

561. *Derivatives of NN-Dialkyldiselenocarbamic Acids.*

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Several sodium *NN*-dialkyldiselenocarbamates have been prepared by reaction of carbon diselenide with secondary amines in alkaline, aqueous dioxan. Treatment of solutions of these with zinc or copper sulphate yielded crystalline compounds, $[R_2N \cdot C(:Se) \cdot Se]_2M$. Oxidation of the sodium salts under a variety of conditions gave equimolar mixtures of bis-(*NN*-dialkyldiselenocarbamoyl) mono- and tri-selenides rather than the expected diselenides.

ZINC DIALKYLDITHIOCARBAMATES have been recognised recently as some of the most potent sulphur-containing antioxidants.¹ It has also been shown that the replacement of sulphur by selenium in many types of compound, particularly disulphides, often markedly increases antioxidant activity, sometimes by a factor of several hundred.² The synthesis of the corresponding *NN*-dialkyldiselenocarbamates was therefore of obvious interest. Bis-(*NN*-dialkyldithiocarbamoyl) disulphides (tetra-alkylthiuram disulphides), the oxidation products of dialkyldithiocarbamates, are of equal importance, since, when heated with rubber in the presence of zinc oxide, they introduce mono- and di-sulphide cross-links^{3,4} and at the same time produce the corresponding zinc dialkyldithiocarbamates.⁵ The vulcanisates so obtained are noted for their resistance to oxidative ageing.⁶ The synthesis of bis-(*NN*-dialkyldiselenocarbamoyl) diselenides would, by analogy, make available rubber vulcanisates which, by virtue of both selenide cross-links and accompanying diselenocarbamate, might be expected to possess even greater resistance to ageing.

Bis-(*NN*-dialkyldithiocarbamoyl) disulphides, first prepared by the oxidation of ammonium or amine salts of dialkyldithiocarbamic acids,⁷ are readily obtained by the oxidation of sodium dialkyldithiocarbamates (formed from carbon disulphide and a secondary amine

¹ Dunn and Scanlan, *Trans. Inst. Rubber Ind.*, 1958, **34**, 228.

² Barnard and Woodbridge, unpublished work.

³ Studebaker and Nabors, *Rubber Chem. Tech.*, 1959, **32**, 941.

⁴ Moore, *J. Polymer Sci.*, 1958, **32**, 503.

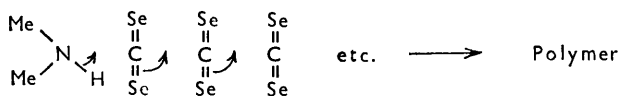
⁵ Scheele, Lorentz, and Dummer, *Kautschuk u. Gummi*, 1954, **7**, WT273; *Rubber Chem. Tech.*, 1956, **29**, 1.

⁶ Fletcher and Fogg, *Rubber Age*, 1959, **84**, 632.

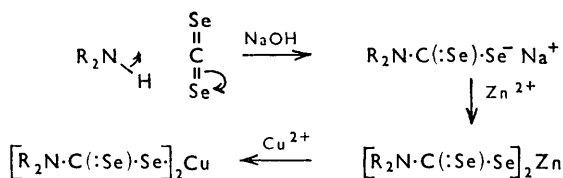
⁷ von Braun, *Ber.*, 1902, **35**, 817.

in alkaline solution) with hydrogen peroxide⁸ or potassium ferricyanide.⁹ Dialkyldithiocarbamates of, for example, zinc or cadmium are prepared by reaction of carbon disulphide with secondary amines in the presence of the required metal ion,¹⁰ or from the sodium dialkyldithiocarbamate and a metal salt.¹¹

The ready polymerisation of carbon diselenide, either alone¹² or in the presence of amines,¹³ has been previously reported. Not unexpectedly, therefore, the addition of carbon diselenide to alkaline solutions of secondary amines, under conditions which with carbon disulphide result in quantitative yields of dithiocarbamates,¹⁴ gave intractable dark resins. Inverse addition gave similar results and a large molar excess of carbon diselenide could be converted into polymer in this way. The resin formation is tentatively ascribed to an amine-catalysed, ionic addition polymerisation of carbon diselenide, *e.g.*:



