TABLE I

SUBSTITUTED 12-AMINOBENZ[*a*]ACRIDINES

No.	Base	Salt	Crystallizing Solvent	M.p.[a] of Salt	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
1	12-*p*-Chloroanilinobenz[*a*]acridine	HCl	Methanol	265	70.58	70.96	4.10	3.98
2	12-*p*-Iodoanilinobenz[*a*]acridine	$C_7H_6O_3$[b]	Benzene-ethanol	212	61.64	61.99	3.60	3.22
3	12-Anilinobenz[*a*]acridine	3 $C_7H_6O_3$	Benzene	220	71.93	71.72	4.63	4.86
4	12-*p*-Toluidinobenz[*a*]acridine	2 $C_7H_6O_3$	50% Ethanol	210	74.75	75.03	4.92	5.23
5	12-*m*-Chloroanilinobenz[*a*]acridine	$C_7H_6O_3$, $2H_2O$[c]	Chloroform	190	68.12	68.00	4.72	4.48
6	12-*m*-Iodoanilinobenz[*a*]acridine	$C_7H_6O_3$	Ethanol	185	61.64	61.85	3.60	3.30
7	12-*m*-Toluidinobenz[*a*]acridine	1.5 $C_7H_6O_3$	Benzene	195	76.53	76.90	4.99	4.97
8	12-*p*-Anisidinobenz[*a*]acridine	1.5$C_7H_6O_3$	Ethanol	207	74.33	74.45	4.85	4.80

[a] All melting points are uncorrected. [b] $C_7H_6O_3$ = salicylic acid. [c] H_2O, calcd., 6.81%; found, 6.72%.

lization from a suitable solvent. The data are recorded in Table I.

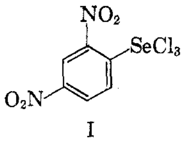
ARMED FORCES MEDICAL COLLEGE
POONA,
INDIA

Derivatives of Sulfenic Acids. XXXIII. 2,4-Dinitrophenyl Selenium Trichloride[1]

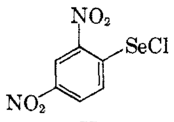
D. DAVID LAWSON AND NORMAN KHARASCH

Received October 27, 1958

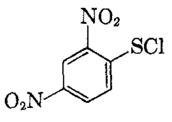
The recent papers of Jenny and co-workers[2] on various seleneny1 derivatives prompt us to report a study, carried out some time ago, concerning 2,4-dinitrophenyl selenium trichloride (I).



I



II



III

Our purpose was to prepare 2,4-dinitrobenzeneselenenyl chloride (II) for comparison with the well known sulfur analog,[3] 2,4-dinitrobenzenesulfenyl chloride (III). While numerous selenenyl halides have been reported, including 2,4-dinitrobenzeneselenenyl bromide[4] and 2-nitrobenzeneselenenyl chloride,[5] II has not been described previously.

The synthesis of III is generally carried out by the catalytic chlorinolysis of bis(2,4-dinitrophenyl) disulfide.[6] This procedure, using chlorine gas, did not permit the convenient chlorinolysis of the very insoluble bis(2,4-dinitrophenyl) diselenide. In the course of the work, however, a superior method for cleaving bis(2,4-dinitrophenyl) disulfide was devised, involving the use of sulfuryl chloride and pyridine. This procedure was succesful in the chlorinolysis of the corresponding diselenide, but the product obtained was not the selenenyl chloride (II), but the trichloride (I). The use of sulfuryl chloride as reagent for chlorinolyses of disulfides and diselenides has been previously reported by Behaghel and Seibert.[4a]

