

Stabilized and Persistent Allenylketenes

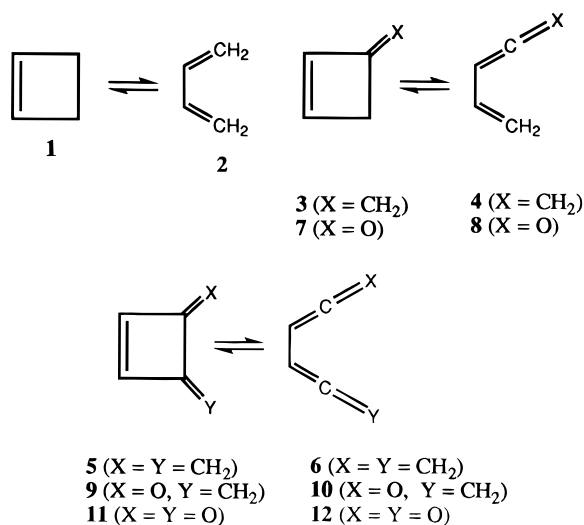
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Abstract: Photolyses of 2,3-bis(trimethylsilyl)-substituted methylenecyclobutenones **22**–**26** give essentially quantitative conversion to the allenylketenes **28**–**32** which have been isolated as long-lived species at room temperature. As predicted by molecular orbital calculations, the methylenecyclobutenones **22** and **26**, with carbethoxy and hydrogen substitution on the methylene group, respectively, undergo thermal equilibration with the corresponding allenylketenes **28** and **32** with equilibrium constants $[22]/[28] = 1.0$ and $[26]/[32] = 0.029$, at 100 °C. The X-ray structure of the phenyl-substituted allenylketene **29** confirms the *anti*-planar conformation as predicted by calculation. The bis-(allenylketene) **35** has been made by an analogous procedure. Hydration rates of the allenylketenes show acceleration by the CO₂Et substituent, but in all cases these are modestly less reactive than the 1,2-bisketene (Me₃SiC=C=O)₂.

The interconversion of cyclobutene (**1**) with 1,3-butadiene (**2**) is a reaction of great synthetic and mechanistic interest,¹ as is the corresponding reaction of the analogous pairs methylenecyclobutene (**3**)/vinylallene (**4**),² bis(methylene)cyclobutene (**5**)/bisallene (**6**),³ cyclobutenone (**7**)/vinylketene (**8**),⁴ methylenecyclobutenone (**9**)/allenylketene (**10**),⁵ and cyclobutenedione (**11**)/1,2-bisketene (**12**).^{6,7} Substituted vinylketenes in particular



have become major synthetic intermediates because of their

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facile intramolecular cyclization with attached unsaturated substituents (Smith–Hoehn reaction).^{4c–h} These reactions have added significance because of their relationships to the cyclization of enediynes, enyneallenes, and enyneketenes, including derivatives with “skipped” conjugation, which have DNA cleaving ability and utility as anticancer antibiotics and are also valuable synthetic intermediates.⁸

Work in our laboratory has concentrated on the reaction forming bisketene (**12**) and has made particular use of the ketene-stabilizing effect of silyl substitution.^{6,7} We now report the first studies of stable and persistent allenylketenes and find that the thermodynamic stability of these species, compared to their isomeric methylenecyclobutenone precursors, as well as the structure determined by X-ray, are accurately predicted by *ab initio* molecular orbital calculations. These highly functionalized molecules are readily available and have great promise as synthetic intermediates.

Allenylketenes have been previously postulated as reactive intermediates,⁵ but they have not been observed as long-lived species at ambient temperatures. The parent **10** was formed by Wolff rearrangement upon photolysis of **13** (eq 1), observed in a matrix at 8 K,^{5a} and was also postulated as an intermediate in the pyrolytic conversion of **14** to **9** (eq 2).^{5b} Photolysis of

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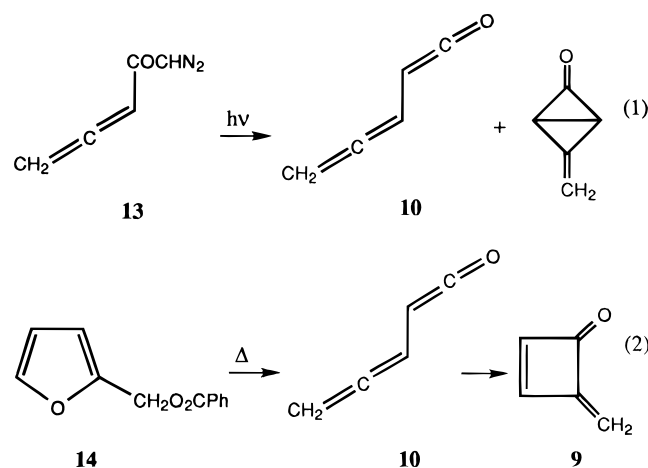
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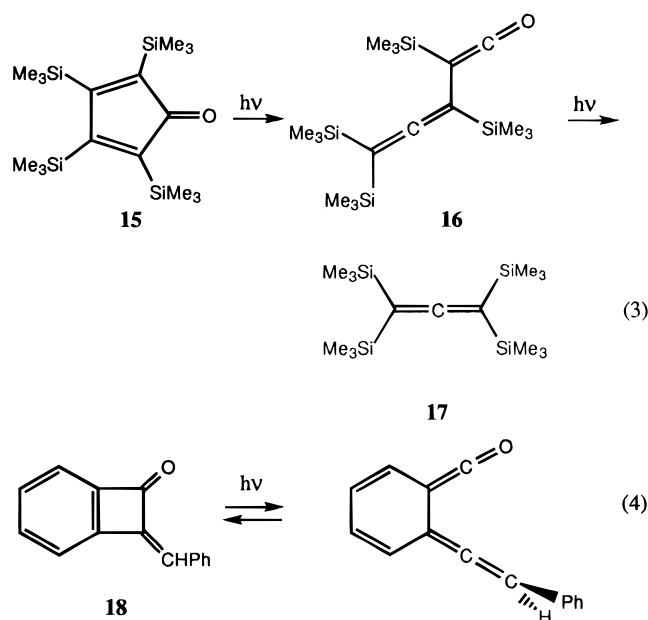
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Table 1. HF/6-31G* Bond Distances (Å), Bond Angles (deg), and Dipole Moments (D) for Allenylketenes

compd	C ₁ C ₂	C ₂ C ₃	C ₃ C ₄	C ₄ C ₅	C ₁ O	C ₁ C ₂ C ₃	C ₂ C ₃ C ₄	C ₃ C ₄ C ₅	OC ₁ C ₂	C ₁ C ₂ C ₃ C ₄	μ (D)
<i>E</i> - 10	1.311	1.471	1.300	1.295	1.145	122.6	124.2	179.7	180.0	180.0	1.43
<i>Z</i> - 10	1.311	1.478	1.300	1.296	1.144	123.5	125.9	179.8	179.5	26.7	1.54
TS 10	1.308	1.494	1.299	1.295	1.146	122.0	123.1	179.5	179.8	104.7	
9	1.498	1.338	1.485	1.315	1.180	91.9	95.2 ^a	138.7	136.9	0.0	3.74
TS 9	1.381	1.402	1.368	1.308	1.151	100.8	105.9	149.9	159.8	20.4	

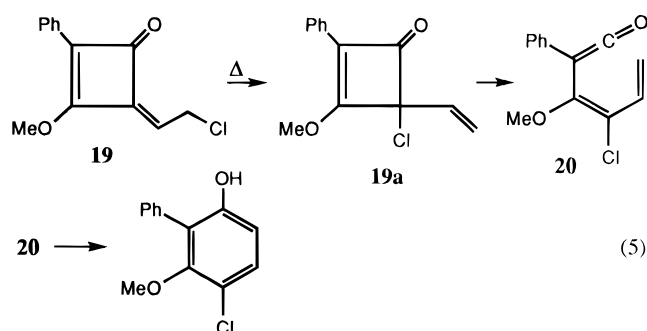
^a C₃C₄C₁ = 87.4.

