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 yields[10] 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

$$R{-}CO_2^{\bullet} \longrightarrow R^{\bullet} + CO_2 \qquad (1)$$

$$R = \text{Aryl, Alkyl}$$

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 viscosity[5] and from CIDNP observations[6] 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 Wolf[8] found secondary isotope effects that support it, Pryor and Smith[9] observed consistent solvent viscosity dependence, and Neuman and Behar[10] 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.

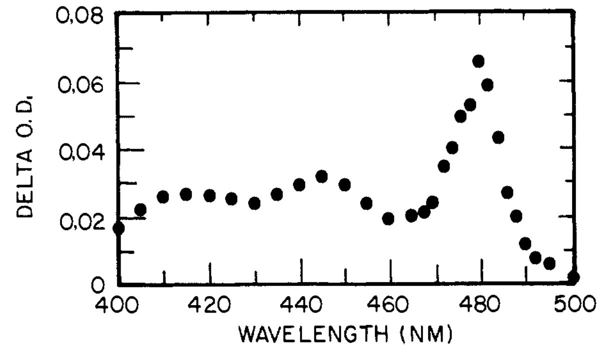


Figure 1. Absorption spectrum of radical **2** obtained by triplet-sensitized photolysis of **1** in CH_3CN.

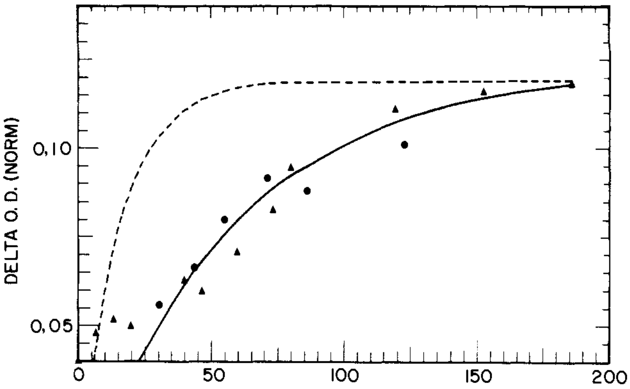
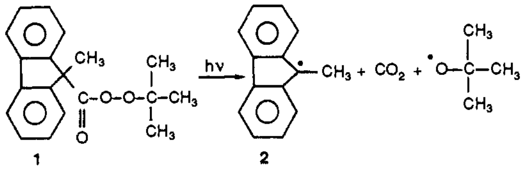


Figure 2. Absorption vs. time plot for the rise of radical **2** after picosecond photolysis of perester, **1** in CH_3CN (▲) and cyclohexane (●). The solid line was fitted to CH_3CN data. The dashed line represents the limit of instrument response as determined by the rise of benzophenone triplet.



1 **2** (2)

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) CO_2, 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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(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 68–83.

(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.* **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.* **1972**, *94*, 6280.

(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, 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 (CCl_4) 1718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.77 (s, 3 H) 7.2–7.8 (m, 8 H).

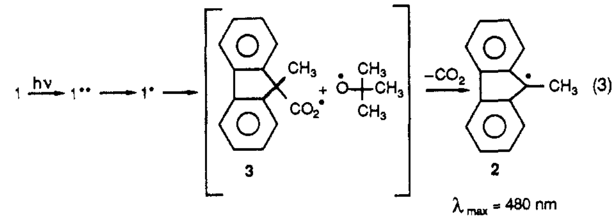
(12) Lorand, J. P.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, *88*, 3294.

(13) Sheldon, R. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 5175.

implicated by the formation of the aforementioned ether, 9,9-dimethylfluorene (6%); the symmetrical coupling product 9,9'-dimethyl-9,9'-bifluorene (67%); and 9-(cyanomethyl)-9-methylfluorene (12% from reactions in acetonitrile). The relative yields of these products depend on the extent of reaction since the ether and the dimer are both photolabile.

The 9-methylfluorenyl radical was also detected spectroscopically. Direct or triplet-sensitized irradiation of perester **1** with a laser pulse of ca. 15-ns duration (direct, 266 nm; triplet sensitized with *p*-methoxyacetophenone at 337 nm) generates a transient intermediate with absorption maxima at 445 and 480 nm. On the timescale of these experiments, the intermediate is formed instantaneously and then decays over a period of several microseconds in a kinetically complex way. The structure of the intermediate was assigned to radical **2** by comparison of its spectrum with that of an authentic sample prepared independently by laser irradiation of di-*tert*-butyl peroxide containing a small amount of dissolved 9-methylfluorene.[14] This spectrum is shown in Figure 1.

Irradiation of perester **1** with the quadrupled output of a mode-locked Nd:YAG laser (266 nm, 18 ps, 4 mJ) similarly leads to the formation of fluorenyl radical **2**. However, on this time scale the radical does not appear instantaneously, Figure 2. Its absorption grows according to a first-order rate law from a precursor that has a 55 ± 15 ps lifetime. There are several chemical and physical processes that must occur between the absorption of a photon at 266 nm by peroxide **1** and the appearance of the methylfluorenyl radical. The kinetic result reports the rate of the slowest of these steps. The proposed reaction sequence is outlined in eq 3.



