Photochemistry of Di-π-silanes

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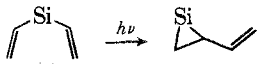
The excited-state chemistry of di-π-silane systems, in which two vinyl or π moieties are attached to a quaternary silicon atom, has been studied in an exploratory and mechanistic fashion. The compounds investigated are *trans*-β-styryltriphenylsilane (**3t**), *trans,trans*-bis(β-styryl)dimethylsilane (**1tt**), and *trans,trans*-bis(β-styryl)diphenylsilane (**2tt**). Our results from studies of the direct and triplet-sensitized irradiations of these compounds have demonstrated that (1) these di-π-silanes, having structures closely analogous to hydrocarbon systems which undergo the di-π-methane rearrangement, fail to isomerize to corresponding π-substituted silacyclopropanes, (2) cis–trans isomerization about π bonds are the energy dissipating and exclusive reaction modes observed upon excitation of **1–3**, and (3) the preferred mechanism for cis–trans isomerization for the bis(β-styryl)silane **1tt** does not appear to involve interaction between the two "nonconjugated" π chromophores.

Organic photochemistry remains one of the more potent areas of synthetic innovation in organic chemistry. Photochemical methods in many cases offer convenient routes for the preparation of highly strained compounds, which normally do not survive common ground-state reaction conditions. Our interests in this area are focused on the development of methods for the preparation of small-ring heterocyclic systems.

The specific aim of the present study was to design simple and efficient synthetic sequences for the preparation of silacyclopropanes.[1] The plan was to utilize the general di-π-methane rearrangement,[2] which transforms 1,4-dienes into corresponding vinylcyclopropanes, as the key ring-building step. Thus, the photochemistry of di-π-silanes, in which the central quaternary carbon atom of di-π-methanes is replaced by silicon, might offer a simple entry into the viylsilacyclopropanes (eq 1). Our interest in investigating the excited state chemistry of di-π-silanes was further stimulated by the lack of literature examples of di-π-methane type reactions of systems containing heteroatoms other than oxygen in the reactive chromophores.[3]

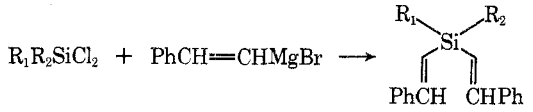


(1)

The recent reports of Connolly[4] and Koch[5] on the excited-state chemistry of compounds closely related to the ones to be described prompts us to relate the results of the photochemical study of several di-π-silanes. We have observed (1) a reluctance of di-π-silanes, having structures closely analogous to reactive hydrocarbon systems which undergo the general di-π-methane rearrangement, to isomerize to π-substituted silacyclopropanes upon either direct or sensitized irradiation; (2) that cis–trans isomerization about the π bonds is an efficient energy-dissipating process upon both direct and triplet-sensitized excitation; and (3) that the preferred mechanism for cis–trans isomerization for bis(β-styryl)silanes does not appear to involve interaction between the two "nonconjugated" π chromophores.[6]

Results

Syntheses. The di-π-silanes used in these studies are prepared by reaction of dichloro- and monochlorosilanes with β-styryl Grignard reagents (eq 2 and 3). Compounds prepared in this way are bis(β-styryl)dimethylsilane (**1**), bis(β-styryl)diphenylsilane (**2**), and β-styryltriphenylsilane (**3**).



$$R_1R_2SiCl_2 + PhCH{=}CHMgBr \longrightarrow R_1R_2Si(CH{=}CHPh)_2 \qquad (2)$$

1, $R_1, R_2 = CH_3$
2, $R_1, R_2 = Ph$

$$Ph_3SiCl + PhCH{=}CHMgBr \longrightarrow \underset{\mathbf{3}}{Ph_3SiCH{=}CHPh} \qquad (3)$$

The proton NMR and ultraviolet spectral data for these compounds, recorded in Table I, serve as strong confirmation of both the expected structures and π-bond stereochemistries in **1–3.** Isomerically pure samples of the trans,trans isomer of **2** and the trans isomer of **3** were obtained by fractional recrystallization. The three stereoisomers of the dimethyldistyrylsilane **1** (**1tt**, **1ct**, and **1cc**) were separated and removed from significant quantities of the coupling by-product, 1,4-diphenylbutadiene, by spinning band distillation. Proton magnetic resonance spectra were definitive in establishing the stereochemistry about the π bonds in each of the synthesized compounds. The cis and trans coupling constants were easily identified as 15.0 Hz and 19.0 Hz, respectively. In addition, the ultraviolet spectra of silanes **1–3** were all similar and nearly superimposable on that of the models, *cis*- and *trans*-(β-styryl)trimethylsilane. These observations support the fact that no strong interaction exists between the "nonconjugated" π chromophores in the ground or initially populated singlet excited states of these systems.

Preparative Photochemistry. Exploratory photochemical studies of the di-π-silanes were undertaken. These initial investigations were not specifically designed to detect the potentially labile π-substituted silacyclopropanes (eq 1).[1,8] The conditions utilized, however, would have allowed detection of secondary products whose structure would have suggested the type of excited-state process occurring.

