Table I. Differences in Chemical Shift for Protons of
n-Hexanoic Acid on Treatment with Eu(fod)$_3$[a]

$$CH_3-CH_2-CH_2-CH_2-CH_2-COOH$$
$$6 \quad 5 \quad 4 \quad 3 \quad 2 \quad 1$$

			Proton no.			
	1	2	3	4	5	6
Untreated hexanoic acid	11.89	2.32	~1.6	~1.4	~1.4	0.89
Hexanoic acid + Eu(fod)$_3$	16.31	4.79	3.70	2.60	2.03	1.30
Δδ		4.42	2.47	2.1	1.2	0.6	0.41

[a] The treated samples were run at a lanthanide/substrate mole ratio of 0.43 in carbon tetrachloride.

Table II. Differences in Chemical Shift for Protons of
2,4-Xylenol on Treatment with Eu(fod)$_3$[a]

OH
|
CH$_3$
CH$_3$
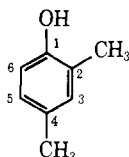
			Proton no.			
	1	2	3	4	5	6
Untreated 2,4-xylenol	5.42	2.12	6.80	2.17	6.72	6.48
2,4-Xylenol + Eu(fod)$_3$		3.47	7.40	2.42	7.12	8.10
Δδ		1.35	0.60	0.25	0.40	1.62

[a] The samples were run at a lanthanide/substrate mole ratio of 0.18 in carbon tetrachloride. All spectra were obtained on a Varian Associates A60 spectrometer.

for those of the acid, and the chemical shift differences are not as great. The phenolic hydroxyl proton resonance could not be located in the spectrum, but this is not surprising in view of the broadness of this resonance in the untreated phenol. In any event, use of the reagent leads to considerable spectral clarification. As expected, the magnitude of the shifts and the amount of paramagnetic broadening is in the order ortho > meta > para. A more detailed account of the results obtained for both acids and phenols will be published at a later date.

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Decomposition of Diazo Compounds in Alkylthio- and Alkoxytrimethylsilanes. A Possible 1,2-Trimethylsilyl Shift in Unstable Silylsulfonium and Silyloxonium Ylides

Sir:

There has been considerable interest in the rearrangement of organometallic compounds in the past few years. Several 1,2-shifts of the trialkylsilyl group have been established by the studies of West and coworkers.[1,2]

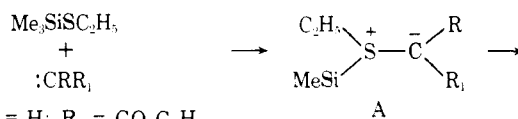(1) R. West and P. Boudjouk, J. Amer. Chem. Soc., 95, 3983, 3987 (1973), and references cited therein.
(2) For review of silane rearrangements, see R. West, Pure Appl. Chem., 19, 291 (1969).

Recently, 1,2-anionic rearrangements from oxygen and sulfur to carbon in alkoxy- and alkylthiosilanes were reported.[3,4] These were shown to be examples of a Wittig-type rearrangement involving migration of a silyl group from oxygen and sulfur to a negatively charged carbon. However, no analogous rearrangement has been described for trialkylsilylsulfonium and -oxonium ylides.

We find that the photolysis of diazo compounds in alkylthio- and alkoxytrimethylsilanes produces the insertion products of the carbene into the Si–S and Si–O bonds. These reactions are probably initiated by carbene attack on lone pair electrons of sulfur and oxygen atoms to form the corresponding onium ylides[5] followed by a 1,2-trialkylsilyl shift from onium sites to the carbanionic center. If this mechanism is correct, this is the first example of a 1,2-migration of an organometallic group in either anion or radical.

