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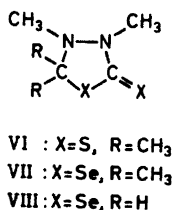
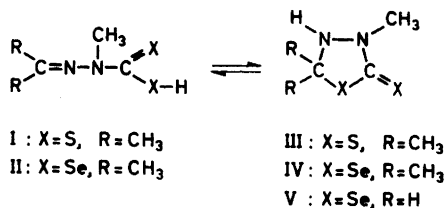
Derivatives of Hydrazine

IX. Conclusive Nuclear Magnetic Resonance Evidence for the Cyclic Structure of Isopropylidenediselenocarbazic Acids

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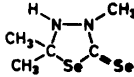
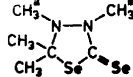
In a recent paper from this laboratory,¹ it was shown that the attempted preparation of isopropylidene-methyldithiocarbazic acid (I) gave a product which, according to ¹H NMR and IR spectroscopic evidence, has the tautomeric 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione structure (III), both in the solid state and in solution. This conclusion was reached by comparing the spectra with those of 3,4,5,5-tetramethyl-1,3,4-thiadiazolidine-2-thione (VI) for which the alternative open-chain dipolar form is highly improbable.



The reaction between acetone and the hydrazinium salts of 2-methyl- or 2,3-dimethyldiselenocarbazic acid furnished the corresponding selenium compounds, IV, and VII, respectively. When recording the ¹H NMR spectra of these compounds (Table 1), it was noted that, in addition to peaks analogous to those observed for III and VI, two small satellites were always present grouped symmetrically around the (CH₃)₂C signal (mutual separation varying between 7.7 and 8.2 Hz, depending on the solvent). An estimate of the intensities of the satellites based upon their heights compared with that of the main signal showed that each corresponds to ca. 3.5%. This shows that the satellites are due to coupling with ⁷⁷Se (natural abundance). The corresponding coupling constant for diethylselenide is 10.8 Hz,² and values around 7 Hz have been found for 2-alkylamino-5-methyl-1,3,4-selenadiazoles.³ Provided that a ⁷⁷Se long range coupling can be excluded these observations are only consistent with a cyclic structure for IV and VII. Since such long range coupling was not observed for the methyl ester of the open-chain form II (*cf.* experimental part), the ¹H NMR spectra furnish conclusive evidence for the cyclic structure IV (and VII). The solvent shifts of IV and VII closely parallel the results obtained for the sulfur analogues and the previous conclusions concerning the cyclic structure of III (and VI) are therefore strongly reinforced.

The product (VIII) from the reaction between formaldehyde and 1,2-dimethyl-

Table 1. Solvent dependence of the chemical shifts (τ , ppm) of the methyl protons and the $J_{\text{Se-C-C-H}}$ coupling constants (Hz) in 3,5,5-trimethyl- and 3,4,5,5-tetramethyl-1,3,4-selenadiazolidine-2-selone (IV and VII, respectively).^a

	 IV			 VII			
Solvent	(CH ₃) ₃ C	$J_{\text{Se-C-C-H}}$	CH ₃ N	(CH ₃) ₂ C	$J_{\text{Se-C-C-H}}$	CH ^a ₃ N	CH ^b ₃ N
CDCl ₃	8.16 (8.31)	7.9	6.36 (6.41)	8.22 (8.36)	7.7	7.33 (7.28)	6.45 (6.49)
CCl ₄	8.14 (8.34)	7.8	6.38 (6.50)	8.21 (8.37)	ca. 7.8	7.32 (7.54)	6.50 (6.56)
C ₆ H ₆	8.77 (8.88)	7.8	6.75 (6.80)	8.81 (8.93)	7.8	8.02 (8.01)	6.85 (6.92)
C ₆ H ₅ NO ₂	8.14	8.0	6.27	8.25	8.2	7.36	6.41

^a Values in parentheses refer to the corresponding sulfur compounds III and VI.¹

hydrazinium 2,3-dimethyldiselenocarbamate⁴ was proved to be cyclic in the same manner. The ¹H NMR spectra of VIII show the coupling constant $J_{\text{Se-C-H}} = \text{ca. } 13$ Hz. When the ¹H NMR spectra of the product (V) from the reaction between formaldehyde and methylhydrazinium 2-methyldiselenocarbamate⁴ were recorded in the solvents mentioned in Table 1, the ⁷⁷Se satellites were difficult to discern. This is due to both a low signal intensity and to the coupling of the methylene group with the N-H proton. However, in saturated CD₃NO₂ solution and in saturated CD₃CN solution (with two drops of D₂O added to remove the NH coupling) the ⁷⁷Se satellites were easily observable ($J_{\text{Se-C-H}} = 13.2$ Hz in both cases).

The infrared spectra (KBr) of IV and V were in accordance with the assigned cyclic structure, showing a strong N-H stretching vibration around 3130 cm⁻¹.

Experimental. 3,5,5-Trimethyl-1,3,4-selenadiazolidine-2-selone* (IV). A suspension of

* To avoid confusion with "selenone", which designates a compound of the type R₂SeO₂, the IUPAC Commission on the Nomenclature of Organic Chemistry has recommended "selone" as the suffix name for the group >C=Se.

methylhydrazinium 2-methyldiselenocarbamate⁴ in an excess of dry acetone was stirred for $\frac{1}{2}$ h. The reaction mixture was filtered and the solvent evaporated. The oily residue was dissolved in dry ether, the solution dried (MgSO₄) and taken to dryness. A solution of the yellow residue in the minimum amount of dry, peroxide-free ether was filtered, if necessary, after an interval of 15 min. Pentane was added and a yellow, crystalline compound separated on cooling to -80°C. M.p. 98-102°C. (Found: C 23.70; H 3.92; N 10.97; Se 61.60. Calc. for C₈H₁₀N₂Se₂: C 23.45; H 3.93; N 10.94; Se 61.66).

