

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUIMICA, FACULDADE DE FILOSOFIA, CIENCIAS E LETRAS, UNIVERSIDADE DE SÃO PAULO]

Sulfenyl Selenocyanates

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Aromatic sulfenyl selenocyanates, ArSSeCN , are easily obtained by the reaction of the correspondent sulfenyl chlorides or bromides, at room temperature, with dry, powdered potassium selenocyanate, suspended in an inert solvent, such as benzene. In this way the selenocyanates of 2-nitrobenzenesulfenyl, 2-nitro-4-methylbenzenesulfenyl and 2-nitro-4-chlorobenzenesulfenyl were prepared.

These compounds do not show a definite melting point, as the sulfenyl thiocyanates do; they decompose, on heating, into the disulfide, cyanogen and cyanogen triselenide, $\text{Se}_3(\text{CN})_2$, this last decomposing, at a higher temperature, with separation of selenium. Another difference in relation to the thiocyanates, is the sensibility of the sulfenyl selenocyanates toward alcohols and cold water (even moisture in the air), toward which the thiocyanates are very resistant.¹ On treatment with cold water, selenocyanates do not give, however, sulfenyl oxides, as the correspondent sulfenyl halides do, but give chiefly aryl thiocyanates, besides a small amount of disulfide. This behavior may be explained by the hydrolysis of the sulfenyl selenocyanate with formation of sulfenic and selenocyanic acids, the last of which decomposes into selenium and hydrocyanic acid; the hydrocyanic acid so formed gives, with the sulfenic acid, the aryl thiocyanate; a small part of the sulfenic acid may form disulfide and sulfenic acid. With cold aliphatic alcohols sulfenic esters are formed. Alcoholic ammonia causes a rupture of the sulfur-selenium bond with a practically quantitative yield of the disulfide; the formation of compounds of the type ArSSeSeAr is not observed. With bromine in dry chloroform there also are formed disulfides, besides selenium monobromide and cyanogen bromide; it was not possible to isolate compounds of the type ArSSeBr .

The sulfenyl selenocyanates react with acetone, acetophenone and N-dimethylaniline in the same manner as the corresponding halides² or thiocyanates,^{1,3} only that the selenocyanic acid formed in these condensations decomposes into selenium and hydrogen cyanide. With dry ammonia in benzene solution, sulfenamides and ammonium selenocyanate are formed. The reactions are described in detail in the experimental part in the case of *o*-nitrobenzenesulfenyl selenocyanate.

Experimental

2-Nitrobenzenesulfenyl Selenocyanate.—A solution of 35.1 g. (0.15 mole) of *o*-nitrobenzenesulfenyl bromide

(1) H. Lecher and K. Simon, *Ber.*, **54**, 632 (1921).

(2) Cf. N. Kharasch, S. Potempa and H. L. Wehrmeister, *Chem. Rev.*, **39**, 269 (1946).

(3) N. Kharasch, H. L. Wehrmeister and H. Tigerman, *This Journal*, **69**, 1612 (1947).

(m. p. 85°)^{4,5} in 250 cc. of dry benzene was mechanically shaken, during fifteen hours, in an opaque closed flask at about 20°, with 21.6 g. (0.15 mole) of dry, finely powdered potassium selenocyanate. The benzene solution was filtered and the remaining solid was washed with dry benzene. After evaporation under reduced pressure a yellow oil separated which after two hours solidified completely; yield 34 g. or 87.5% of the theoretical amount. By recrystallization from dry carbon tetrachloride, protecting against light and moisture, small yellow, odorless needles were obtained.

Anal. Calcd. for $\text{C}_7\text{H}_4\text{O}_2\text{N}_2\text{SSe}$: Se, 30.47; N, 10.81. Found: Se, 30.24, 30.30; N, 11.00.

The substance is very soluble in benzene and acetic ester, slightly soluble in petroleum ether, chloroform, carbon tetrachloride; very slightly soluble in methanol and ethanol, in which it decomposes slowly at room temperature and very quickly at higher temperatures; in cold acetone it decomposes rapidly with separation of selenium. The solid substance separates selenium when exposed to light and moisture. Cold alcoholic potassium hydroxide gives a dark brown solution while with the corresponding sulfenyl thiocyanate it gives, under the same conditions, a dark green color.

Thermal Decomposition.—The substance, heated in a sealed capillary, begins to decompose at about 85°, and becomes first soft, and then more and more fluid, the reddish color becoming more and more pronounced. At 150–160° it separates selenium and the residue melts at about 175°. A sample of the selenocyanate was heated in a test-tube at 120–130° for ten minutes. The cold substance, after being thoroughly ground, was extracted with a small amount of boiling chloroform in which the disulfide is very slightly soluble. Yellowish crystals separated from this solution, which melted at 132° and decomposed at about 150°, with separation of selenium, in accordance with the behavior of the cyanogen triselenide.⁶ In the residue, the disulfide was identified by the mixed melting point with an authentic sample of *o*-nitrophenyl disulfide.

