

Preliminary communication

ORGANOMETALLIC COMPOUNDS

XXVI*. FERROCENOPHANE-7-CARBOCATIONS AND THEIR
REARRANGEMENT

MASAO HISATOME and KOJI YAMAKAWA*

*Faculty of Pharmaceutical Sciences, Science University of Tokyo, Ichigaya-funagawara-machi,
Shinjuku-ku, Tokyo 162 (Japan)*

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Summary

The PMR spectra of 7-s-hydroxyl derivatives of [4]ferrocenophanes (I-IV, X) in trifluoroacetic acid (TFA) indicated formation of stable 7-carbocations (XIX), and the starting alcohols were recovered by treatment of the TFA solutions with aq. Na_2CO_3 . On the other hand, the PMR spectral patterns of [4]ferrocenophane-6-carbocations (XX) appeared in the TFA solutions of 7-t-hydroxyl derivatives (V-IX), and quenching the species gave the corresponding 6-ols (XIII-XVII), rearrangement products.

There have been many studies [1] on the NMR spectra of stable ferrocenyl-6-carbocations which were formed by dissolving the corresponding 6-hydroxyferrocenes in strong acids. Richards et al. [2] and the present authors [1d] have already suggested generation of ferrocenyl-7-carbocations and a participation of the Fe atom with the 7-cationic center. In the present communication, formation of stable 7-s-carbocations and easy rearrangement of 7-t-carbocations to 6-carbocations in [4]ferrocenophanes are described.

In the PMR spectra of 7-s-hydroxyl derivatives of [4]ferrocenophanes (I-IV, X) in 100% trifluoroacetic acid (TFA), the resonance signals of the ring protons appeared separately in the wide region of the magnetic field (δ 3.8–5.8 ppm) as sharp lines. The wide spread of the ring proton signals characterizes formation of carbocations [1]. Their spectral patterns were distinct from the ones of the 6-carbocations generated from the corresponding 6-ols (XI, XII etc.); rearrangement of the cationic center into 6-position did not occur, being different from the behavior of 7-t-hydroxyl derivatives in TFA as mentioned below. Furthermore, treatment of the species with aq. Na_2CO_3 recovered the precursor alcohols.

* For part XXV, see Ref. 7.

TABLE 1
THE PMR SPECTRAL DATA^a OF [4]FERROCENOPHANOLS IN TRIFLUOROACETIC ACID

Compounds	Bridge and substituent protons		Cp ring protons										
	G-CH ^b	7:R ¹	7:II	R ²	2:H	3:H	4:H	5:H	2':H	3':H	4':H	5':H	
I			4.65m		4.03	6.01	5.77	3.89	5.05	5.21	5.37	4.76	
<i>cis</i> -III			4.5m	1.58d	$J_0 = 2.8, J_m = 1.3$	4.05	5.99	5.71	3.80	5.31	5.20	5.31	4.76
<i>trans</i> -III			4.5m	1.27d	$J_0 = 2.8, J_m = 1.3$	c	c	c	c	c	c	c	
<i>cis</i> -X			4.45m	J = 7.5	3.74	5.74	3.88	4.86	4.75	5.15	4.57		
<i>trans</i> -X			4.45m	J = 7.5	$J_0 = 2.8, J_m = 1.4$	3.74	5.58	3.64	4.75	4.88	4.88		
XI	6.67dd				$J_0 = 2.8, J_m = 1.4$	4.78	6.11	6.22	4.50	5.38	4.80	5.06	
V and XIII	J = 12.3, 4.0				$J_0 = 3.2, J_m = 1.3$	4.82	6.12	6.19	4.48	5.35	4.82	5.12	
VI ^{b,c} and XIV ^c	6.44d	1.59d	1.80m	1.04d	$J_0 = 3.1, J_m = 1.3$	4.75	6.08	6.10	4.39	4.54	5.28	4.74	
VII ^{c,d} and XVI ^c	J = 10.1	J = 4.5	1.90m	J = 7.5	$J_0 = 2.9, J_m = 1.4$	4.98	6.16	6.16	4.42	4.66	5.35	4.83	
IX ^{b,c,d} and XVII ^c	6.39d	1.54d	2.84m	1.14d	$J_0 = 3.1, J_m = 1.3$	4.99	6.15	6.15	4.39	4.67	5.36	4.82	
	J = 10.8	J = 6.0		J = 7.5	$J_0 = 3.0, J_m = 1.2$	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	
	5.58d	ca. 7.4		J = 7.5	$J_0 = 3.0, J_m = 1.5$	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	
	J = 11.1	ca. 7.4		J = 7.5	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	
	6.61d			J = 7.5	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	
	J = 10.7			J = 7.5	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	J ₀	

