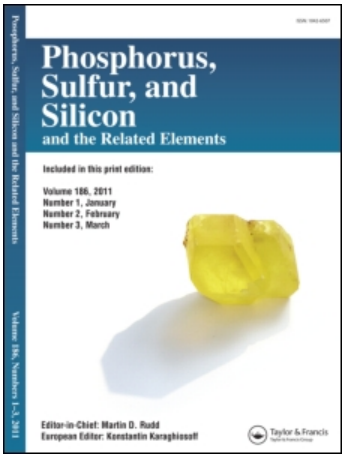

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PREPARATION OF SYMMETRICAL SUBSTITUTED DIPHENYL DISELENIDES

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Review

PREPARATION OF SYMMETRICAL SUBSTITUTED DIPHENYL DISELENIDES

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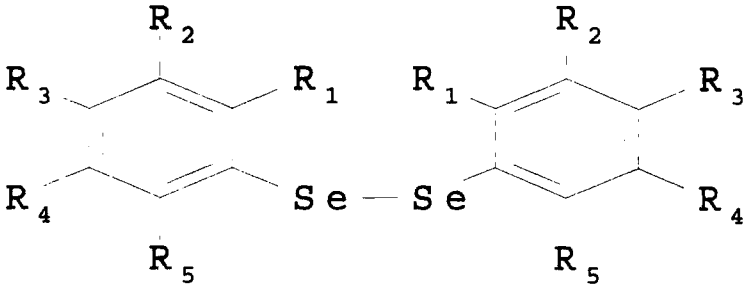
The preparations of 254 known title compounds are fully documented and the 27 different synthetic methods for their preparation are discussed in detail.

INTRODUCTION

Substituted diphenyl diselenides have received much attention recently. Not only as important reagents and intermediates in organic synthesis[1,2,3] or promising donor molecules for conductive and photoconductive organic materials,[4] but also as mimics for important biological systems.[5]

This review covers all title compounds reported up to mid-1993 concerning their preparation, and an examination of all the synthetic methods which are available today will be given.

The paper contains a section that reviews 27 different methods to prepare substituted diphenyl diselenides of the general structure and five tables divided into



derivatives of aniline, phenol, benzamide, toluene, halogen benzene, respectively, and a table for miscellaneous compounds that did not fit into any of the above.

The number given in the third column of the tables represents each method examined in Section 1. In the same way a cross reference is available since each compound is mentioned by a number (in parentheses) in Section 1.

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TABLE I

Preparation of diselenides derived from aniline

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
1	NCH(2-OH-3,5-$(OMe)_2$-Ph),H,H,H,H	22	rf			60
2	NCH(2-OH-Ph),H,H,H,H	22	rf			60
3	NMe_2,H,H,H,H					72
4	NHMe,H,H,H,H	17	rf	2		54
5	NH_2,H,H,CH(OH)Ph,H	17	rf	2	50	54
6	NH_2,H,H,CH_2Ph,H	17	rf	2	70	54
7	NH_2,H,H,CO(4-Cl-Ph),H	17	rf	2	60	54
8	$NHCONMe_2$,H,H,COPh,H	17	rf	17	50	54
9	NH_2,H,H,$COCH_3$,H	17	rf	2	40	54
10	$NHCH_3$,H,H,COPh,H	17	rf	2	60	54
11	NH_2,H,H,COPh,H	17	rf	2	80	54
12	$NHCONMe_2$,H,H,H,H	17	rf	14	50	54
13	4-NO_2-Ph,H,H,NO_2,H	4			50	73
14	4-NO_2-Ph,H,NO_2,H,H	4			60	73
15	H,H,Ph,NO_2,H	4			39	74
16	NO_2,H,NO_2,CH_3,H	4	rf			75
17	H,H,H,NMe_2,H (^{75}Se)	1	35-40	1/2	40	76
18	H,H,H,NMe_2,H	1	35-40	1/2	54	76
19	NO_2,H,Br,H,H	5	rt	1/2	25	37
		6	rt	24	20	37
20	NO_2,H,CH_3,H,H	5	50	3	2	37
		6	60	24	60	37
21	H,H,NO_2,CN,H	25				69
22	H,H,NO_2,H,COOH	4	0	3/4	87	20
23	H,H,NH_2,H,CN	4				77
24	NH(3,6-Cl_2-pyrazin),H,Cl,H,H	23				61
25	NO_2,H,H,H,NO_2	4	-20	1/2	66	17
26	H,H,H,NO_2,H					78
27	NH_2,H,H,H,H					60,79
28	H,H,NO_2,H,CF_3	4	rf	4	67	80

TABLE I (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
29	H, NH_2, CH_3, H, H					81
30	H, H, NMe_2, H, H	4			89	22,82
		25				69
31	$NH(Et)COCH_3, H, H, H, H$					83
32	$NH(Me)COCH_3, H, H, H, H$					83
33	NO_2, H, H, Cl, H	4	rt	1	50	25
34	NH_2, H, H, CH_3, H	4	rf	7/2	91	25
35	H, H, NO_2, H, H	5	20	24	83	36
		4				84
36	H, H, NH_2, H, H	mo				85
37	NO_2, H, CH_3, CH_3, H	pu				86
38	NO_2, H, H, H, H	5	rt	3	16	37
		5	20	20	86	36
		6	rt	5	60	37
		24			92	87,63
39	NH_2, H, Cl, H, H					88
40	NO_2, H, CF_3, H, H	5	rt	1/2	40	37
41	NO_2, H, NO_2, H, H	5	5	1/2	97	36

pu=patent unavailable, mo=mentioned only, rf=reflux, rt=room temperature

TABLE II

Preparation of diselenides derived from phenol

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
42	OCH_3, H, H, H, OCH_3	2	rt	15	60	89
43	$OCH_3, H, H, H, CONH\text{-}t\text{-}Bu$	2	-78	4	65	90
44	$OCH_3, H, H, H, CONHCH_3$	2	-78	4	2	90
45	OCH_3, H, OCH_3, H, H	1				91
46	$H, OCH_3, H, H, CONEt_2$	2	rt	ov		92
47	$OCH_3, H, H, H, CONEt_2$	2	rt	ov		92
48	$OCH_3, OCH_3, H, H, CONHPh$	2	-78	4	41	92
		16	rt	1/4	55	52

TABLE II (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
49	OCH_3,H,H,H,CONHPh	16	rt	1/4	32	52
50	H,H,OCH_3,H,CONHPh	16	rt	1/4	60	52
51	H,t-Bu,OH,t-Bu,H	4				93
52	H,OCH_3,H,$CH_3(CH_2)_4$,H	13	rf	8	63	48
53	H,OCH_3,H,Se-n-Bu,H	13	rf	8	52	48
54	H,H,O-n-Bu,H,H	13	rf	8	72	48
55	H,OCH_3,H,H,H	13	rf	8	65	48
		4				94
56	H,OCH_3,OCH_3,H,$COCH_3$					95
57	OPh,H,H,H,H	8			95	40
58	OCH_3,H,H,H,H	13	rf	8	47	48
		1				96,97
59	H,OCH_3,H,H,NH_2					98
60	OH,H,H,H,H					98
61	H,H,OEt,H,H	13	rf	8	67	48
		1				99
62	H,H,OCH_3,H,NH_2					100
63	H,OCH_3,OCH_3,H,NO_2	10	rf	1	88	42
64	H,OCH_3,OCH_3,H,H	4		6	41	101
65	F,F,OCH_3,F,F					102
66	H,H,OCH_3,H,H	13	rf	8	58	98
		1				103
		4				104
		25				69
67	H,H,OCH_3,SO_3H,H	4				105
68	H,H,OCH_3,H,NO_2	6	60	24	63	37,95
69	H,H,OCH_3,H,NHCOOH					106

rf=reflux, rt=room temperature

TABLE III

Preparation of diselenides derived from benzamide

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
70	$CONHCH_2CH(OCH_3)_2$,H,H,H,H	15	rt	2	86	50
71	CONH(2-pyrimidinyl),H,H,H,H	15				107
72	H,H,$CONH(CH_2)_{17}CH_3$,H,H	5				107
73	H,H,$CONH(CH_2)_{11}CH_3$,H,H	5				107
74	H,H,$CONH_2$,H,H	5				107
75	$CONH(CH_2)_{17}CH_3$,H,H,H,H	5	120	26	52	107
76	$CONH(CH_2)_{11}CH_3$,H,H,H,H	5	120	25	45	107
77	$CON(Et)_2$,H,H,H,H	2	rt	ov	31	91
78	CON(Et)-p-F-Ph,H,H,H,H					108
79	CONH(5-Me-3-isoxazolyl),H,H,H,H	16	rt	1/2	35	52
80	CONH(2-thiazolyl),H,H,H,H	16	rt	1/2	27	52
81	CONH(3-pyridinyl),H,H,H,H	16	rt	1/2	36	52
		15				107
82	CONH(2-thienylmethyl),H,H,H,H	16	rt	1/2	50	52
83	CONH(2-pyridinylmethyl),H,H,H,H	16	rt	1/2	60	52
84	CONH(2-pyridinyl),H,H,H,H	16	rt	1/2	50	25
		15				107
85	CONH(2-furanylmethyl),H,H,H,H	16	rt	1/2	75	52
86	$CONH(2\text{-}CH_3OCO\text{-}Ph)$,H,H,H,H	16	rt	1/4	33	53
87	$CONH(4\text{-}CF_3\text{-}Ph)$,H,H,H,H	16	rt	1/4	44	53
88	$CONHPh,H,H,H,CH_3$	16	rt	1/4	75	53
89	CONH(2-COOH-Ph),H,H,H,H	16	rt	1/4	31	53
90	$CONH(2\text{-}CH_3O\text{-}Ph)$,H,H,H,H	16	rt	1/4	47	53
91	$CONH(3,4\text{-}(CH_3O)_2\text{-}Ph)$,H,H,H,H	16	rt	1/4	25	53
92	CONHPh,H,H,H,H	15	rt	2	85	53
		2	0	1	79	109
		16	rt	1/4	90	53
93	CONH-t-Bu,H,H,H,H	16	rt	1/4	71	53
94	$CONH(CH_2)_6CH_3$,H,H,H,H	16	rt	1/4	78	53
95	CONH-p-F-Ph,H,H,H,H	16	rt	1/4	87	53
96	CONH-c-Hexyl,H,H,H,H	16	rt	1/4	50	53
97	CONH-c-Pentyl,H,H,H,H	16	rt	1/4	66	53
98	CONH-p-CN-Ph,H,H,H,H	16	rt	1/4	25	53
99	CONH-o-Cl-Ph,H,H,H,H	16	rt	1/4	64	53

