

SHORT COMMUNICATIONS

5-Bromo-2,3-diphenyl-1-vinyl-1*H*-pyrrole and 2,3,5-Triphenyl-1-vinyl-1*H*-pyrrole

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Received March 17, 2008

DOI: 10.1134/S1070428008090273

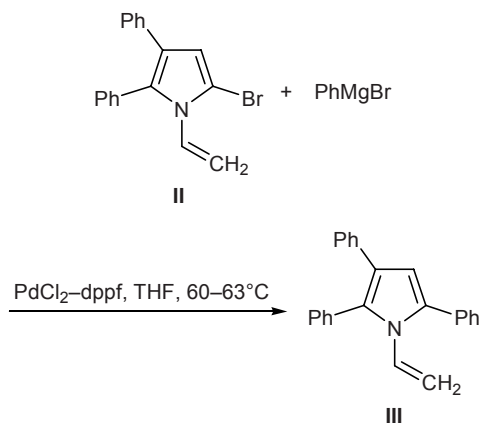
1-Vinylpyrroles are promising as monomers for the preparation of materials for photoelectronics, as well as highly reactive building blocks for the synthesis of various pyrrole derivatives [1]. 1-Vinylpyrroles having several aryl substituents and polymers derived therefrom attract specific attention due to their enhanced ability to transmit electronic excitation. In addition, di- and triarylpyrroles exhibit specific biological activity, and they are widely used in the design of hypoglycemic and antisclerotic drugs (an example is atorvastatin) [2].

1-Vinylpyrroles are commonly prepared by vinylation of NH-pyrroles with acetylene [3] or by one-pot Trofimov reaction from ketone oximes and acetylene [1, 4]. However, introduction of an aryl substituent into the 5-position of the pyrrole ring (provided that the 2-position is already occupied) involves difficulties: for example, the yield of 2,5-diphenylpyrrole from acetophenone oxime and phenylacetylene is as poor as 17% [5]. We have found that accessible 2,3-diphenyl-1-vinyl-1*H*-pyrrole (**I**) [4] can be used as initial compound for the synthesis of 5-substituted 2,3-diphenyl-1-vinyl-1*H*-pyrroles. Pyrrole **I** was selectively brominated at C⁵ by the action of *N*-bromosuccinimide under the conditions described in [6] to give 5-bromo-2,3-diphenyl-1-vinyl-1*H*-pyrrole (**II**) in 65% yield, i.e., the

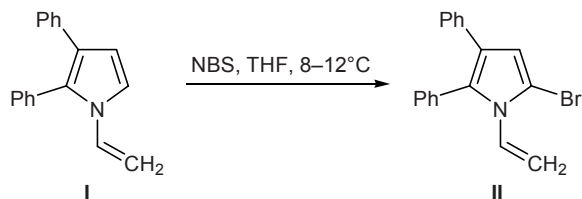
vinyl group in the initial compound remained intact (Scheme 1).

Bromopyrrole **II** can be used as base compound for the preparation of various 5-substituted 2,3-diphenyl-1-vinyl-1*H*-pyrroles, including 5-aryl-2,3-diphenyl-1-vinyl-1*H*-pyrroles, via cross coupling and nucleophilic substitution reactions. As an example, we describe here palladium-catalyzed cross-coupling of bromopyrrole **II** with phenylmagnesium bromide according to the procedure reported in [7] (Scheme 2). As catalyst we used [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride (PdCl₂·dppf). The yield of 2,3,5-triphenyl-1-vinyl-1*H*-pyrrole (**III**) was 75%.

Scheme 2.



Scheme 1.



5-Bromo-2,3-diphenyl-1-vinyl-1*H*-pyrrole (II**).** A solution of 1.227 g (5.0 mmol) of 2,3-diphenyl-1-vinyl-1*H*-pyrrole (**I**) in 20 ml of THF was cooled to 10–12°C, 1.068 g (6.0 mmol) of *N*-bromosuccinimide was added, and the mixture was stirred until it became homogeneous (10–15 min) and kept for 18 h in the

cold (8–10°C). Sodium sulfate, 1.00 g, was then added, the solvent was removed under reduced pressure, the residue was treated with 5 ml of carbon tetrachloride, and the precipitate was filtered off and washed with 3 ml of carbon tetrachloride. The solvent was removed from the filtrate, and the residue was purified by chromatography on aluminum oxide using petroleum ether (bp 40–70°C) as eluent. Yield 1.05 g (65%), mp 70–71°C (from hexane). ^1H NMR spectrum, δ , ppm: 7.40 m (3H, H_{arom}), 7.24 m (2H, H_{arom}), 7.15 m (2H, H_{arom}), 7.10 m (3H, H_{arom}), 6.62 d.d (1H, H_X , $J = 9.0$, 15.6 Hz), 6.51 s (1H, 4-H), 4.98 d (1H, H_A , $J = 9.0$ Hz), 4.96 d (1H, H_B , $J = 15.6$ Hz). ^{13}C NMR spectrum, δ_{C} , ppm: 135.9, 133.1, 132.2, 132.0, 131.6, 129.3, 129.0, 128.9, 128.8, 126.8, 113.8, 111.4. Found, %: C 66.46; H 4.25; Br 24.98; N 4.38. $\text{C}_{18}\text{H}_{14}\text{BrN}$. Calculated, %: C 66.68; H 4.35; Br 24.65; N 4.32.

2,3,5-Triphenyl-1-vinyl-1H-pyrrole (III).

5-Bromo-2,3-diphenyl-1-vinyl-1H-pyrrole (II), 1.85 g (5.7 mmol), was dissolved in 5 ml of THF, 0.042 g (5.7×10^{-5} mmol) of $\text{PdCl}_2 \cdot \text{dppf}$ and 13.2 ml of a 1 M solution of phenylmagnesium bromide in THF were added under argon, and the mixture was heated for 3 h at 60–63°C. The mixture was cooled, diluted with water (1:3), and extracted with diethyl ether. The extract was dried over Na_2SO_4 and evaporated, and the residue was subjected to column chromatography on Al_2O_3 using hexane as eluent. Yield 1.37 g (75%), mp 141–142°C. ^1H NMR spectrum, δ , ppm: 7.49 m (2H, H_{arom}), 7.38–7.30 m (7H, H_{arom}), 7.17 m (5H, H_{arom}), 7.09 m (1H, H_{arom}), 6.67 d.d (1H, H_X , $J = 8.8$, 15.8 Hz), 6.50 s (1H, 4-H), 4.70 d (1H, H_A , $J = 8.8$ Hz), 4.46 d (1H, H_B , $J = 15.8$ Hz). ^{13}C NMR spectrum, δ_{C} ,

ppm: 136.6, 135.1, 134.1, 133.7, 132.5, 132.1, 130.1, 129.2, 129.1, 128.9, 128.5, 127.9, 126.4, 124.9, 112.1, 109.7. Found, %: C 89.86; H 5.92; N 4.20. $\text{C}_{24}\text{H}_{19}\text{N}$. Calculated, %: C 89.68; H 5.96; N 4.36.

The ^1H and ^{13}C NMR spectra were recorded from solutions in CDCl_3 on a Bruker DPX 400 instrument at 400.13 and 100.6 MHz, respectively, using HMDS as internal reference.

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