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Silyl Stabilization of Unsymmetrical Bisketenes: 3-(Trimethylsilyl) and 3-(Triisopropylsilyl)-2-substituted-1,3-butadiene-1,4-diones

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ABSTRACT

*The bisketenes 2-phenyl and 2-methyl-3-(trimethylsilyl)-1,3-butadiene-1,4-dione (***8** *and* **10***) are calculated on the basis of additivity of substituent effects to be less stable than the 3-phenyl and 3-methyl-4-(trimethylsilyl)cyclobut-3-ene-1,2-diones (***7** *and* **9***) by 1.9 and 2.6 kcal/mol, respectively. In agreement with this prediction,* **8** *and* **10** *are formed by photolysis of* **7** *and* **9***, respectively, and undergo thermal reversion to their precursors at similar rates. The concentration of* **8** *in thermal equilibrium with* **7** *in* $CDCl_3$*, as measured by* ^1H *NMR spectroscopy, varied from 2.8% (161°C) to 0.5% (100.5°C), whereas the amount of* **10** *present at equilibrium with* **9** *was distinctly less. These measurements allowed the calculation of values of* ΔG° *(25°C) = 4.4 kcal/mol,* ΔH° *= 6.9±(1.3) kcal/mol, and* ΔS° *= 8.5 (±3.2) cal/deg mol for the conversion of* **7** *to* **8***, and the equilibrium concentration of* **8** *at 25°C was estimated to be 0.06%. The triisopropylsilyl analog* **12** *of* **8** *was prepared and at 66°C was 2.6 times more reactive in ring closure to the corresponding cyclobutenone compared to* **8***. Reactions of* **8** *and* **10** *with MeOH in* $CDCl_3$ *give the isolable monoketenes 3-phenyl and 3-methyl-2-(trimethylsilyl)-3-carbomethoxy-1-ene-1-one (***20,21***). Reaction of* **20** *with excess MeOH or* H_2O *gave the diastereomeric dimethyl 2-(trimethylsilyl)-3-phenylsuccinates (***22***) or ester-acids* **24***, respectively. Reaction of* **8** *with excess N-methylaniline gave the diamide* **25***.*

The preparation and properties of 2,3-bis(trimethylsilyl)-1,3-butadiene-1,4-dione (**2**) by the thermolysis of the cyclobutenedione **1** have recently been reported from this laboratory [1,2]. It was predicted [1] on the basis of ab initio molecular orbital calculations [3a] that the parent cyclobutenedione **3** is more stable than **4** by 6.9 kcal/mol, whereas the stabilizing effect of the SiH_3 group on a ketene relative to the effect on an alkene is 7.6 kcal/mol more, compared to hydrogen. Thus, on the basis of additivity of these effects, the bisketene would be more stable than the cyclobutenedione by 8.3 kcal/mol for $R = R^1 = SiH_3$. Thus, it was expected qualitatively that **1** bearing two silyl groups should be less stable than **2**, and this prediction was verified experimentally [1]. Further calculations for $R = R^1 = SiH_3$ led to the prediction that, for this substituent, the bisketene structure is more stable than the cyclobutenedione by 4.9 kcal/mol, and the lack of additivity was attributed partly to a contribution to ground state stabilization of the cyclobutenedione by SiH_3 [1d].

Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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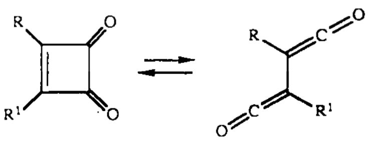
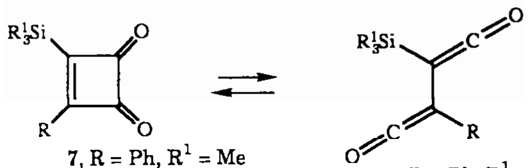


1,3,5,7,9 2,4,6,8,10

1,2 R,R^1 = Me$_3$Si
3,4 R,R^1 = H
5,6 R = Ph, R^1 = H
7,8 R = Me$_3$Si, R^1 = Ph
9,10 R = Me$_3$Si, R^1 = Me

(1)

It is of interest to examine the properties of bisketenes substituted with a single stabilizing silyl substituent [3b–d] and another substituent with different properties [3a,4]. Previous reports of unsymmetrical bisketenes include the formation of dimethyl 2-phenylsuccinate on heating of phenylcyclobutenedione **5** in MeOH, which was proposed to possibly involve the phenylbisketene **6** [4d]. The photochemical generation of O=C=CHC(OH) = C=O has also been reported [4e]. Calculations of the effect of the phenyl and methyl groups on ketene stability compared to the effect on an alkene indicate [3a] that these groups are destabilizing as ketene substituents relative to hydrogen by 2.6 [4c] and 3.3 [3a] kcal/mol, respectively. Assuming an additivity of substituent effects leads to the estimate that 3-phenyl and 3-methyl-4-(trimethylsilyl)cyclobut-3-ene-1,2-diones **7** and **9** will be more stable than the corresponding bisketenes **8** and **10** by only 1.9 and 2.6 kcal/mol, respectively. Therefore, we have undertaken a study of the preparation and reactivity of **8** and **10**, as a test of the validity of these predictions [5]. Also, in order to ascertain if steric effects play a major role in these equilibria, we have prepared **11** and **12** bearing the bulky *i*-Pr$_3$Si substituent [6].



(2)

7, R = Ph, R^1 = Me
9, R = Me, R^1 = Me
11, R = Ph, R^1 = *i*-Pr

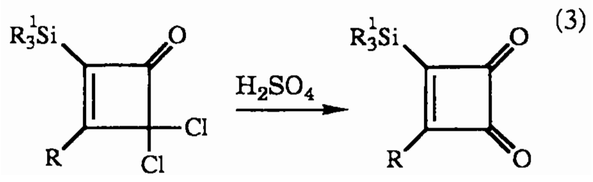
8, R = Ph, R^1 = Me
10, R = Me, R^1 = Me
12, R = Ph, R^1 = *i*-Pr

RESULTS

The reactions of 1-phenyl- and 1-methyl-2-(trimethylsilyl)acetylenes **13** and **14** with dichloroketene generated from CCl$_3$COCl and activated Zn gave the cyclobutenones **16** and **17**, respectively, as previously reported by Danheiser and Sard [7a]. Reaction of phenylethynyllithium with triisopropylsilyl chloride gave **15**, which was converted to **18** by a similar procedure. Of the various procedures for zinc activation [7], it was found most convenient to activate the zinc by simple heating in an adaptation of the procedure reported by Stenstrøm [7c]. Reaction of the cyclobutenones with H$_2$SO$_4$ gave the cyclobutenediones **7**, **9**, and **11**.

$$R^1_3SiC{\equiv}CR \xrightarrow{CCl_3COCl,\ Zn}$$

13 (R = Ph, R^1 = Me)
14 (R = Me, R^1 = Me)
15 (R = Ph, R^1 = *i*-Pr)



(3)

