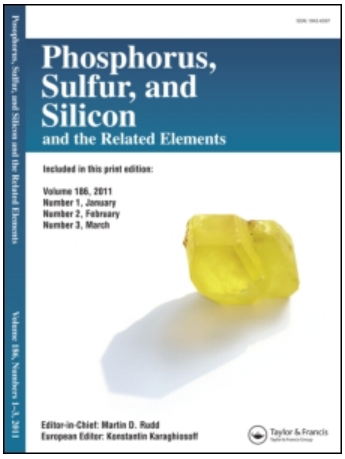

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A FACILE, ONE-POT SYNTHESIS OF NOVEL 2,2′-BI(4,5-DIHYDRO-1,3,4-SELENADIAZOLE) DERIVATIVES VIA DIHYDRAZONOYL DIHALIDES

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N,N′-Diaryloxalodihydrazonoyldichlorides **1** react with potassium selenocyanate (or selenourea), in ethanol, leading to the formation of the hitherto unreported 2,2′-bi(4-aryl-4,5-dihydro-5-imino-1,3,4-selenadiazoles **3** in good yields. Compounds **3** undergo nitrosation, acetylation and benzoylation to afford the N-nitroso, N-acetyl and N-benzoyl derivatives **6, 8** and **9**, respectively. Thermolysis of **6** afforded the corresponding 2,2′-biselenadiazol-5-ones **7** in high yields. The latter products were also obtained directly from acid hydrolysis of **3**. Compounds **8** and **9** were alternatively prepared, in one-step, from the reaction of **1** with N-acetyl-N′-phenylselenourea and benzoylselenourea, respectively.

Key words: Diaryloxalodihydrazonoyl dihalides, 2,2′-biselenadiazoles.

INTRODUCTION

Recently, we have undertaken a comprehensive study directed towards the exploration of the utility of N,N′-diarylglyoxaldihydrazonoyl dihalides **1** as highly versatile intermediates for the synthesis of a variety of heterocyclic systems *viz*: bi-1,2,4-triazoles,[1] bi-(2-pyrazolines),[2] bipyrazoles,[2] bi-1,3,4-thiadiazoles[3] and 1,4-benzothiazine derivatives.[3] As an extension of this study and in continuation of our previous work on the synthesis of selenium heterocycles,[4–6] we now report a facile, one-step synthesis of the title compounds *via* the reactions of **1** with potassium selenocyanates, selenourea and acylseneoureas.

DISCUSSION

The reaction of N,N′-diaryloxalodihydrazonoyl dichlorides **1a–d** with potassium selenocyanate, in ethanol at reflux, afforded products for which three possible isomeric structures **2, 3** or **4** can be written (Scheme I). A lack of absorption in the region 2100–2200 cm^{-1} (the selenocyanato absorption) in the infrared spectra

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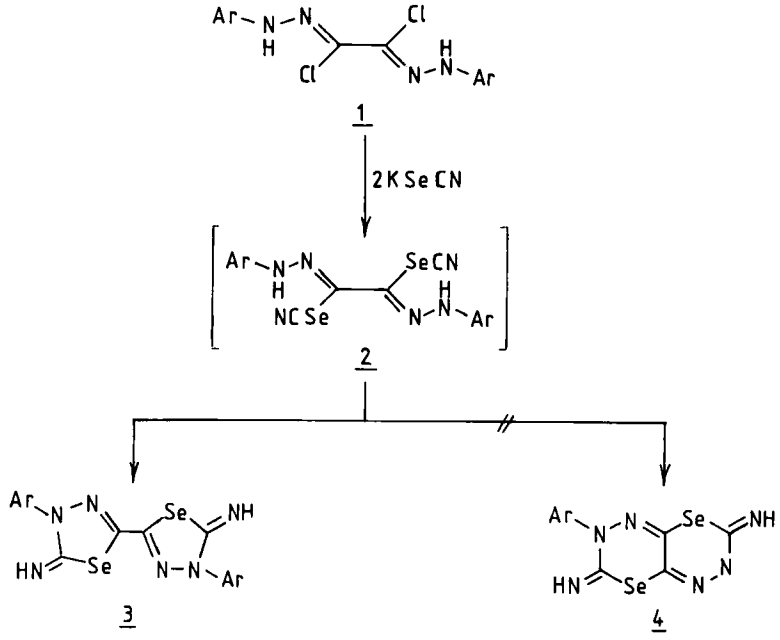
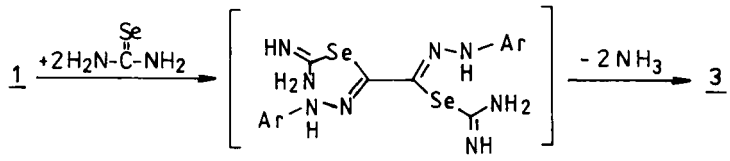