The UV absorption spectrum of perester **1** is nearly superimposable on that of model compound 9-carbomethoxy-9-methylfluorene (**4**) except for a broad, weak band characteristic of peroxides[15] which extends the absorption out past 400 nm. When perester **1** absorbs a 266-nm photon, the initially formed excited state (**1****) is heavily localized in the π-system of the fluorenyl chromophore. It is conceivable that the slow step in the formation of radical **2** is the "transfer" of energy to the lowest excited singlet state (**1***) localized on the peroxide group. This possibility was excluded by comparison of the behavior of **1** with ester **4** and other model compounds. The fluorescence efficiency of the perester is 0.8% that of the ester, but the lifetime of this weak emission is approximately the same (6.9 ns) as the ester. Since it is unlikely that the purity of the perester is greater than 99.2%, the residual emission is logically assigned to a trace of ester (or acid) in the perester sample. Irradiation of either ester **4**, fluorene, or 9-methylfluorene with the picosecond laser forms similarly absorbing transient species assigned by correlation of lifetime to the excited singlet state of the common fluorene-like chromophore. Irradiation of perester **1** under identical conditions gives no trace of this absorption. Thus, as expected from studies of analogous examples of intramolecular energy transfer,[16] the lifetime of **1**** is too short to allow detectable fluorescence or excited-state absorption. And, concomitantly, the formation of **1*** is too fast to be the slow step in the formation of radical **2**.

The second step in the sequence is cleavage of the O–O bond of the excited perester to form acyloxy radical **3** and the *tert*-butoxy radical. All theoretical[17] and experimental[15,18] analyses of the lowest excited states of peroxides have identified them as dissociative. This appears to be the case for perester **1** from consideration of the distinctive shape of its absorption spectrum. Thus it seem likely that cleavage of this bond is instantaneous and thus cannot be the slow step in the sequence that gives radical **2**.

These considerations identify decarboxylation of radical **3** as the rate-determining step in the reaction sequence shown in eq 3. Molecular symmetry analyses for simpler examples of this decarboxylation reveal a barrier caused by an intended state crossing.[19] The height of this barrier is predicted to decrease as the stability of the radical formed increases. Our results reveal that the rate constant for this reaction is about 20 times greater for the formation of the methylfluorenyl radical (1.8×10^{10} s^{-1}) than that estimated for methyl radical formation but still far from instantaneous.[20] It is difficult to imagine a carbon-centered radical that is more highly stabilized than the methylfluorenyl radical. Thus it appears that all such acyloxy radicals will have a definable, if brief, lifetime.

Acknowledgment. This work was supported by a grant from the National Science Foundation for which we are grateful.

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(14) Paul, H.; Small, Jr., R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(15) (a) Holt, R. B.; McLane, C. K.; Oldenberg, O. *J. Chem. Phys.* **1948**, *16*, 225. (b) Silbert, L. S. In *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1970; Vol. II, pp 678–683.

(16) (a) Schnepp, O.; Levy, M. *J. Am. Chem. Soc.* **1962**, *84*, 172. (b) Anderson, R. W.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *Chem. Phys. Lett.* **1975**, *32*, 204.

(17) (a) Evleth, E. M. *J. Am. Chem. Soc.* **1976**, *98*, 1637. (b) Rauk, A.; Barriel, J. M. *Chem. Phys.* **1977**, *25*, 409. (c) Chevaldonnet, C.; Cardy, H.; Dargelos, A. *Chem. Phys.* **1976**, *102*, 55.

(18) (a) Encinas, M. V.; Lissi, E. A. *J. Photochem.* **1982**, *20*, 153. (b) Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640.

(19) Pacansky, J.; Brown, D. W. *J. Phys. Chem.* **1983**, *87*, 1553.

(20) The lifetime of the acyloxy radical could conceivably be longer if 266-nm photolysis generates a vibrationally excited species.

Organocopper–Lewis Acid Mediated 1,3-Chirality Transfer of Acyclic γ,δ-Dioxygenated (*E*)-α,β-Enoates. Regio-, (*E*)-Stereo-, and Diastereoselective α-Alkylation Approaching 100% Selectivity

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The enantio- or diastereoselective α-alkylation of esters and lactones is a crucial problem in the synthesis of biologically active natural products. During the last few years, stereoselective alkylations of chiral metal enolates,[1] intra- and extraannular chirality transfer reactions,[2] asymmetric syntheses via chiral oxazolines,[3] asymmetric hydrogenations,[4] and sigmatropic rearrangements such as Claisen-[5] and Ireland–Claisen[6] rearrangements have been shown

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(1) (a) For an excellent review, see: Evans, D. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed; Academic Press: New York, 1984; Vol. 3, p 1. (b) Fleming, I.; Hill, J. H. M.; Parker, D.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1985**, 318.

(2) (a) For a report on the 1,3-chirality transfer of 5-alkenyl-γ-lactones and their congeners with alkyl cyanocuprates, see: Trost, B. M.; Klun, T. P. *J. Org. Chem.* **1980**, *45*, 4256. (b) Narasaka, K.; Ukaji, Y. *Chem. Lett.* **1986**, 81 and references cited.

(3) (a) Evans, D. A.; Dow, R. L. *Tetrahedron Lett.* **1986**, *27*, 1007. (b) Evans, D. A.; Dimare, M. *J. Am. Chem. Soc.* **1986**, *108*, 2476 and references cited.

(4) (a) For a review, see: Koenig, K. E. In *Asymmetric Synthesis*; Morrison, J. D., Ed; Academic Press: New York, 1985; Vol. 5, p 71. (b) Evans, D. A.; Morrissey, M. M.; Dow, R. L. *Tetrahedron Lett.* **1985**, *26*, 6005.