Phenyldimethylsilyl-Substituted Ketenes and Bisketenes

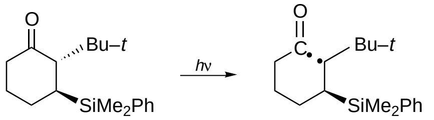
Ronghau Liu, Romeo M. Marra, and Thomas T. Tidwell*

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Received March 18, 1996[⊗]

The phenyldimethylsilyl-substituted monoketene $PhMe_2SiCH{=}C{=}O$ (**1**) and bisketene $(PhMe_2SiC{=}C{=}O)_2$ (**3**) have been prepared and compared to the corresponding Me_3Si- and *t*-$BuMe_2Si$-substituted species. The ^{13}C, ^{17}O, and ^{29}Si NMR spectra fit the pattern shown by other silylketenes and provide no evidence for transmission of a substituent effect of the Ph group through the silicon to the ketenyl group, as has been proposed for $PhMe_2Si$-substituted radicals. The UV spectrum of **1** does show a longer λ and greater ϵ than for *t*-$BuMe_2SiCH{=}C{=}O$, and this may indicate some interaction of the phenyl group with the ketene chromophore, while the greater reactivity of **1** in hydration compared to *t*-$BuMe_2SiCH{=}C{=}O$ is ascribed to the inductive effect of the phenyl. The very similar ring-opening reactivity of the bis(phenyldimethylsilyl)cyclobutenedione (**6**) to form **3** compared to the bis(Me_3Si) analogues also provides no evidence of a significant interaction of the phenyl with the ketene. A new type of stabilized 1,8-bisketene based on the arylbis(dimethylsilyl) grouping, namely, 1,4-bis(ketenyldimethylsilyl)benzene (**12**), has been prepared for the first time.

As part of our studies of silylated ketenes and bisketenes, we have examined the properties of different silyl subsituents, including trimethylsilyl, *tert*-butyldimethylsilyl, and triisopropylsilyl.[1] Extension of these studies to include the phenyldimethylsilyl (PDMS) substituent is of interest for a variety of reasons including the possibility that these derivatives might be more highly crystalline than those bearing other silyl substituents, the utility of this group in synthesis as a masked hydroxy group,[2] the formation of metal-complexed aryl derivatives,[3] other synthetic applications of the PDMS group,[4] and the possibility of electronic transmission of the aryl group through the silyl group to affect the properties of the ketene.[5] Specifically it has been proposed[5a] that the p orbitals of the phenyl in β-PDMS-substituted cyclohexanones can enhance photochemical Norrish Type I cleavage by homoconjugative p−d−p orbital overlap with the developing radical center (eq 1). Two mechanisms have been proposed for silyl stabilization of ketenes,[1a] namely, (a) π donation from the ketene to the d orbitals on silicon[5b] and (b) σ_π−p_π donation from the carbon−silicon bond to the electron deficient in-plane p orbital on the carbonyl carbon.[5c] Thus a study of PDMS-substituted ketenes could provide evidence regarding the viability of d_π−p_π interactions in ketenes, and by implication in developing radicals as in eq 1 as well.



(1)

Therefore we have examined the properties of ketenes and bisketenes substituted with the PDMS group including their ^{13}C, ^{17}O, and ^{29}Si NMR spectra, which we have found to be a sensitive probe of electronic effects in these ketenes.[6a] We have also previously shown that cyclobutenedione precursors to bisketenes can be linked to aryl groups to give precursors to tetraketenes[1f] and have now studied the 1,4-bis(dimethylsilyl)phenyl group as a linking agent for stabilized 1,8-bisketenes.

Results

Previous reports[7a−c] of the preparation of $PhMe_2SiCH{=}C{=}O$ (**1**) have appeared, but none of these gives a thorough characterization of this ketene. Thus **1** has been prepared by dehydrochlorination of the corresponding acyl chloride,[7a] pyrolysis of the alkynyl ether **2** at 115 °C and vacuum distillation (eq 2),[7b] and pyrolysis of the anhydride $(PhMe_2SiCH_2CO)_2O$.[7c]

$$\underset{\mathbf{2}}{PhMe_2SiC{\equiv}COEt} \xrightarrow[-CH_2{=}CH_2]{115\ ^\circ C} \underset{\mathbf{1}}{PhMe_2SiCH{=}C{=}O} \qquad (2)$$

We find that the ketene **1** may be conveniently obtained in pure form directly from **2** by pyrolysis in a preparative gas chromatograph and collection. The ketene was characterized by ^1H, ^{13}C, ^{17}O, and ^{29}Si NMR and showed the distinctive bands for silylketenes in ^{13}C NMR at δ −0.7 (C_β) and 178.9 (C_α), an ^{17}O signal at δ 256.1, and a ^{29}Si signal at δ −5.4. These band positions are consistent with those for other silylketenes.[6]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

[1] (a) Tidwell, T. T. *Ketenes*; Wiley: New York, 1995. (b) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265−271. (c) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097−10103. (d) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625−2626. (e) Allen, A. D.; Ji, R.; Lai, W.-Y.; Ma, J.; Tidwell, T T. *Heteroatom Chem.* **1994**, *5*, 235−244. (f) Liu, R.; Tidwell, T. T. *Can. J. Chem.* **1995**, *73*, 1818−1822. (g) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021−6028.

[2] (a) Fleming, I.; Henning, R.; Parker, D. C.; Plaut, H. E.; Sanderson, P. E. J. *J. Chem. Soc., Perkin Trans. 1* **1995**, 317−337. (b) Taber, D. F.; Yet, L.; Bhamidipati, R. S. *Tetrahedron Lett.* **1995**, *36*, 351−354.

