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Received June 11, 1979

A series of 4-aryl (or heterocyclic)-3-buten-2-one semicarbazones as well as 6-phenyl-3,5-hexadien-2-one semicarbazone were reacted with selenium dioxide to give the corresponding 4-substituted vinyl and 4-phenyl-1,2-butadienyl-1,2,3-selenadiazoles. The selenadiazoles were converted to the corresponding 1,4-diselenafulvenes. Pyrolysis of 4-styryl-1,2,3-selenadiazole gave 2,5-distyrylselenophene.

J. Heterocyclic Chem., **16**, 1405 (1979).

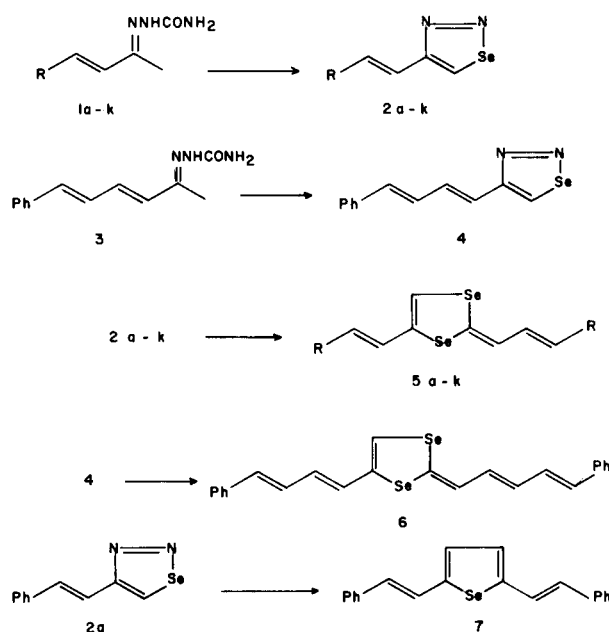
The general method for the synthesis of 1,2,3-selenadiazoles reported in our previous papers (2-7) was used for the preparation of a series of 1,2,3-selenadiazoles with unsaturated chains at the 4-position. The readily available 4-aryl (or heterocyclic)-3-buten-2-one semicarbazones (1a-k and 3) were reacted with molar portions of selenium dioxide in hot glacial acetic acid to give good yields of the desired 1,2,3-selenadiazoles (2a-k and 4).

The mass spectra of the 1,2,3-selenadiazoles prepared had a relatively weak molecular ion bond. The base peak represented the corresponding acetylenic radical ion (M-Se, N₂). The fragment M-N₂ existed in all selenadiazoles prepared as a medium intensity series exhibiting the selenium isotopes pattern. The nmr spectra of the 1,2,3-selenadiazoles synthesized showed sharp singlets at about 9 ppm assigned to proton 5. In all cases a weak doublet centered around the singlet was observed. The doublet was assigned to the coupling of the selenium isotope ⁷⁷Se with a natural abundance of 7.5%. The coupling constant was found to be 40 ± 3 cps, which is in agreement with our previous reports (4).

The 1,2,3-selenadiazoles prepared were treated with potassium hydroxide pellets in alcohol until the evolution of nitrogen gas ceased. The precipitate formed in each case consisted of the corresponding 1,4-diselenafulvene (5a-k and 6), as a mixture of *cis* and *trans* isomers (6).

The decomposition product of 4-styryl-1,2,3-selenadiazole (2a) was heated at 180° for 2 hours to give 2,5-distyrylselenophene (7). The mechanism of this type of ring transformation was discussed in an earlier report (8) (see Scheme 1).

The physical properties of the 1,2,3-selenadiazoles which were prepared and those of the related 1,4-diselenafulvenes are reported in Tables I and II.



a, R = Phenyl; b, R = 4-Chlorophenyl; c, R = 4-Bromophenyl;
d, R = p-Tolyl; e, R = 4-Methoxyphenyl; f, R = 3-Nitrophenyl;
g, R = 3,4-Dimethoxyphenyl; h, R = 3,4-Methylenedioxyphenyl;
i, R = 2-Furyl; j, R = 2-Thienyl; k, R = 2-Pyridyl.

