Electrophilic reactivity of bisketenes: an experimental and theoretical study, and photoinduced hydration

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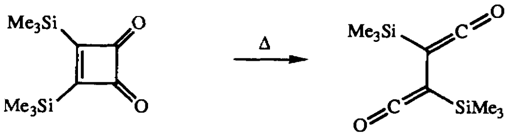
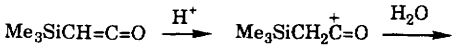
The kinetics of the acid-catalysed hydration of the bisketene $[C(SiMe_3){=}C{=}O]_2$ (**1**) are indicative of rate limiting protonation at C_β followed by hydration to form the (monoketenyl)acetic acid **5**, previously proposed as an unobserved intermediate in the neutral hydrolysis of **1**. On further reaction **5** undergoes a slower uncatalysed conversion to form the stereoisomeric 2,3-bis(trimethylsilyl)succinic anhydrides **4**. Confirmation of the intermediacy of **5** is obtained by its formation and observation on photohydration of **1**. Reaction of **1** with one equivalent CF_3CO_2H yields the (monoketenyl)acetic trifluoroacetic anhydride **8**. *Ab initio* MO calculations at the MP2/6–31G*//MP2/6–31G* level for proton addition and at the HF/6–31G*//HF/6–31G* level for chloronium ion addition to the parent bisketene buta-1,3-diene-1,4-dione (**9**) indicate that the most stable products result from attacks at C_α, the carbonyl carbon, while the ions from attack at C_β are at least 4.7 and 18.4 kcal mol^{-1} less stable, respectively. Further calculations at the MP2/3-21G//HF/3-21G level indicate that silylation of the bisketene causes a relative favouring of electrophilic attack at C_β, in agreement with the experimental results.

The preparation from cyclobutenedione **2** of 2,3-bis(trimethylsilyl)buta-1,3-diene-1,4-dione (**1**), a stable and persistent bisketene, and its reaction with nucleophiles and oxygen have recently been investigated.[1a,b] Experimental photoelectron and dipole moment studies, and *ab initio* calculations, indicate that **1** prefers a non-planar almost perpendicular geometry.[1c,d] 2-Phenyl- and 2-methyl-3-(trimethylsilyl)buta-1,3-diene-1,4-dione have also been prepared as relatively long-lived but unstable intermediates.[1e,f] We have previously studied the protonation of ketenes,[2,3] and now report the reactivity of **1** with protic acids.



2 **1** (1)

The acid-catalysed hydration of simple ketenes has been interpreted as involving rate-limiting proton attack at C_β.[3] For (trimethylsilyl)ketene (**3**) the rate ratio k_{H^+}/k_{H_2O} dm^3 mol^{-1} is 1.7 × 10^5 [eqn. (2)],[3d] and this high value was interpreted as indicating enhancement of the rate of protonation of the silylketene by the stabilizing effect of the β-silicon substituent on the forming carbocation.[3d]



$$\mathrm{Me_3SiCH{=}C{=}O} \xrightarrow{\mathrm{H^+}} \mathrm{Me_3SiCH_2\overset{+}{C}{=}O} \xrightarrow{\mathrm{H_2O}} \mathrm{Me_3SiCH_2CO_2H} \quad (2)$$

3

Electrophilic additions to ketenes have been reviewed,[3a] and other experimental and theoretical examples of ketene protonation in the gas phase[4] and solution,[5,6] reaction of ketenes with carbocations,[5a] and of ketene halogenation[7] also evidently involve electrophilic attack at C_β. This is expected because of the large coefficients of the HOMO of ketenes at C_β and oxygen, whereas the largest coefficient of the LUMO, and the site of nucleophilic attack, is at C_α.[3a,b] In the photoreaction of certain crowded ketenes evidence for protonation at C_α was obtained, and was attributed to the presence of significant negative charge density at C_α in the first excited state of ketenes.[8a] Photolysis of O=C=C=C=O in cyclohexanol gives dicyclohexyl malonate indicating that C_α undergoes nucleophilic attack and not protonation in this case.[8b]

Table 1 Acid-catalysed hydration of **1** in 50% H_2O–CH_3CN (25 °C)

[HCl]/mol dm^{-3}	k^1_{obs}/s^{-1} [a]	k^2_{obs}/s^{-1}
0	0.013 3	
0.099 4	0.023 3	0.005 48
0.199	0.032 5	0.005 74
0.235	0.036 0	0.006 00
0.398	0.072 2	0.006 90
0.471	0.083 6	0.005 75
0.795	0.144	0.005 83

[a] k^1_{obs} = 0.181 ± (0.008) dm^3 mol^{-1} s^{-1} [H$^+$] − 0.09 ± (0.34) s^{-1}, r = 0.996.