Since selenocyanates are known to undergo brominolysis to selenenyl bromides,[7] the direct chlorinolysis of 2,4-dinitrophenyl selenocyanate was attempted. The reaction proceeded smoothly, the product again being the selenium trichloride (I). Further study established that the trichloride is in equilibrium with the monochloride (Equation 1);

$$\underset{\text{I}}{ArSeCl_3} \rightleftharpoons \underset{\text{II}}{ArSeCl} + Cl_2 \qquad (Ar = 2,4\text{-dinitrophenyl}) \quad (1)$$

and that pure I can be prepared by using excess sulfuryl chloride in the chlorinolysis of the selenocyanate or bis(2,4-dinitrophenyl) diselenide; and II results by heating I in an evacuated atmosphere. The reverse reaction was demonstrated by converting the monochloride (II) to trichloride, by reaction of the former with excess chlorine. Such reversible relations of the trichloride and monochloride derivatives have been noted previously, both in the selenium[8] and the sulfur series.[9]

2,4-Dinitrophenyl selenium trichloride (I) is an excellently crystalline solid, which may be stored for long periods without change. As expected, however, I decomposes on heating and does not exhibit a sharp melting point. The bright yellow crystals begin to turn orange at 70°; at 80–85°, chlorine is evolved and at 100°, the whole mass turns to an

---

(1) The research reported in this document was made possible, in part, through support extended by the Office of Scientific Research, Air-Research and Development Command, under Contract No. AF-49-638-330.

(2) W. Jenny, *Helv. Chim. Acta*, **41**, 317 (1958); G. Hölzle and W. Jenny, *Helv. Chim. Acta*, **41**, 331 (1958), and earlier papers.

(3) N. Kharasch, *J. Chem. Ed.*, **33**, 585 (1956). *Cf.* also R. B. Langford and D. D. Lawson, *J. Chem. Ed.*, **34**, 510 (1957) and reference cited therein.

(4) W. S. Cook and R. A. Donia, *J. Am. Chem. Soc.*, **73**, 2275 (1951). (4a) *Cf.* also O. Behaghel and H. Siebert, *Ber.*, **66**, 708 (1933).

(5) N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946). *Cf.* also ref. 3a.

(6) N. Kharasch, G. I. Gleason, and C. M. Buess, *J. Am. Chem. Soc.*, **72**, 1796 (1950).

(7) O. Behaghel and H. Seibert, *Ber.*, **65B**, 812 (1932).

(8) O. Behaghel and K. Hofmann, *Ber.*, **72**, 582 (1939).

(9) Houben-Weyl, "Methoden der Organischen Chemie," 4th ed., Vol. IX, p. 270, Georg Thieme Verlag, Stuttgart, Germany (1955).

orange melt. The proportion of II, in equilibrium with I was not estimated. In cyclohexane there is no appreciable apparent deviation from Beer's law at selected wave lengths, at room temperature, suggesting that the proportion of II in this solvent, at room temperature, is probably fairly low.

The equilibrium of Equation 1 and the reactivity of the monochloride are also shown by the fact that the products found when I is treated with various reagents are those expected for the monochloride (II). Thus, reactions of I with cyclohexene, ethanol, acetone, aniline, or dimethylaniline gave high yields of the products expected for the monochloride with these reagents. The product from cyclohexene is undoubtedly *trans*-2-chlorocyclohexyl 2′4′-dinitrophenyl selenide[10]; and with ethanol, I gave ethyl 2,4-dinitrobenzeneselenenate, which was identical with the product reported by Cook and Donia,[4] who prepared it by reaction of the sulfenyl bromide and the alcohol, in the required presence of silver salts to remove hydrogen bromide formed in the reaction. The product from acetone was acetonyl 2,4-dinitrophenyl selenide, while aniline and dimethylaniline, respectively, gave 2,4-dinitrobenzeneselenanilide and 4-dimethylaminophenyl 2′-4′-dinitrophenyl selenide. The reactions to obtain these products were conducted under conditions identical to those which readily yield the corresponding derivatives from the sulfenyl chloride (III).[3] The results therefore suggest that the readily prepared trichloride (I) may be used as the *in situ* precursor for reactions requiring the selenenyl chloride (II). However, if desired, II may be made from I and isolated as a crystalline, reactive substance, which can be kept for extended periods.

