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SHORT COMMUNICATIONS

Structure of the Reduction Products of *N*-(*m*-Tolyl)*exo*-2,3-epoxybicyclo[2.2.1]heptane-*endo*-5,*endo*-6-dicarboximide with Lithium Tetrahydridoaluminate

L. I. Kas'yan¹, O. V. Krishchik¹, A. O. Kas'yan², and I. N. Tarabara¹

¹ Dnepropetrovsk National University, per. Nauchnyi 13, Dnepropetrovsk, 49625 Ukraine ² Rheinisch–Westfälische technische Hochschule, Aachen, Germany

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Reduction of epoxynorbornanes is accompanied by heterocyclization processes [1]. Gray and Heitmeier [2] reported on the reduction with lithium tetrahydridoaluminate of stereoisomeric epoxy derivatives I (R = Et, PhCH₂CH₂, PhCH₂CH₂CH₂) obtained from norbornanedicarboximides; however, the structure of azabrendanes II thus obtained was not confirmed by NMR spectroscopy.

We examined the reduction of *N*-(*m*-tolyl)-*exo*-2,3epoxybicyclo[2.2.1]heptane-*endo*-5,*endo*-6-dicarboximide (**III**) under analogous conditions (molar ratio substrate-reducing agent 1:5, solvent dimethoxyethane or tetrahydrofuran) [2]. Compound **III** was prepared by oxidation with peroxyformic acid of N-(m-tolyl)bicyclo[2.2.1]hept-2-ene-endo-5,endo-6-dicarboximide (**IV**) which is available via aminolysis of endic anhydride. The reduction of epoxy imide **III** with 5 equiv of LiAlH₄ afforded diol **V** whose structure was confirmed by the IR and ¹H and ¹³C NMR spectra (including two-dimensional NMR techniques).



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When the reduction of **III** was carried out with the use of 3 equiv of LiAlH₄ in tetrahydrofuran (65°C, 40 h) or dimethoxyethane (80°C, 25 h), we isolated by column chromatography on silica gel diol **V** and compound **VI** in 7.5 and 38.3 or 9.2 and 57.2% yield, respectively.

The ¹H NMR spectrum of diol V contained a doublet and a singlet from 8-H and 9-H (& 3.85 and 3.74 ppm), signals from the methylene protons on C^3 (δ 2.68 and 3.69 ppm) and C⁵ (δ 2.83 and 3.99 ppm), a singlet from the methyl group in the aromatic ring (δ 2.32 ppm), and signals from the aromatic protons (δ 6.65–7.16 ppm). In the ¹³C NMR spectrum of V, the C⁸ and C⁹ signals were located at $\delta_{\rm C}$ 85.3 and 78.4 ppm, respectively. The 5-H signal in the ¹H NMR spectrum of VI appeared at δ 5.50 ppm (due to deshielding by the oxygen and nitrogen atoms), and the corresponding carbon nucleus gave a signal at $\delta_{\rm C}$ 94.0 ppm in the ¹³C NMR spectrum. Compound **VI** is a probable intermediate in the synthesis of diol V; it represents a new polyheterocyclic system, 4-oxa-6azatetracyclo $[5.2.1.1^{3,5}.0^{8,9}]$ undecane. The structure of **VI** was proved by the X-ray diffraction data.

N-(*m*-Tolyl)-*exo*-2,3-epoxybicyclo[2.2.1]heptane*endo*-5,*endo*-6-dicarboximide (III) was synthesized by oxidation of imide IV with peroxyformic acid according to the procedure reported in [3]. Yield 99%, mp 216–218°C. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.31–6.92 (4H, H_{arom}), 3.24 m (2H, 2-H, 3-H), 3.12 m (2H, 5-H, 6-H), 3.06 m (2H, 1-H, 4-H), 2.31 s (3H, CH₃), 1.65 d (1H, *syn*-7-H), 1.05 d (1H, *anti*-7-H). Found, %: C 71.32; H 5.54; N 5.16. C₁₆H₁₅NO₃. Calculated, %: C 71.38; H 5.58; N 5.20.

N-(*m*-Tolyl)bicyclo[2.2.1]hept-2-ene-*endo*-5,*endo*-6-dicarboximide (IV) was prepared as described in [4] from endic anhydride and *m*-toluidine in boiling glacial acetic acid. Yield 81%, mp 123–125°C. IR spectrum, v, cm⁻¹: 2980, 1686, 1360, 1186, 1045, 845. ¹H NMR spectrum (DMSO), δ, ppm: 7.26, 7.12, 6.86 (4H, H_{arom}); 6.22 m (2H, 2-H, 3-H); 3.38 m (4H, 1-H, 4-H, 5-H, 6-H); 2.38 s (3H, CH₃); 1.72 d (1H, *syn*-7-H); 1.63 d (1H, *anti*-7-H). Found, %: C 75.83; H 5.96; N 5.58. C₁₆H₁₅NO₂. Calculated, %: C 75.89; H 5.93; N 5.53.

