

SHORT
COMMUNICATIONS

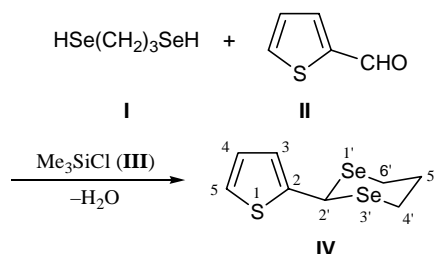
Synthesis of 2-(1,3-Diselenan-2-yl)thiophene from 1,3-Propanediselenol and 2-Thiophenecarbaldehyde

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We previously reported on reactions of aldehydes of the thiophene series in the system thiol–chlorotrimethylsilane [1], which lead to formation of thioacetals, while there are no published data on reactions of 1,3-propanediselenol with 2-thiophenecarbaldehyde and its analogs. We were the first to reveal that 1,3-propanediselenol (**I**) reacts with 2-thiophenecarbaldehyde (**II**) in chlorotrimethylsilane (**III**) to give a new heterocyclic compound, 2-(1,3-diselenan-2-yl)thiophene (**IV**). The yield of **IV** depends on the order of mixing of the reactants.



2-(1,3-Diselenan-2-yl)thiophene (IV). *a.* 1,3-Propanediselenol (**I**), 1.8 g (0.0089 mol), was added dropwise at -3 to -5°C to a solution of 0.996 g (0.0089 mol) of 2-thiophenecarbaldehyde (**II**) in 10.2 ml (0.08 mol) of chlorotrimethylsilane (**III**). The mixture was stirred for 1 h at 0°C and was allowed to warm up to room temperature. The progress of the reaction was monitored by GLC. The grey precipitate, 1 g, was filtered off and repeatedly washed with chloroform; the fractions were combined and evaporated under reduced pressure. The residue was crude 2-(1,3-diselenan-2-yl)thiophene (**IV**) as a brown crystalline substance, 0.49 g (18.6%). It was treated with hexane, the solution was cooled, and the precipitate was filtered off to obtain 0.32 g (12.1%)

of pure compound **IV** as light cream crystals with mp 89°C . IR spectrum, ν , cm^{-1} : 3071 (C–H, thiophene); 2922, 2887 (C–H, CH_2); 1419, 1242, 1213, 1032 ($\delta\text{C–H}$, CH_2); 971 ($\delta\text{C–H}$, thiophene); 843 (C–Se). ^1H NMR spectrum, δ , ppm: 6.91 d.d (1H, 4-H, $^3J_{4,3} = 3.3$, $^3J_{4,5} = 5.0$ Hz), 7.11 d (1H, 3-H), 7.22 d (1H, 5-H), 2.07 d.t.t (1H, 5'- H_{ax} , $^2J_{5'-ax, 5'-eq} = 14.25$, $^3J_{5'-ax, 4'(6')-ax} = 11.45$, $^3J_{5'-ax, 4'(6')-eq} = 2.40$ Hz), 2.22 d.t.t (1H, 5'- H_{eq} , $^3J_{5'-eq, 4'(6')-eq} = 5.9$, $^3J_{5'-eq, 4'(6')-ax} = 2.8$ Hz), 2.95 d.d.d [2H, 4'(6')- H_{eq} , $^2J_{4'(6')-eq, 4'(6')-ax} = 13.4$ Hz], 3.11 d.d.d [2H, 4'(6')- H_{ax}], 5.69 s (1H, 2- H_{ax}); the ^1H NMR parameters of the 1,3-diselenane fragment correspond to a six-membered ring in a *chair* conformation with equatorial orientation of the phenyl substituent. ^{13}C NMR spectrum, δ , ppm: 25.26 ($\text{C}^{4(6')}$), 25.05 ($\text{C}^{5'}$), 20.92 ($\text{C}^{2'}$), 126.75 ($\text{C}^{5'}$), 125.84 ($\text{C}^{4'}$), 125.03 ($\text{C}^{3'}$), 144.66 ($\text{C}^{2'}$). Mass spectrum, m/z (I_{rel} , %) (^{80}Se): 298 (4) [M^+], 176 (100), 137 (41), 95 (6), 45 (3), 39 (15). Found, %: C 32.72; H 3.73; S 11.18; Se 52.94. $\text{C}_8\text{H}_{10}\text{SSe}_2$. Calculated, %: C 32.43; H 3.38; S 10.81; Se 53.38.

b. A mixture of 0.773 g (0.0069 mol) of compound **II** and 3.5 ml (0.0274 mol) of silane **III** was cooled to 0 – 5°C and was added dropwise to 1.39 g (0.0069 mol) of diselenol **I** cooled to 0°C . The mixture was kept at 3 – 5°C , and a solid began to precipitate in 20 min. The mixture was kept at that temperature over a period of 1 h with intermittent shaking and was then allowed to warm up to room temperature. The precipitate was filtered off and treated as described above in *a*. We thus obtained 0.69 g (34.0%) of pure product **IV**.

Diselenol **I** was synthesized by reductive cleavage of poly(trimethylenediselenide) $\text{Br}[\text{SeCH}_2\text{CH}_2\text{CH}_2\text{Se}]_n\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ in a system hydrazine hydrate–base (by analogy with alkanedithiols [2]).

The ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400.1 and 100.6 MHz, respectively, using CDCl_3 as solvent and HMDS as internal reference. The IR spectrum was measured on a Bruker IFS-25 instrument in KBr. The mass spectrum (electron impact, 57 eV) was obtained on an LKB-2091 mass spectrometer with direct sample admission into the ion source.

REFERENCES

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2. Alekminskaya, O.V., Russavskaya, N.V., Korchevin, N.A., Deryagina, E.N., and Trofimov, B.A., *Russ. J. Gen. Chem.*, 2000, vol. 70, p. 732.