photolysis of *tert*-butyl trimethylsilyl peroxide.[2]

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(3) An improved preparation of the bis(trialkylsilyl) peroxides has recently been reported.[4]
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(6) Between −120 and −40 °C, a second triplet was apparent with a slightly higher g value ($\Delta g = 0.0006$) and showing only a 19.4 G (2 H); this is probably to be ascribed to an $-O\dot{C}H_2$ radical.
(7) We are grateful to Dr. J. A. Howard for discussions concerning the origin of these peroxyl radicals.
(8) Intermolecular abstraction of hydrogen by the photolysis of di-*tert*-butyl peroxide in the presence of hexapropyldisiloxane in cyclopropane at −120° showed the spectra of only the radicals $Pr_3SiOSi(Pr_2)\dot{C}HCH_2CH_3$ (a (Hα) 20.0 (1 H), a (Hβ) 25.3 G (2 H)) and $Pr_3SiOSi(Pr_2)CH_2\dot{C}HCH_3$ (a (Hα) 21.0 (1 H), a (Hβ) 16.7 (2 H), a (CH$_3$) 24.2 G (3 H)), but no radical resulting from abstraction of hydrogen from the methyl group.
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(14) The relative reactivity of the methyl and ethyl silicon compounds (MeSi < EtSi) by reaction 2 correlates with the relative ease of homolysis of the Me–H and Et–H, or Me–Sn and Et–Sn bonds,[15] and can be related to the higher bond dissociation energy in the methyl compounds.
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(16) Preliminary results show that the behavior of the germyl peroxides is similar to that of the silyl peroxides. When bis(triethylgermyl) peroxide is photolyzed in cyclopentane at −120 °C, a strong spectrum of the ethyl radical is observed; in cyclopropane at −120 °C, the ethyl radical is still present but the radical $CH_3\dot{C}HGeEt_2OOGeEt_3$ is the dominant species (a (CH$_3$) 26.1, a (CH) 20.7 G). The peroxide $Et_3GeOOCMe_3$ at −120 °C in cyclopropane gave no evidence for the formation of the ethyl radical.

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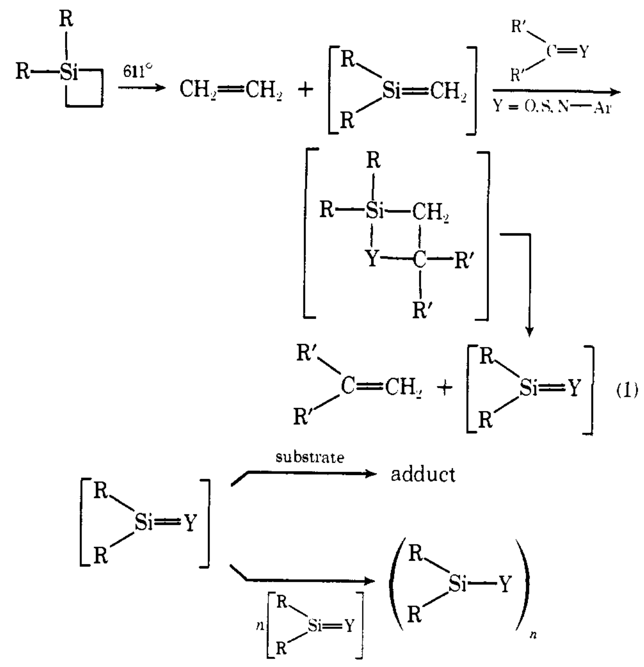
Photolysis of Silyl Azides. Generation and Reactions of Silicon–Nitrogen (p_π–p_π) Doubly Bonded Intermediates. [$R_2Si{=}NR$]

Sir:

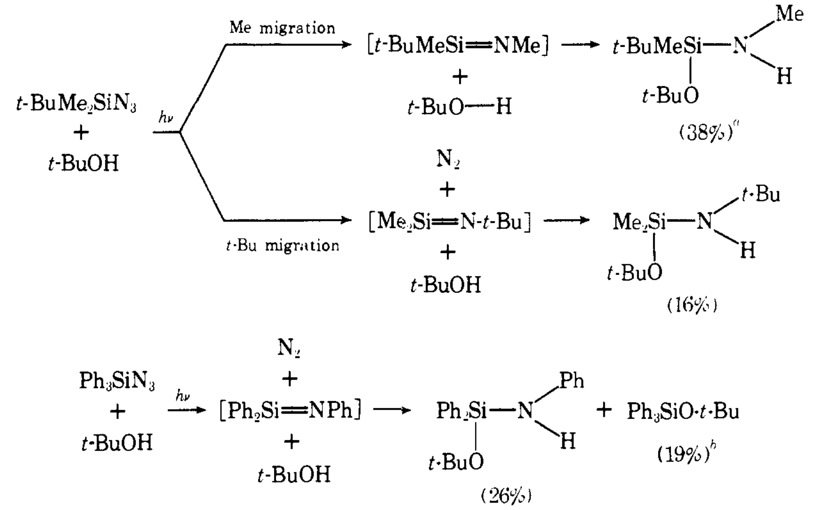
Much interest has been expressed recently in multiply bonded silicon species.[1,2] Silicon has been shown to form (p_π-p_π) double bonds with carbon,[2a] silicon,[2b] oxygen,[2c,2d] nitrogen,[2e] and sulfur.[2f] The usual mode of generation involves *gas phase* copyrolysis of a silacyclobutane, solvent, and substrate (eq 1). Thermolysis of the silacyclobutane forms a silicon–carbon doubly bonded intermediate which then reacts with the desired π-bonded heteroatom. The newly formed multiply bonded silicon species then further reacts either with substrate or with itself in a head to tail manner to give dimer or polymer. The first definitive evidence for thermally generated silicon-nitrogen (p_π-p_π) doubly bonded species, silaimines, [$R_2Si{=}NR$] was obtained via this method.[2e]



(1)

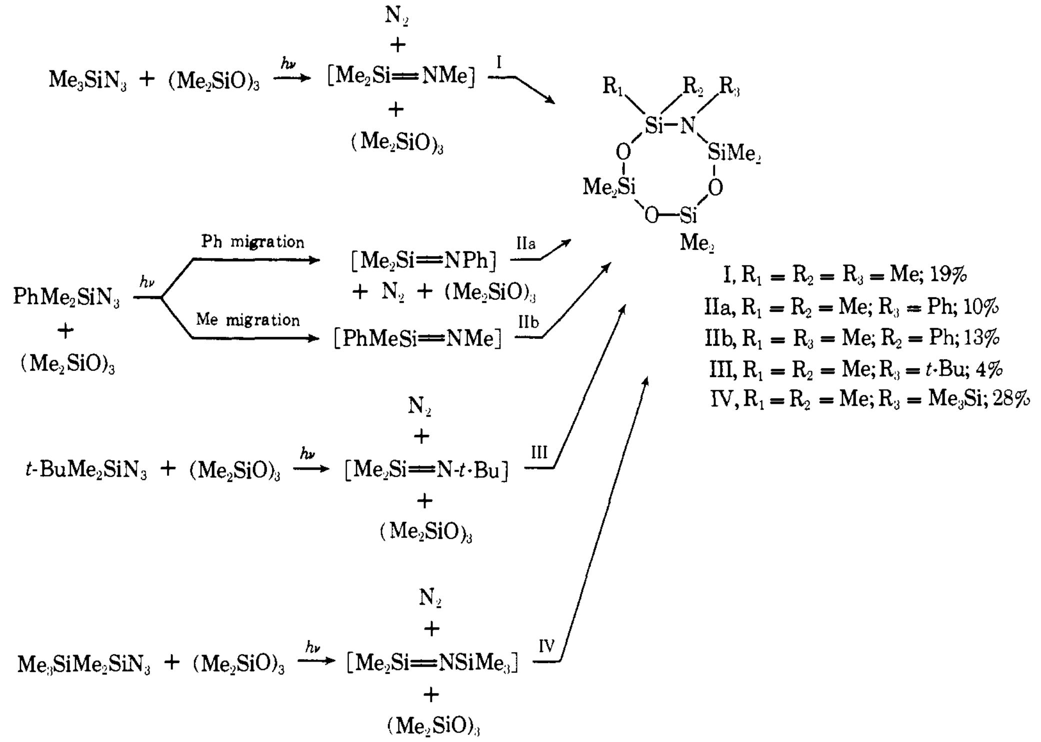
We would like to report the first conclusive evidence for the photochemical generation of silaimines and their reactions in the *condensed phase*. The generation involves irradiation of a silyl azide in the presence of a trapping reagent and solvent (when desired) in a quartz tube under a nitrogen atmosphere. The photolyses were carried out in a Rayonet reactor using Rayonet RPR-2537 lamps. Photolysis of silyl azides in *tert*-butyl alcohol afforded the products shown in Scheme I. These adducts are believed to be the first clear evidence of a silaimine insertion into a σ bond. The products obtained are in accord with analogous ther-

Scheme I



[a] All yields were based on amounts of material isolated by preparative GLPC and assume 100% decomposition of silyl azide unless otherwise noted. [b] From a nonphotochemical silylation reaction.