1-4	
a	C_6H_5
b	$4-CH_3C_6H_4$
c	$4-ClC_6H_4$
d	$2,4-Cl_2C_6H_3$

SCHEME I

of the isolated products excludes the acyclic structure **2**. The bi-selenadiazol-5-imine structure **3** was assigned to the products isolated while the other possible fused-ring structure **4** was ruled out based on their mass spectra. The latter spectra showed in addition to the molecular ion peak, a fragment ion of m/e ratio corresponding to $M/2^+$. For example, the mass spectrum of **3a**, showed a molecular ion peak at m/e 446 and a fragment ion of m/e 223 corresponding to 4-phenyl-4,5-dihydro-1,3,4-selenadiazol-2-yl cation ($M/2^+$). This mode of fragmentation has been employed for distinguishing pendant from alternative fused-ring systems.[3] Compounds **3** are assumed to be formed *via* a nucleophilic substitution of the selenocyanate anion to afford the non-isolable intermediates **2** which readily undergo intramolecular cyclization under the reaction conditions to afford the final isolable products **3** (Scheme I). All attempts to isolate the acyclic intermediate **2** were unsuccessful.

Alternatively, compounds **3** were obtained from the reaction of **1** with selenourea, in one-step, but in rather low yields. The formation of **3** in this reaction is assumed to proceed via the non-isolable intermediates **5** which undergo spontaneous cyclization with elimination of ammonia (Scheme II).



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SCHEME II

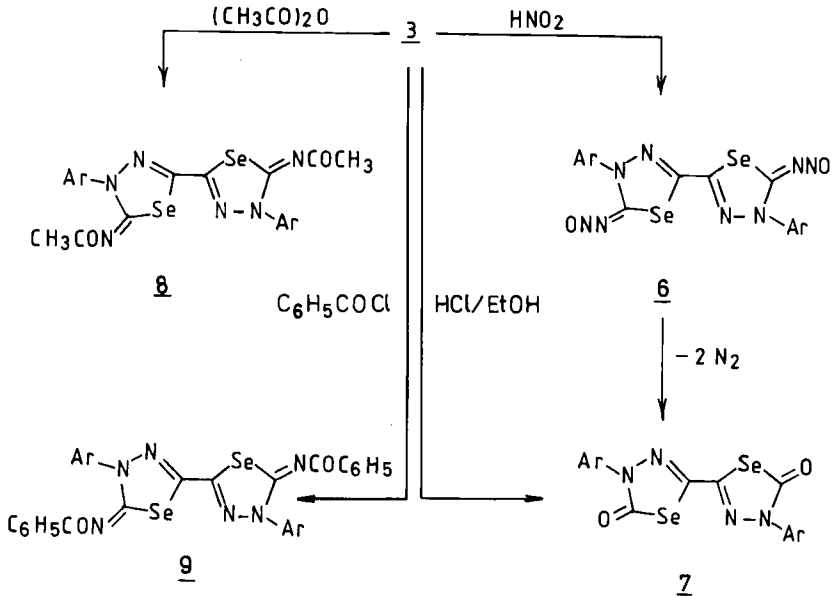
TABLE I

Infrared and ^{1}H nmr spectral data of compounds **3** and **7–9**

Comp. no.	IR (KBr), cm^{-1}	^{1}H nmr, δ(ppm)
3a	3315, 1610	9.24(s, 2H), 7.2-8.2(m, 10H)
3b	3320, 1618	9.3(s, 2H), 7.1-8.0(m, 8H), 2.21(s, 6H)
3c	3316, 1605	9.23(s, 2H), 7.2-8.1(m, 8H)
3d	3318, 1614	9.32(s, 2H), 7.1-7.9(m, 6H)
7a	1688, 1590	7.2-8.1(m)
7b	1680, 1595	7.1-8.0(m, 8H), 2.23(s, 6H)
7c	1686, 1598	7.0-8.1(m)
7d	1685, 1593	7.1-7.9(m)
8a	1630, 1592	7.2-8.0(m, 10H), 2.36(s, 6H)
8b	1635, 1590	7.1-8.1(m, 8H), 2.37(s, 6H), 2.20(s, 6H)
8c	1633, 1595	7.2-8.0(m, 8H), 2.36(s, 6H)
8d	1632, 1596	7.1-7.9(m, 6H), 3.38(s, 6H)
9a	1623, 1581	a
9b	1625, 1584	a
9c	1622, 1590	a
9d	1625, 1586	a

[a] insoluble in the usual nmr solvents.

