

Selenium Heterocycles VIII.
Pyrolysis of Cycloalka-1,2,3-selenadiazoles (1)

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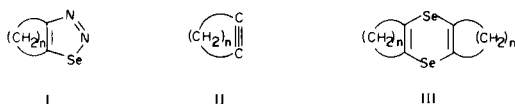
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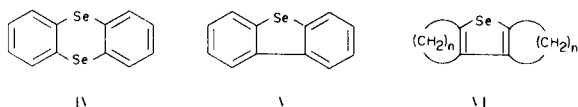
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As part of our study of the chemistry of the 1,2,3-selenadiazoles (2), we have converted a series of cyclic ketone semicarbazones by oxidation with selenium dioxide to the corresponding cycloalka-1,2,3-selenadiazoles (1) in high yields.



In analogy with our previous report (3), ring strain permitting, the cycloalka-1,2,3-selenadiazoles on pyrolysis should have given cyclic acetylenes. Accordingly when cycloocta-1,2,3-selenadiazole (I, $n = 6$) was pyrolysed in boiling toluene or carbon tetrachloride, two products were obtained, one, a hydrocarbon analysing for C_8H_{12} in 55% yield, was found to be cyclooctyne (II, $n = 6$) by comparison with authentic material (4). The second component, a selenium containing hydrocarbon, had an empirical formula of $C_8H_{12}Se$ with a molecular ion at 376 m/e. The two peaks observed in the nmr spectrum of this compound at 2.9 and 2.0 ppm with a ratio of 1:2 are in agreement with the dimeric structure (III, $n = 6$). Further evidence for this structure was obtained from the dimer obtained on pyrolysis of cyclohexa-1,2,3-selenadiazole in refluxing benzene. When this cyclohexa-dimer was heated for a prolonged time at 250° , hydrogen selenide was evolved and two further selenium containing hydrocarbons were produced. These showed molecular ions at 312 and 232 m/e both with a large fragment ion peak at 152 m/e, probably for the biphenylene ion. They were shown by comparison with authentic material to be selenanthrene (IV) (5) and dibenzoselenophene (V) (6), respectively.



Dicyclohepta- and octaselenophenes (VI, $n = 5$ and 6) could be smoothly obtained from the corresponding 1,4-diselenin derivatives on pyrolysis at 250° . Cycloalkaselenadiazoles with large ring size behaved as open chain analogs, giving in high yields the cyclic acetylenes, e.g. cyclododeca-1,2,3-selenadiazole gave in 90% yield cyclododecyne (II, $n = 10$). The physical data for the cycloalka-1,2,3-selenadiazoles and dicycloalka-1,4-diselenins are reported in Table I and Table II.

EXPERIMENTAL

General Procedure for the Synthesis of Cycloalka-1,2,3-selenadiazoles.

All of the cycloalka-1,2,3-selenadiazoles were prepared by dissolving or suspending the corresponding semicarbazone in about 10 times its volume of glacial acetic acid followed by the addition of equimolar selenium dioxide. When gas evolution ceased, the mixture was heated gently on a water bath for a few minutes and filtered to remove the slight amount of metallic selenium. The filtrate was added to water and extracted with chloroform. The chloroform layer was extracted with sodium bicarbonate solution and dried over sodium sulfate. Purification was achieved by distillation under reduced pressure. The yields, boiling points, and analytical data for the selenadiazoles obtained in this way are given in Table I.

General Procedure for the Synthesis of Dicycloalka-1,4-diselenins.

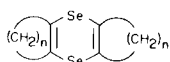
The cycloalka-1,2,3-selenadiazole (about 10 mmoles) was dissolved in 50 ml. of toluene and refluxed for 3 hours. The toluene was evaporated and the residue was crystallized from the appropriate solvent (acetone was used in most cases). The yields, melting points, and analytical data for the 1,4-diselenins obtained are given in Table II. Their mass spectra were characterized by the loss of selenium from the parent ion and less intense fragments corresponding to consecutive loss of CH_2 radicals. The nmr spectrum of these compounds generally showed the methylene hydrogens adjacent to the carbon bearing the double bond at lower field from the remaining methylene hydrogens. Dicyclopenta-1,4-diselenin was exceptional in that all of the hydrogens appeared as a multiplet centered at about 2.2 ppm.

