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Mechanistic Investigation on the Reactivity of the Silicon–Silicon Double Bond with Epoxides. Reaction of Tetramesityldisilene with *cis*- and *trans*-Stilbene Oxides

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Starting from either *cis*- or *trans*-stilbene oxide, the products of reaction with tetramesityldisilene, **1**, in benzene at 100 °C were (a) an *E*/*Z* mixture of the disilyl enol ethers, 1,2-diphenyl-1-[(1,1,2,2-tetramesityldisilanyl)oxy]ethylene, **4**, (b) the five-membered ring, 1,1,2,2-tetramesityl-*trans*-4,5-diphenyl-3-oxa-1,2-disilacyclopentane, **5**, and (c) the products of deoxygenation, stilbene and 1,1,2,2-tetramesityl-3-oxa-1,2-disilacyclopropane, **3**. From the *cis*-epoxide the ratio of **4**:**5**:stilbene was 5.25 (*E*:*Z*, 21:1):3.28:1(c:t, 1.6:1), and from *trans*-stilbene oxide, 1.12 (*E*:*Z*, 5.9:1):1:1.25 (*E* only). A mechanism is proposed for formation of **4** and **5** involving a ring-opened zwitterionic intermediate, allowing carbon–carbon bond rotation and the observed stereoselectivity. Two pathways are considered for deoxygenation. The stereochemistries of **Z4** and **5** were determined by X-ray crystallography. Both crystallized in the triclinic space group $P\bar{1}$ with $Z = 2$. Lattice constants for **Z4** were $a = 11.3064(14)$ Å, $b = 12.4175(8)$ Å, $c = 14.9490(11)$ Å, $\alpha = 88.477(6)°$, $\beta = 79.070(6)°$, and $\gamma = 79.470(10)°$, and for **5**, $a = 12.0524(12)$ Å, $b = 12.0670(9)$ Å, $c = 15.5685(9)$ Å, $\alpha = 86.663(9)°$, $\beta = 70.44(4)°$, and $\gamma = 73.255(9)°$.

Many reactions of the silicon–silicon double bond have been chronicled since the isolation of the first stable disilene over ten years ago, and the reaction chemistry of tetramesityldisilene, **1**, is now rather well developed.[1] Information about reaction mechanisms, however, is rather sparse. Besides in-depth studies on the air oxidation of **1** and 1,2-di-*tert*-butyl-1,2-dimesityldisilene,[1a,2] and more recently, on the reaction of transient disilenes with alcohols,[3] few mechanistic studies have been conducted.

We became interested in the reactions of three-membered organic heterocycles with **1** in hopes of generating more complete mechanistic information on disilene reactions. We anticipated that epoxides and episulfides might act simply as heteroatom sources to give known three- and possibly four-membered silicon ring compounds and alkene. Thus stereochemical and structural variation in the heterocycle could relay mechanistic information by inspection of the product alkenes.

We recently reported the reactions of **1** with cyclohexene oxide and cyclohexene sulfide[4] and found that while simple sulfur transfer occurred for the latter, the epoxide reacted to give the disilyl enol ether, 1-[(1,1,2,2-tetramesityldisilanyl)oxy]cyclohexene, **2**, the net result of nucleophilic attack of the epoxide oxygen on silicon followed by intramolecular proton abstraction and epoxide ring-opening (Scheme 1). Oxygen transfer with formation of cyclohexene and 1,1,2,2-tetramesityl-3-oxa-1,2-disilacyclopropane, **3**, was only a minor side reaction.

We have since continued our investigation into the epoxide reaction to expand its scope and to elucidate mechanistic details of product formation. The results of the reaction of **1** with *cis*- and *trans*-stilbene oxides are reported here.

Results

Heating **1** with *cis*- or *trans*-stilbene oxide in benzene at 100 °C gave a complex mixture of products. An *E*/*Z* mixture of disilyl enol ethers, 1,2-diphenyl-1-[(1,1,2,2-tetramesityldisilanyl)oxy]ethylene, **4**, was formed as were the deoxygenation products, stilbene and **3** (Scheme 2). In contrast to the cyclohexene oxide results, the five-membered ring compound, 1,1,2,2-tetramesityl-*trans*-4,5-diphenyl-3-oxa-1,2-disilacyclopentane, **5**, a single diastereomer, was also seen. Isolated yields are given in Table 1 along with those for side products from known disilene hydrolysis[1e] and unimolecular, thermal rearrangement.[5]

The basic structure of **5** could be assigned using mass spectral and NMR data. The five-membered ring proton signals came at δ 5.81 (d, $J = 11.8$ Hz) and 4.41 (d, $J = 11.8$ Hz), while the ring ^{13}C peaks were at δ 82.33 and

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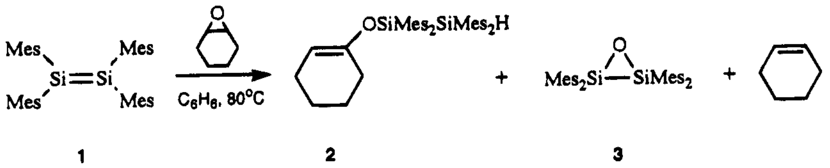
Scheme 1



Scheme 2

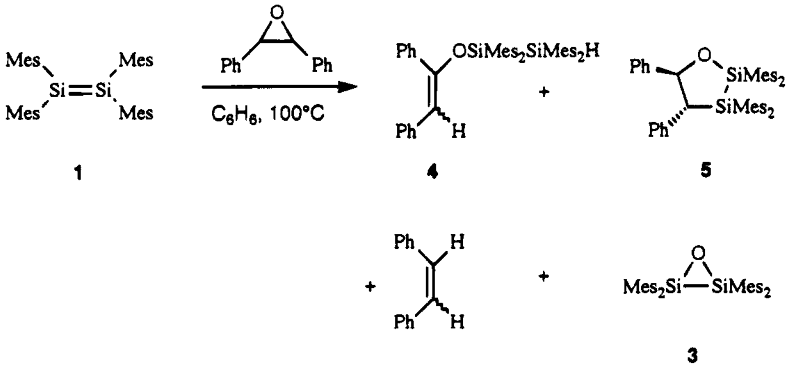


Table 1. Isolated Percent Yields[a] from the Reaction of Mes_4Si_2 with Stilbene Oxides[b]

	starting epoxide	
	cis	*trans*
4 (*E*:*Z*)	26.0 (20:1)	18.7 (6.5:1)
5	24.0	19.6
stilbene	8.8 (*Z* only)	24.4 (*E* only)
disilene hydrolysis	14.9	8.0
disilene rearrangement	3.3	10.5

[a] Yields are based on disilene. [b] Compound **3** could not be isolated by chromatography but was observed in the ^{29}Si NMR spectrum of the crude reaction mixture. See ref 1a for its ^{29}Si data.

