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Disilanylketenes and -bisketenes

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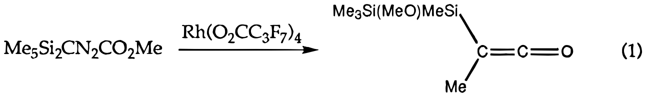
Pyrolysis of $Me_5Si_2C{\equiv}COEt$ (**5**) and $(SiMe_2C{\equiv}COEt)_2$ (**6**), prepared by reaction of $EtOC{\equiv}CLi$ with Me_5Si_2Cl and $ClMe_2SiSiMe_2Cl$, respectively, at 180 °C gave $Me_5Si_2CH{=}C{=}O$ (**1**), and $(SiMe_2CH{=}C{=}O)_2$ (**2**), respectively, which are long lived and were completely characterized by spectroscopic means. The novel 1,6-bisketene $(CH_2SiMe_2CH{=}C{=}O)_2$ (**3**) was prepared similarly. The UV spectra of **1**−**3** and the known $(Me_3Si)_2C{=}C{=}O$ (**4**) show longer wavelength absorption for the disilanylketenes, attributed to a lowering of the π^* orbital by interaction with the Si−Si σ^* orbital, while shifts to shorter wavelength in $Me_3SiCH{=}C{=}O$ and **4** compared to alkylketenes are attributed to a raising of the π^* level by the C−Si σ orbital. Isodesmic comparisons using *ab initio* molecular orbital calculated energies indicate that the Si_2H_5 substituent is essentially equal to the SiH_3 group in ketene-stabilizing ability, while $(SiH_2CH{=}C{=}O)_2$ is only destabilized by 0.6 kcal/mol compared to $SiH_3CH{=}C{=}O$. The rates of hydration of **1** and **2** exceed that of **3** by factors of 2−4, while **3** has a reactivity similar to that of $Me_3SiCH{=}C{=}O$. By contrast theoretical and experimental studies of $(Me_3Si)_2C{=}C{=}O$ (**4**) reveal that the effects of the two silyl groups on the stability and spectra are largely additive but that the second Me_3Si group greatly lowers the reactivity in both neutral and acid catalyzed hydration. This ketene ranks with $t\text{-}Bu_2C{=}C{=}O$ among the least reactive known in hydration, a property attributed to steric inhibition to nucleophilic attack and ground-state stabilization of the ketene by the silyl substituents.

The extraordinary stability of silyl-substituted ketenes was first reported by Shchukovskaya *et al*, in 1965,[1a] and since that time, these species have been widely studied[1−3] and their chemistry has been reviewed.[3a] Our own studies of silylketenes have dealt with kinetic studies of their hydration reactivity,[2a] theoretical studies of the origin of the stabilizing effect of silicon,[2b,c] their ^{13}C, ^{17}O, and ^{29}Si NMR spectra,[2d] long-lived silicon-substituted allenylketenes,[2e] and silylated 1,2- and 1,3-bisketenes and polyketenes.[3]

There have been extensive studies of disilanes[4] but few reports of disilanylketenes.[5] These include the isolation of a disilanylketene from the rhodium heptafluorobutyrate catalyzed reaction of a diazoester as shown in eq 1,[5a] and the formation of disilanylketenes



$$Me_5Si_2CN_2COR \xrightarrow[-N_2]{h\nu} Me_5Si_2CR{=}C{=}O \xrightarrow{MeOH} Me_5Si_2CHRCO_2Me \qquad (2)$$

$Me_5Si_2CH{=}C{=}O$ **1**

$(SiMe_2CH{=}C{=}O)_2$ **2**

$(CH_2SiMe_2CH{=}C{=}O)_2$ **3**

as shown in eq 2, although these were not isolated but were trapped by MeOH.[5b] We now report theoretical calculations to assess the substituent effects of the disilanyl group and the stability of disilanyl ketenes and the preparation and isolation of a ketenyldisilane **1** and a bis(ketenyl)disilane **2**. The bisketene **3**, which is a homologue of **2** with a dimethylene spacer, was also prepared, and this is the first persistent and stabilized 1,6-bisketene. For comparison bis(trimethylsilyl)ketene (**4**), $(Me_3Si)_2C{=}C{=}O$, which has been known for some time[6] but has only been the subject of a few quantitative

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Table 1. Calculated (RHF/6-31G*//RHF/6-31G*) Energies and Dipole Moments of Silyl- and Disilanyl-Substituted Ketenes and Bisketenes

	E (hartrees)	0.9 (ZPVE)	*E* + ZPVE	μ (D)
$CH_2{=}C{=}O$	−151.7247	0.0308	−151.6939	1.63
$CH_3C^+{=}O$	−152.0593	0.0434	−152.0159	2.75
$CH_2{=}C{=}OH^+$	−151.9857	0.0420	−151.9437	1.88
$SiH_3CH{=}C{=}O$	−441.8176	0.0470	−441.7706	1.39
$SiH_3CH_2C^+{=}O$	−442.1525	0.0586	−442.0939	2.00
$SiH_3CH{=}C{=}OH^+$	−442.0892	0.0580	−442.0312	3.39
$Si_2H_5CH{=}C{=}O$	−731.8962	0.0637	−731.8325	1.34
$(SiH_2CH{=}C{=}O)_2$[a]	−882.4874	0.0798	−882.4076	1.25
$(SiH_2CH{=}C{=}O)_2$[b]	−882.4877	0.0798	−882.4079	2.27
$(SiH_3)_2C{=}C{=}O$	−731.9113	0.0630	−731.8483	1.18
$(SiH_3)_2CHC^+{=}O$	−732.2438	0.0739	−732.1699	1.18
$(SiH_3)_2C{=}C{=}OH^+$	−732.1930	0.0739	−732.1191	3.25
$CH_3SiH_2CH{=}C{=}O$	−480.8661	0.0749	−480.7912	1.88
$SiH_3CH{=}CH_2$	−368.1125	0.0648	−368.0477	0.80
$(SiH_3)_2C{=}CH_2$	−658.1928	0.0622	−658.1306	1.00
$Si_2H_5CH{=}CH_2$	−658.1914	0.0815	−658.1099	0.89
$CH_3SiH_2CH{=}CH_2$	−407.1601	0.0926	−407.0675	0.71
CH_3CH_3	−79.2288	0.0718	−79.1570	
H_3SiSiH_3	−581.3051	0.0474	−581.2577	
CH_3SiH_3	−330.2724	0.0587	−330.2137	
SiH_4	−291.2251	0.0301	−291.1950	
$CH_2{=}CH_2$	−78.0317	0.0493	−77.9824	
CH_4	−40.1952	0.0430	−40.1522	
H_2O	−76.0107	0.0207	−75.9900	2.20
H_3O^+	−76.2893	0.0330	−76.2563	1.59

[a] *gauche*. [b] *anti*.

studies, has been examined in spectroscopic and reactivity studies.

