RECYCLIZATION OF SELENOPHENOPYRYLIUM SALTS IN ALKALINE MEDIA

V. I. Dulenko, N. N. Alekseev,
and L. M. Kapkan

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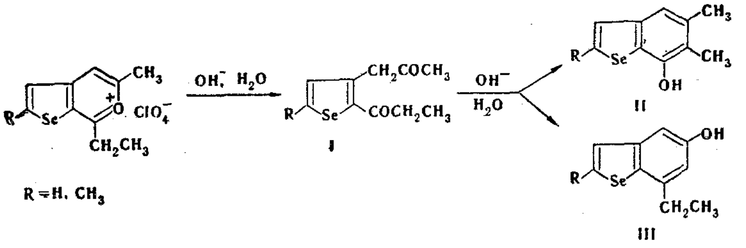
Hydroxy derivatives of benzoselenophene that contain a hydroxyl group in the benzene ring are formed by the action of aqueous alcoholic sodium hydroxide on selenophenopyrylium perchlorates. The structure of the synthesized compounds was proved by IR and NMR spectroscopy.

Selenophenopyrylium salts [1,2] display the high reactivity characteristic for pyrylium salts [3, 4]. Thus they are converted to selenophenopyridines by the action of ammonia [1,2], while treatment of them with secondary amines gives dialkylamino derivatives of benzoselenophene [5]. It seemed of interest to study the recyclization of selenophenopyrylium salts in alkaline media and, as in the case of thienopyrylium salts [6], to obtain the corresponding hydroxy derivatives. In fact, 7-hydroxy derivatives of benzoselenophene were isolated by heating aqueous alcohol solutions of selenopheno[2,3-c]pyrylium salts in the presence of excess sodium hydroxide. Considering the fact that the reaction proceeds through the intermediate formation of a diketone (I) and subsequent intramolecular crotonic condensation with the possible formation of isomeric products II and III, the position of the hydroxy group was proved by a study of the NMR spectra of the hydroxybenzoselenophenes obtained from 7-ethyl-substituted selenopheno[2,3-c]-pyrylium salts.



When R = H, the presence of two singlets (2.22 and 2.34 ppm) and the regions of their chemical shifts, which coincide well with the known data on the chemical shifts of the methyl groups of toluenes [7], make it possible to unambiguously assign the spectra to structure II. In the opposite case (structure III), the NMR spectra should have contained a triplet and quartet of signals of the ethyl group, which are due to the spin–spin coupling between the methyl and methylene groups [8, 9]. The NMR spectra when R = CH_3 give three singlets; this is also in agreement with structure II. Under similar conditions, selenopheno[3,2-c]-pyrylium salts form 4-hydroxy derivatives of benzoselenophene in the same yields (40-60%). As in the case of the preparation of 7-hydroxy derivatives of benzoselenophene, the position of the hydroxy group

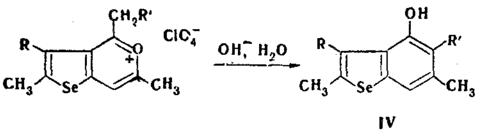


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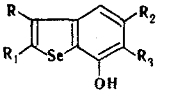
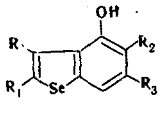
TABLE 1. 4- and 7-Hydroxybenzoselenophenes



