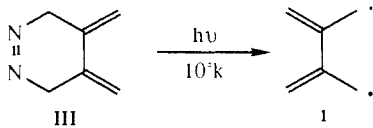


Figure 2. Curie-Weiss plot according to least-squares analysis ($r = 0.997$) of the signal intensity of the $\Delta m = 2$ line of tetramethylethane vs. the reciprocal absolute temperature. The temperature range was 16–65 K; the solvent was 2-methyltetrahydrofuran.

shows vinyl and allylic carbon triplets at δ 109 ($J = 159$ Hz) and δ 65 ($J = 129$ Hz) together with a quaternary carbon singlet at δ 133. Both spectra are free of extraneous peaks.

A solution of the azo diene III in a methyltetrahydrofuran glass was irradiated with a 1000-W dc xenon lamp using a Jarrell-Ash monochromator to control the wavelength of the light to ± 25 nm. Irradiation at the wavelength expected for the azo chromophore (370–380 nm) yielded a very weak triplet ESR spectrum. The strong clean (and identical) spectrum shown in Figure 1 is the result of irradiating at 265 nm.¹² The triplet spectrum in Figure 1 has peaks at 3041, 3164, 3451, and 3577 G (microwave frequency 9.26 GHz) with zero-field parameters $|D/hc| = 0.025$ cm⁻¹ and $|E/hc| < 0.001$ cm⁻¹. The appearance of the spectrum is identical with that observed earlier;¹ however, the D value is twice as large as that reported.¹ We believe that the earlier value was measured incorrectly. The new value is in better accord with theoretical estimates^{13,14} and with the value reported for the cyclic analogue.¹⁰ The $\Delta m = 2$ line (Figure 1, inset) was readily observed at 1651 G, and it exhibited the detailed hyperfine splitting pattern shown. The nine lines are in accord with expectation for a diradical bearing eight hydrogens, provided the inside and outside hydrogens of I are approximately magnetically equivalent.¹⁵ This establishes the structure of the diradical I beyond question.



A Curie-Weiss law plot¹⁶ of the intensity of the $\Delta m = 2$ line vs. $1/T$ over the range 16–65 K¹⁷ gives the straight line ($r = 0.997$)

(12) The same spectrum is observed in a methylcyclohexane glass.

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(15) Considering the close similarity in the a values of the inside and outside hydrogens on the allyl radical, this assumption seems to be reasonable. Strong support is also provided by the nine-line hyperfine splitting pattern ($a_H = 7.17$ G) of the tetramethylethane anion radical observed by: Bauld, N. L.; Stevenson, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3675.

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shown in Figure 2. We conclude that tetramethylethane is a ground-state triplet.¹⁸

It has been suggested⁴ that tetramethylethane (I) might not be the ideal test of theory if the two halves are canted 90° to one another. Indeed, if in the spectrum of Figure 1, the absence of splitting between the x and y lines is interpreted to mean that $E = 0$,¹⁹ this would be consistent with a diradical I of D_{2d} symmetry.²⁰ The two ends of the system would then be isolated by geometric rather than orbital geographic circumstances but the electronic problem would be very closely related to that discussed above. The situation would still consist of two spatially isolated electrons and the question whether singlet or triplet is the preferred ground state in the absence of spatial overlap remains an important and relevant one. Clearly, the triplet is preferred in the present instance.

Acknowledgment. This work was generously supported by the National Science Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We thank Professors S. I. Weissman, J. A. Berson, and D. W. Pratt for their helpful comments.

(17) A Rosemount Model 146MB platinum resistance thermometer immersed in the sample was used to measure the temperature during the Curie-Weiss law experiments. We estimate that the temperature was accurate to 0.02 K in these experiments.

(18) The Curie-Weiss plot is such that a linear plot would also be obtained if the singlet-triplet splitting were 10 cal/mol or less. So, it is also possible that the singlet and triplet are degenerate.

(19) Kindly suggested by Professor S. I. Weissman.

(20) The hyperfine splitting value in I is approximately 10.5 G, somewhat smaller than the 13–14 G of the allyl radical. This might argue for a more delocalized structure in which the two halves maintain some orbital overlap. At the SCF level [which yields calculated hyperfine splittings of 14 and -4.25 G for the allyl radical and 9.4 G for trimethylenemethane (expt.²¹ 8.9 G)] the calculated hyperfine splitting for tetramethylethane I is 8.7 G.