Results

Ab initio calculations of the structure and energy of $Si_2H_5CH{=}C{=}O$, the bisketene $(SiH_2CH{=}C{=}O)_2$, the bis(silylated) ketene $(SiH_3)_2C{=}C{=}O$, and appropriate reference compounds were carried out at the RHF/6-31G* + ZPVE//RHF/6-31G* level using Gaussian 92[7] as we have done previously,[2b,c,3d,h] and the calculated energies and geometries are reported in Tables 1 and 2, respectively. This level of theory has been demonstrated to give good agreement with experimental geometries and energies of ketenes[3a−d] and to be of reliable predictive value. Two minimum energy conformations for $(SiH_2CH{=}C{=}O)_2$ were found, namely *anti* and gauche forms (Figure 1), and the former was calculated to be more stable by 0.2 kcal/mol. The corresponding bond distances and bond angles in the conformations are very similar (Table 2).

New ketenes were prepared using the well-known procedure of ethoxyalkyne pyrolysis.[3a] Thus reaction of chloropentamethyldisilane with EtOC≡CLi gave pentamethyldisilanyl ethyl ether **5**, which upon pyrolysis

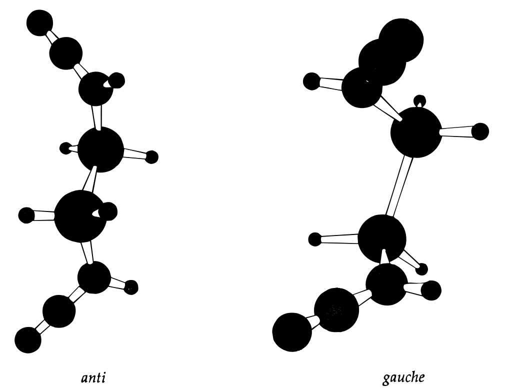
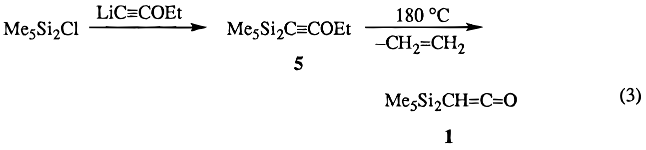


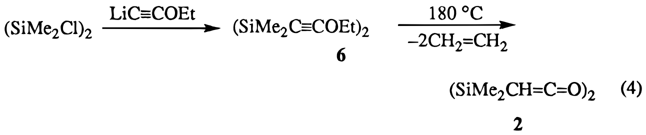
Figure 1. Calculated (RHF/6-31G*) *anti* and *gauche* conformations of $(SiH_2CH{=}C{=}O)_2$.

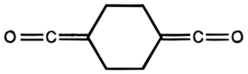
at 180 °C in a gas chromatograph[3e,h] gave **1** (eq 3), whose



structure was confirmed by its distinctive spectral properties as compared to those for $Me_3SiCH{=}C{=}O$ (parentheses);[1a,2d,3a] in particular the characteristic ketenyl IR band at 2108 (2112) cm^{-1}, the ^{1}H NMR signal at C_β at δ 1.73 (1.65), the ^{13}C NMR signals of C_α and C_β at δ 178.7 (179.2) and −2.4 (−0.2), respectively, the ^{17}O NMR absorption at δ 252.2 (255.0), and the ^{29}Si NMR signals at δ −18.3 and −18.8 (0.8),[1d] respectively.

Reaction of 1,2-dichlorotetramethyldisilane with EtOC≡CLi gave 1,2-bis(ethoxyethynyl)tetramethyldisilane (**6**), which upon pyrolysis in a gas chromatograph gave **2** (eq 4) which also showed the distinctive spectral characteristics of a silylketene: IR 2108, 2052 cm^{-1}; NMR δ $^1H_\beta$ 1.76; $^{13}C_\alpha$ δ 178.2, $^{13}C_\beta$ δ −2.2; ^{17}O δ 253.6; ^{29}Si δ −18.6. This is the first example of an isolable acyclic 1,4-bisketene. Previously observed cyclic 1,4-bisketenes include **7** and a few analogous compounds.[8]





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The same strategy was utilized for the preparation of the novel 1,6-bisketene **3**, namely reaction of 1,2-bis(chlorodimethylsilyl)ethane with lithium ethoxyacetylide to form the bis(ethoxyalkyne) **8**, which on pyrolysis in a gas chromatograph gave a 70% yield of **3** (eq 5).

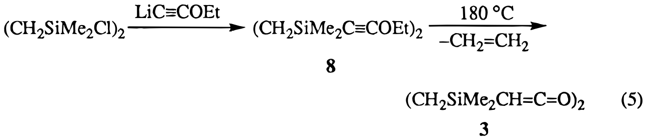

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Table 2. Ab Initio Calculated Geometries for Disilanylketenes and -bisketenes

	bond distances (Å)					
	C−C	C=O	Si−C	Si−Si	C−H	Si−H[c]
$CH_2=C=O$	1.306	1.145			1.071	
$CH_3C^+=O$	1.464	1.095			1.085	
$CH_2=C=OH^+$	1.271	1.216			1.079	(0.969)[k]
$SiH_3CH=C=O$	1.308	1.143	1.860		1.077	1.475
$SiH_3CH_2C^+=O$	1.425	1.101	2.002		1.088	1.461
$SiH_3CH=C=OH^+$	1.256	1.227	1.971		1.081	1.461
$Si_2H_5CH=C=O$	1.308	1.143	1.867	2.353	1.076	1.478
$(SiH_2CH=C=O)_2$[a]	1.308	1.143	1.866	2.353	1.077	1.479
$(SiH_2CH=C=O)_2$[b]	1.308	1.142	1.867[c]	2.351	1.076	1.479
$(SiH_3)_2C=C=O$	1.305	1.143	1.873			1.475
$(SiH_3)_2CHC^+=O$	1.394	1.107	1.993		1.090	1.462
$(SiH_3)_2C=C=OH^+$	1.243	1.238	1.960		1.960	(0.962)[k]
$CH_3SiH_2CH=C=O$	1.308	1.143	1.856[d]		1.077	1.478
$SiH_3CH=CH_2$	1.325		1.874		1.078[c]	1.478
$(SiH_3)_2C=CH_2$	1.333		1.881		1.079	1.478
$Si_2H_5CH=CH_2$	1.325		1.879	2.355	1.078[c]	1.480
$CH_3SiH_2CH=CH_2$	1.325		1.876[e]		1.080[c]	1.480
CH_3SiH_3			1.888		1.086	1.478
Si_2H_6				2.352		1.478

