SYNTHESIS AND STUDY OF INDOLO[2,3-b]QUINOXALINE DERIVATIVES

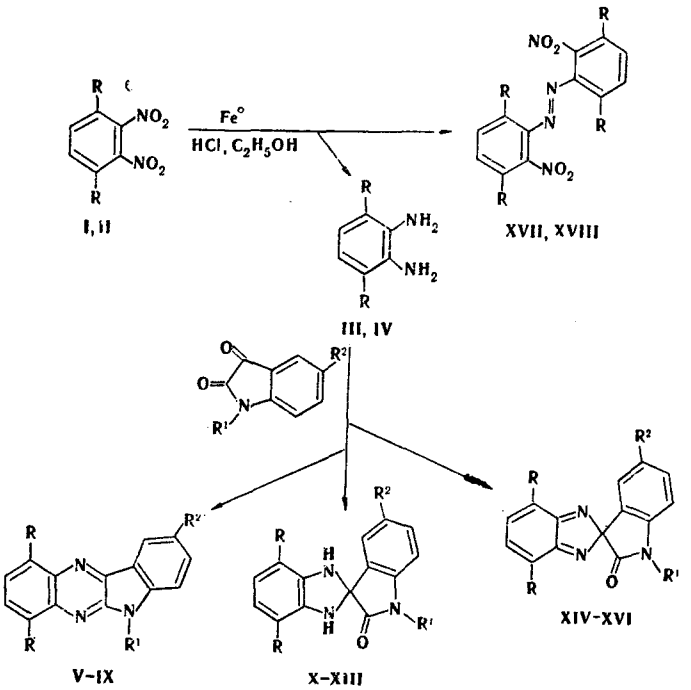
A. V. Ivashchenko and I. F. Agafonova

UDC 547.759.3'863.07

The corresponding indolo[2,3-b]quinoxalines and spiro(benzimidazoline-2,3'-indoline)-2'-ones are formed in the reaction of 2,5-dibutoxy-o-phenylenediamine (I) with 5-nitro- and N-acetylisatin in 50-80% acetic acid, while the corresponding spiro(2H-benzimidazole-2,3'-indole)-2'-ones are formed additionally in the reaction of 2,5-dibutoxy- and 2,5-diheptyloxy-o-phenylenediamine with isatin and N-methylisatin. 6-Acyl and 6- and 5-alkyl derivatives were obtained as a result of acylation and alkylation of a number of 6H-indolo[2,3-b]quinoxalines; the 5-substituted compounds are formed in trace amounts. The IR and electronic spectra of the synthesized compounds were studied.

Continuing our research on the synthesis and study of indolo[2,3-b]quinoxalines [1, 2], which are of considerable practical interest [3], we studied the reactions of 2,5-dibutoxy- and 2,5-diheptyloxy-o-phenylenediamines (III, IV),* obtained by reduction of the corresponding o-dinitrobenzenes (I, II), with isatin and 5-nitro-, N-acetyl-, and N-methylisatins in acetic acid (50-80%), and also by acylation and alkylation of some indolo[2,3-b]quinoxalines.

The corresponding indolo[2,3-b]quinoxalines (V, VI) and spiro(benzimidazoline-2,3'-indolin)-2'-ones (X, XI) in a V:X ratio of 1:18 and a VI:XI ratio of 1:89 are formed in the



I, III, XVII, R=C_4H_9O; II, IV, XVIII R=$C_7H_{15}O$; V, X R=C_4H_9O, R^1=H, R^2=NO_2; VI, XI R=C_4H_9O, R^1=CH_3CO, R^2=H; VII, XII, XIV R=C_4H_9O, R^1=CH_3, R^2=H; VIII, XIII, XV R=$C_7H_{15}O$, R^1=R^2=H; IX, XVI R=$C_7H_{15}O$, R^1=CH_3, R^2=H

*In connection with the fact that dialkoxy-o-phenylenediamines are unstable compounds [4], as in [2], we subjected them to reaction without prior purification immediately after reduction of the component o-dinitrobenzenes (I, II) with iron filings in ethanol in the presence of hydrochloric acid by dilution of the reaction mixture with water, extraction with benzene, and evaporation of the extract *in vacuo*.

Scientific-Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 249-254, February, 1981. Original article submitted May 22, 1980.

