1220, 1100 (COC); 730 cm^{-1}; NMR δ 7.49 (q, 1 H, 3-H), 2.94 (t, 2 H, 1′-H), 2.62 (t, 2 H, 3′-H), 2.51 (q, 2 H, SCH_2), 1.93 (p, 2 H, 2′-H), 1.83 (d, 3 H, 2-CH_3), 1.23 (t, 3 H, CH_3), $^4J_{3,2\text{-}CH_3}$ = 1.0.

Some spectral data of the other products include the following. **6b**: IR 1750 cm^1 (C═O); *m/e* 220 (M^+), 119. **6c**: IR 1740 (C═O); 1220, 1020 (COC); 1470, 730, 695 (Ph); 905 cm^{-1} (DT); NMR δ 4.52 (d, 1 H, 2-H), 3.91 (d, 1 H, α-H); $^3J_{2,\alpha}$ = 11. **18c**: IR 1700 (C═O); 1560 (C═C); 1600, 1480, 730, 700 (Ph); 1220, 1030 cm^{-1} (COC); NMR 7.80 (s, 1 H, 3-H). **19b**, main absorptions in IR identical with those of **18b**; NMR 7.45 (q, 1 H, 3-H), 1.84 (d, 3 H, 2-CH_3), $^4J_{3,CH_3}$ = 1; *m/e* 219 ($^1/_2M^+$), 197, 135, 103. **19c**: IR as for **18c**; NMR 7.70 (s, 1 H, 3-H).

Common spectral data for $CO_2C_2H_5$ groups of all ethyl esters: IR 2980, 1440 (CH) cm^{-1}; NMR δ 4.1–4.2 (q, 2 H, OCH_2), 1.2–1.3 (t, 3 H, CH_3).

Anions of Monoesters 4–6. A solution of the requisite ester in THF (5 mmol in 2 mL) was added dropwise at −78 °C to a stirred solution of lithium diisopropylamide[14] in THF (5.5–6.5 mmol in 8 mL). The slightly yellow solutions were stirred at −78 °C for 20 min in the case of monosubstituted esters **4a**, **5a**, and **6a** and for 1 h in the case of disubstituted esters **4b** and **5b**. Aliquots were quenched with a mixture of aqueous ammonium chloride and ether. GC analysis of the organic layer revealed that ring opening had occurred only in the case of THF esters **4a**,**b**. Workup afforded in 95% yield of a mixture of **4a**,**b** (20%), **11a**,**b** (65%), and **12a**,**b** (15%) as determined with GC and NMR. In the case of THT esters **5a**,**b** and DT ester **6a**, a mixture of ethyl iodide (6.5 mmol) and HMPA (5 mmol) was added. The reactions with monosubstituted esters were quenched after 5 min of stirring at −78 °C, and in the case of **5b** after 30 min of stirring at −78 °C and then at 20 °C. Standard workup yielded crude products containing 5–10% of starting esters **5a**,**b** and **6a** and 80–90% of products **25a**,**b** and **18a**, respectively. The yields were calculated from NMR and GC. Pure samples were obtained by preparative GC (**25a**,**b**) or column chromatography (**18a**).

(*E*)-Ethyl 6-(Ethylthio)hex-2-enoate (25a): 80%; $n^{23}{}_D$ = 1.4843; IR 2940, 1440 (CH); 1650 (C═C); 1720 (C═O); 1250, 1180, 1030 (COC); 970 cm^{-1} ((*E*)-HC═CH); NMR δ 6.92 (dt, 1 H, 3-H), 5.82 (dt, 1 H, 2-H), 4.16 (q, 2 H, OCH_2), 2.52 (t, 2 H, 6-H), 2.51 (q, 2 H, SCH_2), 2.36 (dq, 2 H, 4-H), 1.74 (p, 2 H, 5-H), 1.28 (t, 3 H, OCH_2CH_3), 1.24 (t, 3 H, SCH_2CH_3), $^3J_{2,3}$ = 16, $^3J_{3,4}$ = 7, $^4J_{2,4}$ = 1.5.

