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PREPARATIVE SYNTHESIS OF BENZO[b]THIO(SELENO,TELLURO)PHENE DERIVATIVES*

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A preparative synthesis of aminomethyl derivatives of benzo[b]thio(seleno,telluro)phenes and their hydrohalides by the reaction of sulfur, selenium, and tellurium halides with 1-phenylpropynamines was developed.

As we previously reported, benzo[b]selenophene derivatives were obtained in good yields under conditions of two-phase selenohalogenation of phenylacetylene derivatives [2]. The introduction of a methyleneamino group into phenylacetylene could facilitate the reaction and make it possible to expand the limits of applicability of the method. With this end in mind, we studied the reactions of 1-phenylamino derivatives Ia-e of 1-propyne with selenium and tellurium tetrahalides and sulfur dichloride. The starting amines were obtained from phenylacetylene, paraformaldehyde, and the corresponding amine under the catalytic action of cuprous chloride [3, 4]. It is known that the use of two-phase seleno- or tellurohalogenation [5] markedly increases the yields of products, shortens the reaction time, and makes these reactions preparatively advantageous for the synthesis of benzo[b]seleno(telluro)phene derivatives IIa-m (see scheme on page 1108).

Benzo[b]thiophene derivatives IIn-q are formed in good yields in the reaction of amine derivatives Ia-e with sulfur dichloride in an organic medium (see scheme on page 1108).

It was established that the order of addition of the reagents does not affect the way in which the reaction proceeds – the only reaction products are benzo[b]thio(seleno,telluro)phene derivatives (see Table 1). In contrast to starting amines Ia-e, the IR spectra of IIa-q do not contain bands of stretching vibrations at 2100-2250 cm^{-1} ($C\equiv C$) but do contain bands of stretching vibrations at 1590-1640 and 1260-1580 cm^{-1}, which characterize the stretching vibrations of the C=C group and the benzo[b]thio(seleno,telluro)phene system [6], respectively, and bands of stretching vibrations of the C–A (A = Se, Te) and C–Hal bonds (see Table 1). In the PMR spectra the protons of the methylene group show up in the form of a doublet at 4.32-4.96 ppm (J = 4.0-6.0 Hz), in contrast to the position of the same group in starting amines Ia-e (3.35-3.58 ppm, singlet).

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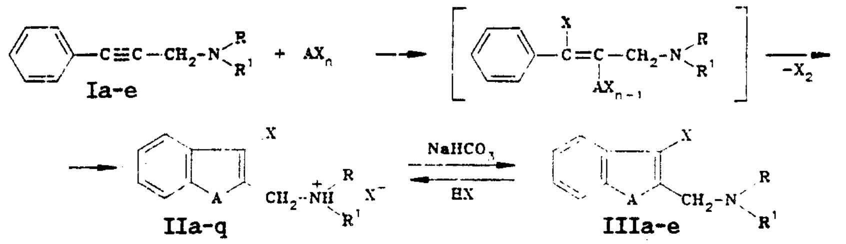
TABLE 1. Properties of IIa-q