Results and discussion

Experimentally the kinetics of HCl catalysed hydration of **1** in 50% H_2O–CH_3CN were measured by monitoring the change in the UV absorption with time, and the data are reported in Table 1. Two consecutive processes were observed, and the rate of the second is independent of the acid concentration [eqn. (3)]. The rate of the first process was correlated by $k_{obs} = k_{H^+}[H^+] + k_{H_2O}$ with a derived value of $k^1_{H^+}$ = 0.181 ± 0.008 dm^3 mol^{-1} s^{-1} and a correlation coefficient r = 0.996. The known[1b] anhydrides **4** were observed as metastable products of the reaction.

Previously the reaction of **1** with neutral H_2O had been found to occur with only one kinetically observable step to form the *cis*- and *trans*-2,3-bis(trimethylsilyl)succinic anhydrides **4**, whose structures were proved by X-ray crystallography.[1b] The pathway of this process could not be specified with certainty, but the α-(ketenyl)acetic acid **5** was suggested as a possible intermediate.[1b]

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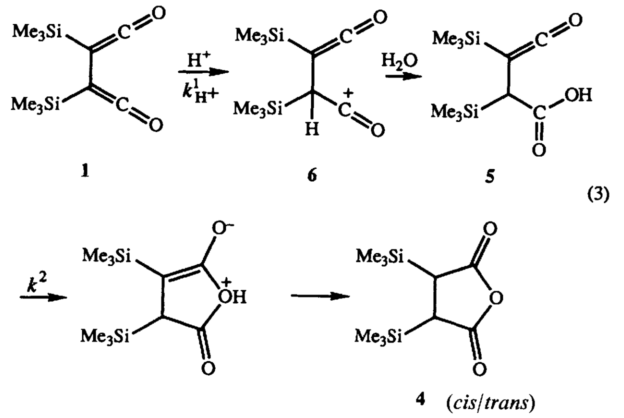
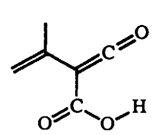


This observation of two distinct steps in the reaction of **1** in aqueous acid solves the mechanistic question of the pathway for neutral hydration of **1**.[1b] The acid-catalysed process is assigned to rate-limiting protonation of the bisketene at C_β to form an acylium ion **6**, which then forms **5** [eqn. (3)], which is directly observable by UV spectroscopy. The rate constant observed[1b] for neutral hydration of **1** in 50% H_2O–CH_3CN at 25 °C is 1.33×10^{-2} s^{-1}, which is 2.2 times greater than the average value of 5.95×10^{-3} s^{-1} of the rate constant for the uncatalysed second process observed in the presence of HCl (Table 1). The small absorbance change of the modestly slower second step at 210 nm precluded its observation previously.[1b]

Independent evidence for the formation of **5** is found by the photolysis of **1** with 300 nm light in $CDCl_3$ containing traces of H_2O, which leads to a product mixture containing unchanged **1** (36%), $Me_3SiC{\equiv}CSiMe_3$ (16%) and **5** (30%), as analysed by ^1H NMR spectroscopy. The structure of **5** was confirmed by its ^1H NMR spectrum δ ($CDCl_3$) 0.19 (s, 9 H), 0.27 (s, 9 H), 2.55 (s, 1 H), and particularly the ^{13}C NMR peaks at δ 12.40 and 179.66, which are very characteristic of C_β and C_α of ketenes, respectively,[1b,9] and by the IR bands ($CDCl_3$) at 2093 (C=C=O) and 1766 (CO_2H) cm^{-1} and by its further slow conversion into **4**. For comparison the ketene carboxylic acid **7** generated by flash vacuum pyrolysis and observed by IR at 77 K showed[9e] the ketenyl band at 2125 cm^{-1} and the carboxylic acid carbonyl at 1770 cm^{-1}. The ^{13}C NMR signal of the carboxylic acid carbon of **5** was at δ 175.32, as compared with a reported[9f] value of 179.2 for $Me_3SiCH_2CO_2H$.



