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PHOTOCHEMICALLY GENERATED SILICON—CARBON DOUBLE-BONDED INTERMEDIATES

III *. THE REACTION OF *p*-TOLYLPENTAMETHYLDISILANE WITH METHANOL AND METHANOL-d_1

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Summary

Photolysis of *p*-tolylpentamethyldisilane in the presence of methanol or methanol-d_1 has been studied. With unlabeled methanol, 1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,3-cyclohexadiene (IVa) and 1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,4-cyclohexadiene (Va) were obtained as main products, along with a small amount of *p*-trimethylsilyltoluene (II) and *p*-methoxydimethylsilyltoluene (IIIa). With methanol-d_1, monodeuteriated products, deuteriomethyl(methyl)(*p*-tolyl)methoxysilane (IIIb), 5-deuterio-1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,3-cyclohexadiene (IVb) and 3-deuterio-1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,4-cyclohexadiene (Vb) were produced in addition to II. The formation of the products II—V can be best explained by assuming either silicon—carbon double-bonded intermediates or loss of dimethylsilylene species from the starting disilane.

Introduction

In previous papers in this series, we have reported that the photolysis of aryldisilanes in the presence of olefins [1] and dienes [2] gives addition products of a novel type. These reactions have been postulated to proceed via photochemical isomerization of arylpentamethyldisilanes to silicon—carbon double-bonded reactive intermediates. The reaction of such intermediates with olefins [1] proceeds in a different fashion from that of the thermally generated silicon—carbon double-bonded intermediates which undergo formal [2 + 2] cycloaddition yielding silacyclobutane derivatives [3,4].

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* For part II, see ref. 2.

In an attempt to learn more about the chemical behavior of the photochemically generated silicon—carbon double-bonded intermediates, we have investigated the reaction of one of these intermediates with methanol and methanol-d_1.

