SYNTHESIS AND TRANSFORMATIONS OF POLYHEDRAL COMPOUNDS.

16.* SYNTHESIS AND SOME REACTIONS OF 7-AROYL- AND 7-HETEROYL-1,3,5-TRIAZAADAMANTANES

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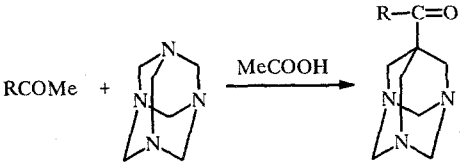
7-Aroyl- and 7-heteroyl-1,3,5-triazaadamantanes were obtained by condensation of aromatic and heterocyclic compounds containing an acetyl group with hexamethylenetetramine in the presence of acetic acid. Reactions with 7-benzoyl- and 7-(4-nitrobenzoyl)-1,3,5-triazaadamantanes at both the carbonyl group and in the triazaadamantane ring were carried out. Ring-deuterated 7-nitro- and 7-(4-nitrobenzoyl)-1,3,5-triazaadamantanes were synthesized in order to ascertain the pathway of mass-spectrometric fragmentation, as well as a possible mechanism for the construction of the triazaadamantane ring.

The known [2] methods for construction of the 1,3,5-triazaadamantane ring and its 7-alkyl derivatives are based either on condensation of the difficult-to-obtain tris(aminomethyl)methane or its homologs with aldehydes or on obtaining 7-nitro-1,3,5-triazaadamantane by condensation of nitromethane with formaldehyde and ammonia or hexamethylenetetramine (HMTA).

We have developed a one-step method for the synthesis of the previously unknown 7-aroyl- and 7-heteroyl-1,3,5-triazaadamantanes I-XI by condensation of various aromatic and heterocyclic compounds containing an acetyl group with HMTA in the presence of acetic acid.



I-XI

I R = Ph; II R = 4-$O_2NC_6H_4$; III R = 4-ClC_6H_4; IV R = 4-$MeOC_6H_4$; V R = 4-$O_2NC_6H_4$; VI R = =4-EtC_6H_4; VII R = α-furyl VIII R = β-pyridyl IX R = γ-pyridyl X R = α-naphthyl XI R = β-naphthyl

Substituents in the acetophenone have an appreciable effect on the yields of the triazaadamantane derivatives (Table 1). Electron-acceptor groups increase the yields of desired products as compared with the unsubstituted acetophenone, while electron-donor groups decrease the yields. Steric factors evidently have a pronounced effect on the yields of the final products in the case of 1- and 2-acetylnaphthalenes. An attempt to carry out this reaction with 3-acetyl- and 1,3-diacetylindole was unsuccessful. The latter can be explained by the marked decrease in the electron density on the carbon atom of the carbonyl group due to its conjugation with the nitrogen atom of the pyrrole ring of indole, which remains significant even when the hydrogen atom attached to the nitrogen atom is replaced by an acetyl group.

*For Communication 15 see [1].

A. L. Mndzhoyan Institute of Fine Organic Chemistry, Academy of Sciences of the Republic of Armenia, Yerevan 375014. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1565-1571, November, 1992. Original article submitted November 4, 1991.

 0009-3122/92/2811-1340$12.50

TABLE 1. 7-Aroyl- and 7-Heteroyl-1,3,5-triazaadamantanes I-XI, XIII-XVI, and XXI-XXIII and Triazabicyclonanes XVII-XX

