PHOTOCHEMICALLY GENERATED SILICON-CARBON DOUBLE-BONDED INTERMEDIATES
VIII*. PHOTOLYSIS OF PHENYLDISILANE DERIVATIVES IN THE PRESENCE OF
OLEFINS

MITSUO ISHIKAWA, TAKAMASA FUCHIKAMI and MAKOTO KUMADA

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

Summary

Photolysis of phenylpentamethyldisilane, 1,1-diphenyltetramethyldi-
silane and 1-isopropyl-1-phenyltetramethyldisilane in the presence of a
wide variety of olefins has been studied. All reactions investigated,
with the exception of those with 1-methylcyclohexene and tetramethylethyl-
ene, afforded the corresponding 1/1 addition products. Yields of the
adducts depended highly on the structure of the olefins used. In the
photolysis of phenylpentamethyldisilane in the presence of an equimolar
mixture of 1,1- and 1,2-bis(trimethylsilyl)ethene under competitive reac-
tion conditions, the main product was the one arising from the 1,1-isomer.
A possible mechanism for the process of addition of olefin to the photo-
chemically generated silicon-carbon double-bonded intermediate (A) is
discussed.

Introduction

One of the fascinating areas of organosilicon chemistry in the past
decade is that concerned with the formation and reactions of reactive
intermediates that may possess a formal silicon-carbon double bond [1].
In 1967 Gusel'nikov and Flowers first reported that gas-phase pyrolysis of
1,1-dimethylsilacyclobutane generates a reactive silicon-carbon double-
bonded intermediate, dimethylsilaethene [2]. Since then many papers con-

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* For Part VII, see ref. [11].

cerning the generation and reactions of the thermally generated silaethenes have been published. Meanwhile, Sommer and his co-workers reported that photolysis of pentaphenylmethyldisilane [3] and 1,1-diphenyl-1-silacyclo-butane [4] also leads to the silaethene type of intermediates.

In 1975 we discovered that photolysis of aryldisilanes produces a novel type of the silicon-carbon double-bonded intermediate (A) [5]. Subsequently, we demonstrated that the intermediate A reacts with various substrates such as dienes [6], alcohols [7], carbonyl compounds [8], and alkynes [9] in a different fashion than do the silaethene intermediates (B) generated either by photolysis of 1-alkenyldisilanes [10,11] or by thermolysis of the silacyclobutanes.
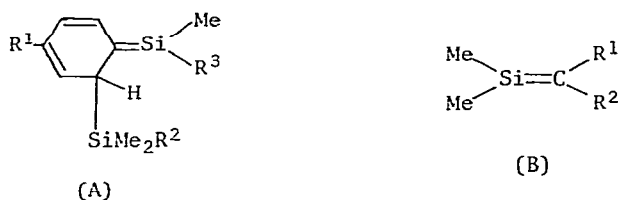


In an effort to learn more about the chemical behavior of the inter-mediates of type A, we have investigated the photolysis of phenylpenta-methyldisilane, 1,1-diphenyltetramethyldisilane and 1-phenyl-1-isopropyl-tetramethyldisilane in the presence of a wide variety of olefins.

## Results and discussion

### Reaction with terminal olefins

In a recent brief report [5] we have shown that the photolysis of phenylpentamethyldisilane (I) in the presence of a large excess of 2-methylpropene afforded a 1/1 addition product which was identified as $o$-trimethylsilyl(isobutyldimethylsilyl)benzene. We now find that the photol-ysis of I in the presence of ethylene or any of its monosubstituted deriva-tives always gives the respective 1/1 adducts (IIa-IIf) in moderate yields (Scheme 1 and Table 1).
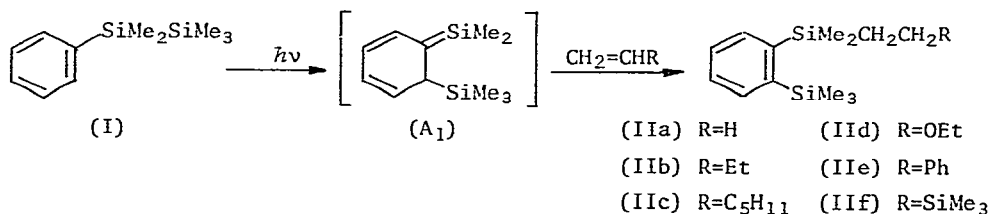
SCHEME 1



(I)  (A$_1$)  (IIa) R=H    (IId) R=OEt
               (IIb) R=Et   (IIe) R=Ph
               (IIc) R=C$_5$H$_{11}$  (IIf) R=SiMe$_3$

TABLE 1

PHOTOLYSIS OF PHENYLPENTAMETHYLDISILANE (4.8 mmol) IN THE PRESENCE OF TERMINAL OLEFINS IN BENZENE (2537 Å)