	bond angles (deg)						
	CCO	SiCC	SiSiC	CCH	SiCH	CCSiSi	SiCCO
$CH_2=C=O$	180.0			119.3			
$CH_3C^+=O$	180.0			107.8			
$CH_2=CH=OH^+$	175.8			119.5		(116.9)[l]	(180.0)[m]
$SiH_3CH=C=O$	178.9	121.9		115.6	122.5		0.0
$SiH_3CH_2C^+=O$	177.5	113.4		107.2	109.7		1.3
$SiH_3C=C=OH^+$	174.9	120.5		119.7	119.8	(116.3)[l]	49.9[n]
$Si_2H_5CH=C=O$	178.7	121.8	111.3	115.7	122.6	122.1	12.2
$(SiCH_2CH=C=O)_2$[a]	178.7	121.7	111.6	115.7	122.6	120.1[f]	10.0[c]
$(SiH_2CH=C=O)_2$[b]	178.7	121.8	111.2	115.7	122.5	121.6[g]	12.6[c]
$(SiH_3)_2C=C=O$	180.0	118.0	(124.0)[h]				0.0
$(SiH_3)_2CHC^+=O$	177.9	111.3	(111.5)[h]	106.4	107.9[c]		66.6, 58.7
$(SiH_3)_2C=C=OH^+$	176.2	119.7	(120.6)[h]			(115.8)[l]	88.6, 90.3[o]
$CH_3SiH_2CH=C=O$	178.8	121.9	(111.8)[i]	115.5	122.6	(120.1)[j]	6.0
$SiH_3CH=CH_2$		123.5		117.7	118.7		
$(SiH_3)_2C=CH_2$		119.0	(121.9)[h]	122.7			
$Si_2H_5CH=CH_2$		123.8	111.9	122.2	118.5		
$CH_3SiH_2CH=CH_2$		123.7	(111.8)[i]	122.3		(120.4)[j]	

[a] *gauche.* [b] *anti.* [c] Average. [d] CH_3-Si 1.884. [e] CH_3-Si 1.889. [f] CSiSiC 65.3. [g] CSiSiC 171.6. [h] SiCSi. [i] CSiC. [j] CCSiC. [k] OH. [l] COH. [m] C-COH. [n] CCOH 141.2. [o] CCOH 180.0.

Table 3. Hydration Rates (s^{-1}) for $Me_5Si_2CH=C=O$ (1), $(SiMe_2CH=C=O)_2$ (2),and $(CH_2SiMe_2CH=C=O)_2$ (3) in H_2O/CH_3CN Mixtures at 25 °C

	1		**2**		**3**	
$[H_2O]$ (M)	k_{obs}[a]	k_{rel}[b]	k_{obs}[c]	k_{rel}[b]	k_{obs}[d]	k_{rel}[b]
33.3	1.27×10^{-2}	1.90	3.74×10^{-2}	5.60	6.22×10^{-3}	0.94
27.8	9.31×10^{-3}	3.28	1.52×10^{-2}	5.35	5.19×10^{-3}	1.82
27.8 (D_2O)	4.25×10^{-3} (2.2)[e]	4.92	4.56×10^{-3} (3.3)[e]	5.28	7.80×10^{-4} (6.7)[e]	0.90
22.2	4.72×10^{-3}	2.32	7.75×10^{-3}	3.82	1.56×10^{-3}	0.77
16.7	1.19×10^{-3}	2.26	2.91×10^{-3}	3.37	9.28×10^{-4}	1.07
11.1	6.36×10^{-4}	0.96	1.28×10^{-3}	1.94	3.94×10^{-4}	0.60

[a] $\log k = 0.0630[H_2O] - 3.87$ ($r = 0.978$). [b] k_{rel} to $Me_3SiCH=C=O$. [c] $\log k = 0.0658[H_2O] - 3.62$ ($r = 0.999$). [d] $\log k = 0.0567[H_2O] - 4.01$ ($r = 0.996$). [e] k_{H_2O}/k_{D_2O}.

The bisketene was identified by its characteristic spectral properties: IR 2115, 2052 cm^{-1}; NMR ($CDCl_3$) δ $^1H_\beta$, 1.77; $^{13}C_\alpha$ 179.0, $^{13}C_\beta$ −1.6; ^{17}O 253.8, ^{29}Si 3.1.

For comparative purposes the UV spectra for known monoketenes were measured as follows: $Me_3SiCH=C=O$, $\lambda_{max}^{isooctane}$ 213 ($\epsilon = 1300$) and 308 ($\epsilon = 56$) nm; $(Me_3Si)_2C=C=O$, $\lambda_{max}^{isooctane}$ 213 ($\epsilon = 1000$) and 278 ($\epsilon = 27$) nm. The ^{17}O NMR shift of the latter was also measured as δ 211.2, and the ^{29}Si shift (δ −1.5) is known.[1d]

To assess the reactivity of ketenes **1**−**3**, their rates of hydration in H_2O/CH_3CN mixtures were measured as we have done for other silylketenes,[2a,3e,h] and the results are given in Table 3, along with comparisons to the reactivity of $Me_3SiCH=C=O$.[2a] The rates of reaction gave reasonably linear empirical correlations of log k with $[H_2O]$, with slopes of 0.057 to 0.066, as has been observed in other cases,[3a,e,h] and solvent isotope effects k_{H_2O}/k_{D_2O} in the range 2.2−6.7.

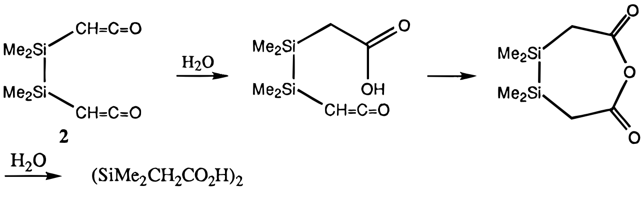
The reactivity of $(Me_3Si)_2C=C=O$ (**4**) in H_2O/CH_3CN mixtures was also measured but in contrast to **1**−**3** and $Me_3SiCH=C=O$ showed a rather irregular and more modest dependence of the reactivity on the $[H_2O]$ (Table 4). In 55.6 M H_2O the kinetic isotope effect k_{H_2O}/k_{D_2O} had a value of 1.4. The acid-catalyzed rate constants k_{H^+} and k_{D^+} were also measured (Table 4) and gave $k_{H^+}/k_{D^+} = 1.44$.

Table 4. Hydration Rates for $(Me_3Si)_2C{=}C{=}O$ (4) at 25 °C

$[H_2O]$ (M)	k_{obs} (s^{-1})	k_{rel}[d]
55.6	2.46×10^{-4} 1.80×10^{-4} [a] 4.92×10^{-4} [b,c]	0.97×10^{-3}
50.0	4.60×10^{-4}	3.03×10^{-3}
44.4	2.21×10^{-4}	4.00×10^{-3}
38.9	1.63×10^{-4}	7.75×10^{-3}
33.3	5.62×10^{-5}	8.40×10^{-3}

[a] D_2O, $k_{H_2O}/k_{D_2O} = 1.37$. [b] $\mu = 0.05$ (NaCl). [c] $k_{H^+} = 0.856$ M^{-1} s^{-1}; $k_{D^+} = 0.594$ M^{-1} s^{-1}, $k_{H^+}/k_{D^+} = 1.44$ (determined using HCl and DCl solutions, respectively). [d] k_{rel} to $Me_3SiCH{=}C{=}O$.