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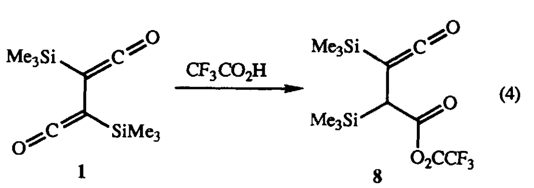
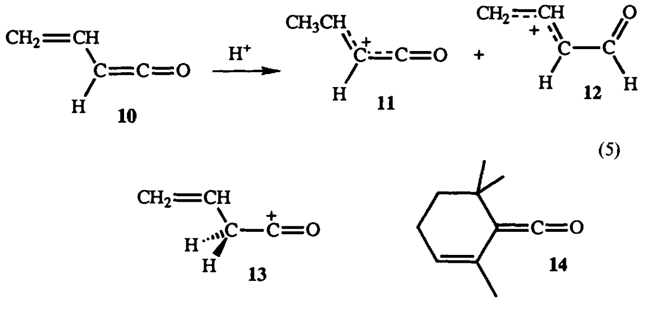
No reaction of **1** with moist $CDCl_3$ was observed without photolysis, and the photochemical formation of **5** is evidently the only reported photoenhanced nucleophilic addition at C_α of a ketene besides the reaction of C_3O_2 noted above.[8b] The photohydrations of alkynes,[8c] allenes,[8d] and alkenes[8c] have been studied, and generally interpreted in terms of initial protonation of the photoexcited substrates. In a previous study[8a] the observation of rearranged aldehydes as products of photoreaction of crowded ketenes in methanol provided good evidence that the reactions proceeded by initial protonation. However for the photohydration of **1** to **5** the evidence does not differentiate whether the reaction occurs by initial protonation, or by nucleophilic attack. The formation of alkynes from the photochemical bis(decarbonylation) of **1** and other bisketenes has been observed before.[1b,e]

Consistent with the intermediacy of the acylium ion **6** in the reaction of **1** with HCl, the reaction of **1** in $CDCl_3$ with 1 equivalent of trifluoroacetic acid in $CDCl_3$ at 25 °C led to formation of the ketenyl mixed anhydride **8** [eqn. (4)], as identified by its spectral characteristics δ_H($CDCl_3$) 0.19 (s, 9 H), 0.24 (s, 9 H), 2.21 (s, 1 H); ν_{max}($CDCl_3$)/cm^{-1} 2095 (C=C=O) and 1837, 1767 (anhydride); δ_C($CDCl_3$) 9.93 and 179.46 (ketenyl carbons).



As a guide to the understanding of the protonation of **1** *ab initio* calculations of the parent bisketene $(CH{=}C{=}O)_2$ (**9**) were undertaken. In a previous study we examined by calculation at the HF/6-31G*//HF/3-21G level the reactivity of $CH_2{=}CHCH{=}C{=}O$ (**10**),[2b] and found that protonation at C_δ forming $CH_3CH{=}CHC^+{=}O$ (**11**) was 38.1 and 15.8 kcal mol^{-1} more favourable than protonation at C_α and C_β, forming $CH_2{=}CHCH^+CH{=}O$ (**12**) and $CH_2{=}CHCH_2C^+{=}O$ (**13**), respectively [eqn. (5)]. This prediction of protonation at the δ-carbon was confirmed experimentally in a model substrate **14**.[2c]



To evaluate the possible course of electrophilic attack on the bisketene **1** the structures and energies of the various energy minimum isomeric ions resulting from addition of H^+ and Cl^+ to the parent **9** were calculated at the MP2/6-31G*//MP2/6-31G* and HF/6-31G*//HF/6-31G* levels of *ab initio* theory, respectively, as we have done previously.[2a,b,10] The calculated energies of the ions are given in Table 2, and relative energies (kcal mol^{-1}) obtained for the fully optimized geometries **15**–**18** are summarized in Fig. 1. Calculated structural details are given in Tables 3–6 which have been deposited as supplementary material.§ [Supp. Pub. No. 57071 (8 pp.)].

The most stable calculated ion from protonation at C_β of **9** is the twisted structure **15c** which resembles the most stable conformers of the bisketenes **1** and **9**, which are also both twisted as revealed by theoretical, photoelectron, and dipole moment studies.[1c,d] However, protonation at C_α produces four minimum-energy isomeric structures, and of these the s-*Z* conformer **16d** is more stable by 4.7 kcal mol^{-1} than **15c** at the MP2/6-31G* level.

