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Synthesis and transformations of 1,3,5-triazabicyclo[3.1.0]hexanes*

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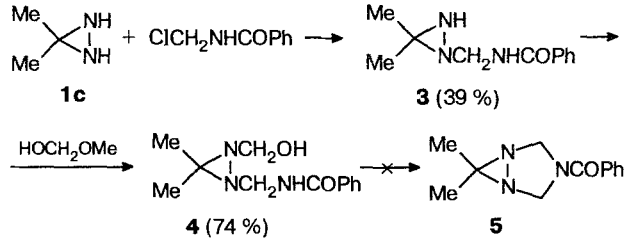
The conditions for the condensation of 1,2-nonsubstituted diaziridines with CH_2O and NH_3 (or $AlkNH_2$) to the corresponding 1,3,5-triazabicyclo[3.1.0]hexanes have been found and 3-phenylsulfonyl, 3-trimethylsilyl, 3-nitroso, and 3-nitro derivatives of the latter have been obtained.

Key words: diaziridines, condensation; 1,3,5-triazabicyclo[3.1.0]hexanes, α-aminomethylation, nitrosation, denitrosation, silylation, nitration.

It has been shown previously[2—4] that 1,2-nonsubstituted diaziridines (**1**) and 1-alkyldiaziridines (**2**) behave as NH acids in the Mannich reaction and only undergo α-aminomethylation. For example, diaziridines **2** do not react either with each other or with aziridine,[3] and alkoxymethyldiaziridine does not react with compounds having an active H atom, *viz.*, imidazole or CD_3OD in the presence of CD_3CO_2D (*cf.* Ref. 5). The absence of α-aminomethylating ability has been also observed for aziridines[6—8] and oxaziridines.[5] Presumably, this is a general property of three-membered nitrogen-containing heterocycles.[5]

Likewise, we could not overcome this restriction when both the diaziridinoalcohol fragment required for α-diaziridinomethylation and a group with an active H atom (PhCONH) were present in the same molecule: 1-benzamidomethyl-2-hydroxymethyl-3,3-dimethyldiaziridine (**4**), obtained as shown in Scheme 1, did not undergo cyclization into 3-benzoyl-6,6-dimethyl-1,3,5-triazabicyclo[3.1.0]hexane (**5**).

Scheme 1



* For the previous communication, see Ref. 1.

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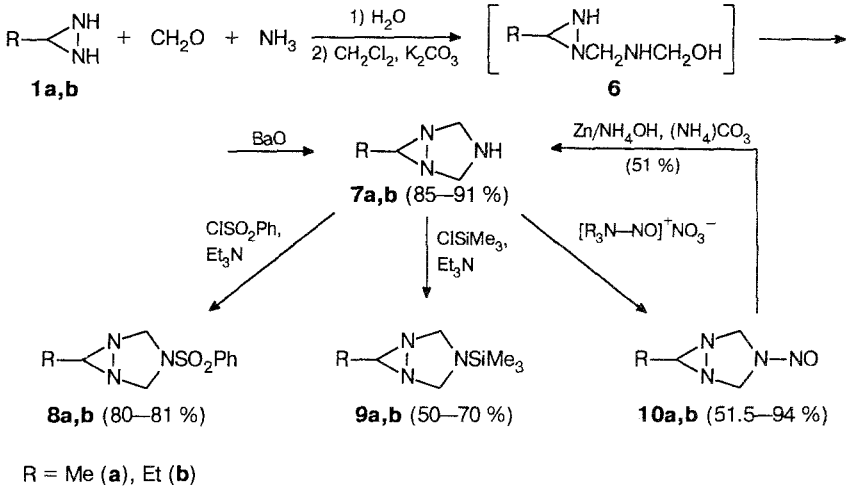
Scheme 2



R = Me (**a**), Et (**b**)

The Mannich condensation of diaziridines **1** with more basic ammonia resulted in the hitherto unknown 2,3,4-nonsubstituted 1,3,5-triazabicyclo[3.1.0]hexanes (**7**), which were then transformed to N(3)-derivatives of type **5**. Only 3-*N*-unsubstituted 2,4,6-trialkyl-1,3,5-triazabicyclo[3.1.0]hexanes have been reported in the literature so far.[9,10] Attempts to perform the condensation of 3-alkyldiaziridines **1a,b** and 3,3-dimethyldiaziridine **1c** both in aqueous or methanolic media and in aprotic organic solvents were undertaken. In both cases, an appreciable amount of urotropin was obtained. It turned out that the best conditions for synthesizing **7a,b** were: the condensation of **1a,b** with CH_2O and NH_3 in water with subsequent transfer of the reaction mixture into an organic solvent and exposure to a basic dehydrating reagent such as K_2CO_3 or BaO (Scheme 2). The yield of compounds **7** under these conditions was 85—91 %, and the side formation of urotropin did not exceed 5 %. Presumably, the first step in water is the α-aminomethylation of diaziridine (a kinetically controlled process) to give an intermediate of type **6**. If the reaction is not interrupted, then compound **6**, which is in equilibrium with the starting compounds **1a,b**, CH_2O, and NH_3, gradually decomposes, and urotropin, the product of the reaction of CH_2O and NH_3 (a thermodynamically controlled process), is the final reaction product. However, the transfer of intermediate **6** into an aprotic organic solvent containing dehydrating reagents facilitates its condensation into **7**.