16 (R = Ph, R^1 = Me)
17 (R = Me, R^1 = Me)
18 (R = Ph, R^1 = *i*-Pr)

7, 9, 11

On heating of **7** and **9** in various non-nucleophilic solvents, no major changes were detected. However, on photolysis of **7** at 350 nm, there was a color change to a deeper yellow and a new UV absorption at λ_{max} 257 nm appeared, whereas that at 287 nm due to **7** essentially disappeared. On heating of the photolyzed sample, the band at 257 nm almost disappeared with concomitant reappearance of the absorption at 287 nm. Some absorption due to the alkyne **13** was also observed in the sample, and this is attributed to arise from photolysis of the bisketene, as has been observed in other examples [1b]. The spectral changes are assigned to photochemical conversion of **7** to the bisketene **8**, which undergoes thermal reformation of **7** (Equation 2). Photolytic conversions of **7** to **8** of 87 to 95% were measured by ^{1}H NMR spectroscopy. Photolysis of **9** at 350 nm similarly gave rise to **10** in 55% yield, and, on photolysis of **11** at 350 nm, the cyclobutenedione disappeared completely with formation of the bis(ketene) **12**.

Evidence for the structures of **8**, **10**, and **12** includes the presence of the ketene bands in the IR spectra at 2093, 2101, and 2092 cm^{-1}, respectively, which are comparable to the band at 2084 cm^{-1} for **2** [1a]. The ^{1}H NMR spectra show peaks at δ 0.18 due to the Me$_3$Si group, 7.05–7.40 due to the phenyl for **8**, and 0.20 (Me$_3$Si) and 1.74 (Me) for **10**, together with residual absorption for the respective cyclobutenediones **7** and **9** and signals due to the original alkynes **13** and **14**. The ^{1}H NMR spectrum of **12** shows a singlet at δ 1.09 due to 21 protons of the *i*-Pr$_3$Si group, which are coincidentally equivalent, and the phenyl absorption at δ 7–7.5. The ^{13}C NMR spectra show the very distinctive peaks for the Me$_3$Si and Ph substituted ketenyl car-

TABLE 1 Thermal Equilibration of **7** and **8** in $CDCl_3$

T (°C)	[**8**]/[**7**]	K^a
161.3	2.2 ($\pm$0.1)/97.8	2.25×10^{-2}
161.0	2.8 ($\pm$0.1)/97.2	2.88×10^{-2}
143.1	1.4 ($\pm$0.2)/98.6	1.42×10^{-2}
142.2	1.6 ($\pm$0.2)/98.4	1.63×10^{-2}
100.5	0.5 ($\pm$0.1)/99.5	5.02×10^{-3}
100.3	0.9 ($\pm$0.1)/99.1	9.08×10^{-3}
25.0^b	0.06/99.94	6.00×10^{-4}

[a] $\Delta G°$ (25°C) = 4.4 kcal/mol; $\Delta H° = 6.9 \pm (1.3)$ kcal/mol; $\Delta S°$ = 8.5 ($\pm$3.2) cal/mol K.
[b] Extrapolated

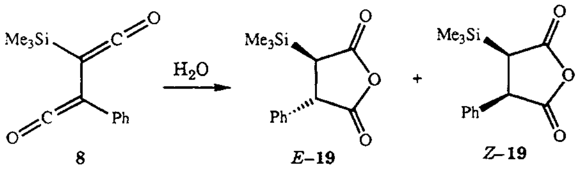
bons at δ 7.9 and 33.5, respectively, for **8**; at 10.7 and 18.9 for the Me_3Si and Me substituted carbons of **10**; and at δ 2.6 and 33.5 for the *i*-Pr_3Si and Ph substituted carbons of **12**. These are comparable to the corresponding carbons for **2** (δ 5.6) [1a], $Me_3SiCH{=}C{=}O$ (−0.1) [8a], $PhCMe{=}C{=}O$ (33.8) [8b], and $MeCH{=}C{=}O$ (10.9) [8b].

Upon heating of **7** in $CDCl_3$, followed by rapid cooling, the presence of the phenyl substituted bisketene **8** could be detected by the appearance of the ^1H NMR peak of the Me_3Si at δ 0.18 and of the IR band at 2093 cm^{-1}. The relative concentrations of **7** and **8** were determined by integration of the NMR spectra, and the data were used to calculate equilibrium constants and thermodynamic parameters (Table 1). Comparable values of the equilibrium constants were measured starting with photolyzed samples containing mostly **8**. Equilibrium constants at elevated temperatures measured by this method may underestimate the concentration of the less stable isomer, as some equilibration will occur during cooling, and the fraction of the less stable isomer is less at lower temperatures. However, the cooling time was fast compared to the rate of thermal equilibration, and no noticeable effect on the measured concentration as a function of cooling rate was seen. Therefore, the observed product ratios are thought to be accurate within the limit of the NMR measurements. Heating of the methyl substituted bisketene **10** also resulted in reformation of **9**, but the ^1H NMR signals due to **10** remaining at equilibrium at 142°C were barely observable and corresponded to the presence of less than 0.5% of **10**, as compared to 1.5$\pm$0.3% of the phenyl bisketene **8** at the same temperature (Table 1).

The thermal reversion of **8** to **7** could be observed by ^1H NMR or UV measurements, and the kinetics of this process in hexane solvent were measured by monitoring the appearance of the UV λ_{max} of **7** at 287 nm. At 65.4°C, the rate constant for the disappearance of **8** at 257 nm was also measured as 1.54×10^{-4} s^{-1}, as compared to the rate constant for the appearance of **7** of 1.70×10^{-4} s^{-1}, and these are the same within the experimental uncertainty. The kinetics of the reversion of **10** to **9** in $CDCl_3$ were measured by ^1H NMR spectroscopy. All the kinetics data are collected in Table 2.

Photolysis of the cyclobutenedione **11** bearing the bulky triisopropylsilyl group [6] to give the bis(ketene) **12** was qualitatively faster than the corresponding reaction of the trimethylsilyl analog **7**. Thermal conversion of **12** back to **11** was 2.6 times faster at 66°C than the corresponding reaction of the trimethylsilyl analog **8** (Table 2), but none of **12** could be detected in thermal equilibrium with **11**. Although the rates of cyclization of the trimethylsilyl and triisopropyl bis(ketenes) **8** and **12** were similar, the respective $\Delta S\ddagger$ values were −14.9 and −3.7 cal/mol K. The significantly more negative value of the former may indicate that the trimethylsilyl bis(ketene) is less conformationally restricted than the triisopropyl derivative but loses more of this freedom on cyclization. Thus, the net effect of the triisopropylsilyl group appears to be to favor modestly the cyclobutenedione form, but the effects due to the increased bulk of this group on the formation and stability of the bis(ketene) are surprisingly small.