Hydrolysis by Water.—A mixture of 2.6 g. of the selenocyanate, 40 cc. of water and some glass beads was shaken for five hours in an opaque flask. The dark brown, disagreeably smelling solid was filtered off, thoroughly dried and extracted with boiling glacial acetic acid, leaving red selenium. From the cold solution yellowish needles (1.3 g.) separated which melted at 130–132°, leaving, however, a very small amount which only melted at 196°. The substance was then extracted with boiling ethanol, leaving a very small amount of *o*-nitrophenyl disulfide, identified by the mixed melting point with an authentic sample. The alcoholic solution gave yellowish needles (71% yield), which melted at 131–132.5°, and were identified as being *o*-nitrophenyl thiocyanate by the mixed melting point with an authentic sample of this substance.

Reaction with Methanol.—A mixture of 2.6 g. of the selenocyanate and 5 cc. of cold anhydrous methanol was shaken for ten hours in an opaque flask. Red selenium and hydrogen cyanide were formed. From the filtered solution, the solvent was evaporated under reduced pressure, at 15–20°, leaving a yellow oil, that soon crystallized (1.5 g. or 80.7% yield). Recrystallization from petroleum ether (50–70°) yielded small yellow needles, whose melting point 54–55° corresponded to that of the known methyl 2-nitrobenzenesulfenylate.⁴

Reaction with Ammonia in Methanol.—A rapid stream of ammonia was introduced in a suspension of 8 g. of the

(4) Th. Zincke and Fr. Farr, *Ann.*, **391**, 57 (1912).

(5) K. Fries and G. Schürmann, *Ber.*, **47**, 1199 (1914).

(6) W. Muthmann and E. Schröder, *ibid.*, **33**, 1767 (1900).

selenocyanate in 100 cc. of dry methanol, while the temperature was held at 10°. The solution slowly became reddish and the solid brown. The filtered and dried solid (4.5 g. or 94.6% yield) melted at 192–196° and contained only a very small amount of free selenium. After recrystallization from benzene and then from glacial acetic acid this substance (m. p. 195.5–196.3°) was identified as *o*-nitrophenyl disulfide. The red methanolic filtrate had a disagreeable smell and split off selenium and hydrogen cyanide immediately when acidified by a mineral acid. When a large amount of water was added to the filtrate, a very small amount (200 mg.) of an orange substance deposited, which, after two recrystallizations from methanol, melted at 120–122° and contained besides sulfur only 1.5% of selenium.

Reaction with Bromine in Chloroform.—To a solution of 5.2 g. (0.02 mole) of the selenocyanate in 10 cc. of dry chloroform, cooled in ice-water, 3.2 g. (0.02 mole) of bromine slowly was added, while stirring. The bromine was absorbed rapidly and a clear brown solution was obtained. By removing the solvent immediately at 15–20° under reduced pressure, an irritatingly smelling residue, consisting of yellow crystals (m. p. 195–196°) and a thick dark-red liquid were obtained. By letting the brown solution stand over night at room temperature, yellow crystals separated (2.6 g. or 84% yield). In both cases the crystals were identified as *o*-nitrophenyl disulfide by the mixed melting point with an authentic sample of this substance. In the chloroformic solution the presence of selenium dibromide and cyanogen bromide could be proved.

Reaction with Dry Ammonia.—In 50 cc. of dry benzene, protected against moisture and cooled in ice-water, dry ammonia was introduced for ten minutes, and then, without interrupting the gas stream, a solution of 5.2 g. of the selenocyanate in 50 cc. of dry benzene was added, drop by drop. A red oil appeared under the benzene layer. The benzene layer was separated and dried over anhydrous sodium sulfate. After removing the solvent, there remained an orange solid (3 g. or 89% yield) melting at 122–124°, which, recrystallized from a mixture of benzene and petroleum ether, yielded yellow needles, whose melting point (124–125°) corresponded to that of the known *o*-nitrobenzenesulfenamide.^{1,4,7} The red oil (consisting of ammonium selenocyanate and ammonia),¹ decomposed by water, deposited selenium and gave off hydrogen cyanide.

