CHEMISTRY LETTERS, pp. 743-744, 1977. Published by the Chemical Society of Japan

TETRABRIDGED FERROCENOPHANES AND A PRECURSOR OF PERFERROCENOPHANE[1]

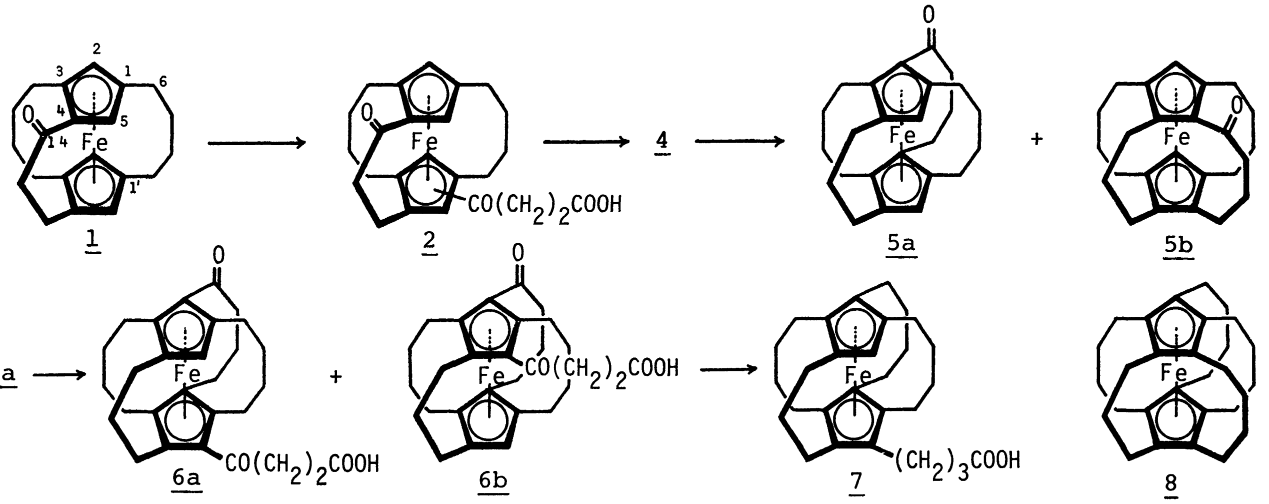
Masao HISATOME, Naoyuki WATANABE, and Koji YAMAKAWA
Faculty of Pharmaceutical Sciences, Science University of Tokyo,
Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162

[4][4][4][3]Ferrocenophanes (5a and 5b), tetrabridged ferrocenophanes, have been synthesized *via* lactic acid derivatives of [4][4][3]ferrocenophanes. A precursor of perferrocenophane, 5-(3-carboxypropyl)[4][4][4][3]ferrocenophane (7), has been derived from 5a.

Perferrocenophanes are very interesting as a new type of cage compounds containing a metal at the center of the molecule. The pentabridged ferrocenophanes are so distinct from empty [4.4.4.4.4.4](1,2,3,4,5,6)cyclophane synthesized by Stephens[2] that it need to be synthesized by stepwise additional bridging. Preparations of tribridged ferrocenophanes have been reported by three groups.[3] An attempt to synthesize tetrabridged ferrocenophane was described,[3a] and the evidence that it was a homoannular cyclization product was provided by Bublitz and Rinehart.[4] We wish to report the first synthesis of tetrabridged ferrocenophanes and its derivation to a precursor of perferrocenophane.

The Friedel-Crafts reaction of deoxo derivative of [4](1,1')[4](3,3')[3](4,4')-ferrocenophan-14-one[3c,5,6] (1) with succinic anhydride and $AlCl_3$ in CH_2Cl_2 afforded a complex mixture of unknown products in a low yield. However, the same reaction of the ketone 1 (r.t., 14 hr) gave 2'- and 5'-acylated [4][4][3]ferrocenophanes (2a and 2b) in a total yield of 87%. The 2'-isomer (2a) was isolated by fractional crystallization from benzene. [2a: orange-red prisms, mp 204-205.5°C; MS: Observed M^+, 448.1346. $C_{25}H_{28}O_4Fe$ requires 448.1335; IR (KBr) cm^{-1}: $\nu_{c=o}$ 1712, 1678, and 1660.] The 5'-isomer (2b) could not be isolated. Methyl esters of the crude mixture of 2a and 2b were separated into 2'- and 5'-isomers (3a and 3b, in 3:1 ratio) by column chromatography on silica gel. The mixture of 2a and 2b was reduced with H_2/PtO_2 in AcOH (4.8 atm, 4 days, r.t.) to give a mixture of isomeric carboxylic acids (4a and 4b), yellow crystals, mp 130-150°C. [4; MS: Observed M^+, 420.1752. $C_{25}H_{32}O_2Fe$ requires 420.1750; IR (KBr) cm^{-1}: $\nu_{c=o}$ 1705.] Further purification of 4 and separation into two isomers could not be carried out, because they were very sensitive to oxygen in solution.