The reaction of **8** with H_2O produced a mixture of the stereoisomeric succinic anhydrides *E*-**19** and *Z*-**19** in a variable ratio that depended upon the reaction conditions (Equation 4). The stereoisomers were readily differentiated on the basis of the J_{H-H} values for vicinal protons, which are 3.6 and 10.4 Hz, respectively, for the structures assigned as *E*-**19** and *Z*-**19**. For the corresponding 2,3-bis(trimethylsilyl)succinic anhydrides, X-ray crystal structures revealed dihedral angles of 108° between the C–H bonds in the *E*-isomer and 38.8° in the *Z*-isomer [1b], and the $\cos^2$ values of these angles, 0.10 and 0.61, respectively, were consistent with the observed coupling constants.



(4)

Samples of the bisketenes **8** and **10** in $CDCl_3$ in NMR tubes were generated by photolysis of **7** and **9**, respectively, and 1.6 equiv of CH_3OH was added at −78°C, followed by warming to RT and evaporation of the solvent. After addition of more $CDCl_3$, the photolysis and methanolysis procedure was repeated one or two times, resulting in formation of the monoketenes **20** and **21**, respectively, in yields of 75 to 95%, as observed by ^1H NMR measurements, together with residual diketones (Equation 5).

TABLE 2 Kinetics of the Conversion of Bisketenes to Cyclobutenediones

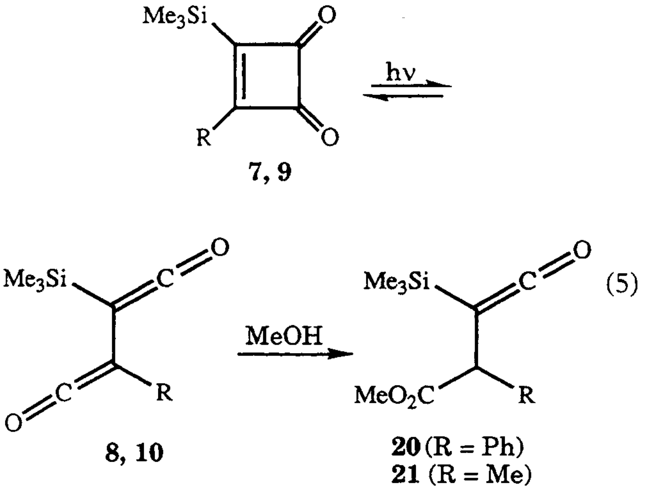
T (°C)	k_{obs} (s^{-1})[a] (**8** *to* **7**)	*T* (°C)[b]	k_{obs} (s^{-1})[b] (**10** *to* **9**)	*T* (°C)	k_{obs} (s^{-1}) (**12** *to* **11**)[c]
82.4	$(7.78 \pm 0.90) \times 10^{-4}$	70.5	1.39×10^{-3}	78.2	$(1.80 \pm 0.03) \times 10^{-3}$
65.4	$(1.70 \pm 0.10) \times 10^{-4}$	69.6	1.31×10^{-3}	66.0	$(4.44 \pm 0.14) \times 10^{-4}$
65.4	$(1.54 \pm 0.01) \times 10^{-4}$[d]	55.5	$(3.61 \times 0.09) \times 10^{-4}$	54.5	$(1.42 \pm 0.04) \times 10^{-4}$
50.0	$(3.54 \pm 0.14) \times 10^{-5}$	39.8	$(7.60 \pm 0.60) \times 10^{-5}$		

[a] Duplicate runs in hexanes at each temperature were measured at 287 nm unless noted. ln $k_{obs} = -10{,}960/T + 23.65$, $E_{act} = 21.8$ kcal/mol; $\Delta G\ddagger = 25.2$ kcal/mol; $\Delta H\ddagger = 21.1$ kcal/mol; $\Delta S\ddagger = -13.6$ cal/mol K.

[b] Duplicate runs in $CDCl_3$ except as noted, measured by ^1H NMR. ln $k_{obs} = -10{,}190/T + 23.09$, $E_{act} = 20.3$ kcal/mol; $\Delta G\ddagger = 24$ kcal/mol, $\Delta H\ddagger = 19.6$ kcal/mol, $\Delta S\ddagger = -14.9$ cal/mol K.

[c] Duplicate runs in isooctane, measured at 290 nm. ln $k_{obs} = -12{,}000/T + 23.76$; $E_{act} = 24.4$ kcal/mol; $\Delta G\ddagger = 24.9$ kcal/mol; $\Delta H\ddagger = 23.8$ kcal/mol, $\Delta S\ddagger = 3.7$ cal/mol K.

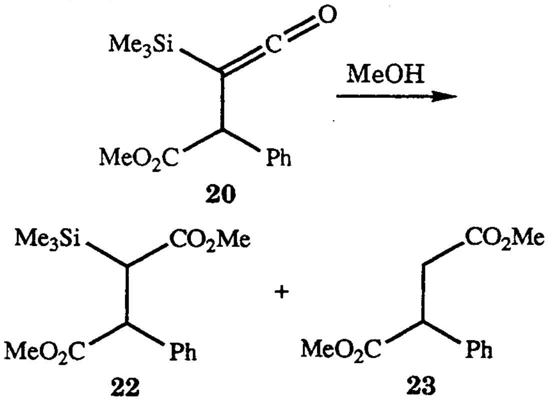
[d] Measured at 257 nm.



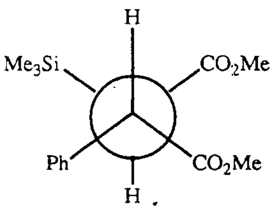
The monoketenes **20** and **21** were purified by VPC and obtained pure as rather stable colorless liquids. Their structures were confirmed by their IR absorptions at 2093 and 2100 cm^{-1}, respectively, their ^{13}C NMR signals for the Me_3Si substituted carbons at δ 8.5 and 17.5, respectively, and by other consistent spectral data.

The kinetics of the reaction of **8** in 5 and 10% EtOH in CH_3CN solutions at 25°C were measured by observing the decrease in the UV absorption at 257 nm. The rate constants obtained were 0.0408 and 0.156 s^{-1}, respectively. By analogy with the reaction of **8** with MeOH (Equation 5), this reaction is considered to be formation of the ethyl ester analog of **20**.

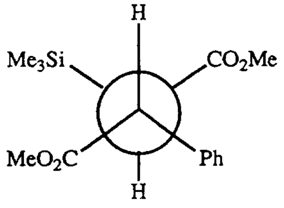
Reaction of the monoketene **20** with methanol in $CDCl_3$ at RT for 10 hours gave the two stereoisomeric dimethyl succinates **22** in a 2/1 ratio (Equation 6), which were isolated after separation by liquid chromatography. These were also formed by heating the diketone **7** in methanol at 100°C for 18 hours and were observed along with the desilylated ester **23**, as 28, 26, and 20%, respectively, of the total product by integration of ^1H NMR spectral data.



