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# SPECTRA AND SOME REACTIONS OF ORGANOPOLYSILANES

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## Prologue

In 1962, when I had an appointment as an associate professor at the Department of Synthetic Chemistry, Kyoto University, the new laboratories which I was to occupy had not yet been finished, and I shared an old office for about six months with Professor Makoto Kumada who also had just moved there. In these circumstances we had a plenty of time for discussion, just like people on sabbatical leave.

Although free-radical chemistry was my main interest, and I had very little knowledge of organosilicon chemistry at that time, I took a great interest in Kumada's collection of his "as yet unexplained" experimental data. One of them was, for example, a greater reactivity of (chloromethyl)pentamethyldisilane (I) than of (chloromethyl)trimethylsilane (II) in the Finkelstein reaction.

$$R(CH_3)_2SiCH_2Cl + I^- \rightarrow R(CH_3)_2SiCH_2I + Cl^- \qquad (1)$$

(I, $R = (CH_3)_3Si$;
II, $R = CH_3$)

While trying to devise an explanation for the enhanced reactivity of I [1], I became convinced that there was some kind of conjugation between the silicon—silicon bond and the reaction center, and suspected that such conjugation might be observed in other phenomena. A straightforward test of such a conjugation seemed to be an inspection of spectroscopic properties of compounds having both silicon—silicon and double bonds.

In the beginning of 1963, I moved to the new building where I prepared phenylpentamethyldisilane [2], the first organosilicon compound I ever made, in an attempt to compare its UV spectra with that of trimethylphenylsilane. It was already known that the trimethylsilyl group had only very small bathochromic effect on benzene [3] or ethylene [4]. Since we had no automatic recording UV spectrometer in Kyoto at that time, I borrowed a new Hitachi U machine at Osaka City University, where I took the UV spectra of phenylpentamethyldisilane on March 26, 1963, and found an intense absorption at 231 nm

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which disclosed a large — an unexpectedly large — red shift of the absorption maxima of 28 nm. I was rather cautious in announcing this discovery, mainly because of a possible doubt about the purity of the samples, so that I awaited the delivery of a GLC apparatus which had just appeared on the Japanese market. Eventually, my first note on the UV spectra of polysilanes appeared in October, 1963 [1,5], and the full account was published in 1964 [6].

## Ultraviolet spectra of phenylpentamethyldisilane and related compounds

Encouraged by the discovery, I recorded the UV spectra of a number of polysilanes, some of which are listed in Table 1. The most striking facts are the red shifts observed for phenylpentamethyldisilane and vinylpentamethyldisilane compared to phenyltrimethylsilane and vinyltrimethylsilane, respectively.

Before our observation on the UV spectra of polysilanes, Hague and Prince [7] had reported an intense absorption of hexaphenyldisilane at 246.5 nm. They described this absorption as an interaction between phenyl groups through the Si—Si bond, but we thought that the most important structural unit responsible for the red shift must be the Ph—Si—Si moiety.

At the same time, Gilman, Atwell and Schwebke suggested that if such an interaction occurred between phenyl groups on different atoms through the Si—Si bond, a smaller red shift should be observed for $Ph(Me_2Si)_nPh$ with a longer polysilane chain. However, this was not the case [8], and instead when $n$ was greater than two, intense absorption maxima were observed, and Gilman et al. concluded as we did that the most dramatic increase in $\lambda_{max}$ was observed when one methyl group of hexamethyldisilane was replaced by a phenyl group [9] *.

Hague and Prince also concluded, in 1964, that the Ph—Si—Si group must be the origin of the intense absorption [10]. Thus, the Si—Si bond was recognized to be able to conjugate with phenyl and vinyl groups by three independent sets of workers.

These conjugated properties were first explained in terms of the "$d$—$\pi$" interaction in the excited state only [6,9,10—15]. However, ground state interaction between the Si—Si $\sigma$ bond and the $\pi$ system has also been recognized as an important factor in addition to the $d$—$\pi$ interaction. I describe below how this was recognized, and how the finding has opened up fascinating new lines of research in organosilicon chemistry, by using selected examples, mostly invoking results from my own laboratory.

## The substitutent effect in the UV spectra of phenylpentamethyldisilane

We prepared a number of $p$- and $m$-substituted phenylpentamethyldisilanes and measured the UV spectra. The $\lambda_{max}$ and molar absorptivities of these compounds are listed in Table 2 [16].

The involvement of $\pi$-symmetric orbitals in the transition is shown by the fact that $p$- but not $m$-substituted phenylpentamethyldisilanes exhibit batho-

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* I learned of the reasoning behind their work through a conversation with Dr. Atwell.

TABLE 1

UV SPECTRA OF SOME POLYSILANES

| Polysilane | $\lambda_{max}$ m$\mu$ | $\epsilon_{max}$ |
|---|---|---|
| $PhSiMe_2SiMe_3$ | 231.0 | 10,900 |
| $PhSiMe_2SiMe_2Ph$ | 238.0 | 18,500 |
| $Ph_2SiMeSiMePh_2$ | 240.0 | 25,900 |
| $CH_2{=}CH{-}SiMe_2SiMe_3$ | 223.2 | 5,200 |
| $CH_2{=}CH{-}SiMe_2SiMe_2{-}CH{=}CH_2$ | 227.0 | 9,790 |
| $PhSiMe_2SiMe_2SiMe_3$ | 240.0 | 15,400 |
|  | 221.3 | 13,000 |
| $Me_3SiSiMePhSiMe_3$ | 243.0 | 13,000 |

chromic shifts relative to phenylpentamethyldisilane. For example, both *m*-nitro and *m*-pentamethyldisilanyl substituents cause essentially no bathochromic shift, while *p*-nitro and *p*-pentamethyldisilanyl groups produce large red shifts in the absorption maximum of phenylpentamethyldisilane, of 57 and 18 nm, respectively [15].

Many experimental and theoretical studies on the UV spectra of mono- and di-substituted benzenes have been reported [17,18]. One of the most successful approaches for benzene derivatives has been the conjugation-interaction method developed by Nagakura and his coworkers [19—21]. They have dealt with the substituent effects on both the UV absorption frequencies and the intensities as a result of the configuration interaction among ground, locally excited and intra-molecular charge transfer (CT) configurations. We have collected UV data for *p*-disubstituted benzenes in addition to our own data and analyzed the substituent effects based on the configuration interaction theory.

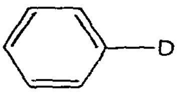
TABLE 2

UV SPECTRAL DATA FOR SUBSTITUTED PHENYLPENTAMETHYLDISILANES IN HYDROCARBON SOLVENT [a]

| Substituent | $\lambda_{max}$(nm) | $\bar{\nu}_{max} \times 10^{-4}$ (cm$^{-1}$) | $\epsilon$ |
|---|---|---|---|
| H | 230.5 | 4.34 | 12,200 |
| *p*-$NMe_2$ | 270 | 3.70 | 31,200 |
| *p*-MeO | 239 | 4.18 | 21,100 |
| *p*-$CH_2SiMe_3$ | 240.5 | 4.16 | 21,100 |
| *p*-$SiMe_2SiMe_3$ | 248 | 4.03 | 24,500 |
| *p*-Me | 233 | 4.29 | 12,800 |
| *p*-Cl | 237.5 | 4.21 | 17,800 |
| *p*-$CF_3$ | 241 | 4.15 | 10,000 |
| *p*-$CH_3CO$ | 264 | 3.80 | 17,200 |
| *p*-$NO_2$ [b] | 287.5 | 3.48 | 12,000 |
| *m*-$SiMe_2SiMe_3$ | 231 | 4.33 | 24,400 |
| *m*-Me | 232 | 4.31 | 14,700 |
| *m*-Cl | 236 | 4.24 | 9,690 |
| *m*-$CF_3$ | 234 | 4.27 | 9,900 |
| *m*-$NO_2$ [b] | 234 | 4.27 | 15,500 |

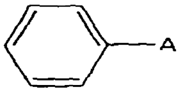
[a] Isooctane was used unless otherwise stated. [b] In cyclohexane.

Monosubstituted benzenes may be classified into two groups, donor-substituted benzenes (D-benzenes) and acceptor-substituted benzenes (A-benzenes).



D = $NR_2$ , OR , Cl , Br etc

D-benzene



A = $NO_2$ , C(O)R etc

A-benzene

In monosubstituted benzenes the nature of the charge-transfer excited configuration should be different for D- and A-benzenes, since in A-benzenes the important CT configuration should be the electron transfer from benzene to the substituent, while in D-benzenes it should be from the substituent to benzene. We expected that *p*-substituents would affect the $^1L_a$ bands of A-benzenes differently from those of benzenes. In fact, we found a very good linear relationship between the wave numbers of the $^1L_a$ band of *p*-substituted anisoles and those of other D-benzenes for the same substituent. A similar

