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PHOTOCHEMICALLY GENERATED SILICON—CARBON DOUBLE-BONDED INTERMEDIATES

II *. PHOTOLYSIS OF ARYLDISILANES IN THE PRESENCE OF DIENES

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Summary

Photolysis of eight aryldisilanes in the presence of 1,3-conjugated dienes (butadiene, isoprene and 2,3-dimethylbutadiene) has been studied. All of the aryldisilanes bearing a hydrogen on an *ortho* carbon atom in the aryl ring reacted upon UV irradiation with the conjugated dienes to give *o*-silyl-substituted (3-butenylsilyl)arene derivatives in high yields. The ^{13}C and ^{1}H NMR, and mass spectroscopic studies of the products are also described.

Introduction

There has been a considerable interest recently in reactive intermediates having a carbon-silicon double bond, generated by pyrolysis of various silacyclobutanes [1—5]. It has been shown that these thermally generated intermediates react with many of substrates such as ketones [6—8], amines [9], alcohols [9—11], imines [12], acetonitrile [9], silicon halides [13] and thiobenzophenone [14]. Photolysis of 1,1-diphenyl-1-silacyclobutane [15], 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene [16] and pentaphenylmethyldisilane [17] has also been shown to lead to the silicon-carbon double-bonded intermediates. However, studies with these intermediates have been limited to the reaction with methanol or acetone.

Recently, we have reported that photolysis of phenyl- and *p*-tolyl-pentamethyldisilane in the presence of a large excess of an olefin such as isobutylene in benzene solution affords a novel type of addition product, 1,2-disilyl substituted arenes. We have postulated a mechanism for their production involving photoisomerization of the disilanes to silicon-carbon double-bonded intermediates,

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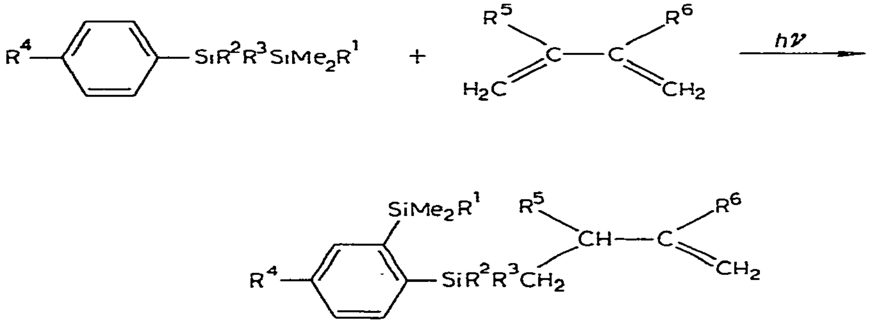
* For Part I, see ref. 18.

followed by addition to the olefins [18]. As part of studies on the scope and limitations of the reaction of these reactive intermediates with unsaturated compounds, we have now investigated the photolysis of eight aryldisilanes in the presence of three conjugated 1,3-dienes.

Results and discussion

In the previous paper [18] we briefly reported that irradiation of phenylpentamethyldisilane in the presence of 2,3-dimethylbutadiene in benzene with a low-pressure mercury lamp afforded a 1/1 adduct which was identified as *o*-(trimethylsilyl)(2,3-dimethyl-3-butenyl)dimethylsilylbenzene (I) in high yield. The present study demonstrates that the photochemically induced addition of the aryldisilanes to the conjugated dienes such as butadienes, isoprene and 2,3-dimethylbutadiene is quite a general, remarkably clean reaction; all of the aryldisilanes bearing a hydrogen atom on the *ortho* carbon in the aryl ring reacted upon UV-light (2537 Å) irradiation with the 1,3-dienes to give adducts whose structures are similar to the structure of I. Thus the irradiation of 1,1- and 1,2-diphenyltetramethyldisilane and *p*-tolylpentamethyldisilane in the presence of 2,3-dimethylbutadiene at 0° C gave adducts II, III and IV, respectively, in high yields. These results sharply contrast with those observed in the reaction of thermally generated silicon—carbon double-bonded intermediates with conjugated dienes, where [2 + 4] cycloaddition took place to give the corresponding 1-silacyclohex-3-enes [1].

Interestingly, the photolysis of aryl-substituted hydrodisilanes such as $H(Ph_2)SiSiMe_3$, $H(Me)(p\text{-}MeC_6H_4)SiSiMe_3$ and $(p\text{-}MeC_6H_4)Me_2SiSiMe_2H$ in the presence of 2,3-dimethylbutadiene under similar conditions gave analogous results to those of the arylpermethyldisilane systems. 1,2-Disilyl-substituted arenes V, VI and VII, respectively, were obtained in high yields. No hydrodisilanylation products which might be derived from the reaction of the starting hydrodisilanes



(I) $R^1 = R^2 = R^3 = R^5 = R^6 = Me, R^4 = H$
(II) $R^1 = R^3 = R^5 = R^6 = Me, R^2 = Ph, R^4 = H$
(III) $R^1 = Ph\ R^2 = R^3 = R^5 = R^6 = Me, R^4 = H$
(IV) $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = Me$
(V) $R^1 = R^5 = R^6 = Me, R^2 = R^4 = H, R^3 = Ph$
(VI) $R^1 = R^3 = R^4 = R^5 = R^6 = Me, R^2 = H$
(VII) $R^1 = H, R^2 = R^3 = R^4 = R^5 = R^6 = Me$
(VIII) $R^1 = Ph, R^2 = R^3 = Me, R^4 = R^5 = R^6 = H$
(IX) $R^1 = Ph, R^2 = R^3 = R^5 = Me, R^4 = R^6 = H$
(X) $R^1 = Ph, R^2 = R^3 = R^6 = Me, R^4 = R^5 = H$

with the diene were observed. In particular, it should be noted that the photolysis of $(p\text{-MeC}_6\text{H}_4)\text{Me}_2\text{SiSiMe}_2\text{H}$ in the presence of 2,3-dimethylbutadiene gave only VII as an addition product. This fact demonstrates amply that the formation of the adduct does not involve reaction of the hydrosilane, which might be expected from intramolecular hydrogen shift of the silicon—carbon double-bonded intermediate, with the diene as shown in Scheme 1. Consequently, our product must be produced from direct reaction of the silicon—carbon double-bonded intermediate with the diene.

