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Preliminary communication

ON THE EVIDENCE FOR THE GENERATION OF A FERROCENYLSILICENIUM ION

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Summary

A previous claim for the generation of a metallocenyl-substituted silicenium ion is shown to be based on insufficient evidence.

We recently presented "prima facie evidence" [1] for the generation of ferrocenyldiphenylsilicenium ion (I). Briefly, reaction of $FcPh_2SiH$ (II) with triphenylcarbenium perchlorate at —60°C in methylene chloride generates a dark green solution; addition of this solution to $NaBD_4$ in diglyme discharges the color (to orange) and produces triphenylmethane and $FcPh_2SiD$ (III). Recognizing at the time that "the possibility cannot be strictly excluded that ferrocenyldiphenylsilyl perchlorate might be a covalent compound which is reduced, with Si—O bond cleavage, by $NaBD_4$", we performed additional experiments to test our original claim.

We have found that triphenylsilyl perchlorate, first prepared by Wannagat et al. [2] and generally assumed to be a covalent compound, is readily reduced by $NaBH_4$ to triphenylsilane under conditions similar to those described above, with no detectable (NMR) formation of triphenylsilanol. This result invalidates any conclusions predicted on the assumption that I is a required intermediate in the trapping reaction, i.e., in the $NaBD_4$ reduction; perchlorate is therefore unsuitable as a gegenion in tests for I. Reaction of II with triphenylcarbenium hexafluorophosphate (IV) under the above conditions also generates a persistent (> 1 hour) green solution whose color is instantly discharged upon quenching with $NaBD_4$ in diglyme. The products of this reaction are triphenylmethane and $FcPh_2SiF$ (V), m.p. 91—92°C, M^+ (based on ^{56}Fe) *m/e* 386, $\delta(^{19}F)$ 163 ppm (in $CDCl_3$) downfield from $CFCl_3$. No detectable amounts (>2%) of II or III are found. When the reaction mixture is quenched within 1 min after mixing of II and IV, the products are again triphenylmethane and V, with no II or III. Since formation of V is essentially

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complete within 1 min, it follows that the green color, whatever its origin, cannot be due to any substantial concentration of I.

In combination, these experiments demonstrate the insufficiency of the evidence originally [1] adduced for I, and by implication for the silicenium ion derived from a silepin [3]. Although the described hydrogen transfer reactions are not inconsistent with the intermediacy of silicenium ions, a verdict of "not proven" must be rendered at this time.

Acknowledgment

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References

1 J.Y. Corey, D. Gust and K. Mislow, J. Organometal. Chem., 101 (1975) C7.
2 U. Wannagat and W. Liehr, Angew. Chem., 69 (1957) 783; U. Wannagat, F. Brandmair, W. Liehr and H. Niederprüm, Z. Anorg. Allg. Chem., 302 (1959) 185; cf. also U. Wannagat and F. Brandmair, ibid., 280 (1955) 223.
3 J.Y. Corey, J. Amer. Chem. Soc., 97 (1975) 3237.

Note added in proof. After this work was completed, we learned that Professors T.J. Barton and J. Lambert had each independently arrived at similar conclusions.