| Olefin | mmol | Time (h) | Yield of adduct (%)[a] | Recovered disilane (%) |
|--------|------|----------|------------------------|------------------------|
| $CH_2=CH_2$ | b | 4 | IIa 20 (24) | 17 |
| $CH_2=CHEt$ | 50 | 4 | IIb 29 (37) | 22 |
| $CH_2=CHC_5H_{11}$ | 5.0 | 4 | IIc 17 (18) | 8 |
| $CH_2=CHOEt$ | 34 | 5 | IId 22 (24)[c] | 9 |
| $CH_2=CHPh$ | 5.1 | 6 | IIe 29 (43) | 35 |
| $CH_2=CHSiMe_3$ | 100 | 4 | IIf 30 (37)[d] | 19 |
| $CH_2=CHSiMe_3$ | 4.8 | 4 | IIf 34 (41)[e] | 16 |
| $CH_2=C(Me)CN$ | 4.8 | 4 | IIg 12 (15) | 21 |
| $CH_2=C(Me)COOMe$ | 5.0 | 10 | IIh 22 (25) | 15 |
| $CH_2=C(Me)OSiMe_3$ | 7.4 | 4 | IIi 30 (35) | 14 |
| $CH_2=C(Me)SiMe_2H$ | 5.4 | 4 | IIj 31 (38) | 20 |
| $CH_2=C(Me)Bu-tert$ | 4.8 | 3 | IIk 19 (19) | 5 |
| $CH_2=CMe_2$ | 50 | 2 | IIl 59 (54) | 27 |
| $CH_2=C(Me)Ph$ | 4.8 | 15 | IIm 45 (46)[f] | 2 |
| $CH_2=C(SiMe_3)_2$ | 4.8 | 4 | IIn 41 (45) | 9 |
| $CH_2=C(Ph)SiMe_3$ | 4.8 | 12.5 | IIo 54 (56) | 4 |

[a] Determined by GLC analysis using tetradecane as an internal standard on the basis of disilane used. Yields given in parentheses based on unrecovered disilane. [b] Under bubbling ethylene. [c] Silepin IIIa was also obtained in 9% yield. [d] Silepin IIIb was also obtained in 6% yield. [e] Product IIIb was obtained in 4% yield. [f] m-Trimethylsilyl-1-(2'-phenylpropyl)dimethylsilylbenzene (IIp) was obtained in 7% yield.

As can be seen from Table 1, trimethylsilyl- and phenyl-substituted ethylenes produced adducts in better yields (40-45%) than others. 1-Heptene afforded a low yield (18%) of the product. These results suggest that the steric as well as the electronic effect is important.

It is of interest to note that in the photolysis of an aryldisilane in the presence of olefin, a stoichiometric amount of the latter can trap the intermediate A as effectively as its excess amount under the conditions used. For instance, irradiation of a benzene solution of I with a 20-fold excess of vinyltrimethylsilane afforded o-trimethylsilyl(2'-tri-

methylsilylethyl)dimethylsilylbenzene (IIf) and silepin IIIb [12] in 37 and 6% yield, respectively. Under identical conditions I reacted with 1 molar equivalent of vinyltrimethylsilane to give IIf and IIIb in 41 and 4% yield, respectively. This indicates that the intermediate $A_1$ (Scheme 1) has a liftime long enough to allow it to find a partner in a dilue solution. Silepin IIIa was also formed in 9% yield, in addition to 24% yield of the normal adduct IId, when I was irradiated in the presence of ethyl vinyl ether at room temperature. The production of the silepin may be explained in terms of the Walk rearrangement of a bicyclic intermediate produced by sequential pathways as shown in Scheme 2 [12]. In all reactions reported here other than those with vinyltrimethylsilane and ethyl vinyl ether, neither silepin derivatives nor any other isomers could be detected by either ^{1}H NMR spectroscopic method or GLC analysis.

SCHEME 2



I + CH$_2$=CHR    $h\nu$

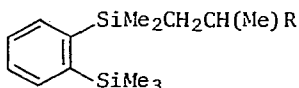R = EtO or Me$_3$Si

(IIIa) R=EtO
(IIIb) R=Me$_3$Si
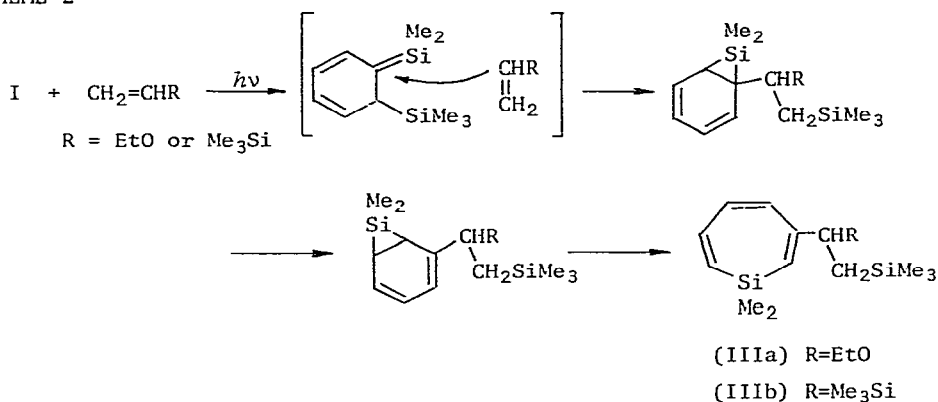
The structures of the products which could be isolated as colorless liquids by GLC techniques were determined by IR, mass and ^{1}H NMR spectroscopic studies. The results of elemental analysis and the spectral data of the products are given in Tables 5 and 6.

Next, we examined the ability of 1,1-disubstituted olefins to trap the intermediate. The reaction of intermediate $A_1$ with 1,1-disubstituted olefins in benzene generally afforded better yields of the adducts than those from the monosubstituted olefins (Table 1). However, with olefins having an electron-withdrawing substituent such as CN or COOMe, yields of the adducts were lower. Thus, the photolysis of I in the presence of 1 molar equivalent of methacrylonitrile gave IIg in 15% yield as the sole volatile product. With methyl methacrylate, product IIh was obtained in 25% yield. None of the product resulting from addition of intermediate $A_1$ to cyano or carbonyl group was formed.

