IMIDAZOLINE RING CLEAVAGE IN 1,3,6,10-TETRAAZATETRACYCLO-[7.3.1.$0^{2,7}$.$0^{6,13}$]TRIDECA-4,11-DIENES, LEADING TO THE FORMATION OF DIQUINOXALINO[1,2-*a*:2',3'-d]PYRROLE DERIVATIVES

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

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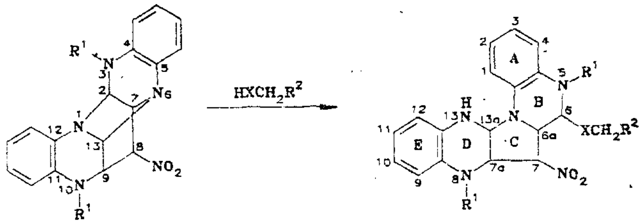
Dibenzo[d,k]-1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}$.$0^{6,13}$]trideca-4,11-dienes undergo addition reactions at the $C_{(2)}$ carbon atom with alcohols and thiols, accompanied by cleavage of the C—N bond of the imidazoline ring, to generate diquinoxalino[1,2-*a*:2',3'-d]pyrrole derivatives.

We have previously described the one-step synthesis of derivatives of a complex polycyclic system, namely, dibenzo[d,k]-1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}$.$0^{6,13}$]trideca-4,11-diene (I), via the cyclization of simple and accessible reagents, i.e., quaternary N-alkylquinoxalinium salts and nitroalkanes [1, 2]. In the present paper we wish to report the conversion of compounds of the type I, upon reaction with alcohols and thiols, in which the molecular skeleton is altered as a consequence of cleavage of the $N_{(1)}$—$C_{(2)}$ bond and transformed to partially hydrogenated diquinoxalino[1,2-*a*:2',3'-d]pyrrole derivatives.



Ia, b

IIa-g

I a $R^1=CH_3$, b $R^1=C_2H_5$; II a c, d, f $R^1=CH_3$, b, e, g $R^1=C_2H_5$, a, b $R^2=H$, c $R^2=CH_3$, d, e $R^2=C_2H_5$, f, g $R^2=C_3H_7$; a–e X=O, f, g X=S

Analysis of the spectral characteristics of compounds Ia, b indicated that their UV spectra differed in heptane and ethanol solutions; further studies of the UV spectral changes with time in a heptane—ethanol (1:4) solvent mixture revealed that compounds Ia, b were converted in ethanol solution to give compounds with altered structures (Fig. 1). This observation prompted us to investigate in more detail the nature of the reaction of compounds Ia, b with alcohols and their thio analogs, in order to determine the structures of the reaction products and to learn about the chemical behavior of the polycyclic compounds Ia, b, with the possibility of being able to prepare novel heterocyclic compounds on this basis.

Reaction of compounds Ia, b with methyl, ethyl, n-propyl alcohols, as well as with n-butylmercaptan, gave compounds IIa-g, whose elemental analyses and mass spectra yielded molecular formulas consistent with the composition of addition products (Table 1). These adducts are characterized by lower mp values than their precursors (Table 1, compare the mp of compounds IIa-g and compounds Ia (177-178°C) and Ib (176-178°C) [2]). The IR spectra of compounds IIa-f exhibit absorption bands due to N—H stretching vibrations in the 3380-3430 cm^{-1} region (Table 1), which are not present in the IR spectra of the starting materials Ia, b. The presence of N—H groups presumes cleavage of one of the C—N bonds in the imidazoline ring in compounds Ia, b: either $C_{(2)}$—$N_{(1)}$ or $C_{(13)}$—$N_{(6)}$, which would be accompanied by the addition of alcohols or mercaptans to the $C_{(2)}$ or $C_{(13)}$ carbon atoms, respectively. ^1H and ^{13}C

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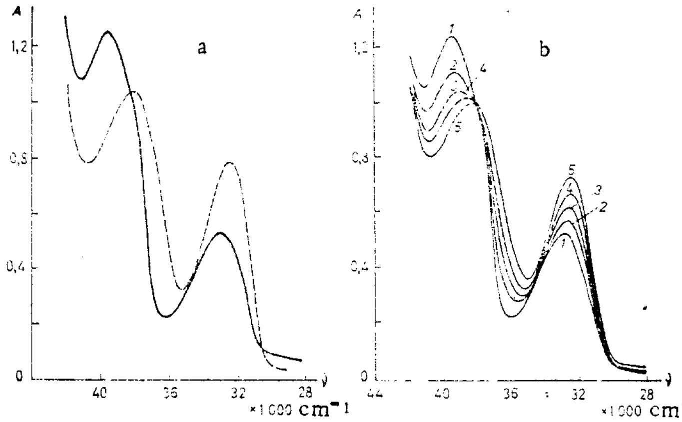

Fig. 1. UV spectra of compound Ia ($c = 4\cdot10^{-4}$ mole/liter, l = 0.2 cm) in heptane (a, continuous line) and in 1:4 heptane—ethanol (b), immediately after mixing (1), after 30 min (2), after 3 h (3), after 5 h (4), and after 22 h (5); the dotted line in (a) represents the spectrum of compound IIc ($c = 4\cdot10^{-4}$ mole/liter, l = 0.2 cm) in heptane.

NMR spectra of compounds IIa-g (Tables 2 and 3) did not permit unequivocal discrimination between these two reactive sites; the structures of the reaction products were therefore established by x-ray structural analysis of one of the products.

