

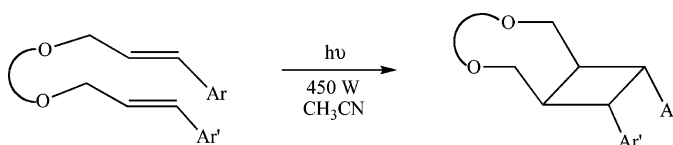
Mechanistic Analysis of the Photocycloaddition of Silyl-Tethered Alkenes

Steven A. Fleming,* Alexander A. Parent, Ephraim E. Parent, James A. Pincock, and Lise Renault

Department of Chemistry & Biochemistry, Brigham Young University, Provo, Utah 84602, and
Department of Chemistry, Dalhousie University, Halifax, NS B3H 4J3, Canada

steve_fleming@byu.edu

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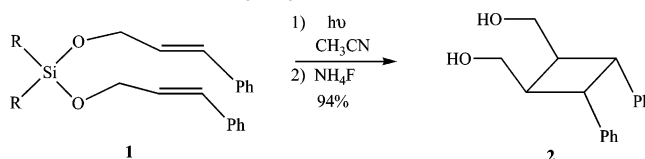


The photochemistry of substituted cinnamyloxy silanes has been examined in both cyclohexane and acetonitrile solvents. Alkene isomerization occurs in addition to cycloaddition. Fluorescence quantum yields and excited singlet state lifetimes have been determined for each compound. We have used the information in order to better understand the regio- and stereoselectivity of photocycloaddition between silyl-tethered cinnamyl groups. This study allows us to conclude that the 2 + 2 photocycloaddition between alkenes is not a Woodward–Hoffmann orbital symmetry controlled event. The most consistent explanation for the excellent regio- and stereoselectivity is that the photocycloaddition is conformationally controlled.

Introduction

We have been interested in the synthetic utility of 2 + 2 photocycloaddition using silyl tethered alkenes. One of our first observations was that irradiation of dicinnamyloxysilane (**1**) results in nearly quantitative formation of the cis-substituted cyclobutane (**2**) as shown in Scheme 1.¹ We were encouraged by the efficiency of this reaction and promptly explored the generality of this carbon–carbon bond-forming methodology. We have found that this cycloaddition is effective between a styrenyl group and other extended π systems (e.g., styrenyl, dienyl, furanyl, cyclopropyl, alkynyl).^{1,2} In all cases we found that the π -containing groups are obtained very selectively cis to each other on the cyclobutane. However, a number of issues indicated that a more thorough mechanistic study was necessary to expand the methodology to include all alkenes. For instance, cycloaddition was not observed between a styrenyl and a non- π -extended alkene (e.g., allyl, 3-methylallyl, and 3,3-dimethylallyl). The fact that the non-extended π -substituted alkenes are not found to undergo photocycloaddition has limited the scope of the reaction.

SCHEME 1. Dicinnamyloxysilane Irradiation



Enone–alkene and carbonyl–alkene (Paterno–Buchi) photocycloadditions have been studied extensively and have been found useful in numerous synthetic applications.³ Alkene–alkene photocycloadditions have been studied less and present challenges that the triplet pathway of enones and Paterno–Buchi reactions are able to avoid. One of the most significant obstacles in alkene photochemistry is the short excited singlet state lifetime. However, we have found that tethering the alkenes is a logical and effective way to deal with this issue. Interestingly, the triplet excited-state alkene + alkene cycloadditions give trans-substituted cyclobutanes as the major products.⁴

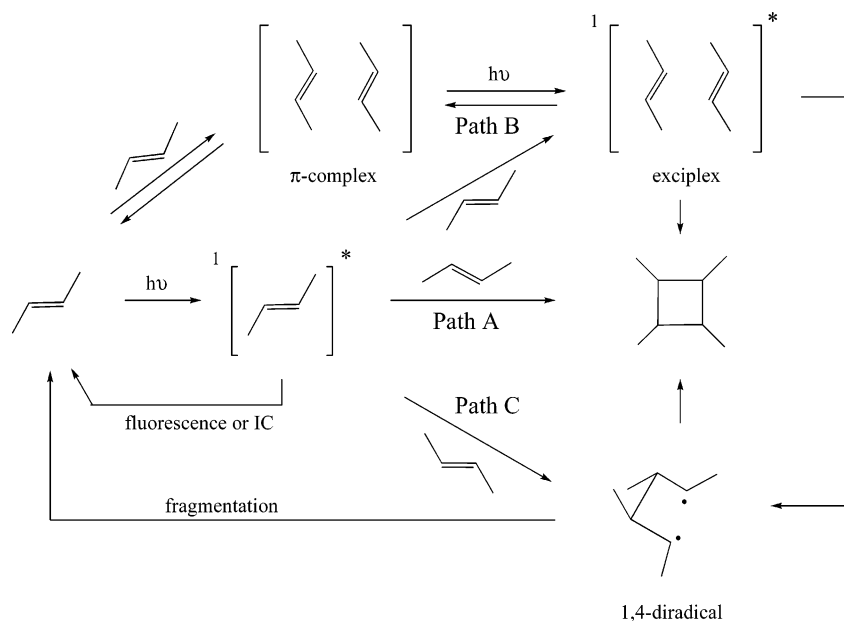
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SCHEME 2. Mechanistic Pathways Available for Alkene–Alkene 2 + 2 Photocycloaddition