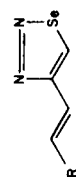
EXPERIMENTAL

Melting points were determined on a Kofler hot stage microscope and are uncorrected. Nmr spectra were determined using a Varian T60A spectrometer. Mass spectra were run on a Varian-Mat Ms-311 instrument.

4-Styryl-1,2,3-selenadiazole (2a).

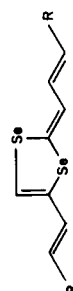
To a hot solution of 20.3 g. (0.1 mole) of methyl styryl ketone semicarbazone (1a) in 200 ml. of glacial acetic acid, 11.2 g. (0.1 mole) of powdered selenium dioxide was added portionwise.

Table I



Compound No.	R	M.p. °C	Yield %	Formula	C%		H%		N%	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
2a	Phenyl	70	60	C ₁₀ H ₈ N ₂ Se	50.84	50.91	3.38	3.30	11.86	12.02
2b	4-Chlorophenyl	125	42	C ₁₀ H ₇ ClN ₂ Se	44.36	44.40	2.58	2.63	10.35	10.20
2c	4-Bromophenyl	100	46	C ₁₀ H ₇ BrN ₂ Se	38.09	38.02	2.22	2.30	8.88	8.58
2d	4-Tolyl	85	45	C ₁₁ H ₁₀ N ₂ Se	52.80	52.89	4.00	4.09	11.20	11.37
2e	4-Methoxyphenyl	95	55	C ₁₁ H ₁₀ N ₂ OSe	49.62	49.46	3.75	3.60	10.52	10.80
2f	3-nitrophenyl	138	66	C ₁₀ H ₇ N ₃ O ₂ Se	42.70	42.39	2.49	2.55	14.94	14.73
2g	3,4-Dimethoxyphenyl	140	67	C ₁₂ H ₁₂ N ₂ O ₂ Se	48.64	48.50	4.05	3.98	9.45	9.64
2h	3,4-Methylenedioxyphenyl	120	71	C ₁₁ H ₈ N ₂ O ₂ Se	47.14	47.38	2.85	2.89	10.00	9.83
2i	2-Furyl	55	52	C ₈ H ₆ N ₂ OSe	42.47	42.63	2.65	2.59	12.38	12.60
2j	2-Thienyl	74	58	C ₈ H ₆ N ₂ SSe	39.66	39.70	2.47	2.43	11.57	11.50
2k	2-Pyridyl	78	53	C ₉ H ₇ N ₃ Se	45.56	45.73	2.95	2.86	17.72	17.91

Table II



Compound No.	R	M.p. °C (a)	Yield %	Formula	C%		H%	
					Calcd.	Found	Calcd.	Found
7a	Phenyl	179-184	60	C ₂₀ H ₁₆ Se ₂	57.69	57.57	3.82	3.91
7b	4-Chlorophenyl	180-185	65	C ₂₀ H ₁₄ Cl ₂ Se	49.48	49.38	2.88	2.71
7c	4-Bromophenyl	182-187	65	C ₂₀ H ₁₄ Br ₂ Se ₂	41.81	41.73	2.43	2.50
7d	4-Tolyl	160-166	71	C ₂₂ H ₂₀ Se ₂	59.45	59.70	4.50	4.44
7e	4-Methoxyphenyl	180-183	70	C ₂₂ H ₂₀ O ₂ Se ₂	55.46	55.30	4.20	4.31
7f	3-Nitrophenyl	210-215	72	C ₂₀ H ₁₄ N ₂ O ₂ Se ₂	47.43	47.66	2.76	2.83
7g	3,4-Dimethoxyphenyl	188-196	75	C ₂₄ H ₂₄ O ₄ Se ₂	53.73	53.60	4.47	4.41
7h	3,4-Methylenedioxyphenyl	178-186	64	C ₂₂ H ₁₆ O ₄ Se ₂	52.38	52.59	3.17	3.22
7i	2-Furyl	169-173	58	C ₁₆ H ₁₂ O ₂ Se ₂	48.48	48.33	3.03	2.89
7j	2-Thienyl	183-187	65	C ₁₆ H ₁₂ S ₂ Se ₂	44.85	44.77	2.80	2.90
7k	2-Pyridyl	160-166	60	C ₁₈ H ₁₄ N ₂ Se ₂	51.67	51.80	3.34	3.31

