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PHOTOCHEMICALLY GENERATED SILICON-CARBON DOUBLE-BONDED INTERMEDIATES
XI. THE REACTION OF UNSATURATED SILICON COMPOUNDS WITH METHYLLITHIUM AND METHYLMAGNESIUM BROMIDE

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Summary

The silicon-carbon double-bonded intermediate generated photochemically from phenylpentamethyldisilane reacted with methyllithium and with methylmagnesium bromide to give a mixture of 1,2- and 1,3-bis(trimethylsilyl)benzene. Both the yield and the product ratio depended highly on the solvent used. Similar reactions with a silicon-carbon double-bonded intermediate from 1-phenyl-1-(pentamethyldisilanyl)ethene afforded 1-phenyl-1,2-bis(trimethylsilyl)ethene in good yields.

Introduction

Recently, it has been demonstrated that photolysis of organopolysilanes bearing a π-electron system such as an aryl or alkenyl group on a silicon atom affords a convenient route to the production of reactive silicon-carbon double-bonded intermediates in solution [1-6], and that the silicon-carbon double-bonded intermediates generated from aryldisilane derivatives react with many organic substrates to give novel adducts. In this paper we report the first examples of the reaction of silicon-carbon double-bonded intermediates derived from phenylpentamethyldisilane and 1-phenyl-1-(pentamethyldisilanyl)ethene with methyllithium and with methylmagnesium bromide.

Results and discussion

Photolysis of phenylpentamethyldisilane (I) in the presence of methyllithium with a low-pressure mercury lamp bearing a Vycor filter in diethyl

TABLE 1

PHOTOLYSIS OF PHENYLPENTAMETHYLDISILANE (I) IN THE PRESENCE OF Me-M

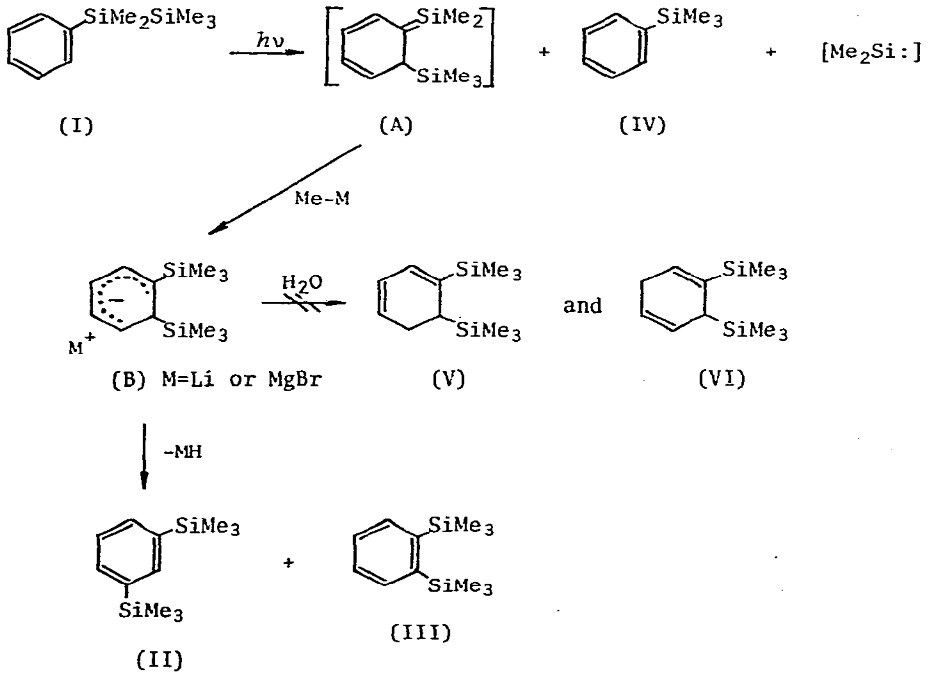
Disilane I	Me-M	Solvent	Time	Products(%)			Recovered
g(mmol)	2.3 mmol	20 ml	h	$PhSiMe_3$	1,3-isomer(II)	1,2-isomer(III)	I(%)
0.209(1.00)	MeLi	ether	7	8	60	2	9
0.211(1.01)	MeLi	THF	5	2	1	9	4
0.208(1.00)	MeLi	dioxane[a]	2	15	43	3	2
0.208(1.00)	MeMgBr	ether	6	10	12	14	3
0.208(1.00)	MeMgBr	THF	6	5	38	1	4
0.210(1.01)	MeMgBr	dioxane[b]	2.5	7	2	25	5

