SYNTHESIS AND SOME PROPERTIES OF 1-(1'-PHTHALAZINYL)-3-PHENYL-5-ARYLFORMAZANS

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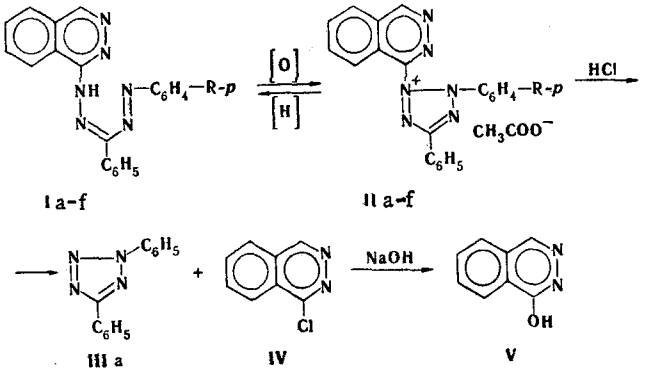
A number of N-phthalazinylformazans with donor and acceptor substituents in the para position of the phenyl ring attached to the 5-N atom of the formazyl grouping were synthesized. The absorption spectra of these formazans and their ions are discussed.

The properties of two series of formazans containing isomeric heterocyclic groupings — quinoxalinyl [1] and quinazolinyl [2] — have been examined. In the present paper the synthetic methods and the results of a study of the properties of formazans with a phthalazinyl grouping are presented for comparison:



I a-f II a-f

III a IV V

I-II a R=H; b R=CH_3; c R=OCH_3; d R=$N(CH_3)_2$; e R=COOH; f R=NO_2

Phthalazinylformazans Ia-f (Table 1) were obtained by diazo coupling of benzaldehyde 1-phthalazinylhydrazone with the corresponding arenediazonium chlorides.

The structure of formazans I was confirmed by their oxidation with Pb_3O_4 to tetrazolium acetates II by the method in [3] and by mild reduction of the latter to the starting formazans by the method in [4]. The product of oxidation of formazan Ia — tetrazolium acetate IIa — like quinoxalinyltetrazolium salts [1], readily undergoes fragmentation in 18% HCl to give 2,5-diphenyltetrazole III in 72% yield and 1-chlorophthalazine IV; the latter gave 1-phthalazone V when it was treated with alkali. Compounds III and V were identified by comparison with authentic samples [5, 6].

Like other hetarylformazans [7], I forms blue complexes with heavy metal ions (Ni^{2+}, Cu^{2+}, Pb^{2+}, and Co^{2+}).

The UV spectra of the phthalazinylformazans contain two intense peaks at 260-290 and 430-470 nm (Table 2). The long-wave absorption maximum of formazans I in ethanol is shifted bathochromically 15-46 nm as compared with the spectra of cyclohexane solutions. In ethanol the contribution of the polar structure of formazan probably increases delocalization of the electron density. The absorption maxima of the corresponding quinoxalinylformazans in ethanol undergo a hypsochromic shift [1], while quinazolinylformazans display clearly expressed solvatochromism [2].

It is interesting to note the rarely observed instance of a bathochromic shift in dioxane (15-50 nm) for I. Under the same conditions, the isomeric formazans [1, 2] undergo the usual

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TABLE 1. Compounds Ia-f

Compound	mp, °C *	R_f	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
Ia	138—139	0,60	$C_{21}H_{16}N_6$	71,9	4,6	23,6	71,6	4,6	23,8	85
Ib	101—102	0,51	$C_{22}H_{18}N_6$	72,4	5,1	23,1	72,2	4,9	22,9	76
Ic	134—136	0,57	$C_{22}H_{18}N_6O$	69,2	4,9	21,6	69,1	4,7	21,9	67
Id	163—165	0,41	$C_{23}H_{21}N_7$	69,7	5,1	24,6	69,9	5,4	24,8	86
Ie	140—143	0,13	$C_{22}H_{16}N_6O_2 \cdot 2H_2O$†	62,9	4,6	20,4	63,2	4,8	20,1	75
If	150—153	0,53	$C_{21}H_{15}N_7O_2$	63,6	4,1	24,4	63,5	3,8	24,7	56

*The compounds were crystallized: Ia-c,f from cyclohexane, Id from diethyl ether, and Ie from ethanol.
†This compound underwent decomposition during vacuum drying at 100°C over P_2O_5.

TABLE 2. Absorption Spectra of Phthalazinylformazans

Compound	λ_{max}, nm (ε×10⁴)				
	cyclohexane	dioxane	ethanol	KOH + ethanol (pH > 14)	conc. H_2SO_4
Ia	282 (2,3); 410 (2,14)	285 (3,1); 292 (3,06)*; 410 (3,4)*; 425 (3,6)*; 445 (4,0)	287 (2,04); 438 (2,14)	531 (1,3)	551 (0,86)
Ib	280 (2,0); 407 (2,48)	293 (1,34); 440 (1,94)	288 (2,04); 414 (2,1); 444 (2,26)	526 (0,6)	—
Ic	282 (1,84); 330 (1,96); 410 (2,84)	282 (1,60); 330 (1,82); 395 (2,44); 425 (2,44)*; 437 (2,46)	285 (2,2); 335 (2,4); 425 (2,9)*; 440 (3,1)	529 (1,12)	—
Id	263 (3,2); 370 (0,72); 470 (0,2)	267 (3,6); 375 (1,72); 462 (0,72); 520 (0,52)*	255 (3,7); 275 (4,2); 370 (1,54); 462 (0,46); 485 (0,44)*; 516 (0,4)*	547 (0,13)	—
Ie	—	290 (2,22); 460 (2,62)	276 (1,2)*; 290 (1,34); 330 (1,24); 460 (1,74)	541 (0,26)	—
If	280 (1,84); 397 (1,16)*; 465 (1,78)	280 (2,1); 288 (2,0)*; 402 (1,76); 422 (1,71)*; 480 (1,9)	270 (3,1); 400 (1,84); 475 (1,26)	590 (0,63)	—

*Shoulder.

hypsochromic shift. The bathochromic effect in our case is possibly associated with the formation of molecular complexes between formazans I and dioxane.