In contrast to the thermally generated silicon—carbon double-bonded intermediates, the present intermediates are thought to polymerize in the absence of a trapping agent. No product that might be expected from dimerization of the intermediates could be observed at all.

Yields of the adducts and reaction conditions are summarized in Table 1. Refractive indices and analytical data for isolated products are shown in Table 2.

All attempts to produce the silicon—carbon double-bonded reactive intermediate from mesitylpentamethyldisilane in the presence of dienes or olefins were unsuccessful. Always, the starting disilane was recovered unchanged. Presumably, large steric hindrance of the methyl groups on the *ortho* carbons prevent migration of the trimethylsilyl group from silicon to the *ortho* carbon.

Next we examined the ability of the conjugated dienes as an acceptor. 1,3-Butadiene reacted with 1,2-diphenyltetramethyldisilane under similar conditions to give the corresponding adduct VIII. With isoprene, two possible isomers, IX and X, were obtained in the ratio of 2.3/1. Interestingly, the abundant iso-

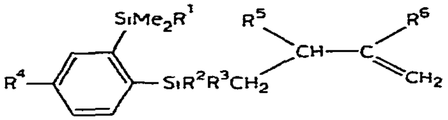
TABLE 1

PHOTOLYSIS OF ARYLDISILANES IN THE PRESENCE OF 1,3-DIENES IN BENZENE (2537 Å)

Aryldisilane (g (mmol))	1,3-Diene (mol)	Time (h)	Adduct (yield (%))	Recovered disilane (%)
$\text{PhMe}_2\text{SiSiMe}_3$ 1.0213(4.90)	2,3-Dimethylbutadiene (0.24)	16	I (37)	47
$\text{Ph}_2\text{MeSiSiMe}_3$ 0.9603(3.55)	2,3-Dimethylbutadiene (0.24)	15.5	II (49)	15
$\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ 0.9941(3.68)	2,3-Dimethylbutadiene (0.24)	16.5	III (61)	9
$p\text{-CH}_3\text{C}_6\text{H}_4(\text{Me}_2)\text{SiSiMe}_3$ 0.9496(4.27)	2,3-Dimethylbutadiene (0.24)	16	IV (60)	19
$\text{Ph}_2(\text{H})\text{SiSiMe}_3$ 1.0231(3.99)	2,3-Dimethylbutadiene (0.24)	15	V (46)	38
$p\text{-CH}_3\text{C}_6\text{H}_4(\text{Me})(\text{H})\text{SiSiMe}_3$ 0.9884(4.74)	2,3-Dimethylbutadiene (0.24)	15	VI (40)	25
$p\text{-CH}_3\text{C}_6\text{H}_4(\text{Me}_2)\text{SiSiMe}_2\text{H}$ 0.9819(4.71)	2,3-Dimethylbutadiene (0.24)	15	VII (47)	13
$\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ 1.0272(3.80)	Butadiene (0.37)	8	VIII (24)	24
$\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ 1.0077(3.73)	Isoprene (0.29)	13	IX (32) X (14)	11

