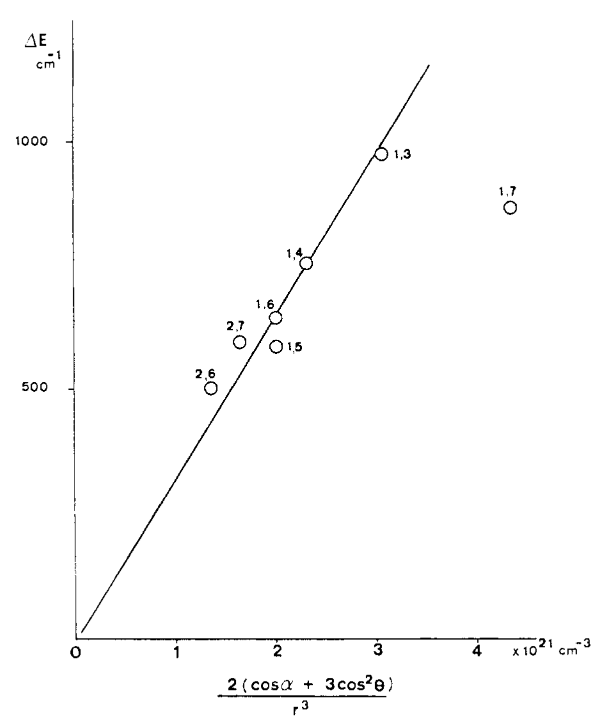

Figure 3. Plot of exciton coupling energy ΔE vs geometrical parameters, $2(\cos\alpha + 3\cos\theta_1\cos\theta_2)/r^3$.

the porphyrin rings relative to each other.[5] These systematic spectral changes are qualitatively in accord with the simple selection rule[6] predicted from the theory of exciton coupling,[7] which has often been used to explain the unusual electronic spectral properties of noncovalent porphyrin aggregates[8] and covalently linked porphyrin dimers.[2,9] However, to the best of our knowledge, there exists no reliable and systematic synthetic model for certification of the theory in fluid solution containing porphyrins, particularly on the dependence of coupling energy upon the geometrical parameters. According to the theory,[7] the dipole-dipole exciton splitting energy, ΔE, in the oblique geometry as shown in Figure 2, is given by the equation:

$$\Delta E = \frac{2|M|^2(\cos\alpha + 3\cos\theta_1\cos\theta_2)}{r^3} \tag{1}$$

where M is the transition dipole moment of the monomer.[10] As shown in Figure 3, a plot of (ΔE) vs the geometrical parameter,[11] $2(\cos\alpha + 3\cos\theta_1\cos\theta_2)/r^3$, showed a good linear correlation between these two quantities.[12] From the slope, the magnitude of the transition dipole moment of the monomer effective for the exciton coupling was determined to be 7.9 D. This is in good agreement with the value (9.7 D) of the transition dipole moment of the monomer, which is calculated from the absorption spectra of 1-NP(Zn). These results indicate the appropriateness of the treatment of the simple exciton theory for this covalently linked system in solution.

The fluorescence properties of NDP(Zn_2) were virtually identical with those of 1-NP(Zn) and 2-NP(Zn) except for 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2), indicating the absence of significant perturbation in their S_1 states in contrast to the strong exciton coupling of their S_2 states. The slightly perturbed fluorescence spectra and reduced fluorescence lifetimes[13] of 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2), which is in line with their red-shifted Q bands, may be due to through-bond interaction. The fluorescence quantum yield of 1,8-ADP(Zn_2) was about one-third those of NP(Zn), and 1,8-BDP(Zn_2) was nearly nonfluorescent. These observations indicated the maximal exciton interaction in the face-to-face geometry, which resulted in the significant perturbation even in their S_1 states.

Geometry-restricted dimeric porphyrins described in this paper will be useful for studies on intramolecular excitation energy transfer and electron-transfer processes. We are currently using fast optical techniques to prove the orientation dependence of these processes in these dimeric porphyrins.

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(5) Restricted geometry of NDP is also deduced from the fact that all their monozinc complexes exhibit a single rapidly decaying component (10–30 ps) in the fluorescence of the zinc porphyrin, which is due to an efficient excitation energy transfer from the zinc porphyrin to the free-base porphyrin. A. Osuka and K. Maruyama, unpublished results.

