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Steven E. Diamond, Henry Taube*
Department of Chemistry, Stanford University
Stanford, California 94305

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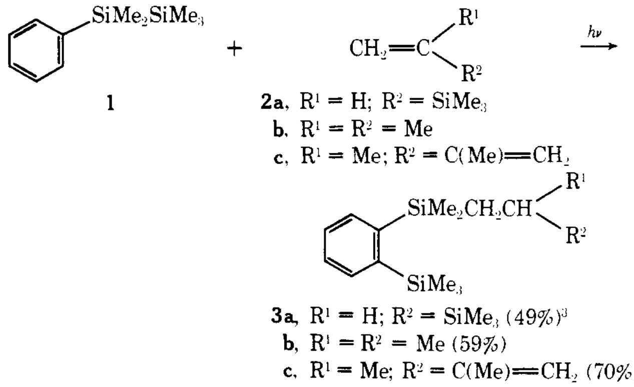
Photolysis of Organopolysilanes. A Novel Addition Reaction of Aryl Substituted Disilanes to Olefins

Sir:

There has been a considerable interest recently concerning the photolysis of organopolysilanes.[1] This paper is concerned with a novel photochemical addition involving arylpentamethyldisilanes and olefins.

When a solution of phenylpentamethyldisilane (**1**) (4.80 mmol) and trimethylvinylsilane (**2a**) (0.20 mol) in 110 ml of dry benzene was irradiated at 0° for 4 hr with a low pressure mercury lamp bearing a Vycor filter under a nitrogen atmosphere, 80% of **1** reacted to give *o*-(trimethylsilyl)(*β*-trimethylsilylethyl)dimethylsilylbenzene (**3a**) in 49% yield (based on unrecovered **1**).[2]

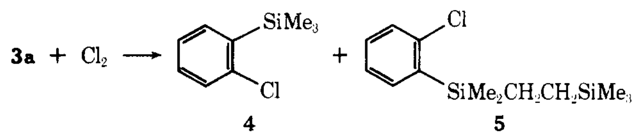


1

2a, $R^1 = H$; $R^2 = SiMe_3$
b, $R^1 = R^2 = Me$
c, $R^1 = Me$; $R^2 = C(Me){=}CH_2$

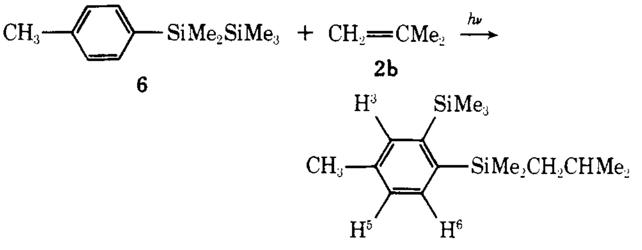
3a, $R^1 = H$; $R^2 = SiMe_3$ (49%)[3]
b, $R^1 = R^2 = Me$ (59%)
c, $R^1 = Me$; $R^2 = C(Me){=}CH_2$ (70%)

The NMR spectrum of **3a** showed proton absorptions at δ −0.07 (CH_3–$SiMe_2$, s, 9 H), 0.28 (CH_3–SiMe, s, 6 H), 0.31 (CH_3–$SiMe_2C_6H_4$, s, 9 H), 0.43–0.61 (CH_2CH_2, m, 4 H), and 7.40–7.56 (ring protons, m, 4 H). The mass spectrum of **3a** showed peaks for $C_6H_4(SiMe_3)(SiMe_2^+)$ at *m/e* 207 (49.3%) and for $C_{10}H_{15}Si_2^+$ at 191 (48.9%) as well as a peak at 308 corresponding to the molecular ion. Further support for the structure of the adduct comes from the reaction of **3a** with chlorine in carbon tetrachloride at room temperature, which gave known *o*-(trimethylsilyl)chlorobenzene (**4**)[4,5] (21%) and a new compound (17%) identified as *o*-(*β*-trimethylsilylethyl)chlorobenzene (**5**) by ir, NMR, and mass spectroscopic studies.[6] No other isomers such as *m*- or *p*-silyl-substituted chlorobenzene were detected by GLC analysis of the reaction mixture.[7]