Results of the x-ray analysis experiment revealed that the adduct of compound Ia with n-butylmercaptan exhibits the structure diquinoxalino[1,2-*a*:2',3'-d]pyrrole (IIf). The molecular structure of compound IIf is shown in Fig. 2, and the bond lengths and bond angles are given in Tables 4 and 5. Five condensed rings A-E are found in the structure. The central pyrrolidine ring C exhibits an almost symmetrical gauche conformation; the deviations of the $C_{(7a)}$ and $C_{(7)}$ carbon atoms from the plane of the other three atoms are 0.26 and 0.31 Å, respectively (Table 6). The nitro group exhibits conventional geometric parameters (Tables 4 and 5). One of the tetrahydropyrazine rings (D) occupies an asymmetric tub conformation with deviations of the $C_{(13a)}$ and $C_{(7a)}$ carbon atoms from the $N_{(8)}C_{(8a)}C_{(12a)}N_{(13)}$ plane of 0.61 and 0.97 Å, respectively (Table 6), and with cis-annelation with the pyrrolidine ring. The $H_{(7a)}C_{(7a)}C_{(13a)}H_{(13a)}$ torsional angle is 19.49° (Table 7). The second tetrahydropyrazine ring (B) shares a common nitrogen atom with the pyrrolidine ring, and is characterized by a twisted half-chair conformation, with the $C_{(6)}$ and $C_{(6a)}$ atoms oriented in different directions away from the plane of the remaining four atoms by 0.51 and −0.21 Å, respectively (Table 6). The torsional angles characterizing the mutual three-dimensional orientation of substituents attached to the saturated bonds are summarized in Table 7. For the most part, the

TABLE 1. Properties of Diquinoxalino[1,2-*a*:2',3'-d]pyrrole Derivatives

Compound*	mp, °C (dec.)	IR spectrum, cm⁻¹		UV spectrum in heptane, λ_{max}, nm (log ε)	Found, %			Molecular formula	Calculated, %			Yield, %
		NH	NO₂		C	H	N		C	H	N	
IIa	150—151	3400	1517, 1363	225 (4,78), 262 (4,11), 308 (3,99)	63,3	6,0	18,2	$C_{20}H_{23}N_5O_3$	63,0	6,0	18,4	75
IIb	145—147	3422	1518, 1376	226 (4,75), 262 (4,11), 310 (3,98)	64,7	6,7	17,1	$C_{22}H_{27}N_5O_3$	64,5	6,7	17,1	69
IIc	136—137	3430	1517, 1380	225 (4,79), 263 (4,11), 309 (3,99)	64,2	6,3	17,7	$C_{21}H_{25}N_5O_3$	63,8	6,4	17,7	78
IId	131—132	3428	1518, 1379	225 (4,78), 263 (4,11), 308 (3,99)	64,3	6,6	16,7	$C_{22}H_{27}N_5O_3$	64,5	6,7	17,1	63
IIe	125	3382	1507, 1370	226 (4,71), 259 (4,15), 311 (3,96)	65,8	7,0	16,4	$C_{24}H_{31}N_5O_3$	65,9	7,1	16,0	70
IIf	128	3413	1517, 1380	277 (4,40), 257 (4,03), 310 (4,00)	62,6	6,6	15,8	$C_{23}H_{29}N_5O_2S$	62,8	6,6	15,9	30
IIg	103				64,1	6,9	14,7	$C_{25}H_{33}N_5O_2S$	64,2	7,1	15,0	36

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*Values of M^+ obtained by mass spectroscopy for compounds IIb (409) and IIc (395) correspond to the molecular formulas given above.

TABLE 2. PMR Spectra of Diquinoxalino[1,2,-*a*:2'3'-d]pyrrole Derivatives IIa-g in $CDCl_3$

Compound	Proton chemical shifts, δ, ppm									SSCC, Hz			
	6-H, d	6*a*-H, d of d	7-H, d of d	7*a*-H, d of d	$N_{(13)}$—H, br.s	13*a*-H, br.s	N—R^1	XCH_2R^2	benzene ring protons	$^3J_{6,6a}$	$^3J_{6a,7}$	$^3J_{7,7a}$	$^3J_{7a,13}$
IIa	4,56	4,05	5,12	4,73	4,38	5,52	2,98 (s, 3H); 3,12 (s, 3H)	3,25 (s, 3H)	6,4—6,9 (m, 8H)	2,1	7,8	8,8	5,8
IIb	4,54	3,95	5,10	4,74	4,30	5,34	1,21 (t, 3H); 1,19 (t, 3H); 3,0—3,9 (*m*, two N—CH_2)	3,18 (s, 3H)	6,4—6,9 (m, 8H)	2,1	7,8	9,0	5,8
IIc	4,65	4,07	5,10	4,76	4,37	5,55	2,99 (s, 3H); 3,08 (s, 3H)	0,90 (t, 3H); 3,2—3,8 (m, 2H)	6,4—6,9 (m, 8H)	2,0	7,6	8,8	5,8
IId	4,62	4,05	5,09	4,73	4,37	5,54	2,98 (s, 3H); 3,07 (s, 3H)	0,90 (t, 3H); 3,2—3,8 (m, 2H)	6,3—6,9 (m, 8H)	2,1	7,6	8,8	5,8
IIe*	—	—	—	—	—	—	0,9—1,5 (m, 6H); 3,0—3,8 (m, 4H)	0,65 (t, 3H); 0,9—1,5 (m, 2H)	6,4—7,2 (m, 8H)	—	—	—	—
IIf	4,46	4,48	5,33	4,81	4,40	5,50	2,91 (s, 3H); 2,99 (s, 3H)	0,9—1,7 (m, 7H); 2,3—2,8 (m, 2H)	6,4—7,0 (m, 8H)	2,4	8,3	8,8	6,7
Calc.†										2,2	7,6	8,2	7,3
IIg	4,57	4,35	5,32	4,86	4,45	5,38	1,22 (*t*, 6H); 3,0—3,7 (*m*, 4H)	0,9—1,6 (*m*, 7H); 2,3—2,7 (m, 2H)	6,4—7,0 (m, 8H)	2,5	8,3	8,8	6,2

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*It was impossible to assign unambiguously the methine group proton signals in compound IIe due to the overlap of multiplets in the 3.0-5.5 ppm region.

†Values of SSCC (spin—spin coupling constants) calculated using the Karplus equation, $^3J = 8.5 \times \cos^2 \varphi - 0.28$ (for $0° \leq \varphi \leq 90°$) and $^3J = 9.5 \times \cos^2 \varphi - 0.28$ (for $90° \leq \varphi \leq 180°$).

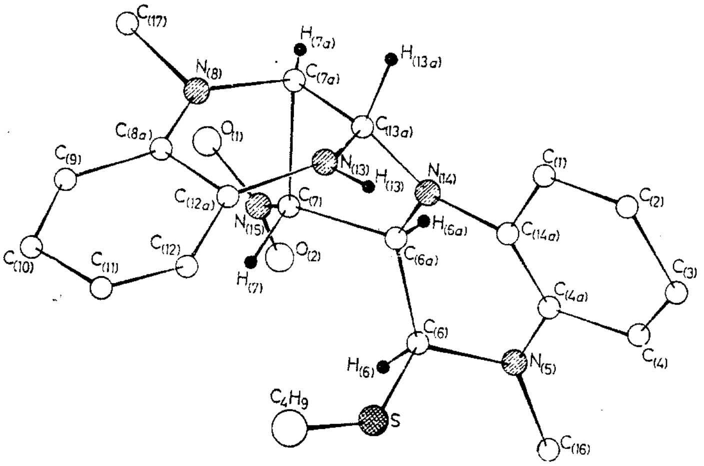

Fig. 2. Molecular structure of Compound IIf.