Table 2. Summary of Crystal Data Collection for 5

empirilca formula	$C_{50}H_{56}OSi_2$
formula weight	729.1
crystal system	triclinic
space group	$P\bar{1}$
a, Å	12.0524(12)
b, Å	12.0670(9)
c, Å	15.5685(8)
α, deg	86.663(9)
β, deg	70.44(4)
γ, deg	73.255(9)
V, Å^3	2041.3(3)
Z	2
d(calcd), g/cm^3	1.186
cryst size, mm	0.1 × 0.3 × 0.5
color; habit	colorless prism
abs coeff, mm^{-1}	1.06
F(000)	784
T, °C	−160(2)
2*θ* range, deg	4.0−114.0
scan type	Wyckoff
scan speed, deg/min	variable, 3.00−40.00
scan range (*ω*), deg	0.86
index ranges	$0 \le h \le 12$, $-12 \le k \le 13$, $-15 \le l \le 16$
no. of reflns collected	5698
no. of indep reflns	5388 (R_{int} = 2.49%)
final *R* indices (obs data), %	*R* = 4.30, R_w = 6.75
goodness of fit	1.24
largest and mean Δ/*σ*	0.009, 0.001
data-to-parameter ratio	9.8:1
largest diff peak/hole, e Å^{-3}	+0.5/−0.23

50.28. Peaks in the ^{29}Si spectrum came at δ 1.86 and −11.72, uncharacteristic of a disilaoxetane,[1f] another possible structure. Stereochemical assignment and structure confirmation were made by X-ray crystallography. The two views in Figure 1 show the five-membered ring with the phenyl groups *trans* to each other, occupying pseudoequatorial positions on the ring (note the dihedral angles). Additional crystallographic data is presented in Tables 2 and 3.

The generation of **5**, although somewhat unexpected based on the cyclohexene oxide results, has precedent in the reactions of transient main group multiple bonds with epoxides. For example, double bonds of germanium to phosphorus, nitrogen, and oxygen have been trapped with epoxides to give the corresponding five-membered rings.[6] Silylenes also react with epoxides to give, among other products, 2,5-dioxa-1-silacyclopentanes, rationalized by silylene abstraction of oxygen to give a silanone which then could insert into the C—O bond of a second equivalent of epoxide.[7]

Compound **4** was identified by comparison of its ^{29}Si spectrum to that of **2**[4] and its ^{13}C data to the trimethylsilyl enol ethers of deoxybenzoin prepared by Davis and co-workers.[8] Peaks in the ^{29}Si spectrum were at δ −4.37 and −56.63 ($J_{Si-H} = -179.4$ Hz) for **E4** and δ 1.02 and −49.29 ($J_{Si-H} = -181.3$ Hz) for **Z4**. These compare to δ −8.36 and −56.67 ($J_{Si-H} = -179$ Hz) for **2**. The characteristic vinyl ^{13}C resonances came at δ 112.8 and 152.4 for **E4** and δ 114.6 and 153.3 for **Z4**. The Davis compounds gave peaks at δ 114.5, and 151.5 for *E* and 110.5 and 150.7 for *Z*.

X-ray diffraction on **Z4** (Figure 2, Tables 4 and 5), the minor isomer from either epoxide (see Table 1), established stereochemistry. Crystals were grown from a 2.3:1 **Z4**:**E4** mixture, a photostationary state obtained by photolysis of a 1:3 **Z4**:**E4** solution in benzene, λ = 350 nm.[9]

In retrospect, the X-ray data was particularly important to define the stereochemistry of **4**, since the vinyl ^{13}C shifts of **E4** and **Z4** are in the opposite order to the

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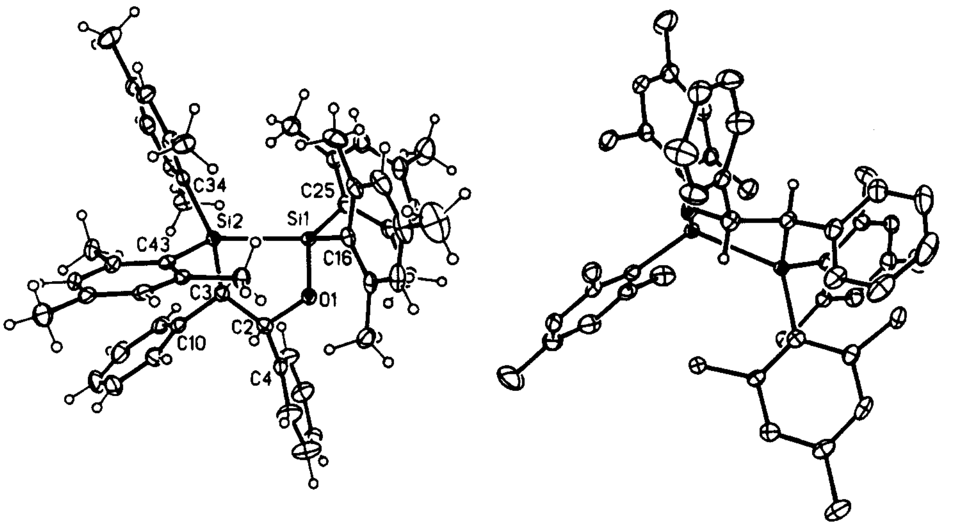

Figure 1. Thermal ellipsoid diagrams of **5**. Selected bond distances (Å) and angles (deg): Si(1)−Si(2), 2.480; Si(1)−O(1), 1.652; Si(2)−C(3), 1.953; C(2)−C(3), 1.549; Si(2)−Si(1)−O(1), 89.8; Si(1)−Si(2)−C(3), 86.4; Si(1)−O(1)−C(2), 124.5; Si(2)−C(3)−C(2), 104.9; O(1)−C(2)−C(3), 110.2; H(2)−C(2)−C(3)−H(3), 178.5; C(4)−C(2)−C(3)−C(10), 55.8; Si(2)−Si(1)−O(1)−C(2), 7.7; O(1)−Si(1)−Si(2)−C(3), 18.9.