(6) A simple selection rule for dimers of dye molecules was given by Kasha in ref 7a as follows: a spectral blue-shift for the face-to-face dimer, a spectral red-shift for the head-to-tail dimer, and band splitting for the oblique dimer.

(7) (a) Kasha, M. *Radiat. Res.* **1963**, *20*, 55–71. (b) Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1961**, *35*, 1059–1071; **1964**, *41*, 2280–2286.

(8) (a) Sauer, K.; Smith, J. R. L.; Schultz, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 2681–2688. (b) Shipman, L. L.; Norris, J. R.; Katz, J. J. *J. Phys. Chem.* **1977**, *80*, 877–882.

(9) (a) Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516–533. (b) Collman, J. P.; Anson, F. C.; Barnes, C. E.; Bencosme, C. S.; Geiger, T.; Evitt, E. R.; Kreh, R. P.; Meier, K.; Pettman, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 2694–2699. (c) Gouterman, M.; Holton, D.; Lieberman, E. *Chem. Phys.* **1977**, *25*, 139. (d) Wasielewski, M. R.; Svec, W. A.; Cope, B. T. *J. Am. Chem. Soc.* **1978**, *100*, 1961–1962. (e) Bucks, R. R.; Boxer, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 340–343. (f) Paine, J. B. III; Dolphin, D.; Gouterman, M. *Can. J. Chem.* **1978**, *56*, 1712–1715. (g) Selensky, R.; Holten, D.; Windsor, M. W.; Paine, J. B. III; Dolphin, D.; Gouterman, M.; Thomas, J. C. *Chem. Phys.* **1981**, *60*, 33–46. (h) Tabushi, I.; Sasaki, T. *Tetrahedron Lett.* **1982**, *23*, 1913–1916. (i) Sessler, J. L.; Hugdahl, J.; Johnson, M. R. *J. Org. Chem.* **1986**, *51*, 2838–2840. (j) Heiler, D.; McLendon, G.; Rogalskyj, P. *J. Am. Chem. Soc.* **1987**, *109*, 604–606.

(10) On the basis of the C_{2v} symmetry of π-system of the zinc 5-aryl-2,3,7,8,12,13,17,18-octaalkylporphyrin, it may be appropriate to place the Soret transition (π–π^*) dipole moment of the monomer to the 5–15 direction.

(11) The split Soret bands of NDP were fitted to two gaussian bands, from which the exciton splitting energy ΔE was estimated. The geometrical parameters were estimated from space-filling models.

(12) The deviation of 1,7-NDP(Zn_2) from the plot may indicate the limitation of the theory based on the dipole–dipole approximation, which may fail at very small separation r.

(13) From picosecond time-correlated single photon counting measurement, the fluorescence lifetimes of 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2) were determined to be 1.25 and 1.28 ns, respectively, while those of 1-NP(Zn), 2-NP(Zn), and the other NDP(Zn_2) were found to be 1.5 ns.

A Novel Photorearrangement of 1-Silyl 1,2-Diones: Generation of Siloxyketenes

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Received January 28, 1988

The photochemistry of acylsilanes has been extensively studied.[1] Upon excitation a 1,2-shift of silicon from the carbonyl carbon to oxygen occurs which results in a siloxycarbene.[2] The siloxycarbene then undergoes a chemical reaction with an added trapping agent, or thermally reverts back to the initial acylsilane.[3]

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† This paper is contribution No. 1575 from the Corporate Research Laboratories, 3M.