TABLE 3. ^{13}C NMR Spectra of Diquinoxalino[1,2-*a*:2'3'-d]pyrrole Derivatives IIa, b, g in Deuterochloroform

Carbon atom	Chemical shift,* δ, ppm (SSCC, Hz)		
	IIa	IIb	IIg
$C_{(6)}$	84,3^a	82,9 ($^1J_{CH}$=156)	64,6
$C_{(6a)}$	63,5^b	63,5 ($^1J_{CH}$=145)	64,5 c
$C_{(7)}$	84,6^a	85,6 ($^1J_{CH}$=157)	86,5
$C_{(7a)}$	64,7^b	63,1 ($^1J_{CH}$=145)	63,4 c
$C_{(13a)}$	66,5	65,6 ($^1J_{CH}$=165)	65,9
N—R^1	38,0; 40,0	13,0; 45,5; 13,6; 46,9	12,7; 45,1; 13,6; 45,4
OCH_3	56,7	55,2	—
SC_4H_9	—	—	13,2; 21,8; 31,8; 32,2
$C_{(1)}$—$C_{(4)}$, $C_{(9)}$—$C_{(12)}$	112,2; 112,9; 113,4; 114,3; 119,2; 119,6; 119,8; 119,9	112,6; 114,1; 114,4; 115,1; 119,4; 119,5; 119,6; 119,7	110,9; 113,7; 114,7; 115,2; 119,7†; 120,3
$C_{(4a)}$, $C_{(8a)}$, $C_{(12a)}$, $C_{(14a)}$	129,6; 131,9; 132,4; 133,0	130,0; 130,7; 130,8; 133,1	130,3; 131,3; 132,1; 133,6

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*The assignment of signals designated by the same letters may be interchanged.

†Position of signals due to three carbon atoms.

SC_4H_9 group occupies a pseudo-axial orientation. We note also that the main geometric parameters for a molecule of IIf are very similar to standard values [3].

The x-ray structure data allowed us to interpret unambiguously the ^1H and ^{13}C NMR spectra of compound IIf. The values of the vicinal spin-spin coupling constants (SSCC) for the protons attached to the junction atoms, $^3J_{6,6a}$ and $^3J_{7a,13a}$, calculated using the Karplus equation [4], differed significantly from one another; this reflects the different modes of annelation of the two tetrahydropyrazine rings with the central pyrrolidine ring: cis-annelation for the [b]-annelated pyrazine ring D, with a H—$C_{(7a)}$—$C_{(13a)}$—H dihedral angle of 19.49°, whereas in the [*a*]-annelated tetrahydropyrazine ring B the 6-H and 6*a*-H protons are oriented in different directions from the plane of the ring, with a H—$C_{(6)}$—$C_{(6a)}$—H dihedral angle of 57.7° (Tables 2 and 7, Fig. 2). The difference in the values of the vicinal coupling constants $^3J_{6,6a}$ and $^3J_{7a,13a}$ enabled us to differentiate the doublet signals due to the terminal protons 6-H and 13*a*-H in the chain from the subsequent five attached methine fragments, and thus to assign all of the signals in the PMR spectrum of compound IIf (Table 2). The SSCC values obtained from the PMR spectrum of compound IIf were in excellent agreement with the calculated values (Table 2). The PMR spectra of compounds IIa-e, g were similar to that of compound IIf,

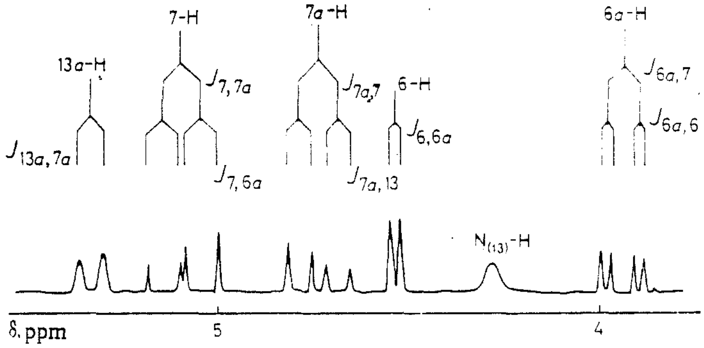

Fig. 3. Portion of the PMR spectrum of 5,8-diethyl-7-nitro-6-methoxy-7H-5,6,6*a*,7*a*,8,13,13*a*,14-octahydroquinoxalino[1,2-*a*:2',3'-d]pyrrole (IIb) in deuterochloroform (90 MHz).

TABLE 4. Bond Lengths, d, in a Molecule of Compound IIf (numbering of atoms given in Fig. 2)

Bond	d, Å	Bond	d, Å	Bond	d, Å
$C_{(1)}—C_{(2)}$	1,40(2)	$C_{(6a)}—N_{(14)}$	1,45(2)	$N_{(8)}—C_{(17)}$	1,46(2)
$C_{(2)}—C_{(3)}$	1,35(2)	$N_{(14)}—C_{(14a)}$	1,38(2)	$N_{(8)}—C_{(8a)}$	1,41(2)
$C_{(3)}—C_{(4)}$	1,39(3)	$C_{(6a)}—C_{(7)}$	1,53(2)	$C_{(8a)}—C_{(12a)}$	1,41(2)
$C_{(4)}—C_{(4a)}$	1,41(2)	$C_{(7)}—N_{(15)}$	1,50(2)	$C_{(12a)}—N_{(13)}$	1,38(2)
$C_{(4a)}—C_{(14a)}$	1,41(2)	$N_{(15)}—O_{(1)}$	1,21(2)	$N_{(13)}—C_{(13a)}$	1,46(2)
$C_{(1)}—C_{(14a)}$	1,41(2)	$N_{(15)}—O_{(2)}$	1,13(2)	$C_{(8a)}—C_{(9)}$	1,40(3)
$C_{(4a)}—N_{(5)}$	1,41(2)	$C_{(7)}—C_{(7a)}$	1,54(2)	$C_{(9)}—C_{(10)}$	1,38(3)
$N_{(5)}—C_{(16)}$	1,53(2)	$C_{(7a)}—C_{(13a)}$	1,55(2)	$C_{(10)}—C_{(11)}$	1,36(3)
$N_{(5)}—C_{(6)}$	1,44(2)	$C_{(13a)}—N_{(14)}$	1,44(2)	$C_{(11)}—C_{(12)}$	1,36(3)
$C_{(6)}—C_{(6a)}$	1,53(2)	$C_{(7a)}—N_{(8)}$	1,45(2)	$C_{(12)}—C_{(12a)}$	1,39(2)
$C_{(6)}—S$	1,84(2)				