4　　5

Compound **1** also reacted with isobutylene (**2b**) and 2,3-dimethylbutadiene (**2c**) under similar conditions to give adducts **3b** and **3c**, respectively. These were characterized by NMR and mass spectroscopic studies.[8,9]



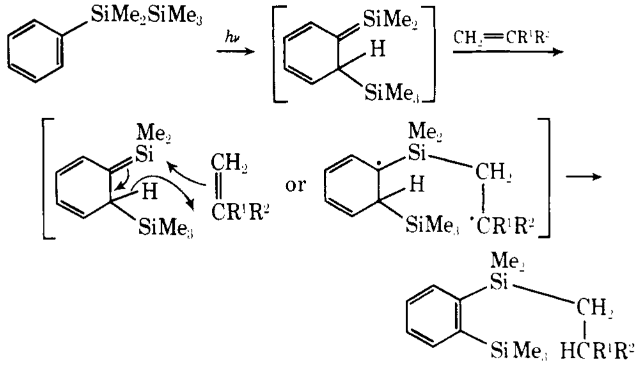
6　　2b

7

Photolysis of *p*-tolylpentamethyldisilane (**6**) in the presence of isobutylene afforded crucial evidence for the migration of the trimethylsilyl group from silicon to the ortho carbon in the aromatic ring. Thus 2-trimethylsilyl-4-methylisobutyldimethylsilylbenzene (**7**)[10] was obtained in 58% yield as a single product.

The NMR spectrum of the phenyl ring protons in **7** clearly indicates that it must have the 1,2,4-trisubstituted benzene structure. Thus H^3 (δ 7.36, s) and H^5 (δ 7.03, d, J = 7.6 Hz) protons showed broadening due to long-range coupling with the methyl and H^3 or H^5 protons, while the H^6 proton occurred at δ 7.45 (J = 7.6 Hz) as a sharp doublet. Protodesilylation of **7** by dry hydrogen chloride in ethyl ether gave *m*-(trimethylsilyl)toluene (**8**)[11] (17%) and *p*-(isobutyldimethylsilyl)toluene (**9**)[12] (5%) as monodesilylated products. Again, no other isomers were detected by GLC analysis.

Recently, Sommer and his coworkers have reported that in the photolysis of pentaphenylmethyldisilane $Ph_2Si{=}CH_2$ or its close equivalent, diradical species $Ph_2\dot{S}i\text{-}\dot{C}H_2$ is formed with loss of triphenylsilane.[11] The production of our adducts can best be explained in terms of photoisomerization of arylpentamethyldisilane to an unstable intermediate having the silicon–carbon double bond, followed by addition of this intermediate to the olefin or diene as shown below.[13,14]



3

The photolysis of various disilane derivatives in the presence of unsaturated compounds is currently being examined and will be reported elsewhere.

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(2) Satisfactory elemental analyses were obtained for all new compounds reported here.

(3) In this reaction, 7% of an unidentified product was also obtained.

(4) Compound **4**: NMR δ (CCl_4) 0.35 (CH_3–Si, s, 9 H), 7.13–7.53 (ring protons, m, 4 H); ir (cm^{-1})(neat) 730, 750, 840 (lit.[5] 730, 750, 840).

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(6) Compound **5**: NMR δ (CCl_4) −0.04 (CH_3–$SiMe_2$, s, 9 H), 0.31 (CH_3–SiMe, s, 6 H), 0.44–1.01 (CH_2CH_2, m, 4 H), 7.08–7.56 (ring protons, m, 4 H); ir (cm^{-1})(neat) 725, 745, 835.

(7) In addition to **4** and **5**, $C_6H_3Cl(SiMe_3)SiMe_2CH_2CH_2SiMe_3$ was also obtained in 60% yield; M^+ 342; NMR δ (CCl_4) −0.07 (CH_3–$SiMe_2$, s, 9 H), 0.31 (CH_3–SiMe, s, 6 H), 0.35 (CH_3–SiC_6H_3, s, 9 H), 0.45–0.95 (CH_2CH_2, m, 4 H), 7.12–7.62 (ring protons, m, 3 H).

