19. D. Pitre, S. Boveri, and E. B. Grabitz, Chem. Ber., 99, 364 (1966).
20. B. Klein, J. Berkowitz, and N. E. Hetman, J. Org. Chem., 26, 126 (1961).
21. W. Ried and R. M. Gross, Chem. Ber., 90, 2646 (1957).
22. H. I. X. Mager and W. Berends, Rec. Trav. Chim., 77, 827 (1957).
23. W. J. Schult, H. I. X. Mager, and W. Berends, Rec. Trav. Chim., 80, 391 (1961).
24. B. Klein and J. Berkowitz, J. Am. Chem. Soc., 81, 5160 (1959).

HETEROADAMANTANES AND THEIR DERIVATIVES.

9.* SYNTHESIS OF 1,5-DINITRO-3,7-DIAZABICYCLO[3.3.1]NONANE AND DERIVED 2,2-DISUBSTITUTED 5,7-DINITRO-1,3-DIAZAADAMANTANES

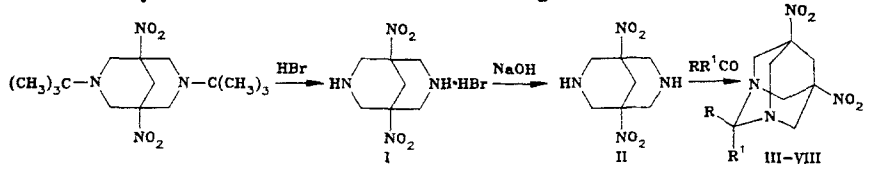
A. I. Kuznetsov, K. I. Romanova,
E. B. Basargin, A. S. Moskovskii,
and B. V. Unkovskii

UDC 547.853.5.07;543.51

Heating 1,5-dinitro-3,7-di(tert-butyl)-3,7-diazabicyclo[3.3.1]-nonane with concentrated hydrobromic acid gives 1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane. Cyclization of the latter with various aldehydes and ketones gave a series of 2,2-disubstituted 5,7-dinitro-1,3-diazaadamantanes. The behavior of the synthesized compounds under electron impact has been studied.

1,3-Diazaadamantanes with substituents at nodal positions have been little studied up to this time because of the absence of convenient methods of preparation.

2,2-Disubstituted 5,7-dinitro-1,3-diazaadamantanes have been synthesized from the bicyclic precursor 1,5-dinitro-3,7-di(tert-butyl)-3,7-diazabicyclo[3.3.1]nonane, which has been synthesized previously [2]. For the first time we have shown how to split off the N-tert-butyl substitutents from this compound using concentrated hydrobromic acid. Brief heating under these conditions leads to practically quantitative formation of the hydrobromide of 1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane (I). The free base II was prepared by treatment of hydrobromide I with aqueous sodium hydroxide. A similar conversion of 2-(tert-butyl)-amino-5,6-dihydro-4H-1,3-thiazine to a 2-amino-5,6-dihydro-4H-1,3-thiazine salt using concentrated hydrobromic and hydrochloric acids has been given in [3].



I II

III R=R¹=H; IV R=R¹=CH_3; V R=C_2H_5, R¹=CH_3; VI R=R¹=C_2H_5; VII R=C_6H_5, R¹=H; VIII R=*p*-$NO_2C_6H_4$, R¹=H

The IR spectra of the dinitrobispidine II shows absorption bands for the stretching (3295) and deformation (1615) vibrations of the amino group and also the symmetric (1340) and asymmetric (1540 cm^{-1}) vibrations of the nitro group. The PMR spectra of II are characterized by an AB- spin coupled system for resonance absorption signals of the eight protons of the N—CH_2—C fragments (H_a 3.71, H_e 3.22 ppm, $^2J_{ae}$ = 12.0 Hz), a singlet signal at 2.85 ppm for the two protons of C—CH_2—C, and a broadened signal near 2.58 ppm corresponding to the absorption of the two amino group protons. The mass spectrum of II shows a characteristic ion peak at M^+ 216.