Compounds **7a,b** can be easily derivatized at the nonsubstituted N(3) atom to give phenylsulfonyl (**8a,b**), trimethylsilyl (**9a,b**), and nitroso derivatives (**10a,b**). Silylation of **7a,b** was performed in a dry aprotic solvent by the action of Me_3SiCl in the presence of Et_3N. Compounds **10a,b** were obtained by a procedure earlier elaborated by us[11] for nitrosation of secondary amines with complexes of N_2O_4 with Et_3N or pyridine at low temperatures (see Scheme 2).

Attempts to reduce the NO group in compound **10a** to NH_2 group by the action of $LiAlH_4$ by a procedure given in Ref. 12 resulted in complete decomposition of the original nitroso derivative **10a**. The reaction of **10a** with Zn in the presence of NH_4OH and $(NH_4)_2CO_3$ under the conditions reported in Ref. 13 results in its denitrosation to give compound **7a** (see Scheme 2).

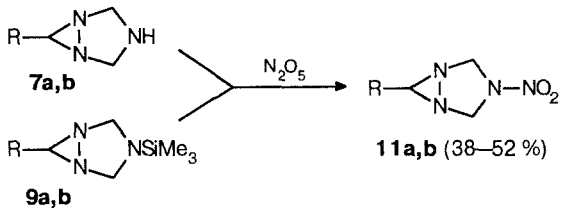
Acidic nitrating agents are not suitable for nitration of compounds **7** due to the instability of diaziridines to acids. Therefore, a series of nonacidic nitrating reagents (acetonecyanohydrine nitrate, nitronium salts, and N_2O_5) which are used for obtaining *N*-nitramines[14—16] from R_2NH or their *N*-trimethylsilyl derivatives[17] were studied in order to find a way to access the 3-*N*-nitro derivatives (**11a,b**). Acetonecyanohydrine nitrate did not react with compounds **7a** or **9a** for 70 h at 60—70 °C. Reactions of nitronium salts with compounds **7a** or **9a** in aprotic organic solvents at −35÷−30 °C result either in a mixture of compounds **10a** and **11a** or solely **10a** in low yields (Table 1).

The formation of *N*-nitroso derivatives is a typical side process in the nitration of R_2NH with nitronium tetrafluoroborate.[18] This is explained by the reduction of the nitronium cation by the amine to give the $NO_2^{\cdot}$ radical stabilized as N_2O_4. The target 3-*N*-nitro deriva-

Table 1. Yields of compounds **10a** and **11a** in the nitration of compounds **7a** and **9a** with nitronium salts

Starting compound	Nitronium salt	The yield of the product (%)	
		10a	**11a**
7a	Tetrafluoroborate	14.0	—
9a	The same	20.0	—
7a	Hexafluorosilicate	14.9	21.3
9a	The same	15.7	30.5
7a	Neutral pyrosulfate	23.1	15.1
9a	The same	20.5	20.5

Scheme 3

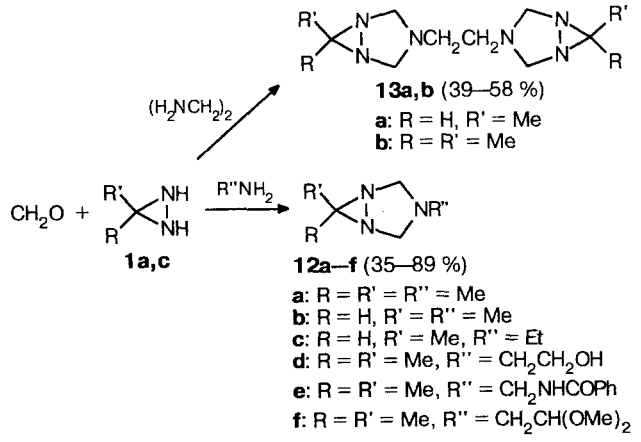


tives **11a,b** were obtained in satisfactory yields by nitration of either compounds **7** or **9** by the action of N_2O_5 in aprotic organic solvents at low temperatures (Scheme 3). These reactions are the first example of the introduction of a NO_2 group into diaziridine-containing systems with the retention of the diaziridine cycle.