[3] Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 954−955.

[4] (a) Barrett, A. G. M.; Hill, J. M.; Wallace, E. M. *J. Org. Chem.* **1992**, *57*, 386−400. (b) Barrett, A. G. M.; Flygare, J. A.; Hill, J. M.; Wallace, E. M. *Org. Synth.* **1995**, *73*, 50−60.

[5] (a) Hwu, J. R.; Chen, B.-L.; Huang, L. W.; Yang, T.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 299−300. (b) Runge, W. *Prog. Phys. Org. Chem.* **1981**, *13*, 315−484. (c) Brady, W. T.; Cheng, T. C. *J. Org. Chem.* **1977**, *42*, 732−734.

[6] (a) Allen, A. D.; Egle, I.; Janoschek, R.; Liu, H. W.; Ma, J.; Marra, R. M.; Tidwell, T. T. *Chem. Lett.* **1996**, 45−46. (b) Valenti, E.; Pericas, M. A.; Serratosa, F. *J. Org. Chem.* **1990**, *55*, 395−397.

[7] (a) Baukov, Yu. I.; Burlachenko, G. S.; Kostyuk, A. S.; Lutsenko, I. F. *Dokl. Vses. Konf. Khim Atsetilena, 4th* **1972**, *2*, 130−133; *Chem. Abstr.* **1973**, *79*, 78904y. (b) Himbert, G.; Henn, L. *Liebigs Ann. Chem.* **1984**, 1358−1366. (c) Kostyuk, A. S.; Boyadzhan, Zh. G.; Zaitseva, G. S.; Sergeev, V. N.; Savel'eva, N. I.; Baukov, Yu. I.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1979**, *49*, 1543−14552. (d) Sommer, L. H.; Gold, J. R.; Goldberg, G. M.; Marans, N. S. *J. Am. Chem. Soc.* **1949**, *71*, 1509.

S0022-3263(96)00519-1 CCC: $12.00

Table 1. Hydration Rates (s^{-1})^a of $RMe_2SiCH{=}C{=}O$ in H_2O/CH_3CN at 25 °C

$[H_2O]$ (M)	R = Ph (**1**)	R = Me^b	R = *t*-Bu^b	Ph/Me	Ph/*t*-Bu
38.9	2.23×10^{-2}	2.11×10^{-2}	5.21×10^{-3}	1.06	4.28
33.3	1.03×10^{-2}	6.68×10^{-3}	2.08×10^{-3}	1.54	4.94
27.9	5.40×10^{-3}	2.84×10^{-3}	9.58×10^{-4}	1.90	5.64
22.2	3.10×10^{-3}	2.03×10^{-3}	5.52×10^{-4}	1.53	5.62
16.7	1.77×10^{-3}	8.63×10^{-4}	2.81×10^{-4}	2.05	6.30
11.1	8.24×10^{-4}	6.61×10^{-4}	1.28×10^{-4}	1.25	6.44

[a] Measured by the decrease in absorbance at 243 nm, $\log k_{obs} = 0.0498[H_2O] - 3.62$ (see text). Duplicate rates at each concentration, maximum deviations ±2%. [b] Reference 1c.

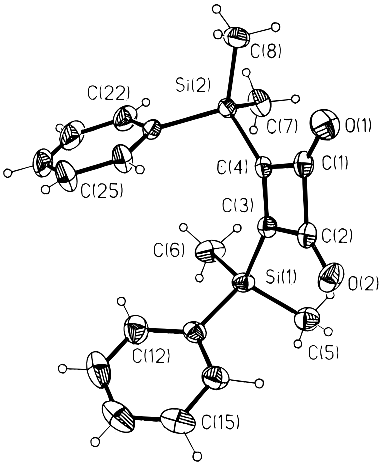
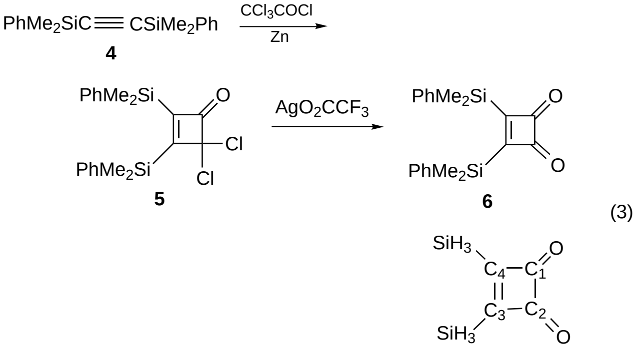


Figure 1. X-Ray structure of 3,4-bis(phenyldimethylsilyl)cyclobut-3-ene-1,2-dione (**6**).

To evaluate the reactivity of **1**, kinetics of its hydration with H_2O/CH_3CN mixtures were measured at different H_2O concentrations by observing the decrease in the absorption at 243 nm. This reaction proceeds to the known acid $PhMe_2SiCH_2CO_2H$,[7d] which was isolated and its structure confirmed from its spectroscopic properties. The results are collected in Table 1, along with comparative data for other silylketenes.[1c]

For the preparation of the PDMS-substituted 1,2-bisketene **3**, the sequence shown in eq 3 was followed. This procedure is analogous to those used for other silylated 1,2-bisketenes, using bis(phenyldimethylsilyl)acetylene (**4**)[8a] and activation of the zinc by heating,[8b] and utilizes AgO_2CCF_3[8c] for conversion of the dichloride **5** to the diketone **6**. The use of the latter regent is necessary instead of the H_2SO_4-catalyzed hydrolysis procedure used in other cases[1] because cleavage of the phenyl group by protodesilylation occurs if **5** is treated with acid. The X-ray crystal structure of the cyclobutenedione **6** was determined and is shown in Figure 1, and some bond distances and bond angles are given in Table 2, along with some *ab initio* calculated values for bis(SiH_3)-substituted cyclobutenedione (**6a**).[9]

