CYCLIZATIONS OF N-ALKYL-SUBSTITUTED AZINIUM CATIONS WITH BIFUNCTIONAL NUCLEOPHILES.

28.* ORIENTATION OF THE NUCLEOPHILE IN THE REACTION OF QUINOXALINIUM SALTS WITH INDAN-1,3-DIONE

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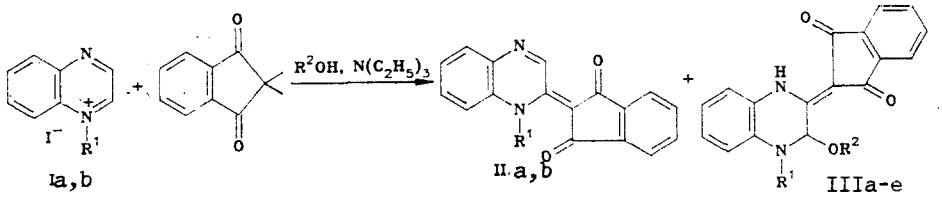
In reactions with quinoxalinium salts in alcoholic-base media indan-1,3-dione acts as a C nucleophile, adding at the 2 or 3 position of the heterocycle to give the corresponding ylidene derivatives; attack by the nucleophile at the $C_{(3)}$ atom (the β position relative to the quaternary nitrogen atom) is preceded by addition of alcohol at the α position. Dissociative substitution at the $C_{(2)}$ atom in 2-alkoxy-3-(1,3-dioxoindan-2-ylidene)-1,2,3,4-tetrahydroquinoxalines by another nucleophile makes it possible to regard lyate complexes as probable intermediates in cyclizations of 1,4-diazinium salts with dinucleophiles.

Reactions involving the diaddition of bifunctional nucleophiles to azines are of interest as simple and convenient methods for the construction of complex heterocyclic compounds [2]. In research involving cyclizations of 1,4-diazinium salts with 1,3- and 1,4-dinucleophiles it was noted that the outcome of these outwardly simple but essentially complicated (by the bifunctional character of the nucleophiles) reactions depends on a large number of internal and external factors, among which the geometrical parameters of the bifunctional reagents play no small role [2]. The geometry of the dinucleophile determines the possibility of its participation in the formation of cyclic adducts with the azine ring. It is no mere coincidence that the overwhelming majority of research on annelation to azines of other rings has been carried out with such 1,3- and 1,4-dinucleophiles, in which the reaction centers are not a part of cyclic systems that restrict their mobility [2].

In the present research we investigated the reactions of quinoxalinium salts with indan-1,3-dione, in which the β-diketone fragment is a part of a cyclic system. This predetermines the peculiarity of its reactions with quinoxalinium salts as compared with other β-dicarbonyl compounds.

The reactions of N-alkylquinoxalinium salts I with indan-1,3-dione in alcoholic media in the presence of bases (diethylamine or triethylamine) lead not to cyclic adducts or to addition products, as usual, but rather to 2- and 3-substituted 1,3-dioxoindan-2-ylidene derivatives II and III of tetrahydroquinoxaline with an approximately twofold preponderance of III (Table 1).



I, II a $R^1=CH_3$; b $R^1=C_2H_5$; III a $R^1=CH_3$, $R^2=CH_3$; b $R^1=CH_3$, $R^2=C_2H_5$; c $R^1=CH_3$, $R^2=C_3H_7$; d $R^1=C_2H_5$, $R^2=C_2H_5$; e $R^1=CH_3$, $R^2=i\text{-}C_3H_7$

*See [1] for Communication 27.

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TABLE 1. Characteristics and Yields of the Synthesized II and III

Compound	Empirical formula	T_{mp}, °C	R_f*	Yield, %
IIa	$C_{18}H_{12}N_2O_2$	295 ... 296	0,73	19
IIb	$C_{19}H_{14}N_2O_2$	220	0,77	15
IIIa	$C_{19}H_{16}N_2O_3$	190 ... 191	0,83	50
IIIb	$C_{20}H_{18}N_2O_3$	189 ... 190	0,84	33
IIIc	$C_{21}H_{20}N_2O_3$	186 ... 187	0,86	31
IIId	$C_{21}H_{20}N_2O_3$	150	0,88	29
IIIe	$C_{21}H_{20}N_2O_3$	136 ... 138	0,89	90**

*On Silufol UV-254 plates in an ethanol–chloroform–amyl acetate system (1:1:1).

