LITERATURE CITED

1. V. D. Orlov, I. Z. Papiashvili, M. V. Povstyanoi, V. A. Idzikovskii and O. M. Tsyguleva, Khim. Geterotsikl. Soedin., No. 1, 93 (1983).
2. P. S. Reddi, C. V. Patham, and S. N. V. Rao, Indian J. Chem., 10, 982 (1972).
3. J. Herbert and H. Suschiky, J. Chem. Soc., Perkin Trans., I, No. 23, 2657 (1974).
4. V. D. Orlov, S. M. Desenko, and N. N. Kolos, Khim. Geterotsikl. Soedin., No. 1, 126 (1984).
5. A. Hetzheim, O. Peters, and H. Bayer, Chem. Ber., 100, 3418 (1967).
6. V. A. Bren', Author's Abstract of dissertation of the degree of Candidate of Chemical Sciences, Rostov-on-Don (1969).
7. V. D. Orlov, N. N. Kolos, S. M. Desenko, and V. F. Davrushin, Khim. Geterotsikl. Soedin., No. 6, (1982).

REACTION OF AROMATIC o-DIAMINES WITH ISATINS.

2.* 2,3-DIAMINONAPHTHALENE

A. G. Drushlyak, A. V. Ivashchenko,
and V. V. Titov

UDC 547.756'781.5'863.1'654.1:542.956.1

The reaction of 2,3-diaminonaphthalene with isatins gives a mixture of indolo[2, 3-b]benzo[g]quinoxalines, 3-(2-aminophenyl)-2(1H)-benzo[g]quinoxalines, and spiro (2,3-d]imidazoline)-2,3'-indolin-2'ones. The ratio between the products is influenced by the solvent and the relative value of the positive charge on the α-carbon atom in the isatin.

It was previously reported [2] that 2,3-diaminonaphthalene (I) reacts with N-methyl- (IIb) and N-acetylisatin (IIe) in ethanol to form spiro compounds IVb and e, with N-methylisatin (IIb) in acetic acid to form indoloquinoxaline VIb, and with N-acetylisatin (IIe) in acetic acid to form spiro compound IVe with traces of the corresponding indoloquinoxaline. In [1] we showed that the reaction of o-phenylenediamine with N-methylisatin gives a mixture of products and that the reaction of N-acetylisatin results in the formation of aminophenylquinoxaline, rather than the spiro compound.

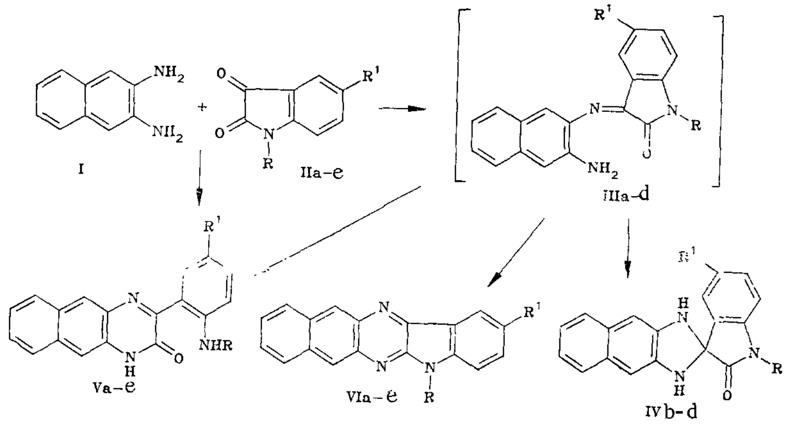
Investigating the reaction of 2,3-diaminonaphthalene (I) with isatins, we found that spiro compounds IVb-d mainly form with N-methylisatins IIb-d in ethanol, that indoloquinoxalines VIa-c form with isatins IIa-c in acetic acid, and that a mixture of aminophenylquinoxalinones Vd-e and indoloquinoxalines VId and e forms with isatins IId and e in acetic acid. In benzene the reactions with all the isatins investigated predominantly produce aminophenylquinoxalinones Va-e (Table 1).