15 led to **16**, as identified by its IR bands at 1890 and 2080 cm^{-1} , and this formed **17** upon further photolysis (eq 3).^{5c} Flash photolysis of **18** led to a transient species detected by its UV absorption near 395 nm, which was identified as an allenylketene and reverted rapidly back to **18** (eq 4).^{5d} Formation of an allenyl(seleno)ketene has also been proposed.^{5e}

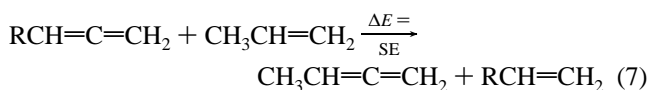
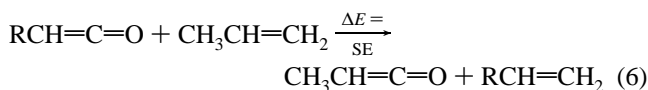


Other cases of ring openings of alkylidenecyclobutenones were, however, proposed not to involve allenylketene intermediates. For example, **19**, upon thermolysis, was suggested to undergo rearrangement to **19a** prior to ring opening to the unobserved ketene **20**, as shown in eq 5.^{5g} There are other studies of the relative stabilities of vinylallenes and the ring-closed isomeric methylenecyclobutenes,² including the effects of silyl substituents^{2a} and a continuing interest in the synthetic utility of silylated allenes.⁹

We have recently reported *ab initio* calculated substituent stabilization energies (SE) of ketenes⁶ and allenes,^{6a} as defined

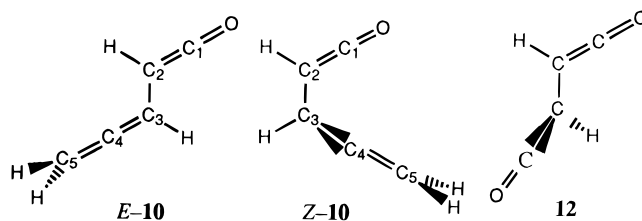


by the isodesmic reactions in eqs 6 and 7, respectively. As part of these calculations, we obtained the energy and structure of allenylketene (**10**), as well as the stabilization energies of the SiH₃ group on ketene (eq 6) and allene (eq 7), of 11.5 (MP2/6-31G*//MP2/6-31G* level) and 4.1 (HF/6-31G*//HF/6-31G* level) kcal mol⁻¹, respectively.^{6a}



Results and Discussion

For the determination of the barriers for interconversion and the relative stabilities of allenylketene (**10**) and the isomeric methylenecyclobutenone (**9**), we have examined the structures and energies of these intermediates and their connecting transition structures using *ab initio* molecular orbital calculations, as we have done previously (Tables 1 and 2).^{6,10} Two minimum energy structures for **10** were found, and the *anti* structure *E*-**10** is found to be planar, but the *syn* structure *Z*-**10** is not, with a dihedral angle for C₁C₂C₃C₄ of 26.7°.



Thus, allenylketene favors an *anti*-periplanar geometry (*E*-**10**), as does vinylketene **8**,¹¹ but by only 1.1 kcal/mol. By contrast, 1,2-bisketene is calculated to prefer the twisted geometry **12**,^{6,7a,b} and this has been confirmed by the X-ray structure of an analogous tetraketene.^{7e}

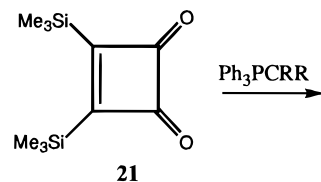
To examine the methylenecyclobutenone/allenylketene interconversion experimentally, 3,4-bis(trimethylsilyl)cyclobut-3-ene-1,2-dione (**21**)^{7c} was reacted with Wittig reagents Ph₃PCRR¹ to give methylenecyclobutenones **22–25**. For **22** and **24**, mixtures of *E/Z* isomers were obtained, and the lower field vinyl hydrogen or methyl group in each pair, which cor-

Table 2. Energies^a of Methylene-cyclobutenone **9**, **TS 9** for Ring Opening, Allenylketenes **E-10** and **Z-10** and **TS 10** for Their Interconversions

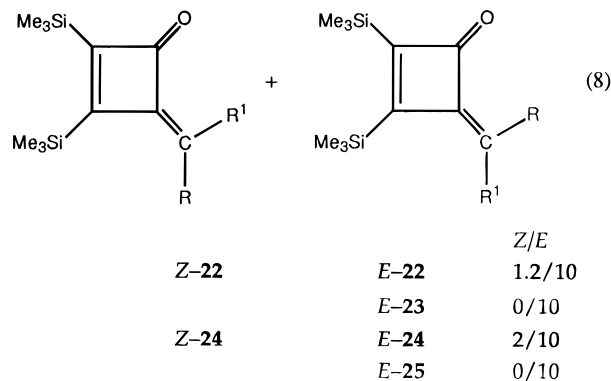
	9	TS 9	Z-10	TS 10	E-10
HF/6-31G*	-266.45062 (0)	-266.37289 (48.78)	-266.43033 (12.73)	-266.42702 (14.81)	-266.43221 (11.55)
ZPVE	0.07044	0.07774	0.06773	0.06899	0.06776
HF/6-31G* + Z	-226.38023 (0)	-226.30596 (46.56)	-226.36259 (11.04)	-226.35804 (12.93)	-226.36445 (9.91)
MP2//HF/6-31G* + Z	-267.17134 (0)	-267.11763 (33.66)	-267.15248 (11.80)	-267.14762 (14.86)	-267.15427 (10.68)

^a Hartrees, relative energies (kcal/mol) in parentheses.