Copper coordination has also been used to bring alkenes together for photocycloaddition. Steric interactions and heteroatom coordination control this useful reaction.⁵ Ramamurthy and co-workers⁶ have reported the selectivity of photocycloadditions in caged systems. This very useful methodology, however, does not easily extend to photocycloaddition between two differing alkenes. Solid-state photochemistry⁷ has also been used for providing stereocontrol of cycloadducts. Once again, this approach is difficult to apply when cycloaddition between two different alkenes is desired.

Silicon is not the only tethering moiety available for alkene photocycloadditions. Carbon-tethered styryl groups also give high yields of stereoselectively formed cyclobutanes,⁸ although this tether unit is more difficult to remove. It is worth noting that these examples, and the earlier work by many others,⁹ consistently show a preference for formation of the *cis*-substituted cyclobutanes. Also worth noting is that the use of cinnamyl groups for photo-cross-linking in polymer systems has been reported by Nakayama and Matsuda.¹⁰ A better under-

standing of the reaction would improve the utility of polymer cross-linking.

Possible Mechanisms

There are at least three mechanistic pathways (see Scheme 2) that one might consider for the silyl-tethered photocycloaddition. Path A is the concerted, symmetry allowed, $2 + 2$ process. This should, however, lead to *trans*-diphenylcyclobutanes or *trans*-fused bicyclo[5.2.0] ring systems. Path B is a concerted π -stacking pathway. It is possible that the *cis* selectivity might arise from a π -stacking phenomenon. Good evidence has been presented for this type of interaction in the vinyl anthracene case reported by Nishimura and co-workers.¹¹ If one assumes that the π interaction is necessary, either in the ground or the excited state, the lack of reactivity of non-extended π -substituted alkenes would be explained. Path C that should be considered, is a stepwise radical mechanism proceeding through a 1,4-diradical.¹² This mechanism is consistent with the need for radical-stabilizing extended π -groups on the reacting alkenes and fits particularly well with the cross $2 + 2$ results from the irradiation of silyl enol ether **3** shown in Scheme 3.¹ To further elucidate the mechanism of this reaction, we have synthesized a number of silyl-tethered alkenes and, on the basis of their photophysical properties and photochemical outcome, are prepared to draw conclusions concerning the reaction pathway.

Results and Discussion

1. Bis-Silyl Enol Ether (Z,Z-4). The bis-silyl enol ether (Z,Z-4, R = CH₃) was reported to undergo bond formation through

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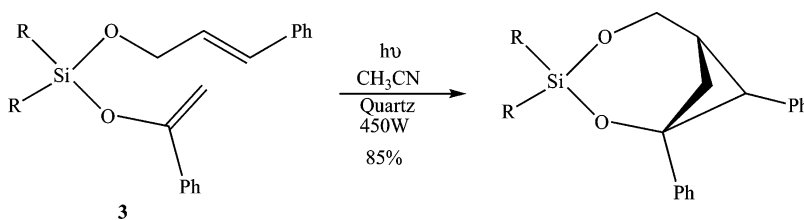
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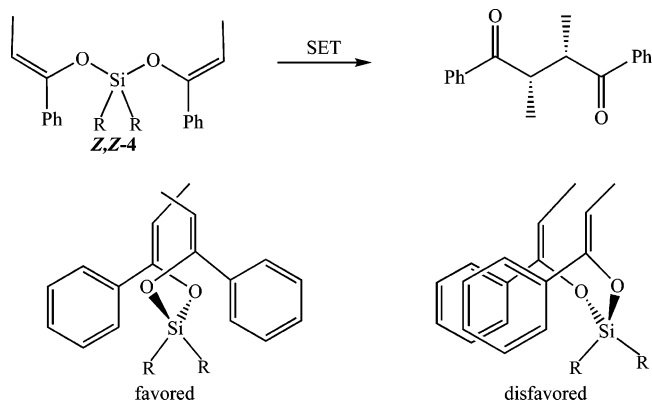
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SCHEME 3. Cinnamyloxysilyl Enol Ether and the Cross 2 + 2 Cycloaddition Product