**Obtained by an exchange reaction from IIIa.

TABLE 2. Data from the PMR Spectra of II and III in $CDCl_3$

Compound	Chemical shifts, δ, ppm					
	2-H, s	3-H, s	NH, brs	R¹	R²	aromatic protons, m
IIa	—	9,87	—	4,07 s	—	7,5 ... 7,9 (8H)
IIb*	—	9,53	—	1,28 t, 4,87 q		7,5 ... 8,2 (8H)
IIIa	6,48	—	12,22	3,26 s	3,46 s	6,5 ... 7,2 (4H), 7,2 ... 7,7 (4H)
IIIb	6,54	—	12,18	3,26 s	1,12 t, 3,77 q	6,5 ... 7,3 (4H), 7,3 ... 7,7 (4H)
IIIc	6,61	—	12,35	3,32 s	0,81 t, 1,55 t.q, 3,70 t	6,8 ... 7,3 (4H), 7,5 ... 7,8 (4H)
IIId	6,75	—	12,36	1,38 t, 3,79 q	1,11 t, 3,71 q	6,6 ... 7,3 (4H), 7,5 ... 7,9 (4H)
IIIe	6,65	—	12,35	3,27 s	1,10 d, 1,20 d, 4,09 m	6,7 ... 7,3 (4H), 7,4 ... 7,9 (4H)

*In d_6-DMSO.

The structures of dihydroquinoxalines II were determined on the basis of data from the PMR and ^{13}C NMR spectra. Singlet signals of a 3-H proton (9.87 ppm) and an N-methyl group (4.07 ppm), as well as a multiplet (8H) of two benzene rings at 7.5–8.2 ppm, are clearly displayed in the PMR spectrum of IIa. The position of the 3-H signal corresponds to the resonance of the proton of an azomethine bond conjugated with an electron-acceptor substituent, while the chemical shift of N–CH_3, which is located at weaker field as compared with previously studied tetrahydroquinoxaline structures [3], indicates the ylidene structure of II. Signals of an N-methyl group at 43.7 ppm and a methylidyne $C_{(3)}$ atom at 151.4 ppm, as well as signals (8CH) of two benzene rings at 116.5, 127.5, 130.7, and 131.9 ppm, which correspond to the unsymmetrical dihydroquinoxaline part of the molecule, and more intense signals at 121.5 and 133.2 ppm, which are related to CH of the symmetrical indandione fragment, appear in the ^{13}C NMR spectra of these substances at first glance are simple to interpret. Thus, the PMR spectrum of IIIa contains singlets of N–CH_3 (3.30 ppm) and OCH_3 (3.49 ppm) groups, a signal of a proton attached to a tetragonal carbon atom (6.01 ppm), and a multiplet of aromatic protons (6.6–7.9 ppm), as well as a broad singlet of the proton of an NH group at 12.2 ppm. The absence of a constant of spin-spin coupling (SSC) between the proton attached to the tetragonal carbon atom and the NH groups makes it possible to assume the presence of an indandione residue attached to the $C_{(3)}$ atom. The chemical shift of the NH signal, which is shifted to weak field due to the formation of a hydrogen bond with one of the carbonyl groups, is then understandable. However, the arguments presented above do not make it possible to completely exclude the possibility of the existence of III in an isomeric form with the opposite mutual orientation of the substituents attached to the $C_{(2)}$ and $C_{(3)}$ atoms, since the $^3J(H_{(3)}, H_{(N)})$ vicinal constants are not always displayed in the spectra of tetrahydroquinoxalines [2].

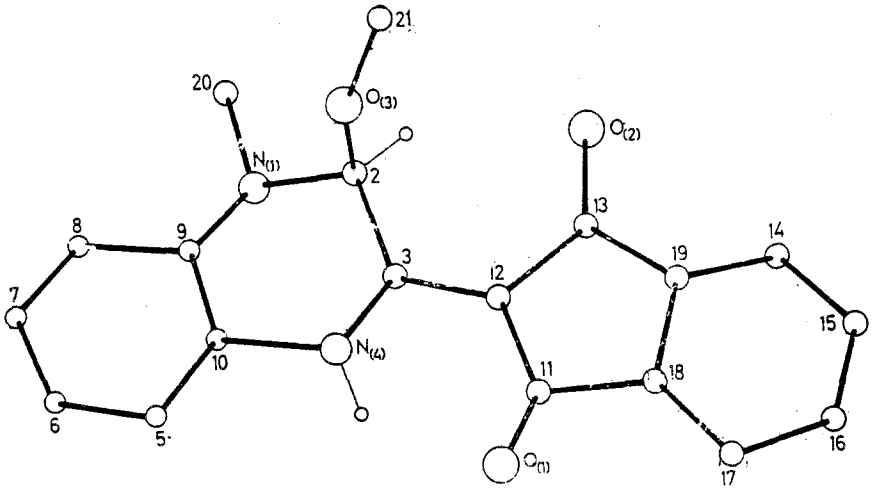


Fig. 1. Structure of the IIIa molecule.

