Intramolecular Cyclization Reaction of 1,1′-Bis-(α-hydroxyisopropyl)ferrocene

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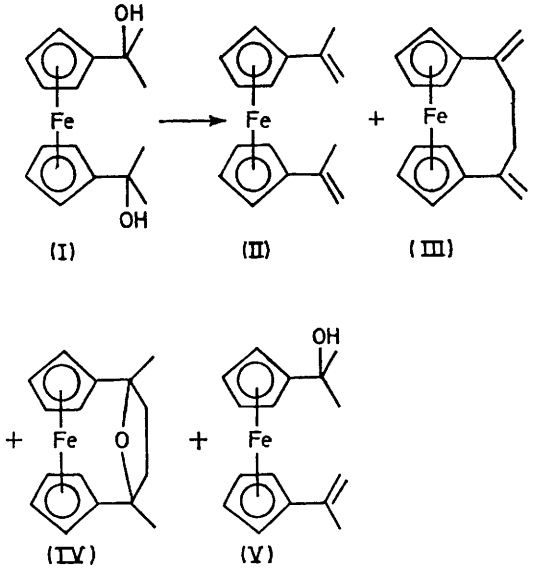
Summary Treatment of 1,1′-bis-(α-hydroxyisopropyl)ferrocene (I) with acid gave the novel [4]ferrocenophanes (III) and (IV) together with the vinyl derivatives (II) and (V); reduction of (III) and (IV) afforded *cis*- and *trans*-6,9-dimethyl[4]ferrocenophane, which was also synthesized from (VII) by an alternative route.

THE reaction of ferrocene derivatives through stable carbonium ions, carbenes, and radicals has been studied recently.[1] We reported[2] that treatment of 1,1′-bis-(α-hydroxyalkyl)ferrocenes with acid initially formed stable α-hydroxyalkyl-α′-ferrocenylcarbonium ions as intermediates and then gave 7-oxa[3]ferrocenophanes by intramolecular cyclization. On the other hand, Pittman[3] reported that 1,1′-bis-(α-hydroxyisopropyl)ferrocene (I) in magic acid (FSO_3H-SbF_5) had the ^1H n.m.r. signals of a dication. The product expected from the intermediate is 1,1′-bis-(α-methylvinyl)ferrocene (II).

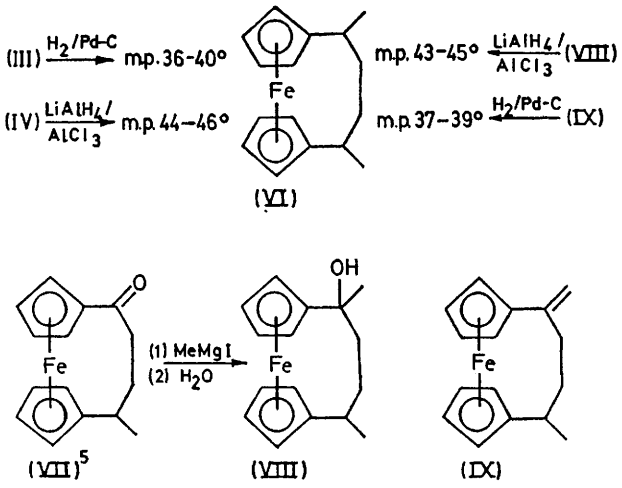
However, we found that treatment of (I) with 3—6N-HCl in benzene gave the novel [4]ferrocenophanes (III) and (IV) together with the vinyl derivatives (II) and (V). Typical results are given in the Table. Ascorbic acid and O_2 gas were added to make the conditions either oxidising or reducing.

TABLE

Conditions	Reaction time (*t*/min)	Products (%) (II)	(III)	(IV)	(V)
3N-HCl	30	10	—	15	—
4N-HCl	5	34	—	6	32
6N-HCl	30	—	6	16	—
3N-HCl+ascorbic acid ..	30	31	—	—	—
6N-HCl + O_2	7	—	3	3	—



The reaction products were separated by column chromatography into four compounds; red plates, m.p. 59—61° (II, lit.[4] m.p. 58—59°), yellow needles, m.p. 123—124° (III), orange yellow needles, m.p. 137—138° (IV), and a red oil (V). The oil was shown to be (V) from its ^1H n.m.r. and i.r. spectra [δ 1·49(s, Me), 2·06(m, :CMe), 4·89 and 5·20 (complex AB system, $:CH_2$), ν_{OH} 3550 and 3450 cm^{-1}, $\nu_{C=C}$ 1613 cm^{-1}]. Compound (III) showed $\nu_{C=C}$ bands (1613 and 1628 cm^{-1}), and methylene [δ 2·55(4H, s)] and terminal methylene signals [δ 4·87 and 5·03 (4H, AB system)].



Compound (IV) had a C–O–C [ν_{C-C-C} 1020—1110 cm^{-1} (four peaks)], two methyl [δ 1·62(s)], and two methylene groups [δ 1·75—2·45 (AA'BB' system)]. The high-resolution mass spectrum of (IV) gave M^+ = 282·0706 ($C_{16}H_{18}OFe$: 282·0706). Compounds (III) and (IV) were both converted into 6,9-dimethyl[4]ferrocenophane (VI) on reduction with H_2/Pd-C and $LiAlH_4$–$AlCl_3$, respectively. Compound (VI) was also synthesized by an alternative route: Grignard reaction of (VII)[5] with MeMgI gave two compounds, (VIII) (oil) and (IX) (m.p. 73·5—75°), which were reduced with $LiAlH_4$–$AlCl_3$ and H_2/Pd-C, respectively, to give (VI). The reduction product of (IV) [δ 1·04(6H, d, Me), 2·33(2H, m, CH)] is assigned the *cis* configuration from the way in which it reacted, while the products from (III), (VIII), and (IX) are considered to be mixtures of *cis* and *trans* isomers from their ^1H n.m.r. spectra [δ 1·04 (d, Me) and 1·11(d, Me), 2·33(m, CH) and 2·57(m, CH)].

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