TABLE 2

PHOTOLYSIS OF PHENYLPENTAMETHYLDISILANE (4.8 mmol) IN THE PRESENCE OF
INTERNAL OLEFINS IN BENZENE

| Olefin | mmol | Time (h) | Yield of adduct (%)$^a$ | Recovered disilane (%) |
|---|---|---|---|---|
| *trans*-2-butene | 50 | 4 | IVa 14 (17) | 20 |
| *cis*-2-butene | 50 | 4 | IVa 21 (32) | 34 |
| 2-methyl-2-butene | 28 | 4 | IVb 9 (12) | 23 |
| cyclohexene | 4.8 | 4 | IVc 11 (13) | 12 |
| cyclooctene | 4.8 | 4 | IVd 30 (34) | 10 |
| 1,2-bis(trimethyl-silyl)ethene | 4.8 | 4 | IVe 28 (32) | 10 |
| 2,3-dimethyl-2-butene | 4.8 | 4 | 0 | 8 |
| 1-methylcyclohexene | 4.9 | 4 | 0 | 3 |

$^a$ Determined by GLC analysis using tetradecane as an internal standard.
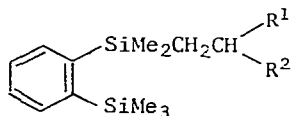Yields given in parentheses based on unrecovered disilane.

SiMe$_2$CH$_2$CH(Me)R

SiMe$_3$

SiMe$_2$CH$_2$CH$\langle$R$^1$, R$^2$

SiMe$_3$

(IIg) R=CN    (IIk) R=tert-Bu    (IIn) R$^1$=R$^2$=Me$_3$Si

(IIh) R=COOMe    (IIl) R=Me    (IIo) R$^1$=Ph,

(IIi) R=OSiMe$_3$    (IIm) R=Ph    R$^2$=Me$_3$Si

(IIj) R=SiMe$_2$H

Introduction of an electron-donating group such as Me$_3$SiO onto the
unsaturated carbon atom did not show any remarkable change in the yield of
addition product. This result is in line with that obtained from the
reaction of A$_1$ with ethyl vinyl ether. The reaction of A$_1$ with olefins
such as 1,1-dimethyl-, 1,1-bis(trimethylsilyl)-, 1-methyl-1-phenyl- and
1-phenyl-1-trimethylsilylethene, gave good yields of the adducts (IIl-IIo).
The yield was highly influenced by introducing a bulky substituent onto
the olefinic carbon atom. Thus, the photolysis of I in the presence of
2-tert-butylpropene afforded adduct IIk in only 19% yield, as a single
volatile product. Interestingly, the $^1$H NMR spectrum of non-volatile
polymeric substances produced in this photolysis showed complex signals in
a methylsilyl region, but no resonances attributed to tert-butyl protons
and CH$_3$-C protons were observed.

*Reaction with internal olefins*

The reaction of intermediate $A_1$ with internal olefins is of interest, because the yield of adducts depends highly on the structure of olefins used in a different sense than do the yields from terminal olefins. Thus, irradiation of I with *cis*-2-butene produced adduct IVa in 32% yield, as the sole volatile product. On the other hand, with *trans*-2-butene under identical conditions, I afforded IVa in only 17% yield. No other isomer was detected by GLC analysis. The ^{1}H NMR spectrum of polymeric substances from the photolysis product again showed that they contained no alkyl moiety arising from 2-butene. This fact suggests that if a biradical species such as C is produced as intermediate in the addition step, it must be stabilized to give the final product by an intramolecular hydrogen



(IVa)

(C)
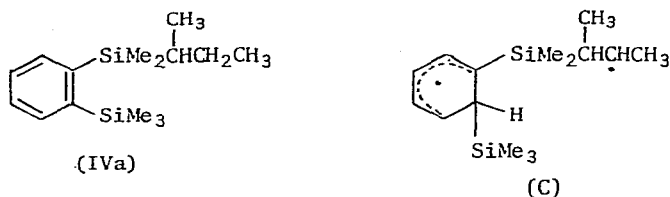
shift, but not polymerize to non-volatile substances. Further discussion about the addition step will be given later in this article.

Similar irradiation of I with 2-methyl-2-butene gave adduct IVb in 12% yield, as a single volatile product. Again, non-volatile polymeric substances produced in this photolysis contained no alkyl moiety from the olefin used.

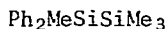The reaction of I with *trans*-1,2-bis(trimethylsilyl)ethene under
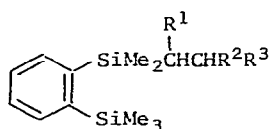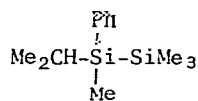


(IVb)  $R^1=R^2=R^3=Me$
(IVe)  $R^1=R^2=Me_3Si$,  $R^3=H$

photolysis conditions gave adduct IVe in 32% yield. In this case, *cis/trans* isomerization of bis(trimethylsilyl)ethene could not be excluded, although no *cis* isomer was detected by either GLC or spectroscopic methods under the conditions used.

Non-substituted cyclic olefins also react with intermediate $A_1$ to give the corresponding adducts. Thus, the reaction of $A_1$ with cyclohexene gave adduct (IVc) in 13% yield, while with cyclooctene, $A_1$ afforded IVd in 32% yield, as the sole volatile product. The photolysis of I with 1-methylcyclohexene or tetramethylethylene produced no volatile products.