The considerable deepening of the color of formazans I in alcoholic alkali (77-125 nm) is explained by the formation of the corresponding phthalazinyl anions. The latter are more highly colored (12 nm) than quinoxalinyl anions but are more deeply colored (7-16 nm) than quinazolinyl anions [1, 3]. Like the anions of the isomeric formazans [1, 2], the phthalazinyl anions undergo a deepening in color as the donor character of the substituent in the para position of the phenyl ring attached to the 5-N atom of the formazyl grouping increases. The anions from Ia,f, which deviate from this series, constitute exceptions: The ion from Ia probably deviates because of the high degree of conjugation of the phenyl ring attached to the 3-C atom with the overall conjugation chain of the ion, and the ion from If is deeply colored due to the formation of the aci form of the nitro group in alkaline media. The phthalazinyl anions are quite stable in alcoholic alkali (pH > 14) at 20-25°C and do not decompose in 24 h. On the other hand, phthalazinyl cations in concentrated H_2SO_4 undergo decomposition relatively easily at 20-25°C to give colorless products after 5-10 min. The cation from Ia is stable for 1 h. Quinazolinyl cations are also easily decomposed under these conditions [2].

It should be noted that of the three series of isomeric formazans compared in this paper, only quinoxalinylformazans form quite stable cations in sulfuric acid [1]; this is probably associated with the low basicity of quinoxaline.

EXPERIMENTAL

The absorption spectra of $5 \cdot 10^{-5}$ M solutions of formazans I were recorded with an SF-4A spectrophotometer, and the absorption spectra of $1 \cdot 10^{-4}$ M solutions of I in alcoholic KOH and concentrated H_2SO_4 were recorded with an SF-10 spectrophotometer.

The Rf values of the formazans were determined on Silufol plates in an ethanol–chloroform–hexane system (3:5:10).

1-(1'-Phthalazinyl)-3,5-diphenylformazan (Ia). Sodium hydroxide solution (2 N) was added dropwise to a cooled mixture of solutions of 1.24 g (5 mmole) of benzaldehyde 1-phthalazinylhydrazone [8] in 40 ml of DMF and (5 mmole) of benzenediazonium chloride in 20 ml of 18% HCl in such a way that the temperature of the solution did not exceed 0°C. The mixture was allowed to stand for 2 h, after which it was diluted with a threefold amount of water and neutralized to pH 7. The resulting red precipitate was removed by filtration, washed with water, and dried to give 1.4 g of product. The formazan was purified by chromatography with a column filled with Al_2O_3 by elution twice with benzene. The excess solvent was removed by vacuum distillation, and the residue was crystallized. Compounds Ib,c,f were eluted with benzene, Id was eluted with propanol, and Ie was eluted with dioxane. Data on I are presented in Table 1.

LITERATURE CITED

1. Yu. A. Sedov, A. I. Zabolot-skaya, and N. V. Kova, Khim. Geterotskol. Soedin., No. 12, 1705 (1973).
2. Yu. A. Sedov, N. I. Shumova, and N. I. Gogoleva, Khim. Geterotsikl. Soedin., No. 5, 709 (1976).
3. I. I. Kratky and V. Svoboda, Chem. Zvesti, 11, 153 (1957); Chem. Z., 8139 (1959).
4. R. Kuhn and H. M. Weitz, Chem. Ber., 86, 1199 (1953).
5. O. Dimroth and S. Mazzbacher, Chem. Ber., 40, 2402 (1907).
6. S. Gabriel and A. Neumann, Chem. Ber., 26, 521 (1893).
7. N. P. Bednyagina, I. Ya. Postovskii, A. D. Garnovskii, and O. A. Osipov, Usp. Khim., No. 6, 1052 (1975).
8. I. Druey and B. H. Ringier, Helv. Chim. Acta, 34, 204 (1951).

SYNTHESIS OF 1,4-DIAZABICYCLO[2.2.2]OCTANE

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Double intramolecular cyclization of N,N'-bis(2-chloroethyl)-N-N'-bis(2-cyanoethyl)ethylenediamine leads to 1,4-bis(2-cyanoethyl)-1,4-diazoniabicyclo[2.2.2]-octane dichloride, which undergoes decyanoethylation to 1,4-diazabicyclo[2.2.2]-octane when it is heated. The structures of the compounds were confirmed by their IR and PMR spectra.

The literature contains a great deal of data on the synthesis of 1,4-diazabicyclo[2.2.2]-octane (I) and its practical applications (see reviews [1, 2]). However, up until now there has been no information on compounds with functional groups attached to the carbon atom of this heterocycle. Communications [3, 4] on the synthesis of quaternary salts of 1,4-diazabicyclo[2.2.2]octane containing C-hydroxymethyl and carboxyl groups appeared only recently. This situation is explained to a great degree by the absence of sufficiently reliable and convenient methods for the construction of heterocyclic system I under relatively mild conditions.

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