INVESTIGATION OF THE STRUCTURAL PECULIARITIES AND CHEMICAL TRANSFORMATIONS OF CARBAZOLE AND ITS DERIVATIVES

XXXVI.* SYNTHESIS OF CARBAZOLE THIOETHERS

N. I. Baranova and V. I. Shishkina

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A method for the synthesis of thioethers of the carbazole series by the reduction of 3-thiocyanato- and 3,6-dithiocyanatocarbazoles with sodium sulfide and subseqent condensation of the reduction products with alkyl halides is described.

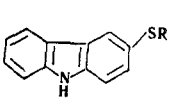
Thioethers of the carbazole series have not yet been obtained. They are of interest as substances with potential inhibiting properties [2,3] and as intermediates in the synthesis of dyes and biologically active compounds.

In this paper we describe the synthesis of thioethers of the carbazole series starting from 3-thiocyanato- and 3,6-dithiocyanatocarbazoles [4]. The reaction of the thiocyanates of carbazole with sodium sulfide, in analogy with that which is described in [5], forms the sodium salts of thiocarbazoles, which give thioethers with the appropriate halo derivatives (see Table 1).

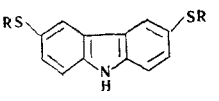
The IR spectra of all of the thioethers demonstrated the presence of an absorption band at 3415-3430

*See [1] for communication XXXV.

TABLE 1.



I - VI



VII - XII

Compound	R	Mp, deg C	Empirical formula	Found, %				Calc., %				Yield, %
				C	H	N	S	C	H	N	S	
I	CH_3	117—119	$C_{13}H_{11}NS$	73,0	5,1	6,2	16,0	73,2	5,2	6,6	15,0	49
II	C_2H_5	128—130	$C_{14}H_{13}NS$	74,2	5,8	5,8	13,9	74,0	5,7	6,2	14,1	40
III	i-C_3H_7	125—126	$C_{15}H_{15}NS$	74,2	6,0	6,2	12,9	74,7	6,2	5,8	13,3	36
IV	C_4H_9	95—96	$C_{16}H_{17}NS$	75,5	6,6	5,5	11,7	75,3	6,7	5,5	12,6	42
V	$CH_2C_6H_5$	150—152	$C_{19}H_{15}NS$	78,2	5,3	5,0	10,9	78,9	5,2	4,8	11,1	41
VI	CH_2COOH	169—171	$C_{14}H_{11}NSO_2$	65,9	4,4	5,2	12,1	65,4	4,3	5,4	12,4	49
VII	CH_3	89—90	$C_{14}H_{13}NS_2$	64,5	5,0	5,3	24,1	64,9	5,0	5,4	24,7	67
VIII	C_2H_5	69—70	$C_{16}H_{17}NS_2$	67,3	6,2	4,8	22,5	66,9	5,9	4,9	22,3	32
IX	i-C_3H_7	49—50	$C_{18}H_{21}NS_2$	68,3	6,6	4,3	20,5	68,6	6,7	4,4	20,3	66
X	C_4H_9	29—30	$C_{20}H_{25}NS_2$	70,2	7,5	4,1	20,3	70,0	7,3	4,1	18,7	51
XI	$CH_2C_6H_5$	130*	$C_{26}H_{21}NS_2$	75,6	5,2	3,3	15,7	75,9	5,1	3,4	15,6	97
XII	CH_2COOH	194†	$C_{16}H_{13}NS_2O_4$	55,4	3,9	4,2	18,6	55,3	3,8	4,0	18,4	95

*From aqueous alcohol.

†From water.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1076-1077, August, 1971. Original article submitted January 3, 1969.

cm^{-1} characteristic for the NH bond in carbazoles [6]. The absence of substitution at nitrogen was also confirmed by chemical means; thus alkylation of I with dimethyl sulfate gave 3-methylthio-9-methylcarbazole (XIII).

EXPERIMENTAL

3-(Methylthio)carbazole (I). A 6.72-g (0.03-mole) sample of 3-thiocyanatocarbazole was added with stirring at 70 deg to a solution of 14.4 g (0.06 mole) of sodium sulfide in 12 ml of water. The reaction mass was stirred for 1 h, heated to 80 deg, and 1.95 ml (0.03 mole) of methyl iodide was added. The mixture was held at 80 deg for 2 h, cooled, acidified with hydrochloric acid until it was weakly acidic, and filtered. The filtered solid was washed with water, dried, and recrystallized from petroleum ether to give 3.15 g (49%) of shiny leaflets with mp 117-119 deg.

The other monothioethers (see Table 1) were similarly obtained. Compounds III, V, and VI were extracted from the reaction mass by benzene, chromatographed with a column filled with aluminum oxide, and crystallized from aqueous alcohol.

3,6-Di(methylthio)carbazole (VII). This compound [3.45 g (67%)] was similarly obtained from 19.2 g (0.08 mole) of sodium sulfide in 40 ml of water, 5.62 g (0.02 mole) of 3,6-dithiocyanatocarbazole, and 2.6 ml (0.04 mole) of methyl iodide.

The other thioethers were obtained by the same method (see Table 1). Compounds IX and X were extracted from the reaction mass with benzene, and the benzene solution was chromatographed with a column filled with aluminum oxide. Removal of the solvent gave an oily liquid that crystallized to needles in the cold.

3-Methylthio-9-methylcarbazole (XIII). A total of 2 ml of 50% potassium hydroxide and 0.5 ml of dimethyl sulfate was added to a solution of 1 g of I in 10 ml of acetone. The reaction mass was stirred for 1 h at room temperature and for 2 h under reflux, cooled, and diluted with 50 ml of water. The precipitate was removed by filtration, washed with water, and crystallized from petroleum ether to give 1.03 g (90%) of shiny crystals with mp 68-69 deg. Found: C 73.8; H 5.8; N 6.6%. $C_{14}H_{13}NS$. Calculated: C 74.0; H 5.7; N 6.2%.

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