1,3-DIMETHYL-4,4-DICHLORO-5-PYRAZOLONE

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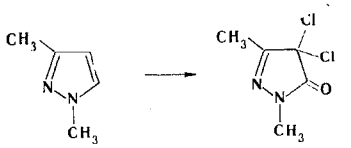
4,4-Dihalo-5-pyrazolones are obtained by the reaction of 1,3-disubstituted pyrazoles with bromine or chlorine in nitric acid [1]. The presence of an electron-acceptor 2,4-dinitrophenyl group in the 1 position of the starting pyrazole is a necessary condition for their formation, since under the same conditions, 4-bromo-1,3-dimethylpyrazole, which contains an electron-donor group in the 1 position, is brominated to 4,5-dibromo-1,3-dimethylpyrazole [2], and the corresponding 4,4-dibromo-5-pyrazolone is not formed.

For the first time we have carried out the chlorination of 1,3-dimethylpyrazole (I) under conditions that differ fundamentally from those previously described by Elguero. Specifically, by the reaction of I with chlorine in acetic acid in the presence of sodium acetate we were able to obtain 1,3-dimethyl-4,4-dichloro-5-pyrazolone (II), which contains an electron-donor methyl group in the 1 position; this is not possible under conditions of halogenation in nitric acid [1, 2].



I II

Chlorine was bubbled for 10 h at 70°C into a mixture of 100 ml of acetic acid, 64 g of sodium acetate, and 19.2 g (0.2 mole) of pyrazole, after which the mixture was diluted with water, and the oil was separated. The residue remaining after neutralization was extracted with chloroform, and the combined oil and extract were dried over sodium sulfate. The solvent was removed by distillation, and the residue was distilled in vacuo to give II (70%) with bp 62-70°C (4 hPa). IR spectrum (CCl_4): 1750 cm^{-1} (C=O). PMR spectrum (CCl_4): 2.19 (3-CH_3) and 3.28 ppm (1-CH_3). Mass spectrum: M^+ 180, 182, and 184.

LITERATURE CITED

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2. J. Elguero, R. Jacquier, G. Tarrago, and H. C. N. Tien Duc, Bull. Soc. Chim. Fr., No. 1, 293 (1966).

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