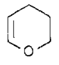
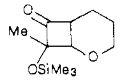
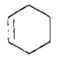
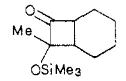
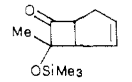
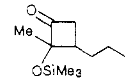
(1) (a) Brook, A G. *Intra-Sci. Chem. Rept.* **1973**, *7*, 131. (b) Watanabe, H.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1972**, *43*, 285. (c) Duff, J. M.; Brook, A. G. *Can. J. Chem.* **1973**, *51*, 2869. (d) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 2148. (e) Porter, N. A.; Hoff, P. M., Jr. *Ibid.* **1974**, *96*, 3200. (f) Brook, A. G.; Pierce, J. B.; Duff, J. M. *Can. J. Chem.* **1975**, *53*, 2874. (g) Brook, A. G.; Kucera, H. W.; Pearce, R. *Ibid.* **1971**, *49*, 1618. (h) Brook, A. G.; Dillon, P. J.; Pearce, R. *Ibid.* **1971**, *49*, 133. (i) Brook, A. G.; Duff, J. M. *Ibid.* **1973**, *51*, 352. (j) Brook, A. G.; Pearce, R.; Pierce, J. B. *Ibid.* **1971**, *49*, 1622. (k) Watanabe, H.; Ohsawa, N.; Sawai, M.; Fukusawa, Y.; Matsumoto, H.; Nagai, Y. *J. Organomet. Chem.* **1975**, *93*, 173.

(2) (a) Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 699. (b) Brook, A. G.; Kivisikk, R.; LeGrow, G. E. *Can. J. Chem.* **1965**, *43*, 1175. (c) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (d) Dalton, J. C. *Org. Photochem.* **1985**, *7*, 149. (e) Scheller, M. E.; Frei, B. *Helv. Chim. Acta* **1984**, *67*, 1734.

(3) Bourque, R. A.; Davis, P. D.; Dalton, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 697.

0002-7863/88/1510-4456$01.50/0

Table I. Products from Photolysis of **1a** in the Presence of Various Alkenes

alkene	product
	
	
	
	

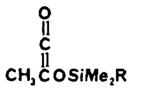
In contrast, 1-silyl 1,2-diones (**1**) are a relatively unexplored class of compounds.[4] Recently prepared by Reich[5] and Bulman Page,[6] these materials have a visible absorption band in the region 450 < λ < 580 nm and are photolytically unstable. Examination of the photochemistry of **1a**,**b** in this laboratory indicates that a significant photoprocess of these compounds involves rearrangement to siloxyketenes **2a**,**b**, respectively.

$CH_3\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}SiMe_2R$

1

(a) R = CH_3

(b) R = *tert*-butyl



$CH_3\overset{\overset{O}{\|}}{\overset{\overset{C}{\|}}{C}}OSiMe_2R$

2

(a) R = CH_3

(b) R = *tert*-butyl

Compounds **1a**,**b** were synthesized according to standard methods[5] and purified by preparative gas chromatography prior to use. Irradiations were performed in deoxygenated borosilicate glass tubes at λ > 475 nm to ensure that absorption was restricted to the long-wavelength band. Products were isolated by preparative gas chromatography and characterized by ^1H, ^{13}C NMR, IR, and high-resolution MS.

Photolysis of **1a** in cyclopentane in the presence of added trapping agents gave the products listed in Table I in high yields.[7] The measured quantum efficiency for photodecomposition was 0.01 ± 0.003. The cyclobutanone ring moiety was identified by its carbonyl stretching band at 1776–1783 cm^{-1} and the presence of corresponding ^{13}C carbonyl resonances at 208–210 ppm.[8] The regiochemistry of the cyclobutanone adducts was established by ^1H NMR spin decoupling experiments; however, stereochemical assignment was not made. As indicated vide infra, these products originate from 2 + 2 cycloaddition of alkenes to **2a**. By analogy to other ketene cycloadditions it seems likely that the methyl group at C-3 and the bridgehead hydrogens are syn.[9] Regardless of the stereochemical assignment, the isolation of only one isomer suggests a highly stereoselective cycloaddition.

The nature of the products suggested the formation of **2a** as a reactive intermediate in the photochemistry of **1a**. This was confirmed by infrared spectroscopy (Figure 1). Photolysis of **1a**,**b** as mulls in Fluorolube, Nujojl, Apiezon, or Vaseline gave transient absorptions at 2106–8 cm^{-1} which are assigned to **2a**,**b**, respectively. The observed signal decay was first order in **2**, apparently resulting from a reaction with unconverted **1**. Since the transient generated from **1a** at room temperature disappeared in seconds when irradiation was stopped, while that from **1b** was still evident after 5 min, the *tert*-butyl substituent in **1b** may serve to slow diffusion or increase the activation energy for reaction. Attempts to observe the ketene intermediate by photolysis in cryogenic hydrocarbon matrices were completely unsuccessful, possibly due to matrix free volume constraints on the photorearrangement.[10]