The dione **6** in $CDCl_3$ was converted upon heating at 100 °C for 2 h to the bisketene **3** (eq 4) as the only product observable by ^1H NMR and was identified by its characteristic ketenyl IR band at 2080 cm^{-1}, the distinctive silylketene bands in the ^{13}C NMR at δ 5.87 (C_β) and 180.88 (C_α), the ^{29}Si signal at δ −2.42, and the ^{17}O band at δ 270. In the ^{13}C spectrum the $(CH_3)_2Si$ resonances at δ −2.73 showed coupling to ^{29}Si, $J = 56$ Hz, and the same coupling was seen in the ^{29}Si spectrum.



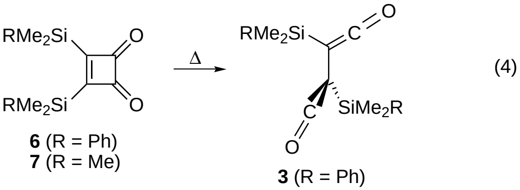
4

5

6

(3)

6a



6 (R = Ph)
7 (R = Me)

3 (R = Ph)
8 (R = Me)

(4)

The kinetics of the conversion of **6** to **3** were measured in isooctane by UV spectroscopy, as reported in Table 3. For comparison with the rates in isooctane the kinetics for **7**, R = Me, were also measured in this medium.

The (aryldimethylsilyl)ketene motif has also been used in the preparation of a new type of bisketene, namely, the bis(silylketene) with a 1,4-disubstituted benzene spacer. Thus 1,4-bis(bromodimethylsilyl)benzene (**9**),[10] prepared as shown in eq 5, reacted with lithium ethoxyacetylene to give the bisalkyne **10**. Upon pyrolysis of **10** in a gas chromatograph, two products were obtained in a variable ratio depending upon the exact conditions. The product of shortest retention time was tentatively identified as monoketene **11** resulting from conversion of one of the alkynyl groups of **10** to a ketenyl function. This assignment was based upon the ^1H NMR spectrum, including the appearance of separate signals for the $EtOC{\equiv}CSiMe_2$ and $SiMe_2CH{=}C{=}O$ moieties, the observation of two separate ^{29}Si NMR resonances, and a ketenyl IR band at 2108 cm^{-1}. Insufficient material was obtained for measuring the ^{13}C NMR spectrum. The major product was identified as the bisketene **12** based upon its complete spectral characterization. Some salient signals and the comparative values for $PhMe_2SiCH{=}C{=}O$ (**1**) (parentheses) are as follows: IR 2115 cm^{-1} (2114 cm^{-1}); ^1H NMR δ 0.44 (0.42), $SiMe_2$; 2.00 (1.98), $CH{=}C{=}O$; ^{13}C NMR δ −0.7 (-0.7) $C_\beta{=}C{=}O$; 178.9 (178.9), $C{=}C_\alpha{=}O$; ^{17}O NMR δ 256.6 (256.1); ^{29}Si NMR δ −5.39 (−5.45).

Discussion

For consideration of the NMR chemical shifts of the $PhMe_2Si$-substituted ketenes and bisketenes, data for the monoketene **1** and the bisketene **3** are collected in Table 4 with data for other ketenes and bisketenes.[6] It is striking from the chemical shifts (Table 4) for silyl groups R_3Si that the ^{13}C shifts for both C_α and C_β, and the ^{17}O shifts, show only very small effects due to the particular

---

(8) (a) West, R.; Quass, L. C. *J. Organomet. Chem.* **1969**, *18*, 55−67. (b) Stenstrøm, Y. *Synth. Commun.* **1992**, *22*, 2801−2810. (c) Wong, H. N. C.; Sondheimer, F.; Goodlin, R.; Breslow, R. *Tetrahedron Lett.* **1976**, 2715−2718.

(9) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233−7238.

(10) (a) Plenio, H. *J. Organomet. Chem.* **1992**, *435*, 21−28. (b) Fink, W. *Helv. Chim. Acta* **1974**, *57*, 1010−1015.

Table 2. Comparison of Measured and Calculated Bond Distances (Å) and Angles (deg) for Bis(silyl)cyclobutenediones

	bond distance							
	C_1O	C_2O	C_1C_4	C_2C_3	C_1C_2	C_3C_4	C_3Si	C_4Si
6 ($PhMe_2Si$)[a]	1.185	1.192	1.511	1.512	1.567	1.375	1.886	1.878
6a (SiH_3)[b]	1.175	1.175	1.511	1.511	1.554	1.352	1.888	1.888

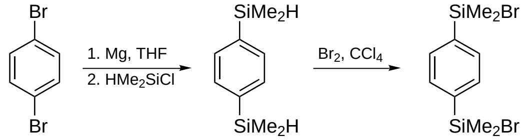
	bond angle							
	C_1C_4Si	C_2C_3Si	OC_1C_4	OC_2C_3	$C_2C_1C_4$	$C_1C_2C_3$	$C_1C_4C_3$	$C_2C_3C_4$
6 ($PhMe_2Si$)[a]	130.0	126.9	136.8	136.6	86.6	86.1	93.4	93.9
6a (SiH_3)[b]	129.6	129.6	136.1	136.1	86.2	86.2	93.8	93.8

[a] Measured. [b] Calculated, HF/6-31G*, ref 9.