(*E*)-Ethyl 2-Methyl-6-(ethylthio)hex-2-enoate (25b): 88%; $n^{20}{}_D$ = 1.4865; IR 2950, 1440 (CH); 1720 (C═O); 1650 (C═C); 1250, 1100 (COC); 740 cm^{-1}; NMR δ 6.72 (tq, 1 H, 3-H), 4.17 (q, 2 H, OCH_2), 2.53 (t, 2 H, 6-H), 2.52 (q, 2 H, SCH_2), 2.29 (q, 2 H, 4-H), 1.85 (d, 3 H, 2-CH_3), 1.72 (p, 2 H, 5-H), 1.29 (t, 3 H, OCH_2CH_3), 1.25 (t, 3 H, SCH_2CH_3), $^3J_{3,4}$ = 7.5, $^4J_{3,CH_3}$ = 1.5.

(*E*)-Ethyl 3-[3′-(Ethylthio)propylthio]propenoate (18a): 70%; $n^{20}{}_D$ = 1.5338; IR 2950, 1440 (CH); 1700 (C═O); 1570 (C═C); 1240, 1150, 1025 (COC); 940 ((*E*)-HC═CH), 825 cm^{-1}; NMR δ 7.70 and 5.80 (AB, 2 H, ^3J = 15.2, 3- and 2-H), 4.18 (q, 2 H, OCH_2), 2.94 (t, 2 H, 1′-H), 2.64 (t, 2 H, 3′-H), 2.53 (q, 2 H, SCH_2), 1.95 (p, 2 H, 2′-H), 1.28 (t, 3 H, OCH_2CH_3), 1.26 (t, 3 H, SCH_2CH_3).

Registry No. 1a, 70398-41-3; **1b**, 70398-42-4; **1c**, 70398-43-5; **1d**, 70576-34-0; **2a**, 70398-46-8; **2b**, 70398-47-9; **2c**, 70398-48-0; **3a**, 63822-64-0; **3b**, 69178-02-5; **3c**, 69178-04-7; **4a**, 2434-02-8; **4b**, 70562-10-6; **4c**, 70562-11-7; **5a**, 65102-19-4; **5b**, 70562-12-8; **5c**, 70562-13-9; **6a**, 70562-14-0; **6b**, 70562-15-1; **6c**, 70562-16-2; **9**, 70562-17-3; **10**, 70562-18-4; **11a**, 13038-15-8; (*E*)-**11b**, 70562-19-5; (*Z*)-**11b**, 70562-20-8; (*E*)-**11c**, 70562-21-9; (*Z*)-**11c**, 70562-22-0; **12a**, 70562-23-1; **12b**, 70562-24-2; **13a**, 21014-26-6; **13c**, 70562-25-3; **14**, 13159-16-5; **15**, 58927-91-6; **16**, 70562-26-4; **17**, 33672-52-5; **18a**, 70562-27-5; **18b**, 70562-28-6; **18c**, 70562-29-7; **19b**, 70562-30-0; **19c**, 70562-31-1; **25a**, 70562-32-2; **25b**, 70562-33-3; MeI, 74-88-4; $PhCH_2Br$, 100-39-0.

Ferrocenyl Carbocations. The Stability of Some [4]Ferrocenophane 6- and 7-Carbocations

Giancarlo Ortaggi,* Paolo Riccio, and Incoronata Tritto

Centro C.N.R. dei Meccanismi di Reazione, c/o Istituto di Chimica Organica, Università di Roma, 00185 Roma, Italy

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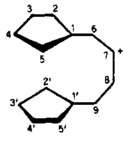
The equilibrium constants for the protonation of [4]ferrocenophan-7-one and -6-one and for the ionization of the corresponding alcohols in aqueous sulfuric acid, as well as the behavior of these molecules as acid–base indicators, suggest that the [4]ferrocenophane 7-carbocations are strongly stabilized by the ferrocenyl group, despite the distance of the positive center from the Cp ring.

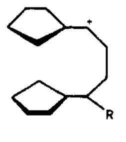
The structure and the stability of the α-ferrocenyl carbocations have been extensively debated on the basis of their physical properties,[1-6] reactivity,[7,8] and equilibria.[9,10]

It seemed of interest to measure the stability of the β-ferrocenyl carbocations, since the investigation of substrates, where the direct conjugation between the positive carbon and the Cp ring is absent, appeared useful for a deeper insight on the role played by the ferrocenyl group in the stabilization of the α-carbocations. [4]-Ferrocenophan-7-ol was taken as a convenient substrate, whose carbocation was found to possess a sufficiently high stability[11] by NMR spectral measurements.

