

Journal of Organometallic Chemistry, 201 (1980) 151–163
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

PHOTOLYSIS OF ORGANOPOLYSILANES. THE REACTION OF PHOTOCHEMICALLY GENERATED METHYLPHENYLSILYLENE WITH CONJUGATED DIENES *

ITSUO ISHIKAWA, KEN-ICHI NAKAGAWA, RYUICHI ENOKIDA and MAKOTO
KUMADA

*Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606
(Japan)*

(Received April 22nd, 1980)

Summary

Photolysis of 2-phenylheptamethyltrisilane (I) in the presence of acyclic and cyclic conjugated dienes has been investigated using both a high-pressure mercury lamp with a quartz filter and a low-pressure mercury lamp with a Vycor filter. Irradiation of I in the presence of 1,3-butadiene, isoprene or 2,3-dimethylbutadiene with a high-pressure mercury lamp gave a product arising from photochemical isomerization of a silacyclopropane derivative and a compound apparently formed by 1,4-silylene addition, along with a 1/1 "ene" adduct of the diene to a photo-rearranged intermediate containing the silicon—carbon double bond. Irradiation of I in the presence of the conjugated diene with a low-pressure mercury lamp, followed by treatment of the product with methanol, afforded a methoxysilane arising from methanolysis of the corresponding silacyclopropane, together with the isomerization product, silacyclopentene and rearranged addition product. Irradiation of I in the presence of cyclopentadiene with a high-pressure mercury lamp produced methylphenylsilylcyclopentadiene, while irradiation of a similar mixture with a low-pressure mercury lamp followed by treatment with methanol gave 4-(methoxymethylphenylsilyl)-1-cyclopentene. With 1,3-cyclooctadiene, the photochemically generated methylphenylsilylene afforded many types of addition product. Photolysis of I in the presence of 1,3-cyclohexadiene, however, afforded none of the silylene addition products.

* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

Introduction

There has been a considerable interest concerning the reaction of silylenes with conjugated dienes. In 1966 Atwell and Weyenberg first reported that thermally generated silylenes reacted with 1,3-butadienes to give silacyclopentenes [1]. Since that time, many papers dealing with the reaction of thermally generated silylene species with cyclic and acyclic conjugated dienes have been reported [2–5]. Most of the silylene reactions with 1,3-dienes are concerned with the formation of 1-silacyclopentene derivatives arising from rearrangement of initially formed 1,2-adducts, although the corresponding alkenylsilacyclopropanes have not been detected by either GLC technique or spectroscopic analysis.

In contrast to the thermally generated silylenes, photochemically generated methylphenylsilylene reacts with 2,3-dimethylbutadiene to give a 1,2-adduct which can be quenched by methanol, together with an apparent 1,4-adduct and a photoisomerization product arising from the 1,2-adduct [6]. Furthermore, trimethylsilylphenylsilylene generated from tris(trimethylsilyl)phenylsilane upon irradiation with a low-pressure mercury lamp adds to 1,3-cyclooctadiene to give the 1,2-adducts as the sole addition product, which can readily be transformed into *syn*- and *anti*-9-phenyl-9-trimethylsilyl-9-silabicyclo[4.2.1]-non-7-ene by irradiating with a high-pressure mercury lamp [7]. In order to learn more about the chemical behaviour of the photochemically generated silylenes, we have investigated the photolysis of 2-phenylheptamethyltrisilane in the presence of a variety of dienes.

Results and discussion

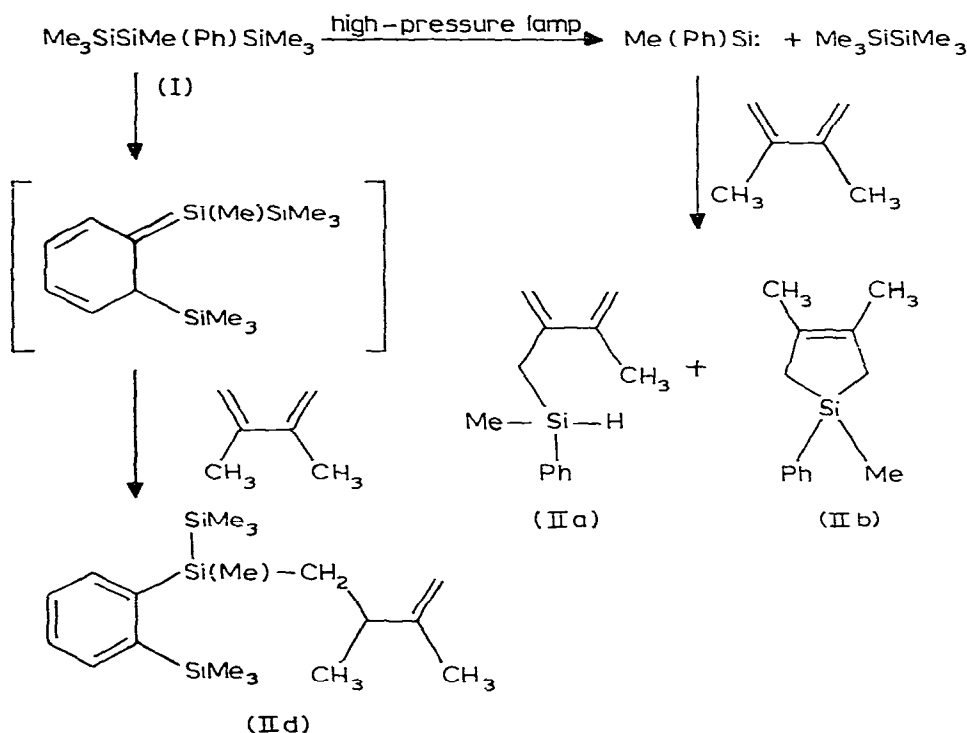
Photolysis of 2-phenylheptamethyltrisilane (I) in the presence of 1,3-butadiene derivatives

We have found that when a hexane solution of 2-phenylheptamethyltrisilane (I) in the presence of 2,3-dimethylbutadiene, isoprene or 1,3-butadiene was photolyzed by irradiating with a high-pressure mercury lamp having a quartz filter, the respective methylphenylsilyl-substituted butadiene was produced, together with a 1-silacyclopentene derivative. On the other hand, similar photolysis of I with a low-pressure mercury lamp bearing a Vycor filter gave an alkenylsilacyclopropane which could be quenched by methanol as the methoxysilane, in addition to the silyl-substituted butadiene and the silacyclopentene.