and the signal assignments were made by analogy (Table 2). A portion of the PMR spectrum of one of these compounds (IIb) is shown in Fig. 3. It is noteworthy that the doublet for proton 13*a*-H, which is broadened due to interaction with the NH group proton, is found at lower field than the signal due to the 6-H proton (Table 2, Fig. 3), although the carbon atom $C_{(6)}$ is bounc to a more electronegative oxygen atom. This can be explained in terms of the different geometries of tetrahydropyrazine rings bridged with five- and six-membered heterocycles [6]. As has been established previously [5, 6], the signals due to the protons attached to the junctior carbon atoms in the ^{1}H NMR spectra of tetrahydroquinoxalines condensed with five-membered ring heterocycles are found considerably downfield from the spectra of tetrahydroquinoxalines condensed with six-membered ring heterocycles or those which do not feature [b]-annelated rings [5, 6]. This probably also explains the observation that the 7*a*-H proton signals in the ^{1}H NMR spectra of compounds IIa-g are found at lower field (4.7-4.9 ppm) than the 6*a*-H proton signals (3.9-4.5 ppm) (Table 2). We should note also, that the signals due to the α- and β-protons (in compounds IIc-d) of the alkoxy and thioalkoxy substituents attached to the $C_{(6)}$ carbon atom absorb upfield relative to the conventional chemical shift values for these fragments, which can be attributed to shielding of these protons due to the magnetic anisotropy of the benzene ring E (Table 2, Fig. 2).

Signal assignments in the ^{13}C NMR spectrum of compound IIb (Table 3) were made on the basis of experiments with selective spin–spin decoupling of the 6-H, 6*a*-H, 7-H, 7*a*-H, and 13*a*-H protons with the corresponding carbon atoms. The coupling constant value for the N—C—N fragment, $^1J[C_{(13a)}\ H_{(13a)}] = 165$ Hz, is large relative to that of the N—C—O fragment, $^1J[C_{(6)}—H_{(6)}] = 156$ Hz, which is explained in the following way: annelation with a five-membered ring pyrrolidine via cis-bridging forces the tetrahydropyrazine ring to adopt a tub conformation, whereas the absence of [b]-annelation, or annelation with a six-membered heterocyclic ring, allows the tetrahydropyrazine ring to adopt the usual twisted half-chair conformation with pseudo-axial and equatorial orientations of the hydrogen atoms attached to the junction carbon atoms. The latter state is characterized by lower $^1J_{CH}$ SSCC values for the junction carbon atoms [6].

TABLE 5. Bond Angles, ω, in a Molecule of Compound IIf (Fig. 2)

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(1)}C_{(2)}C_{(3)}$	121(2)	$C_{(6a)}C_{(6)}S$	112(1)	$C_{(11)}C_{(12)}C_{(12a)}$	121(2)
$C_{(2)}C_{(3)}C_{(4)}$	121(2)	$C_{(7)}C_{(6a)}N_{(14)}$	102(1)	$C_{(12)}C_{(12a)}C_{(8a)}$	119(2)
$C_{(3)}C_{(4)}C_{(4a)}$	120(2)	$C_{(7)}N_{(15)}O_{(1)}$	119(2)	$C_{(12)}C_{(12a)}N_{(13)}$	124(2)
$C_{(4)}C_{(4a)}N_{(5)}$	123(2)	$C_{(7)}N_{(15)}O_{(2)}$	121(2)	$N_{(13)}C_{(13a)}N_{(14)}$	113(1)
$C_{(4)}C_{(4a)}C_{(14a)}$	119(2)	$C_{(7)}C_{(7a)}C_{(13a)}$	102(1)	$C_{(13a)}N_{(14)}C_{(14a)}$	125(1)
$C_{(4a)}N_{(5)}C_{(6)}$	119(1)	$C_{(7)}C_{(7a)}N_{(8)}$	117(1)	$C_{(13a)}N_{(13)}C_{(12a)}$	122(1)
$C_{(4a)}N_{(5)}C_{(16)}$	116(2)	$C_{(7a)}N_{(8)}C_{(8a)}$	114(1)	$C_{(14a)}N_{(14)}C_{(6a)}$	120(1)
$C_{(4a)}C_{(14a)}C_{(7)}$	120(2)	$C_{(7a)}N_{(8)}C_{(17)}$	118(2)	$N_{(14)}C_{(14a)}C_{(1)}$	120(2)
$N_{(5)}C_{(6)}C_{(6a)}$	107(1)	$C_{(7a)}C_{(13a)}N_{(14)}$	103(1)	$N_{(14)}C_{(14a)}C_{(4a)}$	120(2)
$N_{(5)}C_{(6)}S$	113(1)	$C_{(7a)}C_{(13a)}N_{(13)}$	111(1)	$C_{(14a)}C_{(1)}C_{(2)}$	119(2)
$N_{(5)}C_{(4a)}C_{(14a)}$	118(2)	$C_{(7a)}C_{(7)}N_{(15)}$	113(1)	$O_{(1)}N_{(15)}O_{(2)}$	120(2)
$C_{(6)}C_{(6a)}C_{(7)}$	117(1)	$N_{(8)}C_{(7a)}C_{(13a)}$	110(1)	$SC_{(18)}C_{(19)}$*	115(2)
$C_{(6)}C_{(6a)}N_{(14)}$	110(1)	$N_{(8)}C_{(8a)}C_{(12a)}$	116(2)	$SC_{(18)}C_{(19a)}$*	119(3)
$C_{(6)}SC_{(18)}$	110(1)	$N_{(8)}C_{(8a)}C_{(9)}$	125(2)	$C_{(19)}C_{(20)}C_{(21)}$	97(3)
$C_{(6)}N_{(5)}C_{(16)}$	114(1)	$C_{(8a)}C_{(9)}C_{(10)}$	120(2)	$C_{(19a)}C_{(20)}C_{(21)}$	135(4)
$C_{(6a)}N_{(14)}C_{(13a)}$	115(1)	$C_{(9)}C_{(10)}C_{(11)}$	121(2)	$C_{(18)}C_{(19)}C_{(20)}$	112(3)
$C_{(6a)}C_{(7)}C_{(7a)}$	105(1)	$C_{(9)}C_{(8a)}C_{(12a)}$	119(2)	$C_{(18)}C_{(19a)}C_{(20)}$	113(3)
$C_{(6a)}C_{(7)}N_{(5)}$	110(1)	$C_{(10)}C_{(11)}C_{(12)}$	121(2)		

