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HETEROADAMANTANES AND THEIR DERIVATIVES.

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

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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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TABLE 1. Parameters of the PMR Spectra of Compounds I, III–V

Compound	Proton chemical shift, δ, ppm					HFCC, ^2J, Hz	
	$C_{(2)}H_2$ and $C_{(10)}H_2$, d	$C_{(7)}H_2$ and $C_{(11)}H_2$, d	$C_{(9)}H_2$, s	$C_{(4)}H_2$ and $C_{(5)}H_2$, m	others	$H_{(7)}H_{(7)}$; $H_{(11)}H_{(11)}$	$H_{(2)}H_{(2)}$; $H_{(10)}H_{(10)}$
I	4,39; 3,73	3,65; 2,94	3,32	3,30 . . . 3,09	1,26 (C—H), broad s	13,5	13,5
III	4,14; 3,63	3,66; 3,32	3,56	3,28 . . . 3,09	—	13,5	13,5
IV	4,13; 3,63	3,04; 2,71	2,97	3,21 . . . 3,09	1,19 (NH_2), broad s	13,0	13,0
V	4,25; 3,61	3,76; 3,13	3,50	3,24 . . . 3,05	—	12,5	12,5

TABLE 2. Mass Spectra of Compounds I, III-V*

Compound	m/z (I_{rel}, %)
I	153 (100), 125 (99), 111 (19), 96 (23), 82 (81), 68 (43), 57 (45), 56 (18), 55 (20), 42 (75), 41 (43)
III	198 (74), 170 (41), 152 (23), 109 (46), 82 (48), 81 (26), 80 (29), 68 (30), 55 (26), 42 (100), 41 (24)
IV	168 (100), 139 (21), 97 (71), 85 (92), 84 (33), 83 (35), 82 (32), 58 (25), 57 (79), 56 (38), 42 (63)
V	231** (37), 203** (29), 152 (100), 123 (20), 109 (48), 82 (47), 81 (27), 80 (32), 55 (23), 42 (93), 41 (26)

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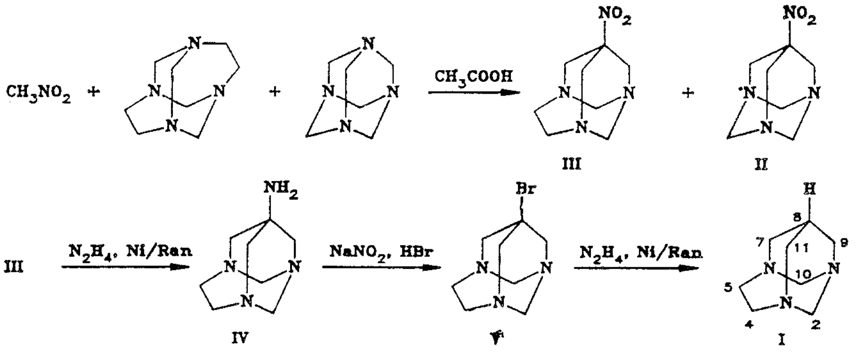
*The M^+ peak and the ten strongest ion peaks in the mass spectra are shown.

**The m/z values are calculated for the ^{79}Br isotope.

Scheme 1



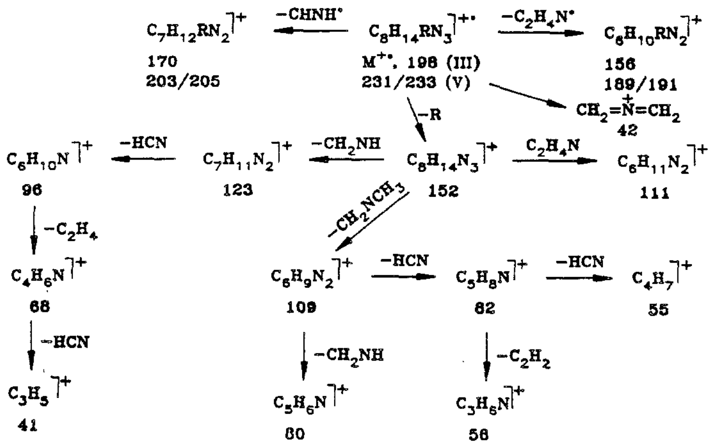
plet in the 3.05–3.30 ppm region. In the spectra of triazahomoadamantane I and amine IV, there are, moreover, broad signals with centers at 1.26 and 1.19 ppm, belonging to the $C_{(8)}$ proton and the amine group protons, respectively.

