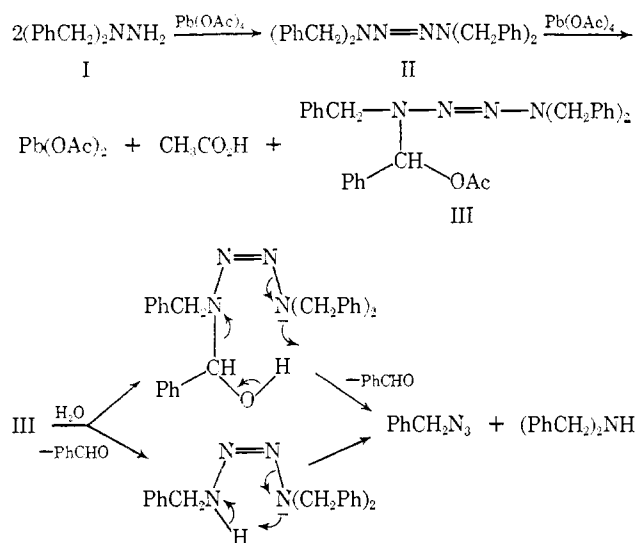


capable of accounting for our reaction is the corresponding tetrazene (II). Indeed, the slow addition of a benzene solution of II to a suspension of 1 equiv of  $\text{Pb}(\text{OAc})_4$  in benzene at  $5\text{--}10^\circ$  resulted in a slightly exothermic reaction until about half-way through the addition of the tetrazene solution. After all the tetrazene solution had been added, a second equivalent of  $\text{Pb}(\text{OAc})_4$  was added in small portions. The yield of lead diacetate was quantitative. The solution was washed with an aqueous solution of sodium bicarbonate and chromatographed on alumina.<sup>4</sup> A 64% yield of benzyl azide and a 20–25% yield of benzaldehyde were obtained. Other products isolated were dibenzylamine (10%) and benzyl alcohol (13%); benzyl acetate was also identified as a very minor component.

When the ratio of  $\text{Pb}(\text{OAc})_4$  to tetrazene was decreased to 1:1 and the reaction mixture treated as previously, only traces of benzaldehyde (less than 5%) were obtained; instead benzyl alcohol was isolated in 34% yield.<sup>5</sup> Benzyl azide was obtained in 76% yield and dibenzylamine was formed in 63% yield. Infrared examination of the yellowish oil *before* chromatography indicated that only small amounts of the products isolated were present at that time; furthermore the component which appeared to be present in the largest quantity, benzaldehyde, was isolated in less than 5% yield *after* chromatography. The oil upon standing at room temperature for 2 days was slowly converted to the products as shown by the examination of the infrared spectrum. Evidently, the oil contained an intermediate which underwent decomposition to benzyl azide and dibenzylamine on standing. It was later discovered that, when pure benzaldehyde was passed through the column, only 16% of it was recovered and a 37% yield of benzyl alcohol was obtained.<sup>6</sup> Thus, benzaldehyde and *not* benzyl alcohol is the main product of the reaction and would amount to 75% yield.<sup>6</sup> On the basis of the information at hand, the mechanism given in Scheme I may be viewed for the reaction. The

Scheme I

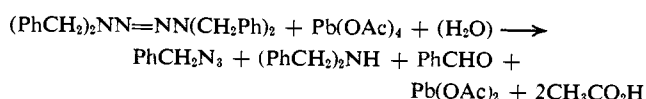


(4) Fisher Scientific Co., alumina A-540.

(5) The yields given for the reaction run with 1 equiv of lead tetraacetate are all corrected for recovered tetrazene (8%).

(6) Presumably the column promoted a Cannizzaro-type rearrangement. Benzoic acid probably remained in the column.

net stoichiometry of the reaction would then be



We are deferring any detailed discussion of this reaction at this time. The scope and the extension of this novel oxidative fragmentation reaction are being currently investigated in our laboratories.

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(7) To whom all inquiries should be addressed. Fellow of the Alfred P. Sloan Foundation.