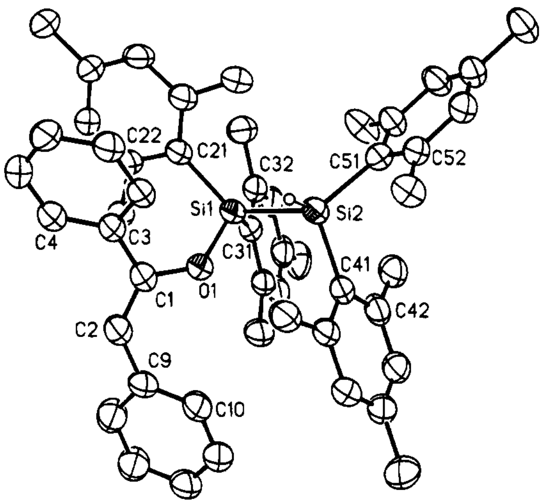

Figure 2. Thermal ellipsoid diagram of **Z4**. Selected bond distances (Å): Si(1)−Si(2), 2.404; Si(1)−O(1), 1.693; C(1)−C(2), 1.337; C(1)−O(1), 1.386.

assignments made by Davis for the trimethylsilyl derivatives. That is, the set of downfield shifts of the isomeric pair here (δ 114.6, 153.3) corresponds to the *Z* isomer, and in their case (δ 114.5, 151.5) to the *E* isomer. The present assignments do, however, follow the general observations of Taskinen.[10] With supporting thermodynamic data, the β vinyl carbon of the *Z* isomers of stereoisomeric methyl enol ethers was found to be downfield of that of the *E* isomers by 11−15 ppm. Inspection of the ^{13}C data of a series of 1,2-disubstituted trimethylsilyl enol ethers reported by Heathcock revealed a similar trend, even though a different method of assignment was used.[11] The chemical shift differences were much smaller than in the Taskinen study, but the β vinyl carbon of the *Z* isomer was consistently deshielded (0.4−1.2 ppm) relative to the *E* isomer.

In addition to isolated yields after chromatographic separation, product ratios were determined for crude reaction mixtures (reactions in sealed NMR tubes). Ample resolution at 500 MHz allowed integration of characteristic peaks from each product, except *trans*-stilbene from *cis*-stilbene oxide. Table 6 gives product ratios for *cis*- and *trans*-stilbene oxide reactions in d_6-benzene. The *cis*- to *trans*-stilbene ratio was determined by ^{1}H NMR after the alkenes were isolated using preparative gel permeation chromatography. The absence of *trans*-stilbene from the preparative *cis*-stilbene oxide run was a consequence of loss during chromatography. The crude mixture did show both stilbene isomers.

Discussion

Although the mechanisms of epoxide reactions can, in general, be quite complex, a number of observations with referral to precedent offer some insight into this reaction. We propose the pathway for formation of **4** and **5** as shown in Scheme 3. Two possible mechanisms for deoxygenation are dealt with later.

A reasonable first step is a Lewis acid−base interaction between **1** and the epoxide oxygen to give intermediates **6**. Sakurai and co-workers have found evidence for a similar intermediate for the reaction of alcohols with cyclic silenes,[12] and more recently with *cis*- and *trans*-1,2-dimethyl-1,2-diphenyldisilene.[3] Ring-opening to **7** would then set up a competition between product-forming steps and conformational changes allowing for the product distributions. Compound **4** would result from intramolecular proton abstraction by the silyl anion of **7** (path a, Scheme 3), while ring-closure from **7t** (path b) would give **5**.

In the reactions of epoxides with electrophilic agents, a carbocation is typically invoked as an intermediate to carbonyl compounds, the result of pinacolic rear-

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(9) The photochemical behavior of **4** is consistent with the known chemistry of stilbene and substituted-stilbene photochemical isomerization. For further reading see (a) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Organic Photochemistry*; Chapman, O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 1. (b) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415.

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Table 3. Atomic Coordinates ($\times 10^5$) and Equivalent Isotropic Displacement Coefficients ($\times 10^4$) for 5

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Si(1)	15526(5)	78165(5)	70974(4)	141(3)
Si(2)	29313(5)	78961(5)	79557(4)	139(3)
O(1)	26585(14)	78510(14)	61296(10)	224(7)
C(2)	37987(21)	80413(21)	60664(15)	199(9)
C(3)	42833(21)	73832(20)	68120(5)	176(9)
C(4)	46472(20)	76833(20)	50978(15)	191(9)
C(5)	51878(25)	65220(22)	48181(17)	303(11)
C(6)	59175(25)	62096(22)	39180(17)	306(11)
C(7)	60930(23)	70374(23)	32961(17)	278(10)
C(8)	55656(28)	81870(24)	35648(18)	391(12)
C(9)	48592(25)	85036(22)	44660(17)	317(11)
C(10)	55355(21)	75152(21)	66892(15)	205(9)
C(11)	57239(23)	86059(23)	66765(16)	263(10)
C(12)	68677(25)	77222(27)	65838(18)	357(12)
C(13)	78487(25)	77563(29)	65078(18)	397(13)
C(14)	76958(23)	66787(27)	64899(17)	348(11)
C(15)	65607(21)	65473(23)	65660(15)	256(10)
C(16)	1326(21)	90614(19)	71438(16)	185(9)
C(17)	−9402(21)	91656(21)	79067(16)	222(10)
C(18)	−19732(23)	101001(23)	80308(19)	310(11)
C(19)	−20123(24)	109608(23)	74084(20)	334(12)
C(20)	−9818(24)	108519(21)	66438(19)	294(11)
C(21)	884(22)	99392(20)	64953(16)	205(9)
C(22)	−10010(24)	82521(23)	86141(18)	309(10)
C(23)	−31440(28)	119885(27)	75524(26)	553(15)
C(24)	11464(23)	99923(21)	56420(16)	253(10)
C(25)	12235(20)	63872(20)	69501(16)	193(9)
C(26)	10435(21)	55252(20)	76059(16)	200(9)
C(27),	8890(23)	45039(21)	73748(17)	258(10)
C(28)	9312(24)	42474(21)	65028(18)	289(11)
C(29)	10678(22)	50880(21)	58744(17)	249(10)
C(30)	12002(20)	61453(20)	60697(16)	199(9)
C(31)	9870(25)	56613(22)	85795(17)	280(11)
C(32)	8621(33)	30899(25)	62500(22)	465(15)
C(33)	13165(24)	69754(21)	53048(16)	252(10)
C(34)	28197(20)	69743(19)	90051(15)	168(9)
C(35)	35639(21)	58382(20)	90259(16)	192(9)
C(36)	34460(21)	52833(20)	98423(16)	217(10)
C(37)	25839(22)	57876(21)	106644(16)	233(10)
C(38)	18285(23)	68958(21)	106410(16)	238(10)
C(39)	19279(21)	74874(20)	98384(15)	189(9)
C(4)	44904(24)	51726(21)	81695(17)	292(10)
C(41)	24521(27)	51467(24)	115349(18)	368(12)
C(42)	10194(23)	86756(21)	99103(16)	252(9)
C(43)	30867(20)	93134(19)	83475(14)	170(9)
C(44)	23408(20)	104294(19)	82791(14)	167(9)
C(45)	24647(22)	114020(20)	86214(15)	195(9)
C(46)	33652(23)	113340(21)	90098(15)	223(10)
C(47)	41176(22)	102447(22)	90581(15)	234(10)
C(48)	39891(21)	92379(20)	87563(15)	202(9)
C(49)	13808(21)	106146(20)	78234(16)	208(9)
C(50)	34994(27)	124159(23)	93478(18)	328(11)
C(51)	48590(23)	81083(22)	88961(17)	262(10)