TABLE III (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
100	CONH-o-NO_2-Ph,H,H,H,H	16	rt	1/4	90	53
101	CONH-m,m-Cl,Cl-Ph,H,H,H,H	16	rt	1/4	84	53
102	CONH$(CH_2)_4$-Ph,H,H,H,H	16	rt	1/4	90	53
103	CONH-p-Cl-Ph,H,H,H,H	16	rt	1/4	72	53
104	CONH-p-OCH_3-Ph,H,H,H,H	16	rt	1/4	63	53
105	CONHCH_2Ph,H,H,H,H	16	rt	1/4	68	53
106	CONH-p-CH_3-Ph,H,H,H,H	16	rt	1/4	72	53
107	CONH-p-NMe_2-Ph,H,H,H,H	16	rt	1/4	50	53
108	CONH(1,3-benzodioxol-5-yl),H,H,H,H	16	rt	1/4	85	53
109	CONH(2,1-phenylenecarbonylimino) bis(α-methyl-,methylester),H,H,H,H	16	rt	1/4	14	53
110	CONH-o-CF_3-Ph,H,H,H,H	16	rt	1/4	51	53
111	CONHCH_2-C-Hexyl,H,H,H,H	16	rt	1/4	86	53
112	CONH-o-OH-Ph,H,H,H,H	16	rt	1/4	8	53
113	CONH-p-OH-Ph,H,H,H,H	16	rt	1/4	46	53
114	CONH-m-OH-Ph,H,H,H,H	16	rt	1/4	12	53
115	CONH-p-NO_2-Ph,H,H,H,H	16	rt	1/4	65	53
116	H,H,CONH-t-Bu,H,H	20	rt	1/4	44	58
117	H,H,CONH-p-F-Ph,H,H	20	rt	1/4	57	58
118	H,H,CONHPh,H,H	20	rt	1/4	57	58
119	H,CONH-p-OH-Ph,H,H,H	20	rt	1/4	35	58
120	H,CONHCH_3,H,H,H	20	rt	1/4	55	58
121	H,CONHPh,H,H,H	20	rt	1/4	68	58
122	H,H,CON$(CH_3)_2$,H,H	20	rt	1/4	77	58
123	H,CON$(CH_3)_2$,H,H,H	20	rt	1/4	49	58
124	CON(CH_3)Ph,H,H,H,H	20	rt	1/4	72	58
125	CON$(CH_3)CH_2$Ph,H,H,H,H	20	rt	1/4	52	58
126	CO-Piperidine,H,H,H,H	20	rt	1/4	78	58
127	CON$(CH(CH_3)_2)_2$,H,H,H,H	20	rt	1/4	93	58
128	CON$(CH_3)_2$,H,H,H,H	20	rt	1/4	75	58
		5	120	24	47	51
129	$CONH_2$,H,H,H,H	5	120	19	70	51
		12	rf	2	92	47
		15				107

rt=room temperature, rf=reflux

TABLE IV

Preparation of diselenides derived from toluene

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
130	CH_2N(2-(2-pyridinyl)ethyl,H,H,H,H	21	rf		37	59
131	$CH(CH_3)_2$CONHPh,H,H,H,H	12			60	46
132	$CH(CH_3)_2$CONHCH_2Ph,H,H,H,H	12			90	46
133	$CH(CH_3)_2$CONHCH_3,H,H,H,H	12			85	46
134	$CH(CH_3)_2$CONH$_2$,H,H,H,H	12			85	46
135	CH_2Cl,,H,H,H,H	4	0	1	69	59
136	CH_2OH,H,H,H,H	4	0	1	87	59
137	$CH_2N(CH_3)$c-Hexyl,H,H,H,H	4	0	1	30	59
138	Et,H,Et,H,Et					110
139	CH_3, CH_3,H,CH_3, CH_3					110
140	H,H,6-Me-Pyridinyl,H,H	5				36
141	H,H,3-quinolinyl,H,H	5				36
142	H,H,2-quinolinyl,H,H	5				36
143	H,H,3-pyridinyl,H,H	5				36
144	H,H,2-pyridinyl,H,H	5				36
145	CF_3,H,H,H,H	1				101
146	CF_3,H,CF_3,H,CF_3	2	rt	9	48	111
147	$CH(CH_3)_2$,H,$CH(CH_3)_2$,H,$CH(CH_3)_2$					110
148	H,H,COPh,H,H	24				33
149	D,D,D,D,D	1				112
150	CONHCOCH_3,H,H,H,H	15				107
		12	50		93	47
151	CONHCOOEt,H,H,H,H	12	rf	3/2	73	47
152	COO$(CH_2)_{17}CH_3$,H,H,H,H	5				36
153	COO$(CH_2)_{11}CH_3$,H,H,H,H	5				36
154	CH_2(1-pyrrolidinyl),H,H,H,H	1	-78	ov	45	5
155	$CH_2N(CH_3)_2$,H,H,H,H	2	-78	2	21	5
156	p-NO_2-Ph,H,H,H,H	4				62,73
157	H,p-NO_2-Ph,H,H,H	4				62,73
158	H,H,p-NO_2-Ph,H,H	4				62,73
159	H,CN,H,H,H	24			51	62
		24			70	62

TABLE IV (*Continued*)

No.	R_1,R_2,R_3,R_4,R_5		Method	Temp C°	Time h	Yield %	Ref.
160	CN,H,H,H,H		24			42	62
			24			59	62
			5	120	6	38	62
161	$COCOOCH_3$,H,H,H,H		25				65
162	Ph,H,H,H,H		1				113
			4				114
163	H,Ph,H,H,H		2				115
			4				116
164	H,$COOCH_3$,H,H,H		4				117
165	COPh,H,H,H,H		4	0-5		52	118
166	$COOCH_3$,H,H,H,H		4	0		46	119
167	Ph,H,Ph,H,Ph		1				120
168	COOH,H,H,H,H	^{75}Se	5	0	30		121
169	H,H,SO_2NH_2,H,H		4	0		29	122
170	H,H,COCl,H,H		19	co			57
171	H,COCl,H,H,H		19	co			57
172	COCl,H,H,H,H		19	40	120	120	56
173	H,H,$COOCH(CH_3)_2$,H,H		20	rt	1/2	63	57
174	H,$COOCH_2Ph$,H,H,H		20	rt	1/2	24	57
175	H,COOEt,H,H,H,H		20	rt	1/2	74	57
176	$COO(CH_2)_3OEt$,H,H,H,H		20	rt	1/2	24	57
177	COOEt,H,H,H,H		20	rt	1/2	63	57
178	COO-n-Bu,H,H,H,H		20	rt	1/2	53	57
179	COO-p-CF_3-Ph,H,H,H,H		20	rt	1/2	14	57
180	COO-t-Bu,H,H,H,H		20	rt	1/2	37	57
181	$COO(CH_2)_5CH_3$,H,H,H,H		20	rt	1/2	32	57
182	$COOCH(CH_3)_2$,H,H,H,H		20	rt	1/2	53	57
183	Et,Et,Et,Et,Et						1
184	Me,Me,Me,Me,Me						1
185	$CH(Ph)_2$,H,Cl,H,H		11	95	1/2	4	44
186	CH(Ph)Ph-d_6,H,H,H,H		11	95	1/2	7	44
187	$CH(Ph)_2$,H,H,H,H		11	95	1/2	11	44

