LETTERS TO THE EDITOR

BROMINATION OF 2,7-DIAZA-1-METHYL-5-PHENYL-BICYCLO[2.2.2]OCTANE-3,8-DIONE

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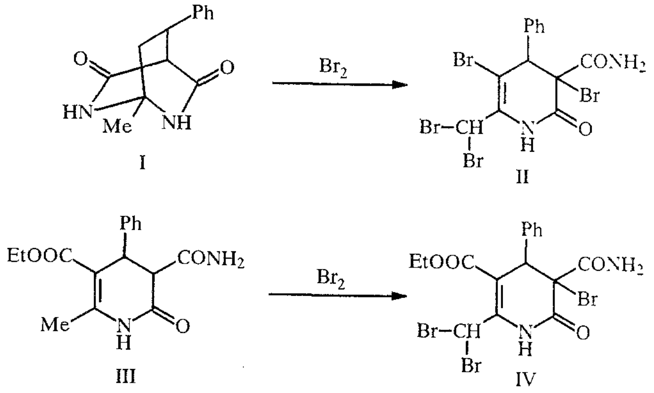
Our recently synthesized 2,7-diazabicyclo[2.2.2]octane-3,8-diones were found to be stable in alkaline medium; they were readily thiolated by the action of a dimer of p-methoxyphenylthionophosphine (the Lowesson reagent) with retention of the bicyclic structure [1].

It was shown in the present work that during the bromination of 1-methyl-5-phenyl-2,7-diazabicyclo[2.2.2]octane-3,8-dione (I) splitting of one of the C–N bonds takes place and a tetrabromo-substituted dihydropyridin-2(1H)-one is formed.



The splitting of the 2,7-diazabicyclo[2.2.2]octane-3,8-dione structure probably precedes bromination; this agrees with the fact that bromine causes 3-carbamoyl-4-phenyl-5-ethoxycarbonyl-6-methyl-3,4-dihydropyridine-2(1H)-one (III) [2] to convert into a tribromo-substituted dihydropyridine-2(1H)-one (IV), the PMR spectrum of which is similar to the PMR spectrum of compound II.

A 50 mmole portion of bromine was added dropwise, with stirring, to 10 mmoles of bicyclo[2.2.2]octane-3,8-dione I or pyridone III, dissolved with heating in 20 ml of acetic acid. The solution was heated to boiling and allowed to stand for 72 h at room temperature, then poured into water and compound II or IV, respectively, was filtered off.

3,5-Dibromo-3-carbamoyl-6-dibromomethyl-4-phenyl-3,4-dihydropyridine-2(1H)-one (II, $C_{13}H_{10}Br_4N_2O_2$). mp 250-251°C (dec., ethanol). PMR spectrum (DMSO-D_6): 4.33 (1H, s, 4CH); 7.04 (1H, s, $CHBr_2$); 7.07-7.31 (5H, m, H_{arom}); 7.68 (1H, br.s, CONHH); 8.07 (1H, br.s, CONHH); 11.6 ppm (1H, s, NH). Yield 57%.

3-Bromo-3-carbamoyl-4-phenyl-5-carbethoxy-6-dibromomethyl-3,4-dihydropyridine-2(1H)-one (IV, $C_{16}H_{15}Br_3N_2O_4$). mp 181-182°C (dec., ethanol). PMR spectrum (DMSO-D_6): 1.14 (3H, t, $\underline{CH_3}-CH_2$); 4.13 (2H, qu, $CH_3-\underline{CH_2}$); 4.77 (1H, s, 4-CH); 7.2 (5H, m, H_{arom}); 7.71 (1H, br.s, CON$\underline{H}$H); 7.93 (2H, s, $CHBr_2$ + CON$\underline{H}$H); 11.5 ppm (1H, s, NH). Yield 60%.

The elemental analysis data for C, H, Br, and N corresponded to the calculated values.

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2. A. A. Krauze, É. É. Liepin'sh, Z. A. Kalme, Yu. É. Pelcher, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 11, 1504 (1984).