1,2-Diaryl Rearrangement in Tetraaryldisilenes

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Tetraaryldisilenes containing silicon atoms that are differently substituted, $A_2Si{=}SiB_2$, (A = mesityl, B = 2,6-xylyl, **12**; A = mesityl, B = 4-*tert*-butyl-2,6-dimethylphenyl, **14**) were generated by cophotolysis of two individual trisilane precursors, $A_2Si(SiMe_3)_2$ and $B_2Si(SiMe_3)_2$. Stereoselective, intramolecular exchange of two aryl substituents between the silicon atoms takes place to give the rearrangement $A_2Si{=}SiB_2 \rightleftarrows ABSi{=}SiAB$, observed by ^{29}Si NMR spectroscopy. 2D ^1H–^{29}Si NMR was used to assign resonances in the reaction mixture. The rearrangement of **12** in benzene is first order with $\Delta H^{\ddagger} = 15 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -36 \pm 4$ eu. A concerted dyotropic mechanism proceeding through a bicyclobutane-like transition state or intermediate is proposed. No evidence for 1,2-diaryl rearrangement was found for the tetraarylethene 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-methoxyphenyl)ethene.

Since the discovery of the first stable disilenes in 1981, studies on the reactivity of the silicon–silicon double bond have revealed a rich and diverse chemistry.[1,2] In a preliminary communication, we described an intramolecular rearrangement of tetraaryldisilenes involving the exchange of two aryl substituents between the silicon atoms of the silicon–silicon bond.[3] In this paper we report kinetic data for the 1,2-rearrangement, an additional example of the reaction, and the use of 2D ^1H–^{29}Si NMR spectroscopy to assign the NMR spectra of the products of one of the rearrangements.

Results

Generation of Disilenes. A series of disilenes containing silicon atoms that are differently substituted, of the types $A_2Si{=}SiB_2$ and $A_2Si{=}SiAB$, were obtained photochemically by irradiation of their trisilane precursors in pentane solution at -60 °C. This procedure follows the now standard method for synthesis of disilenes by dimerization of the photochemically generated silylenes[2b] (Scheme I). The photolysates were examined by ^{29}Si NMR spectroscopy in benzene.

Scheme I. Results from Photolysis of Trisilanes

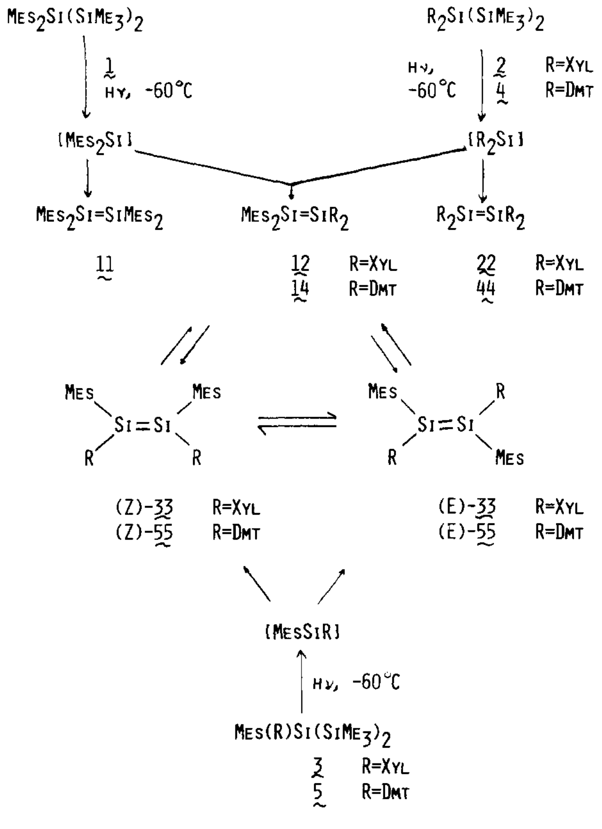

Table I. Notation and ^{29}Si Chemical Shifts for Tetraarylldisilenes

no.	compd	δ
11	$Mes_2Si{=}SiMes_2$	63.67
22	$Xyl_2Si{=}SiXyl_2$	64.05
44	$Dmt_2Si{=}SiDmt_2$	65.15
12	$Mes_2Si{=}SiXyl_2$	65.19,[b] 62.56[c]
14	$Mes_2Si{=}SiDmt_2$	64.22, 64.11
33	(*E*/*Z*)-Mes(Xyl)Si=Si(Xyl)Mes	63.87, 63.86
55	(*E*/*Z*)-Mes(Dmt)Si=Si(Dmt)Mes	64.37, 64.15
13	$Mes_2Si{=}Si(Xyl)Mes$	64.42, 63.14
23	$Xyl_2Si{=}Si(Dmt)Xyl$	64.63, 63.30
24	$Xyl_2Si{=}SiDmt_2$	65.82, 63.24

[a] Mes = 2,4,6-trimethylphenyl; Xyl = 2,6-dimethylphenyl; Dmt = 2,6-dimethyl-4-*tert*-butylphenyl. [b] Mes_2Si. [c] Xyl_2Si.

Disilene **12** was generated from the photolysis of an equimolar mixture of trisilanes **1** and **2** (Scheme I, R = 2,6-xylyl). In the ^{29}Si NMR spectrum, four signals were initially observed in the disilene region (60–65 ppm) in an approximately 1:1:1:1 intensity ratio.[4,5] These four signals were assigned to the three expected disilenes formed by dimerization of the silylenes: disilenes **11** (63.68 ppm) and **22**[6] (64.05 ppm) and mixed disilene **12** (62.56 and 65.19 ppm, Table I and Figure 1a). The nearly equal intensities of the peaks indicate that the disilenes are formed in approximately the statistical 1:1:2 ratio for the dimerization of two silylenes, Mes_2Si: and $(2,6\text{-xylyl})_2Si$:, as expected if the silylenes are formed at the same rate and if the

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[1] For reviews of disilenes, see: (a) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (b) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds., Wiley: New York, 1989; Part 2, pp 1015–1142.

[2] (a) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; Michl, J.; West, R. *Organometallics* **1984**, *3*, 793–800. (b) Michalczyk, M. J.; Fink, M. J.; De Young, D. J.; Carlson, C. W.; Welsh, K. M.; West, R.; Michl, J. *Silicon, Germanium, Tin Lead Comp* **1986**, *9*, 75–80. (c) Michalczyk, M. J.; West, R.; Michl, J. *Organometallics* **1985**, *4*, 826–829. (d) Gillette, G. R.; Maxka, J.; West, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 54.