The structures of **22** were tentatively assigned as the *threo* and *erythro* isomers from their NMR spectral data. The principal differences were the ^1H chemical shifts of the Me_3Si groups at δ −0.21 and 0.13, respectively, of the OMe groups at δ 3.60 and 3.68 for *threo*-**22** and 3.38 and 3.62 for *erythro*-**22**, and of the TMSC*H* proton signals at 2.96 and 3.10, respectively. The coupling constant between the protons at C2 and C3 was 12.4 Hz in each case, and these compounds are proposed to exist predominantly in the conformers shown. The higher field Me_3Si group in *threo*-**22** and the CO_2CH_3 group in *erythro*-**22** are attributed to a shielding influence of the aryl ring on the protons. Nuclear Overhauser effect (nOe) measurements showed that irradiation of the Me_3Si peaks produced a significant (1.4%) enhancement of the absorption of the Ph protons of *threo*-**22** and a smaller effect (0.4%) on the phenyl protons of *erythro*-**22**; separate irradiation of the OMe groups of *threo*-**22** produced no effect on the Me_3Si signal, whereas irradiation of the δ 3.38 and 3.62 MeO groups of *erythro*-**22** gave 0.1 and 0.3% enhancements of the Me_3Si resonances, respectively, consistent with these assignments.

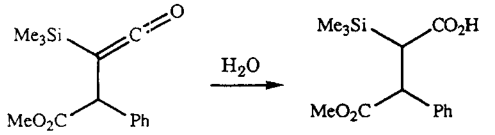


threo–**22**



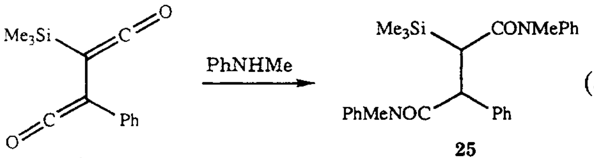
erythro–**22**

Hydrolysis of **20** at 0°C produced the monomethyl succinate esters **24** (Equation 7). These were not separated, but the structures were assigned based on the close similarity of the corresponding peaks of **22** and **24**.



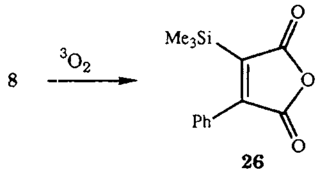
20 **24** (7)

Addition to the bisketene **8**, obtained by photolysis of **7**, to N-methylaniline at 0°C gave a diamide **25** as the only isolated product in 30% yield (Equation 8). Because only one of the stereoisomers was obtained, the stereochemistry could not be reliably assigned.



8 **25** (8)

Reaction of **8** with $^3O_2$ produced the maleic anhydride **26** (Equation 9). This corresponds to the reaction for **2** with $^3O_2$, and a mechanism for this process has been presented [1a,b].



26 (9)

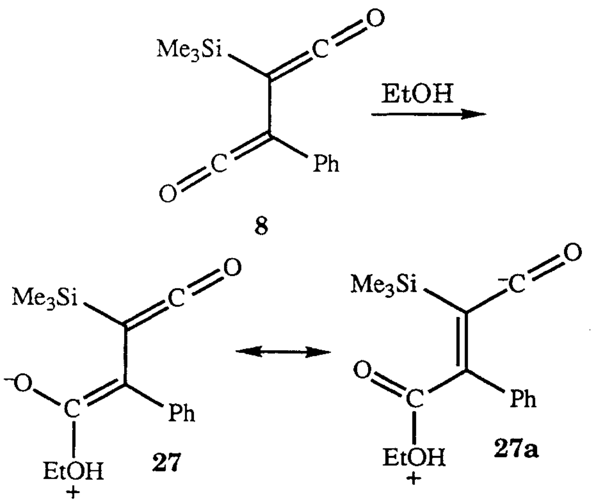
DISCUSSION

The formation of the bisketene **8** on photolysis of **7** is in accord with behavior observed for other cyclobutenediones [1,9], and the thermal reversion of **8** to **7** is consistent with the molecular orbital calculations [3a] discussed previously indicating that **7** is moderately more stable than **8**. Examples in which the kinetics of ring closure of a 1,3-butadiene to a cyclobutene have been measured are rare; another is the perfluoro-1,3-butadiene to cyclobutene reaction [10].

Because the ^1H NMR measurements used for estimating the equilibrium constant for the interconversion of **7** and **8** at elevated temperatures are carried out after cooling the sample to RT, and because of the small amount of **8** present at equilibrium, there is a large uncertainty in the measurement of the fractions of **7** and **8** present. Nevertheless, the $\Delta G°$ value of 4.4 kcal/mol obtained for the interconversion of **7** and **8** is a useful estimate of the energy difference between the two and compares favorably with the ΔE value of 1.9 kcal/mol estimated from the ab initio calculated energies based on the assumption of the additivity of substituent effects. Deviations from estimates based on simple additivity of effects on monoketenes are expected due to ground state stabilization of this cyclobutenedione by the Me_3Si and phenyl substituents, based on the study of more simple systems [1d].

The initial reaction of **8** with nucleophiles at the phenyl substituted ketenyl unit is consistent with the 1.9×10^4 fold greater reactivity of $PhCH{=}C{=}O$ [4b,c] with neutral H_2O compared to $Me_3SiCH{=}C{=}O$ [3b]. The rate constant for reaction of **8** in 5% $EtOH/CH_3CN$ (approximately 1 M) of 0.0408 s^{-1} may be compared to the reported [11] rate constant of $Ph_2C{=}C{=}O$ in 0.99 M EtOH in dioxane of 0.00629 s^{-1}. By this comparison, the bisketene **8** is approximately sixfold more reactive toward nucleophilic addition than $Ph_2C{=}C{=}O$, which is 17-fold less reactive than $PhCH{=}C{=}O$.

Bulky groups R cause major decreases in the reactivity of arylketenes $ArCR{=}C{=}O$ compared to $PhCH{=}C{=}O$ [12]. Thus, $PhC(Pr\text{-}i){=}C{=}O$ is almost 4000 times less reactive than $PhCH{=}C{=}O$ toward H_2O [12]. Based on the comparisons made in the previous paragraph, it appears that the bisketene **8** is within a factor of 10 of being as reactive as $PhCH{=}C{=}O$, and yet on steric grounds, a much lower reactivity of **8** would have been expected. Two conceivable causes for the evident high reactivity of **8** in nucleophilic reactivity are transition state stabilization and ground state destabilization. However, the transition state for EtOH addition to **8** would have the character of **27**, which would be dominated by conjugation of the negatively charged oxygen with the phenyl group, just as for the comparable addition to $PhCH{=}C{=}O$ (Equation 10) [4b,c]. Extended conjugation involving the ketenyl unit as in **27a** suffers from unfavorable acyl anion character, and therefore, enhanced electronic stabilization of the transition state for addition to **8** appears improbable.