 0009-3122/81/1702-0184$07.50

reaction of o-diamine III with 5-nitroisatin and N-acetylisatin. As a result of the reaction of o-diamine III with N-methylisatin and of o-diamine IV with isatin, we obtained, in addition to indolo[2,3-b]quinoxalines (VII, VIII) and spiro(benzimidazoline-2,3'-indolin)-2'-ones (XII, XIII), spiro(2H-benzimidazole-2,3'-indolin)-2'-ones (XIV, XV) in a VII:XII:XIV ratio of 4:1:1.2 and a VIII:XIII:XV ratio of 2.2:1:1.2, whereas only indolo[2,3-b]quinoxaline IX and spiro compound XVI in a ratio of 1:2 are formed in the reaction of o-diamine IV with N-methylisatin.

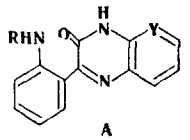
Azobenzenes XVII and XVIII, side products in the reduction of o-dinitrobenzenes I and II, were isolated from the reaction mixtures in all cases. These azobenzenes were also isolated from the reaction mixture obtained immediately after reduction of the starting o-dinitrobenzenes (I, II).

The compositions and structures of the compounds were confirmed by the results of elementary analysis and data from the IR and electronic spectra (Tables 1 and 2).

The IR spectra of dilute solutions of V and VIII contain absorption bands due to stretching vibrations of an NH bond, whereas these bands are absent in the spectra of VI, VII, and IX. The spectrum of VI contains a band of stretching vibrations of a C=O bond. The IR spectra of spiro compounds XI, XII, and XV contain one band of stretching vibrations of N–H bonds, while the spectra of spiro compounds X and XIII contain two such bands. In addition, bands of stretching vibrations of a C=O bond are observed in the spectra of these compounds.

The electronic absorption spectra of solutions of V-XII are identical to the spectra of known analogs or similar to them [1]. The spectra of 1,4-dialkoxy-6-methylindolo[2,3-b]-quinoxalines VII and IX are virtually identical to the spectra of their N-unsubstituted analogs VIII and XIX, and this constitutes evidence for stabilization of the latter in the 6H form in solution.

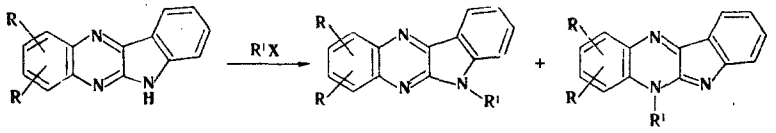
The results of the reactions of o-diamines III and IV with isatins that we carried out are in agreement with the previously published data on the reactions of other o-diamines with isatins [1, 5-7] and confirm the well-known scheme for this reaction [3]. In this connection, it must be noted that, in the opinion of a number of authors [8-11], the products of the reactions of o-diamines with isatins, which take place with splitting out of a molecule of water, are quinoxaline derivatives (A). However, the absence of convincing evidence for the structure of these compounds in the indicated papers and the data obtained in the present research and in [1, 5-7] make it possible to doubt the correctness of the interpretation of the results of the studies indicated above.



A

Y=CH, N; R=H, CH_3CO

The acylation and alkylation of 6H-indolo[2,3-b]quinoxalines VIII and XIX-XXI gave the corresponding 6-acyl- (XXII, XXIII) and 6-alkylindolo[2,3-b]quinoxalines (IX, XXIV-XXVI), the compositions and structures of which are confirmed by the results of elementary analysis and the identical character of their electronic spectra and the spectra of the 6-acetyl- (VI) and 6-methyl (VII, IX) derivatives obtained by condensation of o-diamines III and IV with N-acetyl- and N-methylisatin.



VIII, XIX-XXI IX, XXII-XXVI XXVII, XXVIII

XIX, XXII—XXIV, XXVII R,R=1,4-di-C_4H_9O; XX, XXV R,R=2,3-di-C_4H_9O; XXI, XXVI, XXVIII R,R=H; XXII $R^1=C_2H_5CO$; XXIII $R^1=C_{17}H_{33}CO$; XXIV—XXVI, XXVIII $R^1=C_{18}H_{37}$; XXVII $R^1=CH_3$

In the case of alkylation trace amounts of 5-alkyl derivatives (XXVII and XXVIII) are formed in addition to the 6-alkyl derivatives. The electronic spectra of the former, as in