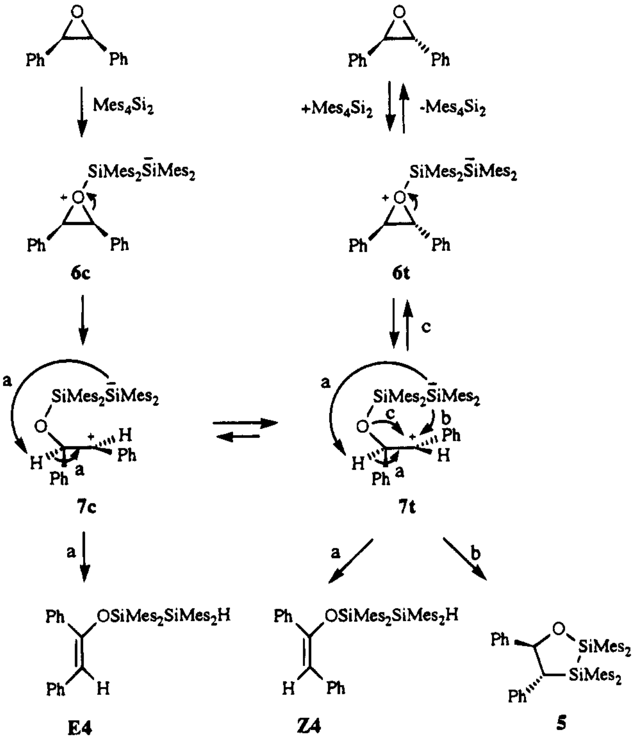
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

rangements.[13] Intermediate **7** is likely formed here without carbocation rearrangement due to the proximity of the silyl anion. Thus with an intramolecular nucleophile/base available, product-forming steps are fast relative to rearrangement, and competitive with conformational changes. Evidence for **7** as a dipolar and not a diradical intermediate comes from work in progress that showed that monoalkyl-substituted epoxides gave the same type of products as the stilbene oxides, while 2-methyl-1,2-epoxypropane gave disilyl enol ether and a disilaoxetane. The latter likely came from four-ring closure after hydride migration to the tertiary cation.

Table 4. Summary of Crystal Data Collection for Z4

empirical formula	$C_{50}H_{56}OSi_2$
formula weight	729.1
crystal system	triclinic
space group	$P\bar{1}$
a, Å	11.3064(14)
b, Å	12.4175(8)
c, Å	14.9490(11)
α, deg	88.477(6)
β, deg	79.070(6)
γ, deg	79.470(10)
V, Å^3	2026.0(3)
Z	2
d(calcd), g/cm^3	1.195
cryst size, mm	0.3 × 0.2 × 0.1
abs coeff, mm^{-1}	1.064
F(000)	784
T, °C	−160(2)
2*θ* range, deg	4.00−114.00
scan type	$\theta-2\theta$
scan speed, deg/min	variable, 3.00−40.00
scan range (*ω*), deg	0.68
index ranges	$-1 \le h \le 12, -13 \le k \le 13, -16 \le l \le 16$
no. of reflns collected	6455
no. of indep reflns	5461 ($R_{int} = 6.11\%$)
final *R* indices (obs data), %	$R = 7.53$, $R_w = 19.30$
goodness of fit on F^2	0.951
largest and mean Δ/σ	0.014, 0.001
data-to-parameter ratio	11.1:1
largest diff peak/hole, e Å^{-3}	+0.427/−0.448

Scheme 3



Thus no five-membered ring compound was produced suggesting that a sufficiently bulky cation can inhibit ring-closure in favor of the typical cationic rearrangement.

Primary evidence for this mechanism is based on the stereochemistry of the products. We now consider this data along with alternate mechanisms.

Intermediate **7** is the most likely precursor to **5**, especially considering the complete stereoselectivity. Sterics likely dictate the conformation of the five-membered ring, and, therefore, in solution, the phenyls probably prefer the pseudoequatorial positions as they

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Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\times 10^3$) for Z4

atom	*x*	*y*	*z*	U_{eq},[a] Å^2
Si(1)	1408(1)	2069(1)	2565(1)	49(1)
Si(2)	2929(1)	2199(1)	3464(1)	49(1)
O(1)	2280(3)	2432(2)	1594(2)	54(1)
C(1)	2672(5)	1989(4)	724(3)	55(1)
C(2)	2786(5)	2631(4)	−8(3)	60(1)
C(3)	3070(5)	780(3)	613(3)	55(1)
C(4)	2733(5)	224(4)	−61(3)	59(1)
C(5)	3161(5)	−884(4)	−202(3)	61(1)
C(6)	3927(5)	−1459(4)	327(3)	61(1)
C(7)	4273(5)	−913(4)	999(3)	60(1)
C(8)	3842(5)	195(4)	1145(3)	55(1)
C(9)	2616(5)	3836(4)	−57(3)	60(1)
C(10)	3177(5)	4431(4)	451(3)	61(1)
C(11)	3062(5)	5548(4)	368(3)	64(1)
C(12)	2375(5)	6090(4)	−223(3)	64(2)
C(13)	1833(6)	5513(4)	−745(4)	73(2)
C(14)	1954(6)	4397(4)	−671(4)	75(2)
C(21)	1015(5)	713(3)	2311(3)	50(1)
C(22)	274(5)	705(3)	1649(3)	50(1)
C(23)	−13(5)	−274(3)	1394(3)	55(1)
C(24)	403(5)	−1264(3)	1779(3)	55(1)
C(25)	1124(5)	−1262(3)	2434(3)	55(1)
C(26)	1427(5)	−305(4)	2701(3)	52(1)
C(27)	−288(5)	1729(3)	1193(3)	56(1)
C(28)	44(6)	−2305(4)	1516(3)	67(2)
C(29)	2208(5)	−384(4)	3426(3)	60(1)
C(31)	−70(5)	3070(3)	2926(3)	54(1)
C(32)	−1122(5)	2742(4)	3469(3)	54(1)
C(33)	−2170(5)	3512(4)	3789(3)	58(1)
C(34)	−2250(6)	4617(4)	3592(3)	61(1)
C(35)	−1253(6)	4943(4)	3057(3)	64(2)
C(36)	−177(5)	4212(3)	2727(3)	55(1)
C(37)	−1217(5)	1574(4)	3746(3)	63(1)
C(38)	−3417(5)	5416(4)	3971(4)	75(2)
C(39)	835(6)	4686(4)	2140(3)	68(2)
C(41)	3385(5)	3589(3)	3213(3)	51(1)
C(42)	2693(5)	4530(4)	3689(3)	55(1)
C(43)	3025(5)	5559(4)	3492(3)	60(1)
C(44)	4003(5)	5686(4)	2825(3)	58(1)
C(45)	4686(5)	4759(4)	2352(3)	54(1)
C(46)	4406(5)	3723(3)	2534(3)	52(1)
C(47)	1579(5)	4466(4)	4402(3)	63(1)
C(48)	4356(6)	6795(4)	2606(4)	75(2)
C(49)	5216(5)	2782(4)	1975(3)	58(1)
C(51)	2926(5)	1820(3)	4704(3)	51(1)
C(52)	4092(5)	1601(3)	4976(3)	51(1)
C(53)	4179(5)	1243(3)	5854(3)	54(1)
C(54)	3159(5)	1100(4)	6494(3)	55(1)
C(55)	2032(5)	1338(4)	6237(3)	57(1)
C(56)	1902(5)	1703(4)	5366(3)	54(1)
C(57)	5259(5)	1738(4)	4346(3)	59(1)
C(58)	3283(6)	706(4)	7437(3)	70(2)
C(59)	617(5)	1973(5)	5188(3)	73(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Crude Product Ratios[a] for NMR-Scale Reactions Run in C_6D_6

