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Preliminary communication

The synthesis of fluoroferrocene

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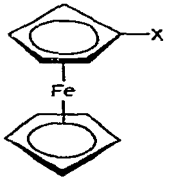
The haloferrocenes have been the subject of considerable interest from both a theoretical and synthetic standpoint in recent years. To date, however, only haloferrocenes containing chlorine, bromine and iodine have been synthesized. Although excellent preparative routes to the monohalo compounds, chloroferrocene (Ib)[1], bromoferrocene (Ic)[2], and iodoferrocene (Id)[2], are available, no fluorine-containing ferrocene has been described in the literature. We now wish to report the preparation of fluoroferrocene (Ia), the first ferrocene derivative containing a fluorine atom directly attached to a ferrocene ring.



(Ia, X = F
Ib, X = Cl
Ic, X = Br
Id, X = I)

A recent publication describes the reaction of a number of organometallic compounds containing lithium and magnesium with perchloryl fluoride to give the corresponding organofluorine derivatives[3]. We have found this reaction also to be applicable to ferrocenyllithium, in spite of the sensitivity of the ferrocene system to oxidants possessing the strength of perchloryl fluoride.

A solution of lithioferrocene (0.01 moles) in ether (125 ml), prepared under a helium atmosphere from bromoferrocene* (0.0100 mole) and n-butyllithium (0.011 mole) according to the procedure recently described by us[4], was cooled to −70° and diluted with 250 ml of dry tetrahydrofuran. When a mixture of perchloryl fluoride (0.040 mole) and helium was bubbled in, the reaction mixture changed from an orange suspension to a deep red solution. While the solution was warmed to 23°, the excess perchloryl fluoride was removed by vigorously bubbling helium through the reaction mixture. Workup consisted of reduction of the mixture by an aqueous solution of sodium thiosulfate, removal of solvent from the organic layer, and column chromatography on alumina. Elution of the column

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*Chloroferrocene was prepared by the procedure reported in ref. 1 while bromo- and iodoferrocene were obtained by the procedures described in ref. 2.

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with hexane afforded 0.20 g (10%) of crude fluoroferrocene, m.p. 113–116°, whose GLPC showed a single peak of slightly longer retention time than ferrocene. Low temperature recrystallization of the crude compound from methanol gave orange crystals, m.p. 116–118°. Elemental analysis and high resolution mass spectral measurement, together with the NMR results reported below provided the structural proof for the compound. (Found: C, 59.05; H, 4.51; F, 9.06; Fe, 27.17%; mol. wt., 204.0041. $C_{10}H_9FFe$ calcd.: C, 58.86; H, 4.44; F, 9.31; Fe, 27.37%; mol. wt. 204.0037.)

RESULTS AND DISCUSSION

While the yield of fluoroferrocene obtained from the reaction was quite low, it is quite possible that this could be raised, since no attempts were made at optimization of reaction conditions. Although some authors have reported the formation of perchlorylbenzene upon reaction of phenyllithium with perchloryl fluoride[5], we found no evidence of any perchlorylferrocene present in the reaction product. Further elution of the chromatographic column with more polar solvents after removal of fluoroferrocene afforded traces of two unidentified substances with nominal masses of 262 and 274, followed by a dark red, polymeric material, possible the product of oxidative decomposition.

The mass spectral fragmentation pattern of fluoroferrocene showed a loss of HF from the molecular ion peak. By comparison, an analogous loss of HCl from chloroferrocene (Ib) and of HBr from bromoferrocene (Ic) was observed in their mass spectra. Iodoferrocene (Id), however, gave an $M^+ I^-$ peak as the primary fragment of its mass spectrum. There are obviously many other comparisons of Ia with Ib–Id which can be made. Our primary interest in Ia is to determine whether its reaction with n-butyllithium involves α-proton abstraction, as occurs with Ib[4], or metal–halogen exchange, as occurs with Ic and Id[4]. The former reaction pathway is desired, since this will make possible the synthesis of perfluoroferrocene, by a route analogous to our recently reported synthesis of perchloroferrocene.

The infrared spectrum of Ia was quite complex in the region usually assigned to C–F stretch, and we were unable to assign a peak to this mode.

The ^{19}F NMR spectrum of Ia consisted of a multiplet centered at 189.3 ppm (all NMR values were obtained in deuterochloroform and are reported as ppm from TMS as internal standard). The ^1H NMR results were consistent with the trends observed in the

TABLE 1

NMR ABSORBANCES OF MONOHALOFERROCENES

	Ia	Ib	Ic	Id
α-protons	4.29	4.35	4.41	4.43
β-protons	3.78	3.98	4.07	4.17
Unsubstituted ring protons	4.26	4.23	4.20	4.17

NMR spectra of the other monohaloferrocenes (Ib–Id). Table 1 shows the results obtained for Ia with the corresponding results obtained for chloroferrocene (Ib), bromoferrocene (Ic), and iodoferrocene (Id), given for comparison*:

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*The assignment of the multiplet upfield from the substituted ring to the β-protons and the multiplet downfield from the substituted ring to the α-protons was demonstrated unequivocally for chloroferrocene recently[7].