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Preparation and Reactivity of Persistent and Stable Silyl-Substituted Bisketenes

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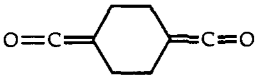
Abstract: 2,3-Bis(trimethylsilyl)-1,3-butadiene-1,4-dione (**1**) is formed as the only product on thermolysis of 3,4-bis-(trimethylsilyl)cyclobut-3-ene-1,2-dione (**2**), and the rate of ring opening of **2** is comparable to that of substituted cyclobutenes and cyclobutenones. Photolysis of **2** also forms **1**, which reacts with ethanol in a stepwise fashion with faster addition of one ethanol molecule to give an isolable monoketene **18**, which reacts in a further slower step to give succinate diesters, accompanied by desilylation. 2,3-Bis(*tert*-butyldimethylsilyl)-1,3-butadiene-1,4-dione (**3**), prepared analogously to **1**, similarly adds one molecule of methanol to give the isolable monoketene **20**, which then reacts to give dimethyl 2,3-bis(*tert*-butyldimethylsilyl)succinate (**21**) as the major product. The reaction of **1** with H_2O is faster than with alcohols and forms (*E*)- and (*Z*)-2,3-bis(trimethylsilyl)succinic anhydrides (**13**) as the first observed products. The reactivity of **1** with different nucleophilic solvents is correlated by the Winstein–Grunwald equation and increases with both solvent ionizing power and solvent nucleophilicity.

The preparation in this laboratory of **1**, the first stable and persistent 1,3-butadiene-1,4-dione, by the thermolysis or photolysis of 3,4-bis(trimethylsilyl)-3-cyclobutene-1,2-dione (**2**) (eq 1) was recently reported.[1] Details of the preparation of **1** and its analogue **3** are reported herein, along with studies of their reaction with nucleophilic water and alcohols, and the properties of intermediate monoketenes formed in these reactions.

(1)

R = Me_3Si (**2**), *t*-$BuMe_2Si$ (**4**), H (**6**) R = Me_3Si (**1**); *t*-$BuMe_2Si$ (**3**), H (**5**)

Bisketenes have been sought since the early days of ketene chemistry. Carbon suboxide (O=C=C=C=O) was prepared in 1906 by Diels and Wolf by dehydration of malonic acid[2a] and in 1908 by Staudinger and Bereza by the bis dehalogenation of $CBr_2(COBr)_2$.[2b] The extensive chemistry of C_3O_2 has been reviewed.[2c–e] Several nonsilylated analogues of **1** have been prepared, usually by photolysis of cyclobutenediones related to **2**, and some of these were directly observed at low temperatures,[3] including the parent **6**.[3a,b] However in all cases these rapidly reverted to the more stable cyclobutenediones at room temperature.[3] A stable metal-complexed ketene of this type was prepared, but from the X-ray structure, the geometry of this species was greatly different from the bisketene structure **5**.[3i] There have also been reports of bisketenes such as **7**[4a] and **8** where the ketenyl groups are further removed from one another,[4] and in the case of **8**,[4b] the species is a long-lived solid at room temperature.



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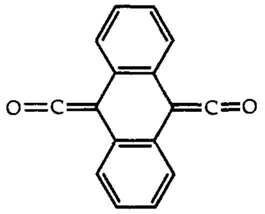

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The stability of **1** was anticipated on the basis of *ab initio* molecular orbital calculations[5a] that indicated that the hydrogen-substituted cyclobutenedione **6** was more stable than the corresponding *anti*-planar bisketene **5** by only 6.9 kcal/mol, while the SiH_3 group was more stabilizing to a ketene compared to an alkene by 7.6 kcal/mol.[5b] If these effects are additive and if the stabilizing effects of the SiH_3 and Me_3Si groups are the same, then the *anti*-planar bisketene **1** would be more stable than **2** by 8.3 kcal/mol. The successful preparation of **1** provides experimental confirmation of this calculation and shows that the effect of the Me_3Si group in stabilizing monoketenes[5] is qualitatively applicable to bisketenes as well. The bisketene structure of **5**, is however, calculated to be destabilized relative to ketene and butadiene; thus, the isodesmic reaction of eq 2 has a calculated ΔE of −11.9 kcal/mol, on the basis of the calculated[5a] energies of the individual species.[5f]

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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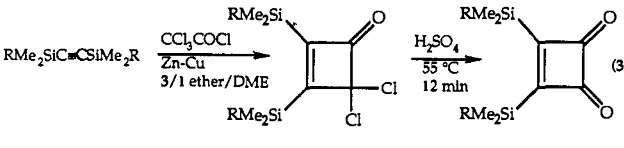
$$\underset{\mathbf{5}}{(CH{=}C{=}O)_2} + 2CH_2{=}CH_2 \xrightarrow[-11.9\ \text{kcal/mol}]{\Delta E\ =} 2CH_2{=}C{=}O + (CH{=}CH_2)_2 \qquad (2)$$

Results

Reaction of bis(trimethylsilyl)acetylene with dichloroketene generated by dechlorination using a zinc–copper couple[6a–c] gave the dichlorocyclobutenone **9** in 88% yield. Simplified procedures involving activation of zinc by ultrasonication[6d] or dry heating[6e] have appeared, and both have subsequently been of use[6f] in the preparation of **9**. The reaction of **9**[6g,h] with concentrated H_2SO_4 at 55 °C gave **2** in 73% yield after chromatography (eq 3).



(3)

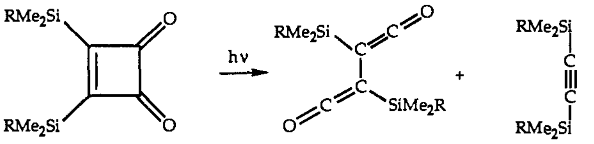
9 (R = Me), **10** (R = *t*-Bu) **2**, **4**

Preparation of the corresponding bis(*tert*-butyldimethylsilyl) derivatives **10** and **4** were carried out similarly, except that the hydrolysis of **10** to **4** proved to be less efficient and gave **4** in 44% yield.

Heating of **2** or **4** in degassed $CDCl_3$ gave complete conversion to **1** and **3**, respectively, as the only products detectable by ^1H NMR. The bisketenes were obtained preparatively by heating samples of **2** or **4** in a N_2 atmosphere. Pure **1** was also obtained by injection of **2** into a gas chromatograph and collection of the pure product. The structures of **1** and **3** follow from their ^1H and ^{13}C NMR spectra,[7] especially the ^{13}C signals of the carbonyl carbons at δ 181.83 and 182.24, respectively, and those of C_β at 5.62 and 4.27, respectively. The ketene $Me_3SiCH{=}C{=}O$ shows the corresponding carbons at δ 179.2 and −0.1, respectively,[7a] while those of t-$BuMe_2SiCH{=}C{=}O$ are at 179.96 and −3.29, respectively.[7c] Characteristic ketene IR bands are at 2084 cm^{-1} for **1** and 2076 cm^{-1} for **3**. These ketenes show broad UV absorptions λ_{max}(hexane) at 325 (ϵ 250) and 376 (ϵ 110) nm (**1**) and 326 (ϵ 160) and 400 (ϵ 88) nm (**3**).

Kinetic data for the ring opening of **2** and **4** to **1** and **3**, respectively, were obtained by monitoring the change in the ^1H NMR spectra and are given in Table I. These lead to E_{act} = 29.3 and 28.5 kcal/mol, respectively.

The photolyses of **2** and **4** at 350 nm also led to the formation of the bisketenes **1** and **3**, accompanied by the formation of the alkynes (eq 4).



(4)

2, **4** **1** (86%), **3** (92%) R = Me (11%), R = *t*-Bu (8%)

The bisketenes **1** and **3** appear to be stable indefinitely at room temperature in the dark in the absence of air. Bubbling of O_2 into a solution of **1** in refluxing toluene gave the anhydrides **11** and **12** in isolated yields of 14 and 7%, respectively, along with small amounts of unidentified products (eq 5).

