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FUNDAMENTAL STUDIES OF SUBSTITUTED FERROCENE SYSTEMS. I. ELECTRONIC EFFECTS OF ELECTRON DONATING GROUPS ON THE FERROCENE SYSTEM[1]

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Pmr spectroscopy has been extensively used in the estimation of electronic effects in metallocene ring systems.[2] For the ferrocene ring system, sufficient data are available including study of deuterium-labeled compounds[3e] to establish unequivocally the strong deshielding effect at the 2,5-positions of substituents containing a carbonyl and other anisotropic groups bonded to the ring.[3] However, substituent effects in the pmr spectra of other types of mono-substituted ferrocenes (particularly those containing electron-donating substituents) have never been rendered secure by the use of deuterium-labeled compounds. A previous report where such assignments were made on other grounds is shown below to be in error.[4]

In this communication we wish to report the syntheses of 2-deuteroaminoferrocene (2), as well as its correspondingly deuterated benzylurethane(3). The $-NH_2$ group in amine 2 serves as a prototype of a strong electron-donating substituent, while the $-NHCO_2Bz$ group in urethane 3 serves as a prototype of a moderate electron-donating substituent. Utilizing a procedure entirely analogous to that used for the lithiation of N-substituted benzene carboxamides,[5] N-phenylferrocenecarboxamide (4)was lithiated with n-butyllithium and hydrolyzed with D_2O.[6] An nmr spectrum of the product revealed the downfield 2-proton triplet of 4 was significantly attenuated. This absorption was assigned to the 2,5-position protons in analogy to the assignment for ferrocenecarboxaldehyde[3e], and to the known fact that directed lithiation takes place at position 2 of such carboxamides[5,6,7]. The deuterium contents of the 2- and 1' positions* were determined by

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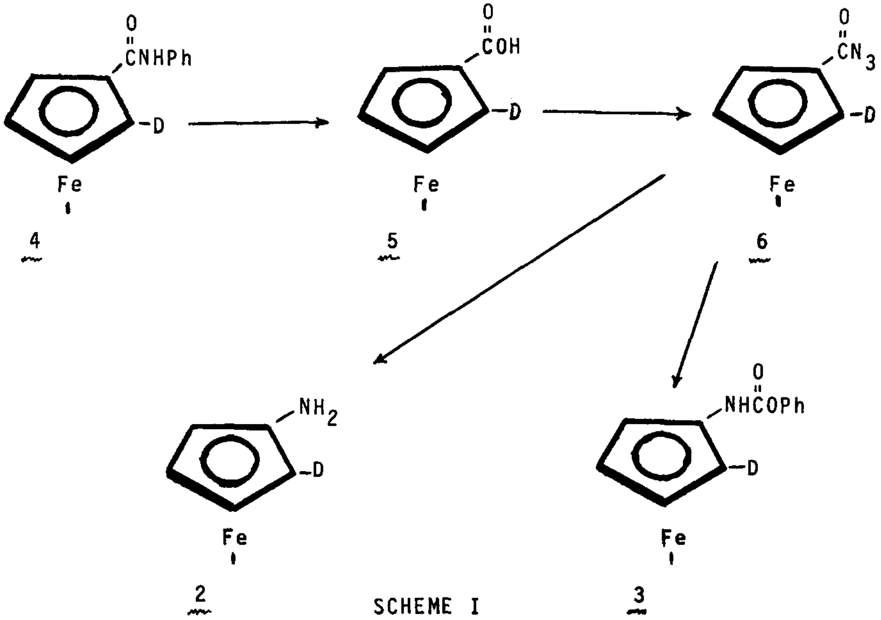
*The fact that 1'-metalation also occurs in this system does not in any way affect our conclusions pmr analysis and were 1.2 and 0.8 deuteriums, respectively. Hydrolysis of the carboxamide 4 to give the deuterated ferrocene carboxylic acid 5 could be achieved only under highly alkaline conditions.[8] Although the deuterium content decreased slightly during the procedure illustrated in Scheme I, the deuterium content at the 2-position could not have changed sufficiently to bring question to our conclusions. Using a modified Curtius rearrangement procedure,[9] the acid 5 was transformed into the 2-deutero amine (3). The pmr spectra of the acid (5), the acid azide (6) and the amine (2) each indicated essentially identical deuterium content at the 2-position. Analysis of these three compounds illustrated the fact that the total deuterium content of these molecules remained unchanged during the rearrangement. In addition, the acid azide (6) was rearranged in the presence of benzyl alcohol to give the benzylurethane (3).

The pmr spectra of both the amine (2) and urethane (3) unequivocally indicate that the 2-position is the less shielded position in the substituted ring of these compounds. Pmr spectra in $CDCl_3$ of 2-D-aminoferrocene(2) and its benzyl urethane derivative(3) were run on a Varian model HR-220 spectrometer. Chemical shift assignments for (2) are: 3,4-position protons, 3.88 ppm, 2,5-position protons(attenuated), 4.02 ppm and 1'- position protons 4.10 ppm. Chemical shift assignments for (3) are: 3,4 -position protons, 3.98 ppm, 1'-position protons, 4.10 ppm and 2,5-position protons (attenuated), 4.47 ppm. This assignment is a direct reversal of the assignment made by Gubin and co-workers[4] based on analogy to the pmr spectrum of aniline, and illustrates the danger of analogies between benzenoid and metallocene-type aromatic compounds. The ferrocene molecule is thus revealed as an aromatic system whose response to an electron withdrawing substituent is principally at the 2,5-positions, but whose response to an electron donating system is principally manifested at the 3,4-positions.



SCHEME I

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