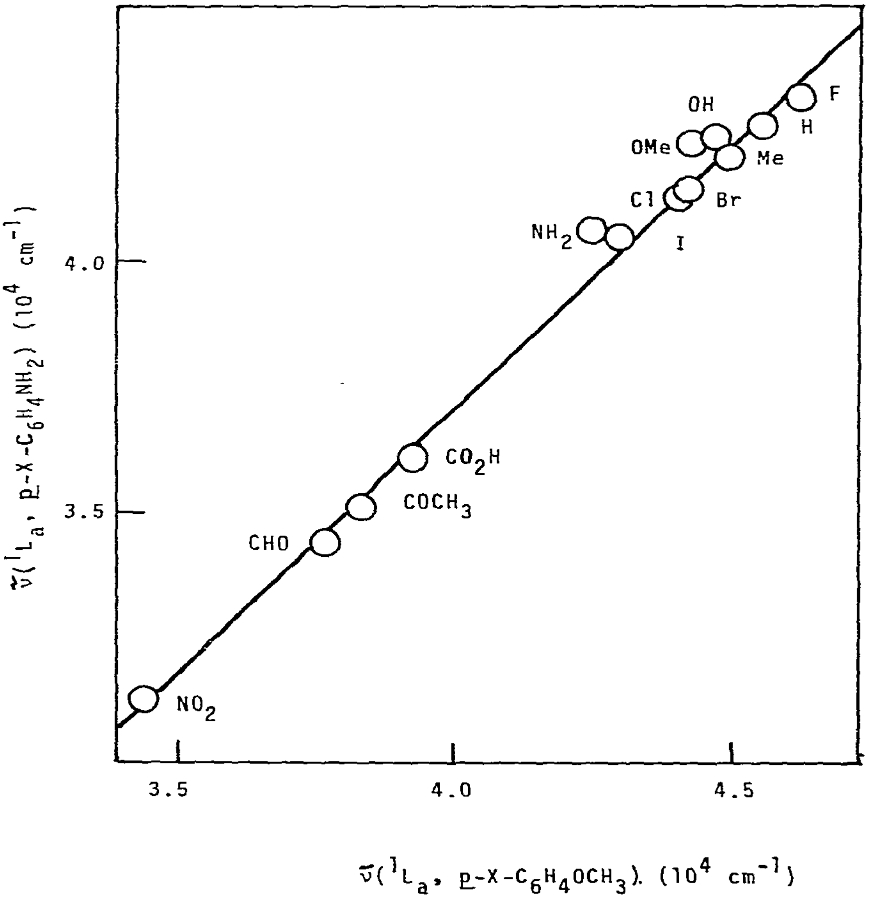


Fig. 1. Plot of $\tilde{\nu}_{max}(^1L_a)$ of *p*-substituted anilines vs. $\tilde{\nu}_{max}(^1L_a)$ of *p*-substituted anisoles.

relationship was found between *p*-substituted nitrobenzenes and other A-benzenes. Here anisoles and nitrobenzenes are taken as standard D- and A-benzenes. A typical example is shown in Fig. 1.

It is interesting to examine the substituent effects on *p*-substituted phenylpentamethyldisilane according to this treatment, since if $(p_\pi—d)$ conjugation is responsible to the intramolecular CT of phenylpentamethyldisilane, the effect should correspond to that on A-benzenes, while the effect should be that for D-benzenes if $(\sigma—p_\pi)$ conjugation is dominant. An excellent linear relationship was found between the wave numbers of the ${}^1L_a$ bands of *p*-substituted phenylpentamethyldisilanes and those of anisoles, as shown in Figure 2. However, no relationship exists between ${}^1L_a$ bands of *p*-substituted phenylpentamethyldisilanes and nitrobenzenes. Thus, it is suggested that only one intramolecular CT configuration, i.e. $(\sigma—p_\pi{}^*)$ need be taken into consideration for the electronic transition of phenylpentamethyldisilane. Table 3 lists such linear relationships for the ${}^1L_a$ bands between *p*-substituted anisoles and D-benzenes, including benzylsilanes, according to equation 2.

$$\tilde{\nu}_{\max}({}^1L_a, p\text{-X-C}_6\text{H}_4\text{D}) = a\tilde{\nu}_{\max}({}^1L_a, p\text{-X-C}_6\text{H}_4\text{OMe}) + b \qquad (2)$$

It is clear from the analysis that the pentamethyldisilanyl group, like the trimethylsilylmethyl group, must be classified as a donor group.

It is noteworthy that the coefficients *a* in eq. 2 are almost unity for X = OH,

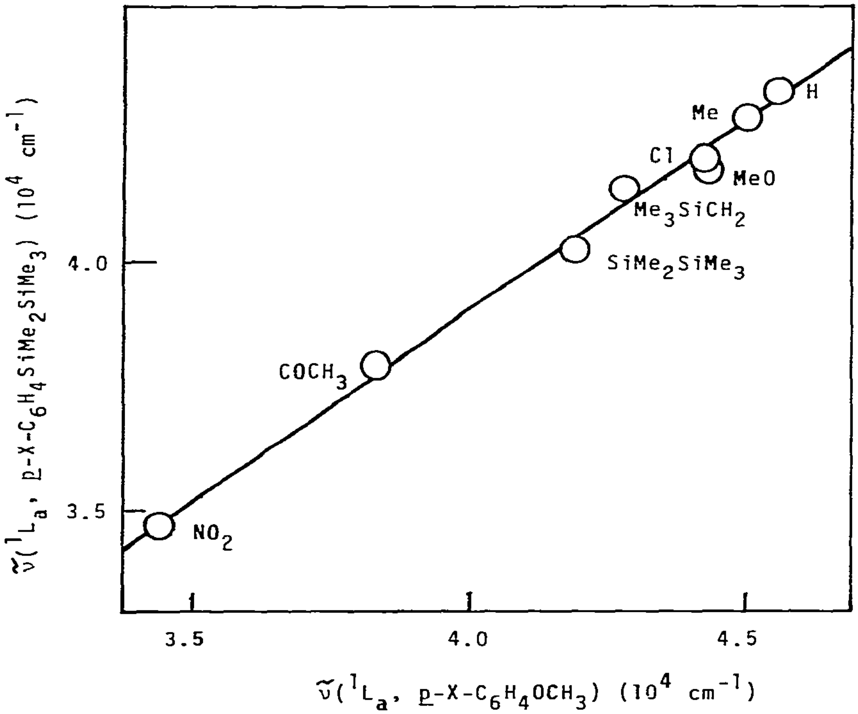


Fig. 2. Plot of $\tilde{\nu}_{\max}({}^1L_a)$ of *p*-substituted phenylpentamethyldisilanes vs. $\tilde{\nu}_{\max}({}^1L_a)$ of *p*-substituted anisoles.

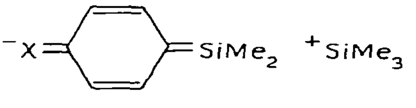
TABLE 3

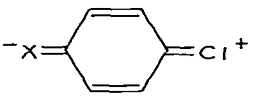
LINEAR RELATIONSHIP IN THE SUBSTITUENT EFFECTS ON $^1L_a$ BANDS BETWEEN *p*-SUBSTITUTED D-BENZENES AND ANISOLES

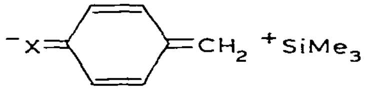
| D | $a$ [a] | $r$ [b] | $n$ [c] |
|---|---|---|---|
| OH | 1.14 | 0.992 | 13 |
| $NH_2$ | 1.08 | 0.994 | 13 |
| $CH_2SiMe_3$ | 0.914 | 0.994 | 8 |
| $Si_2Me_5$ | 0.753 | 0.995 | 8 |
| Cl | 0.722 | 0.957 | 15 |
| I | 0.797 | 0.981 | 14 |

[a] Gradient of eq. 2. [b] Correlation coefficient. [c] Number of points.

$NH_2$ and $CH_2SiMe_3$, but smaller for $Si_2Me_5$, Cl and I. Intramolecular CT from those substituents to benzene involves, in terms of the valence bond theory, the resonance structures shown. The lower ability of second-row elements to form double bonds to carbon is probably reflected in these small *a* values.







## Stereoelectronic aspects of UV absorptions of phenylpentamethyldisilanes

When the ground-state interaction between the Si—Si $\sigma$ bond and the $\pi$ system in aryldisilane was recognized at the most important factor, inductive polarization of benzene molecular orbitals by the $\beta$-trimethylsilyl group was first suggested. However, the importance of $\sigma$—$\pi$ conjugation between the Si—Si bond and the benzenoid $\pi$ system has been now demonstrated in reactions [22], and by UV, CT [16,23] and photoelectron (PE) spectra [24]. In this section, I will describe the stereoelectronic confirmation of the $\sigma$—$\pi$ conjugation in the aryldisilane system, which must be one of the most critical tests of such conjugation.

1,1,2,2-Tetramethyl-3,4-benzo-1,2-disilacyclopentene-3 (III) was prepared [25]. As shown in Fig. 3, both the Si—Si and benzylic C—Si bonds of III are in the nodal plane of the $\pi$ system, so that no $\sigma$—$\pi$ conjugation is possible in this compound since such conjugation requires coplanarity between the $p_\pi$-axis and the interacting $\sigma$ bond, as for $n$—$\pi$ and $\pi$—$\pi$ conjugation. Thus, no intense $^1L_a$ band corresponding to both benzylsilane and phenyldisilane should be observed for III and this was found to be the case. Figure 4 shows the UV spectra of III and some related compounds (IV—VI). Thus, the characteristic $^1L_a$ band of Ph—Si—Si at 230 nm (43,000 cm$^{-1}$), which is found for IV—VI, is absent for III. These results demonstrate unequivocally the importance of $\sigma$—$\pi$ conjugation with the Si—Si bond as well as with the C—Si bond in determining the electronic properties of the ground state.

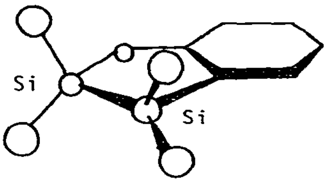
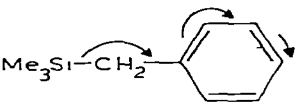


Fig. 3. 1,1,2,2-tetramethyl-3,4-benzo-1,2-disilacyclopentene 3 (III).

The rather large bathochromic effect of the $Me_3Si$ group in benzylsilanes compared to toluenes was recognized previously by Eaborn [26], who explained the effect in terms of the following delocalization, which corresponds to $\sigma$—$\pi$ conjugation *.



