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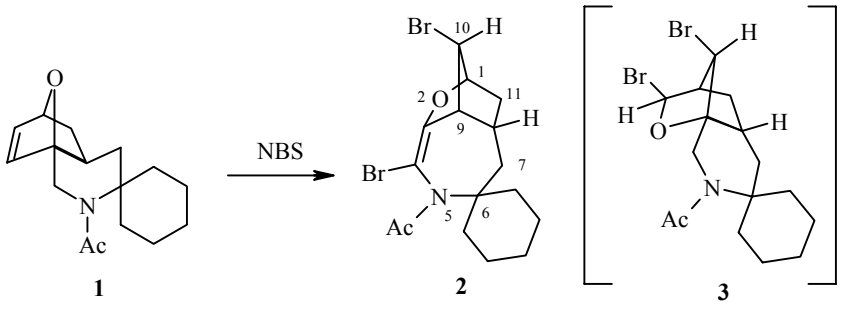
FIRST SYNTHESIS OF 6-SPIRO[5-AZA-2-OXATRICYCLO[6.2.1.0^{3,9}]UNDEC-3-ENE-6,1'-CYCLOHEXANE]

E. V. Nikitina[1], A. A. Safronova[1], A. V. Varlamov[1], F. I. Zubkov[1], G. G. Aleksandrov[2], and K. F. Turchin[3]

Keywords: 5-aza-2-oxatricyclo[6.2.1.0^{3,9}]undecene, 6,8a-epoxyisoquinolines, Wagner–Meerwein rearrangement, skeletal rearrangement of 7-oxabicyclo[2.2.1]heptenes.

We have recently synthesized 3-aza-11-oxatricyclo[6.2.1.0^{1,6}]undec-9-ene (**1**) [1]. In a study of the bromination of this compound by N-bromosuccinimide (NBS) in chloroform, we found that 5-acetyl-4,10-dibromospiro[5-aza-2-oxatricyclo[6.2.1.0^{3,9}]undec-9-ene-6,1'-cyclohexane] (**2**) is formed as the result of a Wagner–Meerwein skeletal rearrangement.



1 **2** **3**

Similar tricyclic structures have not been isolated from rearrangement products. However, the formation of such species as intermediates has sometimes been proposed [2, 3]. A second expected reaction product **3**, whose analogs have most often been isolated in the skeletal rearrangements of simpler bicyclic systems, was not isolated. This failure may result from the high lability of the bromine atoms in **3**. The molecular structure of **2** was established by NMR spectroscopy and X-ray diffraction structural analysis.

5-Acetyl-4,10-dibromospiro[5-aza-2-oxatricyclo[6.2.1.0^{3,9}]undec-3-ene-6,1'-cyclohexane] (2). A sample of NBS (0.66 g, 3.80 mmol) and a catalytic amount of *m*-chloroperbenzoic acid were added to a solution of **1** (0.50 g, 1.90 mmol) in chloroform (25 ml). The reaction mixture was stirred at reflux for 2.5 h and then poured into water (50 ml). The mixture was extracted with five 20-ml chloroform portions. The extract was

[1] Russian People's Friendship University, Moscow 117198; e-mail: avarlamov@sci.pfu.edu.ru. [2] N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Moscow 119991; e-mail: aleks@igic.ras.ru. [3] Center for Pharmaceutical Chemistry, All-Russian Pharmaceutical Chemistry Research Institute, Moscow 119815; e-mail: turchin@drug.org.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 138-140, January, 2003. Original article submitted November 22, 2002.

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dried over $MgSO_4$. The solvent was distilled off and the residue was purified by passing through an alumina column (1 × 10 cm) using 1:10 ethyl acetate–hexane as the eluent to give 0.25 g (0.59 mmol, 30%) **2** as colorless crystals; mp 155°C (dec.), R_f 0.71 (1:1 ethyl acetate–hexane). IR spectrum, δ, cm^{-1}: 1661 (N–C=O), 1694 (C=C). Mass spectrum, *m/z* (I_{rel}, %): 421 (M^+, 3 for Br^{81}), 419 (6), 417 (3), 375 (1), 377 (2), 349 (1), 341 (2), 340 (12), 339 (4), 338 (12), 337 (2), 298 (13), 296 (15), 281 (2), 269 (11), 267 (8), 258 (8), 240 (3), 218 (7), 217 (5), 216 (20), 199 (13), 198 (7), 189 (10), 188 (6), 181 (9), 176 (20), 174 (20), 171 (8), 161 (8), 147 (6), 145 (6), 140 (11), 139 (8), 138 (100), 122 (7), 121 (23), 120 (5), 119 (9), 117 (7), 107 (4), 105 (4), 96 (18), 95 (11), 94 (10), 93 (10), 91 (12), 82 (12), 81 (20), 80 (12), 79 (20), 77 (10), 67 (16), 66 (13), 65 (10), 55 (12), 53 (7), 43 (46), 41 (14), 39 (8), 28 (11). ^1H NMR spectrum ($CDCl_3$, 400 MHz, with TMS as the internal standard), δ, ppm (*J*, Hz): 4.68 (1H, q, ^3J = 1.3 and 1.3, ^4J = 1.3, 1-H); 3.99 (1H, d, ^3J = 1.3, 10-H); 3.38 (1H, m, ^3J = 4.0 and 1.3, ^4J = 1.3, 9-H); 2.97 (1H, m, 6'A-H); 2.75 (1H, dd, ^2J = 15.5, ^3J = 6.6, 7A-H); 2.64 (1H, m, 2'A-H); 2.24 (1H, m, 8-H); 2.23 (3H, s, $NCOCH_3$); 2.14 (1H, m, ^2J = 13.6, ^3J = 9.6 and 1.6, 11B-H); 1.53 (1H, m, 6'B-H); 1.45 (1H, m, 2'B-H); 1.44 (1H, m, ^2J = 13.6, ^3J = 2.8 and ~1.0, 11A-H); 0.99 (1H, m, ^2J = 15.5, ^3J = 8.8, ^4J = 2.4, 7B-H); 1.7-1.2 (6H, m, 3'-, 4'-, 5'-H). ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, TMS as the internal standard), δ, ppm (*J*, Hz): 173.9 (NCO), 154.2 ($C_{(3)}$), 93.1 ($C_{(4)}$), 85.5 ($C_{(1)}$, J = 173.2), 66.3 ($C_{(6)}$), 52.7 ($C_{(9)}$, J = 158.6), 49.3 ($C_{(10)}$, J = 163.2), 38.1 ($C_{(7)}$), 37.5 ($C_{(11)}$), 33.3 ($C_{(2')}$), 28.2 ($C_{(8)}$), 27.7 ($C_{(6')}$), 26.5 ($NCO\underline{C}H_3$, J = 129.0), 23.3, 24.4, 24.6 ($C_{(3')}$, $C_{(4')}$, $C_{(5')}$). Found, %: C 45.55; H 5.37; Br 38.59; N 3.33. $C_{16}H_{23}Br_2NO_2$. Calculated, %: C 45.60; H 5.46; Br 38.20; N 3.32.

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