Reaction of Hydrazine with Aryl and Heterocyclic Selenoamides and Alkylselenone Esters. Synthesis of 2,5-Diaryl and Diheterocyclic-1,3,4-Selenodiazoles and Dialkylselenone Ester-Hydrazones

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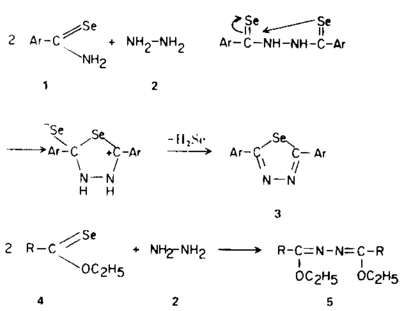
Hydrazine reacted with alkylselenone esters to give dialkylselenone ester-hydrazones. Reaction of selenoamides with the same reagent led to 2,5-disubstituted-1,3,4-selenodiazoles.

J. Heterocyclic Chem., **16**, 365 (1979).

In the preceding paper (1), we reported that the reaction of alkylselenone esters and aryl and heterocyclic selenoamides with an excess of hydrazine hydrate at room temperature gave 3,6-disubstituted-1,2,4,5-tetrazines and 1,2-dihydro-1,2,4,5-tetrazines.

In extending this study, we investigated the addition of 2 moles of selenoamides (**1**) to 1 mole of hydrazine hydrate (**2**) in methanol at room temperature, which after a few days gave 2,5-diaryl-1,3,4-selenodiazoles (**3**). Under the same conditions, the alkylselenone esters (**4**) upon reaction with **2**, provided dialkylselenones ester-hydrazones (**5**) (Scheme 1).

Scheme 1



In agreement with the suggested structure, the mass spectrum of 1,3,4-selenodiazoles exhibited the molecular peaks as well as $Ar\text{-}C{\equiv}\overset{+}{N}$ and $Ar\text{-}C\overset{+Se}{=}N$ fragmentation peaks (Table 3). The structure assignment of the hydrazones was based on nmr and mass spectra (Table 4).

On searching the literature, we discovered that only the parent compound of 2,5-disubstituted-1,3,4-selenodiazoles, 1,3,4-selenodiazole has been prepared (2).

EXPERIMENTAL

The pmr spectra were taken on a Varian EM 360 spectrometer using TMS as internal standard; the chemical shift values were expressed in ppm (δ). The mass spectra were recorded with a Varian Mat instrument at 70 eV and at 25° (dialkylselenone ester-hydrazone), 80-135° (2,5-disubstituted-1,3,4-selenodiazoles) by direct insertion into the ion source. Melting points were determined on a Kofler Hot-Bench and Maquenne Block apparatus. Elemental analyses were performed by the Dornis and Kolbe, Hohenweg 17, West Germany. The method of preparation of the selenone esters is given in reference 3. Aromatic and heterocyclic selenoamides were obtained according to the literature (4).

The following experiments illustrate the general reaction procedures employed.

2,5-Diphenyl-1,3,4-selenodiazole.

To a solution of 3.68 g. (0.02 mole) of benzselenoamide in a minimum quantity of boiling methanol, was added at room temperature, a solution of 0.50 g. (0.01 mole) of hydrazine hydrate in 5 ml. of methanol. After 4 days at room temperature, the selenodiazole was collected by filtration. Recrystallization from ethanol afforded analytically pure **1** (Table 1), m.p. 158°.

Di-*O*-ethylselenoacetate-hydrazone.

To a solution of 3.02 g. (0.02 mole) of *O*-ethyl selenoacetate in 5 ml. of methanol was added at room temperature, a solution of 0.50 g. (0.01 mole) of hydrazine hydrate in 5 ml. methanol. After 4-5 days at room temperature, the elemental selenium was removed by filtration. Evaporation of the solvent left a liquid which on distilation gave **8** (Table 2), b.p. 63° (10 mm).

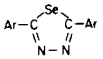
REFERENCES AND NOTES

(1) V. I. Cohen, *J. Heterocyclic Chem.* (1978) (in press).
(2) R. V. Kendall and R. A. Olofson, *J. Org. Chem.*, 35, 806 (1970).
(3) V. I. Cohen, *ibid.*, 42, 2645 (1977).
(4) V. I. Cohen, *Synthesis* (1978) (in press).