Scheme II



mal and photochemical reactions of silicon-carbon double-bonded species and alcohols.[2g,h] A limit to the scope of these reactions was the competing reaction involving silylation of the alcohol by the azide, presumably accompanied by production of hydrazoic acid. For example, the reaction of *tert*-butyl alcohol with trimethylsilyl azide at ambient temperatures yielded only

$$R_3SiN_3 + R'OH \longrightarrow R_3SiOR' + HN_3$$

the silylated alcohol. This reaction occurs in the presence or absence of light. Silylation products were completely eliminated only when t-BuMe$_2$SiN$_3$ and *tert*-butyl alcohol were employed. It is possible that low temperatures might slow silylation sufficiently to allow successful photolysis of a larger number of silyl azides and alcohols.

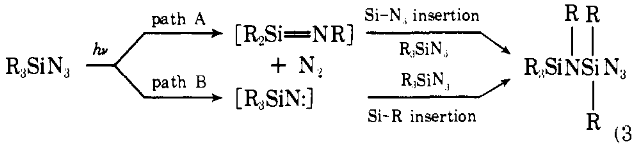
The silicon-nitrogen double bond also undergoes reaction with hexamethylcyclotrisiloxane (Scheme II). Insertion, leading to the expansion of the six-membered ring by one Si-N unit, results in a new, more facile means of generation of N-substituted cyclotrisilazoxanes, a little known class of compounds.[3,4] This reaction which appears to be general for silaimines has precedent in the gas-phase reactions of silanones [R$_2$Si=O][5] and more recently silaethenes [R$_2$Si=CHR].[6]

As shown in eq 2, if all three groups on the silicon azide are not the same, the possibility of generating more than one silaimine intermediate exists.

$$R_2R'SiN_3 \longrightarrow [R_2Si{=}NR'] + [RR'Si{=}NR] \qquad (2)$$

The results presented in Schemes I and II demonstrate this phenomenon. In the reaction of *tert*-butyldimethylsilyl azide with *tert*-butyl alcohol, the methyl and *tert*-butyl migrated products were isolated in almost the statistically expected ratio. The 1:1 adducts formed from the photolysis of phenyldimethylsilyl azide and hexamethylcyclotrisiloxane, however, show a statistical excess of the phenyl migrated product. The photolysis involving pentamethylazidodisilane and hexamethylcyclotrisiloxane yielded exclusively the adduct from trimethylsilyl migration to nitrogen (Scheme II). The ratio of insertion products given by R$_2$R'SiN$_3$ does not necessarily reflect the relative migratory aptitudes of R and R' because of the complication of competitive rates of other reactions (i.e., dimerization) of the silaimines with insertion.

Klein and Connolly, in a recent paper on the photolysis of silyl azides in the absence of trapping agents, were unable to draw a conclusion about the chemical nature of the reactive intermediate from their data.[7] A dilemma existed because, when silyl azides were photolyzed in the absence of reactive substrate, two different mechanistic pathways leading to the observed products could be envisioned (eq 3). Our



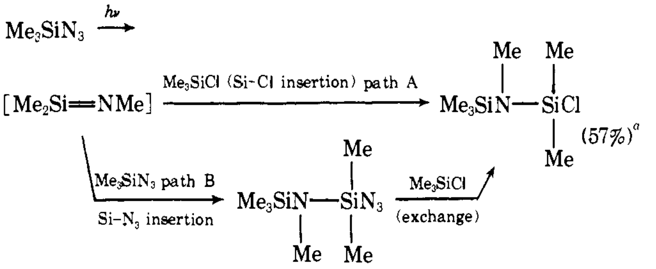
(3)

products derived from photolysis with either *tert*-butyl alcohol or hexamethylcyclotrisiloxane, however, can be rationalized only on the basis of a reactive intermediate containing a (p_π-p_π) silicon-nitrogen double bond. Thus, although no rigorous mechanistic proof exists for either path A or path B, the reactions of silaimines with *tert*-butyl alcohol and hexamethylcyclotrisiloxane when viewed in conjunction with analogous insertions of silaethenes,[2g,6] lead us to favor the mechanism depicted in path A.

Our attempts to demonstrate the insertion of a silaimine into a silicon halide bond have as yet not proven completely successful. The difficulty encountered is that halide-azide exchange renders the mechanistic interpretation equivocal (Scheme III). Although path A is a more direct process and a large (9.8:1) Me$_3$SiCl/Me$_3$SiN$_3$ mole ratio was employed, path B, which involves a halide-azide exchange as well as an insertion reaction, cannot be ruled out.