## Ultraviolet spectra of permethylated polysilanes and interpretation

Shortly after the discovery of the intense absorption of $^1L_a$ bands for phenyl- and vinylpolysilanes, Gilman et al. found that the polysilane skeleton itself has UV absorption [27—29]. For permethylpolysilanes, the absorption maximum of $Me(SiMe_2)_2Me$ at 190 nm moves to 215, 235 and 250 nm in $Me(SiMe_2)_3Me$, $Me(SiMe_2)_4Me$ and $Me(SiMe_2)_5Me$, respectively. Such $\sigma$-bond electronic transitions also have been observed for other Group IVB catenates such as alkanes [30], germanes [31] and stannanes [31]. The UV absorption spectra of compounds corresponding to $Me(MMe_2)_nMe$, where M = C, Si, Ge, Sn; $n$ = 2, 3, 4 ..., show bathochromic shifts as $n$ is increased.

Pitt, Jones and Ramsey considered that the UV absorption involved a transition between a fixed $\sigma$ bonding orbital and the various unoccupied molecular orbitals [14]. They assumed that the excited state of the transition was constructed as a linear combination of unoccupied orbitals of $\pi$ symmetry localized on each $SiMe_2$ unit. Then for a chain of $n$ atoms, the $n$ molecular orbitals will have energies expressed by equation 3.

$$E_j^* = \alpha_{Si}^* + 2\beta_{Si}^* \cos(J\pi/n + 1) \qquad (3)$$

$(J = 1, 2, \ldots n)$

They also assumed $E_\sigma$, the energy level of the $\sigma$ orbitals, to be constant. Then the frequency ($\nu_n$) of the transition from $E_\sigma$ to the lowest unoccupied MO (eq. 3, $J = 1$) is given by equation 4.

$$h\nu_n = (\alpha_{Si}^* - E_\sigma) + 2\beta_{Si}^* \cos(\pi/n + 1) \qquad (4)$$

The plot of transition energies of $H(SiMe_2)_nH$ and $CH_3(SiMe_2)_nCH_3$ against

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* For a brief historical note and references on the concept of $\sigma$—$\pi$ conjugation, see ref. 26b.

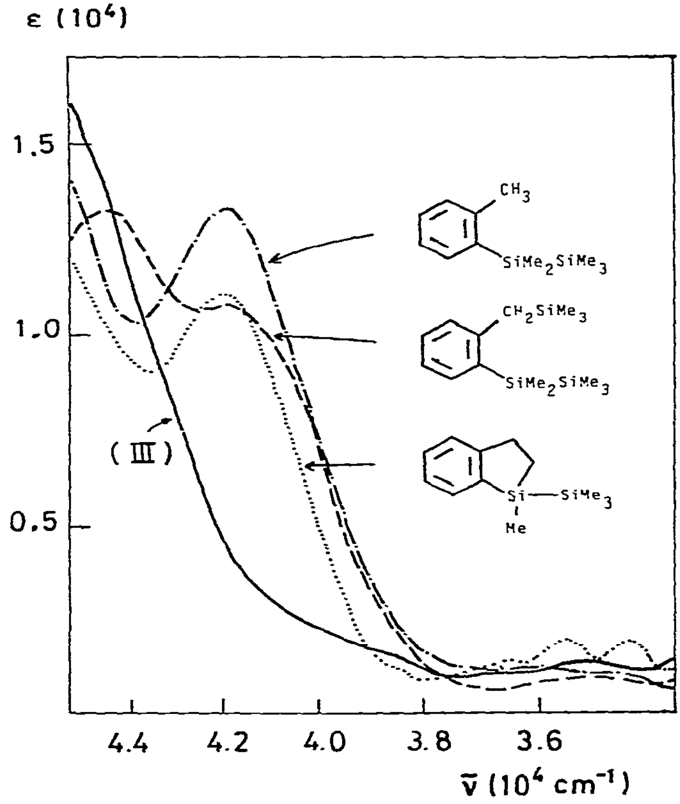


Fig. 4. UV spectra of III and related compounds.

2 cos($\pi/n + 1$) yields a good linear relation except for $n = 2$ [14]. However, later, Pitt et al. demonstrated that the ionization potentials (*IP*) of $Me(SiMe_2)_nMe$ determined by the electron impact method give an excellent linear correlation with $h\nu_n$ [32,33].

The energy not only of the HOMO but also the lower bonding orbital energies of permethylpolysilanes have been determined by PE spectroscopy and analyzed by the LCBO model by Bock et al. [34]. Thus, the eigenvalues of polysilanes are expressed by equation 5 very nicely with $\alpha_{Si-Si} = 8.69$ eV and $\beta_{Si-Si} = 0.5$ eV.

$$E_J = \alpha_{Si-Si} + 2\beta_{Si-Si}\,\mathrm{cis}(J\pi/n + 1) \qquad (5)$$

$$(J = 1, 2, 3 \ldots n)$$

The photoelectron spectra of phenylpentamethyldisilane were also determined by Bock and Pitt and found to show bands at 8.35, 9.07 and 10.03 eV. It is interesting to compare phenylpentamethyldisilane with benzyltrimethylsilane, since the latter has identical energy for the highest occupied molecular orbital (8.35 eV) [24] but a considerably different absorption for the $^1L_a$ band at 233 nm (44,800 cm$^{-1}$). Thus, the energy level of the excited state of phenylpentamethyldisilane is lower than that of benzyltrimethylsilane because of $\pi$—$\sigma^*$ (or *d*) mixing [25].

## Charge transfer spectra

It has been well established that $\pi \rightarrow \pi$ and $n \rightarrow \pi$ electron donor acceptor interactions occur extensively, for example, with tetracyanoethylene (TCNE) as an acceptor [27], but relatively few examples of such interaction with $\sigma$ donors are known. It seemed very interesting to examine the donor properties of permethylpolysilanes by CT spectra. We [38] and West and Traven [39] found that such CT interactions do actually exist in permethylpolysilanes. Table 4 lists the frequencies of band maxima and IP of polysilanes as determined by electron impact [33] and PE spectroscopy [34].

Although the CT interactions between these polysilanes and TCNE are weak, well-defined CT bands were observed. Interestingly, a very good linear relationship between the CT frequencies and the IP's of the respective polysilanes was established.

$$h\nu_{CT}(\text{eV}) = 0.77\, IP(\text{PE}) - 3.71_6\ (r = 0.999) \qquad (6)$$

The energy of the CT interaction can be related to the difference in the energy of the HOMO of the donor ($E_{HOMO}$) and that of the lowest unoccupied molecular orbital (LUMO) of the acceptor ($E_{LUMO}$), namely

$$h\nu_{CT} = E_{LUMO} - E_{HOMO} + 2\beta \qquad (7)$$

where $\beta$ is the interaction energy between HOMO and LUMO. According to the Koopman theory, $E_{HOMO}$ can be equated with the IP of the donor molecule, and for a given acceptor (i.e. TCNE in this case) and a set of donors of similar structure, both $E_{LUMO}$ and $\beta$ can be assumed to be constant. Then equation 7 can be expressed as

$$h\nu_{CT} = aIP + \text{Const.} \qquad (8)$$

Therefore, the observation of a good linear relation between $h\nu_{CT}$ and IP for the polysilanes demonstrates that an electron-transfer from a $\sigma$ bond to a $\pi$ acceptor really occurs.

The CT spectrum of phenylpentamethyldisilane was of considerable interest, since in terms of $\sigma$—$\pi$ conjugation the vertical stabilization by the Si—Si bond

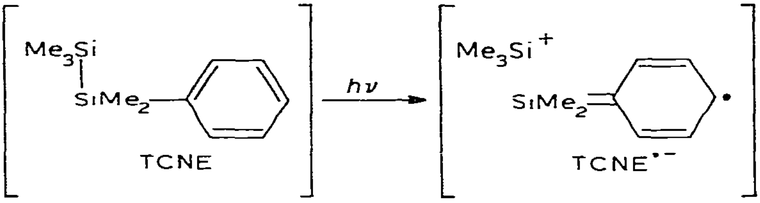
TABLE 4

FREQUENCIES OF CHARGE-TRANSFER ABSORPTIONS IN COMPLEXES OF TCNE WITH PERMETHYLPOLYSILANES, $Me(SiMe_2)_nMe$, IN DICHLOROMETHANE AT ROOM TEMPERATURE

| $n$ | $\tilde{\nu}_{max}$ ($cm^{-1}$) | $\nu_{max}$ (eV) | $IP$(EI) (eV) | $IP$(PE) (eV) |
|---|---|---|---|---|
| 2 | 24,000 | 2.97 | 8.00 | 8.69 |
| 3 | 21,100 | 2.61 | 7.53 | 8.19 |
| 4 | 19,600 | 2.43 | 7.29 | 7.98 |
| 5 | 18,400 | 2.28 | 7.11 | (7.79) |

[a] Calculated from the relationship between $IP$(EI) and $IP$(PE) for linear permethylpolysilane: $IP(\text{PE}) = 1.099\, IP(\text{EI}) + 0.613$ ($r = 0.999$).

in the CT complex must involve a silicon—carbon double bond.



(9)

We examined CT spectra of several α-naphthyl, β-naphthyl and phenyl derivatives of the structure of Ar—X, where X = $Me_3SiSiMe_2$, $Me_3SiCH_2$, MeO and $CH_3$, and determined their ionization potentials [40]. According to the perturbation theory, the extent of the stabilization or destabilization energy, $\Delta E$, can be expressed by the following expression in terms of the change in the ionization potential, where $c_i$ is the coefficient of the atomic orbitals at the

$$\Delta E(IP) = c_i^2\beta'^2/|E_\sigma - E_\pi| \quad (10)$$

point of substituent group attachment in the pertinent π orbitals of benzene or naphthalene and β′ is a measure of the interaction between two orbitals.

