

Selenium Heterocycles IX. Synthesis of Di-1,2,3-selenadiazoles and their Pyrolysis to Diacetylenic Compounds (I)

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In our previous communications (2-5), we reported the synthesis and pyrolysis of 1,2,3-selenadiazoles. Our reports presented the first general route to 1,2,3-selenadiazole ring system.

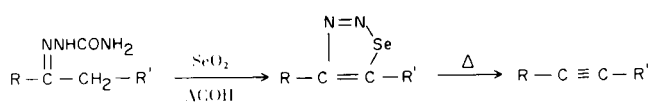


Figure 1

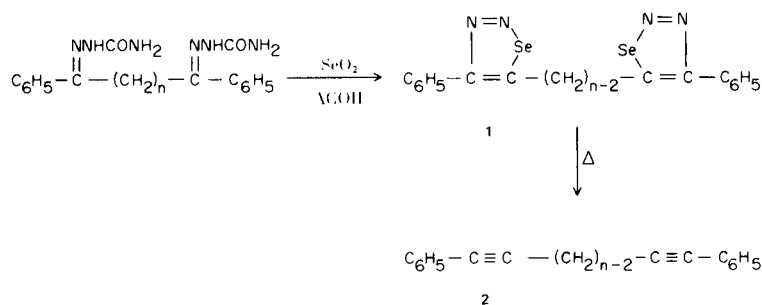
We have extended our work to the synthesis of di-1,2,3-selenadiazoles, which on pyrolysis give high yields of dialkynes. Disemicarbazones of the appropriate diones

were allowed to react with two molar proportions of selenium dioxide in boiling glacial acetic acid. The resulting di-1,2,3-selenadiazoles were pyrolyzed after being mixed with ten times their weights of dry sand. (See Scheme I).

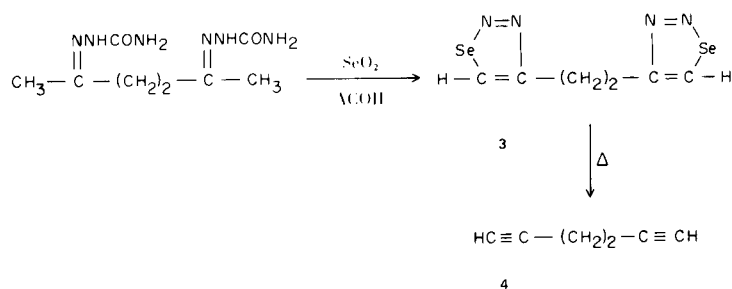
Keto acids, by products in the preparation of diones used in this work, were transformed to the corresponding semicarbazones. Selenium dioxide oxidation of the later, or their corresponding ethyl esters, led to the formation of 1,2,3-selenadiazoles which in turn afforded high yields of alkynecarboxylic acids or esters. (See Scheme II).

The structure of all compounds prepared was confirmed by analytical and spectroscopic methods. Some of the dialkynes or alkynecarboxylic acids were found to be

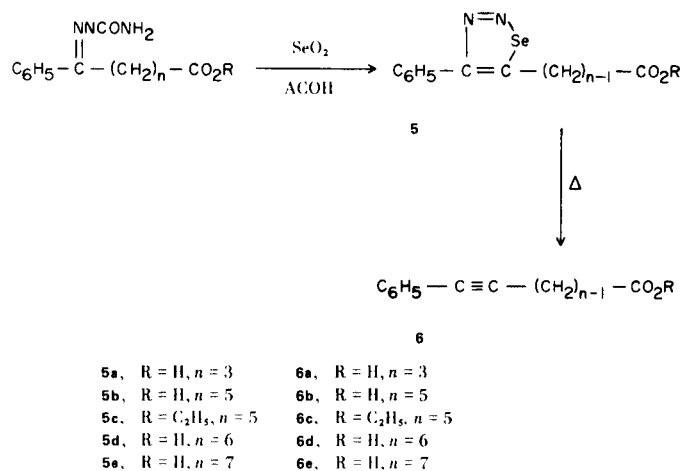
Scheme I



1a.	n	2	2a.	n	2
1b.	n	4	2b.	n	4
1c.	n	5	2c.	n	5
1d.	n	6	2d.	n	6
1e.	n	7	2e.	n	7
1f.	n	8	2f.	n	8
1g.	n	10	2g.	n	10



Scheme II



identical with authentic samples prepared by known methods (6,7).

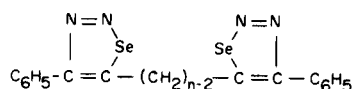
All prepared compounds are listed in Tables I-IV.

