

An example of the facile C-vinylation of pyrroles

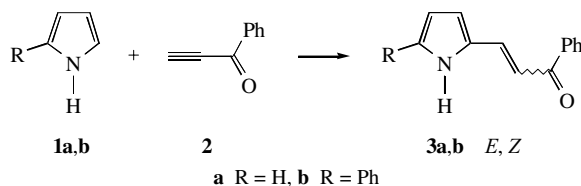
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The reaction of pyrroles with benzoylacetylene affords C-adducts, 2-(2-benzoylethenyl)pyrroles, in yields of up to 80%.

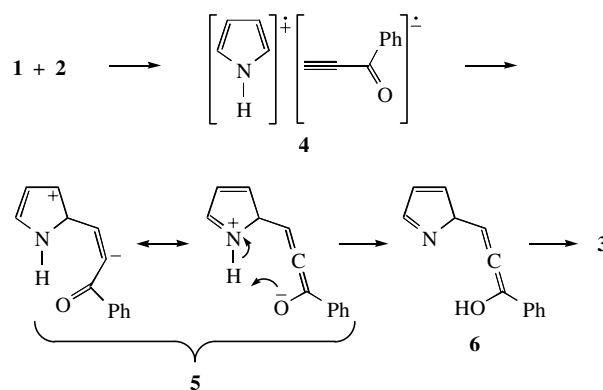
Base-catalysed vinylation of pyrroles with acetylenes is known to be achieved only under relatively harsh conditions (85–100 °C, DMSO) and affords exclusively *N*-vinylpyrroles.^{1,2} At the same time, pyrroles can also act as C-nucleophiles depending on the electrophile nature and the reaction conditions.^{2,3}

We have found that pyrroles **1a,b** readily (without catalyst, room temperature, diethyl ether or benzene) add to benzoylacetylene **2** to give C-adducts [2-(2-benzoylethenyl)pyrroles] **3a,b** (mixtures of *E*- and *Z*- isomers, 2.5:1 for **3a** and 2:1 for **3b**) in yields of up to 80%.[†]



Since pyrroles are typical π -donors and benzoylacetylene is a strong π -acceptor, the reaction can be assumed to begin with the formation of a charge-transfer complex (or the ion-radical pair **4**) to complete the covalent bond in the zwitterionic intermediate **5**, which further rearranges in a prototropic way (either by intra- or intermolecular proton transfer) through **2H**-pyrrole **6** to yield 2-vinylpyrroles **3**.

The orange colour of the reaction mixture and the complicated EPR spectrum recorded in a spin trapping technique with



2-methyl-2-nitrosopropane ($\text{Bu}^\bullet\text{NO}$) may be considered as evidence for the formation of radicals from the supposed ion-radical pair **4**.

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References

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- B. A. Trofimov, *Pyrroles. Part Two: The Synthesis, Reactivity and Physical Properties of Substituted Pyrroles*, ed. R. A. Jones, Wiley, New York, 1992, pp. 131–298.
- R. A. Jones and G. P. Bean, *The Chemistry of Pyrroles*, Academic Press, London–New York–San Francisco, 1977, pp. 143–150.

[†] 2-(2-Benzoylethenyl)pyrrole **3a**. A mixture of pyrrole **1a** (0.14 g, 2.1 mmol) and acetylene **2** (0.26 g, 2 mmol) in 2 ml of diethyl ether was stirred for 30 min and allowed to stand at room temperature for 24 h. After removal of the ether, the residue was washed with ethanol and ether to give 0.26 g (65% yield) of pyrrole **3a** as a mixture of *E*- and *Z*-isomers (2.5:1), mp 128–130 °C. ¹H NMR (250 MHz, [²H₆]DMSO) δ : *E*-isomer, 6.24 (m, 1H, H-4), 6.75 (m, 1H, H-3), 7.15 (m, 1H, H-5), 7.51–7.67 (m, 3H, *p*- and *m*-benzene protons), 7.58 (d, 1H, H, ³J 15.4 Hz), 7.64 (d, 1H, H, ³J 15.4 Hz), 8.05 (m, 2H, *o*-benzene protons), 11.75 (br. s, 1H, NH); *Z*-isomer, 6.34 (m, 1H, H-4), 6.81 (d, 1H, H, ³J 12.3 Hz), 6.83 (m, 1H, H-3), 7.08 (d, 1H, H, ³J 12.3 Hz), 7.28 (m, 1H, H-5), 7.51–7.67 (m, 3H, *p*- and *m*-benzene protons), 8.05 (m, 2H, *o*-benzene protons), 12.82 (br. s, 1H, NH). IR (KBr, ν/cm^{-1}): 604, 632, 689, 704, 732, 777, 849, 881, 928, 977, 1020, 1030, 1077, 1095, 1135, 1181, 1239, 1300, 1336, 1366, 1415, 1446, 1546, 1565, 1586, 1651, 3083, 3114, 3259. MS, m/z : 197 [M]⁺. Found (%): C, 79.02; H, 5.97; N, 7.04. Calc. for C₁₃H₁₁NO (%): C, 79.16; H, 5.62; N, 7.10.

2-(2-Benzoylethenyl)-5-phenylpyrrole **3b**. A mixture of pyrrole **1b** (0.14 g, 1 mmol) and acetylene **2** (0.13 g, 1 mmol) in 2 ml of diethyl ether was stirred for 30 min and allowed to stand at room temperature for 40 h. After removal of the ether, the residue was washed with ethanol and ether to give 0.22 g (80% yield) of pyrrole **3b** as a mixture of *E*- and *Z*-isomers (2:1), mp 188–191 °C. ¹H NMR (250 MHz, [²H₆]DMSO) δ : *E*-isomer, 6.95 and 6.98 (2dd, 2H, H-3 and H-4, ³J 3.7 Hz, ⁴J 2.3 Hz), 7.25–7.80 (m, 8H, Ph, *p*- and *m*-benzene protons), 7.53 (d, 1H, H, ³J 15.3 Hz), 7.68 (d, 1H, H, ³J 15.3 Hz), 8.15 (m, 2H, *o*-benzene protons), 11.78 (br. s, 1H, NH); *Z*-isomer, 6.74 and 6.86 (2dd, 2H, H-3 and H-4, ³J 3.7 Hz, ⁴J 2.3 Hz), 6.90 (d, 1H, H, ³J 12.3 Hz), 7.13 (d, 1H, H, ³J 12.3 Hz), 7.25–7.80 (m, 8H, Ph, *p*- and *m*-benzene protons), 8.05 (m, 2H, *o*-benzene protons), 13.72 (br. s, 1H, NH). IR (KBr, ν/cm^{-1}): 549, 636, 699, 731, 756, 777, 844, 907, 967, 1021, 1043, 1075, 1177, 1225, 1247, 1301, 1353, 1395, 1455, 1507, 1560, 1583, 1597, 1640, 3030, 3059, 3288. MS, m/z : 273 [M]⁺. Found (%): C, 84.01; H, 5.58; N, 5.22. Calc. for C₁₉H₁₅NO (%): C, 83.49; H, 5.53; N, 5.12.

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