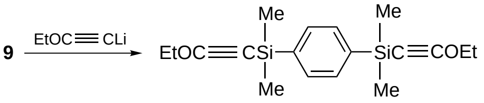
Table 3. Kinetic Data for Conversion of Cyclobutenediones to Bisketenes in Isooctane

cyclobutenedione	T (°C)	k (s^{-1})
6 (R = Ph)[a]	79.0	$(2.36 \pm 0.06) \times 10^{-4}$
	70.7	$(8.30 \pm 0.47) \times 10^{-5}$
	70.2	$(8.64 \pm 0.15) \times 10^{-5}$
	61.0	$(2.50 \pm 0.45) \times 10^{-5}$
	25.0[c]	1.2×10^{-7}
7 (R = Me)[b]	79.0	$(1.44 \pm 0.03) \times 10^{-4}$
	72.6	$(6.01 \pm 0.01) \times 10^{-5}$
	59.0	$(1.19 \pm 0.01) \times 10^{-5}$
	25.0[c]	6.2×10^{-8}

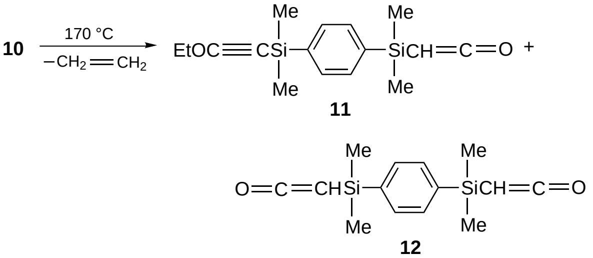
[a] $\ln(k/T) = -14500/T + 27$; $E_{act} = 29.5$ kcal/mol; $\Delta H^{\ddagger} = 28.8$ kcal/mol; $\Delta S^{\ddagger} = 6.3$ eu. [b] $\ln(k/T) = -14100/T + 25$; $E_{act} = 29.5$ kcal/mol; $\Delta H^{\ddagger} = 28.0$ kcal/mol; $\Delta S^{\ddagger} = 3.1$ eu. [c] Calculated from data at other temperatures.



9 (5)



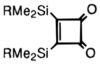
10 (6)



11

12 (7)

Table 4. NMR Chemical Shifts for Ketenes, Bisketenes, and Reference Compounds

	δ ^{13}C (C_α)	(C_β)	δ ^{17}O	δ ^{29}Si	$\Delta\delta$ ^{29}Si Ph/Me	$\Delta\delta$ ^{29}Si t-Bu/Me
$PhMe_2SiC_\beta H{=}C_\alpha{=}O$ (**1**)	178.9	−0.7	256.1	−5.4	-5.2	
$Ph_2MeSiC_\beta H{=}C_\alpha{=}O$[b]	178.5	−3.6				
$Me_3SiCH_\beta{=}C_\alpha{=}O$	179.2	−0.1	255.0	−0.2		
t-$BuMe_2SiCH{=}C{=}O$[b]	180.0	−4.6				
t-$BuMe_2SiCH{=}CH_2$				0.9		7.5
$Me_3SiCH{=}CH_2$				−6.6		
Ph_2SiMe_2				−7.5	-3.0	
$PhSiMe_3$				−4.5		
$(PhMe_2SiC_\beta{=}C_\alpha{=}O)_2$ (**3**)	180.9	5.9	270	−2.4	-5.6	
$(Me_3SiC_\beta{=}C_\alpha{=}O)_2$	181.8	5.6	269.2	3.2		
$(t$-$BuMe_2SiC_\beta{=}C_\alpha{=}O)_2$	182.2	4.3	270.5	10.6		7.4
1,4-$C_6H_4(SiMe_2CH{=}C{=}O)_2$ (**12**)	178.9	-0.7	256.6	-5.4		
 R = Ph (**6**)	201.8	215.9	504	−13.5	-5.2	
R = Me	202.0	217.1	499.1	−8.4		
R = t-Bu	202.1	217.3		0.4		8.8

[a] This work for **1, 3, 6**, and **12**; others ref 6a except as noted. [b] Reference 6b.

groups R. Thus for monoketenes $R_3SiCH{=}C{=}O$ there are variations of 1.5 and 4.5 for δ C_α and C_β, respectively, while for the bisketenes the corresponding variations are only 1.3 and 1.6, respectively, although C_α and C_β average 2.5 and 7.5 ppm, respectively, to lower field for the bisketenes compared to monoketenes. The ^{17}O shifts vary by no more than 1.3 as a function of R for the ketenes and bisketenes, and the latter are on average to lower field by 14.4 ppm.

Just as has been found for other silyl-substituted ketenes and bisketenes,[6a] the C_α and ^{17}O NMR chemical shifts of **1**, **3**, and **12** show upfield shifts of about 20 and 70 ppm, respectively, compared to nonsilylated ketenes, while the ^{29}Si NMR chemical shifts are downfield by 8.1−11.1 ppm compared to the cyclobutenedione **6**. These effects in silylketenes were attributed[6a] to neutral hyperconjugation,[11a] in which there is $\sigma_\pi - p_\pi$ electron donation from the C_β−Si bond to the in-plane p orbital of the carbonyl carbon.[6a]

For the cyclobutenediones the effects of R in RMe_2Si on δ ^{13}C are very small, with a total variation of δ 0.3 for C_α and δ 1.4 for C_β. The corresponding variation on the ^{17}O is δ 4.9.

