

Synthesis of 4,5-Dihydrophenanthro[1,3-d]-1,2,3-selenadiazoles and 10,11-Dihydrophenanthro[1,2-d]-1,2,3-selenadiazoles

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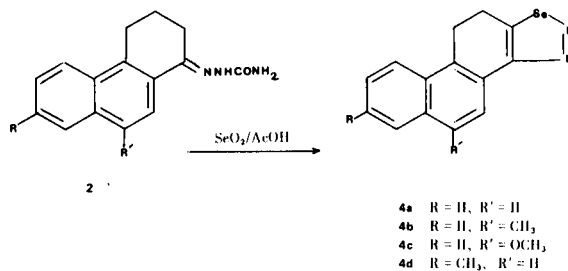
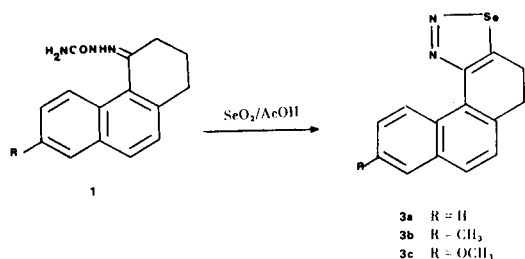
The selenium dioxide oxidation of a series of 1,2,3,4-tetrahydrophenanthrone and 1,2,3,4-tetrahydrophenanthren-4-one semicarbazones afforded 4,5-dihydrophenanthro[4,3-d]-1,2,3-selenadiazoles and 10,11-dihydrophenanthro[1,2-d]-1,2,3-selenadiazoles. The latter series which represent a new type of selenazasteroidal compounds were pyrolyzed and gave the corresponding 1,4-deselenine derivatives.

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In connection with a research program on the synthesis of new azasteroidal compounds, the preparation of several selenadiazacyclopentaphenanthrenes was attempted. The selenium dioxide oxidation of semicarbazones as a simple method for the synthesis of 1,2,3-selenadiazoles which was developed in our laboratory (2-4) was used for the preparation of two series of dihydrophenanthro-1,2,3-selenadiazoles **3** and **4**. Depending on the position of the carbonyl group on the starting tetrahydrophenanthrone derivative, **1** and **2**, 4,5-dihydrophenanthro[4,3-d]-1,2,3-selenadiazoles (**3**) and 10,11-dihydrophenanthro[1,2-d]-1,2,3-selenadiazoles (**4**) were obtained. (See Scheme I).

The nmr spectra appear to be characteristic for compounds **3** and **4**. The spectra of compounds **3a-3c** as well as those of compounds **4a** and **4d** exhibit downfield doublet signals for C₁₁H and C₄H groups respectively. For

Scheme I



compounds **4b** and **4c** the C₄H band appear as singlets on account of the lack of hydrogen in C₅ position.

The structure of compounds are also consistent with the mass spectra. The base peak for compounds **3** and **4** corresponded to M-(N₂,Se) fragment in accordance with their instability towards the heat and light.

The thermal behaviour of compounds **3** and **4** was

Scheme II

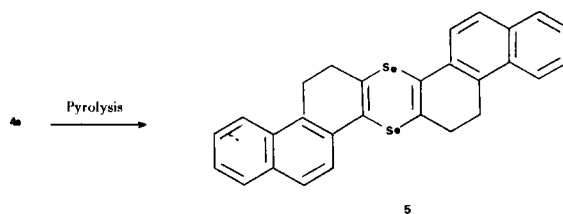
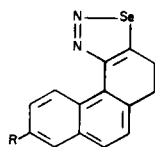
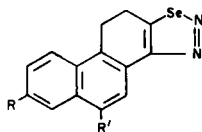


Table I
4,5-Dihydrophenanthro[4,3-d]-1,2,3-selenadiazoles



Compound	R	M.p., °C	Yield %	Formula	C%		Analyses H%		N%	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
3a	H	165 dec.	70	C ₁₄ H ₁₀ N ₂ Se	58.98	58.88	3.51	3.60	9.82	9.69
3b	CH ₃	118	85	C ₁₅ H ₁₂ N ₂ Se	60.20	60.25	4.01	3.99	9.36	9.50
3c	CH ₃ O	105	79	C ₁₅ H ₁₂ N ₂ OSe	57.14	57.09	3.81	3.85	8.89	9.02