[3] Yokelson, H. B.; Maxka, J.; Siegel, D. A.; West, R. *J. Am. Chem. Soc.* **1986**, *108*, 4239–4242.

[4] Product ratios were determined from line intensities obtained from standard acquisition ^{29}Si NMR experiments. Routine spectra were determined by the INEPT technique,[5] optimized for mesityl substituents.

[5] For a discussion of polarization transfer NMR spectroscopy for ^{29}Si, see: Blinka, T. A.; Helmer, B. J.; West, R. *Adv. Organomet. Chem.* **1984**, *23*, 193–218.

[6] Disilene **22** was previously observed, but ^{29}Si NMR data were not reported: Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150–1153.

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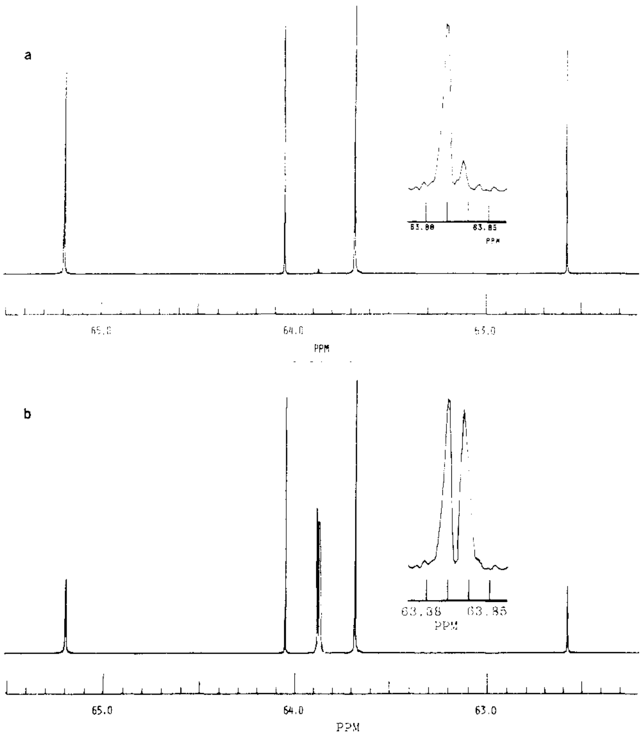

Figure 1. ^{29}Si NMR spectra of disilenes obtained from photolysis of a 1:1 mixture of 1 and 2: (a) After 7 days at 25 °C; the four large peaks are due to **12**, **11**, and **22**; the weak resonances at 68.86 and 68.87 ppm are assigned to **33**. (b) Spectrum of the same sample after 7 days at 70 °C showing growth of **33** and loss of **12**.

dimerization process is not selective for a particular disilene.

Similar results were obtained for the irradiation of an equimolar mixture of trisilanes **1** and **4** to yield the mixed disilene **14**, along with disilenes **11** and **44** (Scheme I, R = 2,6-dimethyl-4-*tert*-butylphenyl).

Photolysis of trisilanes **3** and **5** generated *E*/*Z* mixtures of disilenes **33** and **55**, respectively. The mixture of *E* and *Z* isomers of **33** gave two signals in the ^{29}Si spectrum at 63.87 and 63.86 ppm; the spectrum of the **55** mixture had two signals at 64.15 and 64.37 ppm. In each case the isomer with the more upfield resonance was produced in a slight (4:3) molar excess.

Rearrangement of Disilenes. Evidence for the diaryl rearrangement of disilenes was obtained from changes in the ^{29}Si NMR spectra observed over time. In the mixture of **11**, **22**, and **12** obtained from the cophotolysis of trisilanes **1** and **2**, two new peaks gradually appeared at 63.87 and 63.86 ppm about midway between the resonances for **12** (Figure 1a). These new peaks are assigned to the *Z* and *E* isomers of disilene **33**; the lower field signal appeared first. With time, the two new peaks increased and became more nearly equal in intensity, while those for **12** diminished. The 1,2-diaryl rearrangement process is evidently accompanied by a cis–trans interconversion of (*E*)- and (*Z*)-**33**. Equilibrium was attained after 70 days at 25 °C or 7 days at 70 °C; after this time the concentrations of (*E*)-**33**, (*Z*)-**33**, and **12** were approximately equal (Figure 1b).

The equilibrium can be approached from the opposite direction by photolysis of trisilane **3** (Scheme I). Initially only two signals for (*E*)- and (*Z*)-**33** were present in the ^{29}Si NMR spectrum. No **12** was present after 95% conversion of the trisilane in pentane solution, showing that the rearrangement is not photoinduced. When a solution of (*E*/*Z*)-**33** in benzene was heated to 70 °C, signals for disilene **12** appeared, and after 150 h the same equilibrium mixture of disilenes was established as previously noted for the thermolysis of disilene **12**.

Table II. Rate Constants and Temperatures for the Rearrangement of 12 to 33

T, °C	T, K	k, s^{-1}	log k
70	343	2.0×10^{-5}	-4.70
84	357	5.2×10^{-5}	-4.28
97	370	1.1×10^{-4}	-3.96

Table III. Rate Constants and Temperatures for the Rearrangement of 33 to 12

T, °C	T, K	k, s^{-1}	log k
53	326	3.8×10^{-5}	-4.42
55	328	5.8×10^{-5}	-4.24
60	333	3.4×10^{-5}	-4.47
70	343	5.9×10^{-5}	-4.23
73	346	1.4×10^{-4}	-3.85
82	355	1.0×10^{-4}	-4.00
90	363	3.1×10^{-4}	-3.51
105	378	1.0×10^{-3}	-3.00

The rearrangement of disilene **14**, from the cophotolysis of **1** and **4**, provides a second example of 1,2-diaryl migration. Disilenes **11**, **44**, and **14** were initially formed in the expected 1:1:2 ratio, determined from the four signals of equal intensity between 60 and 65 ppm in the downfield region of the ^{29}Si NMR spectrum (Table I). With time the signals for **14** declined, coincident with the appearance of two new peaks at 64.15 and 64.37 ppm. The identity of the new signals were established as belonging to a mixture of the *E* and *Z* isomers of disilene **55** by the photolysis of the trisilane **5**; the ^{29}Si NMR spectrum showed signals at 64.15 and 64.37 ppm. In the rearrangement of **14** the signal for the more downfield **55** isomer appeared first, as was also the case in the rearrangement of disilene **12**.