In contrast to the data in [2] it was found that the reaction of o-diamine I with isatin IIa results in the formation of the corresponding aminophenylbenzoquinoxalinone (Va) along with benzindoloquinoxaline VIa in all solvents except acetic acid. The main product of the reaction of o-diamine I with N-acetylixatin IIe under all the conditions investigated (Table 1) is acetaminophenylbenzoquinoxalinnone Ve, rather than spiro compound IVe [2]. The hydrolysis of this compound in alkaline medium results in the quantitative formation of compound Va. The latter contains and NH_2 group, which is diazotized, and then the compound is coupled with β-naphthol. The IR spectrum of Va contains a band for νCO at 1675 cm^{-1}, which is characteristic of six-membered lactams [3], and its electronic spectrum is similar to the spectra of other aminophenylbenzoquinoxalinones (Table 2). The acetyl derivative Ve again forms when Va is acylated by acetyl chloride. The formation of Ve when 2,3-diamino-

---

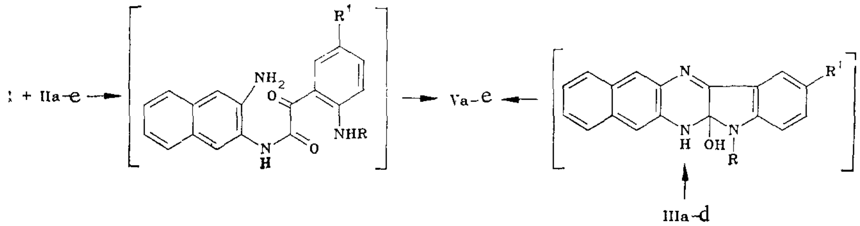
*For report 1 see [1].

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1399-1403, October, 1984. Original article submitted October 17, 1983; revision submitted March 22, 1984.



II—VI a $R=H$, $R^1=H$; b $R=CH_3$, $R^1=H$; c $R=CH_3$, $R^1=Br$; d $R=CH_3$, $R^1=NO_2$; e $R=COCH_3$, $R^1=H$

naphthalene (I) is reacted with N-acetylisatin (IIe) may be attributed to the increase in the positive charge on the α-carbonyl carbon atom and the nitrogen atom in N-acetylisatin (IIe) in comparison to isatins IIa-d, which facilitates the attack of the amino group with the opening of the five-membered ring [4].

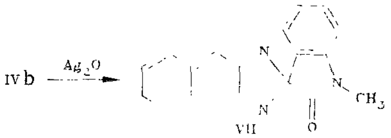


The increase in the yield of aminophenylbenzoquinoxalinones Vb-d in the presence of acids along the series consisting of N-methylisatin (IIb), N-methyl-5-bromoisatin (IIc), and N-methyl-5-nitroisatin (IId) (Table 1) can be explained in a similar manner.

The structure of acetylbenzindoloquinoxaline VIe was confirmed by a back synthesis from benzindoloquinoxaline VIa and acetic anhydride.

As opposed to o-phenylenediamine [1], 2,3-diaminonaphthalene (I) reacts with isatins IIb-d to form the more stable spiro compounds IVb-d, which were recovered even with acid catalysis of the reaction, and in ethanol they are the predominant products (Table 1). This may be attributed to the decrease in the basicity of the amino groups in 2,3-diaminonaphthalene (pK_a 3.99 [5]) in comparison to o-phenylenediamine (pK_a 4.47 [6]). The less basic amino groups in intermediate Schiff bases IIIb-d more readily react with the β carbon atom of the isatin fragment, which apparently bears a large positive charge, to form spiro compounds IVb-d than with the α carbon atom to form aminophenylbenzoquinoxalinones Vb-d or benzindoloquinoxalines VIb-d. Acid catalysis probably facilitates the attack at the α carbon atom, since the yield of spiro compounds IVb-d is diminished (Table 1).