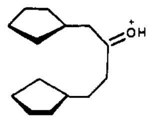
The work reported in this paper concerned the formation of carbocations as obtained from the ionization of [4]ferrocenophan-7-ol (I) and the protonation of [4]ferrocenophan-7-one (IV) in aqueous H_2SO_4. The cations derived from [4]ferrocenophan-6-ol (II) and -6-one (V) and from their 9-methyl derivatives (III and VI) were also



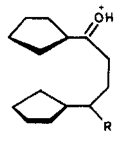
I



II R = H
III R = Me



IV



V R = H
VI R = Me

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(1) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Lett.*, 1695 (1966).

(2) G. H. Williams, D. D. Traficante, and D. Seyferth, *J. Organomet. Chem.*, **60**, C53 (1973).

(3) A. Koridze, P. V. Petrovskii, S. P. Gubin, and E. I. Fedin, *J. Organomet. Chem.*, **93**, C26 (1975).

(4) W. E. Watts, *J. Chem. Soc., Perkin Trans. 1*, 804 (1976).

(5) M. Hisatome and K. Yamakawa, *Tetrahedron*, **27**, 2101 (1971).

(6) G. Ortaggi and R. Marček, *Gazz. Chim. Ital.*, **109**, 13 (1979).

(7) D. W. Hall, E. A. Hill, and J. H. Richards, *J. Am. Chem. Soc.*, **90**, 4972 (1968).

(8) E. A. Hill, *J. Org. Chem.*, **28**, 3586 (1963).

(9) G. Cerichelli, B. Floris, G. Illuminati, and G. Ortaggi, *Gazz. Chim. Ital.*, **103**, 911 (1973).

(10) G. Cerichelli, B. Floris, and G. Ortaggi, *J. Organomet. Chem.*, **78**, 241 (1974).

(11) M. Hisatome and K. Yamakawa, *Tetrahedron Lett.*, 3533 (1971).

0022-3263/79/1944-2920$01.00/0

Table I. Spectral Data for Some Ferrocenyl Ketones and Alcohols in Different Solvents

compd	water max, nm	water log ε	H_2SO_4 70% max, nm	H_2SO_4 70% log ε
[4]ferrocenophan-7-one	260 sh	3.98	260	4.25
	320	2.70	450	2.45
	430	2.15		
[4]ferrocenophan-6-one	260 sh		260	3.96
	275	3.70	350	3.5
	345	3.25	455	2.9
	465	2.80		
9-methyl[4]ferrocenophan-6-one	268	3.74	262	3.94
	344	2.83	350	2.87
	440	2.35	450	2.68
1-acetyl-1′-ethylferrocene[a]	278	3.85		
	346	3.29	360	3.38
	472	2.99	518	2.34
[4]ferrocenophan-7-ol	430	1.78	252	3.7
			430	2.0
[4]ferrocenophan-6-ol	435	2.10	255	3.94
			410	2.68
9-methyl[4]ferrocenophan-6-ol	338	2.55	260	3.8
	440	2.23	342	2.73
			444	2.39

[a] Data from ref 9.

examined as model compounds for the structurally related α-carbocations.

Results and Discussion

Carbocation Formation. The starting alcohols and ketones as well as the corresponding carbocations, generated by dissolution of the parent compounds in sufficiently concentrated sulfuric acid solutions, were characterized by NMR and electronic spectroscopy. The spectroscopic data are collected in Tables I and II.

For all compounds under examination, the reversibility of the equilibrium unprotonated form ⇌ protonated form was ascertained spectroscopically by careful dilution of the solutions containing the carbocations (see Experimental Section). For the carbocations derived from [4]ferrocenophan-7-ol and -7-one, the reversibility of the equilibrium was checked also by the quantitative recovery of the parent compound from the sufficiently concentrated sulfuric acid solution (see Experimental Section). These results indicate that the [4]ferrocenophane 7-carbocation is sufficiently stable to allow the study of its formation by spectrophotometry and to establish that it does not isomerize to the corresponding α-carbocation, i.e., [4]-ferrocenophane 6-carbocation. The lack of isomerization indicates that the difference in stability between the two carbocations is not high.

