2.	Elimination of Aromatically Bonded Fluorine	454
6.2.1.	Nucleophilic Aromatic Substitution	454
6.2.2.	Electrophilic Aromatic Substitution	458
6.2.3.	Substitution Involving Radicals	458
6.2.4.	Substitution Involving Nitrenes	458
6.2.5.	Substitution Involving Aryne Intermediates	459
Bibliography		465
Author Index		485
Subject Index		571