HETEROADAMANTANES AND THEIR DERIVATIVES
19.* SYNTHESES OF 1,3-DIAZAADAMANTANE AND 6,6-DIMETHYL-1,3-DIAZAADAMANTANE BASED ON THE CORRESPONDING 5,7-DINITRO DERIVATIVES

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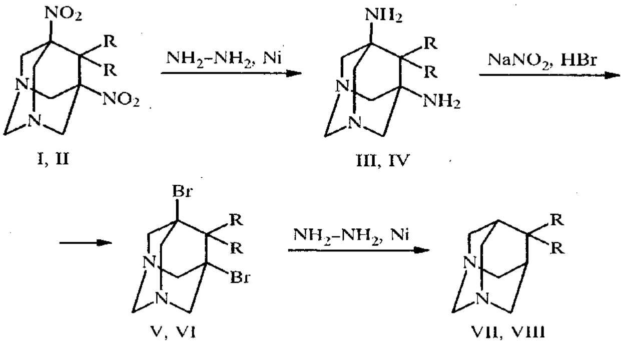
5,7,-Dinitro-6,6-dimethyl-1,3-diazaadamantane was synthesized by condensation of 1,3-dinitro-2,2-dimethylpropane with hexamethylenetetramine. Like the previously prepared 5,7-dinitro-1,3-diazaadamantane, it is converted into the corresponding diamino derivative with hydrazine hydrate in the presence of a nickel catalyst, and the diamino compounds gave the 5,7-dibromo derivatives on treatment with sodium nitrite in conc. HBr. The latter were converted to 6,6-dimethyl-1,3-diazaadamantane and 1,3-diazaadamantane on treatment with hydrazine hydrate in the presence of nickel catalyst in ethanol.

1,3-Diazaadamantanes were previously synthesized [2-4] from the corresponding bispidines which were obtained by a complex and unsatisfactory method. We have shown that 1,3-diazaadamantanes can be obtained from the corresponding dinitro-1,3-diazaadamantanes by a method analogous to that previously used for the synthesis of triazaadamantane [5].



II, IV, VI, VIII R=H; I, III, V, VII R=Me

6,6-Dimethyl-5,7-dinitro-1,3-diazaadamantane (I) was formed on condensation of 2,2-dimethyl-1,3-dinitropropane with hexamethylenetetramine in the presence of acetic acid in n-butanol on heating. Intense absorption bands for the symmetric (1340) and asymmetric (1540 cm^{-1}) vibrations of the nitro group were observed in the IR spectrum of compound I (Table 1). The ^{1}H NMR spectrum contained a singlet at 3.79 (protons of the aminal methylene groups), a singlet at 1.32 (protons of two methyl substituents), and an AB system ($^2J_{ae}$ = 12.0 Hz) with centres of the doublets at 4.16 and 3.30 ppm. The characteristic peak at M$^+$ 256 was observed in the mass spectrum of I.

5,7-Dinitro-1,3-diazaadamantane (II) was prepared by the method developed earlier [6].

Reduction of dinitrodiazaadamantanes I and II with hydrazine hydrate in the presence of a nickel catalyst gave 5,7-diamino-6,6-dimethyl- (III) and 5,7-diamino-1,3-diazaadamantane (IV). Diaminodiazaadamantanes III and IV were converted

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*For Communication 18 see [1].

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TABLE 1. Characteristics of Compounds I and III-VIII

Compound	Molecular formula	M.p., °C	IR spectrum, v, cm^{-1}	^1H NMR spectrum (in $CDCl_3$), ppm (coupling constant, J, Hz)				Yield, %
				$N\text{-}CH_2\text{-}N$, s	$N\text{-}CH_2\text{-}C$, d	R, s	other	
I	$C_{10}H_{16}N_4O_4$	318...319	1540, 1340(NO_2)	3,79	4,16, 3,30(12,0)	1,32	—	22
III	$C_{10}H_{20}N_4$	167...168	3260, 1610(NH2)	3,82	3,34, 2,65(13,0)	1,06	0.91 br.s (NH_2)	97
IV	$C_8H_{16}N_4$	189...192	3280, 1610(NH2)	3,83	2,92, 2,85(13,0)	1,66	1,06 br.s (NH_2)	95
V	$C_{10}H_{16}N_2Br$	259...260	617 (C—Br)	4,06	3,95, 3,49(12,5)	1,45	—	55
VI	$C_8H_{12}N_2Br$	190...191	582(C—Br)	4,06	3,63, 3,49(12,5)	3,05	—	54
VII	$C_{10}H_{18}N_2$	237...239* (picrate)	—	4,08	3,54, 3,22(13,0)	1,17	1,00 s (2H)	88
VIII	$C_8H_{14}N_2$	231...233** (picrate)	—	4,20	3,39, 3,28(13,0)	2,18	1,50 s (2H)	89