TABLE 1. Characteristics of the Synthesized Compounds

Compound	mp,* °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
II	40,0—41,0	60,8	8,3	7,0	$C_{20}H_{32}N_2O_6$	60,6	8,1	7,1	57,3
V	165,0—166,0	65,5	6,1	13,5	$C_{22}H_{24}N_4O_4$	64,7	5,9	13,7	2,3
VI	195,0—196,0	71,1	6,8	10,7	$C_{24}H_{27}N_3O_3$	71,1	6,7	10,4	0,6
VII	176,0—176,5	73,0	7,3	11,0	$C_{23}H_{27}N_3O_2$	73,2	7,2	11,1	15,4
VIII	129,5—130,5	75,5	8,5	9,3	$C_{28}H_{37}N_3O_2$	75,2	8,3	9,4	7,3
IX	128,0—130,0	75,8	8,6	9,2	$C_{29}H_{39}N_3O_2$	75,5	8,4	9,1	5,2
X	219,0—220,0	64,5	6,5	13,8	$C_{22}H_{26}N_4O_5$	64,4	6,3	13,7	41,4
XI	178,0—178,5	68,0	7,1	10,2	$C_{24}H_{29}N_3O_4$	68,1	6,9	9,9	50,6
XII	150,0—151,0	69,6	7,5	10,7	$C_{23}H_{29}N_3O_3$	69,9	7,3	10,6	3,9
XIII	121,5—123,5	72,5	8,4	9,2	$C_{28}H_{39}N_3O_3$	72,3	8,4	9,0	3,3
XIV	172,0—173,0	70,5	6,9	10,8	$C_{23}H_{27}N_3O_3$	70,2	6,9	10,7	4,8
XV	195,0—196,0	72,5	8,1	9,1	$C_{28}H_{37}N_3O_3$	72,6	8,0	9,1	3,8
XVI	132,5—133,5	73,1	8,4	9,1	$C_{29}H_{39}N_3O_3$	73,0	8,2	8,8	10,4
XVII	39,0—40,0	60,1	7,0	10,2	$C_{28}H_{40}N_4O_8$	60,0	7,1	10,0	18,2—21,5
XVIII	Oil	66,0	9,1	7,8	$C_{40}H_{64}N_4O_8$	65,9	8,8	7,7	34,9—35,3
XXII	193,0—194,0	71,8	7,1	10,2	$C_{25}H_{29}N_3O_3$	71,6	6,9	10,0	40,8
XXIII	139,0—139,5	76,5	9,0	6,8	$C_{40}H_{57}N_3O_3$	76,6	9,1	6,7	9,2
XXIV	85,0—86,0	78,1	9,8	7,1	$C_{40}H_{61}N_3O_2$	78,0	9,9	6,8	52,6
XXV	88,5—89,5	78,1	9,2	6,9	$C_{40}H_{61}N_3O_2$	78,0	9,9	6,8	50,5
XXVI	101,0—102,0	81,2	9,5	8,8	$C_{32}H_{45}N_3$	81,5	9,6	8,9	38,9
XXVII	121,7—122,5	75,2	8,5	9,2	$C_{28}H_{37}N_3O_2$	75,2	8,3	9,4	0,8
XXVIII	109,0—110,0	81,7	9,4	9,0	$C_{32}H_{45}N_3$	81,5	9,6	8,9	1,5

*The compounds were recrystallized: II, VII-IX, XI, XII, XIV-XVI, and XXII from ethanol, V from heptane, VI, XVII, XXIII-XXVI, and XXVIII from hexane, X from chloroform, XIII from benzene, and XXVII from carbon tetrachloride.

[12], differ markedly from the spectra of the corresponding 6-alkylindolo[2,3-b]quinoxalines IX and XXVI. Let us note that indolo[2,3-b]quinoxalines XX and XXI, in contrast to 6H-indolo[2,3-b]quinoxalines VIII and XIX, in solutions display prototropic tautomerism, since their electronic spectra differ markedly from the 5-alkyl (XXVIII) and 6-alkyl (XXV, XXVI) derivatives.

EXPERIMENTAL

The IR spectra of 10^{-2}-10^{-3} M solutions of the synthesized compounds in $CHCl_3$ were recorded with a UR-20 spectrophotometer; the electronic spectra of alcohol solutions of these compounds were recorded. The R_f values were determined on Silufol UV-254 plates by elution with $CHCl_3$ (or benzene in the case of the R_f* values).