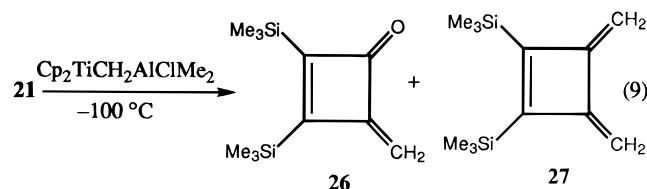
responded to the minor isomer, was assigned to the *Z* isomer, due to deshielding of the *syn*-hydrogen or methyl by the carbonyl group (eq 8).^{12a,b} For **23** and **25** only one stereoisomer was obtained, and these were tentatively assigned the *E* configuration on the basis of the preference for this isomer for **22** and **24** and in related examples.^{12c}



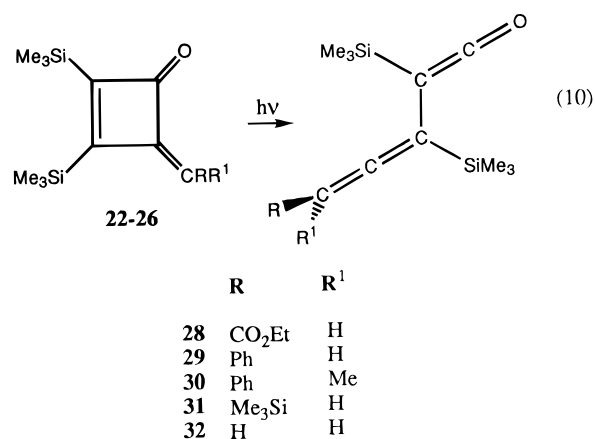
(**R** = CO₂Et, **R**¹ = H) (91%)
 (**R** = Ph, **R**¹ = H) (70%)
 (**R** = Ph, **R**¹ = Me) (66%)
 (**R** = Me₃Si, **R**¹ = H) (32%)



Attempted preparation of the methylene-cyclobutenone **26** by a Wittig reaction was unsuccessful, but this compound was obtained by reaction of **21** with Tebbe reagent^{12d} in 54% yield, along with 34% of the bis(methylene)cyclobutene **27** (eq 9). Recently dimethyltitanocene has also been used for the methylenation of cyclobutenediones.^{12e}



Photolysis of *E*- or *Z*-**22** with 350 nm light in CDCl₃ at 5 °C gave complete consumption of the reactant and led to the carboxy-substituted allenylketene **28** as 98% of the observable product in solution by ¹H NMR (eq 10). Chromatography gave **28** in 93% yield. The identification of **28** follows from its IR spectrum with strong ketenyl and allenyl bands at 2086 and 1919 cm⁻¹, respectively. We have recently reported on the distinctive ¹³C, ¹⁷O, and ²⁹Si NMR spectra of ketenes,¹³ and strong spectral evidence for the structure of **28** are the very characteristic ¹³C NMR chemical shifts of C₁, C₂, C₃, and C₄ at



δ 179.6, 15.5, 92.4, and 208.2, respectively, of ¹⁷O at δ 273, and of ²⁹Si at δ 3.2 and 2.0. For the analogous 1,2-bis(ketenyl)ketene (Me₃SiC=C=O)₂, the ¹³C_α, ¹³C_β, ¹⁷O, and ²⁹Si shifts are δ 181.8, 0.2, 269, and 3.2, respectively.

Thermolysis of pure *E*-**22** at 100 °C in CDCl₃ led to equilibration with *Z*-**22** and to the formation of **28**, and after 2.5 h the relative concentrations of *E*-**22**, *Z*-**22**, and **28** were constant at 0.37, 0.14, and 0.49, respectively. This result indicates that the bis(silylated)allenylketene **28** has essentially the same thermodynamic stability as the isomeric cyclobutenedione **22**, and this is in remarkable agreement with the result calculated from the substituent stabilization parameters (eqs 6 and 7). Thus, the HF/6-31G**/HF/6-31G* *ab initio* calculated stabilization energy values for SiH₃ relative to H on an allene and ketene, and of CH=O on an allene, are 3.0, 7.6,^{14a} and 0.2 kcal mol⁻¹, respectively,^{6a,b} and when the sum of 10.8 kcal mol⁻¹ of these is compared to the 10.7 kcal mol⁻¹ greater stabilization calculated for *E*-**10**, compared to **9** (Table 2), the prediction that **28** is 0.1 kcal mol⁻¹ more stable than **22** is obtained, consistent with the observed similar stability of the species.

Photolyses of the cyclobutenones *E*-**23**, the *E*/*Z*-**24** mixture, *E*-**25**, and **26** with 350 nm light led to allenylketenes **29**–**32**, respectively, in essentially quantitative yields. Allenylketenes **29** and **30** were rather stable solids at room temperature and were purified by chromatography on silica gel, but **31** was unstable to chromatography. The terminal methylene compound **32** was also purified by chromatography, but appeared rather unstable as a neat liquid. The IR and ¹³C, ¹⁷O, and ²⁹Si NMR spectra of **29**–**32** all showed the very characteristic signals for the allenylketene structures. Upon heating, **29**–**31** reformed the original cyclobutenones, along with other as yet unidentified products.

Heating of **32** at 100 °C in CDCl₃ led to clean conversion back to **26**, and after 9 h the ratio of **26**/**32** as measured by ¹H NMR was constant at 97:3. The group stabilizing energies (eqs 6 and 7) cited above for the pair **22**/**28** predict **22** is 0.1 kcal/mol more stable.

Rate constants for the thermal interconversion of **26** and **32** (eq 11) in CDCl₃ were obtained by monitoring the decrease in

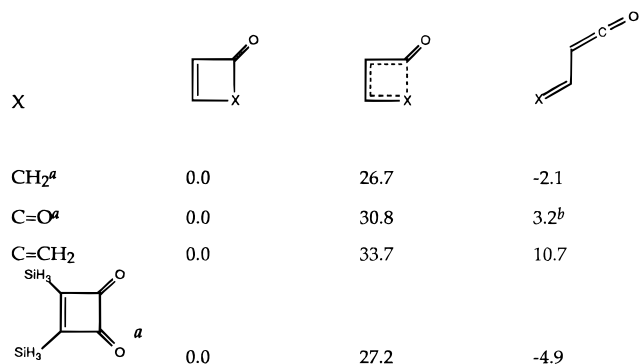


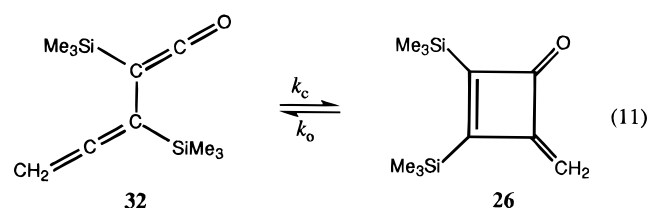
Figure 1. Calculated (MP2/6-31G*) relative energies for reactants, transition states, and products in ketene-forming reactions (kcal/mol). ^aReference 6c. ^bTwisted conformation.