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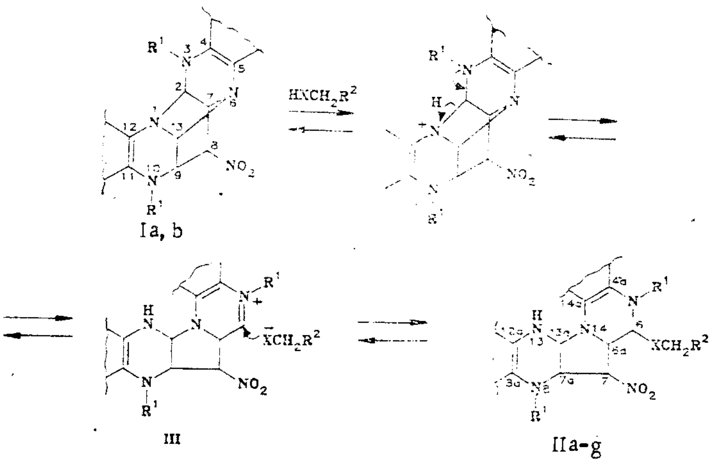
*See citation in Table 8.

The observed conversion of polycyclic compounds Ia, b to diquinoxalinopyrrole derivatives IIa-g upon treatment with alcohols and thioalcohols may be regarded as a nucleophilic substitution reaction at the saturated $C_{(2)}$ carbon atom, in which the alcohol (thiol) acts as the nucleophile and the tetrahydroqyinoxaline residue acts as the leaving group. The mechanism of this reaction was not studied, although it is very likely that cleavage of the $N_{(1)}$—$C_{(2)}$ bond is preceded by protonation of the $N_{(1)}$ atom, with subsequent addition of the nucleophile to an iminium salt III. In this regard, the x-ray structure analysis data lead to the conclusion that the $N_{(1)}$ and $N_{(6)}$ nitrogen atoms in compounds I should have heightened basicity, since they are pyramidal in structure and the degree of conjugation of their unshared electron pairs with the benzene ring is significantly reduced; this latter fact is adduced by the substantially longer $N_{(1)}$—$C_{(12)}$ and $N_{(6)}$—$C_{(5)}$ bond lengths (d = 1.44 Å), relative to the $N_{(10)}$—$C_{(11)}$ and $N_{(3)}$—$C_{(4)}$ bond lengths (d = 1.38 Å) [2]. Conversion of compounds Ia, b to diquinoxalinopyrroles IIa-g is accompanied by a flattening out of the configurations for the junction nitrogen atoms $N_{(1)}$ and $N_{(6)}$ in compounds Ia, b as a result of transition to sp^2 hybridized states and increased conjugation of their electron pairs with the π-electrons of the benzene rings. This is also verified by the x-ray structural data for compound IIf, which gave $C_{(12a)}$—$N_{(13)}$ and $N_{(14)}$—$C_{(14a)}$ bond lengths of 1.38 Å (Table 4).



Based on the data reported in [2], it would follow that the $N_{(1)}$—$C_{(2)}$ bond in compounds Ia, b is lengthened (d = 1.489 Å) and would thus appear to be the weakest C—N bond [2]. The transition to compound IIf is accompanied not only by cleavage of this bond, but also by strengthening of the $C_{(13a)}$—$N_{(14)}$, $C_{(13a)}$—$N_{(13)}$, and $C_{(6a)}$—$N_{(14)}$ bonds; the latter bond lengths in compound IIf are 1.44-1.46 Å (Table 4), in contrast to the corresponding C—N bond lengths in the polycyclic precursor Ia, which are 1.47-1.48 Å [2]. The factors, therefore, which are responsible for the greater thermodynamic stability of adducts IIa-g and which direct the reac-

TABLE 6. Equations of the Plane A-E for Various Planar Fragments of the Molecular Structure of Compound IIf and the Deviations of Atoms, Δ (Å), from these Planes (Fig. 2)

A $9{,}241x+3{,}862y+7{,}086z-1{,}786=0$; B $4{,}107x+11{,}823y-7{,}127z+1{,}471=0$;
C $8{,}663x+3{,}693y+7{,}383z-1{,}838=0$; D $2{,}810x+11{,}953y-5{,}260z+1{,}874=0$;
E $8{,}903x+6{,}290y+6{,}497z-1{,}830=0$

Plane A		Plane B		Plane C		Plane D		Plane E		Dihedral angle between the planes, deg	
atom	Δ	atom	Δ	atom	Δ	atom	Δ	atom	Δ	plane	angle
$C_{(1)}$	0,03	$C_{(4a)}$	−0,01	$C_{(6a)}$	0,00	$C_{(7a)}$*	0,97	$C_{(8a)}$	0,01	AB	2,7
$C_{(2)}$	−0,03	$C_{(14a)}$	0,01	$C_{(7)}$*	0,31	$N_{(8)}$	0,01	$C_{(9)}$	0.00	DE	4,8
$C_{(3)}$	−0,05	$N_{(5)}$	0,00	$C_{(7a)}$*	−0,26	$C_{(8a)}$	−0,02	$C_{(10)}$	0,00	CD	86,8
$C_{(4)}$	0,01	$N_{(14)}$	0,00	$C_{(13a)}$	0,00	$C_{(12a)}$	0,02	$C_{(11)}$	0,00	AE	92,4
$C_{(4a)}$	0,05	$C_{(6)}$*	0,51	$N_{(14)}$	0,00	$N_{(13)}$	−0,01	$C_{(12)}$	0,01		
$C_{(14a)}$	0,05	$C_{(6a)}$*	−0,21	$N_{(15)}$*	−0,28	$C_{(13a)}$*	0,61	$C_{(12a)}$	−0,01		
$N_{(5)}$*	0,13	S	2,34	$H_{(7)}$	1,46			$N_{(13)}$*	−0,16		
$N_{(14)}$*	0,08	$H_{(1)}$	0,21					$N_{(8)}$*	−0,03		

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*Atoms which were not included in the equations of the plane.

tions of compounds Ia, b with alcohols and thiols are as follows: elimination of the strain inherent in the polycyclic compounds Ia, b, strengthening of a series of C—N bonds, and decrease in energy associated with conjugation of the $N_{(13)}$ and $N_{(14)}$ nitrogen atoms with the π-electron systems of the benzene rings.

