UNEXPECTED LOSS OF FUNCTIONALITY DURING THE TROFIMOV SYNTHESIS OF PYRROLES FROM 4-NITRO AND 4-DIMETHYLAMINOACETOPHENONE OXIMES

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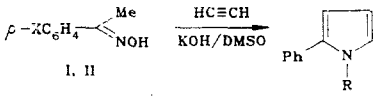
Condensation of ketoximes with acetylene in highly basic media primarily gives rise to pyrroles and N-vinylpyrroles [1]. It has been reported [2] that 4-nitroacetophenone oxime (I) in KOH-DMSO does not give the corresponding pyrroles with acetylene.

In continuation of attempts to synthesize 2-(4-nitrophenyl)pyrroles we have found that condensation of oxime I with acetylene occurs with loss of the NO_2 group and formation of 2-phenylpyrrole (III, yield ~7%) and 1-vinyl-2-phenylpyrrole (IV, yield 1.4%). The reaction was carried out for 3 h at 100°C with a molar ratio of I:KOH of 1:2 using an autoclave and an initial acetylene pressure of 14 atmospheres.



I, II

III, IV

I X=NO_2; II X=NMe_2; III R=H; IV R=CH=CH_2

A similar reaction course was observed when the dimethylamino analog (II) was condensed with acetylene at atmospheric pressure (5 h, molar ratio of II:KOH = 1:3, 100°C). Along with the expected NH and N-vinylpyrroles (2 and 4% yields correspondingly as determined by GLC but with purity insufficient for determination of physical constants) the pyrroles III and IV were also formed in overall 4% yield.

Pyrroles III and IV were separated chromatographically from the reaction mixture on a thin, unbound layer of aluminum oxide using hexane–ether (1:1) as eluent. GLC showed them to have the same retention time as reference samples and their spectra (IR, ^1H and ^{13}C NMR) were identical with the samples prepared by condensation of acetophenone oxime with acetylene [3, 4].

LITERATURE CITED

1. B. A. Trofimov and A. I. Mikhaleva, N-Vinylpyrroles [in Russian], Nauka, Novosibirsk (1984), p. 262.
2. B. A. Trofimov, S. E. Korostova, L. N. Balabanova, and A. I. Mikhaleva, Khim. Geterotsikl. Soedin., No. 4, 489 (1978).
3. B. A. Trofimov, S. E. Korostova, L. N. Balabanova, and A. I. Mikhaleva, Zh. Org. Khim., 14, 2182 (1978).
4. B. A. Trofimov, M. V. Sigalov, V. M. Bzhezovskii, G. A. Kalabin, S. E. Korostova, A. I. Mikhaleva, and L. N. Balabanova, Khim. Geterotsikl. Soedin., No. 6, 798 (1978).

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