

SILICON–CARBON UNSATURATED COMPOUNDS

XVII *. PHOTOCHEMICAL BEHAVIOR OF 1-METHYL-1-(TRIMETHYLSILYL)DIBENZOSILOLE AND 1-PHENYL-1-(TRIMETHYLSILYL)DIBENZOSILOLE **

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Summary

The photolysis of 1-methyl-1-(trimethylsilyl)dibenzosilole (I) and 1-phenyl-1-(trimethylsilyl)dibenzosilole (II) has been investigated. Irradiation of I in the presence of acetone afforded 1-isopropoxy-1-methyl-2-(trimethylsilyl)dibenzosilole (III), while in the presence of isobutene, I afforded 1-isobutyl-1-methyl-2-(trimethylsilyl)dibenzosilole (V). The photolysis of II in the presence of acetone or isobutene gave the rearranged addition products analogous to III and V. Irradiation of I in alcohols such as methyl alcohol, ethyl alcohol and isopropyl alcohol, produced 1-hydro-1-methyldibenzosilole (VII) in high yield. Similarly, irradiation of II in methyl alcohol or ethyl alcohol gave 1-hydro-1-phenyldibenzosilole in high yield.

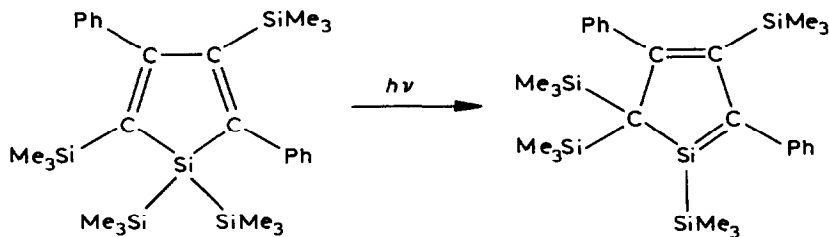
Introduction

There has been a considerable interest in the chemistry of siloles, and many papers that deal with the preparation and reactions of these compounds have been published [2–11]. However, little interest has been shown in the photochemical behavior of the siloles [12,13]. Recently, we have found that the photolysis of 3,5-diphenyl-1,1,2,4-tetrakis(trimethylsilyl)silole affords a silicon–carbon unsaturated compound arising from a 1,2-silyl shift from the silicon in the silole ring to the adjacent unsaturated carbon atom [11,14]. As an extension of our study

* For part XVI see ref. 1.

** Dedicated to Professor R. Calas on the occasion of his 70th birthday on April 8th, 1984.

concerning the photochemistry of π -electron system-substituted polysilanes [15–19], we have examined the photochemical behavior of 1-silyl-substituted dibenzosiloles.

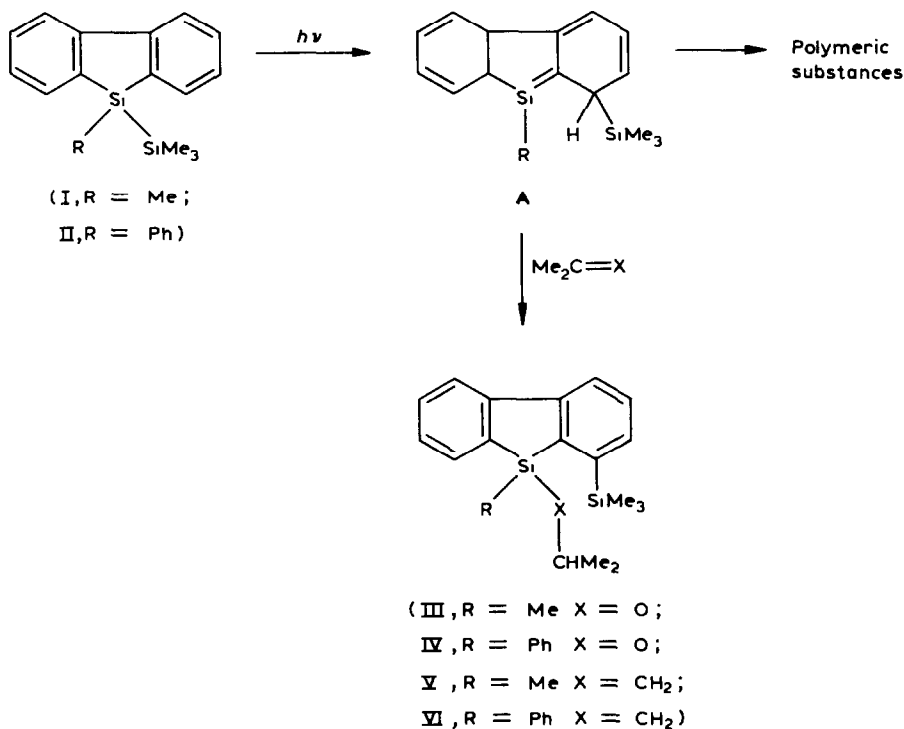


Results and discussion

The 1-silyl-substituted dibenzosiloles, 1-methyl-1-(trimethylsilyl)dibenzosilole (I) and 1-phenyl-1-(trimethylsilyl)dibenzosilole (II), were prepared as described in our previous paper [10].

