CHEMISTRY OF BENZO[b]SELENOPHENE

V.* MERCURATION OF BENZO[b]SELENOPHENE

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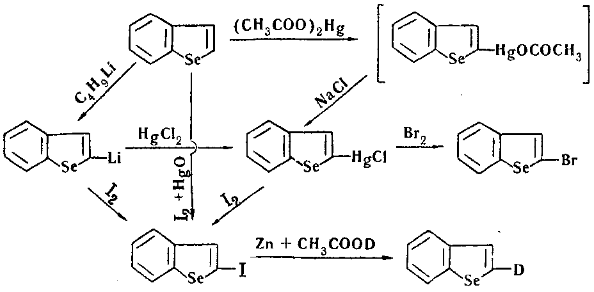
The mercuration of benzo[b]selenophene by mercuric acetate proceeds to form the 2-mercuri derivative, while 2-methyl- and 3-methylbenzo[b]selenophenes give 3-mercuri-2-methyl and 2-mercuri-3-methyl derivatives of benzo[b]selenophene, respectively. The corresponding deutero derivatives of benzo[b]selenophene were obtained by substitution of the chloromercuri group by iodine with subsequent reduction by zinc in deuterated acetic acid.

We have previously shown that the bromination, like acylation [1], of benzoselenophene proceeds to form a mixture of approximately equal amounts of the corresponding 2- and 3-substituted derivatives. In the present paper, we have investigated the mercuration of benzoselenophene and its methyl derivatives under various conditions. We found that the mercuration of this condensed heteroaromatic system with mercuric acetate in methanol at 20°C proceeds at the 2 position, while the mercuration of the isomeric 2- and 3-methylbenzoselenophenes proceeds at the free position of the selenophene ring. Chloromercuribenzo[b]selenophene, obtained by the reaction of acetoxymercuribenzoselenophene with NaCl, was converted to the corresponding halo derivatives by the action of bromine in carbon tetrachloride and of iodine in chloroform. The bromobenzo[b]selenophene obtained by this route proved to be identical to the 2-bromobenzo[b]selenophene previously synthesized [1] through the lithium derivative.

Iodobenzo[b]selenophene was reduced with zinc in deuterated acetic acid to give a deuterobenzoselenophene that proved to be identical to the 2-deuterobenzo[b]selenophene previously obtained [2] through the lithium derivative. The mercuration of the lithium derivative of benzo[b]selenophene with mercuric chloride in absolute ether gave a chloromercuribenzoselenophene that was identical to the monochloromercuri derivative obtained by the direct mercuration of benzo[b]selenophene.



The structures of the mercury derivatives of the isomeric 2-methyl- and 3-methylbenzo[b]selenophenes were proved similarly – by conversion to the corresponding halo and deutero derivatives, which

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*See [1] for communication IV.

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proved to be identical to the corresponding derivatives of methylbenzoselenophene with known positions of the substituents in the selenophene ring.

It was established that the mercuration of 3-methylbenzo[b]selenophene in the 2 position of the selenophene ring proceeds ~10 times faster than mercuration of 2-methylbenzo[b]selenophene in the 3 position. This is in agreement with the fact that the mercuration of unsubstituted benzo[b]selenophene under these conditions proceeds at the α-position of the selenophene ring.

We also accomplished the direct iodination of benzo[b]selenophene and 2-methylbenzo[b]selenophene with iodine in the presence of mercuric oxide; however, it is more expedient to obtain 2-iodobenzo[b]selenophene by the action of iodine on the lithium derivative of benzoselenophene.

The PMR spectrum of 2-chloromercuribenzo[b]selenophene (Fig. 1 and Table 1) in the region of the aromatic protons contains an intense singlet from the unsubstituted proton of the selenophene ring with a chemical shift of 7.68 ppm. Considering that the chloromercuri fragment unshields the signal of the adjacent proton in 2-chloromercuriindole by − 0.23 ppm [3], this singlet can be unambiguously assigned to the signal of an unsubstituted proton in the 3-position of the benzo[b]selenophene molecule.

