Silicon-Carbon Unsaturated Compounds. XVI.[1] Photorearrangement of an Adduct Derived from Reaction of a Silicon-Carbon Unsaturated Compound with *t*-Butyl Alcohol

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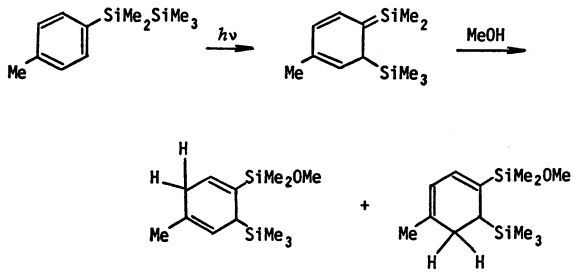
Photolysis of pentamethylphenyldisilane in the presence of *t*-butyl alcohol gave a mixture of adducts which were readily oxidized to 1-(*t*-butoxydimethylsilyl)-2-(trimethylsilyl)benzene by oxygen. Photolysis of *p*-tolylpentamethyldisilane in the presence of *t*-butyl alcohol afforded 4-(*t*-butoxydimethylsilyl)-1-methyl-5-trimethylsilyl-1,3-cyclohexadiene (**4**) as a primary photoproduct. The UV-irradiation of **4** gave ring opened products, 2-(*t*-butoxydimethylsilyl)-5-methyl-1-trimethylsilyl-1,3,5-hexatriene and 2-(*t*-butoxydimethylsilyl)-5-methyl-3-trimethylsilyl-1,3,5-hexatriene in a ratio of 1.8/1.

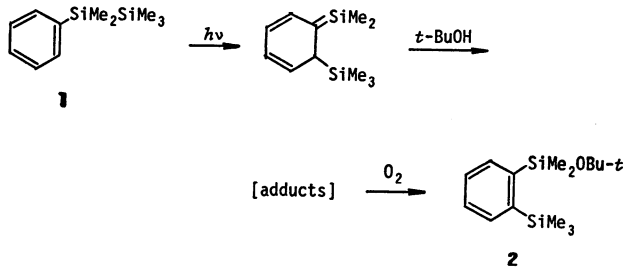
Previous studies in our laboratory have shown that the photolysis of aryldisilanes causes their rearrangement to isomeric silicon–carbon unsaturated compounds, which can react with many types of trapping agent.[2-4] As reported previously, the silicon-carbon unsaturated intermediate generated photochemically from pentamethyl(*p*-tolyl)disilane in a benzene solution reacts with methyl alcohol to give 1-(methoxydimethylsilyl)-4-methyl-6-trimethylsilyl-1,3- and 1,4-cyclohexadiene in the ratio of approximately 1/1 in high yield.[5] We now wish to report the reaction of this intermediate with *t*-butyl alcohol and the photochemistry of the resulting adduct.



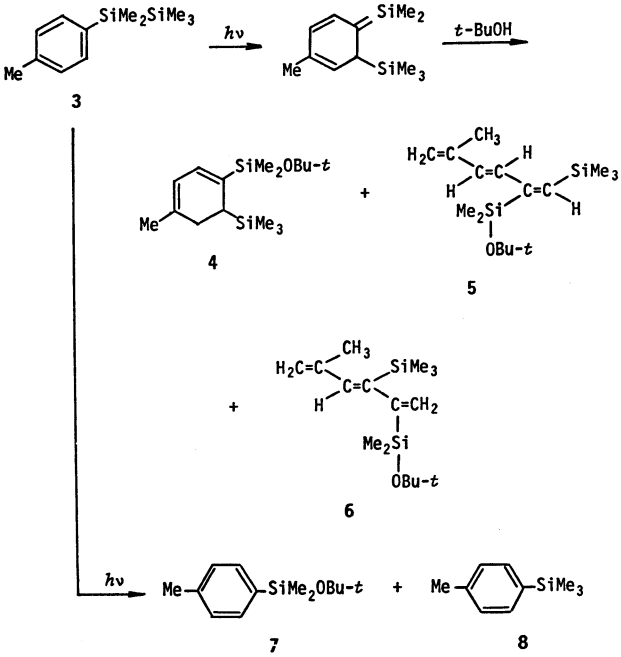
Results and Discussion

Photolysis of Aryldisilanes in the Presence of t-*Butyl Alcohol.* The photochemical studies were carried out with a low-pressure immersion mercury lamp having a Vycor filter.