I-IV



V-VII

Comp.	R	R_1	R_2	R_3	mp, °C[a]	R_f[b]	Empirical formula	Found, %			Calc., %			Yield, %
								C	H	Se	C	H	Se	
I	H	CH_3	CH_3	H	113—114	0,86	$C_{10}H_{10}OSe$	53,6	4,5	34,8	53,3	4,4	35,1	63,8
II	H	CH_3	CH_3	CH_3	150—151	0,89	$C_{11}H_{12}OSe$	55,5	5,2	32,8	55,3	5,0	33,0	51,3
III	H	H	CH_3	CH_3	102—103	0,87	$C_{10}H_{10}OSe$	53,6	4,7	34,8	53,3	4,4	35,1	22,6
IV	H	H	CH_3	H	71—73	0,92	C_9H_8OSe	51,6	4,1	37,1	51,2	3,8	37,4	20,3
V	H	CH_3	H	CH_3	111—112	0,85	$C_{10}H_{10}OSe$	53,6	4,5	34,7	53,3	4,4	35,1	42,5
VI	CH_3	CH_3	H	CH_3	92—93	0,86	$C_{11}H_{12}OSe$	55,6	5,2	32,7	55,3	5,0	33,0	51,5
VII	CH	CH_3	CH_3	CH_3	116—117	0,81	$C_{11}H_{12}OSe$	55,5	5,2	32,8	55,3	5,0	33,0	32,8

[a] From hexane; from hexane–benzene (1:1) in the case of VI. [b] Activity II aluminum oxide with elution with acetone and development with iodine vapors or in UV light.

is determined by a study of the NMR spectra of the product of recyclization of 2,6-dimethyl-4-ethylselenopheno[3,2-c]pyrylium perchlorate (IV, R = H, R' = CH_3).

The IR spectra of 4- and 7-hydroxy derivatives of benzoselenophene contain almost identical absorption bands over a broad range of frequencies. For example, the isomeric dimethylhydroxybenzoselenophenes have the following strong and medium absorption bands: 2,5-dimethyl-7-hydroxybenzoselenophene 1608 (m), 1582 (s), 1560 (s), 1456 (s), 1425 (s), 1335 (s), 1274 (s), 1200 (m), 1160 (s), 1068 (s), 1054 (s), 863 (w), 848 (s), 838 (s), 722 (w) cm^{-1}; 2,6-dimethyl-4-hydroxybenzoselenophene 1610 (m), 1583 (m), 1540 (s), 1468 (s), 1444 (m), 1355 (s), 1268 (s), 1215 (s), 1140 (s), 1040 (w), 977 (m), 867 (m), 838 (s), 821 (s) cm^{-1}. The spectra of products that are not substituted in the selenophene ring additionally contain an absorption band at 690 cm^{-1}. The assignment of the absorption bands at 600-1500 cm^{-1} was previously made in [10]. The absorption band at 3600-3610 cm^{-1} attests to the presence of a phenolic hydroxyl group in all of the compounds obtained. The individuality of the products was confirmed by thin-layer chromatography (TLC) (see Table 1).

EXPERIMENTAL

The NMR spectra of CCl_4 solutions (about 5%) were recorded at 40 MHz with a YaMR-5535 spectrometer at room temperature. The chemical shifts were measured relative to hexamethyldisiloxane as the internal standard and converted to the tetramethylsilane scale. The IR spectra of KBr pellets (600-1800 cm^{-1}) and CCl_4 solutions (3400-3700 cm^{-1}) were recorded with a UR-20 spectrophotometer.

2,5-Dimethyl-7-hydroxybenzoselenophene. A solution of 3.75 g of NaOH in 7.5 ml of water was added to 4.9 g (0.015 mole) of 2,5,7-trimethylselenopheno[2,3-c]pyrylium perchlorate in 25 ml of ethanol, and the mixture was refluxed for 8 h. The alcohol was removed by distillation, and 200 ml of water was added to the residue. The aqueous solution was extracted three times with ether and acidified to pH 2-3 with hydrochloric acid. The resulting oily liquid was extracted with ether, and the extract was dried with sodium sulfate. The ether was removed by distillation, and the residue was crystallized to give 2.15 g (63.8%) of a product with mp 113-114° (from hexane, light-yellow needles) and R_f 0.86. Found,%: C 53.6; H 4.5; Se 34.8. $C_{10}H_{10}OSe$. Calculated,%: C 53.3; H 4.4; Se 35.1.

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