TABLE IV (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
188	$COCH_3$,H,H,H,H	5			27	36
		13	rf	8	68	48
189	H,H,CN,H,H	24			75	62,123,124
		24				63
190	Et,H,H,H,H	1			43	125
191	CH_2Ph,H,H,H,H	25				66
192	CH_2SCH_3,H,H,H,H	26			2	70
193	H,H,t-Bu,H,H	1	rf			126
194	$CH(CH_3)_2$,H,$CH(CH_3)_2$,H,$CH(CH_3)_2$	1	-60		51	127
195	Me,H,Me,H,Me	1	rf	2	47	128
		8			95	40
196	H,Me,H,H,H	8			100	40
		1				16
197	Me,H,H,H,H	1	40	5/2	47	129
198	(2-CH_3OCO-Ph-CO),H,CH_3,H,H	25	20	20	15	67
199	COPh,H,Me,H,H	25			33	68
200	CH_2COOEt,H,H,H,H	12	rf		50	45
201	$CH_2CONHPh$,H,H,H,H	12	rf		60	45
202	CH_2CONH_2,H,H,H,H	12	rf		73	45
203	H,H,CF_3,H,H	1	rt	1/2	45	130,131
204	$COCH(COOEt)_2$,H,H,H,H	27	rf	25	ni	71
205	H,CF_3,H,H,H	1	rt	1/2	88	130
206	F,F,CF_3,F,F	1				42
207	H,H,SO_3H,H,H	4				104,16
208	H,H,COOH,H,H	5				114
		6				132
209	H,COOH,H,H,H	6				132
		4		5/2	85	133,134
210	H,H,SeCN,H,H	4	10-15	3/2	45	135
211	CHO,H,H,H,H	2			13	136
		5	20	18	37	36
212	CHCHCHO,H,H,H,CH_3	18	60	4	50	55

TABLE IV (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
213	$CH_2CHC(CH_3)CHO$,H,H,H,H	18	60	4	50	55
214	$CH_2CHCHCHO$,H,H,H,H	18	60	4	50	55
215	CH_2COOH,H,H,H,H	12	rf		92	45
216	H,H,CH_3,H,H	25	20	20	47	67
		13	rf	8	83	48
		1			61	137
217	H,H,$CO(CH_2)_4CH_3$,H,H	14	rt	5-8	80-85	49
218	H,H,$COCH_3$,H,H	14	rt	5-8	80-85	49
		5				107
219	t-Bu,H,t-Bu,H,t-Bu	2	-78	5/2	64	138
		9	-78	1/2	18	41
						110
220	COOH,H,H,H,H	4		5/2	85	36
		5	<5	2	90	139,140,36
		6				38
221	COOH,H,Br,H,H					141
222	$CONHCH_3$,H,H,H,H	5	120	23	58	36
		16	rt	1/4	64	52
223	H,H,$CONHCH_3$,H,H	4				142
224	2,3-$(CH_3COO)_2$-4-CH_3COO-furan,H,H,H,H	25				66
225		4	100	12	92	19
226		4	90	12	84	19

rt=room temperature, rf=reflux, ni=not isolated, co=claimed only, ov=overnight

TABLE V

Preparation of diselenides derived from halogen benzene

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
227	H,H,F,H,H	1			36	137,143
228	H,H,Cl,H,H					
229	H,H,Br,H,H	1			48	137
		13			71	48
		8	-78	5/2	80	40
230	H,H,I,H,					144
231	F,F,Cl,F,F	5				145
232	F,F,H,F,F					146
233	F,F,F,F,F					147
234	H,Br,H,H,H					148
235	H,Cl,H,H,H					148
236	H,F,H,H,H	1			30	137
237	Br,H,H,H,H					149
238	Cl,H,H,H,H					148
239	I,H,H,H,H	4			9	132

TABLE VI

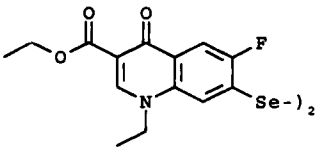
Preparation of diselenides derived from miscellaneous compounds

No.	R_1, R_2, R_3, R_4, R_5	Method	Temp C°	Time h	Yield %	Ref.
240		24				64
241		24				64
242		4	0		40	150
243		7	-60	>1	61	39
244		7			12	39
245		10	rf	2	56	42
246		1	rt	2	65	151
247	(+) (-)	3	-78	1	81	14
248	(+)	3	-78	1		14

TABLE VI (*Continued*)

No.	R_1, R_2, R_3, R_4, R_5		Method	Temp C°	Time h	Yield %	Ref.
249			2	-78	20	84	14
250		(-)	2	-78	1		14
251			4	0	20	16	24
252			4				152
253			4				152
			5				152
254			5			52	153

rt=room temperature, rf=reflux



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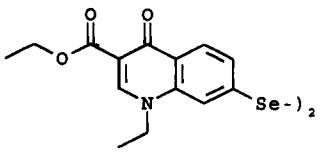

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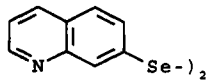

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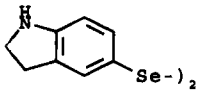

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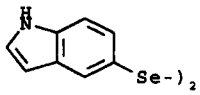

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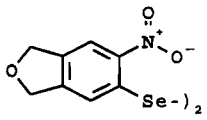

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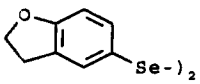

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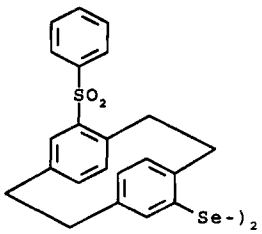
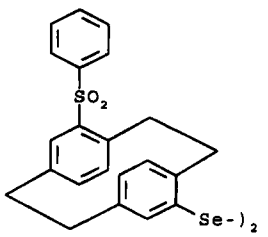
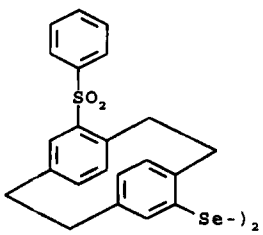


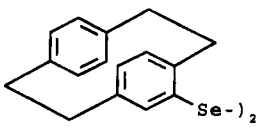
(+)(-) 247



(+) 248



(-) 249



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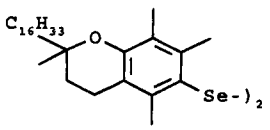

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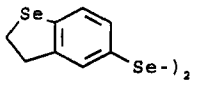
TABLE VI (*Continued*)



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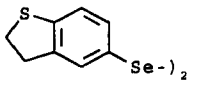

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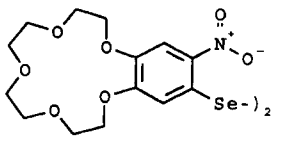

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SYNTHESIS OF SYMMETRICAL DIPHENYL DISELENIDES

This section will deal with the various synthetic approaches for the preparation of diphenyl diselenides.

The section is divided into six categories, where only chapters 1 and 5 actually describe the introduction of selenium into the molecule. Chapters 2, 3, 4 and 6 are all methods to make diselenides from other selenium containing compounds.

1. Introduction of Selenium onto the Aromatic Core

1.1 *With grignard reagents and elemental selenium (method 1).* The reaction of elemental selenium with aromatic grignard reagents, first discovered in 1903 by Taboury[6] and by Wuyts and Cosyns,[7] is a popular way to introduce selenium onto the aromatic core (Equation 1). So far several different compounds (entries 17, 18, 45, 58, 61, 66, 145, 149, 163, 167, 190, 193–197, 203, 205, 206, 216, 227, 229, 236, 246) have been made *via* this route.

$$\mathrm{RMgBr} \xrightarrow[2.\ O_2]{1.\ Se} \mathrm{RSe-)_2} \qquad (1)$$

In the case where it failed to form the grignard reagent from the arylbromide an alternate route was introduced by Wilson *et al.*[5] Here, the grignard reagent is formed by adding magnesium bromide to an ethereal solution of the corresponding aryl lithium (entry 154).

1.2 *With aryl lithium and elemental selenium (method 2).* When the grignard reaction fails a method that has been reported to work, is the reaction of an aryl lithium with elemental selenium, followed by oxidation (Equation 2).[8]

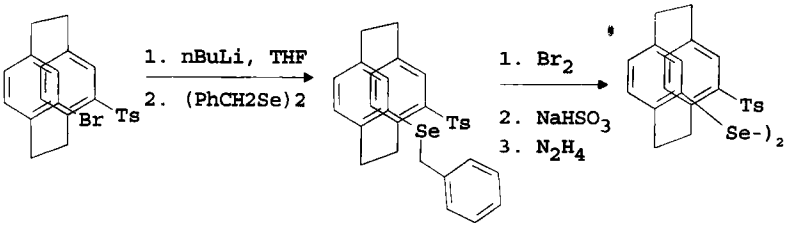
$$\mathrm{RLi} \xrightarrow[2.\ O_2]{1.\ Se} \mathrm{RSe-)2} \qquad (2)$$

The hydrogen/metal or the halogen/metal exchange has been carried out with different solvent/base systems like THF/nBuLi (entries 43, 44, 48, 92, 249, 250), Ether-Hexanes/nBuLi (entries 146, 155, 163, 211, 219), THF-TMEDA/sBuLi (entries 46, 47, 77), THF-TMEDA-LiCl/nBuLi (entry 42).

The exposure of the intermediate lithium selenide or the bromomagnesium selenide (method 1) to atmospheric oxygen[9] is usually sufficient for oxidation but also other oxidizing reagents are known, such as hydrogen peroxide,[1] ferric chloride,[10] chloramine[11] and ferric cyanide.[12]

The formation of the diselenide is often accompanied by the corresponding selenide and triselenide and even the detection of tetraselenides have been reported.[13]

1.3 *With aryl lithium and diselenides (method 3).* In one case it has been reported that the generally reliable *method 2* did not work well; instead dibenzyl diselenide was used as a more reactive selenium source (Equation 3).