Table I. Rate Constants for Formation of Bisketenes by Cyclobutenedione Ring Opening in $CDCl_3$ ($s^{-1} \times 10^4$)

T (°C)	k_1 (**2**)	T (°C)	k_1 (**4**)
99.7	9.47	87.1	7.04
99.0	9.45	79.4	2.86
87.8	2.61	68.0	0.757
87.5	2.52		
81.0	1.17		
80.0	1.11		
E_{act} (kcal/mol)	29.3 ± 0.5		28.5 ± 0.6
$\Delta H^‡$ (kcal/mol)	28.6 ± 0.5		27.8 ± 0.5
$\Delta S^‡$ (eu)	0.2 ± 0.4		3.8 ± 1.5

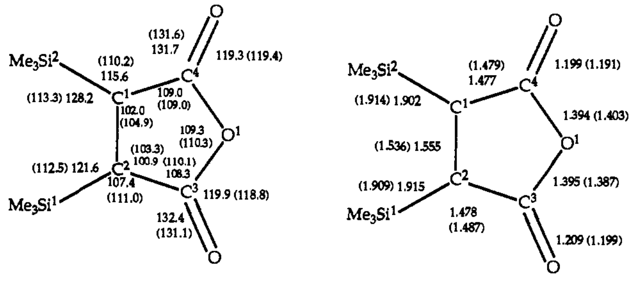
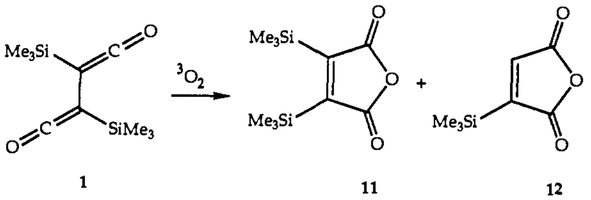


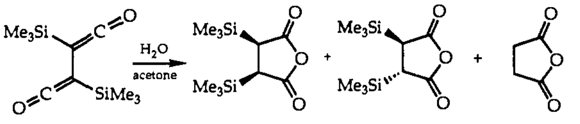
Figure 1. Bond angles and bond lengths for *Z*-**13** and *E*-**13** (in parentheses).



(5)

1 **11** **12**

The reaction of **1** in 1/10 H_2O/acetone for 5 min at 25 °C gave rise to the products **13** and **14** in the relative yields shown of the crude product as observed by ^1H NMR, including 16% unreacted **1**, 2% of the oxidation products of **1**, and further signals tentatively assigned to the mono trimethylsilylated derivative from **13**. After prolonged reaction with H_2O, the observed products were **14** and succinic acid. Both *Z*-**13** and *E*-**13** were isolated as crystalline solids, and their structures were established by X-ray crystallography.[8]



(6)

1 *Z*-**13** (42%) *E*-**13** (8%) **14** (15%)

Some salient bond angles and distances of the structures of *Z*-**13** and *E*-**13** are shown in Figure 1. The greater bond angles of the Me_3Si groups of the C(1)–C(2) bond in the ring for *Z*-**13** (128.2 and 121.6°) compared to those for *E*-**13** (113.3 and 112.5°) are indicative of the repulsion between the Me_3Si groups in *Z*-**13**. The greater C(1)–C(2) bond length for *Z*-**13** of 1.555(10) compared to that for *E*-**13** of 1.536(5) may also result from this repulsion, but the difference only marginally exceeds the combined uncertainties.

Rate constants for the reactions of **1** in H_2O/CH_3CN mixtures were measured by monitoring the change in the UV absorption and are given in Table II, together with comparative data measured for $Me_3SiCH{=}C{=}O$ (**15**) and t-$BuMe_2SiCH{=}C{=}O$ (**16**). The

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(8) The authors have deposited atomic coordinates for these structures 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.

Table II. Hydration Rates of **1** and Comparative Rates of $Me_3SiCH{=}C{=}O$ (**15**) and *t*-$BuMe_2SiCH{=}C{=}O$ (**16**) in H_2O/CH_3CN at 25 °C

	k_{obs} (s^{-1})			k_{rel}	
[H_2O] (M)	**1**[a]	**15**[b]	**16**[c]	**1**/**15**	**15**/**16**
55.5	3.07×10^{-1}	2.54×10^{-1}	1.15×10^{-1}	1.21	2.21
50.0	2.08×10^{-1}	1.52×10^{-1}	3.36×10^{-2}	1.37	4.52
44.4	1.28×10^{-1}	5.52×10^{-2}	1.08×10^{-2}	2.32	5.11
41.7	8.18×10^{-2}				
38.9	4.84×10^{-2}	2.11×10^{-2}	5.21×10^{-3}	2.29	4.05
36.1	3.70×10^{-2}				
33.3	2.31×10^{-2}	6.68×10^{-3}	2.08×10^{-3}	3.46	3.21
30.6	1.89×10^{-2}				
27.8	1.45×10^{-2} [e]	2.84×10^{-3}	9.58×10^{-4} [f]	5.11	2.96
27.8 (D_2O)[d]	6.55×10^{-3}	8.63×10^{-4}	3.01×10^{-4}	7.59	
27.8 (54.6 °C)	9.53×10^{-2}		1.08×10^{-2}		
27.8 (39.6 °C)	3.79×10^{-2}		3.25×10^{-3}		
22.2	9.72×10^{-3}	2.03×10^{-3}	5.52×10^{-4}	4.79	3.68
16.7	5.56×10^{-3}	8.63×10^{-4}	2.81×10^{-4}	6.44	3.07
11.1	2.97×10^{-3}	6.61×10^{-4}	1.28×10^{-4}	4.49	5.16

[a] [**1**] = 2.6×10^{-4} M. Rates measured by UV at 210 nm, at least duplicate runs at each concentration with maximum deviations of ±8%. $\log k = 0.047[H_2O] - 3.09$ and $r = 0.995$. [b] Measured at 206 nm. $\log k = 0.0622[H_2O] - 4.07$ and $r = 0.992$. [c] Measured at 204 or 307 nm. $\log k = 0.0642[H_2O] - 4.70$ and $r = 0.993$. [d] $k(H_2O)/k(D_2O) = 2.2$ (**1**), 3.3 (**15**), and 3.2 (**16**). [e] $\Delta H^{\ddagger} = 11.7$ kcal/mol and $\Delta S^{\ddagger} = -27.6$ eu. [f] $\Delta H^{\ddagger} = 15.5$ kcal/mol and $\Delta S^{\ddagger} = -20.3$ eu.

