is 2-propanol. Plotting Φ_{ac}^{-1} vs. [2-propanol]$^{-1}$ yields a straight line with a slope of 6.9 and an intercept of 1.6, indicating that $\Phi_{ST}\Phi_c$ equals 0.63 while k_a^c/k_d^c is 0.23. We have estimated Φ_{ST} for acylsilane **1** to be 0.9 by using the sensitized dimerization of cyclohexadiene for triplet counting.[9,13] With the τ_T value determined above this allows us to estimate the efficiency ($\Phi_c = 0.70$) and the rate constant ($k_c = 5.4 \times 10^7$ s^{-1}) for formation of siloxycarbene from the acylsilane T_1 state.[14] The ratio of the rate constants for reaction of siloxycarbene **3** with 2-propanol and rearrangement of siloxycarbene **3** to acylsilane **1** ($(k_a^c/k_d^c) = 0.23$) clearly demonstrates that reversion of siloxycarbene to ground-state acylsilane is sufficiently facile that relatively high concentrations of 2-propanol are required for efficient trapping of the siloxycarbene.

In summary, we have shown that acetal formation upon irradiation of acylsilane **1** in the presence of 2-propanol occurs exclusively via reaction of alcohol with an intermediate, presumably siloxycarbene **3**, formed from the acylsilane T_1 state.[15] We are actively engaged in pursuing the generality of this conclusion with respect to other acylsilane photoreactions.[16]

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the Bowling Green State University Faculty Research Committee for support of this research.

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(13) Vesley, G. F.; Hammond, G. S. *Mol. Photochem.* **1973**, *5*, 367.

(14) If siloxycarbene formation involves initial α-cleavage this would be the α-cleavage rate constant.

(15) We have no definitive evidence at present on the multiplicity (singlet or triplet) of the siloxycarbene state which reacts with alcohol.

(16) See: (Dalton, J. C.; Bourque, R. A. *J. Am. Chem. Soc.* **1981**, following paper in this issue) for an interesting example of an acylsilane photoreaction that does not involve siloxycarbene intermediates.

Mechanistic Photochemistry of Acylsilanes. 2. Reaction with Electron-Poor Olefins

J. Christopher Dalton*

Department of Chemistry
Bowling Green State University
Bowling Green, Ohio 43403

Robert A. Bourque

Department of Chemistry, University of Rochester
Rochester, New York 14627

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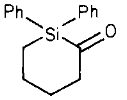
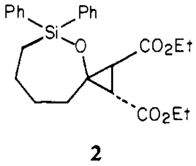
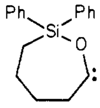
In 1971 Brook and co-workers reported that irradiation of silacyclohexanone **1** in diethyl fumarate results in the formation of the spirocyclopropane **2**.[1] This was taken at the time quite reasonably as prima facie evidence for the formation of siloxycarbene **3** in the photolysis of **1** and was thereby supportive of Brooks's general proposal that a number of acylsilane photoreactions occur via initial formation of a nucleophilic siloxycarbene intermediate.[1-3] Our interest in the photoreaction of acylsilanes and electron-poor olefins was prompted in part by an observation that *trans*-1,2-dicyanoethylene quenches the excited singlet state of simple acyclic acylsilanes with a bimolecular rate constant close to the diffusion-controlled limit.[4] This suggested the interesting possibility that cyclopropane formation might result from reaction of the electron-poor olefin with an acylsilane excited state rather than with a siloxycarbene.



1

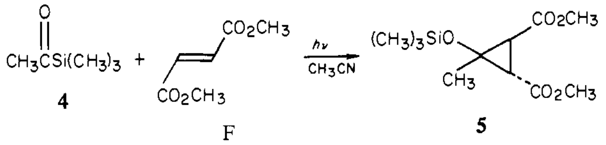


2



3

The photoreaction of acetyltrimethylsilane (**4**) with dimethyl fumarate (F) was chosen for study as a model system. Irradiation of acylsilane **4** in the presence of F leads in good yield to a single photoproduct, the *trans*-cyclopropane **5** (eq 1). No cis-trans isomerization of the fumarate is observed. Interestingly, the photoreaction of **4** with the *cis*-olefin, dimethyl maleate, is nonstereospecific, yielding a 3:2 mixture of *trans*- and *cis*-cyclopropanes, respectively.[5] We describe here experiments designed to determine the identity (S_1, T_1, siloxycarbene formed from S_1, and/or siloxycarbene formed from T_1) of the species, generated on irradiation of acylsilane **4**, which reacts with F to form cyclopropane **5**. The accompanying manuscript[6] demonstrates that acetal formation on irradiation of acylsilane **4** with 2-propanol occurs via reaction of the alcohol with a siloxycarbene formed by rearrangement of the acylsilane T_1 state. This information will be useful to us in unraveling the mechanism for cyclopropane formation.



