The results are shown in Table II. The dehydration was cumulative.

The expected loss of oxygen occurred after long dehydration. The results show clearly that the magnetic dilution of manganese in this substance persists until the temperature is high enough to drive off oxygen. The removal of oxygen is, of course, attended with a reduction of the manganese. Dehydration may be carried a considerable distance without greatly changing the atomic environment of the manganese. It will be noted that at a certain stage of dehydration the product had both X-ray and magnetic properties not unlike that of natural African ore.

Acknowledgment.—It is a pleasure to acknowledge the assistance of Kathryn Wethington in this work.

Summary

Preparation and properties are given for accurately characterized samples of MnO, $Mn(OH)_2$, Mn_3O_4, α-Mn_2O_3, γ-Mn_2O_3, MnOOH, and MnO_2. Some less well characterized products are described.

EVANSTON, ILL. RECEIVED JUNE 22, 1948

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

Selenenyl Selenocyanates

BY HEINRICH RHEINBOLDT AND ERNESTO GIESBRECHT

Members of the new class of aromatic selenenyl selenocyanates, ArSeSeCN, are obtained in a similar way as the correspondent sulfenyl selenocyanates, ArSSeCN,[1] by the reaction of selenenyl bromides with dry, powdered potassium selenocyanate suspended in an inert solvent such as benzene. In this manner the selenocyanates of 2-nitrobenzeneselenenyl, 2-nitro-4-chlorobenzeneselenenyl, 2-nitro-4-bromobenzeneselenenyl and 2-nitro-4-methylbenzeneselenenyl were prepared in a pure state, and 2,4-dinitrobenzeneselenenyl selenocyanate in a less pure state. Attempts to obtain benzeneselenenyl selenocyanate and 4-nitrobenzeneselenenyl selenocyanate were not successful, since these products were not stable under the conditions which were effective for the other selenenyl selenocyanates. Selenenyl selenocyanates, in opposition to the corresponding selenenyl thiocyanates,[2] cannot be obtained by mixing, at 0°, solutions of the selenenyl bromides and potassium selenocyanate in methanol or methanol–ethyl acetate mixtures; an immediate separation of diselenides and selenium is observed in these cases.

The properties of the selenenyl selenocyanates are, under various aspects, very different from those of the sulfenyl selenocyanates. The former compounds melt without decomposition, and at a higher temperature selenium is separated with formation of aryl selenocyanates; no formation of diselenides is observed. The melting points of selenenyl selenocyanates are in general higher than those of the corresponding bromides, with exception of the 2,4-dinitrobenzene compound. This behavior is analogous to that of the corresponding sulfenyl thiocyanate.[3] Another difference is the relative insensibility of the selenenyl selenocyanates against water and methanol, which act only slowly; in this case the selenenyl selenocyanates are similar to the sulfenyl thiocyanates.[4] Alcoholic ammonia or bromine in dry chloroform cause a rupture of the selenium–selenium bond, with practically quantitative formation of the diselenides; this behavior is analogous to that of the sulfenyl selenocyanates.[1] The selenenyl selenocyanates, contrary to the sulfenyl selenocyanates, do not condense with methanol, with dry ammonia in benzene solution, with acetone, acetophenone or N-dimethylaniline. In the three first cases diselenides are formed; in the reaction with acetophenone only a very little amount of diselenide was formed and with N-dimethylaniline no reaction is observed. By hydrolysis selenenyl selenocyanates give aryl selenocyanates. These reactions are described in detail, in the experimental part, in the case of the *o*-nitrobenzeneselenenyl selenocyanate.

Experimental

I. **2-Nitrobenzeneselenenyl Selenocyanate.**—A solution of 11.2 g. (0.04 mole) of *o*-nitrobenzeneselenenyl bromide (m. p. 65°, from petroleum ether; yield 75%)[5] in 50 cc. of dry pure benzene was mechanically shaken in an opaque closed flask for twenty-two hours at about 20° with 7.2 g. (0.05 mole) of dry finely powdered pure potassium selenocyanate. The benzene solution was then filtered off from the solid which was washed with dry benzene. After removing the solvent from the benzene solutions under reduced pressure at 35–40° a crystalline reddish-yellow solid remained which melted at 102–106°; yield 10.5 g. or 86%. After two recrystallizations from dry pure carbon tetrachloride, small canary-colored, odorless needles of melting point 109–110° (microscope hot stage) were obtained.