The reverse process, the rearrangement of the (*E*/*Z*)-**55** disilene mixture to **14** was also observed by ^{29}Si NMR. When the mixture of **55** isomers was examined after heating for several days at 70 °C two new signals, previously identified as the disilene **14**, were present at 64.11 and 64.22 ppm. At equilibrium, the three disilenes **14** and (*E*)- and (*Z*)-**55** are present in equimolar amounts.

Disilenes **13** and **23**, of the type $A_2Si{=}SiAB$, were generated by cophotolysis of trisilane **3** with trisilanes **1** and **2**, respectively. In each case the statistical mixture of disilenes was generated with the (*E*)- and (*Z*)-**33** isomers together accounting for 25% of the mixture. When these two samples were heated, the disilenes **13** and **23** remained unchanged, while the ^{29}Si signals for the **33** isomers diminished with the concurrent appearance of signals correspnding to the disilene **12**. Presumably 1,2-diaryl rearrangements occur with all tetraaryldisilenes but are degenerate and therefore unobservable for **13** and **23**. No rearrangement was observed for disilenes $MesRSi{=}SiRMes$, R = *tert*-butyl or 1-adamantyl; it is probable that the 1,2 migration does not take place with alkyl migrating groups.

Kinetics and Mechanism. The rates of rearrangement of both the forward and reverse reactions were measured as a function of temperature for the **12** ⇌ (*E*/*Z*)-**33** system by ^{29}Si NMR spectroscopy (Tables II and III).

The kinetic system is of the type

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$

where A = **12**, B = (*Z*)- (or (*E*)-) **33**, and C = (*E*)- (or (*Z*)-) **33**. Only a single isomer is observed early in the rearrangement of **12**, so direct conversion of A to C can be excluded.[7] The rate expression for disappearance of A

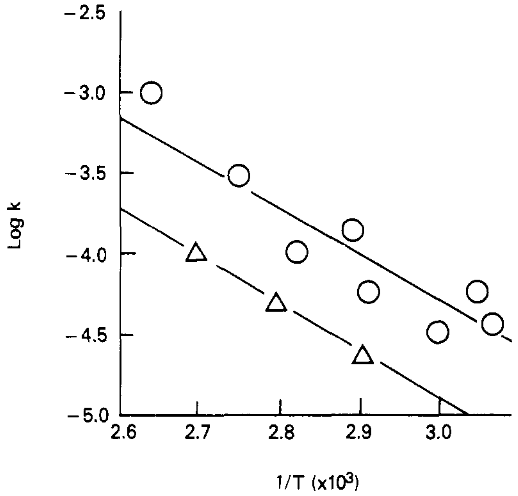

Figure 2. Log k vs $1/T$ plots of diaryl rearrangements: △, **12** → **33**; ○, **33** → **12** (least-squares fit of data).

is $-d[A]/dt = k_1[A] + k_{-1}[B]$. The $Z \rightleftharpoons E$ rearrangement is slower, but not much slower, than the 1,2-diaryl rearrangement. At high conversions the kinetics become quite complicated, but at low (<10%) conversion, the kinetics reduce to a first-order expression in A. A similar analysis applies to the reverse process, the rearrangement of the (E/Z)-**33** mixture to give the disilene **12**.[8]

The activation parameters were $\Delta H^{\ddagger} = 15 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -36 \pm 4$ eu for the reaction **12** to **33** and $\Delta H^{\ddagger} = 14 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = -37 \pm 4$ eu for the reaction of **33** to **12** (Figure 2). The activation energy for cis-trans interconversion in these tetraaryldisilenes cannot be obtained from our measurements, but it probably much larger (>25 kcal mol^{-1}).[9]

The fact that neither of the cross-products **13** and **23** is observed during the rearrangement of the mixture containing **11**, **22**, **12**, and **33** indicates that the rearrangement is intramolecular. As a further test, a benzene solution containing disilenes **11** and **22** was heated for 7 days at 80 °C. The solution was unchanged after this time, with no sign of formation of **12** or **33** in the ^{29}Si NMR spectrum.[10] In addition to eliminating the possibility that the rearrangement is intermolecular, this experiment also shows that thermal fragmentation of the disilenes to silylenes does not take place under these conditions.

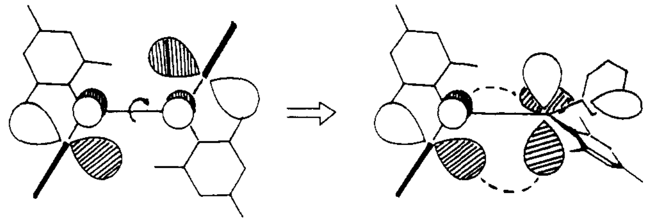

Figure 3. Representation of the orbitals involved in the proposed rearrangement mechanism. As rotation occurs about the Si–Si axis, overlap of the shaded orbitals develops.

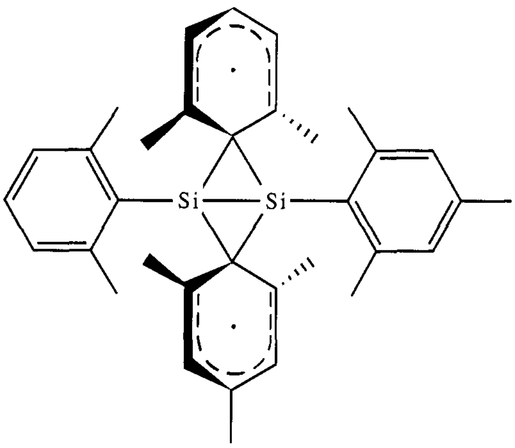

Figure 4. One of the possible resonance contributions to the dibridged structure. The geometry is not implied.

An intramolecular mechanism involving reversible migration of a single aryl group to give a silylsilyene intermediate might be considered (eq 1). However, this

$$Ar_2Si{=}SiAr_2 \rightleftarrows Ar\ddot{S}i{-}SiAr_3 \qquad (1)$$

pathway should lead to loss of stereochemistry, inconsistent with our results. Moreover the rearrangement was found to take place as usual in the presence of excess triethylsilane, a known trapping agent for silylenes that should have intercepted the silylsilylene if it was present.