TABLE I



n	Yield %	B.p., °C (mm Hg)	Formula	C%		H%	
				Calcd.	Found	Calcd.	Found
3	22	80-84 (1 x 10 ⁻³)	C ₅ H ₆ N ₂ Se	34.69	34.60	3.47	3.41
4	60	100-102 (1 x 10 ⁻²)	C ₆ H ₈ N ₂ Se	38.50	38.72	4.28	4.35
5	50	104-106 (1 x 10 ⁻²)	C ₇ H ₁₀ N ₂ Se	41.80	41.69	4.97	4.89
6	80	104-106 (9 x 10 ⁻³)	C ₈ H ₁₂ N ₂ Se	44.65	44.62	5.58	5.47
10	78		C ₁₂ H ₂₀ N ₂ Se	53.17	53.08	7.38	7.31

TABLE II



n	Yield %	M.p., °C	Formula	C%		H%	
				Calcd.	Found	Calcd.	Found
3	30	121-122	C ₁₀ H ₁₂ Se ₂	41.38	41.26	4.14	4.03
4	78	108-109	C ₁₂ H ₁₆ Se ₂	45.28	45.33	5.03	5.09
5	60	99-100	C ₁₄ H ₂₀ Se ₂	48.55	48.68	5.78	5.67
6	75	150-151	C ₁₆ H ₂₄ Se ₂	51.35	51.24	6.42	6.59

Cyclooctyne.

Cycloocta-1,2,3-selenadiazole (4.0 g., 18 mmoles), were mixed with 40 g. of sand and heated in an oil bath to 180° for 5 minutes followed by distillation at 22 mm Hg, yield 1.1 g. (55%); ir identical to authentic cyclooctyne.

Cyclododecyne.

Cyclododeca-1,2,3-selenadiazole (2.0 g., 82 mmoles) was pyrolyzed as above; the yield of cyclododecyne was 0.95 g. (90%), b.p. 238° (lit. (7) 106-109°/11 mm Hg); n_D²⁵ 1.4902; ir and nmr spectra were identical with an authentic sample.

Pyrolysis of Dicyclohexa-1,4-diselenin.

Cyclohexa-1,2,3-selenadiazole (1.0 g.) was heated on sand to 250° for 1 hour, cooled and extracted with chloroform. The chloroform extract was chromatographed on silica gel plates to give two products. The one had a melting point of 180° and a molecular ion at m/e of 312 and was shown to be identical with authentic selenanthrene (mixed melting point undepressed) and the other was an oil with a molecular ion at m/e 232 and was shown to be identical with authentic dibenzoselenophene by comparison with its infrared spectrum.

Dicycloheptaselenophene.

Dicyclohepta-1,4-diselenin (0.35 g., 1.0 mmole) was heated at 250° for ½ hour or until the tlc did not show the presence of starting material. The reaction mixture was chromatographed on a silica gel plate with petroleum ether as the solvent to give 0.16 g. (60%) of dicycloheptaselenophene, m.p. 86-87°.

Anal. Calcd. for C₁₄H₂₀Se: C, 62.91; H, 7.49. Found: C, 63.05; H, 7.38. Molecular weight (by mass spectrum): m/e 268. Dicyclooctaselenophene.

By the above procedure, dicyclooctaselenophene was obtained in 63% yield as a colorless oil.

Anal. Calcd. for C₁₆H₂₄Se: C, 65.09; H, 8.14. Found: C, 65.13; H, 8.22. Molecular weight (by mass spectrum): m/e 296.

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