

Fig. 2. Two photolyses of a 4.00 mM racemic $\text{Cr}(\text{ox})_3^{3-}$ solution in 60% methanol, one with right and one with left circularly polarized light. The same light intensity is used as in the earlier racemization (Fig. 1).

The experiments have been performed at 25.5°. The optical rotation was measured with a modified (see Ref. 6) Perkin Elmer Polarimeter 141. The stop-watch was stopped (for about 30 sec) during the measurement. No decomposition reaction could be detected as the absorption curves (measured with a Hitachi EPS-3T spectrophotometer) were found to be identical (maximum change 0.5 %) before and after irradiation.

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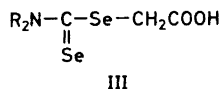
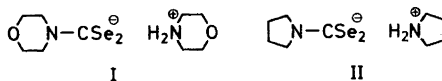
Organic Selenium Compounds

VII. Preparation of Some Derivatives of Diselenocarbamic Acid

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In connection with studies of the infrared¹ and electronic² spectra of organic sulfur and selenium compounds, as well as with studies of coordination compounds with seleniumcontaining ligands,³ we have prepared several diselenocarbamates and their carboxymethyl esters (or [(*N,N*-dialkylselenocarbamoyl)seleno]acetic acids). Most of the diselenocarbamates have previously been described by Barnard and Woodbridge,⁴ and Rosenbaum *et al.*⁵ but two new diselenocarbamates, derived from morpholine and pyrrolidine, respectively, are described in the following. The carboxymethyl esters are new. They were prepared in the same manner as the corresponding carboxymethyl dithiocarbamates.⁶



a: R = C₂H₅

b: R = n-C₃H₇

c: R₂ = H₂C $\begin{array}{l} \diagup \text{CH}_2-\text{CH}_2- \\ \diagdown \text{CH}_2-\text{CH}_2- \end{array}$

d: R₂ = O $\begin{array}{l} \diagup \text{CH}_2-\text{CH}_2- \\ \diagdown \text{CH}_2-\text{CH}_2- \end{array}$

e: R₂ = $\begin{array}{l} \text{CH}_2-\text{CH}_2- \\ | \\ \text{CH}_2-\text{CH}_2- \end{array}$

Experimental. Morpholinium morpholine-4-carbodiselenoate (I). A solution of 3.4 g of carbon diselenide, in 50 ml of petroleum ether, was added gradually with stirring, to a cooled

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solution of 3.5 g of morpholine, also in 50 ml of petroleum ether, the temperature being kept at 0°C. The reaction mixture became deep yellow and after 5 min a flaky yellow precipitate was obtained. After filtering, the precipitate was washed with petroleum ether; it was purified by reprecipitation from an acetone solution, by the addition of ether. Yield 3.7 g (54 %). (Found: C 31.62; H 5.21; Se 45.70. Calc. for $C_8H_{13}N_2O_2Se_2$: C 31.38; H 5.27; Se 45.88).

Pyrrolidinium pyrrolidine-1-carbodiselenoate (II). This compound was prepared by essentially the same procedure as that used for (I). A solution of 3.4 g of carbon diselenide, in 50 ml of petroleum ether, was added to a solution of 2.85 g of pyrrolidine, in 50 ml of petroleum ether. The salt separated as yellow crystals (yield 3.2 g; 51 %). Since it was very unstable, the colour changing to red over a period of 2 h, satisfactory analyses could not be obtained. (Found: C 33.55; H 5.37; Se 51.55. Calc. for $C_4H_{11}N_2Se_2$: C 34.64; H 5.81; Se 50.60).

[(*N,N*-Diethylselenocarbamoyl)seleno] acetic acid (IIIa). A solution of sodium diethyldiselenocarbamate was prepared by dissolving 2.1 g of diethylammonium *N,N*-diethyldiselenocarbamate⁵ in 25 ml of 0.27 M sodium hydroxide solution. A neutralised solution of 0.63 g of chloroacetic acid, in 10 ml of water, was added with stirring to this solution, the temperature being kept at 5°C.

After 3 h 10–15 ml of concentrated hydrochloric acid were added, with both cooling and stirring, to the clear solution, whereupon IIIa separated as fine, lemon-yellow crystals. (Yield 1.2 g). M.p. 72°C after recrystallization from petroleum ether. (Found: C 28.00; H 4.38; N 4.60; Se 51.86. Calc. for $C_7H_{13}NO_2Se_2$: C 27.92; H 4.35; N 4.65; Se 52.40).

The following were prepared in a similar manner:

[(*N,N*-Dipropylselenocarbamoyl)seleno] acetic acid (IIIb). M.p. 53°C. Yield 50 %. (Found: C 33.00; H 5.12; N 4.15; Se 47.70. Calc. for

$C_9H_{17}NO_2Se_2$: C 32.81; H 5.16; N 4.25; Se 47.97).

[(*Piperidinoselenocarbonyl*)seleno]acetic acid (IIIc). M.p. 110–111°C. Yield 62 %. (Found: C 31.16; H 4.46; N 4.41; Se 50.70. Calc. for $C_8H_{13}NO_2Se_2$: C 30.70; H 4.18; N 4.47; Se 50.44).

[(*Morpholinoselenocarbonyl*)seleno]acetic acid (IIIId). M.p. 143–144°C. Yield 55 %. (Found: C 26.85; H 3.56; N 4.58; Se 50.50. Calc. for $C_7H_{11}NO_2Se_2$: C 26.69; H 3.49; N 4.44; Se 50.13).

[(*Pyrrolidyl-1-selenocarbonyl*)seleno]acetic acid (IIIe). M.p. 112°C. Yield 40 %. (Found: C 28.21; H 3.80; N 4.71; Se 53.00. Calc. for $C_7H_{11}NO_2Se_2$: C 28.11; H 3.70; N 4.68; Se 52.79). This compound is the least stable of the carboxymethyl diselenocarbamates prepared.

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