1,4-Dibutoxy-2,3-dinitrobenzene (I) was obtained by the method in [4], 1,4- and 2,3-dibutoxy-6(5)H-indolo[2,3-b]quinoxaline (XIX, XX) were obtained by the method in [1], 5-nitroisatin was obtained by the method in [13], 1-methylisatin was obtained by the method in [14], 1-acetylisatin was obtained by the method in [15], and 6(5)H-indolo[2,3-b]quinoxaline (XXI) was obtained by the method in [8].

1,4-Diheptyloxy-2,3-dinitrobenzene (II). A 107-ml sample of nitric acid (sp. gr. 1.42) was added with stirring at 15-20°C to a solution of 73 g (0.239 mole) of hydroquinone diheptyl ether in 180 ml of acetic acid, after which the mixture was stirred at 15-20°C for 30 min and at 50-55°C for 2 h. It was then cooled to 15°C, and the precipitate was removed by filtration, washed on the filter with water, and dried. The product was dissolved in the minimum amount of boiling ethanol, and the solution was cooled to 20°C. The precipitate was removed by filtration to give 20.3 g of 1,4-diheptyloxy-2,5-dinitrobenzene with mp 107-108°C (ethanol) with R_f*0.98. Found: C 60.3; H 8.2; N 6.8%. $C_{20}H_{32}N_2O_6$. Calculated: C 60.6; H 8.1; N 7.1%. The ethanol mother liquor was evaporated to dryness *in vacuo*, and the residue was crystallized from the minimum amount of ethanol to give 54.4 g of II with R_f* 0.92. The melting points, results of analysis, and the yields are presented in Table 1.

Reaction of 2,5-Dibutoxy-o-phenylenediamine (III) with 5-Nitroisatin. A 26.0-g (0.46 mole) sample of iron filings was added (in 4-5 g portions every 5 min) with stirring to a refluxing solution of 19.0 g (0.062 mole) of dinitro compound I and 1 ml of concentrated HCl in 80 ml of ethanol, and the mixture was refluxed with stirring for 2 h. A 2-g sample of sodium carbonate was added, and the mixture was filtered. The precipitate on the filter was washed with three 10-ml portions of hot ethanol, 200 ml of water was added to the fil-

TABLE 2. Electronic Spectra of $5 \cdot 10^{-4}$ M Solutions of the Compounds in Ethanol and IR Spectra of $1 \cdot 10^{-3}$ M Solutions of the Compounds in Chloroform

Compound	Electronic spectra, λ_{max}, nm (log ε)	IR spectra, cm^{-1}	
		νNH	νCO
V	215 (4,43), 286 (4,13), 333 (3,83), 377 (2,41), 442 (2,64)	3425	
VI	207 (4,39), 225 (4,55), 255 (3,94), 276* (3,98), 299 (4,64), 349 (3,31), 365 (3,40), 417 (2,73)		1700
VII	205 (4,33), 219 (4,44), 243 (4,17), 255 (3,94), 290 (4,72), 349 (3,99), 370* (3,99), 435 (3,38)		
VIII	205 (4,29), 219 (4,41), 238* (4,12), 255* (3,86), 289 (4,64), 349 (4,00), 370* (3,94), 435 (3,57)	3469	
IX	205 (4,28), 219 (4,38), 238* (4,12), 255 (3,89), 290 (4,64), 349 (3,93), 370* (3,81), 435 (3,45)		
X	210 (4,56), 286 (4,33), 327 (4,26), 338* (4,23), 397* (4,32), 412 (4,33)	3450, 3410	1660
XI	208 (4,54), 244* (4,35), 286 (4,19), 357 (4,13)	3370	1705, 1695
XII	207 (4,55), 217* (4,53), 244 (4,27), 289 (4,20), 331* (4,01), 338 (4,03), 354 (4,00), 451 (3,93)	3380	1660
XIII	213 (4,47), 244* (4,09), 286 (4,17), 331* (4,00), 337 (4,01), 352 (3,99), 417 (3,90)	3488, 3383	1665
XIV	222 (4,55), 227* (4,54), 260* (4,36), 266 (4,41), 270* (4,37), 291 (3,83), 325 (4,05), 339 (4,03)		1724
XV	222 (4,53), 265 (4,44), 269 (4,38), 287 (3,86), 325 (4,07), 333* (4,06)	3420	1738
XVI	213 (4,61), 246 (4,80), 250 (4,79), 252 (4,75), 301 (3,91), 425 (3,58)		1738
XVII	227* (4,29), 270 (3,86), 357* (3,55)		
XVIII	220* (4,38), 270 (3,91), 362 (3,60)		
XIX	207 (4,34), 218 (4,49), 238 (4,26), 255* (3,94), 289 (4,70), 349 (4,05), 370* (3,95), 435 (3,45)	3425	
XX	231 (4,64), 238* (4,59), 267 (4,61), 372 (4,26), 400* (4,05)	3432	
XXI	222 (4,16), 267* (4,39), 270 (4,42), 347 (3,96), 355 (4,02), 397 (3,38)		
XXII	207 (4,34), 225 (4,49), 255 (4,05), 276* (4,09), 299 (4,59), 349 (4,25), 365 (4,25), 417 (2,66)		1700
XXIII	207 (4,24), 225 (4,37), 255 (3,94), 276* (3,98), 299 (4,46), 319 (3,11), 365 (4,20), 417 (2,51)		1700
XXIV	205 (4,33), 219 (4,45), 243 (4,19), 255 (3,92), 290 (4,72), 349 (3,96), 370* (3,83), 434 (3,34)		
XXV	231 (3,06), 270 (3,00), 275* (2,97), 377 (2,83), 418 (2,51)		
XXVI	203 (4,09), 205 (4,35), 244 (3,91), 273 (4,48), 278* (4,41), 344 (4,03), 354 (4,08), 359 (4,08), 411 (3,38)		
XXVII	217 (4,75), 272* (4,65), 294 (5,13), 357 (4,35), 369 (4,35), 406 (4,07), 500 (3,53)		
XXVIII	205 (4,54), 220 (4,48), 275 (4,85), 281* (4,77), 347* (4,23), 357 (4,43), 373 (4,24), 481 (4,48)		

