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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

A. I. Kuznetsov, I. A. Vladimirova, E. B. Basargin,
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UDC 547.853.5.07;
543.51'422

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

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*For Communication 10, see [1].

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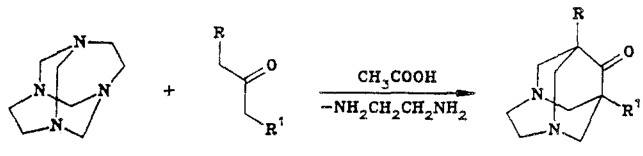
Scheme 1



I–XIV

I $R=R^1=H$; II $R=R^1=CH_3$; III $R=R^1=C_2H_5$; IV $R=R^1=C_3H_7$; V $R=R^1=i\text{-}C_3H_7$; VI $R=R^1=C_6H_5$; VII $R=R^1=C_6H_5CH_2$; VIII $R=H$, $R^1=CH_3$; IX $R=H$, $R^1=C_3H_7$; X $R=H$, $R^1=i\text{-}C_3H_7$; XI $R=H$, $R^1=(CH_3)_2C{=}CH{-}CH_2$; XII $R=H$, $R^1=C_6H_5$; XIII $R=CH_3$, $R^1=C_3H_7$; XIV $R=CH_3$, $R^1=C_6H_5$

Sasaki and coauthors [6] by the condensation of dibenzyl ketone with paraformaldehyde and ammonium acetate in boiling alcohol. One more communication [7] on the synthesis of this compound was also published; this also utilized the condensation of dibenzyl ketone with paraformaldehyde and ethylenediamine acetate, but its characteristics agreed neither with our data nor with the data of [6]. The yield of the compound (VI), obtained under the conditions of our proposed method of the condensation of dibenzyl ketone with TDA in boiling isopropyl alcohol, comprises 67.7%.

The significant increase in the yield of the diazahomoadamantanone (VI) obtained when the formaldehyde and ethylenediamine are replaced by TDA is evidently explained by the fact that the "assembly" of the skeleton of the diazahomoadamantanone from the ketone, formaldehyde, and ammonia includes a whole series of intermolecular reactions. At the same time, when the TDA is utilized, there is the possibility of the formation of the final product as the result of one intermolecular reaction of the protonated form of the TDA with the ketone, after which only the intramolecular conversions with the cleavage of the ethylenediamine molecule may proceed according to Scheme 2

Scheme 2

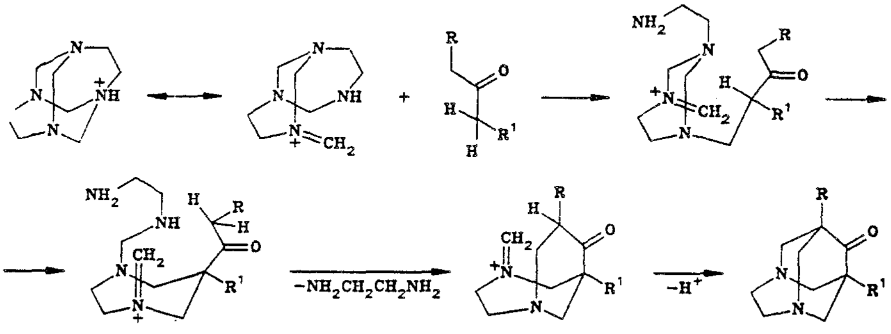


TABLE 1. Characteristics of the 3,6-Diazahomoadamantan-9-ones

Compound	Empirical formula	mp, °C*	IR spectrum, νCO, cm⁻¹	Yield, %
I	$C_9H_{14}N_2O$	77,5...78,5	1705	12
II	$C_{11}H_{18}N_2O$	100...101	1705	66
III	$C_{13}H_{22}N_2O$	110...112**	1705	55
IV	$C_{15}H_{26}N_2O$	58...59	1705	44
V	$C_{15}H_{26}N_2O$	87...88	1705	41
VI	$C_{21}H_{22}N_2O$	181...182	1700, 1600 (arom.)	68
VII	$C_{23}H_{26}N_2O$	188...190	1710, 1595 (arom.)	33
VIII	$C_{10}H_{16}N_2O$	112...113	1705	53
IX	$C_{12}H_{20}N_2O$	40...41	1705	67
X	$C_{12}H_{20}N_2O$	31...32	1705	67
XI	$C_{14}H_{22}N_2O$	68...69	1705, 1630 (C=C)	50
XII	$C_{15}H_{18}N_2O$	160...162	1710, 1600 (arom.)	77
XIII	$C_{13}H_{22}N_2O$	55...56	1705	50
XIV	$C_{16}H_{20}N_2O$	159...160	1710, 1600 (arom.)	56