The condensation of 3,3-dimethyldiaziridine **1c** with CH_2O and NH_3 under the conditions used for the synthesis of compounds **7a,b** gives a complex mixture of compounds. However, when NH_3 is replaced with primary aliphatic amines, the reaction in CH_2Cl_2 in the presence of K_2CO_3 occurs more unambiguously to give 3-alkyl-1,3,5-triazabicyclo[3.1.0]hexanes (**12** and **13**). The condensation of **1a** with CH_2O and RNH_2 occurs under the same conditions (Scheme 4).

The structures of the compounds synthesized were confirmed by physicochemical analysis and (with some exceptions) elemental analysis data. A characteristic feature of the ^1H NMR spectra of all of the 1,3,5-triazabicyclo[3.1.0]hexanes is the presence of the AB-system of protons of the N—CH_2—N group with high $\Delta\delta$ (up to 1 ppm). *N*-Nitroso derivatives **10a,b** display signals for *syn* and *anti* isomers due to hindered rotation of the NO group.

Scheme 4



Experimental

^1H NMR spectra were recorded in $CDCl_3$ (except for compounds **4** and **12c**) on Tesla BS-467, Jeol FX-90Q, Bruker WM-250, and Bruker AM-300 spectrometers with working frequencies of 60, 90, 250, and 300 MHz, respectively. HMDS was used as the internal standard in the former case, and TMS was used in the other cases. ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker AM-300 spectrometer with a working frequency of 75.5 MHz using TMS as the internal standard. Mass spectra were recorded on a Varian MAT CH-6 instrument. TLC was performed on Silufol UV-254 plates. The spots were visualized by spraying with 1 % diphenylamine in acetone followed by heating the plates.

1-Benzamidomethyl-3,3-dimethyldiaziridine (3). Triethylamine (8.2 mL, 0.06 mol) was added dropwise at 0 °C to a stirred solution of 3,3-dimethyldiaziridine **1c** (3.8 g, 0.052 mol) in benzene (20 mL), and then a suspension of *N*-chloromethylbenzamide (8.8 g, 0.052 mol) in benzene (80 mL) was added. The reaction mixture was stirred for 4 h at 5—15 °C, kept at 20 °C overnight, and then stirred for 15 min at 60 °C. The warm mixture was filtered, and the precipitate was washed with benzene. The filtrate was concentrated *in vacuo* until crystallization began and cooled. The resulting precipitate was filtered off, washed with a small amount of benzene, and dried in a vacuum desiccator over KOH to give 4 g (39 %) of diaziridine **3**, m.p. 95—96 °C. ^1H NMR (250 MHz), δ: 1.28 and 1.37 (both s, 6 H, Me); 2.07 (s, 1 H, NNH); 3.74 and 4.57 (both dd, $^2J_{AB}$ = −8.7 Hz, ^3J = 5.3 Hz, 2 H, CH_2); 7.27—7.48 (m, 4 H, *p*-,*m*-H + NHCO); 7.73—7.80 (m, 2 H, *o*-H).

1-Benzamidomethyl-2-hydroxymethyl-3,3-dimethyldiaziridine (4). Methoxymethanol (0.31 mL, 5.5 mmol) was added dropwise to a solution of compound **3** (1 g, 5 mmol) in CH_2Cl_2 (5 mL), and the mixture was boiled for 15 min. The solvent was distilled off. The residue was reprecipitated with ether from hot acetone and washed with ether to give 0.8 g (74 %) of diaziridine **4**, m.p. 99—100 °C. ^1H NMR (250 MHz, $(CD_3)_2SO$), δ: 1.25 and 1.37 (both s, 6 H, Me); 3.88 and 4.24 (both dd, $^2J_{AB}$ = −12 Hz, ^3J = 6.0 Hz and 7.0 Hz, 2 H, NCH_2N); 3.96 and 3.99 (both dd, $^2J_{A'B'}$ = −8.5 Hz, ^3J = 0.8 Hz and 1.0 Hz, 2 H, NCH_2O); 5.6 (t, 1 H, OH); 7.39—7.53 and 7.88—7.94 (both m, 5 H, Ph); 8.85 (t, 1 H, NH).

6-Alkyl-1,3,5-triazabicyclo[3.1.0]hexanes (7) (general procedure). 3-Alkyldiaziridine was added to 25 % aqueous NH_3 (20 mL, 0.2 mol), then paraform (12 g, 0.4 mol) was added portionwise at a temperature ≤ 25 °C, and the mixture was stirred for 10—15 min until paraform dissolved. Then K_2CO_3 (28 g) was added, and the mixture was heated to 60 °C. The upper layer was separated and mixed with CH_2Cl_2 (50 mL). K_2CO_3 (20 g) was added, and the organic layer was separated. This stage was repeated two or three times. The solution was kept over calcined K_2CO_3 for one or two days and over BaO for three or four days. The solvent was distilled off, and the residue was analyzed by ^1H NMR and used in further transformations.