(a) The nmr spectra of the 1,4-diselenafulvenes which were synthesized revealed that they consisted of mixtures of *cis* and *trans* isomers.

The reaction mixture was stirred and heated gently until the evolution of gas ceased. The reaction mixture was diluted with water, neutralized with sodium bicarbonate and extracted with chloroform. After evaporation of the solvent, the residue was recrystallized (charcoal) from aqueous ethanol to give 14.1 g. (60%) of cream plates, m.p., 70°; nmr (deuteriochloroform): 7.23-7.60 (m, 5H, C₆H₅), 7.49-7.71 (m, 2H, CH=CH) and 9.13 (s, 1H, C₅H); ms: m/e (relative intensity) M⁺, 236 (18), M-N₂, 208 (28), M(N₂, Se), 128 (100).

Compounds **2b-k** were prepared similarly. The physical properties of compounds **2** are reported in Table I.

4-(4-Phenyl-1,3-butadienyl)-1,2,3-selenadiazole (**4**).

6-Phenyl-3,5-hexadien-2-one semicarbazone was treated with selenium dioxide as described for compound **2a**. The light brown crystals obtained, m.p. 90-95° (60%), were repeatedly recrystallized from alcohol (charcoal) to give an analytical sample, m.p. 95-96°; ms: m/e (relative intensity) M⁺, 262 (15), M-N₂, 234 (31), M(N₂, Se), 154 (100).

Anal. Calcd. for C₁₂H₁₀N₂Se: C, 54.96; H, 3.81; N, 10.68. Found: C, 55.01; H, 3.76; N, 10.51.

2,5-Distyryl-1,4-diselenafulvene (**5a**).

To a hot solution of 2.36 g. (0.01 mole) of 4-styryl-1,2,3-selenadiazole (**2a**) in 25 ml. of 96 per cent ethanol, 1 g. of potassium hydroxide pellets was added and the mixture was warmed until the evolution of nitrogen gas was ceased. The reaction mixture was diluted with water and the precipitate was filtered, washed with water and recrystallized from acetone to give 1.25 g. (60%) of **5a**, m.p. 179-184°; molecular weight by mass spectroscopy: m/e 416.

Compounds **5b-k** were prepared similarly. The physical properties of compounds **5** are reported in Table II.

2,5-Bis-(4-phenyl-1,3-butadienyl)-1,4-diselenafulvene (**6**).

This compound was also prepared as described for **5a**, m.p. 185-190°; molecular weight by mass spectroscopy: m/e 468.

Anal. Calcd. for C₂₄H₂₀Se₂: C, 61.53; H, 4.27. Found: C, 61.80; H, 4.21.

2,5-Distyrylselenophene (**7**).

4-Styryl-1,2,3-selenadiazole (**2a**) (2.36 g., 0.01 mole) mixed with 25 g. of clean sand was carefully decomposed in a flask preheated in an oil bath at 120°. The temperature of the bath was then raised to 180° and kept at this temperature for 2 hours. After cooling, the mixture was extracted with chloroform and chromatographed on a silica gel column using chloroform in light petroleum ether as eluant. The yellow residue, after evaporation of the solvent, was recrystallized from alcohol to give 0.55 g. (33%) of **7**, m.p. 205-207°; ms: m/e (relative intensity) M⁺, 336 (100), 259 (63), 182 (41) and 130 (66).

Anal. Calcd. for C₂₀H₁₆Se: C, 71.42; H, 4.76. Found: C, 71.33; H, 4.70.

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