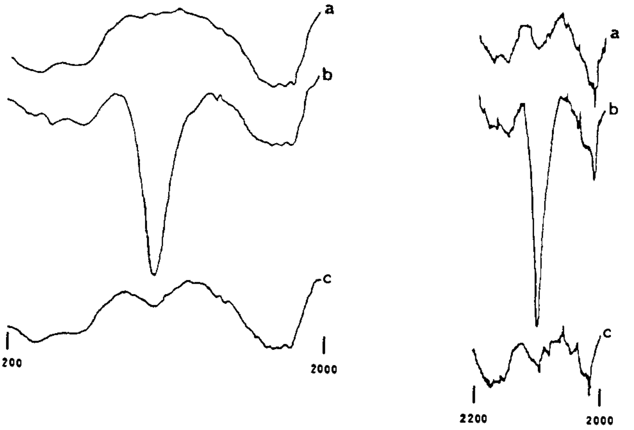


Figure 1. Infrared spectra of **2a**,**b** in vaseline mulls generated by photolysis of **1a**,**b** (cm^{-1}): (a) before photolysis; (b) during photolysis; (c) after sample decay in the dark.

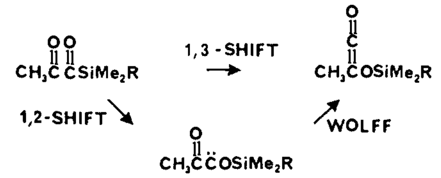


Figure 2. Mechanistic pathways for the rearrangement I → **2**.

Additional trapping agents were tried as well. In the presence of acetaldehyde or benzaldehyde, 2-oxetanone derivatives were formed. Photolysis in the presence of oxygen led to the formation of trimethylsilyl pyruvate.

The mechanism of the photorearrangement is open to speculation; however, two possibilities come to mind (Figure 2). The first involves a 1,3-shift of silicon to the distant carbonyl group in a single step. This process has been shown for some acyl polysilanes.[11] Alternatively, a two-step mechanism in which a 1,2-silyl shift of the type common to acylsilanes is followed by a Wolff rearrangement[12] could be operative. It is noteworthy that all attempts to spectroscopically or chemically implicate the required carbene have been unsuccessful. Therefore, if the latter mechanism applies, the Wolff rearrangement must be faster than reaction of the carbene with added trapping agent.

In conclusion, it has been shown that 1-silyl 1,2-diones can serve as photochemical precursors to siloxyketenes. These ketenes, which have not previously been prepared, are interesting species in their own right, being simultaneously ketenes and silyl enol ethers.

Supplementary Material Available: Table of spectral data for products from photolysis of **1a** in the presence of various alkenes (1 page). Ordering information is given on any current masthead page.

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(4) (a) Sekiguchi, A.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1979**, 575. (b) Sekiguchi, A.; Kabe, Y.; Ando, W. *J. Org. Chem.* **1982**, *47*, 2900. (c) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119.

(5) (a) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949. (b) Reference 4c.

(6) (a) Bulman Page, P. C.; Rosenthal, S. *Tetrahedron Lett.* **1986**, *27*, 2527. (b) Bulman Page, P. C.; Rosenthal, S. *Ibid.* **1986**, *27*, 1947.

(7) Yields were 90–95% determined by GC. Isolated yields were lower (30–80%), due to collection inefficiencies. IR, NMR, and GC/MS of the crude photolysate were consistent with the preparative GC findings. With other trapping agents more complicated product mixtures were observed.

(8) This rules out possible structures involving a β-lactone which might otherwise be considered.

(9) Ward, R. S. In *The Chemistry of Ketenes, Allenes, and Related Compounds*; Patai, S., Ed.; John Wiley and Sons: New York, 1980; Vol. 1.

(10) Matrix imposed limits on molecular motion in photochemical processes have been well documented; for example, see: Schmidt, G. M. J. In *Solid State Photochemistry*; Ginsberg, D., Ed.; Verlag Chemie: New York, 1976.

(11) (a) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Baines, K. M.; Brook, A. G. *Organometallics* **1987**, *6*, 692.

(12) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.