

SHORT
COMMUNICATIONSFormation of 5-Phenyl-1-vinyl-1*H*-pyrrole-2-carbonitrile
in the Vinylation of 5-Phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde
Oxime with AcetyleneE. Yu. Shmidt, A. I. Mikhaleva, E. Yu. Senotrusova, A. M. Vasil'tsov,
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Received February 11, 2008

DOI: 10.1134/S1070428008090261

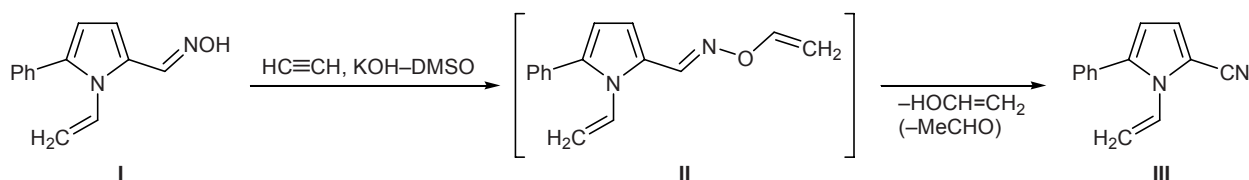
It is known that ketone oximes react with acetylene in the superbasic system KOH–DMSO to give *O*-vinyloximes which readily undergo rearrangement into pyrroles (Trofimov reaction [1–3]). However, vinylation of 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde oxime (**I**) under analogous conditions gave exclusively 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbonitrile (**III**, yield 67%) instead of expected *O*-vinyloxime **II**. It could be presumed that compound **III** was formed via dehydration of initial oxime **I**. Dehydration of aldehyde oximes to the corresponding nitriles in the system KOH–DMSO was described in [4]. However, oxime **I** almost did not undergo dehydration in the absence of acetylene (the yield of nitrile **III** did not exceed 4%). Therefore, we concluded that 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbonitrile (**III**) is formed as a result of elimination of vinyl alcohol (acetaldehyde) from *O*-vinyloxime **II**.

Pyrrole-2-carbonitriles are usually synthesized by dehydration of the corresponding pyrrole-2-carbaldehyde oximes by the action of acid reagents, e.g., acetic anhydride, *p*-toluenesulfonic acid, epichlorohydrin [5], or diethyl chlorophosphate [6]). However, the vinyl group is sensitive to acids [7, 8]; therefore, the observed reaction of 5-phenyl-1-vinyl-1*H*-pyrrole-2-

carbaldehyde oxime (**I**) with acetylene can be used to obtain 1-vinyl-1*H*-pyrrole-2-carbonitriles from 1-vinyl-1*H*-pyrrole-2-carbaldehyde oximes.

Pyrrolecarbonitriles are widely used as nonsteroidal progesterone receptor agonists (e.g., Tanaproget [9]), precursors of conducting polypyrroles with tetrazine spacers, which are characterized by a narrow forbidden zone [10], and intermediate products in fine organic synthesis for the preparation of the corresponding alcohols, acids, esters, amides [11], and heterocyclic compounds [12]. Introduction of a vinyl groups into pyrrolecarbonitrile molecules should further extend their synthetic potential. However, such 1-vinyl-1*H*-pyrrole-2-carbonitriles were previously unknown. The discovered transformation provides a synthetic route to such derivatives.

5-Phenyl-1-vinyl-1*H*-pyrrole-2-carbonitrile (III). A 0.25-l steel rotating high-pressure reactor was charged with 0.50 g (2.4 mmol) of 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde oxime (**I**), 0.16 g (2.4 mmol) of KOH·0.5H₂O, and 50 ml of DMSO, and the mixture was saturated with acetylene at room temperature to a pressure of 14 atm. The mixture was then heated to 70°C and was kept for 10 min at that temperature, the maximal acetylene pressure being



~20–22 atm. After cooling to room temperature, the mixture was diluted with 100 ml of water and extracted with methylene chloride (6×20 ml). The combined extracts were washed with water (4×30 ml) and dried over potassium carbonate. Removal of the solvent gave 0.68 g of a brown tarry material which was subjected to flash chromatography on basic aluminum oxide using hexane as eluent to isolate 0.31 g (67%) of compound **III** as colorless crystalline substance which turned yellow on exposure to air. mp 40–42°C. IR spectrum, ν , cm^{-1} : 2924, 2853, 2214 ($\text{C}\equiv\text{N}$), 1648, 1636, 1458, 1415, 1402, 1329, 1299, 964, 909, 761, 701. ^1H NMR spectrum, δ , ppm: 7.40 m (5H, C_6H_5), 6.96 d (1H, 3-H, $^3J = 3.6$ Hz), 6.76 d.d (1H, H_X , $^3J_{\text{BX}} = 15.8$, $^3J_{\text{AX}} = 6.9$ Hz), 6.29 d (1H, 4-H, $^3J = 3.6$ Hz), 5.67 d (1H, H_B , $^3J_{\text{BX}} = 15.8$ Hz), 5.18 d (1H, H_A , $^3J_{\text{AX}} = 6.9$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 140.2 (C^5 , C^a), 131.7 (C^i), 131.2 (C^b), 130.1 (C^o), 129.7 (C^m), 123.2 (C^3), 115.3 ($\text{C}\equiv\text{N}$), 111.5 (C^4), 109.9 (C^b), 104.7 (C^2). ^{14}N NMR spectrum, δ_{N} , ppm: –203 (N^1), –110 ($\text{N}\equiv\text{C}$). Found, %: C 80.49; H 5.19; N 14.72. $\text{C}_{13}\text{H}_{10}\text{N}_2$. Calculated, %: C 80.39; H 5.19; N 14.42.

The IR spectra were recorded in KBr on a Bruker IFS-25 spectrometer. The NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 MHz for ^1H and 101.61 MHz for ^{13}C using CDCl_3 as solvent and HMDS as internal reference. The ^{14}N chemical shifts (40.53 MHz) were measured relative to MeNO_2 .

This study was performed under financial support by the Russian Foundation for Basic Research (project no. 06-03-39003-GFEN_a) and by the Foundation for Support of Russian Science.

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