SCHEME 4. Bis-Silyl Enol Ether Z,Z-4 SET Results

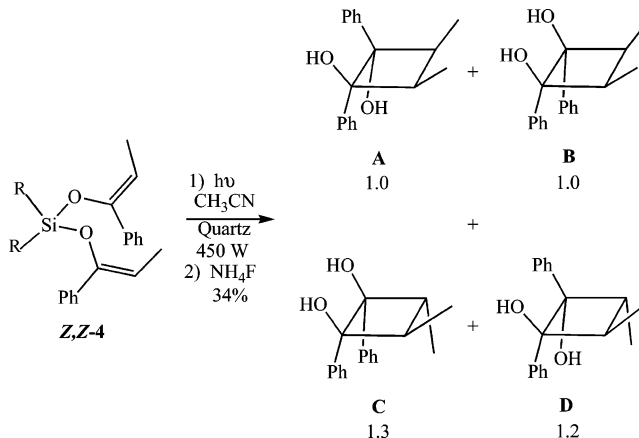


an intermediate radical cation in the presence of ceric ammonium nitrate (CAN) in a regio- and stereoselective fashion under thermal conditions (see Scheme 4) by Schmittel and co-workers.¹³ They found that the product in this reaction resulted from an avoidance of the steric interactions between the phenyl groups. They argued that the favored ground state conformation of this molecule has the phenyl groups not π stacking. On the basis of this work, we felt that a photochemical study of this compound would be an excellent way to establish the role of π stacking in alkene-alkene tethered systems. If cycloaddition occurs and π stacking is required, then π stacking would necessarily be an excited state phenomenon and one would expect the phenyl groups to be *cis* to each other in the resulting cyclobutane. If cycloaddition occurs and π stacking is not required, then the Schmittel-favored conformation would yield *trans* phenyl groups in the resulting cyclobutane. If the cyclobutane product has the phenyl groups *trans* to each other, then we would conclude that the photocycloaddition requires only the radical stabilizing ability of the extended π system.

We synthesized compound **Z,Z-4** ($\text{R} = \text{iPr}$) using the literature procedure¹³ and irradiated the resulting tethered diene. Unfortunately, the cyclobutane products that were obtained included both *cis*- and *trans*-1,2-diphenylcyclobutanes in nearly equal amounts as shown in Scheme 5. These ratios were determined by NMR analysis of the crude mixture of hydrolyzed material. Diols **A** and **C** both have two methyl doublets, one of which is significantly shielded (0.40 and 0.71 ppm, respectively). The symmetrical cyclobutanes **B** and **D** have only one methyl doublet (1.24 and 1.18 ppm, respectively). We believe that the *cis*-diphenyl arrangement in **B** results in less symmetry for the cyclobutyl ring hydrogens which are observed at 3.10 ppm compared to the clean quartet for the ring hydrogens of **D** that appear at 3.07 ppm.

In addition to the nearly equal distribution of cyclobutanes, we observed that the original silyl enol ether undergoes *E-Z*

SCHEME 5. Bis-Silyl Enol Ether Photochemical Results



isomerization during the reaction. For instance, as determined by NMR at 65% conversion of **Z,Z-4**, both **E,Z-4** and **E,E-4** were observed as 60% of the photomixture and less than 5% of the cyclobutanes were formed. It is obvious that this lack of stereochemical integrity complicates what was intended to be an easy answer to the mechanistic question. Our study of compound **4** does not elucidate the mechanism of the silyl-tethered photocycloaddition.

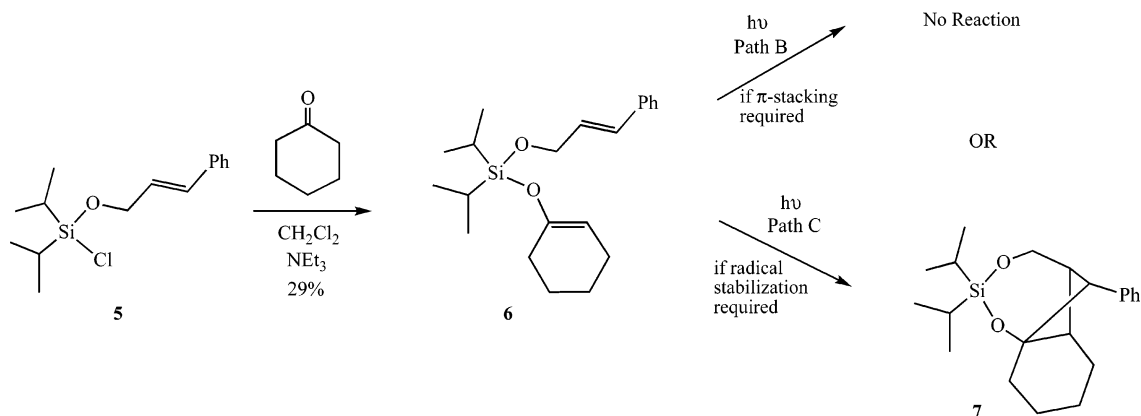
2. Cyclohexenyl Cinnamyl Ether (6). Because the bis-silyl enol ether did not provide an increase in mechanistic understanding, we turned our attention to a tethered silyl enol ether in which one substituent was lacking a conjugated phenyl group. The synthesis of the silyl enol ether of cyclohexanone with use of chlorocinnamyloxydiisopropylsilane (**5**) resulted in formation of the diene **6** (see Scheme 6). We reasoned that this compound would not undergo photocycloaddition if π stacking (Path B) is required. We also felt that the diradical-stabilized pathway (Path C) would lead to formation of the cross 2 + 2 product, compound **7**.