TABLE 3. Coefficients of the General Equation Ax + By + Cz – D = 0 of the Planes of Some Planar Fragments of the IIIa Molecule and Deviations (Å) of the Atoms from Them

Compound	Atoms	A	B	C	D
I	$C_{(18)}$ $C_{(19)}$ $C_{(14)}$ $C_{(15)}$ $C_{(16)}$ $C_{(17)}$ −0,006 0,001 0,006 −0,009 0,004 0,003	3,0353	6,8862	2,5633	5,8675
II	$C_{(18)}$ $C_{(19)}$ $C_{(14)}$ $C_{(15)}$ $C_{(16)}$ $C_{(17)}$ −0,016 −0,009 0,005 −0,001 0,011 0,001 $C_{(13)}$ $C_{(12)}$ $C_{(11)}$ −0,005 0,018 −0,003	3,0101	6,8863	2,6422	5,9253
III	$C_{(18)}$ $C_{(19)}$ $C_{(13)}$ $C_{(12)}$ $C_{(11)}$ −0,001 0,005 −0,007 −0,007 −0,004	2,9827	6,8833	2,7643	5,9953
IV	$C_{(9)}$ $C_{(10)}$ $C_{(5)}$ $C_{(6)}$ $C_{(7)}$ $C_{(8)}$ 0,015 −0,013 0,002 0,008 −0,005 −0,006 $N_{(1)}$* $N_{(4)}$* 0,118 −0,005	4,1125	6,5240	3,8458	7,6242
V	$N_{(1)}$ $N_{(4)}$ $C_{(9)}$ $C_{(10)}$ $C_{(3)}$* $C_{(2)}$* 0,008 −0,008 −0,014 0,014 −0,241 −0,630	4,6608	6,3621	3,8337	8,1159
VI	$N_{(4)}$ $C_{(12)}$ $C_{(13)}$ $C_{(2)}$ −0,006 −0,006 0,017 −0,005	2,5732	6,9693	2,5062	5,5292
VII	$C_{(13)}$ $C_{(12)}$ $C_{(11)}$ $C_{(3)}$ −0,001 0,003 −0,001 −0,001	2,9366	6,8835	2,8694	6,0328

*These are atoms that were not included in the calculation of the equation of the corresponding plane; the dihedral angles between the planes were as follows: I/III 1.09°, IV/V 3.46°, and VI/VII 2.92°.

For the unequivocal determination of the structure of products III we carried out the x-ray diffraction analysis of IIIa (R^2 = OCH_3), which showed that a molecule of the investigated substance consists of tetrahydroquinoxaline and indandione fragments bonded to one another by the $C_{(3)}$=$C_{(12)}$ bond with a length of 1.380(3) Å (Fig. 1). The $C_{(13)}C_{(12)}C_{(11)}C_{(3)}C_{(2)}N_{(4)}$ fragment is virtually planar: the dihedral angle between the $N_{(4)}C_{(12)}C_{(3)}C_{(2)}$ and $C_{(13)}C_{(12)}C_{(11)}C_{(3)}$ planes is 2.9° (Table 3), and the torsion angles about the $C_{(3)}$–$C_{(12)}$ bond are close to 0° and 180° (Table 4). The indandione fragment of the molecule is also almost planar – the angle of bending of the molecule along the $C_{(18)}$–$C_{(19)}$ bond is only 1.1° (Table 3). The tetrahydropyrazine ring has the conformation of a distorted half chair with the $C_{(2)}$ and $C_{(3)}$ atoms at distances of –0.630 Å and –0.241 Å from the mean plane of the remaining four atoms of the ting, which forms a dihedral angle of 3.5° with the plane of the benzene ring $C_{(9)}C_{(10)}C_{(5)}C_{(6)}C_{(7)}C_{(8)}$ (Table 3). The values of the torsion angles characterize the conformation of the tetrahydropyrazine ring (Table 4).