Noteworthy, photolysis of I with either a high-pressure or low-pressure mercury lamp involves the formation of another type of intermediate as well, viz., a silicon—carbon double-bonded intermediate arising from rearrangement of a trimethylsilyl group onto an *ortho* carbon atom in the phenyl ring [8,9]. This intermediate reacts with the conjugated diene to give a 1/1 addition product (hereafter called a rearranged addition product).

Thus, irradiation of a hexane solution of I in the presence of 2,3-dimethylbutadiene with a high-pressure mercury lamp afforded 2-(methylphenylsilylmethyl)-3-methyl-1,3-butadiene (IIa) and 1,3,4-trimethyl-1-phenyl-1-silacyclopentene (IIb) in 11 and 18% yield, respectively. In addition, a rearranged addi-

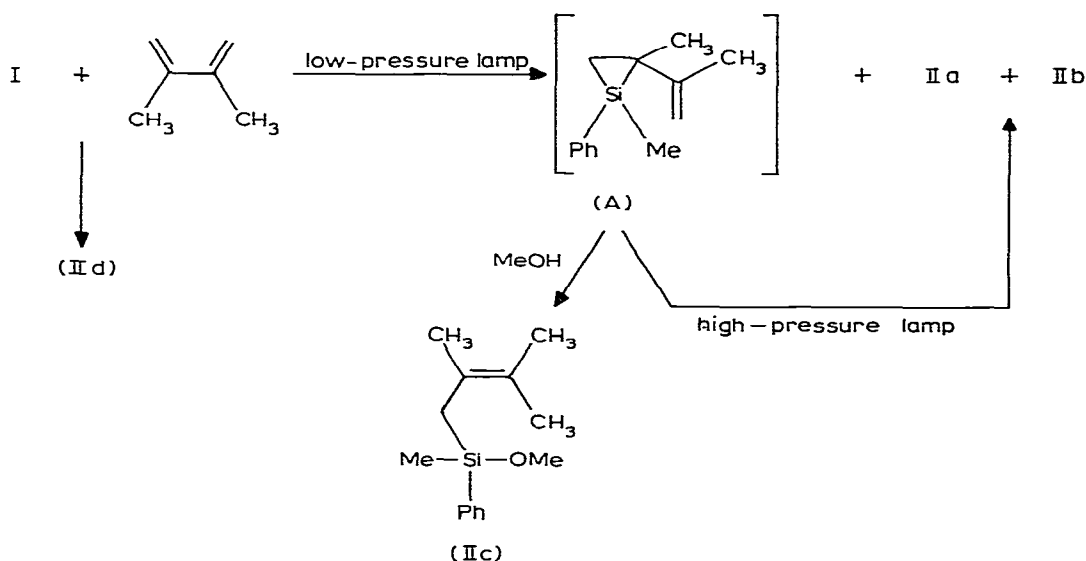
SCHEME 1



tion product (II d) from I and 2,3-dimethylbutadiene was obtained in 16% yield (Scheme 1). In a previous communication [6], we reported the rearranged addition product to be 4-trimethylsilyl-4-(1'-phenyltetramethyldisilanyl)-2,3-dimethylbutadiene. This has turned out to be an erroneous structural assignment. The IR, mass and ^1H NMR spectra of the adduct showed that it must be the disubstituted benzene (II d). The proton-decoupled NMR spectrum of II d showed the presence of two kinds of diastereoisomers in the ratio of approximately 2/1.

Recently, we have demonstrated that irradiation of a hexane solution of I in the presence of an olefin with a low-pressure mercury lamp produces a silacyclop propane in the solution [8]. In the hope of obtaining an alkenyl-substituted silacyclop propane we have studied the photolysis using a low-pressure mercury lamp bearing a Vycor filter. Thus, a solution of I in the presence of 2,3-dimethylbutadiene was photolyzed and a small aliquot taken from the resulting photolysis mixture was treated with methanol. GLC analysis showed that 2-(methoxymethylphenylsilylmethyl)-3-methyl-2-butene (II c) was produced in 10% yield, in addition to II a (8% yield), II b (13% yield) and II d (25% yield) (Scheme 2). Comparison of this result with that obtained from the high-pressure lamp system reveals that the total amounts of the products arising from addition of the silylene to 2,3-dimethylbutadiene are roughly the same in both cases. Irradiation of the above solution involving the intermediate alkenyl-silacyclop propane (A) with a high-pressure mercury lamp led to transformation of A into II a and II b. In this photolysis, II a and II b were obtained in 25 and 32%

