1-METHYL-2,1,3-BENZOTHIA(SELENA)DIAZOLIUM SALTS

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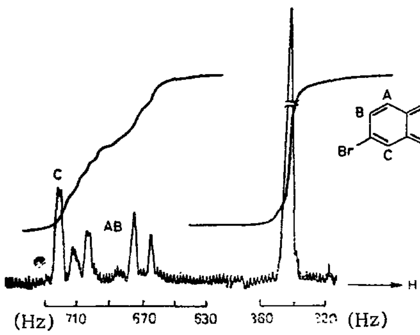

Fig. 1. PMR spectrum of 5-bromo-1-methyl-2,1,3-benzothiadiazolium chloride at 100 MHz (Varian Ha-100) in trifluoroacetic acid with cyclohexane as the internal standard.

We have found the reaction of thionyl chloride or selenious acid with N-methyl-o-phenylenediamines gives 1-methyl-2,1,3-benzothia(selena)diazolium salts I and II.

I II

The structures of the compounds were unambiguously proved by means of the PMR spectra, in which multiplets of aromatic protons and singlets of protons of N-methyl groups are observed. A typical spectrum of I is presented in Fig. 1. Analysis of the spectrum gives ortho and meta spin–spin coupling constants of 9.4 and 1.4 Hz, respectively; the para coupling constant was not recorded in the spectrum.

EXPERIMENTAL

5-Bromo-1-methyl-2,1,3-benzothiadiazolium Chloride. A 1.2-ml sample of thionyl chloride was added to 0.85 g of N_1-methyl-p-bromo-o-phenylenediamine in 10 ml of dry benzene, and the reaction mixture was refluxed for 2 h. The resulting precipitate was removed by filtration, dried, and recyrstallized from methanol.

5-Bromo-1-methyl-2,1,3-benzoselenadiazolium Chloride. A 0.5-g sample of selenious acid was added to 0.76 g of N_1-methyl-p-bromo-o-phenylenediamine dihydrochloride in 15 ml of glacial acetic acid, and the resulting precipitate was removed by filtration, dried, and recrystallized from methanol.

TABLE 1. 1-Methyl-2,1,3-benzothia(selena)thazolium Salts

Compound	R¹	R²	mp (dec.), °C	Empirical formula	Found, %: N	Found, %: Cl+Br	Calculated, %: N	Calculated, %: Cl+Br	Yield, %
I	H	Cl	158—159	$C_7H_6Cl_2N_2S$	12,5	32,4	12,7	32,1	83
II			185—187	$C_7H_6Cl_2N_2Se$	10,6	26,6	10,4	26,5	68
I	Cl	H	188—189	$C_7H_6Cl_2N_2S$	12,8	29,9	12,7	32,1	77
II			200—202	$C_7H_6Cl_2N_2Se$	10,3	26,7	10,4	26,5	85
I	H	Br	143—145	$C_7H_6BrClN_2S$	10,7	43,6	10,6	43,4	74
II			182—183	$C_7H_6BrClN_2Se$	8,7	36,8	9,0	36,9	79
I	Br	H	185—186	$C_7H_6BrClN_2S$	10,7	43,3	10,6	43,4	72
II			196—197	$C_7H_6BrClN_2Se$	8,7	37,2	9,0	36,9	87
I	H	CH_3	179—181	$C_8H_9ClN_2S$	14,1	17,9	14,0	17,7	91
II			199—200	$C_8H_9ClN_2Se$	11,6	14,2	11,3	14,3	69
I	CH_3	H	180—181	$C_8H_9ClN_2S$	13,8	17,6	14,0	17,7	73
II			206—208	$C_8H_9ClN_2Se$	11,0	14,1	11,3	14,3	64
I	H	CH_3O	149—150	$C_8H_9ClN_2OS$	12,7	16,6	12,9	16,4	73
II			180—181	$C_8H_9ClN_2OSe$	10,4	13,3	10,6	13,4	79
I	CH_3O	H	163—164	$C_8H_9ClN_2OS$	13,2	16,5	12,9	16,4	96
II			195—196	$C_8H_9ClN_2OSe$	10,6	13,6	10,6	13,4	89

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