KO-*t*-Bu (1.2 g, 10.7 mmol, 2.16 equiv) dissolved in 10 ml of DMSO was then added dropwise over 2.3 hr at 25°. The resulting dark solution was stirred for an additional 1 hr, poured into water, and extracted with pentane. The aqueous layer was saturated with NaCl to break the emulsion. The pentane extracts were washed twice with water and twice with saturated sodium chloride solution. Removal of pentane in vacuo gave nearly pure **3** (330 mg, 38%): mass spectrum parent ion *m/e* 172; exact *m/e* calcd for $C_9H_{16}O_3$, 172.1099; found, 172.1094.

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Registry No.—**2,** 54276-74-3; **3,** 54276-75-4; **5,** 54276-76-5; ethyl bromide, 74-96-4; 1-butyne, 107-00-6; trimethyl orthoformate, 149-73-5; 2-pentynal dimethyl acetal, 54276-77-6.

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Organometallic Chemistry. VI. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of α-Ferrocenylcarbenium Ions[1]

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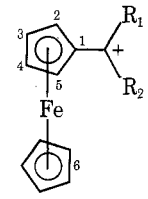
Kinetic studies of the solvolysis of α-ferrocenylcarbinyl derivatives and actual isolation of stable salts demonstrate the remarkable stability of α-ferrocenylcarbenium ions.[2] Although extensive work has been done in the past, the nature of ferrocenyl-stabilized carbocations is still under dispute.[3] Carbon-13 nuclear magnetic resonance spectroscopy provides an understanding of distribution of positive charge in carbocations, in a more quantitative way than does the proton NMR. This is also indicated by several earlier investigations on ferrocenylcarbenium ions.[3,4] Interested in the nature of these ions, we wish to report our further ^{13}C NMR spectroscopic investigation of a series of α-ferrocenylcarbenium ions.

Results and Discussion

Cations 1–4 were prepared in sulfuric acid solution at 0° from their corresponding alcohols.[5] The proton NMR spec-



1, $R_1 = R_2 = H$
2, $R_1 = H$; $R_2 = CH_3$
3, $R_1 = R_2 = CH_3$
4, $R_1 = CH_3$; $R_2 = CH_2CH_3$

tra of α-ferrocenylcarbenium ions were in accordance with those previously reported.[6] The carbon-13 NMR spectra of the cations were obtained by the Fourier-transform method. Carbon shifts (δ ^{13}C, in parts per million from external Me_4Si), multiplicities, and coupling constants (J_{CH}, in hertz) are summarized in Table I. The assignments of the carbon resonances were made with the aid of either off-resonance or proton-coupled spectra.

The present results reveal several interesting features of the carbon-13 NMR spectra of α-ferrocenylcarbenium ions. First of all, the carbocationic centers in these ions are unusually shielded, instead of being deshielded as observed in conventional carbenium ions. Secondly, the replacement of a hydrogen atom in primary ion **1** by a methyl group causes about 30 ppm deshielding of the carbenium center. Further replacement of the second hydrogen by a methyl group causes additional deshielding of about 37 ppm. Ethyl substitution causes about 43 ppm deshielding from **3** to **4**. Thirdly, consecutive methylation at carbenium centers from primary to tertiary ions causes slight shielding at C_1, C_2, and C_3, while C_4 (and C_5) and C_6 (cyclopentadienyl carbons) are almost unaffected. A deshielding of 5 ppm at carbons (C_1) adjacent to the carbenium center is observed for substitution of each methyl going from primary to tertiary ions.

It is also interesting to see that C_3 (and C_4) are more deshielded than the carbenium center (C^+) in the primary

Table I
Carbon-13 NMR Parameters of α-Ferrocenylcarbenium Ions in Sulfuric Acid Solution[a]

Ion	C^+	C_1	C_2	C_3	C_4	C_5	C_6	Δ_1[b]	Δ_2[b]
1	87.8	110.6	84.8	94.5	94.5	84.8	82.4	+22.8	9.7
	(t, 168.9)	(s)	(d, 188.0)	(d, 183.7)	(d, 183.7)	(d, 188.0)	(dt, 184.1, 6.0)		
2[c]	117.9	105.6	81.0[d]	93.9[d]	94.2[d]	81.8[d]	82.3	−12.3	11.9
	(d, 164.9)	(s)	(d, 187.6)	(d, 183.0)	(d, 183.0)	(d, 190.0)	(dt, 182.9, 6.0)		
3[e]	155.1	100.1	78.3	93.6	93.6	78.3	82.2	−55.0	15.3
	(s)	(s)	(dd, 187.5, 5.0)	(d, 185.0)	(d, 185.0)	(as C_2)	(dt, 180.0, 6.0)		
4[f]	160.6	100.3	78.9[d]	93.8[d]	94.0[d]	78.4[d]	82.2	−60.3	15.1
	(s)	(s)	(d, 178.2)	(d, 183.3)	(d, 183.3)	(d, 180.9)	(dt, 182.5, 6.0)		