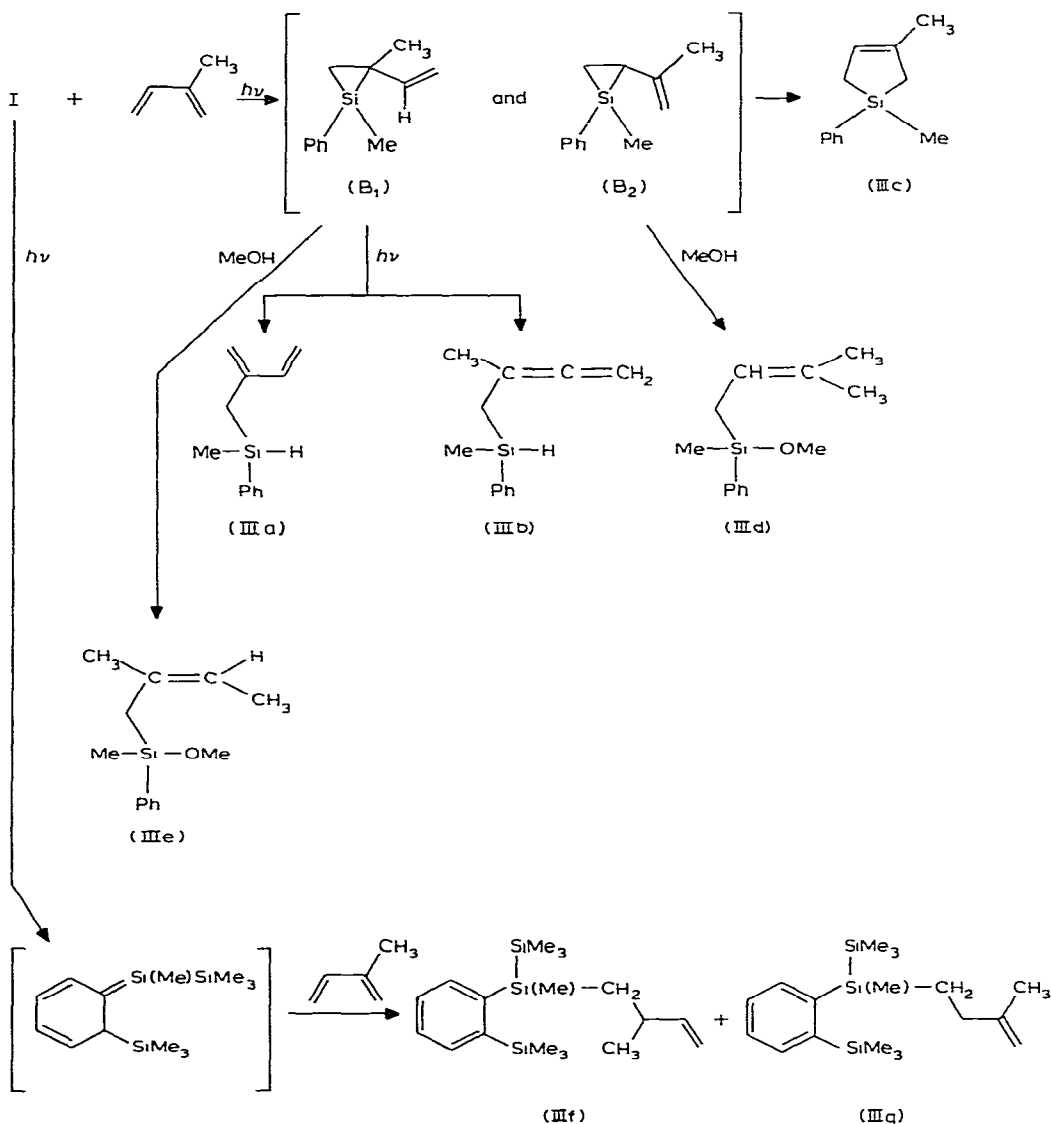
SCHEME 2



yield, respectively, based on silacyclopentane A. The result obtained from low temperature photolysis proved that the isomerization of A to IIa and IIb occurred by a photochemical process. Thus, a mixture of I and 2,3-dimethylbutadiene in hexane was irradiated at -70°C and the resulting mixture was treated with methanol at the same temperature. GLC analysis showed that IIa and IIb were produced in 7 and 12% yield (based on the starting I), respectively, in addition to IIc and II d.

Photolysis of a hexane solution of I in the presence of isoprene by irradiating with a high-pressure mercury lamp afforded 2-(methylphenylsilylmethyl)-1,3-butadiene (IIIa) and 3-methyl-4-(methylphenylsilyl)-1,2-butadiene (IIIb) in a 5% combined yield, along with 1,3-dimethyl-1-phenyl-1-silacyclopentene (IIIc) (23% yield) and two rearranged addition products (III f and III g) in 15 and 4% yield, respectively (Scheme 3). The fact that the addition of methanol to the photolysis mixture after stopping irradiation produced no methanolysis products indicates the absence of alkenylsilacyclopentanes (B) in the solution. Irradiation of a similar mixture of I with a low-pressure mercury lamp bearing a Vycor filter, followed by treatment with dry methanol after the cessation of irradiation, produced 1-(methoxymethylphenylsilyl)-3-methyl-2-butene (III d) and 1-(methoxymethylphenylsilyl)-2-methyl-2-butene (III e) in 10 and 3% yield, respectively, in addition to IIIa (1% yield), IIIb (1% yield), IIIc (10% yield), III f (19% yield) and III g (7% yield). The formation of IIIa can be accounted for by the photochemical rearrangement of a silacyclopentane (B_1), involving a 1,3-hydrogen shift from the methyl group to the silicon atom, while IIIb can be explained in terms of a 1,3-hydrogen shift from the vinyl group in B_1 . All compounds produced, excepting IIIa and IIIb, could easily be separated by preparative GLC. Attempts to isolate IIIa and IIIb in a pure form by preparative GLC were unsuccessful. All columns which were used never gave effective separation of these two compounds. However, the structures of IIIa and IIIb were

SCHEME 3



determined by ^1H NMR, IR and mass spectrometric analysis of the mixture.

Similar photolysis of I in the presence of 1,3-butadiene with a high-pressure mercury lamp afforded 4-(methylphenylsilyl)-1,2-butadiene (IVa), 1-methyl-1-phenyl-1-silacyclopentene (IVb) and a rearranged addition product (IVe) in 6, 22 and 8% yield, respectively. Irradiation of a mixture of I and 1,3-butadiene in hexane with a low-pressure mercury lamp, followed by methanolysis, produced 4-(methoxymethylphenylsilyl)-1-butene (IVc) and 1-(methoxymethylphenylsilyl)-2-butene (IVd) in 1 and 4% yield, respectively, in addition to IVa (5% yield), IVb (16% yield) and IVe (12% yield).

