

Addition of Bromine to Ketenes and Bisketenes: Electrophilic Attack at Carbonyl Carbon and Neighboring Group Participation

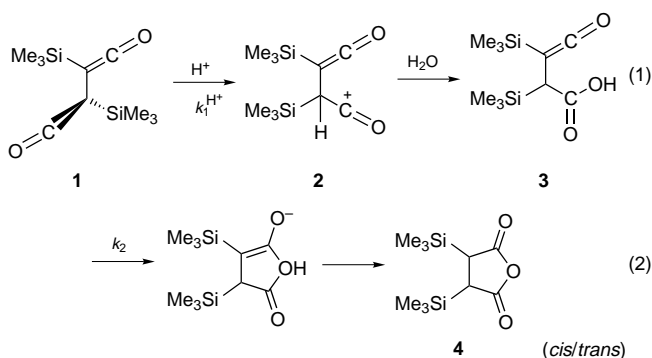
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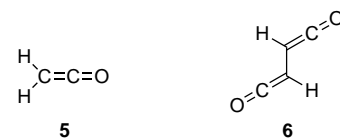
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Addition of bromine to bisketene ($\text{Me}_3\text{SiC}=\text{C}=\text{O}$)₂ (**1**) gave the fumaryl dibromide *E*-**7**, whose stereochemistry was proven by X-ray structure determination. Upon warming, *E*-**7** rearranged to the furanone **8**, and this process was faster in the more polar CD_3CN compared to CDCl_3 , consistent with an ionization pathway for the rearrangement. The bromination of **1** in $\text{CH}_2\text{ClCH}_2\text{Cl}$ followed second-order kinetics with a rate constant $(2.1 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C. The first-order dependence of bromine addition to **1** on $[\text{Br}_2]$ is attributed to intramolecular nucleophilic assistance by the second ketenyl moiety in an initial complex of **1** and Br_2 to give *E*-**7**. A transition structure for this process has been calculated by *ab initio* methods. By contrast $\text{PhMe}_2\text{SiCH}=\text{C}=\text{O}$ **11** and γ -oxoketene **16** underwent bromination by third-order kinetics, second order in $[\text{Br}_2]$, indicating the absence of neighboring group participation in the rate-limiting step. The bisketene $\text{Me}_2\text{Si}(\text{CH}=\text{C}=\text{O})_2$ (**13**) underwent bromination by mixed kinetics with both first- and second-order terms in $[\text{Br}_2]$.

The reactivity of ketenes with electrophiles has recently been reviewed,¹ and as part of our studies of bisketenes, especially those stabilized by trialkylsilyl groups,² we have reported experimental and theoretical studies of the reactions of the 1,2-bis(trimethylsilyl)-bisketene **1** with electrophiles,^{2d} with the results summarized in eqs 1 and 2.



Theoretical studies^{2d,3a,b} of the model ketenes **5** and **6** led to the prediction that electrophilic attack at C_α would be enhanced relative to attack at C_β for 1,2-bisketenes compared to monoketenes, although silylation would tend to favor attack at C_β . The experimental result for **1** was that protonation occurred at C_β (eqs 1 and 2), but the calculations indicated that for Cl^+ attack at C_α would be more likely than for protonation. Experimentally protonation of $\text{Me}_3\text{SiCH}=\text{C}=\text{O}$ at C_β was favored.^{3c} There have been only a few studies of halogenation of ketenes,⁴ and no kinetic investigations or other studies that revealed the position of initial electrophilic attack.



The understanding of the mechanism of bromination of alkenes has undergone a remarkable degree of refinement in recent years,^{5,6} and there is now general agreement that, for the bromination of symmetrical alkenes in halogenated hydrocarbons, the scheme shown in eq 3 is applicable. For unsymmetrical alkenes the various intermediates are of necessity also unsymmetrical, and in the extreme these bridged or π -complexed species are supplanted by open β -bromo-substituted carbocations.

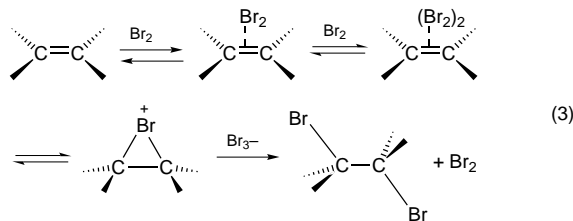
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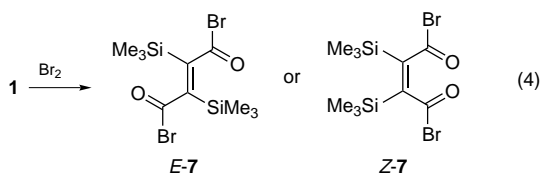
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(2) (a) Zhao, D.-c.; Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1993**, *115*, 10097–10103. (b) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *Acc. Chem. Res.* **1995**, *28*, 265–271. (c) Allen, A. D.; Lai, W.-Y.; Ma, J.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 2625–2626. (d) Allen, A. D.; Ma, J.; McAllister, M. A.; Tidwell, T. T.; Zhao, D.-c. *J. Chem. Soc., Perkin Trans. 2* **1995**, 847–851. (e) McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233–7238. (f) Sung, K.; Tidwell, T. T. *J. Am. Chem. Soc.* **1996**, *118*, 2768–2769. (g) Liu, R.; Marra, R. M.; Tidwell, T. T. *J. Org. Chem.* **1996**, *61*, 6227–6232. (h) Sung, K.; Tidwell, T. T. *Organometallics* **1997**, *16*, 78–85.