(structures at top)

SiMe$_2$R / SiMe$_3$ (benzene ring)
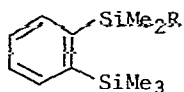
(IVc)  R=cyclo-C$_6$H$_{11}$
(IVd)  R=cyclo-C$_8$H$_{15}$
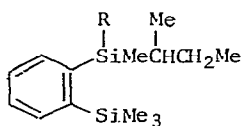
Ph$_2$MeSiSiMe$_3$

(V)
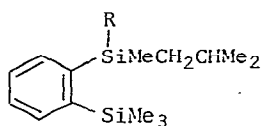
Ph / Me$_2$CH-Si-SiMe$_3$ / Me

(VI)

In order to learn more about the influence of steric hindrance at the unsaturated silicon atom, we carried out the photolysis of 1,1-diphenyl-tetramethyldisilane (V) and 1-isopropyl-1-phenyltetramethyldisilane (VI) in the presence of *cis*- and *trans*-2-butene or 2-methylpropene. Irradiation of V and VI in the presence of *cis*- or *trans*-2-butene gave the respective adducts, VIIa and VIIIa. However, yields of the adducts were lower than those obtained from the reaction of sterically less hindered disilane I with these substrates. Here again, *cis*-2-butene afforded better yields of the adducts than did the *trans* isomer (Tables 3 and 4).

In the photolysis of V and VI in the presence of 2-methylpropene, on the other hand, no influence of the steric hindrance at the unsaturated silicon atom was observed. Yields of adducts VIIb and VIIIb were almost the same as the yield of the adduct resulting from I and 2-methylpropene under similar conditions.

R Me / SiMeCHCH$_2$Me (benzene ring) / SiMe$_3$

(VIIa)   R=Ph
(VIIIa) R=iso-Pr

R / SiMeCH$_2$CHMe$_2$ (benzene ring) / SiMe$_3$

(VIIb)   R=Ph
(VIIIb) R=iso-Pr

·TABLE 3

PHOTOLYSIS OF 1,1-DIPHENYLTETRAMETHYLDISILANE (4.8 mmol) IN THE PRESENCE OF OLEFINS IN BENZENE

| Olefin | mmol | Time (h) | Yield of adduct (%)[a] | Recovered disilane (%) |
|---|---|---|---|---|
| *trans*-2-butene | 50 | 4 | VIIa  4  (4) | 8 |
| *cis*-2-butene | 50 | 4 | VIIa  19  (28) | 32 |
| 2-methyl-1-propene | 50 | 4 | VIIb  59  (62) | 5 |

[a] Determined by GLC analysis using tetradecane as an internal standard on the bases of disilane used. Yields given in parentheses based on unrecovered disilane.

TABLE 4

PHOTOLYSIS OF 1-ISOPROPYL-1-PHENYLTETRAMETHYLDISILANE (4.8 mmol) IN THE
PRESENCE OF OLEFINS IN BENZENE

| Olefin | mmol | Time (h) | Yield of adduct (%)$^a$ | Recovered disilane (%) |
|---|---|---|---|---|
| *trans*-2-butene | 50 | 4 | VIIIa  2  (3) | 25 |
| *cis*-2-butene | 50 | 4 | VIIIa 11 (15) | 26 |
| 2-methyl-1-pentene | 50 | 4 | VIIIb 43 (53) | 20 |

$^a$ Determined by GLC analysis using hexadecane as an internal standard on
the basis of disilane used. Yields given in parentheses based on unrecov-
ered disilane.

Furthermore, we examined competitive addition of a pair of 1,1- and
1,2-disubstituted olefin isomers to an insufficient amount of intermediate
A$_1$. Thus, a benzene solution of I and 0.5 molar equivalent each of 1,1-
and 1,2-bis(trimethylsilyl)ethene was irradiated for 2 h at room tempera-
ture. At this point 63% of the starting I was photolyzed. The major
adduct (51% yield) was found to be IIn arising from 1,1-bis(trimethyl-
silyl)ethene and the minor one (5% yield) was IVe, indicating that the
addition of terminal olefin proceeds much faster than that of internal
olefin.

*Mechanism of addition of intermediate A to olefins*

The addition of intermediate A to the *cis* olefins affords always
better yields of the adducts than those from the *trans* isomers. For
example, a yield (32%) of the adduct of intermediate A to *cis*-butene was
nearly twice higher than that (17%) to the *trans* isomer (*vide supra*).
These results indicate that a model for the addition step which involves
"end-on" approach of olefin to A from the side *trans* to the Me$_3$Si group in
the cyclohexadienyl ring as shown in Fig. 1 would be ruled out, because
there is no appreciable difference in steric interactions for both olefin
isomers. On the other hand, models D (Fig. 2) in which an olefin molecule
"side-on" approaches the intermediate A$_1$ seem to account for the observed
results.

The bonding nature of a silicon-carbon double bond is still uncertain.
However, if this bond can be described in terms of a p$\pi$-p$\pi$ bond, but not a
zwitter-ionic or diradical structure, the present reactions can be con-
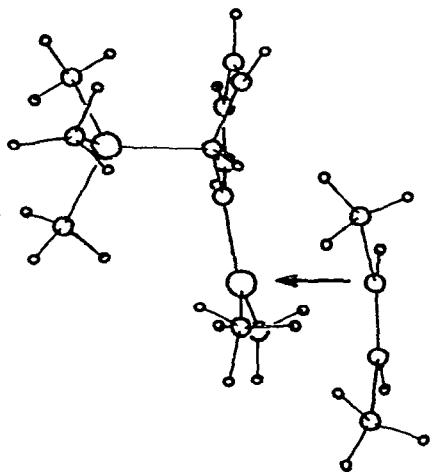sidered as an ene type reaction [13]. Examination of molecular models D

Fig. 1.    Schematic representation of "end-on" approach of olefin
           to intermediate A.