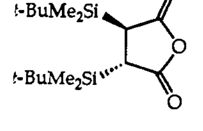
Table III. Alcoholysis Rates of **1** and Comparative Rates of $Me_3SiCH{=}C{=}O$ (**15**) and *t*-$BuMe_2SiCH{=}C{=}O$ (**16**) at 25 °C[a]

	k_{obs} (s^{-1})			k_{rel}	
solvent	**1**	**15**	**16**	**1**/**15**	**15**/**16**
H_2O	3.07×10^{-1}	2.54×10^{-1}	1.15×10^{-1}	1.21	2.21
MeOH	9.21×10^{-3}	6.00×10^{-3}	5.83×10^{-3}	1.54	1.03
EtOH	2.00×10^{-3} [b]	1.50×10^{-4}	1.19×10^{-4} [c]	13.3	1.26
95% EtOH	1.17×10^{-2}	9.12×10^{-4}	5.18×10^{-4}	12.8	1.76
80% EtOH	2.99×10^{-2}	3.58×10^{-3}	1.72×10^{-3}	8.35	2.08
60% EtOH	5.11×10^{-2}	8.37×10^{-3}	3.62×10^{-3}	6.10	2.31
n-HxOH	1.02×10^{-3}	1.72×10^{-4}		5.93	
i-PrOH	5.37×10^{-4}	3.17×10^{-5}		16.9	
t-BuOH[d]	3.59×10^{-5}				
70% TFE[e]	1.74×10^{-3}				
50% TFE[e]	2.70×10^{-3}				
100% HFIP	1.48×10^{-4}				

[a] Averages at least duplicate runs, measured by UV at 390 nm for **1**, and 204 or 307 nm for **15** and **16**. [b] $\Delta H^{\ddagger} = 5.7$ kcal/mol and $\Delta S^{\ddagger} = -50.0$ eu, based on the following rate constants ($s^{-1} \times 10^2$, T (°C) in parentheses): 1.19 (54.6), 0.782 (39.6), 0.428 (25.5), 0.204 (10.9) (measured at 325 nm). [c] $\Delta H^{\ddagger} = 6.9$ kcal/mol and $\Delta S^{\ddagger} = -52.4$ eu, based on the following rate constants ($s^{-1} \times 10^4$, T (°C) in parentheses): 5.84 (54.6), 3.05 (39.6), 25.0 (1.86). [d] Containing 5% CH_3CN. [e] Rates higher by 25–40% were obtained with other batches of solvent.

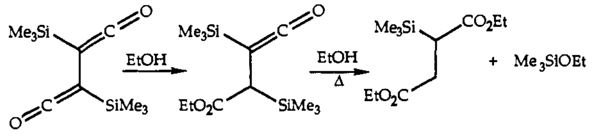
latter substrate, in which nucleophilic attack on the silicon[5c] is minimized, was included to ensure that desilylation of the products did not influence the observed rates.

The reaction of **3** (R = *t*-Bu) with H_2O/acetone proceeded similarly to form the *E* anhydride **17**, but no desilylated product was observed. The stereochemistry of **17** was established by X-ray crystallography. The chemical shift of the methine hydrogens of *E*-**17** (δ 2.68) is midway between those of *Z*-**13** (δ 2.86) and *E*-**13** (δ 2.47) and does not provide a useful criterion of the stereochemistry.



E-**17**

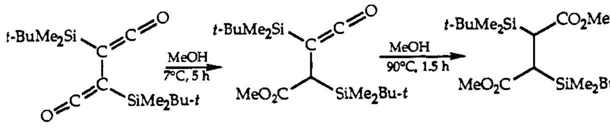
Reaction of **1** in pure EtOH for 15 min at 0 °C and evaporation of the solvent gave the monoketene **18** in 98% purity by ^1H NMR analysis. On reflux for 16 h in EtOH, **1** forms **19**, diethyl succinate, and Me_3SiOEt (eq 7).[9] Reaction of **1** with MeOH and with *i*-PrOH gave the corresponding analogues of **18**, although the isopropyl ester contained the anhydrides *Z*-**13** and **14**, evidently derived from reaction with trace amounts of H_2O.



1 **18** **19** (7)

The structure of the monoketene **18** was established by its spectroscopic data, particularly by the IR bands at 2093 (sh), 2085 (s), and 1711 (s) cm^{-1}, the characteristic ^{13}C NMR chemical shifts of the carbonyl carbon and C_β of the ketene at δ 181.11 and 10.82, respectively, the UV λ_{max} at 205 nm, and its mass spectral data, including the molecular ion at m/z 272 as 28% of the base peak.

The *tert*-butyldimethylsilyl compound **3** reacts similarly with MeOH to form the monoketone **20** and the dimethyl succinate **21** with only trace amounts of desilylated products. The monoketenyl structure of **20** was also established by its characteristic spectral properties, with C_β of the ketene at δ 9.78 in the ^{13}C NMR and the ketenyl IR band at 2085 cm^{-1}. The spectra indicated the presence of only a single isomer of **21**, but its stereochemistry has not been determined.



3 **20** **21** (8)

Rate constants for the addition of some alcohols to **1** were measured by monitoring the change in the UV absorption and are given in Table III. Further reactions occurred with rates at least 10 times less than for the initial step, and presumably correspond to the further reactions of initially formed monoketenes as in eq 7. For comparative purposes, some rates were also determined for $Me_3SiCH{=}C{=}O$ (**15**) and *t*-$BuMe_2SiCH{=}C{=}O$ (**16**) and are included in Table III. The formation of esters from the reactions of **15** and **16** with a variety of alcohols have been reported.[5d,g,h]

Discussion

The kinetics of the ring opening of cyclobutene to butadiene,[10a] and of substituent effects on this reaction,[10b–e] have been measured, as shown in Scheme I, as well as for the conversion of cyclobutenones to vinylketenes.[11] The latter species were not observed but were trapped by nucleophiles and by intramolecular cycloaddition.[11] There was only a modest increase in rate by a factor of 3 for seven solvents of widely different polarities ranging from cyclohexane to DMF for this reaction.[11] The theoretical study of the conversion of cyclobutenes to butadienes is of major

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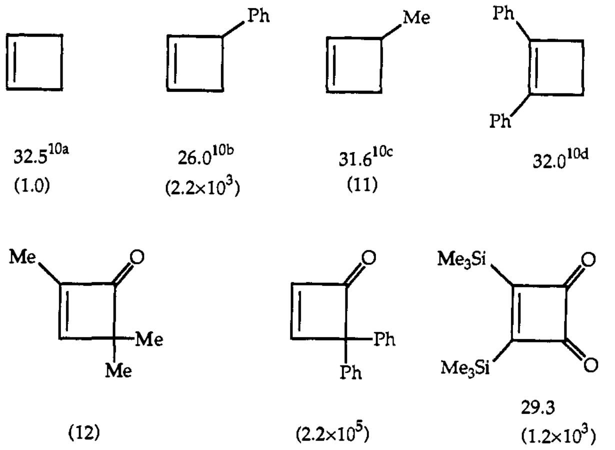
Scheme I. Substituent Effects on E_{act} (kcal/mol) and k_{rel} (at 80 °C)[a] for Conversion of Cyclobutenes to Butadienes



[a] Rates compiled in ref 11b (in parenthesis).

interest,[12] as are the [2+2] cycloadditions[13a] and dimerization[13b] of ketene and the cyclobutenone–vinylketene interconversion.[13c] Calculations predict that this latter reaction has a significant barrier, but with essentially no difference in energy between the reactants and products.[13c]

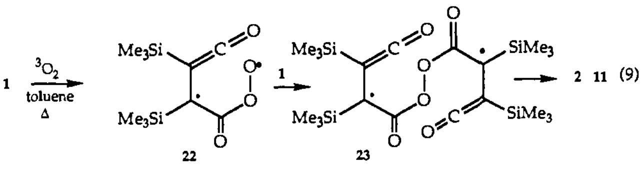
From these results and others for ring openings of cyclobutenes[10c] and cyclobutenones,[11b] the effects of a single methyl group on the double bond decreases the reactivity by a factor of 8, while a methyl or phenyl on carbons 3 or 4 increases the rates by factors of about 10 and 2000, respectively. Large effects of other groups on the 3 or 4 positions have also been observed,[10e,f] but other data for the effects of silyl groups on the rates of ring opening of cyclobutenes are not available.

A comparative study of the ring openings of these systems by *ab initio* molecular orbital calculations has been carried out,[14a] and the barrier calculated for ring opening of the parent cyclobutenedione **6** at the MP2/6-31G*//MP2/6-31G*+ZPVE level is 30.8 kcal/mol, which interestingly is close to the measured E_{act} of 29.3 kcal/mol for **2**. The corresponding calculated[14a] and experimental[10a] barriers for cyclobutene of 35.8 and 32.5 kcal/mol, respectively, are also in good agreement.

