Letters to the Editor

A novel bicyclic system, 1,6-diaza-3,8-dioxabicyclo[4.4.1]undecane

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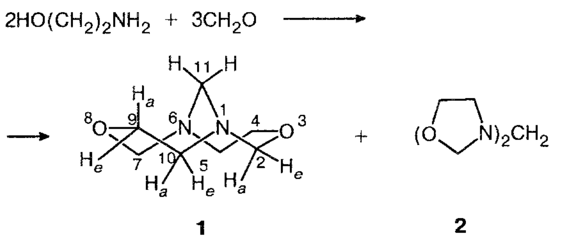
Condensation of monoethanolamine with formaldehyde affords 1,6-diaza-3,8-dioxabicyclo[4.4.1]undecane and *N,N'*-methylene-bis(oxazolidine) in a ratio of 1:8.

Key words: monoethanolamine, formaldehyde, condensation; 1,6-diaza-3,8-dioxabicyclo[4.4.1]undecane, *N,N'*-methylene-bis(oxazolidine), NMR spectra.

We prepared a novel heterocyclic system, 1,6-diaza-3,8-dioxabicyclo[4.4.1]undecane (**1**) by the condensation of monoethanolamine with formaldehyde. Previously it has been reported[1] that this reaction produced *N,N'*-methylene-bis(oxazolidine) (**2**) in a quantitative yield.



A mixture of 0.5 mol of monoethanolamine and 0.75 mol of paraformaldehyde in 100 mL of benzene was boiled for 2 h with a Dean—Stark trap and filtered. The solvent was evaporated and the residue was distilled over metallic Na. The yield of the product was 98 %, b. p. 83—85 °C (1 Torr). ^{1}H NMR and chromato-mass-spectrometry data indicated that the product contained **1** and **2** in the ratio 1:8. In the mass spectrum of **1** (70 eV), peaks at m/z 158 $[M]^+$ (40 %) and 157 (100 %) were observed; in the mass spectrum of **2**, the molecular ion peak was absent, while that of the amine fragment at m/z 86 was the most intense.

The structure of **1** was confirmed by NMR spectra in C_6D_6 (a Bruker WM-400 spectrometer). ^{1}H NMR (Fig. 1), (δ): 2.77 (H-5*e*, 10*e*, $^2J = -12.7$, $^3J_{ee} = 4.1$, $^3J_{ea} = 1.2$ Hz); 3.18 (H-5*a*, 10*a*, $^3J_{aa} = 11.1$, $^3J_{ae} = 2.1$ Hz); 3.30 (H-4*a*, 9*a*, $^2J = -13.4$ Hz); 3.72 (H-4*e*,

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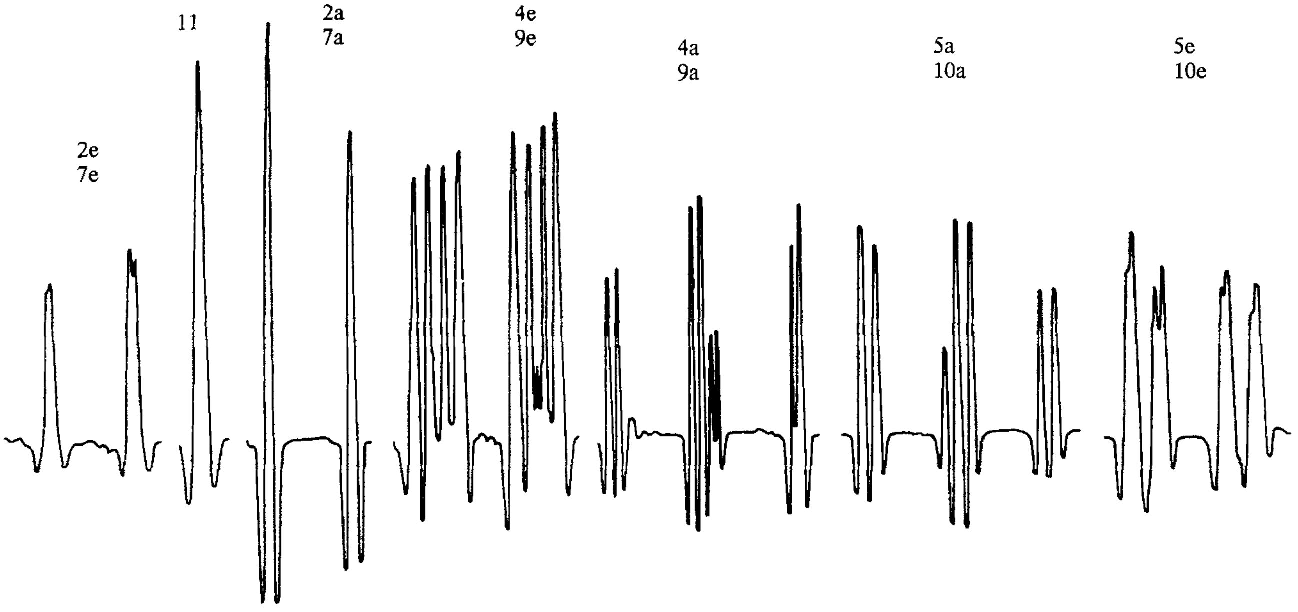