(3)

After cleavage of the benzyl selenide with bromine, the resulting selenenyl bromide was reduced and chromatographed to the diselenide.[14]

Only stereoisomers of the above drawn compound have been reported to be made by this method (entries 247, 248).

1.4 *With selenocyanate (method 4).* One of the most important means by which selenium may be introduced onto the aromatic core is by diazotizing anilinic compounds followed by reaction with selenocyanide anion (Equation 4a).

$$RN_2^+Cl^- \xrightarrow{SeCN^-,\ H_2O} RSeCN \xrightarrow{\text{Decyanation}} RSe-)_2 \qquad (4a)$$

The diazotation and the concomitant selenocyanation are usually carried out in ice water.[15] The decyanation on the other hand has been done in a variety of ways. The most common way is by alkaline hydrolysis of the selenocyanate[16] (entries 13, 14, 15, 16, 23, 35, 55, 64, 66, 156, 157, 158, 162, 163, 164, 165, 169, 207, 209, 210, 220, 223, 239, 253). Other ways include ammonia[17] (entries 25, 67), acidic hydrolysis with $HCl\text{-}H_3PO_3$[18] (entry 242) or $HCl\text{-}H_2O\text{-}EtOH$[19] (entries 225, 226), reduction with (Na/EtOH/DMF)[20] (entry 22), $LiAlH_4$[21] (entries 135, 136, 137), $NaBH_4$[22] (entry 30), Zn/H_2SO_4[33] (entry 166), Zn/HCl[24] (entries 51, 251) or $N_2H_4/H_2O/EtOH$[25] (entries 33, 34). No certain mechanism for the hydrolysis of the selenocyanate has been established but several suggestions have been made. One implicates selenols as the initial product of the hydrolysis followed by air oxidation.[26] Another proposed mechanism views the reaction as proceeding *via* a selenenic acid intermediate.[16] Agenäs reported finding cyanide but no cyanate ion in the alkaline hydrolysis of aryl selenocyanates which mostly points to the mechanism outlined in Equation 4b.[1]

$$OH^- + RSeCN \longrightarrow RSe^- + HOCN$$
$$RSe^- + RSeCN \longrightarrow (RSe-)_2 + CN^- \qquad (4b)$$

There has been reported one case where the diazonium ion as leaving group has been substituted by halogen; namely where the aromatic cation is activated by electron-withdrawing substituents (entry 28).[27] Copper(I) iodide catalyses the reaction of non-activated aryl iodide with potassium selenocyanate and the reaction was used in the preparation of polyalkylated aromatic selenocyanates.[28]

1.5 *With selenium dianion (method 5).* Displacement of halogen or diazonium chloride from an aryl halide or diazonium chloride by an alkali diselenide constitutes a direct method for the synthesis of diselenides (Equation 5).

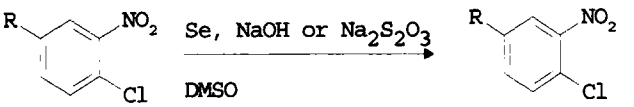
$$2RX + Se_2^{2-} \longrightarrow (RSe-)_2 + 2X^- \quad (5)$$

The diselenium dianion (Se_2^{2-}) can be prepared by either dissolving elemental selenium in an aqueous solution of the alkali-metal selenide[1] or by reduction of elemental selenium. The reduction may be carried out with sodium or lithium in liquid ammonia,[29,30] by Rongalite C (sodium formaldehyde sulfoxylate) in aqueous hydroxide,[31] by magnesium in methanol,[32] electrochemically,[33] or the most convenient manner by reduction with sodium borohydride[34] or lithium triethylborohydride.[35] While the reduction of elemental selenium with sodium borohydride requires ethanol or water as the solvent the lithium triethylborohydride reduction has the advantage of being carried out in THF. Although the latter method seems very convenient and efficient no aryl diselenides have ever been reported prepared by this method. Recently an improved synthesis of lithium diselenide was reported. The reduction of selenium with lithium in THF in the presence of diphenylacetylene as a catalyst afforded lithium diselenide which reacted with aryl halide to give aryl diselenides in good yield.[36]

Four different solvent systems have been reported: THF (entries 19, 20, 35, 38, 40, 41, 208), HMPT (entries 75, 76, 78, 129, 220, 222), THF/HMPT (entries 38, 188) and H_2O (entries 168, 220).

Occasionally no particular solvent system has been reported (entries 72, 73, 74, 140, 141, 142, 143, 144, 149, 151, 152, 153, 211, 218, 231, 253, 254).

1.6 *With elemental selenium and activated aryl halide (method 6).* The use of elemental selenium in the presence of sodium hydroxide in DMSO at room temperature has been reported to be an efficient nucleophile for substitution of unsubstituted *o*-chloronitrobenzene (entry 38) (Equation 6).



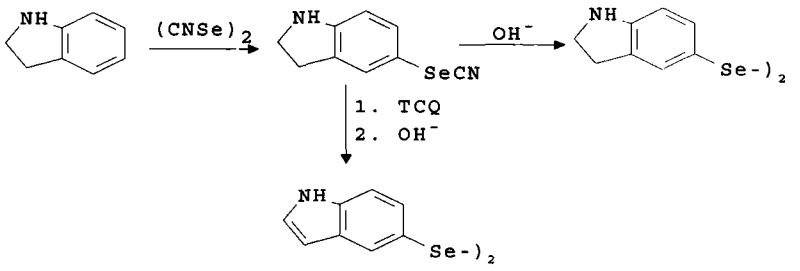
(6)

For substituted *o*-chloronitrobenzenes the yields were even lower or the reaction led to a complex mixture. The use of sodium thiosulphate, instead of sodium hydroxide, in the same solvent represented an improvement of the synthesis when the substituents were Me (entry 20) or OMe (entry 68).

When the substituents were CF_3 (entry 40) or NO_2 (entry 41) (and partly Br (entry 19)) the product was the corresponding disulphide.[37]

In a similar way was diselenobis benzoic acid prepared (entry 208, 209, 220).[38]

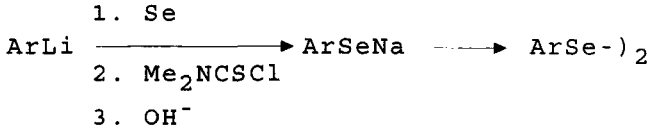
1.7 *With selenocyanogen (method 7).* By reacting bromine with potassium selenocyanate in methanol at low temperature selenocyanogen is formed. The rection of selenocyanogen and indoline results in cyanoselenation at the 5 position (Equation 7) in fairly good yield.



(7)

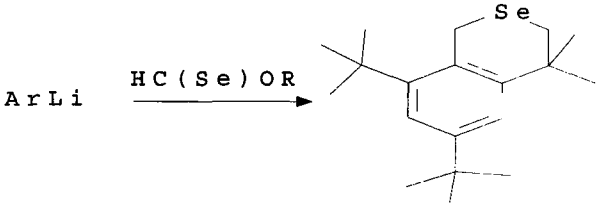
By alkaline hydrolysis the corresponding diselenide was quantitatively formed (entry 244). The 5,5'-diindolyl diselenide (entry 243) was formed by oxidation of the selenocyanatoindoline with tetrachlorobenzoquinone followed by hydrolysis.[39]

1.8 *Via selenothiocarbamate (method 8).* When diselenides are formed by either arylmagnesiumbromide (method 1) or aryllithium (method 2) and elemental selenium one of the major problems was the contamination with monoselenides and triselenides. To overcome that problem Jen and Cava[40] converted the arylselenolithium to a selenothiocarbamate, which was then hydrolysed and oxidized to the diselenide (entries 57, 195, 196, 229) in very high yield (Equation 8).



(8)

1.9 *Via selenoformate (method 9).* When 2,4,6-tributylphenyllithium was allowed to react with butylselenoformate the corresponding diselenide (entry 219) was formed in very low yield (Equation 9).