When a solution of compound I in the presence of a 30-fold excess of acetone in benzene was irradiated with a high-pressure mercury lamp bearing a quartz filter, a rearranged addition product, 1-isopropoxy-1-methyl-2-(trimethylsilyl)dibenzosilole (III) was obtained in 28% yield, as the sole volatile product. The formation of product III can be explained in terms of photochemical isomerization of I to a silicon-carbon unsaturated compound (A, R = Me), via a 1,3-silyl shift, followed by addition to acetone, as shown in Scheme 1.

SCHEME 1



Irradiation of the silyl-substituted dibenzosilole II in the presence of acetone with a high-pressure mercury lamp also gave a rearranged addition product, 1-isopropoxy-1-phenyl-2-(trimethylsilyl)dibenzosilole (IV) in 44% yield. No other volatile product was detected by GLC or TLC analysis.

In contrast to the 1-silacyclopenta-1,3-diene generated photochemically from 3,5-diphenyl-1,1,2,4-tetrakis(trimethylsilyl)silole, which undergoes isomerization to give a silaindene derivative [11], the present unsaturated silicon compound gives no volatile product in the absence of a trapping agent. Such behavior is rather similar to that of the unsaturated silicon compound arising from phenyldisilanes. Like silicon-carbon unsaturated compounds produced photochemically from phenyldisilanes, compound A (R = Me) readily adds to an olefin giving the rearranged addition product. Thus, irradiation of I in the presence of isobutene afforded 1-isobutyl-1-methyl-2-(trimethylsilyl)dibenzosilole (V) in 10% yield. Similar photolysis of II in the presence of isobutene gave 1-isobutyl-1-phenyldibenzosilole (VI) in 20% yield, as the sole volatile product.

The structures of the rearranged addition products, III, IV, V and VI were verified by mass, IR and ^1H NMR spectroscopic analysis (see Experimental section). The 200 MHz ^1H NMR spectrum of V shows resonances at δ 7.52, 7.41 and 7.80 ppm, assigned to hydrogens on the carbon atoms in the 3-, 4- and 5-positions of the dibenzosilole ring, respectively, indicating that the trimethylsilyl group is located on the ring carbon atom in the 2-position (Fig. 1). The ^{13}C NMR spectrum of V (Fig. 2) and the results obtained from selective decoupling are also consistent with the proposed structure.

It has been reported previously that the silicon-carbon unsaturated compound produced from phenyldisilanes reacts with an alcohol to give the rearranged addition products in high yield [1,20]. The photolysis of the silyl-substituted dibenzosiloles in the presence of an alcohol under the same conditions, however, afforded no alcohol adducts. A wholly unexpected compound, 1-hydrodibenzosilole was obtained. Thus, irradiation of I in the presence of a 200-fold excess of methyl alcohol in benzene gave 1-hydro-1-methyldibenzosilole (VII) in 8% yield, as a single reaction product. Interestingly, when I was photolyzed in neat methyl alcohol, 1-hydrodibenzosilole VII was obtained in a much higher yield (53%) (Scheme 2). The ^1H NMR spectrum

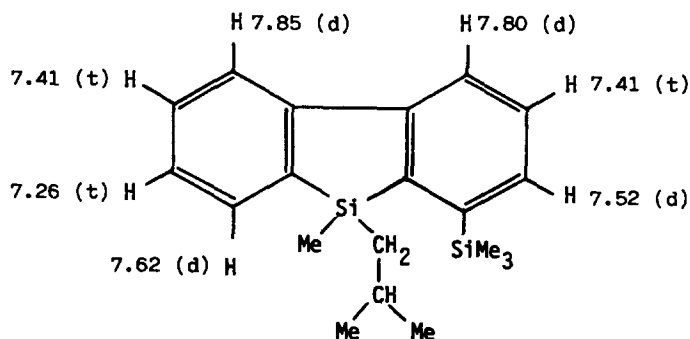
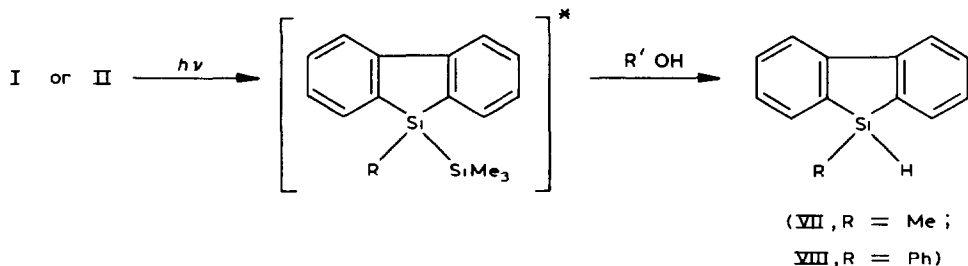


