

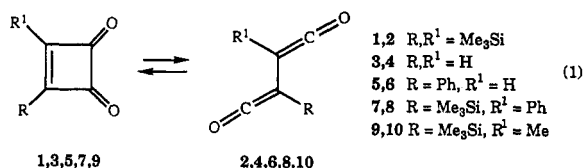
Formation and Reactivity of Unsymmetrical Bis(ketenes): 2-Phenyl- and 2-Methyl-3-(trimethylsilyl)-1,3-butadiene-1,4-diones†

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The preparation and properties of 2,3-bis(trimethylsilyl)-1,3-butadiene-1,4-dione (**2**) from the thermolysis of the cyclobutenedione **1** have recently been reported from this laboratory.^{1,2} It was expected¹ on the basis of *ab initio* molecular orbital calculations^{3a} that the parent cyclobutenedione **3** would be more stable than the *anti*-planar bis(ketene) **4** by 6.9 kcal/mol, whereas the stabilizing effect of the SiH₃ group on a ketene is 7.6 kcal/mol more than on an alkene, compared to hydrogen. Thus it was anticipated that the bis(ketene) **2** bearing two silyl groups should be more stable than **1**, and this prediction was verified experimentally.¹ Further calculations for R = SiH₃ led to the prediction that for this substituent the bis(ketene) structure is more stable than the cyclobutenedione by 4.9 kcal/mol, and the lack of additivity was attributed to ground-state stabilization of the cyclobutenedione by SiH₃.^{1d}

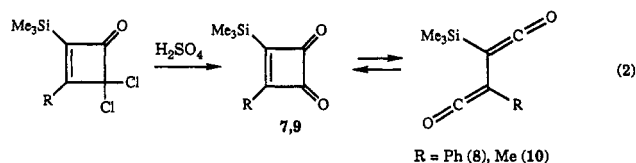


It is of interest to examine the properties of bis(ketenes) substituted with a single stabilizing silyl substituent^{3b-d} and another substituent with different properties.^{3a,4} A few unsymmetrically substituted 1,2-bis(ketenes) have been reported as transient species, including the suggestion by Mallory and Roberts^{4d} that the formation of dimethyl 2-phenylsuccinate from the reaction of the cyclobutenedione **5** with MeOH at 150 °C might occur by way of the bis(ketene) **6**, and a proposal for the formation of O=C=CHC(OH)=C=O by photolysis in an Ar matrix.^{4c} Calculations of the effect of the phenyl and methyl groups on ketene stability compared to the effects of an alkene indicate that these groups are destabilizing as ketene substituents relative to hydrogen by 2.6^{4c} and 3.3^{3a} kcal/mol, respectively. Assuming an additivity of substituent effects leads to estimates that 3-phenylcyclobutenedione (**5**) is 9.5 kcal/mol more stable than the bis(ketene) **6**, but that 3-phenyl- and 3-methyl-4-(trimethylsilyl)cyclobut-3-ene-1,2-dione (**7** and **9**) will be more stable

than the corresponding bis(ketenes) **8** and **10** by only 1.9 and 2.6 kcal/mol, respectively.

As a test of the validity of these calculations, we have undertaken the study of authentic unsymmetrically substituted bis(ketenes), and we now report the generation and direct observation of both **8** and **10** as rather long-lived intermediates at room temperature. The kinetics of the thermal ring closures of these bis(ketenes) to the cyclobutenediones **7** and **9** have been measured, as well as the equilibrium constant for the interconversion of **8** and **7**.

The reaction of the appropriate (trimethylsilyl)acetylene with dichloroketene generated from CCl₃COCl and activated Zn^{5a,b} gave the known cyclobutenones,^{5a} which on reaction with H₂SO₄^{1a,b} gave the cyclobutenediones **7** and **9**. **7**: mp 102.8–103.2 °C; ¹H NMR δ 0.45; ^{7.8}; UV λ_{max} (hexane) 287 nm; IR 1774 cm⁻¹. **9**: oil; ¹H NMR δ 0.36, 2.46; UV λ_{max} (hexane) 222 nm; IR 1771 cm⁻¹.^{5c}



On photolysis of **7** at 350 nm there was a color change to a deeper yellow and a new UV absorption at λ_{max} 257 nm appeared, while that at 287 nm due to **7** essentially disappeared. On heating of the photolyzed sample the band at 257 almost disappeared with concomitant reappearance of the absorption at 287 nm. Some absorption due to the starting alkyne was also observed in the sample, and this is attributed to arise from photolysis of the bis(ketene), as has been observed in other examples.^{1b} The spectral changes are assigned to photochemical conversion of **7** to the bis(ketene) **8**, with conversions of 87–95% as measured by ¹H NMR. Similar photolysis of **9** at 350 nm gave 55% **10**.

