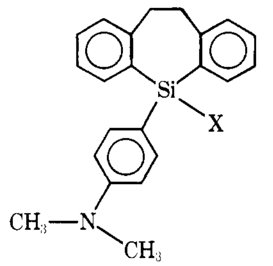
Communications to the Editor

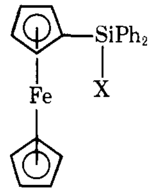
A Reconsideration of the Generation of Silylenium Ions in Solution

Sir:

After years of unsuccessful attempts to gain evidence for the silylenium ion,[1] R_3Si^+, in solution,[2] two reports[3,4] have recently appeared which claim to "provide prima facie evidence for the generation of a silicenium[1] ion in methylene chloride at low temperatures." In both cases an electronically stabilized silylenium ion was supposedly produced by hydride abstraction from silicon by trityl perchlorate in methylene chloride at ca. −50 °C to produce for silane **1a** a yellow-green solution and for **2a** a dark green solution. In the case of **1a** warming to room temperature afforded a brilliant blue-green solution from which no identifiable organosilicon products could be isolated. When the cold trityl perchlorate-silane solutions were added to a solution of $NaBD_4$ in diglyme immediate decoloration was observed and high yields of triphenylmethane and the deuterated silanes **1b** or **2b** were obtained. We would like to raise several points relative to the acceptance of these data as proof of silylenium ion intermediacy. First, it is well known that trityl halides react with silyl hydrides in a variety of solvents, through what has been suggested to be a four-centered transition state,[5,6] to afford the silyl halides and triphenylmethane. The stereochemistry of this hydrogen-halogen exchange reaction has been carefully investigated and found to be extremely solvent dependent.[7] In methylene chloride optically active silane was found to produce completely racemized silyl halide. For the exchange in methylene chloride, a mechanism was suggested where Si-H bond cleavage was somewhat complete before attack by halide from the front or rear was established. The dependency upon the ion dissociating power of the solvent suggests that the freedom of the halide ion may control the stereochemical outcome and a silylenium ion is not demanded. Carey has measured the rates of hydride transfer from substituted silanes to the tris(2,6-dimethoxyphenyl)methyl cation in acetic acid.[8] For a series of triarylsilanes a value of $\rho = -1.87$ was obtained and it was concluded that this was of insufficient magnitude to invoke silylenium ion intermediacy. We have found that a wide variety of silyl hydrides (no exceptions to date) react with trityl perchlorate to instantaneously decolorize the solution and afford triphenylmethane and the silyl perchlorate. For example triethylsilane reacts with trityl perchlorate to produce triphenylmethane and triethylsilyl perchlorate both in essentially quantitative yield. Silyl perchlorates, prepared from silyl halides and silver perchlorate, have been investigated and found to simply be covalent esters of perchloric acid, $R_3Si\text{-}O\text{-}ClO_3$.[9] Thus the observation that both **1a** and **2a** react with trityl perchlorate is hardly surprising.



1a, X = H
b, X = D



2a, X = H
b, X = D

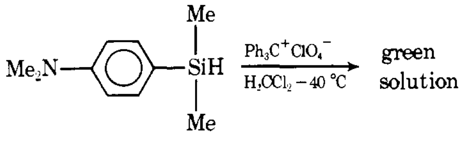
$$Et_3SiH + Ph_3C^+ClO_4^- \xrightarrow{H_2CCl_2} Et_3SiOClO_3 + Ph_3CH$$

Secondly, we felt it hardly unlikely that covalent silyl esters of perchloric acid would react with $NaBH_4$. Indeed we find that $Et_3Si\text{-}OClO_3$ reacts immediately and quantitatively with $NaBH_4$ to afford Et_3SiH under similar conditions as reported in ref 3 and 4. Therefore the formation of **1b** and **2b** is not unexpected as the corresponding silyl perchlorates, whether salts or esters, would be expected to undergo reduction by $NaBD_4$. Steric hinderance for a concerted displacement of perchlorate by hydride is not likely to be sufficient to favor an S_N1 process as we find that tri-*tert*-butylsilyl perchlorate,[10] a molecule whose ^{13}C and ^{29}Si NMR spectra in acetonitrile reveal no evidence for ionic character, is smoothly reduced by $NaBH_4$ in diglyme to tri-*tert*-butylsilane.