The ΔS^* values for the ring openings of **2** (–0.2 eu) and **4** (3.8 eu) are very similar to that of cyclobutene (–0.7 eu)[10c] and are also consistent with those observed for other cyclobutene ring openings.[10e] Cyclobutenedione (**6**) is one of the few cyclobutenes that is more stable than the isomeric 1,3-butadiene **3a,b**, and as reported here, this is reversed by substitution with trimethylsilyl groups. Perfluorocyclobutene is similarly more stable than perfluoro-1,3-butadiene,[10g] and the comparison of the C=CF$_2$ moiety to the C=C=O group in ketenes has been noted before.[10h]

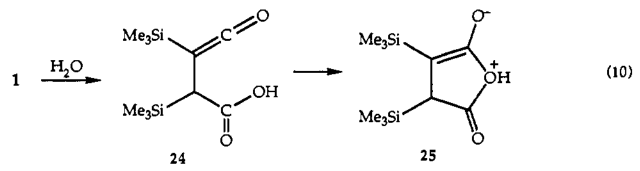
The experimentally determined stability of the bisketene **1** relative to the cyclobutenedione **2** confirms the predictions based on the molecular orbital calculations.[5a] A number of further predictions are implied by these calculations which are being subjected to further tests. The conformational properties of **1** have been the subject of a theoretical and photoelectron spectroscopy study, and this ketene is indicated to prefer a twisted almost perpendicular conformation.[14b] Such a structure is known to be favored for 2,3-bis(trimethylsilyl)-1,3-butadiene.[14c]

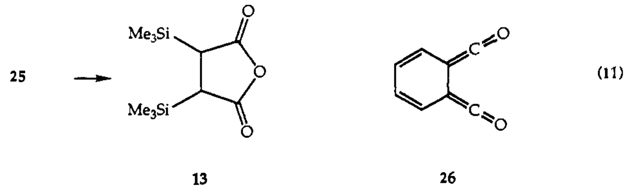
The reactions of ketenes[15] and strained alkenes[16] with O$_2$ have long been of interest and have been interpreted as involving perepoxide and diradical intermediates.[15] A diradical pathway for reaction of **1** with $^3O_2$ could involve an initial triplet diradical, **22**, followed by reaction of a second molecule of **1** to give **23**, which could lead to **11** after intersystem crossing (eq 9). The



formation of anhydrides in the reaction of bisketenes has been observed before,[3f,i] but there has been no discussion of the mechanism of these processes.

The reaction of **1** in CH$_3$CN containing H$_2$O gives the anhydrides **13**, and the rates of reaction of **1** relative to Me$_3$SiCH=C=O (**15**), the solvent isotope effect, and the dependence of the rate on the [H$_2$O] (Table II) are consistent with those measured for other ketenes assigned to react by rate-limiting nucleophilic attack of H$_2$O in the ketene plane.[5c,17] This path appears reasonable for the first step of the conversion of **1** to **13** by H$_2$O and may be represented by the process shown in eqs 10 and 11, in which the monoketene **24**, which was not detected in





these experiments, is formed initially and cyclizes rather rapidly with carboxyl participation via **25** to **13**. The cyclization could also occur from an initially formed enol of a carboxylic acid, and a similar process has been considered in the addition of MeOH to **26**.[3h]

The reactivity of **1** toward alcohols and the much lower reactivity of the monoketene **18** formed initially from ethanol may also be interpreted analogously to previous studies of the reactivity of Me$_3$SiCH=C=O (**15**)[5c] and other ketenes with H$_2$O[17] and alcohols.[18] Thus Me$_3$SiCH=C=O has significant thermodynamic ground-state stabilization due to the presence of the Me$_3$Si group compared to ketenes with only alkyl or hydrogen substituents,[5a] and **18** enjoys the same stabilization. In addition, **18** has the bulky substituent EtO$_2$CCHSiMe$_3$ at C$_\beta$, which will sterically hinder reaction with nucleophiles,[17] and this causes **18**

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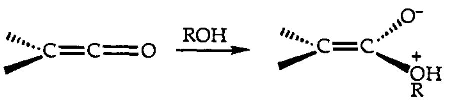
to be significantly less reactive than is $Me_3SiCH{=}C{=}O$. As discussed above, there is evidence that the ground state of **1** is destabilized due to the bisketene structure, and the transition state for nucleophilic addition to **1** is also destabilized, by steric crowding. The net result is that **1** and $Me_3SiCH{=}C{=}O$ have similar reactivities toward nucleophiles. Partial desilylation occurs in the reaction of $Me_3SiCH{=}C{=}O$ with alcohols,[5c] and this also occurs for **18** (eq 7).

The activation parameters for the bisketene **1** and for *t*-$BuMe_2SiCH{=}C{=}O$ (**16**) in 50% H_2O/CH_3CN (Table II) are $\Delta H^* = 11.7$ and 15.5 kcal/mol, respectively, and $\Delta S^* = -27.6$ and -20.3 eu, respectively, and in EtOH (Table III), these are $\Delta H^* = 5.7$ and 6.9 kcal/mol, respectively, and $\Delta S^* = -50.0$ and -52.4 eu, respectively. The parallel between the activation parameters for the two ketenes is indicative of a parallel between the mechanisms as well. Previous kinetic studies of alcohol additions to ketenes[18] have involved dilute solutions of alcohols in other solvents and not neat alcohols, but these other studies are also characterized by large negative entropies of activation, just as for **1** and **16**. The results are all consistent with rate-limiting nucleophilic attack on the carbonyl carbon, with assistance by additional H_2O or alcohol molecules (eq 12).[17]



(12)

The differing rates of addition of water and various alcohols to **1** appear to reflect the effects both of solvent polarity and of solvent nucleophilicity on the reactivity. This result is also consistent with the proposed[17] interpretation that hydroxylic nucleophiles react with ketenes by in-plane approach to give polar transition states, and hence the rates will depend upon both solvent polarity and nucleophilicity.

Quantitative correlation of the rates may be done using the Winstein–Grunwald equation (eq 13), in which the parameters N and Y are measures of the solvent nucleophilicity and ionizing power, respectively.[19] This equation is usually utilized for

$$\log k/k_o = lN + mY \qquad (13)$$

solvolysis, and the N and Y values are specific to leaving groups such as tosylate.[19] However the form of the equation is suitable for application to nucleophilic solvent addition to the carbonyl group of a ketene, and solvolysis parameters may be used, as these are the only ones available.

The best fit of the data for **1** (Table III) was obtained using N_T parameters as reported by Kevill and Anderson,[19c] which are suggested to be superior to previous values[19b,c] and Y_{OTs} values.[19a] The correlation does not include the rates for *n*-hexanol and *tert*-butyl alcohol, for which N and Y values are not available, and gives $l = 0.87 \pm 0.13$, $m = 0.61 \pm 0.10$, intercept, -0.24 ± 0.41, and a correlation coefficient $r = 0.940$ (Figure 2). If the 50 and 70% TFE points are deleted, the l, m, intercept, and r values change to 0.88 ± 0.04, 0.67 ± 0.04, -0.06 ± 0.14, and 0.995, respectively. As noted in Table III, the data for the TFE solvents are somewhat variable. Exclusion of these values has little effect on the l and m values, while changing the intercept and greatly improving the correlation coefficient.

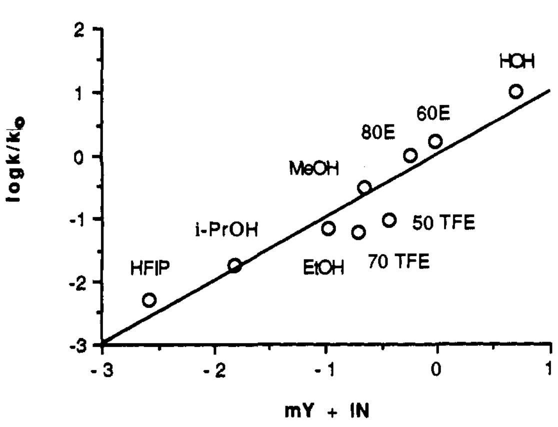


Figure 2. Winstein–Grunwald correlation (eq 13) for **1**.