For addition of Cl^+ calculated at the HF/6-31G*//HF/6-31G* level the products **17a** and **17b** of attack at C_β are much less stable than any of the products **18** of attack at C_α, by at least 11.4 kcal mol^{-1}. This is understandable in terms of the expected inductive destabilization by the β-chlorine of the

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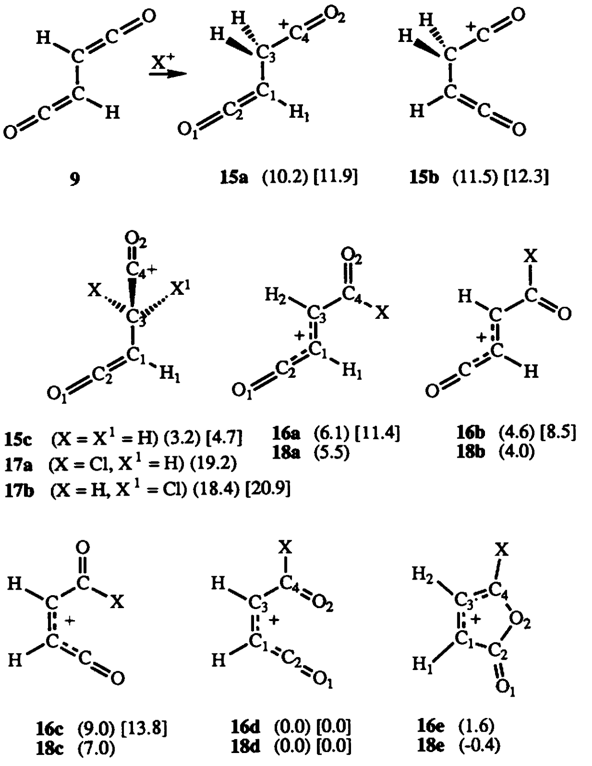
§ For details of the British Library supplementary publications scheme see 'Instructions for Authors (1995),' *J. Chem. Soc.*, *Perkin. Trans. 2*, 1995, issue 1.

Table 2 Calculated total energies (Hartree) and zero-point vibrational energies (ZPVE) (Hartree) of bisketenes and ions derived from addition of H^+ and Cl^+

	MP2/6-31G*[a]	HF/6-31G*[b]	ZPVE[b]		HF/6-31G*[b]	ZPVE[b]
15a	303.4777	302.6140	0.0579	**17a**	761.4990	0.0495
15b	303.4772	302.6120	0.0579	**17b**	761.5002	0.0497
15c	303.4893	302.6252	0.0584	**18a**	761.5207	0.0503
16a	303.4785	302.6206	0.0587	**18b**	761.5231	0.0503
16b	303.4832	302.6230	0.0588	**18c**	761.5184	0.0505
16c	303.4747	302.6159	0.0584	**18d**	761.5295	0.0507
16d	303.4967	302.6303	0.0593	**18e**	761.5302	0.0521
16e		302.6328	0.0611			
	MP2/3-21G[c]	ZPVE[d]			MP2/3-21G[c]	ZPVE[d]
20	878.7741	0.0866		**22**	1335.5205	0.7750
21	878.7681	0.0867		**23**	1335.5287	0.0781

[a] MP2/6-31G*//MP2/6-31G*. [b] HF/6-31G*//HF/6-31G*. [c] MP2/3-21G//HF/3-21G. [d] HF/3-21G//HF/3-21G.



9 **15a** (10.2) [11.9] **15b** (11.5) [12.3]

15c ($X = X^1 = H$) (3.2) [4.7]
17a ($X = Cl, X^1 = H$) (19.2)
17b ($X = H, X^1 = Cl$) (18.4) [20.9]

16a (6.1) [11.4]
18a (5.5)

16b (4.6) [8.5]
18b (4.0)

16c (9.0) [13.8]
18c (7.0)

16d (0.0) [0.0]
18d (0.0) [0.0]

16e (1.6)
18e (-0.4)

Fig. 1 Relative calculated HF/6-31G*//HF/6-31G* (parentheses) and MP2/6-31G*//MP2/6-31G* (brackets) energies (kcal mol^{-1}) of the ions from proton and chloronium ion addition to buta-1,3-diene-1,4-dione (**9**) to form **15** and **16** (X=H) and **17** and **18** (X=Cl)

acylium ion. There are no energy minima for planar geometries resembling the protonated ions **15a**, **b**, and the structures of **17a**, **b** have almost perpendicular geometries with $C_2C_1C_3C_4$ dihedral angles of 93.4 and 116.0°, respectively. The most stable product conformer resulting from chloronium attack at C_α is **18d**, which also corresponds to the most favourable product of proton addition.