Anal. Calcd. for $C_7H_4O_2N_2Se_2$: Se, 51.60; N, 9.15. Found: Se, 51.76; N, 9.27.

The crystals are not very sensitive toward the humidity of the air; however, when exposed for a long time to the daylight and to the atmosphere, they become darker and

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[1] H. Rheinboldt and E. Giesbrecht, THIS JOURNAL, **71**, 1740 (1949).

[2] O. Foss, *ibid.*, **69**, 2236 (1947); Rheinboldt and Madeleine Perrier, unpublished work.

[3] N. Kharasch, H. L. Wehrmeister and H. Tigerman, *ibid.*, **69**, 1612 (1947).

[4] H. Lecher and K. Simon, *Ber.*, **54**, 637 (1921).

[5] O. Behaghel and H. Seibert, *ibid.*, **66**, 713 (1933).

acquire a weak but penetrating odor. Under protection against light and humidity they can be kept unaltered for many months. Heated in an open or sealed capillary the substance melts sharply at 109–110° changing to a red transparent liquid. This melting point is observed only when the capillary is introduced in the bath at about 107° and the temperature increased very slowly. By heating in the customary manner, the substance does not melt, not even at 160°; at 110°, the substance, still solid, becomes darker and, with increasing temperature, turns to a reddish-brown paste. The same phenomenon is observed with slow or rapid heating when the capillary is introduced at room temperature; when the capillary is introduced above 110° (at 112, 115, 120°) no melting is observed. By introducing it exactly at 110°, the substance melts if this temperature is maintained for several minutes. Isolated crystals, observed under a hot stage microscope, melted, in every case examined, sharply at 110°. Identical behavior is shown by compound IV. All other selenenyl selenocyanates reported in this work melt regularly.

The substance is insoluble in water, very slightly soluble in methanol and ethanol, slightly soluble in petroleum ether, ether, chloroform and carbon tetrachloride, soluble in ethyl acetate and glacial acetic acid, very soluble in carbon disulfide, acetone and benzene. Cold alcoholic potassium hydroxide dissolves it with a purple color which does not change during many days. By heating with a 10% sodium carbonate solution, the substance dissolves with a blue color, that soon turns deeper and after a few minutes becomes clearer with precipitation of the yellow diselenide.

Thermal Decomposition.—By heating the melted substance to higher temperatures, the clear red fluid becomes darker, and at 202–203° begins to separate gray selenium, which ends at about 210°; the cooled and solidified material melts then at 140–142°. A sample of the selenocyanate (1.5 g.) was heated in a test-tube at 210° for five minutes; after cooling, the ground material was extracted with boiling carbon tetrachloride, the extract filtered off from the selenium, and the solvent evaporated. There remained a crystalline yellow substance (1.0 g. or 90%), which melted at 142°, and was identified as 2-nitrophenyl selenocyanate by mixed melting point with an authentic sample (m. p. 142.5°).

Hydrolysis.—A suspension of 1.5 g. of the selenenyl selenocyanate in 25 cc. of water was mechanically shaken, with some glass beads, for five hours in a brown closed flask. The flask was then opened and a slight odor of hydrogen cyanide was noted. The filtered and dried reddish-yellow solid was extracted with carbon tetrachloride, leaving as residue a small amount of red selenium and 1.2 g. or 80% of the unaltered selenenyl selenocyanate was recovered from this extract. The rest, 20%, was transformed to the aryl selenocyanate. A sample of the substance, heated with water for ten minutes, in a boiling water-bath, did not show any alteration in its aspect and melting point. The same happens when a current of steam is passed through an aqueous suspension of the selenenyl selenocyanate for ten minutes, or through a benzene solution until the elimination of the solvent.