^aThe spectra were measured with a JEOL JNM-4H-100 spectrometer at 100 MHz with TMS as internal reference and at room temperature. The assignments of the signals were determined by the spin-decoupling technique. Chemical shifts and coupling constants are indicated in δ (ppm) and Hz, respectively (J_0 and J_m : *ortho* and *meta* coupling constants). ^bThe *cis* and *trans* isomers of the alcohol showed the same spectra as each other. ^cThe data in CDCl₃-trifluoroacetic acid. ^dThe spectra were measured in the degassed solutions free from oxygen, because of easy oxidation of the species generated in trifluoroacetic acid. ^eThe chemical shifts or J -values were not definitely determined, because of overlapping with other signals.

The above results suggest strongly that [4]ferrocenophane-7-carbocations (XIX) were generated in the TFA solutions of the 7-hydroxyl derivatives (I–IV, X). Formation of the stable 7-carbocations was supported by the measurement of pK values of [4]ferrocenophan-7-ol and -7-one [I: +0.1, XVIII: -4.0] by Ortaggi [3].

The signals observed at δ 4.4–4.6m in the species formed from 7-s-hydroxyl derivatives (I, III, IV, X) disappeared in the spectrum of 7-deutero-[4]ferrocenophan-7-ol (II). Therefore, it was confirmed that the carbinyl protons at the cationic center in the 7-carbocations resonated at unusually high field.

Reduction of 9-methyl[4](1,1')- and [4](1,1')[4](3,3')ferrocenophan-7-ones with $LiAlH_4$ gave mixtures of the *cis* and *trans** alcohols in isomer ratios of 1 : 2 (III) and 1 : 1 (X), respectively [4]. The PMR spectra of the mixtures in TFA indicated formation of two isomeric species in the same ratios as the alcohols. The 7-hydroxyl derivatives were recovered in the same isomeric ratios as the precursors from the TFA solutions by quenching. According to conformational analysis of the alcohols and the intermediates [5], the retention of the configuration in III indicates that an interannular bridge inversion as shown by Turbitt and Watts [1h] did not occur in the 7-carbocations, at room temperature at least, nor in the case of [3]- and [4]ferrocenophan-6-carbocations [4].

On the other hand, the PMR spectra of 7-t-hydroxyl derivatives (V–IX) in TFA were not those of the expected 7-cationic species. For example, the methyl signals at the 7-position in compounds V–VII were not a singlet line at low field as predicted in the 7-carbocations but doublets at ca. δ 1.5. Furthermore, the signals due to cationic methine protons appeared as doublets at low fields (δ 6.4–6.6) in all t-alcohols (V–IX). The results indicate formation of [4]ferrocenophane-6-carbocations (XX) from 7-carbocations (XIX) via a rearrangement of the cationic center.