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Silicon-Carbon Unsaturated Compounds. 22. The Formation and Reactions of a Nickelasilacyclobutene

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Although the formation of a metalasilacyclobutene has been proposed in the transition-metal-catalyzed reaction of silacyclopropenes with an acetylene,²⁻⁴ no evidence for the existence of this intermediate has been obtained so far. Recently, we have found that the nickel-catalyzed reactions of 1-silacyclopropenes and phenylethynylpolysilanes with phenyl(trimethylsilyl)acetylene afford the products which can be best explained assuming the transient formation of nickel-containing reactive intermediates such as nickelasilacyclobutenes and silapropadiene-nickel complexes.^{5,6} In this paper, we report that the stoichiometric reaction

(1) (a) Kyoto University. (b) Government Industrial Research Institute Osaka.

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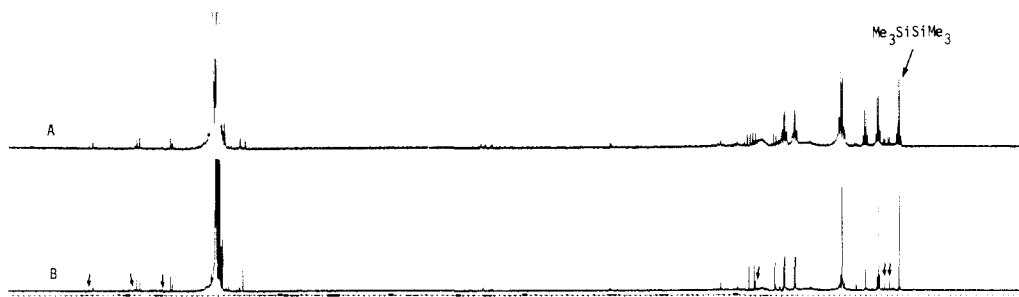


Figure 1. Off-resonance (A) and proton-decoupled (B) ^{13}C NMR spectra of nickelasilacyclobutene (**3**). Arrows indicate resonances due to the starting silacyclopene (**1**).

of a 1-silacyclopene with tetrakis(triethylphosphine)nickel(0) gives the nickelasilacyclobutene in solution. We also report the unique reaction of this compound.

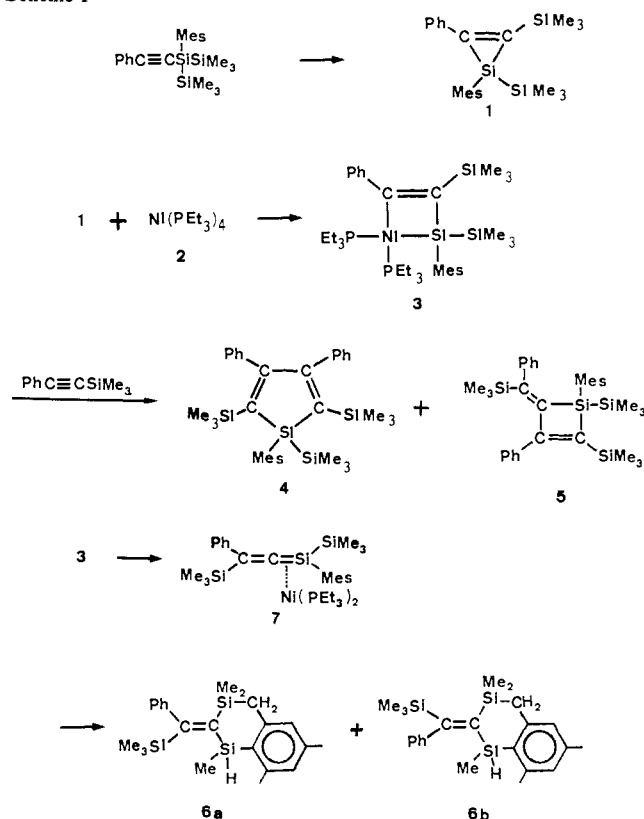
Irradiation of a solution of 2-mesityl-2-(phenylethynyl)-1,1,1,3,3,3-hexamethyltrisilane with a low-pressure mercury lamp in hexane at room temperature gave 1-mesityl-3-phenyl-1,2-bis(trimethylsilyl)-1-silacyclopene (**1**) whose structure was confirmed by spectroscopic analysis,⁷ in 79% yield. First, we treated the 1-silacyclopene **1** with 1 equiv of tetrakis(triethylphosphine)nickel(0) (**2**) in benzene at room temperature, and the reaction was followed by ^1H NMR spectroscopy. The resonances at δ 0.23, 0.36, 2.12, and 2.66, corresponding to two different kinds of trimethylsilyl protons, and para and ortho mesityl methyl protons of the starting **1** decreased gradually with increasing reaction time and were replaced by the resonances at δ 0.20, 0.52, 2.15, 2.83, and 2.96, attributed to two different trimethylsilyl groups and three nonequivalent mesityl protons of the product assigned as 2-mesityl-4-phenyl-1,1-bis(trimethylphosphine)-2,3-bis(trimethylsilyl)-1-nickela-2-silacyclobut-3-ene⁸ (**3**) (Scheme I). Compound **1** was completely transformed into **3** within 1 h at room temperature. The fact that both of the off-resonance and proton-decoupled ^{13}C NMR spectra of **3** show a doublet at δ 143.3 ($^2J_{\text{C-P}} = 51.9$ Hz) and a broad singlet at 151.9 ppm clearly indicates that these resonances can be assigned to the olefinic carbon atoms of C(Ph) and C(SiMe₃), respectively, in the nickelasilacyclobutene ring. The resonances of methylene carbons of two nonequivalent triethylphosphines are also observed at δ 17.5 ($^1J_{\text{C-P}} = 16.5$, $^3J_{\text{C-P}} = 3.1$ Hz) and 19.5 ($^1J_{\text{C-P}} = 16.2$, $^3J_{\text{C-P}} = 4.0$ Hz) as shown in Figure 1. The ^{29}Si NMR spectrum reveals three resonances as expected, one for a silicon atom of the nickelasilacyclobutene ring at δ -105.4 (t, $^2J_{\text{Si-P}} = 2.8$ Hz) and two for trimethylsilyl groups at δ 12.8 (dd, $^3J_{\text{Si-P}} = 4.3$, 1.0 Hz) and 3.1. The ^{31}P NMR spectrum displays two doublets at δ 9.7 ($J = 36.6$ Hz) and 12.4 ($J = 36.6$ Hz), indicating the presence of two nonequivalent phosphines on the nickel atom in the four-membered ring.