Reaction with Methanol.—A suspension of 6.1 g. of the selenenyl selenocyanate in 80 cc. of dry pure methanol was mechanically shaken, with some glass beads, at room temperature, for six hours in a brown closed flask. A reddish liquid and a reddish-yellow solid were formed; the former had a disagreeable, penetrating odor, and a faint odor of hydrogen cyanide was also detected. The solid was collected, carefully dried and then extracted with a small amount of carbon tetrachloride, yielding 2.2 g. or 36.1% of unchanged selenenyl selenocyanate. The subsequent extraction with hot glacial acetic acid gave 2.0 g. of 2-nitrophenyl diselenide, leaving as residue 0.4 g. of selenium. The methanol filtrate, by addition of water, separated a brown oil, which after some time gave off selenium.

Reaction with Ammonia in Methanol and with Bromine in Chloroform.—These reactions, executed exactly as described in the case of the corresponding sulfenyl selenocyanate,[1] gave in both cases more than 90% of the theoretical amount of 2-nitrophenyl diselenide; this, recrystallized from glacial acetic acid melted at 211°, and was identified by the mixed melting point with an authentic sample. In the last reaction, when more than one mole of bromine is used for one mole of the selenocyanate, the selenenyl bromide is formed; with two moles of bromine, 3.1 g. of the selenocyanate gave 2.3 g. of selenenyl bromide (81% yield).

Reaction with Dry Ammonia.—In this reaction, executed as previously described,[1] 1.5 g. of the selenenyl selenocyanate gave 0.9 g. or 91.3% of 2-nitrophenyl diselenide, in addition to a red oil consisting of ammonium selenocyanate and ammonia.

Reaction with Acetone, Acetophenone and N-Dimethylaniline.—A solution of 1.5 g. of the selenenyl selenocyanate in 10 cc. of pure dry acetone was kept in a well-closed brown flask for sixteen hours, at room temperature. A yellow-gray matter separates gradually and hydrogen cyanide is given off. The solid was filtered and the filtrate contained a substance with disagreeable and penetrating odor. The former, well-dried, observed under a microscope, showed to be a mixture of a yellow crystalline substance and red selenium. By extraction with hot glacial acetic acid 0.8 g. or 81% of pure 2-nitrophenyl diselenide was obtained. Acetophenone does not react with the selenenyl selenocyanate by grinding the two substances (2:1 g.) in a mortar. However, by heating this mixture in a boiling water-bath for many hours very little selenium is separated. The 2-nitrophenyl diselenide formed was identified, but about 90% of unaltered selenenyl selenocyanate was recovered. By heating a solution of the substances in ethylene bromide, for an hour, no reaction occurs. A solution of 1.5 g. (0.012 mole) of dimethylaniline and 1.5 g. (0.005 mole) of the selenenyl selenocyanate in 10 cc. of dry benzene, which after standing for twelve hours at room temperature had separated only an insignificant amount of selenium, was heated under reflux for three hours. After distilling off the benzene and dimethylaniline by a current of steam, 1.4 g. (93.3%) of the unaltered selenenyl selenocyanate was recovered.

II. **2-Nitro-4-chlorobenzeneselenenyl** Selenocyanate.—The unknown selenenyl bromide, necessary for the preparation of the selenocyanate, was obtained by bromination of the diselenide.

2-Nitro-4-chlorophenyl diselenide was prepared starting from 2-nitro-1,4-dichlorobenzene. This was transformed, with 90% yield, in 2-nitro-4-chloroaniline (m. p. 116.5–117.5°, from alcohol) by treating with 28% ammonia, at 190–195°.[6] This amine diazotized and treated with potassium selenocyanate in the usual manner, gave a 76% yield of 2-nitro-4-chlorophenyl selenocyanate (m. p. 126.5–127.5°, from ethanol).[7] A stream of ammonia was introduced in a mixture of 92 g. (0.35 mole) of this selenocyanate and 350 cc. of ethyl alcohol, first at room temperature for an hour and then for two and one-half hours at the boiling temperature. After cooling, the deposited solid was filtered off, washed with alcohol and dried *in vacuo* over calcium chloride; yield 73 g., or 88%; melting range 216–218°. For analytical purposes, a sample of this product was extracted with boiling ethanol, washed with ethyl acetate and acetone, and then repeatedly recrystallized from hot benzene or even better from dioxane, yielding brownish-yellow plates, which melted at 221–222° to a thick red liquid.

