ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 9, pp. 1397–1398. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © B.A. Trofimov, O.V. Petrova, L.N. Sobenina, A.I. Mikhaleva, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 9, pp. 1414–1415.

SHORT COMMUNICATIONS

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

B. A. Trofimov, O. V. Petrova, L. N. Sobenina, and A. I. Mikhaleva

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: boris_trofimov@irioch.irk.ru

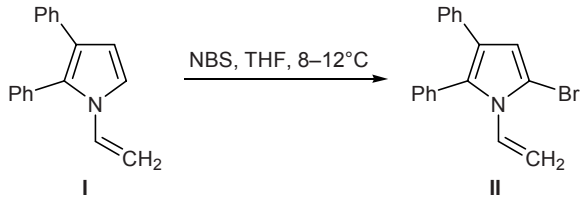
Received March 17, 2008

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 C^5 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).

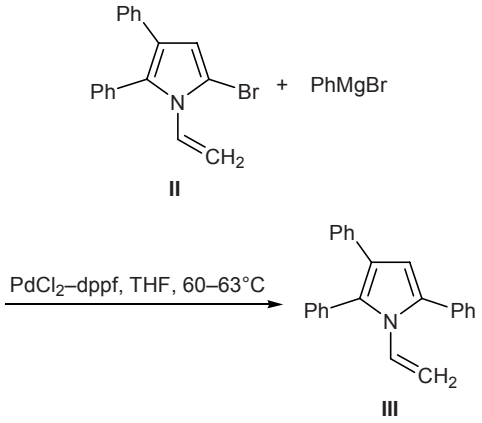
Scheme 1.



I II

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 ($PdCl_2$·dppf). The yield of 2,3,5-triphenyl-1-vinyl-1*H*-pyrrole (**III**) was 75%.

Scheme 2.



II III

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). ^{1}H 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. $C_{18}H_{14}BrN$. Calculated, %: C 66.68; H 4.35; Br 24.65; N 4.32.

2,3,5-Triphenyl-1-vinyl-1*H*-pyrrole (III). 5-Bromo-2,3-diphenyl-1-vinyl-1*H*-pyrrole (**II**), 1.85 g (5.7 mmol), was dissolved in 5 ml of THF, 0.042 g (5.7×10^{-5} mmol) of $PdCl_2\cdot$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. ^{1}H 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. $C_{24}H_{19}N$. Calculated, %: C 89.68; H 5.96; N 4.36.

The ^{1}H 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.

REFERENCES

1. Trofimov, B.A. and Mikhaleva, A.I., *N-Vinilpirroly* (*N*-Vinylpyrroles), Novosibirsk: Nauka, 1984; Trofimov, B.A., *Adv. Heterocycl. Chem*., 1990, vol. 51, p. 177; Trofimov, B.A., *Pyrroles. Part 2. The Synthesis, Reactivity, and Physical Properties of Substituted Pyrroles*, Jones, R.A., Ed., New York: Wiley, 1992, p. 131.
2. Bellina, F. and Rossi, R., *Tetrahedron*, 2006, vol. 62, p. 7213.
3. Trofimov, B.A., Mikhaleva, A.I., Korostova, S.E., Vasil'ev, A.N., and Balabanova, L.N., *Khim. Geterotsikl. Soedin*., 1977, p. 213; Trofimov, B.A., Korostova, S.E., Shevchenko, S.G., Polubentsev, E.A, and Mikhaleva, A.I., *Zh. Org. Khim*., 1990, vol. 26, p. 1110.
4. Trofimov. B.A., Korostova, S.E., Balabanova, L.N., and Mikhaleva, A.I., *Zh. Org. Khim*., 1978, vol. 14, p. 2182.
5. Trofimov, B.A., Mikhaleva, A.I., Korostova, S.E., and Kalabin, G.A., *Khim. Geterotsikl. Soedin*., 1977, p. 994; Korostova, S.E., Mikhaleva, A.I., Trofimov, B.A., Shevchenko, S.G., and Sigalov, M.V., *Khim. Geterotsikl. Soedin*., 1992, p. 485.
6. Gilow, H.M. and Burton, D.E., *J. Org. Chem*., 1981, vol. 46, p. 2221.
7. Bumagin, N.A., Sokolova, A.F., Beletskaya, I.P., and Vol'ts, G., *Zh. Org. Khim*., 1993, vol. 29, p. 162.