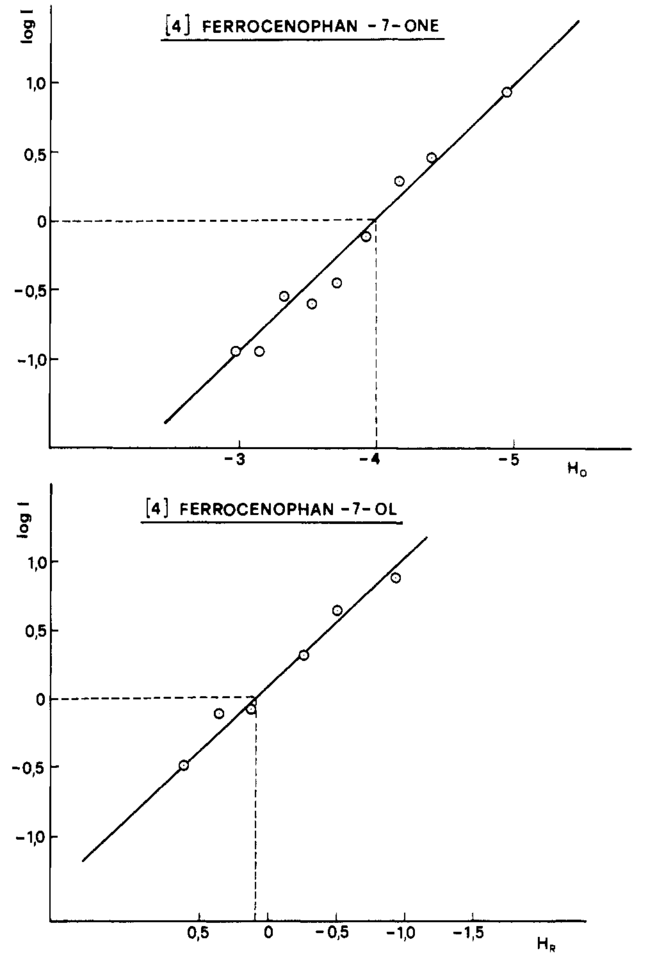

Figure 1. Plots of log I vs. H_0 and H_R for (a) [4]ferrocenophan-7-one and (b) [4]ferrocenophan-7-ol.

Another point to be focused on is the similarity between the UV portions of the spectra of the [4]ferrocenophane 7- and 6-carbocations (Table I), as shown by the presence of an absorption maximum in the 260-nm region, which has been attributed a diagnostic value for the α-ferrocenyl carbocations formation.[10]

Also, the NMR spectra of the two kinds of carbocations show a close similarity, such as the ^+CH signal at lower fields, the splitting of both the α and β hydrogens, and the concomitant shift of their position at lower fields.[10] More significantly, the chemical shift difference between the ^+CH and the tertiary hydrogen CH(OH) signals in the two types of carbocations is similar: for [4]ferrocenophan-6-ol this difference is (6.67 − 4.6) ≃ 2.1; for [4]ferrocenophan-7-ol it is (4.65 − 2.7) ≃ 2. In our opinion these spectral analogies are not fortuitous and indicate that the

Table II. NMR Chemical Shifts (δ) for Some Bridged Ferrocenyl Alcohols and Ketones

compd	in CS_2 H_2H_5	H_3H_4	Cp	bridge protons	CH_3	in H_2SO_4 70% ^+CH	H_2H_5	H_3H_4	Cp	bridge protons	CH_3
[4]ferrocenophan-6-one	4.7	4.55	4.3	1.9-2.2			5.60	6.45	4.0-4.5	2.3-2.8	
			3.8	2.3-2.7			5.20	6.0			
9-methyl[4]ferrocenophan-6-one	4.53	4.37	3.80	1.9-2.25	1.15		5.10	5.95	4.1-4.7	2.2--2.85	1.2
			3.95	2.3-2.7			4.6	5.60			
[4]ferrocenophan-7-ol[a]			4.08			4.65	4.03	6.01	4.76	2.15	
							3.89	5.77	5.37	3.65	
[4]ferrocenophan-6-ol	4.4	4.2	4.0	2.4-1.8		6.67	4.5	6.1	4.55	2.45	
							4.8	6.2	5.38	2.95	
9-methyl[4]ferrocenophan-6-ol	4.4	4.1	3.9	1.6-2.0	1.05	6.5	4.9	6	4.25-4.5	2.10	0.9
				2.1-2.4			5.2		4.55-4.75	2.90	

[a] Data from ref 11.