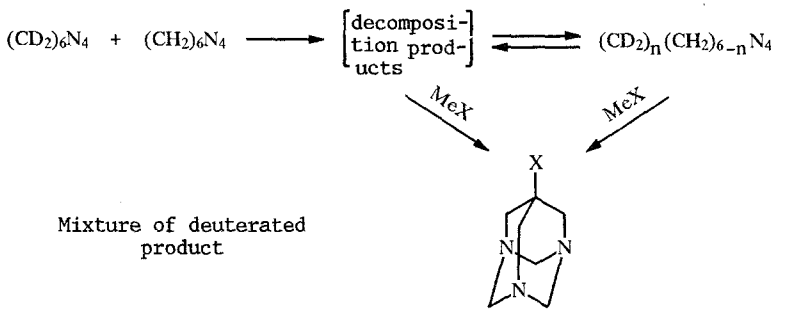
Compound	Empirical formula	mp, °C	IR spectrum, ν, cm^{-1}			Yield, %
			C=O	aromatic ring	functional groups	
I	$C_{14}H_{17}N_3O$	145...146	1655	1600, 1580		22
II	$C_{14}H_{16}N_4O_3$	235...236	1670	1595, 1520	1540, 1350 (NO_2)	57
III	$C_{14}H_{16}ClN_3O$	138...139	1645	1590, 1570		32
IV	$C_{15}H_{19}N_3O_2$	182...183	1640	1595, 1570, 1510	1250, 1040 (C—O—C)	13
V	$C_{14}H_{16}N_4O_3$	174...176,5	1660	1590	1560, 1350 (NO_2)	35
VI	$C_{16}H_{21}N_3O$	95...97	1650	1600, 1560		9
VII	$C_{16}H_{21}N_3O$	139...140	1640	1570		53
VIII	$C_{13}H_{16}N_4O$	176...178	1645	1630, 1590, 1570		24
IX	$C_{13}H_{16}N_4O$	196...198	1660	1630, 1590, 1560		24
X	$C_{18}H_{19}N_3O$	201...203	1660	1610		3
XI	$C_{18}H_{19}N_3O$	189...191	1650	1580		11
XIII	$C_{14}H_{17}N_5O_3$	296 dec.	—		1620 (C=N); 1540, 1350 (NO_2)	20
XIV	$C_{14}H_{19}N_5$	195...197	—	1600, 1580	3330, 3150 broad band NH_2)	51
XV	$C_{14}H_{18}N_6O_2$	234...246	—	1610, 1590, 1510	3380, 3200 (NH_2); 1530, 1350 (NO_2)	58
XVI	$C_{17}H_{22}N_6O_2$	182...184	—	1600, 1520	1620 (C=N); 1520, 1360 (NO_2)	88
XVII	$C_{17}H_{21}N_3O_3$	166...168	1680,1640, 1650	1610,1590		21
XVIII	$C_{17}H_{20}N_4O_5$	169,5...171	1715, 1660, 1650	1610, 1590	1540, 1350 (NO_2)	21
XIX	$C_{17}H_{22}N_4O_5$	246...248	1660, 1640	1600, 1580, 1510	1540, 1350 (NO_2); 3200 broad OH band	82
XX	$C_{27}H_{28}N_4O_7S_2$	228...230	1680	1610, 1580, 1500	1360, 1170 (SO_2); 1540, 1350 (NO_2)	29
XXI	$C_{14}H_{19}N_3O$	250...252	—	1610, 1580, 1520	3350 broad OH band	61
XXII	$C_{14}H_{18}N_4O_3$	300 dec.	—	1610, 1579, 1620	3200 broad OH band; 1540, 1350 (NO_2)	39

In the opinion of Kuznetsov and coworkers [3], in the condensation of nitromethane with HMTA the triazaadamantane carcass may be formed as a result of one intermolecular reaction of protonated HMTA with nitromethane, which is followed by intramolecular rearrangement with splitting out of a nitrogen atom in one of the final steps and the formation of 7-nitro-1,3,5-triazaadamantane (XII).

In order to ascertain the possible mechanism of the construction of the triazaadamantane ring we carried out the reaction of nitromethane and 4-nitroacetophenone with an equimolar mixture of HMTA and deuterated HMTA (d_{12}-HMTA). In the mass spectra of the isolated products II and XII in the molecular-ion region we observed M^+, $[M - 2]^+$, and $[M + 4]$-$[M + 12]^+$ peaks with maximum intensity of the $[M + 6]$ peak and minimum intensities of the M^+ and $[M + 12]^+$ peaks, which corresponds to the mathematical probability of the deuterium distribution under the conditions of fragmentation of HMTA and buildup of the carcass through successive intermolecular transformations. However, further study of these reactions showed that HMTA that, according to the mass-spectral data, is a mixture of HMTA and deuterated HMTA with the most intense peak at 146 (m/z) and the least intense peaks at 140 and 152 (m/z) can be isolated from the reaction mixture 5 min after the start of reflux when amounts of HMTA and d_{12}-HMTA greater than the molar ratio are used. The data obtained show that HMTA and d_{12}-HMTA undergo rapid fragmentation and that HMTA molecules with the corresponding deuterium distribution are built up from their fragmentation products. The possibility that further reaction of nitromethane and 4-nitroacetophenone occurs with their protonated forms in accordance with [3] is not excluded. It is therefore difficult to give preference to any of the examined mechanisms.