Scheme 1



2

11

To test if the kinetic behavior of **4** might indicate a change in reaction mechanism the reaction of **4** with 98% ^{18}O-labeled H_2O was carried out, and the known acid $(Me_3Si)_2CHCO_2H$[6g] was isolated and analyzed by mass spectrometry and found to contain a single ^{18}O, with no detectable dilabeling.

The hydration of **1** and **3** gave the acids $Me_5Si_2CH_2CO_2H$ (**9**) and $(CH_2SiMe_2CH_2CO_2H)_2$ (**10**), as crystalline solids in 53 and 81% yield, respectively, which were characterized by their spectral properties.

In an attempt to ascertain the hydration reaction product of **2** with H_2O a solution of **2** in CD_3CN containing 2 equiv of H_2O was prepared and observed by NMR. Within 2 min new ^1H signals had begun to appear at δ 0.30 and 2.04. After 2 days these peaks and the starting material had disappeared and ^1H singlets at δ 0.32 and 2.30 were present, in a ratio of about 2/1, and the ^{13}C NMR showed signals at δ 2.9, 22.9, and 168.3. These signals represented 90% of the observable material and are consistent with the formation of the diacid $(SiMe_2CH_2CO_2H)_2$ (**11**), which is the expected product of the hydration. Chemical ionization mass spectrometry showed the presence of a weak M^+ ion at m/z 234, with the base peak at m/z 117 ($M^+/2$), corresponding to $^+SiMe_2CH_2CO_2H$. Upon removal of the solvent the product decomposed. These results are consistent with Scheme 1, in which the new ^1H signals observed after 2 min correspond to the acid anhydride. The analogous formation of a transient monoacid leading to an anhydride was observed in the hydration of the 1,2-bisketene $(Me_3SiC{=}C{=}O)_2$.[3e,f] An alternative interpretation is that the new ^1H signals observed are due to the carboxylic acid portion of the monoacid while the signals due to the ketenyl portion of this molecule are coincident with those of **2**, but this appears less likely.

Discussion

The *ab initio* calculated energies at the HF/6-31G* + ZPVE//HF/6-31G* level (Table 1) for disilanylketenes and -bisketenes permit isodesmic energy stabilization comparisons that predict the stability of these species. The comparison of eq 6 indicates that the stabilizing

$$Si_2H_5CH{=}C{=}O + SiH_3CH{=}CH_2 \xrightarrow[-0.2\ \text{kcal/mol}]{\Delta E\,=} Si_2H_5CH{=}CH_2 + SiH_3CH{=}C{=}O \quad (6)$$

$$(SiH_2CH{=}C{=}O)_2 + CH_3CH_3 \xrightarrow[-11.0\ \text{kcal/mol}]{\Delta E\,=} 2CH_3SiH_2CH{=}C{=}O \quad (7)$$

$$(SiH_2CH{=}C{=}O)_2 + 2SiH_4 \xrightarrow[-0.6\ \text{kcal/mol}]{\Delta E\,=} 2SiH_3CH{=}C{=}O + Si_2H_6 \quad (8)$$

$$SiH_3SiH_3 + CH_3CH_3 \xrightarrow[-8.0\ \text{kcal/mol}]{\Delta E\,=} 2CH_3SiH_3 \quad (9)$$

effect of the Si_2H_5 group is essentially identical to the well-known[1,2] stabilizing effect of monosilyl substituents such as SiH_3 and Me_3Si on ketenes as compared to alkenes. The comparison of eq 7 suggests bis(ketenyl)disilanes are thermodynamically destabilized relative to ketenylsilanes, by 11.0 kcal/mol, but this is a manifestation of the lower strength of the Si−Si bond relative to the Si−C bond, and by the comparison of eq 8 the destabilization of the bisketene is only −0.6 kcal/mol. This parallels the effects found for two or three ketenyl groups in the 1,3-bis- or trisketenes $SiH_2(CH{=}C{=}O)_2$ and $SiH(CH{=}C{=}O)_3$, where no decrease in the stabilization of the individual ketenyl groups due to the presence of multiple ketenyl groups was apparent.[3h]

The calculated dipole moments of $Si_2H_5CH{=}C{=}O$ and $SiH_3CH{=}C{=}O$ are essentially identical (1.34 and 1.39 D, respectively), as are the C=O, C=C, Si−C, and C−H bond distances and the C=C=O, SiC−C, C=CH, and SiCH bond angles (Table 2). Similarly for $Si_2H_5CH{=}C{=}O$ and $(SiH_2CH{=}C{=}O)_2$ the calculated C=C, C=O, SiC, SiSi, CH, and SiH bond distances and the CC=O, SiC=C, SiSiC, CCH, SiCH, and CCSiSi bond angles are very similar (Table 2). These results agree with the results of the isodesmic energy comparisons that the effects of the Si_2H_5 and SiH_3 group are similar and there is no evidence of significant interactions between the two ketenyl moieties of the bisketene.

However, an interesting feature of both $Si_2H_5CH{=}C{=}O$ and $(SiH_2CH{=}C{=}O)_2$ is that the Si−C=C=O unit is calculated to be nonplanar, with dihedral angles of 8.3 and 13.9°, respectively. This net pyramidalization at C_β does not result in a significant effect on the energies or the bond distances but suggests some interaction of the Si with the C=C π bond and may affect the UV spectra (*vide infra*).