For naphthalene, two well-separated CT bands were obtained, one from the HOMO ($E_\pi$ = 8.03 eV) and the other from the penultimate occupied MO ($E_\pi$ = 8.78 eV). Therefore, we obtained four sets of CT bands from α- and β-naphthyl derivatives and one from the phenyl derivative for a particular Ar—X. These CT frequencies are converted to $\Delta E(IP)$ values, which give a good linear correlation with $c_i^2/|E_\sigma - E_\pi|$. The β′ values obtained from gradients in eV are: 1.97 for $CH_3$, 2.08 for MeO, 1.69 for $Me_3SiCH_2$, and 0.54 for $Me_3SiSiMe_2$. From these data, it is concluded that a silicon 3*p* orbital is only about one third as effective as carbon or oxygen 2*p* orbital in overlap with carbon π systems. The considerable σ—π interaction seen in phenylpentamethyldisilane and other Si—Si substituted π systems may be attributed to the very high energy of the Si—Si σ orbital.

Another interesting problem in the CT spectra of phenylpentamethyldisilane is the fact that the low energy band (CT-II), which must originate from the HOMO composed of σ(Si—Si) and $\psi_s$ of benzene, has an extremely low intensity compared with the higher energy band (CT-I) (Figure 5), while benzyltrimethylsilane, anisole and even naphthylpentamethyldisilanes show two well-separated CT bands with comparable intensities [23,40,41]. The reason why the intensity of the CT-II band is so low called for explanation.

We measured two CT bands of *p*-R—$C_6H_4SiMe_2SiMe_3$—TCNE (R = H, Me, $Me_3SiCH_2$ and MeO) complexes in dichloromethane and determined the relative intensities of the two bands by computer-aided analysis [42]. As shown in Figure 6, the relative intensity, (Area II/Area I), increases with the increasing donor capcity of the R group. Experimentally the relative intensities can be correlated with the $\sigma^+$ constants of the substituents (Figure 6). The HOMO of a *p*-substituted phenylpentamethyldisilane is constructed from the

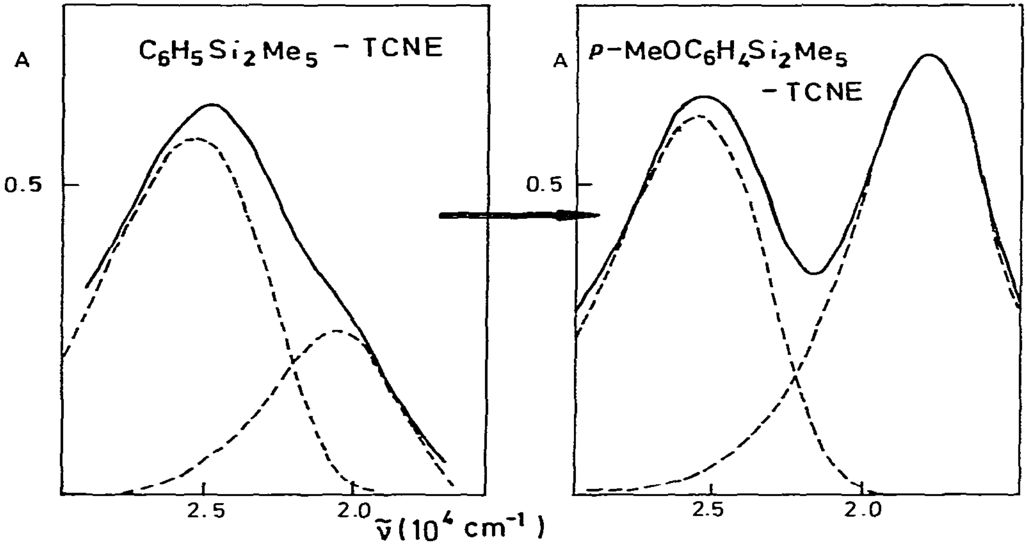


Fig. 5. Change of CT spectra from phenylpentamethyldisilane to $p$-anisylpentamethyldisilane.

symmetric HOMO of benzene ($\phi_s$), the Si—Si $\sigma$ orbital ($\phi_{Si}$) and an appropriate $\pi$-type substituent orbital ($\phi_x$).

$$\psi_{HOMO} = a\phi_s + b\phi_{Si} + c\phi_x \qquad (11)$$

$$(a^2 + b^2 + c^2 = 1)$$

The energy levels and wave functions of the HOMO of the $p$-substituted phenylpentamethyldisilane are calculated as shown in Table 5. Now, the calculated

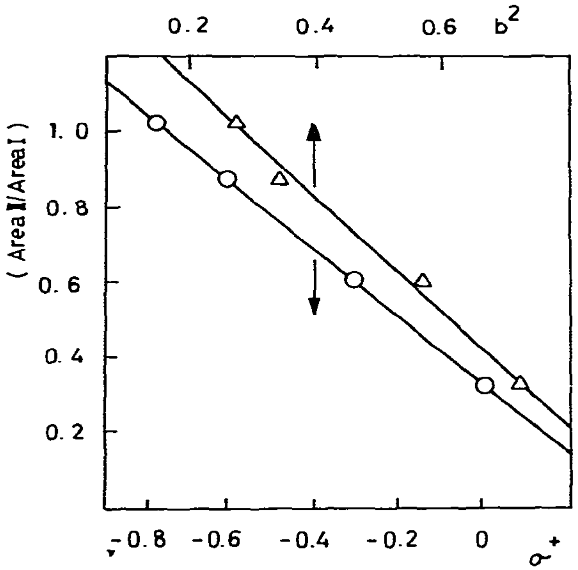


Fig. 6. Plot of relative area (Area II/Area I) for the absorption spectra of substituted phenylpentamethyldisilane-TCNE complexes vs. $\sigma^+$ and $\sigma$(Si—Si) fraction of HOMO of phenylpentamethyldisilanes.

TABLE 5

CALCULATED FIRST IONIZATION POTENTIALS AND WAVE FUNCTIONS OF THE HOMO FOR *para*-SUBSTITUTED PHENYLPENTAMETHYLDISILANES ($X—C_6H_4Si_2Me_5$)

| X | $IP^a$ (eV) | Wave function | σ(Si—Si) fraction |
|---|---|---|---|
| H | 8.35 (8.39) | $0.851\phi_{Si} - 0.526\phi_S$ | 0.72 |
| *p*-Me | 8.23 (8.24) | $0.757\phi_{Si} - 0.631\phi_S - 0.171\phi_X$ | 0.57 |
| *p*-$Me_3SiCH_2$ | 8.02 (7.92) | $0.583\phi_{Si} - 0.710\phi_S - 0.395\phi_X$ | 0.34 |
| *p*-MeO | 7.93 (7.92) | $0.519\phi_{Si} - 0.713\phi_S - 0.471\phi_X$ | 0.27 |

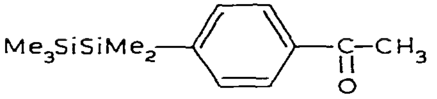
[a] Ionization potentials estimated by the equation of Voigt-Reid are shown in parentheses.

populations of σ(Si—Si) orbitals in the HOMO, $b^2$, show a linear correlation with the relative area (Area II/Area I) (Figure 6). Thus, these facts indicate that the low intensity of the CT-II band of phenylpentamethyldisilane originates mainly in the high σ fraction in the HOMO.

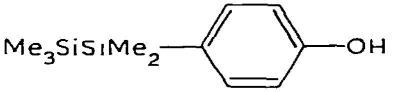
## Pentamethyldisilanyl-substituted phenol and acetophenone (NMR and IR spectra)

The UV, CT and PE spectra of pentamethyldisilanyl-substituted π systems have all indicated that the $Me_5Si_2$ group is a σ donor group as discussed above, although the acceptor character of the $Me_5Si_2$ group due to $\sigma^*$ (or *d*) orbitals always acts to some extent in the opposite direction. The relative importance of the two influences may be determined by the characters of the ground and excited states of a particular system. We have already seen that the $Me_5Si_2$ group affects the levels of both the ground and excited states in the UV absorption of phenylpentamethyldisilane.

A good measure of the electric properties of a particular group is provided by its Hammett σ constant. In particular, $\sigma^+$ and $\sigma^-$ constants represent donor and acceptor properties in systems with enhanced conjugation between the benzene ring and the substituent, respectively. We thus prepared pentamethyldisilanyl-substituted acetophenone (IV) and phenol (V) [43] in the hope of determining $\sigma^+$ and $\sigma^-$ values for $Me_5Si_2$ and related groups, since it was well established that the carbonyl stretching frequencies of *p*-substituted acetophenones [44] and the hydroxyl proton chemical shifts of *p*-substituted phenols [45] are related to $\sigma^+$ and $\sigma^-$ constants of the substituent, respectively.



(IV)



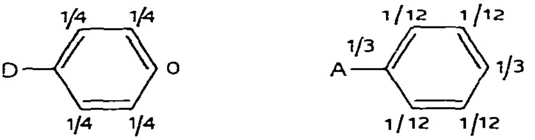
(V)

(12)

The $\sigma^+$ values of $Me_3Si$ and $Me_5Si_2$ thus determined are 0.0 and —0.23, respectively, indicating the stronger electron-releasing nature of the $Me_5Si_2$ than of the $Me_3Si$ group in the ground state. In contrast, the $Me_3Si$ and $Me_5Si_2$ groups have almost the same $\sigma^-$ values, 0.06 and 0.02, respectively. This means that the acceptor property of the $Me_5Si_2$ group is not significantly different from that of the $Me_3Si$ group in the ground state.