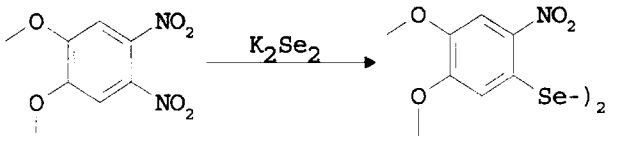


(9)

Ar = 2,4,6-tributylphenyl

Reaction conditions have been greatly varied, but no higher than 18% of the diselenide was ever obtained.[41]

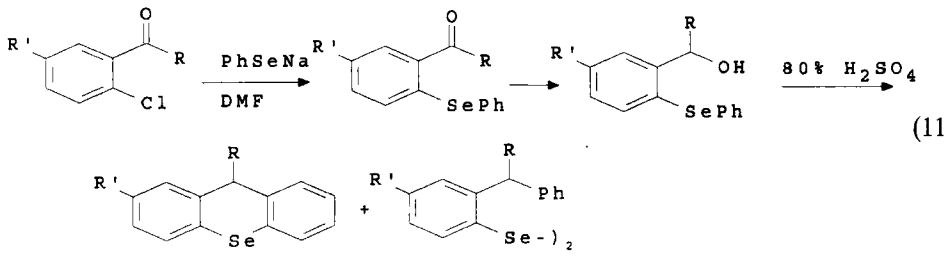
1.10 *By substitution of nitrogroup (method 10).* Without further documentation the reactions of 4,5-dinitroveratrole and 4,5-dinitro-1,3-benzodioxole with potassium diselenide have been claimed to form the 4,5-dimethoxy-2-nitrophenyl diselenide (entry 245) and the 2-nitro-4,5-benzodioxole diselenide (entry 63), respectively in good yield (Equation 10).[42]



(10)

A possible mechanism may be an electron-transfer substitution reaction similar to the conversion of nitro compounds to thiols by sodium disulphide.[43]

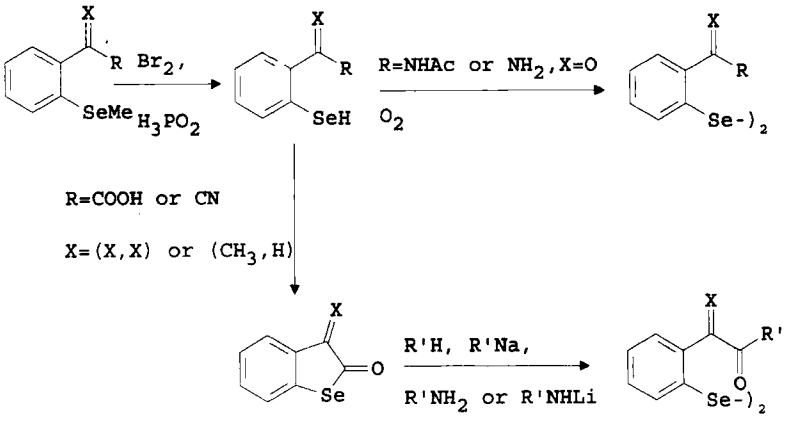
1.11 *Rearrangement of selenide (method 11).* In the reaction of 9-phenylselenoxanthene starting from 2-chlorobenzaldehyde or 2,5-dichlorobenzophenone *via* the phenylseleno intermediate, an interesting side product was formed. When the aldehyde or the benzophenone was converted into the alcohol and attempted cyclized with sulphuric acid, a diselenide (entries 185, 186, 187) was obtained as minor side product (Equation 11).[44]



(11)

2. *Diselenides via Se-Demethylation*

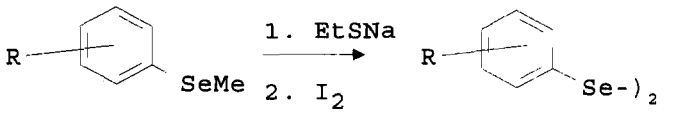
2.1 *By bromination and reduction (method 12).* Bromination of 2-methylselenophenylacetic acid (X = H, H; R = COOH) followed by reduction of the resulting selenenyl bromide with phosphinic acid yields the corresponding selenol. The phosphinic acid also prevents oxidation of the resulting selenol and facilitates its cyclohydration forming the selenolactone. The selenolactone can also be obtained similarly from 2-methylselenobenzylnitril. Under the action of bases (NaOH, NH_3, $PhNH_2$, EtONa, RNH_2, PhNHLi) the selenolactone easily undergoes ringopening through conventional nuclephilic substitution leading to the diselenide[45,46] (entries 131, 132, 133, 134, 200, 201, 202, 215) (Equation 12).



(12)

When the starting compound is 2-methylselenobenzamide no rearrangement occurs but the selenol has been oxidized directly to the diselenide by this approach (entry 129).[47]

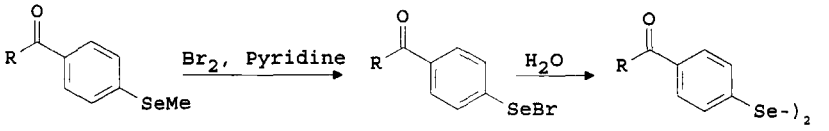
2.2 *With sodium ethanethiolate and iodine (method 13).* The Se-demethylation has been performed on several methylaryl selenides with sodium ethanethiolate and oxidised in situ by iodine to the aryl diselenide (entries 52–55, 58, 61, 66, 188, 216) (Equation 13).[48]



(13)

This method has proven to be efficient for treatment of inactivated arylchlorides with NaSeMe to give aromatic methyl selenides which can then be cleaved to the diselenide by this method (entry 229).

2.3 *By bromination and hydrolysis (method 14).* As in method 12 where the selenobromide was reduced with phosphinic acid, there has been reported two compounds made by hydrolysis of the selenobromide intermediate. The reaction of 4-methylselenophenylalkylketones and bromine in the presence of pyridine forms the selenobromide intermediate which has been hydrolysed to the diselenides (entries 217, 218) in good yield (Equation 14).



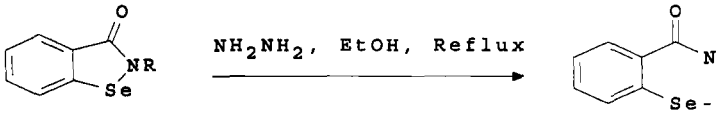
(14)

The overall reaction equation for the hydrolysis of the selenobromide requires three equimolar selenobromide to form one molar diselenide and one molar seleninic acid.[49]

3. *Diselenides by Ringopening*

Many examples of diselenide formation from selenocontaining ringsystems by ringopening are described in the literature. Most of them are formed by ringopening of N-substituted benzoisoselenazolones, but also ringopening of substituted benzoselenazolinone is known.

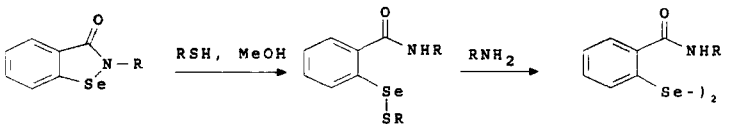
3.1 *Ringopening of benzoisoselenazolone by hydrazine (method 15).* N-Substituted bis(2-carbamoyl)phenyl diselenides (entries 70, 71, 81, 84, 92, 129, 150) were obtained in high yields by the reductive ring cleavage of 1,2-benzisoselenazol-3(2H)-ones with hydrazine (Equation 15).[50]



(15)

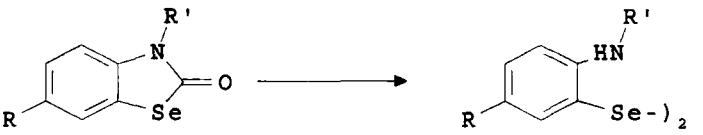
The benzoisoselenazolones were prepared by the reaction of 2-(chloroseleno)benzoyl chloride with various amines.[51]

3.2 *Ringopening of benzoisoselenazolone by thiols (method 16).* In a similar way as method 15 were several diselenides obtained by nucleophilic ringopening of 1,2-benzoisoselenazol-3(2H)-ones by dithioerythrit (entry 79) or ethylmercaptan (entries 48–50, 80–115, 222) followed by sulphur-selenium cleavage with aqueous methylamine (Equation 16).[52,53]



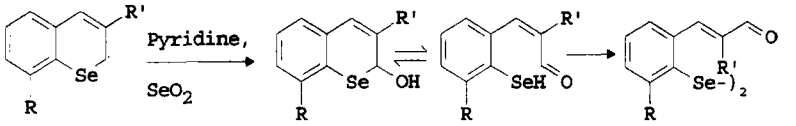
(16)

3.3 *Ringopenings of benzoselenazolinone with base (method 17).* A total number of nine benzosubstituted anilino diselenides have been made *via* the ringopening of substituted benzoselenazolinones (Equation 17) with either dimethylamine and formaldehyde in ethanol (entries 8, 12) or aqueous solution of sodium bicarbonate (4–7, 9–11).[54]



(17)

3.4 *By oxidation of selenochromene (method 18).* When selenochromene was oxidized with selenium oxide a hydroxyl group was introduced at the 2- or the 4-position. Depending on the solvent, the equilibrium may favour either the alcohol or the aldehyde (Equation 18).

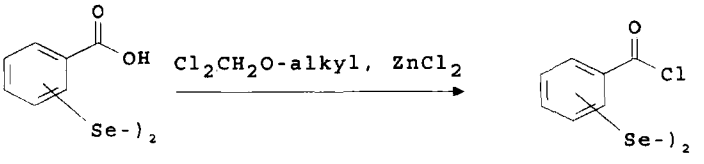


(18)

When the reaction is run in pyridine the major product is the cinnamaldehyde diselenide (entries 212–214).[55]

4. *Diselenides from Diselenides*

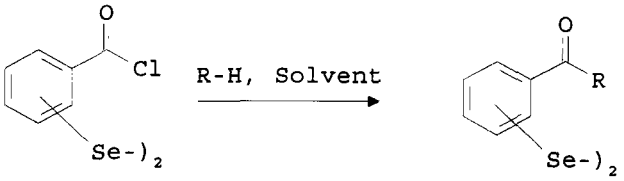
4.1 *Acid chloride from acid (method 19).* A facile approach to obtain diselenide of benzoesters or benzamides is by nucleophilic substitution at the corresponding acid chloride with alcohols or amines, respectively. The starting diselenobis benzoyl chloride has been made by zinc chloride and dichloromethyl alkylether (Equation 19).



