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

XXXI.* SYNTHESIS OF AZOMETHINES FROM 3-AMINOCARBAZOLE

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Ten new azomethine compounds, derivatives of 3-aminocarbazole and aromatic aldehydes, were synthesized. The IR spectra of the compounds were studied.

The azomethine derivatives of various classes of organic compounds have attracted attention as a result of their broad synthetic possibilities and the diversity of the paths for their practical application. The literature contains only limited data on the azomethines of the carbazole series [2].

We have synthesized a number of azomethines of 3-aminocarbazole in high yields by condensing it with equimolecular amounts of various aromatic aldehydes. The condensation was carried out in alcohol, either at room temperature or with heating. The product yield was the criterion for selection of the temperature conditions. The azomethines obtained are yellow to red substances which are satisfactorily crystallized from organic solvents. The results are presented in Table 1.

The IR spectra of the compounds were obtained in order to elucidate several structural peculiarities. An intense absorption band due to the presence of frequencies of the stretching vibrations of the NH bond for the substances in the solid state and in solutions is observed at 3400-3450 cm^{-1}; this is probably due to the presence of an intermolecular $=N-H \ldots N=$ hydrogen bond (Table 2).

All of the azomethines have intense absorption bands at 1612-1621 cm^{-1} which are assigned to the stretching vibrations of the conjugated $C=N$ group [4]. The absence of a band for the stretching vibrations of the OH group, even in solution, is explained by the presence of a strong intramolecular hydrogen bond with the nitrogen of the azomethine group, which is manifested in the form of a broad, diffuse band from 2800 to 2900 cm^{-1}.

EXPERIMENTAL

A. An alcoholic solution of 5 g (0.027 mole) of 3-aminocarbazole in 150 ml of alcohol was mixed with equimolar amounts of the appropriate aromatic aldehyde, and the reaction mass was heated to the boiling point for 2 to 3 h. The precipitate was filtered after cooling and purified by recrystallization.

B. An alcoholic solution of the appropriate aldehyde (0.027 mole) was added with stirring to a suspension of 5 g (0.027 mole) of 3-aminocarbazole in 50 ml of alcohol. The reaction mass was stirred for 3 to 4 h at room temperature, after which the precipitate was filtered and purified by recrystallization.

*For Communication XXX see [1].

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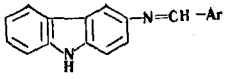
TABLE 1



Comp.	Ar	Method	Color	mp	Solvent	Empirical formula	N, % found	N, % calc.	Yield, %
I	C_6H_5	A	Light-yellow	209	Acetone	$C_{19}H_{14}N_2$	10,1	10,4	81
II	*o*-HOC_6H_4	A	Yellow	223—224	n-Butanol	$C_{19}H_{14}N_2O$	9,4	9,8	93
III	*o*-$CH_3OC_6H_4$	Б	Orange	177—180	Ethanol	$C_{20}H_{16}N_2O$	9,0	9,3	70
IV	*o*-$HOOCC_6H_4$	A	Brown	255—256	Ethanol	$C_{20}H_{14}N_2O_2$	8,7	8,9	82
V	2-Hydroxynaphthyl	A	Red-orange	275—276	Glacial acetic acid	$C_{23}H_{16}N_2O_2$	8,1	8,3	90
VI	2-NO_2-6-HOC_6H_3	Б	Red	> 345	Dimethylformamide	$C_{19}H_{13}N_3O_3$	12,1	12,7	89
VII	2-OH-3-$NO_2C_6H_3$	A	Red-orange	238—239	Ethanol	$C_{19}H_{13}N_3O_3$	12,0	12,7	84
VIII	2-OH-5-$NO_2C_6H_3$	A	Orange	283—285	„ „	$C_{19}H_{13}N_3O_3$	12,3	12,7	87
IX	2-OH-5-BrC_6H_3	A	Yellow	278—281	„ „	$C_{19}H_{13}N_2OBr$	7,3	7,7	94
X	9-Anthracenyl	A	Yellow	218—220	Acetone	$C_{27}H_{18}N_2$	7,2	7,6	72

TABLE 2. Frequencies of the Stretching Vibrations of the NH Bond for Several Azomethines

Compound	Frequency ν, cm^{-1}		$\Delta\nu$, cm^{-1}
	in mineral oil	in dichloroethane	
I	3410	3448	38
II	3400	3450	50
V	3405	3450	45
VIII	3409	3445	36

The IR spectra of the azomethines in the solid state (mineral oil paste) and in dichloroethane solution were obtained with a UR-10 spectrophotometer.

LITERATURE CITED

1. T. I. Proshechkina, V. I. Shishkina, N. D. Negodyaev, and G. M. Novikova, Izv. Vuzov., Ser. Khim., 12, 903 (1969).
2. Ng. Buu-Hoi and Ng. Hoah, J. Org. Chem., 16, 1327 (1951).
3. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
4. N. Jones and C. Sandorfy, Application of Spectroscopy to Chemistry [Russian translation], IL, Moscow (1959), p. 209.