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DISILANYL-SUBSTITUTED FERROCENES

Makoto Kumada, Koji Mimura, Mitsuo Ishikawa and Kyo Shiina
Department of Synthetic Chemistry, Kyoto University, Kyoto and
Department of Applied Chemistry, Osaka City University, Osaka,
Japan

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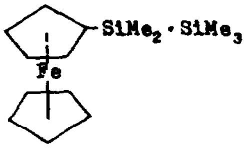
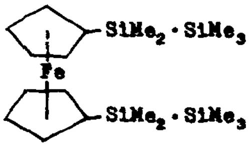
As part of a program concerned with the chemistry of organopolysilanes, it was of primary interest to us to prepare polysilyl-substituted ferrocenes and to study their chemical behavior. We report here the preparation and acid cleavage of the first two examples of disilanyl ferrocenes : pentamethyldisilanylferrocene (I) and 1,1'-bis(pentamethyldisilanyl)ferrocene (II).



I



II

Compound II was prepared through the following sequence of reactions.

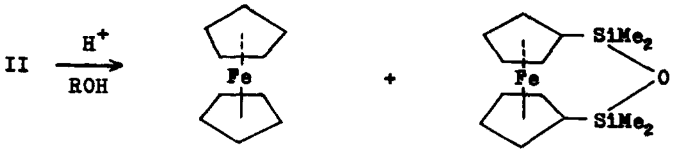
$$Me_3SiSiMe_2Cl \xrightarrow{C_5H_5MgBr} \underset{III}{Me_3SiSiMe_2C_5H_5} \xrightarrow[2)\ FeCl_2]{1)\ n\text{-}BuLi} II$$

The reaction between cyclopentadienylmagnesium bromide and pentamethylchlorodisilane (1) gave (cyclopentadienyl)pentamethyldisilane (III), b.p. 86°/22 mmHg., n_D^{20} 1.4913, d_4^{20} 0.8505, in 65 % yield (Anal. Calcd. for $C_{10}H_{20}Si_2$: C, 61.14; H, 10.26. Found : C, 60.95; H, 10.29). The metalation of III with n-butyllithium, followed by the reaction with ferrous chloride gave ferrocene-like orange-yellow crystals of compound II , m.p. 58.4°, in 65 % yield on the basis of unrecovered III (Anal. Calcd. for $C_{20}H_{38}FeSi_4$: C, 53.77; H, 8.57; mol.wt., 447. Found : C, 53.97; H, 8.55; mol.wt., 437).

Compound I was prepared in a similar way, except that an equimolar mixture of cyclopentadiene and compound III was metalated with n-butyllithium, followed by treatment with ferrous chloride. The reaction gave a mixture consisting of the three possible products, from which a gas-chromatographically homogeneous sample of compound I was isolated by a combination of repeated fractional sublimation *in vacuo* and fractional crystallization from methanol. The yield was 13 %. This compound is also an orange-yellow crystalline solid like ferrocene and, interestingly, has almost the same melting point as that of compound II, 58.0 – 59.6° (Anal. Calcd. for $C_{15}H_{24}FeSi_2$: C, 56.95; H, 7.65; mol.wt., 316. Found : C, 56.91; H, 7.76; mol.wt., 298).

In accordance with the statement by Rosenblum and Woodward (2) that ferrocene derivatives, in which at least one ring remains unsubstituted, exhibit absorption in the infrared spectrum near 9 or 10 μ, the infrared spectrum of compound I did have bands both at 9 and 10 μ, while that of compound II did not.

It was found that although both compounds I and II are very stable to the action of basic reagents, they are extremely sensitive to acid cleavage. Thus, refluxing compound II with 0.012 – 0.14 M sodium methoxide in methanol for several hours gave no appreciable reaction, but refluxing in extremely dilute methanolic or ethanolic solutions of hydrogen chloride for 2 hrs. caused almost complete cleavage to give two compounds: ferrocene and 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane (IV), m.p. 87 – 88° [reported (3) : 87 – 88°]. The relative yields of these two products, which were determined by gas chromatography, depended upon the acid concentration as illustrated in Fig. 1. The lower concentration of the acid favored the formation of 1,3-(1,1'-ferrocenylene)tetramethyldisiloxane, i.e., the selective cleavage of the silicon-silicon linkage.