TABLE 2

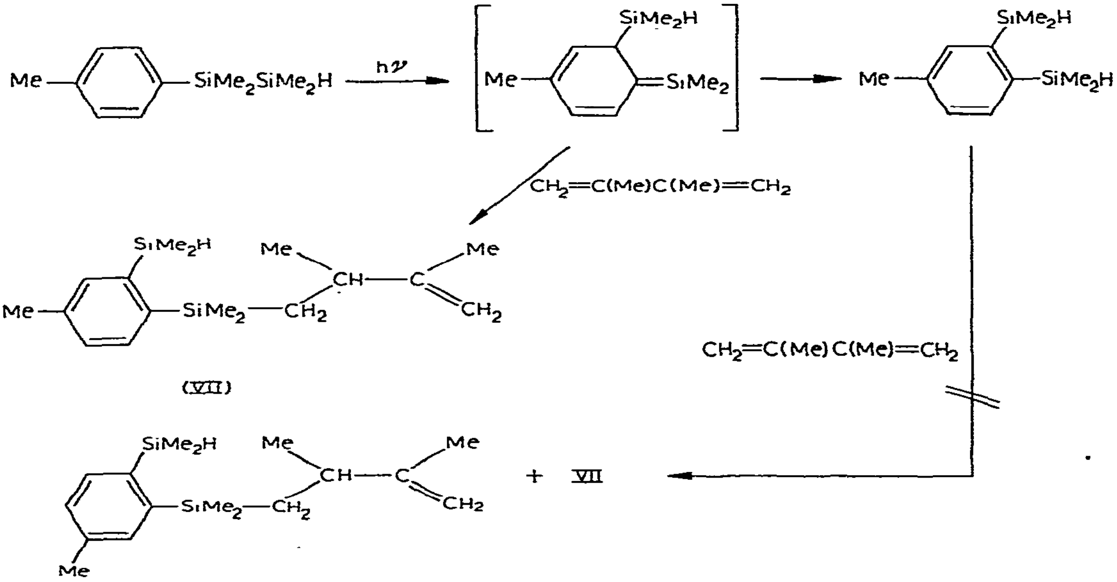
REFRACTIVE INDICES AND ANALYTICAL DATA FOR



Compound [a]		n_D^{25}	C (%) found (calcd.)	H (%) found (calcd.)
I	$R^4 = H$	—	70.53 (70.26)	10.53 (10.41)
II	$R^2 = Ph, R^4 = H$	1.5525	75.23 (74.93)	9.44 (9.15)
III	$R^1 = Ph, R^4 = H$	—	74.68 (74.93)	9.17 (9.15)
IV		1.5171	71.25 (70.97)	10.85 (10.59)
V	$R^2 = R^4 = H, R^3 = Ph$	1.5522	74.41 (74.48)	8.98 (8.93)
VI	$R^2 = H$	1.5133	70.09 (70.26)	10.13 (10.41)
VII	$R^1 = H$	1.5147	70.47 (70.26)	10.34 (10.41)
VIII	$R^1 = Ph, R^4 = R^5 = R^6 = H$	1.5576	73.80 (74.00)	8.87 (8.69)
IX	$R^1 = Ph, R^4 = R^6 = H$	1.5519	74.60 (74.48)	9.10 (8.93)
X	$R^1 = Ph, R^4 = R^5 = H$	—	74.58 (74.48)	9.13 (8.93)

[a] Unless otherwise noted $R^1 \sim R^6$ represent a methyl group.

SCHEME 1



mer was IX resulting from addition of the reactive intermediate to the double bond bearing the methyl group. Analogous results were observed when olefins were used as quenching agents. Thus, isobutylene reacted more easily with the intermediates than ethylene or propylene [19]. These results suggest that the addition of the reactive intermediates to dienes or olefins might proceed by a pathway of radical nature.

All the aryldisilanes described here did not react with 2,5-dimethyl-2,4-hexadiene nor with 1,3-cyclooctadiene, indicating that the quenching agents should contain the terminal carbon—carbon double bond, $CH_2=C(R)—$, for the formation of the adducts.

NMR spectrum of the adducts

The ^1H NMR data for all adducts and ^{13}C NMR data for selected products are listed in Tables 3 and 4. The ^1H and ^{13}C NMR spectra of I are shown in Figs. 1 and 2 as typical examples. The ^1H NMR spectra of the adducts strongly support that one of the silyl groups is attached to the 3-butenyl system. The resonances for aryl ring protons of the adducts V, VI and VII, obtained from the photolysis of *p*-tolyldisilane derivatives, display the coupling patterns characteristic of the 1,2,4-trisubstituted benzene structure which has been noted previously for 1-isobutyldimethylsilyl-4-methyl-2-trimethylsilylbenzene [18].

In the ^{13}C NMR data of the adducts, the aromatic carbon resonances were assigned by comparison with the values reported for silyl-substituted benzenes and toluenes [20—22]. In particular, the chemical shifts of C(1) and C(2) resonances (see Fig. 2 for the numbering of the carbon atoms) were confirmed by the effect exerted by introduction of a hydrogen atom onto the silicon atom, which led to a large upfield shift.

Chemical evidence for structure of the adducts

The structure of the adducts was also confirmed by a chemical reaction. Thus protodesilylation of IV by dry hydrogen chloride in ethyl ether at room temperature gave *m*-(trimethylsilyl)toluene in 55% yield as a monodesilylated product, in addition to an unidentified material (5% yield) *. Neither *o*- nor *p*-(trimethylsilyl)toluene could be detected by GLC analysis.

This clearly indicates that the silyl group originally not linked to the aromatic ring of aryldisilanes rearranged from silicon to the *ortho* carbon to generate the silicon—carbon double-bonded intermediates.

Mass spectra of the adducts

The mass spectra of the adducts shown in Table 5 are quite interesting. The ions at *m/e* 59 (for VII, VIII, IX and X), 73 (for I, II, IV and VI) and 135 (for II, III, VIII, IX and X), corresponding to HMe_2Si^+, Me_3Si^+ and $PhMe_2Si^+$ were observed as important peaks, together with weak parent ions. These ions probably result mainly from cleavage of the aryl—silicon bond, which is frequently observed in the mass spectral fragmentation of the mixed alkyl aryl silicon compounds [23].

The second important fragmentation involves cleavage of the 3-butenyl—silicon bond in the parent ion. This type of fragmentation was observed in all adducts reported here, leading to significant ions (A) (*m/e* 207 for I, VI and VII, *m/e* 221 for IV, *m/e* 255 for V and *m/e* 269 for II, III, VIII, IX and X). The ions thus formed undergo further fragmentation to give ions (B), with loss of hydrogen, methane or benzene.

As shown in Scheme 2, the fragmentation of both ions A_1 and A_2 (from III, VIII, IX and X) leads to the formation of ion B_1 at *m/e* 191, with loss of me-

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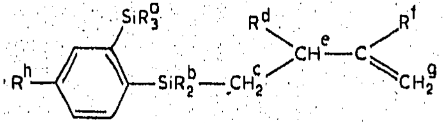
* The retention time of this compound did not coincide with that of either *o*- or *p*-(trimethylsilyl)-toluene.

(continued on p. 148)

TABLE 3.