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*For the compounds (I)–(V), (VIII)–(XI), and (XIII), the mp of the sublimed compound is presented. Compounds (VI) and (VII) were crystallized from toluene; compounds (XII) and (XIV) were crystallized from heptane.

**The bp at 20 mm of Hg stem.

TABLE 2. Parameters of the PMR Spectra of the 3,6-Diazahomoadamantan-9-ones

Compound	Chemical shifts of the protons, δ, ppm		
	NCH_2CH_2N	NCH_2C*, d	R, R^1
I	3,22 s	3,44, 3,15	2,56 br.s, H
II	3,15 s	3,04, 2,90	0,83 s, CH_3
VII	2,91 s	3,17, 2,93	7,32...7,08 m, C_6H_5; 2,87 s, CH_2
VIII	3,12 m	3,68, 3,19, 3,58, 3,35	0,82 s, CH_3; 2,52 br.s, H
XI	3,18 m	3,43, 3,12, 3,09, 2,98	2,57 br.s, H; 1,70 s CH_3; 1,57 s CH_3; 5,16 m, CH; 2,14 d, $^3J_{AB}=14{,}0$ Hz CH_2
XII	3,25 m	3,68, 3,19, 3,58, 3,35	7,37...7,17 m, C_6H_5; 2,70 m, CH_3
XIV	3,27 s	3,72, 3,29, 3,27, 3,05	0,96 s, CH_3; 7,39...7,19 m, C_6H_5

*$^2J_{AB}$ = 14.0 Hz.

The proposed path, indicated on the scheme, for the formation of the diazahomoadamantanones (I)–(XIV) from ketones and TDA is far from being the only one, and may only be realized under optimal conditions; the deviation from these conditions will lead to the breakdown of the intermediate structures and the formation of reaction by-products.

Even more significant than the high yield is the circumstance that [as can be seen from the set of compounds (I)–(XIV) obtained] the condensation of the ketones with TDA allows the isolation of diazahomoadamantanones with practically any of one or two substituents at the angular positions, or without them at all; this is impossible with the condensation of the ketones with paraformaldehyde and ethylenediamine acetate.

The structure of the newly obtained diazahomoadamantanones was confirmed by the combination of the data of the IR, PMR, and mass spectra. The IR spectra contain characteristic absorption bands of the stretching vibrations of the carbonyl group at 1700–1710 cm^{-1} as well as the absorption bands characteristic of the functional groups of the substituents: the aromatic rings in compounds (VI), (VII), (XII), and (XIV) at 1595–1605 cm^{-1}, and the double bond in compound (XI) at 1630 cm^{-1} (Table 1).

The PMR spectra of the diazahomoadamantanones (Table 2) consist of three groups of signals: the singlet or multiplet of protons of the ethylene bridge NCH_2CH_2N in the region 3.29–3.15 ppm, one (in the case of the same substituents at the angular positions) or two (in the case of different substituents) AB-systems corresponding to the protons of the methylene groups NCH_2C at 3.76–2.90 ppm (SSCC $^2J_{AB}$ = 14.0 Hz), and the signals of the protons of the substituents at the angular positions of the corresponding multiplicity. The protons at the angular positions of the unsubstituted (I) and monosubstituted (VIII)–(XII) diazahomoadamantanones appear in the form of a broad singlet in the region of 2.25–2.70 ppm.