	cis-stilbene oxide	*trans*-stilbene oxide
4 (*E*:*Z*)	5.25 (21:1)	1.12 (5.9:1)
5	3.28	1
stilbene (c:t)	1 (1.6:1)	1.25 (t only)

[a] Error was ±3−5% based on multiple runs except for the **Z4**:**E4** ratio where it was 10−15%.

do in the solid. To form the other diastereomer with *cis*-phenyls would be highly unfavorable. A drastic steric interaction in the transition state would likely occur between two *cis*-mesityl groups and one phenyl group forced to be pseudoaxial.

Control experiments showed that isomerization of **4** did not occur under the reaction conditions. With the observed stereoselectivity, then, intermediate **7** must be on the reaction path. Intramolecular proton abstraction likely occurs since the 1,2-dideuterated epoxides gave **4** (and all other epoxide-derived products) with complete deuterium retention.

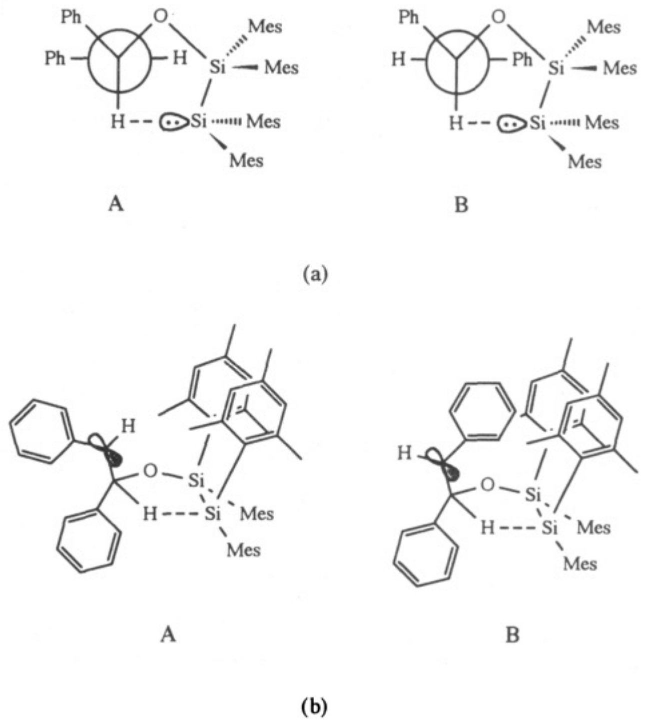

Figure 3. Transition states for proton abstraction to give **4**. (a) Newman projection and (b) alternate view.

The observed stereoselectivity of the formation of **4** can be rationalized with diagrams for the transition state for proton abstraction (Figure 3). With the breaking C−H bond parallel to the empty *p*-orbital of the cation,[14] there are two possible conformations (Figure 3a). In rotational isomer A leading to **E4**, the primary steric interaction is between the two phenyl groups which would not be completely eclipsed. In isomer B, enroute to **Z4**, a severe steric interaction is likely to occur between the phenyl on the cation and the two mesityls of the five-membered ring. Another view (Figure 3b) shows the interacting phenyl to be endo to the five-membered ring in B and exo in A, causing B to be significantly higher in energy, thus making **Z4** formation slower.

As with **4**, the stilbenes showed no isomerization under the reaction conditions. Therefore, 7 must be on the reaction coordinate for formation of *trans*-stilbene from *cis*-stilbene oxide. Two reasonable mechanisms (Scheme 4) are analogous to proposed pathways for epoxide deoxygenations using electrophilic agents. Path a is a concerted, stereospecific oxygen abstraction from **6**. Mechanistic precedent can be found in the stereospecific epoxide deoxygenation by [Cp^*_2TaMe] (eq 1, Scheme 5),[15] and in the stereospecfic carbenoid abstraction of heteroatoms from epoxides, episulfides, and aziridines via proposed intermediate ylids (eq 2, Scheme 5).[16] Path b involves nonstereospecific alkene formation from **7**. The closest analogy is the epoxide deoxygen-