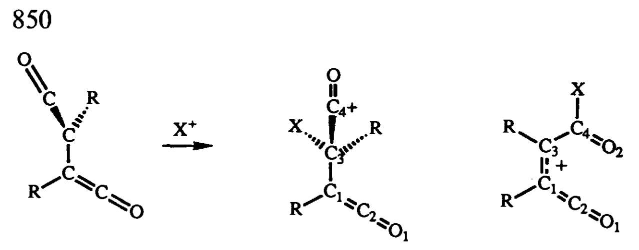
To examine the role of silyl substituents on electrophilic addition to bisketenes the energies of the ions from addition to $(SiH_3C{=}C{=}O)_2$ (**19**) of H^+ to give **20** and **21**, resulting from protonation at C_β and C_α, respectively, and the ions **22** and **23** resulting from Cl^+ addition to C_β and C_α, respectively, were also studied. These ions are much larger than **15**–**18**, and so the calculations could only be done at a lower level of theory, namely MP2/3-21G + ZPVE//HF/3-21G, and the relative energies are reported in Table 2. These results are not quantitatively comparable to those in Fig. 1, but the trends are of value for qualitative interpretations of the results in Fig. 1, and the relative energies are summarized in Fig. 2. Calculated structural details of the product ions **20**–**23** are given in Tables 7 and 8 (Supplementary material), and the structures of **19** and its products of addition of H^+ and Cl^+ are depicted in Figs. 3 and 4.

At the highest level of calculation the most stable ion resulting from protonation of the unsubstituted bisketene **9** is **16d**, resulting from protonation at C_α, which is 4.7 kcal mol^{-1} more stable than the ion **15c** for protonation at C_β (Fig. 1). At the lower level of calculation (Fig. 2) this order of stability is reversed, and **15c** is favoured by 2.5 kcal mol^{-1}, and for protonation of the bis(SiH_3) substituted bisketene **19** the ion **20** for protonation at C_β is favoured by an additional 1.2 kcal mol^{-1} relative to the ion **21** from protonation at C_α. For addition of Cl^+ the ion **18d** from C_α attack on the unsubstituted bisketene is more stable than **17a** for attack at C_β at both levels of theory, and at the lower level of theory for the bis(SiH_3) substituted bisketene the ion **23** from attack at C_α is also more stable, but by 3.1 kcal mol^{-1} less relative to the ion **22** for attack at C_β (Fig. 2). Thus for both protonation and Cl^+ attack the effect of silylation is to favour attack at C_β.

Thus even though the highest level calculations predict that the product of protonation at C_α of the parent bisketene **9** is more stable than the ion from protonation at C_β, the effect of silylation is predicted by calculation to tend to favour protonation at C_β, and experimentally the reaction of the bis(Me_3Si) ketene **1** with protic acids gives the products **5** and **8**, resulting from protonation of **1** at C_β. This result is qualitatively understandable, since the silyl substituents are known experimentally to enhance protonation at C_β,[3d] while protonation at C_α would give allylic cations with coplanar silyl substituents, which are known[11] to have only minor effects. Furthermore the twisted conformation analogous to **19** (Fig. 2) is favoured for the silylated bisketene **1**, and protonation of this species can lead directly to an ion resembling **15c**, whereas bond rotation of the dienyl system is required upon protonation to form an ion corresponding to **16d**. The highest occupied molecular orbital (HOMO) in **9** is also concentrated at C_β, and this will also tend to direct proton attack to that position.

Attack of Cl^+ at C_α is calculated to be significantly more favourable than protonation, although this effect is also diminished by silylation. As a test of this prediction we are examining the reaction of **1** with Br_2. Additions of Br_2 to other dienes such as cyclopentadiene, cyclohexa-1,3-diene, and acylic 1,3-dienes occur with a substantial amount of 1,4-addition,[12a] and so this may occur with **1** as well.

