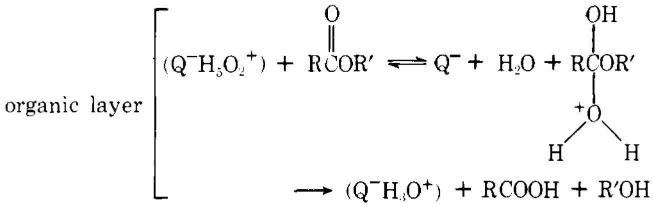
products. Consequently, in a traditional base-mediated PTC reaction, the hydroxide will eventually be neutralized. One must, therefore, replace the hydroxide or begin the reaction with a large excess. In certain acid-mediated PTC reactions, however, the resulting acidic products could serve to increase the rate of the reaction (autocatalysis). Figure 2 illustrates this phenomena for both the catalyzed and uncatalyzed hydrolysis of *p*-toluenesulfonyl chloride in a two-layer aqueous-organic system.[15] The addition of sodium tetraphenylborate greatly increased the rate of hydrolysis while maintaining the autocatalytic nature (Figure 2 insert).[16]

It is likely that there are some mechanistic differences between PTC with a "negatively charged" [10] catalyst and that with a traditional positively charged catalyst. The aforementioned nonlinear relationship of catalyst concentration vs. rate and the extractability of counterions indicate differences. Consider, for example, the hydrolysis of an ester in the organic layer of an acid-catalyzed PTC reaction (Scheme I). The tetraphenylborate anion (Q^-) carries the hydrated proton into the organic layer. The acid-catalyzed reaction occurs (assumed via traditional mechanism). Since protons are not consumed, Q^- gets back the proton at the end of the reaction but looses one molecule of water. Consequently, the ion pair need not return to the aqueous layer, but can continue to catalyze reactions in the organic layer until more water is needed. This is somewhat different from traditional PTC reactions where anions must continually be transferred to the organic layer.

Scheme I



Studies on the use of "negatively charged" [10] phase transfer catalysts in synthesis are currently being completed and will be described in forthcoming publications.[16]

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(10) The sodium tetraphenylborate catalyst is, of course, a neutral salt. The phrase "negatively charged" refers to the tetraphenylborate anion which is responsible for extracting hydrated protons (via ion-pair formation) into the organic solvent.
(11) In a typical reaction 60 mL of 1.5 N HCl was used as the aqueous layer and 60 mL of cyclohexane containing 0.05 M *p*-nitrophenyl acetate was used as the organic layer. All reactions took place in a thermostated constant temperature bath (25 ± 0.1 °C). In the acid-mediated reactions the appearance of *p*-nitrophenol was monitored spectrophotometrically (865 nm) with time. In the traditional base-mediated reactions, the disappearance of *p*-nitrophenyl acetate was monitored spectrophotometrically (267 nm) with time. Each reaction was repeated at least four times to assure reproducible data.
(12) In addition to sodium tetraphenylborate, an anionic surfactant (sodium dioctylsulfosuccinate, Aerosol-OT), a cation-exchange resin (Dowex 50W-X2, for "triphasic" catalysis), and *p*-toluenesulfonic acid were tested to see if they might also be effective negatively charged phase transfer catalysts. However, even at 60 °C they showed little or no catalytic activity.
(13) E. V. Dehmlow, M. Slopianka, and J. Heider, *Tetrahedron Lett.*, **No. 27,** 2361 (1977).
(14) J. H. Fendler, personal communication on unpublished results.
(15) In both of the autocatalytic experiments (with and without 0.01 M sodium tetraphenylborate) 0.136 M *p*-toluenesulfonyl chloride in 60 mL of cyclohexane was used as the organic layer, and 60 mL of distilled water was used as the aqueous layer. The temperature was 25 °C and the stirring rate was 600 rpm.
(16) Patents pending.

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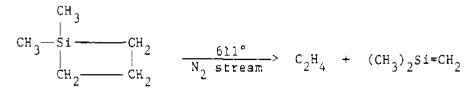
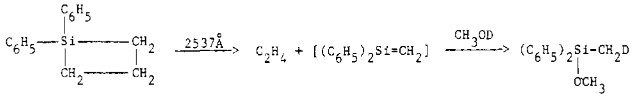
Evidence for Silicon–Carbon and Silicon–Nitrogen Multiple-Bonded (p_π–p_π) Intermediates from Photolysis. Dipolar Character of the Unsaturated Linkages

Sir:

In a previous communication[1] we reported evidence that thermolysis of 1,1-dimethyl-1-silacyclobutane gives an unsaturated intermediate having a highly polarized double bond: $(CH_3)_2Si^{\delta+}\cdots CH_2^{\delta-}$. The nature of the evidence was in strong opposition to a diradical formulation for the species being trapped, when *thermolysis* shown below was used for generation. In this regard our evidence and conclusions were in harmony with the pioneering work of Gusel'nikov and Flowers[2a] and with views expressed in a later review article.[2b]