Fig. 1. ^1H NMR chemical shifts for V. The chemical shifts of substituents on silicon atoms are omitted for clarity. In parentheses, a rough splitting pattern due to $^3J(\text{HH})$ (7.0–7.5 Hz) is shown.

SCHEME 2



of the photolysis mixture showed a sharp signal at δ 0.13 ppm which is consistent with methylsilyl protons of methoxytrimethylsilane, in addition to the resonances attributed to methylsilyl protons of compound VII. The yield of methoxytrimethylsilane was determined to be 62%, when 72% of I was photolyzed. The photolysis of II in the presence of a 160-fold excess of methyl alcohol gave 1-hydro-1-phenyldibenzosilole (VIII) in only 1% yield. Again, it was shown that the yield of VIII is highly dependent on the concentration of methyl alcohol. The highest yield of VIII (55%) was obtained from the photolysis of II in neat methyl alcohol. In all photolyses, no other volatile product bearing the dibenzosilole ring other than the hydrides VII and VIII was detected by either GLC or spectroscopic analysis.

The formation of the 1-hydrodibenzosilole in the photolysis of the 1-silyl-substituted dibenzosilole in an alcohol seems to be quite common. Thus, irradiation of I in ethyl alcohol under similar conditions afforded VII in 43% yield, while in isopropyl alcohol I gave VII in 11% yield. Similarly, irradiation of II in ethyl alcohol produced VIII in 43% yield. The formation of VII and VIII can best be understood in terms of a direct reaction of the photoexcited silyl-substituted dibenzosilole with alcohol. That the yields of the 1-hydrodibenzosilole depend on the concentration of alcohol is presumably due to the short lifetime of the singlet excited state. The low yield of VII in isopropyl alcohol may be attributed to the steric effect of the bulky isopropyl group.

The photolysis of I in acetic acid afforded no 1-hydrodibenzosilole VII, but produced nonvolatile substances.

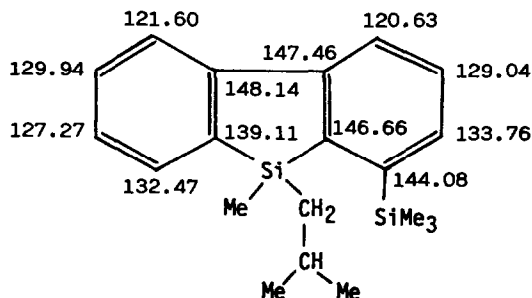


Fig. 2. ^{13}C NMR chemical shifts for V. The methylsilyl carbons and isobutyl carbons are omitted.

Experimental

General procedure

Infrared spectra were obtained with the use of a Hitachi Model EPI-G3 Grating infrared spectrometer. ^1H NMR spectra for III, IV, VI, VII and VIII were determined with a JEOL Model JNM-MH-100 spectrometer, while for V with a JEOL Model JNM-FX-200 spectrometer. The ^{13}C NMR spectrum for V was obtained with a JEOL Model JNM-FX-200. Mass spectra were measured on a JEOL Model JMS-D300 mass spectrometer equipped with a JMA-2000 data processing system. A Varian Aerograph Model 920 gas chromatograph with a thermal conductivity detector was used for separation of the products (SE-30, 3/8 in. \times 10 ft.).

Photolysis of 1-methyl-1-(trimethylsilyl)dibenzosilole (I) in the presence of acetone

A solution of 0.4849 g (1.809 mmol) of I, 3.2 g (55 mmol) of acetone, and 0.144 g (0.637 mmol) of cetane, as an internal standard, in 100 ml of dry benzene was irradiated with a high-pressure mercury lamp bearing a quartz filter for 5 h. The mixture was analyzed by GLC as being III (28% yield) and starting material I (29%). The solvent was distilled off and the residue of the flask was evaporated under reduced pressure (1 Torr) to give III. Pure III was isolated by preparative GLC, M^+ 326 (mol wt. 326.37); IR (cm^{-1}) 1010; ^1H NMR (δ , ppm) 0.30 (Me_3Si , s, 9H), 0.57 (MeSi , s, 3H), 0.98 and 1.00 (MeCH , d, 6H, J 6 Hz), 3.79 (CH-O , sep, 1H, J 6 Hz), 7.0–7.7 (ring protons, m, 7H) (Found: C, 69.60; H, 8.01. $\text{C}_{19}\text{H}_{26}\text{OSi}_2$ calcd.: C, 69.87; H, 8.03%).