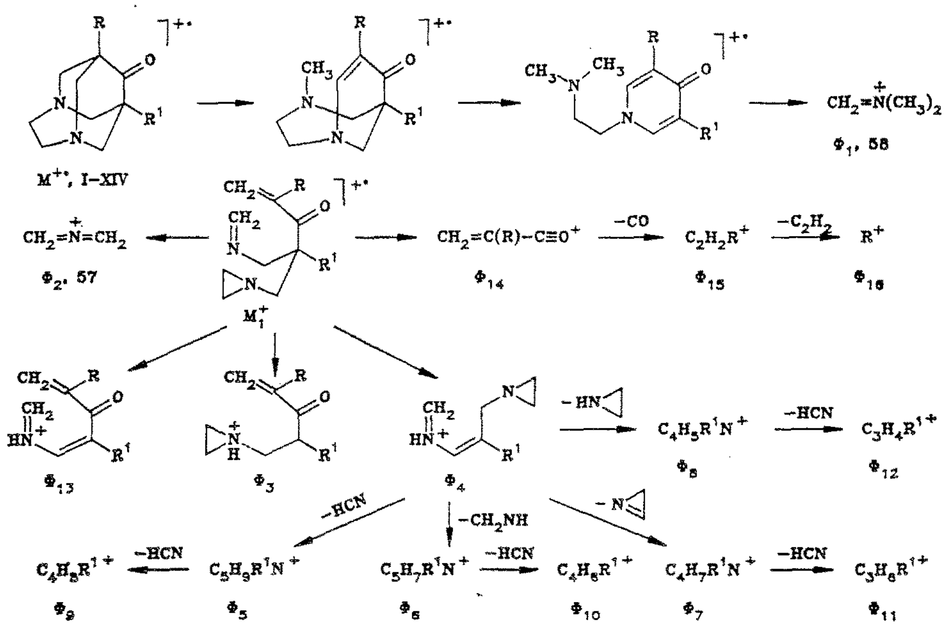
The mass spectra of the diazahomoadamantanones (Tables 3 and 4) are characterized by multilineation, but a comparatively small number of intense ion peaks. Of the compounds studied, the most stable to electron impact is the unsubstituted 9-oxo-3,6-diazahomoadamantane (I); the spectrum of (I) has the peak of the molecular ion (M^+) with the maximal intensity: W_M = 14.7%. The alkyl- and especially the aryldiazahomoadamantanones are less stable, and the values of the W_M are significantly lower for them (see Scheme 3).

The main direction of the decomposition of the M^+ of the diazahomoadamantanones is the rearrangement process accompanied by the migration of hydrogen atoms; this results in the formation of the nitrogen-containing fragment Φ_1 (see Scheme3).This ion has the 30.5% and 36.6% share of the total ion current correspondingly whereby its peak has the maximal intensity in the spectra of the compounds in which one of the substituents or both are represented by the phenyl nucleus. The decomposition of the M^+ of compounds (II)–(XIV) by other routes evidently proceeds from the opened form M_1^+, and leads to the formation of the Φ_2–Φ_{16} fragments (see Scheme 3).

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-71 instrument using mineral oil. The PMR spectra were recorded on a Bruker M-250 instrument using $CDCl_3$ and the internal standard TMDS. The mass spectra were taken on the LKB-2091 chromato-mass spectrometer with the direct input of the sample at the ion source, the accelerating voltage of 3.5 kV, the cathode emission current of 25 μA, the 70 eV energy of the ionizing electrons, and the 200°C temperature of the ionizing chamber.

Scheme 3



The characteristics of the newly obtained diazahomoadamantanones (I), (III)–(VI), (VII), and (IX)–(XIV) are presented in Tables 1–3.

3,6-Diazahomoadamantan-9-one (I). The mixture of 1.58 g (27 mmoles) of acetone, 1.68 g (10 mmoles) of TDA, and 1.26 g (21 mmoles) of glacial acetic acid in 20 ml of isopropyl alcohol is heated with low boiling for 1 h. The reaction mass is condensed in vacuo prior to the separation by chromatography on glass plates (30 × 30 cm) with an unfastened layer of aluminum oxide of the II degree of activity; the eluent is chloroform. The R_f is 0.77. The yield of 0.20 g (12%) of the diazahomoadamantanone (I) is obtained.