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### The Structure of $\alpha$ -Ferrocenylcarbonium Ions<sup>1</sup>

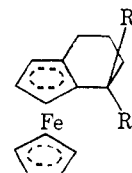
Sir:

The extraordinary stability of  $\alpha$ -metallocenylcarbonium ions as well as the great stereoselectivity of their reactions<sup>2</sup> has given rise to considerable speculation regarding the structural and electronic factors responsible for these properties.<sup>3</sup> It has been suggested<sup>3a</sup> that the cation is stabilized in part by direct interaction of the metal atom with the carbonium ion center, and that as a consequence the metal atom is displaced in the cation toward the  $\alpha$ -carbon atom, as depicted in structure 1.<sup>4</sup> These suggestions have however been questioned.<sup>3b</sup>

The nmr spectra of a series of  $\alpha$ -ferrocenylcarbonium ions have recently been interpreted as providing evidence for such a molecular distortion.<sup>5</sup> Thus, while

(1) Presented in part at the annual meeting of The Chemical Society, Dublin, Ireland, April 1968.

(2) These properties are well illustrated by the reactions of the epimeric acetates (i and ii) both of which undergo solvolysis by uncatalyzed ionization to give the *exo* alcohol (iii) exclusively. The *exo* acetate solvolyzes more rapidly than the *endo* isomer by a factor of 2500 and more rapidly than triphenylcarbinyl acetate by a factor of 28. (a) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 4216 (1961); (b) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, 1 (1960).



- i,  $\text{R}_1 = \text{OAc}$ ;  $\text{R}_2 = \text{H}$   
ii,  $\text{R}_1 = \text{H}$ ;  $\text{R}_2 = \text{OAc}$   
iii,  $\text{R}_1 = \text{OH}$ ;  $\text{R}_2 = \text{H}$

(3) (a) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961), and ref 2a; (b) J. C. Ware and T. G. Traylor, *Tetrahedron Letters*, 1295 (1965); T. T. Tidwell and T. G. Traylor, *J. Am. Chem. Soc.*, **88**, 3442 (1966); **89**, 2304 (1967); J. D. Fitzpatrick, L. Watts, and R. Pettit, *Tetrahedron Letters*, 1299 (1966); M. Rosenblum and F. W. Abbate, *Advances in Chemistry Series*, No. 62, American Chemical Society, Washington, D. C., 1966, p 532.

(4) The magnitude of the shift required to account qualitatively for the nmr spectra of these carbonium ions has been estimated to be about 1 Å: M. I. Levenberg, Ph.D. thesis, California Institute of Technology, 1965.

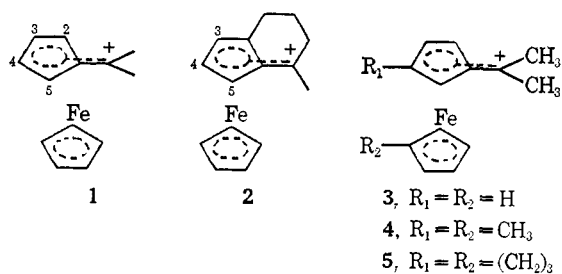
(5) M. Cais, J. J. Dannenberg, A. Eisenstadt, M. I. Levenberg, and J. H. Richards, *Tetrahedron Letters*, 1965 (1966).

Table I. Chemical Shifts of  $\alpha$ -Ferrocenylcarbonium Ions<sup>a</sup>

Carbonium ion	$\overset{+}{C}(CH_3)_2$	Cp <sup>b</sup>	H <sub>2,5</sub>	H <sub>3,4</sub>	Av $\Delta$ , Hz
2	2.28	4.88	5.0 (H <sub>2</sub> ) (q, $J_{35} = 1.5$ , $J_{45} = 3.0$ Hz)	6.12 (H <sub>3</sub> ) (q, $J_{35} = 1.5$ , $J_{34} = 3.0$ Hz) 6.29 (H <sub>4</sub> ) (t, $J_{34} = J_{45} = 3.0$ Hz)	72
3	2.28	4.88	5.0	6.33	80
4	2.20	4.63–4.82	4.73, 4.88	6.07	76
5	2.22, 2.32	4.60–4.80	4.90, 5.05	6.05	65

<sup>a</sup> All spectra were determined in trifluoroacetic acid solution employing tetramethylammonium bromide as internal standard ( $\delta$  3.30). Chemical shifts are given in parts per million (ppm) from tetramethylsilane. <sup>b</sup> Chemical shift of protons on the cyclopentadienyl ring not bearing the cationic center.

protons on C<sub>2,5</sub> in ferrocene derivatives bearing electron-withdrawing groups are normally deshielded by about 20 Hz compared with protons on C<sub>3,4</sub>,<sup>6</sup> the relative chemical shift of these protons is reversed and their shielding difference ( $\Delta$ ) is greatly magnified in the carbonium ions. These observations have been rationalized in terms of structure **1** in which increased metal-ring bonding at C<sub>2,5</sub> and especially magnetic anisotropy effects of the metal atom would lead to increased shielding at H<sub>2,5</sub> and a decrease in shielding at H<sub>3,4</sub>. Furthermore, a progressive decrease in  $\Delta$ , which is observed as substituents at the cationic center increase in their capacity to stabilize the charge, has been interpreted as reflecting a dependence in the extent to which the metal atom shifts on the magnitude of the charge at the  $\alpha$ -carbon atom.



