

Fig. 1. Proton magnetic resonances (at 60 MHz) of the methyl groups of 2% solutions of DL-threonine (a,b) and DL-valine (c,d,e,f) in D_2O . Increasing field from left to right. Chemical shifts in cycles sec^{-1} (cps) relative to internal sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS).

maining spectrum, also recorded by Taddei and Pratt, was interpreted correctly by them by assigning different chemical shifts to the two methyl groups of valine which, in general, are magnetically non-equivalent because of unequal life-times of the rotamers I, II, and III. For the spin-coupling constant, $J(H(\beta), CH_3(\gamma))$, Taddei and Pratt found the same value, 7.0 cps, for each of the two methyl groups, in harmony with values derived from other amino acid spectra, while Aruldas' analysis involves the unusual values of 5.0 and 5.1 cps. Fig. 1, lines c, d, e, and f of this paper, records the methyl group resonances of DL-valine (60 MHz) in D_2O at 28° as re-observed by us. Without prejudice, this spectrum can be interpreted in 3 ways, namely, as consisting of (1) two spin-doublets separated by 3 cps; (2) two spin-doublets separated by 6.8 cps; (3) one spin-doublet separated by 3.8 cps and a second separated by 9.8 cps. Correspondingly, Aruldas' spectrum (Fig. 4b of his paper) shows spin-doublet separations of either 5 cps (2 pairs); 7 cps (2 pairs); or 2 cps for one pair, 12 cps for the remaining. Since spin-couplings are independent on field intensity the acceptable solution is the one (2) common to both formal interpretations, that is, $J(H(\beta), CH_3(\gamma)) = 6.8$ cps. In conclusion no evidence has been presented to disprove that PMR spectra of α -amino acid rotamers at room temperature are effectively averaged to one spectrum. In this respect, the

behavior of aqueous solutions of these acids is quite similar to what is found for solutions in CF_3COOH , even at 220 MHz.⁵ Of course, the molecular species in CF_3COOH are ions ($CH_3CHOHCHNH_3^+COOH$) and not "zwitterions" ($CH_3CHOHCHNH_3^+COO^-$) as in water, but this difference would seem less important in stereochemical respect.

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Organic Selenium Compounds

IV. Esters of Triselenocarbonic Acid

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As a part of a current investigation at this laboratory of the chemistry of carbon diselenide,^{1,4} we have prepared a series of esters of triselenocarbonic acid (I–V).

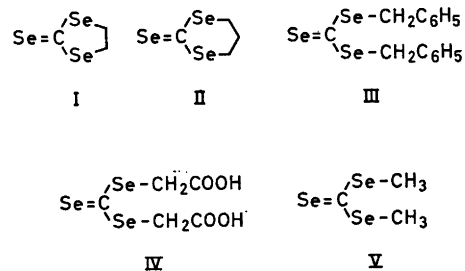


Table I. Esters of triselenocarbonic acid.

Compound	Formula	Base	Yield (%) ^a	M.p. (°C)	λ_{\max} , log ϵ (m μ)	Analyses (C, H, Se)	M.W. ^b
I	C ₃ H ₄ Se ₃	K ₂ CO ₃	45	99–101	565, 2.20 ^c 573, 2.20 ^d	Found: 12.94; 1.60; 85.70 Calc.: 13.01; 1.46; 85.53	264 277
II	C ₄ H ₆ Se ₃	K ₂ CO ₃	23	99–103	554, 2.21 ^c	Found: 16.46; 2.20; 81.35 Calc.: 16.52; 2.08; 81.41	280 291
III	C ₁₅ H ₁₄ Se ₃	KOH	27	69–70	547, 2.03 ^c 551, 2.04 ^d	Found: 41.72; 3.53; 55.00 Calc.: 41.76; 3.25; 54.99	— —
IV	C ₅ H ₆ O ₄ Se ₃	KHCO ₃	48	144–148d	545, 1.95 ^c	Found: 16.70; 1.62 — Calc.: 16.35; 1.63	—
V	C ₃ H ₆ Se ₃	KOH	72	B.p./lmm 99–100	545, 1.96 ^c	Found: 13.25; 2.15 — Calc.: 12.90; 2.15	—

^a The yields were calculated from the amount of selenium initially present as carbon diselenide.

^b Molecular weights were determined by the vapor pressure lowering method. ^c In ethanol. ^d In diethyl ether.