Photolysis conditions and product yields are summarized in Table 1. The ^1H

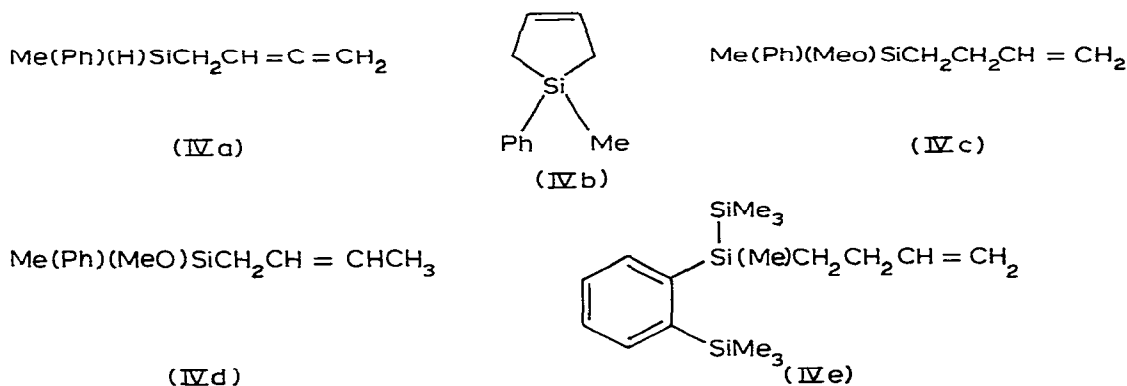
TABLE 1

PHOTOLYSIS OF 2-PHENYLHEPTAMETHYLTRISILANE (I) IN THE PRESENCE OF DIENE IN HEXANE ^a

I (g (mmol))	Diene (mmol)	Time (h)	Product and yield (%)
1.0576 (3.97)	2,3-dimethyl- butadiene(30)	3.5 ^b	IIa(11), IIb(18), IIc(trace), IIId(16)
1.1242 (4.22)	2,3-dimethyl- butadiene(30)	3.5 ^c	IIa(8), IIb(13), IIc(10), IIId(25)
1.0176 (3.82)	isoprene (30)	2.5 ^b	IIIa and IIIb(5) ^d , IIIc(23) IIId(0), IIIf(15), IIIf(4)
1.0630 (3.99)	isoprene (30)	3.0 ^c	IIIa and IIIb(2), IIIc(10), IIId and IIIf(13) ^e , IIIf(19), IIIf(7)
1.0178 (3.82)	1,3-butadiene (5) ^f	2.0 ^b	IVa(6), IVb(22), IVc(0), IVd(0), IVe(8)
1.0629 (3.99)	1,3-butadiene (5) ^f	3.5 ^c	IVa(5), IVb(16), IVc(4), IVd(1), IVe(12)
1.0210 (3.84)	cyclopentadiene (7.6)	3.5 ^b	Va(3), Vb(8), Vc(2)
0.3165 (1.19)	cyclopentadiene (7.6)	2.0 ^c	Va(trace), Vb(11), Vc(19)
1.1615 (4.36)	1,3-cycloocta- diene(20)	5.0 ^b	VIa(3), VIb(7), VIc(4), VIIf(trace) VIf(6), VIf(1), VIf(22)
1.0626 (3.99)	1,3-cycloocta- diene(20)	4.0 ^c	VIa(trace), VIb(1), VIc(trace), VId(3), VIf(9), VIf(3), VIf(21)

^a After irradiation was stopped 1–2 ml of dry methanol were added to the mixture. ^b High-pressure mercury lamp. ^c Low-pressure mercury lamp. ^d The ratio of IIIa/IIIb is 1.3. ^e The ratio of IIId/IIIf is 3. ^f M1.

NMR, analytical, mass spectral and IR data for the isolated compounds are shown in Tables 2 and 3.



Photolysis of I in the presence of cyclic conjugated dienes

Gaspar et al. [10] reported that thermally generated dimethylsilylene added to cyclopentadiene to give 1,1-dimethyl-1-sila-2,4- and -2,5-cyclohexadiene, while the addition to 1,3-cyclohexadiene gave 1-dimethylvinylsilyl-1,3-butadiene and 7,7-dimethyl-7-silanorbornene. We have now found that the reaction of photochemically generated methylphenylsilylene with these two substrates