6-Methyl-1,3,5-triazabicyclo[3.1.0]hexane (7a). Yield 85 %, m.p. 92—93 °C (from hexane). ^1H NMR (60 MHz), δ: 1.15 (d, ^3J = 5.0 Hz, 3 H, Me); 2.18 (q, ^3J = 5.0 Hz, 1 H, CH); 2.54 (br.s, 1 H, NH); 3.39 and 4.12 (both d, $^2J_{AB}$ = −9.4 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 16.1 (Me); 46.5 (CH, ^1J = 166.0 Hz, ^2J = 4.0 Hz); 66.9 (CH_2, ^1J = 156.0 Hz (*cis*-) and 148.0 Hz (*trans*-), ^3J = 5.2 Hz).

6-Ethyl-1,3,5-triazabicyclo[3.1.0]hexane (7b). Yield 91 %, oil. ^1H NMR (60 MHz), δ: 0.85 (t, 3 H, Me); 1.35 (m,

2 H, CCH_2); 2.05 (t, 1 H, CH); 2.64 (br.s, 1 H, NH); 3.82 and 4.10 (both d, $^2J_{AB}$ = −9.0 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 12.7 (Me); 23.6 (CH_2); 51.7 (CH); 67.0 (NCH_2N).

6-Alkyl-3-phenylsulfonyl-1,3,5-triazabicyclo[3.1.0]hexanes (8) (general procedure). Benzenesulfonyl chloride (1.77 g, 0.01 mol) was added dropwise at 0 °C to a stirred solution of compound **7** (0.01 mol) and Et_3N (1.26 mL, 0.01 mol) in $CHCl_3$ (25 mL). Stirring was continued for 1 h at 0 °C and for 3 h at 20 °C. The mixture was left overnight and then washed with water (2×10 mL). The solvent was distilled off, and the residue was recrystallized from an ether—pentane mixture.

6-Methyl-3-phenylsulfonyl-1,3,5-triazabicyclo[3.1.0]hexane (8a). Yield 80 %, m.p. 65 °C. Found (%): C, 50.17; H, 5.44; N, 17.38; S, 13.04. $C_{10}H_{13}N_3O_2S$. Calculated (%): C, 50.19; H, 5.48; N, 17.55; S, 13.40. ^1H NMR (60 MHz), δ: 1.20 (d, ^3J = 5.0 Hz, 3 H, Me); 2.55 (q, ^3J = 5.0 Hz, 1 H, CH); 4.68 and 4.72 (both d, $^2J_{AB}$ = −7.2 Hz, 4 H, NCH_2N); 7.62 (m, 5 H, Ph). ^{13}C NMR, δ: 15.9 (Me); 51.3 (CH, ^1J = 168.0 Hz, ^2J = 5.0 Hz); 66.8 (NCH_2N, ^1J = 159.0 Hz (*cis*-), 148.0 Hz (*trans*-), ^3J = 5.4 Hz); 113.5, 116.0, 119.9, 125.4 (*o*-,*m*-,*p*-,*ipso*-C(Ar)).

6-Ethyl-3-phenylsulfonyl-1,3,5-triazabicyclo[3.1.0]hexane (8b). Yield 81 %, m.p. 66 °C. Found (%): C, 52.4; H, 6.16; N, 16.85; S, 12.56. $C_{11}H_{15}N_3O_2S$. Calculated (%): C, 52.25; H, 6.21; N, 16.77; S, 12.61. ^1H NMR (60 MHz), δ: 0.91 (t, 3 H, Me); 1.40 (m, 2 H, CH_2); 2.36 (t, 1 H, CH); 3.82 and 4.42 (both d, $^2J_{AB}$ = −9.0 Hz, 4 H, NCH_2N); 7.58 (m, 5 H, Ph). ^{13}C NMR, δ: 8.7 (Me); 23.5 (CH_2); 56.6 (CH, ^1J = 167.0 Hz); 67.0 (NCH_2N, ^1J = 158.0 Hz (*cis*-) and 147.0 Hz (*trans*-), ^2J = 5.5 Hz); 129.2, 129.7, 133.0, 138.3 (*o*-,*m*-,*p*-,*ipso*-C(Ar)).

6-Alkyl-3-trimethylsilyl-1,3,5-triazabicyclo[3.1.0]hexanes (9) (general procedure). Me_3SiCl (5.65 g, 0.052 mol) was added dropwise at −10 °C in a flow of dry N_2 to a solution of compound **7** (0.052 mol) and Et_3N (5.25 g, 0.052 mol) in anh. CH_2Cl_2 (5 mL) and abs. ether (75 mL). The mixture was heated to 20 °C and left overnight. The precipitate was filtered off, the solvent was distilled off, and the residue was distilled *in vacuo*.