3,4,5,5-Tetramethyl-1,3,4-selenadiazolidine-2-selone (VII). A suspension of 1,2-dimethylhydrazinium 2,3-dimethyldiselenocarbamate⁴ in an excess of dry acetone was stirred for $\frac{1}{2}$ h. The reaction mixture was filtered and the solvent evaporated. The oily residue was extracted with boiling pentane, the solution dried (MgSO₄) and taken to dryness. The residue was dissolved in the minimum amount of dry ether and pentane added. On cooling to -80°C, VII separated as yellow crystals. M.p. 90.5-92.5°C. (Found: C 26.78; H 4.52; N 10.46. Calc. for C₆H₁₂N₂Se₂: C 26.68; H 4.48; N 10.37).

3,4-Dimethyl-1,3,4-selenadiazolidine-2-selone (VIII). A filtered, aqueous solution (5 ml) of 1,2-dimethylhydrazinium 2,3-dimethyldiseleno-

carbazate 4 (2×10^{-3} mol) was added to a 40 % aqueous formaldehyde solution (4×10^{-3} mol), with stirring. The reaction mixture was filtered immediately and allowed to stand for $\frac{1}{2}$ h. The precipitated yellow oil was isolated by centrifugation, washed with water and dissolved in chloroform (10 ml). The solution was dried (MgSO_4) and taken to dryness. The oily residue was redissolved in chloroform (4 ml), pentane added, and the turbid solution cooled to -18°C . On scratching, a yellow crystalline compound (VIII) precipitated. Yield: 60–70 %. M.p. $60-61^\circ\text{C}$. (Found: C 19.81; H 3.43; N 11.78. Calc. for $\text{C}_4\text{H}_8\text{N}_2\text{Se}_2$: C 19.85; H 3.33; N 11.57).

3-Methyl-1,3,4-selenadiazolidine-2-selone (V). A filtered, aqueous solution (5 ml) of methylhydrazinium 2-methyldiselenocarbazate 4 (10^{-3} mol) was added to a 40 % aqueous formaldehyde solution (2×10^{-3} mol), with stirring. The reaction mixture was allowed to stand for $\frac{1}{2}$ h, after which the yellow precipitate was isolated by centrifugation, washed with water, and dried *in vacuo*. Yield: 90 %. The compound (V) was dissolved in the minimum amount of chloroform and precipitated with pentane. M.p. $124-126^\circ\text{C}$. (Found: C 16.07; H 2.61; N 12.30. Calc. for $\text{C}_5\text{H}_8\text{N}_2\text{Se}_2$: C 15.81; H 2.65; N 12.28).

Methyl isopropylidene-2-methyldiselenocarbazate (IX). Ethanolic solutions of IV (10^{-3} mol) and potassium hydroxide (10^{-3} mol) were mixed, and the equivalent amount of methyl iodide added to the resulting solution. After $\frac{1}{2}$ h the reaction mixture was filtered and the filtrate taken to dryness. The residue was extracted with pentane. This extract was dried (MgSO_4) and the solvent evaporated. The yellow, crystalline residue (IX) was washed with pentane and dried *in vacuo*. Yield: 65 %. M.p. $80-83^\circ\text{C}$. (Found: C 26.43; H 4.53; N 10.49. Calc. for $\text{C}_6\text{H}_{12}\text{N}_2\text{Se}_2$: C 26.68; H 4.48; N 10.37).

Apart from the ^{77}Se satellites around the CH_2-Se signal ($J_{\text{Se}-\text{C}-\text{H}} = ca. 14$ Hz), the ^1H NMR spectra of IX were almost identical to those of methyl isopropylidene-2-methyldithiocarbazate, 1 as was the IR spectrum in the $\text{C}=\text{N}$ stretching region (1601 cm^{-1} and 1624 cm^{-1}). Accordingly, IX is acyclic.

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Aromatic Hydroxylation Resulting from Attack of Lignin by a Brown-Rot Fungus

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A valuable means for studying the aromatic substitution in lignins is the identification of methoxylated aromatic carboxylic acids formed on oxidative degradation of methylated samples. 1,2,c In connection with investigations of the effects of brown-rot fungi on the chemical structure of lignin it was of interest to determine whether any significant differences were to be found between aromatic substitution patterns of sound and fungus-altered lignin.

Lignin isolated from wood of sweetgum (*Liquidambar styraciflua* L.) decayed by the brown-rot fungus *Lenzites trabea* Pers. ex Fries 3 ("enzymatically liberated lignin") has thus been compared with Björkman lignin (milled wood lignin) 4 of sound sweetgum wood. Following methylation, the lignins were oxidized with permanganate at pH 11–12 and then with hydrogen peroxide at pH 9–10, 2b and the resulting acids methylated with diazomethane. The mixtures of methyl esters were examined by gas chromatography-mass spectrometry.

The gas chromatograms indicated close similarity between the two lignins in the products and in the approximate relative proportions of products. The major aromatic acids included veratric acid (I), tri-*O*-methylgallic acid (II), isohemipinic acid (III), meta-hemipinic acid (IV), and 3,4,5-trimethoxyphthalic acid (V). These acids are also major products formed on similar treatment of Björkman lignin of birch (*Betula verrucosa* Ehrh.). 5

In addition to the mutual chromatographic peaks, there were two significant peaks from the enzymatically liberated lignin that were not observed in the case of the ester mixture derived from Björkman lignin. The compounds responsible for

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