We propose that the 1,2-diaryl rearrangement is dyotropic,[11] involving a concerted intramolecular migration of two σ-bonded aryl groups across the silicon–silicon bond. The rearrangement could proceed through a 1,3-disilabicyclobutane-like transition state in which two aryl groups are bridged across the Si–Si bond (Figure 3). Such an ordered transition state is consistent with the large negative entropy of activation observed for the reaction. We envisage that the synchronous migration of the two aryl groups is concurrent with a twist about the Si–Si bond. As rotation takes place about the bond axis, the back lobe of the p orbitals on each silicon begins to interact favorably with the π system of one of the migrating aryl groups (Figure 4). The transition state is reached when the two aryl groups are halfway migrated across the Si–Si bond. By this model the transition state must occur at less than a 90° twist about the Si–Si bond; if this were not the case, then all stereochemical information would be lost (a +90° rotation in the E isomer is the equivalent of a -90° rotation from the Z isomer). In contrast, the transition state for the E/Z interconversion would be at 90°.[12]

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(7) At high conversions the kinetics become much more complicated. See: Szabo, Z. G. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam; Vol. 2, pp 1–80.

(8) The kinetics of the reverse reaction were treated considering that both (E)-**33** and (Z)-**33** are sources of the disilene **12**. However we have shown that the rearrangement of disilene **12** is stereoselective, as only a single isomer of **33** is formed directly, the other **33** isomer being derived from cis to trans interconversion.[2c,7] The reverse rearrangement is probably also stereospecific; only one of the **33** isomers is the source of **12**, the other isomer giving a degenerate 1,2-diaryl rearrangement that cannot be observed. If we assume that only one **33** isomer gives **12**, then the effective concentration of reactant is halved. Therefore the initial concentration of (E/Z)-**33**, $[\mathbf{33}]_0$, for our calculations equals $^1/_2[(E/Z)\text{-}\mathbf{33}]$. This changes the values for the rate constant, k_{-1}, but does not affect the values for the activation energy or entropy. The rearrangement **33** → **12** proceeded more rapidly than **12** → **33**. The reason for the difference is not clear, but possibly the **33** → **12** reaction was subject to adventitious catalysis. On one occasion, a similarly rapid (catalyzed) reaction rate was observed for **12** → **33**. Efforts to identify the catalyst were unsuccessful.

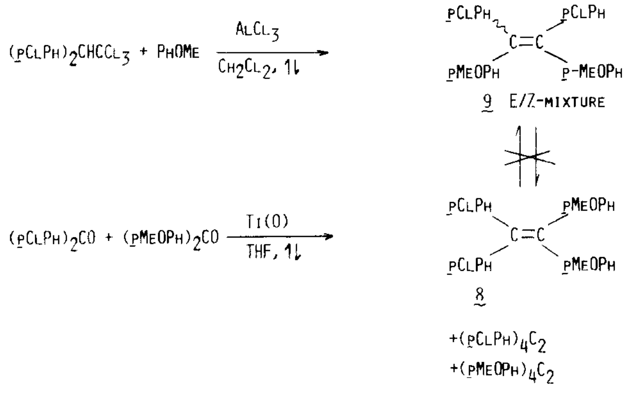
(9) For 1,2-dimesitylbis(2,6-diethylphenyl)disilene, $\Delta H^{\ddagger}$ ($Z \rightarrow E$) is reported to be 27.7 kcal mol^{-1}, and the corresponding values for other disilenes range from 25 to 31 kcal mol^{-1}. See: Masamune, S. In *Silicon Chemistry*; Corey, J. Y., Corey, E. J., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, UK, 1987; pp 257–268. Shepherd, B. D.; Powell, D. R.; West, R. *Organometallics* **1989**, *8*, 2664–2669.

(10) In a related experiment, when trisilane **1** was irradiated at 254 nm for 12 h at -60 °C in a pentane solution containing disilene **22**, only disilenes **12** and **22** were detected in solution. This result shows that there is no formation of a cyclotrisilane intermediate via addition of silylene to a disilene and also that these disilenes do not undergo photochemical fragmentation to give silylenes.

(11) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33–65.

(12) Bridging phenyl groups may be involved in the transition states for E/Z interconversion of 1,2-diarylalkenes as well as 1,2-diaryldisilenes; the result would be lowered rotation barriers for twisting about the C=C or Si=Si bonds relative to the unsubstituted cases.

Scheme II. Synthesis of the Tetraarylethylenes



It is also conceivable that the halfway-migrated structure is actually a shallow minimum on the reaction coordinate, with transition states occurring before and after formation of the dibridged structures. Molecular orbital calculations on the parent disilene, Si_2H_4, indicate that a structure with dibridging hydrogens is a minimum on the singlet energy surface and is only 15 kcal/mol higher in energy than the disilene structure.[13a]

In the proposed pathway, rearrangement of $A_2Si{=}SiB_2$ would produce exclusively the *Z* isomer of ABSi=SiAB. It is clear that one stereoisomer appears first, but there is no direct proof that it is the *Z* isomer.[13b] This assignment seems reasonable, however, because the isomer with the most downfield resonance is produced first. In the several cases where ^{29}Si NMR spectra have been determined for *Z* and *E* disilene isomers with known configuration, the *Z* isomer always appears at lower field than the *E* isomer.[2a]

Efforts to prepare disilenes with electron-donating groups on the aryl substituents were unsuccessful. Trisilanes 6 and 7, with *p*-methoxy substitution on the aryl rings, were synthesized but do not photolyze in the usual fashion to give disilenes. After irradiation for 20 h at −60 °C in pentane solution, the photolysates from trisilanes 6 and 7 were examined by ^{29}Si NMR, and no signals were detected in the downfield region (60–65 ppm) typical of disilenes. Perhaps the methoxy groups provide a mechanism for rapid dissipation of energy from the excited state, returning the molecule to the ground state.[14]

Since the 1,2-diaryl migration takes place readily in disilenes, we looked for a similar reaction in the alkene series. Accordingly we sought to prepare 1,1-bis(*p*-chlorophenyl)-2,2-bis(*p*-methoxyphenyl)ethylene (8) by a literature method,[15] the reaction of DDT with anisole catalyzed by $AlCl_3$ (Scheme II). However, in our hands this synthesis did not give 8 but instead produced the regioisomeric compound 9, as a mixture of its *E* and *Z* stereoisomers, which were separated by thin-layer chromatography. Authentic 8 was prepared by titanium(0)-catalyzed coupling of the two dissimilar diaryl ketones[16] (Scheme II). Ethylene 8 is unequivocally distinguished from the regioisomers (*E*) and (*Z*)-9 by ^{13}C NMR spectroscopy; stereoisomer 8 evidences 11 carbon signals, and (*E*) and (*Z*)-9 show only 10 signals each (see Experimental Section). Rearrangement was not observed in this system even at temperatures up to 285 °C (neat) or at 150 °C in benzene solution; only cis–trans isomerization of the olefin 9 was detected.

