

Figure 2. Curie-Weiss plot according to least-squares analysis (r =0.997) of the signal intensity of the $\Delta m = 2$ line of tetramethyleneethane 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 1,13,14 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

- (13) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty,
 D. A.; Berson, J. A. Tetrahedron 1982, 38, 787.
 (14) Platz, M. S. In Diradicals; Borden, W. T., Ed.; Wiley: New York,
- (15) Considering the close similarity in the a values of the inside and (15) Considering the close similarity in the assumption seems to be reasonable.

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 tetramethyleneethane anion radical observed by: Bauld, N.

i) G) of the tetrametryleneethane anion radical observed by: Bauld, N. L.; Stevenson, G. R. J. Am. Chem. Soc. 1969, 91, 3675.
(16) Cf.: Breslow, R.; Hill, R.; Wasserman, E. J. Am. Chem. Soc. 1964, 86, 5349. Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O'Neill, J.; Breslow, R.; Hoffman, J. M., Jr.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. J. Am. Chem. Soc. 1973, 95, 3017. Breslow, R.; Chang, H. W.; Yager, W. A. J. Am. Chem. Soc. 1963, 85, 2033. Breslow, R.; Chang, H. W.; Hill, R.; Wasserman, E. J. Am. Chem. Soc. 1967, 89, 1112.

shown in Figure 2. We conclude the t tetramethyleneethane is a ground-state triplet.¹⁸

It has been suggested⁴ that tetramethyleneethane (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.

(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 tetramethylenethane I is 8.7 G. (21) Dowd, P.; Gold, A.; Sachdev, K. J. Am. Chem. Soc. **1968**, 90, 2715.

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

Mitsuo Ishikawa,*1a Joji Ohshita,1a Yoshihiko Ito,1a and Jun Iyoda^{1b}

> Department of Synthetic Chemistry Faculty of Engineering, Kyoto University Kyoto 606, Japan Government Industrial Research Institute Osaka Ikeda, Osaka 563, Japan Received June 23, 1986

Although the formation of a metalasilacyclobutene has been proposed in the transition-metal-catalyzed reaction of silacyclo-propenes 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

0002-7863/86/1508-7417\$01.50/0 © 1986 American Chemical Society

⁽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.

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

^{(2) (}a) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Dun an,
D. P. J. Organomet. Chem. 1977, 135, C37. (b) Seyferth, D.; Shannon, M.
L.; Vick, S. C.; Lim, T. F. O. Organometallics 1985, 4, 57.
(3) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. J. Am. Chem. Soc. 1977,

^{99. 3879.} (4) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. J. Organomet.

Chem. 1981, 217, 43. (5) Ishikawa, M.; Matsuzawa, S.; Hirotsu, K.; Kamitori, S.; Higuchi, T.

Organometallics 1984, 3, 1931. (6) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. Organometallics 1985, 4, 2040.



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

of a 1-silacyclopropene 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-silacyclopropene (1) whose structure was confirmed by spectroscopic analysis,⁷ in 79% yield. First, we treated the 1-salicyclopropene 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(triethylphosphine)-2,3bis(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 $(^{2}J_{C-P} = 51.9 \text{ Hz})$ 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 $({}^{1}J_{C-P} = 16.5, {}^{3}J_{C-P} = 3.1 \text{ Hz})$ and 19.5 $({}^{1}J_{C-P} = 16.2, {}^{3}J_{C-P} = 4.0 \text{ Hz})$ as shown in Figure 1. The ²⁹Si NMR spectrum reveals three resonances as expected, one for a silicon atom of the nickelasilacyclobutene ring at δ -105.4 (t, ${}^{2}J_{Si-P} = 2.8$ Hz) and two for trimethylsilyl groups at δ 12.8 (dd, ${}^{3}J_{Si-P} = 4.3$, 1.0 Hz) and 3.1. The ³¹P 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 fourmembered 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.

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(trimethyl-silyl)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 ¹³C 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

⁽⁷⁾ Compound 1 was less sensitive to air than the usual silacyclopropenes, but it still had to be handled under an inert atmosphere: ¹H NMR δ (C₆D₆) 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 (CCl₄) 0.15 (s, 9 H, Me₃Si), 0.29 (s, 9 H, Me₅Si), 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); ²⁹Si NMR δ (C₆D₆, hexamethyldisilane as an internal standard) 3.7 (Me₃Si-C), 8.4 (Me₃Si-Si), 109.5 (Si-SiMe₃). Exact mass calcd for C₂₃H₃₄Si₃, 394.1968; found, 394.1991. (8) Compound 3: ¹H NMR δ (C₆H₆) 0.20 (s, 9 H, Me₅Si), 0.52 (s, 9 H, Me₅Si) 2.15 (s, 3 H, *p*-Me) 2.82 (s, 3 H, *o*-Me) 2.05 (s, 2 H, *o*-Me) ¹³C