The nickelasilacyclobutene **3** can also be prepared in xylene solution from the reaction of **1** with 1 equiv of **2** at room temperature. Unfortunately, all attempts to isolate **3** were unsuccessful, and complicated decomposition products were always obtained.

(7) Compound **1** was less sensitive to air than the usual silacycloprenes, but it still had to be handled under an inert atmosphere: ^1H NMR δ (C_6D_6) 0.23 (s, 9 H, Me₃Si), 0.36 (s, 9 H, Me₃Si), 2.12 (s, 3 H, *p*-Me), 2.66 (s, 6 H, *o*-Me); δ (CCl_4) 0.15 (s, 9 H, Me₃Si), 0.29 (s, 9 H, Me₃Si), 2.20 (s, 3 H, *p*-Me), 2.25 (s, 6 H, *o*-Me), 6.65 (br s, 2 H, Mes ring protons), 7.05–7.52 (m, 5 H, Ph protons); ^{29}Si NMR δ (C_6D_6 , hexamethyldisilane as an internal standard) 3.7 (Me₃Si-C), 8.4 (Me₃Si-Si), 109.5 (Si-SiMe₃). Exact mass calcd for $\text{C}_{23}\text{H}_{34}\text{Si}_3$, 394.1968; found, 394.1991.

(8) Compound **3**: ^1H NMR δ (C_6H_6) 0.20 (s, 9 H, Me₃Si), 0.52 (s, 9 H, Me₃Si), 2.15 (s, 3 H, *p*-Me), 2.83 (s, 3 H, *o*-Me), 2.96 (s, 3 H, *o*-Me); ^{13}C NMR δ (30% C_6D_6 in benzene) 0.16 (Me₃Si), 4.1 (Me₃Si), 8.8 ($\text{CH}_3\text{CH}_2\text{P}$), 8.9 ($\text{CH}_3\text{CH}_2\text{P}$), 17.5 (CH_2P , dd, $^1J_{\text{C-P}} = 16.5$, $^3J_{\text{C-P}} = 3.1$ Hz), 19.5 (CH_2P , dd, $^1J_{\text{C-P}} = 16.2$, $^3J_{\text{C-P}} = 4.0$ Hz), 21.3, 25.2, 26.3, (*o*- and *p*-Me), 123.3, 127.3, 127.5–129.3, 136.8, 137.1 (mesityl and phenyl ring carbons and solvent carbons), 143.3 (d, =C(Ph)Ni, $^2J_{\text{C-P}} = 51.9$ Hz), 151.9 (=C(SiMe₃)); ^{29}Si NMR δ (30% C_6D_6 in benzene, hexamethyldisilane as an internal standard) -105.4 (t, Si-SiMe₃, $^2J_{\text{Si-P}} = 2.8$ Hz), 3.1 (Me₃Si-C), 12.8 (dd, Me₃Si-Si, $^3J_{\text{Si-P}} = 4.3$, 1.0 Hz); ^{31}P NMR δ (30% C_6D_6 in benzene, 85% phosphoric acid as an external standard) 9.7 (d, $J = 36.6$ Hz), 12.4 (d, $J = 36.6$ Hz).

