Calculated, %: C 77.2; H 5.3; N 8.2.

The mass spectra contained ion peaks corresponding to the molecular masses of the ions $[M - HX]^+$. Ion peaks were present with m/z 94:96, confirming the presence of the methyl group on the indole nitrogen atom, and an ion with m/z 207, corresponding to the structure of the substituted indole residue (1-methyl-2-phenylindole, etc.), and fragment ions indicating the presence of a phenyl group in the o-position, in accordance with the process $[M - HX]^+ - C_6H_5$.

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INTERACTION OF 3-ARYLIDENAMINOCARBAZOLES WITH ANTIPYRINE

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UDC 547.838.1'751'773'774'759.3.07:543.422'51

The interaction of 3-arylidenaminocarbazoles with antipyrine in the presence of catalytic amounts of acid leads to the formation of derivatives of indolo[3,2-f]-pyrazolo[4,3-c]quinoline.

Methyl ketones are added at the azomethine bond in the reaction with 3-arylidenaminocarbazoles in the presence of acid. The arylaminoketones formed in this case are cyclized to derivatives of 7H-pyrido[2,3-c]carbazole [1]. In this work antipyrine was used instead of methyl ketone.

Antipyrine was studied previously in reactions with Schiff bases, produced from amines of the benzene series. It was found in this case that it forms addition products at the azomethine bond without their subsequent cyclization [2, 3]; however, as the present investigation showed, antipyrine forms cyclic products with 3-arylidenaminocarbazoles — derivatives of indolo[3,2-f]pyrazolo[4,3-c]quinoline, which undergo supplementary transformations in the course of the reaction, as can be represented by the following scheme:

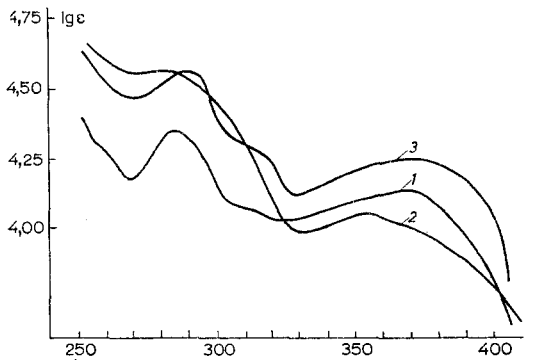

Fig. 1. UV spectra (in methanol): 1) 3-m-chlorobenzylidenaminocarbazole (Id); 2) condensation product of 3-m-chlorobenzylidenaminocarbazole with antipyrine (IIId); 3) condensation product of benzylidene-3-aminocarbazole with antipyrine (IIIa).

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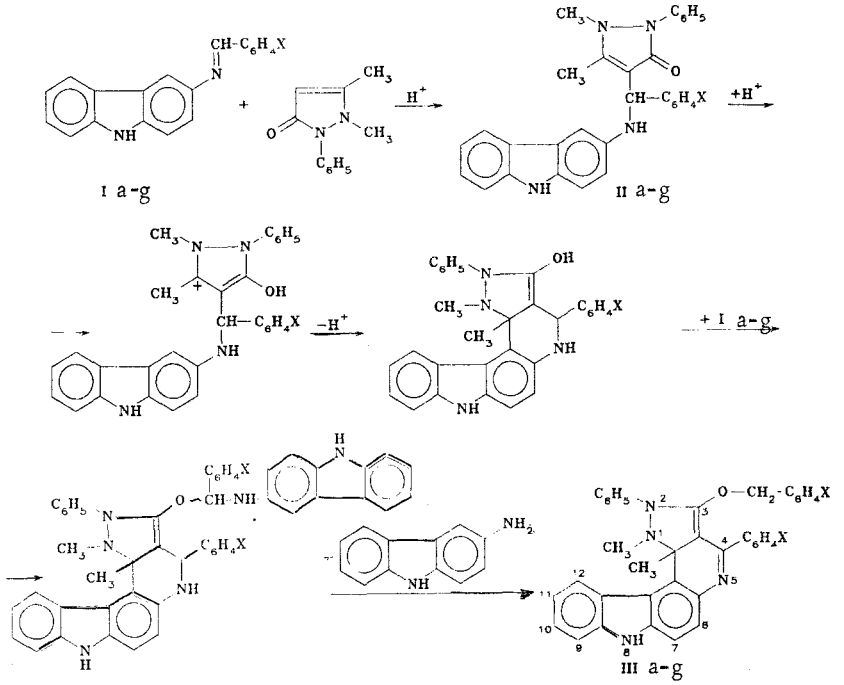
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1657-1659, December, 1983. Original article submitted February 3, 1983.

0009-3122/83/1912-1310$07.50



III a X=H; b X=*p*-Cl, c X=*p*-Br; d X=*m*-Cl; e X=*m*-Br; f X=*o*-Cl; g X=*p*-F

The structure of compounds IIIa-g is confirmed by the UV, IR, PMR, and mass spectra.

The UV spectra of compounds IIIa-g (Fig. 1) have a great similarity to the UV spectra of the carbazoles Ia-g, which is explained by the similarity in the structure of the main chromophores in the molecules.

