SYNTHESIS AND TRANSFORMATIONS OF POLYHEDRAL COMPOUNDS.

15.* TRANSFORMATION OF 1,3-DIAZA- AND 1,3,5-TRIAZA-ADAMANTANES TO 1,4-DIAZA- AND 1,3,6-TRIAZAHOMO-ADAMANTANES

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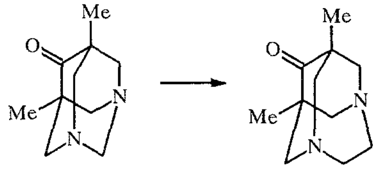
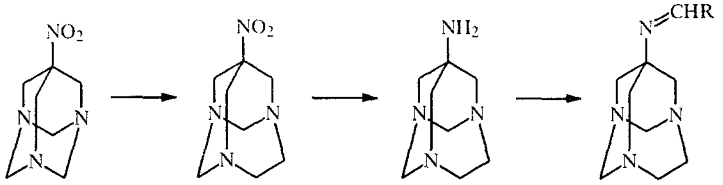
Derivatives of 1,3-diaza- and 1,3,5-triazaadamantanes react with 1,2-dibromoethane in the presence of base to give derivatives of 1,4-diaza- and 1,3,6-triazahomoadamantanes, respectively. Schiff bases were obtained containing the 1,3,6-triazahomoadamantane ring.

In previous work [2, 3] we have shown that the reaction of 1,3-diaza- and 1,3,5-triazaadamantanes with alkyl halides give 3,7-dialkyl derivatives of 3,7-diaza- and 1,3,7-triazabicyclo[3.3.1]nonanes, respectively.

The azaadamantanes indicated above were subjected to reaction with 1,2-dibromoethane in order to synthesize 1,4-diaza- and 1,3,6-triazahomoadamantanes. 5,7-Dimethyl-6-oxo-1,3-diazaadamantane (I) in benzene in the presence of triethylamine and 7-nitro-1,3,5-triazaadamantane (III) upon heating at reflux in aqueous dioxane in the presence of sodium hydroxide react with an equimolar amount of 1,2-dibromoethane to give 6,8-dimethyl-7-oxo-1,4-diazahomoadamantane (II) and 8-nitro-1,3,6-triazaadamantane (IV), respectively, i.e., the methylenediamine group in 1,3-diaza- and 1,3,5-triazaadamantanes is replaced by an ethylenediamine group.



I II



III IV V VI a-f

VIa: R = Ph; b: R = 3-pyridyl; c: R = o-HOC_6H_4; d: R = o-FC_6H_4; e: R = 2-furyl; f: R = 2-oxynaphthyl

The reduction of the nitro group in triazahomoadamantane IV by hydrazine hydrate in the presence of Raney nickel catalyst gave 8-amino-1,3,6-triazahomoadamantane (V). The azeotropic distillation of water from the mixture of V and a series of aromatic aldehydes gave the corresponding Schiff bases containing a 1,3,6-triazahomoadamantane ring VIa-VIf.

The molecular masses of the products determined by mass spectrometry corresponded to the calculated values. The IR spectra of adamantanes VIa-VIf have a band for the C=N bond at 1620-1650 cm^{-1}.

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TABLE 1. 8-Arylidenamino-1,3,6-triazatricyclo[4.3.1.$1^{3,8}$]undecanes (VIa)-(VIf)

Compound	Chemical formula	mp, °C	R_f (B)	M^+	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm	Yield, %
VIa	$C_{15}H_{20}N_4$	160...161	0,28	256	1495, 1595 (C=C), 1620 (C=N)	2,72...3.32 (6H,m, 7,9,11-CH_2); 3,14 (4H,s, 4,5-CH_2); 3,6 (2H, d J = = 14 Hz, 2,10-CH_a); 4,15 (2H,d J = 14Hz , 2,10-CHe); 7,18...7,82 (5H, CH_{arom}); 8,16 (1H, s, CH=N)	58
VIb	$C_{14}H_{19}N_5$	133...134	0,20	257	1610 (C=C), 1630 (C=N), 1690 (C=N pyridine)	2,82...3,45 (6H,m , 7,9,11-CH_2); 3,3 (4H, s, 4,5-CH_2); 3,44...4,26 (4H, m 2,10-CH_2); 7,52...7,62 (4H, m CH_{arom}; 8,2 (1H, s, CH=N)	80
VIc	$C_{15}H_{20}N_4O$	161...162	0,23	272	1500, 1590 (C=C), 1620 (C=N), 2650 (OH)	2,8...3,4 (6H, m, 7,9,11-CH_2); 3,2 (4H, s, 4,5-CH_2); 3,44...4,44 (4H. m, 2,10-CH_2); 6,6...7,28 (4H, m, CH_{arom}); 8,2 (1H, s CH=N); 9,13 (1H s, OH)	81
VId	$C_{15}H_{19}N_4F$	144...145	0,23	274	1490, 1585 (C=C), 1630 (C=N)	2,6...3,45 (6H, m, 7,9,11-CH_2); 3,1 (4H,s , 4,5-CH_2); 3,6...4,26 (4H,m , 2,10-CH_2); 6,8...8,08 (4-H, m, CH_{arom}); 8,45 (1H,s , CH=N)	70
VIe	$C_{13}H_{18}N_4O$	102...103	0,21	246	1590 (C=C), 1650 (C=N)	2,48...3,43 (6H, m , 7,9,11-CH_2); 3,18 (4H, s , 4,5-CH_2); 3,46...4,25 (4-H, m, 2,10-CH_2); 6,40...7,45 (3H m , CH_{arom}); 8,0 (1H, s CH=N)	77
VIf	$C_{19}H_{22}N_4O$	174...175	0,28	322	1595 (C=C), 1625 (C=N), 2650 (OH)	2,18...3,2 (6H,m , 7,9,11-CH_2); 3,04 (4H, s, 4,5-CH_2); 3,47 (2H, d, J = 14 Hz, 2,10-CH_a); 4,07 (2H, d J = 14 Hz, 2,10-CH_e); 6,8...7,85 (7H, m, CH_{arom} CH=N); 9,36 (1H, s, OH)	81