Scheme I



The chemical reaction also supports the nickelasilacyclobutene structure for compound **3**. Thus, when a xylene solution of **3** was heated to reflux with a small excess of phenyl(trimethylsilyl)acetylene for 21 h, 1-mesityl-3,4-diphenyl-1,2,5-tris(trimethylsilyl)silole (**4**) and 1-mesityl-3-phenyl-4-[phenyl(trimethylsilyl)methylene]-2-(trimethylsilyl)-1-silacyclobut-2-ene (**5**) were obtained in 32% and 6% yields, respectively, together with small amounts of unidentified products (less than 3% yields). Compounds **4** and **5** could be readily separated by preparative TLC. The structure of **4** was verified by mass, IR, and ^1H NMR, and ^{13}C NMR spectroscopic analysis, as well as elemental analysis.⁹ All spectral data for compound **5** were identical with those of an authentic sample.¹⁰

To our surprise, when the xylene solution of **3** was heated to reflux in the absence of phenyl(trimethylsilyl)acetylene for 2 h, two isomers, 5,6-benzo-1,3-disilacyclohexene derivatives **6a** and **6b**, were obtained in 47% and 41% yields, respectively. Pure **6a** could be readily separated from **6b** by preparative GLC. All

(9) Compound **4**: mp 180.6; MS, m/e 568 (M^+); ^1H NMR δ (CCl_4) -0.28 (s, 18 H, Me₃Si), 0.36 (s, 9 H, Me₃Si), 2.26 (s, 6 H, *o*-Me), 2.68 (s, 3 H, *p*-Me), 6.65–7.05 (m, 12 H, Mes and Ph ring protons); ^{13}C NMR δ (CDCl_3) 0.9 (Me₃Si), 1.7 (Me₃Si), 19.7, 21.1, 26.2 (*o*- and *p*-Me), 126.0, 126.8, 128.3, 128.7, 128.9 (br), 129.3, 138.8, 143.0, 143.9, 146.6 (Mes and Ph ring carbons). Anal. Calcd for $\text{C}_{34}\text{H}_{48}\text{Si}_4$: C, 71.76; H, 8.50. Found: C, 71.28; H, 8.50.

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spectral data obtained for **6a** and **6b** were identical with those of the authentic samples.¹⁰ The results clearly indicate that the formation of compounds **6a** and **6b** must involve the isomerization of the nickelasilacyclobutene **3** to the silapropadiene-nickel complex (**7**) (see Scheme 1). Although evidence for the production of the intermediate **7** from **3** has not yet been obtained, our recent findings that the reaction of 2-mesityl-2-(phenylethynyl)hexamethyltrisilane with a catalytic amount of **2** affords compounds **6a** and **6b** in high yields¹⁰ also support the isomerization of the nickelasilacyclobutene **3** to the silapropadiene-nickel complex **7**. Numerous examples which have been studied in our laboratory will be described in forthcoming papers.

Acknowledgment. We are grateful to Drs. Y. Kawasaki, M. Wada, and H. Kurosawa, Department of Applied Chemistry, Faculty of Engineering, Osaka University, for useful discussions. We also express our appreciation to Shin-etsu Chemical Co., Ltd., and Toshiba Silicone Co., Ltd., for a gift of organochlorosilanes.

Picosecond Time Scale Dynamics of Perester Photodecomposition: Evidence for an Acyloxy Radical Intermediate in the Photolysis of *tert*-Butyl 9-Methylfluorene-9-percarboxylate

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Much of the experimental basis for the description of free-radical chemistry rests upon studies of organic peroxides.¹ One of the first significant problems to be investigated was the decarboxylation of aryl and alkyl acyloxy radicals, eq 1. Hammond



R = Aryl, Alkyl

and Soffer confirmed the existence of the benzoyloxy radical (R = phenyl) by trapping it with added iodine.^{2a} The lifetime of this radical was later measured by time-resolved ESR to be 250 ns.^{2b} Shine and Slagle interpreted results from thermolysis of acetyl peroxide in cyclohexane in terms of a metastable acetoxy (R = methyl) radical.³ Later, Martin and Taylor showed with definitive isotope tracer experiments that this radical lives long enough to undergo internal return.⁴ Experimental estimates of the lifetime of the acetoxy radical from studies of the effect of varying solvent viscosity⁵ and from CIDNP observations⁶ place it at ca. 1 ns. Until now, no other acyloxy radicals have been directly characterized.