1,8-Diethyl-3,6-diazahomoadamantan-9-one (III). The mixture of 2.28 g (20 mmoles) of dipropyl ketone, 3.36 g (20 mmoles) of TDA, and 3.00 g (50 mmoles) of glacial acetic acid in 10 ml of isopropyl alcohol is heated for 15 min at 50°C. The reaction mass is left for 1 h without heating. It is then concentrated to 0.2 volume in vacuo and extracted with hot heptane (3 × 100 ml). The extract is purified by passing it through a layer of dry aluminum oxide (4 g, II degree of activity) placed on a Schott filter. The extractant is distilled in vacuo, and the solid residue is sublimed in vacuo. The yield of 2.44 g (55%) of the diethyldiazahomoadamantanone (III) is obtained.

TABLE 3. Mass spectra of the 3,6-Diazahomoadamantan-9-ones*

Compound	m/z (I_{rel}, %)
I	166 (100), 110 (30), 84 (38), 82 (27), 70 (23), 68 (22), 58 (45), 57 (31), 55 (40), 42 (60), 41 (54)
II	194 (32), 98 (5), 96 (6), 82 (6), 69 (10), 58 (100), 57 (10), 56 (6), 55 (14), 42 (23), 41 (23)
VI	318 (10), 160 (5), 144 (3), 117 (5), 115 (6), 103 (16), 91 (7), 77 (5), 76 (4), 58 (100), 42 (9)
VII	346 (8), 117 (6), 115 (8), 91 (22), 72 (10), 65 (4), 58 (100), 57 (6), 43 (6), 42 (20), 41 (8)
VIII	180 (87), 71 (39), 70 (66), 69 (40), 58 (100), 57 (93), 56 (22), 55 (65), 43 (73), 42 (27), 41 (57)
XI	234 (65), 84 (15), 82 (11), 72 (100), 69 (10), 58 (92), 57 (15), 55 (29), 43 (11), 42 (41), 41 (42)
XII	242 (57), 241 (13), 115 (13), 103 (27), 84 (24), 77 (19), 58 (100), 57 (55), 55 (19), 42 (34), 41 (18)
XIV	256 (34), 103 (8), 98 (6), 77 (5), 69 (5), 58 (100), 57 (9), 56 (7), 55 (7), 42 (14), 41 (8)

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*The peaks of the M^+ ions and the ten most intense peaks of the ions in the mass spectra are presented.

TABLE 4. Mass Spectra of the 3,6-Diazahomoadamantan-9-ones

Compound	W_M	Intensity of the peaks of the characteristic ions (Σ_{41}, %)															
		Φ_1	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7	Φ_8	Φ_9	Φ_{10}	Φ_{11}	Φ_{12}	Φ_{13}	Φ_{14}	Φ_{15}	Φ_{16}
I	14,7	5,9	7,9	2,0	1,3	5,0	3,6	3,0	2,9	4,1	2,7	1,2	7,1	3,9	2,6	—	—
II	10,0	27,4	6,3	0,7	0,4	1,4	1,7	1,1	1,8	0,4	1,4	2,6	3,8	1,2	1,3	6,3	—
VI	4,4	36,6	3,4	—	0,3	1,8	0,7	0,3	1,1	0,1	0,3	0,2	1,9	0,4	0,2	5,9	1,7
VII	9,3	13,7	4,7	1,1	0,6*	3,5*	1,9*	1,3*	1,7*	7,5	1,5*	1,0*	3,5*	0,4	1,4*	3,7	2,6
VIII	8,1	8,3	3,9	0,6	1,8*	2,9*	1,6	5,5	1,1	11,1*	4,4*	6,1	4,8	0,3	4,3*	Φ_{13}	—
XI	9,8	11,9	5,3	0,3	0,3	2,1*	1,9*	1,2*	2,4*	2,1*	2,2*	1,7*	6,0*	0,5	2,2*	0,9	1,3
XII	9,3	13,7	4,7	1,1	0,6*	3,5*	1,9*	1,3*	1,7*	7,5	1,5*	1,0*	3,5*	0,4	1,4*	3,7	2,6
XIV	12,5	30,5	4,3	0,3	—	1,9	—	—	—	—	0,8	—	—	—	0,8	5,0*	1,4

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*The total intensity of the peaks of the ions with the substituents R and R^1.

1,8-Di-n-propyl-3,6-diazahomoadamantan-9-one (IV). By analogy, the yield of 2.20 g (44%) of the dipropyldiazahomoadamantanone (IV) is obtained from 2.84 g (20 mmoles) of dibutyl ketone, 3.36 g (20 mmoles) of TDA, and 2.86 ml (50 mmoles) of acetic acid in 10 ml of isopropyl alcohol.

