Thermal Rearrangement of Organosilicon-bridged Ferrocenes

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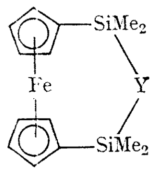
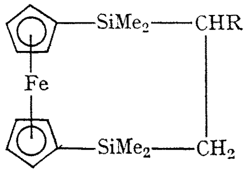
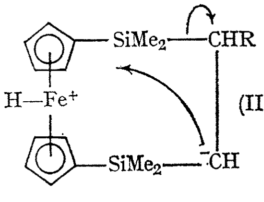
RECENTLY we found[1,2] that, in contrast to ferrocenes of type (I) which are stable at 340° for prolonged periods, 1,1′-bis-organosilyl and -organogermyl ferrocenes undergo intramolecular rearrangement to give equilibrium mixtures with the corresponding 1,3-isomers:



(I) Y = CH_2, O, $SiMe_2$



(II) R = H, Me



(III)

We report now that ferrocenes of type (II) undergo a further type of intramolecular rearrangement, *i.e.* bridge contraction to give three-membered bridged ferrocenes, at high temperatures.

The ferrocene (II; R = H) gave (I; Y = CHMe) (>80%), when heated in a sealed tube at 380° for 500 hr. while a similar thermolysis of (II; R = Me) gave a considerable amount (*ca.* 60%) of nonvolatile material. From the volatile products, however, (I; Y = CHEt) and (I; Y = CH_2) were obtained as the main products, together with small amounts of (I; Y = CMe_2) and other products. The identity of the products was confirmed by their independent synthesis (*i.e.* reaction of 1,1′-dilithioferrocene with an appropriate chlorosilane) as well as elemental analysis and i.r. and ^1H n.m.r. spectroscopy. Further, it was shown that the ferrocene (I; Y = CHEt) can be converted into (I; R = CH_2) in a high yield under similar conditions.

The formation of (I; R = CHEt) and (I; R = CH_2), in preference to (I; R = CMe_2), in the thermolysis of (II; R = Me) suggests a possible mechanism for the rearrangement which involves initial migration of a hydrogen atom, as a proton, from a methylene carbon of the bridge onto an iron nonbonding *d*-orbital, thus leaving a carbanion. This then attacks the vicinal silicon atom to give rise to bridge contraction, which leads to a more stable three-membered bridged structure, as shown by (III). Finally, the proton becomes bonded to the carbanion now generated. The protonation of the metal atom of ferrocene is considered to be a key step and to play twofold roles: first, generation of the carbanion, and second, activation, to the attack of the anion, of a silicon atom bonded to the ferrocene ring.[3]

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[1] M. Kumada, H. Tsunemi, and S. Iwasaki, *J. Organometallic Chem.*, 1967, **10**, 111.

[2] M. Kumada and H. Tsunemi, 3rd International Symposium on Organometallic Chemistry, Munich, Aug. 28-Sept. 1, 1967, Abs., p. 164.

[3] M. Kumada and K. Tamao, *Adv. Organometallic Chem.*, 1968, p. 76.