(19)

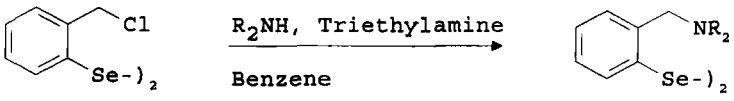
Only the synthesis of 2-diselenobis benzoyl chloride (entry 172) has been reported[56] but 3- and 4-diselenobis benzoyl chloride (entries 170, 171) have been claimed without documentation.[57,58]

4.2 *Esters or amides from acid chloride (method 20).* A number of benzoyl esters[57] and amides[58] have been synthesized by the reaction of diselenobis benzoyl chloride with the respective alcohol or amine in various solvents. The solvent systems have been pyridine (entries 116–119, 121, 124–127), diisopropylether (entries 120, 122–123, 128), *n*-Butanol-pyridine (entries 173–178), *t*-Butanol-pyridine (entries 179–180), and isopropanol (entries 181–182) (Equation 20).



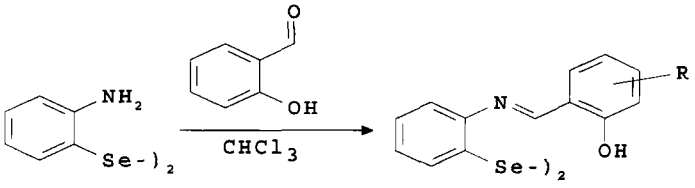
(20)

4.3 *Amine from chloride (method 21).* Even though the reaction between diselenobis benzyl chloride and amine seems like a straight forward method to make benzyl amine diselenides only one synthesis by this method has been reported.[59] Namely the coupling reaction between 2,2′-diselenobis(benzyl chloride) and bis[2-(2-pyridyl)ethyl]amine in benzene in the presence of triethylamine (entry 130) (Equation 21).



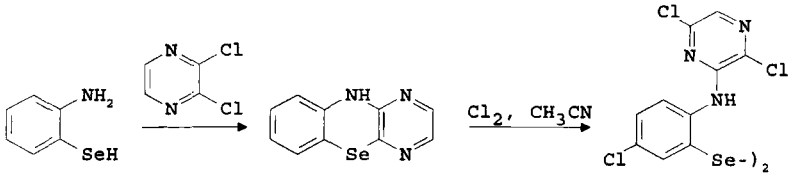
(21)

4.4 *Imine from amine (method 22).* Two examples (entries 1, 2) are given in the literature on formation of imino diselenides by dehydration of bis(2-aminophenyl)diselenide and substituted salicylaldehydes (Equation 22).[50]



(22)

4.5 *Arylation on bis(2-aminophenyl) diselenide (method 23).* When the Zn salt of 2-aminoselenophenol was reacting with 2,3-dichloropyrazine in ethanol 1,4-diazaphenoselenazine was obtained. Treatment of 1,4-diazaphenoselenazine with excess of chlorine in acetonitrile gave bis(2-[N-(3,6-dichloropyrazine)-5-chloro-aniline) diselenide (entry 24) (Equation 23).[61]



(23)

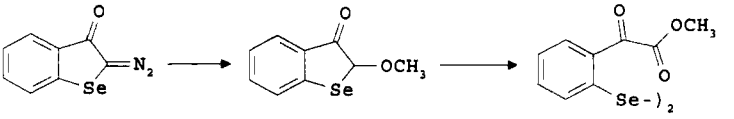
5. *Diselenides by Photo/Electro Chemistry*

5.1 *By reductive transfer of Se (method 24).* An alternate clean route to the synthesis of aromatic diselenides is the electrochemical strategy outlined in Equation 24. The overall process corresponds to a reductive transfer of Se units from a readily available aliphatic or aromatic diselenide (Equation 24).[62]

$$RSeSeR + 2ArX + 4e^- \longrightarrow ArSeSeAr + 2R^- + 2X^- \quad (24)$$

Different electrodes and solvents have been used under various conditions: Pt/DMF/− (entry 160), $C/CH_3CN/Bu_4NSO_4H$ (entry 160), Hg/DMF/− (entry 159), Hg/DMF/PhOH (entry 159), Pt/DMF/Fluorene (entry 189), Pt/DMF/PhOH (entry 189), Se/DMF/$NaClO_4$ (entries 189, 38)[63] and $Se/CH_3CN/Bu_4NPF_6$, $Et_4NF \cdot 2H_2O$ (entries 240, 241).[64]

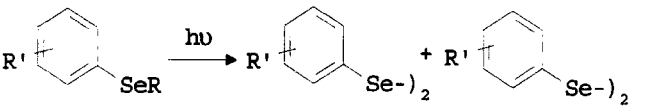
5.2 *Photolysis on selenium containing compounds (method 25).* When 2-diazobenzo[*b*]selenophen-3(2H)-one was exposed to photolysis in methanol the major product formed was 2-methoxybenzo[*b*]selenophen-3-(2H)-one which on air oxidation gave mainly the diselenide (entry 161) (Equation 25a).



(25a)

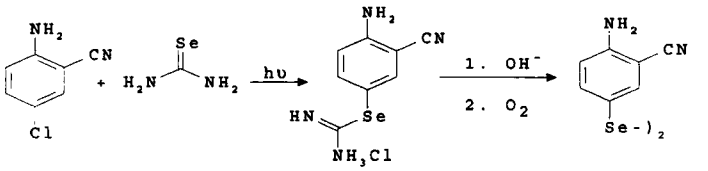
A possible mechanism for the formation of the diselenide is an oxidation of the selenophenone to the selenoxide followed by a seleno-Pummerer rearrangement to the selenol which is readily oxidized to the diselenide.[65]

The photorearrangement of benzyl phenyl selenide, phenyl ribosyl selenide and benzoyl phenyl selenide derivatives afford 2-benzyl phenyl diselenide (entry 191), 2-ribosyl phenyl diselenide (entry 224)[66] and 2-benzoyl phenyl diselenides (entries 198, 199),[67,68] respectively (Equation 25b).



(25b)

Also, it has been established that diaryl diselenides (entry 21, 30, 66) can be obtained by photochemical substitution of halogen by selenourea followed by thermal transformation of the Se-arylisoselenoureas in an alkaline medium into diaryl diselenides (Equation 25c).[69]

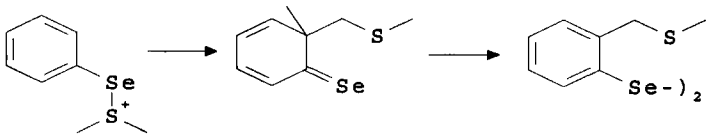


(25c)

6. *Miscellaneous*

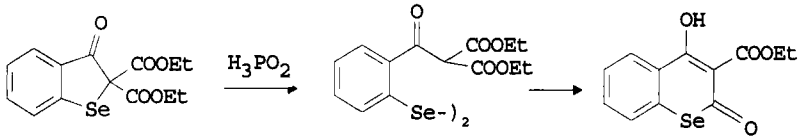
6.1 *Rearrangement of seleno-sulfonium (method 26).* Reaction between (phenylseleno)trimethylsilane and DMSO gave besides the expected dimethyl sulfide,

diphenyl diselenide and hexamethyldisiloxane a fourth product in 2% yield. The product was assigned as bis[2-[(methylthio)methyl]phenyl] diselenide (entry 192) and was presumably formed by rearrangement analogues to the classical Sommerlet-Hauser Rearrangement or the Gassman Azasulfonium Salt Rearrangement (Equation 26).[70]



(26)

6.2 *From substituted benzoselenophene and H_3PO_2 (method 27).* When Di(ethoxycarbonyl)-2,2-oxo-3-dihydro-2,3-benzo[1]selenophene was treated with an aqueous solution of hypophosphoric acid a diselenide was reported, assigned as bis(*o*-selenobenzoyl diethylmalonate) (entry 204), as an intermediate on the route to hydroxy-4-methyl-3-seleno-1-coumarine (Equation 27).[71]



(27)

