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# DEPROTONATION OF FERROCENYLCARBONIUM IONS.*
# A POTENTIAL SOURCE FOR METALLOCENYLCARBENES?

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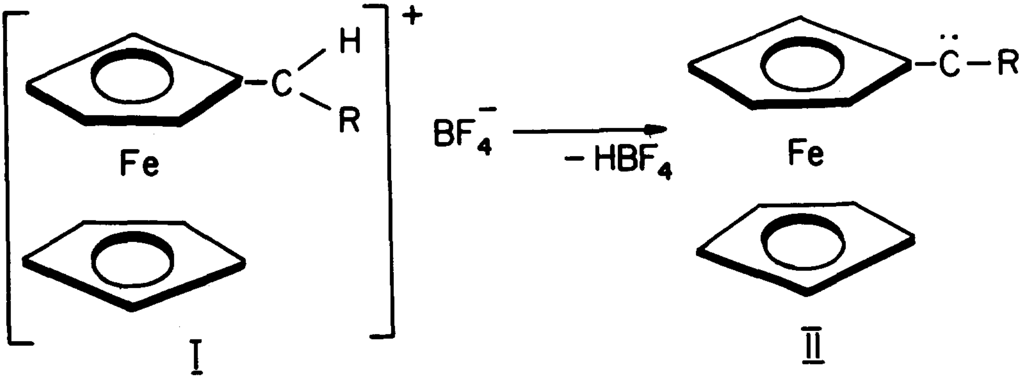
The easy access to the highly stable, isolable, α-ferrocenylcarbonium ions, I, (1), led us to investigate the possibility that deprotonation of I with suitable bases might lead to nucleophilic carbene intermediates of structure II :-



A brief report of some of our preliminary results is made necessary at this time by the recent appearance of a communication (2) describing experiments in which stable "carbonium" ion salts, such as $[(CH_3S)_2CH]^+ BF_4^-$ have been deprotonated with base to yield postulated carbene intermediates, such as $CH_3S\text{-}\ddot{C}\text{-}SCH_3$.

An instantaneous reaction occurred, as shown by an immediate colour change from deep blue to yellow, when a methylene chloride solution of ferrocenyltropylium fluoroborate, III, (3) was reacted with diisopropylethylamine as the proton-abstracting base [chosen for its reported

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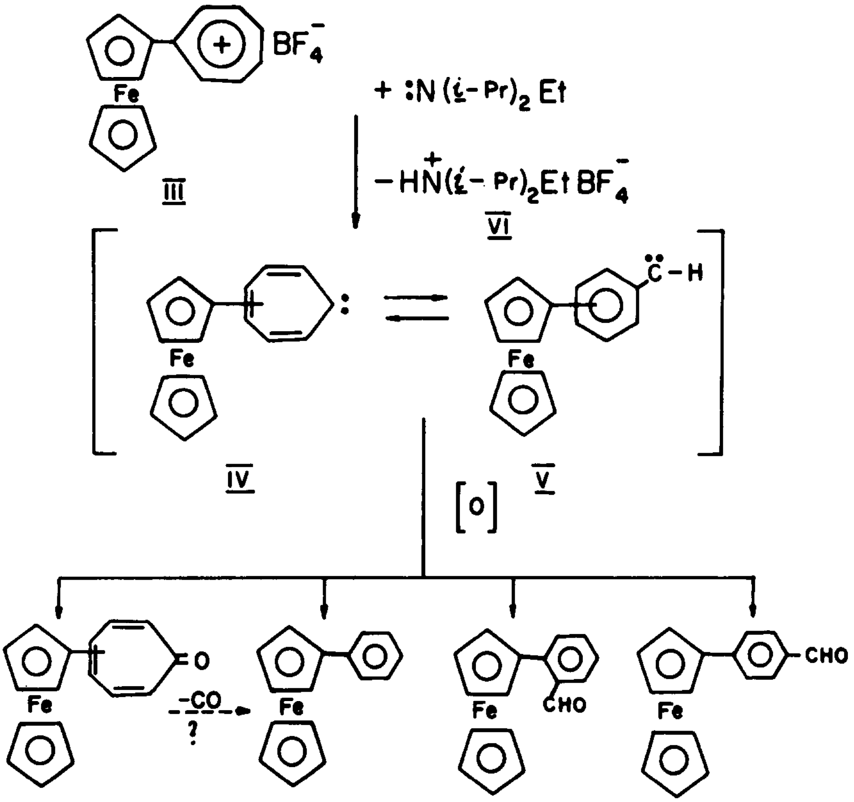
reluctance (4) to enter into alkylation reactions whilst having good proton-abstracting properties]. Work-up of the reaction mixture (shown by thin layer chromatography to contain at least seven different compounds) produced a quantitative yield of the quaternary salt VI in addition to o-ferrocenylbenzaldehyde (22%), p-ferrocenylbenzaldehyde (30%), x-ferrocenyltropone (12%), and phenylferrocene (32%) as the major products.