Although $(Me_3Si)_2C{=}C{=}O$ (**4**) has long been known as a stable species,[6] there have been no quantitative theoretical or experimental studies of its stability and reactivity that allow a comparison of the properties of this disilylated compound to those of monosilylated ketenes. In particular it has not been known whether the second trimethylsilyl group has a further stabilizing influence on this ketene compared to $Me_3SiCH{=}C{=}O$. This question may now be addressed, on the basis of ab initio calculated energies (Table 1), which allow the isodesmic comparisons shown in eqs 10−15.

$$(SiH_3)_2C{=}C{=}O + CH_2{=}CH_2 \xrightarrow[15.1\ \text{kcal/mol}]{\Delta E\,=} (SiH_3)_2C{=}CH_2 + CH_2{=}C{=}O \quad (10)$$

$$(SiH_3)_2C{=}C{=}O + SiH_3CH{=}CH_2 \xrightarrow[7.9\ \text{kcal/mol}]{\Delta E\,=} (SiH_3)_2C{=}CH_2 + SiH_3CH{=}C{=}O \quad (11)$$

$$SiH_3CH{=}C{=}O + CH_2{=}CH_2 \xrightarrow[7.2\ \text{kcal/mol}]{\Delta E\,=} SiH_3CH{=}CH_2 + CH_2{=}C{=}O \quad (12)$$

$$(SiH_3)_2C{=}C{=}O + 2CH_4 \xrightarrow[19.7\ \text{kcal/mol}]{\Delta E\,=} 2SiH_3CH_3 + CH_2{=}C{=}O \quad (13)$$

$$(SiH_3)_2C{=}C{=}O + CH_4 \xrightarrow[10.2\ \text{kcal/mol}]{\Delta E\,=} SiH_3CH_3 + SiH_3CH{=}C{=}O \quad (14)$$

$$SiH_3CH{=}C{=}O + CH_4 \xrightarrow[9.5\ \text{kcal/mol}]{\Delta E\,=} SiH_3CH_3 + CH_2{=}C{=}O \quad (15)$$

These comparisons show that not only is the second silyl substituent effective at further stabilizing the ketene but the stabilizing effect of the second silicon of 7.9 kcal/mol (eq 11) is calculated to slightly exceed that of a single silyl group, by 0.7 kcal/mol. Such additivity of substituent stabilization by electron donation to an electron deficient center in aliphatic systems has been found before, for example in the generation of carbocations by alkene protonations.[9]

A cumulative effect of the second silyl group may also be seen in the ^{17}O NMR chemical shift of $(Me_3Si)_2C{=}C{=}O$ of δ 211.2, which is 44 ppm upfield from that of $Me_3SiCH{=}C{=}O$, which is in turn 74 ppm upfield from that of $Me_2C{=}C{=}O$.[2d]

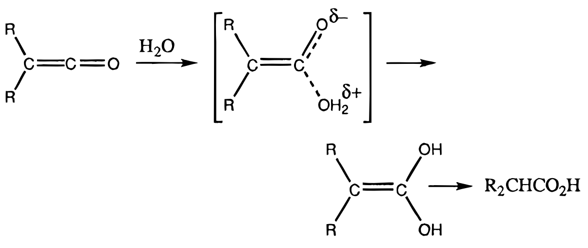
Silyl groups have a conspicuous effect on the UV/visible spectra of ketenes, in that these compounds are colorless, in contrast to the yellow color observed for alkylketenes. Evidently no interpretation of this behavior has been advanced, despite the appearance of many theoretical studies of ketenes.[3a] This behavior may be understood on the basis of the following perturbational molecular orbital arguments. The ketenyl C−Si σ bond is in-plane with the carbonyl π and π^* orbitals and interacts strongly with them, lowering the energy of the former and raising that of the latter. However there is little interaction with the n orbitals on oxygen, so the $n \rightarrow \pi^*$ energy is therefore raised.

This effect is seen in the UV spectrum of $(Me_3Si)_2C{=}C{=}O$, which shows $\lambda_{max}^{isooctane}$ 213 (ϵ = 1,000) and 278 (ϵ = 27) nm, as compared to $\lambda_{max}^{isooctane}$ 213 (ϵ = 1,300) and 308 (ϵ = 56) nm for $Me_3SiCH{=}C{=}O$ and $\lambda_{max}^{isooctane}$ 225 (ϵ = 1,200) and 360 (ϵ = 12) for $t\text{-}Bu_2C{=}C{=}O$.[3a] A single Me_3Si substituent thus causes a shift to shorter wavelength for both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands of ketenes near 220 and 300 nm, respectively, and the effect on the latter compared to $t\text{-}Bu_2C{=}C{=}O$ is 52 and 30 nm for the first and second Me_3Si groups.

As a test[10a] of this interpretation, we have calculated by CIS/6-31+G* the effect of a SiH_3 substituent on the UV spectrum of ketene, and this method predicts a decrease in the λ_{max} for the $n \rightarrow \pi^*$ trnsition of 20 nm, as compared to the observed decrease of 17 nm for $SiMe_3$ substitution. This method is known[10b] not to be always quantitatively accurate for UV λ_{max} values (calculated for $CH_2{=}C{=}O$ 279 nm, observed 325 nm; calculated for $SiH_3CH{=}C{=}O$ 259 nm, observed for $Me_3SiCH{=}C{=}O$ 308 nm) but is qualitatively predictive.

No such effect is seen in the alkenes $Me_3SiCH{=}CH_2$ and $t\text{-}BuCH{=}CH_2$, which have almost the same λ_{max} around 182 nm but with a greater intensity for $Me_3SiCH{=}CH_2$.[4c,d] For disilanes the reported λ_{max} values of $Me_3SiSiMe_3$, $Me_5Si_2CH{=}CH_2$, and $(SiMe_2CH{=}CH_2)_2$ are 193, 224, and 230 nm, respectively, and the increase to longer wavelength was interpreted as indicating σ-(Si−Si)−π conjugation.[4d] This interaction could involve the σ^*(Si−Si) orbital and the π^* orbital, lowering the energy of the latter. The disilanyl monoketene **1** shows $\lambda_{max}^{isooctane}$ 317 nm (ϵ = 210), which is shifted significantly to longer wavelength compared to the values of 292 (ϵ = 35) for $t\text{-}BuSiMe_2CH{=}C{=}O$[3a] and 308 nm for $Me_3SiCH{=}C{=}O$. As noted above the calculated structures of $Si_2H_5CH{=}C{=}O$ and $(SiH_2CH{=}C{=}O)_2$ indicate some pyramidalization around the alkenyl CH carbon, suggesting an interaction with the disilanyl function. The Si−Si bond has a dihedral angle of about 30° with the C=C π bond, and interaction between the σ^*(Si−Si) orbital and the π^*(C=O) and π^*(C=C) orbitals could cause a lowering in energy of both of the latter and would thereby lower the energy of the observed $n \rightarrow \pi^*$ transition. The bisketene **2** has UV $\lambda_{max}^{isooctane}$ 308 nm (ϵ = 610), and the shorter wavelength absorption compared to the value of 317 nm for **1** suggests that the σ^*(Si−Si)−π^* interaction is diminished when the disilane is symmetrically substituted with acceptor groups. The bisketene $(CH_2SiMe_2CH{=}C{=}O)_2$ (**3**) has essentially the same λ_{max} (309 nm) as does $Me_3SiCH{=}C{=}O$ (308 nm), suggesting the two halves of the former are behaving independently.

This kinetic behavior observed in the hydration of **1**−**3** is consistent with these ketenes reacting by the accepted mechanism for these compounds,[2a,3a,e,h] namely rate limiting attack of H_2O in the ketene plane leading to an enediol intermediate (eq 16). Only one kinetic step is observed in the reaction of the bisketene **2**, and apparently the initial hydration results in the conversion of both ketenyl groups. This could involve a transient monoacid as shown in Scheme 1, as occurred in the hydration of $(Me_3SiC{=}C{=}O)_2$.[3e,f] The hydration product from **2** was quite unstable, but the spectral



(16)

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[9] Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252−258.