Direct irradiation of the di-π-silanes, **1tt** and **3**, at room temperature in either methanol or cyclohexane led only to recovered starting materials together with products of cis–trans isomerization about the π bonds. Similar results were obtained when the reactions were triplet sensitized with various ketone sensitizers.

Mechanistic Photochemistry. In an attempt to more closely investigate the reasons for the lack of π-substituted silacyclopropane forming photoprocesses upon irradiation of these di-π-silane systems, a more thorough study of the excited-state behavior of the dimethyldistyrylsilane, **1tt**, was undertaken. One factor which could contribute to the low rearrangement and high isomerization efficiencies upon direct irradiation is an enhanced intersystem-crossing efficiency from the initially populated di-π-silane singlet excited state. In analogy with carbon systems, this pathway would effectively block rearrangement by producing a "free-rotor" di-π-silane triplet capable of energy dissipation by π-bond isomerization.[10] Quenching experiments were carried out to explore this possibility. No reduction in the conversion of **1tt** to its isomers, **1ct** and **1cc**, was ob-

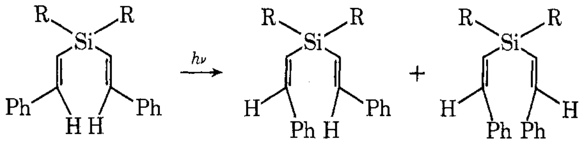
Table I
NMR and Uv Data for the Di-π-silanes 1-3

	Proton NMR				
	Chemical shifts[a]				Uv[b]
Compd	H_a	H_b	$SiCH_3$	J_{ab}, Hz	λmax (log ε)
$Me_2Si(CH_a{=}CH_bPh)_2$					
trans, trans (1tt)	6.50 (d)	6.95 (d)	0.32 (s)	19.0	265 (4.64) 294 (3.83)
cis,	5.89 (d)	7.44 (d)	0.16 (s)	15.0	260 (4.43)
trans (1ct)	6.40 (d)	6.86 (d)		19.0	286 (3.84) 294 (3.55)
cis, cis (1cc)	5.86 (d)	7.32 (d)	0.01 (s)	15.0	255 (4.36) 295 (3.29)
$Ph_2Si(CH_a{=}CH_bPh)_2$					
trans, trans (2tt)	6.86 (d)	7.08 (d)		19.0	263 (6.69) 294 (5.99)
$PhSi(CH_a{=}CH_bPh)$					
trans (3t)	7.18 (d)	7.21 (d)		18.5	252 (6.37) 262 (6.44) 294 (5.67)

[a] Chemical shifts measured in parts per million (ppm) downfield from tetramethylsilane (internal). Letters in parentheses represent multiplicities: d, doublet; s, singlet. [b] Uv spectra were run in cyclohexane solvent.

served when direct irradiations were performed in the presence of 2,3-dimethyl-1,3-butadiene. These results suggest, but do not conclusively prove, that the singlet and not the triplet of the di-π-silane is the excited state responsible for cis–trans isomerization.

In order to evaluate how substitution on the silicon might affect the preferred photochemical pathways followed by these systems, the diphenylsilane, **2**, was irradiated under direct and triplet-sensitized conditions (eq 4).



1tt, R = CH_3 **1ct** **1cc**
2tt, R = Ph **2ct** **2cc**

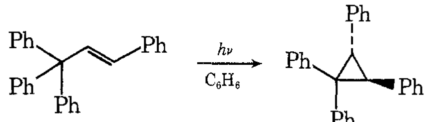
(4)

Surprisingly, no products of rearrangement were detected. As with **1tt**, cis–trans isomerization was the only observed reaction, resulting in a mixture of the three stereoisomers of **2**.

These observations raise the interesting question of the mechanism for cis–trans isomerization in the distyrylsilanes 1 and **2**. The absence of di-π-methane-like reactivity could very well be a result of the inability of these systems to undergo C-2–C-4 carbon–carbon bonding in the singlet or triplet manifold (eq 4). The ability of these systems to undergo C-2–C-4 carbon–carbon bond formation might be reflected in whether or not cis–trans isomerization proceed via a common bridged intermediate as has been proposed for related carbon systems.[11,12] With this in mind, varying conversion direct and sensitized irradiations were conducted on rigorously purified **1tt** (99.6% isomeric purity) using Pyrex filtered light for the direct runs and uranium glass filtered light for the benzophenone runs. The results of these experiments are summarized in Tables II and III and plotted in Figures 1 and 2 in terms of the relative percentage of **1tt**, **1ct**, and **1cc** vs. irradiation time.