Carboethoxycarbene (Ia) was produced by photolysis of ethyl diazoacetate in ethylthiotrimethylsilane as solvent. In this reaction, the expected sulfonium ylide could not be observed upon analysis of the nmr spectrum of the reaction mixture. Product analysis by glpc showed the formation of ethyl trimethylsilyl(ethylthio)-acetate (IIa) and ethyl ethylthioacetate (IIIa) in 38 and 29% yields, respectively;[6] structure IIa was established by comparison of its spectra with those of an authentic sample[7] prepared by the reaction of ethyl trimethylsilyldiazoacetate with ethyl mercaptan.
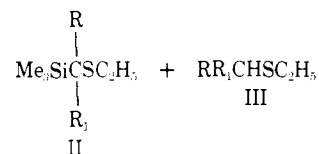
With phenylcarbene (Ib) produced by photolysis of phenyldiazomethane, trimethylsilyl(ethylthio)phenylmethane (IIb) and benzyl ethyl sulfide (IIIb) were formed in 28 and 8% yields, respectively. Product IIb was identified by nmr (CCl$_4$): τ 9.94 (CH$_3$Si–, singlet), 8.93 (–CH$_3$, triplet), 7.75 (–SCH$_2$–, quartet), 6.81 (SiCHS–, singlet), and 2.86 (Ph, broad singlet), intensity ratio 9:3:2:1:5. The ir absorption spectrum of IIb showed no Si–S band at 638 cm^{-1}. Similarly, photolysis of diphenyldiazomethane in ethylthiotrimethylsilane gave 29% trimethylsilyl(ethylthio)diphenylmethane (IIc) and 50% ethyl benzhydryl sulfide (IIIc).

Me$_3$SiSC$_2$H$_5$
+
:CRR$_1$

C$_2$H$_5$
S—C
MeSi
R
R$_1$
A

Ia. R = H; R$_1$ = CO$_2$C$_2$H$_5$
b, R = H; R$_1$ = Ph
c, R = R$_1$ = Ph

R
|
Me$_3$SiCSC$_2$H$_5$ + RR$_1$CHSC$_2$H$_5$
|
R$_1$
III
II

Since ylide formation in the reaction of a carbene with

(3) R. West, R. Lowe, H. F. Stewart, and A. Wright, J. Amer. Chem. Soc., 93, 282 (1971).
(4) A. Wright, D. Ling, P. Boudjouk, and R. West, J. Amer. Chem. Soc., 94, 4784 (1972).
(5) (a) W. Ando, T. Yagihara, S. Tozune, and T. Migita, J. Amer. Chem. Soc., 91, 2786 (1969); (b) W. Ando, S. Kondo, K. Nakayama, K. Ichibori, H. Kohoda, H. Yamato, I. Imai, S. Nakaido, and T. Migita, ibid., 94, 3870 (1972); (c) W. Ando, M. Yamada, E. Matsuzaki, and T. Migita, J. Org. Chem., 37, 3791 (1972), and references cited therein.
(6) Direct insertions of the carbene into C–H bonds were also observed in 14% yields.
(7) W. Ando, T. Hagiwara, and T. Migita, J. Amer. Chem. Soc., 95, 7518 (1973).

a heteroatom is a well-known reaction in carbene chemistry,[5,8-10] an attractive mechanism for the formation of an insertion product may involve sulfonium ylide formation (A) followed by a 1,2-migration of the silyl group involving a geminate radical pair intermediate (B), which collapses to II.[11-13] The radical (C) which escaped the geminate pair provides, *via* hydrogen abstraction reaction, the product III. However, no evidence exists for the mechanism cited save that it may account for the products. The geminate ion pair mechanism has never been established for 1,2-migration of the silyl group. A concerted 1,2-migration of the
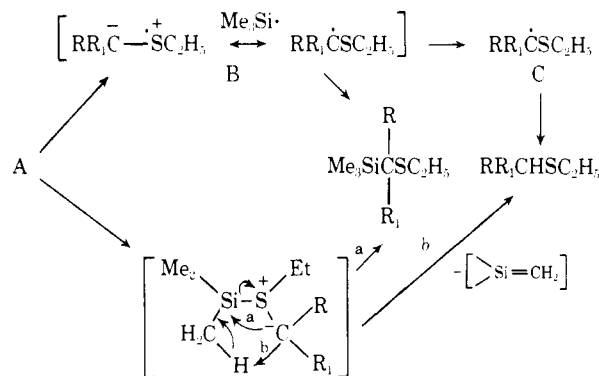
trimethylsilyl group might be involved in these reactions since silicon may expand its valence shell (d orbitals of appropriate symmetry are available to stabilize the transition state or intermediate for such rearrangement) (process a), and the eliminative decomposition of sulfonium ylide (A), *via* a concerted five-member cyclic transition state,[13,14] led to the product III and [>Si=CH$_2$], the fate of which is unknown (process b).

The 1,2-migration of the silyl group from the oxonium site to carbon center may also take place in the reaction between carbenes and alkoxytrimethylsilanes. Irradiation of ethyl diazoacetate in alkoxytrimethylsilanes gave three major products, IV, V, and VI. Product VI may be rationalized in terms of C–H insertion of carboethoxycarbene. The products IV and V are quite analogous to those which were obtained in the reaction with ethylthiotrimethylsilane. These products are apparently formed through a trimethylsilyloxonium ylide intermediate (D) followed by 1,2-migration of the trimethylsilyl group in either anion or radical.