First, we investigated the photolysis of pentamethylphenyldisilane (**1**) in the presence of *t*-butyl alcohol in benzene. In this case, a mixture of two isomers was obtained in 38% yield as reaction products; the ^{1}H NMR spectrum of the mixture showed two resonances in a ratio of 1/3 for *t*-butoxyl protons. Preparative GLC and column chromatography were used to isolate each isomer from the mixture, but they could not be separated under any of the conditions used. The mass spectrum of the mixture showed a parent peak at *m/e* 282, corresponding to the calculated molecular weight for $C_{15}H_{30}OSi_2$. The alcohol adducts can readily be oxidized by atmospheric oxygen. Thus, when the mixture of the adducts was allowed to stand for a week at room temperature in an oxygen atmosphere, 1-(*t*-butoxydimethylsilyl)-2-(trimethylsilyl)-benzene (**2**) was obtained in 65% yield, in addition to 17% of the starting adducts.



We then turned our attention to pentamethyl(*p*-tolyl)disilane (**3**) as a source of the silicon–carbon double-bonded intermediate. As we reported earlier, the photolysis of **3** in the presence of methyl alcohol afforded two addition products which could easily be separated by preparative GLC.[5] Interestingly, the photolysis of **3** in the presence of *t*-butyl alcohol in benzene at room temperature gave 4-(*t*-butoxydimethylsilyl)-1-methyl-5-trimethylsilyl-1,3-cyclohexadiene (**4**) as a primary photoproduct in 27% yield, when 70% of the starting disilane was photolyzed. At this stage, 2-(*t*-butoxydimethylsilyl)-5-methyl-1-trimethylsilyl-1,3,5-hexatriene (**5**) (6% yield) and 2-(*t*-butoxydimethylsilyl)-5-methyl-3-trimethylsilyl-1,3,5-hexatriene (**6**) (6% yield) were formed as secondary photoproducts. Small amounts of *t*-butoxydimethyl(*p*-tolyl)silane (**7**)



(3% yield) and *p*-tolyltrimethylsilane (**8**) (2% yield) were also produced. However, no isolable amount of the disilyl-substituted 1,4-cyclohexadiene isomer was obtained, whereas under similar conditions but using a lower primary alcohol such as methyl alcohol[5] and ethyl alcohol (see Experimental section) as a quencher, both the analogous 1,3- and 1,4-cyclohexadiene isomers were found to be produced.

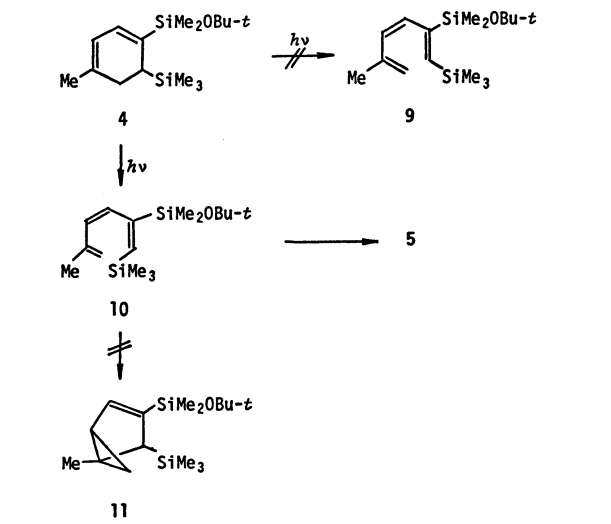
At present, no convincing explanation for the absence of the 1,4-cyclohexadiene in the product is available, but steric interactions arising from an approach of the alcohol to the silicon–carbon unsaturated compound would be important for the product distribution. We found that the adducts to the less hindered alcohols are photochemically more stable than those to the hindered alcohols under the used conditions. Thus, the photolysis of **3** in the presence of methyl alcohol afforded no isolable amounts of the ring opened products when 80% of **3** was photolyzed. On the other hand, compound **4** decomposed slowly to give photoproducts, **5** and **6**, under prolonged irradiation.

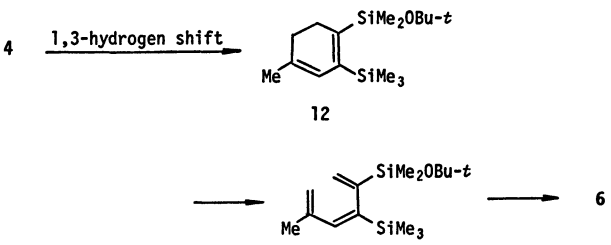
Compound **4** was identified by mass and NMR spectroscopic methods. Compound **4** exhibited proton absorptions at δ 0.01 (CH_3–$SiMe_2$, s, 9H), 0.23 (CH_3–SiOBu-*t*, s, 6H), 1.28 (*t*-BuO–Si, s, 9H), 1.6—2.0 (H–$CSiMe_3$, m, 1H), 1.76 (CH_3–C, broad s, 3H), 2.3—2.6 (H_2C–$CSiMe_3$, m, 2H), 5.59 (H–C=CMe, m, 1H) and 6.07 (H–C=CSiOBu-*t*, broad d, 1H, J=5 Hz).