Analysis of the mass spectra of the compounds synthesized showed that, as in the electron impact fragmentation of 1-substituted adamantanes [4] and 7-substituted 1,3,5-triazaadamantanes [5], decomposition of the molecular ions (M^+) of nitrotriazahomoadamantane III and bromotriazahomoadamantane V occurs basically by splitting off substituent R (Scheme 2).

The further decomposition of the $[M–R]^+$ ion formed here takes place through the breaking off of the neutral fragments CH_3N, C_2H_3N, and C_2H_5N. Other directions of the decomposition of the M^+ ion of compounds III and V are connected with the breaking off of CH_2N and C_2H_4N radicals. Fragmentation of the M^+ of aminotriazahomoadamantane IV takes place in the first step with the cleavage of the homoadamantane skeleton and is accompanied by elimination of the nitrogen-containing species CH_2NH and C_2H_4N. In this, the amino group is preserved in all of the basic ionic fragments.

The predominant path of the decomposition of M^+ of unsubstituted triazahomoadamantane I (Scheme 3) is the sequential loss of a CH_2N radical and of CH_3N and C_2H_4 molecules. The elementary composition of the basic ions in the spectra of compounds I, III–V was established by means of high-resolution mass spectra (Table 3). Thus, the sole difference between

Scheme 2



Scheme 3

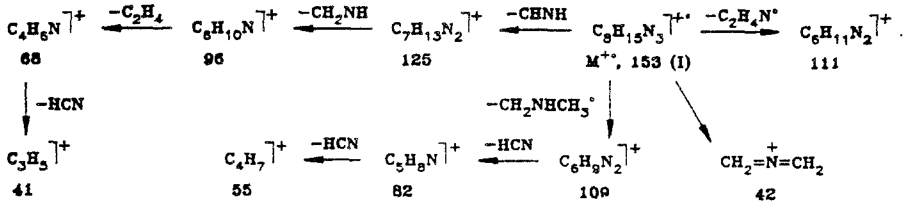


TABLE 3. High-Resolution Mass Spectra of Compounds I, III, and IV

Found for compound			Elemental composition	Calculated
I	III	IV		
	198,1126 M+		$C_8H_{14}N_4O_2$	198,1116
	170,0921		$C_7H_{12}N_3O_2$	170,0929
	—	168,1375 M+	$C_8H_{16}N_4$	168,1374
153,1272 M+	—	—	$C_8H_{15}N_3$	153,1265
—	152,1193	—	$C_8H_{14}N_3$	152,1187
—	—	139,1116	$C_7H_{13}N_3$	139,1109
125,1081	—	—	$C_7H_{13}N_2$	125,1078
—	123,0930	—	$C_7H_{11}N_2$	123,0922
111,0915	111,0923	111,0912	$C_6H_{11}N_2$	111,0922
—	—	110,0836	$C_6H_{10}N_2$	110,0843
109,0770	109,0769	109,0772	$C_6H_9N_2$	109,0765
—	—	97,0770	$C_5H_9N_2$	97,0765
96,0808	—	—	$C_6H_{10}N$	96,0813
—	—	96,0689	$C_5H_8N_2$	96,0687
—	—	85,0776	$C_4H_9N_2$	85,0765
—	—	84,0695	$C_4H_8N_2$	84,0687
—	—	83,0621	$C_4H_7N_2$	83,0609
82,0657	82,0659	—	C_5H_8N	82,0656
—	—	82,0563	$C_4H_6N_2$	82,0531
68,0502	68,0501	—	C_4H_6N	68,0500
57,0580	—	57,0581	C_3H_7N	57,0578
—	56,0498	56,0501	C_3H_6N	56.0500
55,0546	—	—	C_4H_7	55,0547
55,0421	—	—	C_3H_5N	55,0422
42,0339	42,0343	—	C_2H_4N	42,0344
41,0393	—	—	C_3H_5	41,0391

the mass spectra for triazahomoadamantane I and its derivatives III–V and the spectra of the corresponding 7-substituted, 1,3,5-triazaadamantanes [5] is the shift of the signals from the basic ions by 14 amu to higher m/z values.

