# New Tricks from an Old Dog: Bisketenes after 90 Years

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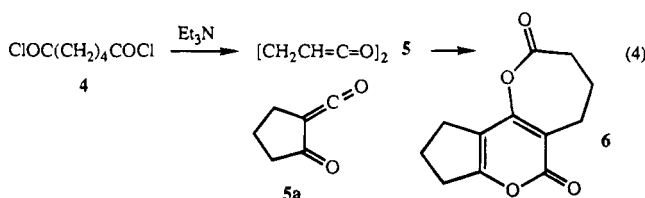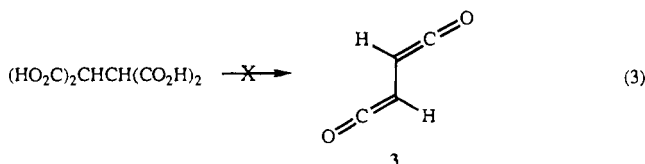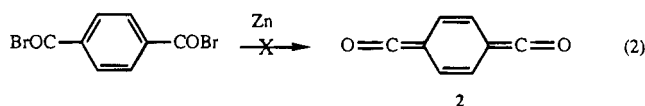*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1*

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Carbon suboxide (1), the first bisketene, was prepared from the dehydration of malonic acid by Otto Diels and B. Wolf in 1906[1a] less than one year after the announcement of the preparation of the first ketene, $Ph_2C=C=O$, by Hermann Staudinger.[1b] In 1908 Staudinger and Bereza[1c] reported an alternative synthesis by a double debromination using zinc (eq 1). The chemistry of 1 has been pursued ever since, and this work has been reviewed periodically.[1d–g]

$$CH_2(CO_2H)_2 \xrightarrow{P_2O_5}$$

$$O=C=C=C=O \xleftarrow{Zn} CBr_2(COBr)_2 \quad (1)$$
$$\mathbf{1}$$
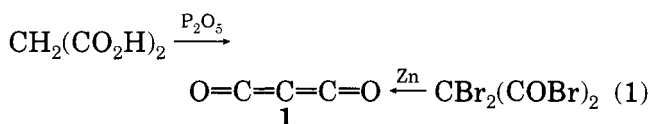
As part of his comprehensive studies of ketenes Staudinger pursued the preparation of bisketenes, including unsuccessful efforts to prepare "quinoketene" 2 (eq 2)[2a] and 1,2-bis(ketene) (3) (eq 2).[2b] Staudinger also reported[2c] that in early work of Wedekind (not published until much later[2d]) the reaction of adipyl chloride (4) with Et_3N may have formed the diketene 5, which led to a dimeric structure shown later by Baldwin to be that of 6 (eq 4).[2e] However, as suggested by later investigators, it appears unlikely that 5 is formed in appreciable amounts from 4, and 5a is a more likely precursor to 6.[2f]

Eventually other workers succeeded in the preparation of the 1,4-bis(ketene) 7[3a] and the dibenzo analogue of 2[3b] as crystalline solids, although both are quite reactive toward nucleophiles, and 7 polymerizes readily at room temperature. The formation of the parent 1,2-bis(ketene) (3) was achieved by different routes, including the photolysis of 9 or 10[4a,b] (eq 5), but 3 was a short-lived intermediate that was only observed in an argon matrix[4a] and formed cyclobutenedione (11) on warming.[4a] Substituted 1,2-bis(ketenes) have been generated as unobserved reactive intermediates from the corresponding cyclobutenediones,[4c–f] and the *ortho*

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$$BrOC—\text{⟨⟩}—COBr \xrightarrow[\text{X}]{Zn} O=C=\text{⟨⟩}=C=O \quad (2)$$
$$\mathbf{2}$$

$$(HO_2C)_2CHCH(CO_2H)_2 \xrightarrow{X} \quad (3)$$
$$\mathbf{3}$$

$$ClOC(CH_2)_4COCl \xrightarrow{Et_3N} [CH_2CH=C=O]_2 \; \mathbf{5} \longrightarrow \quad (4)$$
$$\mathbf{4} \qquad \qquad \qquad \mathbf{5a} \qquad \qquad \mathbf{6}$$

isomer 8 of 2 was a transient but observable intermediate.[4a,g–i] Possibly 2 itself has been generated as an unobserved intermediate in the electrochemical reduction of terephthaloyl chloride leading to a polymeric material.[4j] Reactions of a variety of other