N-(*m*-Tolyl)-4-azatricyclo[5.2.1.0^{2,6}]decaneendo-8,exo-9-diol (V). *a*. Epoxy derivative III, 2.70 g (0.01 mol), was added to a mixture of 1.90 g (0.05 mol) of lithium tetrahydridoaluminate and 40 ml of anhydrous dimethoxyethane, and the mixture was stirred under reflux until the reaction was complete

(according to the TLC data). Excess LiAlH₄ was carefully decomposed with moist diethyl ether and ice water, the precipitate was filtered off and washed with chloroform, and the organic phase was dried and evaporated. Yield of diol V 2.45 g (94%), mp 136-138°C, R_f 0.45 (diethyl ether). IR spectrum, v, cm⁻¹: 3344, 3293, 1604, 1583, 1496, 1480, 1365, 1306, 1015, 787. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.16– 6.65 (4H, H_{arom}), 3.99 d (1H, 5-H_A), 2.83 d.d (1H, 5-H_B), 3.69 d (1H, 3-H_A), 2.68 d.d (1H, 3-H_B), 3.85 d (1H, 8-H), 3.74 s (1H, 9-H), 2.81 m (1H, 2-H), 2.66 m (1H, 6-H), 2.42 m (1H, 1-H), 2.32 s (3H, CH₃), 2.30 m (1H, 7-H), 1.89 d (1H, syn-10-H), 1.41 d (1H, anti-10-H). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 149.1– 113.6 (C_{arom}), 85.4 (C^8), 78.4 (C^9), 51.7 (C^5), 51.0 (C^3), 48.2 (C^1), 45.0 (C^7), 42.9 (C^2), 41.1 (C^6), 37.5 (C^{10}), 22.1 (CH₃). Found, %: C 74.18; H 8.14; N 5.45. C₁₆H₂₁NO₂. Calculated, %: C 74.13; H 8.11; N 5.41.

b. Epoxy derivative III was reduced with 3 equiv of LiAlH₄ in anhydrous tetrahydrofuran. After appropriate treatment, the products were separated by column chromatography on silica gel using petroleum etherdiethyl ether mixtures at different ratios. From the first fraction we isolated N-(m-tolyl)-4-oxa-6-azatetracyclo- $[5.2.1.1^{3,6}.0^{8,9}]$ undecan-*exo*-2-ol (**VI**), yield 38.3%, mp 132–134°C, R_f 0.52 (diethyl ehter). IR spectrum, v, cm⁻¹: 3360, 2949, 1604, 1372, 1195, 1015, 761. ¹H NMR spectrum (CDCl₃), δ, ppm: 7.05–6.45 (4H, H_{arom}), 5.50 d (1H, 5-H), 3.84 d (1H, 3-H), 3.42 d.d (1H, 7-H_A), 3.32 s (1H, 2-H), 3.30 s (1H, OH), 3.12 d (1H, 7-H_B), 2.98 m (1H, 9-H), 2.63 m (1H, 8-H), 2.62 m (1H, 10-H), 2.22 s (3H, CH₃), 2.18 m (1H, 1-H), 1.94 d (1H, syn-11-H), 1.48 d (1H, anti-11-H). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 146.6–111.5 (C_{arom}), 94.0 (C⁵), 88.8 (C³), 75.4 (C²), 49.6 (C⁸), 48.7 (C⁷), 48.3 (C⁹), 47.1 (C¹⁰), 42.1 (C¹), 35.8 (C¹¹), 22.8 (CH₃). Found, %: C 74.76; H 7.33; N 5.51. C₁₆H₁₉NO₂. Calculated, %: C 74.71; H 7.39; N 5.45. From the second fraction we obtained diol V, yield 7.5%, $R_{\rm f}$ 0.45 (diethyl ether), mp 136–138°C.

The IR spectra were recorded in KBr on a Specord 75IR spectrometer. The ¹H and ¹³C NMR spectra were measured on a Gemini-BB instrument (400 MHz for ¹H and 100.7 MHz for ¹³C) from solutions in DMSO- d_6 or chloroform-d; tetramethylsilane was used as internal reference. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates using diethyl ether as eluent; development with iodine vapor. The elemental compositions were determined on a Carlo Erba analyzer.

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