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Short Communications

Organoselenium Compounds Obtained from 1-Bromocyclobutane-1-carboxylic Acid

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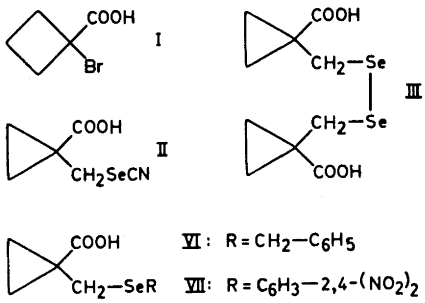
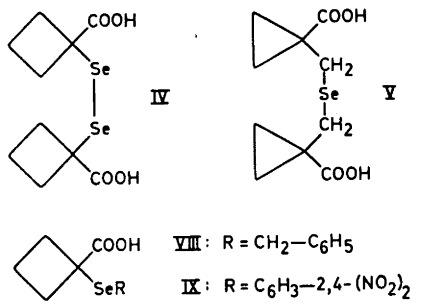
Reaction of 1-bromocyclobutane-1-carboxylic acid (I) with potassium selenocyanate in neutral solution at room temperature gave in good yield a selenocyanato-substituted acid, which analysed correctly, but the rather good stability in acid solution indicated that the SeCN-group was not situated in the α-position.[1,2] Determination of the acidity constant gave $pK_a = 4.1$. Since α- and β-selenocyanatopropionic acid have $pK_a = 2.63$ and 3.85, respectively,[1,3] the β-position is probable. Finally, the NMR-spectrum was quite different from that of the cyclobutane derivative I but gave strong evidence for the formula II. No isomeric selenocyanato acid was found.

The bromo acid I was also reacted with a solution of sodium diselenide. The reaction gave a yellow oil which gradually crystallized. The solid product had a wide melting-point interval. Extraction and recrystallization, using various solvents and finally methanol, gave two diselenide acids, m.p. 182–183° and 155–156°, and one monoselenide acid, m.p. 185–186°. Analyses and NMR-spectra showed that the diselenide acids had the formulas III and IV, respectively, and the monoselenide acid the formula V. The properties of the crude product indicated that it contained a certain amount of the possible unsymmetrical diselenide acid, which during the recrystallization was converted into the symmetrical compounds III and IV. The acid III was also obtained by treating the selenocyanato acid II with alkali.

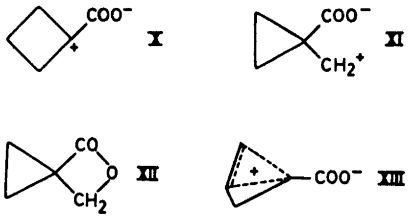




Reaction of the bromo acid I with sodium monoselenide gave as main product the acid V and small quantities of other monoselenide acids, which have not yet been investigated.

Reduction of the diselenides with Rongalite in aqueous ammonia and subsequent reaction with benzyl chloride or 1-chloro-2,4-dinitrobenzene gave the acids VI–IX.

The cyclopropane derivatives are obviously formed by some kind of Demjanov rearrangement but the role of the ionised carboxy group is not clear. Since the bromine in I is bound to a tertiary carbon atom, the first step is probably the formation of the dipolar ion X. Rearrangement to the ion XI does not seem very probable, but this ion may be an intermediate in the



formation of a more stable β-lactone XII, which should give the cyclopropane derivatives II, III, and V. On the other hand, the formation of a non-classical pyramidal structure (XIII) of the type discussed by Roberts *et al.*[4,5] cannot be excluded. The formation of the cyclobutane derivative IV could be explained either by an S_N2 reaction on the bromo acid I or by an S_N1 reaction *via* the unrearranged dipolar ion X. Both possibilities are in agreement with the fact that the very reactive diselenide ion yields in part an unrearranged product, while the less reactive selenocyanato ion gives only a cyclopropane derivative. At present it would be premature to discuss the mechanism in more detail. Experiments with esters of the bromo acid I, now in progress, will probably throw more light upon the rearrangement.

Experimental. The NMR-spectra were recorded with a Varian A 60 instrument. The analyses were carried out by the Analytical Department of the Institute.

