ELECTROPHILIC REACTIONS OF GROUP SIX ELEMENT HALIDES.

11.* SYNTHESIS OF THE CONDENSED SYSTEM SELEN(TELLUR) AZINO-[2, 3-g, h] CARBAZOLE

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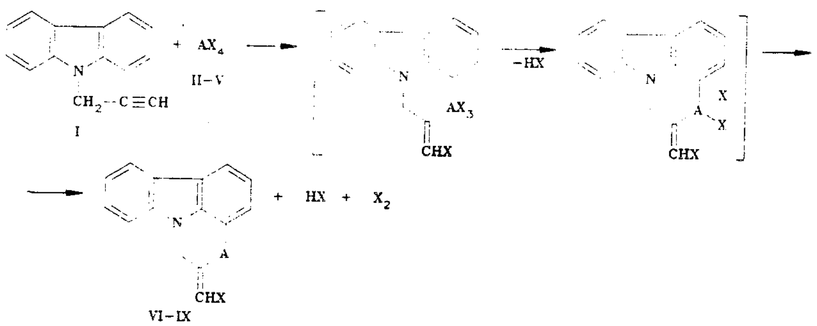
UDC 547.869.6/7'759.3.07:543.422

2-Halomethylidene-1,4-selen(tellur)azino[2,3-g, h]carbazoles are prepared by the seleno(telluro)halogenation of N-propargylcarbazole under heterogeneous reaction conditions.

In order to prepare hitherto unknown 2-halomethylidene-1,4-selen(tellur) azino[2, 3-g, h] carbazoles, we have studied the reaction of N-propargylcarbazole (I) with selenium and tellurium tetrahalides II-V. We have established that these halides, under conditions for two-phase seleno- or tellurohalogenation [2, 3], enter into a reductive heterocyclization reaction with N-propargylcarbazole, I:



II, III, VI, VII A=Se; IV, V, VIII, IX A=Te; II, IV, VI, VIII X=Br; III, V, VII, IX, X=Cl

It is known [4, 5] that electrophilic substitution in the carbazole molecule depends on the nature of the substituent and usually occurs at the 1 position. In our case, too, electrophilic substitution in the carbazole nucleus occurs at position 1 under the influence of selenium or tellurium tetrahalides. As a result of the reaction, halogen molecules split out spontaneously, as described, in particular, for 3-halobenzotellurophenes [6, 7].

The structure of compounds VI-IX were confirmed by IR and PMR spectroscopy (Table 1). Thus, in the IR spectra of compounds VI-IX, the bands from ≡C-H and C≡C bond stretching at 3250 and 2140 cm^{-1}, respectively, are absent, and a C=C stretch band appears [6]. In the PMR spectra of compounds VI-IX, a signal is detected confirming the formation of a selen(tellur)azinocarbazole system (Table 1).

Thus, selenium and tellurium tetrahalides enter into an electrophilic addition reaction at the triple bond in an anti-Markovnikov sense with a subsequent electrophilic substitution of the carbazole in the 1 position and formation of a new selenium (tellurium)-containing condensed system.

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*See [1] for Communication 10.

Uzhgerod State University, Uzhgerod 294000. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 126-128, January, 1990. Original article submitted March 23, 1988; revision submitted July 27, 1988.

0009-3122/90/2601-0108

TABLE 1. Characteristics of 2-Halomethylidene-1,4-selen(tellur)azino[2,3-g, h]carbazoles VI-IX

Compound	Empirical formula	T_{mp}, °C (from benzene)	IR spectrum, cm^{-1}	PMR spectrum ($CDCl_3$), δ, ppm					Yield, %
				N-CH_2	=CHX	5-H, 6-H, 7-H	2-H, 3-H, 4-H	8-H	
VI	$C_{15}H_{10}BrNSe$	161...163	1630 (C=C), 565 (C—Br), 762 (C—Se)	5,00, t J=10,0 Hz	6,38, m	7,07, m 3H	7,45, m 3H	8,08, m	52
VII	$C_{15}H_{10}ClNSe$	136...138	1632 (C=C), 845 (C—Cl), 760 (C—Se)	5,79, t J=13,0 Hz	7,14, m	7,24, m 3H	7,43, m 3H	8,09, m	41
VIII	$C_{15}H_{10}BrNTe$	126	1630 (C=C), 565 (C—Br), 495 (C—Te)	5,17, t J=10,0 Hz	7,13, m	7,37, m 3H	7,54 m 3H	8,11, m	48
IX	$C_{15}H_{10}ClNTe$	113	1615 (C=C), 845 (C—Cl), 510 (C—Te)	5,50, t J=13,0 Hz	7,08, m	7,40, m 3H	7,40, m 3H	8,22, m	39

EXPERIMENTAL

The IR spectra were taken in KBr tablets on an IKC-29 spectrophotometer, and the PMR spectra, in $CDCl_3$, on a WP-100SY spectrometer with TMS as an internal standard. The purity of the compounds and the composition of the reaction mixture were checked by TLC on Silufol-254 plates developed with iodine vapor. The C, H, and N elementary analyses of the compounds obtained correspond to the calculated values.

N-Propargylcarbazole (I, $C_{15}H_{11}N$) was prepared by the method in [8], as improved by us. In a three-necked flask 450 mmoles carbazole, 500 mmoles sodium amide, and 1500 ml liquid ammonia were placed. The mixture was stirred for 2.5 h at −33°C, then cooled to −55°C and at this temperature 630 mmoles propargyl bromide were added dropwise over one hour and stirred for 5 h, then the reaction mixture was allowed to stand until the ammonia had completely evaporated. The residue was extracted (without decomposition with water) with hexane (4 × 3 liters), and stirred for 5 h at 20°C. After distilling off the solvent, four fractions were obtained having T_{mp} 94-106°C, T_{mp} 103-106°C, T_{mp} 100-106°C, and T_{mp} 104-106°C. All fractions were recrystallized from hexane (100 ml of hexane per 7 g of material). Yield 65%, T_{mp} 104-107°C. IR spectrum: 3250 (≡C-H), 2120 (C≡C), 1620-1590 (arom. ring), 1480 (CH_2), 1450-1320 (C—N), and 680-660 cm^{-1} (C≡CH). PMR spectrum: 2.34 (t, 1H, J = 2.4 Hz, CH), 5.04 (d, 2H, J = 2.4 Hz, NCH_2), 7.64 (m, 6H, 6CH), and 8.36 ppm (m, 2H, 1-H, 8-H).

Reaction of Selenium Tetrahalides (II, III) with N-Propargylcarbazole (I). Selenium tetrahalide (II, III) (3.9 mmoles), prepared from selenium dioxide and the calculated amount of hydrohalic acid was added at 0°C with vigorous stirring to a solution of 3.9 mmoles carbazole I in 100 ml diethyl ether. At the end of the reaction (checked by TLC), the precipitate of compounds VI or VII was filtered off and dried in a vaccum desiccator. An additional amount of compound VI or VII separates from the organic layer (Table 1).

Reaction of Tellurium Tetrahalides (IV or V) with N-Propargylcarbazole (I). Tellurium tetrahalide (IV, V) (10 mmoles), prepared from tellurium dioxide and the calculated amount of hydrohalic acid, was added at 0°C with vigorous stirring to a solution of 10 mmoles carbazole I in 100 ml diethyl ether. After 48 h (checked by TLC), the ether layer was separated and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the oily residue was washed with benzene. Compound VIII or IX was obtained (Table 1).

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