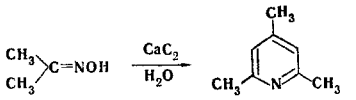
NEW PATHWAY IN THE CONDENSATION OF ACETONE OXIME WITH ACETYLENE

B. A. Trofimov, A. I. Mikhaleva,
A. S. Atavin, and E. G. Chebotareva

UDC 547.821.2 : 542.953

We recently reported that acetylene reacts with ketoximes to give N-vinylpyrroles in high yields [1]. It was found that if the acetylene is obtained directly in the reaction flask from calcium carbide, the reaction in aqueous medium under the autogenic acetylene pressure (~30 atm) gives substituted pyridines. For example, 2,4,6-trimethylpyridine was obtained in ~10% yield from acetone oxime.



A mixture of 50 g of acetone oxime, 7 g of KOH, 110 g of CaC_2 (in oil paper, as described in [2]), and 150 ml of H_2O was heated at 200-220°C in a rotating autoclave for 8 h (the maximum pressure was 27 atm). The organic products were extracted from the reaction mixture by steam distillation and subsequent extraction of the condensate with ether. The extract was dried with K_2CO_3 and distilled to give 8.9 g of 2,4,6-trimethylpyridine. According to gas–liquid chromatography (effected with a 2.4-m long column 3 mm in diameter filled with polyethylene glycol on Chromatone N-AW-DMCS with a helium flow rate of 2.5 liter/h; the apparatus used was an LKhM-8M chromatograph with a thermal-conductivity detector), the 2,4,6-trimethylpyridine was no less than 95% pure. Its IR, UV, and PMR spectra and pK_a values (in water and methanol) were identical to those of an authentic sample.

LITERATURE CITED

1. B. A. Trofimov, A. S. Atavin, A. I. Mikhaleva, G. A.Kalabin, and E. G. Chebotareva, Zh. Organ. Khim., 10, 2205 (1973).
2. A. S. Atavin and B. A. Trofimov, Zh. Prikl. Khim., 2706 (1964).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1427, October, 1975. Original article submitted September 17, 1974.