

REACTION OF o-PHENYLENEDIAMINE WITH ISATINS

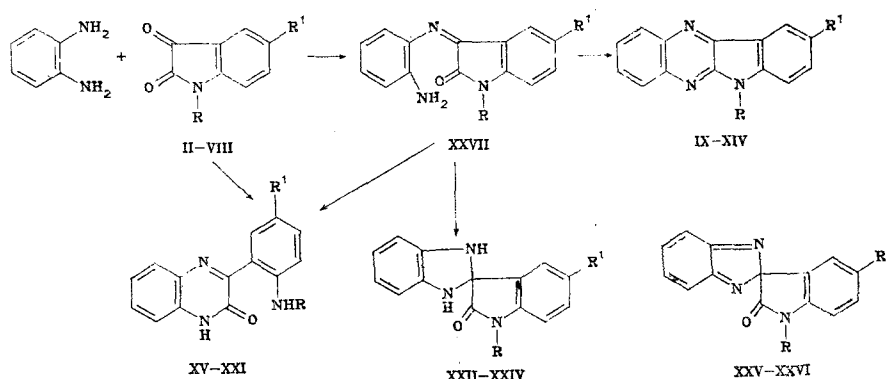
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It is shown that the reaction of o-phenylenediamine with isatins in the general case leads to mixtures of indolo[2,3-b]quinoxalines, 3-(2'-aminophenyl)-2(1H)-quinoxalinones, and spiro[2H-benzimidazoline-2,3'-indolin-2'-ones]. Spiro[2H-benzimidazole-2,3'-indolin-2'-ones] were isolated in individual cases.

Indolo[2,3-b]quinoxalines [1-3], 3-(2'-aminophenyl)-2(1H)-quinoxalinones [4-6], spiro[H-benzimidazoline-2,3'-indolin-2'-ones] [8], or mixtures of these compounds [8, 9] are formed in the reaction of aromatic o-diamines with isatins, depending on the structures of the reacting substances and the conditions under which the reaction is carried out. However, rigorous proof of the structures of the compounds obtained is absent in [1, 4, 7], and the different experimental conditions do not make it possible to correlate the data available in the literature.

In an investigation of the reaction of isatins II-VIII with o-phenylenediamine in various solvents we have established that the following three types of reaction products are formed in the general case: indolo[2,3-b]quinoxalines (IX-XIV), 3-(2'-aminophenyl)-2(1H)-quinoxalinones (XV-XXI), and spiro[2H-benzimidazoline-2,3'-indolin-2'-ones] (XXII-XXIV) (Table 1).



II, IX, XV, XXV R=H, R<sup>1</sup>=H; III, X, XVI R=H, R<sup>1</sup>=Br; IV, XI, XVII R=H, R<sup>1</sup>=NO<sub>2</sub>;  
V, XII, XVIII, XXII, XXVI, XXVII R=CH<sub>3</sub>, R<sup>1</sup>=H; VI, XIII, XIX, XXIII R=CH<sub>3</sub>,  
R<sup>1</sup>=Br; VII, XIV, XX, XXIV R=CH<sub>3</sub>, R<sup>1</sup>=NO<sub>2</sub>; VIII, XXI R=COCH<sub>3</sub>, R<sup>1</sup>=H

As a result of chromatographic separation of the products of the reaction of N-methylisatin (V) with o-phenylenediamine on aluminum oxide we were able to isolate Schiff base XXVII. According to the results of thin-layer chromatography (TLC), it is readily converted to spiro compound XXII when it is heated briefly in benzene, whereas it is converted to a mixture of indoloquinoxaline XII, aminophenylquinoxalinone XVIII, and spiro compound XXII when it is heated in alcohol and under conditions of chromatographic separation on silica gel. We were unable to isolate Schiff bases in the remaining cases, but we observed their formation during monitoring of the course of the reaction (TLC) and from the appearance of the dark-red color of the reaction mixture that is characteristic for these compounds [10] at the start of the reaction.