PROTON NMR CHEMICAL SHIFTS FOR



Compound	Chemical shift in CCl_4 (δ, ppm) [a]							
	a	b	c	d	e	f	g	ring proton
I	0.42 (s, 9H)	0.44 (s, 3H) 0.46 (s, 3H)	0.94 (dd, J_{gem} 14.8, J_{vic} 7.8, 1H), 1.11 (dd, J_{gem} 14.8, J_{vic} 6.5, 1H)	1.05 (s, J 6.9, 3H)	2.43 (m, 1H)	1.71 (s, 3H)	4.58 ~ 4.74 (m, 2H)	7.18 ~ 7.68 (m, 4H)
II	0.21 (s, 9H)	0.70 (s, 3H) 0.71 (s, 3H)	1.21 (dd, J_{gem} 14.9, J_{vic} 5.9, 1/2H), 1.47 (dd, J_{gem} 14.9, J_{vic} 5.9, 1/2H), 1.30 (dd, J_{gem} 14.6, J_{vic} 6.0, 1/2H), 1.41 (dd, J_{gem} 14.6, J_{vic} 6.0, 1/2H)	1.01 (d, J 6.9, 3H)	2.44 (m, 1H)	1.71 (s, 3H)	4.57 ~ 4.72 (m, 2H)	7.22 ~ 7.79 (m, 9H)
III	0.61 (s, 6H)	0.15 (s, 3H) 0.18 (s, 3H)	0.68 (dd, J_{gem} 15.1, J_{vic} 7.9, 1H), 0.84 (dd, J_{gem} 15.1, J_{vic} 6.7, 1H)	0.89 (d, J 6.9, 3H)	2.24 (m, 1H)	1.57 (s, 3H)	4.47 ~ 4.67 (m, 2H)	7.16 ~ 7.76 (m, 9H)
IV	0.36 (s, 3H)	0.37 (s, 3H) 0.39 (s, 3H)	0.87 (dd, J_{gem} 14.9, J_{vic} 7.7, 1H), 1.04 (dd, J_{gem} 14.9, J_{vic} 6.5, 1H)	0.99 (d, J 6.8, 3H)	2.35 (m, 1H)	1.66 (s, 3H)	4.52 ~ 4.67 (m, 2H)	2.34 ($R^h = CH_3$) 7.03 (d, J 7.7, 1H) 7.37 (s, 1H) 7.44 (d, J 7.7, 1H)

V[b]	0.33 (s, 9H)	—	0.93 ~ 1.55 (m, 2H)	1.08 (d, J 6.8, 3/2H), 1.10 (d, J 6.8, 3/2H)	2.40 (m, 1H)	1.69 (s, 3H)	4.54 ~ 4.67 (m, 2H)	7.11 ~ 7.66 (m, 9H)
VI[c]	0.36 (s, 9H)	0.31 (s, J 4.5, 3H)	0.80 (m, 2H)	1.06 (d, J 6.8, 3/2H), 1.07 (d, J 6.8, 3/2H)	2.38 (m, 1H)	1.69 (s, 3H)	4.57 ~ 4.81 (m, 3H)[c]	2.36 ($R^h = CH_3$) 7.07 (d, J 7.6, 1H) 7.30 (s, 1H) 7.33 (d, J 7.6, 1H)
VII[d]	0.35 (s, J 3.8, 3.8, 6H)	0.36 (s, 6H)	0.91 (dd, J_{gem} 14.7, J_{vic} 7.9, 1H), 1.09 (dd, J_{gem} 14.7, J_{vic} 6.5, 1H)	0.99 (d, J 6.9, 3H)	2.33 (m, 1H)	1.66 (s, 3H)	4.51 ~ 4.66 (m, 2H)	2.38 ($R^h = CH_3$) 7.05 (d, J 7.6, 1H) 7.29 (s, 1H) 7.39 (d, J 7.6, 1H)
VIII	0.63 (s, 6H)	0.18 (s, 6H)	0.71 ~ 0.83 (m, 2H)	—	1.81 ~ 2.07 (m, 2H)	5.72 (m, J_{trans} 16.8, J_{cis} 9.8, J_{vic} 6.1, 1H)	4.82 (m, J_{cis} 9.8, J_{gem} 2.1, 1H), 4.86 (m, J_{trans} 16.8, J_{gem} 2.1, 1H)	7.19 ~ 7.74 (m, 9H)
IX[e]	0.58 (s, 6H)	0.14 (s, 6H)	0.48 ~ 0.90 (m, 2H)	0.87 (d, J 7.0, 3H)	2.17 (m, 1H)	5.55 (m, J_{trans} 17.5, J_{cis} 10.0, 1H)	4.69 (m, J_{cis} 10.0, J_{gem} 1.8, 1H), 4.75 (m, J_{trans} 17.5, J_{gem} 1.8, 1H)	7.14 ~ 7.72 (m, 9H)
X[e]	0.58 (s, 6H)	0.11 (s, 6H)	0.60 ~ 0.90 (m, 2H)	—	1.72 ~ 1.91 (m, 2H)	1.61 (s, 3H)	4.50 ~ 4.57 (m, 2H)	7.13 ~ 7.69 (m, 9H)

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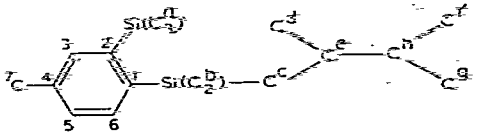
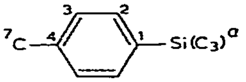
[a] Chemical shifts are reported relative to CH_2Cl_2 at 100 MHz unless otherwise noted; s, singlet; d, doublet; dd, double doublet; m, multiplet. [b] Si—H, 5.20 (triplet, J 4.0). [c] Si—H (overlap with g). [d] Si—H, 4.78 (septet, J 3.8). [e] TMS as internal standard.