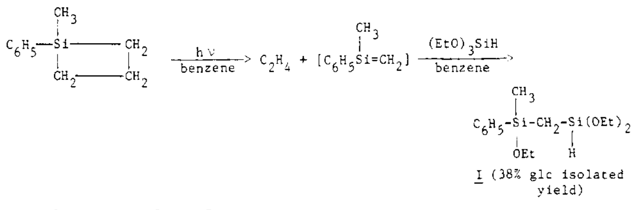


We have previously reported[3] that the *photolysis* of 1,1-diphenyl-1-silacyclobutane yields an unsaturated silicon–carbon intermediate which was trapped with CH_3OD.

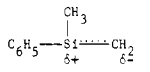


(90% yield)

However, the nature of the *photochemical* intermediate was really unknown, since a diradical might also give the observed product. To resolve the problem we took under consideration the following well-known and well-documented differences between ≡Si—H and ≡Si—OEt bonds: (1) H^- is a poorer leaving group than EtO^- when silicon undergoes nucleophilic attack;[4] (2) H· is far more easily abstracted from silicon by free-radical attack than ·OEt.[5,6] The higher Si—O bond dissociation energy compared with Si—H is probably responsible for this difference. Based on these considerations the experiments shown were done to clarify the nature of the photochemical intermediate being trapped.[7,8] Product I, from trapping with triethoxysilane, clearly results from addition of EtO to the silicon and $Si(H)(OEt)_2$ to the carbon portion of a highly reactive unsaturated silicon–carbon linkage having considerable dipolar character; nucleophilic or electrophilic attack on an Si—O—C grouping is well known, whereas radical attack under ordinary liquid-phase conditions is unknown for Si—O—C and well known for Si—H. Thus, we are inclined to formulate the photolytic intermediate which is



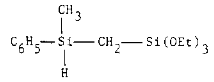
I (38% glc isolated yield)


$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\delta+}{Si}}\cdots\underset{\delta-}{CH_2}$

i

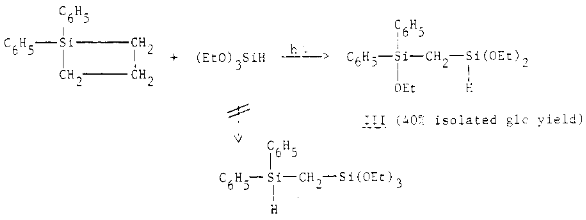
trapped by reaction with $(EtO)_3SiH$ as i. If the unsaturated silicon species is photochemically generated as a triplet diradical, it must rapidly change to the polarized double bond shown in i (the more stable ground-state form; see ref 9).

If trapping had involved addition of the silicon-hydrogen bond across the unsaturated linkage—thus suggesting a diradical structure—the product obtained would have had structure II. From NMR, IR and mass spectral data the product was found to have structure I. An especially significant spectral observation was found to be a clean *triplet* at δ 4.56 for the silicon-hydrogen bond in the product. Structure II would have given a sextet for the Si—H.


$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{Si}}-CH_2-Si(OEt)_3$

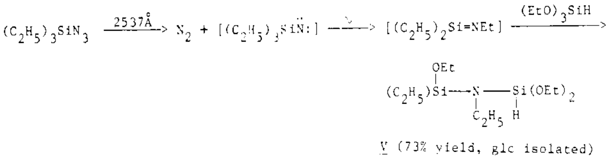
II

The product III from trapping 1,1-diphenyl-1-silaethene with triethoxysilane, shown in the reaction scheme below, also was characterized by NMR, IR, and mass spectral data and also had a clean triplet for the silicon-hydrogen bond at δ 4.56. In this case, the chemical shift of the Si—H in III being the same as for I, when considered along with Si—H chemical shifts of δ 4.84 for $(C_6H_5)_2(CH_3)SiH$ and 4.16 for $(EtO)_3SiH$, established III as the product instead of IV which would have resulted from addition of the Si—H bond across the unsaturated linkage.

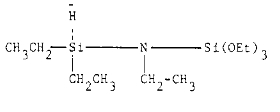

III (40% isolated glc yield)

IV (not found)

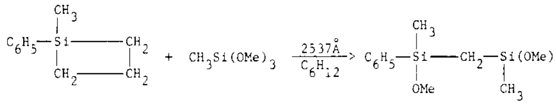
We next turned to the problem of the nature of the unsaturated linkage generated by *photolysis* of silyl azides.[10] Facile reaction of such intermediates with silicon-oxygen bonds in substances such as $(Me_2SiO)_3$ previously led us to assign a polarized double-bond structure to these unsaturated intermediates: $R_2Si^{\delta+}\cdots NR^{\delta-}$. We now report confirmation of this view by the experiment shown.