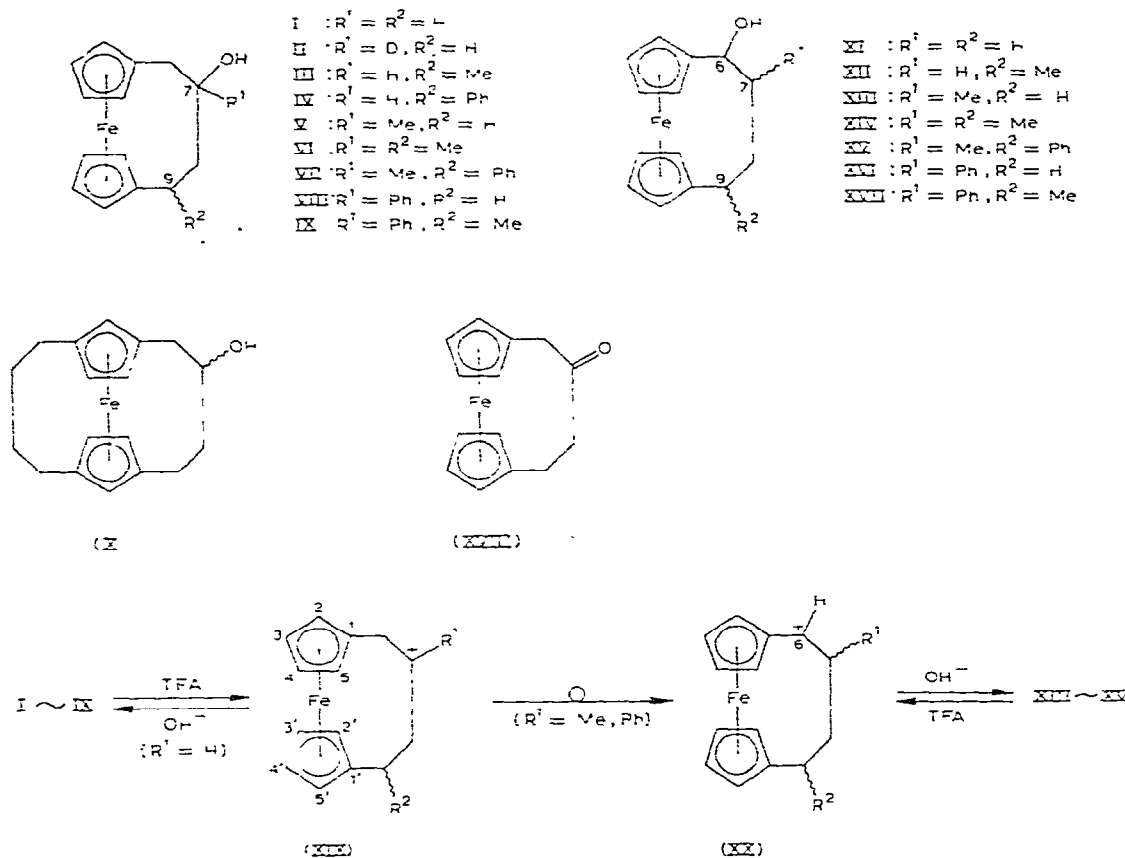
Treatment of the TFA solutions of 7-t-hydroxyl derivatives (V–IX) with alkali gave the corresponding rearrangement products (XIII–XVII). The spectra of the TFA solutions of the 6-ols (XIII–XVII) obtained above were identical with those of the original 7-t-ols (V–IX) in TFA, respectively. Accordingly, the rearrangement of the cationic center from the 7-position to the 6-position in TFA was shown.

Two stereo isomers** were isolated from both 7-t-ols VI and IX [4]. The spectrum of the one isomer of each of the 7-t-ols in TFA was the same as that of the other; only the single 6-carbocation was formed from the two isomers in spite of the possibility of several isomers in the 6-carbocation. Quenching the TFA solution of each alcohol (VI, IX) gave only one isomer of 6-ol (XIV, XVII).

The different behavior of the 7-t-ols from the 7-s-ols in TFA is particularly interesting. The unusually high field shift of the 7-protons in the 7-s-carbocations suggests the presence of the proton in a deshielding zone of the Fe atom [6]. If one of the stabilization factors of the 7-carbocations is a participation of the Fe atom with the cationic center accompanied by approaching each other, it is reasonable that the 7-t-carbocations cannot be stabilized by the metal-participation due to steric hindrance of the bulky substituent at the 7-position, and that

*The indication of *cis* and *trans* in this paper means the configurational relation of the substituents R^1 and R^2 except for X, in which *cis* and *trans* indicate the direction of the 7-hydrogen to the other bridge.
** *cis*-VI: m.p. 116–117°C; *trans*-VI: m.p. 134–135°C; *cis*-IX: m.p. 81–83°C and *trans*-IX: m.p. 90–91°C.

the cationic center was then rearranged into the 6-position to give more stable 6-carbocation (see Scheme 1 and Table 1.)



SCHEME 1. Generation of 7-carbocations and their rearrangement.

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