The biselenadiazol-5-imines **3** were characterized by their elemental analyses and spectral data. The IR spectra of **3a–d** exhibited, in each case, an imino NH absorption band near 3320 cm^{-1}. Their ^{1}H nmr revealed the presence of =NH signal near δ 9.3 ppm (Table I). Structure **3** was further confirmed by their chemical reactions outlined in Scheme III.



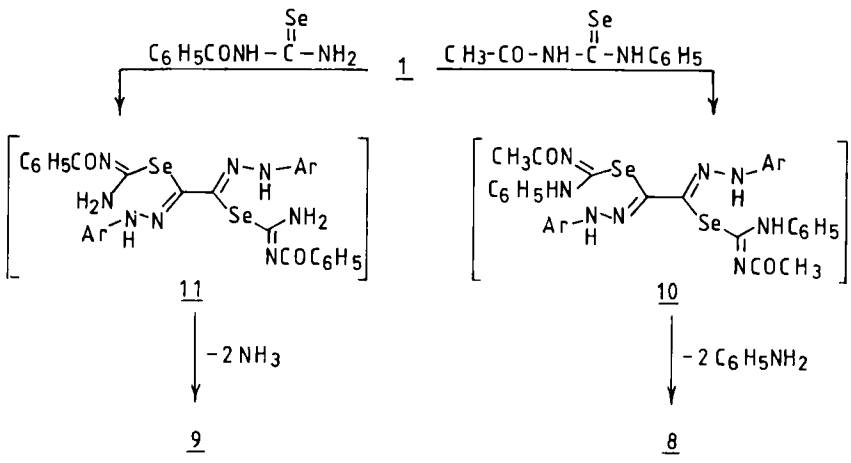
3,6-9	Ar
a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-ClC_6H_4
d	2,4-$Cl_2C_6H_3$

SCHEME III

Thus, treatment of **3** with sodium nitrite in acetic acid furnished the N-nitrosoimino derivatives **6** in high yields. Heating **6** in ethylene glycol afforded the corresponding bi-selenadiazol-5-one derivatives **7** *via* the elimination of nitrogen. The infrared spectra of the latter products showed, in each case, a characteristic ring carbonyl absorption band near 1690 cm^{-1} (Table I). Compounds **7** were also obtained, in one-step, by direct hydrolysis of **3** upon reflux with hydrochloric acid in ethanol (Scheme III).

Heating **3** with acetic anhydride or benzoyl chloride, in pyridine afforded the corresponding N-acetyl derivatives **8** and N-benzoyl derivatives **9**, respectively. The structures of the products **8** and **9** were consistent with their elemental analyses and spectral data. Their infrared spectra revealed carbonyl absorption bands near 1635 and 1625 cm^{-1} assignable to the N-acetyl and N-benzoyl groups, respectively.^{1}H nmr spectra of **8** revealed, in each case, a resonance signal near δ 2.37 ppm corresponding to CH_3CO protons (Table I).

On the other hand, compounds **8** and **9** were obtained, in one-step, from the reaction of the dihydrazonoyl dichlorides **1** with N-acetyl-N′-phenylselenourea and benzoyl selenourea in ethanol through the non-isolable intermediates **10** and **11**, *via* the elimination of aniline and ammonia, respectively (Scheme IV).



SCHEME IV

EXPERIMENTAL

Melting points were determined on a Gallenkamp melting point apparatus. The infrared spectra were recorded on a Perkin-Elmer 1430 spectrophotometer. The ^1H nmr spectra were measured in dimethyl sulfoxide-d_6 on a Varian EM-390 (90 MHz) spectrometer using tetramethylsilane as internal reference. Mass spectra were recorded on GCMS-QP 1000 Ex spectrometer. Elemental analyses were carried out at the Microanalytical Center of Cairo University. N,N'-Diaryloxalodihydrazonoyl dichlorides **1a–d** were prepared as previously described.[3,7] N-Acetyl-N'-phenylselenourea and benzoylselenourea were prepared according to literature procedures.[8,9]

Preparation of 2,2'-bi(4-aryl-4,5-dihydro-5-imino-1,3,4-selenadiazoles) **3a–d**.