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difunctional precursors that could lead through bis-(ketenes) have been reported,[4k-r] including the pyrolysis of bis(isopropenyl) esters,[4k] double Wolff rearrangements,[4l] cleavage of bis(azo) compounds,[4m] thermolysis of a bis(dioxinone),[4n] photolysis of a bis-(methylene)cyclobutenedione,[4o] and dehydration of an azulenedicarboxylic acid, which gave ^{1}H NMR and IR spectra attributed to the interesting dication **12**.[4p]
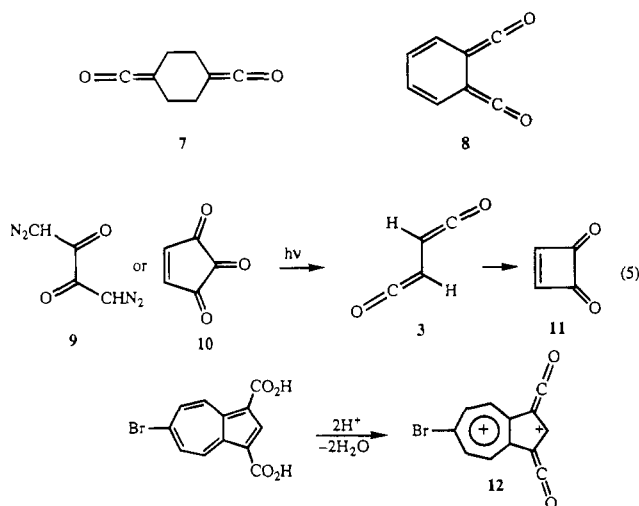
In 1961 reports appeared that ring opening of cyclobutenediones **13** and **14** might also involve bisketene intermediates **15** and **16**, respectively, although these were trapped and not directly observed.[4q,r] In later studies of the photolysis of **14** the IR band of **16** was observed at low temperatures.[4f,s]
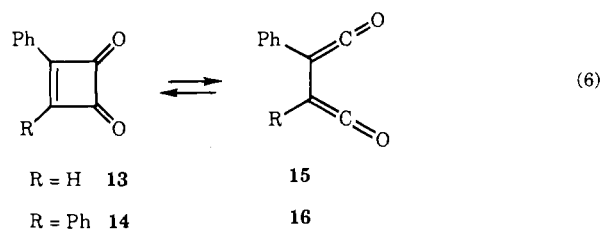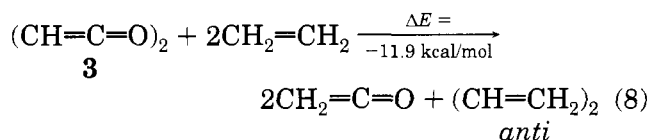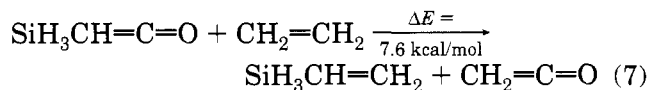

Pyrolysis of cyclobutenediones leads to alkynes,[4t] evidently through the intermediacy of bisketenes, and in the case of the attempted synthesis of cyclo-C_{18} by irradiation of **17** an intermediate IR band at 2115 cm^{-1} may arise from the hexaketene **18**.[4u,v]
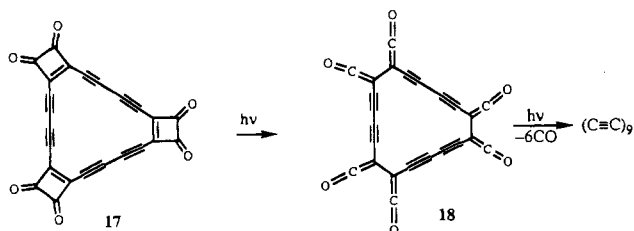

Thus the interesting structural features of bisketenes have stimulated the imagination of chemists since the days of Staudinger; however, due to their difficulty of preparation and apparent short lifetimes these species have remained as chemical curiosities about which rather little is known. Nevertheless, their polyfunctionality and their readily apparent potential utility in practical applications make them attractive candidates for further study.

Our group in Toronto has been pursuing ketene chemistry since 1979[5] and in 1991 reported *ab initio* molecular orbital calculations of the effects of substituents on ketene stabilities.[6a] Comparisons of isodesmic reactions showed that ketenes are stabilized by electropositive substituents; for example, the comparison of eq 7 indicates that SiH_3 is stabilizing by 7.6 kcal/mol relative to H on a ketene as compared to an alkene. Furthermore, these calculations predicted that the anti conformation of the parent bisketene 1,3-butadiene-1,4-dione (**3**) was only 6.9 kcal/mol less stable than cyclobutenedione (**11**). However, the calculated energies of the individual species indicate that bisketene **3** is destabilized relative to ketene and butadiene by 11.9 kcal/mol (eq 8).[6a,b]

$$SiH_3CH{=}C{=}O + CH_2{=}CH_2 \xrightarrow[\text{7.6 kcal/mol}]{\Delta E =}$$
$$SiH_3CH{=}CH_2 + CH_2{=}C{=}O \quad (7)$$

$$\underset{\textbf{3}}{(CH{=}C{=}O)_2} + 2CH_2{=}CH_2 \xrightarrow[\text{-11.9 kcal/mol}]{\Delta E =}$$
$$\underset{anti}{2CH_2{=}C{=}O + (CH{=}CH_2)_2} \quad (8)$$

These considerations led us to the expectation that 1,2-bis(ketenes) could be prepared that were more stable than the isomeric cyclobutene-1,2-diones and, in particular, that the use of the known ketene-stabilizing influence of the Me_3Si group[6] would permit the preparation of **19**. Assuming additivity of substituent effects and an equivalence of the properties of the substituents SiH_3 and Me_3Si leads to an initial estimate that **19** would be 8.3 kcal/mol more stable than **20** (eq 9). As noted below (*cf.* Table 1) more direct calculations indicate a ΔE of −4.9 kcal/mol for two SiH_3 groups.
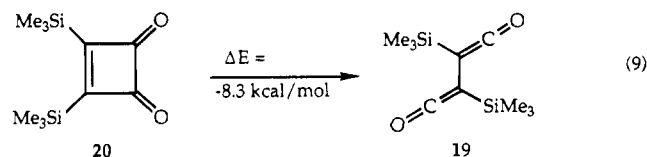
In our first attempt to prepare **19**, acid **21** was synthesized, but attempted formation of the corresponding bis(acyl chloride) as a precursor to **19** led instead to uncharacterized products (eq 10).[6i] Analogous efforts to prepare bisketenes by similar routes by others were also unsuccessful.[4r,7] However, the preparation of **20** was achieved starting with alkyne **22** as shown in eq 11, and heating of **20** at 100 °C in CDCl$_3$ led to quantitative conversion to **19**, as indi-