[10] (a) This test was suggested by an anonymous reviewer. (b) Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian*; p. 173, Gaussain, Inc.: Pittsburgh, PA, 1993.

evidence, as discussed above, is consistent with the formation of the diacid **11** as shown in Scheme 1.

The disilanylketene **1** is more reactive toward hydration than is $Me_3SiCH{=}C{=}O$ by a variable factor that averages 2.6 in the different solutions studied (Table 3). This small difference is in agreement with the isodesmic comparison of eq 6, which indicates that the gas-phase substituent effects of the Si_2H_5 and SiH_3 groups are esentially the same. Bis(ketenyl)disilane **2** is similarly more reactive than the monoketene **1** by a very modest average factor of 1.9, and this also is in agreement with the very small difference in stability indicated by eq 8.

By contrast $(Me_3Si)_2C{=}C{=}O$ (**4**) is measured to have a very low reactivity with H_2O, with a rate constant in pure water of 2.46×10^{-4} s^{-1} at 25 °C (Table 4), which is 1000 times less than the rate for $Me_3SiCH{=}C{=}O$ in H_2O[2a] and is comparable to the rate for t-$Bu_2C{=}C{=}O$ of 1.57×10^{-4} s^{-1}, which is the smallest rate constant recorded for hydration of a ketene in pure H_2O.[11a] The hydration of $(Me_3Si)_2C{=}C{=}O$ has been shown to produce $(Me_3Si)_2CHCO_2H$ as the product.[6g]

Two causes for the origin of the low reactivity of **4** may be considered, namely steric and electronic effects. For bulky alkyl groups the effect of substituents on hydration reactivity is largely steric.[3a] Thus while the hydration rate ratio $k(n\text{-}BuCH{=}C{=}O)/k(CH_2{=}C{=}O)$ is 2.6, that for $k(t\text{-}BuCH{=}C{=}O)/k(CH_2{=}C{=}O)$ is 0.40, and the decrease in reactivity for the t-Bu group may result from steric inhibition of solvation. However the rate ratios for $CH_2{=}C{=}O/Me_3SiCH{=}C{=}O$ and $Me_3SiCH{=}C{=}O/(Me_3Si)_2C{=}C{=}O$ are 160 and 1030, showing that the replacement of both the first and the second hydrogens of $CH_2{=}C{=}O$ by Me_3Si groups each cause significant rate effects, by a factor which is 6-fold greater for the second. This latter factor may be taken as a measure of the steric effect, while the factor of 160 for the first Me_3Si is evidently largely electronic and a result of the ground-state stabilization of the ketene by Me_3Si.

The steric effects of groups such as Me_3Si depend upon the property being measured, and this group has been found to be larger than C_2H_5 in nucleophilic additions to ketenes[11b] and in other studies.[11c] As depicted in eq 16, there are many indications that ketene hydration largely involves formation of a ketene hydrate, and because of the rather long carbon−silicon bond, the steric interactions with the Me_3Si are evidently rather small compared to those for *tert*-butyl.

The hydration of **4** also shows a very low sensitivity to the concentration of H_2O in H_2O/CH_3CN mixtures, so that the rate ratio $k(\mathbf{4})/k(Me_3SiCH{=}C{=}O)$ increases from 0.97×10^{-3} to 8.4×10^{-3} for the change from 55.6 to 33.3 M H_2O in CH_3CN (Table 4). This is in contrast to **1**−**3** and many other ketenes, which show linear dependences of log k_{obs} on $[H_2O]$.[2a,3a,11a] The other exceptions to this behavior are t-$BuC(CO_2Et){=}C{=}O$ and C_3O_2,[11d,e] and in the former case the absence of a strong dependence of reaction rate on the $[H_2O]$ was attributed to the intervention of a rather nonpolar transition state because of coordination of the nucleophilic water molecule to the ester carbonyl during nucleophilic attack on the ketene.[11d] For **4** other factors must be important. One possibility is that enhanced reversibility of the hydration reaction becomes significant in this case. Thus for diarylketenes it has been found that substrate recovered after partial reaction in $H_2{}^{18}O$ was enriched in ^{18}O while some of the product carboxylic acid contained more than one ^{18}O label, although the product itself did not undergo exchange.[11f] This is convincing evidence for the reversibility of ketene hydration in some cases, as shown in eq 16. However, as noted above, this possibility was tested in the case of $(Me_3Si)_2C{=}C{=}O$, and no double incorporation of ^{18}O was observed in the product $(Me_3Si)_2CHCO_2H$, thus excluding significant reversibility of the hydration under these conditions.

In the acid-catalyzed hydration the second Me_3Si group also does not have as large a rate enhancing factor as does the first. Thus the ratio of k_{H^+}/k_{H_2O} (M^{-1}) for $Me_3SiCH{=}C{=}O$ of 1.7×10^5 was rather larger than that observed for other ketenes and was interpreted as an enhancement of the formation of the β-silylacylium ion $Me_3SiCH_2C^+{=}O$ upon protonation.[2a] In the case of **4** this ratio has a value of 3.5×10^3. A possible explanation of this behavior is that the stabilization of the ketene by the two silyl groups is quite strong, but upon carbon protonation the favorable coplanar arrangement of the two Si−C bonds with the carbonyl π orbital is disrupted, so that the silicon stabilization of the developing cation is not so favorable as for the ketene.

As a test[10a] of this interpretation, we have calculated the relative heats of carbon and oxygen protonation of $CH_2{=}C{=}O$, $SiH_3CH{=}C{=}O$, and $(SiH_3)_2C{=}C{=}O$ (Table 1). In the case of carbon protonation there is a slight stabilization for one SiH_3, whereas the second is slightly destabilizing (eqs 17−19). However for oxygen protonation both Si−C bonds remain essentially coplanar with the electron-deficient p orbital on the carbonyl carbon, and there is strong stabilization by both SiH_3

$$CH_2{=}C{=}O + H_3O^+ \xrightarrow[-35.0\text{ kcal/mol}]{\Delta E\,=} CH_3C^+{=}O + H_2O \tag{17}$$

$$SiH_3CH{=}C{=}O + H_3O^+ \xrightarrow[-35.8\text{ kcal/mol}]{\Delta E\,=} SiH_3CH_2C^+{=}O + H_2O \tag{18}$$

$$(SiH_3)_2C{=}C{=}O + H_3O \xrightarrow[-34.7\text{ kcal/mol}]{\Delta E\,=} (SiH_3)_2CHC^+{=}O + H_2O \tag{19}$$

$$CH_2{=}C{=}O + H_3O^+ \xrightarrow[10.4\text{ kcal/mol}]{\Delta E\,=} CH_2{=}C{=}OH^+ + H_2O \tag{20}$$

$$SiH_3CH{=}C{=}O + H_3O^+ \xrightarrow[3.6\text{ kcal/mol}]{\Delta E\,=} SiH_3CH{=}C{=}OH^+ + H_2O \tag{21}$$

$$(SiH_3)_2C{=}C{=}O + H_3O^+ \xrightarrow[-2.8\text{ kcal/mol}]{\Delta E\,=} (SiH_3)_2C{=}C{=}OH^+ + H_2O \tag{22}$$