Anal. Calcd. for $C_{12}H_6O_4N_2Cl_2Se_2$: Se, 33.53; N, 5.95. Found: Se, 33.57; N, 6.06.

Alcoholic potassium hydroxide dissolves the substance very slowly at room temperature and rapidly by heating, giving to the solution a blue color.

2-Nitro-4-chlorobenzeneselenenyl Bromide.—To a mixture of 70.6 g. (0.15 mole) of the diselenide (raw product) with 180 cc. of chloroform, 48 g. (0.3 mole) of bromine was added, at room temperature, in little portions and

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[6] A. I. Kiprianow and M. M. Daschewski, *Ukrain. Khem. Zhur.*, **5**, Tech. pt., 241 (1930); *Chem. Zentr.*, **102**, II, 426 (1931); *C. A.*, **25**, 5034 (1931).

[7] F. Challenger and A. T. Peters, *J. Chem. Soc.*, 1374 (1928).

under vigorous stirring. After standing for twelve hours, with occasional stirring, the brown solution was filtered off from a little dark residue; it was concentrated *in vacuo*, at room temperature, separating brownish-red crystals, which were dried *in vacuo* over silica gel; yield 88 g. or 93%, m. p. 98–99°. After repeated recrystallizations from petroleum ether (b. p. 90–110°), dark red needles of melting point 102.5–103.5° were obtained.

Anal. Calcd. for $C_6H_3O_2NClBrSe$: Se, 25.03; N, 4.44; Br, 25.35. Found: Se, 24.91; N, 4.51; Br, 25.13.

The substance is soluble in cold chloroform, carbon tetrachloride, ether, acetone, acetic ester, benzene; in hot petroleum ether, glacial acetic acid, methanol and ethanol (with separation of diselenide, after some time). Alcoholic potassium hydroxide dissolves it with a deep blue color.

For the preparation of **2-nitro-4-chlorobenzeneselenenyl selenocyanate**, a solution of 12.6 g. (0.04 mole) of the selenenyl bromide in 120 cc. of dry benzene was shaken for twenty hours with 7.2 g. (0.05 mole) of potassium selenocyanate. After removing the benzene from the filtered solution, at 40°, under reduced pressure, a dark brown oil resulted, which soon solidified (9.5 g. or 70%; melting range 105–110°). By recrystallization from a small amount of benzene, small brownish-yellow needles with the melting point 114–115° were obtained. At 172°, the melted substance begins to separate selenium with formation of 2-nitro-4-chlorophenyl selenocyanate.

Anal. Calcd. for $C_7H_3O_2N_2ClSe_2$: Se, 46.38; N, 8.23. Found: Se, 46.40; N, 8.30.

The freshly crystallized substance is odorless, but acquires a penetrating odor when exposed to air and light. It is much less soluble than compound I. Alcoholic potassium hydroxide dissolves it with a deep blue color.

III. **2-Nitro-4-bromobenzeneselenenyl Selenocyanate.**—From 14.4 g. (0.04 mole) of 2-nitro-4-bromobenzeneselenenyl bromide (m. p. 115–116°, from chloroform; yield 92%),[8] shaken for twenty-four hours with 7.2 g. (0.05 mole) of potassium selenocyanate, in 120 cc. of dry benzene, 11.2 g. (73% yield) of the selenenyl selenocyanate (m. p. 120–122°) was obtained. After repeated recrystallizations from benzene, the compound gave odorless yellow-brown little needles, which melted sharply at 125° to a dark red clear liquid, which, at 182°, begins to separate selenium, giving 2-nitro-4-bromophenyl selenocyanate (m. p. 140–141°).

Anal. Calcd. for $C_7H_3O_2N_2BrSe_2$: Se, 41.02; N, 7.28. Found: Se, 40.91; N, 7.30.

The solubilities of this substance are similar to those of compound II. Alcoholic potassium hydroxide dissolves it, giving to the solution a very persisting red-blue color.