(8) Compound **3b**: M^+ 264, *m/e* 207 (55.7), 191 (100); NMR δ (CCl_4) 0.36 (CH_3–$SiMe_2$, s, 9 H), 0.39 (CH_3–SiMe, s, 6 H), 0.83 (CH_2–C, d, 2 H, J = 6.8 Hz), 0.91 (CH_3–CMe, d, 6 H, J = 6.6 Hz), 1.81 (H–CMe_2, m, 1 H), 7.16–7.64 (ring protons, m, 4 H).

(9) Compound **3c**: M^+ 290, *m/e* 207 (17.9), 191 (59.2); NMR δ (CCl_4) 0.42 (CH_3–$SiMe_2C_6H_4$, s, 9 H), 0.44 (CH_3–SiMe, s, 3 H), 0.46 (CH_3–SiMe, s, 3 H), 0.91 (CH_2–CHMe, dd, 1 H, J_{gem} = 14.8 Hz, J_{vic} = 7.8 Hz), 1.13 (CH_2–CHMe, dd, 1 H, J_{gem} = 14.8 Hz, J_{vic} = 6.5 Hz), 1.05 (CH_3–CH, d, 3 H, J = 6.9 Hz), 1.71 (CH_3–C, s, 3 H), 2.43 (H–C(Me)–CH_2, sext, 1 H, J = 6.9 Hz), 4.58–4.74 (CH_2=C, m, 2 H), 7.18–7.68 (ring protons, m, 4 H). Irradiation of the sextet signal at 2.43 changed the two double doublets at 0.91 and 1.13 into two doublets.

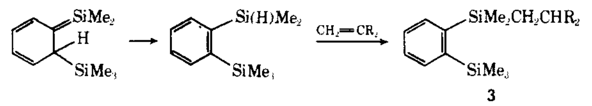
(10) Compound **7**: NMR δ (CCl_4) 0.35 (CH_3–$SiMe_2$, s, 9 H), 0.37 (CH_3–SiMe, s, 6 H), 0.81 (CH_2, d, 2 H, J = 6.8 Hz), 0.90 (CH_3–CMe, d, 6 H, J = 6.6 Hz), 1.79 (H–CMe_2, m, 1 H), 2.33 (CH_3–C_6H_3, s, 3 H).

(11) Ir spectrum of **8** was fully consistent with that reported[5] for the same substance.

(12) Compound **9**: NMR δ (CCl_4) 0.25 (CH_3–Si, s, 6 H), 0.74 (CH_2–C, d, 2 H), 0.90 (CH_3–CMe, d, 6 H), 1.80 (H–CMe_2, m, 1 H), 2.33 (CH_3–C_6H_4, s, 3 H), 7.08–7.52 (ring protons, m, 4 H); ir (cm^{-1})(neat) 745, 780, 830, 850.

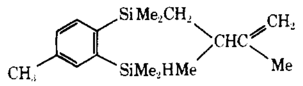
(13) Photolysis of **1** (2537 Å) in the absence of olefin gave a polymeric substance as a main product. When **1** was photolyzed in the presence of methyl alcohol, addition products (M^+ 240) consisting of two isomers were obtained in 33% yield. Attempts to isolate these in a pure form have been unsuccessful.

(14) For the production of **3**, one of the referees has suggested a possibility of an alternative mechanism outlined by the sequence as follows.

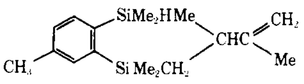


3

Photolysis of p-$CH_3C_6H_4SiMe_2SiMe_2H$ in the presence of 2,3-dimethylbutadiene under the same conditions gave compound **10** in 54% yield as a single product. If hydrosilylation reaction were involved leading to the observed products, compound **11** also should be formed. However, no evidence for the formation of **11** was obtained.