TABLE 4

^{13}C NMR CHEMICAL SHIFTS (from TMS, ppm) FOR



	Compound				
	I	IV	VI	VII	
a	2.07	2.07	1.21	−2.31	
b	0.73	0.79	−3.33 −3.57	−0.53	−0.99
c	23.47	24.09	21.54	23.97	
d	18.58	18.51	18.87 18.76	18.63	
e	37.62	37.62	37.92 37.56	37.62	
f	22.94	22.88	22.45	22.82	
g	108.42	108.30	108.60	108.18	
h	151.92	151.05	151.31	152.04	
1	145.37	141.67	139.85 139.60	142.22	137.87
2	145.79	145.74	146.58 146.46	144.22	133.18
3	135.18	136.15	135.11	135.18	128.48
4	127.53	136.88	137.30	137.18	136.21
5	127.53	128.32	128.62	128.81	
6	135.30	135.54	134.81	134.57	
7	—	21.36	21.30	21.30	21.29

[a] See ref. 21.

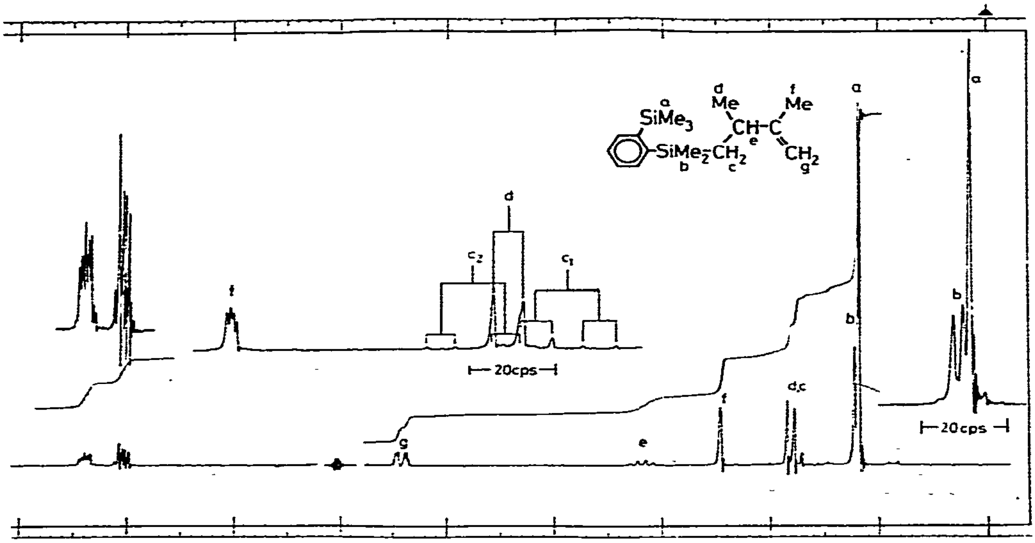


Fig. 1. ^{1}H NMR spectrum of I.