It should also be mentioned at this point, however, that the reaction appears to be reversible. This was detected by following the changes with time of the ^1H NMR spectra of dilute solutions of compounds IIa-3 in $CDCl_3$. For instance, the methanol adduct IIa, dissolved in deuterochloroform at a concentration of 10^{-2} mole/liter, cyclized at 20°C to give compound Ia and elimination of a methanol molecule. The degree of conversion is more than 2/3 after 24 h. Cyclic compound Ia which was formed in this manner was identified, along with the cast-off methanol molecule, by comparison of the spectrum of the reaction mixture with the spectra of pure compounds. Addition of deuterated methanol-D_4 to the reaction mixture did not result in a significant shift of the equilibrium in the direction of compound IIa, although the addition of catalytic quantities of acetic acid did effect complete conversion of compound Ia to its deuteromethanol adduct IIa, which is entirely consistent with the scheme presented above for the reaction, which incorporates protonation of the $N_{(1)}$ nitrogen atom.

Compounds IIa-e are capable of splitting off alcohol molecules not only upon standing in dilute solution, but also in the crystalline state upon heating. Thus, when crystals of IId were maintained at 100°C for 3 h, their color changed from yellow-orange to gray and polycyclic compound Ia was regenerated completely, as evidenced by overlap of its IR and PMR spectra with those of Ia, and also by the absence of mp depression for a mixed sample.

It has been noted in the literature, that the course of a reaction in the crystalline state is determined by the geometry of the crystal lattice of the reagent [7-9]. It has been estimated that the distance between the hypothetical reactive sites in the crystals should not exceed 4.2 Å [8, 9]. The experimentally determined distance between the $C_{(6)}$ and $N_{(13)}$ atoms in the crystal structure of IIf was found to be 4.2 Å, i.e., the limiting distance for interaction in the cyrstalline state. It has been shown, therefore, that the necessary proximity of the reactive sites in the adducts IIa-f is achieved both in solution as well as in the crystalline state.

The reversible interconversions of polycyclic compounds Ia, b and their convalent adducts IIa-g are a rare example of cleavage of an imidazoline ring accompanying nucleophilic addition to a saturated carbon atom.

EXPERIMENTAL

^1H NMR spectra were recorded on Perkin-Elmer R 12B (60 MHz) and Bruker WH-90 spectrometers for $CDCl_3$ solutions at 40°C and with TMS as internal standard. ^{13}C NMR spectra were ob-

TABLE 7. Torsional Angles, τ (Fig. 2)

Angle	τ°	Angle	τ°
$H_{(6)}C_{(6)}C_{(6a)}H_{(6a)}$	−57,70	$C_{(13a)}N_{(14)}C_{(6a)}C_{(7)}$	−12,12
$N_{(5)}C_{(6)}C_{(6a)}H_{(6a)}$	62,70	$H_{(6a)}C_{(6a)}C_{(7)}H_{(7)}$	155,62
$SC_{(6)}C_{(6a)}H_{(6a)}$	−173,58	$H_{(6a)}C_{(6a)}C_{(7)}N_{(15)}$	33,14
$H_{(6)}C_{(6)}C_{(6a)}N_{(14)}$	−177,03	$H_{(6a)}C_{(6a)}C_{(7)}C_{(7a)}$	−89,21
$SC_{(6)}C_{(6a)}N_{(14)}$	67,08	$H_{(7a)}C_{(7a)}C_{(7)}H_{(7)}$	−160,43
$N_{(5)}C_{(6)}C_{(6a)}N_{(14)}$	−56,59	$H_{(7a)}C_{(7a)}C_{(7)}N_{(15)}$	−38,56
$H_{(6)}C_{(6)}C_{(6a)}C_{(7)}$	66,36	$H_{(7a)}C_{(7a)}C_{(7)}C_{(6a)}$	86,57
$SC_{(6)}C_{(6a)}C_{(7)}$	−49,53	$H_{(13a)}C_{(13a)}C_{(7a)}H_{(7a)}$	19,49
$N_{(5)}C_{(6)}C_{(6a)}C_{(7)}$	−173,20	$H_{(13a)}C_{(13a)}C_{(7a)}N_{(8)}$	−89,12
$N_{(14)}C_{(6a)}C_{(7)}C_{(7a)}$	29,54	$H_{(13a)}C_{(13a)}C_{(7a)}C_{(7)}$	146,19
$C_{(6a)}C_{(7)}C_{(7a)}C_{(13a)}$	−35,58	$H_{(13a)}C_{(13a)}N_{(13)}H_{(13)}$	−79,27
$C_{(7)}C_{(7a)}C_{(13a)}N_{(14)}$	27,59	$H_{(6a)}C_{(6a)}N_{(14)}C_{(13a)}$	106,93
$C_{(7a)}C_{(13a)}N_{(14)}C_{(6a)}$	−10,06	$H_{(6a)}C_{(6a)}N_{(14)}C_{(14a)}$	−77,40

tained on a Bruker WH-90 (22.62 MHz) spectrometer. ^{13}C chemical shifts were measured relative to solvent signals (δ_{CDCl_3} 77.0 ppm). ^{13}C NMR spectra of compounds IIa and g were taken using full spin–spin carbon–proton decoupling. In order to measure SSCC for compound IIb, its spectrum was recorded both with proton coupling and also with selective decoupling of individual protons and their attached ^{13}C carbon nuclei. IR spectra of vaseline mulls were obtained on a UR-20 spectrophotometer, electronic spectra on a Specord UV-vis. Mass spectra were obtained using a Varian MAT 311 A with direct sample introduction via a stream of ions and at an accelerating voltage of 3 kV and an ionization energy of 70 eV; the current emission at the cathode was 1 mA. The vaporization temperature was 120-130°C.