Unsaturated silicon intermediates in this manuscript and in our previous ones have been postulated to be p_π-p_π bonded because their chemical behavior does not at all suggest radical character. In agreement with this considerable body of chemical data, the methods we have used to generate these species (i.e., thermolysis at 530-610 °C or direct ultraviolet irradiation) are consistent with initial formation of singlet p_π-p_π intermediates. For very reactive chemical in-

Scheme III



[a] Yield based on recovered starting material.

termediates, ample precedent exists for the reaction of initially formed singlet species as such, without undergoing intersystem crossing (assuming, of course, that the triplet is the ground state). In the present work, a p_π–p_π bonded unsaturated silicon-nitrogen intermediate is also suggested by the well-known analogy of carbon-nitrogen double bond formation from carbon azides. Thus, the results in the present paper appear predictable only on the basis that silicon and carbon azides can behave analogously—an assumption which had to be tested since it is certainly not true in many other comparisons between silicon and carbon analogues.

Work is continuing on the photochemical as well as thermal generation and reactions of this interesting class of reactive intermediates.

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Laser Fluorimetry. Sub-Part-per-Trillion Detection of Solutes

Sir:

While conventional fluorimetry[1] has a typical detection limit of part-per-billion (1 part in 10^9) or in some cases sub-part-per-billion, the replacement of blackbody excitation sources (discharge lamps) by pulsed lasers and the use of gated-detection electronics can substantially increase the detection sensitivity.[2] We report here a study on the use of this detection technique applied to solutions of the dye, rhodamine 6G, and the carcinogenic mold metabolite, aflatoxin. Linear analytical curves are obtained which extend from a molar concentration of 10^{-6} to 10^{-13} M. This represents more than three orders of magnitude improvement over conventional means of detection. The analytic detection of dyes is used extensively in studies of pollution and water flow monitoring by fluorescent tracer techniques.[3] The analytic detection of toxins, such as aflatoxin, is of serious concern in the processing of food and feed stocks,[4] as well as in the analysis of tissue and body fluids. However, the significance of this work is thought to transcend the individual substances investigated; rather, laser fluorimetry holds the promise of dramatically extending the sensitivity limits of liquid chromatography as an analytic tool.

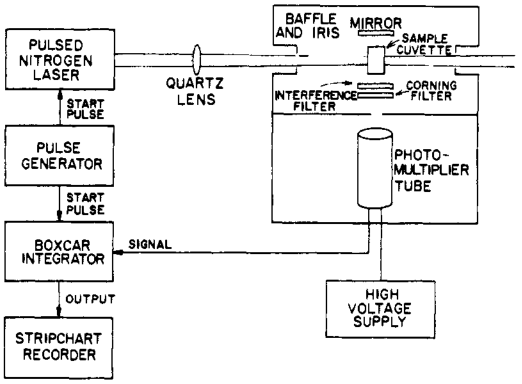

Figure 1. Schematic of laser fluorimeter.

Figure 1 shows a schematic of the experimental setup. The excitation source is a 337.1-nm pulsed nitrogen laser (AVCO-Everett Model C950). The laser power supply is charged from a 1000-W voltage regulator (SOLA). This stabilization is found to be important to the reproducible detection of dye concentrations below 10^{-10} M. The laser is fired 15 pps, each pulse having a 12-ns width, and operated at a power level of about 80 kW.

The laser beam is collimated and focused onto a 2-ml Suprasil quartz cuvette that holds the sample. To ensure signal reproducibility, the cuvette must be rinsed and filled with sample in situ. Baffles at the entrance and exit slits of the sample housing reduce scattering of laser light. A Centronix 4238 S-20 photomultiplier, shielded in a separate housing, views the sample fluorescence at right angles to the laser beam. To detect the dye solutions, an Optics Technology interference filter (6258-450) and a Corning filter (3-66) are placed in front of the photomultiplier to reduce scattered light and to eliminate Raman bands from the solvent, respectively. The interference filter, which cuts off light below 355 nm and transmits higher wavelengths through 700 nm was found to be more effective at diminishing the background of scattered laser light than comparable Corning filters. The latter were also found to fluoresce strongly when exposed to the laser. To detect the aflatoxin solutions, a different Corning filter (4-96) which transmits light from 345 to 650 nm is used. A boxcar integrator (PAR Model 162) receives the pulsed signal from the photomultiplier as well as the start pulse from the pulse generator that triggers the nitrogen laser. The signal-averaged output is displayed by a stripchart recorder (Hewlett-Packard Model 7100B). Rhodamine 6G (mol wt = 479) was obtained from New England Nuclear-Pilot Chemical Division (laser dye grade) and was used without further purification. The molar extinction coefficient at 337.1 nm is 8 × 10^3 M^{-1} cm^{-1} and the fluorescence quantum yield is 0.95.[5] The fluorescence