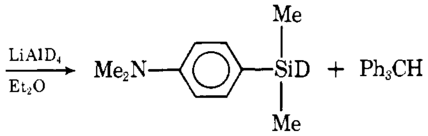
$$R_3SiOClO_3 \xrightarrow{NaBH_4} R_3SiH$$

Lastly we have to deal with the colors generated by the reaction of trityl perchlorate and **1a** and **2a** in methylene chloride solution. Since in all cases investigated by us, including triphenylsilane, the reaction of silyl hydride and trityl perchlorate produced no color whatsoever, we suspected the amino function of **1a** to be the culprit in that case. Indeed we find that *N,N*-dimethylaniline produces a deep green color when mixed with trityl perchlorate in methylene chloride. Further addition of trityl perchlorate turns this solution a deep blue. The aromatic ring is not necessarily involved in this reaction as triethylamine produces a deep violet solution with trityl perchlorate in methylene chloride. The reaction, or lack of reaction, of trityl salts with tertiary amines has been a subject of some controversy.[11] Certainly our colors are not due to quaternization of the amine since these salts should not be colored. One could assume that an electron transfer process is occurring to produce the amine radical cation in a charge-transfer complex. This idea is dimmed but not totally eliminated by the fact that the deep blue solution from triethylamine and trityl perchlorate in methylene chloride produces no ESR signal. We will continue to investigate the nature of the amine-trityl ion interaction, but we do feel that this interaction with the dimethylamino group of **1a** could account for the colors reported in ref 3. Further we note that addition of the cold, blue solution resulting from triethylamine to a cold solution of $NaBH_4$ in diglyme resulted in immediate decoloration. Perhaps the color reported in ref 3 can also be explained by an electron transfer to trityl ion as we find that addition of trityl perchlorate to a methylene chloride solution of ferrocene instantly yields a deep green solution which presumably involves the green ferrocenyl cation.[14]

We have examined a mimic system of **1a**, **3a**,[15] which would not be expected to produce nearly as stable a cation. Reaction of **3a** with trityl perchlorate in methylene chloride at −40 °C produces a deep green solution which when quenched with a cold, ether solution of $LiAlD_4$ affords only the deuterated silane (**3b**), according to the ir and NMR spectra, and undeuterated triphenylmethane. Silane **3a** did not exchange with $LiAlD_4$ under these conditions in the absence of trityl perchlorate.



3a



3b

In summary, while it is still possible that silanes **1a** and **2a** do form the silylenium ions, all of the evidence thus far presented can be reproduced with systems for which there is no particular reason to presume silylenium ion involvement.

Note Added in Proof. Well after this work was submitted for publication, we learned that Professors J. Lambert and K. Mislow had each independently arrived at similar conclusions.

Acknowledgment. Financial support was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) Although the cation R_3Si^+ is referred to as a silicenium ion in ref 3 and 4, if a protonated carbene is to be called a carbenium ion a protonated silylene (R_2Si:) should be named a silylenium ion.

(2) See R. J. P. Corriu and M. Henner, *J. Organomet. Chem.*, **74**, 1 (1974), for a review of previous attempts.

(3) J. Y. Corey, *J. Am. Chem. Soc.*, **97**, 3237 (1975).

(4) J. Y. Corey, D. Gust, and K. Mislow, *J. Organomet. Chem.*, **101**, C7 (1975).

(5) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 2430 (1963).

(6) J. D. Austin and C. Eaborn, *J. Chem. Soc.*, 2279 (1964).

(7) L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7076 (1969).

(8) F. A. Carey and C.-L. Wang Hsu, *J. Organomet. Chem.*, **19**, 29 (1969).

(9) V. Wannagat and W. Liehr, *Angew. Chem.*, **69**, 783 (1957).

(10) The synthesis and chemistry of this compound will be reported separately.

(11) C. G. Swain and Y. Okamoto, *J. Am. Chem. Soc.*, **92**, 3409 (1970), and references therein.

(12) The failure to observe the amine radical $Et_3N\cdot^+$ could be due to band-broadening due to rapid electron exchange with other molecules of Et_3N.[13]

(13) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969, p 312.

(14) M. Rosenblum, "Chemistry of Iron Group Metallocenes", Wiley, New York, N.Y., 1965.

(15) J. Hetflejš, F. Mareš, and V. Chvalovský, *Collect. Czech. Chem. Commun.*, **30**, 1643 (1965).