A similar shift is observed in the PMR spectrum of 2-iodobenzoselenophene (Fig. 2). The shift in the H_3 signal to weak field under the influence of the adjacent iodine atom (− 0.34 ppm) is comparable to the similar shift of the adjacent proton in iodobenzo[b]thiophene [4] (− 0.34 ppm).

EXPERIMENTAL

2-Methyl-3-acetoxymercuribenzo[b]selenophene. A solution of 15.8 g (0.045 mole) of mercuric acetate in ethanol was added to a solution of 8.71 g (0.045 mole) of 2-methylbenzo[b]selenophene in 50 ml of alcohol, and the mixture was allowed to stand at 20° for 20 days. The reaction mixture was then poured into water (~1 liter), and the precipitate was washed with water to give 18.92 g (93%) of 2-methyl-3-acetoxymercuribenzo[b]selenophene as colorless crystals with mp 144.5-145° (from toluene). Found: C 29.1; H 2.5%. $C_{11}H_{10}O_2HgSe$. Calculated: C 29.1; H 2.2%.

2-Methyl-3-chloromercuribenzo[b]selenophene. A mixture of 1 g (0.002 mole) of 2-methyl-3-acetoxymercuribenzo[b]selenophene and 0.41 g (0.007 mole) of sodium chloride in 10 ml of alcohol was heated to the boiling point. The mixture was then cooled to room temperature and poured into water (~100 ml). The precipitate was removed by filtration and washed with water to give 0.95 g (94%) of 2-methyl-3-chloromercuribenzo[b]selenophene as colorless crystals with mp 232-233° (from toluene). Found: C 25.3; H 1.7%. $C_9H_7ClHgSe$. Calculated: C 25.1; H 1.6%.

2-Chloromercuri-3-methylbenzo[b]selenophene. Treatment of 1.5 g (0.008 mole) of 3-methylbenzo[b]selenophene and 2.85 g (0.008 mole) of mercuric acetate in 10 ml of alcohol at 20° for 2 days according to the method described for the synthesis of 2-chloromercuribenzo[b]selenophene gave 3.22 g (93.5%) of 2-chloromercuri-3-methylbenzo[b]selenophene as colorless crystals with mp 214-214.2° (from tuluene). Found: C 25.2; H 2.0%. $C_9H_7ClHgSe$. Calculated: C 25.1; H 1.6%.

2-Chloromercuribenzo[b]selenophene. A) A methanol solution of 19.2 g (0.06 mole) of mercuric acetate was added to a solution of 10.86 g (0.06 mole) of benzo[b]selenophene in 50 ml of methanol, and the mixture was allowed to stand at 20° for 4 days. Sodium chloride [4.1 g (0.07 mole)] was added, and the mixture was heated to the boiling point. The mixture was then cooled to 20° and poured into 1 liter of water. The precipitate was removed by filtration and washed with water (until it gave a negative reaction for Hg^{2+}) to give 22 g (88%) of 2-chloromercuribenzo[b]selenophene as colorless crystals with mp 252-253° (from toluene).

B) A solution of 1.81 g (0.01 mole) of benzo[b]selenophene in 50 ml of absolute ether was added at − 70° with stirring under nitrogen to an ether solution of n-butyllithium, obtained from 0.46 g (0.066 g-atom) of lithium and 2.8 g (0.03 mole) of n-butyl chloride. The mixture was stirred at − 70° for 30 min and for another 30 min at 35°. The ether solution was filtered under nitrogen and added to 4.1 g (0.015 mole) of mercuric chloride. The mixture was stirred for 35° for 1 h, the ether was removed by distillation, and the residue was washed with water and dried. Vacuum sublimation gave 1.1 g of unchanged benzo[b]selenophene. Crystallization of the residue from toluene gave 0.75 g (46%) of 2-chloromercuribenzo[b]selenophene with mp 252-253°. Found: C 23.1; H 1.2%. $C_8H_5ClHgSe$. Calculated: C 23.1; H 1.2%.

