ONE-STEP SYNTHESIS OF 2,2'-THIENYLPYRROLES FROM METHYL 2-THIENYL KETOXIME AND ACETYLENE

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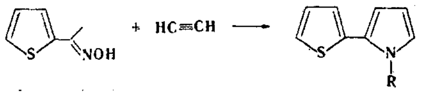
The reaction of methyl 2-thienyl ketoxime with acetylene in the presence of potassium hydroxide at 100-140°C gave 2-(2-thienyl)pyrrole (I), with mp 62°C (from 50% aqueous methanol), in 60% yield. The previously unknown 1-vinyl-2-(2-thienyl)pyrrole (II), with bp 110-111°C (1 mm), n_D^{20} 1.6350, and d_4^{20} 1.0526, was obtained in 50% yield in the presence of excess acetylene.



I R=H; II R=CH=CH$_2$ I-II

The reaction was carried out in an autoclave at an initial acetylene pressure of 8-15 atm. The structures of the products (particularly the site of ring fusion) follow from the results of previous studies [1, 2] and are also confirmed by the analytical and spectral data. The IR spectra of I and II contain characteristic bands of thiophene (705, 1040, and 1515 cm^{-1}) and pyrrole (716, 1380, and 1470 cm^{-1}) rings, bands at 598, 850, 935, 1580, and 1645 cm^{-1} from a N-vinyl group, and a multiplet at 3075-3140 cm^{-1} from the C–H stretching vibrations of the heterorings and the N-vinyl group. UV spectrum, λ_{max} (log ε): 200 (4.28), 250 (4.10), and 2.94 nm (4.04). The first two bands are characteristic for N-vinylpyrroles [1], and the third maximum is the bathochromically shifted absorption of a thiophene ring in conjugation with a pyrrole ring.

^{13}C NMR spectrum of the N-vinylpyrrole skeleton (in parts per million relative to tetramethylsilane, pure liquid): 133.48 (2-C), 111.55 (3-C), 110.34 (4-C), 118.35 (5-C), 130.94 (C-α-vinyl), and 98.74 (C-β-vinyl). This spectrum is in agreement with the ^{13}C NMR spectra of other N-vinylpyrroles [2]. The signals at 127.16, 126.30 (doubled intensity) and 125.14 ppm belong to the carbon atoms of the thienyl ring. In the absence of decoupling with the protons, the 2-C signal appears as a singlet; this constitutes evidence for the presence of a 2-thienyl substituent in this position.

LITERATURE CITED

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