AZIRIDINYL KETONES AND THEIR CYCLIC ANILS.

10.* 2,4,6-TRIARYL-1,3-DIAZABICYCLO[3.1.0]HEX-3-ENES

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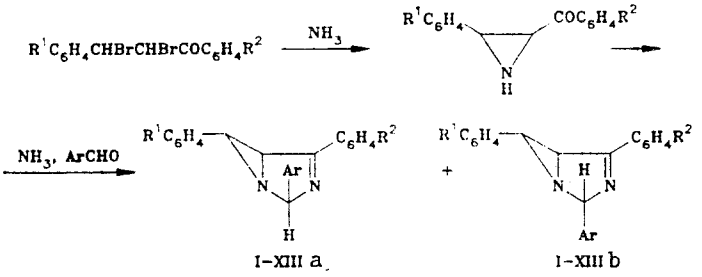
2,4,6-Triaryl-1,3-diazabicyclo[3.1.0]hex-3-enes were prepared by the reaction of α,β-dibromochalcones with aromatic aldehydes and ammonia. The exo- and endo-isomers were isolated and characterized. X-ray structural analysis of the endo-6-(4-nitrophenyl)-2,4-diphenyl derivative was performed.

The *exo*- and *endo*-isomerism† of 2-monosubstituted 1,3-diazabicyclo[3.1.0]hex-3-ene was investigated in the present study. Examples of the isolation of individual *exo*- and *endo*-isomers of this series were previously described in [2-6].

2,4,6-Triaryl-1,3-diazabicyclo[3.1.0]hex-3-enes (I-XIII) were either prepared by direct reaction of α,β-dibromochalcones with the corresponding aldehyde and excess of ammonia similar to [1], or by stages with isolation and purification of the intermediate aziridinyl ketones. Although the intermediate aziridinyl ketones are more soluble in alcohol than the starting dibromides, it is advantageous to conduct the reaction in one stage. Aziridinyl ketones prepared from 1-aryl-2,3-dibromo-3-(4-nitrophenyl)propan-1-ones do not satisfy this condition; in these cases, the stage method is preferred. The reactions of 2- and 2′-nitro-, 4-nitro-2-bromochalcone dibromides stop in the stage of formation of aziridinyl ketones, while compound IVa can be obtained from 2-fluorochalcone dibromide without isolation of the intermediate aziridinyl ketone. Absolute methanol should be used in all syntheses.



I, III R^1=H, IV R^1=2-F, V R^1=4-Cl, VI R^1=4-Br, VII—XIII R^1=4-NO_2; I, IV—XI, XIII R^2=H, III R^2=Br, XII R^2=4-OCH_3; I—XII Ar=$C_6H_4R^3$, XIII Ar=CH_3; I, III, IV, VII, XII R^3=H, V, VIII R^3=2-F, VI R^3=2-NO_2, IX R^3=4-Cl, X R^3=4-OCH_3, XI R^3=4-$N(CH_3)_2$; II 6-D-analog I

A mixture of *endo*- (a) and *exo*- (b) isomers is formed in this reaction with predominance of the *endo*-isomer. The isomers were separated by crystallization, and the *endo*-isomer usually precipitates first (with a lower R_f and frequently a lower melting point, see Table 1). The pairs Ia, b, IVa, b, IXa, b, Xa, b, and XIIIa, b were separated in this way. In the other cases, it was possible to isolate individually only the *endo* form, although formation of the *exo*-isomer was also identified on the chromatograms (except for compound III).

*See [1] for Communication 9.

†The terms "*exo*" and "*endo*" refer to isomers with *trans*- and *cis*-orientation of the substituent in position 2 of the aziridine ring relative to the imidazoline nucleus.