1,4-Addition to a bisketene has been observed in the addition



R	R, X	E_{rel}	E_{rel}
H (**9**)	H, H	0.0 (**15c**)	2.5 (**16d**)
SiH$_3$ (**19**)	SiH$_3$, H	0.0 (**20**)	3.7 (**21**)
	H, Cl	7.9 (**17a**)	0.0 (**18d**)
	SiH$_3$, Cl	4.8 (**22**)	0.0 (**23**)

Fig. 2 Relative calculated MP2/3-21G + ZPVE//HF/3-21G energies (kcal mol^{-1}) of the ions from proton and chloronium ion addition to **9** and **19**

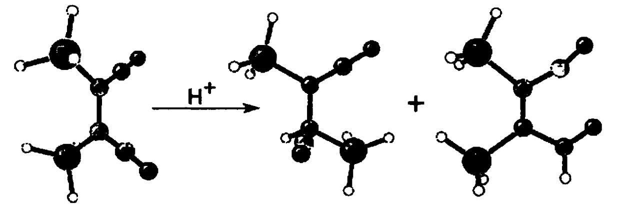
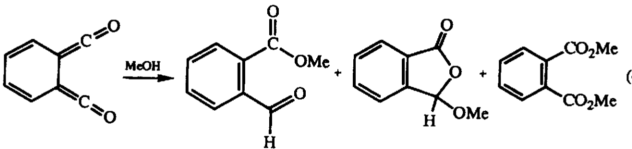


Fig. 3 Protonation of 2,3-disilanylbuta-1,3-diene-1,4-dione

of methanol to the intermediate **24**, generated by photolysis in an Ar matrix at 11 K, which gave the products **25**–**27** in the yields shown [eqn. (6)].[12b] A route to **25** was depicted involving a 1,4-addition as shown in **28**, while **26** was proposed to arise *via* **29**, and **27** was formed *via* an oxidative process.[12b] However there is no direct evidence for the process shown in **28**, and stepwise electrophilic or nucleophilic attack of solvent on **24** could give **30** or **31**, respectively, and either one of these intermediates can give rise to both **25** and **26**, without the need to postulate two completely distinct competing reactions. Thus it appears there is also an opportunity for additional study of **24** to elucidate further the possible addition mechanisms of bisketenes.



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24 **25** (38%) **26** (45%) **27** (17%)

In summary the additions of H$_3$O$^+$ and CF$_3$CO$_2$H to the bis(ketene) **1** occur by protonation at C$_\beta$ to yield unique acylketenes, and the intermediacy of the (α-ketenyl)acetic acid **5** in the neutral hydration of the bisketene **1** is confirmed through the generation and observation of this species by acid and by photoinduced hydration. *Ab initio* calculations confirm a greatly enhanced tendency for electrophilic attack of bisketenes to occur at C$_\alpha$, while silylation favours attack at C$_\beta$. The search for authentic electrophilic attack at C$_\alpha$ of ketenes will continue.

Experimental

General procedures

All reactions were carried out under N$_2$ or Ar in glassware that was oven dried and cooled in a desiccator. Solvents and reagents were obtained from Aldrich, and **1** was prepared as described.[1a,b]

Kinetics of hydration

The procedures followed those used previously for Me$_3$SiCH=C=O[3d] and **1**.[1b] Stock acid solutions were prepared by diluting 100 cm^3 of 3.98 mol dm^{-3} HCl to 200 cm^3 with CH$_3$CN, or 5 cm^3 of 0.942 mol dm^{-3} HCl to 10 cm^3 with CH$_3$CN. Aliquots of these solutions were diluted with appropriate volumes of a solution made by diluting 50 cm^3 of H$_2$O to 100 cm^3 with CH$_3$CN. The bisketene **1** was freshly prepared[1b] by gas chromatographic thermolysis of **2**, and 4 μl of an 0.08 mol dm^{-3} solution of **1** was injected into 1.2 cm^3 of an acid solution and the decrease in the absorbance at 210 nm was observed. There was an initial first-order decrease in the absorbance of 0.5 units that was linearly dependent on [HCl], and this was followed by a slower first-order decrease in the absorbance of 0.05 units that was independent of [HCl].