Irradiation of **6** leads to two major cyclobutanyl products **8** and **9** (1:1) and two diastereomeric cyclohexanones **10** (see Scheme 7). Identification of the photoproducts was accomplished by several NMR methods including COSY, HETCOR, and NOE. The fact that the cross 2 + 2 product (**7**) is not formed establishes that the most stable diradical intermediate is not involved (Path C). Interestingly these products implicate the need for a minimum energy conformational arrangement of the alkenes in order for the cycloaddition to occur. Thus, a π stacking of the alkenes is needed, but not necessarily a stacking of aromatic rings.

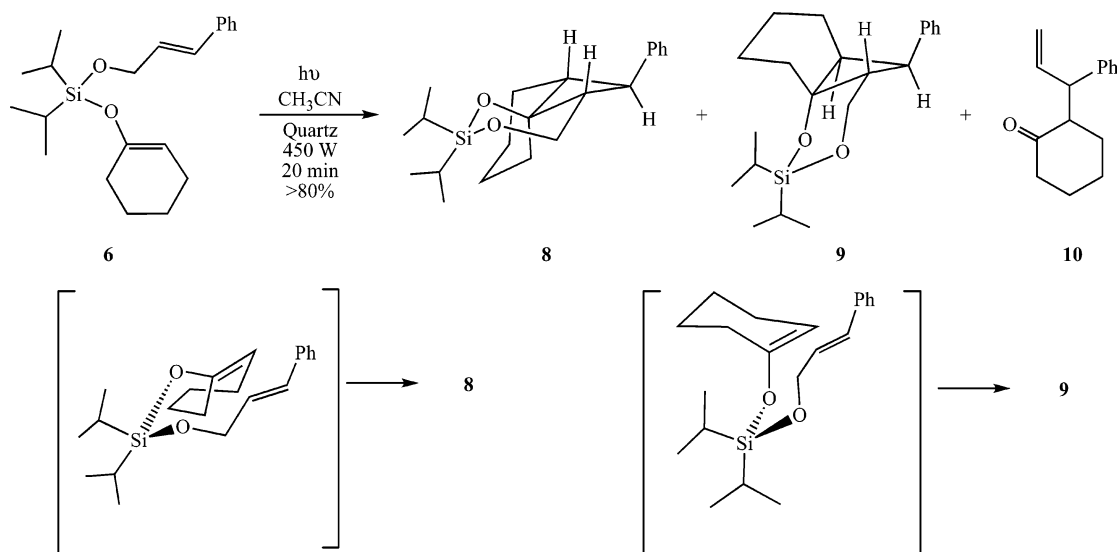
The cyclohexanone products are thought to arise from hydrolysis and ring-opening of the initially formed cyclobutane products. We have found that the cyclobutane products are photochemically stable and do not appear to be undergoing secondary photochemistry to give the 2-(1-phenylallyl)cyclohexanone.

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SCHEME 6. Synthesis and Predicted Photochemistry of Cinnamyloxysilyl Enol Ether (6)



SCHEME 7. Photochemical Results of Dialkoxysilane 6



3. Cinnamyloxy Silanes 11a,b and 12a–e. To probe for a possible interaction between the rings in diaryl derivatives, we have examined the photochemistry and photophysics of two ring-substituted dicinnamyloxysilanes, **11a** and **11b**. These were designed with an electron donor on one ring (methoxy group) and an electron-withdrawing group on the other (trifluoromethyl group) to test for the possibility of π stacking with this push–pull type system.¹⁴ We also speculated that the alkenes would more efficiently undergo cycloaddition in this type of tethered system. The synthesis of the dialkoxy silanes was performed as with previous tethering of alkenes proceeding through reaction of dichlorodiisopropylsilane with 1 equiv of the appropriate cinnamyl alcohol to give the alkoxy chlorodiisopropylsilane, which was then distilled and finally reacted with a second alcohol. In this fashion, (4-methoxycinnamyloxy)(4-trifluoromethylcinnamyloxy)diisopropylsilane (**11a**) and (3-methoxycinnamyloxy)(3-trifluoromethylcinnamyloxy)diisopropylsilane (**11b**) were synthesized (see Figure 1).

