CHLORONITROACETYL CHLORIDE IN THE SYNTHESIS OF 3-CHLOROISOXAZOLES

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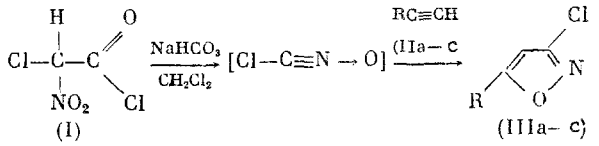
UDC 547.786.1:547.22

The cycloaddition of chloronitrile oxide generated *in situ* from dichloroformaldoxime to acetylenes leads to the formation of 3-chloroisoxazoles, which had been difficult to prepare [1].

We have shown that chloronitroacetyl chloride (I), which is readily obtained by the nitration of trichloroethylene using HNO_3–H_2SO_4 as a nitrating mixture [2], may be a source of chloronitrile oxide. Carrying out the reaction of (I) with a twofold excess of monosubstituted acetylenes (II) in methylene chloride in the presence of an equimolar amount of sodium bicarbonate gave the corresponding 5-substituted 3-chloroisoxazoles (III) in 30-45% yield.



R=Ph (a), CH_2Br (b), OEt (c).

A solution of 19.6 ml (0.02 mole) (I) in 40 ml CH_2Cl_2 was added dropwise with stirring over 4 h to a mixture of 0.04 mole (IIa)-(IIc) and 1.7 g (0.02 mole) $NaHCO_3$ in 10 ml CH_2Cl_2. The reaction mixture was washed with water and dried over magnesium sulfate. The solvent was distilled off. The residue was distilled in vacuum. The yield of isoxazole (IIIa) was 1.1 g (30%), bp 100-102°C (1 mm). PMR spectrum in $CDCl_3$ (δ, ppm): 7.8-7.6 m (2H), 7.5-7.3 m (3H), 6.5 s (1H).

The yield of isoxazole (IIIb) was 1.4 g (35%), bp 90-91°C (10 mm). PMR spectrum in $CDCl_3$ (δ, ppm): 6.41 t (1H, J = 0.6 Hz), 4.46 d (2H, J = 0.6 Hz).

The yield of isoxazole (IIIc) was 1.3 g (45%), bp 60-61°C (1 mm). PMR spectrum in $CDCl_3$ (δ, ppm): 5.32 s (1H), 4.28 q (2H, J = 8 Hz), 1.48 t (3H, J = 8 Hz).

LITERATURE CITED

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Institute of Physiologically Active Compounds, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, p. 1454, June, 1989. Original article submitted March 14, 1989.

0568-5230/89/3806-1335$12.50