1 H, H-6'); 7.64 (dd, $J_{5,4}$ = 8.5 Hz, $J_{5,7}$ = 1.8 Hz, 1 H, H-5); 7.94 (d, $J_{4,5}$ = 8.5 Hz, 1 H, H-4); 8.00 (d, $J_{7,5}$ = 1.8 Hz, 1 H, H-7).

References

1. A. I. Kiprianov, Tsvet i stroenie tsianinovykh krasitelei (Color

and Structure of Cyanine Dyes), Naukova Dumka, Kiev, 1979, 23-106 (in Russian).

2. B. I. Shapiro, L. I. Mikheeva, A. G. Vakar, Yu. L. Slominskii, and A. I. Tolmachev, V Vsesoyuz. simp. "Fizika i khimiya polimetinovykh krasitelei" (Vth All-Union Symp. "Physics and Chemistry of Polymethine Dyes), Chernogolovka, December 4-8, 1989, Moscow, 1989, 231-233 (in Russian).

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Palladium-catalyzed synthesis of 3-substituted pyrroles from 3-pyrrolylmagnesium bromide

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It is known that pyrroles with free α -(2,5) positions can be used for synthesizing porphyrins. However, the preparation of 3-substituted pyrroles encounters difficulties due to the tendency of the pyrrole ring to undergo electrophilic substitution at position 2. Therefore, various indirect methods for synthesizing these compounds are being developed.^{1,2}

We were the first to obtain 3-1-(triisopropylsilyl)pyrrolylmagnesium bromide (1) from the respective 3-bromo derivative and elaborate an efficient procedure for the synthesis of 3-substituted pyrroles (2) based on cross-coupling of the above Grignard reagent with organic halides. The reaction is catalyzed by $PdCl_2(dppf)$ [dppf = 1,1'-bis(diphenylphosphino)ferrocene].

If the aryl bromide contains a hydroxyl and carboxyl group sensitive to the action of organomagnesium compounds, then the organic halide is pretreated with a stoichiometric amount of any Grignard reagent, *e.g.*, *p*-methoxyphenylmagnesium bromide, in order to protect these groups. In all cases, the cross-coupling was completed in 1-1.5 h, and the 3-substituted pyrroles were obtained in 65-90% yields.



2a: R = Ph **2b**: $R = 4-HOOCC_6H_4$ **2c**: $R = 4-HOC_6H_4$ **2d**: $R = 4-FC_6H_4$

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p-Bromobenzoic acid (0.201 g, 1 mmol) and THF (2.5 mL) were placed under argon into a flask equipped with a magnetic stirrer and a reflux condenser. Then, a solution of *p*-methoxyphenylmagnesium bromide (1.2 mL) in THF (~1 M) was added with cooling $(-5 \div 0^{\circ}C)$, and a hot solution (2.5 mL) of compound 1 in THF [obtained from Mg (0.216 g, 9 mmol) and 3-bromo-1-(triisopropylsilyl)pyrrole (1.5 mL, 6 mmol) in THF (8 mL)] and PdCl₂(dppf) (0.0073 g, 0.01 mmol) were added at ~20°C. The reaction mixture was stirred for 1.5 h with heating. After the reaction was completed, a 10% solution of H_2SO_4 was added with cooling (0°C) to the reaction mixture to pH 4, and the product was extracted with ether. The ethereal extract was dried with anhydrous Na_2SO_4 , the solvent was distilled off, and the residue was chromatographed on a column packed with SiO_2 (Silpearl, pentane:ether = 4:1) to give 0.31 g (90%) of 3-(4'-carboxyphenyl)-1-(triisopropylsilyl)pyrrole. The product turns dark above 160°C and melts with decomposition at 203.0-203.5°C. Found (%): C, 70.09; H, 8.48; Si, 7.87. C₂₀H₂₉NO₂Si. Calculated (%): C, 69.91; H, 8.53; Si, 8.18. ¹H NMR (CDCl₃), δ: 1.14 (d, J = 7.2 Hz, 18 H, Me); 1.52 (m, 3 H, CH); 6.68 (m,)1 H, H-4); 6.86 (m, 1 H, H-5); 7.21 (m, 1 H, H-2); 7.63 (d, $J_{2',3'} = 8.3$ Hz, 2 H, H-2', H-6'); 8.03 (d, $J_{3'2'} = 8.3$ Hz, 2 H, H-3', H-5').

⁷The following compounds were obtained in a similar way.

3-Phenyl-1-triisopropylsilylpyrrole, an oil. Yield 80%. Found (%): C, 76.29; H, 9.75; Si, 9.36. $C_{19}H_{29}NSi$. Calculated (%): C, 76.17; H, 9.78; Si, 9.38. ¹H NMR ((CD₃)₂CO), & 1.16 (d, J = 7.0 Hz, 18 H, (CH₃)₂CH); 1.59 (sept, J = 7.0 Hz, 3 H, Me₂CH); 6.66 (m, 1 H, H-4); 6.90 (dd, $J_{5,4} = J_{5,2} = 2.4$ Hz, 1 H, H-5); 7.13 (tt, $J_{4',3'} = 7.6$ Hz, 1 H, H-4'); 7.28 (m, 1 H, H-2); 7.31 (dd, H-5', $J_{3',2'} = J_{3',4'} = 7.6$ Hz, 2 H, H-3'); 7.60 (dd, H-6', $J_{2',3'} = 7.6$ Hz, 2 H, H-2').

3-(4'-Hydroxyphenyl)-1-(triisopropylsilyl)pyrrole, an oil. Yield 65%. ¹H NMR (CD₂Cl₂), δ : 1.14 (d, J = 8.0 Hz, 18 H, Me₂CH); 1.50 (sept, J = 8.0 Hz, 3 H, Me₂CH); 6.55 (m, 1 H, H-4); 6.82 (m, 1 H, H-2); 6.82 (d, $J_{3'2'} = 8.8$ Hz, 2 H, H-3', H-5'); 7.00 (m, 1 H, H-5); 7.42 (d, $J_{2'3'} = 8.8$ Hz, 2H, H-2', H-6').

3-(4'-Fluorophenyl)-1-triisopropylsilylpyrrole, an oil. Yield 87%. ¹H NMR (CD₂Cl₂), δ : 1.04 (d, J = 7.45 Hz, 18 H, (CH₃)₂CH); 1.31 (m, 3 H, Me₂CH); 6.81 (dd, $J_{4,5} = 2.77$ Hz, $J_{4,2} = 1.52$ Hz, 1 H, H-4); 7.07 (dd, $J_{5,4} = 2.77$ Hz, $J_{5,2} = 2.12$ Hz, 1 H, H-5); 7.29 (m, 1 H, H-2); 7.29 (dd, $J_{3',2'} = J_{3',F} = 8.9$ Hz, 2 H, H-3', H-5'); 7.75 (dd, $J_{2',3'} = 8.9$ Hz, $J_{2',F} = 5.4$ Hz, 2 H, H-2', H-6').

References

- 1. P. T. Gallagher, J. L. Palmer, and S. E. Morgan, J. Chem. Soc., Perkin Trans. 1, 1990, 11, 3212.
- B. L. Bray, P. H. Mathies, R. Naef, D. R.Solas, T. T. Tidwell, D. R. Artis, and J. M. Muchowaski, J. Org. Chem., 1990, 55, 6317.

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