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TABLE 1. Characteristics of Compounds I, III-XIII

Compound	T_m, °C*1	R_f ($CHCl_3$)	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) molecular form	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$) bipolar form	IR spectrum (KBr), ν, cm^{-1} C=N	IR spectrum (KBr), ν, cm^{-1} NO_2	IR spectrum (KBr), ν, cm^{-1} 	Yield, %
Ia	144...145	0,22	247 (19,3)	516	1613	—	875	84*2
Ib	156...157	0,25	250 (21,0)	512	1600	—	882	
IIIb	167...168	0,35	261 (24,9)	518	1600	—	842	56
IVa	139...140	0,22	249 (19,7)	508	1608	—	868	95*2
IVb	126...127*3	0,36	258 (19,2)	520	1603	—	873	
Va	145...146	0,33	244 (22,5)	520	1609	—	882	78
VIa	142...143	0,21	244 (28,3)	—*4	1611	1536, 1362	855	42
VIIa	172...173	0,17	254 (20,7), 287 пл (15,1)	640	1610	1512, 1345	869	92
VIIIa	192...193	0,20	255 (23,0), 283 (15,1)	614	1617	1519, 1347	885	67
IXa	151...152	0,23	254 (21,0), 289 (14,1)	608	1602	1515, 1352	862	96*2
IXb	181...182	0,30	256 (22,1), 289 (15,0)	626	1604	1515, 1344	862	
Xa	142...143	0,19	255 (25,2), 280 (22,0)	624	1605	1513, 1348	861	94*2
Xb	168...169	0,23	256 (27,0), 280 (21,0)	622	1607	1520, 1350	867	
XIa	161...162	0,13	265 (40,0), 298 (14,7)	626	1615	1524, 1349	868	47
XIIa	171...172	0,21	282 (27,0)	638	1609	1514, 1349	859	52
XIIIa	172...173	0,12	255 (18,0), 285 (13,7)	604	1612	1516, 1344	861	74*2
XIIIb	169...170	0,14	253 (18,0), 292 (13,4)	622	1602	1511, 1348	857	

*1 Ia T_m 143-144°C [4, 5], Ib T_m 154-155°C [4, 5], mixture of Ia and Ib T_m 153-154°C [7]; VIIa T_m 173-174°C [5], VII T_m 175- 176°C [7]; X T_m 154-155°C [7]; XIII T_m 166-167°C [7]: without consideration of their isomeric composition.

*2 Yield of a mixture of isomers.

*3 According to TLC data, the compound contains a difficult to separate impurity of the corresponding chalcone dibromide.

*4 No photochromic effect was detected.

Both isomers correspond to a derivative of 1,3-diazabicyclo[3.1.0]hex-3-ene according to the data from elementary analysis and the spectral characteristics [see Table 1]. The isomers were most distinctly identified with the PMR spectra (see Table 2), particularly with the $\delta_{2\text{-H}}$. It was shown in [4] for compounds Ia, b that the signal of this proton for the *exo*-isomer should be in a stronger field than for the *endo*-isomer due to the shielding effect of the three-member ring. As Table 2 indicates, the difference in the chemical shifts of the 2-H proton is relatively large (0.42-0.54 ppm) and is characteristic of all isomeric pairs of compounds. Unambiguous assignment of the signals of the 5-H and 6-H protons is obtained by comparing the PMR spectra of compounds Ia, b and the 6-deuterated analog of Ia (IIa). The data in Table 2 also show that the isomers differ sharply with respect to the $^4J_{25}$ (1.3-1.6 Hz for the *endo*- and 2.5-3.1 Hz for the *exo*-isomer). The vicinal constants are $^3J_{56}$ = 2.0-2.5 Hz, which indicates the *trans*-orientation of protons from the three-member ring [7].

X-ray structural analysis of 6-(4-nitrophenyl)-2,4-diphenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene (VIIa) was performed for independent confirmation of the structure. This compound was assigned in [3] to the *exo*-isomer, although the analysis of its PMR spectrum in [7] with the above criteria corresponds to the *endo*-isomer. The x-ray structural study primarily confirms the result of this analysis (See Fig. 1 and Tables 3-5). The nitrophenyl substituent and imidazoline ring are *trans*-oriented relative to the aziridine ring, which corresponds to the data in the PMR spectrum. The imidazoline ring has the shape of a simplified envelope in which the $C_{(2)}$ atom maximally diverges from the median plane (to the side opposite the aziridine ring). The phenyl substituent at the $C_{(4)}$ atom lies in the same median plane, while the three-member ring forms a 73.7° dihedral angle with it.