The correlation is surprisingly good, especially considering that the N and Y values are derived for solvolysis, a quite different process. The large l value shows the large nucleophilic component expected for solvent addition as in eq 12, while the sizeable m value shows there is also a major polar effect on the reaction, also consistent with eq 12.

This method of the correlation of nucleophilic attack by the solvent on unsaturated carbon using the solvent nucleophilicity and polarity parameters may have greater applicability to related processes. There is widespread interest in such reactions as additions to carbon–carbon double bonds,[20a,b] solvolysis of acyl halides,[20c] and nucleophilic attack on carbonyl groups.[20d]

Tests of the application of eq 13 to monoketenes such as **15** and **16** will be made when a more complete set of data is obtained. From the results available (Table III), there is a progressive increase in the reactivity of **1** relative to the monoketenes as the overall reactivity decreases, so different correlations by eq 13 for bisketenes and monoketenes are expected.

Summary

Stable and persistent bis(silyl)-substituted bisketenes have been prepared by ring opening of cyclobutenediones, and their stability is as predicted by *ab initio* molecular orbital calculations. The reactions of these bisketenes reveal that anhydride products are formed on reaction with H_2O or $^3O_2$, whereas reactions with alcohols proceed by selective addition to one ketene moiety to give isolable monoketenes, which react by slower processes to give succinate esters. The rates of reaction of bisketenes with nucleophilic solvents are successfully correlated with parameters for the solvent nucleophilicity and ionizing power. The rich chemistry of these and related bisketenes is being actively pursued in this laboratory.

Experimental Section

General Procedures. Radial chromatography was carried out on silica gel plates using a Chromatotron from Harrison Research. Gas chromatography was performed using 1 cm × 3 m OV-17 columns, unless indicated otherwise. Reagents and solvents were obtained from Aldrich and used as supplied unless indicated. Trifluoroethanol (TFE) was distilled from phosphorus pentoxide, and hexafluoroisopropyl alcohol (HFIP) was dried over 3-Å molecular sieves and distilled. X-ray crystal structures were determined by Dr. Alan Lough at the University of Toronto. Elemental analyses were by Galbraith Laboratories.

Activated Zinc. Water, acetone, and diethyl ether were degassed by bubbling in N_2 for 30 min. Zinc dust (Fisher, 20 g, 0.31 mol) under N_2 in a sintered glass crucible was washed with 20 mL of H_2O and then with two 15-mL portions of a degassed solution of $CuSO_4{\cdot}5H_2O$ (4.64 g, 0.0186

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mol) in 30 mL of H_2O with vigorous stirring. After 2 min, the $CuSO_4$ solution was removed by suction and the zinc was further washed twice each with 20-mL portions of degassed H_2O, acetone, and diethyl ether, and was dried at 1 Torr and 100 °C for 4 h and stored under N_2.

2,3-Bis(trimethylsilyl)-4,4-dichlorocyclobut-2-enone (9). A 200-mL flask fitted with a dropping funnel and magnetic stirrer was heated and evacuated several times under argon. Bis(trimethylsilyl)acetylene (9.6 g, 56 mmol) was added, followed by 50 mL of ether and 10 g of activated zinc. Through the dropping funnel was added trichloroacetyl chloride (21.8 g, 120 mmol) in 30 mL of dimethoxyethane over 1 h at 25 °C, and the solution was stirred for 3 days. The reaction mixture was filtered through celite which was rinsed with pentane, and the filtrate was washed with H_2O and $NaHCO_3$, dried over $MgSO_4$, and evaporated to give 16.8 g of a brownish oil. Radial chromatography (7% EtOAc in hexane, R_f = 0.7) of a 100-mg portion of the crude product afforded 82 mg (88%) of **9**, mp 35.0–35.5 °C, after recrystallization from pentane. ^{1}H NMR ($CDCl_3$): δ 0.278, 0.421. ^{13}C NMR ($CDCl_3$): δ −1.64, −1.06, 96.8, 169.1, 184.1, 196.7. IR (film): 1776 cm^{-1}. EIMS: m/z 284, 282, 280 (20, M$^+$), 197, 195 (20), 174, 172 (25), 131, 129 (35), 73 (100, Me_3Si^+). HRMS: m/z calcd for $C_{10}H_{18}Cl_2OSi_2$, 280.0273; found, 280.0283. Direct crystallization of the remaining crude product from cold pentane gave a first crop of **9** (2.1 g, 18%).

3,4-Bis(trimethylsilyl)cyclobut-3-ene-1,2-dione (2). To concentrated H_2SO_4 (3 mL) in a vigorously stirred Erlenmeyer flask in a water bath (55 °C) was added crude **9** (0.95 g, 3.36 mmol), the solution was stirred for 12 min, and one quarter of the mixture was quenched with ice and extracted three times with ether. The combined ether extracts were washed with $NaHCO_3$ and H_2O, dried over $MgSO_4$, and evaporated. The product was chromatographed on silica gel (7% EtOAc in hexane, R_f = 0.5) to give **2** (0.14 g, 0.619 mmol, 73%) as a yellow solid, mp 50–52°, after recrystallization from pentane. ^{1}H NMR ($CDCl_3$): δ 0.370. ^{13}C NMR ($CDCl_3$): δ −1.57, 201.97, 217.09. IR (solid film): 1769 cm^{-1}. UV (pentane): λ_{max} 222 (ϵ 14 000), 268 (sh), 354 (ϵ 37) nm. EIMS: m/z 226 (M$^+$, 39), 170 (M$^+$ − C_2O_2, 17), 155 (M$^+$ − CH_3, C_2O_2, 100), 97 (18), 73 (59). HRMS: m/z calcd for $C_{10}H_{18}O_2Si_2$, 226.0845; found, 226.0844. Anal. Calcd: C, 53.05; H, 8.02. Found: C, 52.72; H, 8.11. The yield of **2** decreased with longer reaction times.

2,3-Bis(trimethylsilyl)buta-1,3-diene-1,4-dione (1). A sample of **2** (20 mg) in $CDCl_3$ (0.6 mL) was degassed in a tube by three vacuum freeze–thaw cycles, and the tube was sealed under N_2. Heating at 100 °C for 60 min gave **1** as the only detectable product. ^{1}H NMR ($CDCl_3$): δ 0.206. ^{13}C NMR ($CDCl_3$): δ −0.94 (Me_3Si), 5.62 (sp^2 C), 181.83 (sp C). IR (film): 2084 cm^{-1}. UV (hexane): λ_{max} 376 (ϵ 110), 325 (ϵ 250), 248 (sh, ϵ 770) nm. EIMS: m/z 226 (M$^+$, 28), 170 (M$^+$ − C_2O_2, 14), 155 (M$^+$ − CH_3, C_2O_2, 100), 97 (17), 73 (54). HRMS: m/z calcd for $C_{10}H_{18}O_2Si_2$, 226.0845; found, 226.0836. The preparation of **1**, mp 10 °C, was also done by VPC by injecting samples of **2** in hexane onto a 3 m × 1 cm OV-17 column at 130 °C (injector temperature 250 °C) and collecting the product with a retention time 7 min and also by heating **2** (18 mg) in degassed hexane (1.3 mL) for 80 min at 100 °C.

