UNEXPECTED FORMATION OF DERIVATIVES OF 1-AZA-5,7-DIOXATRICYCLO[4.3.1.-$O^{4\cdot 8}$]-DECANE IN THE INTRAMOLECULAR CYCLIZATION OF 1-(2-OXOALKYL)-4-PIPERIDONES

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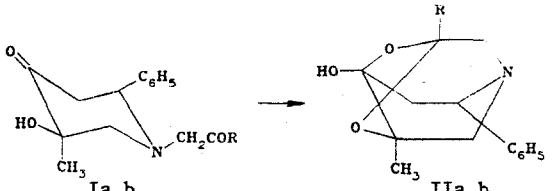
It is known that N-acetonyl(phenacyl)substituted arylpyridines are cyclized in acid media with the formation of benzo[a]quinolizinium salts [1]. We have established that 3-hydroxy-4-piperidones Ia,b on keeping in 80% H_2SO_4 for 48 h at 20°C are converted into 1-aza-5,7-dioxatricyclo[4.3.1.$O^{4\cdot 5}$]decanes IIa, b.



I, IIa R = CH_3; b R = C_6H_5

6β,8α-Dimethyl-2α-phenyl-1-aza-5,7-dioxatricyclo[4.3.$10^{4\cdot 5}$]decan-4α-ol (IIa). mp 114-116°C; yield 84%. IR spectrum ($CHCl_3$): 3590 cm^{-1}. PMR spectrum ($CDCl_3$): 1.17 (s, 8-CH_3); 1.41 (s, 6-CH_5); 1.89 (d. d, J = 13.4 and 9.6 Hz, 3α-H); 2.70 (d, J = 13.8 Hz, 9β-H); 2.78 (d.d, J = 13.4 and 7.8 Hz, 3β-H); 2.79 (d, J = 13.5 Hz, 10α-H); 2.94 (d, J = 13.5 Hz, 10β-H); 3.20 (d, J = 13.8 Hz, 9α-H); 4.39 (d. d, J = 9.6 and 7.8 Hz, 2β-H); 7.22-7.46 ppm (m, 5H).

8α-Methyl-2α,6β-diphenyl-1-aza-5,7-dioxatricyclo[4.3.1.$O^{4\cdot 5}$]decan-4α-ol (IIb). mp 122-123°C; yield 94%. IR spectrum ($CHCl_3$): 3580 cm^{-1}. PMR spectrum ($CDCl_3$); 1.21 (s, 8-CH_3); 1.96 (d. d. J = 13.4 and 9.6 Hz, 3α-H); 2.74 (d, J = 13.8 Hz, 9β-H); 2.87 (d.d, J = 13.4 and 7.8 Hz, 3β-H); 2.95 (d, J = 13.4 Hz, 10α-H); 3.08 (d, J = 13.4 Hz, 10β-H); 3.34 (d, J = 13.8 Hz, 9α-H); 4.50 (d.d, J - 9.6 and 7.8 Hz, 2β-H); 7.19-7.56 ppm (m, 10H).

The initial previously unknown, piperidones Ia (mp 89-91°C) and Ib (mp 77-79°C) were prepared by heating a mixture of 3-hydroxy-3-methyl-6-phenylpiperidone [2] with an equimolar quantity of bromoacetone or phenacyl bromide and a 20% excess of diisopropylethylamine at bp in CH_3CN for 10 min.

Elemental analyses of all the compounds prepared were in agreement with those calculated.

LITERATURE CITED

1. C. K. Bradsher and L. E. Bevers, J. Am. Chem. Soc., 77, 453 (1955).
2. L. S. Stanishevskii, I. G. Tishchenko, and A. M. Zvonok, Khim. Geterotsikl. Soedin., No. 5, 670 (1975).

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