As Jenny has shown,[2] the ultraviolet and visible spectra of corresponding sulfur and selenium compounds are nearly superimposable, but with definite shifts in both position of maxima and absorbancy. This is also borne out by the several pairs of sulfur and selenium compounds whose ultraviolet spectra were compared in this study. In general, the selenium analogs showed a somewhat higher extinction and absorbed at slightly longer wave lengths than the corresponding sulfur analogs. Comparisons of the infrared spectra of these same pairs of compounds also showed them to be practically superimposable with only minor displacements of the bands (in both directions, toward longer and shorter wave lengths). Indeed, the spectral comparisons of analytical samples of the selenium compounds (with authentic sulfur analogs) served as good indications of whether the analytical results could be expected to conform to the calculated values. Samples showing deviations in the infrared patterns invariably failed to give satisfactory elementary analyses.

EXPERIMENTAL[11]

In view of the toxicities and vile odors of selenium compounds, a powerful hood and scrupulous avoidance of contact was assured throughout the work. To avoid accumulation, preparative runs involving possible volatilization were generally conducted on alternate days.

Chlorinolysis of bis(2,4-dinitrophenyl) disulfide by sulfuryl chloride in presence of pyridine. The disulfide (100 g.) was pulverized and dried in an oven (80–90°) for 12 hr. It was then suspended in 600 ml. carbon tetrachloride, in a 1-l. flask with a reflux condenser. Sulfuryl chloride (40 ml.) was added, followed by 5 ml. of dry pyridine. The mixture was refluxed (steam bath) for 1 hr., and 50 ml. more sulfuryl chloride was added, in 10 ml. portions, about every half hour. An additional 2 ml. of pyridine was also added during the course of the reaction, which was generally complete in 3 to 5 hr., as shown by the near disappearance of the insoluble disulfide. In some runs, tar may appear at the surface of the reactions mixture; but causes no difficulty.

The hot reaction mixture was treated with *ca.* 5 g. "Norit A" and filtered (hot) through "filter-aid." The filtrate was concentrated and the product collected; 91 g. (m.p. 97–98°). Six g. more were obtained from the mother liquor by further concentration. Total yield: 97 g.; 82.5%.

Runs of up to 500 g. disulfide were made, as above, with minor variations required in time of heating and proportion of pyridine for a particular batch. Yields of 80–90% of good product were obtained in these batches. Similarly as reported by Kharasch, Gleason, and Buess,[6] the mother liquor from one batch can be used advantageously in succeeding runs, to improve the over-all yield of product.[12]

2,4-Dinitrophenyl selenium trichloride (I). The above method was adapted to the chlorinolysis of 2,4-dinitrophenyl selenocyanate, as follows. To 200 ml. of redistilled sulfuryl chloride was added 27.2 g. (0.1 mole) of dry 2,4-dinitrophenyl selenocyanate, prepared in 70–75% yields from dinitrochlorobenzene and potassium selenocyanate[13] by the method of Fromm and Martin.[14] The mixture was refluxed for 10 min., filtered hot, and cooled slowly, giving a crop of bright yellow crystals. The liquid was decanted and the crystal crop was dried *in vacuo,* for 24 hr., over a mixture of calcium chloride and sodium hydroxide. Yield 30 g. (86%). The decomposition characteristics of this product were described in the introduction.

Anal. Calcd. for $C_6H_3N_2O_4SeCl_3$: C, 20.44; H, 0.85; Cl, 30.15; N, 7.96. Found: C, 20.63; H, 0.88; Cl, 30.39; N, 8.31. Cryoscopic mol. wt. (in benzene): 350 ± 8.5; Calcd. 352.

While the direct chlorination of bis(2,4-dinitrophenyl)-diselenide[15] failed to give I, in suitable yield, reaction of the diselenide with sulfuryl chloride and pyridine gave I.

Conversion of 2,4-dinitrophenyl selenium trichloride (I) *to 2 4-dinitrobenzeneselenenyl chloride* (II). The yellow trichloride (0.9665 g.) was placed in an Abderhalden pistol, evacuated to 1 ml. pressure, and heated at the reflux tem-

---

[10] For the proof of structure of trans-2-chlorocyclohexyl 2′4′-dinitrophenyl sulfide, *Cf.* A. J. Havlik and N. Kharasch, *J. Am. Chem. Soc.,* **78,** 1207 (1956). The sulfide and the selenide showed identical x-ray powder diagrams, made with the kind assistance of Dr. J. Donohue.