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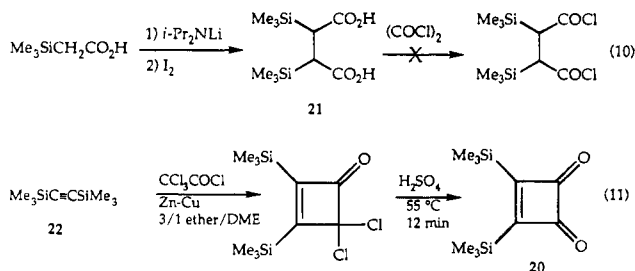
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Table 1. Summary of MP2/6-31G* Relative Energies (kcal/mol)^a and Entropy Changes (cal mol^{-1} K^{-1}) in Ring Opening of Cyclobutenes, Cyclobutenones, and Cyclobutenediones

	E_a	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔE	ΔG	ΔH	ΔS
23	35.8	35.1	35.0	-0.2	-20.9	-23.0	-21.5	5.0
24	26.7	25.7	25.8	0.2	-2.1	-4.0	-2.7	4.4
11	30.8	29.2	29.4	0.8	3.2	0.9	3.2	7.5
(F)	31.0	30.3	30.7	1.2	13.7	11.2	12.8	5.5
(F,F)	29.9	29.2	29.5	1.0	20.4	17.4	19.5	7.0
(SiH₃)	28.8	28.0	28.5	1.7	-0.5	-2.5	-1.2	4.5
(SiH₃,SiH₃)	27.2	26.3	26.9	2.0	-4.9	-6.1	-5.3	2.9
(SiH₃,F)	31.0	32.0	31.2	-2.8	11.9	9.7	11.2	5.1

^{a} MP2/6-31G* + ZPVE//MP2/6-31G* for **11**, **23**, and **24**; otherwise MP2/6-31G* + ZPVE//HF/6-31G*.

cated by the complete disappearance of the ^{1}H NMR signal of **20** at δ 0.37, the appearance of the signal of **19** at δ 0.21, and the generation of a ketenyl band in the IR at 2100 cm^{-1}.[8a,b] The photolysis of **20** with 350 nm light also led to the formation of bisketene **19**, accompanied by the formation of the alkyne **22**,[8b] which was shown to result from the photolysis of **19**.[8b]

$$\text{Me}_3\text{SiCH}_2\text{CO}_2\text{H} \xrightarrow[\text{2) I}_2]{\text{1) }i\text{-Pr}_2\text{NLi}} \underset{\mathbf{21}}{\text{Me}_3\text{Si}}\text{C(CO}_2\text{H)}_2\text{SiMe}_3 \xrightarrow[\text{X}]{\text{(COCl)}_2} \text{Me}_3\text{Si}\text{C(COCl)}_2\text{SiMe}_3 \quad (10)$$

$$\underset{\mathbf{22}}{\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3} \xrightarrow[\text{3/1 ether/DME}]{\underset{\text{Zn-Cu}}{\text{CCl}_3\text{COCl}}} \text{[} \text{cyclobutenone} \text{]} \xrightarrow[\text{12 min}]{\underset{55\,^\circ\text{C}}{\text{H}_2\text{SO}_4}} \underset{\mathbf{20}}{\text{[bisketene]}} \quad (11)$$

A comparison of the calculated energies of ring opening of cyclobutene (**23**) and cyclobutenone (**24**)

was made by Nguyen, Ha, and More O'Ferrall,[8c] and to further elucidate the ring opening of eq 9 we have extended this theoretical study to include cyclobutenedione (**11**) and its derivatives substituted with the ketene-stabilizing SiH₃ and ketene-destabilizing fluoro groups.[8d] It was found[8d] that energies calculated at the MP2/6-31G* level were essentially the same for either MP2/6-31G* or HF/6-31G* optimized geometries, and so it was concluded that energies calculated at the MP2/6-31G*//HF/6-31G* level in cases where calculation of MP2/6-31G* optimized geometries was impractical were sufficiently accurate for direct comparison to other structures calculated at the latter level. Frequencies of the species were calculated so that enthalpies and entropies of activation and reaction could also be calculated by the method of Jorgensen et al.,[8f] as summarized in Table 1. The calculated structures of the reactant, transition structure, and product for ring opening of cyclobutenedione (**11**) are depicted in Figure 1.