The dinitrobispidine II was used as starting material for synthesis of a series of 2,2-disubstituted 5,7-dinitro-1,3-diazaadamantanes III-VIII by cyclization with various aldehydes

*For Communication 8 see [1].

M. V. Lomonosov Institute of Fine Chemical Technology, Moscow 119831. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 538-542, April, 1990. Original article submitted August 8, 1988.

0009-3122/90/2604-0461$12.50

TABLE 1. Parameters for 1,5-Dinitro-3,7-diazabicyclo[3.3.1]nonane (II) and 2,2-Disubstituted 5,7-dinitro-1,3-diazaadamantanes (III-VIII)

Compound	Empirical formula	mp, °C	IR spectrum, ν, cm^{-1}	PMR spectrum (in $CDCl_3$), ppm, (spin-spin ^2J, Hz)			Yield, %
				$N-CH_2-C$, d	$C-CH_2-C$, s	R, R'	
II	$C_7H_{12}N_4O_4$	159...161	3295, 1615 (NH); 1540, 1340 (NO_2)	3,71*, 3,22 (12,0)	2,85	2,58 br s **	95
III	$C_8H_{12}N_4O_4$	286...287	1530, 1335 (NO_2)	3,71; 3,41 (13,5)	3,05	4,02 s	88
IV	$C_{10}H_{16}N_4O_4$	187...189	1525, 1330 (NO_2)	4,16; 3,26 (13,5)	2,96	1,64 s	83
V	$C_{11}H_{18}N_4O_4$	127...128	1525, 1330 (NO_2)	4,10; 3,22 (13,5); 4,15; 3,26 (13,5)	2,97	1,56 s; 1,00 t; 1,97 q (8,0)	92
VI	$C_{12}H_{20}N_4O_4$	131...132	1525, 1330 (NO_2)	4,10; 3,20 (13,5)	2,96	0,90 t; 1,94 q (8,0)	64
VII	$C_{14}H_{16}N_4O_4$	196...197	1525, 1335 (NO_2), 1595 (arom)	3,92; 3,69 (13,5); 3,69; 3,24 (13,5)	3,03	7,56...7,31 m; 5,06 s	71
VIII	$C_{14}H_{15}N_5O_6$	325...327	1525, 1330 (NO_2), 1595 (arom)	3,95; 3,76 (12,5); 3,44, 3,34 (12,5)	3,10	8,29 d; 7,75 d (9,0); 5,41 s	70

*Here and subsequently d = AB doublet.