Evidence for the structures of **8** and **10** includes the presence of the strong ketene bands in the IR at 2093 and 2101 cm⁻¹, respectively, which are comparable to the band at 2084 cm⁻¹ for **2**.^{1a} The ¹H NMR spectra show peaks at δ 0.181 (Me₃Si) and 7.05–7.40 (Ph) for **8** and 0.203 (Me₃Si) and 1.744 (Me) for **10**, together with residual absorption for **7** and **9**, and the original alkynes. The ¹³C NMR shows the very distinctive peaks for the Me₃Si- and Ph-substituted ketenyl carbons at δ 7.9 and 33.5, respectively, for **8**, while the Me₃Si- and Me-substituted ketenyl carbons for **10** are at δ 10.7 and 18.9, respectively, at -20 °C. These may be compared to the corresponding carbons for **2** (δ 5.6),^{1a} Me₃SiCH=C=O (-0.1),^{6a} PhCMe=C=O (33.8),^{6b} and MeCH=C=O (10.9).^{6b}

Upon heating of **7** in CDCl₃ followed by rapid cooling, the presence of the phenyl-substituted bis(ketene) **8** could be detected by the appearance of the ¹H NMR peak of the Me₃Si at δ 0.181 and the appearance of the IR band at 2093 cm⁻¹. The relative concentrations of **7** and **8** were determined by integration of the NMR spectra, and the data were used to calculate equilibrium constants and thermodynamic parameters (Table 1). Comparable values of the equilibrium constants were measured starting with photolyzed samples containing mostly **8**. Heating of the methyl-substituted bis(ketene) **10** also resulted in re-formation of **9**; but while the ¹H NMR signals of **10** were still barely observable, the amount remaining at equilibrium at 142 °C was estimated to be less than 0.5%, as compared to 1.5 ± 0.3% for the phenyl bis(ketene) **8** at the same temperature (Table 1). The greater percentage of the phenyl bis(ketene) **8** present at equilibrium

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† Dedicated to Professor A. R. Katritzky on the occasion of his 65th birthday.

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(2) As discussed in refs 1c,d, approximately perpendicular conformations are found to be favored for bis(ketenes) on the basis of photoelectron and dipole moment measurements as well as calculation.

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Table 1. Thermal Equilibration of Cyclobutenedione **7** and Bis(ketene) **8**^a

<i>T</i> (°C)	[8]/[7]
161.3	2.2(±0.1)/97.8
161.0	2.8(±0.1)/97.2
143.1	1.4(±0.2)/98.6
142.2	1.6(±0.2)/98.4
100.5	0.5(±0.1)/99.5
100.3	0.9±(0.1)/99.1
25.0 ^b	0.06/99.94

^a ΔG° (25 °C) = 4.4(±1.6) kcal/mol, ΔH° = 6.9(±1.3) kcal/mol, ΔS° = 8.5(±3.2) cal/(deg mol). ^b Extrapolated.

compared to the methyl bis(ketene) **10** is consistent with the respective ΔE values of 1.9 and 2.6 kcal/mol for ring opening (eq 2) predicted on the basis of additivity of substituent effects.

The formation of the bis(ketenes) **8** and **10** on photolysis of **7** and **9** is in accord with behavior observed for other cyclobutenediones,^{1,7} and the thermal reversion of the bis(ketenes) is consistent with the greater stability of **7** and **9** predicted by molecular orbital calculations^{3a} as discussed above. This is the first observation of thermodynamically unstable bis(ketenes) as rather long-lived species of room temperature, and these results validate the supposition that calculated ketene-stabilizing effects from monoketenes may be used to predict the stability of bis(ketenes).

The kinetics of the thermal reversion of the bis(ketenes) to the cyclobutenediones were measured by monitoring the appearance of the UV λ_{max} of **7** at 287 nm and the ¹H NMR spectra of **9** and **10**, resulting in values of E_{act} of 21.8 (hexanes) kcal/mol for **8** (R = Ph) and 20.3 (CDCl₃) kcal/mol for **10** (R = Me). Examples in which the kinetics of ring closure of a 1,3-butadiene to a cyclobutene have been observed are rare; another is the perfluoro-1,3-butadiene to cyclobutene reaction.⁹

Samples of the bis(ketenes) **8** and **10** in CDCl₃ in NMR tubes were generated by photolysis of **7** and **9**, respectively, and 1.6 equiv of CH₃OH was added at -78 °C followed by warming to room temperature and evaporation of the solvent. After addition of more CDCl₃ the photolysis and methanolysis procedure was repeated one or two more times, resulting in formation of the monoketenes **11** and **12** in yields of 75–95%, together with residual diketone.

