IMPROVED METHOD FOR THE SYNTHESIS OF 1-ALKOXYAZIRIDINE-2,2-DICARBOXYLIC ACID ESTERS

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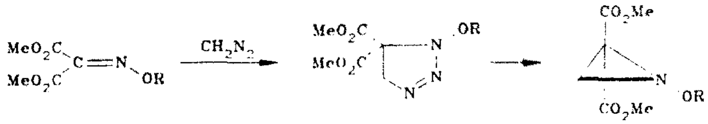
1-Alkoxyaziridine-2,2-dicarboxylic acid esters III are of interest in connection with the high pyramidal stability of the nitrogen atom [1]. The principal method for their synthesis is the reaction of alkoxyiminomalonates with diazomethane at 20°C [2]; the intermediate formation of 1-alkoxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylic acid esters, the spontaneous decomposition of which leads to a mixture of esters III and alkoxyiminosuccinates, is assumed [2]. The reaction products were separated by chromatography, and the yields of esters III generally did not exceed 75% [2].

By the reaction of isonitrosomalonates Ia, b with diazomethane at −10°C we obtained for the first time stable (at low temperatures) triazolines IIa, b, the decomposition of which in the presence of boron trifluoride etherate gives esters III in close-to-quantitative yields.



I a,b   II a,b   III a,b

I–III a R=Me; b R=CH$_2$Ph

The PMR spectra of solutions in $CDCl_3$ were obtained with an RYa-2305 spectrometer (60 MHz) at −10°C with hexamethyldisiloxane (HMDS) as the internal standard.

Dimethyl 1-Methoxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylate (IIa). A 10-ml sample of a 10% solution of diazomethane in ether was added at −10°C to 1.75 g (0.01 mole) of dimethyl (methoxyimino)malonate [2], and the mixture was maintained at this temperature for 1.5 months. PMR spectrum, δ: 3.70 (s, $2CO_2Me$), 3.94 (s, OMe), 4.72 ppm (s, CH_2).

Dimethyl 1-Benzyloxy-Δ^2-1,2,3-triazoline-5,5-dicarboxylate (IIb). This compound was similarly obtained. PMR spectrum, δ: 3.80 (s, $2CO_2Me$), 4.66 (s, CH_2), 5.26 ppm (s, CH_2O).

Dimethyl 1-Methoxyaziridine-2,2-dicarboxylate (IIIa). One drop of $Et_2O \cdot BF_3$ was added to the reaction mixture obtained in the synthesis of triazoline IIa, after which the mixture was maintained for 24 h at −10°C. It was then treated with 100 ml of ether and filtered, the filtrate was washed with water (two 20-ml portions) and dried with Na_2SO_4, and the ether was evaporated. The residue was recrystallized from benzene–hexane (1:4) to give 1.85 g (97%) of a product with mp 42°C (mp 41-42°C [2]).

Dimethyl 1-Benzyloxyaziridine-2,2-dicarboxylate (IIIb). This compound was similarly obtained in 98% yield and had mp 61°C (mp 60-61°C [2]).

LITERATURE CITED

1. R. G. Kostyanovskii and V. F. Rudchenko, *Dokl. Akad. Nauk SSSR*, 231, 878 (1976).
2. R. G. Kostyanovskii, A. V. Prosyanik, A. M. Mishchenko, G. V. Shustov, I. I. Chervin, N. L. Zaichenko, P. N. Belov, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1980 (1979).

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