To compare the photophysical properties of the methoxy- and trifluoromethyl-substituted compounds, we also synthesized and studied the TMS ethers **12a–d** (Figure 1) of the para- and meta-substituted cinnamyl alcohols.

Although we thought we might see evidence of a charge-transfer interaction in the ground state between the two arms of the tethered silane, none was found. For instance, the UV spectrum in acetonitrile (AN) for (4-methoxycinnamyloxy)(4-trifluoromethylcinnamyloxy)diisopropylsilane **11a** (ϵ at the λ_{max} of 258 nm = $3.95 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) was superimposable on the sum of the normalized UV spectra of 4-trifluoromethylcin-

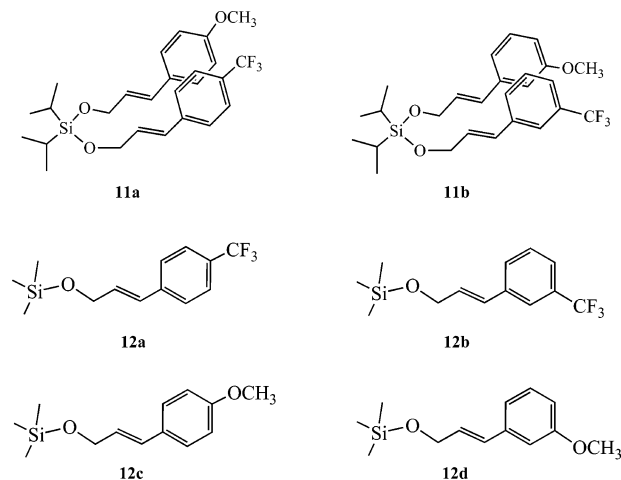


FIGURE 1. Alkenes **11a,b** and **12a–d** synthesized for photophysics.

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TABLE 1. Photophysics of Silanes in Acetonitrile (AN) and Cyclohexane (CX) at 25 °C

compd	quantum yield of fluorescence		lifetime (ns) ^a	
	AN	CX	AN	CX
4-CF ₃ cinnamyloxy silane, 12a	0.17	0.26	3.0	3.7
3-CF ₃ cinnamyloxy silane, 12b	0.31	0.22	5.4	4.2
4-MeO cinnamyloxy silane, 12c	0.36	0.50	6.3	6.5
3-MeO cinnamyloxy silane, 12d	0.50	0.44	6.5	5.8
4-H, 4-H dicinnamyloxy silane, 1	0.01		0.47 (98); 8.4 (2)	
4-MeO, 4-CF ₃ dialkoxy silane, 11a	0.035	0.043	0.31 (96); 5.7 (4)	0.35 (97); 4.4 (3)
3-MeO, 3-CF ₃ dialkoxy silane, 11b	0.12	0.064	0.95 (98); 7.7 (2)	0.72 (98); 5.1 (2)

^a The fluorescence decay of the dicinnamyl derivatives was biexponential and both lifetimes are given. The numbers in parentheses give the relative contribution of each decay to the total decay.

TABLE 2. Photoproducts (% Yield) from Irradiation of TMS Ethers for 1 h at 254 nm

compd	solvent	E-starting material	Z-starting material	E-1,3 H-	Z-1,3 H-	unknown
4-CF ₃ TMS, 12a	CX			51	40	9
4-CF ₃ TMS, 12a	AN			< 5	30	20 (ald)
3-CF ₃ TMS, 12b	CX		trace	37	35	25 (ald)
3-CF ₃ TMS, 12b	AN	trace	6	17	22	55 (ald)
4-methoxy TMS, 12c	CX	59	34	3	4	
4-methoxy TMS, 12c	AN	60	40	trace	trace	
3-methoxy TMS, 12d	CX	28	25	24	8	15
3-methoxy TMS, 12d	AN	21	21	46	12	
cinnamyl TMS, 12e	CX	12	9	38	40	
cinnamyl TMS, 12e	AN	13	14	45	29	

namyloxy trimethylsilyl ether **12a** ($\lambda_{\text{max}} = 252$ nm, ϵ at 250 nm = 1.96×10^4 M⁻¹ cm⁻¹) and 4-methoxycinnamyloxy trimethylsilyl ether **12c** ($\lambda_{\text{max}} = 261$ nm, ϵ at 250 nm = 1.90×10^4 M⁻¹ cm⁻¹). In fact the UV spectra were all very similar to that expected for styrene derivatives with a lower intensity, long wavelength band exhibiting vibrational fine structure between 270 and 310 nm and a broad, higher intensity short wavelength band around 250 nm; the relative intensity of these two bands was about 10:1.