0022-152X/79/020365-04$02.25

Table 1

Physical Properties and Microanalytical Data of 2,5-Diaryl and Diheterocyclic 1,3,4-Selenodiazoles



Compound No.	Ar	M.p. °C	Crystallization solvent	Yield %	Formula		Analysis (%) C	H	N	Se
1	C_6H_5	158	Ethanol	17	$C_{14}H_{10}N_2Se$	Calcd.	58.97	3.50	9.82	27.69
						Found	59.00	3.53	9.88	27.68
2	4-BrC_6H_4	284	*n*-Butanol	24	$C_{14}H_8Br_2N_2Se$	Calcd.	37.92	1.80	6.32	17.83
						Found	38.06	1.90	6.33	17.90
3	4-ClC_6H_4	259	*n*-Butanol	18	$C_{14}H_8Cl_2N_2Se$	Calcd.	47.45	2.25	7.90	22.31
						Found	47.53	2.30	7.79	22.18
4	4-$CH_3C_6H_4$	187	*n*-Butanol	23	$C_{16}H_{14}N_2Se$	Calcd.	61.34	4.47	8.94	25.23
						Found	61.23	4.48	9.04	25.18
5	4-$CH_3OC_6H_4$	212	Ethanol	35	$C_{16}H_{14}N_2O_2Se$	Calcd.	55.67	4.05	8.11	22.87
						Found	55.58	4.06	8.06	22.90
6	3,5-$(CH_3O)_2C_6H_3$	179	*n*-Butanol	45	$C_{18}H_{18}N_2O_4Se$	Calcd.	53.33	4.44	6.91	19.50
						Found	53.43	4.52	7.01	19.54
7	2-Thienyl	181	*n*-Butanol	15	$C_{10}H_6N_2S_2Se$	Calcd.	40.40	2.02	9.42	26.59
						Found	40.46	2.11	9.50	26.40

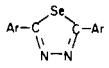
Table 2

Physical Properties and Microanalytical Data of Dialkylselenone Ester-Hydrazones $R\text{-}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}\text{=N-N=}\underset{\displaystyle OC_2H_5}{\underset{|}{C}}\text{-}R$

Compound No.	R	B.p. °C (mm)	Yield %	Formula		Analysis (%) C	H	N
8	CH_3	63 (10)	42	$C_8H_{16}N_2O_2$	Calcd.	55.83	9.29	16.27
					Found	55.84	9.30	16.33
9	$CH_3(CH_2)_2$	102 (12)	56	$C_{12}H_{24}N_2O_2$	Calcd.	63.17	10.52	12.27
					Found	62.94	10.45	12.39
10	$CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}$	97 (21)	62	$C_{12}H_{24}N_2O_2$	Calcd.	63.17	10.52	12.27
					Found	63.16	10.48	12.33
11	$CH_3(CH_2)_3$	121 (12)	67	$C_{14}H_{28}N_2O_2$	Calcd.	65.64	10.93	10.93
					Found	65.49	10.89	10.92
12	$CH_3(CH_2)_4$	134 (6)	72	$C_{16}H_{32}N_2O_2$	Calcd.	67.62	11.26	9.85
					Found	67.56	11.40	10.05