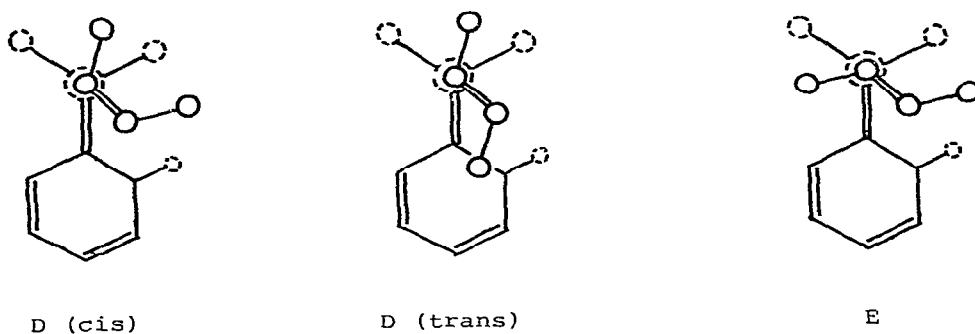D (cis)              D (trans)                    E

Fig. 2.    Schematic representation of "side-on" approaches of
           olefin to intermediate A.

shows that a *trans* isomer of olefin experiences a significant steric
interaction as compared with the *cis* isomer.  Model E showing an alterna-
tive mode of approach of the *trans* isomer also exhibits a larger steric
interaction.  Consideration of orbital interactions in the addition step
between the highest occupied molecular orbital (HOMO) of olefin and the
lowest unoccupied molecular orbital (LUMO) of intermediate A (Fig. 3a)
which can be made up by the orbitabl mixing rule [14] supports such mecha-
nism.  As can be seen from a schematic representation of the HOMO-LUMO
interaction in Fig. 3a, the positive overlap of orbitals shows that the
pathway leading to the adduct iş particularly favorable [15].  The inverse
HOMO-LUMO interactions (Fig. 3b) also favarable, even though the contribu-
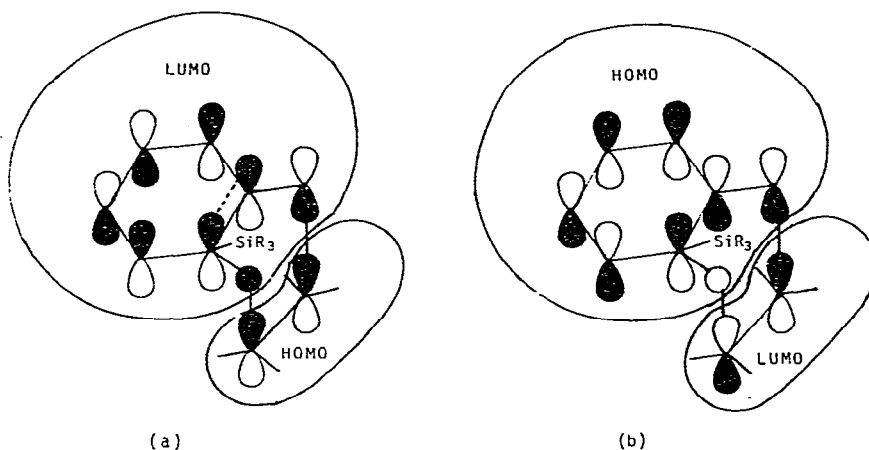tion is small.  Based on the HOMO-LUMO interaction, it can easily be

Fig. 3.    Schematic representation of the orbital interactions;
(a) interaction between HOMO of olefin and LUMO of
intermediate A, (b) interaction between HOMO of A and
LUMO of olefin.

understood that the product yield would be affected by the structure of an
olefin used, because the ease with which orbitals overlap in the transi-
tion state depends highly on the steric requirement of the olefin.    The
observed large difference in product yield obtained from cyclohexene and
cyclooctene can also be explained by steric consideration.

Experimental

*General procedures*
    Infrared spectra were determined on thin liquid films using a Hitachi
Model EPI-G3 Grating infrared spectrometer.  $^1$H NMR spectra were deter-
mined with a JEOL Model JNM-MH-100 and a Varian Model HA-100 spectrometer
using carbon tetrachloride solutions containing cyclohexane as an internal
standard.  Mass spectra were measured on a JEOL Model JMS-D 300 equipped
with a JMA-2000 data processing system.  Ionizing voltage was 24 eV for
all compounds.  Gas chromatographic analyses were carried out using a
Shimazu GC-4B gas chromatograph (30% Silicone grease SE-30 on Celite 545).
    The internal standard method was used for quantitative analyses, with
response factors [RF=(mol of product)×(area of standard)/(mol of standard)
×(area of product)] determined separately under the analysis conditions by
means of a standard solution.
    An Aerograph Model 90-P gas chromatograph with a thermal conductivity
detector was used for separating the reaction products.  Most of the