Gas phase studies of alkene-halogen complexes have recently been reported,⁷ and the IR spectrum of the Br₂-ethylene complex in an argon matrix has been measured and calculated by theoretical methods.^{8a} Other theoretical studies of bromine addition to alkenes include calculations of bromine-ethylene π -complexes,^{5d,e,8b} a transition state for formation of the bromonium ion from the CH₂=CH₂ + Br₂ reaction,^{8c} and bromonium ions from ethylene,^{5c} adamantylideneadamantane,^{5c} 2-methylpropene,^{8d} cyclohexene,^{8e} and benzobicyclo[2.2.2]octadiene.^{8f} We now report a study of the kinetics and mechanism of ketene bromination which, for **1**, demonstrate both electrophilic attack at C _{α} and neighboring group participation by the second ketenyl group.



Results

The reaction of **1** in CDCl₃ or pentane at -78 °C with an equal amount of Br₂ led to the immediate formation of one major product. This could be assigned as a product **7** of net 1,4-addition of Br₂ to **1** based on the single ¹H NMR signal (CDCl₃) at δ 0.42, the three signals in the ¹³C NMR spectrum at δ 0.11, 154.7, and 165.8, and the IR band at 1795 cm⁻¹ (eq 4). This spectral evidence does not however define the stereochemistry of **7** which could be *E* or *Z*. However, upon evaporation of the solvent at low temperature crystals were formed, and these were



determined by X-ray analysis to have the *E* configuration of a fumarate derivative (Figure 1).^{9a}

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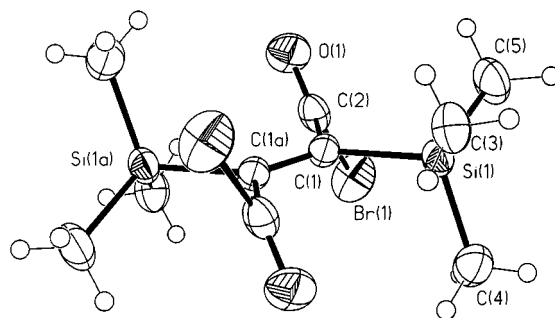
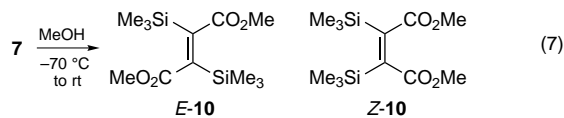
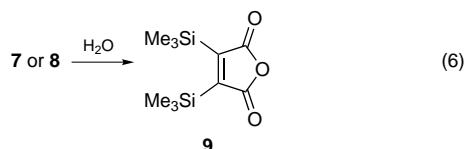
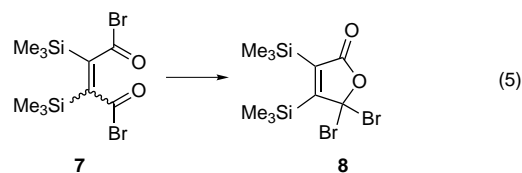


Figure 1. Molecular structure of *E*-**7** obtained by X-ray crystallography.

On standing at 4 °C for 3 days in CDCl₃ **7** rearranged to the $\Delta^{3,4}$ -butenolide **8** (eq 5) identified by its NMR, IR, and mass spectra and the UV absorption at 252 nm for the unsaturated lactone function. The kinetics of the rearrangement were measured by ¹H NMR using *E*-**7** recrystallized from pentane and gave $k_1 = 4.13 \times 10^{-4}$ and $4.24 \times 10^{-5} \text{ s}^{-1}$ at 22 °C in CD₃CN and CDCl₃, respectively. Hydrolysis of **7** or **8** led to formation of the known^{2a} maleic anhydride **9** (eq 6), and reaction with MeOH led to the dimethyl ester *E*-**10** (eq 7), whose structure was confirmed by X-ray crystallography.^{9b} When the bromination of **1** was carried out in the presence of MeOH, both *E*-**10** and *Z*-**10** were formed, in 28 and 53% yields, respectively.

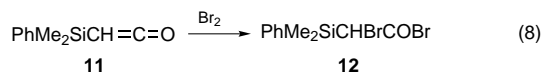


For kinetic studies of the bromination, solutions of bisketene **1** were generated in CH₂ClCH₂Cl by heating degassed solutions of 3,4-bis(trimethylsilyl)cyclobutene-1,2-dione under Ar at 100 °C. Aliquots of these solutions using stopped flow techniques were mixed with solutions of Br₂ in CH₂ClCH₂Cl for kinetic measurements. The results (Table 1, Supporting Information) gave a derived