If so desired, one can rationalize the formation of all the above compounds by postulating the carbene IV (and the rearranged carbene V) as the intermediate leading eventually to the reaction products.

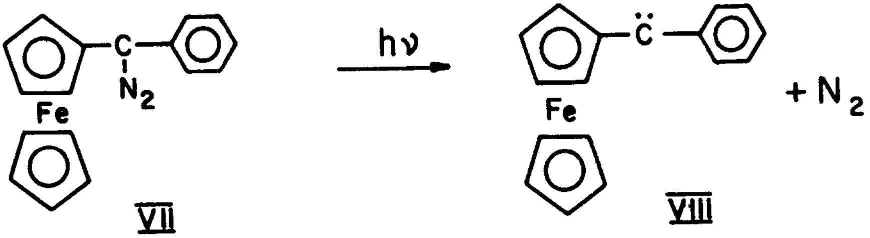


The same reaction carried out as control on phenyltropylium fluoroborate produced a mixture of at least four compounds, containing inter alia substituted benzaldehydes.

When the carbonium ion salt I ($R = C_6H_5$) was used in the deprotonation reaction, the reaction product mixture contained mainly the quaternary salt VI, benzoylferrocene and benzylferrocene. By employing a carbonium ion salt, I, in which the carbinyl hydrogen had been replaced by a deuterium atom, it was possible to show (by NMR spectroscopy) that the quaternary salt VI contained only deuterium, thus providing evidence that deprotonation takes place exclusively at the carbinyl carbon atom.

The use of nitromethane as solvent in any of the deprotonation reactions described above results in the incorporation of the $-CH_2NO_2$ moiety in the reaction products. It must be pointed out that this does not necessarily involve the insertion of a carbene intermediate in the C-H bond of nitromethane; instead, it could well be the result of attack by the aci-nitromethane on the carbonium ion.

Hoping to produce a ferrocenylcarbene, e.g. VIII, by way of a less equivocal reaction, a non-deoxygenated methanolic solution of ferrocenylphenyldiazomethane, VII was subjected to UV irradiation. The major reaction products were benzoylferrocene and, presumably, 1,2-diferrocenyl-1,2-diphenylethane. In preliminary experiments, UV irradiation of VII in a frozen methanolic matrix (150°K) resulted in the production of an ESR signal which persisted strongly even one hour after the UV irradiation had been stopped. The nature and source of the ESR signal are presently under investigation.



Other experiments currently in progress are aimed at:- (i) Extending the deprotonation reaction to a large number of ferrocenylcarbonium ions (including diferrocenylcyclopropenylium fluoroborate) under a variety of reaction conditions; (ii) Obtaining direct experimental evidence that carbene intermediates are indeed formed in the deprotonation of stabilized carbonium ions;

(iii) Investigating the singlet or triplet nature of metallocenylcarbenes, should the evidence point to their actual formation either in the deprotonation or photolysis reactions; (iv) Enlarging upon the potential synthesis applications of the deprotonation reactions.

Finally, we find it necessary to sound a strong note of caution. Although the postulation of carbene intermediates may seem rather attractive at this time, both in our deprotonation examples as well as those recently published by Olofson and co-workers (2), conclusive and unequivocal evidence for carbene formation has yet to be produced (5). At present, we are far from having satisfied ourselves that the intervention of other intermediates can be excluded (7).

## REFERENCES AND NOTES

1. For a review see M. Cais, *Organometal. Chem. Rev.*, *1*, 435(1966).
2. R.A. Olofson, S.W. Walinsky, J.P. Marino, and J.L. Jernow, *J.Am.Chem.Soc.*, *90*, 6554(1968).
3. M. Cais and A. Eisenstadt, *ibid.*, *89*, 5468(1967).
4. S. Hunig and M. Kiessel, *Chem. Ber.*, *91*, 380(1958).
5. The nature of the Wanzlick carbenes [see H.W. Wanzlick and H.J. Kleiner, *Angew. Chem. Intern. Ed. Engl.*, *3*, 65(1964)], which are similar structurally to those reported by Olofson and co-workers (2), is still a matter of controversy (6).
6. See for instance D.M. Lemal, R.A. Lovald, and K.I. Kawano, *J.Am.Chem.Soc.*, *86*, 2518(1964).
7. The rapid α-hydrogen exchange in heterocyclic nitrogen ylides, may serve as one example for consideration in this connection: see R.A. Olofson, W.R. Thompson, and J.S. Michelman, *ibid.*, *86*, 1865(1964); H.A. Staab, M.-Th. Wu, A. Mannschreck, and G. Schwalbach, *Tetrahedron Letters*, *15*, 845(1964).
8. The compounds isolated in the reported reactions have been characterized by elemental analysis, infrared, ultraviolet, mass spectrometry as well as by comparison with authentic samples prepared by independent syntheses.