A complete structure report will be made.

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The Photochemistry of Silicon Compounds. II. The Photolysis of Methylsilane as a Source of Methylsilene

Sir:

The photochemistry of silicon compounds has attracted little attention to date. In part I of this series[1] the mercury-photosensitized decomposition of the methylated silanes had been shown to involve exclusive Si–H bond cleavage and to exhibit, in this and other respects, behavior similar to paraffins. The direct photolysis of alkylsilanes in the vacuum uv, however, would be expected to proceed rather by molecular mode of eliminations if the analogy with paraffins[2] can be further extended, and thus provide a convenient source for the generation of the little investigated family of silenes, the silicon analog of carbenes. As far as can be ascertained from the literature, no previous study has been reported on the vacuum uv photolysis of alkylsilanes.

We photolyzed methylsilane in the gas phase with the 1470-Å radiation of a low-pressure Xe resonance lamp using a conventional vacuum uv photolysis apparatus with LiF windows.

The products of the reaction were hydrogen (1.03), methane (0.23), dimethyldisilane (0.48), methyldisilane (0.26), and a solid polymer along with small amounts of dimethylsilane, ethane, and traces of an oxygenated silane. The figures in parentheses indicate quantum yield values extrapolated to zero exposure time (which was necessitated by the attenuation of the incident light intensity due to polymer deposition on the LiF window) and are based on CO_2 actinometry[3] ($\phi(CO) = 1.0$).

Addition of nitric oxide in concentrations of up to 10% hardly affected the dimeric product yields, indicating that monoradicals are not principal precursors.[4] Addition of ethylene had little effect on the hydrogen yield, but experiments with CH_3SiD_3 revealed that ethylene retarded D_2 formation and increased that of H_2 and HD. These increases are due to the decomposition of ethylene. From these experiments it can be concluded that the disilane products arise from carbene-like precursors, and only a fraction of the hydrogen is scavengeable.

Further insight into the mechanism comes from deuterium-labeling studies using CH_3SiD_3 and CH_3SiH_3–CH_3SiD_3 mixtures.

From CH_3SiD_3, the isotopic composition of hydrogen was ~8% H_2, 29% HD, and 63% D_2. The methane contained 90% CH_3D and 10% CH_4, the latter being formed partly from isotopic impurities in CH_3SiD_3. From a comparison of the photolyses of pure CH_3SiH_3 and CH_3SiD_3, no significant H/D isotope effect appeared on the over-all reaction at a pressure of 100 torr. When the isotopic composition of the hydrogen product was determined from the mixtures of CH_3SiD_3 and CH_3SiH_3, corrected for absorption by each component and plotted against mole per cent of CH_3SiH_3, the relative yield of D_2 exhibited a decline from 0.63 to 0.31 and that of HD an increase from 0.29 to 0.67 on going from 100% CH_3SiD_3 to 100% CH_3SiH_3. These scavenging experiments suggest the following hydrogen-producing primary steps

$$\begin{aligned} CH_3SiD_3 + h\nu &\longrightarrow CH_3SiD + D_2\ (0.32, 0.32) && \text{(1a)} \\ &\longrightarrow CH_3SiD + 2D\ (0.17, 0.00) && \text{(1b)} \\ &\longrightarrow CH_2SiD_2 + HD\ (0.30, 0.00) && \text{(1c)} \\ &\longrightarrow CH_2SiD_2 + H + D\ (0.00, 0.32) && \text{(1d)} \\ &\longrightarrow CHSiD_3 + H_2\ (0.08, 0.08) && \text{(1e)} \end{aligned}$$

where the figures in parentheses indicate limiting quantum yields. The formation of methane, which is also unaffected by NO, requires a fifth primary step

$$CH_3SiD_3 + h\nu \longrightarrow CH_3D + SiD_2 \qquad (2)$$

The two silane products can now be rationalized as being formed by the insertion of the silenes into the Si–H bonds of the methylsilane molecule.

$$CH_3SiH + CH_3SiH_3 \longrightarrow CH_3SiH_2SiH_2CH_3 \qquad (3)$$

$$SiH_2 + CH_3SiH_3 \longrightarrow CH_3SiH_2SiH_3 \qquad (4)$$

Insertion of the 1,2 diradical, CH_2SiH_2, into an Si–H bond would be a sterically unfavorable process, but its isomerization to the silene structure

$$CH_2\text{—}SiH_2 \longrightarrow CH_3SiH \qquad (5)$$

should be energetically feasible.[5] The mass spectrometric analysis of the disilane product from the CH_3SiD_3 reaction indicates a composition of $CH_3SiD_2SiD_2CH_3$ favoring the insertion of the primary CH_3SiD silene and militating against the importance of the isomerization reaction 5. This is also in agreement with the near coincidence of the quantum yield of primary steps 1a and 1b with that of dimethyldisilane appearance. The main mode of the 1,2-diradical removal is probably by polymerization.

The insertion reactions 3 and 4 are strongly exothermic since their net result is an additional bond formation, and the resulting hot molecules require pressure stabilization. This is clearly evident from the fact that the disilane yields exhibit an increase and the hydrogen yield a decrease with pressure from 10 to 100 torr, but all product yields are invariant with pressure between 100 and 400 torr.

The insertion mechanism indicates that the silenes in reactions 1a and 1b and 2 are formed in a singlet state,

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(1) M. A. Nay, G. N. C. Woodall, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **87**, 179 (1965).

(2) J. R. McNesby and H. Okabe, *Advan. Photochem.*, **3**, 157 (1964); R. E. Rebbert and P. Ausloos, *J. Chem. Phys.*, **46**, 4333 (1967); H. Akimoto, K. Obi, and I. Tanaka, *ibid.*, **42**, 3864 (1965).