The calculated E_{act} values of 35.8 kcal/mol for cyclobutene and of 27.2 kcal for bis(silyl)-substituted cyclobutenedione are in reasonable agreement with the experimental $\Delta H^{\ddagger}$ values of 32.9 kcal/mol for cyclobutene and 29.4 kcal/mol for the bis(silyl)-substituted cyclobutenedione **20**.[8b,d]

Comparison of the results for ring openings of cyclobutene, cyclobutenone, and cyclobutenedione

(8) (a) Zhao, D.-c.; Tidwell, T. T. *J. Am. Chem. Soc.* **1992**, *114*, 10980–10981. (b) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097–10103. (c) Nguyen, M. T.; Ha, T.; More O'Ferrall, R. A. *J. Org. Chem.* **1990**, *55*, 3251–3256. (d) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233–7238. (e) Werstiuk, N. H.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 3383–3390. (f) Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936–2942. (g) Allen, A. D.; Liu, R.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Pure Appl. Chem.*, in press.
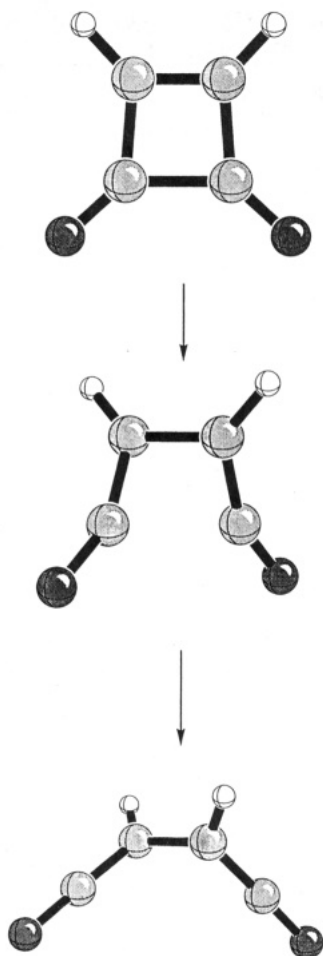
Figure 1. Calculated structures of the reactant, transition structure, and product for ring opening of cyclobutenedione (**11**).

(Table 1) reveals that there is no parallel between the free energies of activation and of reaction, for while the cyclobutene to 1,3-butadiene conversion has the most favorable ΔG, −23.0 kcal/mol, it also has the highest barrier, $\Delta G^{\ddagger} = 35.1$ kcal/mol. For all the compounds in Table 1 the calculated magnitudes of the entropies of activation are rather small, while the entropies of reaction ΔS are all positive and of significantly greater magnitude, ranging from 2.9 to 7.5 cal mol^{-1} K^{-1}. These results are plausible and consistent with there being only a minor increase in conformational mobility in the ring-opening transition state, but a larger effect in the product.

The calculations reveal that the substituent effects are not always additive, as the first and second fluoro substituents increase the ΔG relative to the parent **11** by 10.3 and a further 6.2 kcal/mol, respectively, while SiH$_3$ groups cause corresponding decreases of 3.4 and 3.6 kcal/mol, respectively. These effects are about half of the isodesmic effects of these groups on monoketenes (*cf.* eq 7), and the differences are attributed at least in part to destabilization of the precursor cyclobutenedione by F and stabilization by SiH$_3$.[8d] Cyclobutenedione possesses aromatic stabilization due to the 2π-electron contributing structure **11a**,[9] but it is evidently destabilized by the σ-acceptor effect of fluorine[10a,b] and may be stabilized by SiH$_3$, as evidenced by the generation of a number of electron deficient species bearing trialkylsilyl substituents bonded to sp^2 carbon.[10c-f] The substrate with (SiH$_3$, F) substituents has a larger ΔG of 8.8 kcal/mol than

11, and this is only 1.5 kcal/mol less than the effect of fluorine alone.
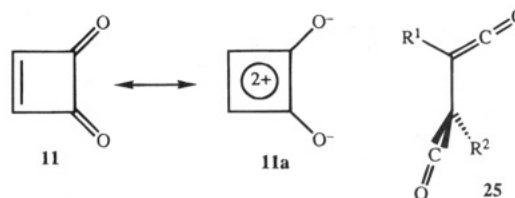
These calculations show that in all cases the bis-ketenes prefer twisted, almost perpendicular conformations, **25**, as shown in Figure 1, as opposed to the planar *s-E* (**3**) or *s-Z* conformations.[8d] These conclusions are confirmed experimentally by the measured photoelectron spectrum of **19**, which is uniquely consistent with a twisted conformation, and by the dipole moment of **19** of 2.7 D, compared to the value of 1.7 D for Me$_3$SiCH=C=O.[8e] This significant dipole moment excludes an *s-E* conformation and is consistent with the twisted conformation.[8e] The unexpected conclusion that the *s-E* conformation is not favored cannot be ascribed primarily to steric effects, as the calculations show that **25** is favored even for R^1 = R^2 = H.[8d] The instability of the planar structure may be attributed to the unfavorable $\pi-\pi$ repulsion between the electrons in the p orbitals at the central carbons of **3**, due to the high negative charge density (*vide supra*) on these carbons, and the absence of any plausible conjugatively stabilizing interactions in a planar 1,3-dienyl unit.

