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FUNDAMENTAL STUDIES OF SUBSTITUTED FERROCENE SYSTEMS III.*

STEREOCHEMISTRY OF THE DIASTEROMERIC 2,2'-BIS(DIMETHYLAMINOMETHYL) BIFERROCENYLS

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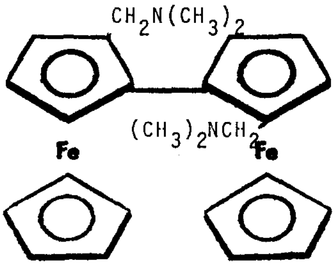
In a recent paper, Marr, Moore and Rockett[1] reported the synthesis of both possible diastereoisomers of 2,2'-bis(dimethylaminomethyl)biferrocenyls. To the higher melting isomer, m.p. 203-205.5°, was assigned the unsymmetric configuration and to the lower melting isomer, m.p. 103-105.5°, the centrosymmetric configuration. Later these workers cited[2] reversal of the assignments, the experimental evidence for which has now been published by Schlögl and Waiser.[3]



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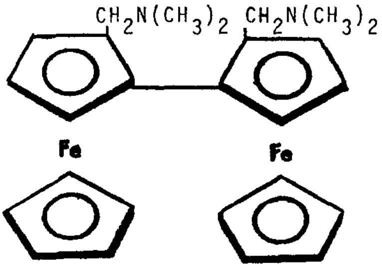

II

We were interested in a method of determining the structures of these two diastereomeric dimers unequivocally. Resolution did not offer an acceptable distinction in this case since exhibition of atropisomerism by the symmetric compound II was a possibility. Only two other methods of doing this appeared feasible; (1) an X-ray determination of (2) synthesis of these compounds via a stereospecific route from optically active precursors. If an optically active

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*For Part II, cf D. S. Slocum, S. P. Tucker and T. R. Engelmann, Tetrahedron Letters, 621 (1970).

(but not optically pure) 1,2-disubstituted ferrocene were allowed to dimerize, both the symmetric and asymmetric diastereomers would be formed, but the only optically active product would be the asymmetric dimer (unless atropisomerism in biferrocenyls could be demonstrated). Since it also offered the opportunity to study an aryl coupling reaction taking place at a site essential to the optical activity of both the precursor and the product, the latter alternative was chosen.

2-Dimethylaminomethylferroceneboronic acid was prepared by the method of the original authors.[1] The amino acid was dissolved in a minimum volume of acetone and added to an equimolar quantity of (+)-tartaric acid, also dissolved in acetone. A light yellow precipitate of the tartrate-amine salts immediately appeared. The salts were not isolated; rather the diastereomeric mixture was separated in a Soxhlet extractor by virtue of the different solubilities in acetone. Recovery of the amino acids was accomplished by hydrolysis with dilute aqueous NaOH. In a typical run, the yield of optically active boronic acid, $\alpha^{25}_{\mathrm{Hg}}$ (EtOH) = -110°, m. 150-162°, was 10%. The boronic acid thereby obtained could be optically enriched by recrystallization from chloroform/petroleum ether, the mother liquor containing boronic acid being of higher optical purity than the crystals.

Dimethylaminomethylferroceneboronic acid, $[\alpha]^{25}_{\mathrm{Hg}}$(ether)-165° (optical purity unknown) was converted to a mixture of dimers I and II by treatment with aqueous cupric acetate for one hour. Both the higher melting and lower melting dimer were isolated. The data for the optically inactive isomer was identical in every respect to the data reported for the centrosymmetric isomer, thus substantiating the revised assignment of both Rockett et al[2] and Schlögl and Waiser[3] and reversing the original assignment.[1] The other isomer possessed an nmr spectrum which duplicated the nmr data reported for the lower melting isomer, i.e., it contained a singlet for the methylene protons, but was an oil rather than a crystalline solid, and demonstrated $[\alpha]^{25}_{\mathrm{Hg}}$(EtOH)-842°.

Clearly, isomer I, which exhibits a singlet for the methylene protons in its nmr spectrum and is optically active is the asymmetric (R,R or S,S) isomer;

isomer II, which exhibits an AB quartet for its methylene protons and is optically inactive is the symmetric R,S isomer. This work also demonstrates the first example of a coupling reaction involving asymmetric ferrocenes, a phenomenon possible only because of the novel stereochemistry of these molecules.

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2. G. Marr, R. E. Moore and B. W. Rockett, Tetrahedron, 25, 3477 (1969).
3. K. Schlögl and M. Waiser, Monatshefte für Chemie, 100, 1515 (1969).