Table 3. Rate ($\times 10^5$ s⁻¹) and Equilibrium Constants for the Interconversion of **26** and **32** (eq 11) in CDCl₃

T (°C)	k_{obsd} (= $k_c + k_o$)	k_c^a	k_o	K_{eq} (= k_c/k_o) ^b
98.8	30.5	29.6	0.85	34.7
98.7	28.8	28.0	0.84	33.5
87.3	9.61	9.40	0.21	44.5
87.1	9.00	8.81	0.19	46.6
77.3	3.29	3.22	0.066	49.0
77.2	3.39	3.32	0.064	51.6
25.0		4.5×10^{-3} ^c	0.028×10^{-3} ^c	160 ^c

^a $\ln k = -13\,200/T + 27.3$, $E_{\text{act}} = 26.2$ kcal/mol, $\Delta H^\ddagger = 25.6$ kcal/mol, $\Delta S^\ddagger = -6.3$ cal K⁻¹ mol⁻¹. ^b $\Delta H = -4.7$ kcal/mol, $\Delta S = -5.6$ cal K⁻¹ mol⁻¹. ^c Extrapolated.

the ¹H NMR absorption of the vinyl protons of **32** generated by photolysis of **26** in an NMR tube, as reported in Table 3. The rate expression for this process is given in eq 12^{14b} and from the relations $k_{\text{obsd}} = k_c + k_o$ and $K_{\text{eq}} = k_c/k_o$ lead to eq 13. From the measured value of k_{obsd} and K_{eq} , values of k_c and k_o may be obtained (Table 3). For comparison, the measured^{7c} rate constant for the ring opening of the cyclobutenedione **21** to form the bisketene (Me₃SiC=C=O)₂ at 99.0 °C in CDCl₃ of 9.45×10^{-4} s⁻¹ is 110 times greater than that for the ring opening of **26** at 98.8 °C.



$$\ln([\mathbf{32}] - [\mathbf{32}]_{\infty})/([\mathbf{32}]_0 - [\mathbf{32}]_{\infty}) = -(k_o + k_c)t \quad (12)$$

$$k_o = k_{\text{obsd}}/(K_{\text{eq}} + 1) \quad (13)$$

In Figure 1 the calculated barriers and energies for interconversion of the pairs cyclobutenone/vinylketene, cyclobutenedione/1,2-bisketene, and methylenecyclobutenone/allenylketene

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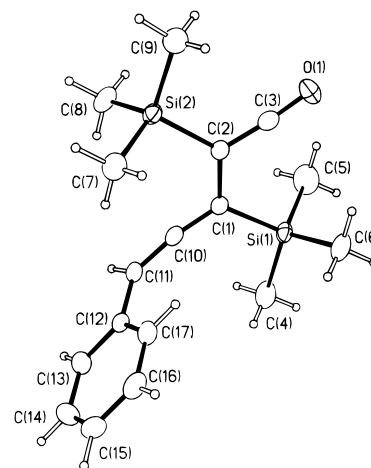


Figure 2. X-ray crystal structure of **29**.

are compared. Previous calculations^{6c} showed that for cyclobutenedione the substitution of first and second SiH₃ groups lowered the barrier for ring opening by 2.0 and 1.6 kcal/mol and lowered ΔE for ring opening by 3.7 and 4.4 kcal/mol, respectively. The experimental E_{act} for ring opening of the bis(Me₃Si)-substituted cyclobutenedione in CDCl₃ of 29.3 kcal/mol is in rather good agreement with the calculated value for the bis(SiH₃) derivative of 27.2 kcal/mol. Thus, similar agreement might be expected for the allenylketene. For ring closure of bisketenes (RC=C=O)₂, the effect of two SiH₃ substituents relative to hydrogen is calculated to increase the barrier by 4.5 kcal/mol, and if the effect of two SiH₃ groups on the ring closure of an allenylketene were the same, this would give a calculated barrier of 27.5 kcal/mol for ring closure of **32**, as compared to the experimental value of 26.2 kcal/mol.

The structure and the conformation of the phenyl-substituted allenylketene **29** were confirmed by an X-ray determination, as shown in Figure 2.¹⁵ Not only is the *anti*-planar conformation predicted by the molecular orbital calculations confirmed but also the observed bond distances and bond angles as noted below are in good agreement with the calculated values from Table 1 (parentheses): C₁=C₂ 1.310 (1.311), C₁=O 1.170 (1.145), C₂=C₃ 1.491 (1.471), C₃=C₄ 1.310 (1.300), C₄=C₅ 1.313 (1.295), C₁C₂C₃ 121.5 (122.6), C₂C₃C₄ 122.7 (124.2), C₂C₁O 175.7 (180.0), and C₁C₂C₃C₄ 175.7 (180.0). The calculated structure does not possess the bis(trimethylsilyl) and phenyl substituents of **29**, but evidently these have only small effects of the geometry.

By analogy to the preparation by Ried et al.^{12c} of unsubstituted 1,4-bis(4'-oxo-2'-cyclobuten-1'-ylidene)-1,4-dimethylbenzene the

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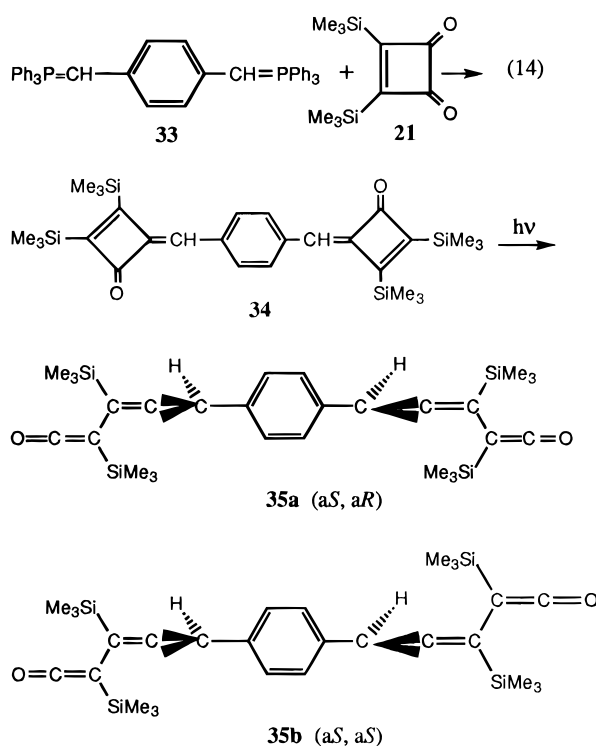
(15) X-ray data for **29**: C₁₇H₂₄O_{Si}₂; formula weight, 300.54; crystal system, monoclinic; space group, C2/c; color, pale yellow; unit cell dimensions, $a = 26.625(5)$ Å, $\alpha = 90^\circ$, $b = 6.1358(10)$ Å, $\beta = 96.011(13)^\circ$, $c = 22.04(3)$ Å, $\gamma = 90^\circ$; volume, Z, 3581.8(11) Å³, $R = 0.0370$, GOF = 0.925. Full crystallographic data are given in the Supporting Information.

Table 4. Hydration Rates of Allenylketenes in H₂O/CH₃CN Mixtures at 25 °C

[H ₂ O] (M)	<i>k</i> (28) ^{a,b}	<i>k</i> (29) ^{a,c}	<i>k</i> (30) ^{a,d}	<i>k</i> (32) ^{a,e}
38.9	72.4			
33.3	34.7			
27.8	21.6			
22.2	12.4			
16.7	8.28	0.400	0.225	0.508
11.1	4.80			

^a Rates in 10⁴ s⁻¹ (average of duplicate runs, ±5%). ^b Measured at 225 nm, log *k* = 0.0412[H₂O] - 3.79. ^c Measured at 251 nm. ^d Measured at 257 nm. ^e Measured at 210 nm.

