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.

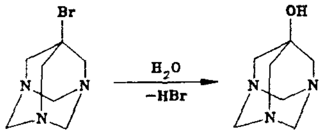
## 10.* HYDROLYSIS OF 7-BROMO-1,3,5-TRIAZAADAMANTANE

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.

TABLE 1. Hydrolysis of Triazaadamantane I ($T_{react}$ 50°C; starting solution: 1.0905 g of triazaadamantane in 50 ml of water)

| Expt. duration, min | Solution pH | Emf of concn. cell, V | $c_{Br^-}$, M | lg $(c_0 - c_{Br^-})$* |
|---|---|---|---|---|
| 0 | 4,86 | 0,184 | — | — |
| 10 | 5,01 | 0,172 | $1{,}07 \cdot 10^{-4}$ | −1,000465 |
| 20 | 5,10 | 0,163 | $1{,}48 \cdot 10^{-4}$ | −1,000643 |
| 30 | 5,16 | 0,160 | $1{,}63 \cdot 10^{-4}$ | −1,000708 |
| 40 | 5,23 | 0,153 | $1{,}99 \cdot 10^{-4}$ | −1,000865 |
| 50 | 5,24 | 0,151 | $2{,}08 \cdot 10^{-4}$ | −1,000904 |
| 60 | 5,25 | 0,148 | $2{,}29 \cdot 10^{-4}$ | −1,000996 |
| 70 | 5,26 | 0,146 | $2{,}39 \cdot 10^{-4}$ | −1,001039 |
| 90 | 5,28 | 0,143 | $2{,}57 \cdot 10^{-4}$ | −1,001118 |
| 110 | 5,32 | 0,139 | $3{,}09 \cdot 10^{-4}$ | −1,001344 |
| 165 | 5,36 | 0,136 | $3{,}55 \cdot 10^{-4}$ | −1,001544 |

*$c_0$ = 0.1 M is the initial concentration of triazaadamantane I.

TABLE 2. Rate Constants of Hydrolysis* of Triazaadamantane I

| $T$, K | $k$, 1/sec | lg $k$ | $\tau_{1/2}$, h |
|---|---|---|---|
| 298 | $7{,}2 \cdot 10^{-9}$** | −8,15 | 26747 |
| 323 | $2{,}3 \cdot 10^{-7}$ | −6,64 | 837 |
| 353 | $5{,}0 \cdot 10^{-6}$ | −5,30 | 38,5 |

*k is the hydrolysis rate constant, and $\tau_{1/2}$ is the time to 50% conversion.

**Calculated according to the Arrhenius equation.

The activation energy calculated according to the Arrhenius equation $E_{act}$ = 105 ± 5 kJ/mole, and the value of the preexponential factor in the Arrhenius equation $B = 1.8 \cdot 10^{13}$ (cm$^3$/mole)·sec.

A comparison of the calculated rate constant of hydrolysis of bromotriazaadamantane I in water at 25°C with the rate constant of hydrolysis of 1-bromoadamantane in 60% alcohol at 25°C presented in [3] ($k = 4.56 \cdot 10^{-6}$ 1/sec) indicates that even under more favorable conditions bromotriazaadamantane I hydrolyzes more than 600-fold more slowly than 1-bromoadamantane. The higher inertness of bromotriazaadamantane I is explained by the inductive effect of the nitrogen atoms of the triazaadamantane ring system, lowering the electron density on the carbon atom in the cross-linked position [4].

We took into account the experimental data in the synthesis of 7-hydroxy-1,3,5-triazaadamantane (II) obtained in 47.8% yield during heating of bromotriazaadamantane I in an aqueous-alkaline medium for 6 h. The structure of hydroxytriazaadamantane II was confirmed by data of IR and PMR spectra. The IR spectrum contained absorption bands at 1135 and 1315 cm$^{-1}$, characteristic of bending vibrations of the hydroxyl group, and also a wide absorption band in the region of 2500-3160 cm$^{-1}$. In the PMR spectrum, the peak of six protons of $N{-}CH_2{-}C$ methylene groups was manifested in the form of a singlet at 2.71 ppm. The peaks of six protons of three $N{-}CH_2{-}N$ aminal methylene groups formed an AB system with a center at 3.71 ppm ($^2J$ = 13.5 Hz). A broadened peak at 2.1 ppm was due to the hydroxyl-group proton.

## EXPERIMENTAL

The IR spectrum was recorded on a UR-20 instrument (in a KBr tablet), the PMR spectrum was recorded on a Bruker WM-250 spectrometer (in $CDCl_3$), and the internal standard was TMS.