When o-phenylenediamine and dialkoxy-o-phenylenediamines were reacted with isatins, spiro (benzimidazole)indolinones were recovered in [2,7]. However, such compounds were not discovered among the products of the reaction of 2,3-diaminonaphthalene (I) with isatins IIa-e. Spiro(naphthimidazole)indolinone VII was obtained as a result of the oxidation of spiro compound IVb by silver oxide:



The electronic spectra of spiro(naphthimidazoline)indolinones IVb-d and spiro(naphimidazole) indolinone VII (Table 2) are similar to the spectra of the corresponding spiro(ben-

TABLE 1. Yields of Products of the Reaction of 2,3-Diaminonaphthalene with Isatins

Isatin	Reaction product	Yield, %				
		ethanol	0.1 N HCl in ethanol	benzene	3% solution of CH_3COOH in benzene	CH_3COOH
IIa	Va	15	33	57	63	—
	VIa	25	34	21	11	68
IIb	IVb	77	traces	12	10	—
	Vb	traces	—	33	34	—
	VIb	2	41	3	33	82
IIc [9]	IVc	65	5	19	—	—
	Vc	3	4	31	91	—
	VIc	7	43	10	4	91
IId [10]	IVd	17	6	20	—	—
	Vd	33	18	29	96	58
	VId	6	26	traces	1,5	40
IIe	Ve	88	—	80	83	89
	VIe	—	—	—	—	0,2

zimidazoline)indolinones and spiro(benzimidazole)indolinones [1], but the band with the longest wavelength undergoes a bathochromic shift. In the electronic spectra of aminophenylbenzoquinoxalinones Va-e the absorption bands with the shortest and longest wavelengths undergo 20-25-nm bathochromic shifts in comparison to the aminophenylquinoxalinones [1]. As in the case of the aminophenylquinoxalinones [1], the long-wavelength band in N-methyl derivative Vb undergoes a strong (35 nm) bathochromic shift, disappears in N-acyl derivative Ve, and may be assinged as a band for the intramolecular charge transfer from the amino group of the phenyl substituent to the quinoxaline fragment. The electronic spectra of benzindoloquinoxalines VIa-e show four absorption maxima. They have all undergone bathochromic shifts relative to the corresponding maxima of the indoloquinoxalines [1], the long-wavelength absorption band being shifted most strongly (by approximately 60 nm). This is attributed to the lowering of the energy for intramolecular charge transfer from the indole fragment to the quinoxaline fragment [8]. The presence of a methyl group at the indole nitrogen atom in benzindoloquinoxalines VIb and c causes a certain bathochromic shift of the long-wavelength band, and the decrease in the donor capacity of the indole fragment upon the introduction of a nitro group (compound VId) or acetylation at the indole nitrogen (compound VIe) causes a hypsochromic shift.

EXPERIMENTAL

The individuality of the compounds synthesized was monitored by TLC on Silufol UV-254 plates. The electronic absorption spectra of solutions of the compounds in ethanol (10^{-4} M) were recorded on a Specord UV-VIS spectrometer. The IR spectra of the substances in KBr tablets were recorded on a UR-20 spectrophotometer.

Reaction of 2,3-Diaminonaphthalene with Isatins. A heated solution of 3 mmole of the respective isatin (IIa-e) in a minimal quantity of the solvent is given an addition of 3 mmole of 2,3-diaminonaphthalene in a minimal quantity of the same solvent, and the mixture is boiled until the original substances vanish (TLC). The reaction mass is cooled, and the precipitate is filtered out. If it is an individual substance, it is recrystallized from an appropriate solvent. Otherwise the mixture along with the evaporated filtrate is separated by column chromatography on aluminum oxide (the pH of an aqueous extract is 9-10) with a 1:10 acetone—chloroform mixture. The sparingly soluble mixture of nitrobenzindoloquinoxaline VId and aminophenylbenzoquinoxalinone Vd is separated by boiling in 50 ml of a 3:1 mixture of ethanol and an aqueous 20% NaOH solution. The insoluble residue, which consists of nitrobenzindoloquinoxaline VId, is washed with water, the filtrate is neutralized by 1 N HCl, and aminonitrophenylbenzoquinoxalinone Vd is filtered out. The yields of the compounds are given in Table 1, and the characteristics are given in Table 2.