Table 3

Mass Spectra of 2,5-Diaryl and Diheterocyclic 1,3,4-Selenodiazoles



Compound No.	Ms m/e (%)	Molecular Formula
1	51 (25); 77 (100); 103 (59) $C_6H_5\text{-}C\equiv N$; 181 (130) $C_6H_5\text{-}C^{+Se}(=N)$; 183 (60); 284 (20); 286 (40)	$C_{14}H_{10}N_2Se$ (284-286)
2	50 (23); 51 (22); 75 (60); 76 (43); 102 (100); 155 (43); 157 (36); 180 (33); 181 (62) $p\text{-}BrC_6H_4\text{-}C\equiv N^+$; 182 (72); 183 (61); 259 (41) $p\text{-}BrC_6H_4\text{-}C^{+Se}(=N)$; 261 (90); 263 (68); 440 (24); 442 (56); 444 (68); 446 (35)	$C_{14}H_8Br_2N_2Se$ (440-442-444-446)
3	75 (36); 102 (27); 111 (38); 113 (12); 137 (100) $p\text{-}ClC_6H_4\text{-}C\equiv N^+$; 139 (33); 215 (36) $p\text{-}Clc_6H_4\text{-}C^{+Se}(=N)$; 217 (75); 219 (34); 352 (18); 354 (41); 356 (26)	$C_{14}H_8Cl_2N_2Se$ (352-354-356)
4	65 (25); 91 (100); 116 (40); 117 (50) $p\text{-}CH_3C_6H_4\text{-}C\equiv N^+$; 195 (30) $p\text{-}CH_3C_6H_4\text{-}C^{+Se}(=N)$; 197 (60); 312 (23); 314 (46)	$C_{16}H_{14}N_2Se$ (312-314)
5	90 (20); 103 (15); 133 (100) $p\text{-}CH_3OC_6H_4\text{-}C\equiv N^+$; 170 (12); 196 (26); 198 (52); 211 (31) $p\text{-}CH_3OC_6H_4\text{-}C^{+Se}(=N)$; 213 (62); 344 (40); 346 (80)	$C_{16}H_4N_2O_2Se$ (344-346)
6	65 (12); 77 (20); 90 (11); 103 (27); 108 (16); 120 (10); 122 (13); 133 (22); 134 (17); 163 (100) $3,5\text{-}(CH_3O)_2C_6H_3\text{-}C\equiv N^+$; 203 (8); 212 (10); 214 (18); 241 (17) $3,5\text{-}(CH_3O)_2C_6H_3\text{-}C^{+Se}(=N)$; 243 (33); 404 (33); 406 (65)	$C_{18}H_{18}N_2O_2Se$ (404-406)
7	39 (10); 43 (13); 45 (15); 58 (16); 69 (7); 82 (5); 95 (6); 109 (100)  175 (7); 187 (25)  189 (50); 296 (30); 298 (60)	$C_{10}H_6N_2S_2Se$ (296-298)

Table 4

Nmr and Mass Spectra of Dialkylselenone Ester-Hydrazone R-C(OC$_2$H$_5$)=N-N=C(OC$_2$H$_5$)-R

Compound No.	Nmr (in carbon tetrachloride) δ in Ppm	Ms m/e (%)	Molecular Formula
8	1.25 (6H, t); 1.95 (6H, s); 4.05 (4H, q)	27 (15); 29 (29); 42 (66); 43 (100); 45 (29); 59 (27); 60 (40); 74 (30); 116 (21); 127 (13); 144 (7); 172 (36)	$C_8H_{16}N_2O_2$ (172)
9	0.90 (6H, t); 1.25 (6H, t); 1.65 (4H, m); 2.42 (4H, t); 4.05 (4H, q)	27 (24); 29 (33); 41 (35); 43 (100); 59 (34); 70 (41); 71 (53); 88 (20); 102 (15); 144 (13); 183 (16); 185 (15); 228 (27)	$C_{12}H_{24}N_2O_2$ (228)
10	1.05 (12, d); 1.26 (6H, t); 3.38 (2H, m); 4.06 (4H, q)	43 (100); 56 (18); 70 (27); 71 (39); 84 (36); 88 (14); 116 (7); 129 (10); 157 (13); 182 (13); 185 (11); 228 (31)	$C_{12}H_{24}N_2O_2$ (228)
11	0.92 (6H, t); 1.24 (6H, t); 1.42 (8H, m); 2.47 (4H, t); 4.07 (4H, t)	29 (97); 41 (67); 43 (36); 57 (100); 59 (28); 84 (34); 85 (55); 116 (25); 144 (54); 172 (23); 181 (22); 256 (33)	$C_{14}H_{28}N_2O_2$ (256)
12	0.95 (6H, t); 1.27 (6H, t); 1.35 (12H, m); 2.40 (4H, t); 4.05 (4H, q)	29 (38); 41 (30); 43 (100); 55 (20); 71 (30); 99 (38); 127 (80); 144 (27); 172 (20); 195 (11); 213 (10); 228 (8); 240 (9); 256 (5); 284 (18)	$C_{16}H_{32}N_2O_2$ (284)