The bisketene **19** appears to be stable indefinitely at room temperature in the dark in the absence of air. Bubbling of O$_2$ into a solution of **19** in refluxing toluene gave the anhydrides **26** and **27** in isolated yields of 14 and 7%, respectively, along with small amounts of unidentified products (eq 12).[8a,b]
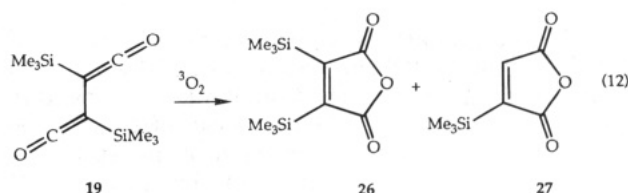
The reactions of ketenes[11] and strained alkenes[12] with O$_2$ have long been of interest and have been interpreted as involving perepoxide and diradical intermediates.[11] A diradical pathway for reaction of **19** with ^{3}O$_2$ could involve an initial triplet diradical **28** followed by reaction of a second molecule of **19** to give **29**, which could cleave to two molecules of **26** (eq 13). The formation of similar anhydrides in the

(9) (a) *Oxocarbons*; West, R., Ed.; Academic Press: New York, 1980. (b) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967.

(10) (a) Allen, A. D.; Tidwell, T. T. *Adv. Carbocation Chem.* **1989**, *1*, 1−44. (b) McAllister, M. A.; Tidwell, T. T. *Croat. Chem. Acta* **1992**, *65*, 633−653. (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677−2689. (d) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317−1320. (e) Siehl, H.-U.; Kaufmann, F.-P. *J. Am. Chem. Soc.* **1992**, *114*, 4937−4939. (f) Prakash, G. K. S.; Reddy, V. P.; Rasul, G.; Casanova, J.; Olah, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 3076−3078.

(11) (a) Bartlett, P. D.; Gortler, L. *J. Am. Chem. Soc.* **1963**, *85*, 1864−1869. (b) Bartlett, P. D.; Cluney, R. E. *J. Org. Chem.* **1983**, *48*, 4165−4168. (c) Turro, N. J.; Chow, M. *J. Am. Chem. Soc.* **1980**, *102*, 5058−5064.

(12) Bartlett, P. D.; Banavali, R. *J. Org. Chem.* **1991**, *56*, 6043−6050. (b) Pasto, D. J.; Yang, D. S.; Muellerleile, J. A. *J. Org. Chem.* **1992**, *57*, 2976−2978.

reaction of bisketenes with O_2 has been observed before,[4f,o] but there has apparently been no discussion of the mechanism of these processes.
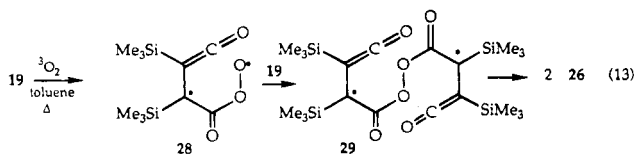
The reaction of **19** in 1/10 H_2O/acetone for 5 min at 25 °C gave rise to the anhydrides *Z*- and *E*-**30** in a 5/1 ratio in the crude product as observed by ^{1}H NMR. After prolonged reaction with H_2O the observed products were succinic anhydride (**31**) and succinic acid. Both *Z*-**30** and *E*-**30** were isolated as crystalline solids, and their structures were established by X-ray crystallography.[8b]
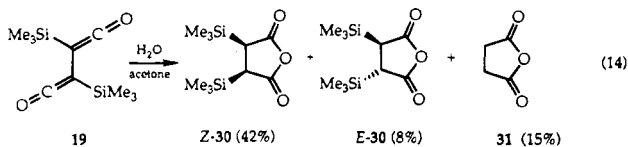

Reaction of **19** in pure EtOH for 15 min at 0 °C and evaporation of the solvent gave monoketene **32** in 98% purity by ^{1}H NMR analysis. Upon refluxing for 16 h in EtOH, **19** forms **33**, diethyl succinate, and Me_3-SiOEt (eq 15).[8b] The structure of monoketene **32** was established by its spectroscopic data, particularly by the IR bands at 2093 (sh), 2085 (s), and 1711 (s) cm^{-1}, and by 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. Comparable reactions of **19** with MeOH and *i*-PrOH gave the corresponding methyl and isopropyl monoester monoketenes.[8b]
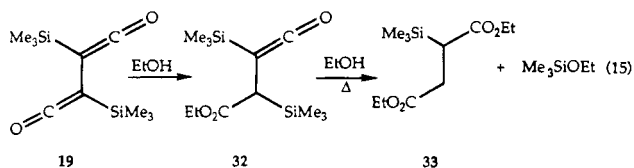
The reaction of **19** in CH_3CN containing H_2O gives the anhydrides **30**, and the rates of reaction of **19** relative to $Me_3SiCH=C=O$, the solvent isotope effect, and the dependence of the rate on $[H_2O]$[8b] are consistent with those measured for other ketenes assigned to react by rate-limiting nucleophilic attack of H_2O in the ketene plane leading through a planar polar transition state with enolate or enol character (eq 16).[5a-c,13] This path appears reasonable for the first step of the conversion of **19** to **30** by H_2O, and it was proposed[8b] that this process occurs as shown in eq 17, in which monoketene **34**, which was not detected in these experiments, is formed initially and cyclizes to **30**.