According to the data from the x-ray structural analysis, the related system — 2,2-dimethyl-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene [1] — is a more flattened bicycle: the dihedral angle formed by the five-

TABLE 2. PMR Spectra of Compounds I-XIII

Compound	δ, ppm*1			J, Hz*2		Compound	δ, ppm.*1			J, Hz*2	
	2-H	5-H	6-H	5,6	2,5		2-H	5-H	6-H	5,6	2,5
Ia	6,76	3,70	2,44	2,2	1,4	VIIIa	6,87	3,71	2,52	2,0	1,5
Ib*3	6,20	3,70	2,69	2,2	2,9	IXa	6,71	3,72	2,41	~2	
IIa	6,76	3,70	—	—	1,4	IXb	6,21	3,72	2,77	2,2	2,9
IIIb	6,17	3,64	2,67	2,1	2,9	Xa	6,73	3,71	2,49	2,0	1,3
IVa	6,76	3,68	2,66	2,0	1,4	Xb	6,19	3,71	2,74	2,2	2,9
IVb	6,21	3,70	2,96	2,2	2,9	XIa	6,71	3,71	2,53	~2	
Va	6,85	3,62	2,44	2,1	1,4	XIIa	6,73	3,70	2,45	2,1	1,3
Vb	6,43	3,69	2,69	2,2	3,1	XIIIa	5,70	3,58	2,63	2,3	1,3
VIa	7,28	3,62	2,71	~2	—	XIIIb	5,24	3,61	2,53	~2,5	~2,5
VIIa*4	6,79	3,75	2,49	2,0	1,3						

*1 Xa δ_{CH_3} 3.76; Xb δ_{CH_3} 3.80; XIa δ_{CH_3} 2.90; XIIa δ_{CH_3} 3.85; XIIIa δ_{CH_3} 1.60 (d, J = 7.0 Hz); XIIIb δ_{CH_3} 1.51 ppm (d, J = 6.5 Hz).

*2 Ia $J_{2.6}$ = 0.8; Va $J_{2.6}$ = 0.9; Vb $J_{2.6}$ = 0.6; VII $J_{2.6}$ = 0.8 Hz.

*3 The *exo*-configuration was demonstrated with the Overhauser intramolecular effect [5].

*4 The data are in agreement with the results reported in [7].

TABLE 3. Bond Lengths (l) in Molecule VIIa

Bond	l, Å	Bond	l, Å	Bond	l, Å
$N_{(1)}$—$C_{(2)}$	1,492(9)	$C_{(10)}$—$C_{(11)}$	1,356(12)	$C_{(21)}$—$C_{(16)}$	1,381(10)
$N_{(1)}$—$C_{(5)}$	1,439(9)	$C_{(11)}$—$C_{(12)}$	1,382(11)	$C_{(4)}$—$C_{(16)}$	1,465(9)
$N_{(1)}$—$C_{(6)}$	1,466(9)	$C_{(12)}$—$C_{(7)}$	1,394(10)	$C_{(2)}$—$C_{(22)}$	1,520(10)
$C_{(2)}$—$N_{(3)}$	1,489(9)	$N_{(13)}$—$O_{(14)}$	1,227(11)	$C_{(22)}$—$C_{(23)}$	1,364(11)
$N_{(3)}$—$C_{(4)}$	1,275(9)	$N_{(13)}$—$O_{(15)}$	1,212(12)	$C_{(23)}$—$C_{(24)}$	1,385(12)
$C_{(4)}$—$C_{(5)}$	1,532(10)	$C_{(16)}$—$C_{(17)}$	1,383(11)	$C_{(24)}$—$C_{(25)}$	1,345(12)
$C_{(5)}$—$C_{(6)}$	1,493(9)	$C_{(17)}$—$C_{(18)}$	1,379(11)	$C_{(25)}$—$C_{(26)}$	1,356(13)
$C_{(6)}$—$C_{(7)}$	1,488(9)	$C_{(18)}$—$C_{(19)}$	1,380(12)	$C_{(26)}$—$C_{(27)}$	1,381(13)
$C_{(7)}$—$C_{(8)}$	1,380(10)	$C_{(19)}$—$C_{(20)}$	1,373(13)	$C_{(27)}$—$C_{(22)}$	1,372(13)
$C_{(8)}$—$C_{(9)}$	1,387(10)	$C_{(20)}$—$C_{(21)}$	1,385(12)	$C_{(10)}$—$N_{(13)}$	1,478(10)
$C_{(9)}$—$C_{(10)}$	1,373(11)				