*Shoulder.

trate, and the mixture was extracted with benzene (three 80-ml portions). The benzene was removed by vacuum distillation, 100 ml of 50% acetic acid and 10 g (0.052 mole) of 5-nitroisatin were added to the residue, and the mixture was refluxed for 1 h. It was then cooled and treated with 200 ml of water, and the precipitate was removed by filtration, washed with water, dried, and dissolved in the minimum amount of chloroform. The solution was chromatographed on L 40/100 μ silica gel (Chemapol) with chloroform, during which four fractions were collected. The solvent was removed from these fractions by vacuum distillation, and the residues were recrystallized from appropriate solvents (Table 1) to give 0.84 g (R_f 0.75) of starting I, 3.44 g (R_f 0.66), 2,2',5,5'-tetrabutoxy-6,6'-dinitroazobenzene (XVII), 0.25 g (R_f 0.35) of 1,4-dibutoxy-9-nitro-6(5)H-indolo[2,3-b]quinoxaline (V), and 9.44 g (R_f 0.11) of 4,7-dibutoxy-5'-nitrospiro(benzimidazoline-2,3'-indolin)-2'-one (X).

Reaction of 2,5-Dibutoxy-o-phenylenediamine (III) with 1-Acetylisatin. The reaction was carried out as described above with 19.0 g (0.062 mole) of dinitro compound I and 10 g (0.053 mole) of 1-acetylisatin. Workup gave 1.37 g (R_f 0.75) of starting I, 3.74 g (R_f 0.66) of XVII, 0.13 g (R_f 0.268) of 6-acetyl-1,4-dibutoxyindolo[2,3-b]quinoxaline (VI), and 11.34 g (R_f 0.032) of 1'-acetyl-4,7-dibutoxyspiro(benzimidazoline-2,3'-indolin)-2'-one (XI).

Reaction of 2,5-Dibutoxy-o-phenylenediamine (III) with 1-Methylisatin. The reaction was carried out as described above with 26.7 g (0.087 mole) of I and 8.7 g (0.054 mole) of 1-methylisatin. Chromatographic separation of the reaction products yielded four fractions. Workup of fractions 1, 2, and 4 gave 0.8 g (R_f 0.75) of starting I, 4.44 g (R_f 0.66) of XVII, and 3.24 g (R_f 0.21) of 1,4-dibutoxy-6-methylindolo[2,3-b]quinoxaline (VII). Workup of

fraction 3 (R_f 0.34) gave a mixture of 4,7-dibutoxy-1'-methylspiro(benzimidazoline-2,3'-indolin)-2'-one (XII) and 4,7-dibutoxy-1'-methylspiro(2H-benzimidazole-2,3'-indolin)-2'-one (XIV), which was dissolved in the minimum amount of refluxing ethanol. The solution was cooled, and the precipitate was removed by filtration. The mother liquor was evaporated to dryness. Two recrystallizations of the precipitate and the residue obtained from the mother liquor from the minimum amount of ethanol gave, respectively, 0.85 g of XII and 1.04 g of XIV.

