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LETTERS TO THE EDITOR

REACTION OF METHYL 4,9-DIOXOBICYCLO[3.3.1]NONANE-2-CARBOXYLATE WITH HYDRAZINE HYDRATE

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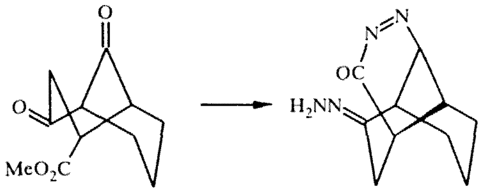
The reaction of β-dicarbonyls with nitrogen containing nucleophiles gives rise to a variety of heterocyclization products [1]. We have reported previously the synthesis of polyfunctional esters β,β'-dioxobicyclo[3.3.1]nonane I [2], the reactions of which with hydrazine and analogous nucleophiles might be expected to give polycyclic compounds.

The reaction of the dioxoester I with hydrazine hydrate in methanol gave a compound with the molecular formula $C_{10}H_{14}N_4O$. The tricyclic structure of this compound followed from the NMR spectra. The ^1H NMR spectrum did not contain a signal for methylene protons and the ^{13}C NMR spectrum did not have a signal corresponding to an ester group. Ten signals were observed in the ^{13}C NMR spectrum, the most characteristic of which were at 159.2, 139.4 and 76.9 ppm, corresponding to carbon atoms in CON, $=C-N$, and $C-N=N$ fragments respectively [3]. The remaining signals are shifted to weak field relative to those in the starting material which indicates a more rigid structure and the presence of nitrogen atoms in this structure. The IR spectrum contains bands at 3200 and 3280 (NH_2), 1705 (CO) and 1670 cm^{-1} (N=N). On the basis of these data the compound obtained from the reaction of I with hydrazine hydrate is assigned structure II. This structure is an isomer of the strained structure with a C=N double bond at the bridgehead. Rearrangement of the latter leads to the more stable structure II. An analogous example of rearrangement of a product from the reaction of bicyclo[3.3.1]nonadienedione with hydrazine has been described [4].

An indication that the initial bicyclic skeleton is not prone to rearrangement is that boiling compound II with potassium hydroxide solution gave bicyclo[3.3.1]nonane-2-carboxylic acid [5].



Interaction with phenylsubstituted hydrazines, hydroxylamine and other nitrogen containing nucleophiles gave complex mixtures of products which have not been fully characterized.

10,11-Diaza-2-hydrazino-tricyclo[4.3.2.1]dodecen-10-one-12 (II, $C_{10}H_{14}N_4O$). A mixture of compound I (1 g, 5 mmol), hydrazine hydrate (1.6 cm^3, 30 mmol) and *p*-toluenesulfonic acid (0.01 g) in methanol (6 cm^3) was stirred for 12 h at room temperature. The reaction mixture was evaporated to dryness to give II (1 g, 98%. M.p. >300°C. IR spectrum (KBr): 3280, 3200, 1705, 1670 cm^{-1} (Specord M-80). ^1H NMR spectrum (80 MHz, DMSO-D_6): 4.1 (3 H, br.s, NH and NH_2), 2.0-1.1 ppm (11 H, m, hydrogens of the carbocyclic skeleton). ^{13}C NMR spectrum (20 MHz, D_2O, methanol as internal standard): 159.2, 139.4, 76.9, 49.2, 43.8, 43.0, 36.5, 30.9, 30.4, 23.7 ppm (Tesla BS-587A).

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