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SELENOPHENE CHEMISTRY

LIX. Synthesis of Mono-, Di-, and Tetradeuteroselenophenes*

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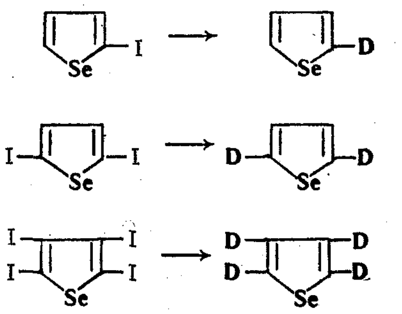
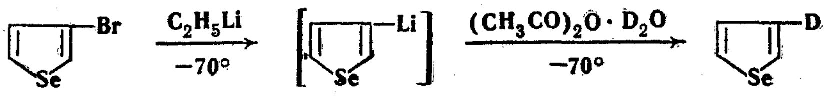
2-Deutero-, 2,5-dideutero- and 2,3,4,5-tetradeuteroselenophenes are synthesized by reducing 2-iodo-, 2,5-diiodo- and 2,3,4,5-tetraiodoselenophene respectively with zinc and deuterated acetic acid, and 3-deuteroselenophene is prepared by hydrolysis of 3-selenienyllithium with the same acid.

Study of the microwave spectra of thiophene and its deuterated derivatives enabled peculiarities in the electronic spectra of thiophene to be established [2,3]. It was of interest to obtain the corresponding data for selenophene, too.

Mono-, di-, and, tetradeuteroselenophenes were synthesized in order to investigate their vibration spectra. 2-Deutero-, 2,5-dideutero-, and 2,3,4,5-tetradeuteroselenophene were prepared by reducing the corresponding iodo derivatives with zinc and deuterated acetic acid.



3-Deuteroselenophene was synthesized by hydrolyzing 3-selenienyllithium with acetic acid at – 70° C.



2,3,4,5-Tetraiodoselenophene was prepared by an exchange reaction between 2,3,4,5-tetrachloromercuriselenophene and potassium iodide and iodine.

The purities of the deuteroselenophenes prepared were shown from data relating to the intensities of peaks in IR and Raman spectra [4,5]. The deuterium contents of the deuteroselenophenes were determined by the drop method [6], and the results obtained are given in the table.

Experimental

2-Deuteroselenophene. 25 g D_2O, 7 g Ac_2O (freshly distilled over P_2O_5), 13 g 2-iodoselenophene [7] and 16 g Zn dust (dried over P_2O_5) were heated together for 6 hr on a boiling water-bath, the 2-deuteroselenophene was steam-distilled off, dried over $MgSO_4$, and distilled over Na. Yield 4.4 g (66.5%), bp 107°–108° C (757 mm); n_D^{20} 1.5710, d_4^{20} 1.5413. Raman spectrum data showed the reaction product to contain ~6% undeuterated selenophene.

2,5-Dideuteroselenophene. 47 g D_2O, 13 g Ac_2O, 34.5 g 2,5-diiodoselenophene [8], and 30 g Zn dust, were heated together for 10 hr on a boiling water-bath, the 2,5-dideuteroselenophene steam-distilled off, dired over $MgSO_4$, and distilled over Na. Yield 7 g (59.5%), bp 107°–107.5° C 753 mm); n_D^{20} 1.5726; d_4^{20} 1.5440. It contained ~8% 2-dideuteroselenophene.

2,3,4,5-Tetraacetoxymercuriselenophene. 213 g HgO in 325 ml AcOH was boiled and stirred, and a solution of 30 g selenophene in 115 ml AcOH added, the whole heated for 15 min on a boiling water-bath, left for 10 hr at 20° C, 500 ml water added, and the whole left for 24 hr. The precipitate was washed with water until it gave a negative reaction for Hg, then dried at 130° C. Yield 233.7 g (79%); mp 238° C (ex AcOH). Found: C 12.43, 12.28; H 1.56, 1.38;

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* For Part LVIII see [1].

Hg 68.50, 68.70%. Calculated for $C_{12}H_{12}O_8Hg_4Se$: C 12.36; H 1.04; Hg 68.84%.

2, 3, 4, 5-Tetrachloromercuriselenophene. A boiling saturated aqueous solution of 40 g NaCl was added to 233.7 g tetraacetoxymercuriselenophene, and the whole stirred for 4 hr while heated on a water-bath. The solid was separated off, washed with water, and dried at 130° C. Yield 189 g (94.5%); mp 213° C (ex AcOH). Found: C 4.01, 4.19; Hg 74.51, 74.79%. Calculated for $C_4Cl_4Hg_4Se$: C 4.48: Hg 74.90%.

Deuterium Contents of Deuteroselenophenes

Deuteroselenophene	D content of water of combustion (% D per mole)	D content of deuteroselenophene (% D per bond)
2-Deuteroselenophene	22.75 23.25 Mean 23.0	92.0
2, 5-Dideuteroselenophene	46.5 47.5 Mean 47.0	94.0
3-Deuteroselenophene	21.80 22.70 Mean 22.25	90.0
2, 3, 4, 5-Tetradeuteroselenophene	96.10 96.90 Mean 96.5	96.5

2, 3, 4, 5-Tetraiodoselenophene. 188.9 g tetrachloromercuriselenophene was stirred at 20° C with 200 g iodine and 400 g KI in 250 ml water until decolorization ensued (~7 hr). The precipitate was washed with saturated KI solution, yield 94 g (75%); mp 203° C (ex dioxane). Found: C 8.06, 7.99%. Calculated for C_4I_4Se: C 7.67%.

2, 3, 4, 5-Tetradeuteroselenophene. 94 g tetraiodoselenophene, 70 g Zn dust, 110 g D_2O, and 62 g Ac_2O were heated together for 20 hr at 130° C, the tetradeuteroselenophene was steam-distilled off, dried over $MgSO_4$, and distilled over Na. Yield 17.1 g (85.5%), bp 108°–108.5° C (743 mm); n_D^{20} 1.5765; d_4^{20} 1.6072, containing about 5% of hydrogen-containing deuteroselenophenes.

3-Deuteroselenophene. 5 g Li was stirred in 300 ml dry ether under nitrogen, and 30.3 g EtBr in 50 ml dry ether added. The EtLi solution was filtered under nitrogen, cooled to –70° C, stirred, and 21 g 3-bromoselenophene [9] in 100 ml dry ether added, along with a solution of deuterated AcOH (prepared by heating 13 g D_2O and 48 g Ac_2O) in 100 ml dry ether. The mixture was stirred for 30 min more at –70° C, allowed to warm up to 10° C, for example, and 150 ml water added. The ether layer was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$, and a cut boiling up to 112° C taken, and then distilled over Na, to give 3 g (22.5% or 70% on the 3-bromoselenophene used), bp 108°–109° C (749 mm); n_D^{20} 1.5699; d_4^{20} 1.5467; contained about 10% undeuterated selenophene.

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