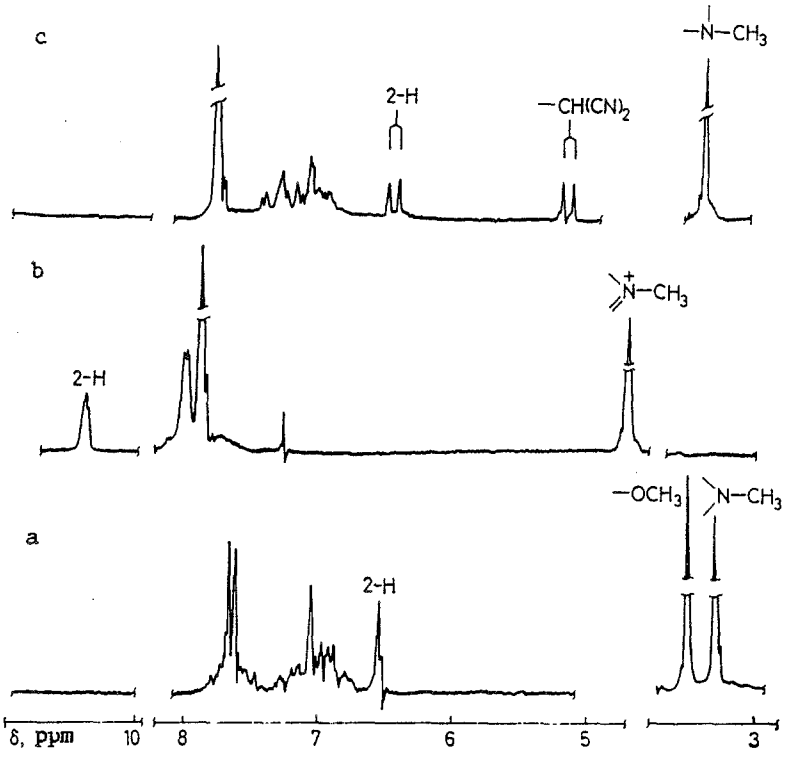


Fig. 2. Fragments of the PMR spectra of solutions in $CDCl_3$: a) IIIa; b) its conversion to salt VIII on acidification of the solution with CF_3COOH; c) formation of adduct IX on treatment of salt VIII with malonodinitrile.

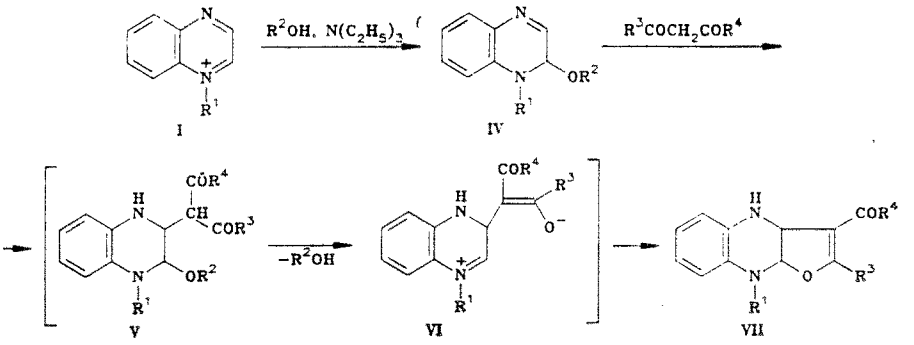
TABLE 4. Values of Some Torsion Angles in the Structure of IIIa

Atoms	Angle, deg	Atoms	Angle, deg
$C_{(3)}N_{(4)}C_{(10)}C_{(9)}$	1.0,0	$C_{(12)}C_{(3)}C_{(2)}O_{(3)}$	−87,9
$N_{(4)}C_{(10)}C_{(9)}N_{(1)}$	3,2	$C_{(12)}C_{(3)}C_{(2)}H_{(2)}$	32,4
$C_{(10)}C_{(9)}N_{(1)}C_{(2)}$	−32,8	$H_{(N4)}N_{(4)}C_{(3)}C_{(12)}$	5,7
$C_{(9)}N_{(1)}C_{(11)}C_{(10)}$	46,0	$H_{(N4)}N_{(4)}C_{(3)}C_{(2)}$	−171,2
$N_{(1)}C_{(2)}C_{(3)}N_{(4)}$	−32,0	$C_{(13)}C_{(12)}C_{(3)}C_{(2)}$	−4,0
$C_{(12)}C_{(3)}N_{(4)}C_{(10)}$	5,6	$C_{(11)}C_{(12)}C_{(3)}C_{(2)}$	175,5
$C_{(20)}N_{(1)}C_{(2)}O_{(3)}$	80,0	$C_{(13)}C_{(12)}C_{(3)}N_{(4)}$	180,0
$C_{(20)}N_{(1)}C_{(2)}H_{(2)}$	−43,2	$C_{(11)}C_{(12)}C_{(3)}N_{(4)}$	−1,2

The bond lengths and bond angles in the tetrahydroquinoxaline and indandione fragments are in good agreement with the data found in similar systems [4]. The only exception is the $N_{(4)}$–$C_{(3)}$ bond, which has a length of 1.324(3) Å, which is substantially shorter than the lengths of the three analogous C–N bonds (1.406, 1.391, and 1.429 Å). This shortening of the C–N bond is evidently due to delocalization of the π-electron density in the $N_{(4)}$–$C_{(3)}$ = $C_{(12)}$ fragment. This assumption is confirmed by the fact that the $C_{(3)}$–$C_{(12)}$ bond is somewhat elongated (1.380 Å) as compared with the standard C=C bond (1.337 Å) [5]. An N_4–H···O(1) intramolecular hydrogen bond (H···O 1.95 Å, N···O 2.740 Å, angle N–H···O 136°) is present in the IIIa molecule in the crystalline state. According to the PMR spectral data, this hydrogen bond is also retained in solutions of III (Table 2).