## The effect of the pentamethyldisilanyl group on the benzene anion and cyclopentadienyl radicals

The substituent effects on the electron spin resonance (ESR) spectra of anion radicals of monosubstituted benzenes have been well established [46]. In the simple approach within a framework of the Hückel MO theory, the benzene anion radical has doubly degenerate singly occupied antibonding orbitals, i.e. symmetric (S) and antisymmetric (A) orbitals, the degeneracy of which is changed by a substituent. The nature of the substituent determines which of the S and A orbitals has the lower energy. A donor group prefers the A orbital, simply as a result of the substituent occupying a node to minimize electron respulsion interactions, while in the case of an acceptor group the S orbital may be preferred because the group can be located at the position of high spin density. The theoretical spin distributions are shown below.



(13)

Although there exist obvious discrepancies between theoretical and experimental spin distributions, it is useful to assess the electronic nature of a substituent from the hyperfine coupling constants (hfcc, $a_H$) (which is related to the spin density, $\rho$, by the McConnell equation, $a_H = Q\rho$) of the given anion radical. Table 6 lists the hfcc for some anion radicals. The *para* coupling constants are particularly diagnostic as a measure of the electron-accepting capacity of the substituents, and it is obvious from the results that both $Me_3Si$ and $Me_5Si_2$ groups are acceptors in the benzene anion radical, in which the unpaired electron resides in the antibonding orbital which interacts with the low-lying vacant orbitals of silyl groups.

However, in cyclopentadienyl radicals an unpaired electron must occupy the bonding orbital as shown in Figure 7, and therefore we can expect different substituent effects from those on benzene anion radicals. Recently we generated a number of silyl- [49,50]and alkyl-substituted [51] cyclopentadienyl radicals and analyzed the ESR spectra.

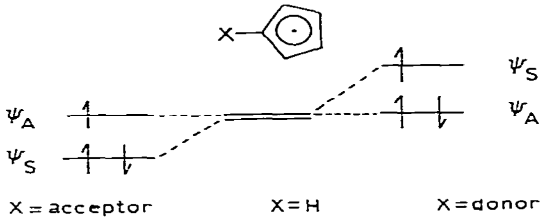
As shown in Figure 7, the lowest energy $\pi$-electron configuration of the planar, symmetrical cyclopentadienyl radical is doubly degenerate. Degeneracy of the two bonding orbitals, $\psi_A$ and $\psi_S$, is removed by a substituent for the reason discussed in the case of benzene anion radicals. Thus in the case of an acceptor group, the level of $\psi_S$ is lowered as it can be located at the position of high electron density. It should be noted that the unpaired electron should occupy $\psi_A$ orbital to have an electron configuration $\psi_S{}^2\psi_A{}^1$. In the case of a donor-substituted cyclopentadienyl radical, $\psi_S$ is destabilized by the electron-

TABLE 6

HYPERFINE COUPLING CONSTANTS OF GROUP IVB ELEMENT-SUBSTITUTED BENZENE ANION RADICALS IN GAUSS

| X in X—Ph | $a_o$-H | $a_m$-H | $a_p$-H | Ref. |
|---|---|---|---|---|
| $Me_3C$ | 4.66 | 4.66 | 1.74 | 47 |
| $Me_3Si$ | 2.66 | 1.06 | 8.13 | 47 |
| | 2.65 | 1.06 | 8.09 | 48 |
| $Me_5Si_2$ | 2.67 | 0.93 | 8.15 | 48 |
| $Me_3Ge$ | 2.33 | 1.46 | 7.61 | 47 |

repelling effect, so that it prefers the $\psi_A{}^2\psi_S{}^1$ configuration.



The energy difference between the two configurations is small and appreciable mixing of the two forms occurs. For example, $\psi_A{}^2\psi_S{}^1$ (S form), the electronic configuration of the donor-substituted cyclopentadienyl radical, may be mixed with $\psi_A{}^1\psi_S{}^2$ (A form).

$$\psi_A{}^2\psi_S{}^1 \rightleftharpoons \psi_A{}^1\psi_S{}^2 \tag{14}$$

From the analysis of the coupling constants, the relative probabilities that the

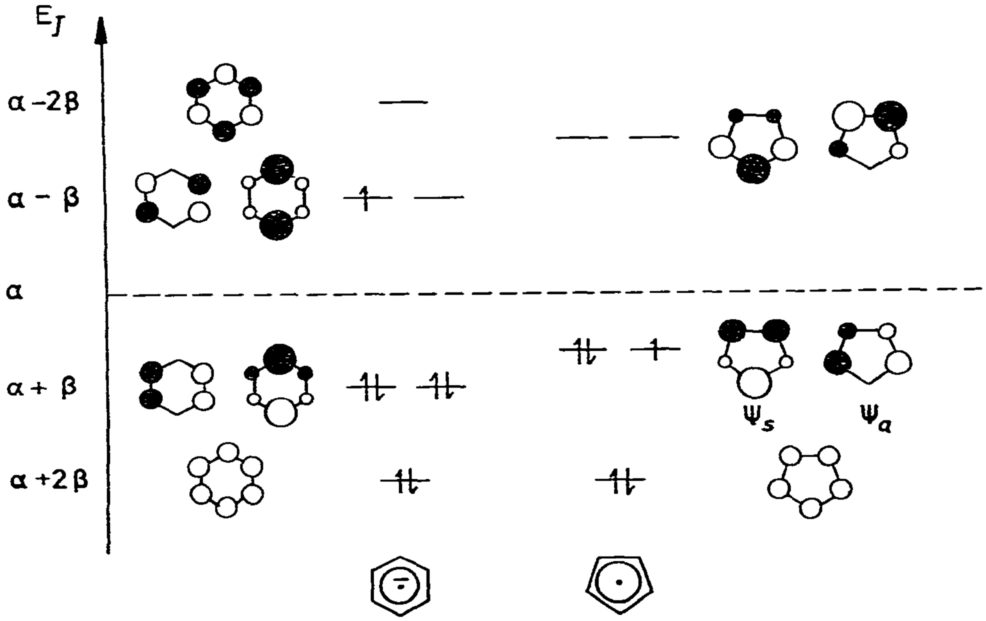
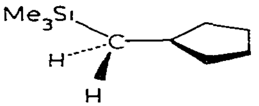


Fig. 7. HMO energy diagram for cyclopentadienyl and benzene anion radicals.

radical is in the S and A forms, $P_S$ and $P_A$, are obtained. $P_S$ (or $P_A$) is a measure of the capacity of the donor (or acceptor). Thus, the larger is the $P_S$, the more electron donating is the substituent. For the unsubstituted cyclopentadienyl radical, $P_S$ is equal to $P_A$ (= 1/2).

The $P_S$ values are very sensitive to the nature of substituents, varying from almost 1 for $Me_3SiCH_2$ to almost 0 for $Cl_3Si$. The order of electron-releasing capacity of a variety of substituent is: $Me_3SiCH_2$ (the strongest donor) > $CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C > Me_3SiSiMe_2SiMe_2 > Me_3SiSiMe_2 >$ H (neutral) $\approx Me_3Ge > Me_3Si > Me_2(t\text{-}BuO)Si > Me_2PhSi > Me_2(Me_3SiO)Si > MePh_2Si > Me_2ClSi > MeCl_2Si > Cl_3Si$ (the strongest acceptor).

It is interesting to note that all monosilyl groups are electron accepting for a singly occupied MO of the cyclopentadienyl radical and that the electron accepting ability is greatly affected by substituent(s) on the silicon atom. Both n-$Me_7Si_3$ and $Me_5Si_2$ groups are electron donating owing to the predominant contribution of $\sigma$(Si—Si)—$\pi$ conjugation. However, the ability of polysilanyl groups to donate electrons to the singly occupied MO is smaller than that of alkyl groups. The Baker-Nathan order applies among the alkyl groups, and the $Me_3SiCH_2$ group is the strongest donor of these examined. The trimethylsilyl group of VI preferentially eclipses the *p*-orbital on the $C_1$ atom of the cyclopentadienyl ring throughout the temperature range studied.



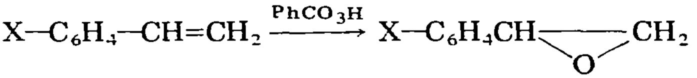
(VI)

### Some reactions of the silicon—silicon bond

During the course of the spectroscopic and related chemical studies on organopolysilanes, the so-called "double bond character" of the silicon—silicon bond came to our notice. For example, organodisilanes are oxidized by perbenzoic acid to give the corresponding disiloxanes [52].

$$X\text{—}C_6H_4\text{—}SiMe_2SiMe_3 \xrightarrow{PhCO_3H} X\text{—}C_6H_4\text{—}SiMe_3\text{—}O\text{—}SiMe_3 \qquad (15)$$

The reaction is analogous to the well-known epoxidation of olefins.



$$X\text{—}C_6H_4\text{—}CH{=}CH_2 \xrightarrow{PhCO_3H} X\text{—}C_6H_4CH\underset{O}{\text{——}}CH_2 \qquad (16)$$

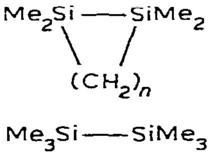
Insertion of an oxygen atom is characteristic of both reactions. Such analogy in the nature of the reactions of Si—Si $\sigma$ and C=C $\pi$ bonds can be seen for other electrophiles, and may be rationalized in terms of the donor property of both $\sigma$ and $\pi$ electrons.

Moreover, the rate of oxidation of $X\text{—}C_6H_4Si_2Me_5$ with perbenzoic acid (eq. 16) is nicely correlated with Brown's $\sigma^+$ constants [52].

$$\log(k/k_H) = -0.29\sigma^+ \ (r = 0.999) \qquad (17)$$

The dependence on the $\sigma^+$ constants has been demonstrated for numerous reactions with electrophiles, including epoxidation, so that the naive concept of the "double bond character" of the Si—Si bond receives support from kinetic studies.