IV. **2-Nitro-4-methylbenzeneselenenyl Selenocyanate.**—This compound cannot be obtained by the same manner as substances I, II and III, because the substance, in benzene solution, decomposes after some time.

2-Nitro-4-methylbenzeneselenenyl bromide was prepared by adding 32 g. (0.2 mole) of bromine, under vigorous stirring, to a solution of 24.1 g. (0.1 mole) of 2-nitro-4-methylphenyl selenocyanate (m. p. 152.5°, from acetic ester; yield 62%)[9] in 50 cc. of dry chloroform. The solution after standing for a night, was concentrated at room temperature, under reduced pressure, until a thick paste was formed. After filtration, 24 g. (81.4%) of a crystalline solid, which melted at 80–82°, was obtained. By repeated recrystallizations from petroleum ether (b. p. 70–90°), brownish-red needles of the melting point 86.2° were obtained.

Anal. Calcd. for $C_7H_6O_2NBrSe$: Se, 26.77; N, 4.75; Br, 27.09. Found: Se, 26.70; N, 4.72; Br, 26.99.

The substance is insoluble in cold methanol and ethanol (by heating it decomposes with formation of the diselenide), slightly soluble in petroleum ether and glacial acetic acid at room temperature, but soluble by heating; soluble in cold chloroform, carbon tetrachloride, carbon disulfide, ether, acetone, acetic ester and benzene. Alcoholic potassium hydroxide dissolves it with a deep blue color.

When a solution of this bromide (11.8 g. or 0.04 mole) in 50 cc. of dry benzene was shaken, for twenty hours, with potassium selenocyanate (7.2 g. or 0.05 mole), a quantity of selenium equivalent to the amount of the selenocyanate added was precipitated. After removing the solvent from the filtered solution, under reduced pressure, at room temperature, an orange colored crystalline solid (9 g.), melting at about 150°, was obtained; this, crystallized from carbon tetrachloride, gave lustrous yellow plates of the m. p. 152–153° which were identified as 2-nitro-4-methylphenyl selenocyanate by analysis (Se, 32.82; calcd., 32.75) and by its mixed melting point with an authentic sample; yield 93.3%.

This unexpected result, similar to the hydrolysis or thermal decomposition of the selenenyl selenocyanates, having been verified many times by using carefully purified and dried reagents and special precautions against humidity of the air, a more detailed study of this reaction was carried on as follows: 2.95 g. (0.01 mole) of the selenenyl bromide in 15 cc. of benzene, was shaken with 1.8 g. (0.0125 mole) of potassium selenocyanate, once for sixteen hours and another time for three hours. In the first case, a 96% yield of the aryl selenocyanate was obtained, but in the second case 2.8 g. or 87.5% of 2-nitro-4-methylbenzeneselenenyl selenocyanate was formed. This same substance was prepared by heating, under reflux, for two and one-half hours, a solution of 5.9 g. (0.02 mole) of the selenenyl bromide with 3.6 g. (0.025 mole) of potassium selenocyanate in 30 cc. of dry benzene, under protection against light and humidity. After removing the benzene from the filtered solution, under reduced pressure, at 40°, a red oil remained, which soon solidified; yield 6.0 g. or 94%, melting range 115–118°. After repeated recrystallizations from dry pure carbon tetrachloride, dark-yellow needles, which melted sharply at 122.7–123.5°, were obtained. However, by heating a mixture of 2.95 g. of the selenenyl bromide with 1.8 g. of potassium selenocyanate in 15 cc. of benzene for seven hours, no selenenyl selenocyanate resulted, but 2.1 g. (91%) of the aryl selenocyanate, with separation of selenium, was formed.

Anal. Calcd. for $C_8H_6O_2N_2Se_2$: Se, 49.34; N, 8.75. Found: Se, 49.30; N, 8.71.