(3) B. H. Mahan, *ibid.*, **33**, 959 (1960).

(4) In the mercury photosensitization of methylsilane, the methylsilyl radicals could be scavenged with a few torr of NO, as evidenced by the complete suppression of their recombination product, $CH_3SiH_2SiH_2CH_3$, and the appearance of the new product, $CH_3SiH_2OSiH_2CH_3$; *cf.* ref 1.

(5) *Cf.* E. W. Dasent, "Nonexistent Compounds," Marcel Dekker Inc., New York, N. Y., 1965, pp 26, 61–65, 71–74.

which may or may not be the ground electronic state.[6] A similar insertion reaction for dimethylsilene,[7,8] trimethylsilylsilene,[9] and SiH_2[1] has been postulated earlier. In these, as in the present study, the silenes exhibited a strong preference for Si–H over C–H bond insertion. This preference is not restricted to silenes; it has been observed with singlet methylene from the photolysis of ketene[10] and with singlet-D sulfur atom from the photolysis of COS. This increased reactivity of the Si–H bond in insertion reactions may be related to its hydridic character and the availability of the vacant d orbitals of the silicon atom.

The Xe-sensitized decomposition of CH_3SiH_3 has also been examined; it appears to be indistinguishable from the direct photolysis.

The effect of wavelength on the photolysis has been studied using the 1236-Å resonance line of Kr. While the nature of products remained unaltered, a marked increase in the hydrogen yield resulted, an effect which has been observed with paraffins[2] and can be attributed to the greater importance of atomic hydrogen production in the primary step.

A preliminary vacuum uv ($\lambda > 1200$ Å) flash photolysis study with kinetic mass spectrometry[11] of some other silanes indicated a similar though less efficient reaction for dimethylsilane (products H_2, CH_4, C_2H_6, and $((CH_3)_2SiH)_2$), and, interestingly, an even less efficient decomposition for trimethylsilane. This feature of the silane photolysis is a significant departure from the behavior of paraffins and can possibly be understood only in the light of sufficient spectral data.

The vacuum uv photolysis of a series of other silicon compounds are currently under study.

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(6) A recent semiempirical calculation predicts a $^1A_1$ ground state for SiH_2 with a lowest excited state, $^3B_1$, lying at $\sim$48 kcal/mole; *cf.* P. C. Jordan, *J. Chem. Phys.*, **44**, 3400 (1966).

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Biosynthesis of Lycopodine[1]

Sir:

The hypothesis that the lycopodium alkaloids are of polyketide origin[2] has gained general currency.[3–6] The carbon skeletons of the structural variants found among these alkaloids (*e.g.*, lycopodine (**12**), α-obscurine (**10**), and annotinine (**13**)) may be formally derived[2,4] from two tetraacetyl chains (**11**).[7] This hypothesis lacks experimental foundation.[10] We now propose a new hypothesis of the origin of the lycopodium alkaloids and offer experimental evidence in its support.

In separate experiments samples of lysine-2-^{14}C and -6-^{14}C were administered to *Lycopodium flabelliforme*. In each case radioactive lycopodine was isolated which, after purification to constant radioactivity, was converted to phenyldihydrolycopodine.[11] Permanganate oxidation then gave benzoic acid, representing the carbonyl carbon of lycopodine. One-fourth of the activity of the intact alkaloid derived from lysine-2-^{14}C as well as from lysine-6-^{14}C was localized at this carbon atom (Table I). In a further experiment labeled lycopodine was obtained from plants which had been infused with lysine-4,5-^{3}H-6-^{14}C (^{3}H:^{14}C 10.7 ± 0.2). The alkaloid showed a ^{3}H:^{14}C ratio (^{3}H:^{14}C 8.4 ± 0.1) which was 22% lower than that of the doubly labeled lysine.

Table I

	DL-Lysine-2-^{14}C[a]		DL-Lysine-6-^{14}C[a]	
	SA[b]	RSA[c]	SA[b]	RSA[c]
Lycopodine	1.30 ± 0.03	100 ± 2	1.22 ± 0.03	100 ± 2
Benzoic acid	0.33 ± 0.01	26 ± 1	0.31 ± 0.01	25 ± 1

[a] Precursor. [b] Specific activity (counts min^{-1} $mmole^{-1}$) × 10^{-4}. [c] Per cent relative specific activity.

The results demonstrate that lysine (**1**) serves as a specific precursor of lycopodine (**12**). This is compatible with the hypothesis that the lycopodium alkaloids are generated from two isopelletierine (**4**) units, whose piperidine nucleus is derived from lysine.[12] The steps of a plausible reaction sequence are shown in Scheme I. Recovery at the carbonyl carbon of 25% of the activity of the intact lycopodine, obtained from lysine-2-^{14}C and -6-^{14}C, is consistent with the view that the alkaloid represents a modified dimer of isopelletierine and that incorporation of lysine into this isopelletierine takes place by way of a symmetrical intermediate. Such symmetrical incorporation of lysine-4,5-^{3}H-6-^{14}C into lycopodine would be expected to be accompanied by loss of one-fourth to one-half of the tritium from C-5, *i.e.*, by a loss of 12.5–25% of the tritium, relative to ^{14}C, of the doubly

(1) This investigation was supported by a grant from the National Research Council of Canada.

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(7) Mention has been made also of several compounds other than acetate as possible precursors of lycopodium alkaloids.[3,8,9]

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(10) Label from acetate-1-^{14}C was indeed incorporated nonrandomly into annotinine (**13**) in *Lycopodium annotinum*. However, the observed distribution of this activity was not in accord with the polyketide hypothesis.[9]

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