Condensation with Acetone.—To 5 cc. of dry pure acetone, 1 g. of the selenocyanate was added at room temperature. Selenium deposited immediately while hydrogen cyanide was given off. From the filtered acetone solution the solvent was evaporated, and the yellow solid residue, recrystallized from ethanol, yielded very small yellow needles whose melting point (81–82°) corresponded to that of the known 2-nitrophenyl acetyl sulfide.^{3,4}

Condensation with Acetophenone.—With acetophenone the selenocyanate does not react immediately at room temperature. However, by grinding the two substances (2:1 g.) in a mortar for about ten minutes, a dark mass was obtained, from which, after separation of the remaining acetophenone by filtration, a small amount of *o*-nitrophenyl phenacyl sulfide⁸ was isolated, by extraction with hot chloroform, leaving red selenium as residue. From a solution of the selenocyanate (1 g.) and acetophenone (2 g.) in 10 cc. of chloroform, after standing twenty-four hours at room temperature, in a closed dark flask, the selenocyanate was entirely recovered by boiling off the solvent at low temperature. By the following procedure the condensation product was obtained in a satisfactory yield: A solution of 1 g. of the selenocyanate and 2 g. of acetophenone in 10 cc. of ethylene bromide was heated for thirty

minutes in a boiling water-bath. Selenium deposited and hydrogen cyanide was given off. The warm solution, filtered off from selenium and tarry by-products, separates, on cooling, yellow crystals. These were recrystallized from a mixture of chloroform with a small amount of petroleum ether (70–90°) and yielded a substance whose melting point (141–142°) corresponded to that of the known *o*-nitrophenyl phenacyl sulfide.⁸

Condensation with *N*-Dimethylaniline.—To a solution of 2.6 g. (0.01 mole) of the selenocyanate in 25 cc. of dry benzene, 3 g. (0.025 mole) of dry, recently distilled dimethylaniline were added. Some heat was evolved, while the solution became red. After standing for forty-five minutes at room temperature, the solution was heated for fifteen minutes in a water-bath. Red selenium deposited and hydrogen cyanide was given off. After cooling, the solution was shaken with a 10% solution of sodium carbonate, and the benzene and excess of dimethylaniline were distilled off by a current of steam. The solid residue was extracted with hot glacial acetic acid and the crystals, separated from this solvent, after recrystallization from benzene, yielded 1.9 g. (69%) of orange red crystals, presenting the melting point 187–188° of the known 2-nitro-4'-dimethylaminodiphenyl sulfide.^{1,4}

2-Nitro-4-methylbenzenesulfenyl Selenocyanate.—From 45.5 g. (0.18 mole) of 2-nitro-4-methylbenzenesulfenyl bromide (m. p. 94–95°),^{5,8} shaken for twenty hours with 27 g. (0.19 mole) of potassium selenocyanate in 200 cc. of dry benzene, 34 g. (68% yield) of the sulfenyl selenocyanate were obtained. Recrystallized from carbon tetrachloride, the compound formed odorless yellow needles which began to decompose at 110°, separating selenium at about 153°.

Anal. Calcd. for C₈H₈O₂N₂SSe: Se, 28.91; N, 10.26. Found: Se, 28.63, 28.88; N, 10.40.

The solubilities and reactions are analogous to that of the previous compound; however, this substance is more resistant against acetone and alcohols, dissolves in cold acetone without rapid decomposition and is not quickly transformed by cold methanol and ethanol. With alcoholic potassium hydroxide, the substance forms a green solution which soon turns to brown.

2-Nitro-4-chlorobenzenesulfenyl Selenocyanate.—By shaking 54 g. (0.2 mole) of 2-nitro-4-chlorobenzenesulfenyl bromide (m. p. 111–112°)⁹ with 29 g. (0.2 mole) of potassium selenocyanate in 300 cc. of dry benzene for twenty-four hours, 42 g. (71% yield) of the sulfenyl selenocyanate was obtained. Recrystallization from warm benzene yielded odorless yellow microcrystalline needles that began to decompose at 118°.

Anal. Calcd. for C₇H₅O₂N₂ClSSe: Se, 26.89; N, 9.54. Found: Se, 26.76, 26.89; N, 9.64.

The solubilities of this substance are analogous with that of *o*-nitrobenzenesulfenyl selenocyanate, but of a lower degree. It is easily soluble in acetic ester, but only slightly soluble in benzene, insoluble in petroleum ether, chloroform and in carbon tetrachloride. It reacts rapidly with cold methanol, ethanol and acetone. With alcoholic potassium hydroxide it gives a brown solution.

Summary

The preparation of some members of the new class of aromatic sulfenyl selenocyanates, ArSSeCN, and the chemical behavior of these compounds are described.

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RECEIVED DECEMBER 23, 1948

(7) J. H. Billman and E. O'Mahony, *THIS JOURNAL*, **61**, 2341 (1939).

(8) Th. Zincke and H. Röse, *Ann.*, **406**, 111 (1914).

(9) Th. Zincke and J. Baeumer, *ibid.*, **416**, 95 (1918).