[11] Melting points were taken on a Fisher-Johns block.

[12] The same procedure, using sulfuryl chloride, was applied advantageously to the synthesis of 2-nitrobenzenesulfenyl chloride, 2-chloro-4-nitrobenzenesulfenyl chloride and benzenesulfenyl chloride. Only very small amounts of pyridine are required in these preparations. In the case of benzenesulfenyl chloride, we prefer not to use any pyridine or solvent, since this gives a product which appears to have better keeping qualities. The excess sulfuryl chloride serves as a good solvent medium for the reaction.

[13] G. R. Waitkins and R. Shutt, *Inorganic Synthesis,* Vol. II, p. 186; John Wiley and Sons Inc., New York, N. Y.

[14] E. Fromm and Martin, *Ann.,* **401,** 177 (1917).

[15] D. F. Twiss, *J. Chem. Soc.,* **105,** 1672 (1914).

perature of acetone. After 9 hr., a weight loss of 22.65% was observed (calcd. for full conversion of I to II, 21.50%). The resulting orange solid was collected and recrystallized from carbon tetrachloride. The m.p. was 88–89°.

Anal. Calcd. for $C_6H_3(NO_2)_2SeCl$: Cl, 12.58. Found: Cl, 13.42.

2,4-Dinitrophenyl selenium trichloride (I) *from 2,4-dinitrobenzeneselenenyl chloride.* The orange monochloride (0.3330 g.) was placed in an atmosphere of dry chlorine for 3 days at room temperature. A weight gain of 7.80% was noted, and a somewhat amorphous material resulted. Recrystallization from carbon tetrachloride gave an orange product, which lost chlorine typically at 80–85°, and turned to an orange melt at 100°.

Anal. Calcd. for $C_6H_3N_2O_4SeCl_3$: Cl, 30.15. Found: Cl, 30.54.

Acetonyl 2,4-dinitrophenyl selenide. 2,4-Dinitrophenyl selenium trichloride (3.52 g., 0.01 mole) was added to 10 ml. of acetone. The mixture was refluxed for 5 min., filtered, cooled, and the yellow product collected and recrystallized from absolute ethanol. The product melted at 116–118°.

Anal. Calcd. for $C_9H_8N_2O_5Se$: N, 9.54. Found: N, 9.94.

Ethyl 2,4-dinitrobenzeneselenate. Into 10 ml. of absolute ethanol 3.52 g. (0.01 mole) of I was added. Addition of 1 ml. of dry pyridine caused formation of an orange color. The volume of the solution was reduced to one third on the steam bath and the remaining solution cooled, causing deposits of orange needles, which were collected and washed with a few ml. of absolute alcohol. After recrystallizing from absolute alcohol, the product melted at 128–129°, which corresponds exactly to the literature value[4] for the ethyl ester.

2,4-Dinitrobenzene selenenalide. Into 15 ml. of dry ether was added 3.52 g. (0.01 mole) of 2,4-dinitrophenyl selenium trichloride. One g. of dry aniline was then added slowly, whereupon a deep red color was noted. The volume was reduced by one fifth and the residue taken up in 50 ml. of 95% ethanol. This was treated with decolorizing charcoal, the mixture was reduced to about two thirds of the original volume and the remaining solution was cooled. The red-orange crystals were collected, washed, and dried; m.p. 187–189°.

Anal. Calcd. for $C_{12}H_9N_3O_4Se$: N, 12.41. Found: N, 12.59.

2-Chlorocyclohexyl, 2,4-dinitrophenyl selenide. Into 10 ml. of dry cyclohexene, was added 3.52 g. of 2,4-dinitrophenyl selenium trichloride (0.01 mole). The reaction mixture became warm and turned a deeper yellow color. It was let stand for one hour and then, by using a stream of dry air, the solvent was removed. The residue was taken up in 10 ml. of 95% ethanol, filtered, and the filtrate cooled, yielding, 1.10 g. of yellow needles, m.p. 114–115°.