Two separate tricks were employed to confirm the formation of **34** in the thermal hydration. The first trick was independent generation of **34** by hydration of **19** induced by acid catalysis (*vide infra*), and the second was the generation of **34** by photochemical hydration.[14] The structure of **34** was established by its spectroscopic characterization, and the kinetics of

(13) Skancke, P. *J. Phys. Chem.* **1992**, *96*, 8065−8069.
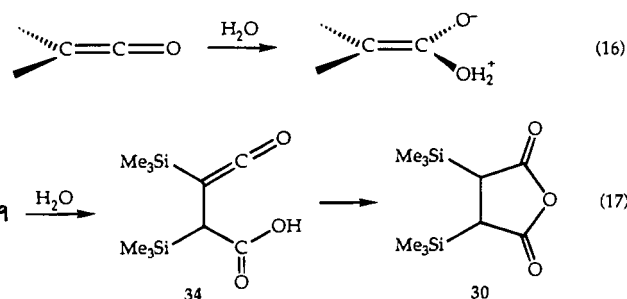
the uncatalyzed conversion of **34** to **30** were measured.[14] Photohydrations of certain crowded ketenes have been reported previously,[15a] as well as similar reactions of carbon suboxide,[15b] alkynes,[15c] allenes,[15d] and alkenes.[15c] These reactions have usually been interpreted in terms of initial protonation of the photoexcited substrate,[15a,c,d] but in the case of **19** the available evidence does not differentiate between initial protonation at C_β or nucleophilic attack at C_α as in eq 16.

The thermal reactivity of **19** toward alcohols and the much lower reactivity of monoketene **32** formed initially from ethanol may be interpreted analogously to previous studies of the reactivity of $Me_3SiCH=C=O$[6c] and other ketenes with H_2O[5a-c] and alcohols.[8b] Thus $Me_3SiCH=C=O$ and **32** have significant thermodynamic ground state stabilization due to the presence of the Me_3Si group compared to ketenes with only alkyl or hydrogen substituents,[6a] and **32** has the bulky substituent $EtO_2CCHSiMe_3$ at C_β, which will sterically hinder reaction with nucleophiles,[5a-c] and this causes **32** to be significantly less reactive than is Me_3-SiCH=C=O. As discussed above there is evidence that the ground state of **19** is destabilized due to the bisketene structure, and the transition state for nucleophilic addition to **19** is also destabilized, by steric crowding. The net result of these different effects is that **19** and $Me_3SiCH=C=O$ have similar reactivity toward nucleophiles. Partial desilylation occurs in the reaction of $Me_3SiCH=C=O$ with alcohols,[6c] and this also occurs for **32** (eq 15).[8b]

The rates of addition of water and various alcohols to **19** are quantitatively correlated by the effects of solvent polarity and of solvent nucleophilicity on the reactivity, using the Winstein−Grunwald equation 18,[16] in which the parameters N and Y are measures of the solvent nucleophilicity and ionizing power, respectively.[8b] This result is consistent with the interpretation that hydroxylic nucleophiles react with ketenes by in-plane approach to give polar transition states (eq 16), and hence the rates will depend upon both solvent polarity and nucleophilicity.

$$\log k/k_0 = lN + mY \qquad (18)$$

The values of the parameters are $l = 0.87 \pm 0.13$, $m = 0.61 \pm 0.10$, intercept -0.24 ± 0.41, and a correlation coefficient $r = 0.940$. The correlation is

(14) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847−851.

(15) (a) Kirmse, W.; Spaleck, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 776−777. (b) Hageloch, G.; Feess, E. *Chem. Ber.* **1951**, *84*, 730−733. (c) McEwan, J.; Yates, K. *J. Am. Chem. Soc.* **1987**, *109*, 5800−5808. (d) Raizadeh, K.; Yates, K. *J. Org. Chem.* **1984**, *49*, 1500−1506.

(16) (a) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667−7674. (b) Kevill, D. N.; Abduljaber, M. H. *Croat. Chem. Acta* **1992**, *65*, 539−549. (c) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1991**, *56*, 1845−1850.

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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 16, while the sizable m value shows that there is also a major polar effect on the reaction, also consistent with eq 16.

This method of the correlation of nucleophilic attack by solvent on unsaturated carbon atoms using the solvent nucleophilicity and polarity parameters may have greater applicability to related processes. These include additions to carbon–carbon double bonds,[17a,b] solvolysis of acyl halides,[17c] and nucleophilic attack on carbonyl groups,[17d] in which there is widespread interest. A term for the ability of the solvent to act as a general base could also be added to eq 18, as there has also been a recent report[17e] that the reaction of 4-nitrobenzenesulfonyl chloride in alcohol–water mixtures showed a bimolecular term in $[H_2O]$, due to H_2O acting both as a nucleophile and as a general base. However, for ketenes it remains to be seen if this factor can be distinguished.