6-Methyl-3-trimethylsilyl-1,3,5-triazabicyclo[3.1.0]hexane (9a). Yield 50 %, b.p. 42 °C (1 Torr). ^1H NMR (60 MHz), δ: 0.1 (s, 9 H, Me_3Si); 1.56 (d, 3 H, MeC); 2.82 (q, 1 H, CH); 4.04 and 4.64 (both d, $^2J_{AB}$ = −7.2 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 1.1 (Me_3Si); 16.4 (Me); 47.1 (CH, ^1J = 167.0 Hz, ^2J = 7.5 Hz); 66.3 (NCH_2N, ^1J = 157.0 Hz (*cis*-), 143.0 Hz (*trans*-), ^3J = 4.9 Hz and 6.4 Hz).

6-Ethyl-3-trimethylsilyl-1,3,5-triazabicyclo[3.1.0]hexane (9b). Yield 70 %, b.p. 49—50 °C (1 Torr). ^1H NMR (60 MHz), δ: 0.1 (s, 9 H, Me_3Si); 1.0 (t, 3 H, Me); 1.5 (m, 2 H, CH_2); 2.35 (t, 1 H, CH); 3.72 and 4.26 (both d, $^2J_{AB}$ = −9.0 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 1.2 (Me_3Si); 8.0 (Me); 23.6 (CH_2); 52.50 (CH, ^1J = 166.0 Hz); 66.50 (NCH_2N, ^1J = 157.0 Hz (*cis*-), 147.0 Hz (*trans*-), ^3J = 5.4 Hz).

6-Alkyl-3-nitroso-1,3,5-triazabicyclo[3.1.0]hexanes (10) (general procedure). ***A.*** A solution of N_2O_4 (4.6 g, 50 mmol) in anh. CH_2Cl_2 (15 mL) was added dropwise at −60 °C in a flow of dry argon to a solution of compound **7** (50 mmol) and Et_3N (5.05 g, 50 mmol) in anh. CH_2Cl_2 (15 mL). The mixture was heated to 20 °C, stirred for 0.5 h, and cooled to 0 °C, and then water (20 mL) was added. The organic layer was dried with K_2CO_3, the solvent was distilled off, and the residue was distilled *in vacuo*.

B. A solution of N_2O_4 (1.45 g, 14.6 mmol) in CH_2Cl_2 (10 mL) was added dropwise at −60 °C to a solution of pyridine (1.16 g, 14.6 mmol) in CH_2Cl_2 (15 mL), then compound **7a** (14.6 mmol) was added at the same temperature. The reaction mixture was worked up as in the above procedure.

6-Methyl-3-nitroso-1,3,5-triazabicyclo[3.1.0]hexane (10a). Yield 62 % according to procedure *A*; 51 % according to procedure *B*. R_f 0.2 (ether : pentane = 6 : 1), m.p. 30 °C, b.p. 42 °C (1 Torr), d = 1.2 g cm^{-3} (in a melt). Found (%): C, 37.40; H, 6.23; N, 43.38. $C_4H_8N_4O$. Calculated (%): C, 37.50; H, 6.25; N, 43.78. ^1H NMR (250 MHz), δ: 1.22 (d, 3 H, Me); 1.98 (q, 1 H, CH); 3.82 and 5.34, 4.86 and 5.62 (all d, $^2J_{AB}$(*syn*-) = −12.0 Hz, $^2J_{A'B'}$(*anti*-) = −10.5 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 15.6 (Me); 53.0 (CH, ^1J = 169.0 Hz, ^2J = 6.0 Hz); 61.6, 67.1 (NCH_2N, *syn*-, *anti*-, ^1J = 168.0 Hz (*cis*-), 154.0 Hz (*trans*-), ^3J = 4.9 Hz).

6-Ethyl-3-nitroso-1,3,5-triazabicyclo[3.1.0]hexane (10b). Yield 94 % according to procedure *A*, b.p. 60 °C (1 Torr), d = 1.14 g cm^{-3}. Found (%): C, 42.26; H, 7.18; N, 39.80. $C_5H_{10}N_4O$. Calculated (%): C, 42.24; H, 7.09; N, 39.41. ^1H NMR (60 MHz), δ: 0.94 (t, 3 H, Me); 1.05 (m, 2 H, CH_2); 2.36 (t, 1 H, CH); 3.87 and 5.31, 4.89 and 5.67 (all d, $^2J_{AB}$(*syn*-) = −11.4 Hz, $^2J_{A'B'}$(*anti*-) = −9.9 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 12.4 (Me); 27.5 (CH_2); 62.20 (CH, ^1J = 169.0 Hz); 66.7, 71.7 (NCH_2N, *syn*-, *anti*-, ^1J = 163.0 Hz (*cis*-), 159.0 Hz (*trans*-), ^3J = 4.9 Hz).