Results and discussion

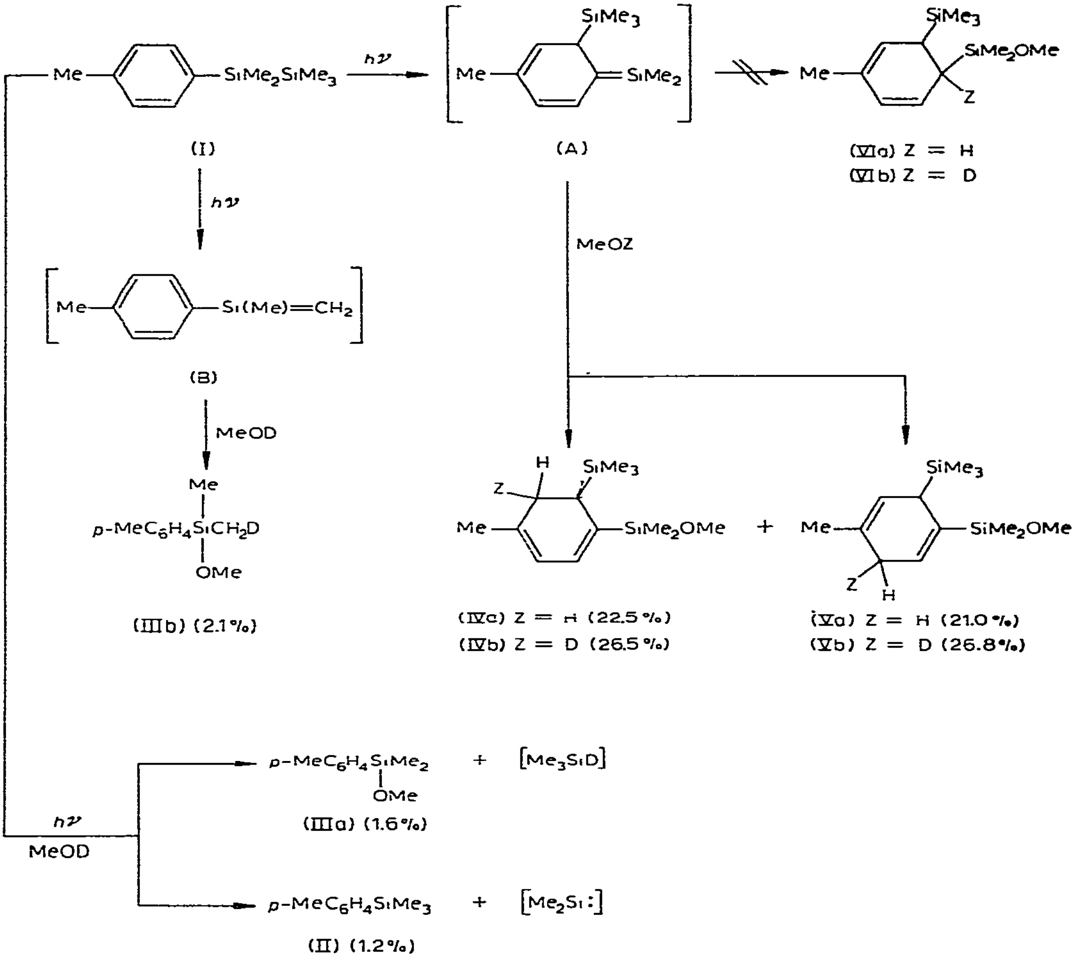
When a solution of *p*-tolylpentamethyldisilane (I) in the presence of a large excess of dry methanol in dry benzene was photolyzed for 6 h with a low-pressure mercury lamp bearing a Vycor filter, five products were obtained: 1.0% yield of *p*-trimethylsilyltoluene (II), 3.1% yield of *p*-methoxydimethylsilyltoluene (IIIa), 22.5% yield of 1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,3-cyclohexadiene (IVa) and 21.0% yield of 1-methoxydimethylsilyl-4-methyl-6-trimethylsilyl-1,4-cyclohexadiene (Va), in addition to 3.2% yield of an unidentified substance. Some amounts (20.5%) of unchanged I were recovered. Products II and IIIa were identified by comparison of their IR and mass spectra with those of authentic samples, while IVa and Va were characterized by mass, IR and NMR spectroscopic methods as shown in Table I. The production of IVa and Va may be rationalized in terms of transient formation of the sillicon—carbon double-bonded intermediate (A) followed by reaction with methanol as shown in Scheme I. Interestingly, no product that might be expected from 1,2-addition of methanol to the intermediate (A) could be observed at all. We believe that steric approach control is the most important in this addition reaction. Approach of a methanol molecule to the silicon—carbon "double" bond from the *cis* side with respect to the trimethylsilyl group must experience significant steric interaction with this group and therefore an attack from the *trans* side would be favored (Fig. 1). Furthermore, examination of molecular models shows that the formation of *cis*-5,6-disilyl-1,3-cyclohexadiene (VI) which might be expected from

TABLE 1

PROTON NMR, MASS AND IR SPECTRAL DATA FOR COMPOUNDS IV AND V

Compound	Chemical shifts (δ, ppm) in CCl_4	M^+	C=C (cm^{-1})
IVa	—0.02 (CH_3—$SiMe_2$, s, 9H), 0.15 (CH_3—SiMeOMe, s, 6H), 1.73 (CH_3—C=C, broad s, 3H), 1.7—2.0 (H—$CSiMe_3$, m, 1H), 2.3—2.7 (H_2C, m, 2H), 3.34 (CH_3—O, s, 3H), 5.59 (H—C=CMe, m, 1H), 6.09 (H—C=CSiOMe, d, 1H, *J* 4.7Hz)	254	1643
IVb	—0.04 (CH_3—$SiMe_2$, s, 9H), 0.12 (CH_3—SiMeOMe, s, 6H), 1.74 (CH_3—C=C, broad s, 3H), 1.8—2.0 (H—$CSiMe_3$, m, 1H), 2.2—2.5 (H—CD, m, 1H), 3.34 (CH_3—O, s, 3H), 5.60 (H—C=CMe, m, 1H), 6.10 (H—C=CSiOMe, broad d, 1H, *J* 4.9Hz)	255	1643
Va	—0.01 (CH_3—$SiMe_2$, s, 9H), 0.12 (CH_3—SiMeOMe, s, 3H), 0.16 (CH_3—SiMeOMe, s, 3H), 1.69 (CH_3—C=C, broad s, 3H), 2.47 (H—$CSiMe_3$, m, 1H), 2.53 (H_2C, m, 2H), 3.34 (CH_3—O, s, 3H), 5.42 (H—C=CMe, m, 1H), 5.97 (H—C=CSiOMe, t, 1H, *J* 7Hz)	254	1600
Vb	—0.01 (CH_3—$SiMe_2$, s, 9H), 0.12 (CH_3—SiMeOMe, s, 3H), 0.16 (CH_3—SiMeOMe, s, 3H), 1.67 (CH_3—C=C, broad s, 3H), 2.44 (H—$CSiMe_3$, m, 1H), 2.54 (H—CD, m, 1H), 3.32 (CH_3—O, s, 3H), 5.41 (H—C=CMe, m, 1H), 5.96 (H—C=CSiOMe, m, 1H)	255	1599