Photolysis of 2. A degassed solution of **2** (0.02 M) in $CDCl_3$ in a sealed NMR tube was irradiated with 350-nm light at 5 °C. After 12 min, the ^{1}H NMR showed 71% of the diketene **1**, 18% of residual **2**, and $Me_3SiC{\equiv}CSiMe_3$ absorbing at δ 0.170 (11%). After irradiation for 48 min, the peak for **1** constituted 86% of the total, that at 0.170 still constituted 11%, and others were 3%.

Kinetics of Ring Opening. Solutions of **2** or **4** (0.3 M) in $CDCl_3$ in NMR tubes were degassed by three vacuum freeze–thaw cycles, and the sealed tubes were heated by direct contact with the vapors of vigorously refluxing liquids in an insulated glass tube protected from light and equipped with a thermometer and condenser. The liquids employed were H_2O (99 °C), CH_3CN (80 °C), the 2.26/1 (w/w) azeotropic mixture of H_2O/dioxane (87 °C), and hexane (68 °C). The tubes were removed at intervals over three half-lives for measurement of the ^{1}H NMR spectra. After heating for 10 half-lives only **1** could be detected by ^{1}H NMR. The compositions of the mixtures were determined from the relative integrations of the signals for reactants and products, and no other signals were detected.

Reaction of 1 with Oxygen. Oxygen was bubbled into a solution of **1** (0.139 g, 0.615 mmol) in refluxing toluene for 18 h. Then the toluene was evaporated and the residue separated by radial chromatography to give **11** (14%), mp 58–59.5 °C (^{1}H NMR ($CDCl_3$): δ 0.390. ^{13}C NMR ($CDCl_3$): δ 0.03, 161.6, 168.5. IR ($CDCl_3$): 1830 (w), 1814 (w), 1752, 1747 (d, s) cm^{-1}. CIMS: m/z 243 (M$^+$ + 1). EIMS: m/z 227 (M$^+$ − CH_3, 11), 155 (M$^+$ + H − TMS, 100), 73 (Me_3Si^+, 47). HRMS: m/z calcd for $C_{10}H_{18}O_3Si_2$ − CH_3 (M$^+$ − CH_3), 227.0560; found, 227.0567), and **12** (7%) as an oil (^{1}H NMR ($CDCl_3$): δ 0.345 (9), 6.985 (1). ^{13}C NMR ($CDCl_3$): δ −2.3, 142.8, 155.6, 164.7, 167.5. IR ($CDCl_3$): 1855 (w), 1816 (w), 1764 (s) cm^{-1}. CIMS: m/z 171 (M$^+$ + 1, 100), 155 (M$^+$ − CH_3, 72). HRMS: m/z calcd for $C_6H_7O_3Si$ (M$^+$ − CH_3), 155.0164; found, 155.0152).

(*E*)-2,3-Bis(trimethylsilyl)succinic Anhydride (*E*-13). The bisketene **1** (20 mg, 0.088 mmol) was dissolved in 0.7 mL of $CDCl_3$ in an NMR tube, one drop of H_2O (ca. 50 mg, 2.8 mmol) was added, and the heterogeneous mixture was shaken vigorously for 1 min and then left at room temperature. The decrease of the ^{1}H NMR signal of **1** was monitored until it had disappeared (15 days), at which time the mixture contained by ^{1}H NMR analysis 90% ***E*-13**, 1% ***Z*-13**, 2% **11**, and 7% **12**. The top aqueous layer was removed with a pipet, the organic layer was filtered through a pad of anhydrous $MgSO_4$ and concentrated to 0.2 mL, and 0.2 mL of ether and 0.3 mL of pentane were added. After 1 day at −20 °C, colorless crystals of ***E*-13** (2 mg, 0.0082 mmol, 9%) were collected, mp 97–99 °C. ^{1}H NMR ($CDCl_3$): δ 0.198 (s, 18, Me_3Si), 2.470 (s, 2 C*H*TMS). ^{13}C NMR ($CDCl_3$): δ −3.51, 35.78, 173.59. IR ($CDCl_3$): 1835 (w), 1818 (w), 1753 (s), cm^{-1} (C=O). EIMS: m/z 244 (M$^+$, 7), 215 (7, M$^+$ − H, CO), 201 (25, M$^+$ − CH_3, CO), 173 (23), 147 (99), 73 (100). HRMS: m/z found, 244.0948.

(*Z*)-2,3-Bis(trimethylsilyl)succinic Anhydride (*Z*-13). The bisketene **1** (164 mg, 0.78 mmol) was added to 3.6 mL of acetone containing H_2O (360 μL, 20 mmol) and kept 30 min at 22 °C. The solution was poured into ice cold ether over solid anhydrous $CaSO_4$, left for 10 min, filtered, and evaporated. The residue was triturated with pentane, giving solid succinic anhydride (**14**), and evaporation of the pentane gave ***Z*-13** (0.028 g, 0.115 mmol, 15%) as white needles, mp 73–74 °C. ^{1}H NMR ($CDCl_3$): δ 0.279 (s, 18 Me_3Si), 2.856 (s, 2, C*H*TMS). ^{13}C NMR ($CDCl_3$): δ −0.946, 37.03, 173.65. IR ($CDCl_3$): 1827 (w), 1758 (s) cm^{-1} (C=O). EIMS: m/z 244 (M$^+$, 6), 215 (8, M$^+$ − H, CO), 201 (40, M$^+$ − CH_3, CO), 173 (26), 147 (100), 133 (26), 73 (81). HRMS: m/z calcd for $C_{10}H_{20}O_3Si_2$, 244.0951; found, 244.0941.

In experiments in which the entire product was collected and examined by ^{1}H NMR, the ratio ***Z*-13**/***E*-13** was 5/1 after 5 min, but the conversion of both to succinic anhydride was observed, with ***E*-13** reacting more rapidly.

3-Carboethoxy-2,3-bis(trimethylsilyl)prop-1-en-1-one (18). The bisketene **1** (0.020 g, 0.088 mmol) was dissolved in 0.7 mL of cold EtOH and kept 20 min at 0–5 °C. The ethanol was evaporated while the solution warmed to room temperature, giving **18** (98% pure). ^{1}H NMR ($CDCl_3$): δ 0.143 (s, 9, Me_3Si), 0.151 (s, 9, Me_3Si), 1.266 (t, 3, J = 7.12 Hz, CH_3), 1.962 (s, 1, CH), 4.155 (q, 2, J = 7.12 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ −2.27, −0.91, 10.82, 14.38, 30.20, 60.80, 175.05, 181.11. IR ($CDCl_3$): 2093 (sh), 2085 (s), 1711 (s) cm^{-1}. UV (CH_3CN/EtOH, 5/1): λ_{max} 205 nm. EIMS: m/z 272 (M$^+$, 28), 243 (M$^+$ − Et, 38), 147 (35), 73 (TMS$^+$, 100). HRMS m/z calcd for $C_{12}H_{24}O_3Si_2$ (M$^+$), 272.1263; found, 272.1264. Refluxing for **1** for 16 h in EtOH, evaporation of the solvent, and examination by ^{1}H NMR indicated the presence of diethyl succinate and diethyl 2-(trimethylsilyl)succinate (**19**) in a ratio of 1/3. The latter product was separated by VPC. ^{1}H NMR ($CDCl_3$): 0.100 (s, 9, Me_3Si), 1.251 (t, 6, J = 7.1 Hz, CH_3), 2.34 (dd, 1, J = 16.7, 3.3 Hz), 2.48 (dd, 1, J = 11.4, 3.3 Hz), 2.8 (dd, 1, J = 16.7, 11.4 Hz), 4.13 (q, 4, J = 7.13 Hz). ^{13}C NMR ($CDCl_3$): δ −2.86, 14.1, 14.4, 31.3, 32.9, 60.0, 60.6, 172.9, 174.5. IR (film): 1758, 1733, 1722, 1715. EIMS: m/z 246 (M$^+$, 1), 201 (M$^+$ − OEt, 39), 173 (M$^+$, Me_3Si, 73), 129 (41), 103 (51), 73 (Me_3Si^+, 95). HRMS: m/z calcd for $C_{10}H_{19}O_4Si$ (M$^+$ − CH_3), 231.1053; found, 231.1048.

