STRUCTURE AND PROPERTIES OF 1-(2-PYRIDYL)-3-PHENYL-5-ARYLFORMAZANS

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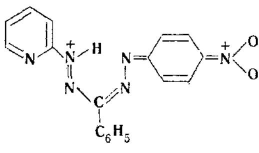
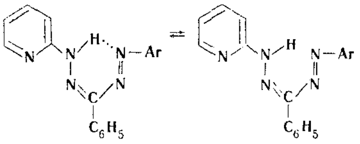
A series of 1-(2-pyridyl)-3-phenyl-5-arylformazans, which form deeply colored complexes with Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} salts, were obtained by coupling of arenediazonium salts, containing various substituents in the phenyl ring, with benzaldehyde 2-pyridylhydrazone. The presence of a nitro group causes deepening of the color and leads to the appearance of negative solvatochromism.

Of the formazans that contain heterocyclic residues, pyridyl derivatives are also known [1, 2]. There is no information available regarding the synthesis of 1-(2-pyridyl)-3-phenyl-5-arylformazans that have substituents in the benzene ring.

In the present study we have established that the synthesis of formazans of this series can be accomplished by coupling arenediazonium salts with benzaldehyde 2-pyridylhydrazone (Table 1). Formazan I is also formed in low amounts in the reaction of sodium 2-pyridyldiazotate with benzaldehyde phenylhydrazone.

Formazans I-VIII absorb light at 464-480 nm, and neither the substituents nor the nature of the solvent appreciably affect the absorption maximum (Table 1). An exception to this is the more deeply colored formazan VII (which contains a nitro group), which, in contrast to 1-benzazolyl-3-phenyl-5-(p-nitrophenyl)-formazans [3], displays a clearly expressed negative solvatochromism: λ_{max} 530 nm (benzene), 510 nm (nitrobenzene), 504 nm (chloroform), and 488 nm (ethanol). A dipolar structure apparently takes on considerable weight for VII. It is remarkable that only VII forms salts in alcoholic alkali, and a deepening of the color to 603 nm is observed in the process.


VII


A B

Compounds I-VIII form deeply colored complexes with metal salts in alcohol solution (Table 1). The IR spectra of the formazans contain absorption bands corresponding to the NH bond at both 3050-3080 and 3330-3350 cm^{-1}, on the basis of which it can be assumed that structures A and B are in tautomeric equilibrium.

Since replacement of the phenyl group in the 3 position of the formazan by a methyl group has an appreciable effect on the properties of the compound, an attempt was made to obtain 1-(2-pyridyl)-3-methyl-5-phenylformazan by coupling benzenediazonium chloride with acetaldehyde 2-pyridylhydrazone; however, disproportionation occurred as a result of the reaction, and 1,5-diphenyl-3-methylformazan was isolated.

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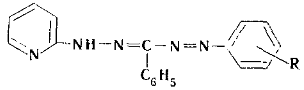
TABLE 1



Compound	R	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %	Spectra (ethanol)		λ_{max} of complexes in ethanol solution			
				C	H	N	C	H	N		λ_{max}	lg ε	$ZnCl_2$	$Cu(CH_3COO)_2$	$Co(CH_3COO)_2$	$NiSO_4$
I	H	153—154*	$C_{18}H_{15}N_5$†	—	—	—	—	—	—	50	464	4,565	627	630	670	618
II	$4\text{-}CH_3$	130—131	$C_{19}H_{17}N_5$	72,3	5,3	22,1	72,4	5,4	22,2	79	470	4,484	630	626	672	608
III	$2\text{-}CH_3$	158—159	$C_{19}H_{17}N_5$	71,9	5,6	22,3	72,4	5,4	22,2	69	472	4,581	—	604	688	586
IV	$4\text{-}OCH_3$	105—106	$C_{19}H_{17}N_5O$	69,1	5,3	21,0	68,9	5,2	21,1	92	480	4,632	634	650	678	612
V	$4\text{-}OC_2H_5$	135—136	$C_{20}H_{19}N_5O$	69,3	5,5	20,2	69,6	5,5	20,3	86	472	4,660	632	640	664	610
VI	4-Br	145—146	$C_{18}H_{14}BrN_5$	57,2	4,2	18,3	56,9	3,7	18,4	42	472	4,552	638	632	660	612
VII	$4\text{-}NO_2$	177—178	$C_{18}H_{14}N_6O_2 \cdot {}^1/_2H_2O$	61,3	4,1	23,6	60,8	4,3	23,7	41	488	4,527	662	662	702	640
VIII	$4\text{-}N(CH_3)_2$	178—180	$C_{20}H_{20}N_6$	70,0	5,9	24,3	69,7	5,9	24,4	48	482	4,618	635	648	690	615

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* According to [1], this compound has mp 154°.

† Formazans I-VI and VIII were purified by crystallization from ethanol, while formazan VII was crystallized from aqueous ethanol.

EXPERIMENTAL

The visible spectra of the substances were recorded with an SF-14 spectrophotometer, while the IR spectra were obtained with an IKS-14 spectrophotometer. The solvent was carbon tetrachloride.

1-(2-Pyridyl)-3-phenyl-5-(o-tolyl)formazan (III). A 1-g (5 mmole) sample of benzaldehyde 2-pyridylhydrazone was dissolved in 30 ml of ethanol–pyridine (4 : 1), and a diazonium solution, prepared from 0.5 ml (5 mmole) of o-toluidine in 15% HCl (4 ml) and 0.3 g of $NaNO_2$ in 1 ml of water, was added to the cooled solution. The pH of the solution was brought up to 6-7 with 2 N NaOH, and the mixture was allowed to stand for 24 h. The resulting red needles of formazan III were removed by filtration. Compounds I, II, and IV-VIII (Table 1) were similarly obtained.

Coupling of Sodium 2-Pyridyldiazotate with Benzaldehyde Phenylhydrazone. A solution of 2.6 g of sodium 2-pyridyldiazotate in 100 ml of ethanol was added to a solution of 2 g of benzaldehyde phenylhydrazone in 20 ml of absolute ethanol. Carbon dioxide was bubbled through the solution periodically, after which the mixture was allowed to stand for 24 h. Water (300 ml) was then added, and the resulting red precipitate was removed by filtration. Chromatography in a thin layer of aluminum oxide with chloroform–diethyl ether (1 : 1) demonstrated the presence of formazan I with R_f 0.83.

Reaction of Benzenediazonium Chloride with Acetaldehyde 2-Pyridylhydrazone. A 2.5-g sample of sodium acetate and a diazonium solution, prepared from 1 ml of aniline, 8 ml of 15% HCl, and 0.6 g of $NaNO_2$ in 8 ml of water, were added to an alcohol solution of acetaldehyde 2-pyridylhydrazone, prepared from 2 g (18 mmole) of hydrazinopyridine and 1 ml of acetaldehyde. The solution was allowed to stand for 24 h and was then diluted with water. The precipitated yellow-orange crystals of 1,5-diphenyl-3-methylformazan were removed by filtration and crystallized from aqueous ethanol to give 1.54 g (35%) of a product with mp 125-127° (mp 123-123.5° [4]).

LITERATURE CITED

1. D. Jerchel and H. Fischer, Ber., 89, 563 (1956).
2. A. Kawase, Bunseki Kagaku, 16, (12), 1364 (1967); Chem. Abstr., 69, 64,285.
3. N. P. Bednyagina, N. V. Serebryakova, and G. N. Lipunova, Khim. Geterotsikl. Soedin., 342 (1967).
4. E. Bamberger and H. Pemsel, Ber., 36, 88 (1903).