TABLE 4. Valence (β) and Torsion (τ) Angles of the Bicyclic Part of Molecule VIIa

Angle	β°	Angle	β°	Angle	τ°
$N_{(1)}C_{(2)}N_{(3)}$	106,6(5)	$C_{(5)}C_{(6)}C_{(7)}$	119.4(5)	$N_{(1)}C_{(2)}N_{(3)}C_{(4)}$	6,0(7)
$N_{(1)}C_{(5)}C_{(4)}$	104,9(6)	$C_{(2)}N_{(1)}C_{(6)}$	114,3(5)	$C_{(2)}N_{(3)}C_{(4)}C_{(5)}$	−4,1(7)
$C_{(2)}N_{(1)}C_{(5)}$	106,6(5)	$C_{(4)}C_{(5)}C_{(6)}$	111,1(6)	$N_{(3)}C_{(4)}C_{(5)}N_{(1)}$	−0,1(7)
$C_{(2)}N_{(3)}C_{(4)}$	109,6(6)	$C_{(6)}C_{(7)}C_{(8)}$	123,2(6)	$C_{(4)}C_{(5)}N_{(1)}C_{(2)}$	3,1(7)
$N_{(3)}C_{(4)}C_{(5)}$	112,0(6)	$C_{(6)}C_{(7)}C_{(12)}$	118,9(6)	$C_{(5)}N_{(1)}C_{(2)}N_{(3)}$	−4,8(7)
$N_{(1)}C_{(5)}C_{(6)}$	60,0(4)	$N_{(1)}C_{(2)}C_{(22)}$	111,9(6)	$N_{(1)}C_{(6)}C_{(7)}C_{(8)}$	29,3(7)
$N_{(1)}C_{(6)}C_{(5)}$	58,2(4)	$N_{(3)}C_{(2)}C_{(22)}$	110,8(6)	$C_{(5)}C_{(6)}C_{(7)}C_{(12)}$	142,3(8)
$C_{(5)}N_{(1)}C_{(6)}$	61,8(4)	$C_{(5)}C_{(4)}C_{(16)}$	123,9(6)	$N_{(3)}C_{(4)}C_{(16)}C_{(21)}$	−179,8(9)
$N_{(1)}C_{(6)}C_{(7)}$	115,4(5)	$N_{(3)}C_{(4)}C_{(16)}$	124,1(6)	$N_{(3)}C_{(4)}C_{(16)}C_{(17)}$	0,7(8)

member rings is 46.8°. On the contrary, the phenyl nucleus in position 4 is turned by 12.6° relative to the C=N bond. These findings undoubtedly reflect the role of the steric effects of the two methyl groups. The structure of the molecule is similar in other respects.

The presence of isolated chromophoric fragments is a common feature of compounds I-XIII: aromatic nuclei and an arylazomethine group, responsible for the lack of significant differences in the absorption spectra of the *exo*- and *endo*-isomers. This allows modeling the absorption spectra by the additive method using the published data on the absorption of the corresponding fragments, which additionally confirms the structure. Analysis of the electron absorption spectra of isomeric compounds Xa and XIIa can be cited as an example. 4-Nitro- and 4-methoxytolyl