Method A: General Procedure: To a solution of the appropriate **1** (5 mmol) in dimethylformamide (30 ml) was added a solution of potassium selenocyanate (15 mmol) in water (10 ml) and the mixture was heated under reflux for 2 hours then left to cool. The reaction mixture was diluted with water (50 ml) and the precipitated solid was collected, washed with water and crystallized from dimethylformamide to afford **3** in 66–81% yields. The compounds prepared together with their physical constants are listed in Table II.

Method B: General Procedure: To a solution of selenourea (20 mmol) in ethanol (60 ml) was added the appropriate dichloride **2** (5 mmol) and the reaction mixture was stirred at room temperature for 1 hour, then refluxed for 2 hours and left to cool. The produced solid was filtered off, washed with water and dried. Recrystallization from dimethylformamide afforded products identical in all respects (mp., mixed mp. and infrared spectra) with those obtained by method A above, except the yields are much lower (20–35%).

Nitrosation of **3**: *General Method*: To a solution of **3** (3 mmol) in acetic acid (30 ml) was added a saturated solution of sodium nitrite (2 g in 5 ml water) dropwise with stirring. The mixture was left to stand at room temperature for 3 hours then diluted with water. The reddish solid that separated was filtered off, washed with water and dried. Rapid crystallization from dioxane afforded the N-nitroso derivatives **6** in 76–88% yields (Table II).

2,2'-Bi(4-aryl-4,5-dihydro-1,3,4-selenadiazol-5-ones) **7**.

Method A: Thermolysis of **6**. *General Procedure*: The appropriate N-nitroso derivative **6** (2 mmol) in ethylene glycol (15 ml) was heated until the evolution of N_2 ceased and the reddish colour disappeared then left to cool and diluted with water (20 ml). The precipitated crude product was filtered off, washed with water and dried then crystallized from dimethylformamide to afford the bi-selenadiazolone derivatives **7** in 88–91% yields (Table II).

TABLE II

2,2′-Bi(4-aryl-4,5-dihydro-5-imino-1,3,4-selenadiazoles) **3**, 2,2′-Bi(4-aryl-4,5-dihydro-5-nitrosoimino-1,3,4-selenadiazoles) **6** and 2,2′-Bi(4-aryl-4,5-dihydro-1,3,4-selenadiazol-5-ones) **7**

Comp. no.	M.p. °C	Yield %	Formula (M.W.)	Analysis calcd/found		
				C	H	N
3a	250-2	81	$C_{16}H_{12}N_6Se_2$	43.06	2.71	18.84
			(446.23)	(43.2)	(2.6)	(19.0)
3b	216-18	78	$C_{18}H_{16}N_6Se_2$	45.58	3.40	17.72
			(474.28)	(45.3)	(3.5)	(17.6)
3c	258-60	72	$C_{16}H_{10}Cl_2N_6Se_2$	37.30	1.95	16.31
			(515.12)	(37.5)	(2.1)	(16.5)
3d	264-66	66	$C_{16}H_{18}Cl_4N_6Se_2$	32.90	1.38	14.39
			(584.02)	(33.1)	(1.4)	(14.2)
6a	160	88	$C_{16}H_{10}N_8O_2Se_2$	38.11	1.99	22.22
			(504.23)	(37.9)	(2.1)	(22.4)
6b	152	85	$C_{18}H_{14}N_8O_2Se_2$	40.61	2.65	21.05
			(532.28)	(40.8)	(2.6)	(20.9)
6c	145	79	$C_{16}H_8Cl_2N_8O_2Se_2$	33.53	1.40	19.55
			(573.12)	(33.7)	(1.5)	(19.3)
6d	158	76	$C_{16}H_6Cl_4N_8O_2Se_2$	29.93	0.94	17.45
			(642.02)	(30.2)	(1.1)	(17.3)
7a	211-12	91	$C_{16}H_{10}N_4O_2Se_2$	42.87	2.24	12.05
			(448.19)	(43.0)	(2.4)	(11.9)
7b	204-6	89	$C_{18}H_{14}N_4O_2Se_2$	45.39	2.96	11.76
			(476.24)	(45.2)	(3.1)	(11.9)
7c	278-80	90	$C_{16}H_8Cl_2N_2O_2Se_2$	37.16	1.56	10.83
			(517.08)	(37.3)	(1.7)	(11.0)
7d	242-44	88	$C_{16}H_6Cl_4N_4O_2Se_2$	32.79	1.03	9.56
			(585.98)	(33.0)	(1.1)	(9.7)