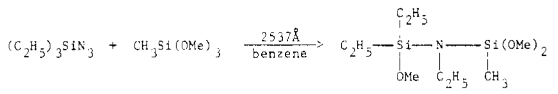

V (73% yield, glc isolated)

The NMR, IR, and mass spectral data were all consistent with structure V for the high-yield product. In the NMR spectrum a clean *singlet* for the silicon-hydrogen bond at δ 4.35 served to dispose of structure VI which would result from addition of the Si—H grouping across the unsaturated linkage and which would have a quintet for its Si—H bond. In further support of analogous highly polarized (p_π-p_π) double bonds for photochemically generated silicon-carbon and silicon-nitrogen unsaturated linkages, we carried out the experiments shown in which the unsaturated species both reacted similarly with $CH_3Si(OMe)_3$ which is an excellent trap. Products were characterized by NMR, IR, and mass spectra, consistent with the assigned structures. In the NMR, for both products, different chemical shifts for -SiOMe and for $-Si(OMe)_2$ were found, thus showing that alternate structures resulting from addition of CH_3Si across the unsaturated linkages were not formed since such additions would give an $-Si(OMe)_3$ grouping.


$CH_3CH_2-\overset{\overset{H}{|}}{\underset{\underset{CH_2CH_3}{|}}{Si}}-\underset{\underset{CH_2-CH_3}{|}}{N}-Si(OEt)_3$

VI (not found)


(45% glc isolated yield)


(72% glc isolated yield)

Photolyses were carried out in a Rayonet photochemical reactor equipped with 16 RPP 2537-Å lamps. Irradiations varied from ~10 to 24 h and were carried out on samples in quartz tubes.

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(4) The greater polarity of $\equiv Si^{\delta+}-OEt^{\delta-}$ compared with $\equiv Si^{\delta+}-H^{\delta-}$ is no doubt responsible, in part at least, for this difference. An example is the fact that ≡Si—OEt reacts readily with RMgX to give ≡Si—R, whereas ≡Si—H reacts slowly or not at all with RMgX. See C. Eaborn, "Organosilicon Compounds", Butterworths, London, 1960, Chapters 2 and 6; A. G. MacDiarmid, "The Synthesis and Reactions of the Silicon-Carbon Bond", C. Eaborn and R. W. Bott, Ed., Marcel Dekker, New York, 1968, Part 1, Chapter 2.

(5) See Chapter 6 in C. Eaborn publication[4] for the high reactivity of Si—H in homolytic (free-radical) reactions.

(6) For a listing, with references, of almost 300 hydrosilylation reactions involving radical initiated addition of Si—H across carbon—carbon double bonds, see pp 148–171 in Table 4 of "Organic Insertion Reactions of Group IV Elements" by E. Y. Lukevits and M. G. Voronkov, translated from Russian by M. J. Newlands, Consultants Bureau, New York, 1966.

(7) For listings in ref 6 *specifically* dealing with radical initiated hydrosilylations of $(EtO)_3SiH$ with alkenes, see Table 4, ref 6, reactions 585, 586, 632, 650, 678, and 696. *No additions of ≡Si—OEt were observed!*

(8) We have corroborated the conclusion from ref 5–7 by demonstrating hydrogen-chlorine exchange between $(EtO)_3SiH$ and CCl_4 to give $(EtO)_3SiCl$ and $HCCl_3$ using both a radical initiator and 2537-Å light. This type of free-radical reaction of -Si—H has been well documented; see H. Sakurai, M. Murakami and M. Kumada, *J. Am. Chem. Soc.*, **91**, 519 (1969), for an interesting paper on the pyramidal, configurational stability of the $R_3Si^{\bullet}$ radical and references to earlier silicon free-radical work involving radical exchange between ≡Si—H and ≡C—Cl.

(9) For a detailed and convincing theoretical treatment of $CH_2{=}SiH_2$ which showed the ground-state singlet, π-bonded species to be more stable than the lowest triplet diradical by ~28 kcal/mol, the bond strength of the $2p_\pi$-$3p_\pi$ bond to be ~46 kcal/mol, and also showed the silicon-carbon double bond to have considerable polarity: $C^{-0.4}\cdots Si^{+0.5}$. See R. Ahlrichs and R. Heinzman, *J. Am. Chem. Soc.*, **99**, 7452 (1977).

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A Spirocyclophosphazene with Iron–Phosphorus Bonds and a P-Fe-Fe Three-Membered Ring

Sir:

We report here the synthesis and structure proof of an unusual new spirocyclophosphazene compound that contains

0002-7863/79/1501-2492$01.00/0