Journal of Organometallic Chemistry, 55 (1973) C82–C84
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Organometallic Compounds
XIV*. Formation of novel [4]ferrocenophanes by the acid-catalyzed reaction of 1,1′-bis(α-hydroxy-α-phenylethyl)ferrocene

MASAO HISATOME, SHIKŌ MINAGAWA and KOJI YAMAKAWA**

Faculty of Pharmaceutical Sciences, Science University of Tokyo, Shinjuku-ku, Tokyo, 162 (Japan)

(Received April 25th, 1973)

SUMMARY

The acid-catalyzed reaction of 1,1′-bis(α-hydroxy-α-phenylethyl)ferrocene gave several [4] ferrocenophanes including a peroxide derivative. Their structures have been confirmed by spectrometric methods and from a study of their reaction behavior.

In a previous communication[1], we reported that the acid-catalyzed reaction of 1,1′-bis(α-hydroxyisopropyl)ferrocene gave [4]ferrocenophanes by intramolecular cyclization. The present communication describes the production of a peroxide derivative and several other novel derivatives of [4]ferrocenophane by treatment of 1,1′-bis(α-hydroxy-α-phenylethyl)ferrocene (I) (m.p. 134–135°) with acid.

The products obtained by vigorous stirring of a benzene solution of (I) (1.000 g) and 7*N* HCl were separated into a fraction (241 mg) soluble in ethyl acetate, and an insoluble crystalline product (II) (609 mg). Column chromatographic separation of the soluble fraction gave three [4]ferrocenophanes [(III), 49 mg; (IV), 7 mg; and (V), 26 mg] and 30 mg of unidentified products.

The IR (KBr) and ^{1}H NMR spectra*** of compound (IV) (m.p. 174–174.5°) possess characteristic ether bands at 960–1050 cm^{-1} (5 peaks) and methylene signals of a typical ABCD system at δ 2.0–2.9 ppm.

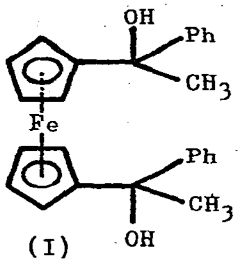
Reduction of (IV) with $LiAlH_4/AlCl_3$ gave compound (VI) [m.p. 82.5–83°, δ 1.8–2.8 (6H, m, CH_2), 3.70 ppm (1H, m, CH)], which was identical to the product obtained by reduction of compound (VII) with $LiAlH_4/AlCl_3$. The ferrocenophane (VII)

---

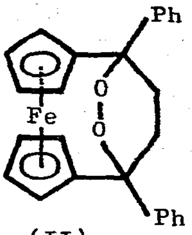
* For part XIII see ref. 5.

** Author to whom correspondence should be addressed.

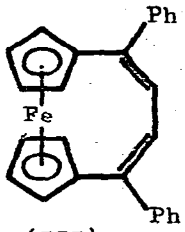
*** All ^{1}H NMR spectra were measured at 100 MHz in $CDCl_3$ unless otherwise stated.



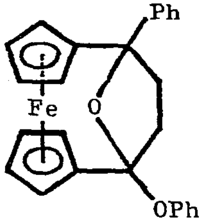
(I)



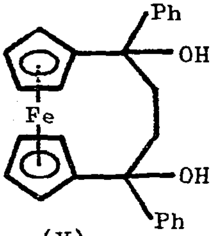
(II)



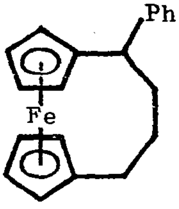
(III)



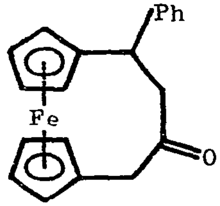
(IV)



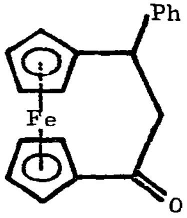
(V)



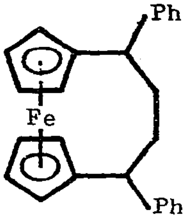
(VI)



(VII)



(VIII)



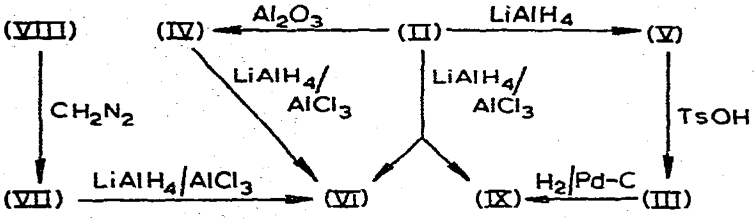
(IX)

(m.p. 162.5–163°) was prepared by treating 6-phenyl-8-oxo[3]ferrocenophane (VIII)[2] with diazomethane. The spectra of compound (V) (m.p. 168–169°) indicated OH bands at 3505 and 3385 cm^{-1}, and a methylene signal at δ 2.62 ppm (4H, s). Compound (III) (m.p. 220.5–221.5°) which had a vinyl proton signal at δ 6.11 ppm (2H, s), was also obtained by dehydration of the diol (V) with *p*-toluenesulfonic acid, and it was converted into compound (IX) [m.p. 155–160°, a mixture of *trans* and *cis* isomers in a 2/1 ratio; *trans*, δ 3.56 ppm (m, CH); and *cis*, δ 3.80 ppm (m, CH) in CS_2] on catalytic reduction. The molecular ion peak was apparent in the mass spectrum of each compound described above.

The insoluble crystalline compound (II) [m.p. 164.5–165.5°, δ 2.64 ppm (4H, s)] had a composition of $C_{26}H_{22}O_2Fe$ according to the elemental analysis and mass spectrum [m/e: 422, M^+; 406, $(M{-}O)^+$; 394, $(M{-}C_2H_4)^+$; 390, $(M{-}O_2)^+$; 388, $(M{-}H_2O_2)^+$]. Treatment of (II) with alumina gave the ether (IV), a rearrangement product. It has been reported[3] that the same rearrangement reaction occurred in the thermal decomposition of 9,10-epidioxyanthracene derivatives in alkylbenzene with formation of two ether bonds.

Furthermore, (II) was converted into either (V) or a 1/6 mixture of (VI) and (IX) on reduction with $LiAlH_4$ or $LiAlH_4/AlCl_3$, respectively. The reduction product (IX) (m.p. 176–177°) consisted only of *cis* isomer in analogy with the products of the reduction of peroxides of anthracene[3,4]. The reaction behavior of (II) (Scheme) suggests that the peroxide (II) is initially formed in the present acid-catalyzed reaction and that it is then converted into compounds (III)–(V).

Scheme



REFERENCES

1 M. Hisatome and K. Yamakawa, *J. Chem. Soc., Chem. Commun.*, (1973) 199.
2 J.W. Huffman and R.L. Asbury, *J. Org. Chem.*, 30 (1965) 3941.
3 P.F. Southern and W.A. Waters, *J. Chem. Soc.*, (1960) 4340.
4 J. Rigaudy, *Pure Appl. Chem.*, 16 (1968) 169.
5 K. Yamakawa and M. Moroe, *J. Organometal. Chem.*, 50 (1973) C43.