REFERENCES

1. D. L. Klayman and W. H. H. Günther, "Organic Selenium Compounds: Their Chemistry and Biology," Wiley: New York, 1973.
2. H. J. Reich, in "Oxidation in Organic Chemistry," W. S. Trahanovsky, Ed., Academic Press: New York, 1978; Part C, Chapter 1.
3. H. J. Gysling, in "The Chemistry of Organic Selenium and Tellurium Compounds," S. Patai and Z. Rappoport, Eds., Wiley: New York, 1986; Vol. 1, p. 679.
4. B. Gautheron, G. Tainturier and C. Degrand, *J. Am. Chem. Soc.*, **107,** 5579 (1985 and references therein).
5. S. R. Wilson, P. A. Zucker, R.-R. C. Huang and A. Spector, *J. Am. Chem. Soc.*, **111,** 5936 (1989).
6. F. Taboury, *Bull. Soc. Chim. Fr.*, **29,** 761 (1903).
7. H. Wuyts and G. Cosyns, *Bull. Soc. Chim. Fr.*, **29,** 689 (1903).
8. E. S. Gould and J. D. McCullough, *J. Am. Chem. Soc.*, **73,** 1109 (1951).
9. L.-B. Agenäs, *Ark. Kemi*, **24,** 415 (1965).
10. G. Bergson and A. Biezais, *Ark. Kemi*, **18,** 143 (1961).
11. H. H. Sisler and N. K. Kotia, *J. Org. Chem.*, **36,** 1700 (1971).
12. L. Engman, *J. Org. Chem.*, **54,** 2964 (1989).
13. S. R. Wilson, M. Ankersen, A. Pasternak, R. R. Wang, N. J. Kleiman, A. L. Block and A. Spector, *Investigative Opthalmology and Visual Science*, **31,** (4 Abstr. Issue) (1990).
14. H. J. Reich and K. E. Yelm, *J. Org. Chem.*, **56,** 5672 (1991).
15. O. Behaghel and M. Rollmann, *J. Prakt. Chem.*, **123,** 336 (1929).
16. Houben-Weyl, "Methoden der Organischen Chemie," Band 9, 972 (1955).
17. J. M. Renga, *U.S. US 4242285 30 Dec 1980*, CA94(17):139188b.
18. E. Sekido and I. Fujiwara, *Talanta*, **19,** 647 (1972).
19. M. R. Bryce, C. D. Reynolds, P. Hanson and J. M. Vernon, *J. Chem. Soc. Perkin Trans.*, **1,** 607 (1981).
20. N. P. Luthra, R. B. Dunlap and J. D. Odom, *Anal. Biochem.*, **117,** 94 (1981).
21. M. Iwaoka and S. Tomoda, *Phos. Sulf. Relat.*, **67,** 125 (1992).
22. B. M. Pinto, J. Sandoval-Ramírez and R. D. Sharma, *Synth. Commun.*, **16,** 553 (1986).
23. D. Hellwinkel and S. Bohnet, *Chem. Ber.*, **120,** 1151 (1987).
24. A. S. Csallany and H. H. Draper, *Int. J. Vitam. Nutr. Res.*, **41,** 516 (1971).

25. S.-K. Yao, *Ger. Offen. DE 2054802 19 May 1971*, CA76(22):128839s.
26. F. Challenger, A. T. Peters and J. Halevy, *J. Chem. Soc.*, 1648 (1926).
27. K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40,** 947 (1975).
28. A. Toshimitsu and S. Uemura, in "The Chemistry of Organic Selenium and Tellurium Compounds," Vol. 2, Ed. S. Patai, 1987, John Wiley & Sons, Ltd.
29. L. Brandsma and H. E. Wijers, *Recl. Trav. Chim. Pays-Bas*, **82,** 68 (1963).
30. Y. N. Shlyk, G. M. Bogolyubov and A. A. Petrov, *Zh. Obshch. Khim.*, **38,** 1199 (1968).
31. L.-B. Agenäs, *Acta. Chem. Scand.*, **16,** 1809 (1962).
32. W. H. H. Günther, *J. Org. Chem.*, **32,** 3929 (1967).
33. C. Degrand and R. Prest, *J. Electroanal. Chem.*, **282,** 281 (1990).
34. D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **95,** 197 (1973).
35. J. A. Gladysz, J. L. Hornby and J. E. Garbe, *J. Org. Chem.*, **43,** 1204 (1978).
36. L. Syper and J. Mlochowski, *Tetrahedron*, **44,** 6119 (1988).
37. P. Battistoni, S. Bompadre, P. Bruni and G. Fava, *Gazz. Chim. Ital.*, **111,** 505 (1981).
38. Jpn. Kokai Tokkyo Koho JP 59128368 A2 24 Jul 1984 Showa.
39. L.-B. Agenäs, *Ark. Kemi*, **31,** 159 (1969).
40. K.-Y. Jen and M. P. Cava, *J. Org. Chem.*, **48,** 1449 (1983).
41. A. Ishii, R. Okazaki and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **59,** 2529 (1986).
42. P. J. Keogh, G. E. Ficken and C. J. Cough, *Brit GB 1411957 29 Oct 1975*, CA84(12):75713c.
43. N. Kornblum and J. Widmer, *J. Am. Chem. Soc.*, **100,** 7086 (1978).
44. K. Tomimatsu, T. Kataoka, H. Shimizu and M. Hori, *Phosphorus and Sulfur*, **16,** 97 (1983).
45. M. Evers, P. Weber, Ph. Thibaut, L. Christiaens, M. Renson, A. Croisy and P. Jacquignon, *J. Chem. Soc., Perkin Trans.*, **1,** 2452 (1976).
46. P. V. Jacquemin, L. Christiaens and M. J. Renson, *Tetrahedron Lett.*, **33,** 3863 (1992).
47. M. Mbuyi, L. Christiaens and M. Renson, *Bull. Soc. Chim Belg.*, **98,** 395 (1989).
48. M. Evers and L. Christiaens, *Tetrahedron Lett.*, **24,** 377 (1983).
49. E. Hannig and H. Ziebandt, *Pharmazie*, **23,** 552 (1968).
50. F. Dallacker and A. Peisker, *Chem.-Zeitung*, **115,** 169 (1991).
51. J. Mlochowski, K. Kloc, L. Syper and A. D. Inglot, *Phosphorus, Sulfur, and Silicon*, **59,** 267 (1991).
52. A. Welter, H. Fischer, L. Christiaens, A. Wendel and E. Etschenberg, *Ger. Offen DE 3513070 A1 30 Oct. 1986*, CA106(11):84181c.
53. A. Welter, A. Römer, D. Leyck and J. M. Parnham, *Ger. Offen DE 3626554 A1 18 Feb 1988*, CA109(7):265s.
54. M.-P. Vaccher, D. Lesieur, P. Renard, D.-H. Caignard, J.-F. Renaud de la Faverie and G. Adam, *Eur. Pat. Appl. EP 487423 A1 27 May 1992*, CA117(9):90302m.
55. A. Ruwet, J. Meessen and M. Renson, *Bull. Soc. Chim. Belges*, **78,** 459 (1969).
56. H. Fischer and N. Dereu, *Bull. Soc. Chim. Belg.*, **96,** 757 (1987).
57. N. Dereu, M. Renson, S. Leyck and E. Etschenberg, *Ger. Offen. DE 3513072 A1 23 Oct. 1986*, CA106(3):18122h.
58. H. Fischer, N. Dereu, P. Kuhl, E. Graf and A. Wendel, *Ger. Offen. DE 3513071 A1 23 Oct. 1986*, CA106(5):32613a.
59. M. Iwaoka and S. Tomoda, *J. Chem. Soc., Chem. Commun.*, **17,** 1165–7 (1992).
60. E. Labisla, J. Romero, M. L. Duran, J. A. Garcia-Vazquez, A. Sousa, U. Russo, R. Pritchard and M. Renson, *J. Chem. Soc. Dalton Trans.*, **5,** 755 (1993).
61. G. W. H. Cheeseman and G. Rishman, *Tetrahedron*, **36,** 2681 (1980).
62. C. Degrand, C. Gautier and M. Kharroubi, *Tetrahedron*, **44,** 6071 (1988).
63. P. Jeroschewski, W. Ruth, B. Struhbing and H. Berge, *J. Prakt. Chem.*, **324,** 787 (1982).
64. C. Thobier-Gautier, C. Degrand, M. Nour and P.-L. Compagnon, *J. Electroanal. Chem.*, **344,** 383 (1993).
65. S. Yamazaki, K. Kohgami, M. Okazaki, S. Yamabe and T. Arai, *J. Org. Chem.*, **54,** 240 (1989).
66. J. L. Fourrey, G. Henry and P. Jouin, *Tetrahedron Lett.*, **21,** 455 (1980).
67. J. Martens, K. Praefcke and H. Simon, *Chem.-Zeitung*, **102,** 108 (1978).
68. J. Martens, K. Praefcke, H. Simon and A. Schönberg, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **31B,** 1717 (1976).
69. E. M. Klokova, A. N. Frolov and A. V. El'tsov, *J. Org. Chem. USSR*, **17,** 2171 (1981).
70. M. R. Detty, *J. Org. Chem.*, **44,** 4528 (1979).
71. R. Weber, L. Christiaens, Ph. Thibaut, M. Renson, A. Croisy and P. Jacquignon, *Tetrahedron*, **30,** 3865 (1974).
72. Inconsistency between name and structure in CAS.
73. Magelli and Passerini, *Boll. Sedute Accad. Gioenia Sci. Catania*, **4,** 185 (1956).
74. A. Cermani and R. Passerini, *Boll. sci. fac. chim. ind. Bologna*, **14,** 107 (1956).
75. M. Giua and R. Bianco, *Gazz. Chim. Ital.*, **89,** 693 (1959).