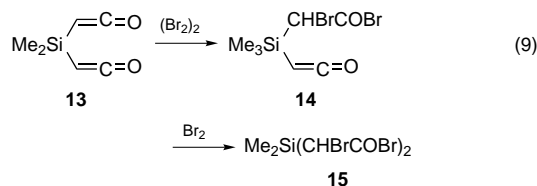
(9) (a) X-ray data for *E*-**7**: C₁₀H₁₈Br₂O₂Si₂; formula weight, 386.24; crystal system, monoclinic; space group, *P2₁/n*; color, colorless; unit cell dimensions, $a = 9.2960(1) \text{ \AA}$, $\alpha = 90^\circ$, $b = 8.7600(1) \text{ \AA}$, $\beta = 105.93^\circ$, $c = 9.7680(1) \text{ \AA}$, $\gamma = 90^\circ$; volume, 764.89(14) \AA^3 , $Z = 2$, $R = 0.0701$, $\text{GOF} = 1.023$. (b) This X-ray structure has been independently reported: Maas, G.; Gimmy, M.; Alt, M. *Organometallics* **1992**, *11*, 3813–3820. (c) X-ray data for **17a** and **17b**: C₁₈H₁₈Br₂O₄; formula weight, 458.16; **17a** crystal system, orthorhombic; space group, *Pbc*; color, morphology, colorless plate, unit cell dimensions, $a = 10.957(2) \text{ \AA}$, $b = 15.599(3) \text{ \AA}$, $c = 20.403(4) \text{ \AA}$; volume = 3487.1(1) \AA^3 , $Z = 8$, $R_w = 0.094$, 0.077 , $\text{GOF} = 2.440$. **17b** crystal system, orthorhombic; space group, *P2₁2₁2₁*; color, morphology, colorless lump; unit cell dimensions, $a = 9.096(2) \text{ \AA}$, $b = 9.488(1) \text{ \AA}$, $c = 20.746(3) \text{ \AA}$; volume = 1790.4(5) \AA^3 , $Z = 4$, $R_w = 0.047$, 0.040 , $\text{GOF} = 1.505$. Full crystallographic data are given in the Supporting Information.

second-order rate constant of $(2.1 \pm 0.1) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and showed no second-order dependence on $[\text{Br}_2]$. Examination of the solution by ^1H NMR revealed that the fumaryl dibromide **E-7** was the only observable product.

As a further guide to the reactivity of ketenes with bromine the monoketene **11**^{2g} was examined. The addition of Br_2 in CDCl_3 led to formation of the dibromo compound **12** (eq 8), as evidenced by ^1H and ^{13}C NMR spectra and the IR absorption at 1797 cm^{-1} for the acyl bromide. In contrast to the behavior of **1**, the reaction of **11** in $\text{CH}_2\text{ClCH}_2\text{Cl}$ followed third-order kinetics, with a second-order dependence on $[\text{Br}_2]$, $k_3 = (6.1 \pm 0.3) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ (Table 2, Supporting Information).

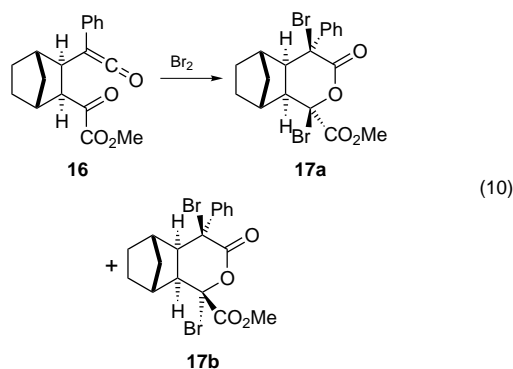


The bromination of the 1,3-bisketene **13**^{2f} was also studied. The reaction was monitored by ^1H NMR, and upon addition of 1 equiv of Br_2 , unreacted **13** and both the monoadduct **14** and the diadduct **15** could be observed, in a ratio of 2.3/1.7/1.0 (eq 9). After addition of 2 equiv of Br_2 the tetrabromide **15** was the only observed product, and this was fully characterized spectrally. At $[\text{Br}_2] = 2.6 \text{ to } 5.6 \times 10^{-3} \text{ M}$, the bromination followed third-order kinetics, second-order in $[\text{Br}_2]$, with $k_3 = (3.5 \pm 0.1) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$ (Table 3, Supporting Information). However, at $[\text{Br}_2] = 5 \times 10^{-4} \text{ M}$ or less, the reaction showed evidence of a significant bromination pathway that was first order in $[\text{Br}_2]$ (see Experimental Section).

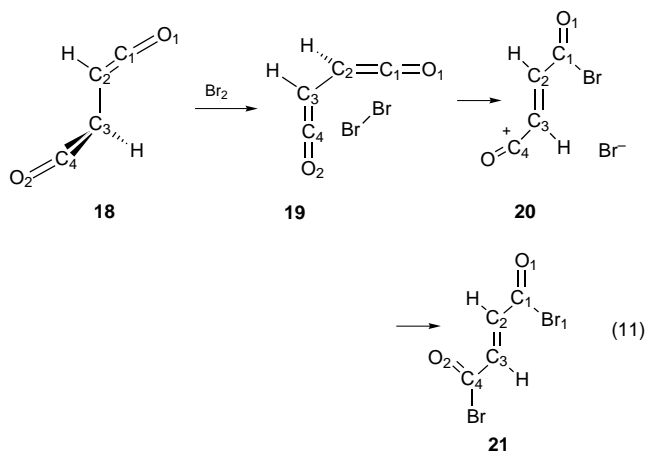


The γ -oxoketene **16**,¹⁰ which is readily prepared by treatment of norbornene with methyl 6-oxo-5-phenyl-1,3,4-oxadiazine-2-carboxylate,^{10a} was also studied. A variety of reactions of **16** have been carried out,^{10b-f} and in most of these processes a cooperation of the ketene and the ketone functionalities was observed. The addition of Br_2 in CH_2Cl_2 to **16** gave a mixture of the diastereomeric lactones **17a** and **17b** in the ratio of 1.0:2.3 in 75% yield (eq 10), the configurations of which were established by X-ray analyses.^{9c} The kinetics of the reaction were third order overall, with $k_3 = (1.10 \pm 0.25) \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$ (Table 4, Supporting Information). By comparison the third-order rate constants for the reaction of Br_2 with cyclohexene and 1,2-diphenylethylene in dichloroethane at 25°C are reported to be 2.4×10^5 and $1.7 \times 10^7 \text{ M}^{-2} \text{ s}^{-1}$.^{5f,g}