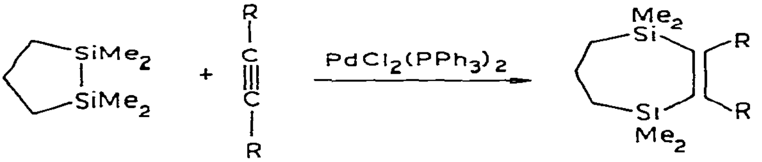
Next, we have examined oxidation of cyclic carbodisilanes [53]. The CT energies of these carbodisilanes with TCNE increase regularly with increasing ring size, so that it is clear that the HOMO is raised by decreasing ring size, probably because of ring strain.



| | $n$ | $\tilde{\nu}_{CT}$(cm$^{-1}$) |
|---|---|---|
| VII | 3 | 21,600 |
| VIII | 4 | 27,500 |
| IX | 5 | 23,500 |
| | | 24,000 |

Reflecting the difference in the HOMO levels, the most strained disilacyclopentane (VII) was oxidized more than 1000 times faster than the open-chain hexamethyldisilane by *m*-chloroperbenzoic acid. Interestingly, a good linear relationship was observed between $\Delta H^{\neq}$ of the reaction and $E_{CT}$ which demonstrates the importance of the donor-acceptor interaction between disilane and peracid.

Recently, we have observed interesting cycloaddition reactions between σ(Si—Si) and C≡C π bond catalyzed by palladium complexes [54].

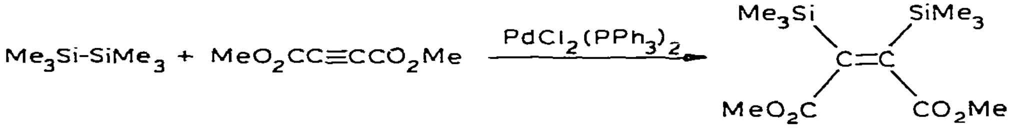


(18)

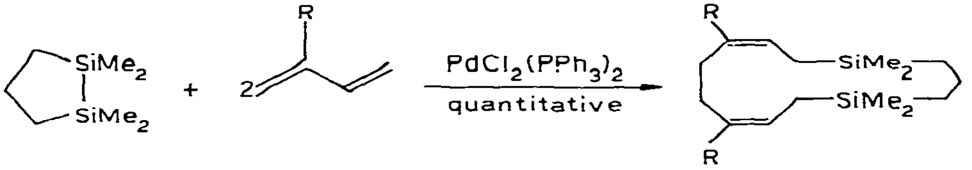
(VII) (X)

a; R = COOMe; Y = 83 4%
b; R = H ; Y = 53.3%

Since the reaction of hexamethyldisilane with dimethylacetylene dicarboxylate gave only the *cis* adduct (XI), the mode of the reaction resembles formally a thermally forbidden [$\sigma^2_s + \pi^2_s$] reaction, which may become allowed by the action of a catalyst.



(19)



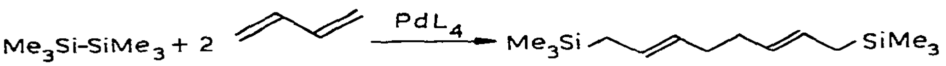
(20)

(VII) (XIII)

a; R = H, b; R = Me

Disilanes also undergo a 1 : 2 cycloaddition with dienes as illustrated below [55].

The reactivity of hexamethyldisilane is rather low, but the yield of the following reaction to give the synthetically useful adduct (XIV) is improved to more than 85% [56].

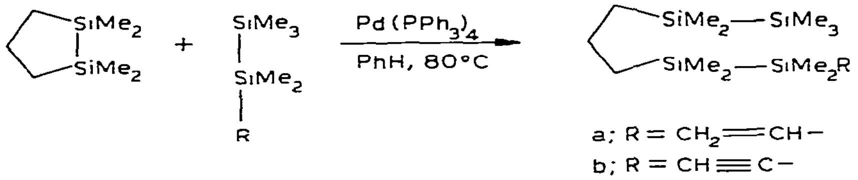


(21)

(XIV)

Thermal (forbidden) and catalyzed (allowed) metatheses of organodisilanes have been observed [57,58].

$$\text{i-PrMe}_2\text{Si—SiMe}_2\text{—i-Pr} + \text{Me}_3\text{Si—SiMe}_2 \underset{180\ \text{days}}{\overset{190°\text{C}}{\rightleftharpoons}} 2\ \text{i-PrMe}_2\text{Si—SiMe}_3 \qquad (22)$$

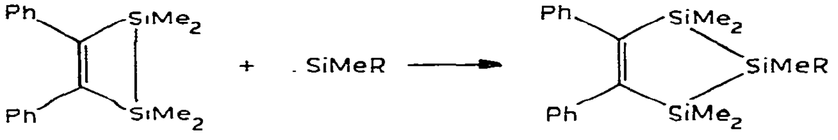


(23)

a; R = $CH_2{=}CH-$

b; R = $CH{\equiv}C-$

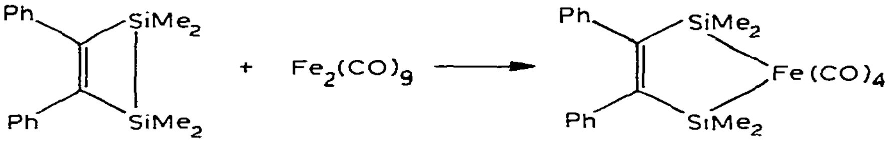
Insertion of divalent species such as $Me_2Si$ and $Fe(CO)_3$ into the Si—Si bond occurs for strained disilacyclobutenes [59].



(24)

(XVI) (XVII)

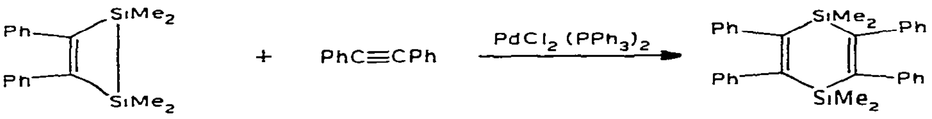
a; R = Me, b; R = Ph



(25)

(XVI) (XVIII)

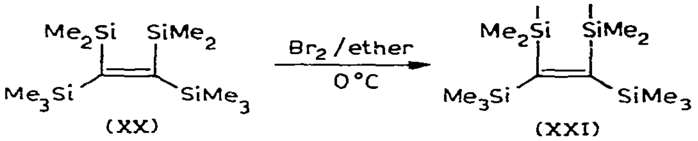
It is interesting to note that the palladium-catalyzed addition of an acetylene to XVI occurs with the Si—Si but not with the C=C bond of disilacyclobutene [59].



(26)

(XVI) (XIX)

An important development of the chemistry of disilacyclobutene can be seen in the preparation of very crowded tetrakis(trimethylsilyl)ethylene (XXII) and related compounds as depicted by the following equations [60,61]. *



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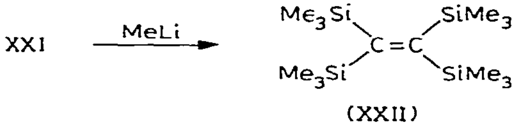

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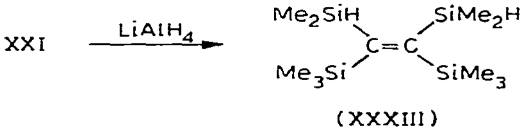

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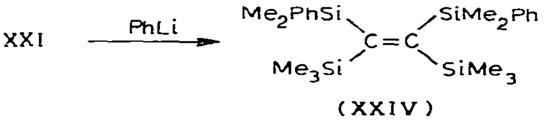

(30)

These hindered olefins show interesting reversible thermochromism and unusual spectral properties. (*z*)-XXXIV isomerizes to the (*E*)-isomer very rapidly and the activation energy of the *cis—trans* isomerization is estimated to be 33 kcal/mole [61].

The $S_H2$ reaction of disilanes with bromine derived from 1,2-dibromoethane, which formally resembles free radical addition of bromine, occurs very smoothly to give bromosilanes [64,65]

$$\begin{aligned} &Br^{\cdot} + R{-}Me_2SiSiMe_2R \rightarrow RMe_2Si^{\cdot} + RMe_2SiBr \\ &RMe_2Si^{\cdot} + BrCH_2{-}CH_2Br \rightarrow RMe_2SiBr + {}^{\cdot}CH_2CH_2Br \qquad (31) \\ &{}^{\cdot}CH_2CH_2Br \rightarrow CH_2{=}CH_2 + Br^{\cdot} \end{aligned}$$

## Photochemistry of organopolysilanes

Because phenyl and vinylpolysilanes as well as aliphatic polysilanes have characteristic UV absorption, their photochemistry is of considerable interest. Since we have recently reviewed the photochemistry of organosilicon compounds [66], only selected examples, mostly from our laboratory, will be reviewed.

In 1969, when I have moved to Tohoku University in Sendai, we initiated the photochemical studies of organopolysilanes. Kumada and his coworkers

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* The preparation of XXII has been recorded without structural evidence [62]. See also ref. 63.