**Two proton signal for N_3 and N_7 protons.

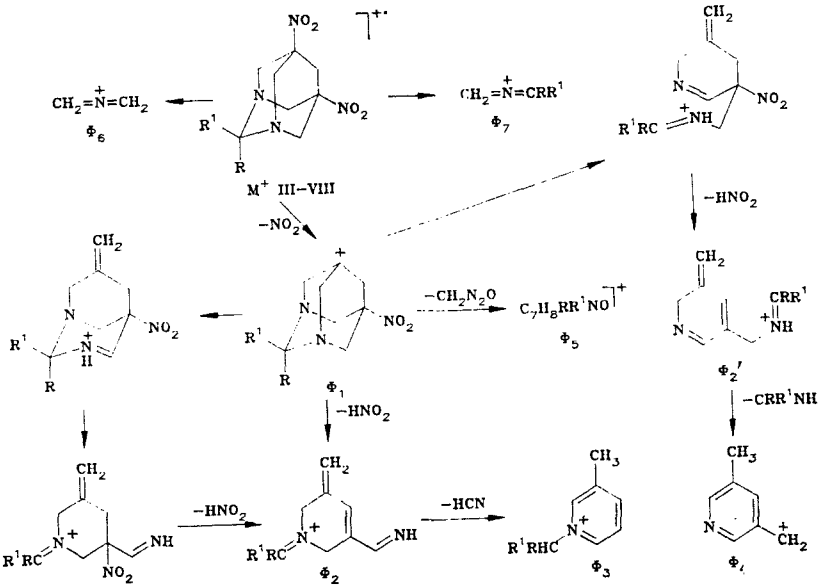
TABLE 2. Mass Spectra of III-VIII*

Compound	m/z, (I_{rel}, %)
III	228 (57), 182 (100), 168 (11), 135 (52), 108 (52), 107 (19), 106 (29), 94 (12), 79 (13), 42 (29), 41 (13)
IV	256 (46), 210 (85), 152 (61), 136 (40), 107 (45), 106 (66), 94 (55), 79 (43), 70 (94), 42 (100), 41 (82)
V	270 (51), 224 (100), 166 (74), 150 (49), 106 (67), 84 (62), 79 (45), 56 (50), 55 (55), 42 (85), 41 (71)
VI	284 (37), 238 (84), 180 (55), 108 (42), 106 (58), 98 (44), 94 (51), 79 (45), 53 (40), 42 (80), 41 (100)
VII	304 (100), 258 (96), 211 (65), 200 (63), 184 (39), 118 (43), 107 (39), 106 (82), 91 (91), 79 (40), 77 (42)
VIII	349 (55), 303 (100), 256 (35), 108 (36), 107 (30), 106 (53), 93 (22), 79 (27), 77 (23), 42 (27)

*The M^+ ion and ten most abundant ion peaks in the mass spectrum are given.

and ketones (just as used by the authors of [4, 5] for obtaining 5,7-diphenyl- [4] and 5,7-dimethyl-1,3-diazaadamantanes [5] with $C_{(2)}$ substituents via the corresponding bispidines). The dinitrobispidine II was reacted with the aldehydes in refluxing n-butanol. In the case of the ketones, they were used in excess as solvent. The yields of the target dinitrodiazaadamantanes III-VIII were 64-92%.

The IR spectra of III-VIII (Table 1) showed the presence of characteristic symmetric (1335-1330) and asymmetric (1530-1525 cm^{-1}) vibrations for the nitro group and the spectra for VII and VIII showed aromatic ring absorptions at 1595 cm^{-1}.



The PMR spectra of the dinitrodiazaadamantanes III-VIII (Table 1) show characteristic absorption signals for eight methylene protons for $N-CH_2-C$ fragments formed due to the symmetry of the C_2 AB system (compounds III, IV, VI) or two AB systems (V, VII, VIII) in the region 3.22-4.16 ppm. The singlet signal at 2.96-3.10 ppm corresponds to the methylene fragment $C-CH_2-C$. Signals for the protons of the substituents at C_2 are found in a group with the appropriate multiplicity at 0.9-4.02 ppm (III-VI) or 5.06-7.75 ppm (VII, VIII).

According to literature data [6-9] the first stage of the dissociation of 1-nitroadamantane under electron impact conditions is the elimination of the nitro group. The same is found for molecular ion dissociation of 7-nitro-1,3,5-triazaadamantane [10].

The mass spectra of III-VIII (Table 2) show the analogous process from the molecular ion M^+. As expected, the most typical process for the dissociation of the dinitro disubstituted 1,3-diazaadamantanes III-VIII is loss of the NO_2 radical. The associated peak for fragment Φ_1 is significant and, for compounds III, V, VIII is the most intense (Table 2, 3). Typical of dinitro substituted adamantanes [9] is the subsequent loss of the HNO_2 fragment

TABLE 3. Mass Spectra of III-VIII

Compound	Peak ion intensities*							
	$M^+(W_M)$	Φ_1	Φ_2, Φ'_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
III	9,7	15,3	7,9	7,9	4,4	1,0	4,4	Φ_6
IV	2,8	4,4	1,5	2,4	3,4	3,2	5,2	4,9
V	3,0	5,1	1,6	2,5	3,4	3,7	4,3	3,1
VI	2,2	4,3	1,1	1,6	3,0	2,8	4,1	2,3
VII	6,7	5,4	3,7	2,2	4,6	3,6	1,8	2,4
VIII	5,7	8,7	3,0	1,1	4,6	2,1	2,3	1,2

*Percent of total ion current.

from Φ_1 in III-VIII, evidently leading to formation of the two ions Φ_2 and Φ'_2. The latter further dissociates with elimination of the neutral molecules HCN and CRR'NH respectively. Peaks for the amino fragments Φ_6 and Φ_7 are also seen in the spectra of the dinitrodiazaadamantanes III-VIII, again typical of other 1,3-diazaadamantanes [11].