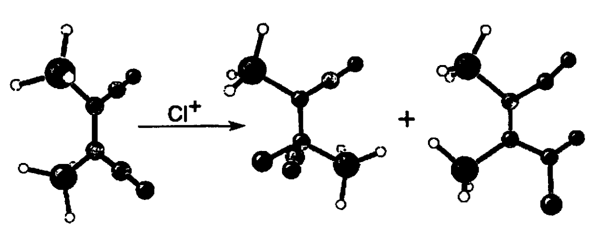
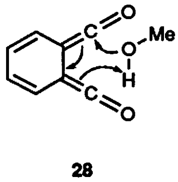


Fig. 4 Reaction of Cl$^+$ with 2,3-disilanylbuta-1,3-diene-1,4-dione



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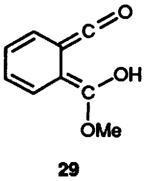

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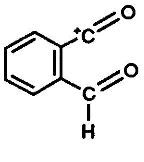

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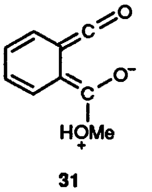

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2,3-Bis(trimethylsilyl)-4-oxobut-3-enoic acid (5)

Bisketene **1**[1b] (25 mg, 0.11 mmol) was dissolved in 1 cm^3 CDCl$_3$ and H$_2$O (0.79 mg, 0.044 mmol) was added, and the solution was irradiated at 4 °C with 300 nm light for 5 h. Analysis of the product by ^{1}H NMR spectroscopy showed the presence of unchanged **1** (36%), **5** (30%), Me$_3$SiC≡CSiMe$_3$ (16%), and other minor products. The identity of **5** was confirmed by its spectral signals in the mixture: δ_H(CDCl$_3$) 0.19 (s, 9 H, Me$_3$Si), 0.27 (s, 9 H, Me$_3$Si) and 2.55 (s, 1 H, CHCO); δ_C(CDCl$_3$) −1.99, −1.03, 12.40, 43.79, 175.32 and 179.66; ν_{max}(CDCl$_3$)/cm^{-1} 2093 and 1766. After a while the signals due to **5** disappeared and were replaced by those of the anhydride *trans*-**4**. A sample of **1** kept under the same conditions except for the absence of irradiation showed almost no change.

2,3-Bis(trimethylsilyl)-4-(trifluoroacetoxy)but-1-ene-1,4-dione (8)

To the bisketene **1** (28.0 mg, 0.124 mmol) in 0.5 cm^3 CDCl$_3$ in an NMR tube at room temperature was added CF$_3$CO$_2$H (14.1 mg, 0.124 mmol). The NMR spectra revealed the formation of **8** as the sole product: δ_H(CDCl$_3$) 0.19 (s, 9 H, Me$_3$Si), 0.24 (s, 9 H, Me$_3$Si) and 2.21 (s, 1, CHO); δ_C(CDCl$_3$) −2.31, −1.14, 9.93, 32.14, 113.80 (q, 1, $J_{^{13}C-^{19}F}$ = 286.2 Hz), 167.22, 174.16 (q, 1, $J_{^{13}C-^{19}F}$ = 63.3 Hz, COCF$_3$) and 179.46; ν_{max}(CDCl$_3$)/cm^{-1} 2095, 1837 and 1767; *m*/*z* (ei) 340 (M$^+$, 1), 226 (M$^+$ − CF$_3$CO$_2$H, 40), 155 (TMSC≡CSiMe$_2^+$, 99), 73 (TMS, 100) (Found: M$^+$ 340.0761. Calc. for C$_{12}$H$_{19}$Si$_2$O$_4$F$_3$: *M*, 340.0774).

Computational methodology

The *ab initio* molecular orbital calculations were carried out using the GAUSSIAN 90 and GAUSSIAN 92 series of programs [10a] on Hewlett Packard 9000–750 and IBM RS/6000–530 minicomputers. The geometries of **9** and **15–18** were gradient optimized using the standard split valence 6-31G* basis set.[10c] There were no geometrical constraints during optimization. The orders (number of negative diagonal elements of the Hessian matrix) of all critical points were determined at the HF/6-31G* level by analytical differentiation of the restricted Hartree–Fock wavefunction, and were found to be zero in all cases except for **16a** and **16b**, which have order 1 (one). Geometries of **15** and **16** which were optimized at the MP2/6-31G* level, were also order checked at that level of theory. The frozen core approximation was not used. Calculations of **9** and **19** are given in detail elsewhere.[1c,d]

Calculations on **20–23** were carried out similarly using the MP2/3-21G//HF/3-21G basis set, with the inclusion of corrections for zero-point vibrational energies (ZPVE) at the HF/3-21G level.

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