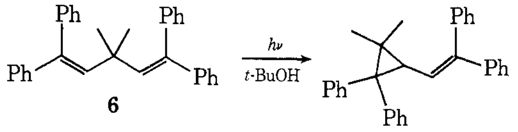
Discussion

The di-π-silanes that have been prepared and studied contain structural features which make them closely related to hydrocarbon analogs which undergo efficient di-π-methane photorearrangements. For example, Griffin[13] has shown that the carbon counterpart of β-styryltriphenylsilane (**3**), 1,3,3,3-tetraphenylpropene (**4**), affords the tetraphenylcyclopropane **5** upon direct irradiation (eq 5). Similarly, a host of hydrocarbons related to the distyrylsilanes **1** and **2**, e.g., the tetraphenyldiene **6**,[10] react efficiently to yield vinylcyclopropane products from their corresponding singlet excited states (eq 6). Thus, these examples serve



4 **5**

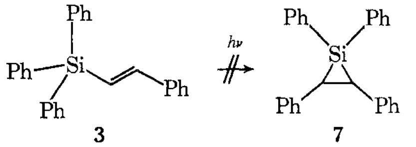
(5)



6

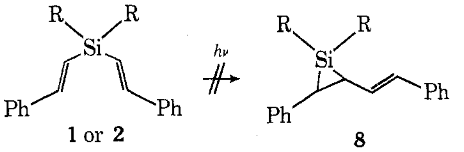
(6)

as strong precedents for the postulated photochemical reactions of di-π-silanes leading to π-substituted silacyclopropanes and, therefore, for postulated reaction sequences yielding convenient entries into the silacylopropane series. The complete inertness to photorearrangement of the styrylsilanes **1–3**, however, indicates that the silicon heteroatom in these systems introduces factors which cause the pathway to π-substituted silacyclopropanes, such as **7** and **8**, to be less efficient than in the carbon analogs (eq 7 and 8).



3 **7**

(7)



1 or **2** **8**

(8)

Several factors can be considered in assessing how the silicon heteroatom blocks di-π-methane-like reactivity in

Table II
The *cis,trans*- to *cis,cis*-Bis(β-styryl)dimethylsilane Isomer Compositions from Direct Irradiations of the Trans,Trans Isomer, 1tt, at Low Conversions (<50%) and at the Photostationary State

% conversion[a]	% cis,trans isomer[b] (1ct)	% cis,cis isomer[b] (1cc)	Cis,cis to cis,trans isomer ratio[b] (1cc/1ct)
2.0	2.0	0.0	0.00
9.7	9.7	0.0	0.00
14.2	13.9	0.3	0.02
17.6	20.6	0.6	0.03
28.0	28.0	0.8	0.03
35.9	34.0	2.0	0.06
43.0	39.6	3.4	0.09
Photostationary state	43.5	46.1	1.06

[a] Calculated as 100% minus the percent 1tt measured. [b] See Experimental Section for method of analysis.

Table III
The *cis,trans*- to *cis,cis*-Bis(β-styryl)dimethylsilane Isomer Compositions from Benzophenone-Sensitized Irradiations of the Trans,Trans Isomer, 1tt, at Low Conversions (<50%) and at the Photostationary State

% conversion[a]	% cis,trans isomer[b] (1ct)	% cis,cis isomer[b] (1cc)	Cis,cis to cis,trans isomer ratio[b] (1cc/1ct)
4.0	4.1	0.0	0.00
14.2	13.4	8.8	0.06
18.3	17.2	1.0	0.06
21.0	19.1	1.9	0.10
26.9	25.0	2.0	0.08
35.0	31.5	3.5	0.11
37.9	33.2	4.7	0.14
47.0	41.2	5.8	0.14
Photostationary state	50.2	33.8	0.67

[a] Calculated as 100% minus the percent 1tt measured. [b] See Experimental Section for method of analysis.

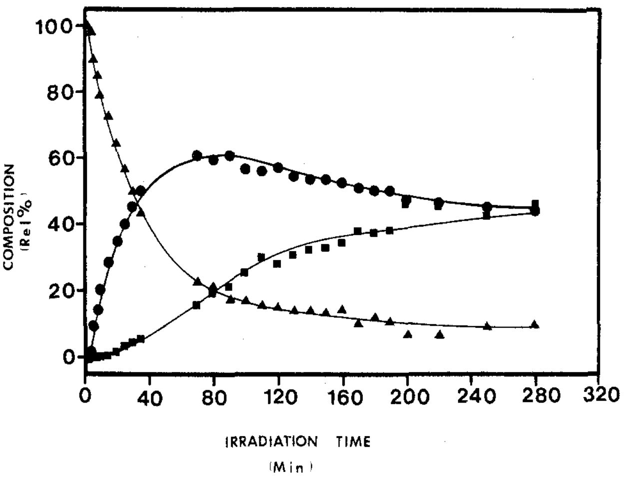


Figure 1. Direct irradiations of the *trans,trans*-distyrylsilane 1tt. Plots of isomer composition (1tt, ▲; 1ct, ●; 1cc, ■) as relative percentages vs. irradiation time in cyclohexane.