7-Hydroxy-1,3,5-triazaadamantane (II, $C_7H_{13}N_2O$). A solution of 2 g (9.2 mmoles) of triazaadamantane I, obtained according to [2], and 0.4 g (10 mmoles) of NaOH in 30 ml of water was heated to 70-80°C and held with stirring for 6 h. The water was driven off in vacuo. The residue was extracted with hot toluene (6 × 30 ml), and the solvent was driven off. The dry residue was washed with 10 ml of warm toluene, dried under vacuum, and purified by sublimation. We obtained 0.68 g (47.8%) of hydroxytriazaadamantane II, mp 262-263°C. IR spectrum: 2500-3160, 1315, and 1135 $cm^{-1}$ (OH). PMR spectrum ($CDCl_3$): 2.1 (1H, broadened signal, C—OH); 2.71 (6H, singlet, $N—CH_2—C$); 3.47 and 3.95 ppm (6H, 2 doublets, $N—CH_2—N$, $^2J = 13.5$ Hz). Found: mol. wt. 155. Calculated: mol. wt. 155.

Kinetic Measurements. The rate of hydrolysis of bromotriazaadamantane I was monitored according to the increase of the concentration of $Br^-$ ions. A concentration cell consisting of a silver bromide electrode (in the reaction solution) and a saturated silver chloride electrode (reference electrode) was used for the measurement. A graph of the relation of the emf of the cell to the concentration of $Br^-$ ions was plotted. In this case, it was impossible to monitor the reaction rate according to the pH change because the hydrolysis product, triazaadamantane II, is more basic (pK 8.50) than the starting bromotriazaadamantane I (pK 10.11); therefore, the concentration of $H^+$ ions decreased during the reaction, i.e., could not be used to plot concentration—time relations.

## LITERATURE CITED

1. A. I. Kuznetsov, K. I. Romanova, E. B. Basargin, A. S. Moskovkin, and B. V. Unkovskii, Khim. Geterotsikl. Soedin., No. 4, 538 (1990).
2. A. I. Kuznetsov, V. A. Kosmakov, and B. V. Unkovskii, Khim. Geterotsikl. Soedin., No. 6, 837 (1985).
3. H. Stetter, J. Mayer, M. Schwarz, and K. Wulf, Chem. Ber. 93, 226 (1960).
4. W. N. Speckamp, J. Dijkin, and A. W. Dekkers, Tetrahedron Lett., No. 24, 1853 (1974).

---

# RECYCLIZATION OF INDOLO[2,3-c]PYRYLIUM SALTS BY REACTION WITH SECONDARY AMINES

V. I. Dulenko, A. V. Kibal'nyi,
Yu. A. Nikolyukin, V. I. Luk'yanenko,*
A. V. Goncharov, S. A. Sidorova,
D. S. Yufit, and Yu. T. Struchkov

UDC 547.759.3'816.07:548.737

1-R-3-methylindolo[2,3-c]pyrylium salts react with cyclic secondary amines (morpholine, piperidine, and N-methylpiperazine) to give, depending on the structure of the alkyl substituent R, either 1- (when R = Me) or 3-aminocarbazoles (when R = i-Pr), or mixtures of both (when R = Et). The position of the amino-substituent in 1-morpholino-3,9-dimethylcarbazole has been established by x-ray diffraction examination.

The conversion of pyrylium salts into N,N-dialkylanilines was first reported by Diels and Alder in 1927, as exemplified by the reaction of 2-methylpyrylium salts bearing various substituents in the 2- and 4-positions with secondary amines (dimethylamine and piperidine) [1]. This reaction was subsequently used for the development of novel syntheses of dialkylamino-derivatives of naphthalene [2], benzo[b]thiophene [3], benzo[b]selenophene [3], dibenzofuran [4], dibenzothiophene [4], and isomeric thiobenzo[b]thiophenes [5]. The postulated reaction mechanism involves addition of the amine at one of the α-positions of the pyrylium ring, electrocyclic cleavage of the resulting intermediate, and aldol condensation of the cleavage products to give a new aromatic ring [6].

This communication reports the reactions of secondary amines with the indolo[2,3-c]-pyrylium salts (Ia-c) to give the aminocarbazoles (IIa-f), (IIIa-f), or their mixtures (Table 1).

---

*Deceased.

Institute of Physical Organic and Coal Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk 340114. P. I. Lebedev-Polyanskii Vladimir State Pedagogical Institute, Vladimir 600024.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 546-551, April, 1990. Original article submitted November 1, 1988.