

## Contents

**Preface** *IX*

**Glossary and Abbreviations** *XI*

**Journal Abbreviation List** *XIII*

**1 Electrophilic Alkylation of Arenes** *1*

1.1 General Aspects *1*

1.1.1 Catalysis by Transition-Metal Complexes *2*

1.1.2 Typical Side Reactions *5*

1.2 Problematic Arenes *7*

1.2.1 Electron-Deficient Arenes *7*

1.2.2 Phenols *9*

1.2.3 Anilines *13*

1.2.4 Azoles *19*

1.3 Problematic Electrophiles *19*

1.3.1 Methylations *19*

1.3.2 Olefins *20*

1.3.3 Allylic Electrophiles *21*

1.3.4 Epoxides *23*

1.3.5  $\alpha$ -Halo ketones and Related Electrophiles *25*

1.3.6 Nitroalkanes *26*

1.3.7 Ketones *27*

1.3.8 Alcohols *32*

References *34*

**2 Electrophilic Olefination of Arenes** *45*

2.1 General Aspects *45*

2.2 Olefinations with Leaving-Group-Substituted Olefins *45*

2.3 Olefinations with Unsubstituted Olefins *46*

2.4 Olefinations with Alkynes *52*

References *57*

**3 Electrophilic Arylation of Arenes** *61*

3.1 General Aspects *61*

3.2 Arylations with Aryl Halides *61*

3.2.1	Via Cationic Intermediates	61
3.2.2	Via Radicals	63
3.2.3	Via Transition-Metal Chelates	65
3.2.4	By Transition-Metal Catalysis	67
3.3	Arylations with Diazonium Salts	69
3.4	Arylations with Other Functionalized Arenes	73
3.5	Arylations with Unsubstituted Arenes	78
	References	79
<b>4</b>	<b>Electrophilic Acylation of Arenes</b>	<b>85</b>
4.1	General Aspects	85
4.2	Problematic Arenes	88
4.2.1	Dealkylation/Isomerization of Arenes	88
4.2.2	Styrenes	88
4.2.3	Anilines, Phenols, and Thiophenols	90
4.2.4	Electron-Deficient Arenes	92
4.2.5	Azoles	93
4.3	Problematic Electrophiles	95
4.3.1	Problematic Acyl Halides	95
4.3.2	Carboxylic Esters and Lactones	98
4.3.3	Carbonic Acid Derivatives	101
4.3.4	Formic Acid Derivatives	106
4.3.5	Mixed Carboxylic Anhydrides and Other Polyelectrophiles	110
	References	112
<b>5</b>	<b>Electrophilic Halogenation of Arenes</b>	<b>121</b>
5.1	General Aspects	121
5.2	Typical Side Reactions	121
5.3	Regioselectivity	125
5.4	Catalysis	128
5.5	Fluorinations	129
5.6	Electron-Deficient Arenes	132
5.6.1	Pyridines	133
5.6.2	Benzoic Acid Derivatives	134
5.7	Electron-Rich Arenes	137
5.7.1	Phenols and Arylethers	138
5.7.2	Anilines	138
5.7.3	Azoles	144
5.8	Sensitive Functional Groups	147
5.8.1	Alkenes	148
5.8.2	Amines	148
5.8.3	Ethers	149
5.8.4	Thiols and Thioethers	149

5.8.5	Aldehydes, Ketones, and Other C–H Acidic Compounds	151
5.8.6	Amides	152
	References	152
<b>6</b>	<b>Electrophilic Formation of Aromatic C–N Bonds</b>	<b>161</b>
6.1	Nitration of Arenes	161
6.1.1	Mechanisms	161
6.1.2	Regioselectivity	164
6.1.3	Catalysis	167
6.1.4	Electron-Deficient Arenes	167
6.1.5	Electron-Rich Arenes	169
6.1.5.1	Anilines	171
6.1.5.2	Indoles	173
6.1.5.3	Phenols	173
6.2	Electrophilic Aromatic Aminations	175
6.2.1	Typical Side Reactions	177
6.3	Electrophilic Aromatic Amidations	177
6.3.1	Typical Side Reactions	177
	References	184
<b>7</b>	<b>Electrophilic Formation of Aromatic C–S Bonds</b>	<b>191</b>
7.1	Sulfonylation	191
7.1.1	General Aspects	191
7.1.2	Typical Side Reactions	193
7.2	Sulfinylation	195
7.2.1	General Aspects	195
7.2.2	Typical Side Reactions	195
7.3	Sulfenylation	199
7.3.1	General Aspects	199
7.3.2	Typical Side Reactions	200
	References	201
<b>8</b>	<b>Aromatic Nucleophilic Substitutions</b>	<b>205</b>
8.1	General Aspects	205
8.1.1	Mechanisms	205
8.1.2	Regioselectivity	205
8.1.3	Acid-/Base-Catalysis	211
8.1.4	Transition-Metal Catalysis	211
8.2	Problematic Electrophiles	216
8.2.1	Incompatible Functional Groups	216
8.2.2	Non-Activated Arenes	217
8.2.3	Nitroarenes	219
8.2.4	Diazonium Salts	226
8.2.5	Phenols	229
8.2.6	Arylethers and Arylthioethers	229

8.2.7	Other Phenol-Derived Electrophiles	231
8.2.8	Arynes	232
8.3	Problematic Nucleophiles	233
8.3.1	Enolates	233
8.3.2	Organomagnesium and Related Organometallic Compounds	235
8.3.3	Ammonia	241
8.3.4	Primary and Secondary Amines	242
8.3.5	Tertiary Amines	244
8.3.6	Azides	247
8.3.7	Hydroxide	248
8.3.8	Alcohols	250
8.3.9	Thiols	252
8.3.10	Halides	253
	References	260
<b>Epilogue</b>	<b>Economics, Politics, and the Quality of Chemical Research</b>	277
	Prosperity	277
	Slavery and Freedom	279
	The Quality of Chemical Research	281
	References	283
<b>Index</b>		285