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To elucidate the reaction pathway of **1**, *ab initio* calculations for the bromination of the parent bisketene **18** (eq 11) at the HF/6-31G*//RHF/6-31G* and MP2/6-31G*//RHF/6-31G* levels were carried out using Gaussian 94,¹¹ the results being reported in Table 5 (Supporting Information). An initial complex, **19**, was observed in



which the 1,2-bisketene structure was barely changed, with the Br_2 molecule bridging between the two ketenyl units. The energy of **19** was 4.2 kcal/mol below the reactants (MP2/6-31G*//RHF/6-31G*) while the energy of the ethylene/ Br_2 complex in which the $\text{C}=\text{C}$ and $\text{Br}-\text{Br}$ bonds are parallel is calculated^{5d} to be 1.8 kcal/mol below the reactants (MP2/6-31G*//MP2/6-31G*), with $\text{C}-\text{Br}$ distances of 3.631 Å, while **19** has $\text{C}-\text{Br}$ distances of 3.789 and 3.808 Å. Transition structure **20**, with one imaginary frequency, was located (Figure 2) in which the *anti* geometry, approaching the fumaryl structure of the product **E-7**, had already been adopted, but with one short and one long $\text{C}-\text{Br}$ distance. The energy of the transition structure, **20**, is 39.9 kcal/mol above the reactants, and the conversion of **18** to **21** is exothermic by 48.8 kcal/mol at the MP2/6-31G*//HF/6-31G* level. The calculated barrier for the gas phase formation of the ethylenebromonium ion bromide ion pair from $\text{CH}_2=\text{CH}_2 + \text{Br}_2$ is 61.4 kcal/mol (MP3/3-21G//RHF/3-21G),^{8c} and the π -complex and intermediate from this reaction are calculated to be stabilized by 7.7 and 26.3 kcal/mol, respec-

(11) Gaussian 94. Revision B 3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zuckewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1995.

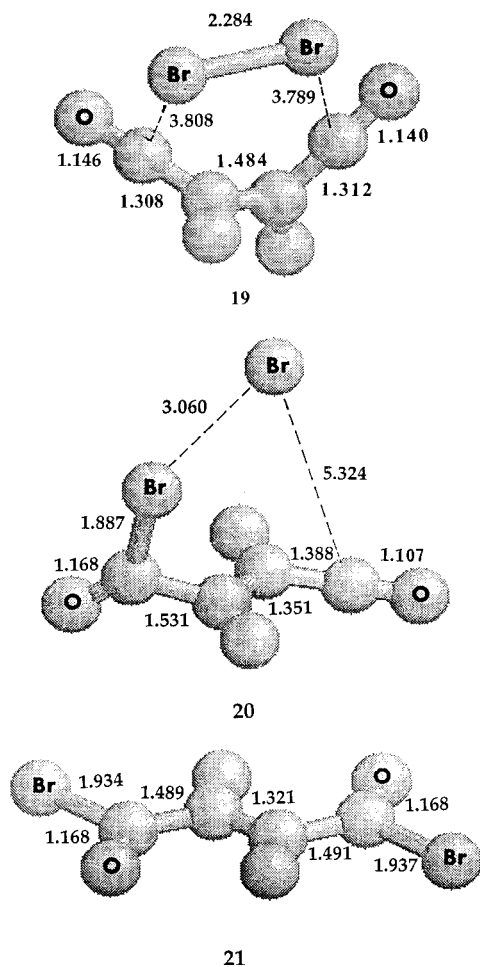


Figure 2. HF/6-31G* calculated structures for the complex **19**, transition structure **20**, and fumaryl bromide **21**, with bond distances in angstroms.

tively, by transfer from vacuum to $\text{ClCH}_2\text{CH}_2\text{Cl}$ solution.^{8b} Significant stabilization of **19** and **20** by solvation is also expected.

As already noted^{8c} calculation of transition structures for formation of alkene bromonium ions + Br^- is ordinarily not possible in the gas phase, but in the case of **20** the complexation of Br^- with the second ketenyl moiety makes this feasible. Calculations for the addition of Br_2 to benzobicyclo[2.2.2]octadiene revealed an "ion-pair transition structure" with some resemblance to **20** in which C,C bond migration has already occurred and the C- Br_1 , C- Br_2 , and Br-Br bond distances were 2.010, 3.172, and 3.260 Å, respectively.^{8f}

Discussion

While bromination of ketenes has not been extensively studied, the results presented above provide convincing evidence that they behave as reactive alkenes with some special features that influence both the kinetic behavior and pathways leading to products. We deal first with the bromination of the prototypical monoketene **11**, which reacts with a second-order dependence on $[\text{Br}_2]$, with a value of k_3 that is 25 times that of cyclohexene^{5f} and 2.8 times less than that of 1,2-diphenylethylene.^{5g} Protonation at C_β of $\text{Me}_3\text{SiCH}=\text{C}=\text{O}$ is known to be accelerated by silicon,^{3c} and by analogy formation of a β -bromoacylium ion $\text{PhMe}_2\text{SiCHBrC}^+=\text{O}$ in the reaction of **11** appears likely.