TABLE 2

PROTON NMR CHEMICAL SHIFTS FOR ISOLATED COMPOUNDS

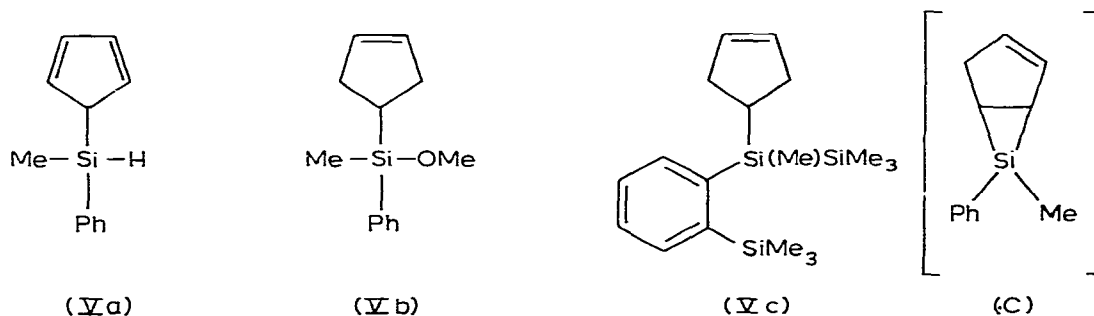
Compound	Chemical shifts (δ , ppm) in CCl_4
IIa	0.30 ($\text{CH}_3\text{—Si}$, d, 3 H, $J = 4$ Hz), 1.89 ($\text{CH}_3\text{—C}$, s, 3 H), 2.01 ($\text{CH}_2\text{—Si}$, double d, 2 H, $J = 4$ Hz), 4.36 (H—Si , m, 1 H), 4.76, 4.92, 4.95, 5.01 ($\text{CH}_2=\text{C}$, broad s, 4 H), 7.16–7.48 (ring protons, m, 5 H)
IIb	0.40 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.53 ($\text{CH}_2\text{—Si}$, broad s, 4 H), 1.72 ($\text{CH}_3\text{—C}$, broad s, 6 H), 7.51–7.95 (ring protons, m, 5 H)
IIc	0.34 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.50 ($\text{CH}_3\text{—C}$, broad s, 3 H), 1.60 ($\text{CH}_3\text{—C}$, broad s, 6 H), 1.77 ($\text{CH}_2\text{—Si}$, broad s, 2 H), 3.41 ($\text{CH}_3\text{—O}$, s, 3 H), 7.17–7.51 (ring protons, m, 5 H)
IId	Abundant isomer: 0.09 ($\text{CH}_3\text{—Si}$, s), 0.35 ($\text{CH}_3\text{Si—Si}$, s), 0.53 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s), 0.87 ($\text{CH}_3\text{—CH}$, $J = 6.8$ Hz), 1.04 ($\text{CH}_2\text{—Si}$, $J = 6.6$ Hz), 1.63 ($\text{CH}_3\text{—C}$, s), 2.31 (HC—CH_3 , m), 4.53 ($\text{CH}_2=\text{C}$, s), 7.05–7.60 (ring protons, m); other isomer: 0.06 ($\text{CH}_3\text{—Si}$, s), 0.35 ($\text{CH}_3\text{Si—Si}$, s), 0.53 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s), 0.83 ($\text{CH}_3\text{—CH}$, $J = 6.8$ Hz), 1.15 ($\text{CH}_2\text{—CH}$, $J = 5.3$ Hz), 1.63 ($\text{CH}_3\text{—C}$, s), 2.31 (CH—CH_3 , m), 4.60 ($\text{CH}_2=\text{C}$, s), 7.05–7.60 (ring protons, m)
IIIa	0.38 ($\text{CH}_3\text{—Si}$, d, 3 H, $J = 4$ Hz), 1.88–2.00 ($\text{CH}_2\text{—Si}$, m, 2 H), 4.75–5.25 ($\text{CH}_2=\text{C}$, m, 2 H), 6.15–6.45 (CH(C)=C , m, 1 H), 7.22–7.52 (ring protons, m, 5 H)
IIIb	0.33 ($\text{CH}_3\text{—Si}$, d, 3 H, $J = 4$ Hz), 1.55–1.70 ($\text{CH}_2\text{—Si}$ and $\text{CH}_3\text{—C=C}$, m, 5 H), 4.33–4.52 (H—Si and $\text{CH}_2=\text{C}$, m, 3 H), 7.22–7.52 (ring protons, m, 5 H)
IIIc	0.35 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.50 ($\text{CH}_2\text{—Si}$, broad s, 4 H), 1.82 ($\text{CH}_3\text{—C}$, broad s, 3 H), 5.50 (CH=C , broad s, 1 H), 7.16–7.52 (ring protons, m, 5 H)
IIId	0.31 ($\text{CH}_3\text{—Si}$, s, 3 H), 15.1 ($\text{CH}_3\text{—C}$, broad s, 3 H), 1.68 ($\text{CH}_3\text{—C}$, broad s, 3 H), 1.45–1.78 ($\text{CH}_2\text{—Si}$, double d, 2 H), 3.42 ($\text{CH}_3\text{—O}$, s, 3 H), 5.08 (CH=C , m, 1 H), 7.22–7.54 (ring protons, m, 5 H)
IIIe	0.35 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.40–1.80 ($\text{CH}_3\text{—C}$ and $\text{CH}_2\text{—Si}$, m, 8 H), 3.42 ($\text{CH}_3\text{—O}$, s, 3 H), 5.05 (CH=C , m, 1 H), 7.25–7.56 (ring protons, n, 5 H)
IIIf	0.08 ($\text{CH}_3\text{Si—Si}$, s, 9 H), 0.35 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s, 9 H), 0.55 ($\text{CH}_3\text{—Si}$, s, 3 H), 0.95 ($\text{CH}_3\text{—C}$, d, 3 H, $J = 7$ Hz), 0.86–1.17 ($\text{CH}_2\text{—Si}$, m, 2 H), 2.28 (CH—C , m, 1 H), 4.77 ($\text{CH}_2=\text{C}$, m, 2 H), 5.58 (CH=C , m, 1 H), 7.06–7.60 (ring protons, m, 4 H)
IIIg	(0.10 ($\text{CH}_3\text{Si—Si}$, s, 9 H), 0.35 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s, 9 H), 0.50 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.13 ($\text{CH}_2\text{—Si}$, m, 2 H), 1.71 ($\text{CH}_3\text{—C}$, broad s, 3 H), 1.93 ($\text{CH}_2\text{—C}$, m, 2 H), 4.60 ($\text{CH}_2=\text{C}$, broad s, 2 H), 7.10–7.60 (ring protons, m, 5 H)
IVa	0.28 ($\text{CH}_3\text{—Si}$, d, 3 H, $J = 4$ Hz), 1.38–1.62 ($\text{CH}_2\text{—Si}$, m, 2 H), 4.38 (H—Si , m, 1 H), 4.56 ($\text{CH}_2=\text{C}$, m, 2 H), 4.98 (CH=C , m, 1 H), 7.20–7.57 (ring protons, m, 5 H)
IVb	0.33 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.53 ($\text{CH}_2\text{—Si}$, broad s, 4 H), 5.88 (CH=C , broad, s, 2 H), 7.10–7.56 (ring protons, m, 5 H)
IVc	0.35 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.61 ($\text{CH}_2\text{—Si}$, m, 2 H), 2.11 ($\text{CH}_2\text{—C}$, m, 2 H), 3.42 ($\text{CH}_3\text{—O}$, s, 3 H), 4.73–5.03 ($\text{CH}_2=\text{C}$, m, 2 H, $J_{\text{trans}} = 17$ Hz, $J_{\text{cis}} = 11$ Hz), 5.51–6.02 (CH=C , m, 1 H), 7.20–7.57 (ring protons, m, 5 H)
IVd	0.33 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.48 ($\text{CH}_3\text{—C}$, broad d, 3 H, $J = 4$ Hz), 1.75 ($\text{CH}_2\text{—Si}$, m, 2 H), 3.45 ($\text{CH}_3\text{—O}$, s, 3 H), 5.38 (CH=CH , m, 2 H), 7.22–7.60 (ring protons, m, 5 H)
IVe	0.09 ($\text{CH}_3\text{Si—Si}$, s, 9 H), 0.36 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s, 9 H), 0.50 ($\text{CH}_3\text{—Si}$, s, 3 H), 0.74–1.30 ($\text{CH}_2\text{—Si}$, m, 2 H), 2.01 ($\text{CH}_2\text{—C}$, m, 2 H), 4.74–5.04 ($\text{CH}_2=\text{C}$, m, 2 H), 5.57–5.93 (CH=C , m, 1 H), 7.07–7.60 (ring protons, m, 4 H)
Va	0.12 ($\text{CH}_3\text{—Si}$, d, 3 H, $J = 4$ Hz), 3.02 (CH—Si , broad s; 1 H), 4.18 (H—Si , m, 1 H), 6.55 (cyclopentadienyl ring protons, m, 4 H), 7.20–7.55 (phenyl ring protons, m, 5 H)
Vb	0.30 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.50 (CH—Si , m, 1 H), 2.40 (ring CH_2 , m, 4 H), 3.43 ($\text{CH}_3\text{—O}$, s, 3 H), 5.66 (vinyl protons, s, 2 H), 7.20–7.55 (phenyl ring protons, m, 5 H)
Vc	(0.07 ($\text{CH}_3\text{Si—Si}$, s, 9 H), 0.35 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s, 9 H), 0.43 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.35–2.65 (cyclopentenyl ring protons, m, 5 H), 5.68 (vinyl protons, s, 2 H), 7.10–7.65 (phenyl ring protons, m, 5 H)
Vib	0.12 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.41 ($\text{CH}_2\text{—C—Si}$, m, 4 H), 1.73 ($\text{CH}_2\text{—C—Si}$, m, 4 H), 1.93 (CH—Si , m, 2 H), 6.00 (vinyl protons, d, 2 H, $J = 4$ Hz), 7.12–7.52 (phenyl ring protons, m, 5 H)
Vic	0.57 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.60–1.95 ($\text{CH}_2\text{CH}_2\text{CH—Si}$, m, 10 H), 5.99 (vinyl protons, d, 2 H, $J = 4$ Hz), 7.10–7.45 (phenyl ring protons, m, 5 H)
VId	0.43 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.56 (methylene protons, m, 4 H), 2.27 (allyl protons, m, 4 H), 5.70 (CH(=C)—Si , d, 2 H, $J = 14$ Hz), 6.58 (CH=C , double t, 2 H, $J = 14$ Hz and $J = 7$ Hz), 7.13–7.59 (phenyl ring protons, m, 5 H)