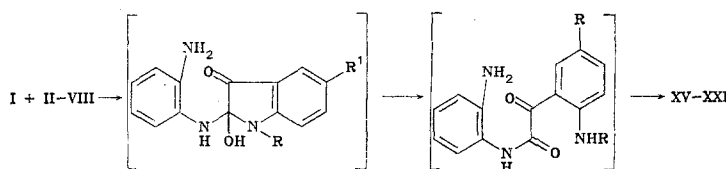
Aminophenylquinoxalinones XVII and XX are formed at a higher rate than the Schiff bases (according to TLC) in the reaction of o-phenylenediamine with 5-nitroisatins IV and VII. It may therefore be assumed that, in addition to the intermediate formation of Schiff bases, a rearrangement leading to aminophenylquinoxalinones occurs:

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TABLE 1. Yields of the Products of the Reaction of Isatins with o-Phenylenediamine

Starting isatin	Reaction product	Yield, %				
		alcohol	0.1 N HCl in alcohol	benzene	benzene + 3% CH <sub>3</sub> COOH	CH <sub>3</sub> COOH
II	IX	68	18	9	15	80
	XV	6	15	70	78	—
	XXV	—	8	—	—	—
III	X	42	39	—	2	52
	XVI	8	5	97	94	24
IV	XI	19	16	—	—	15
	XVII	25	19	95	91	66
V	XII	40 <sup>a</sup>	25	35	50	92
	XVIII	4	21	42	26	—
	XXII	20	13	2	—	—
	XXVI	—	3	—	—	—
	XXVII	12	1	—	—	—
VI	XIII	34	—	30	23	80
	XIX	13	—	59	60	2
	XXIII	17	—	2	—	—
VII	XIV	28	19	8	5	46
	XX	25	14	82	81	44
	XXIV	3	—	7	—	—
VIII	XXI	77	—	95	95	93

<sup>a</sup>Separation by column chromatography on aluminum oxide.



This is in agreement with data on the reaction of 2,3-diaminopyridine with isatins [5].

The reaction of N-methylisatins V-VII with o-phenylenediamine in ethanol leads to mixtures of indoloquinoxalines XII-XIV, aminophenylquinoxalinones XVIII-XX, and spiro compounds XXII-XXIV. Mixtures of only indoloquinoxalines IX-XI and aminophenylquinoxalinones XV-XVII are formed in the case of N-unsubstituted isatins II-IV. The yields of indoloquinoxalines IX-XIV and, especially, spiro compounds XXII-XXIV decrease in a less polar solvent (benzene), and the yields of aminophenylquinoxalinones XV-XX increase significantly (Table 1). The reaction times increase somewhat as the polarity of the solvent increases (3-4 h in alcohol and 4-6 h in benzene). The addition of small amounts of acid accelerate the process significantly (1-2 h) without substantially affecting the ratios of the reaction products. Colorless luminescing substances, viz., spiro[2H-benzimidazole-2,3'-indolin-2'-ones] XXV and XXVI, were isolated in the reaction of isatin (II) and N-methylisatin (V) with o-phenylenediamine in alcohol in the presence of hydrochloric acid.

The reaction proceeds rapidly in acetic acid; it is complete in 1 h and leads primarily to mixtures of indoloquinoxalines IX-XIV and aminophenylquinoxalinones XV-XX. The reaction of N-acetylisatin (VIII) with o-phenylenediamine, which leads only to acetamidophenylquinoxalinone XXI in all of the investigated solvents, constitutes an exception. This fact, as well as the increase in the yields of aminophenylquinoxalinones and the decrease in the yields of indoloquinoxalines as the acceptor properties of the substituents in the 5 position of the isatin ring become more pronounced and on passing from N-methylisatins to N-unsubstituted isatins, can be explained by an increase in the positive charge on the C<sub>(2)</sub> atom. This facilitates attack by the amino group at this position [5, 11] with opening of the five-membered ring and the formation of aminophenylquinoxalinones either directly in the reaction of o-phenylenediamine with the isatins or in the intermediate Schiff base:

TABLE 2. Characteristics of the products of the Reaction of o-Phenylenediamine with Isatins