However, the fluorescence spectra did give evidence for a π -stacking interaction in the excited state. Table 1 shows the fluorescence quantum yields for each of the cinnamyl compounds in both acetonitrile (AN) and cyclohexane (CX). The mono-cinnamyloxy silanes (**12a–d**) are similar in fluorescence quantum yield in both solvents although the meta-substituted compounds **12b** and **12d** fluoresce somewhat more efficiently than the para analogues **12a** and **12c** in AN but less efficiently in CX. In addition, the methoxy cinnamyl derivatives **12c** and **12d** are more efficient fluorophores than the trifluoromethyl compounds **12a** and **12b**. This is a consequence of the extended π system available to the alkoxy-substituted rings.

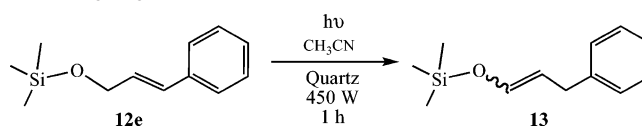
As indicated by their decreased fluorescence yields, the dialkoxy-substituted silanes clearly have a pathway of deactivation that is not available for the monomers, which is clear evidence of π - π interaction between the chromophores. Interestingly, the meta-disubstituted silane **11b** is more fluorescent than the para-substituted one (**11a**). We suspect this is due to increased overlap between the two styrenyl chromophores in the para-substituted isomer. This overlap may enhance the alternative, nonradiative pathway for deactivation of the excited state.

The excited state lifetime data provide additional evidence of π -stacking. Each of the tethered dienes exhibited a biexponential fluorescence decay. In all cases, the short-lived component is the major contributor to the decay (>95%). Moreover, the long-lived component is similar in lifetime to the corre-

sponding mono-ene, where determined. This observation is perhaps indicative of two conformers, a major one that is short-lived because of π -stacking and a stretched one that is long-lived. This implies that the dienes have a rapid decay route that is unavailable to the monomers, presumably a rapid and efficient cycloaddition process with a rate constant on the order of 10^9 s⁻¹ that competes with fluorescence. Although the differences are small, this decay pathway is most efficient for the case that has the tethered cinnamyloxy groups substituted in the para positions (lifetime of 0.31 ns for **11a**) compared to the isomeric meta compound (lifetime of 0.95 ns for **11b**). This decay route is also faster than that of the unsubstituted dicinnamyloxy silane (lifetime of 0.47 ns for **1**), although the difference is not as significant. The data for the dialkoxy-tethered silanes determined in cyclohexane shows similar lifetime behavior.

The photoproducts from each of the trimethylsilyl ethers are provided in Table 2 from irradiations in both cyclohexane and acetonitrile. Along with rapid photochemical *E* to *Z* isomerization, the major product formed upon irradiation of the unsubstituted cinnamyl TMS ether **12e** in both cyclohexane and acetonitrile was the 1,3-hydride shift product, 3-phenyl-1-propenyl TMS ethers (**13E** and **13Z**, see Scheme 8). This compound was independently synthesized to verify its identity.

SCHEME 8. Photoisomerization of Cinnamyloxy Trimethylsilyl Ether



The 3-methoxy-substituted derivative **12d** behaves similarly to the unsubstituted cinnamyl silyl ether, providing evidence of poor communication between the chromophore, which is the

styrene moiety, and the meta substituent.¹⁵ In contrast, the trifluoromethyl analogues (**12a** and **12b**) were much more photoactive than the unsubstituted TMS ether (**12e**), both undergoing essentially complete conversion to the 1,3-hydride shift product in the 1 h of irradiation. Presumably this is a reflection of the significant inductive effect that the CF₃ group provides from both the 3- and 4-positions. The aldehyde that is observed in these reactions is detected by NMR and likely arises from hydrolysis of the moisture-sensitive silyl enol ethers.

Irradiation of the 4-methoxy analogue, compound **12c**, results in *cis/trans* isomerization as the predominant pathway in either solvent, with only low yields of the 1,3-shift product. A low yield of the comparable product was also observed for the photochemistry of 4-methoxycinnamyl acetate in both cyclohexane and methanol.¹⁵

The photochemistry of the tethered alkenes provides strong evidence for the importance of the interaction between the two chromophores. The dicinnamyl silane, as previously reported,¹ undergoes a very efficient cycloaddition. In fact, we were forced to reduce the rayonet photoreactor light intensity by reducing the number of lamps from 16 to 4 in order to see partial conversion (less than 40%) after 5 min of irradiation. Even compound **11b**, with the *m*-trifluoromethylcinnamyl group tethered to the *m*-methoxycinnamyl, reacted with a similar efficiency to compound **1**. In contrast, the 4-methoxycinnamyl-4-trifluoromethylcinnamyl silane, **11a**, was significantly more photoactive. In the same photolysis setup, a 75% conversion resulted after only 5 min. We interpret this as evidence of increased π stacking and more conformational control between the styrenyl groups in the excited state for the para-substituted analogue (Path B). Both tethered systems **11a** and **11b** give the corresponding cyclobutanes as single products with the same regio- and stereochemical outcome as the unsubstituted compound **1** (see Scheme 1). The yield for the photocycloaddition is >95% based on NMR analysis. Prolonged irradiation does result in loss of the original cyclobutane.