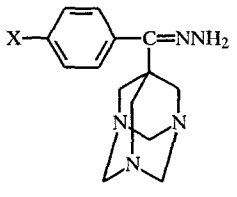
TABLE 2. PMR Spectra of I-XI, XIII-XIX, and XXI-XXIII in $CDCl_3$

Compound	Chemical shifts of the protons, δ, ppm		
	NCH_2C, s	NCH_2N, d	R
I	3,85	4,26, 4,55	7,53 m, C_6H_5
II	3,78	4,19, 4,50	7,65 m, 8,3 m, C_6H_4
III	3,66	4,04, 4,35	7,34 m, 7,6m, C_6H_4
IV	3,85	4,28, 4,55	6,9 m, 7,9 m, C_6H_4
V	3,85	4,24, 4,55	7,9 m, 8,4 m, C_6H_4
VI	3,88	4,29, 4,58	1,28 t, CH_3, 2,73 q, CH_2 (J = 7 Hz); 7,26m, 7,73 m, C_6H_4
VII	3,93	4,29, 4,59	6,57 q, 4-H; 7,28 q, 3-H; 7,63 q, 5-H, C_4H_3O (J_{45} = 2 Hz, J_{34} = 4 Hz, J_{35} = 1Hz)
VIII	3,85	4,24, 4,54	7,4 d.d, 5-H; 7,95 m., 4-H; 8,76 d.d, 6-H; 9,0 d, 2-H, C_5H_4N (J_{25} = 2 Hz, J_{56} = 4 Hz, J_{45} = 8 Hz
IX	3,75	4,24, 4,53	7,03 d.d, 3-H, 5-H; 8,66 d.d 2-H, 6-H; C_5H_4 (J_{23} = = 4 Hz, J_{25} = 2Hz)
X	3,90	4,24, 4,54	8,14...7,58 m, $C_{10}H_7$
XI	3,91	4,53, 4,26	8,16...7,5 m, $C_{10}H_7$
XIII	3,46	4,40, 4,0	3,9 br.s, OH; 7,4 m, 8,35 m, C_6H_4
XIV	3,51	4,44, 4,09	5,06 br.s, NH_2; 7,1m, 7,5m, C_6H_5
XV	3,68	4,66, 4,29	(DO_2) 7,6m, 8,5 m, C_6H_4
XVI	3,62	4,49, 4,14	1,77 s, CH_3; 1,9 s, CH_3; 7,1 m, 8,16 m, C_6H_4
XVII	3,0...5,6		1,93 s, CH_3; 7,6 m, C_6H_5
XVIII	3,0...5,9		2,11 s, CH_3; 7,83 m, 8,4 m, C_6H_4
XIX	3,0...5,9		2,0 s, CH_3; 4,6 br.s, OH
XXI	2,96, 319	4,05, 3,72	3,9 s, H; 4,6 br.s OH; 7,3 m, C_6H_5
XXII	3,09, 3,37	4,31, 3,87	(DMSO d_6) 4,63 s, H; 5,7 br.s, OH; 7,6 m, C_6H_4
XXIII	3,16	4,0, 4,4	2,16 s, CH_2; 7,1 m, 7,3 m, C_6H_5

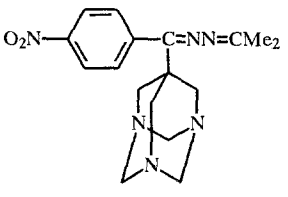


X=NO_2, 4-$O_2NC_6H_4CO$; n=0...6

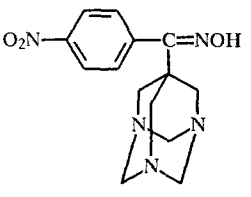
7-Benzoyl- and 7-(4-nitrobenzoyl)-1,3,5-triazaadamantanes I and II were subjected to various reactions. Oxime XIII and the corresponding hydrazones XIV-XVI were obtained through reactions of the keto group. The keto group was reduced to a hydroxy group by sodium borohydride (to give XIX, XXII, and XXIII) and to a methylene group (to give XXIII) via the Kishner reaction. The reactions of triazaadamantanes I and II with acetic anhydride and of triazaadamantane II with toluene-4-sulfonyl chloride lead to, respectively, 3,7-diacetyl (XVII and XVIII) and 3,7-ditosyl (XX) derivatives of 3,7-diazabicyclo-[3.3.1]nonanes.