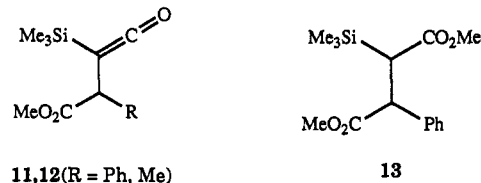
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(8) Rate constants ($s^{-1} \times 10^4$) measured by UV for conversion of **8** to **7** in mixed hexanes (*T* (°C) in parentheses): 7.78 (82.4), 1.62 (65.4), 0.354 (50.0). $\ln k_{\text{obs}} = -10960/T + 23.65$, $E_{\text{act}} = 21.8$ kcal/mol; $\Delta H^\circ = 21.1$ kcal/mol, $\Delta S^\circ = -13.6$ eu. Rate constants ($s^{-1} \times 10^4$) measured by ¹H NMR for conversion of **10** to **9** in CDCl₃ (*T* (°C) in parentheses): 13.5 (70.1), 3.61 (55.5), 0.760 (39.8). $\ln k_{\text{obs}} = -10194/T + 23.1$, $E_{\text{act}} = 20.3$ kcal/mol; $\Delta H^\circ = 19.6$ kcal/mol, $\Delta S^\circ = -14.9$ eu.

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The monoketenes **11** and **12** were purified by VPC and obtained pure as rather stable colorless liquids whose structures are confirmed by their ketenyl IR absorptions at 2093 and 2100 cm⁻¹, respectively, their ¹³C NMR signals for the Me₃Si-substituted carbons at δ 8.5 and 17.5, respectively, and other consistent spectral data.^{5c} Such long-lived monoketenes were previously observed from the reaction of the bis(trimethylsilyl) bis(ketene) **2** with alcohols, but these α -silylated esters decomposed on attempted isolation by gas chromatography.^{1b}

Reaction of the monoketene **11** with methanol in CDCl₃ at room temperature for 10 h gave the two stereoisomeric dimethyl succinates **13**^{5c} in a 2/1 ratio, each of which was isolated after separation by liquid chromatography. These were also formed by heating the bis(ketene) **8** in methanol at 100 °C for 18 h, along with the desilylated ester, as 28, 26, and 20%, respectively, of the total product as measured by ¹H NMR integration.



The kinetics of the reaction of the phenyl bis(ketene) **8** in 5 and 10% EtOH in CH₃CN solutions at 25 °C were measured by observing the decrease in the UV absorption at 257 nm. The rate constants obtained were 0.0408 and 0.156 s⁻¹, respectively. This fast reaction corresponds to the initial reaction of **8** with EtOH on the phenyl-substituted ketenyl unit and is consistent with the (1.9 × 10⁴)-fold greater reactivity of PhCH=C=O^{4c} in neutral H₂O compared to Me₃SiCH=C=O.^{3b} The rate constant for reaction of **8** in 5% EtOH/CH₃CN (approximately 1 M EtOH) of 0.0408 s⁻¹ may be compared to the reported¹⁰ rate constant of Ph₂C=C=O in 0.99 M EtOH in dioxane of 0.006 29 s⁻¹. By this comparison the bis(ketene) **8** is approximately 6-fold more reactive toward nucleophilic addition than Ph₂C=C=O, which is 17-fold less reactive than PhCH=C=O.

In conclusion this work demonstrates that unsymmetrically substituted bis(ketenes) bearing one trimethylsilyl group are readily accessible reactive intermediates from photolysis of cyclobutenediones, and these bis(ketenes) are relatively long-lived at room temperature. The observation of a measurable thermal equilibrium of the phenyl-substituted cyclobutenedione **7** and the bis(ketene) **8** and the lower relative stability of the methyl bis(ketene) **10** are convincing demonstrations of the utility of published molecular orbital calculations^{3a} in the prediction of substituent effects on ketenes. The reactivities of the two ketenyl groups of **8** and **10** show high selectivity and lead to isolable but reactive monoketenes, and this behavior is understandable in terms of the properties we have determined for the model monoketenes.

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