3-(2-Aminophenyl)-2(1H)-benzo[g]quinoxalinone (Va). A solution of 0.33 g (1 mmole) of acetaminophenylbenzoquinoxalinone Ve in 6 ml of a 10% aqueous solution of NaOH is boiled for 4 h. After cooling the reaction mixture is neutralized with acetic acid to pH 7. The precipitate is filtered out and recrystallized from 30 ml of a 5:1 ethanol—DMFA mixture. The yield of Va is 0.28 g (97%). According to the spectral characteristics and the melting point of a mixed sample, the substance is similar to the 3-(2'-aminophenyl)-2(1H)-benzo[g]-

TABLE 2. Characteristics of Products of the Reactions of 2,3-Diaminonaphthalene with Isatins

Compound	mp,[a] °C	R_f[b]	UV spectrum, λ_{max}, nm (log ε)	IR spectrum, cm^{-1}		Found, %				Empirical formula	Calculated, %			
				C=O	N=H	C	H	N	Br		C	H	N	Br
IVb	210—212	0,47	215 (4,62), 253 (4,80), 352 (4,03)	1735 c	3420 c	75,9	5,0	13,6	—	$C_{19}H_{15}N_3O$	75,7	5,0	13,9	—
IVc	209	0,52	218 (4,61), 254 (4,81), 352 (4,04)	1750 c	3410 c	60,2	3,8	10,9	20,9	$C_{19}H_{14}BrN_3O$	60,0	3,7	11,1	21,0
IVd	220 (decomp.)	0,24	215 (4,45), 253 (4,79), 350 (4,25)	1745 c	3395 c	66,0	4,2	16,2	—	$C_{19}H_{14}N_4O_3$	65,9	4,1	16,2	—
Va	275—276	0,28	241 (4,66), 298 (4,29), 360 (4,15), 425 (3,90)	1675	3420, 3335, 3150	75,3	4,6	14,5	—	$C_{18}H_{13}N_3O$	75,2	4,6	14,6	—
Vb	257—258	0,56	241 (4,66), 298 (4,30), 360 (4,08); 461 (3,86)	1680	3150	75,5	4,9	14,0	—	$C_{19}H_{15}N_3O$	75,7	5,0	13,9	—
Vc	271	0,77	244 (4,68), 298 (4,33), 360 (4,17), 470 (3,94)	1680	3150	59,9	3,8	11,2	20,8	$C_{19}H_{14}BrN_3O$	60,0	3,7	11,1	21,0
Vd[d]	337 (decomp.)	0,70		1670	3150	65,8	4,0	16,3	—	$C_{19}H_{14}N_1O_3$	65,9	4,1	16,2	—
Ve	332	0,22	243, 294, 355[e]	1660, 1680	3150	72,7	4,7	12,7	—	$C_{20}H_{15}N_3O_2$	72,9	4,6	12,8	—
VIa	370 [2]	0,42	238 (4,53), 293 (4,86), 395 (4,34), 461 (3,47)	—	3120									
VIb	238	0,88	237 (4,51), 296 (4,92), 395 (4,26); 467 (3,44)	—	—	80,5	4,5	14,9	—	$C_{19}H_{13}N_3$	80,6	4,6	14,8	—
VIc	260	0,94	238 (4,48), 299 (4,93), 394 (4,25), 476 (3,36)	—	—	63,1	3,4	11,4	22,0	$C_{19}H_{12}BrN_3$	63,0	3,3	11,6	22,1
VId	365—366	0,95	238 (4,53), 290 (4,93), 355 (4,65), 450 (3,50)	—	—	69,3	3,7	17,0	—	$C_{19}H_{12}N_4O_2$	69,5	3,7	17,1	—
VIe	256 [2]	0,93	238 (4,75), 302 (4,93), 394 (4,46), 425 (3,57)	1725	—									
VII	250—251	0,80	232 (4,62), 275 (4,73), 348 (4,39), 365 (4,18)	1715 c	—	76,3	4,5	14,0	—	$C_{19}H_{13}N_3O$	76,2	4,4	14,1	—