Photochemical Isomerization of **4**. In order to learn more about the photoisomerization of **4** to **5** and **6**, we investigated the photochemistry of **4**. When a solution of **4** in benzene was photolyzed at room temperature for 13.5 h, **5** and **6** were obtained in 43 and 24% yield, respectively, in addition to 24% of the starting substance. No other isomer such as a bicyclo[3.1.0]hexene derivative (**11**), which might be expected to be formed from formal intramolecular [2+4] cycloaddition of 1,3,5-triene (**10**), could be detected by spectroscopic analysis.[6–8] Furthermore, it was shown that compound **5**, which could easily be isolated by preparative GLC, did not undergo isomerization at all when irradiated under similar conditions. These results indicate that both the products, **5**, and **6**, must come independently from the photoisomerization of **4**. The *trans* triene structure for **5** is based on its NMR spectrum: δ=0.17 (CH_3–$SiMe_2$, s, 9H), 0.25 (CH_3–SiOBu-*t*, s, 6H), 1.25 (*t*-Bu–O, s, 9H), 1.87 (CH_3–C=C, broad s, 3H), 4.98 (H_2C=CMe, broad s, 2H), 6.17 (H–$CSiMe_3$, broad s, 1H), 6.48 (H–C–CMe, d, 1H, J=16 Hz), and 6.72 (H–C–CSi, d, 1H, J=16 Hz). The magnitude of the coupling constant requires that the geometrical configuration of **5** is *trans*.

Compound **6** can also be shown unambiguously to have the proposed structure by proton NMR spectroscopy: (δ) 0.17 (CH_3–$SiMe_2$, s, 9H), 0.29 (CH_3–SiOBu-*t*, s, 6H), 1.28 (*t*-Bu–O, s, 9H), 1.84 (CH_3–C=C, broad s, 3H), 4.91 (H_2C=CMe, broad, s, 2H), 6.30 (H_2C=CSi, s, 2H), and 6.64 (H–C=C, s, 1H).

Two modes of conrotatory motion are possible in the ring opening of **4**.[9,10] One involves the formation of the triene **9**, in which the two silyl groups are brought into a *cis* relationship, and the other comprises the production of the triene **10** having *E*-configuration for the two silyl groups. Unfortunately both compounds **9** and **10** could not be detected either by GLC or spectroscopic analysis. However, the former process seems to be unlikely, because *Z*-configuration of the two bulky silyl groups about the carbon-carbon double bond is sterically very unfavorable. Compound **10** thus formed would undergo rapid isomerization to afford the observed product **5**. The formation of **6** can be explained in terms of successive 1,3-sigmatropic hydrogen shifts in the compound **4**, followed by rapid ring opening and rearrangement of the resulting product (**12**).





Experimental

^{1}H NMR spectra were determined with a JEOL JNM-MH-100 spectrometer in carbon tetrachloride. Mass spectra were measured on a JEOL JMS-300 mass spectrometer equipped with a JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. A Shimazu Model GC-4B gas chromatograph with a column containing 30% methylsilicon polymer (5 mm×1.5 m) was used for analysis of the products. An Aerograph Model 90 gas chromatograph with a thermal conductivity detector was used for separation of the products reported here.

Materials. Pentamethylphenyldisilane[11] and pentamethyl(*p*-tolyl)disilane[12] were prepared as described in the literature. *t*-Butyl alcohol was purified fractional distillation. Benzene was dried over lithium aluminum hydride and distilled just before use.

*Photolysis of Pentamethylphenyldisilane (***1***) in the Presence of t-Butyl Alcohol.* A solution of 1.00 g (4.8 mmol) of **1** and 20 ml of *t*-butyl alcohol in 80 ml of dry benzene was photolyzed for 3 h at room temperature under bubbling nitrogen. The solvent benzene and unchanged *t*-butyl al-

cohol were evaporated, and the residue was distilled under reduced pressure. GLC analysis of the distillate showed that 37% yield of the adduct consisting of two isomers was produced in addition to phenyltrimethylsilane (2%), 1-(*t*-butoxydimethylsilyl)-2-(trimethylsilyl)benzene (**2**) (2.5%) and the starting compound (11.5%). The adduct was isolated by preparative GLC as a mixture. MS *m/e* 282; Found: C, 63.77; H, 10.54%. Calcd for $C_{15}H_{30}OSi_2$: C, 63.90; H, 10.70%.