We wish now to report nmr spectral data for several  $\alpha$ -ferrocenylcarbonium ions<sup>7</sup> which suggest that the proposed distortion does not occur. These are summarized in Table I.

The nmr spectrum of the tricyclic cation (**2**) allows an unequivocal assignment of resonance signals in this ion and provides confirmation for the earlier assignment<sup>5</sup> of the low-field signals in such ions to H<sub>3,4</sub>. Identification of resonance signals for H<sub>2,5</sub> and hence for H<sub>1</sub> in cations **4** and **5** was made possible by a comparison of the nmr spectra of these ions with those specifically deuterated at C<sub>2</sub> and C<sub>5</sub>. The labeled cations were prepared by treatment of the respective carbinols with excess butyllithium followed by quenching with D<sub>2</sub>O, a method previously shown to lead to specific deuteration at C<sub>2</sub> and C<sub>5</sub>.<sup>8</sup>

Comparison of the chemical shifts for the geminal methyl protons in the cations **3** and **4** suggests that the presence of methyl substituents on the cyclopentadienyl

rings in **4** does not appreciably alter the charge distribution at the carbonium ion center. Similarly, substitution of a trimethylene bridging element for the methyl substituents on the rings does not result in a significant change in positive charge at the tertiary cationic center.

The bridged cation (**5**) is however structurally significantly different from **4** in that a molecular distortion such as that depicted for the ion **1**, which is not precluded for **4**, can only be imposed on the ion **5** at the cost of considerable valence angle distortion within the bridging element. Nevertheless, the near identity of geminal methyl resonances in these cations as well as those signals due to the cyclopentadienyl ring not substituted by the carbonium ion center suggest a close similarity both in charge distribution within the cations and in their structures.

Furthermore, the average signal for H<sub>2,5</sub> in **5** is shifted downfield by only 0.17 ppm compared with this resonance in **4**, and the values of  $\Delta$  for these ions are very similar notwithstanding the very different structural constraints in each ion toward deformation as in **1**. It is unlikely that the metal atom alone is displaced toward the carbonium ion center in **5**, since under these circumstances significant differences in shielding of protons on both cyclopentadienyl rings would be anticipated. Finally, the downfield shift of resonances for H<sub>2,5</sub> in **5** compared with those in **4** is not accompanied by a corresponding reciprocal effect on the signals for H<sub>1</sub> in these ions. Such an effect is to be anticipated if the differences in ring proton shielding are largely due to the magnetic anisotropy of the iron atom. In fact calculations suggest that the effect of a shift such as that depicted in **1** should be greater on the shielding of ring proton H<sub>3,4</sub> than on H<sub>2,5</sub>.<sup>4</sup>

These observations suggest that the disparate shielding of ring protons in  $\alpha$ -ferrocenylcarbonium ions is not to be accounted for in terms of molecular distortions such as depicted by **1**, but are either the consequence of very different molecular deformations<sup>9</sup> or derive from a charge distribution and metal-ring bonding interactions which are significantly different in the ion compared with uncharged derivatives.

**Acknowledgment.** This research has been generously supported by the National Institutes of Health through grants (GM-05978 and GM-16395) which are gratefully acknowledged.

(9) E. A. Hill and R. Wiesner, *J. Am. Chem. Soc.*, **91**, 509 (1969).

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(6) The nmr spectrum of acetylferrocene, a typical derivative of this class, exhibits absorption at  $\delta$  4.76 (H<sub>2,5</sub>) and 4.47 (H<sub>3,4</sub>).

(7) The cations were generated from the corresponding carbinols, which were prepared from their respective methyl ketones of well-defined structure. All compounds gave satisfactory analyses.

(8) R. A. Benkeser, W. P. Fitzgerald, and M. S. Meltzer, *J. Org. Chem.*, **26**, 2569 (1961).