SCHEME 1



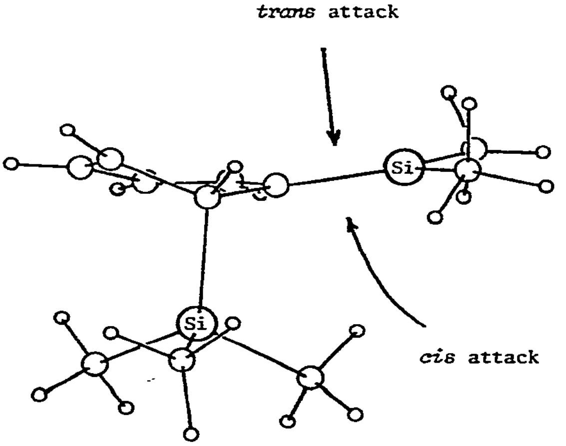


Fig. 1. A schematic representation of *cis* and *trans* attack of a methanol molecule on the silicon—carbon double-bonded intermediate (A).

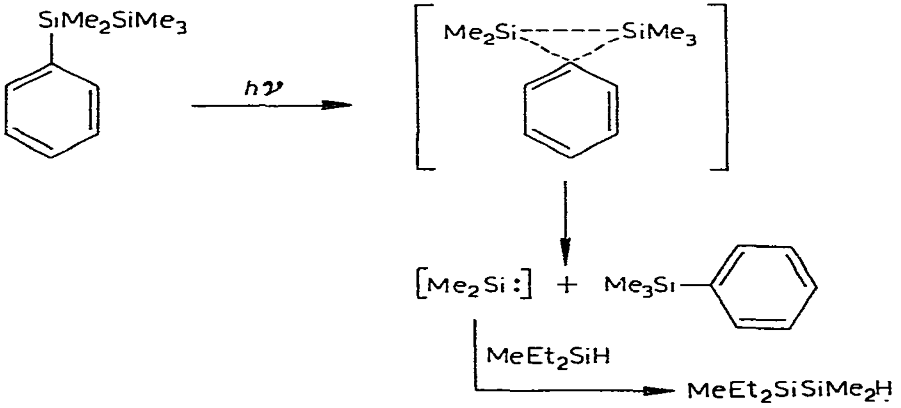
the *trans* attack is sterically very unfavorable. On the other hand, there is no such steric interaction when the addition of methanol takes place, as actually observed, in a 1,4- and a 1,6-fashion to give IVa and Va, respectively.

In order to obtain further information concerning the production of IVa and Va, I was photolyzed in the presence of methanol-d_1 in benzene solution under the same conditions. Compounds IVb and Vb were obtained in 26.5 and 26.8% yield, respectively, together with compounds II (1.2%) and III (3.7%). The mass and NMR spectral data of IVb and Vb are shown in Table 1. The proton decoupled NMR spectra of IVb and Vb were fully consistent with the proposed structures. Irradiation of the multiplet signal at δ (ppm) 5.60 in IVb changed the broad doublet at δ 6.10 into a singlet. Double irradiations of the δ 1.74 and 2.31 resonances changed the broad doublet at δ 6.10 and the multiplet at δ 5.60 into sharp doublets. Similarly, irradiation of the δ 2.54 resonance in Vb caused the multiplet at δ 5.96 to collapse to a singlet. Double irradiations of the δ 1.67 and 2.44 resonances changed the multiplet at δ 5.41 into a singlet.

The isotopic purity for IVb and Vb was found to be 98 and 96% respectively. However, in the case of III, its isotopic purity was determined to be 58%, indicating that 2.1% yield of p-$CH_3C_6H_4Si(Me){=}CH_2$ (B) would be produced in this photolysis. This type of intermediate has been reported by Sommer et al. in the photolysis of pentaphenylmethyldisilane [5]. The formation of the unlabeled *p*-methoxydimethylsilyltoluene (IIIa) (1.6%) may be explained by solvolysis of photo-excited I.