TABLE 5. Coordinates of Nonhydrogen Atoms ($\times 10^4$) in Molecule VIIa*

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	4971(10)	2126(3)	5479(3)	$O_{(15)}$	814(14)	5494(4)	3938(4)
$C_{(2)}$	5713(10)	1349(3)	5519(3)	$C_{(16)}$	10922(10)	2086(4)	6868(3)
$N_{(3)}$	8116(10)	1313(3)	6025(3)	$C_{(17)}$	12589(13)	1539(4)	7097(4)
$C_{(4)}$	8703(12)	1935(4)	6314(4)	$C_{(18)}$	14750(14)	1661(4)	7593(4)
$C_{(5)}$	6796(13)	2509(4)	6003(4)	$C_{(19)}$	15252(14)	2343(5)	7896(4)
$C_{(6)}$	6643(12)	2605(3)	5163(3)	$C_{(20)}$	13588(17)	2886(5)	7682(4)
$C_{(7)}$	5521(12)	3275(4)	4791(4)	$C_{(21)}$	11446(14)	2768(4)	7168(4)
$C_{(8)}$	3530(13)	3613(4)	5004(4)	$C_{(22)}$	5844(15)	1043(4)	4734(4)
$C_{(9)}$	2570(13)	4254(4)	4673(4)	$C_{(23)}$	7807(15)	662(4)	4582(4)
$C_{(10)}$	3682(13)	4550(4)	4114(4)	$C_{(24)}$	7793(15)	358(4)	3870(5)
$C_{(11)}$	5616(16)	4230(4)	3878(4)	$C_{(25)}$	5841(17)	436(4)	3311(4)
$C_{(12)}$	6531(12)	3585(4)	4204(4)	$C_{(26)}$	3882(17)	818(5)	3451(3)
$N_{(13)}$	2729(18)	5244(4)	3772(5)	$C_{(27)}$	3864(15)	1121(5)	4159(4)
$O_{(14)}$	3900(15)	5537(4)	3334(4)				

*The coordinates of the hydrogen atoms and temperature factors can be obtained from the authors.

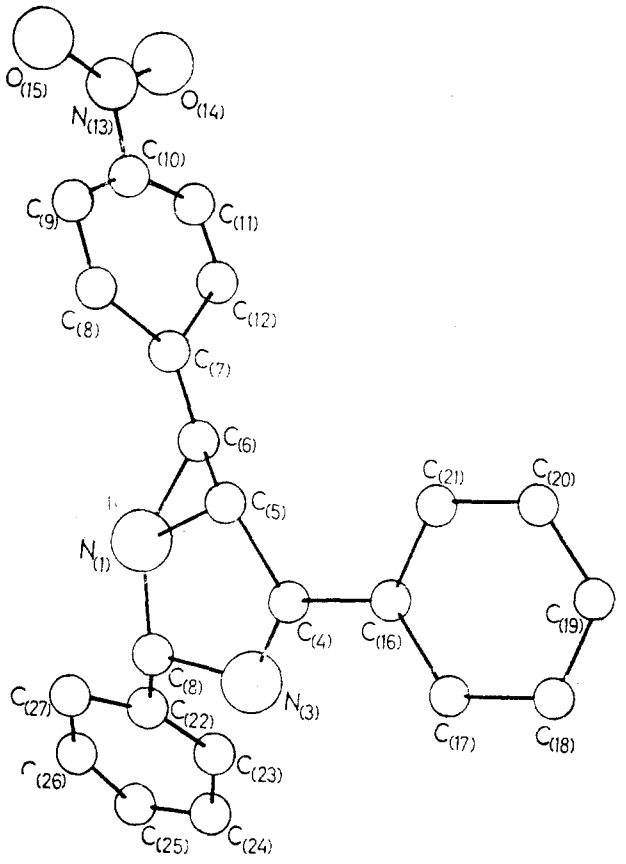


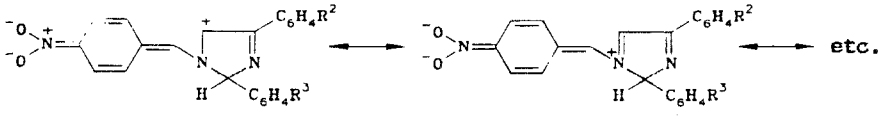
Fig. 1. Structure of the molecule of compound VIIa.

and phenylazomethine fragments with λ_{max} ($\varepsilon \cdot 10^{-3}$) of 273 (11.3), 285 (2.6), and 246 nm (13.2)* can be distinguished in the molecule of Xa; 4-nitrotolyl, tolyl, and 4-methoxyphenylazomethine fragments with λ_{max} ($\varepsilon \cdot 10^{-3}$) of 273 (11.7), 207 (9.3), and 276 nm (15.5) can be distinguished analogously in the molecule of XIIa [8, 9]. The experimental λ_{max} of compounds Xa and XIIa (see Table 1) are in good agreement with these data.