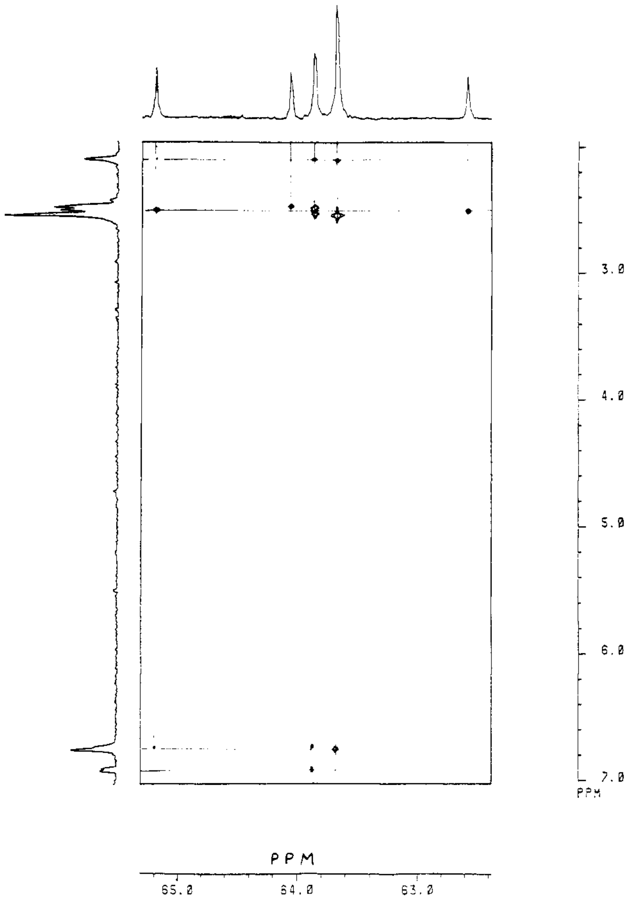


Figure 5. 2D ^1H–^{29}Si NMR spectrum of rearranged mixture containing disilenes **12**, **22**, (*E*)- and (*Z*)-**33** and **11** (see text).

Assignment of ^{29}Si NMR Spectra. Silicon-29 chemical shifts for the disilenes are summarized in Table I. For **14**, the two resonances lie close together and fall between those for the corresponding symmetrical compounds, **11** and **44**. For **12**, however, the resonances are separated by 2.6 ppm and lie *outside* the values for the symmetrical disilenes **11** and **22**.

To assign the resonances in **12**, a 2D ^1H–^{29}Si experiment[17] was carried out on the equilibrium mixture containing **11**, **22**, **12**, and (*Z*)- and (*E*)-**33**. The ^{29}Si NMR spectrum for this mixture (shown in Figure 1b) is projected in the F2 dimension at the top of the 2D plot in Figure 5; the ^1H spectrum is shown in the vertical F1 dimension. In the latter, resonances appear at 2.25, 2.7, 6.9, and 7.1 ppm, due to the *p*-CH_3, *o*-CH_3, *m*-H, and *p*-H protons, respectively. It is now possible to make correlations, first for the known compounds. Disilene **11**, having δ ^{29}Si at 63.67 ppm, shows ^1H–^{29}Si correlation to the *p*-CH_3, *o*-CH_3, and *m*-H protons as expected. For **22**, no cross peak is found for the *p*-CH_3 protons.[18] The ^{29}Si resonances for

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[13] (a) The proposed hydrogen-dibridged structure is however rotated by 90°. See: Lischka, H.; Kohler, H.-J. *Chem. Phys. Lett.* **1984**, *112*, 33–40. (b) A dyotropic pathway involving initial formation of the *E* isomer is also permitted by symmetry considerations. See: Halevi, E. A. *Orbital Symmetry and Reaction Mechanism-The OCAMS View*; Springer-Verlag: Heidelberg, FRG, in press. It is also conceivable that both of these pathways are operational, but if this is so, then one must be much faster than the other.

[14] McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905.

[15] Mitchell, R. H.; Mazuch, L.; Shell, B.; West, P. R. *Can. J. Chem.* **1978**, *56*, 1246–1252. From the data given in this publication it is not possible to tell whether the authors actually had 8 or (*E*/*Z*)-9.

[16] McMurray, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411.

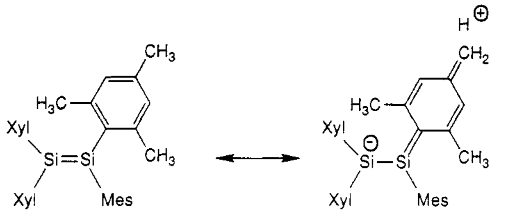
[17] The Bruker XHCORR program was employed, with D1 = 3.0 s; D3 = 0.16 s; D4 = 0.032 s.

[18] Some of the expected cross peaks for the aromatic protons do not appear in Figure 5; these peaks are broadened but are observable at lower levels on the 2D contour plot.

[19] Cagniant, P.; Hoi, B. *Bull. Chim. Soc. Fr.* **1942**, *9*, 889–892.

(*Z*)- and (*E*)-**33** near 63.9 ppm are not separated in the 2D spectrum but show correlations to all four types of protons. This leaves the resonances for **12** at 65.19 and 62.56 ppm. The resonance at 65.19 ppm shows a cross peak for the *p*-CH_3 protons, whereas the 62.56 ppm resonance does not. The 65.19 ppm resonance is therefore due to the silicon-bearing the mesityl groups, and the 62.56 ppm resonance is derived from the silicon attached to the 2,6-xylyl groups.