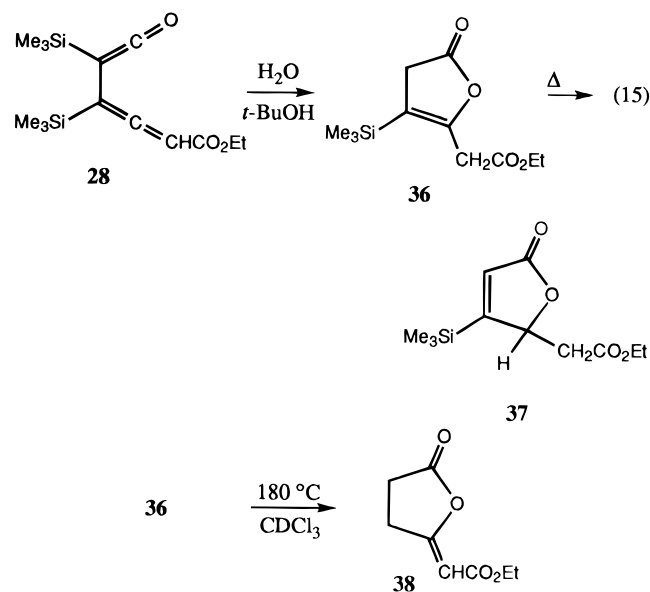
reaction of **21** with the bis Wittig reagent **33** gave the tetrasilylated analogue **34**, which upon photolysis gave the bis-(allenylketene) **35** as shown by the appearance of the characteristic IR bands and ¹³C NMR absorptions (eq 14).



The allene moieties in **35** each possess axial chirality; therefore, there should be two diastereomeric forms of this molecule,^{16a} as has been observed for other bis(allenes).¹⁶ The *meso* form **35a** and the *chiral* aS,aS isomer **35b** are depicted, and there is also a *chiral* aR,aR form.^{16a} The ¹H NMR signals for both *meso* **35a** and the racemic mixture of **35b** are observed as a 1:1 mixture in the crude product. Recrystallization of the mixture gave one of the stereoisomers in pure form, with characteristic IR bands at 2080 (ketene) cm⁻¹ and 1912 (allene) cm⁻¹ and ¹³C NMR signals at δ 16.4 and 181.4 (ketene) and δ 92.57, 92.59, and 205.7 (allene).

As a measure of the reactivity of the allenylketenes, the rates of hydration of **28–30** and **32** were obtained in H₂O/CH₃CN mixtures, as we have done previously,^{7c} and are reported in Table 4. For **28** the dependence of the reactivity on the [H₂O] in CH₃CN was determined over the range of 11.1–38.9 M H₂O (10–70%) and the rate increased by a factor of 15 over this

range and displayed the empirical correlation of log *k*_{obsd} with [H₂O] typical of many ketenes.^{7a–c} This behavior has been interpreted as indicating that the hydration proceeds through a highly polar transition state. There is a significant variation in the reactivity of the different substrates in 30% (16.7 M) H₂O/CH₃CN, with a maximum rate ratio *k*(**28**)/*k*(**30**) of 37:1. Examination of the product resulting from hydration of the carboxy-substituted allenylketene **28** (performed in H₂O/*t*-BuOH because of the limited solubility of **28**) showed that there was an initial, rather unstable, and not completely pure product formed in about 70% yield, identified as the desilylated lactone **36** on the basis of its spectral properties. Upon attempted purification by vapor phase chromatography, this was partially converted to another isomeric material identified as **37**, and upon heating in CDCl₃ and chromatography on silica gel, **36** gave the lactone **38** in 73% yield (eq 15).



Salient spectral features upon which these assignments are based include distinctive ¹H NMR signals of two allylic CH₂ groups in **36** with a mutual coupling of 1.4 Hz and IR absorptions at 1802, 1741, and 1648 cm⁻¹ consistent with lactone, ester, and alkenyl groups, respectively. Lactone **37**, in a mixture containing 33% residual **36**, showed a UV λ_{max} at 217 nm and ¹H NMR signals and couplings for the 3 distinct protons in the CHCH₂ unit and allylic coupling between the methine and vinyl H. The assignment was verified by decoupling of the methine H.

In accord with previous studies^{7a,c} and with the rate evidence favoring a highly polar transition state, these ketenes may be interpreted as reacting through rate-limiting nucleophilic attack of H₂O on the ketene.

In summary, long-lived allenylketenes **28–32** and bis-(allenylketene) **35** have been generated from the readily available bis(trimethylsilyl)cyclobut-3-ene-1,2-dione **21**, and characterized by their distinctive IR and NMR properties. The stability of **28–32** and **35** and the X-ray structure of **29** are in remarkable agreement with predictions based on calculated substituent stabilization energies and calculated structures, respectively.

Experimental Section

Infrared (IR) spectra were recorded on a Nicolet FTIR-8210E spectrometer. ¹H NMR spectra were recorded on a Varian VXR-200 at 199.975 MHz referenced to residual CHCl₃ (7.26 ppm), and are reported as follows: ppm (multiplicity, number of protons, assignment).

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^{13}C NMR spectra were recorded on a Varian VXR-200 at 50.289 MHz or a Varian UNITY-400 at 100.577 MHz and referenced to the center line of CDCl_3 (77.00 ppm). ^{17}O NMR and ^{29}Si NMR spectra were recorded on a Varian UNITY-400 at 54.219 and 79.459 MHz, respectively. Thin layer chromatography was performed on precoated silica gel 60F 254 on aluminum. The products were detected by ultraviolet light and by iodine vapor. Flash column chromatography was performed using silica gel (230–400 mesh) and hexanes/EtOAc as eluent. UV irradiation was performed in a Rayonet Photochemical Reactor using five RPR 3500 A 8 W lamps at about 5 °C.

2,3-Bis(trimethylsilyl)-4-(carbethoxymethylene)cyclobuten-1-one (22). A solution of ethyl (triphenylphosphoronylidene)acetate (0.774, 2.22 mmol) and cyclobutenedione **21** (0.502 g, 2.22 mmol) in 50 mL of CHCl_3 was stirred for 18 h under N_2 at 25 °C. The solvent was evaporated, and the viscous product was separated by column chromatography to give *Z*-**22** (0.070 g, 0.24 mmol, 11%), $R_f = 0.68$, and *E*-**22**, (0.529 g, 1.79 mmol, 80%), $R_f = 0.31$. For *Z*-**22**: IR (neat) 1764 (C=O) 1715 (CO_2Et) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.31 (s, 9, Me_3Si), 0.35 (s, 9, Me_3Si), 1.29 (t, 3, $J = 7.2$ Hz, CH_3), 4.19 (q, 2, $J = 7.2$ Hz, CH_2), 5.69 (s, 1, C=CH); ^{13}C NMR (CDCl_3) δ -0.67, -0.42, 14.3, 60.7, 99.4, 165.2, 169.2, 189.1, 191.1, 201.2; UV λ_{max} (cyclohexane) 253 (ϵ 15 000), 280 (sh) nm; EIMS m/z 296 (M^+ , 19), 267 ($\text{M}^+ - \text{C}_2\text{H}_5$, 39), 73 (Me_3Si^+ , 100); HRMS m/z calcd for $\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si}_2$ 296.1264, found 296.1254. For *E*-**22**: IR (neat) 1767 (ketone), 1707 (CO_2Et) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.28 (s, 9, Me_3Si), 0.33 (s, 9, Me_3Si), 1.32 (t, 3, $J = 7.1$ Hz, CH_3), 4.22 (q, 2, $J = 7.1$ Hz, CH_2), 5.44 (s, 1, C=CH); ^{13}C NMR (CDCl_3) δ -1.47, -1.28, 14.0, 60.3, 104.3, 164.6, 172.5, 184.6, 190.2, 198.1; UV λ_{max} (cyclohexane) 248 (ϵ 21 000), 275 (sh) nm; EIMS m/z 296 (M^+ , 8), 267 ($\text{M}^+ - \text{C}_2\text{H}_5$, 31), 73 (Me_3Si^+ , 100); HRMS m/z calcd 296.1264, found, 296.1261.