Table III. Equilibrium Data for Some Ferrocenyl Carbocations in Aqueous H_2SO_4 at 25 °C

ferrocene compd	$-pK_{R^+}$	m_{OH}[a]	$-pK_a$	m_{CO}[b]
[4]ferrocenophan-7-ol	−0.1	0.94		
[4]ferrocenophan-6-ol	−0.15	0.95		
9-methyl[4]ferrocenophan-6-ol	−1.8	0.99		
[3]ferrocenophan-6-ol[c]	3.20	0.68		
1′-ethyl-1-(α-hydroxyethyl)ferrocene[c]	0.13	0.85		
[4]ferrocenophan-7-one			4.0	0.98
[4]ferrocenophan-6-one			2.50	0.99
9-methyl[4]ferrocenophan-6-one			2.15	0.99
1′-ethyl-1-acetylferrocene[d]			2.53	0.98
acetylferrocene[d]			2.80	1.00

[a] From the slope of the plots log *I* vs. H_R. [b] From the slope of the plots log *I* vs. H_0. [c] Data from ref 10. [d] Data from ref 9.

electronic structures of the two types of carbocations are essentially similar.

A brief comment on the molecular conformations imposed by the interannular bridge is necessary. For [4]ferrocenophan-6-one and its 9-methyl derivative, the bridge does not introduce any relevant strain, as is shown from the close similarity of their electronic spectral data with those of 1-acetyl-1′-ethylferrocene (Table I) and from their carbonyl stretching frequencies (1647 and 1650 cm^{-1}, respectively), which reveal a good conjugation between the carbonyl group and the Cp ring. The same conclusion was reached from the analysis of the NMR spectrum of [4]ferrocenophan-6-one.[12] For [4]ferrocenophan-7-one, the C=O stretching band falls at the expected higher frequency (1710 cm^{-1}), and the Dreiding models show no relevant ring strain. For the free alcohols, the NMR pattern of the Cp hydrogens may be interpreted in agreement with the absence of strain.[12]

On the contrary, the NMR spectra of the carbocations show that the signals of the Cp hydrogens, especially of the H_1'–H_5' protons, are spread in a wide δ range. This pattern indicates that the relative ring motion is permitted only to a limited extent in the carbocations, probably since the interaction between the ferrocenyl group and the positive carbon is forcing the molecules in a more rigid conformation.

The p*K* values. The p*K* values of the compounds were determined spectrophotometrically by recording the increase in absorbance at 252 nm for the alcohols and at 260 nm for the carbonyl derivatives. The standard procedure employed in these determinations is described in the Experimental Section.

The p*K* values for the acid–base equilibria of the compounds I–VI in aqueous sulfuric acid are reported in Table III, together with the *m* values, which measure the slopes of log *I* vs. H_R (or H_0) plots. Typical plots of log *I* vs. H_R or H_0 values are shown in Figure 1. The equilibria data for a number of α-ferrocenyl carbocations are also reported in the table for the appropriate comparisons.

The comment suggested by the data of the table is that [4]ferrocenophane 7-carbocation I has nearly the same stability as carbocations II and III derived from [4]ferrocenophan-6-ol and as the open-chain α-ferrocenyl carbocations where peculiar structural effects are absent.[10] Accordingly, the pK_{R^+} values of carbocations I and II are nearly identical (0.1 and 0.15, respectively) and their difference from the stability constant of 1′-ethyl-1-α-hydroxyethylferrocene (which is the related open-chain term) is very small (ca. 0.2 pK_{R^+} units). These numbers nicely account for the absence of isomerization I → II.

As to the ferrocenyl ketones, carbocation IV is only 1.5 pK_a units (ca. 30 times) less stable than carbocation V, the pK_a values being −4.0 and −2.5, respectively, while acetylferrocene has −2.8. In our opinion, the difference in stability between IV and V is unexpectedly small, taking into account that the conjugated acid of [4]ferrocenophan-6-one may delocalize the positive charge into the ferrocenyl group (as all α-ferrocenyl carbocations), the interannular bridge being not so highly constrained as for [3]ferrocenophan-6-one (Table III). On the contrary, for the protonated [4]ferrocenophan-7-one, any possibility of conjugation with the Cp ring is precluded. By comparing, for example, the stability of IV with the protonated acetone ($pK_{app} = -7.86$),[13] it can be seen that IV acquires a high stabilizing effect (ca. 4 p*K* units), which must be a consequence of the interaction of the carbocation with the iron or with the electron-rich region between the metal and the Cp ring.