Isolated crystals of the substance, observed under a hot-stage microscope, melted sharply at the indicated temperature. The same melting point is observed in an open or sealed capillary, when this is introduced in the bath at about 110° and the temperature increased by 1° per minute. If the capillary is introduced at 121° or at the temperature of the melting point, no melting is observed, but is seen only above 140°. The same phenomenon is observed when the capillary is introduced 5 or 10° above the melting temperature, but in the hot stage the substance melts immediately in the latter cases. This phenomenon is similar to the behavior of substance I. By heating above its melting point, the melted substance becomes more and more red and at 173–175° begins to separate gray selenium; the cooled and solidified substance melts then at 151–153°, the melting point of 2-nitro-4-methylphenyl selenocyanate. The solubilities of this substance are similar to those of compound I. Alcoholic potassium hydroxide dissolves it with a deep blue color.

V. **2,4-Dinitrobenzeneselenenyl Selenocyanate.**—By shaking a solution of 3.3 g. (0.01 mole) of 2,4-dinitrobenzeneselenenyl bromide (m. p. 117–118°, yield 87%),[10] in 25 cc. of dry benzene, with 1.7 g. (0.012 mole) of potassium selenocyanate for eighteen hours no separation of selenium was noted. The solid residue, which had a light yellow color, was filtered from the benzene solution, washed with dry benzene and dried *in vacuo* (1.6 g.). It consisted of 1.0 g. of unaltered potassium selenocyanate and 0.6 g. of potassium bromide, so that only 41.2% of the potas-

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(8) O. Behaghel and K. Hofmann, *Ber.*, **72**, 709 (1939).

(9) S. Keimatsu and I. Satoda, *J. Pharm. Soc. Japan*, **55**, 233 (1935); *C. A.*, **31**, 6662 (1937); *Chem. Zentr.*, **107**, I, 2745 (1936).

(10) O. Behaghel and W. Müller, *Ber.*, **68**, 1544 (1935).

sium selenocyanate reacted. The benzene solutions, after concentration under reduced pressure, at 40°, gave a red thick matter, which solidified after two hours, and showed a melting range from 70 to 115°. It consisted of a mixture of selenenyl bromide and selenenyl selenocyanate; after two recrystallizations from hot carbon tetrachloride, small yellow plates of the melting range 81.0–83.8° and with the selenium content of 42.21% were obtained. This melting range, after two more recrystallizations from the same solvent, remained the same, but the selenium content of the substance was raised to 44.33%, and after three more recrystallizations, to 44.46% (calcd. 44.99%).

On account of the low reactivity of this selenenyl bromide at room temperature, an attempt was made, at higher temperature, to increase the yield of the reaction: by heating under reflux, for twelve hours, a mixture of 6.5 g. (0.02 mole) of the bromide in 45 cc. of dry benzene with 3.6 g. (0.025 mole) of potassium selenocyanate and a small amount of "Drierite," under protection against light and humidity of the air, no separation of selenium was noted. After evaporation of the solvent from the filtered solution *in vacuo*, a red thick matter remained, which solidified after several hours. This material, showing a melting range of 70–116°, was again a mixture of the selenenyl bromide and selenenyl selenocyanate, from which, after three recrystallizations from carbon tetrachloride, by heating to 45° and cooling to 0°, yellow plates which melted at 82–84° were isolated. Repeated recrystallizations did not alter this melting range.

Anal. Calcd. for $C_7H_3O_4N_3Se_2$: Se, 44.99; N, 11.97. Found: Se, 44.69; N, 12.04.

At about 150° the substance separates selenium and gives 2,4-dinitrophenyl selenocyanate, which melts at 163°. By heating the substance in glacial acetic acid for some time, at about 120°, selenium is separated, with formation of the aryl selenocyanate. Even in petroleum ether or carbon tetrachloride, heated for long time, the substance separated selenium.

The substance is easily soluble in ether, carbon disulfide, benzene, toluene and xylene, slightly soluble in carbon tetrachloride, acetone, acetic ester, methanol, ethanol and petroleum ether. By heating with methanol or ethanol it separates selenium and gives the diselenide. Alcoholic potassium hydroxide dissolves it with a brownish-red color.