Preparation of NN-Dialkyldiselenocarbamates.—Resin formation was reduced to negligible proportions by the slow addition of a dioxan solution of carbon diselenide to a vigorously stirred, alkaline solution of the secondary amine at low temperature, and high yields of the required dialkyldiselenocarbamates were thus obtained. It is apparently essential to avoid a localised excess of diselenide. Zinc dialkyldiselenocarbamates, precipitated by the addition of zinc sulphate, are stable, pale brown or yellow, crystalline materials, insoluble in water but soluble in organic solvents, their solubility increasing with the size of the alkyl groups. The intensely red copper diethyldiselenocarbamate was prepared in quantitative yield by shaking a chloroform or methylene chloride solution of the zinc derivative with aqueous copper sulphate.



The spectra of the metal diselenocarbamates in both the visible and the ultraviolet region closely resemble those of the corresponding dithiocarbamates,^{15,16} with absorption maxima similar in intensity and position except for a slight shift to longer wavelengths. The lower absorption of the copper diethyldiselenocarbamate in the visible region, λ_{max} 495 μ (ϵ 11,780), leaves dithiocarbamates as the preferred reagents for the quantitative estimation of copper.¹⁶

Oxidation of sodium dialkyldiselenocarbamates gave a mixture of the bis-(*NN*-dialkyldiselenocarbamoyl) tri- and mono-selenides. Thus, although the theoretical quantity of oxidant was consumed and the initial product gave correct analyses for the expected diselenide, fractional crystallisation gave in each case well-defined crystalline materials (yield *ca.* 50 mole %) which contained 5 rather than 4 selenium atoms per molecule. That these contained two *NN*-dialkyldiselenocarbamoyl residues and were therefore the

⁸ Houben-Weyl, "Methoden der Organischen Chemie," Georg Thieme, Stuttgart, 1955, 4th edn., Vol. IX, p. 853.

⁹ Rothstein and Binovic, *Rec. Trav. chim.*, 1954, **73**, 561.

¹⁰ Whitby and Matheson, *Trans. Roy. Soc. Canada*, 1924, **18**, Sect. III, 111.

¹¹ Saville, *J.*, 1959, 2749.

¹² Ives, Pittman, and Wardlaw, *J.*, 1947, 1080.

¹³ Grimm and Metzger, *Ber.*, 1936, **69**, 1356.

¹⁴ Houben-Weyl, *op. cit.*, p. 825; Mathes, U.S.P. 2,117,619.

¹⁵ Koch, *J.*, 1949, 401.

¹⁶ Näsänen and Tamminen, *Suomen Kem.*, 1950, **23**, B, 28.

(0.0259 g., 0.00065 mole) in water (5 ml.), under the previous conditions, gave an orange-brown precipitate (0.92 g., 85% based on CSe_2), m. p. 150—170°, insoluble in all common solvents.

Optimum Conditions for the Preparation of Sodium NN-Dialkyldiselenocarbamate Solutions.—Carbon diselenide (2.11 g., 0.0124 mole) in dioxan (20 ml.) was added to a stirred solution of sodium hydroxide (0.5 g., 0.0124 mole) and the secondary amine (0.0124 mole) in water (20 ml.) at -10° during 30 min. in an atmosphere of nitrogen. The solution was filtered and used immediately. Addition of the amine solution to the carbon diselenide in dioxan gave a marked reduction in yield when dimethylamine was used, owing to formation of an insoluble polymer. All the following reactions were carried out with the quantities described above.