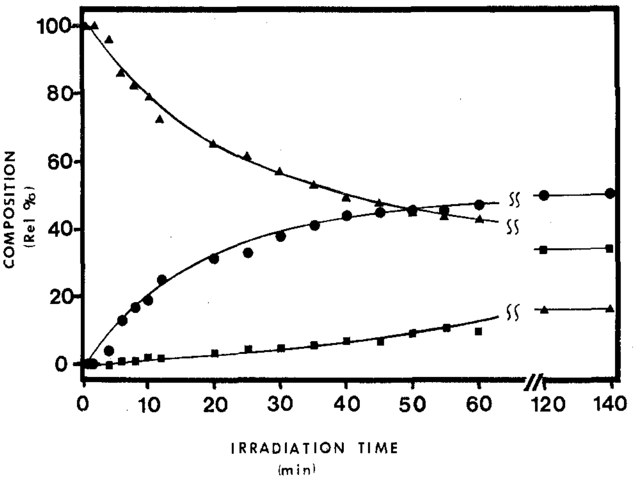


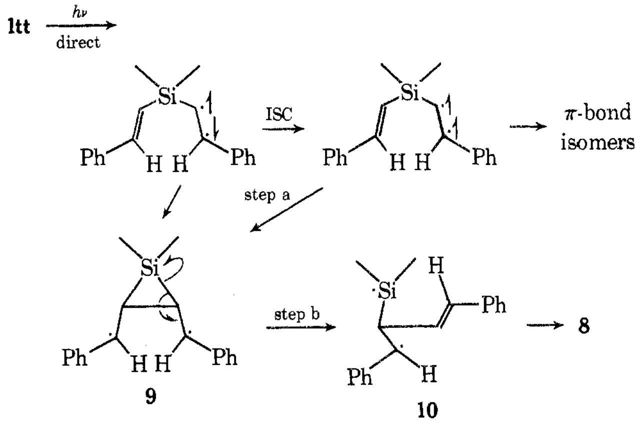
Figure 2. Benzophenone-sensitized irradiations of the *trans,trans*-distyrylsilane 1tt. Plots of isomer composition (1tt, ▲; 1ct, ●; 1cc, ■) as relative percentages vs. irradiation time in cyclohexane.

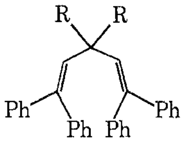
these systems. Silicon can either enhance the efficiency of alternate excited state deactivation modes or decrease the efficiency of di-π-methane reaction by destabilizing intermediates along the reaction coordinate.

One possible consequence of replacement of carbon by silicon in these systems might be a silicon-induced, enhanced intersystem crossing efficiency from the initially populated singlet excited states of **1**–**3**. This would be expected to have a dramatic effect on the efficiency of potential di-π-silane reactions, since it has been well documented that acyclic 1,4-diene triplet excited states utilize cis–trans isomerization as a major energy-dissipating, reaction mode.[2,10] Unfortunately, evidence accumulated to determine whether the silicon atom in these systems serves to enhance the intersytem crossing rate is minimal. High concentrations of the known triplet quencher, 2,3-dimethyl-1,3-butadiene ($E_T \simeq 58$ kcal/mol) appear to have absolutely no effect upon the efficiency of cis–trans isomerization of **1tt** (note Experimental Section). However, this observation might be explained by either a singlet isomerization mechanism or by the fact that the triplet state of **1tt** is shortlived. Another observation which concerns this point is the nondetectable fluorescence of the distyrylsilane **1tt** under conditions in which a reasonable model, β-methylstyrene, displays strong fluorescence. This decreased efficiency of singlet emission might very well be a reflection of a silicon enhancement of k_{ISC}. Our results, however, offer no firm conclusions on this point.

Another possibility for the absence of di-π-silane reactivity in the systems studied may be related to the effect silicon has on the ease with which silacyclopropyldicarbinyl diradicals, like **9** in Scheme I, undergo bond rupture to produce 2-vinylsilatrimethylene diradicals, e.g., **10**.[14] Zimmerman and coworkers[15] have demonstrated the effect of central carbon atom substitution on the efficiency of the di-π-methane process. In the absence of radical stabilizing groups on the central carbon atom, the di-π-methane reaction efficiency drops to zero. Demonstrative of this effect is the comparison of the quantum yields for rearrangement of the series of 1,4-dienes **11**. Interestingly, the di-π-silane rearrangement is inefficient for styrylsilanes **2** and **3** in spite of phenyl substituents on silicon, which might have the potential of increasing the stability of diradicals like **10**. In addition, estimates of silicon–carbon vs. carbon–carbon bond dissociation energies in silacyclopropanes vs. cyclopropanes yield the conclusion that step b in the hypothetical di-π-silane reaction pathway (see Scheme I) should be *more* facile for silicon.[16]

Scheme I

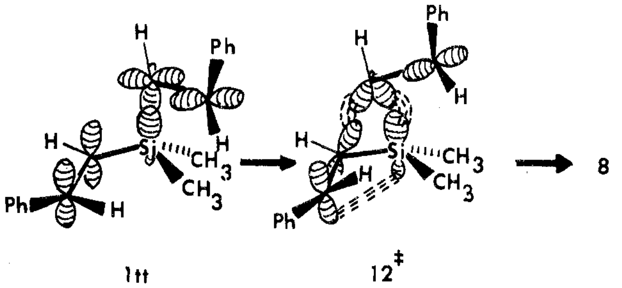




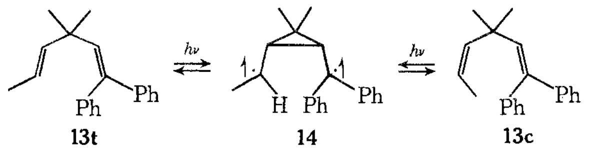
11

R = H, $\Phi = 0.002$
R = CH_3, $\Phi = 0.10$
R = Ph, $\Phi = 0.42$

Probably the most important effect of silicon on the excited state reactivity of di-π-silane systems may be a result of its ability to *decrease* the direct (through space) interaction between the nonconjugated diene (or π) chromophores in the excited states of **1**–**3**. It seems reasonable to postulate that formation of silacyclopropyldicarbinyl diradicals like **9** in the excited states of distyrylsilanes would suffer from the same prohibitive features of high ring strain as do ground-state silacyclopropanes.[1,16] This ring strain effect due to silicon at early stages in a nonconcerted pathway (step a in Scheme I) or in the transition state **12**‡ of a concerted reaction, could be controlling in causing di-π-silane rearrangements to be of high energy.