The surprising result is that although the resonance for $Xyl_2Si{=}SiXyl_2$ (**22**) falls downfield from that for $Mes_2Si{=}SiMes_2$ (**11**), in **12** the *dimesityl* silicon produces the most downfield resonance. This can be rationalized in terms of electron release by the *p*-CH_3 groups in **12**, leading to slight polarization of the molecule and additional shielding of Xyl_2Si silicon, as illustrated in resonance structure A. The Mes_2Si silicon would be correspondingly deshielded. In **33** the internal polarization from methyl groups would be nil, and in fact the resonances for **33** lie midway between those for **11** and **22**.



Structure A

Experimental Section

All reactions and manipulations were carried out under at atmosphere of dry nitrogen or argon, and solvents were dried and distilled prior to use. Proton NMR spectra were recorded on a Bruker WP-270 (270 MHz) spectrometer. Silicon-29 NMR spectra were recorded on either a Bruker AM-360 (71.55 MHz) or a Bruker AM-500 (100.33 MHz) spectrometer using INEPT pulse sequences and complete proton decoupling.[5] Chemical shifts are reported in parts per million downfield from a tetramethylsilane external standard. All spectra were recorded in benzene solution unless otherwise noted.

All compounds reported below were >98% pure by gas chromatographic analysis. Elemental analyses were performed by Galbraith Laboratories. Melting points are uncorrected.

Photolyses were carried out in a Rayonet Model RPR-100 photoreactor equipped with 254-nm lamps. Low temperatures for photolysis were maintained by the use of a quartz Dewar equipped with a liquid nitrogen blowoff system and temperature controller. Thermal rearrangement reactions were carried out in the dark to preclude the possibility of photoinduced rearrangement.

A least-squares fit of the experimental data points was used to generate the plots of Figure 2 and the values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$. Error limits were calculated assuming ±5% errors in the NMR integrations.

2,6-Dimethyl-4-*tert*-butylbromobenzene[19] and 2,6-dimethyl-4-methoxybromobenzene[20] were prepared by bromination of the corresponding aromatic compounds. Dichlorosilane **1a** was prepared from mesityllithium and silicon tetrachloride according to known procedures and showed spectral properties identical with those reported.[2a,21] The same method was used for the synthesis of **2a**,[22] **4a**, and **6a**. Compounds **5a** and **7a** were prepared in the same manner as **3a**, by the addition of 1 mol equiv of aryllithium to mesityltrichlorosilane.[2a] Trisilanes **1–7** were prepared by the lithium coupling reaction of the diaryldichlorosilanes (**1a–7a**) with trimethylchlorosilane[21,23] and were recrystallized from hexane.

1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT), 4,4′-dimethoxybenzophenone, and 4,4′-dichlorobenzophenone were purchased from Aldrich Chemical Co. and used without further purification.

Mesityl(2,6-xylyl)dichlorosilane (3a). To a suspension of 10.4 g (0.093 mol) of (2,6-xylyl)lithium in 100 mL of dry toluene was added a solution of 15.7 g (0.062 mol) of mesityltrichlorosilane in 100 mL of toluene over 1 h at room temperature. The reaction was monitored by gas chromatography (GLC). After 24 h at 20 °C, no starting material remained. The lithium salts were filtered, and the filtrate evaporated to a pale yellow residue, 23.2 g (77%); mp 68–70 °C; ^{1}H NMR (C_6D_6) δ 1.98 (s, 3 H), 2.42 (s, 6 H), 2.45 (s, 6 H), 6.56 (s, 2 H), 6.75 (AB_2, 2 H), 6.97 (AB_2, 1 H); MS (30 eV) 322 (M^+, 12), 307 ($M^+ - CH_3$, 100); exact mass for $C_{17}H_{20}SiCl_2$ calcd *m*/*e* 322.0711, found *m*/*e* 322.0711.

Bis(2,6-xylyl)dichlorosilane (2a): mp 85–87 °C; ^{1}H NMR (C_6D_6) δ 2.44 (s, 12 H), 6.66 (AB_2, 4 H), 6.89 (AB_2, 2 H); exact mass for $C_{16}H_{18}SiCl_2$ calcd *m*/*e* 308.0560, found *m*/*e* 308.0555.

Bis(2,6-dimethyl-4-*tert*-butylphenyl)dichlorosilane (4a): mp 130–132 °C; ^{1}H NMR (C_6D_6) δ 1.17 (s, 18 H), 2.54 (s, 12 H), 6.98 (s, 4 H); exact mass for $C_{24}H_{34}SiCl_2$ calcd *m*/*e* 420.1807, found *m*/*e* 420.1808.

Mesityl(2,6-dimethyl-4-*tert*-butylphenyl)dichlorosilane (5a): mp 79–84 °C; ^{1}H NMR (C_6D_6) δ 1.17 (s, 9 H), 1.98 (s, 3 H), 2.46 (s, 6 H), 2.54 (s, 6 H), 6.57 (s, 2 H), 6.99 (s, 2 H); exact mass for $C_{21}H_{28}SiCl_2$ calcd *m*/*e* 378.1138, found *m*/*e* 378.1336.

2-Mesityl-2-(2,6-xylyl)-1,1,1,3,3,3-hexamethyltrisilane (3). To a suspension of 3.0 g (0.07 mol, 6 equiv) of lithium metal, cut into small chunks, in 100 mL of dry tetrahydrofuran (THF) was added via syringe 19.9 mL (23.1 g, 2.2 equiv) of chlorotrimethylsilane. The mixture was then cooled in an ice bath, and 23 g (0.07 mol) of mesityl(2,6-xylyl)dichlorosilane in 50 mL of THF was added dropwise over 1.5 h with stirring. After 1 h the ice bath was removed, and the reaction mixture was allowed to warm to room temperature. After stirring for an additional 3 h at 20 °C, at which time GLC analysis showed the reaction to be complete, the solution was filtered to remove any unreacted lithium metal. Next, the filtrate was evaporated to a solid, and 100 mL of hexane was added. The hexane was washed three times with 50-mL portions of water and once with brine and dried over Na_2SO_4. Evaporation of the solvent gave a grey solid. Recrystallization from hexane gave 15 g (54%) of pure **3**: mp 150–151 °C; ^{1}H NMR (C_6D_6) δ 0.22 (s, 18 H), 2.10 (s, 3 H), 1.9–2.4 (br s, 12 H), 6.73 (s, 2 H), 6.89 (AB_2, 2 H), 7.10 (AB_2, 1 H); ^{29}Si NMR (C_6D_6) δ −47.65 (*Si*Ar$_2$), −12.69 (Me$_3$*Si*); MS (30 eV) 398 (M, 22), 383 ($M^+ - CH_3$, 5), 325 ($M^+ - SiC_3H_9$, 100); exact mass for $C_{23}H_{38}Si_3$ calcd *m*/*e* 398.2281, found *m*/*e* 398.2289. Anal. Calcd for $C_{23}H_{38}Si_3$: C, 69.27; H, 9.60. Found: C, 69.32; H, 9.81.