Compound	mp, °C	R <sub>f</sub> <sup>a</sup>	λ <sub>max</sub> , nm (log ε) in ethanol	ν <sub>C=O</sub> (KBr), cm <sup>-1</sup>	ν <sub>N-H</sub> (KBr), cm <sup>-1</sup>
IX	287—289 <sup>b</sup>	0,54	222 (4,48), 271 (4,69), 358 (4,32), 397 (3,62)	—	3150
X	337—338 <sup>b</sup>	0,90	223 (4,58), 272 (4,61), 358 (4,38), 408 (3,58)	—	3150
XI	382—384 <sup>c</sup>	0,77	212 (4,43), 223 (4,42), 257 (4,61), 330 (4,50), 381 (3,94)	—	3150
XII	145—146 <sup>b</sup>	0,91	224 (4,49), 274 (4,69), 358 (4,33), 410 (3,57)	—	—
XIII	189—190 <sup>b</sup>	0,92	228 (4,50), 286 (4,57), 357 (4,35), 420 (3,51)	—	—
XIV	297—298 <sup>c</sup>	0,97	209 (4,33), 229 (4,37), 260 (4,63), 330 (4,51), 392 (3,88)	—	—
XV	260—261 <sup>d</sup>	0,44	217 (4,54), 308 (3,87), 350 (3,92) <sup>e</sup> , 405 (3,79)	1670	3400, 3260, 3150
XVI	254—255 <sup>b</sup>	0,81	222 (4,57), 305 (3,94), 355 (3,91) <sup>f</sup> , 425 (3,80)	1675	3465, 3300, 3150
XVII	331—333 <sup>d</sup>	0,48	213 (4,43), 309 (4,17), 360 (4,17) <sup>e</sup> , 393 (4,17)	1670	3400, 3250, 3150
XVIII	225 <sup>b</sup>	0,66	222 (4,54), 300 (3,89), 354 (3,96) <sup>e</sup> , 442 (3,83)	1660	3180, 3130
XIX	251—253 <sup>d</sup>	0,77	226 (4,55), 310 (3,92), 358 (3,90) <sup>e</sup> , 455 (3,85)	1665	3180, 3130
XX	304—306 <sup>d</sup>	0,82	215 (4,49), 308 (4,10), 396 (4,31) <sup>e</sup>	1660	3140, 3100
XXI	291 <sup>d</sup>	0,20	213 (4,56), 303 (3,96), 362 (4,05)	1655, 1680	3270, 3130
XXII	188—190 <sup>f</sup>	0,60	218 (4,54), 244 (4,14), 300 (4,00) <sup>e</sup>	1725	3390, 3140
XXIII	172 <sup>f</sup>	0,66	219 (4,60), 263 (4,37), 310 (4,00) <sup>e</sup>	1715	3330, 3140
XXIV	170 <sup>f, g</sup>	0,78	218 (4,49), 297 (4,22), 330 (4,20) <sup>e</sup>	1730	3370, 3130
XXV	300—301 <sup>f</sup>	0,48	215 (4,42), 231 (4,54), 246 (4,49), 324 (4,24), 338 (4,19)	1740	3190
XXVI	167—168 <sup>f</sup>	0,74	209 (4,48), 232 (4,58), 248 (4,57), 327 (4,29), 341 (4,21)	1730	—
XXVII	141—144 <sup>f</sup>	0,57	210 (4,50), 253 (4,25), 500 (3,42)	1720	3425, 3325, 3190

<sup>a</sup>Chloroform-acetone (3:1).

<sup>b</sup>From ethanol.

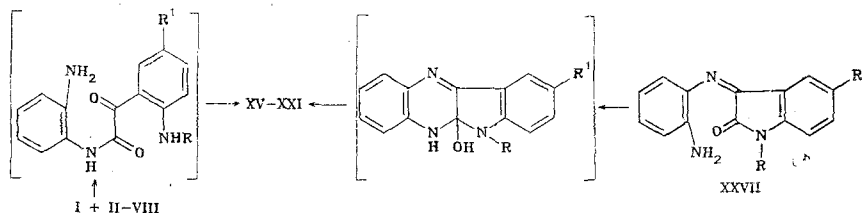
<sup>c</sup>From DMF.

<sup>d</sup>From ethanol-DMF (5:1).

<sup>e</sup>Broad band.

<sup>f</sup>From benzene-hexane (1:1).

<sup>g</sup>With decomposition.



These processes become the predominant processes in the case of N-acetylisatin.

It should be noted that the structures of a Schiff base [1, 4], a spiro compound [7], and an acetamidophenylquinoxalinone [6] were assigned in previous studies to the product of the reaction of o-phenylenediamine with N-acetylisatin (VIII). We have established that the only product of this reaction is 3-(2'-acetamidophenyl)-2(1H)-quinoxalinone (XXI). Compound XV was isolated quantitatively in both cases in the hydrolysis of XXI in acidic and alkaline media. Acylation of XV with acetyl chloride in the cold leads to XXI. Consequently, these compounds should differ only with respect to the presence of an acetyl group. Compound XV contains an NH<sub>2</sub> group, since it is readily diazotized, and the diazotization product couples with β-naphthol. Consequently, the spiro structure assigned in [7] is erroneous.