1tt 12‡



13t 14 13c (9)

A possible experimental test for whether or not the silicon atom prevents interaction between the excited styryl moieties of **1tt** is suggested by the results of Zimmerman and Pratt in which cis–trans ismerization about the higher triplet energy propenyl π bond in the hexadiene **13** was rationalized in terms of a mechanism involving the intermediacy of the bridged cyclopropyldicarbinyl diradical **14** (eq 9).[11] Thus, the mechanism for π-bond isomerization of **1tt** compared to the analogous carbon system should indicate whether the central silicon atom blocks C-2–C-4 carbon–carbon bridging. Specifically, in order to distinguish between a consecutive (eq 10) or a simultaneous (eq 11) mechanism for cis–trans isomerization of **1tt**, measurements of the **1ct** to **1cc** isomer ratios after low-conversion irradiations of **1tt** were made.

$$\mathbf{1tt} \overset{h\nu}{\rightleftarrows} \mathbf{1ct} \overset{h\nu}{\leftrightarrows} \mathbf{1cc} \qquad (10)$$

$$\begin{tikzcd} & & \mathbf{1ct} \\ \mathbf{1tt} \arrow[r, shift left, "h\nu"] & 9 \arrow[l, shift left] \arrow[ur, shift left, "h\nu"] \arrow[dr, shift left, "h\nu"'] & \\ & & \mathbf{1cc} \arrow[ul, shift left] \end{tikzcd} \qquad (11)$$

Note that in the consecutive mechanism no direct pathway exists for the interconversion of **1tt** to **1cc**. However, in the simultaneous mechanism a direct route is available through the intermediate **9**. The results summarized in Table II and Figure 1 demonstrate that the **1cc** to **1tt** isomer ratios at low conversions from direct irradiation of **1tt** remain nearly zero up to 27.9% conversion. After this point the ratio rises to its photostationary state value of 1.06. These observations are consistent with a mechanism for cis–trans isomerization of **1tt** which involves the formation of **1cc** in a second photochemical step from the excited state of the initially formed **1ct** (eq 10). Only after significant quantities of **1ct** are produced and, thus, significant quantities of light are absorbed by **1ct** does the cis–cis isomer appear. Therefore, the consecutive mechanisms seems more probable.

In order to completely rule out the possibility that these results are due to a simultaneous mechanism in which the bridged intermediate **9** decays much more rapidly to **1ct** than **1cc**,[17] the photostationary state compositions of both **1cc** and **1ct** were analyzed. In a simultaneous mechanism, two factors will determine the photostationary ratio of **1cc** to **1ct**, the relative rate constants for collapse of **9** to **1cc** and **1ct** (k_{cc} and k_{ct}) and the relative intensities of light absorbed by **1cc** and **1ct** (I_{cc} and I_{ct}), according to eq 12. The

$$\frac{[\mathbf{1cc}]_{\mathrm{pss,direct}}}{[\mathbf{1ct}]_{\mathrm{pss,direct}}} = \frac{I_{ct}}{I_{cc}} \cdot \frac{k_{cc}}{k_{ct}} \qquad (12)$$

intensity ratio, calculated approximately from relative integrated extinction coefficients of the two isomers,[18] was 1.12 and the photostationary state ratio was 1.06. Therefore, if the simultaneous mechanism were operating, the initial, low-conversion **1cc** to **1ct** ratios, determined by k_{cc}/k_{ct}, should have been about 0.94, a value clearly not observed. These observations support the consecutive mechanism for π-bond isomerization in the distyrylsilane systems and rule out the intermediacy of silacyclopropyldicarbinyl diradical **9**.

Results from benzophenone-sensitized isomerizations can be similarly interpreted.[19] In this case, the predicted intital **1cc** to **1ct** ratio for a simultaneous mechanism can be obtained from eq 13, which relates the photostationary

$$\frac{[\mathbf{1cc}]_{\mathrm{pss,\ sensit}}}{[\mathbf{1ct}]_{\mathrm{pss,\ sensit}}} = \frac{k_{\mathrm{et,ct}}}{k_{\mathrm{et,cc}}} \times \frac{k_{cc}}{k_{ct}} \qquad (13)$$

state isomer ratio to ratios of the rate constants for collapse of a bridged intermediate and the rates of energy transfer (k_{et}) from benzophenone triplets to the cis,cis and cis,trans isomers. We have assumed the latter ratio to be unity based upon measurements of photostationary state isomer ratios from sensitized photolysis using various triplet energy sensitizers (see Experimental Section).[20] According to this estimate, k_{cc}/k_{ct} should be on the order of 0.67. The experimentally observed **1cc** to **1ct** ratios at low conversions in the benzophenone-sensitized runs vary from 0.00 to 0.19 in conversions from 4.0 to 54.0%.