TABLE 1. Chemical Shifts of the Protons of a Number of Benzo[b]selenophenes

Substituent	Solvent	δ, ppm	
		$H_{(2)}$	$H_{(3)}$
H	CCl_4	7,76	7,36
2-I	CCl_4	—	7,70
2-HgCl	$(CH_3)_2SO$	—	7,65
H	$(CH_3)_2SO$	8,15	7,60

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*The chemical shifts are given on the δ scale [the values were obtained by the addition of 0.05 to the chemical shift relative to hexamethyldisiloxane (HMDS)]; the spectra were recorded with an RS-60 spectrometer.

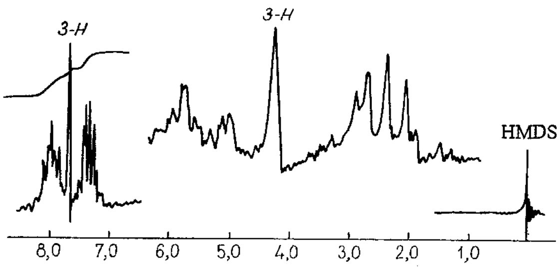

Fig. 1

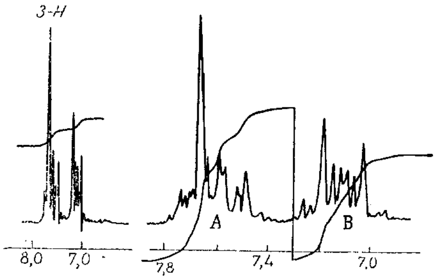

Fig. 2

Fig. 1. PMR spectrum of 2-chloromercuribenzo[b]selenophene [10% solution in dimethylsulfoxide with hexamethyldisiloxane (HMDS) as the internal standard].

Fig. 2. PMR spectrum of 2-iodobenzo[b]selenophene (10% solution in carbon tetrachloride with HMDS as the internal standard).

2-Bromobenzo[b]selenophene. A solution of 0.39 g (0.005 mole) of bromine in 50 ml of carbon tetrachloride was added with stirring in the course of 15 min to 2 g (0.005 mole) of 2-chloromercuribenzo[b]selenophene. The mixture was filtered, and the residue was crystallized from toluene to give 0.83 g of unchanged 2-chloromercuribenzo[b]selenophene. Removal of the carbon tetrachloride by distillation gave 0.55 g (73%) of 2-bromobenzo[b]selenophene with mp 58° (from petroleum ether) (mp 58° [1]).

2-Iodobenzo[b]selenophene. A) A solution of 2.54 g (0.001 mole) of iodine in 500 ml of chloroform was added with stirring in the course of 1 h to 4.16 g (0.001 mole) of 2-chloromercuribenzo[b]selenophene. The mixture was filtered, and the chloroform was removed by distillation to give 2.65 g (86%) of 2-iodobenzo[b]selenophene as colorless crystals with mp 70° (from petroleum ether).

B) A 3.3 g (0.013 mole) sample of finely ground iodine and 1.42 g (0.0066 mole) of mercuric oxide were added alternately in small portions in the course of 2 h to a refluxing solution of 2.4 g (0.0133 mole) of benzo[b]selenophene in 50 ml of benzene. The mixture was stirred and refluxed for another 3 h and filtered. The benzene was removed by distillation, and the residue was fractionally sublimed in vacuo to give 1.2 g of unchanged benzo[b]selenophene and 0.2 g (10%) of 2-iodobenzo[b]selenophene with mp 70° (from petroleum ether).

C) An ether solution of 3.62 g (0.04 mole) of benzo[b]selenophene was added under nitrogen at −70° to an ether solution of n-butyllithium from 1.4 g (0.2 g-atom) of lithium and 10.7 ml (0.1 mole) of n-butyl bromide. The mixture was stirred for 30 min at −70° and for another 15 min at 35°. The mixture was then cooled to −70°, and a solution of 12.7 g (0.1 mole) of iodine in 300 ml of absolute ether was added. The mixture was stirred for 30 min and filtered. The ether was removed by distillation, and the residue was chromatographed with a column filled with silica gel with elution by petroleum ether to give 4 g (65%) of 2-iodobenzo[b]selenophene with mp 70° (from petroleum ether) and R_f 0.56 on Silufol in heptane. Found: C 31.6; H 1.9%. C_8H_5ISe. Calculated: C 31.3; H 1.6%.