TABLE 2 (continued)

Compound	Chemical shifts (δ , ppm) in CCl_4
Vle	0.35 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.44 (methylene protons, m, 7 H), 2.10 (allyl protons, m, 4 H), 3.42 ($\text{CH}_3\text{—O}$, s, 3 H), 5.48 (vinyl protons, m, 2 H), 7.15—7.53 (phenyl ring protons, m, 5 H)
Vlf	0.37 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.57 (methylene protons, m, 8 H), 2.10 (allyl protons, m, 3 H), 3.45 ($\text{CH}_3\text{—O}$, s, 3 H), 5.20—5.70 (vinyl protons, m, 2 H), 7.25—7.55 (phenyl ring protons, m, 5 H)
Vlg	0.09 ($\text{CH}_3\text{Si—Si}$, s, 9 H), 0.36 ($\text{CH}_3\text{—SiC}_6\text{H}_4$, s, 9 H), 0.51 ($\text{CH}_3\text{—Si}$, s, 3 H), 1.50 (methylene protons, m, 7 H), 2.12 (allyl protons, m, 4 H), 5.52 (vinyl protons, m, 2 H), 7.05—7.70 (phenyl ring protons, m, 5 H).

proceeded in a different fashion. Thus, photolysis of a hexane solution of I in the presence of cyclopentadiene with a high-pressure mercury lamp gave methylphenylsilylcyclopentadiene (Va) and a rearranged addition product (Vc) in 3 and 2% yield, respectively, in addition to trace amounts of unidentified products (less than a 2% combined yield). In this case, treatment of the photolysis mixture with methanol produced 4-(methoxymethylphenylsilyl)-1-cyclopentene (Vb) in 8% yield. This result suggests that the rate of photoisomerization of a silacyclopropane (C) to Va is slow. Indeed, similar photolysis of I by irradiating with a low-pressure mercury lamp followed by treatment with methanol afforded Vb and Vc in 11 and 19% yield, together with a trace of Va. No other products were observed by analytical GLC.

Photolysis of I in the presence of 1,3-cyclohexadiene with either a high-pressure or low-pressure mercury lamp did not afford any silylene addition



products or rearranged addition product. Large amounts of white precipitates arising from polymerization of 1,3-cyclohexadiene were produced.

Irradiation of I with 1,3-cyclooctadiene, however, gave many types of silylene insertion product. Thus, irradiation of I in the presence of 1,3-cyclooctadiene with a high-pressure mercury lamp at room temperature followed by addition of methanol to the photolysis mixture after stopping irradiation gave six compounds: 3-methylphenylsilyl-1,4-cyclooctadiene (VIa), *syn* and *anti*-9-methyl-9-phenyl-9-silabicyclo[4.2.1]non-7-ene (VIb and VIc), 4-(methoxymethylphenylsilyl)-1-cyclooctene (Vle), 3-(methoxymethylphenylsilyl)-1-cyclooctene (Vlf) and a rearranged addition product (Vlg), in 3, 7, 4, 6, 1 and 22% yield, respectively, as shown in Scheme 4. When a low-pressure mercury