Compounds XV-XXI are not Schiff bases, since their electronic spectra do not contain the absorption band at 500 nm that is characteristic for azomethines obtained from isatins [10]. The absorption band of a carbonyl group in the IR spectra of these compounds is located at 1660-1680 cm<sup>-1</sup>; this is characteristic for six-membered lactams [12] and confirms the 3-(2'-aminophenyl)-2(1H)-quinoxalinone structure for XV-XXI.

TABLE 3. Results of Elementary Analysis of the Synthesized Compounds

Compound	Found, %				Empirical formula	Calc., %			
	C	H	Br	N		C	H	Br	N
X	56,2	2,8	26,7	14,0	C <sub>14</sub> H <sub>8</sub> BrN <sub>3</sub>	56,4	2,7	26,8	14,1
XI	63,5	3,1	—	21,2	C <sub>14</sub> H <sub>8</sub> N <sub>4</sub> O <sub>2</sub>	63,6	3,1	—	21,2
XIII	57,8	3,3	25,4	13,4	C <sub>15</sub> H <sub>10</sub> BrN <sub>3</sub>	57,7	3,2	25,6	13,5
XIV	64,6	3,5	—	20,0	C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> O <sub>2</sub>	64,7	3,6	—	20,1
XVI	53,1	3,1	25,0	13,1	C <sub>14</sub> H <sub>10</sub> BrN <sub>3</sub> O	53,2	3,2	25,3	13,3
XVII	59,7	3,5	—	19,9	C <sub>14</sub> H <sub>10</sub> N <sub>4</sub> O <sub>3</sub>	59,6	3,6	—	19,9
XVIII	71,6	5,0	—	16,5	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O	71,7	5,2	—	16,7
XIX	54,7	3,5	24,0	12,8	C <sub>15</sub> H <sub>12</sub> BrN <sub>3</sub> O	54,6	3,7	24,2	12,7
XX	60,7	4,1	—	18,7	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O <sub>3</sub>	60,8	4,1	—	18,9
XXII	71,6	5,1	—	16,8	C <sub>15</sub> H <sub>13</sub> N <sub>3</sub> O	71,7	5,2	—	16,7
XXIII	54,5	3,5	24,2	12,6	C <sub>15</sub> H <sub>12</sub> BrN <sub>3</sub> O	54,6	3,7	24,2	12,7
XXIV	60,7	4,0	—	18,7	C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> O	60,8	4,1	—	18,9
XXV	71,4	3,8	—	17,9	C <sub>14</sub> H <sub>9</sub> N <sub>3</sub> O	71,5	3,9	—	17,7
XXVI	72,1	4,4	—	17,0	C <sub>16</sub> H <sub>11</sub> N <sub>3</sub> O	72,3	4,5	—	16,9
XXVII	71,9	5,1	—	16,9	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O	71,7	5,2	—	16,7

The strong bathochromic shift ( $\sim 30$  nm) of the long-wave band in the electronic spectra in the case of methylation of aminophenylquinoxalinones XV-XIX, its disappearance in the case of acylation (XXI), and the hypsochromic shift when a nitro group is introduced (XVII, XX) (Table 2) make it possible to regard it as a band of intramolecular charge transfer from the amino group of the phenyl substituent to the quinoxaline fragment. As expected, absorption bands of a carbonyl group are absent in the IR spectra of indoloquinoxalines IX-XIV. The certain bathochromic shift of the long-wave absorption band in the electronic spectra of 6-methylindoloquinoxalines XII-XIV as compared with 6-unsubstituted indoloquinoxalines IX-XI can be explained by intensification of the donor properties of the indole fragment and a corresponding decrease in the energy of intramolecular charge transfer from the indole fragment to the quinoxaline fragment [13]. The decrease in the donor properties of the indole fragment in the case of 9-nitroindoloquinoxalines XI and XIV leads to a hypsochromic shift ( $\sim 20$  nm) of their electronic spectra as compared with the remaining indoloquinoxalines (Table 2). The presence of N-H absorption at  $3390\text{ cm}^{-1}$  in the IR spectra of spiro[2H-benzimidazoline-2,3'-indolin-2'-ones] XXII-XXIV and of a carbonyl group at  $1715\text{-}1730\text{ cm}^{-1}$ , which is characteristic for five-membered lactams [12], confirms the structure of these compounds. Let us note that the constants of the XXII that we obtained differ from those described in [7]. According to TLC, the substance isolated under the conditions presented in [7] is a mixture of 6-methylindoloquinoxaline (XII), methylaminophenylquinoxalinone XVIII, spiro compound XXII, and unchanged N-methylisatin, which we separated into individual compounds by column chromatography.