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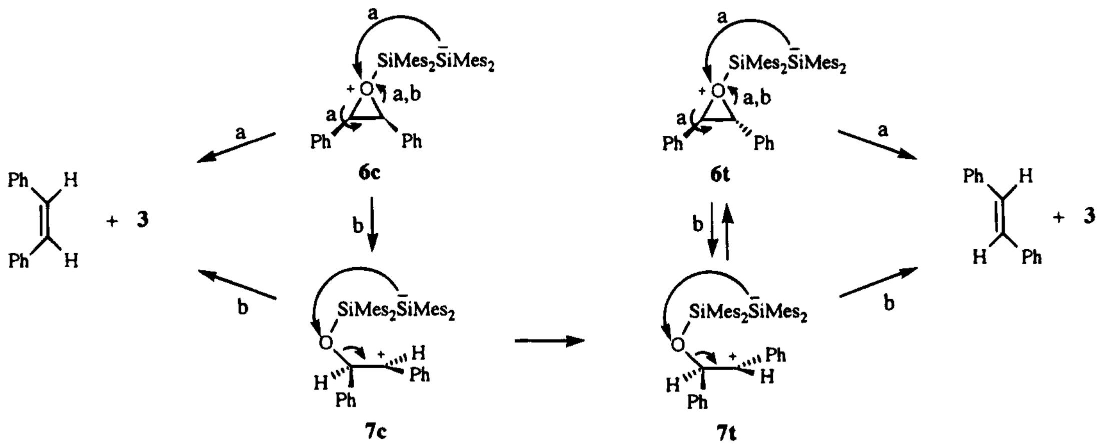
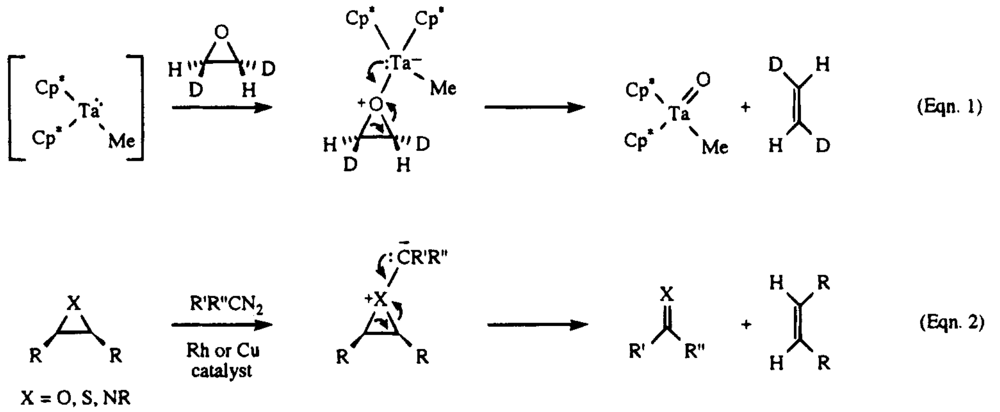
(14) This is a proposed alignment necessary for the deprotonation step of an E1 elimination. Kieboom, A. P. G.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1424.

(15) Whinnery, L. L., Jr.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 7575.

Scheme 4



Scheme 5



ations by transition metals, although these mechanisms normally involve ring-opened radical intermediates.[17]

At first glance, the stereochemical outcome of deoxygenation would indicate a nonstereospecific route: a mixture of *cis*- and *trans*-stilbenes from *cis*-stilbene oxide and only *trans*-stilbene from *trans*-stilbene oxide. However, a small amount of *trans*-stilbene oxide (ca. 2% of the product mixture) was produced from *cis*-stilbene oxide presumably by reversal of **7t** to **6t** and **6t** to *trans*-stilbene and disilene.[18] The observed stereochemical outcome, therefore, could also result from a stereospecific oxygen removal to give *cis*-alkene from the *cis*-epoxide with a small portion of *trans*-stilbene oxide reacting to give *trans*-stilbene.

The greater amount of alkene produced from *trans*-stilbene oxide compared to *cis*-stilbene oxide, if via path a of Scheme 4, could simply result from a more rapid ring-opening from **6c** relative to **6t**. Considering path b one might also expect more alkene, since the transition state for formation of *trans*-stilbene from **7** should be more accessible than for *cis*-stilbene.[18]

Experimental Section

General Procedures. All solvents for reactions of tetramesityldisilene were distilled from sodium or sodium benzophenone ketyl under nitrogen and degassed prior to use. The disilene was prepared by the literature method.[19] Preparative scale runs and reactions in THF used disilene prepared in pentane/THF, while that used for NMR scale runs in d_6-benzene was prepared in pentane. *cis*-Stilbene was prepared as in the literature.[20] The epoxides were made as described in the literature[21] with the following modifications: *m*-chloroperoxybenzoic acid was used as the olefin oxidizing agent instead of peroxybenzoic acid, chloroform was used as the solvent in place of benzene, and the epoxides were purified by column chromatography prior to recrystallization. Reported melting points are uncorrected. ^{1}H and ^{13}C Spectra were referenced to the residual solvent resonances which were calibrated against tetramethylsilane. ^{29}Si NMR spectra were obtained using INEPT pulse sequences and were referenced to external tetramethylsilane.

1,2-Dideuteriostilbene Oxides. To a solution of a 1.3:1

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(16) (a) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron* **1966**, *22*, 3393. (b) Thijs, L.; Zwanenburg, B. *Tetrahedron* **1980**, *36*, 2145. (c) Martin, M. G.; Ganem, B. *Tetrahedron Lett.* **1984**, *25*, 251. (d) Hata, Y.; Watanabe, M. *Tetrahedron Lett.* **1972**, 3827, 4659. (e) Hata, Y.; Watanabe, M.; Inoue, S.; Oae, S. *J. Am. Chem. Soc.* **1975**, *97*, 2553.

(17) Bartók, M.; Láng, K. L. *The Chemistry of Functional Groups, Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Sulfur Analogues*; Patai, S., Ed.; Wiley: New York, 1980; Pt. 2, p 627.

(18) Neither *cis*-stilbene nor *cis*-stilbene oxide was observed in the reaction mixture from *trans*-stilbene oxide. It is, therefore, suspected that **7c** does not revert to **6c**. This is reasonable considering the activation barrier for realignment of the phenyl groups *cis* may be prohibitively high. Note (a) the equilibrium constant of stilbenes at 90 °C is 0.004 *cis/trans*; Fischer, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc. B* **1968**, 1156, (b) electrophilic deoxygenations considered to be stepwise are highly stereoselective for *trans*-stilbene; Fujiwara, Y.; Ishikawa, R.; Akiyama, F.; Teranishi, S. *J. Org. Chem.* **1978**, *43*, 2477, and Kupchan, S. M.; Maruyama, M. *J. Org. Chem.* **1971**, *36*, 1187, and (c) the stepwise epoxidation of stilbenes with [Ru^{III}(hedta)]/tBuOOH, the microscopic reverse of deoxygenation via ring-opened radicals is highly stereoselective for *trans*-stilbene oxide; Shepherd, R. E. *Inorg. Chim. Acta* **1993**, *209*, 201.

(19) Tan, R. P.; Gillette, G. R.; Yokelson, H. B.; West, R. *Inorg. Synth.* **1992**, *29*, 19.