Anal. Calcd. for $C_{12}H_{12}N_2O_4ClSe$: N, 7.74. Found: N, 7.47.

The x-ray powder patterns of the selenide and corresponding sulfide were practically identical, indicating similar space distribution of the substituents and size of unit cells; *Cf.* ref. 9.

4-Dimethylaminophenyl 2,4-dinitrophenyl selenide. This was prepared from reaction of I (3.5 g.) and dimethylaniline (2 ml.) dissolved in dry benzene (10 ml.) at room temperature. The solution was concentrated and the crude deep red product recrystallized from hot methanol, giving bright red needles, m.p. 194–196°.

Anal. Calcd. for $C_{14}H_{13}N_2O_4Se$: N, 11.28. Found: N, 10.88.

Spectra. The ultraviolet and infrared absorption spectra of the several pairs of sulfur and selenium compounds encountered in this work are recorded in a catalog of spectra being prepared for publication from this laboratory. The ultraviolet spectra of I and II are defined by the following absorption coefficients, at the wave lengths stated.

2,4-Dinitrobenzenesulfenyl chloride, in ethylene chloride solution; 4180 Å (max.)/2.4 × 10^3; 3660 Å (min.)/3.5 × 10^3; 3190 Å (max.)/8.9 × 10^3; 2930 Å (min.)/6.4 × 10^3; 2640 Å (max.)/10 × 10^3.

2,4-Dinitrophenyl selenium trichloride (in cyclohexane); 4180 Å (max.)/4.3 × 10^3; 3660 Å (min.)/2.4 × 10^3; 3235 Å (max.)/11.4 × 10^3; 2921 Å (min.)/5.0 × 10^3; 2640 Å (max.)/12.6 × 10^3; 2480 Å (min.)/11.5 × 10^3.

Acknowledgment. We are indebted to Mr. William R. Wilcox for assistance with experiments on the reactions of sulfuryl chloride with bis(2,4-dinitrophenyl) disulfide, to Dr. J. Donohue for help with the x-ray comparisons, to Dr. Adalbert Elek for microanalyses, and to the Office of Scientific Research, Air-Research and Development Command, for partial support of this study.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIF.

Amination of Tertiary Amines by Hydroxylamine-*O*-sulfonic Acid

HARRY H. SISLER, RICHARD A. BAFFORD,
GEORGE M. OMIETANSKI, BERNARD RUDNER,
AND RONALD J. DRAGO

Received November 3, 1958

The reaction of chloramine with tertiary amines to form 1,1,1, trisubstituted hydrazinium chlorides has been clearly established.[1] It seemed desirable to us to investigate the possibility of a similar reaction with another compound of the type NH_2X where X represents an electronegative group other than chlorine. We have, therefore, investigated the reactions of hydroxylamine-*O*-sulfonic acid (NH_2OSO_3H) with a variety of tertiary amines and have found that *N*-aminating reactions of the type

$$R_3N + NH_2OSO_3H \longrightarrow [R_3NNH_2^+]\,[HSO_4^-]$$

do indeed occur. The present communication reports the results of studies of a series of these reactions. Meuwsen and Gösl have very recently reported a similar reaction with trimethylamine and pyridine.[2]

Since our results show that the reaction of tertiary amines with hydroxylamine-*O*-sulfonic takes place in basic media and that it also occurs with the sodium salt, we may postulate the following equation for the reaction

$$R_3N + H_2NOSO_2O^- \longrightarrow R_3NNH_2^+ + SO_4^=$$

The question as to whether the sulfate or hydrogen sulfate crystallizes undoubtedly depends upon solubility factors as well as the basicity of the individual nitrogen base concerned. In the case of dimethylaniline the hydrogen sulfate is obtained. In all other cases studied where crystallization occurred the sulfate was obtained.

---

(1) G. Omietanski and H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

(2) A. Meuwsen and R. Gösl, *Angew. Chem.*, 69, 754 (1957).