The elemental composition of the principal compounds III-VIII was confirmed by high resolution mass spectrometry of VIII.

EXPERIMENTAL

IR Spectra were obtained on a Specord 71 IR spectrometer (in vaseline mull or KBr tablets) and PMR spectra on a Bruker WM-250 instrument ($CDCl_3$ solvent) using HMDS internal standard. Low and high resolution mass spectra were obtained on a Kratos MS-80 instrument with direct introduction of the sample into the ion source, an ionization energy of 70 eV, ionization chamber temperature of 150°C, and perfluorokerosene standard. Resolution $M/\Delta M$ = 10,000.

Parameters for II-VIII are given in Tables 1-3. The elemental analytical data for C, H, and N (Br) agreed with those calculated.

1,5-Dinitro-3,7-diazabicyclo[3.3.1]nonane hydrobromide (I, $C_7H_{12}N_4O_4 \cdot HBr$. A solution of 1,5-dinitro-3,7-di(tert-butyl)-3,7-diazabicylco[3.3.1]nonane (2.3 g, 7 mmole) and concentrated hydrobromic acid (2 ml) was heated under gentle reflux for 20 min. After cooling, the precipitated solid was filtered off and dried in a desiccator over $CaCl_2$. Recrystallization from alcohol gave 2.02 g (97%) of the hydrobromide (I) with mp 178-179°C.

1,5-Dinitro-3,7-diazabicyclo[3.3.1]nonane (II). A solution of sodium hydroxide (0.3 g) in water (1.5 ml) was added dropwise with stirring to a solution of hydrobromide I (2 g, 3.4 mmole) in water (8 ml), extracted with chloroform (6 × 10 ml), and the combined chloroform extracts dried over $MgSO_4$. The extract was distilled in vacuo and the solid residue recrystallized from benzene to give the dinitrobispdine II (1.38 g, 95%).

5,7-Dinitro-1,3-diazaadamantane (III). Dinitrobispidine II (0.4 g, 1.8 mmole) and paraformaldehyde (0.54 g, 1.8 mmole) in n-butanol (30 ml) were heated under gentle reflux for 6 h. The solid formed on cooling was filtered off, dried in a desiccator over $CaCl_2$, and recrystallized from benzene to give the dinitrodiazaadamantane III (0.37 g, 88%).

2,2-Dimethyl-5,7-dinitro-1,3-diazaadamantane (IV). A solution of dinitrobispidine II (0.2 g, 0.9 mmole) and acetone (40 ml) was heated under gentle reflux for 10 h. Acetone was distilled off and the solid residue recrystallized from alcohol to give dinitrodiazaadamantane IV (0.2 g, 83%).

2-Methyl-2-ethyl-5,7-dinitro-1,3-diazaadamantane (V) was obtained similarly to IV from the dinitrobispidine II (0.1 g, 0.45 mmole) in methylethylketone (10 ml) for 6 h. Recrystallization from n-butanol gave the dinitrodiazaadamantane V (0.12 g, 92%).

2,2-Diethyl-5,7-dinitro-1,3-diazaadamantane (VI) was obtained similarly to IV from the dinitrobispidine II (0.5 g, 2.25 mmole) and diethylketone (20 ml) for 8 h. Recrystallization from n-butanol gave the dinitrodiazaadamantane VI (0.4 g, 64%).

2-Phenyl-5,7-dinitro-1,3-diazaadamantane (VII) was obtained similarly to III from the dinitrobispidine II (0.4 g, 1.8 mmole) and benzaldehyde (0.4 g, 4 mmole) in n-butanol (50 ml) for 12 h. Recrystallization from n-butanol gave the dinitrodiazaadamantane VII (0.4 g, 71%).