Now that the structures of II and III are proved, let us attempt to draw some analogies and find the common features in the reactions of quinoxalinium salts with indandione and other β-dicarbonyl compounds. Let us recall that the reactions of quinoxalinium salts and their aza and benzo analogs with acetylacetone, acetoacetic acid esters, and other acyclic β-dicarbonyl compounds have been previously examined in detail [2] and that it was shown that they lead to furo[2,3-b]quinoxalines VII. A scheme proceeding from the C addition of enolates and including the participation of lyate complexes IV, the formation of intermediates V, and the subsequent substitution of the alcohol residue attached to the $C_{(2)}$ atom during intramolecular

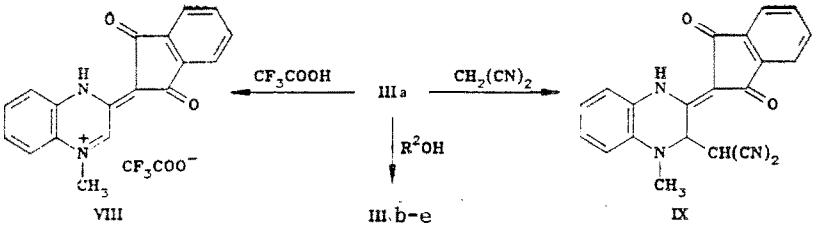
cyclization was proposed in [6] to explain the regioorientation of the furan ring in cyclization products VII. However, tetrahydroquinoxalines V or iminium salts VI could not be detected.



The formation of furo[2,3-b]quinoxalines of the VII type does not occur in the reaction with indan-1,3-dione, most likely because of the fact that the cyclic structure of the diketone hinders the cyclization process. The formation of III can be described by the same scheme, which includes intermediates V, with the difference that in this case dehydrogenation of V to ylidene derivatives III rather than intramolecular cyclization proves to be the more favorable pathway. The quinoxalinium cation or air oxygen may act as the oxidizing agent. A similar example of the oxidative condensation of a pyridinium salt with indandione was described in [7].

Thus, although the reactions of quinoxalinium salts with indandione do not lead to annelation of the furan ring, the very fact of the formation of 2-alkoxy-3-(1,3-dioxoindan-2-ylidene)-1,2,3,4-tetrahydroquinoxalines III is important for an understanding of the mechanism of the cyclization of 1,4-diazinium salts with β-dicarbonyl compounds. Compounds III are analogs of tetrahydroquinoxalines V; the substituent attached to the $C_{(3)}$ atom in them is incapable of dissociation, and they can be used as models in the study of the cyclization of 1,4-diazinium salts with β-dicarbonyl compounds.

In order to ascertain the possibilities of nucleophilic substitution of the alcohol residue attached to the $C_{(2)}$ atom in tetrahydroquinoxalines III we investigated the properties of alkoxy ylidene derivatives III. It was established by PMR spectroscopy that splitting out of an alcohol residue from the $C_{(2)}$ atom of the pyrazine ring occurs when trifluoroacetic acid is added to a solution of IIIa in $CDCl_3$. The resulting 1-methyl-3,4-dihydroquinoxalinium cation VIII is detected in the PMR spectrum from the singlet signal of the 2-H proton of the iminium fragment at 10.29 ppm and from the absorption of a quaternary N-methyl group at 4.63 ppm (Fig. 2). However, salt VIII could not be isolated from the solution.



The chemical transformations of III under the influence of nucleophiles also provide evidence for the ease of splitting out of the alkoxy group from the $C_{(2)}$ atom. Thus, on heating in ethanol and isopropyl alcohol methoxy adduct IIIa is converted completely to IIIb or IIIc (see Experimental), while replacement of the methoxy group attached to the tetragonal carbon atom with the formation of C adduct IX occurs when malonodinitrile is added to a solution of IIIa in chloroform (Fig. 2).