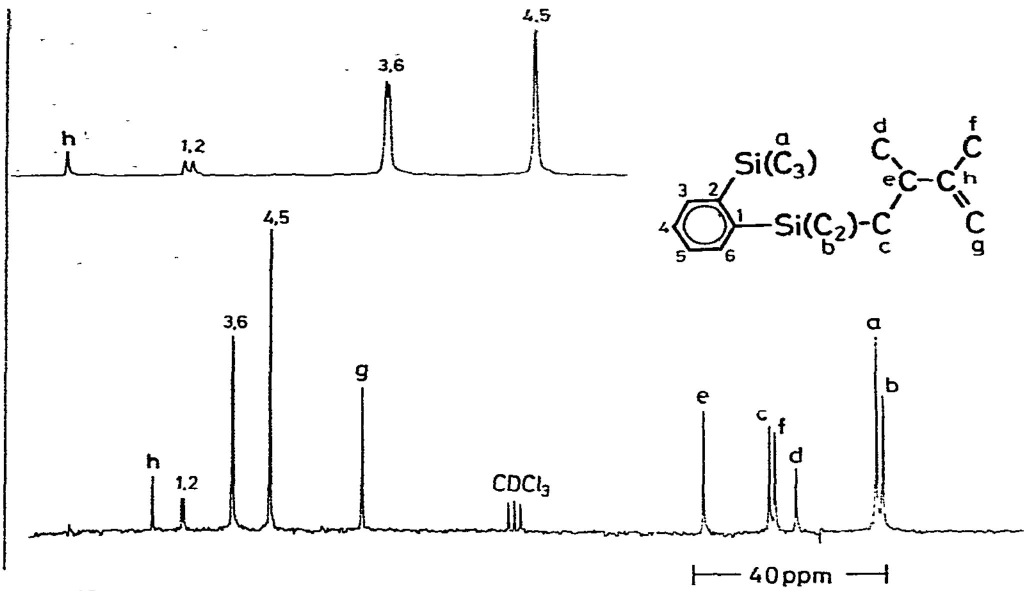


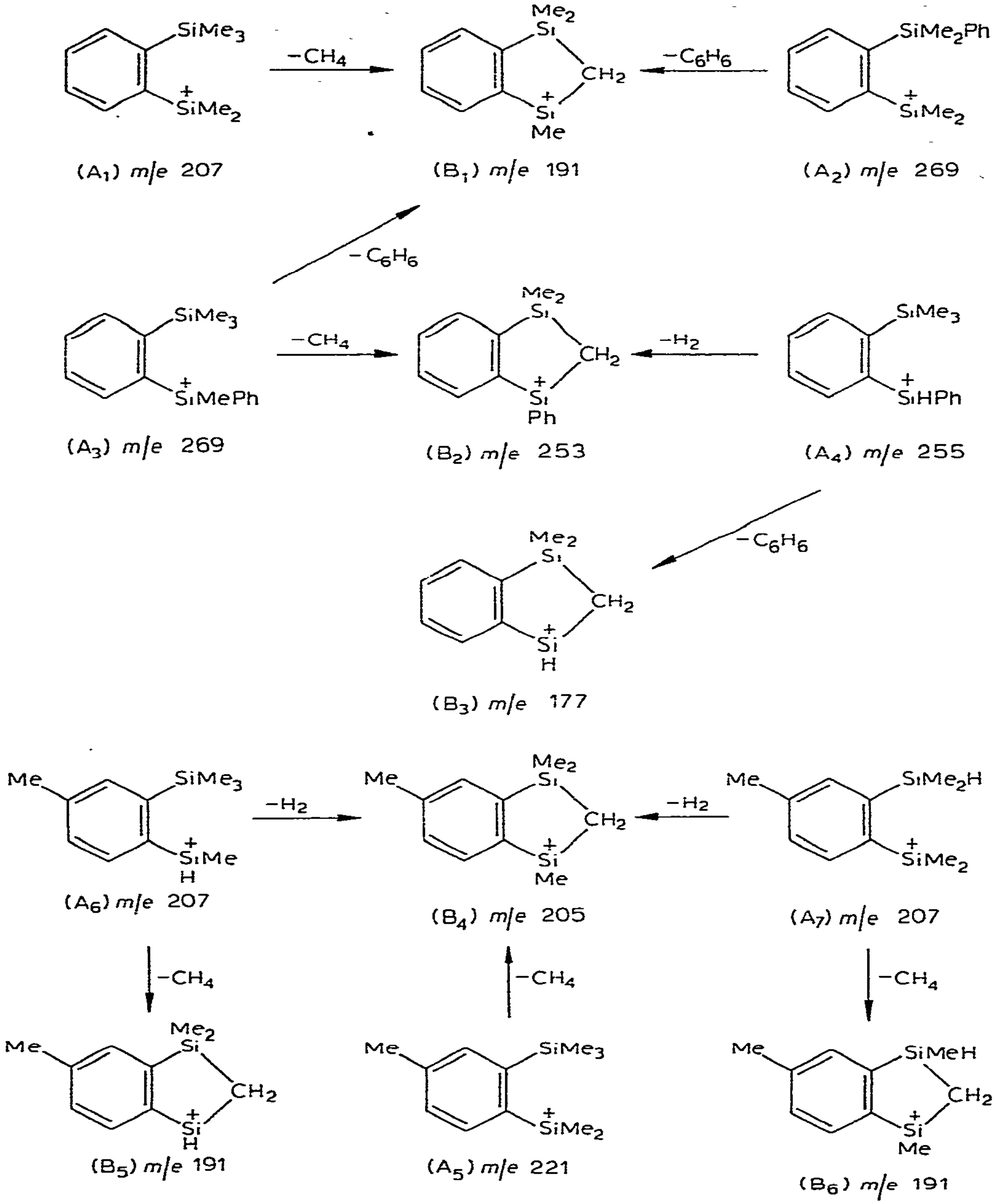
Fig. 2. ^{13}C NMR spectrum of I.

TABLE 5

IMPORTANT PEAKS IN THE MASS SPECTRA OF ADDUCTS AT 70 eV

m/e	Relative intensity (%) of peaks of the adducts									
	I	II	III	IV	V	VI	VII	VIII	IX	X
59	28.4	23.4	30.9	29.1	15.4	32.6	40.9	39.5	46.4	40.5
73	100	95.2	28.6	100	46.3	77.5	57.9	20.2	27.8	26.8
112								18.9		
121		54.0								
126									19.2	9.7
135	30.1	90.3	100		38.1			100	100	100
140	8.9			7.8						
141			6.3							
149				33.6		21.1	26.7			
174						100				
177					62.9					
188					9.2			3.2		
191	59.2	100	46.8		6.3	32.6	34.0	86.0	56.6	55.1
202		12.9	10.0						1.8	10.9
205				59.2		100	57.5			
207	17.9					39.2	100			
217						7.7				
221				20.9						
222					80.4					
231				18.4			17.4			
239					19.8					
253		20.6	8.7		100			9.7	8.2	7.7
255					43.3					
265					4.6					
269		80.7	50.8					87.2	59.7	49.3
279		21.0								
290	0.66					0.70	2.83			
304				0.76						
324								1.03		
338					1.55				0.92	9.84
352		3.18	0.66							

SCHEME 2



thane or benzene respectively. Interestingly, in the latter case, loss of methane is an unimportant pathway (less than 10%). The observation of metastable ions *m/e* 176 (calcd. *m/e* = $(191)^2/207 = 176.2$) and 136 (calcd. *m/e* = $(191)^2/269 = 135.6$) provides evidence in support of these fragmentations. In contrast to the fragmentation of ion A_2, ion A_3 yields two ions, B_1 (100%) and B_2 (20.6%), with loss of either benzene or methane as a neutral fragment, although the elimination of benzene is more favorable than that of methane (metastable ions: at 176 (calcd. 176.2) and at 238 (calcd. 238.0)). Similarly, ion A_4 which is observed in the mass spectrum of V leads to two ions B_2 at *m/e* 253 (100%) and B_3 at *m/e* 177 (62.9%); however, in this case, the elimination of hydrogen is more important than that of benzene. Metastable ions can also be observed at *m/e* 123 (calcd. 122.9) and at *m/e* 251 (calcd. 251.0).