Pioneering work by Bartlett and his students showed that the thermal stability of a series of peresters is inversely related to the stability of the alkyl radical formed in their decarboxylation.⁷ This fact led to the suggestion that concerted two-bond cleavage of the perester occurs whenever a sufficiently stable radical is formed [R = (Ph)₂CH, for example] and that acyloxy radicals are not intermediates in these reactions. This conclusion has stood the test of time. Koenig and Wolf⁸ found secondary isotope effects

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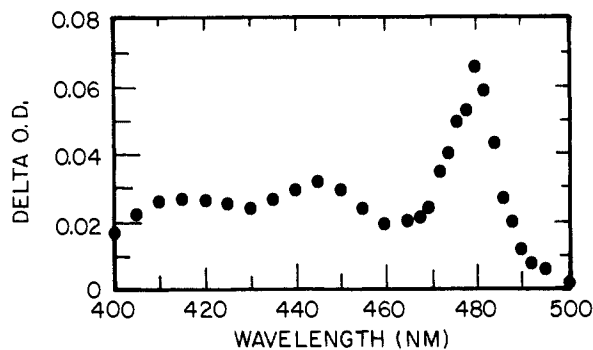


Figure 1. Absorption spectrum of radical **2** obtained by triplet-sensitized photolysis of **1** in CH₃CN.

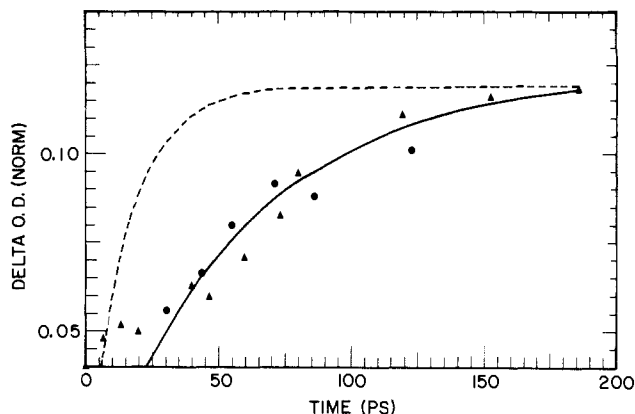
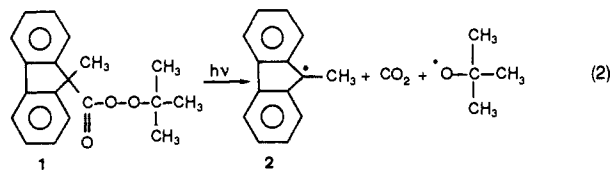


Figure 2. Absorption vs. time plot for the rise of radical **2** after picosecond photolysis of perester, **1** in CH₃CN (▲) and cyclohexane (●). The solid line was fitted to CH₃CN data. The dashed line represents the limit of instrument response as determined by the rise of benzophenone triplet.

that support it, Pryor and Smith⁹ observed consistent solvent viscosity dependence, and Neuman and Behar¹⁰ measured supportive activation volumes. However, these experiments do not directly address the central question of definable existence for these highly reactive acyloxy radicals. They may not be formed in the thermolyses of peresters, and they certainly do not live long enough to escape the solvent cage of their creation, but their independent reactivity toward decarboxylation has remained unknown. Herein we describe experiments that indicate the measurable existence of acyloxy radicals of even very highly stabilized systems.

We have investigated the photochemistry of *tert*-butyl 9-methylfluorene-9-percarboxylate (**1**).¹¹ Photolysis of peresters leads to chemical reactions that appear to mimic those of their more thoroughly studied thermolyses.¹³ As expected, irradiation of **1** in oxygen-free cyclohexane or acetonitrile solution generates the *tert*-butoxy radical, the 9-methylfluorenyl radical (**2**), and (presumably) CO₂, eq 2. The intermediacy of the *tert*-butoxy



radical was verified by analysis of the reaction products which contained *tert*-butyl alcohol (42%), acetone (49%), and *tert*-butyl 9-methylfluorenyl ether (2%). Similarly, fluorenyl radical **2** was

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(11) This perester was prepared from the reaction of the acid chloride with sodium *tert*-butyl peroxide according to the general procedure of Bartlett and Lorand;¹² mp 69.4-71.2 °C dec; IR (CCl₄) 1718 cm⁻¹; ¹H NMR (CDCl₃) δ 1.01 (s, 9 H), 1.77 (s, 3 H) 7.2-7.8 (m, 8 H).

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