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trans/*cis* mixture of 1,2-dideuteriostilbenes[22] (ca. 8.5 g, 0.048 mol) in 150 mL of diethyl ether was added *m*-chloroperoxybenzoic acid (75%, 12 g, 0.052 mol, 1.1 equiv). After stirring at 25 °C for one day, GC showed no d_2-*cis*-stilbene and a small amount of d_2-*trans*-stilbene. An additional 3 g of *m*-CPBA was added. After stirring one more day, the solution was washed with 5–25 mL portions of a saturated aqueous sodium bicarbonate solution, dried over magnesium sulfate, and concentrated in vacuo. The residue was recrystallized from methanol to give only d_2-*trans*-stilbene oxide. A second recrystallization from hexanes gave pure compound, 1.4 g (26.8%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45–7.30 (m, aromatic). Integration of the residual epoxide α protons against the aromatic protons showed >97% deuteration.

The mother liquor from the first recrystallization was concentrated in vacuo to a viscous oil and chromatographed on a 20 × 20 cm preparative silica gel plate, eluted with 3% diethyl ether in hexanes. The second band from the bottom was determined to be d_2-*cis*-stilbene oxide. The material from two plates was combined and recrystallized from methanol to give pure *cis*-epoxide: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20–7.12 (m, aromatic). Deuteration was >97%.

Preparative-Scale Reactions of Tetramesityldisilene with Stilbene Oxides. **1**·THF (80 mg, 0.132 mmol) was dissolved in a solution of epoxide (39 mg, 0.199 mmol, 1.5 equiv) in 4 mL of benzene, and the solution was sealed in a thick-walled glass ampule and heated to 100 °C. When the characteristic yellow-orange disilene color had dissipated (five days for *cis*, sixteen days for *trans*), the tube was cracked open and the solution concentrated in vacuo. The residue was chromatographed on a 20 × 20 cm preparative silica gel plate, eluted with 3% diethyl ether in hexanes.

For *cis*-stilbene oxide, chromatography gave four bands, starting with lowest R_f: (1) presumed to be $HOSiMes_2OSiMes_2H$ from hydrolysis of **3**, 3.4 mg (4.55% based on disilene),[23] (2) *cis*-epoxide[24] and disilene hydrolysis product, 21.5 mg, 1.75:1 ratio, (3) a mixture of **4** and **5**, and (4) stilbene and disilene rearrangement product. Fraction 3 was rechromatographed with 1% diethyl ether in hexanes to give **5**, 23.1 mg (24%), and **4**, 25 mg (26%, *E*:*Z* 20:1). Fraction 4 was rechromatographed with hexanes to give disilene rearrangement product, 2.3 mg (3.3%), and *cis*-stilbene, 2.1 mg (8.8%).

For *trans*-stilbene oxide, chromatography gave five bands: (1) $HOSiMes_2OSiMes_2H$, 10.6 mg (14.2%), (2) disilene hydrolysis, 5.8 mg (8.0%), (3) epoxide, 19.8 mg, (4) a mixture of **4**, **5**, and *trans*-stilbene, and (5) *trans*-stilbene and disilene rearrangement product. Fractions 4 and 5 were rechromatographed to give disilene rearrangement product, 7.4 mg (10.5%); *trans*-stilbene, 5.8 mg (24.4%); **4**, 18 mg (18.7%, *E*:*Z* 6.5:1); and **5**, 18.8 mg (19.6%).

E4, as isolated from the *cis*-stilbene oxide reaction (ca. 95% pure), was a viscous oil. Analytical data: ^{1}H NMR (C_6D_6, 200 MHz) δ 7.53–7.47 (m, 2 H, phenyl H), 7.15–6.63 (phenyl H), 6.71 (s, 4 H, mesityl H), 6.65 (s, 4 H, mesityl H), 5.73, 5.72 (2 s, 2 H, Si-H and vinyl H), 2.50 (s, 12 H, *o*-Me), 2.26 (s, 12 H, *o*-Me), 2.08 (s, 12 H, *p*-Me); ^{13}C NMR (C_6D_6, 125 MHz) δ 152.40 (α vinyl C), 145.87, 145.02, 139.82, 139.31, 138.42, 137.95, 133.88, 131.79, 130.73, 130.23, 129.54, 129.46, 128.87, 128.79, 126.08 (aromatic C), 112.76 (β vinyl C), 25.41, 25.04, 21.64, 21.56 (Me C); INEPT ^{29}Si NMR (C_6D_6, 53.67 MHz) δ −4.37, −56.63 (J_{Si-H} = −179.4 Hz); exact mass for $C_{50}H_{56}OSi_2$ calcd *m*/*e* 728.3863, found 728.3870; IR (cm^{-1}, Nujol) 2133.1 (Si–H), 1631.6, 1603.7.

5 was crystallized from hexane. Analytical data: ^{1}H NMR (C_6D_6, 200 MHz) δ 7.38 (m, 2 H, phenyl H), 7.07–6.82 (m, 5 H, phenyl H), 6.74, 6.65, 6.62, 6.58 (4 s, mesityl H), 5.81 (d, 1 H, *J* = 11.8 Hz, PhCHPhC*H*O), 4.41 (d, 1 H, *J* = 11.8 Hz, PhC*H*PhCHO), 2.75, 2.40, 2.30, 2.12, 2.10, 2.09, 2.08, 2.05 (8 s, Me H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.82, 145.66, 145.04, 144.49, 143.22, 141.47, 139.29, 139.22, 138.58, 134.84, 134.14, 133.86, 129.86, 129.77, 129.65, 129.49, 129.33, 129.16, 129.02, 128.10, 127.99, 127.41, 125.19 (aromatic C), 82.33 (PhCHPh*C*HO), 50.28 (Ph*C*HPhCHO), 26.71, 26.48, 24.86, 24.80, 21.80, 21.76, 21.70, 21.64 (Me C); INEPT ^{29}Si NMR (C_6D_6, 53.67 MHz) δ 1.86, −11.72; exact mass for $C_{50}H_{56}OSi_2$ (M$^+$-Mes) calcd *m*/*e* 609.3009, found 609.2944; mp 270–275 °C.

The reactions of the d_2-epoxides were conducted as described above. ^{1}H NMR (500 MHz) of the fraction from the first chromatography containing the mixture of **4** and **5** showed these products to contain >97% deuteration.