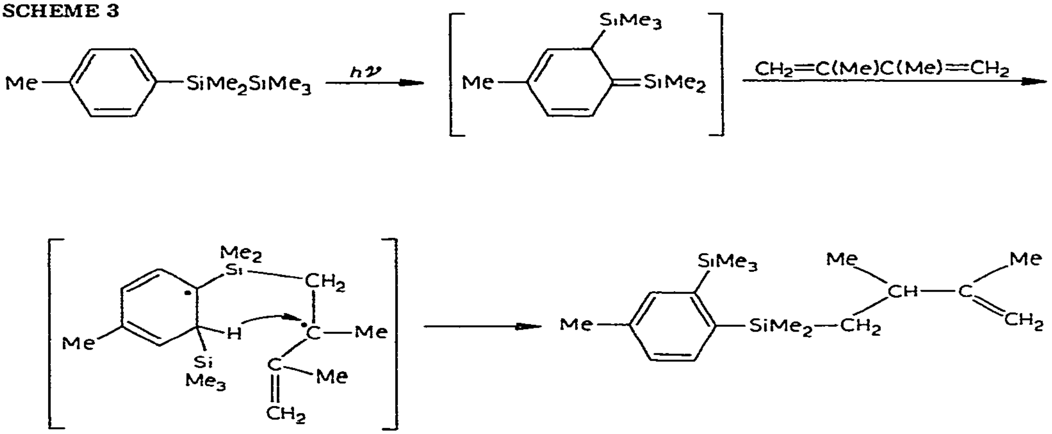
The fragmentation of ion A_5 results in the generation of ion B_4 in a similar manner as A_1. Ions A_6 and A_7 produced from VI and VII with loss of the 3-butenyl group lead to the formation of ion B_4 at *m/e* 205 with loss of hydrogen molecule, and to ions B_5 and B_6 with loss of methane as a minor pathway (metastable ions: at 176 (calcd. 176.2) and at 203 (calcd. 203.0)).

Reaction mechanism

The nature of the intermediates and steps in the addition reaction are not yet clear, but the findings in quenching reaction with alcohols, which will be reported in the succeeding paper, allow one to make certain conclusion of the reaction mechanism of the photochemically induced addition of aryldisilanes to the 1,3-dienes.

As has already been proposed, the reaction may proceed via photoisomerization of an aryldisilane to the unstable silicon—carbon double-bonded intermediate. The intermediate then adds to one of the double bonds in the 1,3-diene, yielding the observed adduct. The reaction of *p*-tolylpentamethyldisilane with 1,3-dimethylbutadiene is exemplified in Scheme 3.

SCHEME 3



Experimental

Spectra

^{1}H NMR spectra were determined with a Varian Model HA-100 spectrometer using carbon tetrachloride solution containing methylene chloride as a lock signal. ^{13}C NMR spectra were determined with a JOEL Model JNM-PFT-100 spectrometer using deuteriochloroform as a solvent. Mass spectra were measured on a Hitachi Model RMU-6D fitted with an all glass direct inlet accessory. Ionizing voltage was 70 eV for all compounds.

Gas chromatography

An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separation of the products. All the products were easily separated as colorless liquids by using a column containing 30% Apiezon L (3/8 in. × 20 ft.).

Materials

2,3-Dimethylbutadiene and isoprene were fractionally distilled before use. 1,3-Butadiene was purified by passing the gas through a column containing $CaCl_2$ and P_2O_5. Benzene was dried over lithium aluminum hydride and distilled before use.

Phenylpentamethyldisilane, 1,2-diphenyltetramethyldisilane and 1,1-diphenyltetramethyldisilane were made as reported in the literature [24]. Other organodisilanes were obtained as described below.

p-Tolylpentamethyldisilane

To a Grignard reagent prepared from 6.3 g (0.25 g-atom) of magnesium and 43 g (0.25 mol) of *p*-tolylbromide in 200 ml of tetrahydrofuran (THF) was added 20 g (0.12 mol) of chloropentamethyldisilane. The reaction mixture was heated to reflux for 3 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. Distillation gave 13 g (49% yield) of *p*-tolylpentamethyldisilane [25], b.p. 119°C/21 torr, n_D^{20} 1.5060; NMR (δ, ppm) 0.10 (s, 9H), 0.35 (s, 6H), 2.37 (s, 3H), 7.08 (d, 2H, *J* 7.7 Hz), 7.29 (d, 2H, *J* 7.7 Hz).

1-Chloro-1,1-diphenyltrimethyldisilane

In a 500-ml three-necked flask was placed a mixture of 8.0 g (0.24 mol) of 1,1,1-trimethyltriphenyldisilane [29] dissolved in 300 ml of chloroform and 1.0 g of anhydrous aluminum chloride. Dry hydrogen chloride was passed into the stirred solution at room temperature over a period of 10 h. Evaporation of the solvent, followed by distillation under reduced pressure gave 57 g of crude product boiling over a range of 107 to 172°C at 5 torr. Fractional distillation of the crude product gave 47 g (67% yield) of 1-chloro-1,1-diphenyltrimethyldisilane, b.p. 135—136°C/2 torr; NMR (δ, ppm) 0.32 (s, 9H), 7.25—7.72 (m, 10H) (Found: Cl, 12.08. $C_{15}H_{19}ClSi_2$ calcd.: 12.19%).

1,1,1-Trimethyl-2,2-diphenyldisilane

To a mixture of 2 g of lithium aluminum hydride with 100 ml of dry ethyl ether was added a solution of 30 g (0.10 mol) of 1-chloro-1,1-diphenyltrimethyldisilane in 100 ml of ether at room temperature. This mixture was refluxed for 5 h and hydrolyzed with water. The organic layer was separated, washed with water and dried over potassium carbonate. After evaporation of the solvent ether, the residue was fractionally distilled under reduced pressure to give 20 g (80% yield) of 1,1,1-trimethyl-2,2-diphenyldisilane [26], b.p. 110°C/2 torr, n_D^{25} 1.5690; NMR (δ, ppm) 0.20 (s, 9H), 4.77 (s, 1H), 7.14—7.67 (m, 10H).