Reduction of compound 10a. ***A.*** A solution of compound **10a** (1.8 g, 0.014 mol) in abs. ether (5 mL) was added dropwise at 0 °C in a flow of an inert gas to a suspension of $LiAlH_4$ (1 g) in abs. ether (25 mL). The mixture was stirred for 1 h at 20 °C (according to TLC data, the original compound disappears almost immediately). The excess $LiAlH_4$ was decomposed by an ether—EtOH mixture (6 : 1) on cooling. The precipitate was filtered off and repeatedly washed with ether. The residue after evaporation of the solvent did not contain compounds of the diaziridine series (a test with an acidic KI solution).

B. A solution of $(NH_4)_2CO_3$ (8 g, 82 mmol) in a minimum amount of water was added to a solution of compound **10a** (2.1 g, 17 mmol) in EtOH (10 mL). The mixture was cooled to 0 °C, zinc dust (4 g) was added, then 25 % aqueous NH_3 (20 mL) was added dropwise, and the mixture was stirred for 1 h at 0 °C. Then an additional amount of zinc dust (4 g) was added, and the mixture was stirred for 4 h at 20 °C. The excess zinc was filtered off and washed with water. The filtrate was concentrated *in vacuo* until precipitation began. Solid KOH was added to the residue until the precipitate dissolved. The product was extracted with ether (3×25 mL), and the extract was dried with K_2CO_3. Evaporation of the solvent gave 0.9 g (51 %) of compound **7a**, m.p. 92—93 °C (from hexane).

Nitration of compounds 7 and 9 with nitronium salts. Nitronium tetrafluoroborate (5 mmol) or neutral nitronium pyrosulfate or hexafluorosilicate (2.5 mmol) was added at −50 °C to a solution of compound **7** or **9** (10 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 8—9 h at −35÷−30 °C. Water (10 mL) and CH_2Cl_2 (20 mL) were added ($T \leq -10$ °C). The organic layer was separated (and washed with 5 % $NaHCO_3$ in the case of nitration of compound **9**), dried with $MgSO_4$, and the solvent was distilled off. The residue was analyzed by ^1H NMR (see Table 1).

6-Alkyl-3-nitro-1,3,5-triazabicyclo[3.1.0]hexanes (11) (general procedure). Compound **7** (0.06 mol) or **9** (0.03 mol) was added at −40÷−35 °C in a flow of an inert gas to a vigorously stirred mixture of CH_2Cl_2 cooled to −40 °C (10 mL) and N_2O_5 (3.24 g, 0.03 mol). The mixture was stirred for 5—7 h at the same temperature and heated to −10 °C. Water

(10 mL, in the case of compound **7**) or 5 % $NaHCO_3$ (10 mL, in the case of compound **9**) and CH_2Cl_2 (20 mL) were added. The organic layer was separated and dried with $MgSO_4$. The solvent was distilled off, and the residue was distilled *in vacuo*.

6-Methyl-3-nitro-1,3,5-triazabicyclo[3.1.0]hexane (11a). Yield 52 % (from **7a**) or 50 % (from **9a**), b.p. 51 °C (0.25 Torr), m.p. 39 °C, d = 1.26 g cm^{-3} (melt). Found (%): C, 33.46; H, 5.80; N, 38.90. $C_4H_8N_4O_2$. Calculated (%): C, 33.33; H, 5.99; N, 38.87. ^{1}H NMR (60 MHz), δ: 1.19 (d, 3 H, Me); 2.10 (q, 1 H, CH); 4.27 and 5.41 (both d, $^2J_{AB}$ = −11.4 Hz, 4 H, NCH_2N).

6-Ethyl-3-nitro-1,3,5-triazabicyclo[3.1.0]hexane (11b). Yield 51.5 % (from **7b**) or 38 % (from **9b**), b.p. 96 °C (0.5 Torr), n_D^{20} 1.4990, d = 1.21 g cm^{-3}. Found (%): C, 37.65; H, 6.09; N, 35.37. $C_5H_{10}N_4O_2$. Calculated (%): C, 37.96; H, 6.37; N, 35.43. ^{1}H NMR (60 MHz), δ: 0.9 (t, 3 H, Me); 1.22—1.82 (m, 2 H, CH_2); 2.0 (t, 1 H, CH); 4.30 and 5.50 (both d, $^2J_{AB}$ = −12.0 Hz, 4 H, NCH_2N).

3-Alkylsubstituted 1,3,5-triazabicyclo[3.1.0]hexanes (12 and 13) (general procedure). An amine (0.02 mol; 0.01 mol, in the case of ethylenediamine) was added to a solution of compound **1a** or **1c** (0.02 mol) in CH_2Cl_2 (20 mL), then methoxymethanol (0.04 mol) prepared from paraform (1 mol) and MeOH (1.5 mol) was added dropwise at 5—10 °C. Ground K_2CO_3 (2.5—3.0 g) was added to the reaction mixture, which was then kept for 3—10 days at ~20 °C. K_2CO_3 was filtered off, and the solvent was evaporated *in vacuo*. The residue was distilled, recrystallized, or purified by chromatography.

