SYNTHESIS OF 3,6-DIAZAHOMOADAMANTAN-9-ONES

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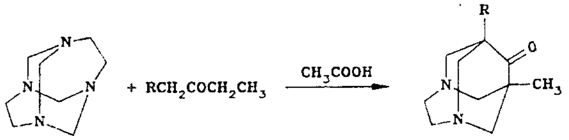
3,6-Diazahomoadamantan-9-ones (I and II), representatives of a practically uninvestigated system [1], were prepared by condensing methyl ethyl ketone and diethyl ketone with 1,4,6,9-tetraazatricyclo[4,4,1,$1^{4,9}$]dodecane (tetramethylenediethylenediamine).



I R=H; II R=CH_3 I, II

The structure of the compounds obtained was confirmed by the IR, UV, and PMR spectral data. In their IR spectra there is a stretching vibration band of the carbonyl group in the region of 1705 cm^{-1}, and in the UV spectra (in heptane), an intense absorption is observed corresponding to the so-called σ-bonded transition with λ_{max} 244 (ε 1580) and 242 m (ε 1630).

<u>1-Methyl-3,6-diazahomoadamantan-9-one (I)</u>. A solution of 3.36 g (20 mmoles) of tetramethylenediethylenediamine, 1.44 g (20 mmoles) of methyl ethyl ketone and 3 g (50 mmoles) of acetic acid in 10 ml of isopropanol is heated to 50°C, and then is left to stand for 2 h without heating. The reaction mixture is evaporated in vacuo to 1/5 of its initial volume, and the viscous residue is extracted by hot toluene (4 × 20 ml). The warm extract is purified by passing it through a layer of anhydrous aluminum oxide (4 g, grade II of activity). The extractant is evaporated and the solid residue is recrystallized from heptane. Yield 1.9 g (53%) of methyldiazahomoadamantanone I, mp 112-113°C. PMR spectrum ($CDCl_3$), δ: 3.12 (4H, m, NCH_2CH_2N); 3.35 and 3.07 (4H, $^2J_{AB}$ = 14 Hz, NCH_2C); 3.01 and 2.86 (4H, $^2J_{AB}$ = 14 Hz, NCH_2C); 0.82 (3H, s, CH_3), and 2.52 ppm (1H br. s, C—H).

<u>1,8-Dimethyl-3,6-diazahomoadamantan-9-one (II)</u> is obtained in a similar way from 1.73 g (20 mmoles) of diethyl ketones. Yield 2.53 (65%), mp 100-101°C (from heptane). PMR spectrum ($CDCl_3$), δ: 3.15 (4H, s, NCH_2CH_2N); 3.04 and 2.90 (8H, $^2J_{AB}$ = 14 Hz, NCH_2C); 0.83 (6H, s CH_3).

The data of the elemental analysis correspond to calculated values.

LITERATURE CITED

1. T. Sasaki, S. Eguchi, T. Kiriyama, Y. Sakito, J. Org. Chem., <u>38</u>, 1648 (1973).

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