Photolysis of 1-phenyl-1-(trimethylsilyl)dibenzosilole (II) in the presence of acetone

A solution of 0.5264 g (1.59 mmol) of II and 0.6 ml of acetone in 100 ml of benzene was irradiated for 15 h. The mixture was analyzed by GLC as being IV (44% yield). Pure IV was isolated by preparative GLC, ^1H NMR (δ , ppm) 0.06 (Me_3Si , s, 9H), 1.10 and 1.16 (MeCH , d, 6H, J 8 Hz), 4.06 (HCMe_2 , sep, 1H, J 8 Hz), 7.1–7.9 (ring protons, m, 12H). (Exact mass: 388.1660. $\text{C}_{24}\text{H}_{28}\text{OSi}_2$ calcd.: 388.1679).

Photolysis of I in the presence of isobutene

A mixture of 0.4184 (1.56 mmol) of I, 7 ml of isobutene and 0.1212 g (0.451 mmol) of nonadecane, as an internal standard, was irradiated for 3 h. The solvent was evaporated and the residue was analyzed by GLC as being V (10% yield). Pure V was isolated by preparative GLC, ^1H NMR (δ , ppm) 0.36 (Me_3Si , s, 9H), 0.50 (MeSi , s, 3H), 0.76 and 0.79 (MeCH , d, 6H, J 6.2 Hz), 1.04 and 1.05 (CH_2Si , d, 2H, J 7.0 Hz), 1.69 (HCMe_2 , nonet 1H, J 6.7 Hz), 7.2–7.9 (ring protons, 7H (see Fig. 1)). (Exact mass: 324.1703, $\text{C}_{20}\text{H}_{28}\text{Si}_2$ calcd.: 324.1730).

Photolysis of II in the presence of isobutene

A mixture of 0.4854 g (1.47 mmol) of II and 10 ml of isobutene in 100 ml of benzene was irradiated for 6 h at room temperature. After the solvent had been evaporated, the residue was analyzed by GLC as being VI (20% yield). Pure VI was isolated by preparative GLC; ^1H NMR (δ , ppm) 0.24 (Me_3Si , s, 9H), 0.92 (Me_2CH , d, 6H, J 6.0 Hz), 1.5–2.0 (CH_2 and HCMe_2 , m, 3H), 7.0–8.0 (ring protons, m, 12H). (Exact mass: 386.1898. $\text{C}_{25}\text{H}_{30}\text{Si}_2$ calcd.: 386.1886).

Photolysis of I in alcohols

The following is typical of the procedures used. A mixture of 0.1462 g (0.562 mmol) of I and 0.1468 g (0.610 mmol) of heptadecane, as an internal standard, in 100 ml of methyl alcohol, was irradiated with a high-pressure mercury lamp for 15 min. At this point, 100% of the starting I had been photolyzed. After the solvent was distilled off and the residue was analyzed by GLC as being VII (53% yield). Pure VII was isolated by preparative GLC, M^+ 196 (mol wt. 196.22); IR (cm^{-1}) 2125; ^1H NMR (δ , ppm) 0.57 (MeSi, d, 3H, J 4 Hz), 4.92 (HSi, q, 1H, J 4 Hz), 7.2–7.9 (ring protons, m, 8H) (Found: C, 79.70; H, 6.18. $\text{C}_{13}\text{H}_{12}\text{Si}$ calcd.: C, 79.53; H, 6.16%) [21]. Irradiation of I (49.3 mg, 0.183 mmol) in 25 ml of ethyl alcohol gave VII in 43% yield. Irradiation of I (55.1 mg, 0.205 mmol) in 25 ml of isopropyl alcohol afforded VII in 11% yield. The retention time on GLC and mass spectrum of both products were identical with those of an authentic sample.

Photolysis of II in methyl alcohol

A solution of 0.1487 g (0.450 mmol) of II and 0.067 g (0.237 mmol) of icosane as an internal standard was irradiated for 15 min. The mixture was analyzed by GLC as being VIII (55% yield). Pure VIII was isolated by preparative GLC, M^+ 258 (mol.wt. 258.27); IR (cm^{-1}) 2130; ^1H NMR (δ , ppm) 5.33 (HSi, s, 1H), 7.1–7.9 (ring protons, m, 13H) (Found: C, 83.67; H, 5.73. $\text{C}_{18}\text{H}_{14}\text{Si}$ calcd.: C, 83.80; H, 5.46%) [21].

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