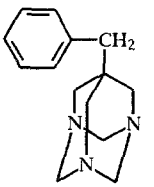
XIV, XV



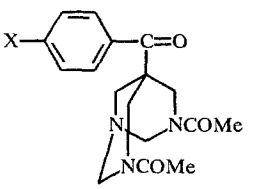
XVI



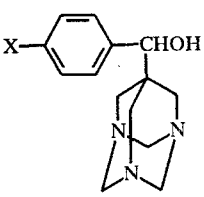
XIII



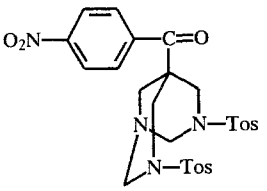
XXIII



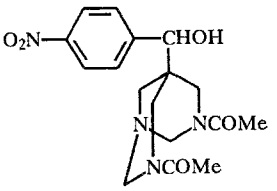
XVII, XVIII



XXI, XXII



XX



XIX

XIV, XVII, XXI X=H; XV, XVIII, XXII X=NO_2

Characteristic absorption bands of a carbonyl group at 1640-1680 cm^{-1} and of aromatic and heterocyclic rings at 1500-1610 cm^{-1}, as well as absorption bands that are characteristic for the functional groups of the substituents, are present in the IR spectra of the triazaadamantanes (see Table 1).

The PMR spectra of I-XI, XIV-XVI, and XIII consists primarily of three groups of signals: a singlet from six NCH_2C protons at 3.51-3.91 ppm; resonance signals from the six protons of NCH_2N methylene groups, which show up in the form of an AB spin system with centers at 4.09-4.29 ppm and 4.35-4.66 ppm (J = 13 Hz); and multiplets from protons of aromatic or heterocyclic rings (Table 2). In the case of 7-(α-hydroxybenzyl)- and 7-(α-hydroxy-4′-nitrobenzyl)-1,3,5-triazaadamantanes (XXI, XXII) the protons of the NCH_2C methylene groups also are not magnetically equivalent and are observed in the form of an AB spin system with centers at 3.1-3.2 ppm and 3.2-3.4 ppm (J = 14 Hz).

The PMR spectra of triazabicyclononane derivatives XVII-XX are quite complex. A doublet at 5.0 ppm belonging to equatorial protons attached to the 2-C and 8-C atoms (J = 12 Hz), doublets of doublets of four protons attached to the 4-C and 6-C atoms at 4.46 and 4.28 ppm (J = 11 Hz), a doublet from axial protons attached to the 2-C and 8-C atoms at 3.56 ppm, and a broad singlet from protons attached to the 9-C atom at 3.43 ppm are observed in the spectrum of ditosyl derivative XX. A singlet of protons of methyl groups at 2.2 ppm and a multiplet from aromatic protons at 7.7-8.4 ppm are also observed.

A singlet from the methyl protons of acetyl groups at 1.9-2.0 ppm and a multiplet of aromatic protons at 7.6-8.4 ppm are observed in the PMR spectra of diacetyltriazabicyclononanes XVII-XIX. Protons of a triazabicyclononane ring are observed at 3.0-5.6 ppm in the form of partially overlapped doublets; according to the integral curve, these signals correspond to 10 protons. The character of the splitting of the signals coincides with that observed in the PMR spectrum of 5-nitro-3,7-acetyl-1,3,5-triazabicyclo[3.3.1]nonane [4]; however, as in the latter case, their interpretation is difficult.

An analysis of the mass spectra of the triazaadamantanes and triazabicyclononanes shows that the former are resistant to electron impact — the molecular-ion peak (M^+) has the maximum intensity (W) in their spectra (Table 3).

It follows from the mass-spectral behavior of triazaadamantane d_{12}-II and the mass spectra of 7-aroyl- and 7-heteroyltriazaadamantanes I-XI that the principal pathway of the fragmentation of the molecular ions (M^+) of the triazaadamantanes is the elimination of a CO group ($[M - 28]^+$). The subsequent fragment ions are associated with products of cleavage of the triazaadamantane ring [5]; the substituents are retained in all of the principal fragment ions.

