Chemistry of Heterocyclic Compounds, Vol. 33, No. 4, 1997

2-SELENOPHENETHIOL AND 5-METHYLTHIO-2-SELENOPHENETHIOL: SYNTHESIS AND AUTOCONVERSIONS

V. Yu. Vvedenskii, E. D. Shtefan, R. N. Malyushenko,
and E. V. Shilkin

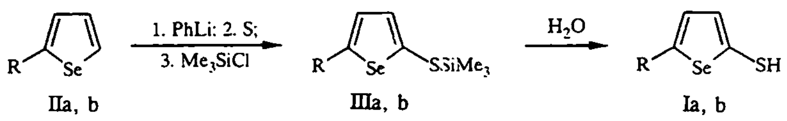
Selenophenethiols have been synthesized by a modified organolithium method. The structures of the products were established by their autothiylation and reaction with phenylhydrazine.

We showed previously that 2-thiophenethiol and 2-furanthiol autothiylate spontaneously into 4-(2-thienylthio)tetrahydrothiophene-2-thione and 4-(2-furylthio)tetrahydrofuran-2-thione respectively [1, 2]. The aim of the present work was to ascertain whether 2-selenophenethiol underwent a similar reaction.

Unsubstituted 2-selenophenethiol (Ia) was synthesized by the sequential treatment of 2-bromoselenophene with butyllithium, sulfur, and acid. The tendency of the product to thicken rapidly was noted. It was concluded on the basis of PMR and IR spectroscopy that thiol (Ia) exists in equilibrium with the tautomeric 5H-selenophene-2-thione [3].

Our attempts to synthesize thiol (Ia) by treating unsubstituted selenophene (IIa) with butyllithium and then sulfur with subsequent acidification proved unsuccessful. Neither the target product (Ia) nor the initial selenophene were detected in the reaction mixture. It is possible that this is linked with inadequate cooling at the lithiation step which leads to destruction of the selenophene ring.

The use of phenyllithium as lithiating agent proved to be more successful. After treating the lithium derivates of selenophene (IIa) with sulfur and alkylating the thiolate formed with methyl iodide 2-(methylthio)selenophene (IIb) was obtained in 37% yield. To synthesize 2-selenophenethiols (Ia, b) we treated a solution of the appropriate lithium 2-selenophenethiolate not with acid but with chlorotrimethylsilane which led to trimethylsilyl ether (IIIa, b) stable on storage. When needed the latter compound is converted readily and almost quantitatively into (Ia, b) by hydrolysis with a strictly stoichiometric quantity of water (this method was used by us previously when investigating the autoconversions of furanthiols and -selenols, and also of 2-thiopheneselenol [2, 4]).

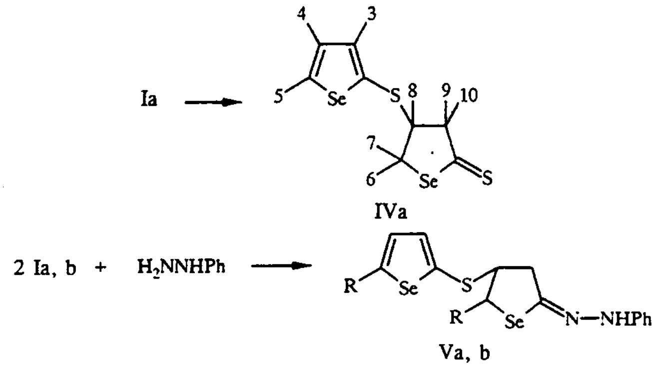


a R = H, b R = MeS

Investigation of a freshly distilled sample of compound (Ia) by PMR showed that in $CDCl_3$ it exists solely in the thiol form. Catalytic addition of HCl and warming to ~50°C only affected the position and width of the SH group signal.

On leaving in the air or by the action of a catalytic quantity of triethylamine the thiol (Ia) is autothiylated with the formation of 4-(2-selenienylthio)tetrahydroselenophene-2-thiol (IVa). The substituted thiol (Ib) is not converted under the conditions indicated into the analogous thione (IVb). However derivatives of the corresponding thiones (IVa) and (IVb), viz. the hydrazones (Va) and Vb), are obtained on treating compounds (Ia, b) with phenylhydrazine.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 500-502, April, 1997. Original article submitted July 4, 1996.



a R = H, b R = MeS

The results obtained previously in [1, 2] and in the present work therefore indicate that the autothiylation reaction is characteristic for 2-furan-, 2-thiophene-, and 2-selenophenethiol, although the first undergoes the conversion most readily.