EXPERIMENTAL

Melting points were taken on a Kofler hot stage microscope and are uncorrected. The ir spectra were obtained on a Leitz Model 111 spectrograph. Mass spectra were recorded on a Varian-Matt 111 spectrometer. Nmr spectra were taken on a Varian A60A instrument using tetramethylsilane as internal standard. 1,2-(bis-4,4'-1,2,3-Selenadiazolyl)ethane (3).

Acetylacetonone disemicarbazone, 4.56 g. (0.02 mole) was suspended in 60 ml. of glacial acetic acid. To the mixture, 4.44 g. (0.04 mole) of selenium dioxide was added. The reaction mixture was warmed gently on a water bath to start the reaction after which the vigorous reaction was kept under control by external

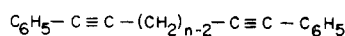
TABLE I



Compound Number	n	M.p., °C (a)	Yield %	Formula	C%		H%	
					Calcd.	Found	Calcd.	Found
1a	2	165	48	C ₁₆ H ₁₀ N ₄ Se ₂	45.93	45.88	2.39	2.41
1b	4	145	60	C ₁₈ H ₁₄ N ₄ Se ₂	48.43	48.50	3.14	3.10
1c	5	98	56	C ₁₉ H ₁₆ N ₄ Se ₂	49.50	49.23	3.48	3.41
1d	6	138	55	C ₂₀ H ₁₈ N ₄ Se ₂	50.63	50.66	3.80	3.90
1e	7	oil	70	C ₂₁ H ₂₀ N ₄ Se ₂	51.64	51.60	4.10	4.12
1f	8	80-82	62	C ₂₂ H ₂₂ N ₄ Se ₂	52.59	52.62	4.38	4.38
1g	10	114	60	C ₂₄ H ₂₆ N ₄ Se ₂	54.34	54.34	4.91	4.99

(a) All solid compounds were recrystallized from aqueous ethanol.

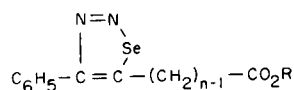
TABLE II



Compound Number	n	M.p., °C or B.p., °C mmHg	Yield % (a)	Formula	C%		H%	
					Calcd.	Found	Calcd.	Found
2a	2	88 (b)	96	C ₁₆ H ₁₀	95.04	95.11	4.95	4.81
2b	4	50-51	98	C ₁₈ H ₁₄	93.91	93.96	6.09	5.99
2c	5	225/20 (c)	93	C ₁₉ H ₁₆	93.44	93.44	6.55	6.66
2d	6	33	95	C ₂₀ H ₁₈	93.02	93.11	6.97	7.02
2e	7	200-205/25 (d)	92	C ₂₁ H ₂₀	92.64	92.66	7.35	7.23
2f	8	260/20	98	C ₂₂ H ₂₂	92.30	92.33	6.69	6.69
2g	10	265-270/20	93	C ₂₄ H ₂₆	91.71	91.70	8.28	8.25

(a) The yields were calculated on the basis of the corresponding di-1,2,3-selenadiazoles. (b) Literature m.p. 88° (6). (c) n_D²⁵ 1.6125. (d) n_D²⁶ 1.5858.

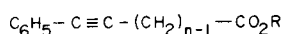
TABLE III



Compound Number	n	R	M.p., °C (a)	Yield %	Formula	C%		H%	
						Calcd.	Found	Calcd.	Found
5a	3	H	145-146	62	C ₁₁ H ₁₀ N ₂ O ₂ Se	46.80	46.70	3.55	3.51
5b	5	H	88	56	C ₁₃ H ₁₄ N ₂ O ₂ Se	50.32	50.40	4.52	4.61
5c	5	C ₂ H ₅	36-37 (b)	51	C ₁₅ H ₁₈ N ₂ O ₂ Se	53.25	53.20	5.32	5.33
5d	6	H	81	58	C ₁₄ H ₁₆ N ₂ O ₂ Se	51.85	52.00	4.94	5.01
5e	7	H	oil	60	C ₁₅ H ₁₈ N ₂ O ₂ Se	53.25	53.26	5.32	5.30

(a) Acids were recrystallized from aqueous ethanol. (b) Recrystallized from light petroleum ether.