The reaction of Br_2 with bisketene **1** follows a very different pathway and involves addition of one molecule of bromine to provide **7** via a pathway that is first order in $[\text{Br}_2]$. The *E* or *Z* assignment of the stereochemistry of **7** proved difficult, as this material underwent facile rearrangement with cyclization to the lactone **8**, as expected for *Z*-**7**. This puzzle has been resolved by the isolation of **7** as a crystalline solid and the determination of its molecular structure by X-ray crystallography, as shown in Figure 1. The *E* stereochemistry observed shows that the configuration was preserved in the reaction of **7** with MeOH (eq 7), whereas the reactions of *E*-**7** on standing to form **8** and with H_2O to form **9** involved reversal of the stereochemistry.

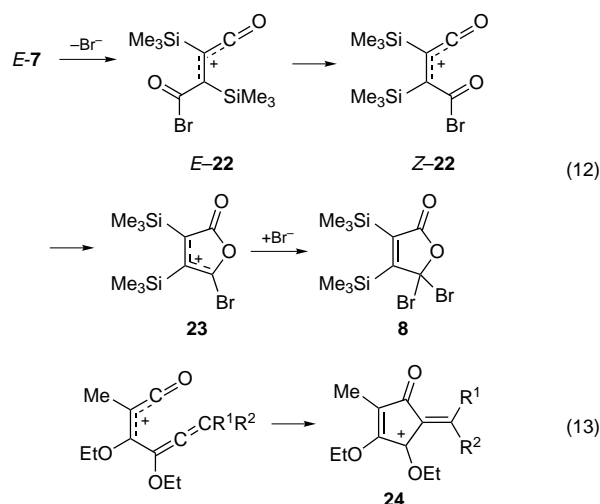
The observed first-order dependence of the rate of the reaction of **1** on $[\text{Br}_2]$ in $\text{ClCH}_2\text{CH}_2\text{Cl}$ is also in contrast to the usual second-order dependence found for alkene bromination in this solvent (eq 3).⁵ The monoketene $\text{PhMe}_2\text{SiCH}=\text{C}=\text{O}$ (**11**) reacts with a second-order dependence on $[\text{Br}_2]$ and evidently follows the normal alkene mechanism. First-order behavior for olefin bromination is common in polar solvents such as MeOH or acetic acid if the $[\text{Br}_2]$ is low but is almost unknown in chlorinated hydrocarbon solvents. Due to the low polarity and ionizing ability of chlorinated hydrocarbons, the $[\text{Br}_2]^2$ dependence can be understood in terms of the second Br_2 acting as an electrophile or Lewis acid in assisting the removal of Br^- from the developing bromonium ion.⁵ Conceptually, one might expect that as the reactivity of the alkene increases, as is the case for some of the bisketenes studied here, the requirement for the second bromine to assist in the ionization might be attenuated. Recently, Chiappe and co-workers have shown that bromination of the very reactive alkene, *trans*-4,4'-dimethoxystilbene, when conducted at low $[\text{Br}_2]$, exhibits mixed first and second order in $[\text{Br}_2]$ kinetic terms.^{5h}

An explanation of the origin of the kinetic behavior and the product stereochemistry in the bromination of **1** is provided by the calculated model pathway (eq 11). Initially Br_2 forms a π -complex, **19**, in which one Br interacts with the HOMO of one ketene (CCCBr dihedral angle 129.3°) and the other Br interacts with the other ketene (CCCBr angle 15.4°). In the HF/6-31G* calculated transition structure **20** (Figure 2) the *anti* geometry of the fumarate product has already been attained and the initial C-Br bond formation is far advanced, involving electrophilic attack at the carbonyl carbon on the HOMO perpendicular to the ketene plane. The C-Br distance for generation of the second acyl bromide moiety is quite long and involves bromide attack on the incipient acylium ion. This latter interaction permits the calculation of this structure. The stereochemistry of the fumarate product is determined by the direction of rotation around the central C-C bond in attaining the transition structure **20**. In the calculated structure for the parent, formation of the fumaryl structure occurs without the need to avoid repulsions between the two bulky Me_3Si groups, and in the presence of these the tendency for **1** to form the fumaryl structure would be enhanced for steric reasons. When the bromination is conducted in the presence of MeOH, solvent attack could occur on the side opposite the bromine on one of the ketenyl units prior to formation of the *anti* geometry of **20**, and the concomitant rotation could lead to the observed *syn* geometry. In the observed product *E*-**7** both acyl bromide moieties are twisted from

the plane of the fumarate carbon skeleton for steric reasons (Figure 1), but in the calculated structure **21** these are coplanar.

