

SHORT
COMMUNICATIONS

First Example of Pyrroles C-Vinylation by an Activated Acetylene Under Catalysis with Bases

L. N. Sobenina, A. I. Mikhaleva, I. A. Ushakov, V. N. Elokhina,
and B. A. Trofimov

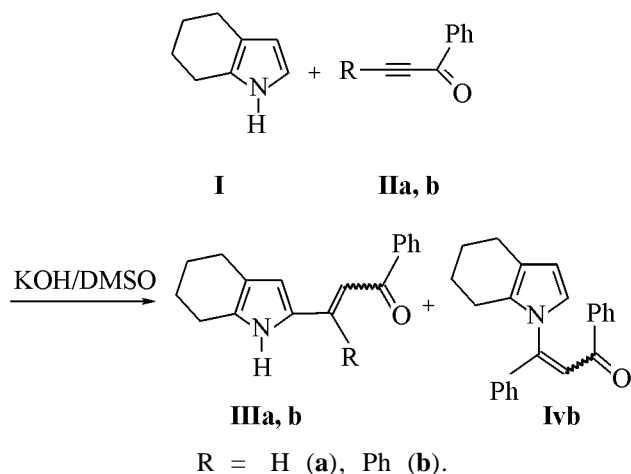
Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia
e-mail: sobenina@irioch.irk.ru

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In noncatalyzed reaction with acylacetylenes pyrroles behave exclusively as C-nucleophiles adding to the triple bond by 2-position [1].

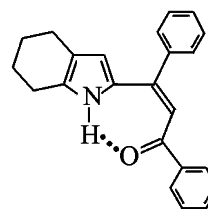
At the same time the nucleophilic addition of azoles to activated acetylenes affords exclusively N-adducts in a high yield [2]. In a similar fashion pyrroles react with acetylene in the presence of bases furnishing *N*-vinylpyrroles [3, 4].

We found that in a superbasic catalytic system KOH-DMSO 4,5,6,7-tetrahydroindole (I) added at room temperature within 3 h to benzoylacetylene (IIa) selectively forming a C-adduct, 2-(2-benzoyl-ethenyl)-4,5,6,7-tetrahydroindole (IIIa) (*E/Z*, 5:1), in 26% yield. The N-adduct was not detected even in traces (according to ¹H NMR spectrum in the reaction mixture were present only pyrrole IIa and the initial compounds).



Addition of pyrrole I to 2-benzoyl-1-phenylacetylene (IIb) under similar conditions affords a mixture of adducts (~1:1) *E/Z* C-(IIIb) and *E/ZN*-(IVb) in an

overall yield 56%. *E*-Isomer of C-vinylpyrrole IIIb in solutions rapidly (approximately within 0.5 h) and completely transforms into the *Z*-form stabilized by an intramolecular hydrogen bond.



The IR spectrum of *E*-isomer of pyrrole IIIb contains a strong band at 3322 cm⁻¹ corresponding to the stretching vibrations of the N-H bond. The carbonyl bond vibrations are observed in the region 1628 cm⁻¹. In the IR spectrum of the *Z*-isomer the characteristic bands of the NH group in the region 3200–3400 cm⁻¹ are lacking, and the absorption of the carbonyl group is still more shifted to the low frequency region (1613 cm⁻¹) indicating the formation of a very strong intramolecular hydrogen bond.

The ¹H NMR spectrum of pyrrole IIIb contains the signals of the olefin proton and of proton from the NH group (7.84 ppm), and also from protons belonging to pyrrole and benzene rings. In the spectrum of the *Z*-isomer the signal of the NH proton is uncommonly shifted downfield (to 13.99 ppm) confirming the presence of a very strong intramolecular hydrogen bond NH-carbonyl. The two-dimensional ¹H NMR spectra unambiguously show that both isomers are present in the *cis*-conformation with respect to the mutual position of the olefin bond and the carbonyl group.

Reaction of 4,5,6,7-tetrahydroindole with benzoylacetylene. A mixture of 4,5,6,7-tetrahydro-

indole (**I**) (0.545 g, 4.5 mmol), KOH (0.250 g, 4.5 mmol), and benzoylacetylene (**IIa**) (0.585 g, 4.5 mmol) was stirred in DMSO (10 ml) at room temperature for 3 h. The reaction mixture was diluted with 20% solution of NaCl, the separated crystals were filtered off (0.650 g) and purified by column chromatography on Al₂O₃ (eluent hexane). We isolated 0.293 g (26%) of 2-(2-benzoyl-4,5,6,7-tetrahydroindole-1-phenylethenyl)-4,5,6,7-tetrahydroindole (**IIIa**), *E/Z*, 5:1, orange crystals, mp 136–137°C. The spectral characteristics of pyrrole **IIIa** are consistent with those published in [1]. On extraction of water-DMSO solution with ethyl ether and removing the latter we recovered 0.232 g of 4,5,6,7-tetrahydroindole (**I**) (conversion 57%).