The signals for the NCH_2CH_2N group protons in the PMR spectra of diaza- and triazahomoadamantanes appear as singlets at 3.0-3.23 ppm, while the signals for the NCH_2N group protons of the triazahomoadamantanes appear as a multiplet or two doublets. The signals for the CCH_2N group protons in diazahomoadamantane appear as two doublets, while these signals for triazahomoadamantane appear as a multiplet at 2.18-3.65 ppm.

EXPERIMENTAL

The IR spectra were taken on a Specord UR-20 spectrometer in Vaseline mull. The PMR spectra were taken on a Varian T-60 spectrometer in $CDCl_3$ with TMS as the internal standard. The mass spectra were taken on an MKh-1320 mass spectrometer. The reaction course and purity of the compounds were monitored by thin-layer chromatography on alumina in 1-butanol saturated with aqueous ammonia (A) and on Silufol UV-254 plates using a 7:3 mixture of 1-propanol and water (B) and 1-butanol saturated with aqueous ammonia (C).

The elemental analysis data for II, IV, V, and VIa-VIf for C, H, and N corresponded to the calculated values.

6,8-Dimethyl-7-oxo-diazatricyclo$[4.3.1.1^{3,8}]$undecane (II, $C_{11}H_{18}N_2O$). A sample of 1.45 g (7.7 mmoles) of 1,2-dibromoethane was added to a solution of 1.4 g (7.7 mmoles) of diazaadamantane I in 100 ml of benzene and heated at reflux for 1 h. Then 2 g (0.02 mole) triethylamine and the mixture were heated at reflux with stirring for an additional 8 h. The reaction mixture was cooled and filtered. The benzene solution was evaporated in vacuum and the residue was recrystallized from heptane, mp 98-99°C [4]. R_f 0.32 (B). IR spectrum: 1710 cm^{-1} (C=O). PMR spectrum: 0.9 (6H, s, $2CH_3$), 2.96 (4H, d, J = 14 Hz, 5,9,10,11-CH_a), 3.1 (4H, d, J = 14 Hz, 5,9,10,11-CH_e), 3.23 ppm (4H, s, NCH_2CH_2N). M^+ 194. The yield of II was 1.1 g (73%).

8-Nitro-1,3,6-triazatricyclo$[4.3.1.1^{3,8}]$undecane (IV, $C_8H_{14}N_4O_2$). A solution of 1.84 g (0.01 mole) triazaadamantane III, 1.88 g (0.01 mole) 1,2-dibromoethane, and 0.8 g (0.02 mole) sodium hydroxide in a mixture of 100 ml dioxane and 20 ml water was heated for 18 h. The organic layer was separated and evaporated. The residue was recrystallized from heptane, mp 189-191°C. R_f 0.37 (B). IR spectrum: 1340, 1545 cm^{-1} ($C-NO_2$). PMR spectrum: 3.0 (4H, s, 4,5-CH_2), 3.2-3.65 (6H, m, 7,9,11-CH_2), 3.41 (2H, d, J = 14 Hz, 2,10-CH_a), 3.95 ppm (2H, d, J = 14 Hz, 2,10-CH_e). M^+ 198. The yield of IV was 0.9 g (45%).

8-Amino-1,3,6-triazatricyclo$[4.3.1.1^{3,8}]$undecane (V, $C_8H_{16}N_4$). A sample of 7.5 g (0.128 mole) 85% hydrazine hydrate was added to a suspension of 7.7 g (0.38 mole) triazahomoadamantane IV in 150 ml methanol. Then a suspension of 1.5 g Raney nickel in 50 ml methanol was added in small portions with stirring over 5 h at 35-40°C. The mixture was heated at reflux on a water bath for 30 min, cooled, and filtered. The filtrate was evaporated in vacuum. The residue was recrystallized from heptane. mp 179-180°C. R_f 0.31 (A). IR spectrum 3100-3500 cm^{-1} (NH_2). PMR spectrum: 2.12 (2H, s, NH_2), 2.66 (3H, d, J = 14 Hz, 7,9,11-CH_a), 3.0 (3H, d, J = 14 Hz, 7,9,11-CH_e); 3.14 (4H,c,4,5-CH_2); 3,6 (2H, d, J = 14 Hz, 2,10-CH_a); 4,1 ppm (2H, d, J = 14 Hz), 2,10-CH_e). M^+ 168. The yield of V was 4.2 g (60%).

8-Arylidenamino-1,3,6-triazatricyclo$[4.3.1.1^{3,8}]$undecanes (VIa)-(VIf). A mixture of 0.1 mole triazahomoadamantane V and 0.1 mole of the corresponding aldehyde in toluene was heated at reflux for 15 h with a Dean–Stark trap in the presence of 0.2 g p-toluenesulfonic acid until no further water was liberated. The residue was filtered and recrystallized from heptane (VIa and VIc). In the other cases, the filtrate was evaporated in vacuum. The residue was recrystallized from heptane (Table 1).

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