There are systematic effects of the groups R in R_4Si on the ^{29}Si chemical shifts (Table 4). Thus for R = Ph compared to R = Me there are upfield shifts in ^{29}Si of δ 3.0−5.6, and for R = t-Bu compared to R = Me there are downfield shifts of δ 7.4−8.8. These trends appear to be largely independent of the rest of the structure. The upfield shift caused by phenyl has been noted previously, as has a similar effect by vinyl groups.[11b] It was also noted previously[11b] that the replacement of the hydrogens on carbon bonded to silicon by alkyl groups caused downfield shifts of about 2 ppm per alkyl group and this is consistent with the trend noted for R = t-Bu compared to R = Me.

Thus for the substrates RMe_2SiX there are no specific interactions of the groups R and ketenyl or cyclobutenedione groups X which affect the chemical shifts in R, X, or Si, at least for the compounds studied. In particular no transmission of electrical effects or conjugation between R and X through Si is apparent.

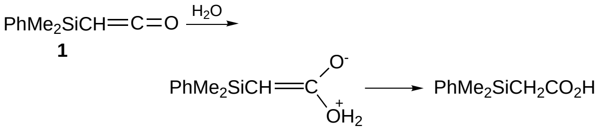
---

(11) (a) Lambert, J. B.; Singer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 10246−10248. (b) Scholl, R. L.; Maciel, G. E.; Musker, W. K. *J. Am. Chem. Soc.* **1972**, *94*, 6376−6385.

The UV spectrum of $PhMe_2SiCH{=}C{=}O$ (**1**) shows that in addition to the aryl absorption of **1** between 240−270 nm the characteristic ketene absorption is at 309 nm, $\epsilon = 110$ L mol^{-1} cm^{-1} in isooctane, as opposed to the absorption for t-$BuMe_2SiCH{=}C{=}O$ at 292 nm, $\epsilon = 35$ L mol^{-1} cm^{-1} in hexane. The shift to longer wavelength and the increased ϵ for **1** suggests there is a measureable interaction between the phenyl group and the ketene chromophore. A similar increase to longer wavelength has been reported in the UV spectra upon the addition of a second and third ketenyl group to silicon in the series t-$BuMe_2SiCH{=}C{=}O$, $Me_2Si(CH{=}C{=}O)_2$, and $MeSi(CH{=}C{=}O)_3$.[12] The UV spectra are thus more sensitive for detecting perturbations due to different substitution patterns in these compounds than are the NMR spectra. The observed shifts to longer wavelength of the carbonyl $n \rightarrow \pi^*$ transition presumably results from a lowering of the π^* levels, as the n orbitals would be relatively unaffected by the remote substituents.

The UV spectrum of the cyclobutenedione **6** shows the long wavelength (visible) band at 355 nm, $\epsilon = 41$, and these values are essentially identical to those for bis(trimethylsilyl)cyclobutenedione (**7**) (λ_{max} 354 nm, $\epsilon = 37$) and the bis(*tert*-butyldimethylsilyl) analogue (λ_{max} 356 nm, ϵ 27).[1c] Thus as far as this measure is concerned there is also no evidence for an interaction between the aryl group and the cyclobutenedione moiety. The bisketenes **3**, **8**,[1c] and $(t\text{-}BuMe_2SiC{=}C{=}O)_2$[1c] all show long wavelength shoulders in their UV spectra near 325 and 380 nm, but any differences appear too indistinct for interpretation.

Upon reaction with H_2O, **1** gives the acid $PhMe_2SiCHCO_2H$,[7d] and the hydration reactivity of **1** is greater than that of $Me_3SiCH{=}C{=}O$ and t-$BuMe_2SiCH{=}C{=}O$ at different $[H_2O]$ in CH_3CN by factors of 1.05−2.05, and 4.28−6.44, respectively (Table 1). A lesser decrease in the reactivity of **1** as the $[H_2O]$ is decreased is expressed in the slopes of plots of log k_{obs} *vs* $[H_2O]$ of 0.0498, 0.0622,[1c] and 0.0642,[1c] respectively. We have found such plots of log k_{obs} *vs* $[H_2O]$ are usually linear and have used these as an empirical measure of the influence of solvent polarity on reactivity. A simple explanation of the greater reactivity of **1** relative to $Me_3SiCH{=}C{=}O$ and t-$BuMe_2SiCH{=}C{=}O$ is that this effect results from inductive electron withdrawal by phenyl stabilizing a negatively charged enolate-like transition state (eq 8).[1a]



$$PhMe_2SiCH{=}C{=}O \xrightarrow{H_2O} PhMe_2SiCH{=}C(O^-)(\overset{+}{O}H_2) \longrightarrow PhMe_2SiCH_2CO_2H \quad (8)$$

Comparison of the kinetics of ring opening of the $PhMe_2Si$-substituted cyclobutenedione **6** to the bisketene **3** (Table 3) reveals a very modest acceleration compared to the corresponding reaction of the Me_3Si-substituted cyclobutenedione **7**, by a factor of 1.6 at 79.0 °C. This small factor could be due to ground state destabilization of the cyclobutenedione **6** by the $PhMe_2Si$ groups, or stabilization of the transition state leading to the bisketene **3**, or a combination of effects, including conformational influences. The magnitude of the net effect is so small as to preclude any convincing assignment to a specific cause.

Thus the reactivity data agree with the analysis of the NMR spectra and indicate that there is no strong evidence for a transmission of electrical effects of the phenyl through the silicon to affect the ketenyl group. Only the UV spectrum of $PhMe_2SiCH{=}C{=}O$ compared that of t-$BuMe_2SiCH{=}C{=}O$ reveals any significant effect attributable to phenyl.