Similar reaction of **1** (0.010 g, 0.044 mol) with 0.5 mL of cold MeOH for 5 min at 0 °C followed by addition of 1 mL of pentane and evaporation gave as the only observed product 3-carbomethoxy-2,3-bis(trimethylsilyl)prop-1-en-1-one. ^{1}H NMR ($CDCl_3$): δ 0.137 and 0.147 (each s, 9, Me_3Si), 1.989 (s, 1, CH), 3.692 (s, 3, MeO). ^{13}C NMR ($CDCl_3$): δ −2.23, −2.19, 10.85, 29.72, 51.90, 175.44, 180.94. IR (CH_2Cl_2): 2091 (sh), 2085 (s), 1716 (s). EIMS: m/z 258 (M$^+$, 25), 243 (M$^+$ − Me, 17), 215 (28), 154 (63), 73 (Me_3Si^+, 100). HRMS: m/z calcd for $C_{11}H_{22}O_3Si_2$ (M$^+$), 258.1108; found, 258.1113. Similar reaction of **1** (0.010, 0.044 mmol) with 0.5 mL of cold *i*-PrOH for 90 min at 7 °C gave a mixture in a 1/1.4/1 ratio as identified by ^{1}H NMR of succinic anhydride, ***Z*-13**, and 3-carboisopropoxy-2,3-bis(trimethylsilyl)prop-1-en-1-one. ^{1}H NMR ($CDCl_3$): δ 0.144 and 0.147 (each s, 9, Me_3Si), 1.23 and 1.25 (each d, 3, Me of *i*-Pr), 1.916 (s, 1, CH), 5.01 (m, 1, Me_2C*H*). ^{13}C NMR ($CDCl_3$): δ −2.14, −0.85, 10.96, 22.03, 30.39, 68.26, 174.45, 181.05. IR (CH_2Cl_2): 2084 (s) 1720 (br). EIMS: m/z 286 (M$^+$, 6), 243 (M$^+$ − *i*-Pr, 30), 147 (32), 73 (Me_3Si^+, 100). HRMS: m/z calcd for $C_{12}H_{26}O_3Si$ (M$^+$), 286.1421; found, 286.1410.

2,3-Bis(*tert*-butyldimethylsilyl)-4,4-dichlorocyclobut-2-enone (10). Reaction of bis(*tert*-butyldimethylsilyl)acetylene (8.6 g, 33.8 mmol)[21] with dichloroketene generated from a Zn–Cu couple (*vide infra*) and purification of the product by radial chromatography on silica gel gave **10** (10.4 g, 28.5 mmol, 84%). ^{1}H NMR (CDCl$_3$): δ 0.261 (s, 6, Me$_2$), 0.410 (s, 6, Me$_2$), 0.933 (s, 9, *t*-Bu), 1.033 (s, 9, *t*-Bu). ^{13}C NMR (CDCl$_3$): δ −4.98, −4.09, 16.91, 17.45, 26.85, 27.37, 96.46, 169.98, 184.77, 194.74. IR (film): 1775 cm^{-1} (C=O). EIMS: *m/z* 368, 366, 364 (M$^+$, 3, 12, 15), 279 (43), 195 (35), 151 (44), 73 (Me$_3$Si$^+$, 100), 57 (*t*-Bu$^+$, 28). HRMS: *m/z* calcd for $C_{14}H_{30}Cl_2OSi_2$, 364.1214; found, 364.1212.

3,4-Bis(*tert*-butyldimethylsilyl)cyclobut-3-ene-1,2-dione (4). Reaction of **10** (0.46 g, 1.25 mmol) in concentrated H$_2$SO$_4$ (1 mL) at 54 °C for 20 min and workup as for **2** gave a yellow solid which by ^{1}H NMR analysis contained **4**, **10**, and other unidentified products. Purification by radical chromatography gave **4** (0.170 g, 0.55 mmol, 44%), mp 43.5–45.0 °C. ^{1}H NMR (CDCl$_3$): δ 0.34 (s, 12, 2Me$_2$), 0.97 (s, 18, 2*t*-Bu). ^{13}C NMR (CDCl$_3$): δ −5.13, 17.31, 26.74, 202.08, 217.28. IR (film): 1766 cm^{-1} (C=O). UV: λ_{max}(hexane) 356 (ϵ 27), 224 (ϵ 6900) nm. EIMS: *m/z* 310 (M$^+$, 100), 294 (M$^+$ − O, 19), 197 (75), 171 (27), 155 (54, $^1/_2$M$^+$), 73 (73, Me$_3$Si$^+$). HRMS: *m/z* calcd for $C_{16}H_{30}O_2Si_2$, 310.1784; found, 310.1776.

2,3-Bis(*tert*-butyldimethylsilyl)buta-1,3-diene-1,4-dione (3). Heating of **4** in CDCl$_3$ in a sealed tube for 60 min at 100 °C gave **3** as the only product. Pure **3** was obtained as a yellow liquid by heating crystalline **4** in a degassed sealed tube for 1.5 h. ^{1}H NMR (CDCl$_3$): δ 0.172 (s, 12), 0.956 (s, 18). ^{13}C NMR (CDCl$_3$): δ −5.42, 4.27, 18.70, 26.38, 182.24. IR (CDCl$_3$): 2076 cm^{-1}. UV (hexane): λ_{max} 400 (ϵ 88), 326 (ϵ 260) nm. EIMS: *m/z* 310 (M$^+$, 81), 197 (MH$^+$ − 2C$_4$H$_9$, 100), 171 (42), 155 (81), 73 (78). HRMS: *m/z* calcd for $C_{16}H_{30}O_2Si_2$, 310.1784; found, 310.1796. Photolysis of **4** as for **2** showed the formation of **3** and the parent alkyne in a ratio of 92/8.

(*E*)-2,3-Bis(*tert*-butyldimethylsilyl)succinic Anhydride (*E*-17). Diketone **4** (20 mg, 0.064 mmol) dissolved in 1.5 mL of hexane in a glass tube was purged with N$_2$ for 5 min and the tube was sealed and heated at 90 °C for 40 min. Evaporation of the solvent gave a yellow oil analyzed by ^{1}H NMR as containing the bisketene **3** (83%) and residual **4** (17%). To this was added 10 mL of 1/1 H$_2$O/acetone, and the resulting emulsion was stirred at room temperature overnight. Acetonitrile (0.8 mL) was added, the mixture was stirred 1 h more and extracted with CH$_2$Cl$_2$ (2 × 6 mL), and the organic extracts were dried over MgSO$_4$ and evaporated. ^{1}H NMR analysis showed *E*-**17** (55%), **4** (17%), **3** (10%), and a few unidentified products. In a separate experiment, a drop of H$_2$O was added to **4** (7.1 mg, 0.023 mmol) in 0.7 mL of CDCl$_3$ and the heterogeneous mixture was kept at room temperature for 38 days, dried over MgSO$_4$, and evaporated. Radial chromatography afforded colorless crystals of *E*-**17** (5.1 mg, 0.0156 mmol, 68%) which on recrystallization from petroleum ether at −25 °C gave mp 70.5–71.5 °C. ^{1}H NMR (CDCl$_3$): δ 0.14 (s, 6H, Me$_2$), 0.15 (s, 6H, Me$_2$), 1.00 (s, 18, 2*t*-Bu), 2.68 (s, 2, 2CH). ^{13}C NMR (CDCl$_3$): δ −7.45, −6.48, 17.90, 26.69, 34.42, 173.92. IR (CDCl$_3$): 1825 (m), 1756 (s) cm^{-1}. EIMS: *m/z* 328 (M$^+$, 16), 243 (20), 147 (25), 73 (Me$_3$Si$^+$, 100), 59 (17, *t*-Bu$^+$). HRMS: *m/z* calcd for $C_{16}H_{32}O_3Si_2$, 328.1890; found, 328.1895. The stereochemistry of *E*-**17** was established by X-ray crystallography, but the quality of the crystals caused sufficient uncertainties in the structural parameters to preclude quantitative comparisons to the structure of *E*-**13**.