These observations can be interpreted in terms of mechanism(s) for π-bond isomerization which do not pass through an intermediate resulting from C-2–C-4 carbon–carbon bridging. It seems likely that the different photochemical reactivity of di-π-silanes and their carbon analogs is due to the ability of silicon to destabilize the first bridged diradical intermediate along the reaction coordinate or the transition state, $12^{\ddagger}$, for a one-step process.

However, it may well be that photochemistry can offer an entry into the silacyclopropane ring system if we take into account the limitations which are apparent from the results presented in this paper. Studies aimed at obtaining more information for silicon containing π systems in which cis–trans isomerization is precluded are continuing.

Experimental Section

General. All NMR spectra were obtained on a Varian Associates Model HA-100 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane (internal). Ultraviolet spectra were obtained on a Beckman Acta III spectrophotometer in 1-cm matched quartz cells. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Gas chromatographic analyses were run using a Varian 940 GC with a flame ionization detector. All melting points are recorded uncorrected.

Bis(β-styryl)dimethylsilane (1). β-Bromostyrene (102.0 g, 0.56 mol; ca. 90% trans and 10% cis) was added over a 2-hr period to a suspension of magnesium turnings (15.0 g, 0.63 g-atom) in a solution of dimethyldichlorosilane (35.0 g, 0.27 mol) dissolved in 400 ml of tetrahydrofuran. After initiation, the temperature of the reaction was maintained between 0 and 15°. After the addition was complete, the reaction mixture was stirred for 2 hr at room temperature and poured into aqueous sodium bicarbonate. The ether layer was separated, dried over calcium chloride, and concentrated in vacuo, giving 88.0 g of crude material which was distilled. The fraction between 192 and 210° (8 mm) was found to contain a mixture of the three stereoisomers and a small amount of the coupling product, 1,4-diphenylbutadiene (37.7 g, 52.7% yield). This fraction was distilled carefully using a spinning band column to give fractions containing a mixture of cis,cis and cis,trans isomers along with 1,4-dipheylbutadiene, and pure trans,trans-bis(β-styryl)dimethylsilane [15.2 g, bp 124–125.5° (0.2 mm)]. Gas chromatographic analysis of this material indicated the absence of stereoisomeric impurities.

Anal. Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62. Found: C, 81.63; H, 7.85.

Bis(β-styryl)diphenylsilane (2). This compound was prepared by essentially the same procedure as described for 1 from β-styrylmagnesium bromide and diphenyldichlorosilane. The crude product was chromatographed on a silica gel column (Davison grade 920, 100–200 mesh) using hexane as eluent. The crystalline material obtained was recrystallized from hexane to yield a white, crystalline product (45.8% yield, mp 67–69°). The spectral data, recorded in Table I, indicate that the structure is *trans,trans*-bis(β-styryl)diphenylsilane (2).

Anal. Calcd for $C_{28}H_{24}Si$: mol wt, 388.165. Found (by high-resolution mass spectrum): mol wt, 388.164.

β-Styryltriphenylsilane (3). This material was prepared from triphenylchlorosilane and β-styrylmagnesium bromide by essentially the same method as described for 1. The crude product was recrystallized from 9:1 ethanol–acetone to yield pure *trans*-β-styryltriphenylsilane (24.8% yield), mp 148.5–150.0° (lit.[7] mp 148–148.5°).

Preparative Photochemical Runs. Direct Irradiations of Bis(β-styryl)dimethylsilane (1). Preparative irradiations of pure *trans,trans*-bis(β-styryl)dimethylsilane (**1tt**) were carried out on degassed, nitrogen-purged solutions of cyclohexane or methanol (500 mg per 500 ml) in an apparatus consisting of a quartz, water-cooled, immersion well containing a Hanovia 450-W medium-pressure lamp and Corex glass filter. Irradiations for ca. 2 hr were sufficient to reach a photostationary state mixture of **1tt**, **1ct** and **1cc**, the presence of which was detected by gas chromatographic analysis (7 ft × 0.125 in. column, 3% SE-30 on Anachrom ABS, 60/70, at 165°). The order of elution and the relative percentages of the three stereoisomers are as follows: **1cc**, 46.1%; **1ct**, 43.5%; and **1tt**, 10.4%. The spectral data for **1cc** and **1ct**, collected by preparative gas chromatography, are recorded in Table I.

Anal. (**1cc**). Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62; Si, 10.63. Found: C, 81.65; H, 7.86; Si, 10.45.