2-Methyl-3-iodobenzo[b]selenophene. A) A 2 g (0.009 mole) sample of mercuric oxide and 3.8 g (0.015 mole) of iodine were added alternately in small portions in the course of 2 h to a refluxing solution of 2.9 g (0.015 mole) of 2-methylbenzo[b]selenophene in 25 ml of n-hexane. The mixture was refluxed and stirred for 28 h. Carbon tetrachloride (50 ml) was added, and the mixture was filtered. The filtrate was washed with 2% sodium thiosulfate solution and water and dried with sodium sulfate. The solvent was removed by distillation, and the residue was fractionally sublimed in vacuo to give 1.7 g of unchanged 2-methylbenzo[b]selenophene and 0.15 g (7.5%) of colorless plates of 2-methyl-3-iodobenzo[b]selenophene with mp 63-63.5° (from methanol).

B) A solution of 7.1 g (0.028 mole) of iodine in 500 ml of chloroform was added to 9.3 g (0.028 mole) of 2-methyl-3-chloromercuribenzo[b]selenophene. After 1 h, the mixture was filtered, and the chloroform was removed from the filtrate by distillation to give 6.17 g (90.7%) of 2-methyl-3-iodobenzo[b]selenophene with mp 63-63.5° (from petroleum ether). Found: C 33.7; H 2.2%. C_9H_7ISe. Calculated: C 33.7; H 2.2%.

3-Methyl-2-iodobenzo[b]selenophene. A total of 0.88 g (61%) of 3-methy-2-iodobenzo[b]selenophene was obtained from 2 g (0.004 mole) of 3-methyl-2-chloromercuribenzo[b]selenophene and 1 g (0.004 mole) of iodine by the method (B) described for the synthesis of 2-methyl-3-iodobenzo[b]selenophene. The product was obtained as light yellow crystals with mp 79.5-80° (from petroleum ether). Found: C 33.6; H 2.2%. C_9H_7ISe. Calculated: C 33.7; H 2.2%.

2-Deuterobenzo[b]selenophene. A mixture of 2.5 g (0.125 mole) of deuterium oxide, 0.7 g (0.007 mole) of freshly distilled (over P_2O_5) acetic anhydride, 1.5 g (0.005 mole) of 2-iodobenzo[b]selenophene, and 1.6 g (0.025 g-atom) of dried (over P_2O_5) zinc dust was heated for 6 h on a boiling-water bath. The mixture was cooled and poured into ice water. The aqueous mixture was extracted with ether, and the ether extract was dried with sodium sulfate. The ether was removed by distillation to give 0.8 g (89%) of the deutero compound with mp 50° (vacuum sublimation) (mp 50° [1]).

2-Methyl-3-deuterobenzo[b]selenophene. A total of 2.24 g (93.8%) of 2-methyl-3-deuterobenzo[b]-selenophene was obtained from 3.65 g (0.0114 mole) of 2-methyl-3-iodobenzo[b]selenophene, 1.3 ml (0.014 mole) of acetic anhydride, 2.3 ml (0.125 mole) of deuterium oxide, and 3.2 g (0.25 g-atom) of Zn by the method described for the synthesis of 2-deuterobenzo[b]selenophene. The product was obtained as colorless crystals with mp 61° (vacuum sublimation) (mp 61° [2]).

3-Methyl-2-deuterobenzo[b]selenophene. A total of 2.19 g (92%) of 3-methyl-2-deuterobenzo[b]selenophene was obtained from 3.21 g (0.01 mole) of 3-methyl-2-iodobenzo[b]selenophene, 1.2 g (0.013 mole) of acetic anhydride, 2.06 ml (0.12 mole) of deuterium oxide, and 2.6 g (0.04 g-atom) of zinc dust by the method described for the synthesis of 2-deuterobenzo[b]selenophene. The product had bp 131° (13 mm) and n_D^{20} 1.6570 (n_D^{20} 1.6570 [2]).

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