⁽⁸⁾ Compound 3: ¹H NMR δ (C₆H₆) 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); ¹³C NMR δ (30% C₆D₆ in benzene) 0.16 (Me₃Si), 4.1 (Me₃Si), 8.8 (CH₃CH₂P), 8.9 (CH₃CH₂P), 17.5 (CH₂P, dd, ¹J_{C-P} = 16.5, ³J_{C-P} = 3.1 Hz), 19.5 (CH₂P, dd, ¹J_{C-P} = 16.2, ³J_{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_{C-P} = 51.9 Hz), 151.9 (=C(SiMe₃); ²⁸Si NMR δ (30% C₆D₆ in benzene, hexamethyldisilane as an internal standard) –105.4 (t, Si-SiMe₃, ²J_{Si-P} = 2.8 Hz), 3.1 (Me₃Si-C), 12.8 (dd, Me₃Si-Si, ³J_{Si-P} = 4.3, 1.0 Hz); ³¹P NMR δ (30% C₆D₆ in benzene, 85% phosphoric acid as an external standard 9.7 (d, J = 36.6 Hz).

⁽⁹⁾ Compound 4: mp 180.6; MS, m/e 568 (M⁺); ¹H NMR δ (CCl₄) -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); ¹³C NMR δ (CDCl₃) 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 C₃₄H₄₈Si₄; C, 71.76; H, 8.50. Found: C, 71.28; H, 8.50. (10) Ishikawa, M.; Ohshita, J.; Ito, Y. Organometallics **1986**, 5, 1518.

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 I). 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

Daniel E. Falvey and Gary B. Schuster*

Department of Chemistry, University of Illinois Urbana, Illinois 61801 Received August 20, 1986

Much of the experimental basis for the description of freeradical 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

$$R - CO_2 \cdot \qquad R \cdot + CO_2 \quad (1)$$

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



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 (\blacktriangle) and cyclohexane (\bigcirc). 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 9methylfluorene-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

^{(1) (}a) Koenig, T. In Free Radicals; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. I, p 113. (b) Wentrup, C. Reactive Molecules; Wiley-Interscience: New York, 1984; pp 63-83.
(2) (a) Hammond, G. S.; Soffer, L. M., J. Am. Chem. Soc. 1950, 72, 4711.
(b) Yamauchi, S.; Hirota, N.; Takahara, S.; Sakuragi, H.; Tokumaru, K. J. Am. Chem. Soc. 1986, 107 5021

Am. Chem. Soc. 1985, 107, 5021.

 ⁽³⁾ Shine, H. J.; Slagle, J. R. J. Am. Chem. Soc. 1959, 81, 6309.
 (4) Taylor, J. W.; Martin, J. C. J. Am. Chem. Soc. 1967, 89, 6904.
 (5) Braun, W.; Rajbenbach, L.; Eirich, F. R. J. Phys. Chem. 1962, 66,

^{1591.} (6) Kaptein, R.; Brokken-Zijp, J.; de Kanter, F. J. J. J. Am. Chem. Soc.

 ⁽¹⁾ Raptelli, R., Biokes, E., P., C. L. M., Chem. Soc. 1958, 80, 1398. (b)
 (7) (a) Bartlett, P. D.; Hiatt, R. R. J. Am. Chem. Soc. 1958, 80, 1398. (b)
 Bartlett, P. D.; Simons, D. M. Ibid. 1960, 82, 1753. (c) Bartlett, P. D.;
 Rüchardt, C. Ibid. 1960, 82, 1756. (d) Bartlett, P. D.; Benzing, E. P.; Pincock,
 Bartlett, P. D. 1726. (c) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. Ibid. 1960, 82, 1762. (e) Bartlett, P. D.; Pincock, R. E. Ibid. 1960, 82, 1769.

⁽⁸⁾ Koenig, T.; Wolf, R. J. Am. Chem. Soc. 1967, 89, 2948.
(9) Pryor, W. A.; Smith, K. J. Am. Chem. Soc. 1970, 92, 5403.
(10) Neuman, Jr., R. C.; Behar, J. V. J. Am. Chem. Soc. 1969, 91, 6024. (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

 ⁽¹²⁾ Lorand, J. P.; Bartlett, P. D. J. Am. Chem. Soc. 1966, 88, 3294.
 (13) Sheldon, R. A.; Kochi, J. K. J. Am. Chem. Soc. 1970, 92, 5175.