Compound	Empirical formula	mp, °C	IR spectrum, cm^{-1} χ	PMR spectrum, δ, ppm (J, Hz)			Yield, %
				$-CH_2N$, d	$\gt NH^+$, m	Remaining H	
IIa	$C_{10}H_{11}Br_2NSe$	243...245	775 (C—Se), 580 (C—Br)	4,75 (6,0)	9,97	2,88 (s, 3H, $2CH_3$); 7,40...7,72 (m, 2H, 2CH); 7,87 (m, 1H, CH); 8,25 (m, 1H, CH)	90
IIb	$C_{10}H_{11}Br_2NTe$	126...128	585 (C—Br), 445 (C—Te)	4,48 (4,0)	8,68	2,78 (s, 3H, CH_3); 7,35...7,68 (m, 2H, 2CH); 7,78 (m, 1H, CH); 8,21 (m, 1H, CH)	83
IIc	$C_{11}H_{13}Br_2NSe$	187...189	780 (C—Se), 575 (C—Br)	4,70 (6,0)	10,55	2,78 (s, 6H, $2CH_3$); 7,35...7,62 (m, 2H, 2CH); 7,85 (m, 1H, CH); 8,15 (m, 1H, CH)	70
IId	$C_{13}H_{17}Br_2NSe$	181...183	770 (C—Se), 600 (C—Br)	4,68 (6,0)	11,5	1,50 (t, 6H, $2CH_3$, $J=7,0$); 3,25 (q, 4H, $2CH_2$, $J=7,0$); 7,29...7,60 (m, 2H, 2CH); 7,68 (m, 1H, CH); 8,02 (1H, CH)	62
IIe	$C_{13}H_{17}Cl_2NSe$	113...115	830 (C—Cl), 760 (C—Se)	4,36 (6,0)	12,25	1,51 (t, 6H, $2CH_3$, $J=7,0$); 3,25 (q, 4H, $2CH_2$, $J=7,0$); 7,20...7,38 (m, 2H, 2CH); 7,40 (m, 1H, CH); 7,63 (m, 1H, CH)	54
IIf	$C_{14}H_{17}Br_2NSe$	139...141	740 (C—Se), 560 (C—Br)	4,96 (6,0)	8,50	2,03 (m, 6H, $3CH_2$); 3,63 (m, 4H, $2CH_2$); 7,65...7,85 (m, 2H, 2CH); 7,98 (m, 1H, CH); 8,18 (m, 1H, CH)	65
IIg	$C_{14}H_{17}Cl_2NSe$	194...196	810 (C—Cl)	4,69 (6,0)	8,95	2,08 (m, 6H, $3CH_2$); 3,65 (m, 4H, $2CH_3$); 7,25...7,85 (m, 2H, 2CH); 7,92 (m, 1H, CH); 8,18 (м, 1H, CH)	60
IIh	$C_{13}H_{15}Br_2NOSe$	229...230	780 (C—Se), 585 (C—Br)	4,84 (6,0)	11,34	2,50 (m, 4H, $2CH_2$); 3,62 (m, 4H, $2CH_2$); 7,22...7,62 (m, 2H, 2CH); 7,75 (m, 1H, CH); 8,06 (m, 1H, CH)	94
IIj	$C_{13}H_{17}Br_2NTe$	96...98	530 (C—Br), 440 (C—Te)	4,37 (4,0)	9,65	1,45 (t, 6H, $2CH_3$); 3,44 (q, 4H, $2CH_2$, $J=7,0$); 7,34 (4H, 4CH)	70
IIk	$C_{13}H_{17}Cl_2NTe$	118...120	839 (C—Cl), 425 (C—Te)	4,50 (4,0)	8,41	1,65 (t, 6H, $2CH_3$, $J=7,0$); 3,48 (q, 4H, $2CH_2$, $J=7,0$); 7,39 (м, 4H, 4CH)	40
IIℓ	$C_{13}H_{15}Br_2NOTe$	169...171	580 (C—Br), 432 (C—Te)	4,68 (4,0)	8,35	2,75 (m, 4H, $2CH_2$); 3,65 (m, 4H, $2CH_2$); 7,55...8,01 (m, 4H, 4CH)	66
IIm	$C_{13}H_{15}Cl_2NOTe$	126...128	825 (C—Cl), 450 (C—Te)	4,34 (4,0)	8,48	2,73 (m, 4H, $2CH_2$); 3,65 (m, 4H, $2CH_2$); 7,55...8,11 (m, 4H, 4CH)	68
IIn	$C_{10}H_{11}Cl_2NS$	210...211	860 (C—Cl)	4,68 (5,0)	11,22	2,82 (s, 3H, CH_3); 7,45...7,78 (m, 2H, 2CH); 7,83 (m, 1H, CH); 8,13 (m, 1H, CH)	43
IIo	$C_{13}H_{17}Cl_2NS$	161...163	850 (C—Cl)	4,60 (5,0)	11,12	1,55 (t, 6H, $2CH_3$, $J=8,0$); 3,23 (q, 4H, $2CH_2$, $J=8,0$); 7,33...7,55 (m, 2H, 2CH); 7,68 (m, 1H, CH); 8,03 (m, 1H, CH)	73
IIp	$C_{14}H_{17}Cl_2NS$	178...180	868 (C—Cl)	4,64 (5,0)	10,42	1,79 (m, 6H, $3CH_2$); 2,52 (m, 4H, $2CH_2$); 7,42...7,68 (m, 2H, 2CH); 7,87 (m, 1H, CH); 8,14 (m, 1H, CH)	68
IIq	$C_{13}H_{15}Cl_2NOS$	202...204	790 (C—Cl)	4,59 (5,0)	11,68	2,48 (m, 4H, $2CH_2$); 3,92 (m, 4H, $2CH_2$); 7,05 (t); 7,23 (m, 2H, 2CH); 7,35 (m, 1H, CH); 7,60 (m, 1H, CH)	48



IIa—H $n=4$; IIo—c $n=2$

Compound	R	R¹	A	X	Compound	R	R¹	A	X
Ia	H	Me			IIh	$(CH_2)_2$—O—$(CH_2)_2$		Se	Br
Ib	Me	Me			IIj	Et	Et	Te	Br
Ic	Et	Et			IIk	Et	Et	Te	Cl
Id	$(CH_2)_5$				IIℓ	$(CH_2)_2$—O—$(CH_2)_2$		Te	Br
Ie	$(CH_2)_2$—O—$(CH_2)_2$				IIm	$(CH_2)_2$—O—$(CH_2)_2$		Te	Cl
IIa	H	Me	Se	Br	IIn	H	Me	S	Cl
IIb	H	Me	Te	Br	IIo	Et	Et	S	Cl
IIc	Me	Me	Se	Br	IIp	$(CH_2)_5$		S	Cl
IId	Et	Et	Se	Br	IIq	$(CH_2)_2$—O—$(CH_2)_2$		S	Cl
IIe	Et	Et	Se	Cl	IIIa	$(CH_2)_2$—O—$(CH_2)_2$		Se	Br
IIf	$(CH_2)_5$		Se	Br	IIIb	H	Me	S	Cl
IIg	$(CH_2)_5$		Se	Cl	IIIc	Et	Et	S	Cl
					IIId	$(CH_2)_5$		S	Cl
					IIIe	$(CH_2)_2$—O—$(CH_2)_2$		S	Cl