TABLE 5

REFRACTIVE INDICES AND ANALYTICAL DATA FOR ISOLATED PRODUCTS

| Product | $n_D^{20}$ | H (%) | | C (%) | |
|---------|-----------|-------|--------|-------|--------|
| | | Found | (calcd) | Found | (calcd) |
| IIa | 1.5167 | 10.36 | (10.23) | 65.87 | (66.02) |
| IIb | 1.5112 | 10.97 | (10.67) | 68.19 | (68.10) |
| IIc | 1.5067 | 11.36 | (11.18) | 70.41 | (70.51) |
| IId | 1.5099 | 10.27 | (10.06) | 64.39 | (64.22) |
| IIe | 1.5525 | 9.11 | (9.03) | 72.70 | (73.00) |
| IIf | 1.5068 | 10.27 | (10.45) | 62.44 | (62.26) |
| IIg[a] | 1.5219 | 9.26 | (9.15) | 65.44 | (65.39) |
| IIh | 1.5083 | 9.20 | (9.15) | 62.20 | (62.28) |
| IIi | 1.4994 | 10.36 | (10.12) | 60.76 | (60.28) |
| IIj | 1.5143 | 10.74 | (10.45) | 62.39 | (62.26) |
| IIk | 1.5111 | 11.37 | (11.18) | 70.58 | (70.51) |
| IIl | 1.5106 | 10.80 | (10.67) | 67.88 | (68.10) |
| IIm | 1.5493 | 9.50 | (9.26) | 73.66 | (73.54) |
| IIn | 1.5160 | 10.69 | (10.59) | 60.19 | (59.92) |
| IIo | 1.5445 | 9.52 | (9.43) | 68.91 | (68.67) |
| IIp | 1.5312 | 9.39 | (9.26) | 73.37 | (73.54) |
| IIIa | 1.5049 | 10.25 | (10.06) | 64.23 | (64.22) |
| IIIb | 1.5058 | 10.59 | (10.45) | 62.13 | (62.26) |
| IVa | 1.5219 | 10.80 | (10.67) | 67.99 | (68.10) |
| IVb | 1.5174 | 11.06 | (10.85) | 68.70 | (68.98) |
| IVc | 1.5320 | 10.23 | (10.41) | 70.49 | (70.26) |
| IVd | 1.5438 | 11.04 | (10.76) | 71.64 | (71.62) |
| IVe | 1.5156 | 10.68 | (10.59) | 59.73 | (59.92) |
| VIIa | 1.5571 | 9.31 | (9.26) | 73.84 | (73.54) |
| VIIb | 1.5460 | 9.42 | (9.26) | 73.47 | (73.54) |
| VIIIa | 1.5178 | 11.32 | (11.02) | 69.89 | (69.78) |
| VIIIb | 1.5120 | 11.15 | (11.02) | 69.72 | (69.78) |

[a] N, 4.99 (5.08).

products were easily separated as colorless liquids by using a 3/8" × 10' column containing Silicone grease SE-30 on Celite 545.

*Materials*

Phenylpentamethyldisilane [16], 1,1-diphenyltetramethyldisilane [16], trimethylvinylsilane [17], 1-trimethylsilylstyrene [18], 2-trimethyl-siloxypropene [19], 1,1-bis(trimethylsilyl)ethene [20] and 1,2-bis(tri-