These transformations are similar to the substitution reactions in series of anionic σ complexes of polynitro aromatic compounds [8, 9] or neutral σ adducts of azines [10], for which an S_N1 dissociative mechanism was assumed [11]. Substitution of the alcohol residues in the 2 position of ylidene derivatives III confirms the previously proposed scheme of the formation of furo[2,3-b]quinoxalines, which includes the participation of lyate complexes IV, with a subsequent step involving intramolecular substitution of the nucleophilic group in the 2 position by the second nucleophilic center of the β-dicarbonyl compound.

TABLE 5. Coordinates of the Atoms* ($\cdot 10^4$; $\cdot 10^3$ for H) of IIIa

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	9965(2)	1265(3)	7693(2)	$C_{(18)}$	7892(3)	1746(5)	8822(3)
$O_{(2)}$	5648(2)	3580(5)	6519(2)	$C_{(19)}$	6033(3)	2445(5)	8465(3)
$O_{(3)}$	7165(2)	1835(3)	4042(2)	$C_{(20)}$	7610(3)	5772(5)	2451(3)
$N_{(1)}$	8374(3)	4580(4)	3410(2)	$C_{(21)}$	5797(4)	1832(7)	3918(4)
$N_{(4)}$	9760(3)	2446(4)	5226(2)	$H_{(N1)}$	1028(4)	184(6)	592(4)
$C_{(2)}$	7826(3)	3540(5)	4382(3)	$H_{(2)}$	682	448	464
$C_{(3)}$	8492(3)	2858(4)	5472(3)	$H_{(5)}$	1226	125	464
$C_{(5)}$	11653(3)	2073(5)	3850(3)	$H_{(6)}$	1324	199	256
$C_{(6)}$	12227(3)	2412(5)	2679(3)	$H_{(7)}$	1196	382	84
$C_{(7)}$	11499(4)	3411(5)	1728(3)	$H_{(8)}$	969	491	119
$C_{(8)}$	10215(4)	4102(5)	1927(3)	$H_{(14)}$	452	298	922
$C_{(9)}$	9624(3)	3814(5)	3103(3)	$H_{(15)}$	509	219	1121
$C_{(10)}$	10365(3)	2746(4)	4049(3)	$H_{(16)}$	725	99	1184
$C_{(11)}$	8780(3)	1804(5)	7709(3)	$H_{(17)}$	910	57	1034
$C_{(12)}$	7980(3)	2588(4)	6659(3)	$H_{(20-1)}$	278	492	808
$C_{(13)}$	6641(3)	2969(5)	7103(3)	$H_{(20-2)}$	817	685	206
$C_{(14)}$	5606(4)	2589(7)	9310(3)	$H_{(20-3)}$	679	631	276
$C_{(15)}$	5876(4)	1988(7)	10545(3)	$H_{(21-1)}$	464	−82	633
$C_{(16)}$	7139(4)	1317(6)	10902(3)	$H_{(21-2)}$	526	215	455
$C_{(17)}$	8161(4)	1183(5)	10049(3)	$H_{(21-3)}$	564	303	323

*The coordinates of the H atoms [with the exception of the $H_{(N4)}$ atom] were not refined. The temperature factors of the atoms can be obtained from the authors.

TABLE 6. Bond Lengths in the IIIa Molecules

Bond	d, Å	Bond	d, Å
$N_{(1)}$—$C_{(1)}$	1,429(3)	$C_{(9)}$—$C_{(10)}$	1,407(3)
$N_{(1)}$—$C_{(9)}$	1,391(3)	$C_{(11)}$—$C_{(12)}$	1,461(3)
$N_{(1)}$—$C_{(20)}$	1,464(3)	$C_{(11)}$—$C_{(18)}$	1,490(4)
$C_{(2)}$—$C_{(3)}$	1,520(3)	$C_{(11)}$—$O_{(1)}$	1,235(3)
$C_{(2)}$—$O_{(3)}$	1,435(3)	$C_{(12)}$—$C_{(13)}$	1,445(4)
$C_{(3)}$—$N_{(4)}$	1,324(3)	$C_{(13)}$—$C_{(19)}$	1,459(4)
$C_{(3)}$—$C_{(12)}$	1,380(3)	$C_{(13)}$—$O_{(2)}$	1,236(3)
$N_{(4)}$—$C_{(10)}$	1,406(3)	$C_{(14)}$—$C_{(15)}$	1,399(4)
$N_{(4)}$—$H_{(N4)}$	0,98(4)	$C_{(15)}$—$C_{(16)}$	1,386(4)
$C_{(5)}$—$C_{(6)}$	1,389(4)	$C_{(16)}$—$C_{(17)}$	1,379(4)
$C_{(6)}$—$C_{(7)}$	1,385(4)	$C_{(17)}$—$C_{(18)}$	1,387(4)
$C_{(7)}$—$C_{(8)}$	1,379(4)	$C_{(18)}$—$C_{(19)}$	1,391(4)
$C_{(8)}$—$C_{(9)}$	1,400(4)	$C_{(21)}$—$O_{(3)}$	1,400(4)

EXPERIMENTAL

The PMR spectra of the compounds were recorded with Perkin–Elmer R-12B (60 MHz) and Bruker WP-80 (80 MHz) spectrometers, while the ^{13}C NMR spectra were recorded with a Bruker WP-80 spectrometer (20.13 MHz) with tetramethylsilane (TMS) as the internal standard.