Bis(2,6-xylyl)-1,1,1,3,3,3-hexamethyltrisilane (2): mp 164–166 °C; ^{1}H NMR (C_6D_6) δ 0.21 (s, 18 H), 1.9–2.5 (br, 12 H), 6.88 (AB_2, 4 H), 7.03 (AB_2, 2 H); ^{29}Si NMR (C_6D_6) δ −47.41 (SiAr$_2$), −12.57 (Me$_3$Si); exact mass for $C_{22}H_{36}Si_3$ calcd *m*/*e* 384.2125, found *m*/*e* 384.2115. Anal. Calcd for $C_{22}H_{36}Si_3$: C, 68.67; H, 9.43. Found: C, 69.32; H, 9.78.

Bis(2,6-dimethyl-4-*tert*-butylphenyl)-1,1,1,3,3,3-hexamethyltrisilane (4): mp 185–186 °C; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H), 1.26 (s, 18 H), 2.0–2.5 (br, 12 H), 7.15 (obscured by solvent), ($CDCl_3$) δ 0.14 (s, 18 H), 1.26 (s, 18 H), 1.8–2.4 (br, 12 H), 6.87 (s, 4 H); ^{29}Si NMR (C_6D_6) δ −47.90 (*Si*Ar$_2$), −12.66 (Me$_3$*Si*); exact mass for $C_{30}H_{52}Si_3$ calcd *m*/*e* 496.3377, found *m*/*e* 496.3394.

Mesityl(2,6-dimethyl-4-*tert*-butylphenyl)-1,1,1,3,3,3-hexamethyltrisilane (5): mp 90–92 °C; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H), 1.26 (s, 9 H), 2.11 (s, 3 H), 2.0–2.5 (br, 12 H), 6.73 (s, 2 H), 7.10 (s, 2 H); ^{29}Si NMR (C_6D_6) δ −47.92 (*Si*Ar$_2$), −12.78 (Me$_3$*Si*); exact mass for $C_{27}H_{46}Si_3$ calcd *m*/*e* 454.2907, found *m*/*e* 454.2911.

Bis(2,6-dimethyl-4-methoxyphenyl)-1,1,1,3,3,3-hexamethyltrisilane (6): mp 142–144 °C; ^{1}H NMR (C_6D_6) δ 0.25 (s, 18 H), 1.0–2.5 (br, 12 H), 3.34 (s, 6 H), 6.62 (s, 4 H); ^{29}Si NMR (C_6D_6) δ −48.30 (*Si*Ar$_2$), −12.76 (Me$_3$*Si*); exact mass for $C_{24}H_{40}O_2Si_3$ calcd *m*/*e* 444.2336, found *m*/*e* 444.2324. Anal. Calcd for

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(22) Compound **2a** was reported by S. Masamune and co-workers, but no experimental details nor characterization data were given. See ref 6.

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$C_{24}H_{40}Si_3O_2$: C, 64.80; H, 9.06. Found: C, 64.88; H, 9.22.

Mesityl(2,6-dimethyl-4-methoxyphenyl)-1,1,1,3,3,3-hexamethyltrisilane (7): mp 152–154 °C; ^1H NMR (C_6D_6) δ 0.25 (s, 18 H), 2.12 (s, 3 H), 2.0–2.4 (br, 12 H), 3.34 (s, 3 H), 6.61 (s, 2 H), 6.74 (s, 2 H); ^{29}Si NMR (C_6D_6) δ −48.11 (*Si*Ar$_2$), −12.79 (Me$_3$*Si*); exact mass for $C_{24}H_{40}OSi_3$) calcd *m/e* 428.2427, found *m/e* 428.2384.

Photolysis of Trisilanes. A solution of 0.5 g (1 mmol) of trisilane in 20–40 mL of pentane in a quartz photolysis tube was irradiated at −60 °C. The solution immediately turned yellow, and precipitation of the disilene product began within a few hours. After 12–16 h of photolysis the reaction was complete, as determined by GLC and ^{29}Si NMR on the crude photolysate. The solvent volume was then reduced under vacuum, and the bright yellow solid collected on a glass frit. The crude disilene (50–80%) was maintained under vacuum for 1 h to remove any volatile impurities. ^1H and ^{29}Si NMR analysis on the semicrystalline solid indicated >95% purity.

44: mp 247–250 °C; ^1H NMR (C_6D_6) δ 1.19 (s, 36 H), 2.25 (s, 24 H), 7.03 (s, 8 H); ^{29}Si NMR (C_6D_6) δ +65.14; exact mass for $C_{48}H_{68}Si_2$ calcd *m/e* 700.4859, found *m/e* 700.4812.

Pure disilenes **11** and **22** were produced by photolysis of trisilanes **1** and **2**. Disilenes **33** and **55**, from **3** and **5**, respectively, were isolated and characterized as *E*/*Z* mixtures only.

33: ^{29}Si NMR (C_6D_6) δ +63.86, +63.87; exact mass for $C_{34}H_{40}Si_2$ calcd *m/e* 504.2668, found *m/e* 504.2655.

55: ^{29}Si NMR (C_6D_6) δ +64.37, +64.15; exact mass for $C_{42}H_{56}Si_2$ calcd *m/e* 616.3921, found *m/e* 616.3920.

Cophotolysis of Trisilanes. An equimolar mixture two trisilanes (0.5 g total) in 20–40 mL of pentane in a quartz tube was irradiated at −60 °C. The solution immediately turned yellow, and precipitation of the disilene products began within a few hours. After 12–16 h of photolysis the reaction was complete, as determined by GLC and ^{29}Si NMR on the crude photolysate. Workup, as described above, gave disilene mixtures that were analyzed by ^{29}Si NMR in benzene solution. The data are summarized in Table I.