76. G. Walschulzik, H. Schuldes and H. Oelschlager, *Ger. Offen. DE 3125296 A1 13 Jan 1983*, CA98(25):215600e.
77. A. N. Frolov, E. V. Smirnov, O. V. Kul'bitskaya and A. V. Eltsov, *Zh. Org. Khim.*, **16,** 2302 (1980).
78. F. L. Pyman, *J. Chem. Soc.*, **115,** 166 (1919).
79. J. Prachar and V. Dalecky, *Czech CS 217354 B 1 Sep 1984*, CA193(11):87883g.
80. K. B. Sharpless and M. W. Young, *J. Org. Chem.*, **40,** 947 (1975).
81. J. T. Groves, S. M. Lindenauer, B. J. Haywood, J. A. Knol and J. S. Schultz, *J. Med. Chem.*, **17,** 902 (1974).
82. L.-B. Agenäs, *Ark. Kemi*, **30,** 417 (1969).
83. A. H. Herz and E. R. Westcott, *Fr. Demande FR 2135176 19 Jan 1973*, CA79(4):25677v.
84. H. Bauer, *Ber.*, **46,** 92 (1913).
85. M. A. Lardon, *Ann. N.Y. Acad. Sci.*, **192,** 132 (1972).
86. A. H. De Cat and L. H. Manssens, *Belg. BE 758241 30 Apr 1971*, CA76(17):99646u.
87. C. Degrand, R. Prest and M. Nour, *Phosphorus Sulfur, Volume Date 1987*, **38,** 201 (1988).
88. A. E. Rosenoff, *U.S. US 3354170 21 Nov 1967*, CA68(23):105207e.
89. M. Wada, K. Kajihara, T. Morikawa and T. Erabi, *Chem. Express*, **6,** 875 (1991) CA116(7):59528v.
90. C. Lambert, M. Hilbert, L. Christiaens and N. Dereu, *Synth. Commun.*, **21,** 85 (1991).
91. Y. Ye, D. H. R. Barton, X. Lusinchi and P. Milliet, *Chin. J. Chem.*, 274 (1990).
92. M. Watanabe, M. Date, M. Tzukazaki and S. Furukawa, *Chem. Pharm. Bull.*, **37,** 36 (1989).
93. E. Mueller, H. B. Stegmann and K. Scheffler, *Justus Liebigs Ann. Chem.*, **657,** 5 (1962).
94. K. H. Pfoertner, *J. Chem. Soc., Perkin Trans.*, **2,** 523 (1991).
95. D. E. Ames, A. G. Singh and W. F. Smyth, *Tetrahedron*, **39,** 831 (1983).
96. I. Kuwajima, M. Shimizu and H. Urabe, *J. Org. Chem.*, **47,** 837 (1982).
97. W. Nankanishi and I. Yoshitsugu, *Bull. Chem. Soc. Jpn.*, **56,** 1661 (1983).
98. B. Kh. Stretlets, M. M. Gel'mont, Yu. I. Akulin and L. S. Efros, *Khim. Geterotsikl. Soedin.*, 1205 (1979).
99. S. A. Mbogo, T. S. Lobana, W. R. McWhinnie, M. R. Graves and T. A. Hamor, *J. Organomet. Chem.*, **395,** 167 (1990).
100. J. Prachar and V. Dalecky, *Czech. CS 217354 B 1 Sep 1984*, CA103(11):87883g.
101. T. Weiss, W. Nitsche, F. Boehnke and G. Klar, *Justus Liebigs Ann. Chem.*, 1418 (1973).
102. G. G. Furin, T. V. Terent'eva and G. G. Yakobson, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 78 (1972).
103. A. McKillop, D. Koyunchu, A. Krief, W. Dumont, P. Renier and M. Trabelsi, *Tetrahedron Lett.*, **31,** 5007 (1990).
104. S. I. Kagn and C. P. Colin, *J. Med. Chem.*, **30,** 597 (1987).
105. W. Clauss and H. G. Todt, *Ger. Offen. DE 2053860 8 Jun 1972*, CA77(10):69450d.
106. The compound was listed as commercially available from Aldrich Chemical Co. in 1967, but is not available anymore.
107. J. Mlochowski, K. Kloc, L. Syper and A. D. Inglot, *Phosphorus, Sulfur Silicon Relat. Elem.*, **59,** 561 (1991).
108. A. Wendel, G. Tiegs, C. Werner and N. Dereu, *Phosphorus and Sulfur*, **38,** 59 (1988).
109. L. Engman and A. Hallberg, *J. Org. Chem.*, **54,** 2964 (1989).
110. A. Martens-Von Salzen, H. U. Meyer and W. W. Du Mont, *Sulfur Silicon Relat. Elem.*, **67,** 67 (1992).
111. N. Bertel, H. W. Roesky, F. T. Edelmann, M. Noltemeyer and H. G. Schmidt, *Z. Anorg. Allg. Chem.*, **586,** 7 (1990).
112. A. Krief, G. Evrard, E. Badaoui, V. De Beys and R. Dieden, *Tetrahedron Lett.*, **30,** 5635 (1989).
113. Campbell and McCullough, *J. Am. Chem. Soc.*, **67,** 1965 (1945).
114. Behagel and Hofmann, *Chem. Ber.*, **72,** 582 (1939).
115. Gould and McCullough, *J. Am. Chem. Soc.*, **73,** 1109 (1951).
116. Cerniani and Passerini, *Boll. Sci. Fac. Chim. Ind. Bologna*, **14,** 107 (1956).
117. Keimatsu, Yokota and Suzuki, *Yakugaku Zasshi*, **52,** 961 (1932).
118. Rheinboldt and Giesbrech, *Chem. Ber.*, **89,** 631 (1956).
119. D. Hellwinkel and S. Bohnet, *Chem. Ber.*, **120,** 1151 (1987).
120. Kataewa and Kataev, *J. gen. Chem. USSR*, **32,** 2667 (1962).
121. R. Cantineau, G. Tihange, A. Plenevaux, L. Christiaens, M. Guillaume, A. Welter and N. Dereu, *J. Labelled Compd. Radiopharm.*, **23,** 59 (1986).
122. S. I. Kagn and C. P. Colin, *J. Med. Chem.*, **30,** 597 (1987).
123. C. Degrand, *J. Org. Chem.*, **52,** 1421 (1987).
124. B. Gautheron, G. Tainturier and C. Degrand, *J. Am. Chem. Soc.*, **107,** 5579 (1985).
125. W. M. Maxwell and K. J. Wynne, *Inorg. Chem.*, **20,** 1707 (1981).
126. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **44,** 4204 (1979).

127. M. Bochmann, K. J. Webb, M. B. Hursthouse and M. Mazid, *J. Chem. Soc., Dalton Trans*., 2317 (1991).
128. I. Kuwajima, M. Shimizu and H. Urabe, *J. Org. Chem.*, **47,** 837 (1982).
129. K. Hiroi and S. Sato, *Synthesis*, 635 (1985).
130. H. J. Reich, J. M. Renga and I. L. Ieva, *J. Am. Chem. Soc.*, **97,** 5434 (1975).
131. *Organic Synthesis*, Collect. **3,** 771 (1955).
132. *Jpn. Kokai Tokkyo Koho JP 59128368 A2 24 Jul 1984*, Showa CA101(21):191354e.
133. J. W. Baker, G. F. C. Barrett and W. T. Tweed, *J. Chem. Soc.*, 2331 (1952).
134. A. Fredga and C. Evertsdotter, *Acta. Chem. Scand.*, **13,** 1042 (1959).
135. Y. Okamoto, T. Yano and R. Homsany, *Ann. N.Y. Acad. Sci.*, **192,** 60 (1972).
136. L. Christiaens and M. Renson, *Bull. Soc. Chim Belg.*, **79,** 133 (1970).
137. G. C. Pappalardo, K. J. Irgolic and R. A. Grigsby, *J. Organomet. Chem.*, **133,** 311 (1977).
138. W. W. DuMont, S. Kubiniok, L. Lange, S. Pohl, W. Saak and I. Wagner, *Chem. Ber.*, **124,** 1315 (1991).
139. N. Kamigata, H. Iizuka, A. Izuoka and M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **59,** 2179 (1986).
140. F. Dallacker and A. Peisker, *Chem.-Ztg.*, **115,** 135 (1991).
141. Vafai and Renson, *Bull. Soc. Chim. Belg.*, **75,** 145 (1966).
142. Wagner and Nuhn, *Pharm. Zentralhalle*, **104,** 328 (1965).
143. B. M. Pinto, B. D. Johnson, J. Sandoval-Ramirez and R. D. Shama, *J. Org. Chem.*, **53,** 3766 (1988).
144. L. A. Sorokina, T. I. Chebotar and L. M. Kataeva, *Zh. Fiz. Khim.*, **50,** 775 (1976).
145. P. G. Jones and C. Thoene, *Z. Naturforsch., B: Chem. Sci.*, **47,** 600 (1992).
146. G. G. Furin, O. I. Andreevskaya and G. G. Yakobson, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 100 (1980).
147. A. V. Zibarev, S. N. Konchenko, G. G. Furin and M. A. Fedotov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2101 (1986).
148. V. Z. Latypova, A. A. Chichirov, V. V. Zhuikov, O. G. Yakovleva, R. Vinokurova, I. A. Ustyugova and Yu. M. Kargin, *Zh. Obshch. Khim.*, **59,** 1344 (1989). *No synthesis given.*
149. T. Kitao and M. Masaru, *Jpn. Kokai Tokkuo Koho JP 63079884 A2 9 Apr. 1988.*
150. E. Sekido and I. Fujiwara, *Talanta*, **19,** 647 (1972).
151. S. A. Sadek, G. P. Basmadjian, J. A. Rieger, P. M. Hsu and R. D. Ice, *Int. J. Appl. Radiat. Isot.*, **35,** 35 (1984).
152. M. Vafai and M. Renson, *bull. Soc. Chim. Belges*, **75,** 145 (1966).
155. H. Xu, D. Pan, T. Yu and W. Du, *Youji Huaxue*, **12,** 64 (1992).