The multiplet at 8.35-11.50 ppm characterizes the $-\overset{+}{N}H$ group. The ^{13}C NMR spectra (Table 2) do not contain signals in the region that characterizes carbon atoms in the sp-hybridized state (at 78.74 ppm in the starting compounds), while signals that characterize eight nonequivalent carbon atoms are found at 100-150 ppm. These data are in good agreement with the literature data [7, 8].

The benzo[b]thio(seleno)phene halide derivatives IIh, n-q obtained were subjected to reaction with aqueous sodium bicarbonate solution. As a result of the reaction we isolated free bases IIIa-e. Compounds IIh, n-q were isolated in quantitative yields by the action of the corresponding hydrohalic acid on IIIa-e.

The structures of the bases obtained were confirmed by the PMR spectra, while the compositions were confirmed by elementary analysis.

TABLE 2. ^{13}C NMR Spectra of II

Compound	Chemical shifts, δ, ppm					
	$C_{(2)}$	$C_{(9)}$	$C_{(4)}$	$C_{(3)}$	$C_{(10)}$	remaining C
IId	140,25	137,92	133,35	130,43	51,52	126,57; 126,17; 125,71; 125,35; 46,08; 8,52
IIb	140,28	137,69	131,69	129,47	51,28	128,30; 126,18; 125,82; 125,13; 47,81; 9,49
IIg	140,36	137,81	131,81	129,53	49,93	128,30; 127,57; 125,56; 123,48; 22,52; 21,29
IIo	137,80	134,60	131,01	126,81	47,07	126,12; 125,64; 123,13; 121,73; 46,14; 8,46
IIp	137,91	134,42	128,50	126,75	51,28	125,53; 123,42; 123,01; 121,78; 22,08; 20,79
IIq	136,70	135,51	128,67	128,15	51,34	125,43; 124,12; 123,12; 121,00; 62,74; 21,34

EXPERIMENTAL

The IR spectra of KBr pellets and $CHCl_3$ solutions of the compounds were recorded with an IR-75 spectrometer. The ^1H and ^{13}C NMR spectra were recorded with Tesla BS-487 (80 MHz) and Bruker WP-100SY spectrometers with tetramethylsilane (TMS) as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates. Column chromatography was carried out on 40-100 μm silica gel (Czechoslovakia).

The characteristics of the synthesized compounds are presented in Tables 1 and 2. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

Reactions of Selenium and Tellurium Tetrahalides with 3-Amino-1-phenyl-1-propynamines. A 10-mmole sample of selenium or tellurium tetrahalide, obtained from selenium or tellurium dioxide and the calculated amount of hydrohalic acid, was added with cooling to 0°C and vigorous stirring to a solution of 10 mmoles of Ia-e in 100 ml of diethyl ether. At the end of the reaction (according to TLC data) the precipitated IIa-m were removed by filtration and dried in a vacuum desiccator.

Reactions of Sulfur Dichloride with 3-Amino-1-phenyl-1-porpynamines. A 20 mmole sample of the corresponding amine was added in the course of 1 h with vigorous stirring to a solution of 20 mmoles of sulfur dichloride in 20 ml of chloroform. At the end of the reaction (24 h, according to TLC data) 100 ml of diethyl ether was added to the reaction mixture. The precipitates were removed by filtration, and IIn-q were dried in a vacuum desiccator.

Reactions of Benzo[b]thio(seleno)phenyl Halide Derivatives with Sodium Bicarbonate. A suspension of 2.0 mmoles of the corresponding II in 30 ml of diethyl ether was added to a solution of 20 mmoles of sodium bicarbonate in 20 ml of water, and the reaction mixture was stirred vigorously for 1 h. At the end of the reaction (according to TLC) the resulting base was extracted with diethyl ether. The organic layer was separated and dried over anhydrous sodium sulfate, and the ether was removed with a vacuum rotary evaporator. The following compounds were obtained. Compound IIIa, with mp 85-86°C (ether) was obtained in 93% yield. Compound IIIb, with bp 136-138°C (3.0 mm), was obtained in 85% yield. Compound IIIc, with bp 129-130°C (2 mm), was obtained in 89% yield. Compound IIId, with mp 66-68°C (methanol), was obtained in 91% yield. Compound IIIe, with mp 117-118°C (methanol), was obtained in 90% yield.

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