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*Lit. 236-238 °C

**Lit. 235 °C

TABLE 2. Mass Spectra of Compounds I and III-VIII*

Compound	m/z (I_{rel}, %)
I	256 (56), 210 (21), 164 (43), 163 (21), 136 (100), 121 (18), 91 (29), 67 (19), 55 (19), 42 (19), 41 (20)
III	196 (34), 181 (23), 125 (14), 112 (17), 84 (14), 83 (100), 57 (12), 56 (15), 43 (14), 42 (49), 41 (17)
IV	168 (54), 124 (21), 112 (35), 109 (17), 97 (21), 83 (100), 82 (24), 57 (20), 56 (27), 44 (16), 42 (63)
V	326 (37), 324 (74), 322 (34), 243 (52), 222 (100), 163 (60), 135 (31), 134 (20), 122 (47), 108 (19), 94 (21), 42 (50), 41 (22)
VI	298 (36), 296 (75), 294 (37), 215 (100), 214 (46), 186 (22), 135 (34), 108 (14), 107 (15), 106 (18), 94 (20), 42 (28), 41 (12)
VII	166 (100), 151 (66), 124 (25), 122 (15), 108 (30), 94 (10), 70 (22), 69 (19), 68 (20), 42 (21), 41 (18)
VIII	138 (100), 110 (19), 96 (66), 95 (24), 94 (32), 82 (20), 68 (25), 58 (48), 44 (23), 42 (46), 41 (23)

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*The values of *m/z* for M^+ and the ten most intense peaks are given.

by substitutive deamination with sodium nitrite in concentrated hydrobromic acid into 5,7-dibromo-6,6-dimethyl- (V) and 5,7-dibromo-1,3-diazaadamantane (VI), reduction of which with hydrazine hydrate in the presence of Raney nickel and base in ethanol gave 6,6-dimethyl-1,3-diazaadamantane (VII) and 1,3-diazaadamantane (VIII) in yields of greater than 80%.

Stretching vibrations of the amino group were observed in the regions of 3260 and 3280 cm^{-1} in the IR spectra of the diamino-1,3-diazaadamantanes III and IV, while the IR spectra of compounds V and VI contained C-Br stretching vibrations at 617 (V) and 582 cm^{-1}.

The ^1H NMR spectrum of the diazaadamantanes III-VIII (Table 1) contained the signals of eight methylene protons of the $N-CH_2-C$ units which form an AB system with atom $C_{(2)}$ in the 2.65-3.95 range, characteristic of the 1,3-diazaadamantane structure. Singlets for the protons of the aminal methylene fragment $N-CH_2-N$ were present in the 3.82-4.20 ppm range. A singlet for the geminal methyl groups at $C_{(6)}$ was observed in the 1.06-1.45 ppm range for compounds III, V, and VII, while the signal for the geminal protons appeared in the range 1.66-3.05 ppm for compounds IV, VI, and VIII. Resonances of the amine protons appeared as broad singlets at 0.91 ppm (III) and 1.06 ppm (IV). The molecular ion peak M^+

is characteristically intense in the mass spectra of all the compounds studied (III-VIII) and is the peak with maximum intensity for compounds VII and VIII (Table 2). As in the previously studied case of 3,7-dinitro-1,3-diaza-adamantanes [6], fragmentation of the M^+ ions of the dibromodiazaadamantanes V and VI proceeds by consecutive loss of a bromine radical, and molecules of HBr and HCN. The $(M - Br)^+$ peak has maximum intensity in the spectrum of compound VI. The other direction of decomposition of the M^+ ions of these compounds is connected with consecutive loss of a hydrogen atom (compound VI) or a methyl radical (compound (V) followed by loss of an HBr molecule. The latter peak is the most intense peak in the spectrum of compound V.

Loss of a methyl radical from the M^+ ion is also characteristic of the spectra of the dimethyldiazaadamantanes V and VII. Decomposition of the M^+ ions in compounds VII and VIII is accompanied by destruction of the nucleus of the molecule to produce the ions $(M - C_2H_4N)^+$ and $(C_2H_4N)^+$ which is typical of the spectra of 1,3-diazaadamantan-6-ones [7]. For the diamines III and IV fragmentation of the M^+ ion is predominantly by consecutive loss of the radical $C_3H_7R_2NH_2$ and the particle CH_2NH. The ion with *m/z* 83 formed in this way has the maximum intensity in the spectra of compounds III and IV.