1,8-Di-isopropyl-3,6-diazahomoadamantan-9-one (V). By analogy, the yield of 2.05 g (41%) of the di-isopropyldiazahomoadamantanone (V) is obtained from 2.84 g (20 mmoles) of di-isobutyl ketone, 3.36 g (20 mmoles) of TDA, and 2.86 ml (50 mmoles) of acetic acid in 10 ml of isopropyl alcohol.

1-n-Propyl-3,6-diazahomoadamantan-9-one (IX). By analogy, the yield of 2.78 g (67%) of the propyldiazahomoadamantanone (IX) is obtained from 2.00 g (20 mmoles) of methyl butyl ketone, 3.36 g (20 mmoles) of TDA, and 2.86 ml (50 mmoles) of acetic acid in 10 ml of isopropyl alcohol.

1-Isopropyl-3,6-diazahomoadamantan-9-one (X). By analogy, the yield of 2.80 g (67%) of the isopropyldiazahomoadamantanone (X) is obtained from 2.00 g (20 mmoles) of methyl isobutyl ketone, 3.36 g (20 mmoles) of TDA, and 2.86 ml (50 mmoles) of acetic acid in 10 ml of isopropyl alcohol.

1-Methyl-8-n-propyl-3,6-diazahomoadamantan-9-one (XIII). By analogy, the yield of 2.19 g (50%) of the methylpropyldiazahomoadamantanone (XIII) is obtained from 2.28 g (20 mmoles) of ethyl butyl ketone, 3.36 g (20 mmoles) of TDA, and 2.86 ml (50 mmoles) of acetic acid in 10 ml of isopropyl alcohol.

1-(3-Methyl-2-butenyl)-3,6-diazahomoadamantan-9-one (XI). The mixture of 2.65 g (20 mmoles) of 6-methyl-5-hepten-2-one, 3.36 g (20 mmoles) of TDA, 2.52 g (42 mmoles) of glacial acetic acid, and 40 ml of isopropyl alcohol is heated for 4 h with low boiling. The reaction mass is concentrated in vacuo prior to the extraction with hot toluene (5 × 30 ml). The extract is purified by its passage through a layer of dry aluminum oxide (4 g, II degree of activity) placed on a Schott filter. The extractant is distilled off, and the solid residue is sublimed in vacuo. The yield of 2.33 g (50%) of the diazahomoadamantanone (XI) is obtained.

1,8-Diphenyl-3,6-diazahomoadamantan-9-one (VI). The mixture of 10.43 g (50 mmoles) of dibenzyl ketone, 8.34 g (50 mmoles) of TDA, and 7.45 g (124 mmoles) of glacial acetic acid in 30 ml of isopropyl alcohol is heated for 4 h with weak boiling. The reaction mixture is cooled to 0°C, and the precipitated crystals are filtered off, washed with cold isopropyl alcohol (4 × 5 ml), and dried in an exsiccator over $CaCl_2$. The yield of 9.53 g of the diphenyldiazahomoadamantanone (VI) is obtained. The mother liquor is concentrated, and the oily residue is extracted with hot toluene (200 ml). The extract is filtered twice through a layer (2 cm) of silica gel L 40/100; the solvent is evaporated. To the residue are added 3 ml of isopropyl alcohol, and the mixture is cooled to 0°C. The precipitated crystals are filtered off, washed on the filter with cold isopropyl alcohol, and dried. The additional yield of 1.06 g of the diphenyldiazahomoadamantanone (VI) is obtained. In all, 10.59 g (68%) of the diphenyldiazahomoadamantanone (VI) are obtained.

1-Methyl-8-phenyl-3,6-diazahomoadamantan-9-one (XIV). By analogy, the yield of 5.75 g (56%) of the methylphenyldiazahomoadamantanone (XIV) is obtained from 7.40 g (50 mmoles) of ethyl benzyl ketone, 8.34 g (50 mmoles) of TDA, and 7.45 g (124 mmoles) of acetic acid in 30 ml of isopropyl alcohol.