Interestingly, the X-ray crystal structure of the cyclobutenedione **6** (Figure 1) reveals that the two aryl groups are found on the same side of the cyclobutenedione ring, in an almost parallel arrangement.[13] However the two groups are too far from one another for any direct interaction, either favorable or unfavorable, and this effect apparently results from the intermolecular stacking of aryl groups seen in the crystal structure. The geometry of **6** obtained from the X-ray crystal structure determination is in reasonable agreement with that obtained earlier for the bis(SiH_3)-substituted cyclobutenedione **6a** by HF/6-31G* calculations (Table 2).[9] Calculations of the structures and energies of 1,2-bisketenes and their cyclobutenedione precursors have played an important part in the elucidation of the chemistry of these novel species,[1,9] and this agreement between the calculated and X-ray structures lends some confidence to the validity of this approach.

The bisketene **12** is the first example to be prepared in which two silyl-stabilized ketene units have been joined by a spacer group to give a stable bisketene and points the way to the utilization of the aryldimethylsilylketene moiety for the preparation of other new types of ketenes. The ketenyl NMR chemical shifts of **12** are essentially identical with the corresponding values for the monoketene $PhMe_2SiCH{=}C{=}O$ (**1**), indicating that there is no detectable interaction of the two ketenyl units in **12** through the phenyl spacer group. This structural unit is of interest because it suggests that a variety of such bis- and polyketenes could be prepared with various spacer groups, and additions to these ketenyl groups could then give further more complex products with predetermined arrays of repetitive structural types. By analogy with the designation of **3** as a 1,2-bisketene, then **12** is a 1,8-bisketene.

In summary the phenyldimethylsilyl group is an effective substituent for the stabilization of ketenes and bisketenes and has very little effect on their ^{13}C and ^{17}O NMR spectroscopic properties or their rates of formation and reaction compared to the corresponding Me_3Si-substituted derivatives. Only the UV spectra show any evidence for interaction of the phenyl with more distant parts of the molecule, and our results provide no evidence for the p−d−p type of overlap proposed[5a] for this substituent in radical systems.

Experimental Section

Unless otherwise stated, reagents were obtained from commercial suppliers and used as received. Ether and THF for use as reaction solvents were dried by refluxing over Na/benzophenone and distilling. Glassware was either dried in an oven at 150 °C and then cooled under N_2 or Ar or flame dried under N_2 or Ar before use.

1-(Phenyldimethylsilyl)-2-ethoxyacetylene.[7b] Ethoxyacetylene (0.0285 mol, 50% by weight solution in hexane) was

---

(12) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1996**, *118*, 2768−2769.

(13) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge, Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

added slowly via a syringe to a solution of *n*-butyllithium (0.03 mol, 20 mL, 1.50 M in hexane) and 30 mL of dry THF at −78 °C under Ar and then HMPA (hexamethylphosphoramide, 5 mL, 1.1 equiv) was added. The mixture was allowed to warm to room temperature and was stirred at room temperature for 2 h, and then phenyldimethylsilyl chloride (5.26 mL, 5.35 g, 0.0314 mol) was added slowly via a syringe and the solution was allowed to stir overnight at room temperature. The mixture was extracted between water and pentane, the pentane layer was washed twice with saturated NaCl solution, dried over $MgSO_4$, and concentrated under vacuum, and the residue was then distilled under reduced pressure (41−55 °C, 0.025 mmHg) to yield 1-(phenyldimethylsilyl)-2-ethoxyacetylene[7b] as a clear colorless liquid (4 g, 70%): ^{1}H NMR ($CDCl_3$) δ 0.41 (s, 6, $SiMe_2$), 1.43 (t, 3, $J = 7$ Hz, CH_3), 4.20 (q, 2, $J = 7$ Hz, CH_2), 7.4, −7.7 (m, 5, Ph).

(Phenyldimethylsilyl)ketene (1).[7a−c] A solution of 1-(phenyldimethysilyl)-2-ethoxyacetylene (40 mg) in 30 μL of pentane was injected into a gas chromatograph (column = 185 °C), and **1** was collected as a clear colorless oil with a retention time of 5.5 min: IR (film) 2114 cm^{-1} (s); UV $\lambda_{\max}^{\text{isooctane}}$ 254, 260, 264, 270, 309 nm (ϵ 200, 290, 280, 210, 110); ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6, $SiMe_2$), 1.98 (s, 1, CH), 7.38−7.56 (m, 5, Ph); ^{13}C NMR ($CDCl_3$) δ −0.72, −0.52, 127.9, 129.5, 133.4, 138.0, 178.9; ^{17}O NMR ($CDCl_3$) δ 256.1; ^{29}Si NMR ($CDCl_3$) δ −5.45; EIMS *m/z* 176 (M^+, 8), 169 ($M^+ - CH_3$, 100), 148 (M^+ − CO, 19), 135 ($PhMe_2Si^+$, 5).

Hydration of 1. Ketene **1** (20 mg, 0.11 mmol) was dissolved in 1 mL of deuterioacetone in an NMR tube, H_2O (40 μL, 2.2 mmol) was added, and the solution was left for 14 h, after which ^{1}H NMR indicated the complete disappearance of **1**. The solution was dried over $MgSO_4$ and evaporated, and the residue was dissolved in ether and dried again with $MgSO_4$ and evaporated to leave $PhMe_2SiCH_2CO_2H$ as a white solid, mp 89 °C (lit.[7d] mp 90 °C): IR (film) 3500−3300 cm^{-1} (br), OH, 1693 cm^{-1} (s), C═O; ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 6, $SiMe_2$), 2.12 (s, 2, CH_2), 7.36−7.57 (m, 5, Ph); EIMS *m/z* 193 (M^+ − H, 2), 135 ($PhMe_2Si^+$, 15), 117 (M^+ − Ph, 100).