Fig. 1. The ^{1}H NMR spectrum of **1** in C_6D_6 in the line narrowing mode with different amplification.

9*e*); 3.88 (H-2*a*, 7*a*, $^2J = -11.1$ Hz); 4.02 (11, $^4J = 0.6$ Hz); 4.24 (H-2*e*, 7*e*, $^4J = 0.6$ Hz). ^{13}C NMR, δ: 51.75 (C-5, 10, $^1J_{C,H} = 133.7$ and 134.2, ^2J, $^3J_{C,H} =$ 3.6; 4.4 Hz); 67.11 (C-4, 9, $^1J_{C,H} = 138.1$ and 143.9, $^2J_{C,H} = 7.9$ Hz); 70.36 (C-11, $^1J_{C,H} = 145.3$ Hz); 86.55 (C-2, 7, $^1J_{C,H} = 153.3$ and 157.3, $^3J_{C,H} = 2.9$ Hz).

In accordance with the C_2 symmetry of molecule **1**, all of the nuclei of the H and the C atoms of the large bridges are pairwise equivalent. The rigid bicyclic structure of **1** was confirmed by the existence of spin coupling constants ^4J of the protons at C-11 with protons 2*e* and 7*e* (see Fig. 1) (according to the analysis of the molecular model, the corresponding fragment of the system had the planar zigzag conformation), as well as by the nonequivalence of the spin-spin coupling constants $^1J_{CHa}$ and $^1J_{CHe}$ of all of the methylene C atoms of the large bridges.

The ^{1}H NMR spectrum of **2** (C_6D_6), δ: 2.68 (NCH_2C, $^3J = 6.9$ Hz); 2.96 (NCH_2N); 3.42 (OCH_2C); 4.33 (OCH_2N). ^{13}C NMR (C_6D_6), δ: 50.22 (NCH_2C, $^1J = 140.9$ Hz, $^2J = 4.4$ Hz); 62.83 (OCH_2C, $^1J =$ 146.8 Hz, $^2J = 4.4$ Hz); 73.97 (NCH_2N, $^1J =$ 141.0 Hz, $^3J = 5.8$ Hz); 84.89 (OCH_2N, $^1J = 158.4$ Hz, $^3J = 4.4$ Hz).

The mixture obtained was enriched in bicycle **1** to a 5:1 ratio of compounds **1** and **2** by chromatography on a column with $Mg(OH)_2$ (petroleum ether as the eluent). When it was treated with a deficiency of AcCl (2/3 of equivalent) in ether, the ratio between **1** and **2** became equal to 2:1. In the latter case, *N*-acetyloxazolidine[2] formed as a mixture of *syn* and *anti* rotamers (CO relative to NCH_2O). ^{1}H NMR (C_6D_6), δ, *syn*: 1.45 1.45 (MeCO); 3.20 (NCH_2C, $^3J = 6.9$ Hz); 3.31 (OCH_2C); 4.16 (OCH_2N); *anti*: 1.55 (MeCO); 2.40 (NCH_2C, $^3J =$ 6.9 Hz); 3.32 (OCH_2C); 4.93 (OCH_2N); *anti*/*syn* = 1.3. Previously, we observed[3] the similar splitting of **2** under the action of nitrosyl chloride.

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