Thomas J. Barton,* Allan K. Hovland, Christopher R. Tully
Department of Chemistry, Iowa State University
Ames, Iowa 50011

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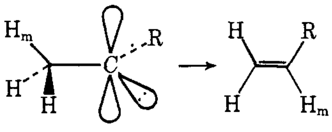
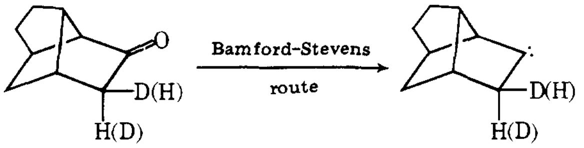
1,2-Hydrogen Shifts in Carbenes. The Question of Stereoelectronic Control of Migration

Sir:

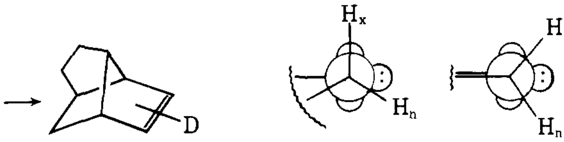
In recent years there have been a number of theoretical investigations concerning stereoelectronic control in the 1,2-hydrogen shift to a carbene center to give the corresponding olefin.[1] The prediction arising from these calculations is that the group which migrates is that which is aligned with the empty orbital as in **1** (H_m migrates). Until recently, this prediction had not been tested experimentally with a relatively rigid, stereochemically well-defined system.[2] The carbene **3** derived from the Bamford–Stevens reactions on the *exo*(x)- and *endo*(n)-4-deuteriobrexan-5-one (**2**) recently described by Nickon and his co-workers[3] appeared to be such a system. It was stated on the basis of examination of models, that the ethylene bridging unit twists the molecules **2** and **3** such that the exo-hydrogen (H_x) tends to align with the empty p-type orbital of the carbene as in **5**, instead of being symmetrically disposed, which is the case in normal [2.2.1] systems (e.g., **6**).



1

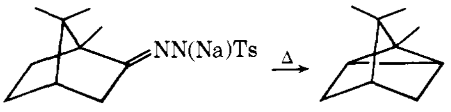


2 **3**



4 **5** **6**

Nickon found the migratory ratio H_x/H_n in **3** to be 138, on the basis of ^1H NMR analysis of the position of the deuterium in **4**. This ratio presumably reflected stereoelectronic migration control in accord with theoretical predictions.[1] In order to conclude this, it is necessary to assume that H_x does not have some "natural" propensity to migrate relative to H_n, which is peculiar to the [2.2.1] system, as is well-known in carbonium ion analogues.[4] There is, to our knowledge, no information concerning carbenic migratory ratios H_x/H_n in unbiased [2.2.1] systems (e.g., **6**), the problem being that intramolecular cyclization (e.g., **7** → **8**[5]) is apparently more facile than H migration to give the olefin. Thus it was necessary to synthesize a [2.2.1] carbene precursor in which the intramolecular cyclization was precluded in order to study the H_x/H_n migratory aptitudes.



7 **8**

The synthesis of appropriately labeled carbene precursors **14** is outlined below. The Diels–Alder adduct **9**[6] obtained from benzoquinone and carbomethoxycyclopentadiene was aromatized (acid-catalyzed) and alkylated (base, dimethyl sulfate) to give the substituted benzonorbornadiene **10**. This was reduced (LAH) and protected with the *tert*-butyldimethylsilyl group[7] to give **11a**, which under hydroboration conditions (disiamylborane, −77°) gave a mixture of regioisomers **13** and **12** in a ratio of 10:1.[8] The alcohols **12** and **13** were readily separated by chromatography, and **13** was oxidized to ketone **14a** (Oppenauer, benzoquinone, $Al(OBu\text{-}t)_3$[9]). Treatment of **14a** with KOBu-*t* (1 equiv) in dioxane-D_2O at 60° for 1.25 h gave **14b**.[10a,11] Similarly, treatment of **14a** under the above reaction conditions for 60 h gave **14c**,[10b] which gave **14d**[10c] upon treatment with KOBu-*t* (1 equiv) in dioxane-H_2O at 60° for 3 h.

The tosylhydrazones of the ketones **14b** and **14d** were obtained under neutral conditions ($TsNHNH_2$ in MeOH at 60° for 1.3 h) and these were converted to the lithium salts (*n*-BuLi in THF at −77°), which were obtained free of solvent by evaporation and pumping on the residue at 60° (2 μ). These salts were then decomposed in cyclohexane at 190° (0.7 h).[12] The regioisomeric mixture of olefins **11b** and **11c** was isolated by chromatography in about 30% yields.[13] ^1H NMR analysis[14]