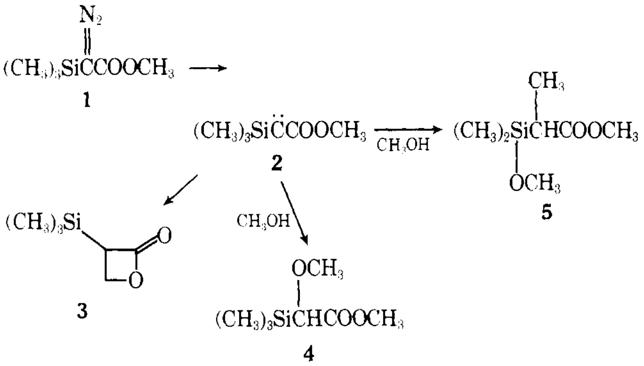
Communications to the Editor

On the Role of Alkoxysilylketenes and the Absence of Carbon–Silicon Double Bonds in the Gas-Phase Decomposition of Trimethylsilyldiazoacetates[1]

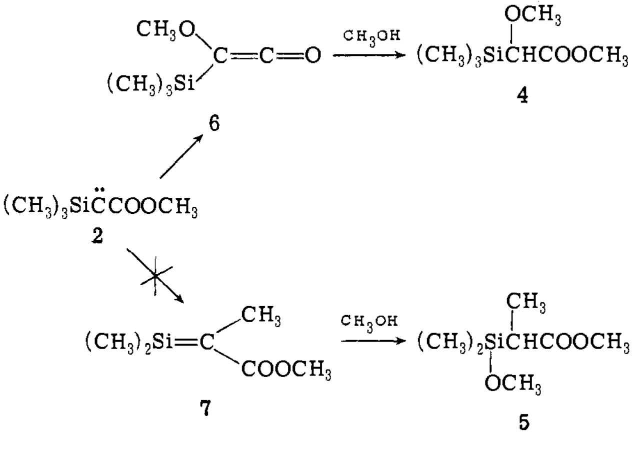
Sir:

It has become recently fashionable[2,3] to claim silaethylenes as intermediates in the formation of products from trimethylsilylcarbenes. We present here a case in which such an inference would be reasonable at first glance, but in which a closer look reveals that more circuitous reaction paths are being followed.

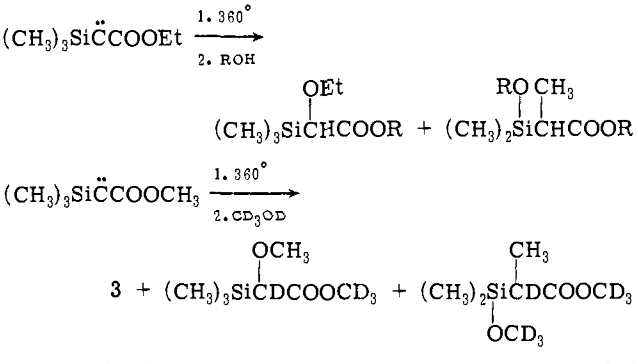
When methyl trimethylsilyldiazoacetate (**1**) was evaporated through a Pyrex tube maintained at 360° and the products then treated with methanol, three compounds were observed.[4] Compound **3** is almost certainly formed by an insertion of carbene **2** into the proximate carbon–hydrogen bond of the methoxyl group. Although β-lactones have not been isolated previously, they have been postulated,[5] and larger ring lactones have been found in similar reactions.[6] The ^1H NMR spectrum of **3** (CCl_4, τ 5.6–5.9, m, 1 H; 5.9–6.3, m, 1 H; 6.5–6.9, m, 1 H; 9.83, s, 9 H) and infrared absorptions at 1813 and 1095 cm^{-1} serve to establish the structure.[7]



Compound **4** is the evident product of methanolysis of the ketene **6**, itself formed by Wolff rearrangement of carbene **2**.[8]



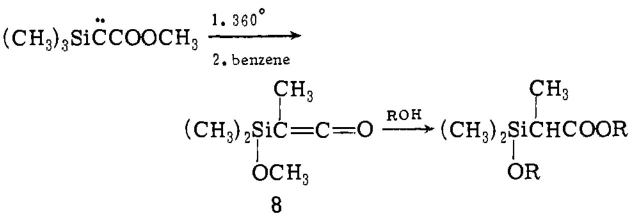
Compound **5** appears to be derived from methanolysis of silaethylene **7** which could arise by methyl shift in **2**. Indeed this compound was so rationalized in earlier work on the photolysis of **1** in solution.[2] However, it is not formed in such a fashion. Trapping of the pyrosylate in alcohols other than methanol shows that *both* alkoxy groups in **5** are derived from the *added* alcohol! This observation led us to attempt the isolation of ketene **8**, the suspected intermediate.



$$\mathrm{(CH_3)_3Si\ddot{C}COOEt} \xrightarrow[2.\ \mathrm{ROH}]{1.\ 360^\circ} \mathrm{(CH_3)_3Si\overset{OEt}{\overset{|}{C}}HCOOR} + \mathrm{(CH_3)_2\overset{RO}{\overset{|}{Si}}\overset{CH_3}{\overset{|}{C}}HCOOR}$$