The bromination of **1** is in contrast to that of 1,3-butadiene, which gives both 1,2- and 1,4-addition.^{12a-c} The reaction of 2,3-di-*tert*-butyl-1,3-butadiene with bromine also occurs with 1,4-addition.^{12d}

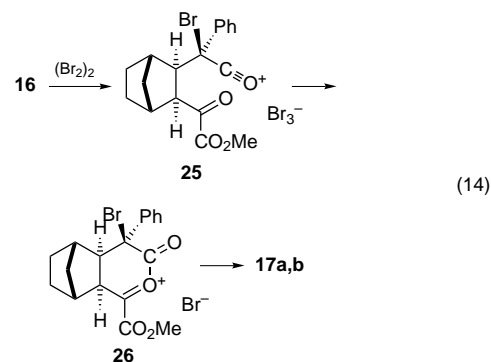
The formation of **8** from *E*-**7** is perhaps most simply explained by ionization to form *E*-**22**, which undergoes bond rotation about the central C–C bond to form *Z*-**22**, which cyclizes to **23** and forms **8** (eq 12). The cyclization of *Z*-**22** has some resemblance to the process shown in eq 13, which has been studied both experimentally and theoretically.^{12e} The 10-fold faster rate of the isomerization of *E*-**7** in the more polar CD₃CN compared to CDCl₃ is also consistent with an ionization process.



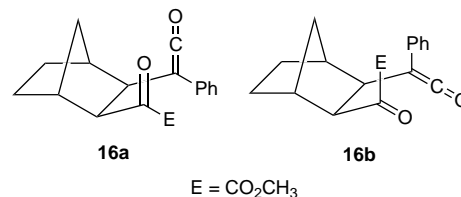
Bromination of the 1,3-bisketene **13** (eq 9) occurs by mixed second- and third-order kinetics. The third-order process occurs at a rate 1.7 times less than that of the monoketene PhMe₂SiCH=C=O (**11**) and gives addition of one molecule of bromine. Under preparative conditions, the product mixture contains unreacted **13** as well as the dibromo and tetrabromo adducts **14** and **15**. This suggests the two ketenyl groups react independently, and there is little difference in the rate of the second bromination. It is also conceivable that the second-order process leads to **15** and the first-order process gives **14**, but the conditions of the product study would favor the higher-order process. The hydration reactivities^{2f} of the two ketenyl groups in **13** are also essentially independent of the other group, which might also suggest that the bromination, by whatever mechanism, proceeds sequentially.

The most likely pathway for the addition of Br₂ to **16** (eq 10) starts with a transfer of a bromine cation from (Br₂)₂ resulting in the acylium ion **25**, which gives the carbenium–oxonium ion **26** and then **17a** and **17b** (eq 14). An analogous mechanism has been proposed for the addition of hydrogen chloride^{10e} and carboxylic acids^{10d}

to γ -oxoketenes. There is no evidence for neighboring group participation in the rate-limiting step, as has been suggested in other cases.¹³



It is known that **16** exists in one of the conformations **16a** and **16b** with the phenyl and the methoxycarbonyl groups in close proximity to each other, as testified by the methyl signal in the ¹H NMR spectrum, which is located at rather high field (δ 3.33^{10a}) due to the ring current of the phenyl group. The same effect, even more pronounced (CH₃, δ 3.07), is operative in **17a** but is absent in **17b** (CH₃, δ 3.89). Only the reaction of **16a** with bromine should eventually lead to the observed products, since only the face of the ketene functionality opposite to the methyl glyoxylate moiety can be attacked for steric reasons. In contrast, **16b** would be converted into a product displaying an inverted C-4 configuration as compared to that of **17**.



In summary the bromination of the ketene PhMe₂SiCH=C=O (**11**) resembles the second order in [Br₂] bromination behavior of ordinary alkenes in halogenated hydrocarbon solvents. Throughout the accessible range of [Br₂] the 1,2-bisketene **1** reacts with bromine in a process first order in [Br₂] in which there is a concerted interaction of both ketenyl groups with the Br₂ molecule, obviating the need for participation of a second Br₂ molecule. This reaction initially forms the fumaryl bromide *E*-**7**, and a transition state for such a process has been calculated by *ab initio* methods. At high [Br₂], the bisketene **13** also reacts by the normal mechanism with a rate dependence on [Br₂]², but at low [Br₂] the reactions of this highly reactive bisketene exhibit kinetic terms that are first order in [Br₂]. After partial consumption of the starting material products of addition of both one and two molecules of Br₂ to **13** are noted. The γ -oxoketene **16** reacts by the second order in [Br₂] mechanism throughout the accessible concentration range, but the γ -oxo group participates in the product-determining step.

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Experimental Section

General Procedures. All reactions were carried out under N₂ or Ar in glassware that was oven dried and cooled in a desiccator. Solvents and reagents were obtained from Aldrich. The 1,2-dichloroethane was 99.8% HPLC grade.

Bromination Kinetics. The rate constants of Br₂ addition to (Me₃SiC=C=O)₂ (**1**),^{2a} PhMe₂SiCH=C=O (**11**),^{2g} Me₂Si(CH=C=O)₂ (**13**),^{2h} and γ -oxoketene **16**^{10a} were measured at 25 °C under pseudo-first- or pseudo-second-order conditions of excess ketene (or bromine) in 1,2-dichloroethane using an Applied Photophysics SX-17MX Stopped Flow instrument. The ketene concentration was varied from 0.5 to 9.32×10^{-3} M (after mixing), and the [Br₂] was varied from 0.05 to 5.6×10^{-3} M (after mixing). Solutions were prepared under Ar and stored with protection from moisture and light. The reactions were monitored by observing the rate of decrease of the Br₂ band at the absorption maximum of 409 nm ($\epsilon(\text{Br}_2) = 211 \text{ M}^{-1} \text{ cm}^{-1}$). In the case of the bromination of **1**, the reactions were strictly first order in [Br₂]. The pseudo-first-order rate constants for this bromination, k_{obs} , were evaluated by nonlinear least-squares fitting of the absorbance versus time traces to a standard exponential model. The k_{obs} values were the averages of 12–14 runs.