[a] Suspension of MeLi. [b] Suspension of MeMgBr.

ether, followed by hydrolysis, led to the formation of wholly unexpected compounds, 1,3-bis(trimethylsilyl)benzene (II) and 1,2-bis(trimethylsilyl)-benzene (III) in 60 and 2% yield, respectively, in addition to an 8% yield of phenyltrimethylsilane (IV) (Scheme 1). Surprisingly, no disilyl-substituted cyclohexadienes [7] such as (V) and (VI), that might be expected from addition of methyllithium to intermediate (A), followed by hydrolysis, were observed. It also was found that both the yield and the product ratio depended on the solvent used. Thus, irradiation of I with methyllithium in tetrahydrofuran (THF) under similar photolysis conditions, followed by treatment with water, afforded III and IV in 9 and 2% yield, along with 4% of unchanged I. In this photolysis, II was produced in ca. 1% yield. In dioxane, however, similar results to those in diethyl ether were obtained.

Photolysis of I in the presence of methylmagnesium bromide in THF gave II in 38% yield, in addition to a 2% yield of IV. In this case, a trace of III was observed. In diethyl ether, intermediate A reacted with methylmagnesium bromide to give II and III in 12 and 14% yield, respectivly, while in dioxane, II and III were formed in 2 and 25% yield, respectively. Reaction conditions and product yields are summarized in Table 1.

Scheme 1

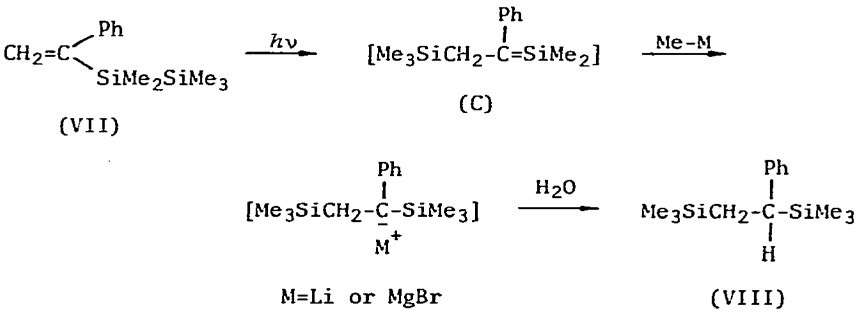


The structures of compounds II-IV are known and were confirmed by mass and ^1H NMR spectrometric analysis. The patterns in the aromatic region of the ^1H NMR spectra of II and III were identical with those reported by Seyferth and White [8]. The IR spectra of II and III were identical with those reported by Clark et al. [9]. In all photolyses, a trace of compound which has the same retention time as that of authentic 1,4-bis(trimethylsilyl)benzene was observed by GLC analysis (less than 1%).

In order to obtain further information concerning the production of II, compound III was photolyzed in the presence of methyllithium in diethyl ether under photolysis conditions similar to those above. No isomerization product II was detected by GLC analysis, with the starting compound III being recovered almost quantitatively after hydrolysis of the reaction mixture. This result indicates that the production of II must involve an anionic rearrangement of the trimethylsilyl group from the *ortho* to the *meta* carbon atom in the organometallic intermediate (B) prior to elimination of the metal hydride, while the metal hydride elimination from the initially formed addition product (B) would lead to the formation of III. The production of IV can be explained in terms of a photochemical 1,2-phenyl migration with simultaneous generation of dimethylsilylene during photolysis of I as reported previously [7,10].

The UV-irradiation of 1-phenyl-1-(pentamethyldisilanyl)ethene (VII) [3] with methyllithium in diethyl ether at 0°C afforded an orange solution. Treatment of the reaction mixture with water, followed by distillation, gave 1-phenyl-1,2-bis(trimethylsilyl)ethene (VIII) in 21% yield, together with 48% of unchanged VII. Similar photolysis of VII in the presence of methylmagnesium bromide, followed by hydrolysis afforded VIII in 36% yield, in addition to 40% of unchanged VII (Scheme 2). No silyl metal derivatives arising from inverse addition of the organometallic compounds to intermediate (C) were detected by spectroscopic analysis.