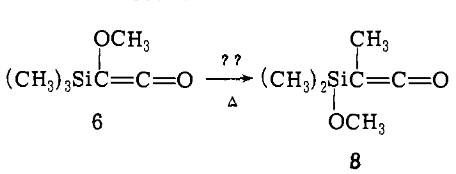
$$\mathrm{(CH_3)_3Si\ddot{C}COOCH_3} \xrightarrow[2.\ \mathrm{CD_3OD}]{1.\ 360^\circ} 3 + \mathrm{(CH_3)_3Si\overset{OCH_3}{\overset{|}{C}}DCOOCD_3} + \mathrm{(CH_3)_2\underset{OCD_3}{\underset{|}{Si}}\overset{CH_3}{\overset{|}{C}}DCOOCD_3}$$

Pyrolysis of **1** at 360° followed by addition of benzene led to **8** in 12% yield.[9] The structure follows from the ^1H NMR spectrum (CCl_4, τ 6.57, s, 3 H; 8.39, s, 3 H; 9.78, s, 6 H) and the presence of infrared bands at 2085 and 1088 cm^{-1}.[7] At 60° in alcohols **8** gave the twice-exchanged products quantitatively. Thus the source of **5** is not the silaethylene but rather ketene **8**, and there is no need to invoke π-bonded silicon species, at least in the gas phase.



$$\mathrm{(CH_3)_3Si\ddot{C}COOCH_3} \xrightarrow[2.\ \mathrm{benzene}]{1.\ 360^\circ} \underset{8}{\mathrm{(CH_3)_2Si\underset{OCH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}{=}C{=}O}} \xrightarrow{\mathrm{ROH}} \mathrm{(CH_3)_2\underset{OR}{\underset{|}{Si}}\overset{CH_3}{\overset{|}{C}}HCOOR}$$

A major question remains as to the source of **8**. It is known that ion pairs are involved in the Wolff rearrangement of carboalkoxycarbenes in solution.[10] It is attractive to speculate that similar species, probably not ionic, are involved in the gas phase. Thus as OCH_3 migrates to the adjacent position on its way to ketene **6**, it finds itself in the neighborhood of a silicon atom and simply adds with or without simultaneous movement of a methyl group. But other possibilities abound.



$$\underset{6}{\mathrm{(CH_3)_3Si\overset{OCH_3}{\overset{|}{C}}{=}C{=}O}} \xrightarrow[\Delta]{??} \underset{8}{\mathrm{(CH_3)_2\underset{OCH_3}{\underset{|}{Si}}\overset{CH_3}{\overset{|}{C}}{=}C{=}O}}$$

Ketone **6** may undergo a rearrangement to **8** of the dyotropic kind, or nitrogen containing species may be involved, or **8** may be formed by rapid rearrangement of **7**.[12]

In sum, it is clear that the immediate source of **5** is not the silaethylene but rather the ketone **8**. There is no requirement that **7** be formed in **2**.

References and Notes

(1) Grant MPS74-05690 from the National Science Foundation to Princeton University and support for one of us (S.K.) by the Dean of Student Affairs Office at Princeton University is gratefully acknowledged. We are further pleased to acknowledge a gift of trimethylchlorosilane by the Shinetsu Chemical Co.

(2) W. Ando, T. Hagiwara, and T. Migita, *J. Am. Chem. Soc.*, **95**, 7518 (1973).
(3) W. Ando, A. Sekiguchi, J. Ogiwara, and T. Migita, *J. Chem. Soc., Chem. Commun.*, 145 (1975).
(4) In Gunma, products were directly condensed in cold alcohol on emergence from the hot zone. In Princeton, they were condensed upon a cold finger maintained at −196° and washed off with alcohol.
(5) D. C. Richardson, M. E. Hendrick, and M. Jones, Jr., *J. Am. Chem. Soc.*, **93**, 3790 (1971).
(6) W. Kirmse, H. Dietrich, and H. W. Bucking, *Tetrahedron Lett.*, 1833 (1967).
(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2nd ed., Wiley, New York, N.Y., 1958.
(8) Spectral characteristics of compounds **4** and **5** are in accord with the proposed structures.
(9) A similar reaction has been carried out for the ethyl ester.
(10) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971, p 490 ff.
(11) M. T. Reetz, *Tetrahedron*, **29**, 2189 (1973).
(12) We appreciate conversations with Professor Philip Shevlin on this point.