Table IV
Irradiations of 1tt in the Presence of 2,3-Dimethyl-1,3-butadiene

Irradiation time, min	Concn of 2,3-dimethyl-1,3-butadiene, M	% conversion	% 1ct	% 1cc
15	0.00	22.0	19.3	2.7
15	0.50	22.3	19.8	2.5
15	1.00	20.7	18.6	2.1
25	0.00	30.4	26.0	4.4
25	0.50	33.2	28.7	4.5
25	1.00	29.1	25.0	4.1
90	0.05	85.2	56.7	28.5
90	0.10	86.0	55.8	30.2
90	0.20	86.5	55.3	31.2

Table V
Triplet-Sensitized Irradiations of 1tt Using Various Triplet Energy Sensitizers

Triplet sensitizer	E_T, kcal/mol	Photostationary state compositions % 1tt	% 1ct	% 1cc
Benzil	54	33.6	11.2	55.2
1-Acetonaphthone	59	19.9	28.3	51.8
Benzophenone	69	16.0	33.8	50.2
Acetone	76	18.7	30.4	50.9

Anal. (**1ct**). Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62; Si, 10.63. Found: C, 81.86; H, 7.47; Si, 10.88.

Sensitized Irradiations of 1tt. Sensitized irradiations were conducted using the apparatus previously described containing cyclohexane solutions (500 ml) of 1.00 g of **1tt** and 2.0 g of benzophenone, and using a uranium glass filter ($T > 320$ nm). The photostationary state mixture of the three stereoisomers, reached after 3.0 hr of irradiation, was found to be 88.8% **1cc**, 50.2% **1ct**, and 16.0% **1tt**.

Varying Conversion Runs. Direct Irradiation of 1tt. Irradiation of 128.1 mg (1.94×10^{-3} mol) of *trans,trans*-bis(β-styryl)dimethylsilane in 250 ml of degassed and nitrogen-purged spectrograde cyclohexane was conducted in the preparative apparatus previously described using a Pyrex glss filter ($T > 290$ nm). One-half milliliter aliquots were removed at varying time intervals during the irradiations through a septum-capped inlet port. Samples were stored in the dark until they were analyzed by gas chromatography using a 5 ft × 0.125 in., 1.5% OV-101 on 100/200 Varaport column at 150°. The peak areas were determined by the triangulation method and were then used to calculate the relative percentages of the three stereoisomers, **1cc**, **1ct**, and **1tt**. The results of these measurements are tabulated in part in Table II and plotted in full in Figure 1.

Sensitized Irradiations of 1tt. Irradiation of a solution of 36.8 mg (5.56×10^{-4} mol) of **1tt** and 12.8 mg (2.8×10^{-4} mol) of benzophenone in 250 ml of degassed and nitrogen-purged Spectrograde cyclohexane was conducted in the preparative apparatus previously described, using a uranium glass filter. These conditions ensured that greater than 99% of the light was absorbed by benzophenone. Relative percentages of **1cc**, **1ct**, and **1tt**, obtained by gas chromatographic analyses, of aliquots removed at varying time intervals during irradiation are tabulated in part in Table III and plotted in full in Figure 2.

Irradiations of 1tt in the Presence of 2,3-Dimethyl-1,3-butadiene. Irradiations were carried out in a "merry-go-round" apparatus with a Corex glass filter on degassed spectrograde cyclohexane solutions, 5.4×10^{-3} M in **1tt** and containing varying concentrations of 2,3-dimethyl-1,3-butadiene, in quartz glass test tubes. Three tubes, containing the three different quencher concentrations, were removed at varying time intervals during the irradiations. Analyses of these solutions were conducted to determine the percent conversion of **1tt** and the relative percentages of the three stereoisomers. The results of this experiment are recorded in Table IV.

Photostationary State Compositions from Irradiations of 1tt with Various Triplet Sensitizers. Spectrograde cyclohexane solutions of *trans,trans*-bis(β-styryl)dimethylsilane (1.0×10^{-2} M) and the various triplet sensitizers (acetone, benzophenone, 1-acetonaphthone, and benzil), each 2.0×10^{-2} *M*, were placed individually in Pyrex test tubes and irradiated with Pyrex-filtered light until the photostationary states were obtained. Analyses of these solutions by gas chromatography yielded photostationary state isomer compositions tabulated in Table V.

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Registry No.—**1tt**, 54366-27-7; **1ct**, 54366-28-8; **1cc**, 54366-29-9; **2**, 54366-30-2; **3**, 33105-34-9; *cis*-β-bromostyrene, 588-73-8; *trans*-β-bromostyrene, 588-72-7; dimethyldichlorosilane, 75-78-5; triphenylchlorosilane, 76-86-8.

References and Notes

(1) The syntheses of highly substituted silacyclopropanes has recently been reported by R. L. Lambert and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972).

(2) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

(3) (a) The oxadi-π-methane rearrangement of β,γ-unsaturated ketones and aldehydes to cyclopropyl ketones and aldehydes was first discussed mechanistically by Swenton[3b] and related to the carbon analog by Givens;[3c] (b) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969); (c) R. S. Givens and W. F. Oettle, *Chem. Commun.*, 1164 (1969).

(4) J. M. Connolly, *J. Organomet. Chem.*, **64**, 343 (1974).

(5) T. H. Koch, J. A. Soderquist, and T. H. Kinstle, *J. Am. Chem. Soc.*, **96**, 5576 (1974).

(6) The initial results of this study, reported at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 26–31, 1973, Abstracts, No. ORGN-153, were found to be in error owing to impurities present in the starting materials which presumably changed the product ratios.