(1)

The following observations clearly indicate that cyclopropane formation in the photoreaction of acylsilane **4** with F does *not* involve reaction of a siloxycarbene intermediate with the electron-poor olefin but rather results from direct reaction of F with both the acylsilane S_1 and T_1 states.

(1) Concentrations of 2-propanol up to 10 M have no effect on the quantum yield for cyclopropane formation from acylsilane **4** and F ([F] ≥ 0.002 M). Acetal, from reaction of siloxycarbene ($(CH_3)_3SiO\ddot{C}CH_3$) with 2-propanol,[6] is observed under these conditions. This observation demonstrates that the siloxycarbene responsible for reaction with 2-propanol to yield acetal is *not* reacting with F to yield cyclopropane.[7]

(2) Benzophenone (E_T = 69 kcal/mol[8a]) sensitization of reaction

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(1) Brook, A. G.; Kucera, H. W.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 1618.

(2) For reviews see: (a) Brook, A. G. *Intra-Sci. Chem. Rep.* **1973**, *7*, 131: (b) Brook, A. G. *Adv. Organomet. Chem.* **1968**, 7, 95.

(3) See, for example: (a) Brook, A. G.; Kucera, H. W.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 1618. (b) Brook, A. G.; Pearce, R.; Pierce, J. B.; *Ibid.* **1971**, *49* 1622. (c) Brook, A. G.; Pierce, J. B., Duff, J. M. *Ibid.* **1975**, *53*, 2874. (d) Brook, A. G.; Duff, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 2118. (e) Brook, A. G.; Dillon, P. J.; Pearce, R. *Can. J. Chem.* **1971**, *49*, 133. (f) Porter, N. A.; Iloff, P. M., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 6200. (g) Brook, A. G.; Duff, J. M. *Can. J. Chem.* **1973**, *51*, 352. (h) Watanabe, H.; Kogure, T.; Nagai, Y. *J. Organomet. Chem.* **1972**, *43*, 285. (i) Watanabe, H.; Ohsawa, N.; Sawai, M.; Kukasawa, Y.; Matsumoto, H.; Nagai, Y. *Ibid.* **1975**, *93*, 1973. (j) Hassner, A.; Soderquist, J. A. *Tetrahedron Lett.* **1980**, 429.

(4) Dalton, J. C.; Evitt, E. R.; Wu, M. M. S., unpublished results.

(5) Only one of the two possible *cis*-cyclopropanes is observed, the exact stereochemistry of which has not yet been determined. No cis-trans isomerization of the maleate occurs.

(6) Bourque, R. A.; Davis, P. D.; Dalton, J. C. *J. Am. Chem. Soc.* **1981**, preceding paper in this issue.

(7) The inability of 2-propanol to quench cyclopropane formation does not rigorously rule out the possibility that siloxycarbene generated from the acylsilane S_1 state reacts with F to yield cyclopropane. (Such a mechanism would require that siloxycarbene generated from acylsilane T_1 state react with 2-propanol but not F, while siloxycarbene generated from the S_1 state reacts with F but not 2-propanol). The observation that F strongly quenches fluorescence of **4**, however, coupled with the fact that the quantum yield for non-acylsilane triplet-derived cyclopropane formation continually increases with increasing F concentration clearly indicates that the non-triplet-derived cyclopropane is coming from reaction of the acylsilane S_1 state with F. The only way significant amounts of cyclopropane could be formed via olefin reaction with siloxycarbene generated from S_1 would be if such a carbene were in equilibrium with the acylsilane S_1 state. This seems an unlikely possibility.

(8) (a) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 3. (b) From phosphorescence spectrum: Dalton, J. C.; Evitt, E. R., unpublished results. (c) Hammond, G. S., et al. *J. Am. Chem. Soc.* **1964**, *86*, 3197. (d) Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cummings: Menlo Park, CA, 1978; p 353.