(10)

Ground state destabilization does appear to be a plausible cause of the high reactivity of **8** relative to model monoketenes. It has been pointed out [1a,b], based on published calculated energies, that the bisketene **4** is destabilized relative to ketene and butadiene, by 11.9 kcal/mol (Equation 11).

$$\underset{\mathbf{4}}{(\mathrm{CH{=}C{=}O})_2} + 2\mathrm{CH_2} = \mathrm{CH_2} \xrightarrow[-11.9\ \mathrm{kcal/mol}]{\Delta E\,=} 2\mathrm{CH_2{=}C{=}O} + (\mathrm{CH{=}CH_2})_2 \qquad (11)$$

The instability of bisketene **4** relative to 1,3-butadiene noted in Equation 11 is evidently one cause of the preference of **4** for a geometry in which the two ketenyl units are almost orthogonal [1c,d,2]. In the case of **8**, steric factors would further contribute to a preference for a perpendicular conformation. Thus, it is known that silyl groups at the 2- and 3-positions of 1,3-butadienes cause a preference for twisted conformations [13a], and the factors favoring planar 1,3-butadiene conformations are small in any case [13b].

In conclusion, the formation of bisketenes **8** and **10** by photolysis of the cyclobutenediones **7** and **9**, respectively, and their thermal conversion back to their precursors are convincing demonstrations of the utility of published molecular orbital calculations [3a] for the prediction of substituent effects on reactions of ketene and bisketenes. The triisopropylsilyl bisketene **12** is readily formed and appears to have similar thermal stability to its trimethylsilyl analog **8**. The reactivities of the two ketenyl groups of **8** show high selectivity, and this is understandable in terms of the properties we have determined for the model monoketenes. The utility of **8** and **10** in the formation of monoketenyl esters, diesters, diamides, and mixed ester-acids is also demonstrated.

EXPERIMENTAL

General Procedures

All reactions were carried out in oven-dried glassware, and $CDCl_3$ used as a reaction solvent was dried over 4A molecular sieves. Alkynes **13** and **14**, and most of the other reagents, were obtained from Aldrich, Milwaukee, WI, and used as received. NMR spectra were measured using Varian Gemini 200 and XL-400 spectrometers. Infrared spectra were measured using a Nicolet FTIR instrument. Photolyses were carried out using a Rayonet RPR-100 reactor. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, TN.

4,4-Dichloro-2-(trimethylsilyl)-3-phenylcyclobut-2-enone (**16**). Zinc dust (20 g, 0.306 mol) was placed in a 500 mL three-neck flask under N_2, and the flask was heated with a flame for 10 minutes, and then allowed to cool to room temperature. 1-Phenyl-2-(trimethylsilyl)acetylene (**13**, 17 g, 0.097 mol) in 200 mL of ether was added, followed by dropwise addition of trichloroacetyl chloride (14 mL, 22.8 g, 0.125 mol) in 70 mL ether over 20 minutes with vigorous stirring, and the reaction mixture was stirred for an additional 3 hours. The mixture was filtered, and the filtrate was washed twice with 50 mL portions of saturated $NaHCO_3$, filtered again, washed twice with 100 mL portions of saturated NaCl solution, dried over $MgSO_4$, evaporated, and purified by flash chromatography (5% EtOAc/hexane) on silica gel to give **16** (23.6 g, 0.0839 mol, 86%), mp 72°C (Ref. [7a] 77–78°C).

3-(Trimethylsilyl)-4-phenylcyclobut-3-ene-1,2-dione (**7**). A solution of **16** (1 g, 3.5 mmol) in 5 mL anhydrous ether was added dropwise to 2.5 mL of stirred concentrated H_2SO_4 at 95°C stirred. The solution was at 95°C for 30 minutes, cooled with Dry Ice/acetone, and added to 100 mL of an ice and water mixture. The solution was extracted three times with 50 mL portions of ether, and the combined ether extract was washed three times with 50 mL portions of H_2O, dried over $MgSO_4$, and concentrated on the rotary evaporator; the crude product (0.73 g) was purified by flash chromatography using 1/1 hexane/dichloromethane to give **7** (0.36 g, 1.26 mmol, 35%) as a bright yellow-green solid, mp 102.8–103.2°C: ^{1}H NMR ($CDCl_3$) δ 0.45 (s, 9, Me_3Si), 7.50–8 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −1.4, 129.8, 130, 134, 157.2, 198.4, 199.9, 201, 203.2; IR ($CDCl_3$) 1776 (s) (C=O), 1601 (C=C), 1541 (m) cm^{-1}; UV (hexane) λ_{max} 287 nm; EIMS m/z 230 (M^+, 10), 174 (M^+ −2CO, 39), 159 (M^+ −2CO, Me, 100); HRMS m/z calcd 230.0763, found 230.0758. Anal. calcd for $C_{13}H_{14}SiO_2$ (230.34): C, 67.79; H, 6.13; Si, 12.19. Found: C, 67.65; H, 6.12; Si, 11.31.

2-(Trimethylsilyl)-3-phenyl-1,3-butadiene-1,4-dione (**8**). A solution of **7** (0.0742 g, 0.322 mmol) in

0.5 mL $CDCl_3$ in an NMR tube under a N_2 atmosphere was photolyzed 1.5 hours with 350 nm light. The ^1H NMR signals due to **7** decreased, and new signals appeared corresponding to 87% isomerization to **8**: ^1H NMR ($CDCl_3$) δ 0.18 (s, 9, Me_3Si), 7.05–740 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −0.23, 7.9, 33.5, 124.4, 125.4, 129.4, 135, 178.8, 202.2; IR ($CDCl_3$) 2076 (s), 2042 (w); UV λ_{max} (hexane) 257 nm.

Thermal equilibration of **7** *and* **8**. The diketone **7** (9 mg, 0.040 mmol) dissolved in 0.6 mL $CDCl_3$ was sealed in an NMR tube and kept in a thermostatted bath until the relative NMR peak areas no longer changed. The sample was withdrawn and cooled in an ice bath, and the areas of the ^1H NMR signals at 0.18 and 0.45 ppm due to **8** and **7**, respectively, were obtained by integration. Equilibrium constants were determined from the peak areas.

2-(Trimethylsilyl)-3-methylcyclobut-2-ene-1,4-dione (**9**). Zinc dust (4.06 g, 62.1 mmol) in a 200 mL three-neck flask equipped with a magnetic stirring bar was heated under N_2 with a flame for 10 minutes. After cooling, a solution of 1-(trimethylsilyl)propyne (**14**, 2.01 g, 17.9 mmol) in 50 mL ether was added, followed by dropwise addition of trichloroacetyl chloride (6.05 g, 33.3 mmol) in 25 mL ether over 30 minutes with stirring, which was continued for 1 day. The mixture was filtered through Celite and washed successively with water, saturated $NaHCO_3$, and water, dried over $MgSO_4$, and evaporated to give the crude dichlorocyclobutenone **17** [7a] as a brown oil (3.87 g, 97%). Crude **17** (1.91 g, 8.6 mmol) was added dropwise to 3 mL concentrated H_2SO_4 vigorously stirred in a 25 mL round bottom flask while being heated at 55°C. The mixture was stirred 15 minutes, and then 5 g of ice was added and the product was extracted with ether. The ether layer was washed successively with water, saturated $NaHCO_3$, and water, dried over $MgSO_4$, and evaporated to give crude **9** (1.10 g, 6.5 mmol, 76%). Radial chromatography (2% EtOAc in hexane on silica gel) gave pure **9** (0.48 g, 2.8 mmol, 33%) as a yellow liquid: ^1H NMR ($CDCl_3$) δ 0.36 (s, 9, Me_3Si), 2.46 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ −2.27, 13.20, 200.08, 201.18, 207.11, 208.70; IR (film) 1771 cm^{-1}; UV (hexane) λ_{max} 222 nm; EIMS *m/z* 168 (M^+, 16), 140 (M^+ −CO, 15), 112 (M^+ $-C_2O_2$, 22), 99 (M^+ $-C_2O_2$, CH_3, 100), 73 (Me_3Si^+, 38); HRMS *m/z* calcd for $C_8H_{12}O_2Si$, 168.0607; found, 168.0615.