Biological investigations did not reveal anticonvulsant activity for I-IV, VII, and IX, antitumorigenic activity for I, II, X, XIV, and XIX, and antibacterial activity for I-III, VII, X, XIV, and XXII.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Varian T-60 spectrometer. The mass spectra were obtained with an MKh-1320 spectrometer with direct introduction of the samples into the ion source at an ionizing-electron energy of 70 eV. Thin-layer chromatography was carried out on Silufol UV-254 plates in the following systems: propanol—water (7:3) (A), methanol—water (1:1) (B), butanol—acetic acid—water (3:1:1) (C), and benzene—ethanol (10:1) (D).

7-Benzoyl-1,3,5-triazaadamantane (I). A solution of 2.8 g (20 mmole) of HMTA, 2.6 g (20 mmole) of acetophenone, and 2.8 g (47 mmole) of acetic acid in 50 ml of dry butanol was refluxed for 15 h, after which the reaction mixture was evaporated in vacuo to 1/5 of its original volume, and the viscous precipitate was extracted with heptane (5 × 50 ml). The warm extract was purified and passed through a layer of aluminum oxide (4 g, activity II) placed in a Schott filter. The precipitate that formed from the heptane extract was removed by filtration to give 1.07 g (22%) of I with R_f 0.34 (D).

TABLE 3. Mass Spectra of I-IV, VI, VII, IX-XI, XIII, XV, XVII-XIX, and XXII*

Compound	W	m/z (I_{rel}, %)
I	27,2	243 (100), 215 (51), 201 (6), 188 (24), 174 (25), 138 (22), 105 (27), 81 (12), 78 (9), 42 (92)
II	20,6	288 (99), 260 (61), 233 (13), 249 (8), 217 (7), 168 (6), 150 (14), 140 (28), 138 (15), 112 (16)
III	20,7	277 (74), 249 (49), 222 (17), 208 (11), 183 (8), 139 (28), 114 (15), 42 (100)
IV	16,3	273 (100), 245 (57), 231 (7), 218 (20), 204 (16), 202 (18), 200 (30), 199 (40), 175 (9), 145 (9), 140 (18), 138 (21), 135 (69), 121 (30), 109 (8), 107 (9), 92 (8), 83 (20), 77 (15), 73 (20), 72 (21), 42 (66)
VI	18,7	271 (100), 243 (72), 216 (26), 197 (26), 169 (12), 145 (48), 138 (18), 133 (44), 92 (20), 83 (20), 82 (48), 51 (99)
VII	20,2	233 (79), 205 (46), 191 (6), 178 (21), 162 (22), 138 (17), 95 (45), 81 (54), 42 (100)
IX	26,1	244 (100), 216 (96), 189 (11), 175 (35), 138 (18), 106 (19), 78 (17), 42 (87)
X	25,3	293 (100), 265 (62), 238(16), 202 (13), 204 (13), 195(8), 155 (41), 141 (15), 138 (15), 127 (43), 42 (64)
XI	25,4	293 (100), 265 (66), 238 (19), 202 (15), 204 (18), 109 (15), 188 (13), 155 (41), 141 (13), 138 (13), 118 (40), 42 (62)
XV	15,3	302 (100), 286 (45), 273 (55), 259 (22), 245 (58), 231 (42), 216 (74), 203 (93), 156 (19), 157 (19), 71 (68), 42 (55)
XIII	12,6	303 (44), 286 (19), 274 (98), 246 (15), 245 (13), 230 (13), 216 (10), 189 (5), 71 (30), 42 (100)
XVIII	9.6	360 (59), 345 (5), 330 (5), 307 (9), 289 (39), 273 (13), 275 (16), 247 (16), 232 (18), 219 (54), 210 (48), 205 (18), 201 (20), 181 (16), 168 (27), 153 (15), 150 (32), 139 (45), 97 (27), 57 (16), 42 (100)
XVII	10,1	315 (42), 273 (8), 244 (38), 229 (11), 210 (31), 174 (30), 169 (42), 160 (19), 128 (27), 105 (23), 72 (38), 42 (100)
XIX	13,4	362 (87), 347 (8), 319 (11), 302 (6), 290 (45), 276 (32), 260 (10), 248 (14), 234 (34), 210 (95), 168 (53), 139 (100), 109 (23), 97 (45), 43 (78)
XXII	17,1	290 (96), 273 (10), 260 (10), 245 (10), 233 (100), 219 (10), 149 (17), 138 (52), 111 (15), 109 (10), 46 (53), 45 (78), 42 (78)

*The peaks with intensities ≥ 5% are presented.