Table II
10,11-Dihydrophenanthro[1,2-d]-1,2,3-selenadiazoles



Compound	R	R'	M.p., °C	Yield %	Formula	C%		Analyses H%		N%	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
4a	H	H	94-96	76	C ₁₄ H ₁₀ N ₂ Se	58.95	58.79	3.51	3.41	9.82	9.66
4b	H	CH ₃	110-115	68	C ₁₅ H ₁₂ N ₂ Se	60.20	60.11	4.01	4.08	9.36	9.80
4c	H	CH ₃ O	165 dec.	55	C ₁₅ H ₁₂ N ₂ OSe	57.14	57.19	3.81	3.90	8.89	8.57
4d	CH ₃	H	120	74	C ₁₅ H ₁₂ N ₂ Se	60.20	60.30	4.01	3.96	9.36	9.48

Table III
Nmr Parameters

Compound	Solvent	Chemical Shift, ppm
3a	Deuteriochloroform	3.42 (s, 4H, CH ₂ CH ₂), 7.33-8.16 (m, 5H, aromatic), 8.65 (d, J 9 Hz, 1H, C ₁₁ H).
3b	Deuteriochloroform	2.40 (s, 3H, CH ₃), 3.10 (s, 4H, CH ₂ CH ₂), 7.00-7.72 (m, 4H, aromatic), 9.35 (d, J 10 Hz, 1H, C ₁₁ H).
3c	Carbon tetrachloride	3.10 (s, 4H, CH ₂ CH ₂), 3.85 (s, 3H, CH ₃ O), 6.82-7.66 (m, 4H, aromatic), 9.42 (d, J 10 Hz, 1H, C ₁₁ H).
4a	Carbon tetrachloride	3.16 (s, 4H, CH ₂ CH ₂), 7.19-7.89 (m, 5H, aromatic), 9.50 (d, J 8 Hz, 1H, C ₄ H).
4b	Carbon tetrachloride	2.50 (s, 3H, CH ₃), 3.10 (s, 4H, CH ₂ CH ₂), 7.10-7.90 (m, 4H, aromatic), 8.03 (s, 1H, C ₄ H).
4c	Deuteriochloroform	3.33 (s, 4H, CH ₂ CH ₂), 4.10 (s, 3H, CH ₃ O), 7.42-8.30 (m, 5H, aromatic).
4d	Carbon tetrachloride	2.50 (s, 3H, CH ₃), 3.40 (s, 4H, CH ₂ CH ₂), 7.16-8.00 (m, 4H, aromatic), 8.50 (d, J 9.5 Hz, 1H, C ₄ H).

similar to that of cycloalka-1,2,3-selenadiazoles (5,6). Careful pyrolysis of 4a resulted in the formation of 5,6,14,15-tetrahydrodiphenanthro[1,2-b:1',2'-e] [1,4]-diselenine (5). (See Scheme II).

Compounds 3 and 4 are listed in Tables I and II and the nmr parameters are reported in Table III.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and are uncorrected. Nmr spectra were determined using a Varian T-60-A spectrometer. Mass spectra were run on a Varian MAT 311 spectrograph. Semicarbazones used were prepared by known methods and dried at room temperature.

General Procedure for the Preparation of 4,5-Dihydrophenanthro[4,3-d]-1,2,3-selenadiazoles (3a-c) and 10,11-Dihydrophenanthro[1,2-d]-1,2,3-selenadiazoles (4a-d).

To a hot solution of 0.02 mole of the appropriate dihydrophenanthrone semicarbazone in 25 ml. of glacial acetic acid, 2.2 g. (0.02 mole) of powdered selenium dioxide was slowly added and the mixture was gently heated with stirring until the evolution of

gas ceased. The reaction mixture was cooled and diluted with 100 ml. of water and the mixture was neutralized with sodium bicarbonate. The selenadiazole derivative was extracted with 25 ml. of chloroform. After evaporation of the solvent, the residue was recrystallized from acetone (charcoal) to give light brown crystals.

The 1,2,3-selenadiazole derivatives obtained turned green upon exposure to the day light.

The physical properties and nmr parameters of the compounds prepared are reported in Tables I, II and III.

5,6,14,15-Tetrahydrodiphenanthro[1,2-b:1',2'-e] [1,4]diselenine (5)

A solution of 0.72 g. (0.025 mmole) of 10,11-dihydrophenanthro[1,2-d]-1,2,3-selenadiazole (4a) in 20 ml. of diethylene glycol dimethyl ether was refluxed for 6 hours. After cooling, a solid was separated which was recrystallized from ethanol to give 0.31 g. (43%) of light brown crystals m.p. 83-85°; ms: 516 (6%) M⁺, 436 (80%) M-Se, 356 (18%) M-2Se, 178 (100%) anthracene molecular ion.

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