[a] Carbon shifts (δ ^{13}C) are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{CH}, in hertz) are given in parentheses: d, doublet; dt, doublet of triplets; t, triplet; dd, doublet of doublets; s, singlet; and q, quartet. [b] $\Delta_1 = \delta\ ^{13}C_1 - \delta\ ^{13}C^+$, $\Delta_2 = \delta\ ^{13}C_3 - \delta\ ^{13}C_2$. [c] δ_{CH_3} = 19.8 (q, 129.8). [d] Interchangeable values. [e] δ_{CH_3}=26.6 (q, 127.5). [f] δ_{CH_3} = 25.7 (q, 129.5), δ_{CH_3}=16.6 (q, 129.1), and δ_{CH_2} = 35.9 (t, 131.0).

cation **1**, and less so or even shielded in the secondary and tertiary ions. Despite the change in carbon shifts at carbocationic centers going from primary to tertiary ions (about 80 ppm), C_3 and C_4 show almost no change. The lack of variation of deshielded cyclopentadienyl carbons, C_3 and C_4, not only indicates positive charge delocalization into the ferrocenyl moiety at these positions, but also shows that the interaction between the iron atom and the carbocationic center is reduced going from primary to tertiary ions. One also finds that carbon–hydrogen coupling constants (J_{CH}, in hertz) at the carbenium centers are smaller than those in the cyclopentadienyl moiety, presumably caused by some interaction between iron and the carbenium center. The magnitude of J_{CH} is significantly different from those in, for example, dimethyl- and diphenylcarbenium ions (J_{CH} = 169 and 164 Hz, respectively).

The observed diastereotropism of the carbon pairs (C_2 and C_5, and C_3 and C_4) in the unsymmetrically substituted α-ferrocenylcarbenium ions (**2** and **4**) undoubtedly indicates slow rotation about the exocyclic C^+–C_1 bond, which could arise from either the double bond character between C^+ and C_1 or the direct interaction between iron and the carbocationic center.

The present ^{13}C NMR studies demonstrate that α-ferrocenylcarbenium ions indeed have the positive charge substantially delocalized into the metallocenyl moiety. Although the detailed mechanism for the interaction between the iron nucleus and the neighboring carbenium center is not yet clear, such interaction seems to be weaker in tertiary than in primary or secondary species.

Experimental Section

Materials. All α-ferrocenylcarbinols were prepared according to literature procedures.[5]

Carbon-13 NMR Spectra. A Varian Associates Model XL-100 NMR spectrometer equipped with a Fourier transform accessory, a spin decoupler, and a variable-temperature probe was used to obtain the carbon-13 NMR spectra. Carbon shifts were referred to external Me_4Si (capillary).

Preparation of the Ions. α-Ferrocenylcarbenium ions were prepared from corresponding alcohols in cold sulfuric acid solution at −10° and carefully transferred to NMR tubes for study.

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Registry No.—**1**, 12129-36-1; **2**, 12129-73-6; **3**, 12295-38-4; **4**, 12295-58-8.

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An Improved Procedure for the N-Demethylation of 6,7-Benzomorphans, Morphine, and Codeine

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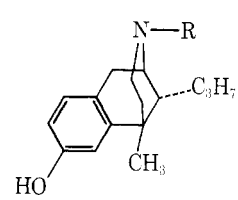
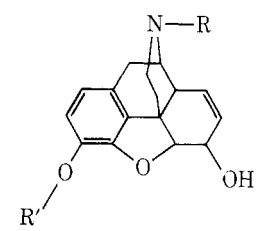
The N-demethylation of tertiary methylamines has been accomplished in several ways. The classic von Braun reaction,[1] using cyanogen bromide, was improved upon for many amines by the use of benzyl or ethyl chloroformate.[2] Further improvement involved the use of phenyl chloroformate;[2,3] the intermediate carbamate formed with this reagent proved easier to hydrolyze. Ethyl azodicarboxylate has been used[4] to demethylate thebaine and various 6-ester derivatives of morphine and codeine in reasonable yield. However, this procedure gave only ca. 40% yields of an *N*-nor-6,7-benzomorphan.[5] Recently, 2,2,2-trichloroethyl chloroformate[6] has been found to give a carbamate intermediate which could be cleaved by zinc in acetic acid or methanol. These reagents N-demethylated morphine in 75% yield. However, in our hands, the trichloroethyl chloroformate procedure gave poor yields (<40%) of the *N*-nor product from 2′-hydroxy-2,5-dimethyl-9α-propyl-6,7-benzomorphan (**1b**).



1a, R = H
b, R = CH_3



2a, R = R′ = H
b, R = CH_3; R′ = H
c, R = H; R′ = CH_3
d, R = R′ = CH_3

We utilized a modified phenyl chloroformate procedure to produce an intermediate carbamate, and have found that the carbamate can be easily cleaved with a 1:1 mixture of 64 and 95% hydrazine. The method has been applied to morphine (**2b**), codeine (**2d**), and 6,7-benzomorphans to give the *N*-nor compounds in excellent yield. Hydrazine has, of course, been used in the past to cleave amides in peptides and other compounds.[7]

The procedure of Abdel-Monem and Portoghese[3] for the preparation of *N*-normorphine involved the hydrolysis of *N*,3,6-tricarbophenoxynormorphine to *N*-carbophenoxynormorphine, its chromatography and crystallization, followed by cleavage with ethanolic KOH, in an overall yield of ca. 40%. We found it unnecessary in our procedure to isolate and purify the intermediate carbamate and, with the benzomorphan, the *N*-nor product precipitated from the hydrazine reaction mixture; washing and drying gave analytically pure product in 95% overall yield. *N*-Normorphine