EXPERIMENTAL

The ^1H NMR spectra were taken on Bruker WP 200 SY and Jeol FX 90 [for compounds (IIIa, b)] instruments in $CDCl_3$. The chromato-mass spectra were taken on an LKB 2091 instrument, 70 eV (capillary column, 25 m, SE-30).

Selenophene (IIa) was obtained by the known procedure of [5].

2-(Methylthio)selenophene (IIb). Selenophene (IIa) (15 g, 0.115 mole) was added dropwise to a solution of PhLi (0.110 mole) in ether (100 ml) and the reaction mixture stirred for 5 h at room temperature. The mixture was then cooled to −20°C, powdered sulfur (3.52 g, 0.110 mole) was added, and the temperature raised slowly to room temperature. After the sulfur had dissolved, the mixture was cooled to −70°C, and methyl iodide (15.62 g, 0.110 mole) added dropwise. The temperature of the reaction mixture was then raised to the boiling point, and the mixture boiled for ~1 h. After evaporation of the ether, the product (IIb) (7.56 g, 37% on the selenophene) was obtained by distillation, bp 88-90°C/16 mm Hg, which corresponds to literature data [6].

2-(Trimethylsilylthio)selenophene (IIIa). Selenophene (IIa) (6.7 g, 0.51 mole) was added dropwise to a solution of PhLi (0.051 mole) in ether (50 ml), the mixture was stirred for 5 h at room temperature, then cooled to −20°C. Powdered sulfur (1.6 g, 0.05 mole) was added and the temperature raised slowly to room temperature. After the sulfur had dissolved the mixture was cooled to −70°C, chlorotrimethyl-silane (5.9 g, 0.054 mole) was added dropwise, and the mixture left for 16 h at 0°C. The ether was then distilled off, the concentrate filtered, and the filtrate distilled in vacuum. Product (IIIa) (5.55 g, 56%) was obtained having bp 76-78°C/3 mm Hg, n_D^{22} 1.5673, d_4^{22} 1.2800. PMR spectrum: 0.3 (9H, s, $SiMe_3$); 7.15 (2H, m, 3- and 4-H); 7.86 ppm (1H, m, 5-H). Found, %: C 35.61; H 5.05; S 13.58; Se 33.72. $C_7H_{12}SSeSi$. Calculated, %: C 35.73; H 5.14; S 13.63; Se 33.56.

5-Methylthio-2-(trimethylsilylthio)selenophene (IIIb). Product (IIIb) was obtained in 15% yield from 2-(methylthio)selenophene (IIb) in the same way as for the synthesis of compound (IIIa), bp 118-120°C/1.5 mm Hg. PMR spectrum: 0.29 (9H, s, Me_3Si); 2.45 (3H, s, MeS); 6.95 ppm (2H, s, 3- and 4-H). Mass spectrum: 282 (M^+, 12), 73 ($SiMe_3$, 100). Found, %: C 33.98; H 4.95; S 22.87; Se 28.21. $C_8H_{14}S_2SeSi$. Calculated, %: C 34.15; H 5.01; S 22.79; Se 28.06.

2-Selenophenethiol (Ia). A solution (9 μl) of 0.005 N HCl (~0.0005 mole H_2O) was added to compound (IIIa) (0.24 g, 0.001 mole) and the mixture stirred vigorously for ~30 min on a magnetic stirrer. The yield of product (Ia) was almost quantitative. A sample of thiol (Ia) was purified from hexamethyldisiloxane and contaminants by distillation of the reaction mixture [obtained from a larger quantity of selenophene (IIIa)], bp 65-67°C/1 mm Hg. Literature bp 50°C/0.6 mm Hg [3]. PMR spectrum: 3.71 (1H, d.d, $J_{SH,3}$ = 1.2, $J_{SH,5}$ = 0.5 Hz, SH); 7.12 (1H, d.d, J_{34} = 3.7, J_{45} = 5.9 Hz, 4-H); 7.23 (1H, d.t, J_{35} = 1.2 Hz, 3-H); 7.94 ppm (1H, d.d.d, 5-H).

5-Methylthio-2-selenophenethiol (Ib) was obtained by hydrolysis of ether (IIIb) as described for compound (IIIa). Yield was ~100%. PMR spectrum: 2.50 (3H, s, MeS); 4.75 (1H, s, SH); 7.07 ppm (2H, s, 3- and 4-H). Found, %: C 28.59; H 2.82; S 30.75; Se 37.91. $C_5H_6S_2Se$. Calculated, %: C 28.71; H 2.89; S 30.66; Se 37.74.

4-(2-Selenienylthio)tetrahydroselenophene-2-thione (IVa). A. Compound (Ia) was left for several days in an open flask. The time was shortened significantly by adding a catalytic quantity of triethylamine. The yield of product (IVa) was practically quantitative (according to PMR data).