Bis(phenyldimethylsilyl)acetylene (4).[8a] *cis*-Dichloroethylene (2.43 g, 0.025 mol) in 50 mL of ether was added dropwise with a pressure-equalizing addition funnel to *n*-butyllithium (50 mL, 1.51 M in hexane, 0.075 mol) in 75 mL of ether at 0 °C, and the mixture was stirred at room temperature for 2 h. The mixture was then cooled to −78 °C, a solution of phenyldimethylsilyl chloride (12.8 g, 0.075 mol) in ether (100 mL) was added dropwise with stirring, and the mixture was stirred at room temperature for 9 h, filtered, and concentrated to yield a yellow oil, which was distilled under vacuum (0.015 mmHg, 110 °C) to yield a clear colorless liquid which crystallized on standing (5.90 g, 0.0200 mol, 80%).

2,3-Bis(phenyldimethylsilyl)-4,4-dichlorocyclobut-2-enone (5). A 3-necked round bottom flask equipped with a magnetic stirring bar, pressure-equalizing addition funnel, gas inlet, and septum was flame dried under Ar. Zinc dust (3.71 g, 0.0567 mol) was added and heated with a Bunsen burner with stirring until it became a fine powder. A solution of **4** (5.30 g, 0.0180 mol) in 120 mL of ether was injected with a syringe, and trichloroacetyl chloride (4.22 g, 0.0232 mol) in 13 mL of ether was added dropwise to the stirring mixture, which was then stirred for 3 days at room temperature. The mixture was quenched with 15 mL of H_2O and washed twice with saturated Na_2CO_3 and twice with saturated NaCl. The combined aqueous washings were extracted once with 15 mL of diethyl ether, and the combined ether extracts were dried over anhydrous $MgSO_4$ and concentrated on a rotary evaporator, leaving a clear yellow-orange oil. Some of the crude product (1.05 g) was chromatographed on silica gel by radial chromatography to yield 890 mg of **5**, mp 95−97 °C: IR (KBr) 1770 cm^{-1}; UV $\lambda_{\max}$ 210 nm, shoulder at 230 nm; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 6, $SiMe_2$), 0.47 (s, 6, $SiMe_2$), 7.21−7.43 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −3.30, −2.47, 128.1, 128.2, 129.9, 130.2, 134.0, 134.3, 134.4, 135.6, 168.5, 184.0, 195.5; ^{29}Si NMR ($CDCl_3$) δ −15.85, −11.68; EIMS *m/z* 408, 406, 404 (M^+, 6), 368 (M^+, − HCl, 16), 353 (M^+, − CH_3, −HCl, 40), 135 (Me_2PhSi^+, 100); HRMS *m/z* calcd for $C_{20}H_{22}Cl_2OSi_2$, 404.0586, found 404.0597.

3,4-Bis(phenyldimethylsilyl)cyclobut-3-ene-1,2-dione (6). Silver trifluoroacetate (0.87 g, 4.0 mol) was dissolved in ethyl acetate (2 mL) in a round bottom flask equipped with a magnetic stirrer and a drying tube. The solution was heated to 65 °C, **5** (291 mg, 0.719 mmol), dissolved in 2 mL of ethyl acetate, was added dropwise to the stirring mixture using a transfer pipette, and the mixture was stirred at 65 °C for 1.5 h and then extracted with H_2O and saturated NaCl. The combined aqueous washings were extracted twice with ether (5 mL), and the combined organic extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator leaving a bright yellow oil. The crude oil was purified by radial chromatography on silica gel to yield **6** (120 mg, 0.342 mmol, 48%) as a pale yellow solid, mp 72.5−81 °C (dec). As an alternate purification method, the crude dione was recrystallized from ether at −20 °C to yield long clear yellow crystals: IR ($CDCl_3$), 1764 cm^{-1}; UV $\lambda_{\max}^{\text{isooctane}}$ 210 (sh, ϵ = 68 000), 270 (sh, ϵ = 3400), 355 (ϵ = 41); ^{1}H NMR ($CDCl_3$) δ 0.42 (s, 12, $SiMe_2$), 7.31−7.38 (m, 10, Ph); ^{13}C NMR ($CDCl_3$) δ −3.38, 128.2, 130.2, 134.0, 201.8, 215.9; ^{17}O NMR ($CDCl_3$) δ 504; ^{29}Si NMR ($CDCl_3$) δ −13.54, EIMS *m/z* 350 (M^+, 60), 335 ($M^+ - CH_3$, 29), 306 ($M^+ - CO_2$, 71), 279 ($M^+ - C_2O_2$, CH_3, 81), 135 ($PhMe_2Si^+$, 100); HRMS *m/z* calcd for $C_{20}H_{22}O_2Si_2$, 350.1158, found 350.1170. Anal. Calcd for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.32. Found: C, 68.53; H, 6.62.