TABLE 3
ELEMENTAL ANALYSIS, MASS AND IR DATA FOR ISOLATED COMPOUNDS

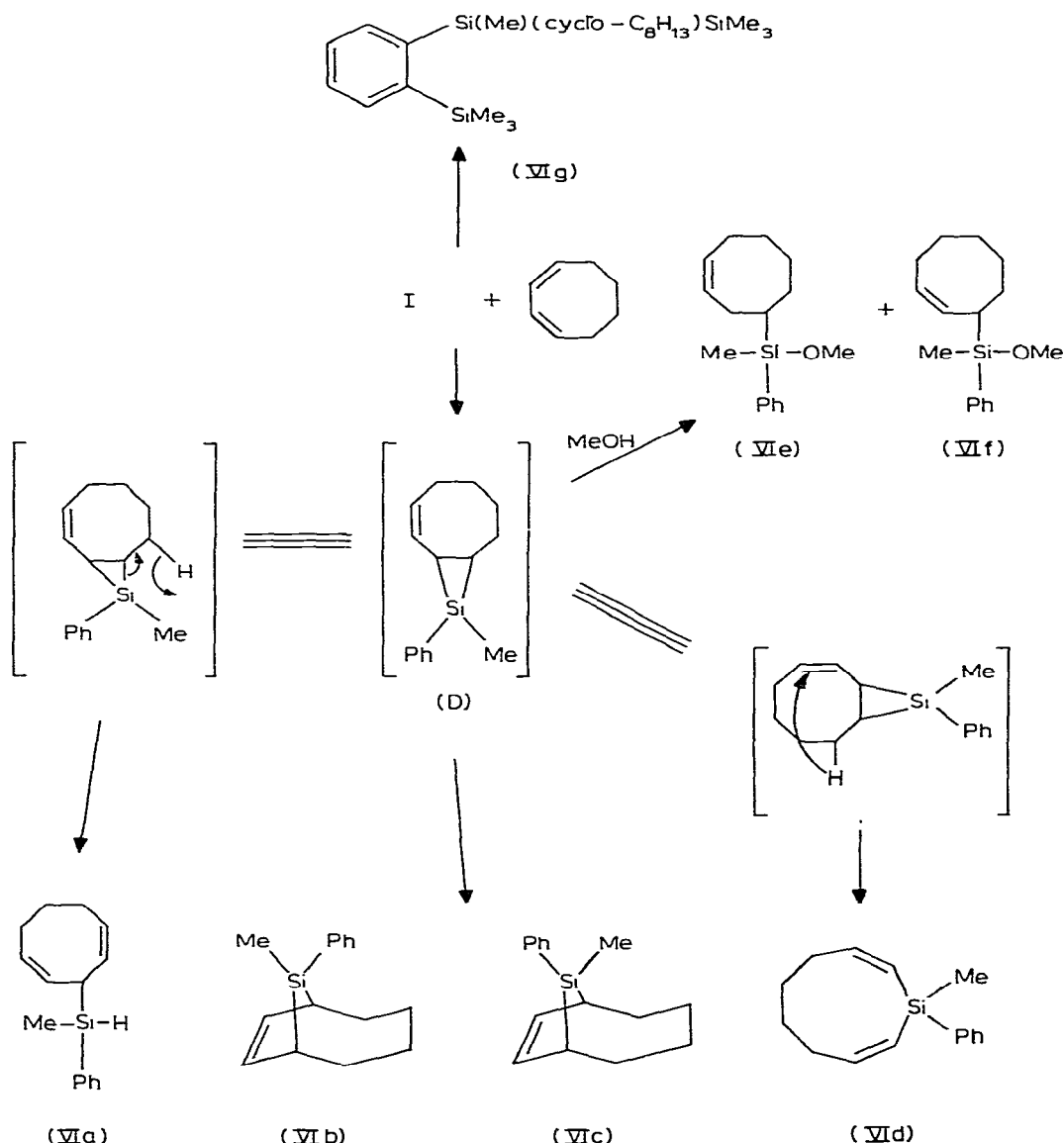
Compound		Found (calcd.) (%)		IR (neat) M^+ (cm^{-1})	M^+	Exact mass (calcd.)
		C	H			
IIa	$\text{C}_{13}\text{H}_{18}\text{Si}$	—	—	2120		202.1184 (202.1178)
IIb	$\text{C}_{13}\text{H}_{18}\text{Si}$	—	—	1650		202.1177 (202.1178)
IIc	$\text{C}_{14}\text{H}_{22}\text{OSi}$	—	—	1090		234.1442 (234.1440)
IIId	$\text{C}_{19}\text{H}_{36}\text{Si}$	65.39(65.44)	10.31(10.40)	1645	348	188.1015 (188.1021)
IIIa, IIIb	$\text{C}_{12}\text{H}_{16}\text{Si}^a$	—	—	2120, 1955		188.1009 (188.1021)
IIIc	$\text{C}_{12}\text{H}_{16}\text{Si}$	76.52(76.52)	8.58(8.56)	1640		188.1009 (188.1021)
IIId	$\text{C}_{13}\text{H}_{20}\text{OSi}$	—	—	1080		220.1279 (220.1284)
IIIe	$\text{C}_{13}\text{H}_{20}\text{OSi}$	—	—	1090		220.1281 (220.1284)
IIIIf	$\text{C}_{18}\text{H}_{34}\text{Si}_3$	64.74(64.59)	10.28(10.24)	1640		334.1970 (334.1968)
IIIg	$\text{C}_{18}\text{H}_{34}\text{Si}_3$	64.89(64.59)	10.29(10.24)	1650	334	
IVa	$\text{C}_{11}\text{H}_{14}\text{Si}$	—	—	2125, 1955		174.0834 (174.0865)
IVb	$\text{C}_{11}\text{H}_{14}\text{Si}$	75.56(75.79)	8.13(8.10)	1610		174.0829 (174.0865)
IVc	$\text{C}_{12}\text{H}_{18}\text{OSi}$	—	—	1640, 1090		206.1122 (206.1156)
IVd	$\text{C}_{12}\text{H}_{18}\text{OSi}$	69.89(69.85)	9.03(8.79)	1650, 1090		206.1156 (206.1127)
IVe	$\text{C}_{17}\text{H}_{32}\text{Si}_3$	—	—	1635		320.1822 (320.1812)
Va	$\text{C}_{12}\text{H}_{14}\text{Si}$	—	—	2120		186.0866 (186.0865)
Vb	$\text{C}_{13}\text{H}_{18}\text{OSi}$	—	—	1620, 1085		332.1837 (332.1812)
VIa	$\text{C}_{15}\text{H}_{20}\text{Si}$	—	—	2120		228.1343 (228.1334)
VIb	$\text{C}_{15}\text{H}_{20}\text{Si}$	78.75(78.88)	8.95(8.83)	1595		228.1326 (228.1334)
VIc	$\text{C}_{15}\text{H}_{20}\text{Si}$	78.83(78.88)	9.07(8.83)	1590		228.1340 (228.1334)
VIId	$\text{C}_{15}\text{H}_{20}\text{Si}$	—	—	1600		228.1330 (228.1334)
VIe	$\text{C}_{16}\text{H}_{24}\text{OSi}$	73.67(73.79)	9.52(9.29)	1080		260.1601 (260.1597)
VIf	$\text{C}_{16}\text{H}_{24}\text{OSi}$	—	—	1080		260.1592 (260.1597)
VIg	$\text{C}_{21}\text{H}_{38}\text{Si}_3$	—	—	—		374.2270 (374.2281)

^a A mixture of IIIa and IIIb.

lamp was used for photolysis of the same solution as above, 1-methyl-1-phenyl-1-silacyclonona-2,8-diene (VIId) was obtained in 3% yield, in addition to VIa, VIb, VIc, VIe, VIf and VIg.

The amount of VIa obtained was insufficient for an NMR spectroscopic

SCHEME 4



study, but this compound was characterized by IR and mass spectrometric analysis. The IR spectrum showed a strong band at 2120 cm^{-1} due to the Si—H stretching vibration. The exact mass of this compound was 228.1343, corresponding to the calculated molecular weight for $\text{C}_{15}\text{H}_{20}\text{Si}$. All of the data were consistent with the proposed structure VIa.

The structures of VIb—VIg were established by ^1H NMR, IR and mass spectrometric analyses. Of isomers VIb and VIc, the ^1H NMR spectrum of one isomer showed an upfield shift for the methyl protons and methylene protons at C-3 and C-4 atoms due to the shielding effect of the olefinic group and the

phenyl ring, respectively. Therefore this isomer can be assigned to VIb and the other to VIc. For a pair of isomers VIe and VIf, one had the ratio of 2/3 for the allylic protons to the methylene protons in the cyclooctenyl ring. It follows that this isomer is assignable to VIe. The ratio of these protons of the other isomer was determined to be 1/4, indicating it to be VIf.