X-Ray Diffraction Analysis. The x-ray diffraction analysis of IIIa was carried out with a Synthex PI diffractometer with $\lambda_{(Mo\,K)}$, a graphite monochromator, $\theta/2\theta$ scanning, and $3 \le 2\theta \le 55°$. The crystals of IIIa were triclinic, and the unit cell parameters were as follows: $a = 1.140(5)$ Å, $b = 7.099(5)$ Å, $c = 11.054(6)$ Å, $\alpha = 81.20(4)°$, $\beta = 87.50(4)°$, $\gamma = 85.89(4)°$, $V = 783.9(8)$ Å^3, $Z = 2$, space group P1. The structure was decoded by the method of least squares within the total-matrix anisotropic approximation up to $R = 0.051$ ($R_w = 0.061$) for 1722 reflections with $F^2 \ge 2\sigma$. The coordinates of the atoms are presented in Table 5, and the bond lengths and bond angles are presented in Tables 6 and 7. The equations of the planes of some fragments of the molecule and the deviations of the atoms from these planes are presented in Table 3.

TABLE 7. Bond Angles in the IIIa Molecule

Angle	ω, °	Angle	ω, °
$C_{(18)}—N_{(1)}—C_{(2)}$	116,2(2)	$N_{(4)}—C_{(10)}—C_{(5)}$	120,8(2)
$C_{(18)}—N_{(1)}—C_{(9)}$	118,8(2)	$C_{(12)}—C_{(11)}—C_{(18)}$	107,1(2)
$C_{(2)}—N_{(1)}—C_{(9)}$	118,3(2)	$C_{(12)}—C_{(11)}—O_{(1)}$	127,2(3)
$N_{(1)}—C_{(2)}—C_{(3)}$	110,2(2)	$C_{(18)}—C_{(11)}—O_{(1)}$	125,7(2)
$N_{(1)}—C_{(2)}—O_{(3)}$	112,0(2)	$C_{(3)}—C_{(12)}—C_{(11)}$	122,8(2)
$C_{(3)}—C_{(2)}—O_{(3)}$	105,2(2)	$C_{(3)}—C_{(12)}—C_{(13)}$	108,1(2)
$C_{(2)}—C_{(3)}—C_{(12)}$	122,1(2)	$C_{(12)}—C_{(13)}—C_{(19)}$	107,1(2)
$N_{(4)}—C_{(3)}—C_{(12)}$	121,2(2)	$C_{(12)}—C_{(13)}—O_{(2)}$	129,2(2)
$C_{(3)}—N_{(4)}—C_{(10)}$	124,6(2)	$C_{(19)}—C_{(13)}—O_{(2)}$	123,7(3)
$C_{(3)}—N_{(4)}—H_{(N4)}$	116,3(3)	$C_{(19)}—C_{(14)}—C_{(15)}$	117,6(3)
$C_{(10)}—N_{(4)}—H_{(N4)}$	119,0(3)	$C_{(14)}—C_{(15)}—C_{(16)}$	121,1(3)
$C_{(10)}—C_{(5)}—C_{(6)}$	119,7(3)	$C_{(15)}—C_{(16)}—C_{(17)}$	121,0(3)
$C_{(5)}—C_{(6)}—C_{(7)}$	119,7(3)	$C_{(16)}—C_{(17)}—C_{(18)}$	118,1(3)
$C_{(6)}—C_{(7)}—C_{(8)}$	121,0(2)	$C_{(17)}—C_{(18)}—C_{(19)}$	120,9(3)
$C_{(7)}—C_{(8)}—C_{(9)}$	120,3(3)	$C_{(17)}—C_{(18)}—C_{(11)}$	130,5(3)
$C_{(8)}—C_{(9)}—N_{(1)}$	124,4(2)	$C_{(19)}—C_{(18)}—C_{(11)}$	108,6(3)
$C_{(8)}—C_{(9)}—C_{(10)}$	117,8(2)	$C_{(18)}—C_{(19)}—C_{(14)}$	121,4(3)
$N_{(1)}—C_{(9)}—C_{(10)}$	117,8(2)	$C_{(18)}—C_{(19)}—C_{(13)}$	109,0(2)
$C_{(9)}—C_{(10)}—N_{(4)}$	117,4(2)	$C_{(14)}—C_{(19)}—C_{(13)}$	129,6(3)
$C_{(9)}—C_{(10)}—C_{(5)}$	121,7(2)	$C_{(2)}—O_{(3)}—C_{(21)}$	115,8(2)