3,6,6-Trimethyl-1,3,5-triazabicyclo[3.1.0]hexane (12a). Yield 89 %, subl.p. 120 °C (3 Torr). Found (%): C, 56.72; H, 10.26; N, 33.12. $C_6H_{13}N_3$. Calculated (%): C, 56.60; H, 10.30; N, 33.04. ^{13}C NMR, δ: 13.2 and 27.3 ($\underline{C}H_3$—C); 38.1 (NCH_3); 60.2 (C(6)); 71.2 (NCH_2N). MS, m/z: 127 [M$^+$].

3,6-Dimethyl-1,3,5-triazabicyclo[3.1.0]hexane (12b). Yield 42 %, b.p. 53—55 °C (10 Torr), n_D^{20} 1.4614, d = 0.971 g cm^{-3}. ^{1}H NMR (90 MHz), δ: 1.14 (d, ^3J = 5.5 Hz, 3 H, Me—C); 2.23 (s, 3 H, Me—N); 3.24 (q, ^3J = 5.5 Hz, 1 H, CH); 3.03 and 4.07 (both d, $^2J_{AB}$ = −8.2 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 17.23 (Me); 35.61 (Me—N); 51.67 (CH); 73.40 (NCH_2N).

3-Ethyl-6-methyl-1,3,5-triazabicyclo[3.1.0]hexane (12c). Yield 38 %, b.p. 62—63 °C (8 Torr). ^{1}H NMR (60 MHz), δ: 0.85—1.35 (m, 6 H, 2Me); 2.43 (m, 3 H, NCH_2, C); 2.95 and 4.06 (both d, $^2J_{AB}$ = −7.5 Hz, 4 H, NCH_2N).

3-(2-Hydroxyethyl)-6,6-dimethyl-1,3,5-triazabicyclo[3.1.0]hexane (12d). Yield 71 %, b.p. 116—117 °C (2 Torr), n_D^{20} 1.4890. Found (%): C, 53.44; H, 9.62; N, 26.70. $C_7H_{15}N_3O$. Calculated (%): C, 53.48; H, 9.62; N, 26.73. ^{1}H NMR (250 MHz), δ: 1.15 and 1.43 (both s, 6 H, CH_3—C); 2.52 (t, ^3J = 7.0 Hz, 2 H, NCH_2); 3.40 (t, ^3J = 7.0 Hz, 2 H, OCH_2); 3.46 and 3.87 (both d, $^2J_{AB}$ = −8.85 Hz, 4 H, NCH_2N). ^{13}C NMR, δ: 14.6 and 28.8 (C—$\underline{C}H_3$); 56.46 (NCH_2); 61.6 (C(6)); 62.4 (OCH_2); 71.7 (NCH_2N).

3-Benzamidomethyl-6,6-dimethyl-1,3,5-triazabicyclo[3.1.0]hexane (12e). Yield 35 %, m.p. 183—184 °C (from MeOH). Found (%): C, 63.29; H, 7.34; N, 22.71. $C_{13}H_{18}N_4O$. Calculated (%): C, 63.41; H, 7.32; N, 22.76. ^{1}H NMR (250 MHz), δ: 1.12 (s, 6 H, Me); 3.22 and 4.0 (both d, $^2J_{AB}$ = −14.7 Hz, 4 H, NCH_2N); 4.79 (d, ^3J = 5.4 Hz, 2 H, $NC\underline{H}_2NH$); 7.30—7.46 (m, 3 H, *m*-,*p*-H(Ar)); 7.72—7.82 (m, 2 H, *o*-H(Ar)); 8.27 (t, NH).

3-(2,2-Dimethoxyethyl)-6,6-dimethyl-1,3,5-triazabicyclo-[3.1.0]hexane (12f). Yield 62 %, b.p. 95—97 °C (1 Torr). Found (%): C, 53.68; H, 9.41; N, 21.04. $C_9H_{19}N_3O_2$. Calculated (%): C, 53.73; H, 9.45; N, 20.90. ^{1}H NMR (60 MHz), δ: 1.20 and 1.48 (both s, 6 H, CH_3—C); 2.56 (d, ^3J = 5.5 Hz, 2 H, NCH_2); 3.28 (s, 6 H, OMe); 3.50 and 3.95 (both d, $^2J_{AB}$ = −8.0 Hz, 4 H, NCH_2N); 4.28 (t, ^3J = 5.5 Hz, 1 H, CH).