TABLE IV



Compound Number	n	R	M.p., °C or B.p., °C/mmHg	Yield % (c)	Formula	C%		H%	
						Calcd.	Found	Calcd.	Found
6a	3	H	99-100 (a)	98	C ₁₁ H ₁₀ O ₂	75.86	75.71	5.75	5.70
6b	5	H	53	97	C ₁₃ H ₁₄ O ₂	77.22	77.21	6.93	7.02
6c	5	C ₂ H ₅	190/15	93	C ₁₅ H ₁₈ O ₂	78.26	78.61	7.82	7.99
6d	6	H	44	99	C ₁₄ H ₁₆ O ₂	77.77	78.01	7.40	7.43
6e	7	H	280/30 (b)	94	C ₁₅ H ₁₈ O ₂	78.26	78.19	7.82	7.79

(a) Literature m.p. 98-99° (7). (b) n_D^{24} 1.5311. (c) Yields were calculated on the basis of the corresponding 1,2,3-selenadiazoles.

cooling (if necessary). When the gas evolution ceased (ca. ½ hour), the reaction mixture was filtered, diluted with 200 ml. of cold water and extracted 3 times with a total of 60 ml. of chloroform. The organic layer was neutralized with a concentrated sodium bicarbonate solution and charcoaled. After evaporation of the solvent under reduced pressure, the residue was crystallized from aqueous ethanol to give 2.5 g. (42.5%) of yellowish crystals, m.p. 129°. Molecular weight m/e 294 (by mass spectroscopy); ir (potassium bromide): 1511, 1438, 1340, 1283, 1181, 962, 810, 793, and 755 cm⁻¹; nmr (deuteriochloroform): δ 3.80 (s, 4H, CH₂) and 8.91 ppm (s, 2H, aromatic H).

Anal. Calcd. for C₆H₆N₄Se₂: C, 28.92; H, 2.04. Found: C, 28.91; H, 2.11.

4,4'-Diphenyl-5,5'-di-1,2,3-selenadiazolyl (**1a**).

A mixture of 3.52 g. (0.01 mole) of dibenzoyl ethane disemicarbazone (prepared from dibenzoyl ethane (8)) and 2.2 g. (0.02 mole) of selenium dioxide in 30 ml. of glacial acetic acid was stirred and warmed until gas evolution ceased. The reaction mixture was worked up as above. The product was recrystallized from aqueous ethanol to give 2 g. (48%) of crystals m.p. 165° dec.; ir (potassium bromide): 1450, 1320, 1250, 928, 805, 760, 723, and 699 cm⁻¹.

δ -(4-Phenyl-1,2,3-selenadiazol-5-yl)valeric Acid Ethyl Ester (**5c**).

ϵ Benzoyl-*n*-caproic acid ethyl ester semicarbazone 6.0 g. (0.02 mole) and 2.2 g. (0.02 mole) of selenium dioxide in 40 ml. of glacial acetic acid was heated gently and worked up as above. The oily residue was crystallized from light petroleum ether to give 3.45 g. (51%) of the ester, m.p. 36-37°; nmr (deuteriochloroform): δ 1.18 (t, 3H, CH₃), 1.7 (m, 4H, CH₂), 2.2 (t, 2H, CH₂), 3.05 (t, 2H, CH₂COO), 4.01 (q, 2H, OCH₂), and 7.5 ppm (m, 5H, aromatic H).

All other di-1,2,3-selenadiazoles were prepared similarly.

δ -(4-Phenyl-1,2,3-selenadiazol-5-yl)valeric Acid (**5b**).

A. By Saponification of the Ethyl Ester.

δ -(4-Phenyl-1,2,3-selenadiazol-5-yl)valeric acid ethyl ester 3.38 g. (0.01 mole) in 50 ml. of 50 percent aqueous ethanol containing 0.4 g. (0.01 mole) of sodium hydroxide was refluxed for 5 hours. After evaporation of the solvent under reduced pressure, the residue was dissolved in 10 ml. of water, charcoaled and acidified to give 2.8 g. (90%) of the desired acid, m.p. 88°. Molecular weight by mass spectroscopy 310; nmr (deuteriochloroform): δ 1.76 (m, 4H, CH₂), 2.30 (t, 2H, CH₂), 3.13 (t, 2H, CH₂COO), 7.56 (m, 5H, aromatic H), and 11.56 ppm (s, 1H, acid H).

B. By Selenium Dioxide Oxidation of the Corresponding Semi-carbazone.

The procedure given for the preparation of 1,2-(bis-4,4'-1,2,3-selenadiazolyl)ethane was followed except that the neutralization with sodium bicarbonate was omitted. The acid obtained in this way was found to be identical with the same compound obtained through the saponification of the ethyl ester.

All other compounds listed in Table III were prepared similarly.

General Procedure for the Preparation of Acetylenes.

Five to 10 g. of di-1,2,3-selenadiazoles or 1,2,3-selenadiazol carboxylic acids or esters were mixed with 10 times their weight of clean dry sand and gradually heated on an oil bath to 180°. Acetylenes could be distilled from the reaction mixture under reduced pressure or extracted by chloroform.

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