The production of II is quite interesting since migration of the tolyl group should be involved with simultaneous formation of dimethylsilylene in the photolysis of I. To confirm this, pentamethylphenyldisilane was photolyzed in the presence of diethylmethylsilane as silylene-trapping agent under the same conditions. The expected silylene-insertion product, 1,1-diethyl-1,2,2-trimethyldisilane (0.8%) [6], and phenyltrimethylsilane (2.7%) were obtained, in addition to 7.6% of the starting disilane and polymeric substances arising from the silicon—carbon double-bonded intermediates.

The migration of the aryl group, but not methyl group, from one silicon atom to the other in aryldisilanes could be evidenced by the fact that the photolysis of 1-(*p*-tolyl)-1,2,2,2-tetramethyldisilane (VII) in benzene solution gave *p*-tolyltrimethylsilane in 3.1% yield as a sole volatile product, in addition to 2.2% of the unchanged starting disilane.



Experimental

Materials

Methanol was dried over magnesium methoxide and distilled from it just before use. *p*-Tolylpentamethyldisilane [2], 1-(*p*-tolyl)-1,2,2,2-tetramethyldisilane [2], phenylpentamethyldisilane [7] and diethylmethylsilane [9] were prepared as described in the literature.

Photolysis of p-tolylpentamethyldisilane (I) in the presence of methanol

A solution of 0.9950 g (4.47 mmol) of I and 10 ml (0.24 mol) of dry methanol in 110 ml of dry benzene was irradiated at ca. 0°C for 6 h with a low-pressure mercury lamp fitted with a Vycor filter, under bubbling purified nitrogen. Most of the benzene was distilled off, and the residue was distilled under reduced pressure to give a distillate boiling up to 180°C/1 torr. The yields (vide ante) of individual products contained in the distillate were determined by GLC using n-pentadecane as an internal standard. The individual products were isolated as a colorless liquid by preparative GLC which had a column containing 20% of methylsilicone polymer (3/8 in. × 20 ft.) on 60—80 mesh celite 545. Products II and IIIa were identified by comparison of their NMR and IR spectra with those of the authentic samples. The mass, IR and NMR data for IVa (Found: C, 61.75; H, 10.61. $C_{13}H_{26}OSi_2$ calcd.: C, 61.35; H, 10.30%) and Va (Found: C, 61.37; H, 10.56. $C_{13}H_{26}OSi_2$ calcd.: C, 61.35; H, 10.30%) are listed in Table 1.

Photolysis of I in the presence of methanol-d_1

A solution of 1.0058 g (4.52 mmol) of I and 10 ml (0.24 mol) of methanol-d_1 in benzene was irradiated for 6 h under the same conditions as above. The yields (based on unrecovered I) of the products, II, III, IVb and Vb and the isotopic purity for III, IVb and Vb determined by mass spectrometry have been described above.

Photolysis of phenylpentamethyldisilane in the presence of diethylmethylsilane

A solution of 0.9567 g (4.59 mmol) of phenylpentamethyldisilane and 10 g (0.098 mol) of diethylmethylsilane in 100 ml of dry benzene was irradiated for 10 h at 2537 Å with ice cooling. Analysis of the distillate from the reaction mixture showed the presence of 1,1-diethyl-1,2,2-trimethyldisilane (0.8%), phenyltrimethylsilane (2.7%) and the starting disilane (7.6%) which were identified by comparison of their GLC retention times with those of the authentic samples.

Photolysis of 1-(p-tolyl)-1,2,2,2-tetramethyldisilane (VII)

A solution of 0.9465 g (4.54 mmol) of VII in 130 ml of dry benzene was irradiated for 16 h at 2537 Å with ice cooling. The mixture was analysed by GLC, indicating the presence of *p*-tolyltrimethylsilane in 3.1% yield. The mixture was then distilled. Pure *p*-tolyltrimethylsilane [8] was isolated by preparative GLC; NMR (δ, ppm) CH_3—Si (0.26, s, 9H), CH_3—C (2.35, s, 3H), H—C—CSi (7.06, d, 2H, *J* 7.8 Hz), H—C—CCH_3 (7.34, d, 2H, *J* 7.8 Hz).

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