A previous suggestion of the formation of an unsymmetrically substituted 1,2-bis(ketene) was the proposal that thermolysis or photolysis of 3-phenylcyclobutenedione (**13**) in methanol to give dimethyl 2-phenylsuccinate may have involved ring opening to bisketene **15** (eq 6) which then reacted with methanol.[4q] The unsymmetrical bisketene $O=C=CHC(OH)=C=O$ was also formed upon photolysis of the corresponding cyclobutenedione in an Ar matrix and observed by IR.[4c]

To form long-lived unsymmetrical bisketenes, cyclobutenediones substituted with one trimethylsilyl group and either phenyl (**35a**) or methyl (**35b**) were prepared, and both formed observable bisketenes **36** upon photolysis.[18a,b] Reaction of these bisketenes with methanol gave monoketenes **37**, which were purified by VPC and obtained pure as rather stable colorless liquids, and further reaction with methanol gave the corresponding dimethyl succinates (eq 19).[18a,b] The kinetics of the reversion of bisketenes **36** to the more stable cyclobutenediones **35** were measured and were faster for R = Me compared to R = Ph, consistent with the predicted stabilization of ketenes by these groups.[18a] For R = Ph the presence of 0.5–1.5% of the bisketene in thermal equilibrium could also be detected,[18a,b] while for **36b** (R = Me) the amount of bisketene present at thermal equilibrium was less, a result consistent with the known stabilizing effects of Ph and Me on ketenes.[18a,b]

Recently we have found that even the unstabilized phenyl and diphenyl bisketenes **15** and **16** generated by photolysis of cyclobutenediones **13** and **14**, respectively (eq 6), are long-lived at room temperature, with half-lives for ring closure at 25 °C in hydrocarbon solvents of 1.1 h and 18 s, respectively.[18c] The greater reactivity of **16** in ring closure is consistent with the
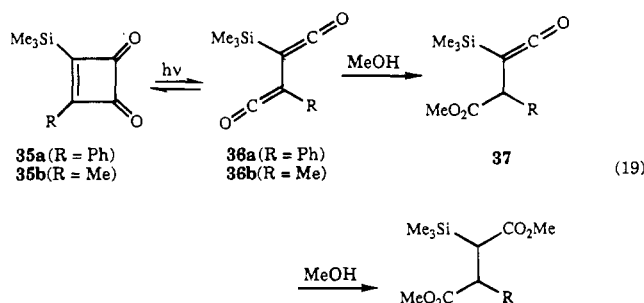
calculated barrier to ring closure of the unsubstituted bisketene,[8d] and the calculated destabilization of monoketenes by phenyl relative to H of 2.6 kcal/mol per phenyl.[6b]

These bisketenes as well as shorter-lived examples have been generated in CH_3CN at 25 °C and directly observed by time-resolved infrared spectroscopy (TR-IR).[18c] This technique is well suited for the observation of ketenes because of their strong absorption near 2100 cm^{-1}. For example, 2,3-dimethyl-1,3-butadiene-1,4-dione $(O=C=CMeCMe=C=O)$[4e,s] was prepared in this way and, in CH_3CN, showed bands at 2092 and 2114 cm^{-1} with relative intensities of 1.82/1.00.[18c] The HF/6-31G*//HF/6-31G* calculated IR frequencies at 2098 and 2113 cm^{-1}, relative intensities 1.41/1.00, for this compound were in good agreement. For the bis(trimethylsilyl) derivative only one band is observed experimentally at 2084 cm^{-1}, while the bis(silyl) compound is calculated[18c] to have closely spaced absorptions at 2088.7 and 2089.5 cm^{-1}.

Electrophilic additions to ketenes have been studied theoretically,[19a] and experimentally in the gas phase[19b] and solution.[19c] For bisketenes calculations of the structures and energies of the products of protonation of **3** show that the three conformations **38a–c** (relative energies, kcal/mol, in parentheses) could result from protonation of C_1, and of these the twisted conformation **38c** is the most stable.[14] However, the most favorable product by 3.3 kcal/mol was **38d**, resulting from protonation of **3** at C_4. This calculated pathway involves electrophilic attack at C_α of a carbonyl group. In an earlier study of the protonation of ketenes it was shown that there is a strong preference for protonation at C_β, but that carbocation-stabilizing groups at C_β decreased the preference for protonation at this position.[19a] Structure **38d** benefits from both allylic and acylium ion character, while structures **38a–c** are destabilized by the presence of the electronegative ketenyl group at C_β. The cyclized ion **38e** is predicted at this level of theory to be 1.6 kcal/mol higher in energy than **38d**.

For the addition of Cl^+ the calculations indicate that ion **39d** from Cl^+ attack at C_4 (C_α) is much more stable than the twisted ions **39a** and **39b** from attack at C_2 (C_β), and that no ion with coplanar C_1–C_4 exists as a minimum energy structure. The cyclized ion **39e** is 0.4 kcal/mol more stable than **39d**.[14]

Further calculations on the 2,3-bis(silyl)-substituted bisketene at a lower level of theory than the results in Scheme 1 revealed that silyl substitution tended to give a relative preference for electrophilic attack

(17) (a) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474–479. (b) Bernasconi, C. F.; Schuck, D. F. *J. Org. Chem.* **1992**, *57*, 2365–2373. (c) Song, B. D.; Jencks, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8470–8479. (d) Cieplak, A. S.; Wiberg, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 9226–9227. (e) Bentley, T. W.; Jones, R. O.; Koo, I. S. *J. Chem. Soc., Perkin Trans. 2* **1994**, 753–759.

(18) (a) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625–2626. (b) Allen, A. D.; Ji, R.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *Heteroat. Chem.* **1994**, *5*, 235–244. (c) Allen, A. D.; Colomvakos, J. D.; Egle, I.; Lusztyk, J.; McAllister, M. A.; Tidwell, T. T.; Wagner, B. D.; Zhao, D.-c. *J. Am. Chem. Soc.*, in press.