2,3-Bis(trimethylsilyl)-5-carbethoxy-1,3,4-pentatrien-1-one (28). A solution of *E*-**22** (110 mg, 0.37 mmol) in 4 mL of CHCl_3 in a glass tube was irradiated with 350 nm light 12 h at 5 °C. The solvent was evaporated, and the product was chromatographed (10% EtOAc in hexanes, $R_f = 0.60$) to give **28** (102 mg, 0.344 mmol, 93%): IR (CCl_4) 2086, 1919, 1711 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.21 (s, 9, Me_3Si), 0.22 (s, 9, Me_3Si), 1.25 (t, 3, $J = 7.1$ Hz, CH_3), 4.17 (q, 2, $J = 7.1$ Hz, CH_2), 5.42 (s, 1, C=CH); ^{13}C NMR (CDCl_3) δ -1.34, -0.78, 14.3, 15.5, 60.5, 85.4, 92.4, 167.1, 179.6, 208.2; ^{17}O NMR (CDCl_3) δ 273.2; ^{29}Si (CDCl_3) δ 2.0, 3.2; UV λ_{max} (cyclohexane) 220 (ϵ 28 000), 348 (ϵ 141) nm; EIMS m/z 296 (M^+ , 6), 267 ($\text{M}^+ - \text{C}_2\text{H}_5$, 15), 73 (Me_3Si^+ , 100); HRMS m/z calcd for $\text{C}_{14}\text{H}_{24}\text{O}_3\text{Si}_2$ 296.1264, found 296.1262. Similar photolysis of *Z*-**22** gave complete conversion to **28**. Heating of *E*-**22** (10 mg, 0.034 mmol) in 0.76 mL of degassed CDCl_3 in an NMR tube at 100 °C for 3 h gave a mixture of *Z*-**22**, *E*-**22**, and **28** in a ratio of 0.14:0.37:0.49, as measured by ^1H NMR. This ratio did not change on further heating.

(E)-2,3-Bis(trimethylsilyl)-4-(phenylmethylene)cyclobuten-1-one (E-23). To a stirred suspension of $\text{PhCH}_2\text{PPh}_3^+\text{Cl}^-$ (0.78, 2.0 mmol) in 40 mL of ether at -78 °C was added *n*-BuLi (1.2 mL, 1.6 M in hexane, 2 mmol), the solution was stirred 10 min at -78 °C and 1 h at 0 °C, and cyclobutenedione **21** (450 mg, 2.0 mmol) in 5 mL of ether was added to the orange suspension. After 15 h of stirring at 25 °C, the mixture was filtered through a small plug of silica gel, the solvent was evaporated, and the product was chromatographed (5% EtOAc in hexanes, $R_f = 0.50$) to give *E*-**23** (0.420 g, 1.4 mmol, 70%): IR (CCl_4) 1750 cm^{-1} (C=O); ^1H NMR (CDCl_3) δ 0.28 (s, 9, Me_3Si), 0.38 (s, 9, Me_3Si), 6.03 (s, 1, CHPh), 7.2–7.8 (m, 5, Ph); ^{13}C NMR (CDCl_3) δ -1.47, -1.27, 116.9, 127.5, 128.4, 129.3, 135.4, 158.6, 177.9, 190.0, 201.4; UV λ_{max} (cyclohexane) 211 (ϵ 17 000), 283 (ϵ 25 000), 294 (ϵ 27 000), 309 (ϵ 20 000); EIMS m/z 300 (M^+ , 23), 285 ($\text{M}^+ - \text{CH}_3$, 8), 272 ($\text{M}^+ - \text{CO}$, 57), 257 ($\text{M}^+ - \text{CO} - \text{CH}_3$, 43), 73 (Me_3Si , 100); HRMS m/z calcd for $\text{C}_{17}\text{H}_{24}\text{OSi}_2$ 300.1366, found, 300.1364.

2,3-Bis(trimethylsilyl)-5-phenyl-1,3,4-pentatrien-1-one (29). A solution of *E*-**23** (150 mg, 5.0 mmol) in 4 mL of CHCl_3 in a glass tube was irradiated with 350 nm light 12 h at 5 °C. The solvent was evaporated, and the product was chromatographed (5% EtOAc in hexanes, $R_f = 0.78$) to give **29** (141 mg, 0.47 mmol, 94%): mp 89–90 °C (dec); IR (CCl_4) 2080, 1908 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.18 (s, 9, Me_3Si), 0.21 (s, 9, Me_3Si), 6.07 (s, 1, C=CH), 7.1–7.4 (m, 5, Ph); ^{13}C NMR (CDCl_3) δ -1.0, -0.7, 14.1, 92.5, 92.6, 126.3, 128.5, 135.0,

181.3, 205.3 (one C not seen); ^{17}O NMR (CDCl_3) δ 274.0; ^{29}Si NMR (CDCl_3) δ 0.7, 2.2; UV λ_{max} (cyclohexane) 249 nm (ϵ 26 000); EIMS m/z 300 (M^+ , 11), 285 ($\text{M}^+ - \text{CH}_3$, 5), 272 ($\text{M}^+ - \text{CO}$, 51), 257 ($\text{M}^+ - \text{CO} - \text{CH}_3$, 43), 73 (Me_3Si^+ , 100); HRMS m/z calcd for $\text{C}_{17}\text{H}_{24}\text{OSi}_2$ 300.1366, found 300.1368. Heating of **29** in CDCl_3 led to a complex mixture.

(E/Z)-2,3-Bis(trimethylsilyl)-4-(1-phenylethylidene)cyclobuten-1-one (E/Z-24). Reaction of $\text{Ph}_3\text{PCHMePh}^+\text{Br}^-$ (0.781 g, 2.0 mmol) with **21** (450 mg, 2.0 mmol) and *n*-BuLi (2.0 mmol), as for *E*-**15**, gave after chromatography a 4.5:1 mixture of *E/Z*-**24** (0.415 g, 66%). For *E*-**24**: $R_f = 0.36$; ^1H NMR (CDCl_3) δ 0.26, (s, 9, Me_3Si), 0.42 (s, 9, Me_3Si), 2.21 (s, 3, CH_3), 7.2–7.4 (m, 5, Ph). For *Z*-**24**: $R_f = 0.47$; ^1H NMR (CDCl_3) δ -0.14 (s, 9, Me_3Si), 0.28 (s, 9, Me_3Si), 2.30 (s, 3, CH_3), 7.2–7.4 (m, 5, Ph).

