SYNTHESIS OF 3,4-DIOXO-2,3,4,5,6,7-HEXAHYDROBENZO[b]FURANS

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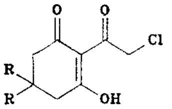
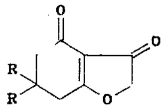
We have synthesized the previously undescribed 2-chloroacetyl-1,3-cyclohexanediones Ia, b by the method in [1] and have investigated their reactions with sodium and silver acetates, as well as with sodium nitrite. We found that nucleophilic intramolecular heterocyclization of the synthesized triketones Ia, b to give the previously unknown 3,4-dioxo-2,3,4,5,6,7-hexahydrobenzo[b]-furans IIa, b takes place under the influence of nucleophilic reagents. The observed reaction is an effective method for the synthesis of hexahydrobenzofuran derivatives, which are of interest for the synthesis of natural and related biologically active compounds.



Ia, b



IIa, b

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

2-Chloroacetyl-1,3-cyclohexanedione (Ia) and 2-Chloroacetyl-5,5-dimethyl-1,3-cyclohexanedione (Ib). These compounds were obtained from, respectively, dihydroresorcinol and dimedone by reaction with monochloroacetyl chloride. Triketone Ia, with mp 76-78°C (from ether—hexane), was obtained in 77% yield. Triketone Ib, with mp 81-82°C (from ether—hexane), was obtained in 65% yield. Bands at 1565 (C=C) and at 1615 and 1655-1660 cm^{-1} (C=O) are observed in the IR spectra of triketones Ia, b (KBr pellets). Signals of OH groups at 17.65 ppm (triketone Ia) and 15.84 ppm (triketone Ib) appear in the PMR spectra.

The structures and compositions of triketones Ia, b were also confirmed by the UV, PMR, and mass spectra and the results of elementary analysis.

3,4-Dioxo-2,3,4,5,6,7-hexahydrobenzo[b]furan (IIa). This compound was obtained by refluxing 1 g (5.3 mmole) of triketone Ia and 0.435 g (5.3 mmole) of sodium acetate in 40 ml of absolute acetone for 30 min. After cooling, the precipitated salt was removed by filtration, and the filtrate was evaporated to dryness *in vacuo* to give chromatographically pure IIa, with mp 127°C (from alcohol—ether), in 99% yield. IR spectrum (KBr): 1575 (C=C); 1655 and 1725 cm^{-1} (C=O). UV spectrum (in alcohol), λ_{max} (log ε): 233 (3.98) and 259 nm (4.03). PMR spectrum ($CDCl_3$): 4.66 (2H, s, 2-H), 2.86 (2H, t, J = 6 Hz, 7-H), 2.48 (2H, t, J = 6 Hz, 5-H), and 2.18 ppm (2H, m, J = 6 Hz, 6-H).

6,6-Dimethyl-3,4-dioxo-2,3,4,5,6,7-hexahydrobenzo[b]furan (IIb). This compound was similarly obtained from triketone Ib and sodium acetate. Recrystallization from a mixture of ethanol and ether gave the product in 72% yield. PMR spectrum ($CDCl_3$): 4.64 (2H, s, 2-H), 2.64 (2H, s, 7-H), 2.30 (2H, s, 5-H), and 1.15 ppm (6H, s, 6-CH_3).

The structure of IIb was also confirmed by the IR and UV spectra. The results of elementary analysis and mass-spectral determination of the molecular masses of IIa, b were in agreement with the calculated values.

Compound IIb was also obtained in virtually quantitative yield by heating equimolar amounts of triketone Ib and silver acetate in acetic acid at 100°C for 8 h, as well as by the addition of sodium nitrite to triketone Ib in absolute methanol at room temperature.

LITERATURE CITED

1. A. A. Akhrem, F. A. Lakhvich, S. I. Budai, T. S. Khlebnikova (Khlebnicova), and I. I. Petrusevich, Synthesis, No. 12, 925 (1978).

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