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(11) (a) Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1987**, *109*, 2774−2780. (b) Baigrie, L. M.; Seikaly, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 5391−5396. (c) Frey, J.; Schottland, E.; Rappoport, Z.; Bravo-Zhivotovskii, D.; Nakash, M.; Botoshansky, M.; Kaftory, M.; Apeloig, Y. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2555−2562. (d) Allen, A. D.; McAllister, M. A.; Tidwell, T. T. *Tetrahedron Lett.* **1993**, *34*, 1095−1098. (e) Allen, A. D.; McAllister, M. A.; Tidwell, T. T. *J. Chem. Soc., Chem. Commun.* **1995**, 2547−2548. (f) Frey, J.; Rappoport, Z. *J. Am. Chem. Soc.* **1995**, *117*, 1161−1162; **1996**, *118*, 5182−5192.

groups upon oxygen protonation, by 6.8 and 6.4 kcal/mol, respectively (eqs 20−22).

In summary the Si_2H_5 and Me_5Si_2 groups are shown to have almost the same stabilizing effect on ketenes as the SiH_3 and Me_3Si groups, as shown by computational and experimental studies, respectively. Similarly the computed stabilities and reactivities of the 1,4-bisketenes $(SiH_2CH{=}C{=}O)_2$ and $(SiMe_2CH{=}C{=}O)_2$ (**2**) are similar to those of the corresponding monoketenes, respectively. The novel 1,6-bisketene $(CH_2SiMe_2CH{=}C{=}O)_2$ (**3**) is also very similar in its properties to $Me_3SiCH{=}C{=}O$. By contrast the disilylated ketenes $(SiH_3)_2C{=}C{=}O$ and $(Me_3Si)_2C{=}C{=}O$ show strongly cumulative effects of the silyl substituents on the stability and on the spectral properties and the hydration reactivity, respectively. The reactivity is affected both by electronic and steric factors.

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. Pyrolyses of ethoxyalkynyl substrates were carried out with a Varian 920 gas chromatograph using a 3 m × 1 cm OV-17 column and injector and detector temperatures of 210 and 230 °C, respectively.

All ^1H and ^{13}C NMR spectra were obtained using a Varian Gemini 200 instrument, and ^{29}Si and ^{17}O NMR spectra were obtained using a Varian XL-400 NMR spectrometer. IR spectra were obtained using a Nicolet 8210E FT-IR spectrophotometer. UV spectra and hydration kinetics were measured with a Perkin-Elmer Lambda 12 spectrophotometer as reported previously.[3e,11a] Preparative radial thin-layer chromatography was carried out using a Chromatron from Harrison Research on silica gel with elution by 5% EtOAc in hexane.

(Ethoxyethynyl)pentamethyldisilane (5). To ethoxyethyne (2.5 g, 36 mmol) in 30 mL ether at 0 °C was added with stirring CH_3Li (24.6 mL, 1.5 M in ether, 37 mmol), and the solution was allowed to warm to 25 °C and stirred 2 h. Then chloropentamethyldisilane (5.4 g, 32.4 mmol) was added, the solution was stirred 24 h and washed 3 times with water, the ether layer was dried and evaporated, and the product was purified by chromatography to give **4** (5.8 g, 29 mmol, 81%): IR (neat) 2171 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 9, 3 CH_3), 0.14 (s, 6, 2 CH_3), 1.36 (t, 3, $J = 7.1$ Hz, CH_3), 4.13 (q, 2, $J = 7.1$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ −2.52, −2.11, 14.3, 35.3, 74.8; 111.3; EIMS m/z 171 ($M^+ - C_2H_5$, 72), 141 (38), 99 ($O{=}C{=}CHSi(CH_3)_2^+$, 32), 73 (Me_3Si^+, 100); HRMS m/z calcd for $C_9H_{20}OSi_2$, 171.0661, found 171.0659.

(Pentamethyldisilanyl)ketene (1). Pyrolysis of **5** (35 mg, 0.175 mmol) by gas chromatography gave **1** (21 mg, 0.12 mmol, 70%): IR (isooctane) 2108 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.097 (s, 9, 3 CH_3), 0.206 (s, 6, 2 CH_3), 1.73 (s, 1, CH); ^{13}C NMR ($CDCl_3$) δ −2.39, −1.93, −2.57, 178.7; ^{17}O NMR ($CDCl_3$) δ 252.2; ^{29}Si NMR ($CDCl_3$) δ −18.8, −18.3; UV $\lambda_{\max}^{\text{isooctane}}$ 317 (ϵ 210); EIMS m/z 157 ($M^+ - CH_3$, 49), 144 ($M^+ - CO$, 55), 129 ($M^+ - CH_3 - CO$, 100), 99 ($O{=}C{=}CHSiMe_2^+$, 56), 73 (Me_3Si^+, 68); HRMS m/z calcd for $C_6H_{13}OSi_2$ 157.0505, found 157.0500.

1,2-(Diethoxyethynyl)-1,1,2,2-tetramethyldisilane (6). Reaction of ethoxyethyne (2.5 g, 36 mmol) with 1,2-dichlorotetramethyldisilane (3.1 g, 16.7 mmol) as described above gave after chromatography **5** (2.9 g, 11.4 mmol, 68%) as a colorless oil: IR (neat) 2171 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 12, 4 CH_3), 1.38 (t, 6, $J = 7.1$ Hz, 2 CH_3), 4.12 (q, 4, $J = 7.1$ Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ −2.11, 14.3, 35.0, 74.9, 111.4; EIMS m/z 225 ($M^+ - C_2H_5$, 2), 197 (88), 99 ($O{=}C{=}CHSiMe_2^+$, 100); HRMS m/z calcd for $C_{10}H_{17}O_2Si_2$ 225.0767, found 225.0746.