The results of Table III also show that both carbocations with the C-9 methyl group are more stable than the unsubstituted ones. Since the methyl group is located far from the positive site, the higher stability is probably ascribed to an electronic effect transmitted through the iron.

The similarity in the p*K* values of the [4]ferrocenophane 6- and 7-carbocations is paralleled by the similarity in the *m* values. The last may be considered a measure of the behavior of a compound as an acid–base indicator, depending on the solvation requirements of the protonation equilibria, and are therefore sensitive to the structure of the base.[13] In particular, bases which may delocalize the positive charge of the protonated form into the molecule are characterized by *m* values higher than bases where the conjugated acids are essentially stabilized by solvation.[13] In this respect, the α-ferrocenyl ketones show the highest *m* values (ca. 1) as compared to acetophenone (0.63) and acetone (0.29). Also, the *m* values relative to the ionization of the α-ferrocenyl alcohols are among the most positive ones.[10]

Since the acid–base equilibria of both [4]ferrocenophan-7-ol and -7-one are characterized by *m* values closely similar to those which are peculiar of the α-ferrocenyl alcohols and ketones, it may be concluded that in [4]ferrocenophane 7-carbocations I and IV the positive charge is extensively delocalized into the ferrocenyl group in order to reach an electronic structure substantially similar to that of the α-ferrocenyl carbocations.

Finally, our conclusions find support in the solvolysis data of the exo and endo isomers of α-tosyloxymethyl-1,2-tetramethyleneferrocene. The endo isomer solvolyzes (without rearrangement) faster than the exo isomer by a factor of 2780. The kinetic and the stereochemical results have been rationalized in terms of an interaction of the electron-deficient carbon atom with the interannular electrons.[14]

In order to elucidate conclusively the stability of the α-ferrocenyl carbocations as compared to the β ones, the formation of the β-carbocation from an open-chain term, 2-ferrocenylethanol, was examined spectrophotometrically by dissolving it in degassed trifluoroacetic acid; in these conditions the substrate appears to be immediately oxidized to the green ferricenium cation, whereas 1-ferro-

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(12) T. H. Barr and W. E. Watts, *Tetrahedron*, **24**, 6111 (1968).

(13) A. Levi, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.*, **90**, 6585 (1974).

(14) M. J. Nugent and J. H. Richards, *J. Am. Chem. Soc.*, **91**, 6138 (1969).

cenylethanol promptly gives the α-carbocation.[10] This result is in agreement with the course of the ionic additions to vinylferrocenes,[15,16] and it seems to substantiate the conclusion by which the similar stability of the α- and β-bridged carbocations examined above is probably due to the ferrocenophane structure, which orients the empty orbital of the carbocation in the proper direction to be stabilized by the ferrocenyl group.

This interaction seems to be specific and is easily perturbed by the substituents in the bridge, as is proved by the observation that by dissolving 7-methyl- and 7-butyl[4]ferrocenophan-7-ol in 50% H_2SO_4 the carbocations derived from 7-methyl- and 7-butyl[4]ferrocenophan-6-ol are obtained.[17]

Another example in the literature of the peculiar interaction of the interannular bridge with the iron is found in the unusual redox potential of [3]ferrocenophane as compared to dialkyl ferrocenes.[18]

Experimental Section

The samples of [4]ferrocenophan-7-ol and -7-one were kindly offered by Professors Hisatome and Yamakawa. [4]Ferrocenophan-6-ol and -6-one were prepared according to literature methods.[19] 9-Methyl[4]ferrocenophan-6-ol and -6-one were prepared by the method of Horspool et al.[20]

The NMR spectra were recorded by a Jeol C-60 HL spectrometer. The electronic spectra and the spectral measurements were made with a Beckmann DB-GT spectrophotometer. The aqueous sulfuric acid solutions were standardized according to the methods described previously.[9,10]

For the assessment of the reversibility of the equilibrium involving [4]ferrocenophane 7-carbocation, 100 mg of the alcohol was dissolved in 3 mL of 30% H_2SO_4; after 15 min, the acid solution was diluted with 10 mL of water, carefully neutralized with aqueous $NaHCO_3$, and extracted with ether; 85 mg of a compound was recovered, mp 160–161 °C ([4]ferrocenophan-7-ol melts at 160–162 °C).[21] [4]Ferrocenophan-7-one was successfully submitted to the same procedure.