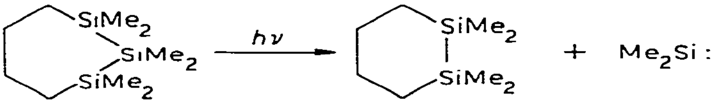
also began photochemical studies in the same year [67], and reported the photolysis of dodecamethylcyclohexasilane and permethylpolysilanes [68].

$$(Me_2Si)_6 \xrightarrow{h\nu} (Me_2Si)_5 + Me_2Si: \qquad (32)$$

$$Me(Me_2Si)_nMe \xrightarrow{h\nu} Me(Me_2Si)_3Me + (n-3)Me_2Si: \qquad (33)$$

$n = 4 \sim 6$

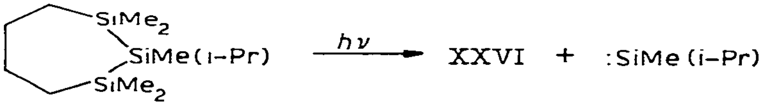
The system we chose first was 1,2,3-trisilacycloheptane, since trisilane was the smallest unit to exhibit UV absorption at a wave length longer than 200 nm.



(34)

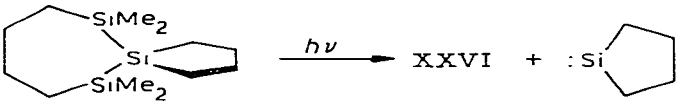
(XXV) (XXVI)

Irradiation of 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloheptane (XXV), which has an absorption maximum at 221 nm, with a low pressure mercury arc lamp under nitrogen gave a single volatile product which was identified as 1,1,2,2-tetramethyl-1,2-disilacyclohexane (XXVI). The fact that the silicon atom involved in the silylene moiety comes from the central silicon atom of XXV is substantiated by the following examples [69].



(35)

(XXVII)

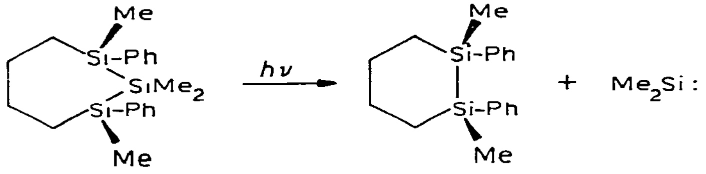


(36)

(XXVIII)

This reaction is not only important for its mechanistic implications but useful as a method of generating a "tailor-made" silylene.

We next demonstrated that extrusion of silylene from the 1,2,3-trisilacycloheptane system occurs highly stereospecifically, with complete retention of the *cis-trans* stereochemistry for both *cis*- and *trans*-1,3-diphenyl-1,2,2,3-tetramethyl-1,2,3-trisilacycloheptane (XXIX) [70].



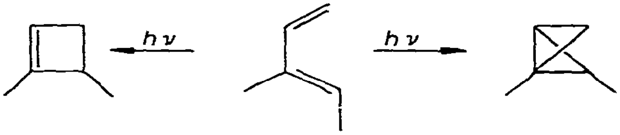
(37)

(XXIXa) *(cis)* (XXXa) *(cis)*

(XXXIXb) *(trans)* $\xrightarrow{h\nu}$ (XXXb) *(trans)*

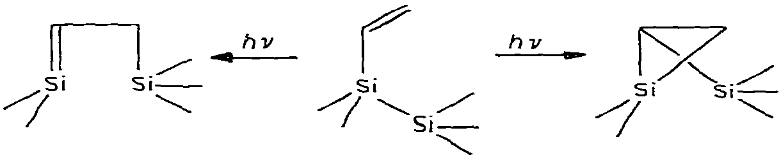
These results are consistent with a concerted elimination of the silylene, and the unique photochemical reaction in cyclic polysilanes may be regarded as a chelatropic reaction in a system composed of only a "σ" electron framework.

Intriguing polysilanes from a photochemical point of view are vinyldisilanes, since in the sense of the "double bond character" of the Si—Si bond, a vinyldisilane may be regarded as an analogue of a 1,4-diene. The photochemistry of 1,4-diene is well-established to be that illustrated below.



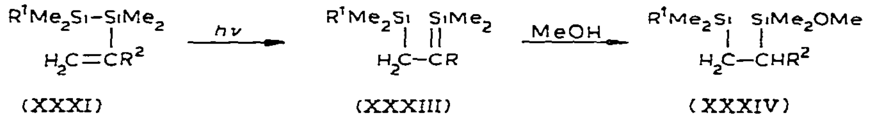
(38)

If a double bond of 1,4-diene is replaced with a Si—Si bond, one gets vinyldisilane, photolysis of which should result in the following two reactions.



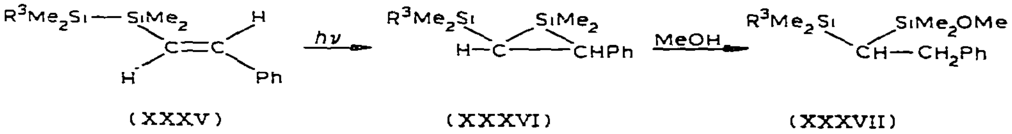
(39)

We have indeed, found these two types of photochemical reactions for vinyldisilanes [71].



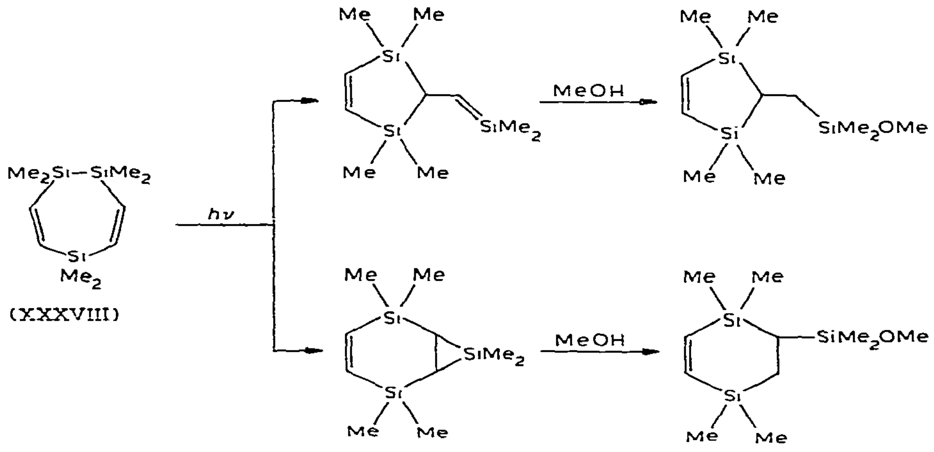
a $R^1 = R^2 = Me$
b $R^1 = Me$; $R^2 = H$
c $R^1 = Me$; $R^2 = Ph$
d $R^1 = CH_2{=}CH-$; $R^2 = H$
e $R^1 = CH_2{=}CMe-$, $R^2 = Me$
f $R^1 = CH_2{=}CPh-$; $R^2 = Ph$

(40)



a $R^3 = Me$
b $R^3 =$ *trans*$-PhCH{=}CH-$

(41)

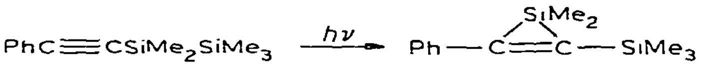


(42)

The intermediate silaethene (XXXIII) and silacyclopropane derivatives (XXXVI) were not isolated, but the nature of the reaction of these unstable molecules with methanol had been established [72,73].

The course of the reaction depends upon the structure of the disilane, but in some case two types of reaction can occur competitively from a single compound (XXXVIII) [74].

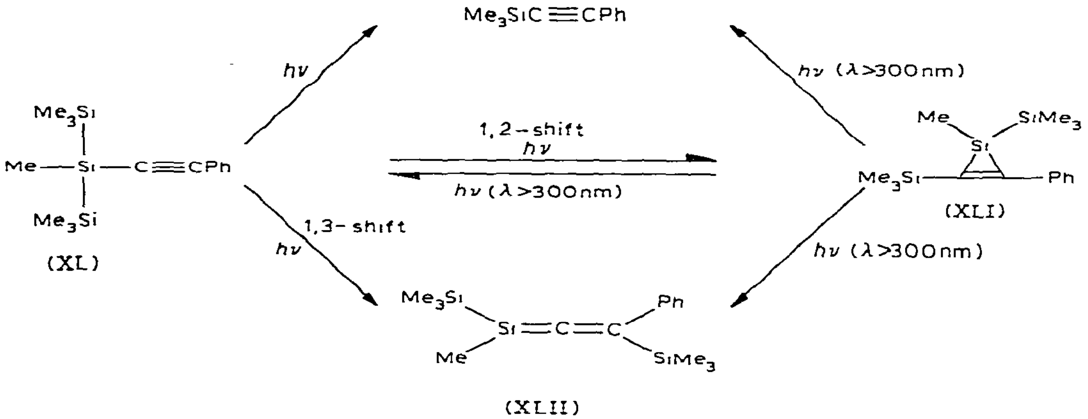
As a logical extension of the studies of the photochemistry of vinyldisilanes, we examined the photolysis of (pentamethyldisilanyl)phenylacetylene, which led to an entirely new route to a silacyclopropene [75].



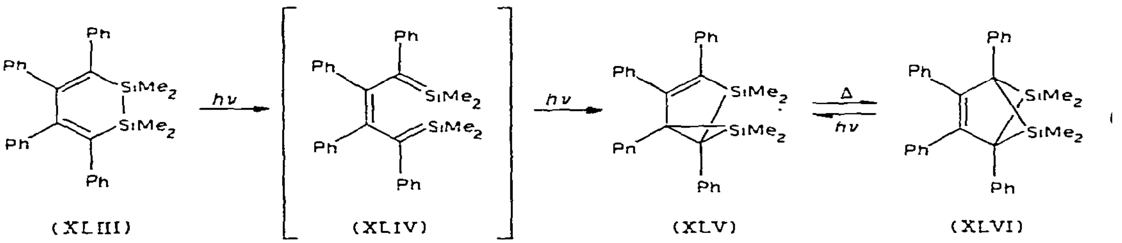
$$PhC\equiv CSiMe_2SiMe_3 \xrightarrow{h\nu} Ph-\overset{SiMe_2}{C{=}C}-SiMe_3 \qquad (43)$$

(XXXIX)

We have prepared a variety of silacyclopropenes, some of which are air stable. The following example shows photochemical transformation of ethynylpolysilane to both silacyclopropene and 1-silapropadiene [76].