The structure of 1'-methylspiro[2H-benzimidazole-2,3'-indolin-2'-one] (XXVI) was confirmed by alternative synthesis by oxidation of 1'-methylspiro[2H-benzimidazoline-2,3'-indolin-2'-one] (XXII) with silver oxide. The similarity in the electronic and IR spectra of XXV and XXVI makes it possible to assign the spiro[2H-benzimidazole-2,3'-indolin-2'-one] structure to XXV also. Unstable XXVII absorbs at 500 nm, and its IR spectrum contains bands of a carbonyl group at  $1720\text{ cm}^{-1}$  and an NH<sub>2</sub> group at  $3425$  and  $3325\text{ cm}^{-1}$ , in good agreement with the Schiff base structure.

#### EXPERIMENTAL

The individuality of the synthesized compounds was monitored by TLC on Silufol UV-254 plates. The electronic absorption spectra of solutions of the compounds in ethanol ( $10^{-4}$  mole/liter) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The substances were characterized by the results of elementary analysis (Table 3). 5-Bromoisatins III and VI were obtained by bromination of, respectively, isatin and N-methylisatin [14], and 5-nitroisatins IV and VII were obtained by nitration [15].

Reaction of o-Phenylenediamine with Isatins. A solution of 3 mmole of o-phenylenediamine in the minimum amount of the solvent was added to a heated solution of 3 mmole of isatin II-VIII in the minimum amount of the same solvent, and the mixture was refluxed until the starting substances vanished (TLC). The reaction mixture was cooled, and the precipitate was removed by filtration. If it was an individual substance, it was recrystallized from ethanol, ethanol-DMF, or DMF; otherwise, it was purified by column chromatography on

silica gel. The filtrates were combined and evaporated to dryness and also separated by column chromatography on L<sup>40</sup>/100 silica gel (Chemapol) by elution with acetone-chloroform (1:10). The yields of the compounds obtained are presented in Table 1, and the characteristics are given in Table 2.

Preparation of Schiff Base XXVII. A 0.48-g (3 mmole) sample of N-methylisatin (V) was dissolved by heating in 10 ml of ethanol, a solution of 0.32 g (3 mmole) of o-phenylenediamine in 1 ml of ethanol was added, and the mixture was refluxed for 20 min. It was then cooled, and the precipitate was removed by filtration. The filtrate was evaporated to dryness, and the residue was combined with the precipitate, dissolved in the minimum amount of benzene, and separated by column chromatography on aluminum oxide (aqueous extract pH 9-10) by elution with acetone-benzene (1:10). The dark-red fraction was evaporated carefully *in vacuo* to a volume of 3-5 ml, and the product was precipitated with 10 ml of hexane. The yield of Schiff base XXVII, with mp 141-144°C, was 0.19 g (26%).

Transformation of Schiff Base XXVII on Silica Gel. A solution of 0.05 g of Schiff base XXVII in 3 ml of chloroform was applied to a column (l = 20 cm, d = 1 cm) packed with L<sup>40</sup>/100 silica gel (Chemapol) and eluted with chloroform-acetone (10:1), during which the red color of the zone of Schiff base XXVII became weaker, and a yellow zone appeared in front of it. An indoloquinoline XII fraction, a mixture of indoloquinoline XII, aminophenylquinoxalinone XVIII, and spiro compound XXII, and, finally, a mixture of spiro compound XXII and Schiff base XXVII (TLC) emerged from the column.

Hydrolysis of 3-(2'-Acetamidophenyl)-2(1H)-quinoxalinone (XXI). A) A 0.14-g (0.5 mmole) sample of acetamidophenylquinoxalinone XXI was refluxed in 3 ml of 10% NaOH for 5 h, during which it gradually dissolved to give a red solution. The solution was cooled and neutralized to pH 5-7, and the yellow precipitate was removed by filtration and recrystallized from 20 ml of ethanol to give 0.11 g (93%) of 3-(2'-aminophenyl)-2(1H)-quinoxalinone (XV) with mp 259-261°C.

B) A 0.14-g (0.5 mmole) sample of acetamidophenylquinoxalinone XXI was refluxed in 5 ml of 6 N HCl for 2 h, after which the mixture was cooled and neutralized to pH 5 with ammonium hydroxide. The precipitate was removed by filtration and recrystallized from 20 ml of ethanol to give 0.11 g (93%) of aminophenylquinoxalinone XV with mp 257-258°C. The substances obtained by variants A and B were identical to 3-(2'-aminophenyl)-2(1H)-quinoxalinone (XV) obtained from isatin and o-phenylenediamine, with mp 260-261°C [4], with respect to the electronic spectra and the results of a mixed-melting-point determination.