The evaluation of the equilibrium constants was carried out according to equations $H_0 = pK_a - \log I$ and $H_R = pK_{R^+} - \log I$, where I is the ionization ratio.[9,10]

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Registry No. I, 34823-20-6; **II**, 70355-46-3; **III**, 70355-47-4; **IV**, 70355-48-5; **V**, 70355-49-6; **VI**, 70355-50-9; [4]ferrocenophan-7-ol, 34870-41-2; [4]ferrocenophan-6-ol, 55522-48-0; 9-methyl[4]ferrocenophan-6-ol, 70355-45-2; [4]ferrocenophan-7-one, 41583-25-9; [4]ferrocenophan-6-one, 31884-28-3; 9-methyl[4]ferrocenophan-6-one, 12182-14-8.

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[15] G. R. Buell, W. E. McEwen, and J. Kleinberg, *J. Am. Chem. Soc.*, 84, 40 (1962).

[16] D. Kaufman and R. Kupper, *J. Org. Chem.*, **39**, 1438 (1974).

[17] Unpublished results of this laboratory.

[18] K. Schlögl and M. Peterlik, *Monatsh. Chem.*, **93**, 1328 (1962).

[19] K. Schlögl, *Monatsh. Chem.*, **95**, 558 (1964).

[20] W. M. Horspool and R. G. Sutherland, *Chem. Commun*, 240 (1967).

[21] M. Rosenblum, A. K. Banerjee, N. Danieli, R. A. Fish, and V. Schlatter, *J. Am. Chem. Soc.*, **85**, 316 (1963).

Reactions of the Nitrosonium Ion. 11. Fluoride Transfer from Complex Fluoride Anions to Carbenium Ions in the Nitrosative Decomposition of Aliphatic Azides[1]

Michael P. Doyle,* JoAnn L. Whitefleet, and Richard J. Bosch

Department of Chemistry, Hope College, Holland, Michigan 49423

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Results from nitrosative reactions of aliphatic azides, azido nitriles, and phenoxy azides with nitrosonium salts in chloroform are reported. The presence of the basic nitrile or ether functional group causes a significant increase in the yield of fluoroalkane products, from 5% with 1-azidohexane to 50–81% in reactions with azido nitriles. Elimination reactions and protonic decomposition (Curtius rearrangement), which are major competing processes in the nitrosative decomposition of aliphatic azides, are minimized or not observed in nitrosative reactions with azido nitriles and phenoxy azides. Fluoride transfer is even competitive with intramolecular Friedel–Crafts alkylation from nitrosative reactions of phenoxy azides, but nitrosative decomposition of benzyl 5-azidopentanoate results in the exclusive formation of lactones. Enhancement of fluoride substitution is explained by intimate association of the basic functional group at the surface of the nitrosonium salt causing nitrosative decomposition of the azide to occur in close proximity to the complex fluoride anion.

Although complex fluoride anions such as tetrafluoroborate are generally regarded as very weak nucleophiles, fluoride transfer from complex fluoride anions to an electron-deficient center has achieved both synthetic and mechanistic importance. Decomposition of arenediazonium tetrafluoroborate salts (the Schiemann reaction[2–6]) has long been regarded for its synthetic value as a selective method for the synthesis of aryl fluorides. However, because of the relative instability of the corresponding alkyl diazonium salts and the concomitant formation of water in diazotization processes with primary amines,[7] attempts to extend this useful process to aliphatic

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[1] Part 9: Doyle, M. P.; Whitefleet, J. L.; DeBruyn, D. J.; Wierenga, W. *J. Am. Chem. Soc.* **1977**, *99*, 494.

[2] Forche, E.; Hahn, W.; Stroh, R. "Methoden der Organischen Chemie" (Houben-Weyl-Müller), 4th ed.; Georg Thieme Verlag: Stuttgart, 1965; Vol. V, Part 3, p 213.

[3] Hudlicky, M. "Chemistry of Organic Fluorine Compounds", 2nd ed.; Ellis Harwood: Chichester, 1976; Chapter 4.

[4] Suschitzky, H. *Adv. Fluorine Chem.* **1965**, *4*, 1.

[5] Roe, A. *Org. React.* **1949**, *5*, 193.

[6] Swain, C. G.; Rogers, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 799.

[7] Friedman, L. In "Carbonium Ions"; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1973; Vol. II, Chapter 16.