X-ray structural analysis of compound IIf was carried out using a Syntex P1 diffractometer ($\lambda_{MoK\alpha}$), with a graphite monochromator, θ/2θ scanning ($2 \leq 2\theta \leq 48°$). Crystals of IIf were monoclinic with the following unit cell parameters: a = 16.131(7), b = 14.515(5), c = 9.576(3), β = 93.40(3)°, V = 2238(2) Å^3, Z = 4 space group $P2_1/c$. The structure was solved by direct methods and refined by least squares with full-matrix anisotropic approximations* to R = 0.090 (R_w = 0.097) for 1620 reflections with $F^2 \geq 3$. Atomic coordinates are given in Table 8.

3-10-Dimethyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo$[7.3.1.0^{2,7}.0^{6,13}]$trideca-4,11-diene (Ia). A suspension of 2 g (7.3 mmole) of N-methylquinoxalinium iodide in 8 ml tetrafluoropropanol HCF_2–CH_2–CH_2OH at about 20°C was stirred and 0.4 ml (7.5 mmole) nitromethane was added, along with 2 ml (14.5 mmole) triethylamine. The starting quinoxalinium salt dissolved upon the addition of base under mild heating of the reaction mixture. After 15 min crystals of Ia began to deposit out of solution; they were filtered after 1 h, washed with ether, and dried in air. Yield 0.55 g (43%), mp 177-178°C (dec.). An analytical sample was prepared by dissolving it at 20°C in a minimum amount of chloroform and adding one and a half times its volume in ethanol. After 5-10 min the resulting light yellow crystalline precipitate was isolated and dried in air. IR spectrum: 1502, 1337 cm^{-1} (NO_2), no N–H absorption bands in the 3300-3500 cm^{-1} region. UV spectrum in heptane, λ_{max} (log ε): 221 (4.53), 252 (4.20), 304 (3.82). PMR spectrum ($CDCl_3$): 3.11 (s, 3H); 3.13 (s, 3H); 4.04 (s, 1H); 4.23 (m, 2H); 4.48 (m, 2H); 6.5-7.4 (m, 8H). ^{13}C NMR spectrum ($CDCl_3$): 37.7, 38.1 (two N–CH_3); 61.1, 65.8 [$C_{(2)}$ and $C_{(9)}$]; 81.7 and 82.8 [$C_{(7)}$ and $C_{(13)}$]; 86.6 [$C_{(8)}$]; 112.1; 113.7; 118.6; 119.0; 125.1; 125.6; 126.5, 128.0 (8 CH, benzene rings); 131.3; 132.2; 135.9; 141.9 (4 quaternary C–N). Mass spectrum, m/e (I ≥ 10%): 77 (17), 130 (11), 131 (13), 145 (100), 146 (30), 171 (34), 303 (96), 304 (24), 349 (M^+, 10). Found, %: C 65.2, H 5.6, N 19.6. $C_{19}H_{19}N_5O_2$. Calculated, %: C 65.3, H 5.5, N 20.0.

3-10-Diethyl-8-Nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo$[7.3.1.0^{2,7}.0^{6,13}]$trideca-4,11-diene (Ib). This was prepared in an analogous manner from N-ethylquinoxalinium iodide and nitromethane according to the perviously described method [2]. The properties of compound Ib have also been reported earlier [2].

5,8-Diemthyl-7-nitro-6-ethoxy-7H,5,6,6a,7a,8,13,13a,14-octahydroquinoxalino[1,2-a:2',3'-d pyrrole (IIc). Compound Ia (0.4 g, 1.15 mmole was dissolved in the minimum amount of

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*Hydrogen atoms, which appeared in a difference synthesis, were not refined. The carbon atoms of the butyl group [one of which was disordered and statistically occupied two equivalent positions $C_{(19)}$ and $C_{(19a)}$ with occupancies of 0.5] were refined using isotropic (thermal) approximations.

TABLE 8. Atomic Coordinates (×10³, for sulfur atoms ×10⁴)

Atom	x	y	z	Atom	x	y	z
$C_{(1)}$	−19(1)	43(1)	258(2)	$N_{(14)}$	100(1)	29(1)	116(1)
$C_{(2)}$	−84(1)	98(2)	303(2)	$C_{(14a)}$	37(1)	82(1)	166(2)
$C_{(3)}$	−92(1)	187(2)	264(2)	$N_{(15)}$	264(1)	−3(1)	−120(2)
$C_{(4)}$	−37(1)	228(1)	177(2)	$O_{(1)}$	289(1)	−77(1)	−160(2)
$C_{(4a)}$	29(1)	175(1)	127(2)	$O_{(2)}$	265(2)	59(1)	−191(2)
$N_{(5)}$	88(1)	212(1)	40(1)	$C_{(16)}$	92(1)	317(1)	35(2)
$C_{(6)}$	168(1)	168(1)	37(2)	$C_{(17)}$	291(1)	−222(1)	54(2)
$C_{(6a)}$	151(1)	66(1)	11(2)	S	2330(3)	1879(3)	1984(5)
$C_{(7)}$	226(1)	1(1)	19(2)	$C_{(18)}$	319(1)	257(2)	128(2)
$C_{(7a)}$	192(1)	−91(1)	67(2)	$C_{(19)}$*	286(2)	203(3)	82(4)
$N_{(8)}$	251(1)	−154(1)	138(2)	$C_{(19a)}$*	403(3)	253(4)	201(6)
$C_{(8a)}$	294(1)	−115(1)	256(2)	$C_{(20)}$	439(2)	155(3)	213(4)
$C_{(9)}$	378(1)	−128(1)	294(2)	$C_{(21)}$	490(3)	103(3)	134(4)
$C_{(10)}$	413(1)	−89(2)	414(3)	$H_{(6)}$	205	188	−57
$C_{(11)}$	366(2)	−36(2)	497(2)	$H_{(6a)}$	121	64	−85
$C_{(12)}$	284(1)	−22(1)	462(2)	$H_{(7)}$	271	31	106
$C_{(12a)}$	245(1)	−62(1)	343(2)	$H_{(7a)}$	164	−140	−16
$N_{(13)}$	161(1)	−58(1)	312(1)	$H_{(13)}$	121	−20	364
$C_{(13a)}$	126(1)	−61(1)	169(2)	$H_{(13a)}$	78	−108	159