Photolysis of E4. After 3–4 weeks of exposure of a solution of **4** (25 mg) in d_6-benzene to ordinary laboratory lighting, the original *E*:*Z* 20:1 ratio changed to 3:1. The sample was photolyzed in a Rayonet photoreactor, λ = 350 nm, at 25 °C for 90 min. An *E*/*Z* ratio of 1:2.3 resulted. An additional 30 min of photolysis caused no further change in the ratio. **Z4** was isolated by crystallization from this solution. Analytical data were: ^{1}H NMR (C_6D_6, 200 MHz) δ 7.70–7.62 (m, 2 H, phenyl H), 7.42–7.34 (m, 2 H, phenyl H), 7.12–6.87 (m, 5 H, phenyl H), 6.67 (s, 4 H, mesityl H), 6.55 (s, 4 H, mesityl H), 6.05, 5.76 (2 s, 1 H each, Si–H and vinyl H), 2.39 (s, 12 H, *p*-Me), 2.20 (s, 12 H, *p*-Me), 2.07, 2.03 (2 s, 12 H, *o*-Me); ^{13}C NMR (C_6D_6, 125 MHz) δ 153.31 (α vinyl C), 145.57, 145.42, 142.32, 139.65, 139.15, 137.27, 134.82, 133.83, 130.24, 129.81, 129.51, 128.82, 127.84, 127.82, 126.80 (aromatic C), 114.60 (β vinyl C), 25.98, 25.65, 21.59, 21.47 (Me C); INEPT ^{29}Si NMR (C_6D_6, 53.67 MHz) δ 1.02, −49.29 (J_{Si-H} = −181.3 Hz); exact mass for $C_{50}H_{56}OSi_2$ (M$^+$ − H) calculated *m*/*e* 727.3791, found 727.3821; IR (cm^{-1}, Nujol) 2143 (Si–H), 1634.6, 1602.7; mp 236–241 °C.

NMR-Scale Reactions. For *cis*-stilbene oxide: **1** (22 mg, 0.041 mmol) was dissolved in a solution of the epoxide (12 mg, 0.061 mmol, 1.5 equiv) in ca. 0.5 mL of d_6-benzene in an NMR tube. The tube was sealed, and its contents heated to 100 °C. Complete loss of color occurred in two days.

For *trans*-stilbene oxide: **1** (42 mg, 0.079 mmol) was dissolved in a solution of the epoxide (3 mg, 0.015 mmol, 0.19 equiv) of ca. 0.5 mL of d_6-benzene in an NMR tube.[25] The tube was sealed and its contents heated to 100 °C. Complete loss of color occurred in 10–14 days.

Isomerization Studies of 4 and *cis*-Stilbene. **E4**, as isolated from the *cis*-stilbene oxide reaction was dissolved in d_6-benzene, the solution sealed in an NMR tube and heated to 100 °C for 24 h. No change in the ^{1}H NMR had occurred. The same procedure was conducted with pure **Z4**. Again no change in the ^{1}H NMR had occurred.

NMR-scale reactions of *cis*-stilbene oxide with **1** were carried out with an excess of epoxide (as above) and an excess of **1** (4 mg, 0.02 mmol of epoxide and 35 mg, 0.066 mmol, 3.3 equiv of **1**). The mixtures were heated to 100 °C until **1** or epoxide was completely consumed (two days). The ratio of **Z4**:**E4**:*cis*-stilbene was determined by ^{1}H NMR. After an additional two days at 100 °C, the ratios of **Z4**:**E4** and **E4**:*cis*-stilbene showed variations of 3.6 and 1.6%, respectively, using excess epoxide, and 7.9 and 4.1%, respectively, using excess disilene.

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[22] The mixture of deuterated stilbenes was obtained from diphenylacetylene by the procedure of Magoon, E. F.; Slaugh, L. H. *Tetrahedron* **1967**, *23*, 4509.

[23] Compound **3** was observed in the NMR-scale reaction of either epoxide with **1**, but not after chromatography. Its suspected hydrolysis product, on the other hand, was observed (INEPT ^{29}Si, δ −30.32, −31.36, J_{Si-H} = −214.8 Hz) after chromatographic workup.

[24] *trans*-Stilbene oxide was observed in the ^{1}H spectrum of the NMR-scale reaction at half and complete reaction. Loss of a small amount of material during chromatography could explain its absence from recovered epoxide in the preparative-scale run.

[25] A 5:1 disilene:epoxide ratio was used here to minimize a secondary oxidation of **3** by *trans*-stilbene oxide, shown to occur by a control experiment. Using a 1:1.5 ratio gave an increase in the amount of *trans*-stilbene without substantial change in the other product ratios. *cis*-Stilbene oxide also reacted with **3** to give a mixture of alkenes and an unidentified product. However, this secondary reaction was shown not to contribute stilbenes to the product ratios from the primary reaction since; almost none of the unidentified product was observed.

Similar experiments were conducted with *trans*-stilbene oxide. An excess of epoxide (same scale and quantities as for *cis*-stilbene oxide) showed a variation of the **Z4**:**E4** ratio of 2.2% upon heating at 100 °C for four days after complete reaction, while an excess of disilene (procedure as above) gave a variation of 6.3%.

X-ray Structure Determinations. X-ray crystallographic analyses was performed on a Siemens P4 diffractometer equipped with a graphite crystal monochromator and a Cu X-ray tube ($\lambda = 1.54178$ Å). Suitable crystals of **5** were grown from *n*-hexane at 25 °C. The orientation matrix and unit cell parameters were determined by the least squares fitting of 26 centered reflections ($55° < 2\theta < 58°$). Intensities of three standard reflections were monitored every 50 reflections with a maximum variation of 0.05. Structure solution and refinement were performed using Siemens SHELXTL PLUS, Version 4.2.[26] The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically by full matrix least-squares analysis on F with weighting scheme, $w^{-1} = \sigma^2(F) + 0.0020\,F^2$. An extinction correction was applied with $\chi = 0.0031(4)$ where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$.[27] The positions of the hydrogen atoms were calculated by idealized geometry and refined using a riding model. Neutral atom scattering factors were taken from ref 28a.

Crystals of **4** were grown by slow evaporation from benzene at 25 °C. The orientation matrix and unit cell parameters were determined by the least squares fitting of 38 centered reflections ($19° < 2\theta < 55°$). Intensities of three standard reflections were monitored every 50 reflections with a maximum variation of 0.06. The structure was solved using the SHELXS-86 program[29] and the non-hydrogen atoms were refined anisotropically using the SHELXL-92 program by full-matrix least-squares analysis on F^2 with weighting scheme, $w^{-1} = \sigma^2(F_0{}^2) + (0.1564\ P)^2$, where $P = [\max(F_0{}^2, 0) + 2F_C{}^2)]/3$.[30] The positions of the hydrogen atoms were calculated by idealized geometry and refined using a riding model. Neutral atom scattering factors were taken from refs 28a and 28b.

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Supplementary Material Available: Tables of all bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients (15 pages). Ordering information is given on any current masthead page.

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