*Data for aromatic aldehydes were used because of the lack of published data for the arylazomethine group.

Pronounced photochromism in the crystals is characteristic of most of these compounds. Photochromism of aziridinyl-containing compounds is due to the formation of 1,3-ylides as a result of photochemical exposure of the C—C bond in the three-member ring [2, 3]. In solutions, this process is accompanied by isomerization into 2,3-dihydro-2,3,5-triarylpyrazines or 1-(4-nitrobenzyl)-2,4-diarylimidazoles, as demonstrated in individual examples in [5]. The process is reversible in crystals.

The reflection spectra of the ylide forms (see Table 1) show that ylides absorb much more deeply than the starting aziridinyl anils. Especially deep intensification of the color (at 320-360 nm) is characteristic of compounds with a 4-nitrophenyl substituent in position 6, which regularly reflects potentiation of the contribution of structures of the type:



The reflection spectra of the *endo*- and *exo*-isomers do not differ significantly. The aromatic nucleus in position 2 weakly affects the reflection spectra, except for the 2-nitrophenyl radical (compound VIa), whose incorporation causes the disappearance of photochromic effects in the crystals. The role of the R^2 substituent is ambiguous.

The crystals of compounds I-XIII are less stable than their 2,2-dimethyl analogs [1], and they are decolorized during prolonged UV irradiation, probably due to isomerization processes similar to those described above for solutions. This suggests that the photochromic processes are not totally reversible in the crystals of these compounds. Photochromic processes only cover the surface molecular layers in crystals, and for this reason, the total number of photocycles remains high. Unfortunately, the slow process of dark return to the molecular form, lasting for 24 h, complicates the study of the number of photocycles, which is a function of the shape and size of the crystals.

EXPERIMENTAL

The IR spectra of compounds I-XIII were measured in KBr pellets on a Specord IR-75 spectrophotometer and the electron absorption spectra were recorded in methanol with a $2\text{-}4\cdot10^{-5}$ *M* concentration of the substances on a Specord UV-vis spectrophotometer; the electron reflection spectra of the ylide forms were made on a Hitachi-330 with an integrating sphere 150 mm in diameter, the samples were prepared by applying crystals of I-XIII to a support with subsequent irradiation with UV light (the irradiation time — from several seconds to minutes — affects the intensity of the reflection bands, while the values of λ_{max} remain constant). The PMR spectra were made in $CDCl_3$ (TMS internal standard) on a Tesla BS-567A (100 MHz). The course of the reactions and purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates; chloroform was the eluent.

The x-ray structural analysis of compound VIIa was conducted at A. Mitskevich University (Poznan, Poland) in the intercollegiate collaboration with Khar'kov University. The crystals of compound VIIa are monoclinic. Crystallographic data: a = 5.558(1), b = 18.485(2), c = 17.801(3) Å, β = 100.101(1)°, V = 1800.49(5) Å^3, d_{calc} = 1.36 g·cm^{-3}, Z = 2, $\mu_{CuK\alpha}$ = 7.2 cm^{-1}, $P2_{1/n}$ space group. The intensity of the diffraction rays was measured at 20°C on a Syntex $P2_1$ four-circuit automatic diffractometer ($\lambda_{CuK\alpha}$-graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$ = 115°). We obtained 2410 independent reflections, including 1210 with $I > 1.96\,\sigma(I)$. The structure was interpreted by a direct method with the MULTAN software and was more precisely defined by the method of least squares in the totally symmetric anisotropic approximation. Only some of the hydrogen atoms were detected in difference synthesis, and the remainder were found by calculation. They were not considered in more precisely defining the structure. The final divergence factor was R = 6.8% (R_w = 7.6%) based on 1210 reflections with $F^2 > 3\sigma$.