3-Carbomethoxy-2,3-bis(*tert*-butyldimethylsilyl)prop-1-en-1-one (20). Bisketene **3** was prepared by heating (100 °C, 50 min) diketone **4** (10 mg, 0.032 mmol) in a sealed tube, followed by evaporation of the hexane. Reaction of **3** with 0.5 mL of MeOH for 5 h at 7 °C followed by evaporation of the solvent gave **20** containing 5% of the anhydride **17** as determined by ^{1}H NMR. **20**: ^{1}H NMR (CDCl$_3$) δ 0.078 (s, 3), 0.111 (s, 3), 0.115 (s, 3), 0.137 (s, 3), 0.892 (s, 9), 0.938 (s, 9), 2.123 (s, 1), 3.677 (s, 3); ^{13}C NMR (CDCl$_3$) δ −6.89, −5.94, −5.60, 9.78 (C$_\beta$), 17.77, 19.04, 26.32, 26.56, 51.73, 176.09, 181.27; IR (CDCl$_3$) 2085 (s), 1720 (s) cm^{-1}; EIMS *m/z* 342 (M$^+$, 23), 257 (52), 196 (40), 73 (100). HRMS: *m/z* calcd for $C_{17}H_{34}O_3Si_2$, 342.2047; found, 342.2054. Attempts to remove the **17** present by chromatography were unsuccessful.

Dimethyl 2,3-Bis(*tert*-butyldimethylsilyl)succinate (21). Reaction of **3** (99 mg, 0.319 mmol) in MeOH at 90 °C for 100 min followed by evaporation of the MeOH and radial chromatography on silica gel gave *E*-**17** (11 mg, 11%) and **21** (100 mg, 84%), mp 78.5–80.5 °C. ^{1}H NMR (CDCl$_3$): δ −0.011 (s, 6), 0.145 (s, 6), 0.924 (s, 18), 2.277 (s, 2), 3.635 (s, 6). ^{13}C NMR (CDCl$_3$): δ −6.14, −6.04, 17.87, 26.85, 30.60, 50.99, 174.85. IR (film): 1733 (s). EIMS: *m/z* 374 (M$^+$, 3), 317 (M$^+$ − *t*-Bu, 15), 289 (16), 143 (39), 389 (41), 73 (100). HRMS: *m/z* calcd for $C_{18}H_{38}O_4Si$, 374.2309; found, 374.2299. Attempts to isolate **19** by VPC (OV-101 column, 150 °C) instead gave as the major product dimethyl 2-(*tert*-butyldimethylsilyl)succinate. ^{1}H NMR (CDCl$_3$): δ 0.005 and 0.074 (each s, 3, Me), 0.927 (s, 9, *t*-Bu), 2.41 (dd, 1, *J* = 17.1, 2.7 Hz), 2.60 (dd, 1, *J* = 12.1, 2.7 Hz), 2.96 (dd, 1, *J* = 17.1, 12.1 Hz), 3.67 and 3.68 (each s, 3, Me). ^{13}C NMR (CDCl$_3$): δ −6.83, −6.71, 17.55, 26.54, 30.02, 32.20, 51.28, 51.87, 173.52, 175.57. IR (CDCl$_3$): 1716 cm^{-1} (C=O).

Hydrolysis of (*tert*-Butyldimethylsilyl)ketene (16). The ketene was prepared from *t*-BuMe$_2$SiC≡COEt as reported[5h] and showed λ_{max} (CH$_3$CN) 305 nm (ϵ 31) with a shoulder at 206 nm (ϵ 2.4 × 10^3). The ketene (26 μL) was placed in a solution of 400 μL of CH$_3$CN and 100 μL of H$_2$O for 18 h at 25 °C. The solution was poured into water and extracted four times with ether. The ether layer was washed with saturated NaCl, dried over CaSO$_4$, and evaporated to give (*tert*-butyldimethylsilyl)acetic acid, mp 72–73.5 °C. ^{1}H NMR (CDCl$_3$): δ 0.11 (s, 6, Me$_2$), 0.92 (s, 9, *t*-Bu), 1.92 (s, 2, CH$_2$). IR (CDCl$_3$): 3400–2800 cm^{-1} (OH), 1686 cm^{-1} (C=O). EIMS: *m/z* 159 (M$^+$ − CH$_3$), 157 (5, M$^+$ − OH), 117 (73, M$^+$ − *t*-Bu), 75 (100, Me$_2$SiOH). HRMS: *m/z* 159.0840 (M$^+$ − CH$_3$ requires 159.0841).

Reaction of 16 with Hexafluoroisopropyl Alcohol (HFIP). Ketene **16** (25 μL) freshly purified by VPC was added to 1 mL of dry HFIP, and after 2 h at room temperature, the sample was kept at 0 °C for 3 days. The solvent was evaporated and the product identified as 1,1,1,3,3,3-hexafluoro-2-propyl (*tert*-butyldimethylsilyl)acetate. ^{1}H NMR (CDCl$_3$): δ 0.092 (s, 6, SiMe$_2$), 0.910 (s, 9, *t*-Bu), 2.074 (s, 2, CH$_2$), 5.763 (septet, 1, $J_{^1H-^{19}F}$ = 6.3 Hz, CH). IR (CDCl$_3$): 1754 cm^{-1} (C=O). CIMS: *m/z* 309 (0.5, M$^+$ − CH$_3$), 267, (23, M$^+$ − C$_4$H$_9$), 157 (11), 129 (31), 77 (100). HRCIMS: *m/z* calcd for $C_{11}H_{19}O_2SiF_6$ (MH$^+$), 325.1054; found, 325.1059.

Ethyl (*tert*-Butyldimethylsilyl)acetate. Ketene **16** (25 μL) was added to 0.5 mL of EtOH and left 18 h at room temperature. The solvent was evaporated and the ester purified by VPC (column 130 °C, retention time 22 min). ^{1}H NMR (CDCl$_3$): δ 0.070 (s, 6), 0.91 (s, 9), 1.24 (t, 3, *J* = 7.2 Hz), 1.88 (s, 2), 4.09 (quartet, 2, *J* = 7.2 Hz). IR (CDCl$_3$): 1711 cm^{-1} (C=O). EIMS: *m/z* 157 (20, M$^+$ − EtO), 145 (49, M$^+$ − *t*-Bu), 103 (100), 73 (39), 75 (73), 59 (24). HRMS: *m/z* calcd for $C_9H_{19}O_2Si$ (M$^+$ − CH$_3$), 187.1154, found, 187.1158.

Kinetics of Ketene Solvolysis. The rates of reaction were measured by following previous methodology of injecting 4 μL of a 0.08 M solution of the bisketene **1** into 1.2 mL of the reaction solvent in a UV cell and observing the decrease in the absorption at 210 or 390 nm, while for **15** and **16**, 5 μL of 0.6 or 0.3 M solutions were similarly observed at 204 or 307 nm, respectively. The rates in 100% EtOH were very sensitive to the method of drying the EtOH, and the rates reported were measured in anhydrous EtOH from Aldrich and are the lowest observed. Activation parameters in EtOH (Table III) were obtained from rates in the same batch of EtOH measured in the same series of experiments. Reproducible rates were not obtained in pure TFE, and rates measured in 50 and 70% TFE from a different batch of purified TFE were 25 and 40% higher, respectively, than those reported in Table III.

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