1-Bromocyclobutane-1-carboxylic acid (I) was prepared according to Perkin and Sinclair [6] and recrystallized from petrol ether. NMR-spectrum in acetone-d_6: multiplet at $\delta = 1.77-3.00$ ppm; singlet at $\delta = 10.73$ ppm (1 carboxy proton).

1-Selenocyanatomethylcyclopropane-1-carboxylic acid (II). Glistening scales from carbon tetrachloride, m.p. 114.5–115.5°. NMR-spectrum in acetone-d_6: A_2B_2-spectrum at $\delta = 1.25$ and 1.45 ppm (4 protons); singlet at $\delta = 3.40$ ppm (2 protons); singlet at $\delta = 10.47$ ppm (1 carboxy proton). For NMR-spectra of cyclopropane derivatives, see Wiberg and Nist.[7] (Found: C 35.31; H 3.51; Se 38.55. Calc. for $C_6H_7NO_2Se$: C 35.31; H 3.46; Se 38.69.)

Diselenide-dicarboxylic acid III. Yellow prisms from dilute methanol, m.p. 182–183°. NMR-spectrum in trifluoroacetic acid: A_2B_2-spectrum at $\delta = 1.31$ and 1.63 ppm (8 protons); singlet at $\delta = 3.37$ ppm (4 protons). (Found: C 33.95; H 4.09; Se 44.23. Calc. for $C_{10}H_{14}O_4Se_2$: C 33.72; H 3.96; Se 44.34.)

Diselenide-dicarboxylic acid IV. Yellow flakes or scales from dilute methanol, m.p. 155–156°. NMR-spectrum in trifluoroacetic acid: multiplet at $\delta = 2.03-3.13$ ppm. (Found: C 33.90; H 4.12; Se 44.23. Calc. for $C_{10}H_{14}O_4Se_2$: C 33.72; H 3.96; Se 44.34.)

Monoselenide-dicarboxylic acid V. Glistening plates from methanol, m.p. 185–186°. NMR in trifluoroacetic acid: A_2B_2-spectrum at $\delta = 1.19$ and 1.63 ppm (8 protons); singlet at $\delta = 3.10$ ppm (4 protons). (Found: C 43.34: H 5.17; Se 28.42. Calc. for $C_{10}H_{14}O_4Se$: C 43.33; H 5.09; Se 28.49.)

1-Benzylselenomethylcyclopropane-1-carboxylic acid (*VI*). Needles from ligroin, m.p. 96–97°. (Found: C 53.57; H 5.30; Se 29.37. Calc. for $C_{12}H_{14}O_2Se$: 53.55; 5.24; Se 29.34.)

1-(2,4-Dinitrophenylselenomethyl)cyclopropane-1-carboxylic acid (*VII*). Yellow, glistening scales from formic acid, m.p. about 234° (dec.). (Found: C 38.17; H 2.93; Se 22.71. Calc. for $C_{11}H_{10}N_2O_6Se$: C 38.27; H 2.92; Se 22.88.)

1-Benzylselenocyclobutane-1-carboxylic acid (*VIII*). Short prisms from ligroin, m.p. 123.5–125°. (Found: Se 29.40. Calc. for $C_{12}H_{14}O_2Se$: Se 29.34.)

1-(2,4-Dinitrophenylseleno)cyclobutane-1-carboxylic acid (*IX*). Yellow prisms from formic acid, m.p. about 214° (dec.). (Found: Se 22.82. Calc. for $C_{11}H_{10}N_2O_6Se$: 22.88.)

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1. Fredga, A. *J. prakt. Chem.* [2] **123** (1929) 129.
2. Fredga, A. *Uppsala Univ:s Årsskrift* **1935**:5, 106.
3. Fredga, A. *J. prakt. Chem.* [2] **121** (1929) 56.
4. Roberts, J. D. and Mazur, R. H. *J. Am. Chem. Soc.* **73** (1951) 3542.
5. Mazur, R. H., White, W. N., Semenow, D. A., Lee, C. C., Silver, M. S. and Roberts, J. D. *J. Am. Chem. Soc.* **81** (1959) 4390.
6. Perkin, W. H. and Sinclair, W. *J. Chem. Soc.* **61** (1892) 41.
7. Wiberg, K. B. and Nist, B. J. *J. Am. Chem. Soc.* **85** (1963) 2788.

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