In the case of bromination of monoketenes **11** and **16**, the kinetics were strictly second order in [Br₂]. In the case when the [ketene] was kept 10–20-fold in excess of the Br₂, the pseudo-second-order rate constants (k_2^{obs}) were evaluated from the slopes of the plots of 1/abs vs time. The third-order rate constants were calculated as $k_3 = k_2^{\text{obs}}\epsilon/[\text{ketene}]$. In this case, we checked the validity of the previous third-order rate constants by running the kinetics under conditions where [Br₂] \gg [ketene]. In these cases, when [Br₂] was 10–20-fold in excess of the ketene, the kinetic behavior is pseudo first order in [Br₂], and one can evaluate the pseudo-first-order rate constants (k_{obs}) by fitting the absorbance vs time traces. The third-order rate constants given in Tables 2 and 4 were calculated as $k_3 = k_{\text{obs}}/[\text{Br}_2]^2$.

The kinetics of bromination of **13** were more complicated since the total absorbance vs time profile did not adhere strictly to first or second order in [Br₂] behavior. In this case, the reported third-order rate constants in Table 3 (Supporting Information) were evaluated under conditions where [ketene] \gg [Br₂] and the disappearance of bromine was monitored only to the extent of 2 half-lives. The linear plot of 1/abs vs time for 2 half-lives of reaction yielded the second order in [Br₂] rate constants (k_2^{obs}) from which was determined $k_3 = k_2^{\text{obs}}\epsilon/[\text{ketene}]$. To check the validity of the k_3 rate constant determined in this way, we also looked at the reaction under conditions where [Br₂] \gg [ketene] as in the case for monoketenes **11** and **16**. The so-determined rate constants agree acceptably well with those determined as above and are also given in Table 3 (Supporting Information). Determination of the rate constants that are first order in [Br₂] cannot be carried out exactly, but a crude value can be determined by fitting the entire absorbance vs time profile to a model containing both first and second order in [Br₂] terms.¹⁴

Products of Bromination of 1. The bisketene **1** (46.0 mg, 0.204 mmol) in 0.5 mL of CDCl₃ was cooled in dry ice/acetone, and Br₂ (32.6 mg, 0.204 mmol) was added with rapid loss of the Br₂ color. The spectra showed only the presence of **2,3-bis(trimethylsilyl)fumaryl dibromide (E-7)**: ¹H NMR (CDCl₃) δ 0.42; ¹³C NMR (CDCl₃) δ 0.11, 154.7, 165.8; IR (CDCl₃) 1795 cm⁻¹. In a separate preparation part of the solvent was removed to give crystals which were used for the X-ray structure determination (Figure 1). The product from the initial bromination of **1** above was left at 4 °C for 3 days and the spectra indicated a 90% conversion to **3,4-bis(trimethylsilyl)-5,5-dibromo-2(5H)-furanone (8)**, which was purified by low-temperature thin-layer chromatography (5% EtOAc in hexane): ¹H NMR (CDCl₃) δ 0.37 (s), 0.53 (s); ¹³C NMR δ 0.1, 1.4, 79.7, 137.8, 165.8, 173.4; IR (CDCl₃) 1792

cm⁻¹; UV $\lambda_{\text{max}}^{\text{CDCl}_3}$ 252 nm ($\epsilon = 5.6 \times 10^4$); EIMS m/z 386 (M⁺, 1), 279/277 (18, 16), 155 (88), 73 (100); HRMS m/z calcd for C₁₀H₁₈Br₂O₂Si₂ 383.9212, found 383.9207.

For kinetic studies of the isomerization, Br₂ (5.3 μL , 0.1 mmol) was added slowly to **1** (23 mg, 0.10 mmol) in 1 mL of pentane at -78 °C. The solution was warmed to room temperature and the solvent evaporated, and the resulting solid was dissolved in 0.5 mL of pentane and recrystallized at -78 °C. The solvent was removed at -78 °C, and the resulting solid was dried 1 min under vacuum at room temperature and dissolved in deuterated solvent. The kinetics of the conversion of **1** to **8** were monitored at 22 °C by observing the decrease of the Me₃Si ¹H NMR signal of **1** (δ 0.53 in CD₃CN, 0.42 in CDCl₃) relative to a toluene (δ 2.3) internal standard and gave first-order rate constants of $(4.13 \pm 0.33) \times 10^{-4} \text{ s}^{-1}$ (CD₃CN) and $(4.24 \pm 0.33) \times 10^{-5} \text{ s}^{-1}$ (CDCl₃).

To a sample of *E-7* (25.2 mg, 0.0652 mmol) in CDCl₃ prepared as above was added 10 μL of H₂O (0.536 mmol), and after 3 days at room temperature the solvent was evaporated and thin-layer chromatography (15% EtOAc in hexane) gave **9^{2a}** (12.7 mg, 0.0525 mmol, 80%); ¹H NMR (CDCl₃) δ 0.39; ¹³C NMR (CDCl₃) δ 0.11, 161.5, 168.4.