EXPERIMENTAL

The PMR spectra were recorded on a WM-250 (250 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard. The low- and high-resolution mass spectra were obtained on a Kratos MS-80 instrument with direct introduction of the sample into the ion source, a 30 kV accelerating potential, a 100 μA cathode emission current, ionizing electrons of 70 eV energy, and an ionization chamber temperature of 150°C. Perfluorokerosene standard; resolution $M/\Delta M = 10{,}000$.

8-Nitro-1,3,6-triazahomoadamantane (III, $C_8H_{14}N_4O_2$). A mixture of 5.43 g (88 mmoles) nitromethane, 5.61 g (40 mmoles) hexamethylenetetramine, 6.72 g (40 mmoles) 1,4,6,9-tetraazatricyclo[4.4.1.1^{4,9}]dodecane, 11.44 ml (200 mmoles) glacial acetic acid, and 40 ml n-butyl alcohol is heated and kept at the boiling point for 1 h. The solvent is distilled off under vacuum. The viscous residue is extracted with boiling heptane (8 × 100 ml). The heptane is distilled off under vacuum. The residue is chromatographed on a column with L 40/100 M grade silica gel. On eluting with 10:1 chloroform:saturated ammoniacal methanol, 3.47 g (44%) of compound III is obtained. T_{mp} 191–192°C (subl.). Found: M^+ 198. Calculated: M 198.

8-Amino-1,3,6-triazahomoadamantane (IV, $C_8H_{16}N_4$). A solution of 0.7 ml of hydrazine hydrate in 1 ml of ethyl alcohol is added dropwise with stirring to a mixture of 1 g (5 mmoles) 8-nitro-1,3,6-triazahomoadamantane (III), 50 ml ethyl alcohol, and 0.15 g freshly prepared Raney nickel at a temperature of 40–50°C. The reaction mixture is held at 40–50°C for 3.5 h. The catalyst is filtered off and the filtrate evaporated to dryness. The residue is purified by vacuum sublimation to obtain 0.79 g (93%) of compound IV. T_{mp} 161–162°C. Found: M^+ 168. Calculated: M 168.

8-Bromo-1,3,6-triazahomoadamantane (V, $C_8H_{14}N_3Br$). A solution of 0.23 g (3.3 mmoles) sodium nitrite in 2 ml water is added with vigorous stirring to a mixture of 0.5 g (3.0 mmoles) 8-amino-1,3,6-triazahomoadamantane (IV) and 2 ml concentrated hydrobromic acid cooled to 0–3°C. The reaction mixture is stirred for 30 min without cooling. Sodium hydroxide solution (40%) is then added dropwise to bring the pH to 9–10. The reaction mixture is evaporated to dryness. The residue is purified by vacuum sublimation to obtain 0.27 g (38.6%) of substance V. T_{mp} 106–107°C. Found: M^+ 232. Calculated: M 232.

1,3,6-Triazahomoadamantane (I, $C_8H_{15}N_3$). A mixture of 0.5 g (2.1 mmoles) 8-bromo-1,3,6-triazahomoadamantane (V), 0.1 g (2.5 mmoles) sodium hydroxide, 0.1 g freshly prepared Raney nickel, and 20 ml ethyl alcohol is heated to boiling and 0.6 ml of hydrazine hydrate in 1.5 ml of water is added to it dropwise with stirring. The mixture is kept barely boiling for 4.5 h. The catalyst is filtered off and the solvent distilled off under vacuum. The dry residue is sublimed under vacuum to obtain 0.28 g (85%) of compound I. T_{mp} 225–226°C. Found: M^+ 153. Calculated: M 153.

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