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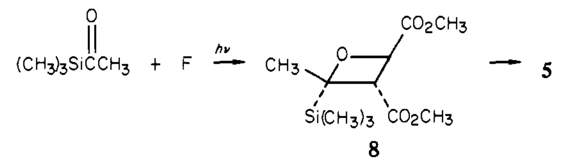
Scheme I



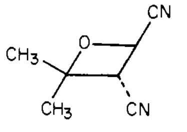
of acylsilane **4** (E_{T} = 61 kcal/mol[8b]) with F (E_{T} = 61 kcal/mol[8c]) results in clean formation of cyclopropane **5**. This, coupled with observation 1, suggests that the T_1 state of **4** is capable of reacting with F to yield cyclopropane **5**.

(3) 1,3-Cyclohexadiene (E_{T} = 54 kcal/mol[8d]) quenches only a fraction of the cyclopropane formation observed on direct irradiation of acylsilane **4** and F. Increasing the initial F concentration lowers the fraction of cyclopropane formation which can be quenched.[9] This clearly indicates that cyclopropane formation occurs from reaction of both the S_1 and T_1 states of acylsilane **4** with F. Increasing the initial F concentration leads to more S_1 (unquenchable) and less T_1 (quenchable) reaction.

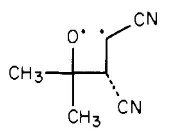
(4) The fluorescence of acylsilane **4** is readily quenched ($k_q\tau_f$ = 46)[10] by F. This observation is consistent with the conclusion from observation 3 that cyclopropane formation occurs in part via reaction of the acylsilane S_1 state with the electron-poor olefin.

This leaves the intriguing question of how reaction of the S_1 and T_1 states of acylsilane **4** with an electron-poor olefin such as F results in formation of cyclopropane **5**. The observed migration of silicon from carbon to oxygen cannot have taken place in the acylsilane excited state since that would yield siloxycarbene, which we have shown above is not involved in cyclopropane formation. Thus either an intermediate formed from interaction of the acylsilane S_1 and T_1 states with F or an initially formed undetected product must have undergone rearrangement. Consideration of the mechanism for photoreaction of other carbonyl compounds with electron-poor olefins offers some insight into these possibilities.

Alkanone ^{1}n,π^* states are well-known to undergo photoreaction with electron-poor olefins to yield oxetanes stereospecifically.[11,12] For example, irradiation of acetone and *trans*-1,2-dicyanoethylene yields oxetane **6**. The reaction is generally pictured as being initiated by interaction of the nucleophilic π system of the carbonyl ^{1}n,π^* state with the electron-deficient olefin.[11,12] Symmetry considerations have led to the suggestion that short-lived biradicals such as **7** should be intermediates in these photocycloaddition reactions.[11c,12,13]



6

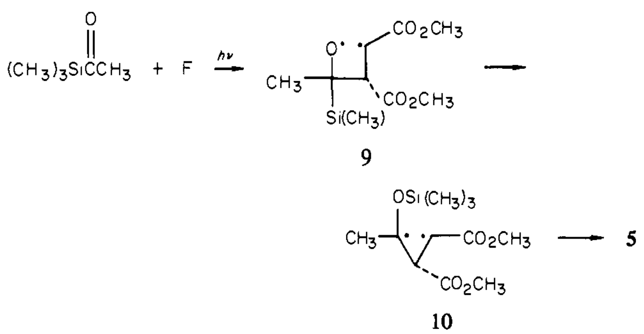


7

By analogy we suggest the two possible pathways for cyclopropane formation from photoreaction of acylsilanes with electron-poor olefins, shown in Schemes I and II.

In Scheme I, an initially formed oxetane (**8**) undergoes rearrangement to cyclopropane **5** under the reaction conditions. We consider this pathway to be unlikely since we know of no literature precedent and see no compelling reason why silicon substitution should render an oxetane such as **8** unstable to rearrangement.