Method B: Hydrolysis of **3**. *General Procedure*: To a solution of the appropriate **3** (1 mmol) in ethanol (40 ml) was added hydrochloric acid (37%, 5 ml) and the reaction mixture was refluxed for 4 hours then left to cool to room temperature. The solid that formed was filtered off, washed with water and dried. Crystallization from dimethylformamide afforded products identical in all respects (mp. mixed mp. and infrared spectra) with compounds **7** obtained above by method A.

2,2′-Bi(4-aryl-4,5-dihydro-5-acetylimino-1,3,4-selenadiazoles) **8**.

Method A: General Procedure: A solution of the appropriate **3** (1 mmol) in acetic anhydride (6 ml) was refluxed for ½ hour then allowed to cool and poured onto crushed ice. The solid product that formed was collected by filtration, washed with water and crystallized from dimethylformamide to give the N-acetyl derivatives **8a–b** in 80–90% yield (Table III).

TABLE III

2,2'-Bi(4-aryl-4,5-dihydro-5-acetylimino-1,3,4-selenadiazoles) **8** and 2,2'-Bi(4-aryl-4,5-dihydro-5-benzoylimino-1,3,4-selenadiazoles) **9**

Comp. no.	M.p. °C	Yield %	Formula (M.W.)	Analysis calcd/found		
				C	H	N
8a	318-20	92	$C_{20}H_{16}N_6O_2Se_2$	45.29	3.04	15.85
			(530.3)	(45.5)	(2.9)	(16.1)
8b	296-8	90	$C_{22}H_{20}N_6O_2Se_2$	47.32	3.61	15.05
			(585.35)	(47.1)	(3.7)	(15.2)
8c	323-25	87	$C_{20}H_{14}Cl_2N_6O_2Se_2$	40.08	2.35	14.03
			(599.2)	(39.9)	(2.4)	(14.1)
8d	313-15	85	$C_{20}H_{12}Cl_4N_6O_2Se_2$	35.95	1.81	12.58
			(668.1)	(36.1)	(2.0)	(12.5)
9a	>350	95	$C_{30}H_{20}N_6O_2Se_2$	55.05	3.08	12.84
			(654.43)	(54.8)	(2.9)	(13.0)
9b	>350	92	$C_{32}H_{24}N_6O_2Se_2$	56.31	3.54	12.31
			(682.48)	(56.1)	(3.4)	(12.4)
9c	>350	89	$C_{30}H_{18}Cl_2N_6O_2Se_2$	49.81	2.50	11.62
			(723.33)	(50.0)	(2.4)	(11.8)
9d	>350	87	$C_{30}H_{16}Cl_4N_6O_2Se_2$	45.48	2.03	10.61
			(792.23)	(45.6)	(2.1)	(10.8)

Method B: General Procedure: To a solution of N-acetyl-N'-phenylselenourea (4 mmol) in ethanol (30 ml) was added the appropriate dichloride **1** (1 mmol) and the mixture was stirred for 1 hour then refluxed for 2 hours and left to cool. The solid that formed was collected, washed with water and crystallized from dimethylformamide to afford products identical in all respect with those obtained by method A above.

2,2'-Bi(4-aryl-4,5-dihydro-5-benzoylimino-1,3,4-selenadiazoles) **9a–d**.

Method A: General Procedure: To a solution of the appropriate **3** (1 mmol) in pyridine (20 ml) was added benzoyl chloride (2 mmol) and the mixture was refluxed for ½ hour then left to cool. The reaction mixture was poured onto crushed ice containing hydrochloric acid (25%, 15 ml) and the precipitated product was filtered off, washed with water and dried. Crystallization from dimethylformamide afforded the N-benzoyl derivatives **9** in 75–90% yield (Table III).

Method B: General Procedure: To a solution of N-benzoylselenourea (4 mmol) in ethanol (30 ml) was added the appropriate **1** (1 mmol) and the mixture was stirred for 1 hour then refluxed for further 2 hours and left to cool. The formed solid was filtered off, washed with water and crystallized from dimethylformamide. The compounds prepared by this method are identical in all respects (mp. mixed mp. and infrared spectra) with compounds **9a–e** obtained from benzoylation of **3** in method A above.

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