2,3-Bis(trimethylsilyl)-5-phenyl-1,3,4-hexatrien-1-one (30). A solution of *E/Z*-**24** (150 mg, 0.50 mmol) in 4 mL of CHCl_3 was irradiated 12 h with 350 nm light at 5 °C and chromatographed ($R_f = 0.77$), as for *E*-**23**, to give **30** (144 mg, 4.6 mmol, 93%): mp 77–78 °C (dec); IR (CCl_4) 2080 cm^{-1} (allenyl band not visible); ^1H NMR (CDCl_3) δ 0.14 (s, 9, Me_3Si), 0.19 (s, 9, Me_3Si), 2.06 (s, 3, CH_3), 7.1–7.4 (m, 5, Ph); ^{13}C NMR (CDCl_3) δ -0.99, -0.97, 16.4, 16.6, 90.5, 97.9, 125.3, 126.0, 128.3, 137.3, 182.0, 205.7; ^{17}O NMR (CDCl_3) δ 273.2; ^{29}Si NMR (CDCl_3) δ 1.76, 1.30; UV λ_{max} (cyclohexane) 257 (ϵ , 23 000) nm; EIMS m/z 314 (M^+ , 40), 299 ($\text{M}^+ - \text{CH}_3$, 12), 286 ($\text{M}^+ - \text{CO}$, 58), 271 ($\text{M}^+ - \text{CO} - \text{CH}_3$, 43), 73 (Me_3Si^+ , 100); HRMS m/z calcd for $\text{C}_{18}\text{H}_{26}\text{OSi}_2$ 314.1522, found 314.1521.

(E)-2,3,5-Tris(trimethylsilyl)-4-methylenecyclobuten-1-one (E-25). To a stirred suspension of $\text{Ph}_3\text{PCH}_2\text{SiMe}_3^+\text{I}^-$ (957 mg, 2.0 mmol) in 40 mL of ether was added *n*-BuLi (1.2 mL, 1.6 M in hexane, 2 mmol), the solution was stirred 10 min at 0 °C and 1 h at 25 °C, and dione **21** (450 mg, 2.0 mmol) in 5 mL of ether was added to the yellow suspension. After 15 h of stirring at 25 °C, the mixture was filtered through a small plug of silica gel, the solvent was evaporated, and the product was chromatographed (5% EtOAc in hexanes, $R_f = 0.68$) to give *E*-**25** (0.189 g, 0.64 mmol, 32%): IR (CCl_4) 1753 cm^{-1} (C=O); ^1H NMR (CDCl_3) δ 0.17 (s, 9, Me_3Si), 0.25 (s, 9, Me_3Si), 0.31 (s, 9, Me_3Si), 5.26 (s, 1, C=CH); ^{13}C NMR (CDCl_3) δ -1.04, -0.80, -0.08, 115.1, 171.3, 181.7, 203.1; UV λ_{max} (cyclohexane) 242 (ϵ 21 000); EIMS m/z 296 (M^+ , 26), 281 ($\text{M}^+ - \text{CH}_3$, 11), 253 (21), 155 (44), 73 (Me_3Si^+ , 100); HRMS m/z calcd for $\text{C}_{14}\text{H}_{28}\text{OSi}_3$ 296.1448, found 296.1445.

2,3,5-Tris(trimethylsilyl)-1,3,4-pentatrien-1-one (31). A solution of *E*-**25** (140 mg, 0.50 mmol) was irradiated as above, and the solvent was evaporated to give **31**: IR (CDCl_3) 2074, 1904 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.09 (s, 9, Me_3Si), 0.13 (s, 9, Me_3Si), 0.21 (s, 9, Me_3Si), 4.69 (s, 1, C=CH); ^{13}C NMR (CDCl_3) δ -1.20, -0.80, -0.31, 14.1, 78.1, 181.6, 208.3; ^{17}O NMR (CDCl_3) δ 270.3; ^{29}Si (CDCl_3) δ -4.9, -0.7, 2.2; EIMS m/z 296 (M^+ , 17), 253 (10), 147 (45), 73 (Me_3Si^+ , 100). Upon attempted purification by chromatography, **31** decomposed.

2,3-Bis(trimethylsilyl)-4-methylenecyclobuten-1-one (26). To a stirred solution of dione **21** (0.401 g, 1.8 mmol) in 8 mL of dry THF at -100 °C was added μ -chloro- μ -methylenebis(η^5 -2,4-cyclopentadienyl)(dimethylaluminum)titanium (Tebbe reagent, 2.0 mL, 0.5 M in toluene, 1 mmol), and the solution was stirred 6 h at -100 °C and then poured into 50 mL of pentane and filtered. The filtrate was concentrated and chromatographed (3% EtOAc in hexanes) to give 1,2-bis(trimethylsilyl)-3,4-bis(methylene)cyclobutene (**27**) (0.038 g, 0.17 mmol, 34% based on Tebbe reagent), **26** (0.124 g, 0.554 mmol, 55% based on Tebbe reagent), and unreacted **21** (0.097 g, 24%). For **26**: $R_f = 0.42$; IR (CCl_4) 1757 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.25 (s, 9, Me_3Si), 0.32 (s, 9, Me_3Si), 4.63 (d, 1, $J = 1.4$ Hz), 4.95 (d, 1, $J = 1.4$ Hz); ^{13}C NMR (CDCl_3) δ -1.09, -0.76, 94.9, 165.0, 181.1, 191.7, 199.9; EIMS m/z 224 ($\text{M}^+ - \text{CH}_3$, 22), 209 ($\text{M}^+ - \text{CH}_3$, 8), 196 ($\text{M}^+ - \text{CO}$, 34), 181 ($\text{M}^+ - \text{CO} - \text{CH}_3$, 65), 155 (62), 147 (34), 108 (31), 73 (Me_3Si^+ , 100). For **27**: $R_f = 0.90$; ^1H NMR (CDCl_3) δ 0.26 (s, 18), 4.63 (s, 2), 4.67 (s, 2); ^{13}C NMR (CDCl_3) δ -0.26, 92.8, 154.7, 173.0; EIMS m/z 222 (M^+ , 39), 207 ($\text{M}^+ - \text{CH}_3$, 100), 179 ($\text{M}^+ - \text{CO} - \text{CH}_3$, 10), 155 (41), 73 (Me_3Si^+ , 91); HRMS m/z calcd for $\text{C}_{12}\text{H}_{22}\text{Si}_2$ 222.1260, found 222.1256.

2,3-Bis(trimethylsilyl)-1,3,4-pentatrien-1-one (32). A solution of **26** (120 mg, 0.54 mmol) in 4 mL of CHCl_3 in glass tubes was irradiated

with 350 nm light for 12 h at 5 °C. The solution was concentrated and chromatographed (3% EtOAc in hexanes, $R_f = 0.80$) to give **32** (101 mg, 0.45 mmol, 84%): IR (CCl₄) 2080.5, 1912 cm⁻¹; ¹H NMR (CDCl₃) δ 0.157 (s, 9, Me₃Si), 0.224 (s, 9, Me₃Si), 4.55 (s, 2, C=CH₂); ¹³C NMR (CDCl₃) δ -1.48, -0.52, 15.5, 76.4, 86.5, 181.2, 208.3; ¹⁷O NMR (CDCl₃) δ 271.5; ²⁹Si NMR (CDCl₃) δ -0.96, 2.40; EIMS m/z 224 (M⁺, 6), 196 (M⁺ - CO, 8), 181 (M⁺ - CO - CH₃, 22), 155 (30), 147 (28), 73 (Me₃Si⁺, 100); HRMS m/z calcd for C₁₁H₂₀OSi₂ 224.1053, found 224.1054.