Acylation of 3-(2'-Aminophenyl)-2(1H)-quinoxalinone (XV). A 0.2-ml (3 mmole) sample of acetyl chloride was added with ice cooling to a solution of 0.12 g (0.5 mmole) of aminophenylquinoxalinone XV in 5 ml of pyridine. After 1 h, the reaction mixture was poured into water, and the aqueous mixture was neutralized to pH 5 with HCl. The colorless precipitate was removed by filtration and recrystallized from 30 ml of ethanol to give 0.08 g (60%) of acetamidophenylquinoxalinone XXI with mp 285-288°C. The product was identical to 3-(2'-acetamidophenyl)-2(1H)-quinoxalinone, with mp 285°C [4] and 291°C [6], from N-acetylisatin (VIII) and o-phenylenediamine with respect to the electronic spectra and the results of a mixed-melting-point determination.

Qualitative Reaction for the Presence of a Primary Amino Group in 3-(2'-Aminophenyl)-2(1H)-quinoxalinone (XV). A 0.024-g (0.1 mmole) sample of aminophenylquinoxalinone XV was dissolved with ice cooling in 2 ml of acetic acid, and 1 ml of a 10% aqueous solution of sodium nitrite and a drop of hydrochloric acid were added. After 30 min, a solution of 0.02 g (0.1 mmole) of β-naphthol in 10 ml of 10% NaOH solution was added to the solution, and a bright-red coloration developed.

Oxidation of 1'-Methylspiro[2H-benzimidazolidine-2,3'-indolin-2'-one] (XXII). A 0.05-g (0.2 mmole) sample of spiro compound XXII was dissolved in 5 ml of benzene, 0.5 g (2 mmole) of silver oxide was added, and the mixture was refluxed for 4 h. The precipitated silver was removed by filtration and washed with 5 ml of benzene. The filtrate was evaporated, and the residue was purified by column chromatography on L<sup>40</sup>/100 silica gel (Chemapol) by elution with chloroform-acetone (10:1) to give 0.029 g (60%) of spirobenzimidazole-indolinone XXVI with mp 167-168°C. The product was identical to the compound obtained from N-methylisatin (V) and o-phenylenediamine with respect to the electronic spectra and the results of a mixed-melting-point determination.

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## AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

## 7.\* SOLVOLYSIS OF 1,2-DIARYL-1,1a-DIHYDROAZIRINO[1,2-a]-

## QUINOXALINES

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543.422'426'51

Refluxing of 1,2-diaryl-1,1a-dihydroazirino[1,2-a]quinoxaline in 1-propanol leads to 3-aryl-1-arylmethyl-2-propoxy-1,2-dihydroquinoxalines or to aryl(3-aryl-1-arylmethyl-1,2-dihydroquinoxalin-2-yl)(3-aryl-2-hydroxy-1,2-dihydroquinoxalin-1-yl)methanes. Both processes are due to opening of the C-C bond of the aziridine ring; however, in the first process the ylids formed react with solvent molecules, whereas in the second process dimerization of the ylids with the participation of the water present in the solvent is observed.

1,1a-Dihydroazirino[1,2-a]quinoxaline derivatives have an interesting chemical peculiarity — their three-membered ring is capable of opening at either of its external bonds. Thus in acidic media these compounds readily undergo rearrangement to quinoxaline derivatives as a result of intermediate opening of the aziridine ring at the C-N bond [2, 3]. The capacity of 1,2-diaryl-1,1a-dihydroazirino[1,2-a]quinoxalines for photochromism [2] is due to opening of the C-C bond of the three-membered ring and the formation of deeply colored 1,1a-ylids [4, 5]. The thermochromism of these compounds noted in [6] is probably due to a similar process (evidence for which is provided by the identical character of the coloration that develops); however, this problem has not been subjected to a detailed study.

It is also known [7] that cleavage of the common bond to give a seven-membered azepine ring is possible to polycyclic systems that contain a 1,2-fused aziridine ring.

In the present research we studied the chemical behavior of 1,2-diaryl-1,1a-dihydroazirino[1,2-a]quinoxalines (I) when they are refluxed in methanol, ethanol, and 1-propanol.

\*See [1] for communication 6.

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