Zinc Dimethyldiselenocarbamate.—A solution of sodium dimethyldiselenocarbamate, prepared as above, was added rapidly to zinc sulphate (1.80 g., 0.0062 mole) in water (10 ml.) at 0° . The resulting precipitate was filtered off and gave a pink solid (3.03 g., 97%), m. p. 236—239°. Recrystallisation from toluene gave light brown crystals, m. p. 242—243° (Found: C, 14.95; H, 2.45; N, 5.5; Se, 63.5; Zn, 13.3; *M*, 520. $C_6H_{12}N_2Se_4Zn$ requires C, 14.6; H, 2.45; N, 5.7; Se, 64.0; Zn, 13.25%; *M*, 493.5).

Other zinc dialkyl diselenocarbamates were prepared in an identical manner and included:

Zinc diethyldiselenocarbamate. The precipitated yellow solid (3.07 g., 90%), m. p. 154—154.5°, was recrystallised from acetone to give a pale yellow salt, m. p. 154.5—155° (Found: C, 21.9; H, 3.85; N, 4.9; Se, 56.9; Zn, 12.1; *M*, 538. $C_{10}H_{20}N_2Se_4Zn$ requires C, 21.85; H, 3.65; N, 5.1; Se, 57.45; Zn, 11.9%; *M*, 549.5), λ_{max} (in methylene chloride) 285 (ϵ 25,850) and 317 $m\mu$ (ϵ 13,040).

Zinc dibutyldiselenocarbamate. The orange precipitate (2.68 g., 65%), m. p. 66—67°, gave, after recrystallisation from aqueous acetone, the pale brown salt, m. p. 68—68.5° (Found: C, 32.6; H, 5.5; N, 4.25; Se, 48.0; Zn, 9.65. $C_{18}H_{36}N_2Se_4Zn$ requires C, 32.7; H, 5.5; N, 4.25; Se, 47.8; Zn, 9.9%).

Copper Diethyldiselenocarbamate.—Zinc diethyldiselenocarbamate (0.498 g.) in chloroform (20 ml.) was shaken with copper sulphate (10 g.) in water (100 ml.). Evaporation of the deep red chloroform layer left a black solid (0.50 g., 100%), m. p. 222—223°, which gave black crystals, m. p. 225—226°, on recrystallisation from acetone–chloroform (Found: C, 22.3; H, 4.0; Se, 57.9. $C_{10}H_{20}N_2Se_4Cu$ requires C, 21.95; H, 3.7; Se, 57.65%), λ_{max} (in methylene chloride) 290 (ϵ 34,800), 324 (ϵ 17,120), and 495 $m\mu$ (ϵ 11,780).

Oxidation of Sodium Diethyldiselenocarbamate Solution.—The oxidation was carried out by using (a) 27% w/v hydrogen peroxide (0.72 ml., 0.0068 mole) in 23% w/v sulphuric acid (2.64 ml., 0.0062 mole) or (b) potassium ferricyanide (4.11 g., 0.0062 mole) in water (20 ml.), either by adding the oxidant dropwise to the standard sodium diethyldiselenocarbamate solution at -10° or by inverse addition. The products of oxidation were identical in yield, composition, and melting characteristics, 90—100% of the added oxidant being consumed in each case. The oxidation product was precipitated as an orange solid (2.50 g., 83%), m. p. 102—112° with shrinkage at 77—78° (Found: C, 24.4; H, 4.2; N, 5.7; Se, 65.8. Calc. for $C_{10}H_{20}N_2Se_4$: C, 24.8; H, 4.15; N, 5.8; Se, 65.25%). This initial product (1 g.) was separated by crystallisation from ethanol–chloroform into two components, the less soluble bis-(NN-diethylselenocarbamoyl) triselenide being obtained as red crystals (0.4 g.), m. p. 136—137° (Found: C, 21.3; H, 3.8; N, 5.0; Se, 70.45. $C_{10}H_{20}N_2Se_5$ requires C, 21.35; H, 3.6; N, 5.0; Se, 70.1%), λ_{max} 287 $m\mu$ (ϵ 55,200), inflexion at ca. 310 $m\mu$ (ϵ 40,500), with a second crop (0.15 g.) of m. p. 126—129°. Evaporation of the mother-liquors gave a pasty solid (0.40 g.), apparently slightly impure bis-(NN-diethylselenocarbamoyl) monoselenide (Found: N, 6.2; Se, 59.1. Calc. for $C_{10}H_{20}N_2Se_3$: N, 6.9; Se, 58.5%). The tri- and mono-selenide gave well-defined infrared absorption spectra almost superimposable in the region 1500—1100 cm^{-1} .