B. The stoichiometric quantity of water was added to thiol (IIIa) followed by triethylamine (1 drop). The latter simultaneously acts as a catalyst for the hydrolysis of compound (IIIa) and for the subsequent autoconversion of thiol (Ia). The PMR spectrum of the obtained mixture contains signals for product (IVa): 2.9 (1H, d.d, $J_{7,10}$ = 9.5, $J_{9,10}$ = 18 Hz, 10-H); 3.4 (1H, d.d, J_{89} = 5.3 Hz, 9-H); 3.7-4.0 (3H, m, 6-, 7-, and 8-H); 7.22 (2H, m, 3- and 4-H); 8.15 ppm (1H, m, 5-H) and also a signal for the protons of HMDS at 0.05 (s, Me_3Si) and of trimethylsilanol at 0.14 (s, Me_3Si) and 1.7 (s, OH). Thiol (IVa) was obtained by evacuating the mixture. Found, %: C 29.48; H 2.43; S 19.83; Se 48.36. $C_8H_8S_2Se_2$. Calculated, %: C 29.46; H 2.47; S 19.66; Se 48.41.

4-(2-Selenienylthio)-2-phenylhydrazonotetrahydroselenophene (Va). Water (45 μl, 0.0026 mole) and phenylhydrazine (0.23 g, 0.0026 mole) were added to selenophene (IIa) (1.2 g, 0.0051 mole). After evolution of hydrogen sulfide had ceased (slight warming of the reaction mixture) the viscous product (Va) was obtained and was purified by keeping in vacuum (1 mm Hg) for 30 min. Yield was ~100% (according to PMR data). PMR spectrum: 2.8 (1H, d.d, $J_{8,10}$ = 10, $J_{9,10}$ = 15.5 Hz, 10-H); 3.1-3.6 (4H, m, 6-, 7-, 8-, and 9-H); 6.1 (1H, s, NH); 6.8-7.2 (6H, m, 3-H and $5H_{Ph}$); 7.35 (1H, d.d, 4-H); 8.12 ppm (1H, d.d, 5-H). Found, %: C 41.88; H 3.48; S 8.15; Se 39.26. $C_{14}H_{14}N_2SSe_2$. Calculated, %: C 42.01; H 3.53; N 7.00; S 8.01; Se 39.45.

4-(5-Methylthio-2-selenienylthio)-2-phenylhydrazono-5-(methylthio)tetrahydroselenophene (Vb). Product (Vb) was obtained analogously to compound (Va) from thiol (Ib) and was a viscous mass. Yield ~100%. PMR spectrum (acetone-D_6): 2.2 (3H, s, 6-MeS); 4.92 (1H, d, 7-H); 3.77 (1H, m, J_{89} = 6, $J_{8,10}$ = 6.5 Hz, 8-H); 3.42 (1H, d.d, $J_{9,10}$ = 16 Hz, 9-H); 3.00 (1H, d.d, 10-H); 2.58 (3H, s, 5-MeS); 6.7-7.3 (7H, m, 4-H and $5H_{ph}$); 7.7 ppm (1H, s, NH). Found, %: C 39.07; H 3.61; N 5.51; S 19.60; Se 32.15. $C_{16}H_{18}N_2S_3Se_2$. Calculated, %: C 39.02; H 3.68; N 5.69; S 19.53; Se 32.07.

REFERENCES

1. V. Yu. Vvedenskii, S. V. Zinchenko, T. A. Shkarupa, N. A. Korchevin, É. N. Deryagina, and M. G. Voronkov, Dokl. Akad. Nauk SSSR, **305**, 624 (1989).
2. V. Yu. Vvedenskii, E. D. Shtefan, R. N. Malyushenko, and É. N. Deryagina, Khim. Geterotsikl. Soedin., No. 7, 891 (1994).
3. J. Morel, C. Paulmier, D. Semard, and P. Pastour, Bull. Soc. Chim. France, No. 10, 3547 (1971).
4. V. Yu. Vvedenskii, S. V. Zinchenko, E. D. Shtefan, M. V. Ul'ev, A. R. Zhnikin, T. A. Shkarupa, É. N. Deryagina, and M. G. Voronkov, Dokl. Akad. Nauk, **320**, 96 (1991).
5. N. A. Korchevin, M. A. Ostroukhova, E. N. Sukhomazova, A. R. Zhnikin, É. N. Deryagina, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 2, 279 (1987).
6. J. Morel, C. Paulmier, M. Garreau, and G. Martin, Bull. Soc. Chim. France, No. 12, 4497 (1971).