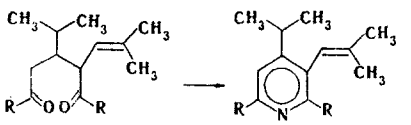
SYNTHESIS OF SUBSTITUTED 3-VINYLPYRIDINES

L. S. Novikov, V. A. Mezhentsev,
and I. G. Tishchenko

UDC 547.442+547.822

We have established that erythro-2-methyl-5-isopropyl-4,6-diaroyl-2-hexenes Ia-d form the corresponding 3-vinylpyridines IIa-d when they are refluxed with hydroxylamine hydrochloride in dioxane–methanol for 30-45 h.



Ia-d IIa-d

I-II a R = C_6H_5; b R = $C_6H_4CH_3$-*p*; c R = $C_{10}H_7$-2; d R = $C_6H_4C_6H_5$-*p*

The following compounds were obtained [the melting points (solvent) and yields (%) are given]: IIa, 65-66°C (methanol), 72; IIb, 84-85°C (methanol), 66; IIc, 143-144°C (ether–methanol), 74; IId, 130-131°C (ether–methanol), 71. The structure of IIa-d was proved by conversion to the corresponding epoxy derivatives.

The carbonyl absorption bands at 1690 and 1695 cm^{-1} vanished in the IR spectra of the products. PMR spectra (CCl_4): 1.19 and 1.77 [two s, 3-$(CH_3)_2$], 6.17 (s, 3H), 1.27 [d, 4-$(CH_3)_2$], 3.2 (m, 4-H), and signals of aryl substitutents and the proton of the pyridine ring. The high-resolution mass spectra confirmed the structures and compositions of the molecular and fragment ions of IIa-d. The results of elementary analysis for C, H, and N were in agreement with the calculated values.

Alkylpyridines are not formed under the reaction conditions; this is probably associated with the difficulty involved in the reduction of the trisubstituted olefin bond. According to the results of thin-layer chromatography [ether–heptane (1:4)], products of oximation of the carbonyl groups are side products. The yields of IIa were 52 and 40%, respectively, when ammonium acetate in acetic acid and formamide in formic acid were used as the cyclizing agents; this is associated with destruction of the starting diketone at the olefin bond, which takes place in an acidic medium. A carbocyclic unsaturated ketone with the composition $C_{21}H_{22}O$, the structure of which was established on the basis of spectral data and chemical transformations, was a side product.

A. M. Gorkii Minsk State Pedagogical Institute, Minsk 220809. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, p. 1693, December, 1979. Original article submitted May 30, 1979.

0009-3122/79/1512-1367$07.50