2-(Trimethylsilyl)-3-methyl-1,3-butadiene-1,4-dione (**10**). A degassed solution of **9** (15 mg, 0.09 mmol) in 0.6 mL $CDCl_3$ in a sealed NMR tube under a N_2 atmosphere was photolyzed 1 hour with 350 nm light at 6°C, and the ^1H NMR spectrum showed the presence of 55% of **10**, 37% of **9**, and 1% of the alkyne **14**. After 3 hours irradiation, the relative peak areas of **10**, **9**, and **14** were 54, 24, and 4, respectively. The spectra confirmed the presence of **10**: ^1H NMR ($CDCl_3$) δ 0.20 (s, 9, Me_3Si), 1.74 (s, 3, CH_3); ^{13}C NMR ($CDCl_3$) δ −0.84, 10.7, 13.5, 18.9, 180.6, 204.2; IR ($CDCl_3$) 2101 cm^{-1}. No distinct UV λ_{max} was observed for **10** in the presence of residual **9**. Thermal equilibration of **9** and **10** and kinetic measurements of the conversion of **10** to **9** were carried out similarly to the interconversion of **7** and **8**, with observation by ^1H NMR.

Kinetics of the Reaction of **8** *with EtOH in CH_3CN.* To 0.6 mL of pentane was added the dione **7** (2.8 mg, 0.00122 mmol), and the vial was shaken to obtain a homogenous solution, which was irradiated for 14 minutes with 350 nm light. For kinetic runs, 10 μL samples of this solution were injected into 1.2 mL of EtOH–CH_3CN solution in a UV cell, and a decrease in absorbance of 0.5 to 1 absorbance units at 257 nm was measured.

Kinetics of the Conversion of **8** *to* **7**. Samples of **8** were prepared by injecting 3 μL aliquots of a 0.019 M solution of **7** in CH_3CN into 1.2 mL of hexanes and irradiating 7 minutes at 350 nm. For runs at 50 and 65.3°C, the change in the UV absorption was monitored continuously, whereas for rates at 82.4°C, a set of 11 ampoules were sealed for each run, placed in the constant temperature bath, and removed at intervals. Rates were monitored by either the increase of the absorption of **7** at 287 nm or the decrease in the absorption of **8** at 257 nm.

Kinetics of the Conversion of **10** *to* **9**. Samples of **9** (1.5 mg) in 1 mL $CDCl_3$ in NMR tubes were deaerated by bubbling in Ar and were then sealed and irradiated 30 minutes with 350 nm light at 6°C. The ^1H NMR spectrum indicated 40% conversion to **10**. The tubes were heated in a constant temperature bath for specified periods and cooled in ice, and the peaks at δ 2.46 and 1.74 due to the methyl groups of **9** and **10** were integrated and used to derive rate constants for the formation of **9**.

1-Phenyl-2-(triisopropylsilyl)-ethyne (**15**). To a solution of phenylacetylene (1.02 g, 0.010 mol) in 15 mL THF in a three-neck flask cooled to −78°C was added dropwise *n*-BuLi (8 mL, 1.6 M in hexane, 12 mmol) and TMEDA (4 drops, ca. 1 mmol), followed by dropwise addition of *i*-Pr_3SiCl (2 g, 0.011 mol) in 15 mL THF, and the solution was refluxed overnight. Then 30 mL saturated NH_4Cl solution was added, and the mixture was extracted with three 20 mL portions of ether; the combined ether layer was washed with H_2O, dried over $MgSO_4$, and evaporated to give **15** (2.44 g, crude yield 95%): ^1H NMR ($CDCl_3$) δ 1.13 (s, 21, $CH(CH_3)_2$, chemical shifts equivalent), 7.20–7.50 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ 11.4, 18.7, 90.4, 107.2, 123.6, 128.1, 128.2, 132; IR (film) 2156 cm^{-1}; EIMS *m/z* 258 (M+, 12), 215 (M^+

-*i*-Pr, 100), 129 (M$^+$ -3*i*-Pr, 23); UV λ_{max} (isooctane) 252 nm.

4, 4-Dichloro-2-(triisopropylsilyl)-3-phenylcyclobut-2-enone (**18**). Reaction of **15** (0.77 g, 0.03 mol) with Zn dust (1.14 g, 0.018 mol) and CCl$_3$COCl (3.27 g, 0.018 mol), as described previously for **14**, gave **18** as a crude solid (1.05 g), which on recrystallization from ether-pentane was pale yellow, mp 89–90°C: ^{1}H NMR (CDCl$_3$) δ 1.03 (d, 18, J = 7.3 Hz, (SiCH(C*H*$_3$)$_2$), 1.40 (sep, 3, J = 7.3 Hz, SiC*H*Me$_2$), 7.4–7.9 (m, 5, Ph); ^{13}C NMR (CDCl$_3$) δ 12, 18.6, 91.1, 128.8, 129.0, 129.4, 132.8, 150.4, 182.9, 183.7; IR (CDCl$_3$) 1772 cm^{-1}; EIMS *m/z* 368 (M$^+$, 4), 333 (M$^+$ -Cl, 7), 325 (M$^+$ -*i*-Pr, 9), 297 (M$^+$ -CO, *i*-Pr, 100); HRMS *m/z* calcd for C$_{19}$H$_{26}$Cl$_2$OSi, 368.1130; found, 368.1126.

2-(Triisopropylsilyl)-3-phenylcyclobut-2-ene-1, 4-dione (**11**). Reaction of **18** (50 mg, 0.14 mmol) in ether with 2 mL H$_2$SO$_4$ as in the preparation of **7** gave, after chromatography, **11** (15 mg, 0.048 mmol, 34%) as a golden yellow solid, mp 92–94°C: ^{1}H NMR (CDCl$_3$) δ 1.13 (d, 18, J = 7.4 Hz, SiCH(C*H*$_3$)$_2$), 1.62 (septet, 3, J = 7.4 Hz, SiC*H*Me$_2$), 7.5–8 (m, 5, Ph); ^{13}C NMR (CDCl$_3$) δ 12, 18.7, 128.8, 129.1, 129.3, 133.3, 197.5, 200.9, 201.3, 203.4; IR (CCl$_4$) 1773 cm^{-1}; UV (isooctane) λ_{max} 291 nm; EIMS *m/z* 314 (M$^+$, 32), 299 (M$^+$ -CH$_3$, 20), 243 (M$^+$ -2CO, CH$_3$, 21), 215 (M$^+$ -2CO, -*i*-Pr, 90), 145 (100); HRMS *m/z* calcd for C$_{19}$H$_{26}$O$_2$Si, 314.1702; found, 314.1700.