2,3-Bis(phenyldimethylsilyl)buta-1,3-diene-1,4-dione (3). A solution of **6** (50 mg, 14 mmol) in 1.5 mL of $CDCl_3$ in an NMR tube was degassed for 15 min by bubbling through Ar. The tube was sealed and heated in an oil bath at 100 °C for 2 h. All NMR signals corresponding to the dione disappeared and were replaced with signals corresponding to the bisketene **3**. Evaporation of the $CDCl_3$ gave **3** as a yellow oil, or alternatively heating **6** at 120 °C for 2 h in an ampule sealed under argon also gave neat **3**: IR ($CDCl_3$) 2080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 12, Me_2Si), 7.35−7.53 (m, 10, Ar); UV $\lambda_{\max}^{\text{isooctane}}$ 210 (sh, ϵ = 16 000), 250 (sh, ϵ = 3,400), 320 (sh, ϵ = 450), 380 (sh, ϵ = 140); ^{13}C NMR ($CDCl_3$) δ −2.73 ($J^{13}C-^{29}Si$ = 56 Hz), 5.9, 128.0, 129.9, 133.9, 136.0, 180.9; ^{17}O NMR ($CDCl_3$) δ 270; ^{29}Si NMR ($CDCl_3$) δ −2.42 ($J\ ^{29}Si-^{13}C$) = 56.4 Hz).; EIMS *m/z* 350 (M^+), 335 ($M^+ - CH_3$), 321 (M^+, − CHO), 306 (M^+, − CO_2), 135 ($PhMe_2Si^+$). Anal. Calcd for $C_{20}H_{22}O_2Si_2$: C, 68.52; H, 6.32. Found: C, 68.41; H, 6.19.

1,4-Bis(bromodimethylsilyl)benzene (9).[10] 1,4-Dibromobenzene (5.9 g, 25.0 mmol) in 5 mL of THF was added dropwise to a mixture of chlorodimethylsilane (5.0 g, 52.5 mmol) in 30 mL of THF and Mg turnings (1.3 g, 52.5 mL) under N_2. The reaction mixture was stirred for 1 h at room temperature and filtered, and the collected solid was washed with hexanes. The combined organic layers were evaporated to give crude 1,4-bis(dimethylsilyl)benzene (4.0 g, 20.4 mmol, 82%). To a sample of this product (1.0 g, 5.1 mmol) in 10 mL of dry CCl_4 was added a Br_2/CCl_4 solution dropwise until the bromine color persisted. Evaporation of the solvent gave crude **9** (1.74 g, 4.9 mmol, 96%): ^{1}H NMR ($CDCl_3$) δ 0.78 (s, 12, Me_2Si), 7.53 (s, 4, Ar).

1,4-Bis(ethoxyethynyldimethylsilyl)benzene (10). Ethoxyacetylene (1 g, 5.7 mol, 50% in hexane) was added by a syringe to *n*-BuLi (6.0 mmol, 3.8 mL in hexane) in 10 mL of dry ether at 0 °C. The solution was stirred for 2 h, and crude **9** (1.0 g, 2.8 mmol) in 5 mL of ether was added via a syringe. The solution was allowed to stir for 3 h at room temperature and was then extracted with ether, and the ether extracts were washed with H_2O, dried, and evaporated to give crude **10** (0.8 g, 2.4 mmol, 86%), which was purified by column chromatography giving a colorless oil: IR ($CDCl_3$) 2176 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.37 (s, 12, $SiMe_2$), 1.40 (t, 6, OCH_2CH_3), 4.18 (q, 4, OCH_2CH_3), 7.64 (s, 4, Ar); ^{13}C NMR ($CDCl_3$) δ 0.0, 14.2, 35.0, 74.8, 110.7, 132.7, 139.1; EIMS *m/z* 330 (M^+, 5), 315 ($M^+ - CH_3$, 40), 301 ($M^+ - C_2H_5$, 53), 259 (100), 99 (50).

Pyrolysis of 10. A solution of **10** (50 mg) in 50 μL of acetone was injected into a gas chromatograph (3 m × 1 cm OV-17 column, 170 °C), and the products **11** and **12** observed in a ratio of 1:3 were collected. The first was tentatively identified as ((4-((ethoxyethynyl)dimethylsilyl)phenyl)dimethylsilyl)ketene (**11**) (t_R 40 min): IR ($CDCl_3$) 2108 cm^{-1}; ^{1}H NMR

($CDCl_3$) δ 0.39 (s, 6, $SiMe_2$), 0.45 (s, 6, $SiMe_2$), 1.20 (t, 3, J = 7 Hz, OCH_2CH_3), 2.00 (s, 1, $CH{=}C{=}O$), 3.68 (q, 2, J = 7 Hz, OCH_2), 7.59 (s, 4, Ar); ^{29}Si NMR ($CDCl_3$) δ −5.48 ($SiMe_2CH{=}C{=}O$), 7.42 ($SiMe_2C{\equiv}COEt$). **1,4-Bis(ketenyldimethylsilyl)benzene** (**12**) (t_R 75 min): IR ($CDCl_3$) 2115 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.44 (s, 12, $SiMe_2$), 2.00 (s, 2, $CH{=}C{=}O$), 7.59 (s, 4, Ar); ^{13}C NMR ($CDCl_3$) δ −0.9, −0.7, 132.8, 139.5, 178.9; ^{17}O NMR ($CDCl_3$) 256.6; ^{29}Si NMR ($CDCl_3$) δ −5.39; EIMS m/z 274 (M^+, 15), 259 ($M^+ - CH_3$, 100), 246 ($M^+ - CO$, 34), 233 ($M^+ - CHCO$, 9), 99 ($SiMe_2CHCO^+$, 17); HRMS m/z calcd for $C_{14}H_{18}O_2Si$, 274.0845, found 274.0845.

Kinetic Studies. The rates of hydration of **1** were measured as described previously[1c] by injecting aliquots of a solution of **1** dissolved in CH_3CN into solutions of H_2O/CH_3CN equilibrated at 25.0 °C and measuring the decrease in the absorption at 243 nm. The kinetics of ring opening of **6** and **7** were measured as described previously[1c] by observing the change in the UV spectrum with time.

Acknowledgment. Financial support by the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research is gratefully acknowledged. We thank Dr. Alan Lough for the X-ray structure of **6**.

Supporting Information Available: Copies of NMR spectra (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO9605197