Dimethyl 2,3-Bis(trimethylsilyl)fumarate (E-10). The bisketene 2,3-bis(trimethylsilyl)-1,3-butadiene-1,4-dione (**1**) (21.6 mg, 0.096 mmol) was dissolved in CCl₄ (2 mL) and cooled to -23 °C (CCl₄/CO₂). One equivalent of bromine (15.4 mg, 0.096 mmol) was added slowly with stirring until the bromine color did not disappear. The reaction mixture was cooled to -78 °C (CO₂/acetone), and methanol (4 mL) was added slowly. The solution was warmed to room temperature, and the solvent was evaporated to give a crude solid product which was purified by thin-layer chromatography on silica gel (3% ethyl acetate in hexane) to give *E-10^{9b}* (26.8 mg, 0.0983 mmol, 97%).

Dimethyl 2,3-Bis(trimethylsilyl)maleate (Z-10). The bisketene **1** (41.0 mg, 0.181 mmol) dissolved in anhydrous ether (2 mL) was added to methanol (4 mL) at -77 °C. One equivalent of bromine (29.0 mg, 0.181 mmol) was added slowly until the bromine color persisted. The solvent was evaporated giving a crude solid product which was purified by thin-layer chromatography (silica gel, 3% EtOAc/hexane) to give dimethyl 2,3-bis(trimethylsilyl)fumarate *E-10^{9b}* (14.4 mg, 0.050 mmol, 28%), *R_f* 0.36, and *Z-10* (27.8 mg, 0.097 mmol, 53%), *R_f* 0.10.

2-(Phenyldimethylsilyl)-2-bromoacetyl Bromide (12). To phenyldimethylsilylketene **11^{2g}** (30 mg, 0.17 mmol) in 1 mL of CDCl₃ at -20 °C under N₂ was added liquid Br₂ (8.7 μL , 0.17 mmol) with stirring. The Br₂ decolorized immediately, and spectral examination revealed complete conversion to **12**: ¹H NMR (CDCl₃) δ 0.70 (s, 6), 4.39 (s, 1), 7.60–7.63 (m); ¹³C NMR (CDCl₃) δ 2.92, 45.9, 128.6, 131.2, 133.2, 134.8, 163.5; IR (CDCl₃) 1797 cm⁻¹ (C=O); EIMS m/z 255/257 (6), 227/229 (10), 199/201/203 (11), 161 (29), 135 (100).

Bromination of 13. To bis(2-oxoethenyl)dimethylsilane (**13^{2f}**) (20 mg, 0.14 mmol) in 0.5 mL of CDCl₃ at -30 °C was slowly added Br₂ (7.3 μL , 0.14 mmol) in 0.5 mL of CDCl₃. The Br₂ was decolorized immediately, and ¹H NMR showed signals attributed to unreacted **13**, (1,2-dibromo-2-oxoethyl)(2'-oxoethenyl)dimethylsilane (**14**), and bis(1,2-dibromo-2-oxoethyl)-dimethylsilane (**15**) in a ratio of 2.3/1.7/1.0. Addition of a further 0.14 mmol of Br₂ in 0.5 mL of CDCl₃ at -30 °C (further rapid decolorization) gave a 1:1 mixture of *meso*- and *d,l-15* as the only products. **14**: ¹H NMR (CDCl₃) δ 0.56 (s, 3), 0.58 (s, 3), 2.20 (s, 1), 4.31 (s, 1). **d,l-15**: IR (CDCl₃) 1793 cm⁻¹; ¹H NMR (CDCl₃) δ 0.69 (s, 6), 4.71 (s, 2); ¹³C NMR (CDCl₃) δ -3.74, 44.4, 162.1. *meso-15*: IR (CDCl₃) 1793 cm⁻¹; ¹H NMR (CDCl₃) δ 0.63 (s, 3, Me), 0.74 (s, 3, Me), 4.72 (s, 2, CHBr); ¹³C NMR (CDCl₃) δ -3.80, -3.23, 44.4, 162.3. *meso* + *d,l-15*: EIMS, m/z (intensity) 377, 379, 381, 383 (5), 257, 259, 261 (95), 99 (59), 84 (35); HRMS m/z calcd for C₆H₈Br₃O₂Si 376.7844, found 376.7877.

(1 α ,4 α ,4 α β,5 α ,8 α ,8 α β)- and (1 α ,4 β ,4 α ,5 β ,8 β ,8 α)-1,4-Dibromooctahydro-3-oxo-4-phenyl-5,8-methano-1H-2-benzopyran-1-carboxylic Acid Methyl Ester (17a and 17b). A solution of bromine (279 mg, 1.74 mmol) in dichloromethane

(14) Glint Analysis Manual, Version 3.20, April 1994, Applied Photophysics Ltd., Leatherhead, U.K.

(2 mL) was added dropwise to a stirred solution of γ -oxoketene **16**^{10a} (520 mg, 1.74 mmol) in dichloromethane (10 mL) at room temperature. At the beginning, the color of bromine disappeared instantaneously; at the end it remained. The mixture was then concentrated *in vacuo*, and the residue was purified by flash chromatography (silica gel, petroleum ether/dichloromethane 2:1 for the first 400 mL of the eluant, 1:1 for the next 1000 mL, and finally 1:2) affording in order of elution **17a** (21 mg, 3%), a 1.0:1.7 mixture of **17a** and **17b** (423 mg, 52%), and **17b** (163 mg, 20%) as solids. Spectral analysis and details of the preparation of samples of **17a** and **17b** for X-ray analysis are in the Supporting Information.

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Supporting Information Available: Tables 1–5, NMR spectra, spectral and analytical data of **17a** and **17b**, and X-ray crystallographic data for *E-7*, **17a**, and **17b** (39 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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