Journal of Organometallic Chemistry, 101 (1975) C7—C8

Preliminary communication

GENERATION OF A FERROCENYLSILICENIUM ION

JOYCE Y. COREY*, DEVENS GUST, and KURT MISLOW**
Department of Chemistry, Princeton University, Princeton, New Jersey 08540 (U.S.A.)

(Received August 11th, 1975)

Summary

Generation of the first metallocenyl-substituted silicenium ion is described.

Demonstration of the elusive trivalent silicenium ion [1] was first achieved [2] by employing a hydride abstraction reaction from a 10,11-dihydrodibenzo-[*b*,*f*]silepin according to eqn. 1.

$$R'_3C^+ + R_3SiH \rightarrow R'_3CH + R_3Si^+ \qquad (1)$$

Silicenium ions (R_3Si^+) are likely to be observed whenever the stability of the analogous carbenium ion (R_3C^+) is substantially greater than that of the hydride abstracting reagent, R'_3C^+. Metallocenylcarbenium ions exhibit unusually high stability [3] and are therefore suitable models for analogous silicenium ions. The recent communication by Corriu et al. [4], pointing to the possibility of forming ferrocenylsilicenium ions, prompts us to disclose our preliminary results describing conditions for the generation of a ferrocenylsilicenium ion.

The starting silane, ferrocenyldiphenylsilane (I), m.p. 66.5-67°***, was prepared in 42% yield from reaction of diphenylchlorosilane with ferrocenyllithium by a reported method [5]. The spectroscopic constants for Si—H were: δ ($CDCl_3$, TMS) 5.49 ppm; IR (CH_2Cl_2) 2140 cm^{-1}. Reaction of I with an equimolar amount of triphenylcarbenium perchlorate at −60°C in methylene chloride under a dry, nitrogen atmosphere generated a dark-green solution from the orange precursors****. Rapid addition of the reaction mixture to a cold solution (−20°C) of $NaBD_4$ in diglyme resulted in an immediate change to an orange color. After removal of the solvents under reduced pressure, the residue was dissolved in CH_2Cl_2, filtered to remove excess $NaBD_4$, and hydrolyzed by addition of water.

---

*Faculty Member of the Department of Chemistry, University of Missouri-St. Louis, St. Louis, Mo. 63121, on sabbatical leave at Princeton University during 1974-75.

**Author to whom correspondence should be addressed.

***Satisfactory analytical data and an NMR spectrum consistent with the product I have been obtained.

****A color change took place on warming this solution to room temperature. The products of this reaction have not yet been characterized.

Separation of the products was effected by removing triphenylmethane (98% crude yield free of deuterium by mass spectrometry), containing a trace of ferrocene, at 130-150°C/0.05 mmHg. After removal of some insoluble material from the remaining viscous oil, crude I containing deuterium on silicon in place of protium was obtained in 86% yield. The oil could be purified by recrystallization from ethanol to give deuteriated I, m.p. 66-67°C, whose NMR spectrum was identical to that of I except in the absence of the SiH resonance at δ 5.49 ppm; M^+ (based on ^{56}Fe), *m/e* 369. Deuteriated I exhibited a new IR band at 1540 cm^{-1} in the region assigned to an Si—D stretch [6]. A trace of undeuteriated I was indicated by a weak residual IR absorption at 2140 cm^{-1}.

The results of this trapping reaction provide prima facie evidence for the generation of ferrocenyldiphenylsilicenium ion (II) in solution at low temperatures, although the possibility cannot be strictly excluded that ferrocenyldiphenylsilyl perchlorate might be a covalent compound which is reduced, with Si—O bond cleavage, by $NaBD_4$.

It was found that reaction of II with water follows an unexpected course. Addition of the dark-green reaction mixture (produced from 0.60 g of triphenylcarbenium perchlorate and 0.64 g of I in 25 ml of CH_2Cl_2) to 25 ml of dioxane containing 0.5 ml of water produced no apparent change in color. After removal of the solvents the dark-green residue was dissolved in CH_2Cl_2 and extracted with water to give a deep blue aqueous layer and a yellow-orange organic layer. Elution of the residue obtained from the organic layer over silica gel (hexanes) afforded ferrocene (identical to an authentic sample), triphenylmethane, and $[(C_6H_5)_2SiO]_x$, in 70%, 98% and 56% yields respectively. These reaction products may arise from protonation of the metal center followed by hydrolytic cleavage of the $(C_6H_5)_2Si$ moiety. The expected product, ferrocenyldiphenylsilanol, was not obtained even though it is reportedly stable under workup conditions similar to those reported here [7]*.

Acknowledgment

We thank the National Science Foundation (grant no. MPS74-18161) for support of this work.

References

1 For a review of previous work see R.J.P. Corriu and M. Henner, J. Organometal. Chem., 74 (1974) 1.
2 J.Y. Corey, J. Amer. Chem. Soc., 97 (1975) 3237.
3 M. Cais, Organometal. Chem. Rev., 1 (1966) 435; E.A. Hill and R. Wiesner, J. Amer. Chem. Soc. 91 (1969) 509.
4 R.J.P. Corriu, F. Larcher and G. Royo, J. Organometal. Chem., 92 (1975) C18.
5 R.A. Benkeser, D. Goggin and G. Schroll, J. Amer. Chem. Soc., 76 (1954) 4025.
6 L. Kaplan, J. Amer. Chem. Soc., 76 (1954) 5880.
7 G.P. Sollott and W.R. Peterson, J. Amer. Chem. Soc., 89 (1967) 5054.

---

[*] A referee has suggested that the blue color in the aqueous phase may be due to the presence of ferrocenium (Fe^{3+}) salts produced by $HClO_4$ oxidation of the ferrocene (Fe^{2+}) moiety.