IV

Compound I was also found to undergo a similar type of cleavage to that described above under nearly the same conditions. By gas chromatography, we were able to detect ferrocene, ethoxydimethylsilylferrocene (V), trimethylethoxysilane and hexamethyldisiloxane in the reaction product, and collect a small amount of a fairly pure sample of compound V, an orange-red liquid, for elemental analysis and spectroscopic study (Anal. Calcd. for $C_{14}H_{20}OFeSi$: C, 58.34; H, 6.99. Found : C, 57.95; H, 6.98). The

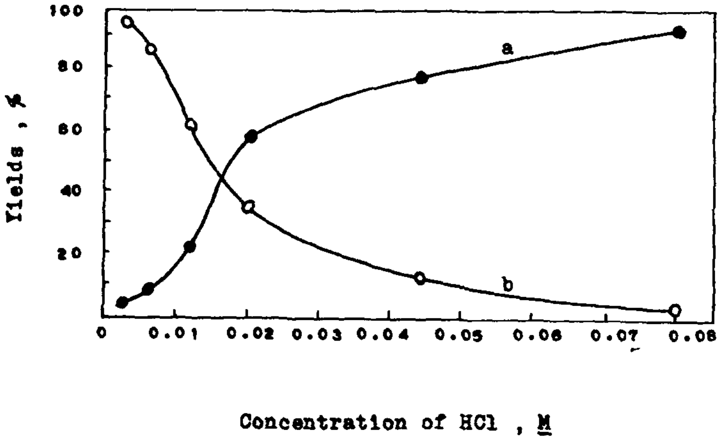
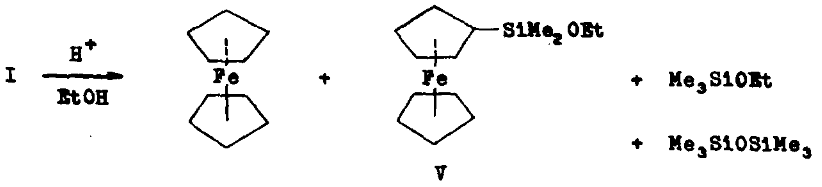


FIG. 1

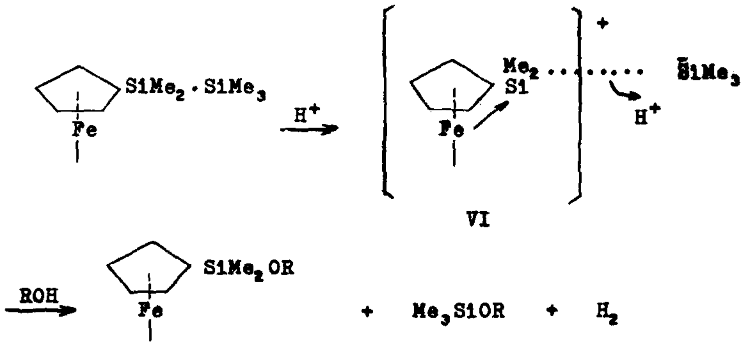
Yields of ferrocene (curve a) and 1,3-(1,1′-ferrocenylene)-tetramethyldisiloxane (curve b) *vs.* the concentration of HCl in methanol.

Yield of V was estimated to be 37 %, by gas chromatography, when compound I was heated to reflux for 1 hr. in a 0.001 *M* ethanolic solution of hydrogen chloride.



The cleavage reactions described here are the first examples of acid cleavage of the silicon-silicon bond in hexaorganodisilanes under mild conditions. Thus, we have recently demonstrated (4) that in phenylmethylpolysilanes, *e.g.*, PhMe$_2$Si·SiMe$_3$ and PhMe$_2$Si-SiMe$_2$·SiMe$_3$, only the phenyl-silicon bond undergoes cleavage by hydrogen chloride in chloroform in the presence of anhydrous aluminum chloride. We also find that cyclopentadienylpentamethyldisilane (III) under the same conditions as used for compounds I and II is mostly recovered unchanged. Only a small amount of cleavage occurs and this is at the cyclopentadienyl-silicon bond.

Apart from the detailed reaction mechanism, the unusual ease with which the silicon-silicon bond adjacent to a ferrocenyl group undergoes acid-catalyzed cleavage in alcohols may be explained by stabilization of the transition state, as symbolized by structure VI, which could result from overlap of filled *d*-orbitals of iron with the electron-deficient *p*-orbital of silicon. Stabilization of carbonium ions adjacent to a ferrocenyl group in a similar way has been proposed by Richards and Hill (5), and supported by many other authors (6).


VI

In order to learn more about the reaction scheme, further investigation is in progress.

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