1,2 Oxygen–carbon silyl group rearrangement in the reaction of phenylcarbene with methoxytrimethylsilane

(8) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1971.

(9) M. Jones, Jr., and R. A. Moss, "Carbenes," Vol. I, Wiley, New York, N. Y., 1973.

(10) Direct insertion of carbenes into the Si–S bond is considered and is also considered likely into Si–H and Si–Cl bonds in some cases. However, the reactivities of the carbene into Si–H and Si–Cl bonds were not even favored over addition on olefin, but ylide formation on sulfur was found to be more rapid than addition on olefin, especially by an electrophilic carbene. Direct insertion may not be involved in these reactions. See ref 5 and D. Seyferth, J. M. Burlitsch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.*, 7, 405 (1967).

(11) U. Schöllkopf, G. Ostermann, and J. Schossing, *Tetrahedron Lett.*, 2619 (1969).

(12) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

(13) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, and T. Migita, *J. Org. Chem.*, 37, 1721 (1972).

(14) W. Ando, T. Yagihara, and T. Migita, *Tetrahedron Lett.*, 1983 (1969).
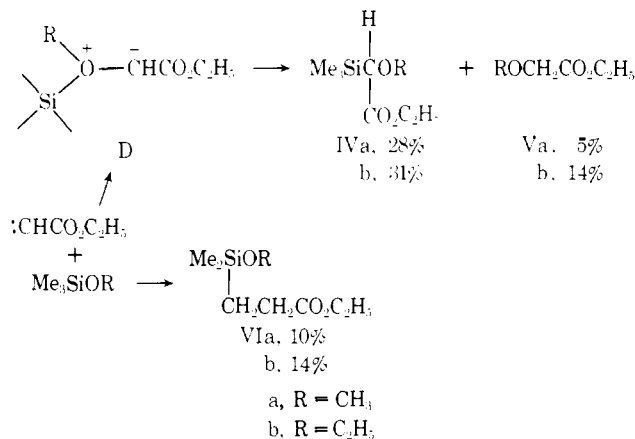
was observed to give the insertion product of phenylcarbene into the Si–O bond in 25% yield;[15] the product was identified by comparison of its spectra with those of an authentic sample.[16]
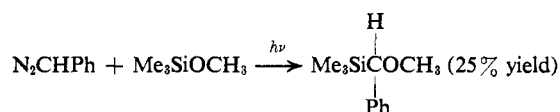
$$N_2CHPh + Me_3SiOCH_3 \xrightarrow{h\nu} Me_3Si\overset{H}{\underset{Ph}{\overset{|}{C}}}OCH_3 \ (25\% \ yield)$$

(15) A few per cent of benzyl methyl ether was also obtained in this reaction.

(16) An authentic sample was prepared by the reaction of phenyltrimethylsilyldiazomethane with methanol.[7]

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Reaction of Sodium Naphthalene with Methylene Halides. The Methylene Radical Anion

Sir:

Alkyl geminal dihalides which possess β- or γ-hydrogens react with sodium naphthalene (1) to yield products of C–H insertion. These reactions reveal the intervention of a carbene (or carbenoid) intermediate.[1,2] Treatment of the methylene halides CH$_2$X$_2$ (X = Cl, Br, I) should thus give methylene (or its carbenoid counterpart), which could be detected by its addition to an olefinic double bond.[2] In fact, reaction of 1 M CH$_2$Cl$_2$ in 60:40 (v/v) cyclohexene–1,2-dimethoxyethane (DME) with excess 1 M sodium naphthalene does yield norcarane, but in yields of less than 1%. The principal products of the reaction (>70%) are low molecular weight hydrocarbons. Alkylated naphthalenes and dihydronaphthalenes are also formed in less than 30% yield.
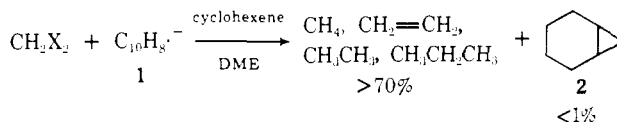
(1) G. D. Sargent, C. M. Tatum, Jr., and S. M. Kastner, *J. Amer. Chem. Soc.*, 94, 7174 (1972).

(2) For a recent, comprehensive, authoritative review of carbene chemistry, see W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.