Reaction of 2,5-Diheptyloxy-o-phenylenediamine (IV) with 1-Methylisatin. The reaction was carried out as described above with 10 g (0.0252 mole) of II and 4.7 g (0.032 mole) of 1-methylisatin and gave 0.39 g of 1,4-diheptyloxy-6-methylindolo[2,3-b]quinoxaline (IX, R_f 0.45), 0.81 g of 4,7-diheptyloxy-1-methyl-spiro(2H-benzimidazole-2,3'-indolin)-2'-one (XVI, R_f 0.40), 0.75 g of starting 1-methylisatin (R_f 0.28), and 3.2 g of azobenzene XVIII (R_f 0.98).

Reaction of 2,5-diheptyloxy-o-phenylenediamine (IV) with Isatin. The reaction was carried out as described above with 40 g (0.102 mole) of II and 18.8 g (0.128 mole) of isatin. Workup gave 2.15 g of 1,4-diheptyloxy-6H-indolo[2,3-b]quinoxaline (VIII, R_f 0.13), 1.0 g of 4,7-diheptyloxyspiro(benzimidazoline-2,3'-indolin)-2'-one (XIII, R_f 0.20), 1.18 g of 4,7-diheptyloxyspiro(2H-benzimidazole-2,3'-indolin)-2'-one (XV, R_f 0.08), 3.12 g of starting isatin (R_f 0.05), and 12.8 g of azobenzene XVII (R_f 0.98).

1,4-Dibutoxy-6-propionylindolo[2,3-b]quinoxaline (XXII). A 0.8-ml sample of propionyl chloride was added dropwise with stirring to a solution of 1 g of XIX in 25 ml of pyridine, and the mixture was maintained at room temperature for 15 h. Water (100 ml) was added, and the precipitate was removed by filtration, washed on the filter with water, dried, and recrystallized from ethanol to give 0.47 g of XXII (R_f 0.60).

1,4-Dibutoxy-6-oleinoylindolo[2,3-b]quinoxaline (XXIII). This compound was similarly obtained from 1 g of XIX and 2 ml of oleinoyl chloride. The precipitate obtained as a result of the reaction was recrystallized successively from the minimum amount of ethanol and hexane. The reaction product was dissolved in the minimum amount of chloroform, and the solution was chromatographed on L 40/100 μ silica gel (Chemapol). The fraction with R_f 0.6 was collected and evaporated to dryness *in vacuo*, and the residue was recrystallized from hexane to give 0.14 g of XXIII.

6- and 5-Octadecylindolo[2,3-b]quinoxaline (XXVI, XXVIII). A solution of 21.9 g (0.1 mole) of XXI, 10 g (0.18 mole) of KOH, and 38 g (0.1 mole) of octadecyl iodide in 400 ml of ethanol was boiled for 5 h, after which it was cooled, and the precipitate was removed by filtration, washed on the filter with water, and dried. The product was dissolved in the minimum amount of chloroform, and the solution was chromatographed on L 40/100 μ silica gel (Chemapol); two fractions were collected. The solvent was removed from them by distillation, and the residues were recrystallized from hexane to give 18.3 g of XXVI (R_f 0.54) and 0.7 g of XXVIII (R_f 0.06). Water (500 ml) was added to the alcoholic mother liquor, and the precipitate was removed by filtration, washed on the filter with water, and recrystallized twice from ethanol to give 10.2 g of starting XXI.

1,4-Dibutoxy-6-octadecylindolo[2,3-b]quinoxaline (XXIV). This compound was obtained by a method similar to that used to prepare XXVI. The reaction of 1.59 g (4.24 mmole) of XIX and 1.8 g (4.74 mmole) of octadecyl iodide gave 1.37 g of XXIV (R_f 0.37) and 0.67 g of starting XIX.

2,3-Dibutoxy-6-octadecylindolo[2,3-b]quinoxaline (XXV). This compound was obtained by a method similar to that used to prepare XXVI. The reaction of 1.59 g (4.24 mmole) of XX and 1.8 g (4.74 mmole) of octadecyl iodide gave 1.23 g of XXV (R_f 0.52) and 0.52 g of starting XX.