1-Chloro-1,1,2,2-tetramethyl-2-(p-tolyl)disilane

To 10 g (0.05 mol) of 1,2-dichlorotetramethyldisilane dissolved in 100 ml of dry THF was added *p*-tolylmagnesium bromide prepared from 10 g (0.06 mol) of *p*-tolyl bromide and 1.5 g (0.06 g-atom) of magnesium in 50 ml of THF. The mixture was then refluxed for 2 h. The magnesium salt was filtered off and the filtrate was distilled under reduced pressure to give 9.7 g (76% yield) of crude 1-chloro-1,1,2,2-tetramethyl-2-(*p*-tolyl)disilane, b.p. 108°C/4 torr. This was used, without further purification, for preparation of the following hydride.

1-(p-Tolyl)-1,1,2,2-tetramethyldisilane

In a 200-ml three-necked flask fitted with a stirrer, a dropping funnel and a reflux condenser were placed 2.0 g (0.053 mol) of lithium aluminum hydride and 40 ml of dry ethyl ether. To this was added a solution of 9.7 g (0.040 mol) of crude 1-chloro-1,1,2,2-tetramethyl-2-(*p*-tolyl)disilane in 30 ml of dry ethyl ether with ice cooling. The mixture was refluxed for 2 h and then hydrolyzed with water. The organic layer was separated, washed with water and dried over potassium carbonate. Distillation under reduced pressure gave 3.4 g (41% yield) of 1-(*p*-tolyl)-1,1,2,2-tetramethyldisilane [27], b.p. 86°C/6 torr, n_D^{25} 1.5091; NMR (δ, ppm) 0.12 (d, 6H, *J* 4.3 Hz), 0.35 (s, 6H), 2.36 (s, 3H), 3.72 (sept, 1H, *J* 4.3 Hz), 7.06 (d, 2H, *J* 7.7 Hz) and 7.30 (d, 2H, *J* 7.7 Hz) (Found: C, 62.92; H, 9.60. $C_{11}H_{20}Si_2$ calcd.: C, 63.38; H, 9.67%).

1,1-Dichlorotetramethyldisilane

In a 500-ml three-necked flask was placed a mixture of 59 g (0.22 mol) of 1,1-diphenyltetramethyldisilane dissolved in 300 ml of dry benzene and 1.0 g of anhydrous aluminum chloride. Dry hydrogen chloride was passed into the stirred solution over a period of 5 h with ice cooling. Evaporation of the solvent, followed by distillation under reduced pressure gave 30 g of crude 1,1-dichlorotetramethyldisilane, b.p. 53°C/34 torr. Fractional distillation gave 24 g (59% yield) of a pure sample, b.p. 144°C; NMR (δ, ppm) 0.26 (s, 9H), 0.78 (s, 3H) (Found: Cl, 37.64. $C_4H_{12}Cl_2Si_2$ calcd.: Cl, 37.87%).

1-(p-Tolyl)-1,2,2,2-tetramethyldisilane

A solution of 8.8 g (0.036 mol) of 1-chloro-1-(*p*-tolyl)-1,2,2,2-tetramethyldisilane prepared from 10 g (0.053 mol) of 1,1-dichlorotetramethyldisilane and an equimolar amount of *p*-tolylmagnesium bromide in 50 ml of THF was added to 1.8 g of lithium aluminum hydride in 50 ml of ethyl ether. The mixture was refluxed for 2 h, and then hydrolyzed with water. The organic layer was separated and washed with water. After evaporation of the solvent ether, the residue was distilled under reduced pressure to give 3.0 g (40% yield) of a colorless liquid, b.p. 88°C/6 torr, n_D^{25} 1.5111; NMR (δ, ppm) 0.13 (s, 9H), 0.38 (d, 3H, *J* 4.3 Hz), 2.38 (s, 3H), 4.18 (q, 1H, *J* 4.3 Hz), 7.09 (d, 2H, *J* 8.1 Hz) and 7.33 (d, 2H, *J* 8.1 Hz) (Found: C, 63.68; H, 9.80. $C_{11}H_{20}Si_2$ calcd.: C, 63.38; H, 9.67%).

Photolysis of aryldisilanes in the presence of 1,3-dienes

The following is typical of the procedures used. A solution of 1.0213 g (4.90 mmol) of phenylpentamethyldisilane and 20 g (0.24 mol) of 2,3-dimethylbutadiene in 110 ml of dry benzene was irradiated for 16 h with a low-pressure mercury lamp (10 watt) having a Vycor filter under bubbling nitrogen with ice cooling. Most of the solvent benzene and unchanged 2,3-dimethylbutadiene were evaporated and the residue was distilled under reduced pressure to give a volatile product boiling up to 200°C/1 torr. The yield of I in the distillate was determined by GLC using n-eicosane as an internal standard. Then I was isolated by preparative GLC.

Protodesilylation of IV

In a 25-ml two-necked flask fitted with a gas inlet tube and a reflux condenser was placed 0.60 g (3.3 mmol) of IV dissolved in 20 ml of dry ethyl ether. Dry hydrogen chloride gas was introduced into the solution with ice cooling. The progress of the reaction was monitored by GLC analysis of small samples extracted periodically from the reaction mixture. The starting compound was completely cleaved by hydrogen chloride after about 0.5 h. The reaction mixture was then washed with water and neutralized with sodium bicarbonate solution. The organic layer was separated and dried over anhydrous calcium chloride. After the solvent ether was evaporated the yield of *m*-(trimethylsilyl)toluene (55% yield) was determined by analytical GLC using n-eicosane as an internal standard. A pure sample of *m*-(trimethylsilyl)toluene was isolated by preparative GLC. M^+ 164 (mol. wt. 164.33); NMR (δ, ppm) 0.27 (s, 9H), 2.37 (s, 3H), 7.01—7.34 (m, 4H); IR (cm^{-1}) 876, 838, 779, 753, 691 (ref. 28: 874, 837, 778, 751, 690).

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