SHORT COMMUNICATIONS

The Synthesis of Glycidylferrocences

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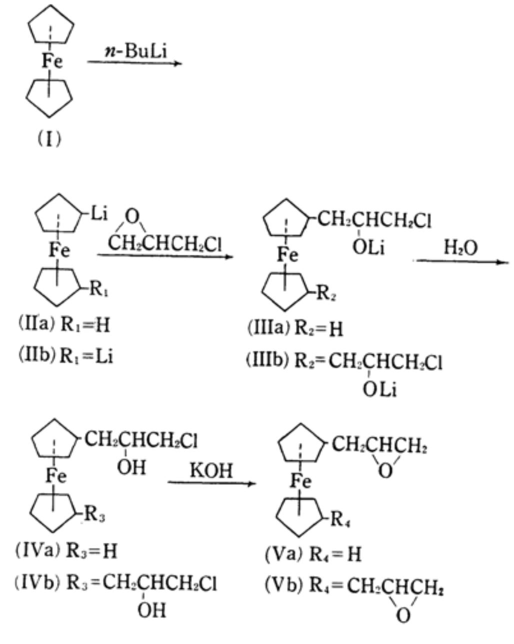
Since the discovery of ferrocene, a great number of its derivatives have been synthesized in studies of their chemical properties. However, only a few ferrocence derivatives have been reported which are available as monomers for polymerization to homopolymers in the presence of an adequate initiator.[1] Ketazine derivatives prepared by the present authors from diacetylferrocene and hydrazine have been shown to be novel polymers, the electric resistivities of which are near to those of organic semi-conductors.[2] Now we wish to report the synthesis of a new type of ferrocene derivatives, with one or two glycidyl substituents to provide promising monomers for the formation of a homopolymer. The sequence of the synthesis and the products of the reactions are as follows:



Ferrocene (I) was converted into the lithium derivative (IIa) by treatment with butyllithium

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[1] F. S. Arimoto and A. C. Haven, Jr., *J. Am. Chem. Soc.*, **77**, 6295 (1955); V. V. Korshak, S. L. Sosin and M. V. Chistyakova, *Vysokomolekularnye Soedineniya*, **1**, 937 (1959); *Chem. Abstr.*, **54**, 19451 (1960); V. V. Korshak, S. L. Sosin and B. P. Alekseeva, *Doklady Akad. Nauk S. S. S. R.*, **132**, 360 (1960); *Chem. Abstr.*, **54**, 20982 (1960).

[2] K. Hata, I. Motoyama and K. Azuma, unpublished, read before the 16th Annual Meeting of The Chemical Society of Japan, Tokyo, April, 1963.

in anhydrous ether under an atmosphere of nitrogen.[3] The suspension was cooled to ca. -50°C. in a dry ice—acetone bath, and the ethereal solution of epichlorohydrin was added slowly.[4] After the reaction was over, the reaction mixture was poured into ice water to hydrolyze the lithium compound IIIa. The ethereal layer was separated and evaporated to remove the ether. On concentration, a large quantity of unreacted ferrocene separated as orange crystals, which were then removed by filtration. The filtrate was further evaporated under reduced pressure to obtain crude chlorohydrin (IVa), which was submitted to vacuum distillation to obtain the pure substance, a very viscous liquid, dark red in color; b.p. 156～158°C/0.8～0.9 mmHg.

Found: C, 56.09; H, 5.33. Calcd. for $C_{13}H_{15}FeClO$: C, 56.05; H, 5.43%.

Glycidylferrocene (Va) was obtained by the epoxidation of the chlorohydrin (IVa) with alkali.[5] An ethanolic solution of the crude chlorohydrin was cooled in an ice water bath, and an aqueous solution of potassium hydroxide was added with vigorous stirring. After the reaction was over, a large quantity of water and ether was added, and the crude epoxide was obtained from the ethereal layer. The crude product was purified by vacuum distillation to a slightly viscous, dark red liquid; b.p. 111～115°C/0.1～0.2 mmHg, n_D^{20} 1.6093. The overall yield of Va was ca. 13% based on ferrocene.

Found: C, 64.41; H, 5.57. Calcd. for $C_{13}H_{14}FeO$: C, 64.50; H, 5.83%. Epoxy equivalent, 0.99 (HCl-dioxane method).

From the residue of the vacuum distillation of Va, a small quantity of diglycidylferrocene (Vb) was obtained. The purification of Vb was unsuccessful by simple vacuum distillation. The distillation residue was treated with a hydrochloric acid dioxane mixture to open the epoxide ring. The products were dissolved in benzene and chromatographed on alumina, followed by elution with the same solvent. The bischlorohydrin (IVb) thus obtained was reconverted into the epoxide (Vb) with potassium hydroxide in the manner described above. The crude epoxide was dissolved in benzene and purified by chromatography on alumina, using a mixture of benzene and ether (1 : 1 by volume) for elution. Pure diglycidylferrocene was obtained as a dark red liquid with a low viscosity. The yield of Vb was ca. 0.3% based on ferrocene.

Found: C, 64.40; H, 6.18. Calcd. for $C_{16}H_{18}FeO_2$: C, 64.45; H, 6.09%.

The chlorohydrins (IVa and IVb) and the epoxides (Va and Vb) were characterized by their infrared absorption spectra (liquid film). The characteristic absorption peaks for the epoxide group in Va and Vb were found at 3050 and 2970 cm^{-1} (ν_{C-H}) and at 1256, 960～900, and 845 cm^{-1} (the epoxy ring). The figures of the two chlorohydrins and of the two epoxides are essentially identical in each pair except for the lack of peaks at 1100 and 1000 cm^{-1} in the disubstituted compounds IVb and Vb, as has been pointed out by Rosenblum in disubstituted ferrocene derivatives.[6]

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[3] R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954); M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[4] H. Gilmann, B. Hofferth and J. B. Honeycutt, *J. Am. Chem. Soc.*, **74**, 1594 (1952).

[5] S. Winstein, T. L. Jacobs, G. B. Linden, D. Seymour, E. F. Levy, B. F. Day, J. H. Robson, R. B. Henderson and W. H. Florsheim, *J. Am. Chem. Soc.*, **68**, 1831 (1946).

[6] M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).