10



11

Mitsuo Ishikawa,* Takamasa Fuchikami
Toru Sugaya, Makoto Kumada*
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University
Sakyo-ku, Kyoto 606, Japan

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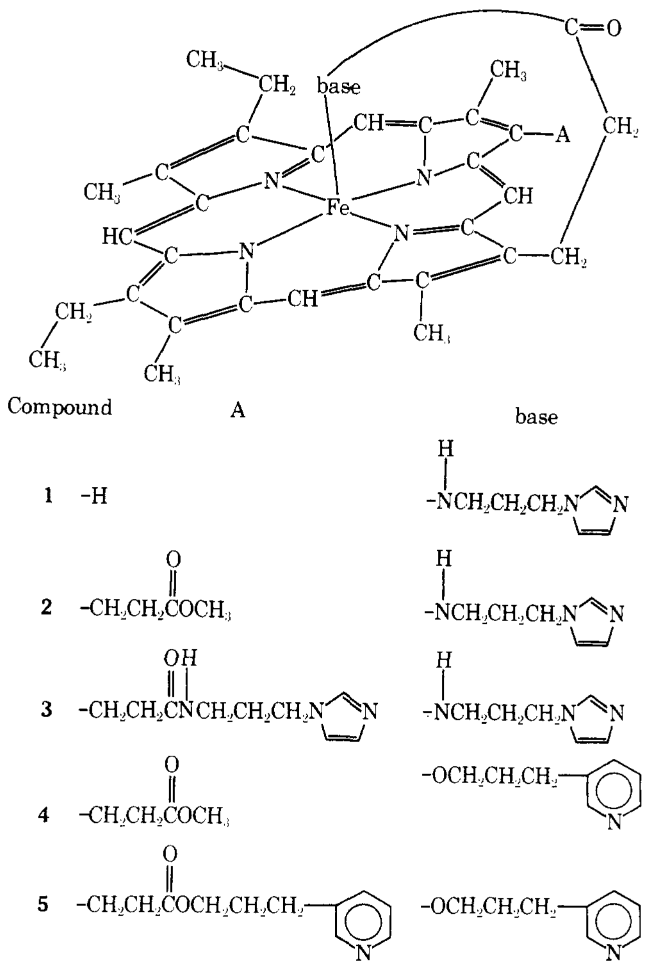
Coordination of Myoglobin Active Site Models in Aqueous Solution as Studied by Kinetic Methods[1]

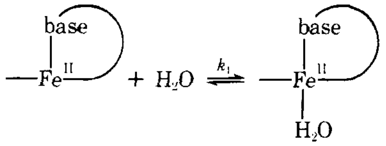
Sir:

The covalent attachment of the "proximal" base to simple hemes,[2-4] as in **1**, has made possible studies of both equilibria[4a-d] and kinetics[4e,f] of reversible heme oxygenation. Although some of the qualitative aspects of reversible oxygenation of **1** and **2** have been duplicated with simple heme-base mixtures,[5-8] quantitative equilibria and kinetic studies of such mixtures have met with limited success[4e,9,10] due to the interference of the competing external bases.[11]



Because our "isolated site" models **1** and **2** showed oxygenation kinetics and equilibria at 20° in water similar to those of myoglobin,[4] and because **3** also binds oxygen reversibly in solution, it seemed interesting to investigate the coordination of **2** and **3** in aqueous solution. We report evidence that **2** is present in aqueous solution *almost entirely as the five-coordinate species* shown, whereas **3** exists as a mixture of five- and six-coordinate species in water.

We have previously reported that **1**, **2**, and **4** react with carbon monoxide as rapidly in water as in anhydrous solvents.[4d,f] This is evidence that, even in aqueous solution, water is not coordinated to the iron in **1** or **4** at room temperature (K_1 is small) (eq 1). However, as the temperature



(1)

of solutions of **1** or **2** in methanol-water or wet methylene chloride is lowered to <0° the broad band at 530 nm splits in α,β bands,[4a] typical of hexacoordinate hemes ($\epsilon_{555}/\epsilon_{528} \approx 1.5$ at −60°C in filtered wet methylene chloride). This indicates that K_1 becomes significant at low temperatures.[15]

Because there is still some disagreement concerning unequivocal correlations of visible spectra with axial ligation in hemes,[13b] we have developed an alternative kinetic meth-