Compounds VIa and VIc may be formed by a hydrogen shift in a silacyclopentane (D), while the formation of VIb and VIc can be explained in terms of a silyl shift in D. Products analogous to VIb and VIc have been observed in the reaction of photochemically generated trimethylsilylphenylsilylene with 1,3-cyclooctadiene [7]. On the other hand, in the reaction of thermally generated methoxymethylsilylene with 1,3-cyclooctadiene, 1-methoxy-1-methyl-1-silacyclonona-2,8-diene analogous to VIc has been reported [11].

Experimental

General procedure

All photolyses were carried out with a 100-W high-pressure mercury lamp surrounded by a quartz jacket, and a 10-W low-pressure mercury lamp bearing a Vycor filter. The progress of photolysis was followed by GLC analysis using a 2 m $\times$ 0.5 cm stainless column with 20% Silicone DC-550 oil, and irradiation was stopped when approximately 90% of the starting 2-phenylheptamethyltrisilane was photolyzed. Yields were determined by GLC using an internal standard on the basis of the unrecovered trisilane. Products were identified by GLC techniques using two different columns (30% Apiezon Grease on Celite 545 and 20% Silicone DC-550 oil on Celite 545).

Proton NMR spectra were determined at ambient temperatures with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solution containing cyclohexane as an internal standard. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JNA-2000 data processing system. Ionizing voltage was 24 eV for all compounds.

Infrared spectra were determined on thin liquid films using a Hitachi Model EPI-G3 Grating infrared spectrometer.

An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products. Most of the products were easily separated as colorless liquids by using a 3/8" $\times$ 20' column containing Silicone Gum SE-30 on Celite 545.

Materials

2-Phenylheptamethyltrisilane (I) was prepared as reported previously [12]. 1,3-Butadiene was purified by passing the gas through a column containing CaCl_2 and P_2O_5 . Other acyclic and cyclic dienes and solvent hexane were dried over lithium aluminium hydride and distilled before use.

Photolysis of 2-phenylheptamethyltrisilane (I) in the presence of a diene with a high-pressure mercury lamp

The following is typical of the procedures used. In a 120-ml reaction vessel with a reflux condenser and nitrogen inlet tube, and fitted internally with a high-pressure mercury lamp having a quartz filter, was placed a solution of

1.0255 g (3.82 mmol) of I and 0.1065 g (0.47 mmol) of cetane in 110 ml of dry hexane. To this solution, ca. 10 ml of dry 1,3-butadiene was added through the nitrogen inlet tube. The mixture was irradiated at room temperature with a slow stream of nitrogen bubbling through the mixture. Upon 2 h irradiation, 94% of the starting I was photolyzed. After the irradiation was stopped, 3 ml of dry methanol was added to the reaction mixture through the condenser by a syringe. Most of the solvent and unchanged 1,3-butadiene was evaporated away. The residue was analyzed by GLC as being 4-(methylphenylsilyl)-1,2-butadiene (IVa) (6% yield), 1-methyl-1-phenyl-1-silacyclopentene (IVb) (22% yield) and 2-trimethylsilyl[1-(3-butenyl)tetramethyldisilanyl]benzene (IVe) (8% yield). After distillation of the residue under reduced pressure pure compounds, IVa, IVb and IVe, were isolated by preparative GLC. The reaction conditions and yields of the products obtained are listed in Table 1.

Photolysis of I in the presence of a diene with a low-pressure mercury lamp

A mixture of 0.3165 g (1.19 mmol) of I, 0.0344 (0.14 mmol) of octadecane and 0.5 g (7.58 mmol) of cyclopentadiene in 100 ml of dry hexane was photolyzed for 1 h. At this stage 90% of the starting I was photolyzed. After the irradiation was stopped, 2 ml of methanol was added to the reaction mixture. The solvent was distilled off, and the residue was analyzed by GLC as being 4-(methoxymethylphenylsilyl)-1-cyclopentene (Vb) (11% yield) and the rearranged addition product Vc (19% yield). Pure Vb and Vc were isolated by preparative GLC as colorless liquids.

Low temperature photolysis of I in the presence of 2,3-dimethylbutadiene

A mixture of 1.1296 g (4.24 mmol) of I, 1.0320 g (12.6 mmol) of 2,3-dimethylbutadiene and 0.1088 g (0.48 mmol) of cetane in 100 ml of hexane was irradiated with a low-pressure mercury lamp surrounded by a Vycor vacuum jacket for 13 h at -70°C . At this stage, 96% of I was photolyzed. After the irradiation was stopped, 1 ml of methanol was added to the photolysis mixture through the reflux condenser by a syringe. The solvent was distilled off, and the residue was then analyzed by GLC as being IIa (7% yield), IIb (12% yield), IIc (2% yield) and IId (17% yield).

Acknowledgements

The cost of this research was defrayed by a Grant-in-Aid for Scientific Research by the Ministry of Education and Toray Science and Technology Grant to which the authors' thanks are due. They also express their appreciation to Toshiba Silicon Co., Ltd. and Shin-etsu Chemical Co., Ltd. for a gift of organochlorosilanes.

References

- 1 W.H. Atwell and D.R. Weyenberg, *J. Organometal. Chem.*, **5** (1966) 594; *J. Amer. Chem. Soc.*, **90** (1968) 3438.
- 2 W.H. Atwell and D.R. Weyenberg, *Angew. Chem. Intern. Edit.*, **8** (1969) 469.
- 3 E.A. Chernyshev, N.G. Komalenkova and S.A. Bashkirova, *Uspek. Khim.*, **45** (1976) 1782.
- 4 M. Ishikawa and M. Kumada, *Review on Silicon, Germanium, Tin and Lead Compounds*, **4** (1979) 7.
- 5 Y.-N. Tang, Private communication.

- 6 M. Ishikawa, F. Ohi and M. Kumada, *J. Organometal. Chem.*, **86** (1975) C23.
- 7 M. Ishikawa, K. Nakagawa and M. Kumada, *J. Organometal. Chem.*, **178** (1979) 105.
- 8 M. Ishikawa, K. Nakagawa, M. Ishiguro, F. Ohi and M. Kumada, *J. Organometal. Chem.*, **152** (1978) 155.
- 9 M. Ishikawa, T. Fuchikami and M. Kumada, *J. Organometal. Chem.*, **162** (1978) 223.
- 10 R.-J. Hwang, R.T. Conlin and P.P. Caspar, *J. Organometal. Chem.*, **94** (1975) C38.
- 11 M.E. Childs and W.P. Weber, *Tetrahedron Lett.*, (1974) 4033.
- 12 M. Kumada, M. Ishikawa and S. Maeda, *J. Organometal. Chem.*, **2** (1964) 478.