Quinoxalinium cations Ia, b were obtained by a previously described method [12]. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

1-Methyl-2-methoxy-3-(1,3-dioxoindan-2-ylidene)-1,2,3,4-tetrahydroquinoxaline (IIIa, $C_{19}H_{16}N_2O_3$). A. From N-methylquinoxalinium iodide (Ia). A 3-ml (0.02 mole) sample of triethylamine was added with stirring at room temperature to a suspension of 3.0 g (0.01 mole) of salt Ia and 1.6 g (0.01 mole) of indan-1,3-dione in 30 ml of methanol. The temperature of the reaction mixture rose 10–15°C, and the starting reagents dissolved. The solution was allowed to stand at room temperature for 48 h, after which it was filtered to give 1.9 g of a brown crystalline precipitate, which was identified as a mixture of two compounds, viz., IIa and IIIa. The mixture was separated by refluxing in ether. Compound IIIa dissolved and IIa, which was only slightly soluble in ether, was removed by filtration. Compound IIIa was obtained from the ether solution after removal of the solvent and was recrystallized from methanol to give yellow needles with mp 190–191°C (decomp.). ^{13}C NMR spectrum (in $CDCl_3$): 37.9 ($N–CH_3$); 57.6 (OCH_3); 82.2 [$C_{(2)}$]; 100.3 [$C_{(3)}$]; 148.3 [$C_{(2)}$ of the indandione fragment]; 113.5, 117.7, 120.0, 121.3, 121.9, 124.4, 126.7, 133.4, 133.7, 134.6, 139.7, 140.6 (12C of two benzene rings); 190.1 and 195.4 ppm (C=O).

Compounds IIIb–e were similarly obtained when the reactions of salts Ia, b with indan-1,3-dione were carried out in the corresponding alcohol.

B. From IIIb–d. A 30-ml sample of methanol was added to 0.5 g of one of IIIb, e, and the mixture was refluxed for 5 min. Crystals of IIIa precipitated in close-to-quantitative yield when the solution was cooled. The results of elementary analysis and the data from the spectra of IIIa obtained by methods A and B were identical.

By replacement of the alcohol residue in IIIa–e one can obtain any of the compounds of this series.

1-Methyl-2-(1,3-dioxoindan-2-ylidene)-1,2-dihydroquinoxaline (IIa, $C_{18}H_{12}N_2O_2$). The insoluble substance remaining after the mixture of IIa and IIIa obtained by method A (see above) was refluxed in ether and was removed by filtration and recrystallized from DMF. This gave an orange fibrous precipitate, which was removed by filtration, washed with ether, and dried at 50°C to give a product with mp 295–296°C. Compound IIb was similarly obtained.

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HETEROADAMANTANES AND THEIR DERIVATIVES

11.* SYNTHESIS OF 3,6-DIAZAHOMOADAMANTAN-9-ONE AND ITS DERIVATIVES WITH SUBSTITUENTS IN THE ANGULAR POSITIONS

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The condensation of ketones with tetramethylenediethylenediamine led to the isolation of 3,6-diazahomoadamantan-9-one and its derivatives with substituents in the angular positions; their structure was confirmed by the data of the IR, PMR, and mass spectra.

The condensation of ketones with hexamethylenetetramine, which we developed [2, 3], produced derivatives of 1,3-diazaadamantan-6-one with one or two substituents at the angular positions with readily available compounds. The substitution of hexamethylenetetramine by its analog 1,4,6,9-tetraazatricyclo[4.4.1.$1^{4,9}$]dodecane [4], which we will conditionally name as tetramethylenediethylenediamine (TDA), in this reaction permits the isolation of the 3,6-diazahomoadamantan-9-one derivatives instead of the corresponding 1,3-diazaadamantan-6-one derivatives [5]. In the present communication, data on the synthesis of the unsubstituted 3,6-diazahomoadamantan-9-one and its derivatives (I)–(XIV) with one or two substituents in the angular positions using this route are presented in Scheme 1.

Two of them – 1-methyl- and 1,8-dimethyl-3,6-diazahomoadamantan-9-ones (VIII) and (II) – were described in our brief communication [5], and the 1,8-diphenyl-3,6-diazahomoadamantan-9-one (VI) was first obtained with the yield of 8.1% by

*For Communication 10, see [1].

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