Scheme 2



The IR, mass and ^1H NMR data of compound VIII were identical with those of the authentic sample [11,12].

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Photolysis was performed using a 10-W low-pressure mercury lamp surrounded by a Vycor filter. Identification of the products by GLC was done by using two different columns (30% Silicone DC-550 on Celite 545 and 30% Apiezon grease on Celite 545).

Proton NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane as an internal standard. IR spectra of thin liquid films were determined using a Hitachi Model EPI-G3 grating spectrometer. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionizing voltage was 24 eV for all compounds. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products. Yields were determined by GLC using an internal standard on the basis of the disilanes used.

Methyllithium was prepared from the reaction of a fine cut lithium metal with methyl bromide in diethyl ether. Methylmagnesium bromide was prepared from methyl bromide and magnesium in diethyl ether.

Photolysis of phenylpentamethyldisilane (I) in the presence of methyllithium or methylmagnesium bromide

The following is typical of the procedures used. A mixture of 0.208 g (1.00 mmol) of phenylpentamethyldisilane (I) [13] and 2.0 ml (2.3 mmol) of methyllithium-ether solution was diluted with 20 ml of diethyl ether and irradiated for 7 h with ice cooling. After irradiation was stopped, the mixture was hydrolyzed with water. The solvent ether was evaporated and the residue was distilled under reduced pressure to give volatile products. GLC analysis of the distillate, using undecane as an internal standard, showed that II, III and IV were produced in 60, 2 and 8% yield, respectively, in addition to 9% of unchanged I. Pure II, III and IV were isolated by preparative GLC. For II: IR (cm^{-1}) 1580, 1405, 1370, 1270, 1255, 1145, 1110, 860, 840, 750, 690 and 620; mass spectrum m/e 222 (M^+); NMR (δ) 0.27 (Me_3Si, s, 18H) and 7.0-7.6 (ring protons, m, 4H). For III: IR (cm^{-1}) 1450, 1415, 1270, 1255, 1120, 1055, 1040, 860, 840, 755, 695, 685, 660 and 620; mass spectrum m/e 222 (M^+); NMR (δ) 0.37 (Me_3Si, s, 18H) and 7.1-7.7 (ring protons, AA'BB', 4H).

Photolysis of 1-phenyl-1-(pentamethyldisilanyl)ethene in the presence of methyllithium in diethyl ether

A solution of 0.240 g (1.02 mmol) of 1-phenyl-1-(pentamethyldisilanyl)ethene (VII) [3] and 2.3 mmol of methyllithium in 20 ml of diethyl ether was irradiated for 6 h with ice cooling. After hydrolysis of the photolysis mixture, the solvent was evaporated and the residue was distilled under reduced pressure. GLC analysis of the distillate showed that 21% yield of 1-phenyl-1,2-bis(trimethylsilyl)ethane (VIII) [11,12] was produced in addition to 48% of unchanged VII. Mass spectrum m/e 250 (M^+); NMR (δ) -0.22 (Me_3Si, s, 9H), -0.01 (Me_3Si, s, 9H), 0.78 ($CH(H)SiMe_3$, dd, 1H), 1.05 ($HC(H)SiMe_3$, dd, 1H), 2.03 (HCPh, dd, 1H) and 6.8-7.4 (ring protons, m, 5H).

Photolysis of VII in the presence of methylmagnesium bromide in diethyl ether

A diethyl ether solution (20 ml) of 0.235 g (1.00 mmol) of VII and 0.8 ml (2.3 mmol) of methylmagnesium bromide-ether solution was irradiated for 6 h with ice cooling. Work-up as above gave VIII in 36% yield, in addition to 40% of unchanged VII.

Attempted isomerization of 1,2-bis(trimethylsilyl)benzene to 1,3-isomer

In a carefully dried 5 ml quartz tube purged with dry nitrogen was placed a mixture of 5 mg of 1,2-bis(trimethylsilyl)benzene (III) and 0.1 mmol of methyllithium in 1 ml of diethyl ether. The mixture was irradiated externally with a low-pressure mercury lamp bearing a Vycor filter for 5 h. Analysis by GLC of the hydrolyzed reaction mixture indicated no production of the 1,3-isomer but a quantitative recovery of the starting compound III.

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