The IR spectra contain absorption bands of the C=O group, but intense and medium-intensity bands are present at 1620-1630 and 3400-3420 cm^{-1}, corresponding to the absorption of the enol double bond and the NH group of the carbazole fragment. Moreover, there is a rather intense band at 810-830 cm^{-1}, indirectly confirming the formation of intermediate products IIa-g of the angular isomers [1, 4].

The PMR spectra contain three singlets in the region of 1.8 and 2.7 (two CH_3) and 3.5 ppm (CH_2), a weak broad signal with chemical shift 10.9-11.1 ppm (NH), and a complex multiplet of signals of the aromatic protons in the region of 7.2-9.0 ppm.

The mass spectra of compounds IIIa-g contain rather intense (∿75%) peaks of the molecular ions. The large number of doubly charged ions is evidence of a high degree of aromaticity of these compounds. The ratio of the isotopic peaks of the molecular ions of compounds IIIb-f, as well as the presence of peaks of the ions due to the elimination of fragments containing halogen atoms, confirms not only the presence of two halogen atoms in the molecules but also that of two phenyl radicals, containing halogen. The presence of rather intense peaks in the spectra (∿40%), corresponding to the ions $XC_6H_6CH_2O^+$ (X = F, Cl), confirms the presence of this fragment in the molecules of the investigated compounds. The antipyrine fragment is confirmed by the presence of a peak with m/z 119 in the spectra, possessing maximum intensity and corresponding to the ion $C_6H_5NCO^+$.

Thus, in contrast to the Schiff bases of amines of the benzene series, 3-arylidenaminocarbazoles give heterocyclic compounds in the reaction with antipyrine. The enol nature of these compounds permits them to interact with the unreacted initial azomethine, forming O-benzyl derivatives.

EXPERIMENTAL

The UV spectra were recorded on an SF-4a spectrophotometer in methanol. The IR spectra were recorded on a UR-20 instrument in liquid petrolatum. The PMR spectra were recorded on a YaMR-5535 instrument at the frequency 40 MHz, internal standard HMDS. The mass spectra were obtained on an LKB-2091 instrument, using direct introduction of the sample into the ion source at an ionization energy 70 eV and temperature 0-200°C.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	X	Mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
IIIa	H	225	81,15	5,39	10,29	$C_{37}H_{30}N_4O$	81,32	5,49	10,25	61
IIIb	*p*-Cl	199	71,87	4,32	9,01	$C_{37}H_{28}Cl_2N_4O$	72,07	4,54	9,09	72
IIIc	*p*-Br	206	62,99	3,68	7,86	$C_{37}H_{28}Br_2N_4O$	63,06	3,97	7,95	45
IIId	*m*-Cl	240	71,89	4,42	9,03	$C_{37}H_{28}Cl_2N_4O$	72,07	4,54	9,09	53
IIIe	*m*-Br	212	62,87	3,87	7,86	$C_{37}H_{28}Br_2N_4O$	63,06	3,97	7,95	31
IIIf	*o*-Cl	251	71,97	4,55	8,88	$C_{37}H_{28}Cl_2N_4O$	72,07	4,54	9,09	74
IIIg	*p*-F	239	76,14	4,66	9,49	$C_{37}H_{28}F_2N_4O$	76,28	4,81	9,62	54

Compounds IIIa-g were produced according to a single procedure, described below on the example of compound IIIb.

1,13d-Dimethyl-2-phenyl-4-(p-chlorophenyl)-3-(p-chlorobenzyloxy)-1,2-dihydro-13dH,8H-indolo[3,2-f]pyrazolo[4,3-c]quinoline (IIIb). A mixture of 1.52 g (0.005 mole) 3-p-chlorobenzylidenaminocarbazole, 0.94 g (0.005 mole) antipyrine, 60 ml of alcohol, and 1.5 ml conc. HCl was heated in a flask with a reflux condenser on a boiling water bath for 3 h. At first everything dissolved; after 2 h a precipitate began to form, which was filtered off at the end of the reaction and cooling of the mixture. It was treated with aqueous ammonia, and after drying was recrystallized from a mixture of toluene and methanol (1:1).

In all cases one spot was observed on the thin-layer chromatograms (aluminum oxide, methanol). The characteristics of the compounds synthesized are cited in Table 1.

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SYNTHESIS AND AMINOMETHYLATION OF DERIVATIVES OF PYRAZINO[3.2.1-jk]CARBAZOLE AND DIAZEPINO[3.2.1-jk]CARBAZOLE

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UDC 547.759.3'863'892.07:543.422

Derivatives of pyrazino- and diazepino[3.2.1-jk]carbazoles were obtained by the Fischer condensation of 1-amino-3-oxo-1,2,3,4-tetrahydroquinoxaline and 1-amino-4-oxo-2,3-dihydrobenzodiazepine(1,5) with cyclohexanone and 3-methylcyclohexanone. A study was carried out on the transformations of derivatives of pyrazino- and diazepino[3.2.1-jk]carbazoles by methylation at the NH group and aminomethylation of the N-methyl derivatives.

In a continuation of a study of the Fischer reaction with the aim of synthesizing condensed heterocycles [1], we obtained derivatives of pyrazino- and diazepino[3.2.1-jk]carbazoles by the reaction of cyclohexanone and 3-methylcyclohexanone with 1-amino-3-oxo-1,2,3,4-

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1660-1663, December, 1983. Original article submitted February 9, 1983; revision submitted July 14, 1983.

0009-3122/83/1912-1312$07.50