A NEW ONE-STEP METHOD FOR THE SYNTHESIS OF THE TRIMETHYL ESTER OF TRANS-ACONITIC ACID

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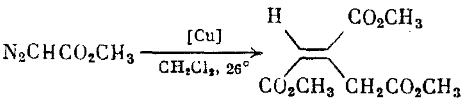
UDC 542.971.2:547.467.2

We have developed a new stereoselective method for the synthesis of the trimethyl ester of trans-aconitic acid (I) in one step by catalytic trimerization of carbomethoxycarbene generated from methyl diazoacetate by the action of catalytic amounts of $Cu(acac)_2 \cdot ZnCl_2 \cdot C_5H_5N$.



(I)

The formation of even traces of (I) is not observed upon the reaction of methyl diazoacetate with dimethyl fumarate or dimethyl maleate or upon the trimerization of methyl diazoacetate without the pyridine·$ZnCl_2$ complex in the catalyst.

A sample of 1.8 g (0.018 mole) $N_2CHCO_2CH_3$ in 5 ml CH_2Cl_2 was added dropwise to the catalytic system obtained by mixing 0.047 g (0.18 mmole) $Cu(acac)_2$, 0.708 g (0.009 mole) pyridine, and 1.23 g (0.009 mole) $ZnCl_2$ in 20 ml CH_2Cl_2 at 26°C. After 2 h, the reaction mixture was washed with water. The organic layer was dried over Na_2SO_4 and the solvent was evaporated. The residue was distilled in vacuum to give 0.91 g (~70%) (I), bp 105°C (1 mm), n_D^{20} 1.4629. The physicochemical indices of our sample of (I) were identical to those reported in the literature [1].

LITERATURE CITED

1. Beilsteins Handbuch der Organischen Chemie, 4th ed., Vol. 2/3, Springer-Verlag, Berlin–Heidelberg–New York (1973), p. 2405.

Institute of Chemistry, Bashkir Science Center, Urals Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 492-493, February, 1990. Original article submitted October 12, 1989.

0568-5230/90/3902-0430$12.50