Preparation of Copper Diethyldiselenocarbamate from Bis(diethylselenocarbamoyl) Triselenide.—The triselenide (0.265 g., 0.00048 mole) in chloroform (20 ml.) was shaken with sodium thiosulphate (0.28 g., 0.00096 mole) and copper sulphate (10 g.) in water (100 ml.), the wine-red chloroform layer being separated at once. On evaporation a black solid (0.203 g., 77%), m. p. 215—220°, was obtained, which after recrystallisation from acetone–chloroform had m. p. and mixed m. p. with copper diethyldiselenocarbamate 224.5—226°.

The yield was also determined spectrophotometrically. The triselenide (10 mg.) in methylene chloride (25 ml.) was shaken with copper sulphate (0.88 g.) and sodium thiosulphate (11.9 mg.) in water (25 ml.) for 10 sec. The organic layer was immediately separated and diluted, and the absorption at 495 $m\mu$ determined. The yield was 88%. In the absence of thiosulphate

the colour developed very slowly and after 20 hr. the yield was 62%; in the presence of quinol (11 mg.), after 2 hr. the yield was 79%. A complicating factor was the rapid destruction of the compound by thiosulphate ion in the presence of excess of cupric ion with the formation of an insoluble brown gum. The monoselenide gave the copper diethylselenocarbamate in 51 mole % yield, estimated spectrophotometrically, under identical conditions.

Bis(dimethylselenocarbamoyl) Triselenide.—The orange solid (2.67 g., 99%) initially obtained from sodium dimethyldiselenocarbamate (0.0124 mole) by oxidation with hydrogen peroxide as above had m. p. 200—210° with shrinkage at 170° (Found: C, 17.2; H, 2.9; Se, 73.1. Calc. for $C_6H_{12}N_2Se_4$: C, 16.8; H, 2.8; Se, 73.8%). Crystallisation from chloroform gave the red *triselenide*, m. p. 223—224° (Found: C, 14.4; H, 2.3; N, 5.65; Se, 77.0. $C_6H_{12}N_2Se_5$ requires C, 14.2; H, 2.4; N, 5.55; Se, 77.9%).

Bis-(NN-dibutylselenocarbamoyl) Triselenide.—Oxidation of sodium dibutyldiselenocarbamate (0.0124 mole) gave a black oil (2.83 g., 76%) from which, after several recrystallisations from ethanol at low temperature, was isolated an orange solid *triselenide* (0.56 g.), m. p. 39—40° (Found: C, 32.1; H, 5.3; N, 4.2; Se, 58.8. $C_{18}H_{36}N_2Se_5$ requires C, 32.05; H, 5.4; N, 4.15; Se, 58.45%).

NN-Dimethyldiselenocarbamic Acid.—A solution of sodium dimethyldiselenocarbamate (0.0124 mole) was acidified with dilute sulphuric acid, and the resulting orange precipitate (1.60 g.; m. p. 98—105°) filtered off in the absence of air (Found: C, 15.65; H, 3.3; N, 6.1; Se, 74.8. $C_3H_7NSe_2$ requires C, 16.8; H, 3.3; N, 6.5; Se, 73.4%). This *acid* was soluble in alkali and oxidised in the air to an orange solid, m. p. 190—210°, from which bis(dimethyldiselenocarbamoyl) triselenide, m. p. and mixed m. p. 223—224°, was obtained by recrystallisation from chloroform or pyridine.

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