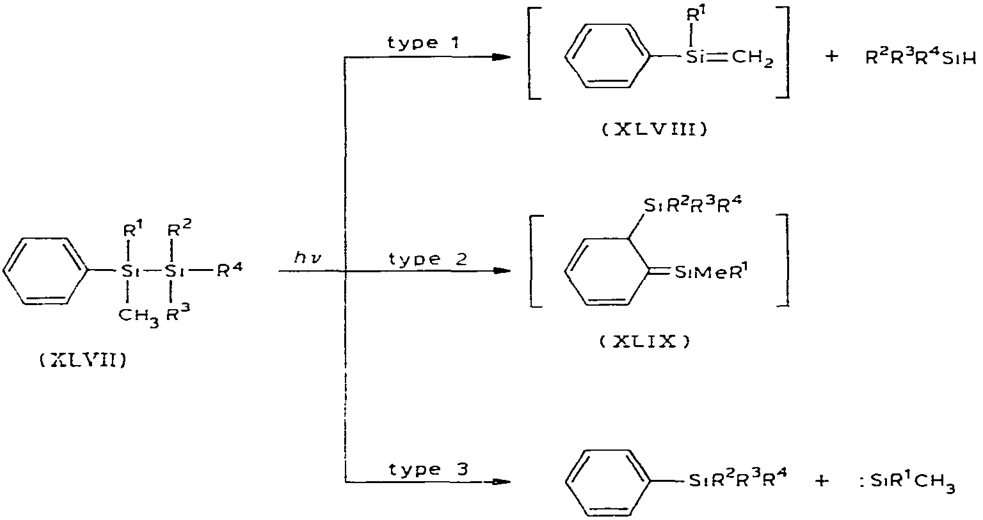


Photochemical reactions of 1,2-disila-3,5-cyclohexadienes such as XLIII [77] and related 1-sila-2,4-hexadienes [78] are of interest in relation to the photochemistry of cyclohexadiene.



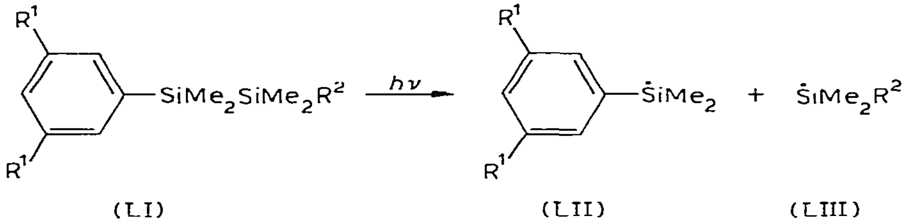
Conversion of XLV into XLVI occurs when XLV is heated. This is the first example of a vinylsilacyclopropane—silacyclopentene rearrangement. Interestingly, XLVI reverts to XLV upon irradiation. In these compounds there is no extensive $\sigma$—$\pi$ conjugation since the Si—Si bond lies in the nodal plane of the diene moiety.

The photolysis of an aryldisilane was reported first by Boudjouk, Roberts, Golino and Sommer for pentaphenylmethyldisilane [79]. Generation of a silicon–carbon double bonded species (XLVIII) is the characteristic feature of the reaction (type 1 reaction), but later Ishikawa, Fuchikami, Sugaya and Kumada reported another type of reaction in which a rather unusual silicon–carbon double bonded species (XLIX) was postulated as a key intermediate (type 2 reaction) [80]. Generation of a silylene (type 3 reaction) has also been noted.



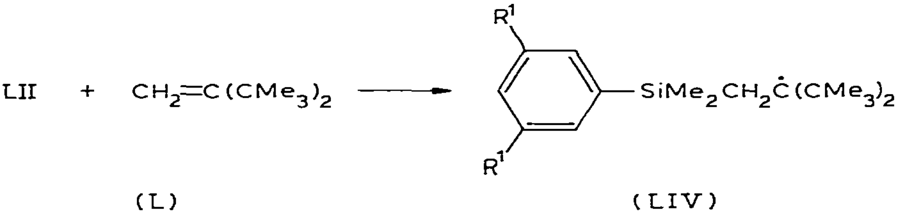
(45)

We have been interested in the photolysis of aryldisilanes in connection with the spectroscopic studies on aryldisilanes as described above, and very recently, we have found that one of the primary steps of the photolysis of aryldisilane is the generation of silyl radicals which can be successfully trapped with 1,1-di-t-butylethylene (L) to give relatively long-lived adduct radicals [81].



(46)

a; $R^1$ = H, $R^2$ = Me
b; $R^1$ = t-Bu, $R^2$ = Me
c; $R^1$ = H, $R^2$ = F
d; $R^1$ = H, $R^2$ = O-t-Bu



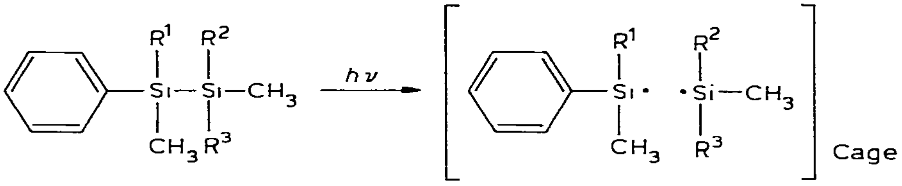
(47)

Particularly in the case of LId, a composite ESR spectrum of LIVd and LVd

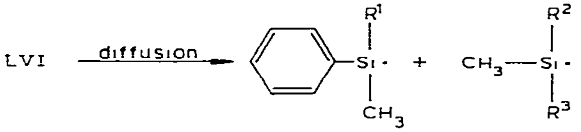
$$\underset{\text{(L)}}{\text{LIII} + CH_2{=}C(CMe_3)_2} \longrightarrow \underset{\text{(LV)}}{R^2Me_2SiCH_2\dot{C}(CMe_3)_2} \qquad (48)$$

with a relative abundance of 1/3 was obtained. A possible route to these adduct radicals by the reaction of hydrosilanes was excluded by control experiments.

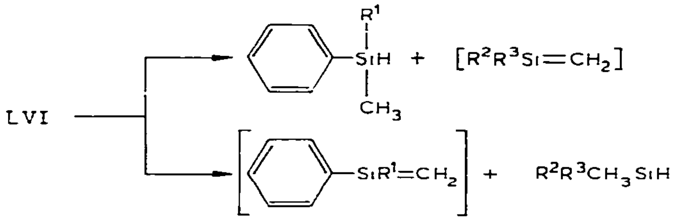
These results indicate clearly the involvement of free silyl radicals in the photo-reaction of aryldisilanes. Although the results do not necessarily show that all of the reaction proceeds by the free radical process, it is now possible to explain the type 1, 2, and 3 reactions in terms of free silyl radicals in a unifying manner, as shown below.



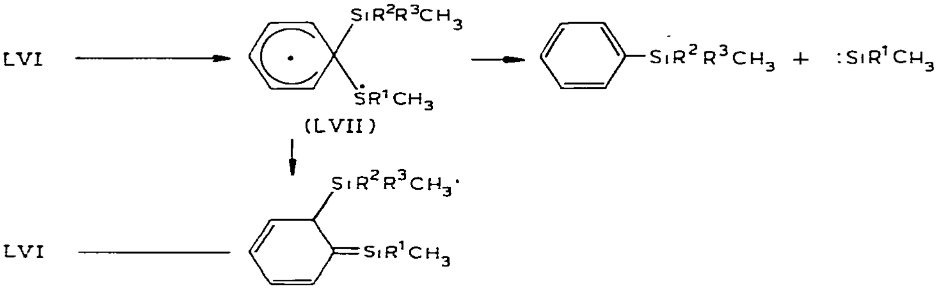
(LI) (LVI) (49)



(50)



(51)



(52)

(53)

Photolysis of an aryldisilane results in the formation of a geminate pair of two silyl radicals, some of which may escape from the solvent cage and be trapped by 1,1-di-t-butylethylene. The pair of radicals may undergo disproportionation to give the type 1 products. Very recently, three groups of workers have reported disproportion of trimethylsilyl radicals [82].

The pair of radicals can also undergo *ipso*-substitution followed by further rearrangement and/or reactions with stable molecules to give type 2 products. The intermediate (LVII) also can be a precursor of the silylene. The facile *ipso*-substitution of silyl radicals has been reported recently [83,84].

## Epilogue

Starting from the examination of UV spectra of phenylpentamethyldisilane, we have enjoyed studying the chemistry of polysilanes, particulary phenyl- and vinyl-substituted disilanes, which led us to recognition of the interesting physical properties of the Si—Si bond, to fruitful investigations of reactions of Si—Si bonded compounds, to new fascinating fields of organosilicon photochemistry and to important information on elusive organosilicon intermediates such as silyl radicals, silylenes, silyl anions, and small-membered ring and double-bonded species. Although there is no space to describe the studies of the important chemistry of free-radical, nucleophilic, anionic, and other photochemical reactions in this laboratory, nor to introduce contributions resulting from other laboratories, especially those from Professors T.J. Barton, H. Bock, A.G. Brook, M. Kumada, Y. Nagai, D. Seyferth, W.P. Weber, and R. West, I hope that this article gives a reasonable compendium of a fascinating story of the birth of a new branch of organosilicon chemistry.

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