Reaction of 4,5,6,7-tetrahydroindole with 2-benzoyl-1-phenylacetylene. In the same way from 4,5,6,7-tetrahydroindole (**I**) (0.303 g, 2.5 mmol), KOH (0.140 g, 2.5 mmol), 2-benzoyl-1-phenylacetylene (**IIb**) (0.515 g, 2.5 mmol), and DMSO (10 ml) we obtained 0.760 bright yellow powder that after washing with ether afforded 0.040 g (5%) of *E*-2-(2-benzoyl-1-phenylethenyl)-4,5,6,7-tetrahydroindole (**IIIb**), yellow crystals, mp 161–162°C. ¹H NMR spectrum (250 MHz, CHCl₃), δ, ppm: 1.75 m (4H, CH₂^{5,6}), 2.45 m (2H, CH₂⁴), 2.75 m (2H, CH₂⁷), 6.24 s (1H, H³), 7.03 s (1H, CH=), 7.35–7.15 m (8H, H_{m,p} CPh, Ph), 7.84 m (3H, NH, H_o CPh). Found, %: C 84.15; H 6.19; N 4.34. C₂₃H₂₁NO. Calculated, %: C 84.37; H 6.46; N 4.28.

The residue after ether removal was subjected to column chromatography on Al₂O₃ (eluent hexane) to isolate 0.295 g (25%) of *Z*-2-(2-benzoyl-1-phenylethenyl)-4,5,6,7-tetrahydroindole (**IIIb**), yellow crystals, mp 111–112°C. ¹H NMR spectrum (250 MHz, CHCl₃), δ, ppm: 1.85 m (2H, CH₂⁵), 1.92 m (2H, CH₂⁶), 2.52 m (2H, CH₂⁴), 2.81 m (2H, CH₂⁷), 5.98 (1H, H³), 6.47 s (1H, CH=), 7.58–7.39 m (8H, H_{m,p} CPh, Ph), 8.07 m (2H, H_o CPh), 13.99 br.s (1H, NH). ¹³C NMR spectrum (100 MHz, CHCl₃), δ, ppm: 22.93 (CH₂⁷), 23.05 (CH₂⁴), 23.61

(CH₂⁶), 23.79 (CH₂⁵), 112.13 (=CH), 120.31 (C³), 122.49 (C⁴), 127.90 (C_o Ph), 128.10 (C_o CPh), 128.20 (C_p Ph), 128.50 (C_m Ph), 129.10 (C_m CPh), 130.57 (C²), 131.76 (C_p CPh), 136.20 (C⁵), 141.13 (C_i CPh), 143.56 (C_i Ph), 150.41 (C=), 189.05 (C=O). Found, %: C 84.45; H 6.08; N 4.11. C₂₃H₂₁NO. Calculated, %: C 84.37; H 6.46; N 4.28.

Also was isolated 0.210 g (26%) of 1-(2-benzoyl-1-phenylethenyl)-4,5,6,7-tetrahydroindole (**IVb**), *E/Z*, 2:1, yellow oily liquid. ¹H NMR spectrum: *E*-isomer 1.70 m (4H, CH₂^{5,6}), 2.52 m (2H, CH₂⁴), 2.81 m (2H, CH₂⁷), 5.78 s (1H, H³), 6.45 s (1H, H²), 6.74 s (1H, CH=), 7.35–7.50 m (8H, H_{m,p,o} Ph, H_{m,p} CPh), 7.75 m (2H, H_o CPh); *Z*-isomer 1.70 m (2H, CH₂^{5,6}), 2.52 m (2H, CH₂⁴), 2.81 m (2H, CH₂⁷), 6.08 s (1H, H³), 6.58 s (1H, H²), 6.76 s (1H, CH=), 7.35–7.50 m (8H, H_{m,p,o} Ph, H_{m,p} CPh), 7.92 m (2H, H_o CPh). Found, %: C 83.87; H 6.16; N 4.04. C₂₃H₂₁NO. Calculated, %: C 84.37; H 6.46; N 4.28.

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