(19) (a) Leung-Toung, R.; Peterson, P.; Csizmadia, I. G.; Tidwell, T. T. *J. Mol. Struct. (THEOCHEM)* (b) Eberlin, M. N.; Majumdar, T. K.; Cooks, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 2884–2896. (c) Olah, G. A.; Alemayehu, M.; Wu, A.; Farooq, O.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1992**, *114*, 8042–8045.

Bisketenes after 90 Years

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Scheme 1. Calculated Relative Energies (MP2/6-31G*//MP2/6-31*) of Products 38 and 39 from Addition of H⁺ and Cl⁺, Respectively (kcal/mol)
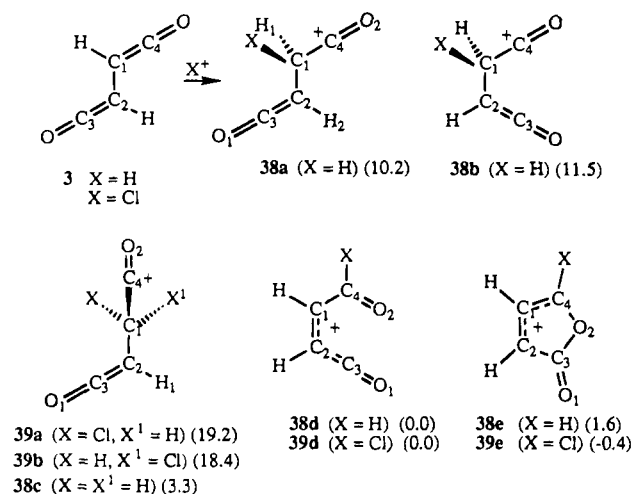
at C_β, so it is expected that for silylated bisketenes the preference for attack of H⁺ or Cl⁺ to give the products of α-attack **38d** and **39d**, respectively, would be less marked.

Experimentally as mentioned above it is found that the reaction of **19** with aqueous acid in CH_3CN proceeded by an initial acid-catalyzed step followed by a slower uncatalyzed step to give the stereoisomeric anhydrides **30**.[14] The acid-catalyzed process is assigned to rate-limiting protonation of the bisketene at C_β to form an acylium ion **40**, which then forms the acid **34** (eq 20). The formation of **34** had been previously inferred to occur in the neutral hydration of **19**, followed by cyclization of **34** to the observed anhydrides **30** (eq 17).[8b] The measured uncatalyzed rate of formation of **30** from **34** in acid is 2.2 times less than that previously found for the neutral reaction of bisketene **19** with H_2O (eq 17),[8b] and since the absorbance of **34** at the wavelength at which the reaction of **19** was monitored was 10-fold less than that of **19**, the slower reaction of **34** was not observed in the study in neutral solution.[8b]
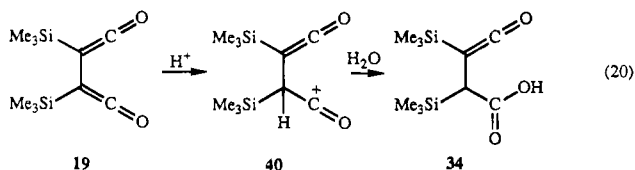
The reaction of **19** in $CDCl_3$ with 1 equiv of CF_3-CO_2H in $CDCl_3$ at room temperature led in 4 min to

(20) Lough, A.; Ma, J. Unpublished results.

complete consumption of **19** and exclusive formation of monoketene **41** (eq 21).[14] The structure of **41** is established by the spectral data, particularly the ¹³C NMR peak at δ 9.93, which is highly characteristic of C_β of ketenes,[8b] and the distinctive ketenyl IR band at 2095 cm⁻¹.
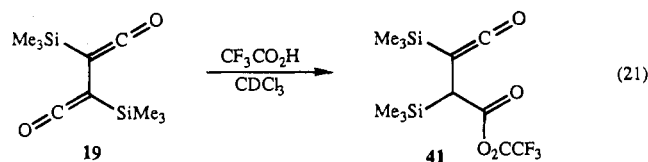
Thus with protic acids products resulting from protonation of **19** at C_β are observed exclusively, and this is not unexpected, since the calculations indicate that the twisted conformation **38c** from protonation at C_β is only 3.3 kcal/mol less stable than the planar ion **38d** resulting from protonation at C_α, and the effect of silicon should favor protonation at C_β. Furthermore, protonation of the twisted conformation favored for the silylated bisketene **19** can lead directly to an ion resembling **38c**, whereas bond rotation of the dienyl system is required upon protonation to form an ion corresponding to **38d**. The highest occupied molecular orbital (HOMO) in **19** is also concentrated at C_β, and this will tend to direct proton attack to that position. Recent studies of the reaction of **19** with Br_2 reveal however that attack at C_α does occur with this reagent, by 1,4-addition, as established by the X-ray structure of the product.[20]

In conclusion, we have been studying bisketenes only since 1992, but have already uncovered a rich chemistry of these species. The stabilities of these species have been uncannily close to that predicted by theory, but their reactivity has frequently been totally different from our naive expectations, and a few tricks have been needed to elucidate their reaction pathways. Further studies underway with these species include cycloaddition reactions with various reagents, their reaction with amines to give amides, and their reaction with difunctional reagents to form polymers. We look forward with delight to the further surprises we know await us in these studies including their conversation to a host of attractive synthetic intermediates, some of which are outlined here.