3,3′-Ethylenebis(6-methyl-1,3,5-triazabicyclo[3.1.0]hexane) (13a) was isolated by column chromatography on L 40/100 silica gel ($CHCl_3$—MeOH, 20 : 1 as the eluent). Yield 58 %, m.p. 109—110 °C (from heptane). Found (%): C, 53.51; H, 9.02; N, 37.64. $C_{10}H_{20}N_6$. Calculated (%): C, 53.57; H, 8.93; N, 37.50. ^{1}H NMR (300 MHz), δ: 0.74 (d, ^3J = 5.2 Hz, 6 H, Me); 2.10 (s, 4 H, CH_2CH_2); 2.69 d+q and 3.70 d (10 H, $^2J_{AB}$ = −7.6 Hz, NCH_2N + CH). ^{13}C NMR, δ: 16.63 (Me); 49.78 (CH_2CH_2); 51.10 (CH); 71.85 (NCH_2N).

3,3′-Ethylenebis(6,6-dimethyl-1,3,5-triazabicyclo[3.1.0]hexane) (13b) was isolated by column chromatography on L 40/100 silica gel ($CHCl_3$—MeOH, 18 : 1 as the eluent). Yield 39.7 %, m.p. 134—135 °C (from hexane). Found (%): C, 57.21; H, 9.58; N, 33.25. $C_{12}H_{24}N_6$. Calculated (%): C, 57.14; H, 9.52; N, 33.33. ^{1}H NMR (300 MHz), δ: 1.03 and 1.31 (both s, 12 H, Me); 2.28 (s, 4 H, CH_2CH_2); 3.27 and 3.37 (both d, $^2J_{AB}$ = −8.2 Hz, 8 H, NCH_2N). ^{13}C NMR, δ: 19.99 and 27.31 (Me); 52.25 (CH_2CH_2); 59.92 (C(6)); 70.03 (NCH_2N).

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Photochemical isomerization of 2*H*-imidazole *N*-oxides*

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1,3-Diaza-6-oxabicyclo[3.1.0]hex-3-enes and their 3-oxides were obtained by the photolysis of 2*H*-imidazole 1-oxides and 2*H*-imidazole 1,3-dioxides. 1,3-Diaza-6-oxabicyclo[3.1.0]hex-3-ene 3-oxides are thermally unstable and are converted to the starting 2*H*-imidazole 1,3-dioxides; their further photolysis affords a mixture of stereoisomeric 1,3-diaza-4,7-dioxatricyclo[4.1.0.$0^{3,5}$]heptanes.

Key words: 2*H*-imidazole *N*-oxides, photolysis; photochemical isomerization; nitrones; oxaziridines.

Photochemical isomerization of nitrones to oxaziridines has been extensively studied for various heterocyclic and acyclic nitrones.[2—4] When this reaction is reversible, its investigation is of interest in view of accumulating luminous energy; the use of cyclic nitrones is the most promising in this respect.[5,6] The synthesis of 2*H*-imidazole 1-oxides and 1,3-dioxides, which we have recently accomplished,[7,8] made it possible to study the photochemical isomerization of these compounds. In analogy with α-dinitrones of the pyrazine series,[9] we could expect that the photolysis of 2*H*-imidazole 1,3-dioxides would afford highly strained tricyclic compounds containing two oxaziridine cycles.

The UV spectra of symmetric 2*H*-imidazole 1,3-dioxides (**1a,b**) exhibit a long-wave absorption band with $\lambda_{max} \approx 360$ nm (Fig. 1).[8] Photolysis of solutions of these compounds with the light (an SS-1 filter) of a high-pressure mercury lamp results in a decrease in the intensity of the long-wave absorption. Simultaneously a band appears with a shorter wavelength, characteristic of the mononitrone group, with maxima at 300 nm in the

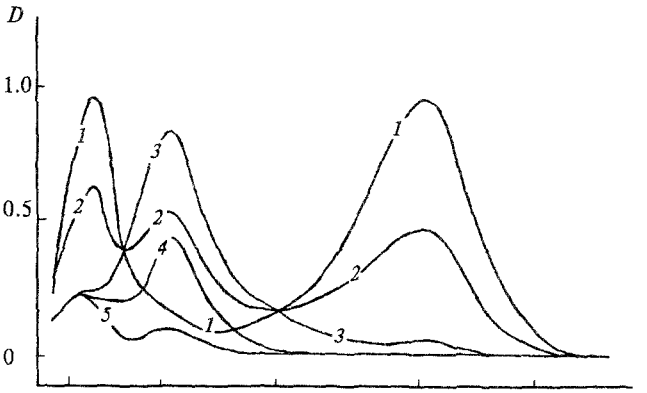

Fig. 1. Changes in the UV spectrum during the photolysis of a 0.1 m*M* solution of compound **1b** in hexane (l = 1 cm): the original spectrum (*1*); after photolysis with an SS-1 filter for 10 s (*2*) and for 45 s (*3*); after continued photolysis with unfiltered light for 30 s (*4*) and for 180 s (*5*).

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