A New Preparation of Iodoferrocene†

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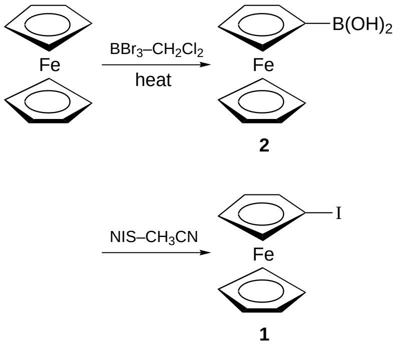
A new synthesis of iodoferrocene *via* ferroceneboronic acid is reported.

Ferrocenes have in recent years gained increasing interest as building blocks for molecular magnets,[1] biosensors[2] or catalysts.[3] Iodoferrocene (**1**) is one of the very useful building blocks for ferrocene chemistry.[4–10] Recently two new methods for the synthesis of **1** were reported,[11,12] both involving lithiation of ferrocene followed by reaction with tributyltin chloride to give a mixture of mono- and bis-tributylstanylferrocene, which had to be separated prior to reaction with iodine or iodine chloride to give **1**. However, these procedures constituted a considerable improvement over the previously reported methods,[13] which include the reaction of ferrocenemercurio compounds with *N*-iodosuccinimide.[14]

The present method, which is shown in Scheme 1, takes advantage of the well known reaction between ferrocene and boron tribromide,[15] which gives ferroceneboronic acid (**2**) after aqueous work-up. Reaction with *N*-iodosuccinimide in acetonitrile is mild and gives **1** in 63% yield. The traditional solvent for the boronation reaction, carbon disulfide, could conveniently be replaced with CH_2Cl_2. We found however, that no reaction occurred if $CHCl_3$ were used as solvent.



Scheme 1

Experimental

Ferroceneboronic Acid (**2**).—Boron tribromide (25 g, 0.1 mol) was added at room temperature to a stirred solution of ferrocene (16.6 g, 89 mmol) in dry CH_2Cl_2 (150 ml). The mixture was heated under reflux for 24 h under argon, cooled to 0 °C and poured into 2 M NaOH (100 ml). The CH_2Cl_2 layer was discarded, the alkaline aqueous layer was washed with diethyl ether (4 × 100 ml) and acidified at 0 °C with 2 M HCl. The yellow-orange precipitate was filtered off, washed with water and air-dried to give ferroceneboronic acid (**2**) (7.8 g, 38%), δ_H (400 MHz; $CDCl_3$) 4.68 (m, 2 H), 4.56 (m, 2 H), 4.18 (m, 5 H) and 1.53 (s, 2 H).

Iodoferrocene (**1**).—To a solution of **2** (0.230 g, 1.0 mmol) in dry acetonitrile (15 ml) was added *N*-iodosuccinimide (0.270 g, 1.2 mmol). After stirring had continued for 20 h at room temperature, the mixture was extracted with hexane (3 × 50 ml). The hexane extract was washed with aqueous $Na_2S_2O_5$ (2 × 30 ml) and water (2 × 50 ml) and finally dried over $MgSO_4$. Concentration *in vacuo* gave an orange-brown oil that was purified by flash-chromatography on silica gel 60 (0.040–0.063 mm) with hexane to give pure iodoferrocene (**1**) (0.197 g, 63% yield). A sample crystallized from methanol–water had mp 48–49 °C (lit.,[16] 49–49.5 °C; lit.,[17] 44–45 °C); m/z (EI) 312 (M^+); δ_H (250 MHz, $CDCl_3$) 4.40 (m, 2 H), 4.18 (s, 5 H) and 4.15 (m, 2 H).

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References

1 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385.
2 P. N. Bartlett, P. Tebbut and R. G. Whitaker, *Prog. React. Kinet.*, 1991, **16**, 55.
3 K.-S. Gan, T. S. A. Hor, T. Hayashi, Y. Butsugan, S. Araki and M. Watanabe, in *Ferrocenes*, ed. A. Togni and T. Hayashi, VCH, Weinheim, 1995, pp. 3-169.
4 J. T. Lin, S.-S. Sun, J. J. Wung, L. Lee, K.-J. Lin and Y. Fong, *Inorg. Chem.*, 1995, **34**, 2323.
5 J. K. Pudelski amd M. R. Callstrom, *Organometallics*, 1994, **13**, 3095.
6 S. Akabori, M. Sato and S. Ebine, *Synthesis*, 1981, 278.
7 M. Sato, S. Ebine and S. Akabori, *Synthesis*, 1981, 472.
8 E. W. Neuse and L. Bednarik, *Macromolecules*, 1979, **12**, 187.
9 P. V. Rolling and M. D. Rausch, *J. Organomet. Chem.*, 1977, **141**, 195.
10 A. Kasahara, T. Izumi and M. Maemura, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1021.
11 I. R. Butler, S. B. Wilkes, S. J. McDonald, L. Hobson, A. Taralp and C. P. Wilde, *Polyhedron*, 1993, **12**, 129.
12 D. Guillaneux and H. B. Kagan, *J. Org. Chem.*, 1995, **60**, 2502.
13 S. B. Wilkes, personal communication.
14 R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 1954, **30**, 1253.
15 R. Epton, G. Marr and G. K. Rogers, *J. Organomet. Chem.*, 1978, **150**, 93.
16 M. D. Rausch, *J. Org. Chem.*, 1961, **26**, 1802.
17 A. N. Mesmeyanov, G. E. Perelova and O. A. Nesmeyanova, *Dokl. Akad. Nauk. SSSR*, 1955, **100**, 1099.

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