EXPERIMENTAL

IR spectra were recorded as Nujol mulls with a Specord 71-IR spectrometer and ^1H NMR spectra were recorded with a Bruker WM-250 instrument (in $CDCl_3$), with HMDS as internal standard. Low and high resolution mass spectra were recorded with a Finnigan MRT-90 with direct insertion of samples into the ion source, ionization energy 70 eV, ionization chamber temperature 200 °C, perfluorokerosene standard, and resolution $M/\Delta M = 10\,000$. Characteristics of the compounds synthesized are given in Tables 1 and 2.

Results of elemental analysis for C, H, N, and Br agreed with calculated values.

6,6-Dimethyl-5,7-dinitro-1,3-diazaadamantane (I). A mixture of 2,2-dimethyl-1,3-dinitropropane (13.0 g, 80 mmol), hexamethylenetetramine (11.2 g, 80 mmol), glacial acetic acid (11.5 g, 190 mmol), and *n*-butanol (40 ml) was heated for 6 h with gentle boiling. The precipitate which formed over a day was filtered off, washed with water (15 ml) followed by isopropanol, dried and sublimed in vacuum to give dimethyldinitrodiazaadamantane I (4.6 g, 22%).

5,7-Diamino-6,6-dimethyl-1,3-diazaadamantane (III). A solution of hydrazine hydrate (10 ml) in isopropanol (10 ml) was added gradually with stirring over 7 h at 50-55 °C to a mixture of dimethyldinitrodiazaadamantane I (1.0 g, 3.9 mmol) and freshly prepared Raney nickel (0.6 g) in isopropanol (30 ml). Additional nickel catalyst (0.2 g) was added every three hours. The catalyst was filtered off, the filtrate evaporated to dryness, and the residue recrystallized from toluene to give the diaminodiazaadamantane III (0.74 g, 97%).

5,7-Diamino-1,3-diazaadamantane (IV) was obtained analogously to compound III from 5,7-dinitro-1,3-diazaadamantane (II) (0.27 g, 1.1 mmol), Raney nickel (0.2 g), and hydrazine hydrate (4.5 ml). 5,7-Diamino-1,3-diazaadamantane (IV) (0.17 g, 95%) was obtained after sublimation in vacuum.

5,7-Dibromo-6,6-dimethyl-1,3-diazaadamantane (V). A solution of sodium nitrite (0.84 g, 12 mmol) in water (4 ml) was added over 20 min at 0-5 °C to a vigorously stirred solution of 5,7-diamino-6,6-dimethyl- 1,3-diazaadamantane (III) (0.6 g, 3.1 mmol) in conc. HBr (8 ml) and stirring was continued for a further hour without cooling. Sodium hydroxide solution (40%) was added dropwise to pH 9-10 and the solution was extracted with chloroform (5 × 50 ml). The solvent was evaporated and the dry residue was sublimed in vacuum to give 5,7-dibromo-6,6-dimethyl-1,3-diazaadamantane (V) (0.54 g, 55%).

5,7-Dibromo-1,3-diazaadamantane (VI) was obtained analogously to compound V from diaminodiazaadamantane IV (0.70 g, 4.2 mmol) and sodium nitrite (1.16 g, 16.6 mmol) in Conc. HBr (10 ml). Dibromodiazaadamantane VI (0.65 g, 54%) was obtained after sublimation in vacuum.

6,6-Dimethyl-1,3-diazaadamantane (VII). Hydrazine hydrate (1.0 ml) was added dropwise with stirring to a mixture of dibromodimethyldiazaadamantane V (0.35 g, 1.1 mmol), Raney nickel (0.05 g), and sodium hydroxide (0.05 g) in ethanol (10 ml) after which the mixture was kept for 3.5 h. The catalyst was filtered off, the solvent evaporated in vacuum, and the dry residue was sublimed in vacuum to give dimethyldiazaadamantane VII (0.15 g, 88%).

1,3-Diazaadamantane (VIII) was prepared analogously to compound VII from dibromodiazaadamantane VI (0.42 g, 1.3 mmol), Raney nickel (0.06 g), and sodium hydroxide (0.06 g) in ethanol (15 ml) and hydrazine hydrate (1.5 ml). 1,3-Diazaadamantane (VIII) (0.17 g, 89%) was obtained after sublimation in vacuum.

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