---

[a] Compounds IVb, Vb, Vc, VIb, and VIc were crystallized from ethanol; IVc, IVd, VIe, and VII were crystallized from a 3:1 chloroform—hexane mixture; Va and e were crystallized from a 5:1 ethanol—DMFA mixture; Vd, VIa, and VId were crystallized from DMFA. [b] 10:1 chloroform—acetone. [c] In chloroform. [d] Not soluble in a spectral concentration. [e] Saturated solution.

quinoxalinone (Va) obtained from isatin IIa and 2,3-diaminonaphthalene (I).

3-(2-Acetaminophenyl)-2(1H)-benzo[g]quinoxalinone (Ve). A 0.14-g portion (0.5 mmole) of aminophenylbenzoquinoxalinone Va is dissolved in 10 ml of pyridine, and 0.2 ml (3 mmole) of acetyl chloride is added with cooling by ice. After 1 h the reaction mixture is poured into water and neutralized by HCl to pH 5. The precipitate formed is filtered out and recrystallized from 40 ml of a 5:1 ethanol–DMFA mixture. The yield of Ve is 0.10 g (60%). According to the spectral characteristics and the melting point of a mixed sample, the substance is similar to the acetaminophenylbenzoquinoxalinone Ve obtained from N-acetylisatin (IIe) and 2,3-diaminonaphthalene (I).

1'-Methylspiro(2H-naphth[2,3-d]imidazole)-2,3'-indolin-2'-one (VII). A 0.15-g portion (0.5 mmole) of spiro compound IVb is dissolved in 10 ml of benzene, 1.0 g (4 mmole) of silver oxide is added, and the mixture is boiled for 2 h. The silver precipitate is filtered out and washed with 5 ml of acetone. The combined filtrate is evaporated and chromatographed on silica gel L 40/100 (Chemapol) with chloroform as the eluent, the first fraction being collected. The yield of VII is 0.06 g (40%).

7-Acetylindolo[2,3-b]benzo[g]quinoxaline (VIe). A solution of 0.135 g (0.5 mmole) of benzindoloquinoxaline VIa in 5 ml of acetic anhydride is boiled for 1 h. After cooling, the precipitate formed is filtered and recrystallized from 50 ml of a 3:1 chloroform–hexane mixture. The yield of VIe is 0.15 g (97%). According to the spectral characteristics and the melting point of a mixed sample, the substance is similar to the acetylbenzindoloquinoxaline VIe recovered following the reaction of N-acetylisatin IIe and 2,3-diaminonaphthalene in acetic acid.

LITERATURE CITED

1. A. V. Ivashchenko, A. G. Drushlayk, and V. V. Titov, Khim. Geterotsikl. Soedin., No. 5, 667 (1984).
2. F. D. Popp, J. Heterocycl. Chem., 6, 125 (1969).
3. L. J. Bellamy, Advances in Infrared Group Frequencies, Methuen, London (1968).
4. G. I. Zhungietu and M. A. Rekhter, Isatin and Its Derivatives, Shtiintsa, Kishinev (1977), p. 44.
5. P. H. Grantham, E. K. Weisburger, and J. H. Weisburger, J. Org. Chem., 26, 1008 (1961).
6. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Wiley, New York (1962).
7. V. M. Dziomko, A. V. Ivashchenko, and R. V. Poponova, Zh. Org. Khim., 10,1326 (1974).
8. V. T. Grachev, A. V. Ivashchenko, S. P. Ivashchenko, B. G. Gerasimov, V. N. Lisyuntenko, and B. E. Zaitsev, Khim. Geterotsikl. Soedin., No. 9, 1259 (1982).
9. W. Borsche and W. Jacobs, Chem. Ber., 47, 354 (1914).
10. H. C. Calwery, C.R. Noller, and R. Adams, J. Amr. Chem. Soc., 47, 3059 (1925).