Scheme II



Therefore, we favor the mechanism outlined in Scheme II in which initial formation of short-lived 1,4-biradical **9** is followed by a migration of silicon from carbon to the oxygen radical center, yielding 1,3-biradical **10** which subsequently closes to the cyclopropane product. This pathway would explain the lack of stereospecificity in the photoreaction of acylsilane **4** with dimethyl maleate if either **9** or **10** is long-lived enough to allow bond rotation prior to closure. It also rationalizes why cyclopropane formation is not observed on irradiation of acylsilanes and electron-rich olefins,[1,14] since formation of 1,4-biradicals such as **9** should occur only upon reaction of carbonyl excited states with electron-poor olefins.[11c,12,13]

Note that although alkanones react with electron-poor olefins only via the carbonyl ^{1}n,π^* state, acylsilane **4** reacts with F from both S_1 and T_1 states. This distinction may be due to the difference in alkanone and acylsilane triplet energies. For alkanones (E_{T} = 78 kcal/mol[16]), energy transfer to electron-poor olefins such as F (E_{T} = 61 kcal/mol[8c]) is diffusion controlled, ruling out all but the most rapid bimolecular ketone–olefin reactions. The much lower triplet energy of acylsilanes (E_{T} = 61 kcal/mol[8b]) makes energy transfer less favorable and bimolecular reactions more probable.

In summary, we have shown that formation of cyclopropane **5** results from reaction of both the S_1 and T_1 states of acylsilane **4** with dimethyl fumarate, rather than via addition of a photochemically generated siloxycarbene to the electron-poor olefin. Although the generality of our results remains to be determined, it is now clear that the observation of cyclopropane formation on irradiation of acylsilanes with electron-poor olefins does not necessarily implicate a siloxycarbene intermediate in these reactions. Since photolysis of acylsilanes yields cyclopropanes only with electron-poor olefins,[1,14] there are no longer any documented examples of addition of siloxycarbenes to olefins.[17] This may make the behavior of siloxycarbenes easier to rationalize.[18]

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the National Science Foundation, and to the Bowling Green State University Faculty Research Committee for support of this research.

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(9) For example, increasing the initial F concentration from 0.021 to 0.083 M decreases the fraction of cyclopropane formation that is quenchable from 50% to 34%. The quenchable and unquenchable portions of the reaction are determined from the Φ^0/Φ values at which the slope of the Stern–Volmer plots for cyclohexadiene quenching of cyclopropane formation becomes zero.

(10) This is the slope of the Stern–Volmer plot (Φ_f^0/Φ_f vs. [F]) for F quenching of the fluorescence of acylsilane **4**.

(11) For reviews see: (a) Turro, N. J. *Pure Appl. Chem.* **1972**, *27*, 697. (b) Turro, N. J., et. al. *Acc. Chem. Res.* **1972**, *5*, 92. (c) Reference 8d, pp 432–446.

(12) See, for example: Yang, N. C., et al. *J. Am. Chem. Soc.* **1977**, *99*, 3023 and references therein.

(13) Dauben, W. G.; Salem, L.; Turro, N. J.; *Acc. Chem. Res.* **1975**, *8*, 41.

(14) Bourque, R. A.; Dalton, J. C., unpublished results. No intermolecular photocycloaddition products have been observed with acylsilanes and electron-rich olfeins. The acylsilane excited singlet state is significantly less electrophilic than alkanone excited singlet states.[15]

(15) Friedrich, L. E.; Hamilton, M. A.; Dalton, J. C. *Mol. Photochem.*, in press; (b) Dalton, J. C.; Bourque, R. A.; Evitt, E. R.; Wu, M. M. S., unpublished results.

(16) Reference 8d, p 290.

(17) Oxycarbenes generated by ring expansion on photolysis of cyclobutanones also appear reluctant to undergo addition to olefins.[19] For both siloxycarbenes and these cyclic oxycarbenes, facile rearrangement to the carbonyl compound may be in part responsible for the low efficiency of cyclopropane formation.[6,20]

(18) See: Moss, R. A. *Carbenes* **1973**, *1* 281.

(19) See, for example: Morton, D. R.; Turro, N. J. *Adv. Photochem.* **1974**, *9*, 235. (b) Morton, D. R.; Turro, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 3947.

(20) (a) Smith, A. B., III; Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5100. (b) Foster, A. M.; Agosta, W. C. *Ibid.* **1972**, *94*, 5777. (c) *Ibid.* **1973**, *95*, 608. (d) Brook, A. G.; Harris, J. W.; Bassindale, A. R. *J. Organomet. Chem.* **1975**, *99*, 379.