The crude product (4a and 4b) was treated with ethyl chlorocarbonate and equimolar triethylamine in dry CH_2Cl_2 below 0°C under an N_2 atmosphere and stirred at 0°C for 30 min. Under the degassed condition, $AlCl_3$ was added to the above solution. The reaction mixture (0°C, 1 hr) was worked-up, and then separated into two isomeric cyclization products by preparative TLC on silica gel. In the FT-PMR spectra of the two products, the ring proton signals appeared only as two singlets. Therefore, the compounds were heteroannularly linked with four carbon chains. The tetrabridged



ferrocenophanes 5a (deep red prisms, mp 183-185°C) and 5b (orange-red prisms, decomp. above 165°C) were assigned to [4](1,1')[4](2,2')[4](3,3')[3](4,4')ferrocenophan-10-one and [4](1,1')[4](3,3')[3](4,4')[4](5,5')ferrocenophan-17-one, respectively, by comparing their yields (5a: 11%, 5b: 2.4%) with the isomer ratio of the precursor and the chemical shifts of their ring protons. [5a; MS: Observed M^+, 402.1642. $C_{25}H_{30}OFe$ requires 402.1644; IR (KBr) cm^{-1}: $\nu_{C=O}$ 1657; FT-PMR ($CDCl_3$) δ: 3.42 (1H, s, 5'-H), 4.27 (1H, s, 5-H). 5b; MS: Observed M^+, 402.1617. $C_{25}H_{30}OFe$ requires 402.1644; IR (KBr) cm^{-1}: $\nu_{C=O}$ 1659; FT-PMR ($CDCl_3$) δ: 3.80 (1H, s, 2'-H), 4.56 (1H, s, 2-H).]

The Friedel-Crafts reaction of 5a with succinic anhydride-$AlCl_3$ (0°C, 2 hr, N_2 gas) gave 5'- and 5-acylated [4][4][4][3]ferrocenophanes (6a and 6b) in 77 and 19% yields. [6a: red crystals, mp 90-92°C; MS: Observed M^+, 502.1825. $C_{29}H_{34}O_4Fe$ requires 502.1804; IR (KBr) cm^{-1}: $\nu_{C=O}$ 1710, 1675, and 1660; PMR ($CDCl_3$) δ: 4.16 (1H, s, 5-H). 6b: red crystals, decomp. above 200°C; MS: Observed M^+, 502.1775. $C_{29}H_{34}O_4Fe$ requires 502.1804; IR (KBr) cm^{-1}: $\nu_{C=O}$ 1740, 1662, and 1622; PMR ($CDCl_3$) δ: 3.22 (1H, s, 5'-H).] The two isomers 6a and 6b were converted to an identical product (7) by hydrogenation with H_2/PtO_2 in AcOH (2.8 atm, 40 hr, r.t.). [7: yellow crystals, decomp. above 162°C; MS: Observed M^+, 474.2227. $C_{29}H_{38}O_2Fe$ requires 474.2220; IR (KBr) cm^{-1}: $\nu_{C=O}$ 1722; PMR ($CDCl_3$) δ: 3.95 (1H, s, 5-H), 9.25 (1H, bs, COOH).]

Cyclization of 7 by treatment with ClCOOEt-Et_3N and then with $AlCl_3$ to form the last bridge for synthesis of perferrocenophane (8) afforded a complex mixture of unknown products. Further experiments are in progress.

References and Notes

1 Organometallic Compounds XXVII. Part XXVI: M. Hisatome and K. Yamakawa, J. Organometal. Chem., in press.

2 R.D. Stephens, J. Org. Chem., 38, 2260 (1973).

3 a) K. Schlögl and M. Peterlik, Tetrahedron Lett., 573 (1962); b) K.L. Rinehart, D.E. Bublitz, and D.H. Gustafson, J. Am. Chem. Soc., 85, 970 (1963); c) M. Hisatome, N. Watanabe, T. Sakamoto, and K. Yamakawa, J. Organometal. Chem., 125, 79 (1977).

4 D.E. Bublitz and K.L. Rinehart, Tetrahedron Lett., 827 (1964).

5 Some attempts to prepare [4][4][4]ferrocenophane by elongation of the three-carbon bridge in 1 were unsuccessful. Therefore, 1 had to be used as the starting material for additional bridging.

6 The numbering system in the rings of the ferrocenophanes in this paper follows that of the starting material 1.

(Received April 26, 1977)