1,2-Bis(2-oxoethenyl)-1,1,2,2-tetramethyldisilane (2). Pyrolysis of **6** (35 mg, 0.138 mmol) by gas chromatography gave **2** (17 mg, 0.086 mmol, 62%): IR (isooctane) 2108, 2052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 12, 4 CH_3), 1.76 (s, 2, CH); ^{13}C NMR ($CDCl_3$) δ −2.52, −2.21, 179.0; ^{17}O NMR ($CDCl_3$) δ 253.6; ^{29}Si NMR ($CDCl_3$) δ −18.6; UV $\lambda_{\max}^{\text{isooctane}}$ 308 (ϵ 610); EIMS m/z 198 (M^+, 1), 183 ($M^+ - CH_3$, 33), 170 ($M^+ - CO$, 38), 155 ($M^+ - CH_3, - CO$, 84); 99 ($O{=}C{=}CHSiMe_2^+$, 100); HRMS m/z calcd for $C_8H_{14}O_2Si_2$ 198.0532, found 198.0527.

1,2-Bis((ethoxyethynyl)dimethylsilyl)ethane (8). Reaction of ethoxyethyne (2.5 g, 36 mmol) with 1,2-bis(chlorodimethylsilyl)ethane (3.6 g, 16.7 mmol) as described above gave after chromatography **8** as a colorless oil (4.2 g, 14.9 mmol, 89%): IR (neat) 2178 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 12, 4 CH_3), 0.54 (s, 4, 2 CH_2), 1.38 (t, 6, $J = 7.1$ Hz, 2 CH_3), 4.12 (q, 4, $J = 7.1$ Hz, 2 CH_2); ^{13}C NMR ($CDCl_3$) δ −1.52, 14.3, 9.2, 36.0, 74.8, 109.7; EIMS m/z 282 (M^+, 3), 253 ($M^+ - C_2H_5$, 3), 225 (37), 99 ($O{=}C{=}CHSiMe_2^+$, 100); HRMS m/z calcd for $C_{14}H_{26}O_2Si$ 282.1471, found 282.1470.

1,2-Bis((2-oxoethenyl)dimethylsilyl)ethane (3). Pyrolysis of **8** (35 mg, 0.124 mmol) by gas chromatography gave **3** (19 mg, 0.084 mmol, 68%): IR (isooctane) 2115, 2052 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 12, 4 CH_3), 0.54 (s, 4, 2 CH_2), 1.77 (s, 2, CH); ^{13}C NMR ($CDCl_3$) δ −1.82, −1.63, 9.47, 179.0; ^{17}O NMR ($CDCl_3$) δ 253.8; ^{29}Si NMR ($CDCl_3$) δ 3.09; UV $\lambda_{\max}^{\text{isooctane}}$ 309 ($\epsilon = 220$); EIMS m/z 211 ($M^+ - CH_3$, 9), 198 ($M^+ - CO$, 16), 183 ($M^+ - CH_3 - CO$, 46), 99 ($O{=}C{=}CHSiMe_2^+$, 100); HRMS m/z calcd for $C_9H_{15}O_2Si_2$ 211.0611, found 211.0614.

Hydration of 1. To **1** (21 mg, 0.13 mmol) in 1.5 mL of CD_3CN in an NMR tube was added H_2O (2.2 μL, 0.12 mmol), and the solution was kept 1 day at 22 °C. The solvent was evaporated, and recrystallization from $CH_3CN-CHCl_3$−hexane gave (pentamethyldisilanyl)acetic acid (**9**) (19 mg, 0.109 mmol, 81%): mp 55 °C; IR (KBr) 3310 −2480, 1672 cm^{-1}; ^1H NMR (CD_3CN) δ 0.08 (s, 9, Me_3Si), 0.13 (s, 6, Me_2Si), 1.86 (s, 2, CH_2), 8.80 (s, 1, OH); ^{13}C NMR (CD_3CN) δ −3.75, −2.38, 24.5, 174.8; EIMS m/z 175 ($M^+ - CH_3$, 24), 117 ($Me_2SiCH_2CO_2H^+$, 50), 73 (Me_3Si^+, 100).

Hydration of 2. To bisketene **2** (15 mg, 0.076 mmol) in 1.5 mL of CD_3CN in an NMR tube was added H_2O (2.7 mg, 0.15 mmol), and the ^1H NMR was observed with time. After 2 min new signals appeared at δ 0.30 and 2.04 in a 3:1 ratio. After 2 days these peaks had disappeared and new signals appeared assigned to 3,3,4,4-tetramethyl-3,4-disilahexanedioic acid (**11**): ^1H NMR (CD_3CN) δ 0.32 (s, 12, Me_2Si), 2.30 (s, 4, CH_2); ^{13}C NMR (CD_3CN) δ 2.9, 22.9, 168.3; CIMS (CH_4) m/z 234 (M^+), 249 ($M^+ + CH_3$), 263 ($M^+ + C_2H_5$). Upon evaporation of the CD_3CN **11** decomposed.

Hydration of 3. To **3** (11 mg, 0.049 mmol) in 1.5 mL of CD_3CN in an NMR tube was added H_2O (1.8 μL, 0.10 mmol), and the solution was kept for 4 days. Evaporation of the solvent and recrystallization from hexane gave 3,3,6,6-tetramethyl-3,6-disilaoctanedioic acid (**10**) (7 mg, 0.027 mmol, 55%): mp 123 °C; IR (KBr) 3500−2500, 1693 cm^{-1}; ^1H NMR (CD_3CN) δ 0.11 (s, 12, CH_3), 0.75 (s, 4, CH_2CH_2), 2.17 (s, 4, CH_2CO_2), 8.80 (bs, 2, CO_2H); ^{13}C NMR (CD_3CN) δ 0.34, 9.4, 22.4, 167.8; EIMS m/z 203 ($M^+ - CH_2CO_2H$, 26), 145 ($C_2H_4SiMe_2CH_2CO_2H^+$, 60), 117 ($Me_2SiCH_2CO_2H^+$, 73).

Hydration of 4. A solution of **4** (10 mg, 0.054 mmol) in 0.5 mL of CH_3CN containing 0.2 mL of $H_2{}^{18}O$ (98%) was sealed in a glass tube under N_2 and heated 36 h at 60 °C. Upon cooling, crystals of $(Me_3Si)_2CHCO_2H\text{-}^{18}O$ (9 mg, 0.045 mmol, 83%) formed and were collected and analyzed by HRMS (CI). Calcd for $C_8H_{20}{}^{16}O^{18}OSi_2$ m/z 207.1123, found m/z 207.1124. Ratio for peaks at m/z 205, 206, 207, 208, 209: 4.3, 14.3, 100, 20.9, 6.7 (found). Calcd for 207, 208, 209: 100, 19.0, 7.2.

Kinetic Studies. The rates of hydration of **1**−**3** were measured as previously[3e,10a] 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 317 nm (**1**), 308 nm (**2**), and 309 nm (**3**). The hydration of **4**[6d] was measured by injecting 5 μL of a 0.15 M solution in CH_3CN into 1.2 mL solvent in a 1 cm UV cell and monitoring the decrease in absorption at 278.7 nm.

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Supporting Information Available: ^{1}H NMR spectra (8 pages). Ordering information is given on any current masthead page.

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