2,4,6-Triphenyl-1,3-diazabicyclo[3.1.0]hex-3-enes (Ia, b). Dry ammonia was passed through a suspension of 1.21 g (3.3 mmole) of 1,3-diphenyl-2,3-dibromopropan-1-one, 0.7 g (6.6 mmole) of benzaldehyde, and 0.1 g of NH_4Cl in 15 ml of dry methanol for 1 h until the starting dibromide had dissolved. The tightly sealed reaction flash was left at room temperature for 2-3 days, then placed in the refrigerator for 24 h (0°C). The precipitated sediment was filtered off, washed with water and aqueous methanol (1:1), and 0.86 g (84%) of a mixture of *endo*- and *exo*-isomers of Ia (R_f 0.22) and Ib (R_f 0.25) was obtained. Then 0.4 g of prismatic crystals of the *endo*-isomer of Ia with T_m of 144-145°C and 0.8 g of needle-shaped crystals of *exo*-isomer Ib with T_m of 156-157°C were obtained by fractional crystallization from dioxane—isopentyl acetate mixture, 2:1.

Compound IIa (T_m 144-145°C), III-IV, and XIII were obtained analogously.

6-(4-Nitrophenyl)-4-phenyl-2-(4-chlorophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (IXa, b). Dry ammonia was passed through a suspension of 2.68 g (0.01 mole) of 3-benzoyl-2-(4-nitrophenyl)aziridine [10], 5.6 g (0.04

mole) of 4-chlorobenzaldehyde, and 0.1 g of NH_4Cl in 30 ml of dry methanol for 1 h. Aziridinyl ketone was dissolved, and sediment of the product of the reaction immediately began to precipitate. The flask was sealed and left at room temperature overnight and then placed in the refrigerator for 2-3 days. The precipitated sediment was filtered off and washed with water, aqueous methanol (1:1), and alcohol. Then 3.7 g (96%) of a mixture of *endo*- and *exo*-isomers of XIa, b was obtained. Fractional crystallization from dioxane—isopentyl acetate mixture, 2:1, produced 1.06 g of prismatic crystals of IXa and 0.3 g of needle-shaped crystals of IXb.

Compounds VIIa, VIIIa, and **X-XII** were obtained analogously.

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N-NITRATION OF 1(2)-SUBSTITUTED 5-AMINOTETRAZOLES WITH TETRANITROMETHANE

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1(2)-Methyl-5-aminotetrazoles and 2-(β-cyanoethyl)-5-aminotetrazole are nitrated by tetranitromethane in the presence of bases with the formation of salts of the corresponding 5-nitroaminotetrazole derivatives. In contrast to this, decyanoethylation takes place in nitration of 1-(β-cyanoethyl)-5-aminotetrazole by tetranitromethane with the formation of 5-nitroaminotetrazole salt. The structure of the 2-methyl-5-nitroaminotetrazole salts (using the 2-methyl-5-nitroaminotetrazole potassium salt) was confirmed by x-ray structural analysis.

Weakly basic aromatic amines are known [1, 2] to react with tetranitromethane in basic medium, forming N-nitroamines. Only anilines containing substituents in the *meta*- or *para*-positions are nitrated. There are published data on N-nitration of unsubstituted 5-aminotetrazole by tetranitromethane [3] and obtaining N-nitroamines from compounds I and II by treatment of the corresponding nitrate salts with sulfuric acid is described [4, 5]. The possibility of N-nitration of 5-aminotetrazole derivatives containing substituents in positions 1 or 2 with tetranitromethane has not yet been studied. We investigated the possibility of N-nitration of 1(2)-substituted 5-aminotetrazoles I-IV, which are weak bases (pK_{BH+} = 1.75 for I and pK_{BH+} = 1.81 for II [6]), with tetranitromethane.

The results of the experiments showed that only compounds I-III are smoothly nitrated into the corresponding 5-nitroaminotetrazole salts (see Table 1).

I-III V-XIV

I R=CH_3-2; II R=CH_3-1; III R=CH_2CH_2CN-2

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