2-(Triisopropylsilyl)-3-phenyl-1, 3-butadiene-1, 4-dione (**12**). A solution of **11** (0.010 g, 0.03 mmol) in 0.5 mL CDCl$_3$ in an NMR tube under N$_2$ was photolyzed 0.5 hours with 350 nm light. The ^{1}H NMR signals due to **11** disappeared and new signals appeared due to **12**: ^{1}H NMR (CDCl$_3$) δ 1.09 (s, 21, CH(CH$_3$)$_2$, chemical shifts equivalent), 7–7.5 (m, 5, Ph); ^{13}C NMR (CDCl$_3$, −30°C) δ 2.6, 11.9, 18.3, 33.5, 124, 124.6, 128.9, 132.1, 178, 201.6; IR (CDCl$_3$) 2092 cm^{-1}; UV (CDCl$_3$) λ_{max} 260 nm.

Kinetics of the Conversion of **12** *to* **11**. Samples prepared from 1 μL aliquots of a 0.011 M solution of **11** in CDCl$_3$ in 1.2 mL isooctane were irradiated 3 minutes at 350 nm, and the cuvette was placed in a thermostatted cell compartment of the UV spectrometer. Rates were determined by monitoring the increase in the absorption of **11** at 290 nm.

2-Phenyl-(3-trimethylsilyl)succinic Anhydride (**19**). Diketone **7** (44.2 mg, 0.20 mmol) in 0.5 mL CDCl$_3$ in an NMR tube was photolyzed 1 hour at 350 nm at 6°C, and then 20 μL H$_2$O was added; the tube was then stored 24 hours in the refrigerator, the solution was dried over MgSO$_4$, and the solvent evaporated. The product was redissolved in 0.5 mL CDCl$_3$ and the procedure repeated. Examination of the product by ^{1}H NMR revealed formation of the anhydride *E*-**19** along with 10% of *Z*-**19** and 5% of **7**. The anhydrides *E*-**19** and *Z*-**19** were not isolated in pure form. *E*-**19**: ^{1}H NMR (CDCl$_3$) δ 0.26 (9, TMS), 2.77 (d, 1, J = 3.6 Hz, C*H*TMS), 4.06 (d, 1, J = 3.6 Hz, C*H*Ph), 7.5 (m, 5, Ph); ^{13}C NMR (CDCl$_3$) δ −3.24, 41.65, 49.99, 126.87, 128.54, 129.54, 136.57, 172.22, 172.41; IR (CDCl$_3$) 1772, 1791 cm^{-1}; EIMS *m/z* 248 (M$^+$, 1), 205 (M$^+$ -C$_2$H$_3$O, 6), 176 (M$^+$ -C$_2$O$_3$, 9), 161 (M$^+$ -C$_3$H$_3$O$_3$, 9), 104 (PhCHCH$_2$$^+$, 100).

Photolysis as above at 45°C led to a product containing predominantly *Z*-**19** with 10% of *E*-**19** and 5% of **7**. *Z*-**19**: ^{1}H NMR (CDCl$_3$) δ −0.13 (s, 9, TMS), 3.09 (d, 1, J = 10.4 Hz, C*H*TMS), 4.69 (d, 1, J = 10.4 Hz, C*H*Ph), 7.1–7.4 (M, 5, Ph); ^{13}C NMR (CDCl$_3$) −1.86, 40.47, 49.69, 128.69, 129.10, 129.15, 133.54, 171.71, 172.33; IR (CDCl$_3$) 1770, 1793 cm^{-1}; EIMS *m/z* 248 (M$^+$, 2) 205 (M$^+$ -C$_2$H$_3$O, 3), 176 (M$^+$ -C$_2$O$_3$, 10), 161 (M$^+$ -C$_3$H$_3$O$_3$, 6), 104 (PhCHCH$_2$$^+$, 100).

2-(Trimethylsilyl)-3-carbomethoxy-3-phenylprop-1-ene-1-one (**20**). A solution of **8** prepared as in the previous section was cooled to −78°C, and CH$_3$OH (20 μL, 0.50 mmol) was added with shaking. The solution was allowed to warm to RT over 10 minutes, and the solvent was removed on the rotary evaporator; the resulting residue was dissolved in CDCl$_3$ again, and the above photolysis and methananolysis were repeated. Purification by VPC on an OV-17 column at 200°C gave pure **20** (57.3 mg, 0.218 mmol, 68%): ^{1}H NMR (CDCl$_3$) δ 0 (s, 9, Me$_3$Si), 3.68 (s, 3, Me), 4 (s, 1, CH), 7.20–7.50 (m, 5, Ph); ^{13}C NMR (CDCl$_3$) δ −0.6, 8.5, 47.7, 53.3, 128.3, 128.4, 129.1, 139.5, 173.9, 194.1; IR (CDCl$_3$) 2093 cm^{-1} (C=O); EIMS *m/z* 262 (M$^+$, 2), 247 (M$^+$ -CH$_3$, 35), 219 (M$^+$ -CH$_3$, CO, 11), 203 (M$^+$ -CO$_2$CH$_3$, 73), 73 (Me$_3$Si$^+$, 100); HRMS *m/z* calcd for C$_{14}$H$_{18}$O$_3$Si, 262.1025, found 262.1009.

2-(Trimethylsilyl)-3-carbomethoxy-3-methylprop-1-ene-1-one (**21**). This product was prepared in the same manner as **20** by irradiating **9** (30 mg, 0.18 mol) in CDCl$_3$ with 350 nm light for 1 hour at 6°C, followed by addition of dry MeOH (16 mg, 0.49 mmol) and evaporation of the solvent. Gas chromatographic separation at 130°C gave **21** with a retention time of 35 minutes: ^{1}H NMR (CDCl$_3$) δ 0.18 (s, 9, Me$_3$Si), 1.38 (d, 3, J = 7.2 Hz, CH$_3$), 2.80 (q, 1, J = 7.2 Hz, CH), 3.72 (s, 3, CH$_3$O); ^{13}C NMR (CDCl$_3$) δ −0.78, 17.5, 20.8, 34.8, 52.6, 176.1, 180.5; IR (film) 2100, 1779 cm^{-1}; EIMS *m/z* 200 (M$^+$, 16), 185 (M$^+$ -CH$_3$, 100), 157 (M$^+$ -CH$_3$, CO, 60), 141 (M$^+$-CH$_3$, CO$_2$, 74), 127 (M$^+$ -TMS, 17), 73 (Me$_3$Si$^+$, 96); HRMS *m/z* calcd for C$_9$H$_{16}$O$_3$Si, 200.0869; found 200.0860.