1-Phenyl-3,6-diazahomoadamantan-9-one (XII). The mixture of 40.25 g (300 mmoles) of methyl benzyl ketone, 50.40 g (300 mmoles) of TDA, and 42.93 ml (750 mmoles) of acetic acid in 200 ml of isopropyl alcohol is maintained for 1 h with stirring at room temperature. The precipitated residue is filtered off and washed with 20 ml of isopropyl alcohol. After the recrystallization from isopropyl alcohol, the yield of 56.27 g (77%) of the phenyldiazahomoadamantanone (XII) is obtained.

1,8-Dibenzyl-3,6-diazahomoadamantan-9-one (VII). The mixture of 2.86 g (12 mmoles) of 1,5-diphenylpentan-3-one, 1.68 g (10 mmoles) of TDA, 1.4 g (23 mmoles) of acetic acid, and 10 ml of n-butyl alcohol is heated for 1 h 30 min with weak boiling. The mixture is then left overnight at room temperature. The precipitated residue is filtered off, washed with 5 ml of n-butyl alcohol, and dried in an exsiccator over $CaCl_2$. After the recrystallization from toluene, the yield of 1.13 g (33%) of the dibenzyldiazahomoadamantanone (VII) is obtained.

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HETEROADAMANTANES AND THEIR DERIVATIVES.

12.* SYNTHESIS OF 1,3,6-TRIAZAHOMOADAMANTANE – A NEW HETEROCYCLIC SYSTEM

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UDC 547.853.5'859:
543.51'422

8-Nitro-1,3,6-triazahomoadamantane was obtained by the condensation of nitromethane with an equimolar mixture of 1,4,6,9-tetraazatricyclo[4.4.1.1^{4,9}]dodecane and hexamethylenetetramine. By reducing it with hydrazine hydrate in the presence of Raney nickel, 8-amino-1,3,6-triazahomoadamantane was synthesized. This was converted to 8-bromo-1,3,6-triazahomoadamantane by the action of sodium nitrite in hydrobromic acid. The 1,3,6-triazahomoadamantane was obtained by reduction of the bromo derivative with hydrazine hydrate in the presence of Raney nickel. The structures of the compounds synthesized were confirmed by PMR and mass spectroscopy.

A scheme has been published in the literature [2] for synthesizing 1,3,5-triazaadamantane, a close structural analog of 1,3,6-triazahomoadamantane (I). In this scheme, 7-nitro-1,3,5-triazaadamantane (II) is used as the starting material.

We chose an analogous scheme to synthesize 1,3,6-triazahomoadamantane (I). The starting material, 8-nitro-1,3,6-triazahomoadamantane (III), was obtained [3] by the condensation of nitromethane with an equimolar mixture of 1,4,6,9-tetraazatricyclo[4.4.1.1^{4,9}]dodecane and hexamethylenetetramine in the presence of acetic acid in n-butyl alcohol. The mixture of nitrotriazahomoadamantane III and nitrotriazaadamantane II formed in the reaction was separated chromatographically on a silica gel column.

8-Nitro-1,3,6-homoadamantane (III) was reduced to aminotriazahomoadamantane (IV) with hydrazine hydrate in alcohol in the presence of Raney nickel. By the action of sodium nitrite on a solution of amine IV in concentrated hydrobromic acid, 8-bromo-1,3,6-triazahomoadamantane (V) was obtained. This was converted to the desired 1,3,6-triazahomoadamantane (I) in an 84% yield by reduction with hydrazine hydrate in the presence of Raney nickel (see Scheme 1).

The structures of the compounds synthesized were confirmed by PMR (Table 1) and mass spectroscopy (Table 2). In the PMR spectra of compounds I, III–V, resonance absorption signals from four protons on atoms $C_{(2)}$ and $C_{(10)}$ appear as an AB system centered in the 3.88–4.06 ppm region. An AB system centered in the 2.88–3.49 ppm region is also formed by the signals from the four protons on atoms $C_{(7)}$ and $C_{(11)}$. A singlet signal in the 2.97–3.56 ppm region is formed by the protons on atom $C_{(9)}$. The signals from the protons on atoms $C_{(4)}$ and $C_{(5)}$ are present in the spectrum as a complex multi-

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[*] See [1] for Communication 11.

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