TABLE 6

$^1$H NMR DATA FOR ISOLATED PRODUCTS

| .Compound | Chemical shift (δ, ppm) in carbon tetrachloride |
|---|---|
| IIa | 0.32 (Me$_2$Si, s, 6H), 0.34 (Me$_3$Si, s, 9H), 0.9 (Et, m, 5H), 7.1-7.6 (ring protons, m, 4H) |
| IIb | 0.34 (Me$_2$Si, s, 6H), 0.35 (Me$_3$Si, s, 9H), 0.9 (SiCH$_2$ and CH$_3$, m, 5H), 1.3 (-(CH$_2$)$_2$-, m, 4H), 7.0-7.7 (ring protons, m, 4H) |
| IIc | 0.36 (Me$_2$Si, s, 6H), 0.37 (Me$_3$Si, s, 9H), 0.9 (SiCH$_2$ and CH$_3$, m, 5H), 1.3 (-(CH$_2$)$_5$-, m, 10H), 7.1-7.6 (ring protons, m, 4H) |
| IId | 0.37 (Me$_3$Si, s, 9H), 0.39 (Me$_2$Si, s, 6H), 1.12 (SiCH$_2$, t, 2H), 1.16 (CH$_3$, t, 3H), 3.31 (OCH$_2$, q, 2H), 3.38 (OCH$_2$, t, 2H), 7.1-7.6 (ring protons, m, 4H) |
| IIe | 0.35 (Me$_3$Si, s, 9H), 0.38 (Me$_2$Si, s, 6H), 1.18 (CH$_2$, m, 2H), 2.61 (CH$_2$, m, 2H), 7.0-7.7 (ring protons, m, 9H) |
| IIf | -0.07 (Me$_3$Si, s, 9H), 0.28 (Me$_2$Si, s, 6H), 0.31 (Me$_3$Si, s, 9H), 0.40 (CH$_2$, m, 2H), 0.58 (CH$_2$, m, 2H), 7.1-7.7 (ring protons, m, 4H) |
| IIg | 0.36 (Me$_3$Si, s, 9H), 0.39 (Me$_2$Si, s, 6H), 0.83 (CH$_2$, d, 2H), 0.91 (CH$_3$, d, 6H), 1.81 (CH, m, 1H), 7.1-7.7 (ring protons, m, 4H) |
| IIh | 0.37 (Me$_3$Si, s, 9H), 0.39 (Me$_2$Si, s, 6H), 0.90 and 1.36 (CH$_2$, dd, 2H), 1.13 (CH$_3$, d, 3H), 2.46 (CH, m, 1H), 3.48 (OMe, s, 3H), 7.1-7.7 (ring protons, m, 4H) |
| IIi | 0.02 (Me$_3$Si, s, 9H), 0.36 (Me$_3$Si, s, 9H), 0.40 (Me$_2$Si, s, 6H), 1.15 (SiCH$_2$ and CH$_3$, d, 5H), 4.02 (CH, m, 1H), 7.0-7.7 (ring protons, m, 4H) |
| IIj | 0.03 (Me$_2$Si, d, 6H), 0.37 (Me$_3$Si, s, 9H), 0.40 (MeSi, s, 3H), 0.41 (MeSi, s, 3H), 0.9 (CH$_2$CHCH$_3$, m, 6H), 3.7 (SiH, m, 1H), 7.0-7.7 (ring protons, m, 4H) |
| IIk | 0.36 (Me$_3$Si, s, 9H), 0.38 (MeSi, s, 3H), 0.39 (MeSi, s, 3H), 0.4-1.5 (CH$_2$CHCH$_3$, m, 6H), 0.82 (tert-Bu, s, 9H), 7.1-7.7 (ring protons, s, 4H) |
| IIl | 0.37 (Me$_3$Si, s, 9H), 0.52 (Me$_2$Si, s, 6H), 1.2 (CH$_2$, m, 2H), 1.30 (Me$_2$, d, 6H), 2.5 (CH, m, 1H), 7.1-7.7 (ring protons, m, 4H) |
| IIm | 0.15 (MeSi, s, 3H), 0.29 (MeSi, s, 3H), 0.36 (Me$_3$Si, s, 9H), 1.23 (SiCH$_2$ and CH$_3$, d, 5H), 2.84 (CH, m, 1H), 6.9-7.6 (ring protons, m, 9H) |
| IIn | -0.11 (CH, t, 1H), -0.06 (Me$_3$Si, s, 18H), 0.38 (Me$_3$Si and Me$_2$Si, s, 15H), 0.87 (CH$_2$, d, 2H), 7.1-7.6 (ring protons, m, 4H) |
| IIo | -0.09 (Me$_3$Si, s, 9H), 0.00 (MeSi, s, 3H), 0.23 (MeSi, s, 3H), 0.35 (Me$_3$Si, s, 9H), 1.2 (CH$_2$, m, 2H), 2.05 (CH, dd, 1H), 6.7-7.7 (ring protons, m, 9H) |
| IIp | 0.10 (MeSi, s, 3H), 0.11 (MeSi, s, 3H), 0.29 (Me$_3$Si, s, 9H), 1.2 (SiCH$_2$ and CH$_3$, m, 5H), 2.8 (CH, m, 1H), 6.9-7.5 (ring protons, m, 9H). |

TABLE 6 (continued)

| Compound | Chemical shift ($\delta$, ppm) in carbon tetrachloride |
|----------|--------------------------------------------------------|
| IIIa | 0.06 (Me$_2$Si, s, 6H), 0.12 (Me$_3$Si, s, 9H), 1.08 (SiCH$_2$, d, 2H), 1.15 (CH$_3$, t, 3H), 3.38 (OCH$_2$, q, 2H), 4.36 (OCH, t, 1H), 5.35, 5.49, 5.77, 5.97 and 6.53 (vinylic protons, m, 5H) |
| IIIb | -0.01 (Me$_2$Si, s, 6H), 0.05 (Me$_3$Si, s, 9H), 0.11 (Me$_3$Si, s, 9H), 0.58 and 1.05 (CH$_2$, m, 2H), 2.24 (CH, m, 1H), 4.93, 5.42, 5.84 and 6.37 (vinylic protons, m, 5H) |
| IVa | 0.31 (Me$_2$Si, s, 6H), 0.35 (Me$_3$Si, s, 9H), 0.9 (Me and Et, m, 8H), 1.5 (CH, m, 1H), 7.1-7.6 (ring protons, m, 4H) |
| IVb | 0.35 (MeSi, s, 3H), 0.36 (Me$_3$Si, s, 9H), 0.38 (MeSi, s, 3H), 0.9 (SiCH and Me, m, 10H), 1.8 (CHMe$_2$, m, 1H), 7.0-7.7 (ring protons, m, 4H) |
| IVc | 0.31 (Me$_2$Si, s, 6H), 0.36 (Me$_3$Si, s, 9H), 0.9-1.9 (cyclo-hexyl, m, 11H), 7.0-7.7 (ring protons, m, 4H) |
| IVd | 0.31 (Me$_2$Si, s, 6H), 0.37 (Me$_3$Si, s, 9H), 1.1-1.8 (cyclo-octyl, m, 15H), 7.0-7.7 (ring protons, m, 4H) |
| IVe | -0.23 (Me$_3$Si, s, 9H), -0.07 (Me$_3$Si, s, 9H), 0.30 (CH, m, 1H), 0.36 (MeSi, s, 3H), 0.38 (Me$_3$Si, s, 9H), 0.44 (MeSi, s, 3H), 0.65 (CH$_2$, m, 2H), 7.1-7.7 (ring protons, m, 4H) |
| VIIa | 0.07 (Me$_3$Si, s, 9H), 0.57 (MeSi, s, 3H), 1.0 (Me and Et, m, 8H), 1.7 (CH, m, 1H), 7.1-7.8 (ring protons, m, 9H) |
| VIIb | 0.13 (Me$_3$Si, s, 9H), 0.64 (MeSi, s, 3H), 0.92 (Me$_2$, dd, 6H), 1.27 (CH$_2$, d, 2H), 1.84 (CH, m, 1H), 7.2-7.7 (ring protons, m, 9H) |
| VIIIa | 0.33 (MeSi, s, 3H), 0.35 (Me$_3$Si, s, 9H), 0.7-1.8 (alkyl, m, 16H), 7.0-7.7 (ring protons, m, 4H) |
| VIIIb | 0.36 (MeSi, s, 12H), 0.7-1.9 (alkyl, m, 16H), 7.1-7.7 (ring protons, m, 4H) |