1,4-Diheptyloxy-6-methyl- and 1,4-Diheptyloxy-5-methylindolo[2,3-b]quinoxalines (IX, XXVII). This compound was obtained by a method similar to that used to prepare XXVI and XXVIII. The reaction of 1.0 g (0.0022 mole) of VIII, 0.093 g (2.3 mmole) of sodium hydroxide, and 0.15 ml (2.3 mmole) of methyl iodide gave 0.33 g of IX (R_f 0.45), 0.004 g of XXVII (R_f 0.39), and 0.4 g of starting VIII.

LITERATURE CITED

1. V. M. Dziomko, A. V. Ivashchenko, and R. V. Poponova, Zh. Org. Khim., 10, 1325 (1974).
2. V. M. Dziomko, A. V. Ivashchenko, V. N. Avilina, and L. I. Nikol'skaya, Zh. Neorg. Khim., 19, 3349 (1974).
3. A. V. Ivashchenko and V. M. Dziomko, Usp. Khim., 44, 228 (1977).
4. S. Kawai, Y. Okawa, Y. Yada. H. Hosoi, T. Murakoshi, and I. Yajima, Nippon Kagaku Zasshi, 80, 551 (1959).
5. F. D. Popp, J. Heterocycl. Chem., 6, 125 (1969).
6. F. D. Popp, J. Heterocycl. Chem., 9, 1399 (1972).
7. R. G. Fenwick and F. D. Popp, Org. Mass Spectrom., No. 8, 1003 (1971).
8. E. Schunk and L. Marchlewski, Ber., 29, 194 (1896).
9. J. W. Armit and R. Robinson, J. Chem. Soc., No. 7, 1604 (1925).
10. M. Seth, A. P. Bhaduri, N. M. Khanna, and M. L. Dhar, Indian J. Chem., 12, 124 (1974).
11. F. Knotz and W. Wendeein, Sci. Pharm., 43, 249 (1975).
12. G. M. Badger and P. Nelson, J. Chem. Soc., No. 10, 3926 (1962).
13. G. I. Zhungietu and M. A. Rekhter, Isatin and Its Derivatives [in Russian], Shtiintsa, Kishinev (1977), p. 67.
14. J. Harley-Mason and P. E. Ingleby, J. Chem. Soc., No. 10, 3639 (1958).
15. Organic Syntheses [Russian translation], Coll. Vol. 4, Inostr. Lit., Moscow (1953), p. 404.

REACTIONS OF N-ALKYLAZINIUM CATIONS.

2.* REACTION OF QUINOXALINIUM SALTS WITH MALONODINITRILE AND CYANOACETIC ESTER

V. N. Charushin, O. N. Chupakhin,
G. M. Petrova, E. O. Sidorov,
N. A. Klyuev, and L. G. Egorova

UDC 547.863

N-Alkylquinoxalinium salts react with malonodinitrile and cyanoacetic ester carbanions to give addition products, which, due to favorably disposed CN groups and active CH centers, subsequently undergo intramolecular cyclization with the formation of a five-membered ring.

N-Alkylazinium cations are capable of readily adding carbanions and heteroatomic anions, as well as uncharged anionoid nucleophiles, to give the corresponding dihydro compounds [2]. The N-alkylquinoxalinium cation, which has a tendency to add two molecules of a nucleophilic reagent [3-5] to give tetrahydroquinoxaline derivatives, occupies a special position among these cations. The reaction of quinoxalinium salts (I) with enamines was investigated in [6], and an unusual cyclization reaction, at the basis of which also lies the ability of the quinoxalinium cation to undergo diaddition, was observed. In the present research we studied the reaction of quinoxalinium salt I with derivatives of cyanoacetic acid, viz., the ester and nitrile, which, according to the literature data, have rather high CH activity that is sufficient for participation in reactions even with less electrophilic azinium cations such as the quinolinium cation [7].

We established that, depending on the reaction conditions, the formation of several products is possible with malonodinitrile. The slow addition of a base to a mixture of quinoxalinium salt I with a twofold excess of malonodinitrile in ethanol at room temperature (method A, see the experimental section) leads to an exothermic reaction that is ac-

*See [1] for Communication 1.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 255-260, February, 1981. Original article submitted June 10, 1980.