Conclusion

Our results indicate that singlet 2 + 2 photocycloaddition between alkenes is dependent on a close relationship between the alkene groups. We have observed that the alkenes can be held sufficiently close as a result of either π stacking or a conformational preference. This is consistent with a short-lived excited state or exciplex, which has the ability to stabilize polar groups. Most importantly, these results indicate that the regio- and stereochemical outcome of the 2 + 2 cycloaddition between tethered alkenes is not dictated by the rules of orbital symmetry nor by stability of radical intermediates.

We are continuing to study the utility of the alkene + alkene photocycloaddition. We expect that a polar group on the para position will produce sufficient π - π interactions between a styrenyl group and a non-aryl-substituted alkene (e.g., allyl, 3-methylallyl, or 3,3-dimethylallyl) to result in efficient photocycloaddition.

Experimental Section

General Synthetic Procedure for Substituted Silanes. The commercially available substituted cinnamic acid was converted to its respective ester by refluxing in 100% ethanol in the presence

of a catalytic amount of *p*-toluenesulfonic acid for 24–36 h. The isolated ester was then treated with 3 equiv of diisobutyl aluminum hydride (DIBAL) in toluene in an ice bath. The reaction was allowed to stir for 2 h. The reaction was quenched with aqueous 5% HCl and extracted with ether. The organic layer was washed with aqueous 5% HCl, water, and brine, and then dried. The resulting alcohol was purified by recrystallization or chromatography. Treatment of the alcohol with excess chlorotrimethylsilane in methylene chloride, then purification by chromatography, yielded the substituted cinnamyl silyl ether. The dialkoxysilanes were synthesized by treating an alcohol with dichlorodiisopropylsilane (4 equiv) and triethylamine (1 equiv) in methylene chloride in an ice bath. The reaction was stirred overnight at rt. The monochlorosilane was isolated by concentration and pentane extraction. Kugelrohr distillation (approximately 120 °C, 0.2 mmHg) gave the pure monochloride, which was treated immediately with 1 equiv of the second alcohol and triethylamine in methylene chloride. The mixture was stirred for 18 h at rt, then concentrated and washed with pentane. Concentration and chromatography (silica gel, 5% ethyl acetate:hexane) gave the desired dialkoxysilane.

(Z,Z)-Diisopropyldi(1-phenyl-1-propenoxy)silane (4).¹³ Synthesis of the bis-silyl enol ether was carried out as indicated in the literature with use of dichlorodiisopropylsilane rather than dimethyldichlorosilane. The crude mixture (41% yield) was purified by chromatography (silica gel, hexane) to give the desired compound in 30% yield.

Diisopropylcinnamyloxysilyl Enol Ether of Cyclohexanone (6). The synthesis of the cinnamyloxysilyl enol ether of cyclohexanone was accomplished by using a modified literature procedure.¹⁶ Sodium iodide (0.60 g, 4.0 mmol, dried in a 200 °C oven for a week) was dissolved in 5 mL of acetonitrile and added to 0.37 g (3.8 mmol) of cyclohexanone in 10 mL of ACN. To this mixture was added 0.55 g (5.4 mmol) of Et₃N, followed by dropwise addition of 1.07 g (3.8 mmol) of diisopropylcinnamyloxysilyl chloride. The resulting solution was diluted to 25 mL with acetonitrile and heated at reflux with stirring for 4 h. The solution was allowed to cool to room temperature, diluted with approximately 20 mL of distilled water, and extracted with pentane three times. The combined organic layers were then washed three times with distilled water, dried over anhydrous sodium sulfate, and concentrated to give a crude yield of 1.16 g (3.4 mmol, 89% yield). Chromatography gave 0.383 g (1.1 mmol, 29% yield) of pure product.

General Photochemical Procedure. The silyl ethers were irradiated in nonpolar (cyclohexane) or polar (acetonitrile) solvents. Irradiations were performed on a rayonet apparatus, using with use of sixteen 254 nm lamps with a quartz well in the center of the irradiation chamber unless otherwise indicated. The samples were approximately 100 mg in 100 mL of solvent. All irradiations were deoxygenated by bubbling with nitrogen for at least 30 min prior to and during the irradiation. In the rayonet setup the solutions were stirred throughout the experiment and a temperature probe maintained the temperature at 25 °C. The solutions were monitored by tlc or GC/MS during the experiment and concentrated after 1 h unless otherwise indicated. NMR analysis was used to determine the components present in each photomixture. For cycloaddition reactions the conversion to cyclobutane was confirmed by GC and NMR. The amount of conversion was based on NMR integration of the -CH₂O- group.