(7) R. A. Benkeser and R. A. Hickner, *J. Am. Chem. Soc.*, **80**, 5298 (1958).

(8) It is very likely that the potential vinylsilacyclopropanes expected in these reactions will not survive the reaction conditions but will either rearrange to silacyclopentenes[9a,9b] or react with the alcoholic solvent to yield methyl allylsilyl ethers.[5,9a]

(9) (a) Y. Nakadaira, S. Kanouchi, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 5621 (1974); (b) Y.-N. Tang, G. P. Gennaro, and Y. Y. Su, ibid., **94**, 4355 (1972).

(10) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).

(11) H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.*, **92**, 6267 (1970).

(12) H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, *J. Am. Chem. Soc.*, **96**, 439 (1974).

(13) G. W. Griffin et al., *Tetrahedron Lett.*, 2951 (1965).

(14) The evidence accumulated to date indicates that the di-π-methane reaction in the singlet excited manifold is most probably a concerted process.[15a,b] However, the effect of central[15c] and terminal[15d] carbon atom substitution indicates that stabilization of diradicaloids along the reaction coordinate is influential in determining the efficiency of the process.

(15) (a) P. S. Mariano and J. K. . Ko, *J. Am. Chem. Soc.*, **95**, 8670 (1973); (b) H. E. Zimmerman et al., ibid., **96**, 1459 (1974); (c) H. E. Zimmerman et al., ibid., **95**, 2155, 2157 (1973); (d) H. E. Zimmerman and A. A. Baum, ibid., **93**, 3646 (1971).

(16) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

(17) The lower limit of our detectability of **1tt** is ca. 0.1% and thus **1cc/lct** ratios of less than 0.01 could not be measured.

(18) The relative integrated extinction coefficients of **1cc** and **1ct** were calculated from considerations of the relative absorption spectra of the two isomers along with the wavelength dependencies of the lamp output and Pyrex glass filter transmittance.

(19) The possibility does exist that the triplet excited state of **1tt** is responsible for π-bond isomerization in both the direct and sensitized irradiations. The quenching studies using 2,3-dimethyl-1,3-butadiene can be interpreted in terms of a direct irradiation singlet process or a fast unquenchable triplet process.

(20) The triplet energies of the three stereoisomers of **1** should all fall in the range of 62 kcal/mol, like that of styrene. Thus, triplet energy transfer from benzophenone (69 kcal/mol) to all three should be highly exothermic and should occur at the diffusion-controlled rates.[21] The constancy of the photostationary state isomer compositions when changing from acetone (76 kcal/mol) sensitization to benzophenone to 1-acetonaphthone (59 kcal/mol) sensitization indicates the correctness of the assumption that $k_{\mathrm{et,cc}} = k_{\mathrm{et,ct}}$ in the benzophenone-sensitized irradiation.[22]

(21) K. Sandros and H. Backstrom, *Acta Chem. Scand.*, **12**, 3 (1958).

(22) G. S. Hammond et al., *J. Am. Chem. Soc.*, **86**, 3197 (1964).

Photochemical Ring-Opening Reactions of Substituted Chromenes and Isochromenes[1]

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Irradiation of a number of substituted chromenes in methanol give products derived from an *o*-quinoneallide intermediate. The fate of the *o*-quinoneallide depends on the experimental conditions. The primary mode of reaction corresponds to 1,4 and 1,6 addition of methanol across the C–C double bonds of the *o*-quinoneallide intermediate. In nonreactive solvents, the *o*-quinoneallide undergoes a 1,7-sigmatropic hydrogen shift. Irradiation of several substituted isochromenes, on the other hand, give indene epoxides which produce ring-opened hydroxy ethers on further irradiation. The mechanism involves opening of the isochromene ring to give an *o*-quinoidal intermediate which undergoes a subsequent intramolecular [4 + 2] cycloaddition reaction. A similar path occurs with 4-phenylisothiochromene, except that in this case the initially formed indene episulfide loses sulfur on further irradiation to give a substituted indene.

Light-induced transformations of cyclic dienes have been the subject of recent intensive study.[2,3] Derivatives of 1,3-cyclohexadiene, for example, have been transformed into a vast array of photoproducts via ring-opening processes,[4–12] valence-bond tautomerization reactions,[13–15] bond-switching mechanisms,[16–22] and dimerization pathways.[23,24] Despite the fact that photochemical isomerizations of cyclic dienes have been well documented, investigation of suitable heterocyclic analogs in light-induced reactions has been somewhat limited.[25] With a desire to discover new photochemical pathways of appropriate heterocyclic dienes, we have examined the photochemical behavior of several substituted chromenes and isochromenes.[26] A number of investigators had previously observed that a ring–chain tautomerization could be established between substituted cis dienones **1** and 2*H*-pyrans **2**.[27–29] Transformations of this type are known to be responsible for the photochromism encountered on irradiation of 2*H*-chromenes[30,31] and *o*-vinylphenones.[32] Extended irradiation of the photoequilibrated dienone–pyran mixture might be expected to afford an oxabicyclo[3.1.0]hex-2-ene (**3**) as the ultimate photoproduct. This transformation would be