Compounds III, IV, and VI-XI, the characteristics of which are presented in Tables 1-3, were similarly obtained.

7-(4′-Nitrobenzoyl)-1,3,5-triazaadamantane (II). A solution of 2.8 g (20 mmole) of HMTA, 3.3 g (20 mmole) of 4-nitroacetophenone, and 2.8 g (47 mmole) of acetic acid in 50 ml of dry butanol was refluxed with moderate heating for 10 h, after which the resulting precipitate was removed by filtration and recrystallized from isopropyl alcohol to give 3.26 g (57%) of II with R_f 0.34 (A).

A similar procedure was used to obtain 7-(3′-nitrobenzoyl)-1,3,5-triazaadamantane (V) (see Table 1) with R_f 0.28 (A).

d_{12}-7-(4′-Nitrobenzoyl)-1,3,5-triazaadamantane (d_{12}-II). This compound was obtained from the method presented above using 3.04 g (20 mmole) of d_{12}-HMTA and 3.3 g (0.20 mmole) of p-nitroacetophenone. Workup gave 3.4 g (57.3%) of d_{12}-II with mp 235-236°C, R_f 0.34 (A), M^+ 300.

A mixture of undeuterated and ring-deuterated 7-nitrobenzoyl-1,3,5-triazaadamantanes was similarly obtained using a mixture of 1.52 g (10 mmole) of d_{12}-HMTA and 1.4 g (10 mmole) of HMTA. Workup gave a 3.3 g of a mixture with mp 235-236°C and R_f 0.34 (A). Mass spectrum: M^+ 288 (3), $[M + 2]^+$ 290 (20.8), $[M + 4]^+$ 292 (65), $[M + 6]^+$ 294 (100), $[M + 8]^+$ 296 (89), $[M + 10]^+$ 298 (43), $[M + 12]^+$ 300 (10) (percent of the maximum [M + 6] peak).

d_{12}-7-Nitro-1,3,5-triazaadamantane (XII). This compound was obtained by a method similar to that in [6] using 1.52 g (10 mmole) of d_{12}-HMTA, 0.67 g (11 mmole) of nitromethane, and 1.38 g (23 mmole) of acetic acid in 25 ml of butanol. Workup gave 4.7 g (58%) of a deuterated product with mp 226°C (subl.), R_f 0.23 (A), and M^+ 196.

A mixture of undeuterated and ring-deuterated 7-nitro-1,3,5-triazaadamantanes was obtained similarly using 0.76 g (5 mmole) of d_{12}-HMTA and 0.7 g (5 mmole) of HMTA. Workup gave 4.9 g of a mixture of deuterated products with mp 226°C (subl.) and R_f 0.23 (A). Mass spectrum: M^+ 184 (8), $[M + 2]^+$ 186 (42), $[M + 4]^+$ 188 (91), $[M + 6]^+$ 190 (100), $[M + 8]^+$ 192 (67), $[M + 10]^+$ 194 (25.5), $[M + 12]^+$ 196 (3).

7-(4′-Nitrobenzoyl)-1,3,5-triazaadamantane Hydrazone (XV). A mixture of 3.9 g (17.3 mmole) of 7-(4-nitrobenzoyl)-1,3,5-triazaadamantane (II), 0.75 g (20 mmole) of 85% hydrazine hydrate, and a drop of acetic acid in 50 ml of dry ethanol was refluxed for 5 h, after which the reaction mixture was evaporated in vacuo to half its original volume. The

precipitate that formed on cooling was removed by filtration and recrystallized from isopropyl alcohol to give 3 g (58%) of XV with R_f 0.2 (B).

7-(Benzoyl)-1,3,5-triazaadamantane Hydrazone (XIV). This compound was similarly obtained. Workup gave 2.7 g (51.4%) of XIV with R_f 0.25 (C).

N^1-[α-(1,3,5-Triazaadamant-7-yl)-4-nitrobenzylidene]-N^2-isopropylidenehydrazine (XVI). A mixture of 3 g (100 mmole) of 7-(4′-nitrobenzoyl)-1,3,5-triazaadamantane hydrazone (XV) in 100 ml of acetone was refluxed until the solid material had dissolved completely (≈2 h), after which the acetone was removed by distillation to half the original volume, and the resulting precipitate was removed by filtration and recrystallized from acetone to give 3 g (88%) of XVI with R_f 0.25 (B).