Dimethyl 2-(trimethylsilyl)-3-phenylsuccinates (**22**). Reaction of the monoketene **20** (9.8 mg, 0.037 mmol) in 0.5 mL CDCl$_3$ containing CH$_3$OH (20 μL, 16 mg, 0.50 mmol) in an NMR tube for 10 hours at RT gave complete conversion to a 1/2 mixture of the two stereoisomers *erythro*-**22** and *threo*-**22**, as assigned by ^{1}H NMR. These esters were also prepared by reaction of the diketone **7** (120 mg, 0.521 mmol) in 4.5 mL CH_3OH for 18 hours in a sealed tube at 100°C. After evaporation of the solvent, ^{1}H NMR analysis showed the presence of *erythro*-**22**, *threo*-**22**, and dimethyl 2-phenylsuccinate (**23**) in a ratio of 1/1/1.1. The esters were separated by radial chromatography using 5/95 EtOAC/hexanes to give *erythro*-**22** (42.3 mg, 0.144 mmol, 28%) and *threo*-**22** (16 mg, 0.0654 mmol, 10%). *erythro*-**22**: mp 59–61°C; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9, Me_3Si), 3.10 (d, 1, J = 12.4 Hz, C*H*TMS), 3.38 and 3.62 (each s, 3, OCH_3), 4.02 (d, 1, J = 12.4 Hz, C*H*Ph), 7.24–7.34 (s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −2.09, 41.05, 49.72, 50.89, 52.15, 127.35, 127.86, 128.43, 138.98, 173.21, 173.21, 173.26; IR ($CDCl_3$) 1719, 1731 cm^{-1} (C=O); EIMS *m/z* (*rel* intensity) 294 (M^+, 1), 279 (M^+ -CH_3, 6), 235 (M^+ -CO_2CH_3, 24), 131 (M^+ -TMS, CO_2Me, OMe, 100), 73 (TMS^+, 26); HRMS *m/z* calcd for $C_{15}H_{22}O_4Si$, 294.1287; found, 294.1275. *threo*-**22**: ^{1}H NMR ($CDCl_3$) δ −0.21 (s, 9, Me_3Si), 2.96 (d, 1, J = 12.4, C*H*TMS), 3.60 and 3.69 (each s, 9, OCH_3), 4.09 (d, 1, J = 12.4 Hz, C*H*Ph), 7.31 (br s, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −2.14, 41.02, 50.34, 51.31, 52.31, 127.95, 128.72, 128.81, 136.96, 174.41, 175.03; IR ($CDCl_3$) 1710, 1736 cm^{-1} (C=O); EIMS *m/z* (*rel* intensity) 294 (M^+, 3), 279 (M^+ -CH_3, 18), 263 (M^+ -MeO, 8), 235 (M^+ -CO_2Me, 47), 131 (M^+ -TMS, CO_2Me, OMe, 100), 73 (TMS^+, 38); HRMS *m/z* calcd for $C_{15}H_{22}O_4Si$, 294.1287; found, 294.1267.

2-Trimethylsilyl-3-phenyl-3-(carbomethoxy)propionic Acids (**24**). A sample of **20** in $CDCl_3$ in an NMR tube on standing at 0°C showed the formation of a mixture of *erythro*- and *threo*-**24** in a 1/2 ratio, as identified by their ^{1}H NMR spectra. *erythro*-**24**: δ 0.16 (s, 9, Me_3Si), 3.11 (d, 1, J = 12.4 Hz, C*H*TMS), 3.62 (s, 3, OMe), 3.99 (d, 1, J = 12.4 Hz, C*H*Ph), 7.20–7.40 (m, 5, Ph). *threo*-**20** δ −0.18 (s, 9, Me_3Si), 2.96 (d, 1, J = 12.3 Hz, C*H*TMS), 3.60 (s, 3, OMe), 4.04 (d, 1, J = 12.3 Hz, C*H*Ph), 7.20–7.40 (m, 5, Ph).

N,N'-Dimethyl-N,N'-diphenyl-2-trimethylsilyl-3-phenylsuccinamide (**25**). The diketone **7** (23.2 mg, 0.101 mol) in 0.5 mL $CDCl_3$ in an NMR tube was photolyzed 1.5 hours with 350 nm light at room temperature. N-Methylaniline (10 µL, 0.92 mmol) was added with shaking, and the sample was left at 0°C for 10 hours. The solvent was evaporated and the residue purified by radial chromatography to give **25** (13.5 mg, 0.0304 mmol, 30%), mp 121.5–123.5°C; ^{1}H NMR (acetone-d_6) d 0.03 (s, 9, Me_3Si), 2.60 (d, 1, J = 11.4 Hz, C*H*TMS), 2.83 and 3.08 (each s, 3, MeN), 4.04 (d, 1, J = 11.4 Hz, PhC*H*), 6.20–7.50 (m, 15, 3 Ph); ^{13}C NMR (acetone-d_6) δ −0.31, 36.77, 37.83, 41.97, 51.20, 127.45, 128.10, 128.17, 128.51, 128.65, 129.37, 129.50, 130.01, 130.07, 142.07, 144.24, 145.17, 172.63, 173.42; IR (film) 1651, 1635 cm^{-1} (C = O); EIMS *m/z* 444 (M^+, 3), 429 (M^+ -CH_3, 11), 338 (M^+ -MeNPh, 100), 310 (M^+ -CONMePh, 32), 107 ($PhNHMe^+$, 20), 106 ($PhNMe^+$, 21); HRMS *m/z* calcd for $C_{27}H_{32}SiN_2O_2$, 444.2233; found, 444.2235.

2-Phenyl-3-(trimethylsilyl)maleic Anhydride (**26**). A solution of the cyclobutenedione **7** (21.1 mg, 0.092 mmol) in 0.5 mL $CDCl_3$ was photolyzed 1 hour with 350 nm light, giving a 93% conversion to the bisketene **8** as measured by ^{1}H NMR. Air was bubbled in for 1.5 hours, the solvent was evaporated, and the crude product was purified by chromatography (5% EtOAc/hexane on silica gel) to give **26** (13.6 mg, 0.055 mmol, 65%) as a colorless solid, mp 80–82°C; ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9), 7.44–7.52 (m, 5); ^{13}C NMR ($CDCl_3$) δ −0.92, 128.37, 128.84, 129.48, 131.01, 144.39, 155.61, 165.59, 167.30; IR ($CDCl_3$) 1754 cm^{-1}; EIMS *m/z* 246 (M^+, 17), 231 (M^+ -CH_3, 17), 174 (M^+ -C_2O_3, 37), 159 (M^+ -C_2O_3, CH_3, 100); HRMS *m/z* calcd for $C_{13}H_{14}O_3$, 246.0712; found, 246.0711.

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