methylsilyl)ethene [20] were prepared as reported in the literature. Other olefins were used as received. Benzene was dried over lithium aluminum hydride and distilled before use.

*Preparation of 1-chloro-1-phenyltetramethyldisilane*

In a 300-ml three-necked flask was placed a mixture of 50 g (0.19 mol) of 1,1-diphenyltetramethyldisilane dissolved in 200 ml of dry chloroform and 1.0 g of anhydrous aluminum chloride. Dry hydrogen chloride was passed into the stirred solution over a period of 5 h at room temperature. Evaporation of the solvent, followed by distillation under reduced pressure gave 32 g (76% yield) of 1-chloro-1-phenyltetramethyldisilane, b.p. 113-115°C/15 Torr, NMR ($\delta$, ppm) 0.16 (Me$_3$Si, s, 9H), 0.70 (MeSi, s, 3H) and 7.2-7.6 (ring protons, m, 5H) (Found: Cl, 15.30. C$_{10}$H$_{17}$ClSi$_2$ calcd.: Cl, 15.49%).

*Preparation of 1-phenyl-1-isopropyltetramethyldisilane (VI)*

To 12 g (0.052 mol) of 1-chloro-1-phenyltetramethyldisilane in 20 ml of dry tetrahydrofuran (THF) was added a Grignard reagent prepared from 5 g·(0.064 mol) of isopropyl chloride and 1.5 g (0.063 g-atom) of magnesium in 20 ml of THF. The mixture was heated at reflux for 24 h and hydrolyzed with dilute hydrochloric acid. The organic layer was washed to neutral and dried over potassium carbonate. After evaporation of the solvent, the residue was distilled under reduced pressure to give 6 g (49% yield) of a colorless liquid, b.p. 69°C/2 Torr, $n_D^{20}$ 1.5135; NMR ($\delta$, ppm) 0.12 (Me$_3$Si, s, 9H), 0.32 (MeSi, s, 3H), 1.1 (iso-Pr, m, 7H), 7.0-7.4 (ring protons, m, 5H); IR (cm$^{-1}$) 1430s, 1390m, 1370m, 1255s, 1100s; mass spectrum m/e 236 (32), 193 (100), 179 (10), 163 (24), 135 (62), 121 (30), 73 (12) (Found: C, 66.07; H, 10.41. C$_{13}$H$_{24}$Si$_2$ calcd.: C, 66.02; H, 10.23%).

*Photolysis of phenylpentamethyldisilane (I) in the presence of ethylene*

In a 100-ml reaction vessel fitted internally with a low-pressure mercury lamp having a Vycor filter was placed a solution of 1.00 g (4.8 mmol) of I in 80 ml of dry benzene. The solution was irradiated with ice cooling for 4 h in a slow stream of dry ethylene bubbling through the mixture. After the irradiation was stopped, 0.14 g of tetradecane as an internal standard was added to the reaction mixture. The solvent benzene was distilled off, and the residue was then analyzed by GLC as being IIa (20% yield) and 8% of the starting disilane I. Pure IIa was isolated by preparative GLC.

*Photolysis of phenyldisilanes (I, V and VI) in the presence of an olefin*

The following is typical of the procedures used. A solution of 1.00 g (4.8 mmol) of I in 80 ml of dry benzene was placed in a reaction vessel similar to that described above. To this solution, 3 g (50 mmol) of 1-butene was added through a nitrogen inlet tube. The mixture was irradiated with ice cooling for 4 h in a slow stream of nitrogen bubbling through the mixture. After the irradiation was stopped, 0.12 g of tetradecane was added to the mixture. The mixture was then analyzed by GLC as being adduct IIb (29% yield) and 22% of the starting disilane I. After distillation of the volatile product, pure IIb was isolated by preparative GLC. The reaction conditions and yields of the products obtained from the photolysis experiments are listed in Tables 1, 2, 3 and 4.

*Photolysis of I in the presence of 1,1- and 1,2-bis(trimethylsilyl)ethene*

A mixture of 1.00 g (4.8 mmol) of I, 0.41 g (2.4 mmol) of 1,1-bis-(trimethylsilyl)ethene and 0.41 g (2.4 mmol) of 1,2-bis(trimethylsilyl)-ethene in 80 ml of dry benzene was photolyzed for 2 h. At this stage 63%

of the starting I was photolyzed. After the irradiation was stopped, 0.12
g of tetradecane was added as an internal standard to the reaction mixture.
The yield of the products, IIm and IVe, was determined by GLC to be 51 and
5%, respectively, on the basis of unrecovered disilane I.

## Acknowledgement

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