2-(p-Nitrophenyl)-5,7-dinitro-1,3-diazaadamantane (VIII) was obtained similarly to III from the dinitrobispidine II (0.4 g, 1.8 mmole) and p-nitrobenzaldehyde (0.3 g, 2.0 mmole) in n-butanol (50 ml) for 10 h. Recrystallization from toluene gave the dinitrodiazaadamantane VIII (0.45 g, 70%).

LITERATURE CITED

1. A. I. Kuznetsov and I. A. Vladimirova, Khim. Geterotsikl. Soedin., No. 12, 1700 (1988).
2. D. A. Cichra and H. G. Adolph, J. Org. Chem., 47, 2474 (1982).
3. A. Schöberl and K. H. Magosh, Annalen, 742, 74 (1970).
4. R. L. Vittory, G. Settimj, F. Gatta, N. Sarti, and S. Chiavarelli, Gazz. Chim. Ital., 97, 1294 (1967).
5. G. S. Saakyan, G. L. Arutyunyan, Ts. E. Agadzhanyan, and R. V. Paronikyan, Arm. Khim. Zh., 39, 242 (1986).
6. Z. Dolejsek, S. Hala, V. Hanus, and S. Landa, Coll. Czech. Chem. Commun., 31, 435 (1966).
7. G. G. Hall, Bull. Soc. Chim. Belg., 73, 305 (1964).
8. A. I. Feinstein, E. K. Fields, P. J. Ihrig, and S. Meyerson, J. Org. Chem., 36, 996 (1971).
9. J. Yinon and S. Bulusu, Org. Mass Spectrom., 21, 529 (1986).
10. A. S. Moskovkin, A. I. Kuznetsov, and I. V. Miroshnichenko, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol., 24, 172 (1981).
11. A. I. Kuznetsov, E. B. Basargin, A. S. Moskovkin, M. Kh. Ba, I. V. Miroshnichenko, M. Ya. Botnikov, and B. V. Unkovskii, Khim. Geterotsikl. Soedin., No. 12, 1679 (1985).

HETEROADAMANTANES AND THEIR DERIVATIVES.

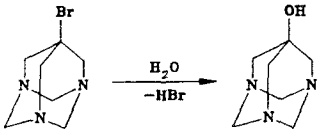
10.* HYDROLYSIS OF 7-BROMO-1,3,5-TRIAZAADAMANTANE

A. I. Kuznetsov, V. A. Tyurikov, and V. A. Kosmakov

UDC 547.853.5'859.04:542.938:541.127

Potentiometric titration was used to determine the rate constants of hydrolysis of 7-bromo-1,3,5-triazaadamantane at 50 and 80°C. It was shown that the rate of this reaction is significantly lower than the rate of hydrolysis of 1-bromoadamantane.

Previously it was shown [2] that 7-bromo-1,3,5-triazaadamantane (I) is formed in the reaction of 7-amino-1,3,5-triazaadamantane with sodium nitrite in a medium of concentrated hydrobromic acid. Attempts to carry out chemical conversions of bromotriazaadamantane I similar to conversions of 1-bromoadamantane showed its low reactivity. To determine the reactivity of bromotriazaadamantane I and 1-bromoadamantane in nucleophilic substitution reactions, we decided to compare the rates of their hydrolysis.



I II

According to the data of [3], 1-bromoadamantane hydrolyzes at a significant rate in 60% alcohol at 25°C. We found that under these conditions bromotriazaadamantane I practically does not hydrolyze. Even in pure water, it hydrolyzes by only 1-2% in 30 days at 25°C. Therefore, the hydrolysis rates of bromotriazaadamantane I were determined in water at 50 and 80°C (Table 1). The first-order rate constant was found graphically according to the curve of log c vs. τ (Table 2).

M. V. Lomonosov Moscow Institute of Fine Chemical Technology, Moscow 119435.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 543-545, April, 1990. Original article submitted August 10, 1988.