Thermal Ring Closure of 32. Allenylketene **32** in a degassed solution of CDCl₃ in sealed NMR tubes was heated and periodically cooled, and the relative amounts of **26** and **32** were measured from the ¹H NMR spectrum. Derived rate and equilibrium constants are given in Table 3.

1,4-Bis[2',3'-bis(trimethylsilyl)-4'-oxo-2'-cyclobuten-1'-ylidene]-methyl]benzene (34). To a stirred solution of 1,4-bis[(triphenylphosphonium)methyl]benzene dibromide (876 mg, 1.1 mmol) in 40 mL of ether at -78 °C was added *n*-BuLi (1.4 mL, 1.6 M in hexane, 2.2 mmol), and the mixture was stirred for 10 min at -78 °C and 1 h at 0 °C. The dione **21** (502 mg, 2.2 mmol) in 5 mL of ether was added to the dark orange mixture, which was stirred 12 h at 22 °C and filtered through a small plug of silica gel. The filtrate was concentrated on a rotary evaporator and the residue chromatographed (5% EtOAc/hexanes, $R_f = 0.45$) to give **34** (0.356 g, 0.682 mmol, 62%), as a solid that isomerized/decomposed at 165 °C: ¹H NMR (CDCl₃) δ 0.278 (s, 18), 0.379 (s, 18), 6.00 (s, 2), 7.75 (s, 4); ¹³C NMR (CDCl₃) δ -1.05, -0.75, 116.8, 129.5, 134.5, 158.7, 177.8, 189.9, 201.6; EIMS m/z 522 (M⁺, 13), 494 (M⁺ - CO, 23), 466 (M⁺ - 2CO, 100), 363 (28), 155 (16), 97 (19), 73 (Me₃Si⁺, 97); HRMS m/z calcd for C₂₈H₄₂O₂Si₄ 522.2262, found 522.2284.

1,4-Bis[2',3'-bis(trimethylsilyl)-1'-oxo-1',3',4'-pentatrien-5'-yl]benzene (35). A solution of **34** (10 mg, 0.019 mmol) in CDCl₃ (4 mL) in three NMR tubes was irradiated with 350 nm light 8 h at 5 °C to give a 1:1 mixture of *meso* and *dl* **35**: ¹H NMR (CDCl₃) δ 0.157 (s, 18, Me₃Si), 0.171 (s, 18, Me₃Si), 0.197 (s, 18, Me₃Si), 0.206 (s, 18, Me₃Si), 6.02 (s, 4, CH=C), 7.11 (s, 8, Ar). Removal of the solvent and recrystallization three times from CHCl₃ gave one of the diastereoisomers of **35** as a white solid that isomerized/decomposed near 158 °C upon fast heating: ¹H NMR (CDCl₃) δ 0.157 (s, 9, Me₃Si), 0.207 (s, 9, Me₃Si), 6.02 (s, 2, CH=C), 7.11 (s, 4, Ar); ¹³C NMR (CDCl₃) δ -1.05, -0.74, 16.42, 92.57, 92.59, 126.59, 133.10, 181.43, 205.70; IR (CDCl₃) 2080, 1912 cm⁻¹; EIMS m/z 522 (M⁺, 6), 494 (M⁺ - CO, 15), 466 (M⁺ - 2CO, 87), 363 (20), 155 (13), 97 (15), 73 (Me₃Si⁺, 100); HRMS m/z calcd for C₂₈H₄₂O₂Si₄ 522.2262, found 522.2244.

Hydration of Allenylketene 28. A sample of **28** (200 mg, 0.68 mmol) was dissolved in a solution of H₂O (1 g) and *t*-BuOH (9 g) and stirred overnight at 22 °C. Then, EtOAc (50 mL) was added and the solution was dried over MgSO₄, evaporated, and chromatographed (20% EtOAc in hexanes) to give slightly impure **36** (114 mg, 0.47 mmol, 69%) as an oil: ¹H NMR (CDCl₃) δ 0.184 (s, 9, Me₃Si), 1.271 (t, 3, $J = 7.0$ Hz, CH₃), 3.19 (t, 2, $J = 1.4$ Hz, CH₂), 3.35 (t, 2, $J = 1.4$ Hz, CH₂), 4.19 (q, 2, $J = 7.0$ Hz, OCH₂); ¹³C NMR (CDCl₃) δ -1.33, 13.83, 34.67, 37.29, 61.16, 111.82, 152.66, 167.75, 176.88; IR (neat) 1802, 1741, 1648 cm⁻¹; EIMS m/z 242 (M⁺, 5), 227 (M⁺ - CH₃, 100), 199 (79), 171 (47), 147 (24), 129 (46), 73 (Me₃Si⁺, 66).

Injection of **36** (10 mg, 0.04 mmol) in 0.1 mL of hexanes into a gas chromatograph (OV-17 column, injector 220 °C, column 200 °C, retention time 35 min) gave a colorless oil showing the ¹H NMR signals of **36** as well as those assigned to **37** in a 33:67 ratio. For **37**: ¹H NMR (CDCl₃) δ 0.26 (s, 9, Me₃Si), 1.28 (t, 3, $J = 7.2$ Hz, CH₃), 2.50 (dd, 1, $J = 16.8, 8.8$ Hz, CHH), 2.85 (dd, 1, $J = 16.8, 3.8$ Hz, CHH), 4.195 (q, 2, $J = 7.2$ Hz, OCH₂), 5.51 (ddd, 1, $J = 8.8, 3.8, 1.9$ Hz, CHO), 6.21 (d, 1, $J = 1.9$ Hz, C=CH). Irradiation of the methine H at 5.51 collapsed the coupling to the alkene proton at 6.21 and the doublet splittings of the protons at δ 2.50 and 2.85 (UV λ_{\max} (cyclohexane) 217 nm ($\epsilon \approx 3000$)).

The lactone **36** (36 mg, 0.15 mmol) in 1 mL of CDCl₃ in a sealed NMR tube under Ar was heated for 15 h at 180 °C, the solvent was evaporated, and purification by chromatography (5% EtOAc/hexanes) gave **38** (18.7 mg, 0.11 mmol, 73%): mp 96–97 °C; ¹H NMR (CDCl₃) δ 1.287 (t, 3, $J = 7.0$ Hz, CH₃), 2.70–2.78 (m, 2, CH₂), 3.34–3.43 (m, 2, CH₂), 4.18 (q, 2, $J = 7.0$ Hz, OCH₂), 5.71 (t, 1, $J = 2.2$ Hz, C=CH); ¹³C NMR (CDCl₃) δ 14.26, 26.10, 60.14, 97.52, 166.64, 167.36, 173.47 (one C not observed); IR (KBr) 1819, 1699 cm⁻¹; UV λ_{\max} (cyclohexane) 227 nm (ϵ 11 500); EIMS m/z 170 (M⁺, 39), 142 (M⁺ - CO, 64), 125 (100), 115 (26), 96 (39), 87 (55), 69 (60), 55 (41); HRMS m/z calcd for C₈H₁₀O₄ 170.0579, found 170.0574.

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Supporting Information Available: ¹H NMR spectra and full X-ray crystallographic data on **29** (32 pages). See any current masthead page for ordering and Internet access instructions.

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