*$C_{(19)}$ and $C_{(19a)}$ have occupancies of 0.5, i.e., one of the carbon atoms of the butyl residue is statistically disordered and occupies two equivalent positions.

ethanol upon heating, refluxed for 15 min, and allowed to stand for several days at ~20°C for crystallization to occur. The crystals were removed, washed with ethanol, and air dried. Yield 0.35 g (78%), mp 136-137°C. Mass spectrum, m/e (I ≥ 10%): 77 (28), 103 (10), 130 (28), 131 (67), 132 (111), 145 (98), 146 (89), 159 (52), 171 (84), 183 (30), 303 (100), 304 (26), 349 (11), 350 (10), 395 (M^+, 24) (Tables 1-3).

The products resulting from addition of methanol and propanol to compounds Ia, b, namely compounds IIa, b, d, e, were prepared in an analogous manner (Table 1-3).

6-Butylthio-5,8-dimethyl-7-nitro-7H,5,6,6*a*,7*a*,8,13,13*a*,14-octahydroquinoxalino[1,2-*a*:2',3'-d]pyrrole (IIf). A mixture of 0.45 g (1.29 mmole) of compound Ia and 5 ml (47.6 mmole) n-butylmercaptan was heated in a water bath for 2 h. The solution stood overnight at 20°C, and then was evaporated to dryness. The residue was dissolved in ether, filtered, evaporated to dryness again, and recrystallized from ethanol. Yield 0.17 g (30%), mp 128°C (dec.). Crystals for x-ray structure analysis were obtained by recrystallization from acetone—isopropyl alcohol (1:5) (Tables 1, 2, 4-8).

6-Butylthio-5,8-diethyl-7-nitro-7H,5,6,6*a*,7*a*,8,13,13*a*,14-octahydroquinoxaline[1,2-*a*:2',3'-d]pyrrole (IIg). A mixture of 0.4 g (1.1 mmole) of compound Ib and 3 ml (28.6 mmole) n-butylmercaptan was refluxed for 15 min, cooled to 20°C, and 10 ml ether was added; the mixture was filtered and evaporated to dryness. The residue was dissolved in a minimum amount of chloroform, diluted with 5 times its volume isopropyl alcohol, and the solution was allowed to stand at 20°C for 2-3 days for crystallization to occur. The resulting crystals were removed and air dried. Yield 0.18 g (36%), mp 103°C (Tables 1-3).

Thermal Cyclization of 5,8-Dimethyl-7-nitro-6-propocy-7H,5,6,6*a*,7*a*,8,13,13*a*,14-oxtahydroquinoxalino[1,2-*a*:2',3'-d]pyrrole (IId) to Give 3,10-Dimethyl-8-nitrodibenzo[d,k]1,3,6,10-tetraazatetracyclo[7.3.1.$0^{2,7}$.$0^{6,13}$]trideca-4,11-diene (Ia). Crystals of IId (0.1 g, 0.24 mmole) were heated in an open steel ampule to 100°C and maintained at this temperature for 3 h. The form of the crystals was retained, although their color changed from yellow-orange to gray. The PMR spectrum recorded at this time was completely identical to that of compound Ia (Table 2). For purification the material was recrystallized from chloroform—isopropyl alcohol (1:5). Yield 0.06 g (64%) compound Ia, mp 175°C (dec.). The substance did not exhibit a mp depression in a mixed probe with an authentic sample of Ia and had an identical IR spectrum.

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STUDY OF PRODUCTS OF REACTION OF DIAROYLETHYLENES WITH o-PHENYLENEDIAMINE AND 1,3-DIMETHYL-5,6-DIAMINOURACIL

V. D. Orlov, S. M. Desenko,
B. Insuasti, K. A. Potekhin,
and Yu. T. Struchkov

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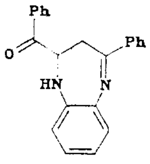
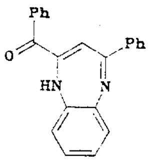
It was shown that the product of the reaction of dibenzoylethylene with o-phenylenediamine has the structure of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline. The steric structure of the dihydroqyinoxaline bicyclic compound was discussed. It was shown that the reaction of di(4-toluyl)ethylene with 1,3-dimethyl-5,6-diaminouracil leads to 5,7-dimethyl-6,8-dioxo-2-(4-methylphenacylidene)-3-(4-tolyl)-1,2-dihydropyrimidino[5,6-b]pyrazine.

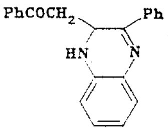
The reactions of o-phenylenediamine with dibenzoylethylene have been dealt with in several contradictory reports [1-6]. This was due first of all to the ambiguous character of the spectral proofs of the proposed sturctures of the compounds formed. In particular, it was difficult to decide between the diazepine [2-4] and quinoxaline [5, 6] structures, corresponding to two alternative paths of cyclocondensation:



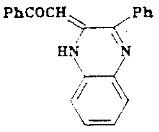
I



II



III



IV

Thus, for one of the compounds obtained in [4], a benzodiazepine structure II was proposed, based on the mass, PMR, IR, and UV spectral data. In a later publication [5], a 2-phenacylidene-3-phenyl-1,2-dihydroquinoxaline structure (IV) was proposed for the same compound, and the only argument refuting structure II was the presence of a carbonyl carbon atom signal with δ 182.4 ppm in the ^{13}C NMR spectrum, whereas the signal of the corresponding carbon nucleus of compound II should be expected in stronger fields. In [5], an intermediate in the formation of compound IV is also described, which can be both oxidized into IV and may split off a molecule of acetophenone to form 2-phenylquinoxaline. Considering these facts and taking also the spectral characteristics of the compound obtained into account, the authors of [5] proposed for it the structure of 2-phenacyl-3-phenyl-1,2-dihydroquinoxaline (III).

A. M. Gor'kii Kharkov State University, Khar'kov 310077. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Moscow 117813. P. I. Lebedev-Polyanskii Vladimir State Pedagogical Institute, Vladimir 600024. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 523-527, April, 1987. Original article submitted December 2, 1986.