7-(4′-Nitrobenzoyl)-1,3,5-triazaadamantane Oxime (XIII). A mixture of 5.8 g (20 mmole) of 7-(4-nitrobenzoyl)-1,3,5-triazaadamantane (III), 2.8 g (40 mmole) of hydroxylamine hydrochloride, and 84 ml of pyridine in 100 ml of dry ethanol was refluxed for 3 h, after which the reaction mixture was cooled, and the resulting precipitate was removed by filtration, washed successively with water, 20% sodium carbonate solution, and water, and recrystallized from DMF to give 1.2 g (20%) of XIII with R_f 0.3 (A).

3,7-Diacetyl-5-(4′-nitrobenzoyl)-1,3,7-triazabicyclo[3.3.1]nonane (XVIII). A solution of 5.8 g (20 mmole) of 7-(p-nitrobenzoyl)-1,3,5-triazaadamantane (II) in 25 ml [2.7 g (264 mmole)] of acetic anhydride was maintained at room temperature for 30 min, after which 20 ml of water was added, and the resulting acetic acid was removed by fractional distillation in vacuo. The precipitate was recrystallized from ethanol—water (1:1) to give 1.5 g (21%) of XVIII and R_f 0.52 (A).

3,7-Diacetyl-5-benzoyl-1,3,7-triazabicyclo[3.3.1]nonane (XVII). This compound was similarly obtained. Recrystallization from water gave 1.35 g (21%) of XVII with R_f 0.34 (A).

7-(α-Hydroxybenzyl)-1,3,5-triazaadamantane (XXI). A 1-g (2.8 mmole) sample of sodium borohydride was added with stirring at room temperature to a solution of 2.4 g (10 mmole) of 7-benzoyl-1,3,5-triazaadamantane in 50 ml of dry methanol. After all of the sodium borohydride had been added, the mixture was evaporated in vacuo to half its original volume, and the concentrate was cooled. The resulting precipitate was removed by filtration and recrystallized from isopropyl alcohol to give 1.9 g (61%) of XXI with R_f 0.23 (A).

7-(α-Hydroxy-4′-nitrobenzyl)-1,3,5-triazaadamantane (XXII). This compound was similarly obtained. Workup gave 2.2 g (39%) of XXII with R_f 0.24 (A).

3,7-Diacetyl-5-(α-hydroxy-4′-nitrobenzyl)-1,3,7-triazabicyclo[3.3.1]nonane (XIX). The compound was obtained via method presented above from 3.6 g (10 mmole) of 3,7-diacetyl-5-(4′-nitrobenzoyl)-1,3,7-triazabicyclo[3.3.1]nonane (XIX) and 0.1 g (3 mmole) of sodium borohydride. Product was recrystallized from hot water to give 3 g (82% XIX) with R_f 0.56 (A).

3,7-Ditosyl-5-(4-nitrobenzoyl)-1,3,5-triazabicyclo[3.3.1]nonane (XX). A solution of 8.56 g (45 mmole) of p-toluenesulfonyl chloride in 50 ml of THF was added dropwise in the course of 1 h to a suspension of 5.8 g (20 mmole) of 7-(4-nitrobenzoyl)-1,3,5-triazaadamantane (II), 8.4 g (100 mmole) of sodium bicarbonate, 30 ml of water, and 100 ml of THF, and the mixture was allowed to stand overnight. The THF layer was separated, the THF was removed by distillation, and the residue was recrystallized from DMF to give 3.5 g (29%) of XX with R_f 0.5 (A).

8-Benzyl-1,3,5-triazaadamantane (XXIII). A mixture of 12.1 g (50 mmole) of 7-benzoyl-1,3,5-triazaadamantane (I), 50 ml of diethylene glycol, 11.25 g (200 mmole) of potassium hydroxide, and 5.53 g (150 mmole) of 85% of hydrazine hydrate was heated until nitrogen evolution ceased (≈2 h). The reaction mixture was then evaporated in vacuo, and the residue was extracted with isooctane (3 × 50 ml). The precipitate that formed from the isooctane extract was recrystallized twice from heptane to give 3.44 g (30%) of XXIII with R_f 0.23 (A).

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