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Catalytic Hydrogenation of 1-Hexene by Rhodium Complexes in the Intracrystal Space of a Swelling Layer Lattice Silicate

Sir:

There has been considerable recent interest[1-14] in converting homogeneous transition metal catalysts into heterogeneous catalysts by anchoring the complexes to insoluble support matrices such as organic polymers and metal oxides. We have been investigating, as an alternative means of achieving some of the combined advantages of homogeneous and heterogeneous catalysis, the feasibility of conducting metal ion-catalyzed reactions in the intracrystal space of naturally occurring swelling layer lattice silicates known as smectites. These relatively abundant minerals possess mica-like structures in which the crystallites are made up of alternating layers of cations and negatively charged silicate sheets[15] as illustrated in Figure 1. Unlike the micas, however, the interlayer cations (mainly Na^+ and Ca^{2+}) are readily exchangeable, and the intracrystal space occupied by the electrostatically bonded cations can be swelled by sorption of water, alcohols, and a variety of other substrates on the large internal surface area (~800 m^2/g). The degree of swelling depends on the nature of the interlayer cation, the substrate, and the negative charge density on the silicate sheets.

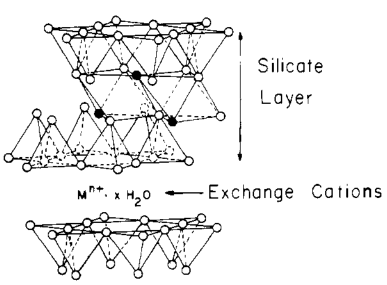

Figure 1. Schematic representation of a smectite structure (adapted from ref 15). Open circles are O^{2-}, dark circles are OH^- or F^-. In hectorite, which has an idealized anhydrous unit cell composition of $Na_{0.66}[Li_{0.66}, Mg_{5.34}](Si_8)O_{20}(OH, F)_4$, Si^{4+} fills the tetrahedral sites, Li^+ and Mg^{2+} fill the octahedral positions, and Na^+ is the interlayer exchange cation.

Electron spin resonance studies[16,17] have shown that fully hydrated Cu^{2+} and Mn^{2+} in smectite interlayers 10-12 Å thick possess local structures and mobilities similar to those found for the ions in bulk solution. The solution-like properties of the ions suggested to us that, with an appropriately designed exchange ion-substrate system, the interlayer ions should be accessible to attack by reagent molecules from solution and that one should be able to conduct cation-catalyzed reactions in the intracrystal environment. This concept is demonstrated by the preliminary results communicated herein for the catalyzed hydrogenation of 1-hexene by rhodium complexes derived from Rh_2^{4+} in the intracrystal space of the mineral hectorite.

Native $[Na_{0.66}{}^+]$-hectorite with the approximate unit cell composition given in the caption to Figure 1 was converted to its proton exchange form by passing a suspension of the microcrystalline, colorless mineral in methanol through a column of acid-exchanged Dowex 50 resin. An amount of Rh_2^{4+} equivalent to ca. 6% of the cation exchange capacity of the mineral was then introduced to the intracrystal surfaces[18] by exchange reaction with 8×10^{-3} *M* Rh_2^{4+} in methanol[2] under oxygen-free conditions. The uv-visible absorption spectrum of the light green $[(Rh_2^{4+})_{0.01}, H_{0.62}{}^+]$-hectorite as a Nujol mull exhibited the same intense charge transfer band found near 256 nm for Rh_2^{4+} in methanol (ϵ 3.1×10^3),[2] though the weak solution bands at 423 (ϵ 61.8) and 612 nm (ϵ 55.0) could not be detected in the mineral environment.

The addition of triphenylphosphine in methanol solution to $[(Rh_2^{4+})_{0.01}, H_{0.62}{}^+]$-hectorite causes the mineral-bound metal ion to be reduced at room temperature to a red rhodium(I)-triphenylphosphine complex of the type $Rh(PPh_3)_x{}^+$. An analogous reduction has been demonstrated by Wilkinson and his coworkers[2] for Rh_2^{4+} in methanol solution and at the exchange sites of a cation exchange

Table I. Hydrogenation Rates for 1.0 *M* Hexene in Methanol at 25°

Initial complex	Mol of Rh/mol of olefin	Mol of PPh_3/mol of Rh	H_2 uptake[a] (ml/min/mmol of Rh)
$[(Rh_2^{4+})_{0.01}, H_{0.62}{}^+]$-Hectorite	1.2×10^{-4}	0	4.9[b]
		6.0	14
		9.0	23
		11.0	22
		14.0	23
$[(Rh(PPh_3)_{2.3}{}^+)_{0.12}, Na_{0.54}{}^+]$-Hectorite	8×10^{-4}		20
$[Rh_2^{4+}, H^+]$-Dowex 50W resin	1.0×10^{-2}	2.0	7[c]
Rh_2^{4+}, homogeneous solution[d]	2.5×10^{-3}	2.0	140

[a] H_2 pressure = 640 Torr, unless otherwise noted. [b] The uncertainty in rates for $[(Rh_2^{4+})_{0.01}, H_{0.62}{}^+]$-Hectorite is ca. ±10% due to comparable uncertainty in the rhodium content of the catalyst. [c] This value is taken from data presented in ref 2; H_2 pressure = 450 Torr. [d] This solution was prepared by protonation of $Rh_2(OOCCH_3)_4 \cdot 2CH_3OH$ with HBF_4.[2]