Irradiations in Cyclohexane: (a) (Z,Z)-Diisopropyldi(1-phenyl-1-propenoxy)silane (4). The bis-silyl enol ether (300 mg, 0.79 mmol) was added to 350 mL of cyclohexane and the mixture was irradiated with a 450 W immersion well apparatus with a quartz jacket for 10 h. The solution was concentrated and transferred to 50 mL of methanol to which NH₄F (105 mg, 2.84 mmol) was added and refluxed. A water/chloroform extraction yielded 180 mg of crude product. The mass lost after the extraction roughly corre-

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sponds to the theoretical amount lost upon cleavage of the silyl tether (120 mg, 1.05 mmol). Separation by chromatotron, using an increasing concentration of an ethyl acetate:hexane solvent, yielded 8 UV active bands. These bands included the four 3,4-dimethyl-1,2-diphenyl-1,2-cyclobutanediol products (42 mg, 0.15 mmol, 19%), propiophenone (57 mg, 0.43 mmol, 27%), polymeric material, and two other minor fractions (<5%) that were unidentified.

(b) (Z,Z)-Diisopropylidi(1-phenyl-1-propenoxy)silane (4), Low Conversion. The bis-silyl enol ether (110 mg) was added to 100 mL of cyclohexane and the mixture was irradiated with a 450 W immersion well apparatus with a quartz jacket for 1 h. The solution was concentrated and an NMR was taken of the crude material. The presence of two major methyl signals in the 1.8 region establish the *E*–*Z* isomerization of the alkene. There is more *E* isomer (1.75 ppm) than the initial *Z* (1.82 ppm) and only a small amount of cycloaddition (methyl doublet at 0.5 and 0.8 ppm) after this short time of irradiation.

Irradiations in Acetonitrile: (a) (Z,Z)-Diisopropylidi(1-phenyl-1-propenoxy)silane (4). The bis-silyl enol ether (488 mg, 1.28 mmol) was added to 510 mL of acetonitrile and the mixture was irradiated with a 450 W immersion well apparatus with a quartz jacket for 11 h. The solution was concentrated and transferred to 50 mL of methanol to which NH_4F (190 mg, 5.14 mmol) was added. This solution was refluxed for 10 h and then concentrated under reduced pressure. A water/chloroform extraction yielded 331 mg of crude product. The mass lost after the extraction corresponds to the theoretical amount lost upon cleavage of the silyl tether (149 mg, 1.30 mmol). Separation by chromatotron, using increasing concentrations of an ethyl acetate:hexane solvent, yielded 13 UV active bands. These bands included the four 3,4-dimethyl-1,2-diphenyl-1,2-cyclobutanediol products (116 mg, 0.44 mmol, 34%), propiophenone (93 mg, 0.70 mmol, 27%), polymer (85 mg, 26 mass percent of crude product), and seven other fractions that were unidentified.

(b) Diisopropylcinnamyloxysilyl Enol Ether of Cyclohexanone (6). Irradiation of the cinnamyloxysilyl enol ether of cyclohexanone (0.242 mg in 250 mL) was carried out with use of a 450 W immersion well with a quartz jacket. Complete conversion of starting material was noted by 15 min. Four major products were obtained. Two are cyclobutanes and two are diastereomeric isomers of desilylated photoproduct (ca. 30%). The diastereomers are known compounds and are very difficult to separate.²² The percent yield of the cyclobutane products is 50%.

(c) Dicinnamyloxydiisopropylsilane (1). Irradiation of 0.099 g of dicinnamyloxy silane¹ in 100 mL of acetonitrile with the standard rayonet apparatus (16 lamps) for 20 min resulted in complete consumption of starting material. Concentration of solvent provided 0.101 g of cyclobutane (>80%). Irradiation of 0.105 g of dicinnamyloxy silane in 100 mL of acetonitrile under the same conditions for 10 min resulted in 0.110 g of material that contained no starting material and ~85% cyclobutane. Irradiation of 0.095 g of dicinnamyloxy silane in 95 mL of acetonitrile for 5 min resulted in complete conversion to ~95% cyclobutane. Irradiation of 0.097 g of dicinnamyloxy silane in 99 mL of acetonitrile with four lamps in the rayonet apparatus for 5 min gave a clean incomplete conversion to cyclobutane. The ratio of dialkenylsilane to cyclobutane was 61.9:38.1. Irradiation of 0.055 g of dicinnamyloxy silane in 75 mL of acetonitrile for 10 min with the four-lamp arrangement gave 0.060 g of cyclobutane (>95% conversion).

Supporting Information Available: Experimental procedures for this work and the spectral data for **4**, **6**, **8**, **9**, **10**, **11a,b**, **12a–e**, and photoproducts of **11a,b** and **12a–e**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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