Thermolysis of 11 and 22. A solution of 50 mg of **11** and 50 mg of **22** in 0.5 mL of benzene was heated at 90 °C for 7 days. The ^{29}Si NMR spectrum showed only two signals in the downfield region at 63.67 and 64.05 ppm for disilenes **11** and **22**, respectively.

Cophotolysis of 1 in the Presence of 22. A solution of 50 mg of **22** and 35 mg of trisilane **1** in 20 mL of pentane was irradiated for 12 h at −60 °C. The ^{29}Si NMR spectrum of the photolysate showed only two signals in the disilene region; these corresponded to disilenes **11** and **22** at 63.67 and 64.05 ppm.

Kinetic Measurements. Sealed NMR samples of disilene mixtures, 50 mg in 0.5 mL of benzene, were heated in a constant-temperature bath, protected from light. Samples were removed at periodic intervals, and the progress of the rearrangement monitored by ^{29}Si NMR. Data shown in Table II for rearrangement of **12** and **33** are from a single preparation of **12**, but five other runs on different samples of **12** gave closely similar results over the same range of temperatures. In one set of experiments for **12** to **33**, the reaction appeared to be catalyzed, and the rates at each temperature were faster by an order of magnitude.

1,1-Bis(*p*-chlorophenyl)-2,2-bis(*p*-methoxyphenyl)ethylene (8). To a suspension of 24.7 g (0.16 mol) of $TiCl_3$ in 400 mL of THF at 0 °C was added 3.2 g (0.08 mol) of $LiAlH_4$ in small portions. The purple solution was refluxed for 1 h and then cooled to room temperature. At this time a solution of 17.7 g (0.08 mol) of 4,4′-dimethoxybenzophenone and 18.1 g (0.08 mol) of 4,4′-dichlorobenzophenone in 300 mL of THF was added dropwise over 15 m. The resulting mixture was refluxed for 5 h, cooled, and poured onto 400 g of ice. The suspension was extracted four times with 300-mL portions of $CHCl_3$. The organic layer was washed four times with 750-mL portions of H_2O, dried over $MgSO_4$, and evaporated to a yellow oil. Three products were detected by thin-layer chromatography and separated by column chromatography on silica gel eluted with 2% ethyl acetate in hexane. The products were identified as the expected mixture of ethylenes:[24] tetrakis(*p*-chlorophenyl)ethylene, tetrakis(*p*-methoxyphenyl)ethylene, and **8**, which was recrystallized from ethyl acetate–hexane as pale yellow crystals, 1.4 g (4%); mp 196–197 °C; ^1H NMR ($CDCl_3$) δ 3.76 (s, 6 H), 6.66 (m, 4 H), 6.8–7.0 (m, 8 H), 6.09 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.10, 113.17, 127.99, 131.99, 132.45, 132.59, 135.60, 136.51, 141.41, 142.33, 158.35; exact mass for $C_{28}H_{22}O_2Cl_2$ calcd *m/e* 460.0997, found *m/e* 460.0980.

(*E*)- and (*Z*)-1,2-Bis(*p*-chlorophenyl)-1,2-bis(*p*-methoxyphenyl)ethylene (9). To a cooled (0 °C) solution of 20 g (56 mmol) of DDT and 25 g (232 mmol) of anisole in 200 mL of CH_2Cl_2 was added in small portions 25 g (56 mmol) of $AlCl_3$ with stirring. The solution was refluxed for 4.5 h, gradually taking on a purple color. At this time, the mixture was cooled, poured over ice, and evolved HCl vigorously.

The organic layer, an orange suspension, was filtered and evaporated to a deep red oil. Thin-layer chromatography showed two new products with similar R_f values. These isomers were separated by column chromatography using silica gel eluted with 2% ethyl acetate in hexane. The products were characterized by ^1H and ^{13}C NMR and HRMS. The isomer with the higher R_f value was isolated as pale yellow crystals, 4.1 g (16%); mp 185–188 °C; ^1H NMR ($CDCl_3$) δ 3.75 (s, 6 H), 6.65 (m, 4 H), 6.8–7.0 (m, 8 H), 6.07 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.06, 113.35, 127.92, 132.11, 132.44, 132.60, 135.49, 139.03, 142.50, 158.37; exact mass for $C_{28}H_{22}O_2Cl_2$ calcd *m/e* 460.0997, found *m/e* 460.0987.

The other regioisomer was recrystallized from cyclohexane as pale yellow crystals, 3.7 g (14%): mp 180–181 °C; ^1H NMR ($CDCl_3$) δ 3.74 (s, 6 H), 6.65 (m, 4 H), 6.8–7.0 (m, 8 H), 6.07 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 55.08, 113.21, 127.97, 132.17, 132.37, 132.60, 135.61, 138.90, 142.31, 158.18; exact mass for $C_{28}H_{22}O_2Cl_2$ calcd *m/e* 460.0997, found *m/e* 460.0990.

Thermolysis of 8. In a thick-walled glass ampule was sealed under vacuum 350 mg (0.76 mmol) of **8**. The sample was heated at 285 °C for 22 h. At that time, the ^{13}C spectra in $CDCl_3$ showed no evidence for the isomers of **9**.

Thermolysis of 9. In separate thick-walled glass ampules were sealed under vacuum 350 mg (0.76 mmol) of each of the two stereoisomers of ethylene **9**. The samples were heated at 285 °C for 22 h. At that time, the ^{13}C spectra in $CDCl_3$ showed, in both samples, a nearly equal mixture of *E* and *Z* isomers of **9** and no **8**.

Thermolysis of 8 in Solution. A sample containing 190 mg (0.41 mmol) of **8** was dissolved in C_6D_6. After three freeze–degas–thaw cycles, the tube was sealed under vacuum. After 22 h at 150 °C, NMR showed no evidence for the isomers of **9**.

Thermolysis of 9 in Solution. A sample containing 150 mg of each of the two isomers of **9** was dissolved in C_6D_6. After three freeze–degas–thaw cycles, the tube was sealed under vacuum. After 22 h at 150 °C, NMR showed no evidence of ethylene **8**.

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