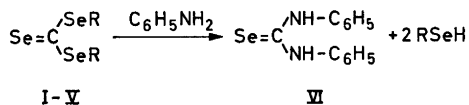
These substances were encountered as by-products when the intermediates from the base-catalyzed reactions between carbon diselenide and active methylene compounds were alkylated. However, under conditions which favoured the latter reactions, the yields of triselenocarbonic esters were low.

In order to raise the yields of the triselenocarbonic esters, a variety of reaction conditions were employed. It was shown that these compounds could be obtained as the main products when dimethyl sulfoxide containing 10–20 % of water was used as solvent, and a wide variety of bases resulted in good yields. So far 1,2-dibromoethane, 1,3-dibromopropane, benzyl chloride, bromoacetic acid and methyl iodide have been used successfully as alkylating agents. This indicates that esters of triselenocarbonic acid can generally be made available by the present method.

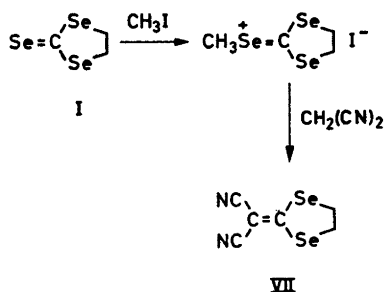
In a typical run, carbon diselenide (2 mmol) and 1,2-dibromoethane (4 mmol) were added to a suspension of finely powdered potassium carbonate (4 mmol) in dimethyl sulfoxide containing 10 % of water (40 ml). The reaction required 4 h at

room temperature. 2-Seleno-1,3-diselenolan or ethylene triselenocarbonate (I) could be isolated in 45 % yield. The bases employed in the preparations of compounds II–V are given in Table 1.

For elemental analyses and some molecular weight determinations, see Table 1. The 60 Mc/s NMR spectra of compounds I–V were in accord with the assigned structures (*cf.* Table 2). The presence of a C=Se group was shown by the ability of I–V to form N,N'-diphenylselenourea (VI)² by reaction with aniline.



Furthermore, the presence of the 1,3-diselenolan ring system in I was demonstrated in the following way. By treatment of I with methyl iodide, followed by malonitrile and triethylamine dissolved in pyridine, 1,3-diselenolan-2-ylidenemalonitrile (VII) was formed.



Cf. Ref. 3 for the corresponding reaction with the thio analogue of I. The IR-spectrum of compound VII was identical with the spectrum of an authentic sample.⁴

The esters I–IV are red or violet, crystalline compounds. (Absorption maxima in the visible region are given in Table 1). Compound I exhibits a remarkable stability towards heat, oxygen and moisture. No detectable decomposition occurred when I was refluxed in toluene for 1 h or was heated in the air to *ca.* 100°C for 5 min. After hydrolysis of I for 14 days at room temperature with hydrochloric acid in aqueous ethanol, substantial amounts

of unchanged material could be recovered. Compounds II and III are somewhat less stable. Compound IV is destroyed in a few days at room temperature when it is kept as the pure solid and even more rapidly when in solution.

Reactions of the esters with bases proceed rapidly and result in replacement of the alkylseleno groups, as demonstrated by the formation of VI when aniline is used as the base.

At present, no direct evidence about the mechanism of formation of the triselenocarbonic esters have been obtained. However, the fact that oxygen does not affect the yields of the esters, even when the alkyl halide is added at the end of the reaction between carbon diselenide and base, indicates that the esters are formed by a route bypassing the triselenocarbonate ion, which is easily oxidized.^{5,6}

In a recent paper by Gattow and Dräger,⁵ the formation of dimethyl triselenocarbonate (V) from barium triselenocarbonate and methyl iodide is reported. The description of V as an insoluble substance led us to prepare this compound by the present method. We have isolated V as a very soluble red oil, which was characterized by its reaction with aniline to form VI. We therefore conclude that the compound described by Gattow and Dräger cannot be dimethyl triselenocarbonate.

The details of this investigation will appear in a forthcoming paper in this journal.

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Table 2. NMR-spectra.^a

Compound	Solvent	τ (ppm)	Relative intensity
I	(CD ₃) ₂ SO	5.72 (s)	—
II	CDCl ₃	6.55–6.80 (m) 7.17–7.52 (m)	2 1
III	CDCl ₃	2.70 (s) 5.30 (s)	5 2
IV	(CD ₃) ₂ CO	–0.03 (s) 6.63 (s)	1 2
V	CCl ₄	7.27 (s)	—

^a The spectra were recorded at 60 Mc/s with TMS as internal reference. s = singlet, m = multiplet.

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