SYNTHESES AND CONVERSION OF POLYHEDRAL COMPOUNDS.

26.* SYNTHESIS OF NEW HETEROPOLYHEDRAL COMPOUNDS BY HETEROCYCLIZATION OF CERTAIN 3,7-DISUBSTITUTED DERIVATIVES OF 3,7-DIAZA- AND 1,3,7-TRIAZABICYCLO-[3.3.1]NONANES

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The following heterocyclization reactions have been carried out: heterocyclization of 3,7-diacryloyl-3,7-diazabicyclo[3.3.1]nonane by benzylamine, heterocyclization of 3,7-diacryloyl-, 3,7-bis(β-bromopropionyl)-, and 3,7-bis(β-chloroethyl)-3,7-diazabicyclo[3.3.1]nonanes by hydrogen sulfide, and heterocyclization of 3,7-bis(bromoacetyl)- and 3,7-diacryloyl-1,3,7-triazabicyclo[3.3.1]nonanes by benzylamine and hydrogen sulfide. New compounds were obtained, based on previously unknown thiadiaza-, triaza-, and tetraazatricyclic systems.

The heterocyclization of 3,7-bis(haloacetyl)-3,7-diazabicyclo[3.3.1]nonanes by ammonia or primary amines leads to the corresponding derivatives of 1,4,7-triazatricyclo[7.3.1.172,13]tetradecane [2, 3]. With the aim of obtaining new heteropolyhedral compounds and studying their biological properties, we have investigated the possibility of heterocyclization of derivatives of 3,7-diazabicyclo[3.3.1]nonane and 1,3,7-triazabicyclo[3.3.1]nonane by benzylamine and/or hydrogen sulfide in an alkaline medium.

It was established that refluxing of equimolar quantities of 3,7-diacryloyl-1,5-dimethyl-9-oxo-3,7-diazabicyclo-[3.3.1]nonane (I) [4] and benzylamine in ethanol results in the formation of 1,5,9-triazatricyclo[9.3.1.17,13]hexadecane (II). Heterocyclization was also accomplished successfully when starting with solutions of 3,7-diacryloyl- (I) and 3,7-bis(β-bromopropionyl)-1,5-dimethyl-9-oxo-3,7-diazabicyclo[3.3.1]nonane (III) [4], in hydrogen sulfide-saturated methanol and dioxane, respectively, by the action of a 28% aqueous solution of sodium hydroxide. As a result of this treatment, we obtained a derivative of 5-thia-1,9-diazatricyclo[9.3.1.17,13]hexadecane (IV).

*For Communication 25, see [1].
Analogously, by refluxing a solution of 3,7-bis(β-chloroethyl)-9,9-dimethyl-1,5-dinitro-3,7-diaza-2,5-bicyclo[3.3.1]nonane (V) in dioxane with hydrogen sulfide in an alkaline medium, we synthesized a derivative of 4-thia-1,7-diazatricyclo[7.3.1.17,11]tetradecane (VI). The original dichloride V was obtained by the action of thionyl chloride on 3,7-bis(β-hydroxyethyl)-9,9-dimethyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane (VII), which in turn was synthesized by the Mannich reaction from 2,2-dimethyl-1,3-dinitropropane, monoethanolamine, and paraformaldehyde.

We were able to use benzylamine and also hydrogen sulfide in an alkaline medium to accomplish the heterocyclization of 3,7-bis(bromoacetyl)- (VIII) and 3,7-diacryloyl-5-nitro-1,3,7-triazabicyclo[3.3.1]nonane (IX) [5]. In the case of compound VIII, we also used sodium sulfide for this reaction. As a result, we obtained derivatives of 1,3,6,9-tetraazatricyclo[7.3.1.13,11]tetradecane (X), 1,3,7,11-tetraazatricyclo[9.3.1.13,13]hexadecane (XI), 6-thia-1,3,9-triazatricyclo[7.3.1.13,11]tetradecane (XII), and 7-thia-1,3,11-triazatricyclo[9.3.1.13,13]hexadecane (XIII).

Thus, as a result of the above-described heterocyclization of derivatives of 1,7-diaza- and 1,3,7-triazabicyclo[3.3.1]nonanes, we have synthesized new heteropolyhedra that differ in the size of one of the rings and also in the number, character, and position of the heteroatoms.

The structures of these compounds were established on the basis of elemental analyses and IR and mass spectra, and in a number of cases by PMR spectra (see Experimental). The mass spectra of all of the synthesized compounds contain peaks of the respective molecular ions. In the PMR spectra of compounds II-VII there is a singlet signal of methyl-group protons in the 1.00-1.35 ppm region. The spectrum of the benzyl-substituted product II also contains a singlet signal of protons of the phenyl group at 7.55 ppm, while the signal of the CH2 groups has the form of a broad multiplet in the 3.00-5.30 ppm region. The PMR data are more informative in the case of compounds IV-VII. In the spectrum of IV, for example, we can clearly distinguish triplets of CH2CO and CH2S groups at 2.70 and 3.30 ppm, respectively (SSCC = 5.5 Hz); however, the signal of the CH2N groups is manifested in the form of a broad multiplet in the 2.80-5.00 ppm region. The clearest picture is observed for compounds V and VII and the product VI that was obtained from them. In addition to triplet signals of the groups CH2O (VII), CH2Cl (V), and CH2S (VI) at 3.65, 3.60, and 3.40 ppm, respectively (SSCC = 5.5-6.0 Hz), the spectra contain well-resolved triplets of CH2N groups of the side chains (V, VII) or the heterocycle formed from these groups (VI), in the 2.70-2.90 ppm region (SSCC = 5.5-6.0 Hz), as well as doublets of axial and equatorial protons of CH2N groups of six-membered heterocycles at 2.95-3.20 and 3.70-3.75 ppm, respectively (SSCC = 11-12 Hz). The PMR spectra of the derivatives of tetraazatricyclic compounds (X, XI) and triazatricyclic compounds (XII, XIII), as would be expected by analogy with the PMR spectra of 3,7-diacetyl-1,3,7-triazabicyclononanes [6] are complex and difficult to decipher. The purities of the compounds were established by TLC data.