Oxidation of the Adduct. The photolysis mixture containing 1.6 mmol of the adduct was concentrated and the residue was allowed to stand in an oxygen atmosphere for a week at room temperature. GLC analysis of the resulting mixture showed that 64% yield of **2** was produced, and 17% of the starting adduct was recovered. Pure **2** was isolated by preparative GLC; MS *m/e* 280; ^{1}H NMR δ=0.37 (CH_3–$SiMe_2$, s, 9H); 0.43 (CH_3–SiMeOBu-*t*, s, 6H), 1.30 (CH_3–CMe_2OSi, s, 9H) and 7.15—7.63(ring protons, m, 4H); Found: C, 64.62; H, 10.1%. Calcd for $C_{15}H_{28}OSi_2$: C, 64.42; H, 10.06%.

Photolysis of p-*Tolylpentamethyldisilane (**3**) in the Presence of Ethyl Alcohol.* A solution of 0.9896 g (4.45 mmol) of **3** and 10 ml of ethyl alcohol in 90 ml of benzene was photolyzed for 3 h at room temperature. The solvent benzene was evaporated and the residue was distilled under reduced pressure to give volatile products. GLC analysis showed the presence of 4-(ethoxydimethylsilyl)-1-methyl-5-trimethylsilyl-1,3-cyclohexadiene (**13**) and 4-(ethoxydimethylsilyl)-1-methyl-3-trimethylsilyl-1,4-cyclohexadiene (**14**) in 27 and 18% yield, respectively, along with 7% of ethoxydimethyl(*p*-tolyl)silane[13] and 27% of the starting **3**. A small amount of unidentified compounds (less than 5%) was also detected. For, **13**: MS *m/e* 268; ^{1}H NMR δ=-0.04 (CH_3–$SiMe_2$, s, 9H), 0.14 (CH_3–SiMeOEt, s, 6H), 1.16 (CH_3–CH_2O, t, 3H, J=6 Hz), 1.76 (CH_3–C, broad s, 3H), 1.85—2.47 (H_2C–CH, m, 3H), 3.65 (CH_2–O, q, 2H, J=6 Hz), 5.64 (H–C=CMe, m, 1H); 6.15 (H–C=CSi, d, 1H); Found: C, 62.89; H, 10.66%. Calcd for $C_{14}H_{28}OSi_2$: C, 62.62; H, 10.51%. For **14**: MS *m/e* 268; ^{1}H NMR δ=−0.03 (CH_3–$SiMe_2$, s, 9H), 0.17 (CH_3–SiMeOEt, s, 6H), 1.15 (CH_3–CH_2O, t, 3H, J=6 Hz), 1.70 (CH_3–C, broad s, 3H), 2.37—2.65 (H_2C and HC, m, 3H), 3.62 (CH_2–O, q, 2H, J=6 Hz), 5.45 (H–C=CMe, m, 1H), 6.00 (H–C=CSi, t, 1H); Found: C, 62.32; H, 10.75%. Calcd for $C_{14}H_{28}OSi_2$: C, 62.62; H, 10.51%.

*Photolysis of **3** in the Presence of* t-*Butyl Alcohol.* A solution of 1.0170 g (4.57 mmol) of **3** and 20 ml of *t*-butyl alcohol in 80 ml of benzene was irradiated for 4 h. The solvent benzene was evaporated and the residue was distilled under reduced pressure to give volatile products. GLC analysis showed that the distillate contained **4** (28%), **5** (6%), and **6** (6%), together with *t*-butoxydimethyl(*p*-tolyl)silane **7** (2%), *p*-tolyltrimethylsilane (**8**) (trace) and the starting disilane (30%). Compound **4** was isolated by preparative GLC. MS *m/e* 296; Found: C, 65.09; H, 11.01%. Calcd for $C_{16}H_{32}OSi_2$: C, 64.79; H, 10.87%. Compounds **7** and **8** were identified by comparison of their retention times on GLC with those of the authentic samples.

*Photoisomerization of **4**.* A solution of 472 mg (1.59 mmol) of **4** in 80 ml of dry benzene was irradiated for 13.5 h at room temperature. Distillation of the reaction mixture afforded **5** and **6** in 43 and 24% yield, respectively, together with 24% of the starting compound. Both **5** and **6** were isolated by preparative GLC. For **5**: MS *m/e* 296; Found: C, 64.59; H, 10.79%. Calcd for $C_{16}H_{32}OSi_2$: C, 64.79; H, 10.87%. For **6**: MS *m/e* 296; Found: C, 64.55; H, 10.64%. Calcd for $C_{16}H_{32}OSi_2$: C, 64.79; H, 10.87%.

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