VI. Reaction of 4-Nitrobenzeneselenyl Bromide with Potassium Selenocyanate.—This selenenyl bromide (m. p. 91.5–92.5°, from petroleum ether)[5] reacts slowly with potassium selenocyanate, at room temperature; thus, the reaction is incomplete. At a higher temperature, the reaction is not practicable, because the selenenyl selenocyanate or the mixture formed in the reaction is very sensitive against the usual solvents and, for the same reason, the formed selenenyl selenocyanate cannot be isolated from this complex mixture. A typical example of various experiments is the following: 28.0 g. (0.1 mole) of *p*-nitrobenzeneselenenyl bromide, dissolved in 125 cc. of dry benzene, was shaken, in the usual manner, with 16.0 g. (0.11 mole) of potassium selenocyanate for twenty hours. The benzene solution was then filtered, under protection against humidity of the air, from the solid residue (A), which was washed with dry benzene. From the benzene solutions, after evaporation of the solvent at cold, *in vacuo*, a lachrymatory oil resulted, which solidified completely after an hour (B). This matter (30 g.) had a melting range from 88 to 136°, with separation of selenium a little under 136°. From the cooled and solidified material, by extraction with a little hot carbon tetrachloride, *p*-nitrophenyl selenocyanate (m. p. 135–136°) was isolated.

The reddish solid residue (A), carefully dried (15.2 g.), gave 7.0 g. of unaltered potassium selenocyanate by extraction with a little cold acetone; thus, only 9 g. or 62.7% of the theoretical amount reacted. It contained also the equivalent quantity of potassium bromide and red selenium (0.8 g.). The reaction product (B) was thus a mixture of selenenyl bromide, selenenyl selenocyanate and aryl selenocyanate, according to the selenium content (41.23%) which is between that of the selenenyl selenocyanate (51.60%) and that of the aryl selenocyanate (34.77%). The mixture product (B), exposed to air, rapidly separates selenium, and loses also its lachrymatory odor. It dissolves in methanolic potassium hydroxide with a deep red color. By heating in dry carbon tetrachloride, the mixture separates selenium; a brownish-yellow matter, which crystallized by cooling the filtered solution, was a mixture of yellow plates and red selenium; by repeating this treatment, pure *p*-nitrophenyl selenocyanate (m. p. 135–136°; Se, 34.61, calcd., 34.77) was isolated. The same result was obtained by dissolving the mixture in ethyl acetate or by precipitating its solution in benzene or carbon disulfide, by addition of petroleum ether.

The reaction of benzeneselenenyl bromide with potassium selenocyanate in benzene gave a similar unseparable mixture product.

Summary

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

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[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY,[1] PEORIA, ILLINOIS]

Preparation and Reactions of Dialkoxytetrahydrofurans[2]

BY JØRGEN FAKSTORP,[3] DOLORES RALEIGH AND L. E. SCHNIEPP

The opening of the furan ring by means of hydrolytic agents has long attracted considerable interest. However, only in the case of methylfuran[4] and dimethylfuran[5] has hydrolytic cleavage led to results of any practical importance. The investigations of Meinel[6] and Clauson-Kaas and co-workers[7] resulting in methods for the preparation of stable dialkoxydihydrofurans which are cyclic acetals of unsaturated 1,4-dicarbonyl compounds and easily convertible into these, represent important advances in this field.

The procedures developed by these authors con-

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented in part before the Division of Organic Chemistry at the 114th National Meeting of the American Chemical Society, Washington, D. C., August 30, 1948.

(3) American-Scandinavian Foundation Fellow 1947–1948.

(4) C. Harries, *Ber.*, **31**, 37 (1898).

(5) F. Dietrich and C. Paal, *ibid.*, **20**, 1085 (1887).

(6) K. Meinel, *Ann.*, **510**, 129 (1934); **516**, 231 (1935).

(7) (a) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Math.-Fys. Medd.*, **22**, [6] (1947), *C. A.*, **42**, 1930 (1948); (b) N. Clauson-Kaas and F. Limborg, *Acta Chem. Scand.*, **1**, 619 (1947); (c) N. Clauson-Kaas and J. Fakstorp, *ibid.*, **1**, 415 (1947); (d) N. Clauson-Kaas, F. Limborg and J. Fakstorp, *ibid.*, **2**, 109 (1948).