

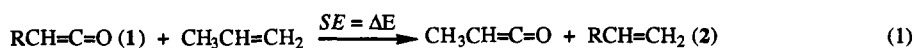
## Silylated bisketenes: Accessible and reactive organic intermediates

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**Abstract.** The thermal or photochemical ring opening of bis(trialkylsilyl) substituted cyclobutenediones **13** gives 1,2-bisketenes **14** which are thermodynamically stable relative to **13**. When only one trialkylsilyl substituent is present the cyclobutenedione **13** is moderately more stable, but has a substantial barrier to ring closure, so that the kinetics of ring closure can be readily measured above room temperature. The observed relative stabilities of **13** and **14** are consistent the substituent effects observed on monoketenes, with some additional effects on the cyclobutenediones **13**, and with *ab initio* calculations on analogues of **13** and **14**. The structures and reactivity of these bis(ketenes) have been studied, including the preparation of tetra(ketenes).

The study of ketene chemistry has continued to blossom, including the examination of the effect of substituents on ketene structure and reactivity (1). The extraordinary stabilizing effect of silyl substituents on ketenes has long been known (2), and the origin of this stabilization has been elucidated by *ab initio* molecular orbital calculations (3). From the MP2/6-31G\*\*//MP2/6-31G\* calculated energies of substituted ketenes **1** and alkenes **2**, ketene stabilization energies *SE* were calculated by the isodesmic reaction of eq. 1, and these are correlated with the group electronegativities  $\chi_{BE}$  (3c) by eq. 2, as illustrated in Fig. 1 (3a,b). Thus ketenes are stabilized relative to alkenes by electropositive substituents, and destabilized by electronegative groups.

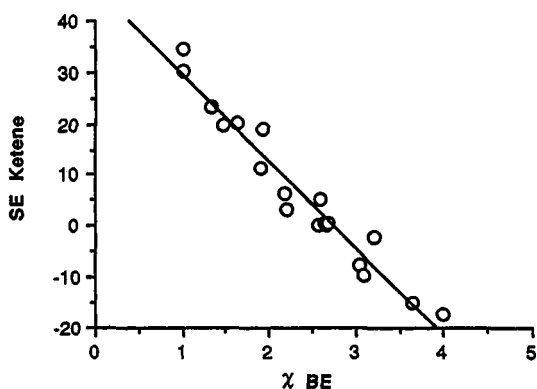


$$SE \text{ (MP2)} = -17.0 \chi_{BE} + 46.4 \quad (r = 0.97) \quad (2)$$

These calculations help to elucidate several important aspects of the effects of substituents on ketenes.  $\pi$ -Acceptor groups such as BH<sub>2</sub>, CH=O, NO, and NO<sub>2</sub> adopt coplanar conformations which permit conjugation between the substituent and the ketene as illustrated in eq. 3.

This interaction results in stabilization of the ketene, as manifested by positive deviations for these substituents above the correlation line of Fig. 1 (3a,b).

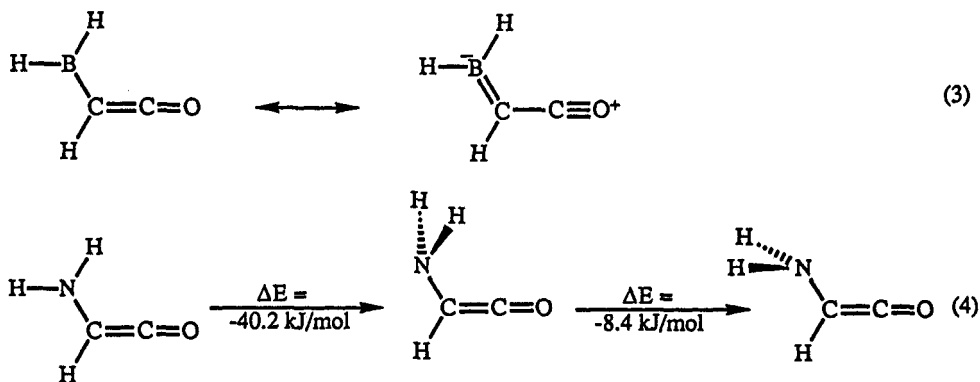
The  $\pi$ -donor substituents cause an unfavorable interaction between the substituent and the excess electron density at C $\beta$  of the ketene, and consequently the substituents NH<sub>2</sub>, OH, PH<sub>2</sub>, and SH favor twisted conformations of the substituent in which this unfavorable interaction is reduced, as shown in eq. 4. As discussed elsewhere (3b) there have been suggestions that this preference for the twisted conformation of the substituents is due to an attractive bonding interaction



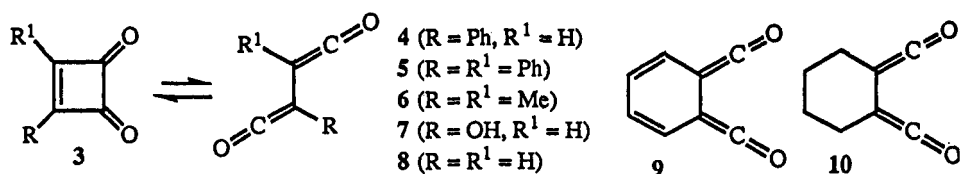
**Figure 1.**

Correlation of MP2/6-31G\*\*/MP2/6-31G\* calculated stabilization energies of bisketenes (eq. 1) with substituent group electronegativities  $\chi_{BE}$ .

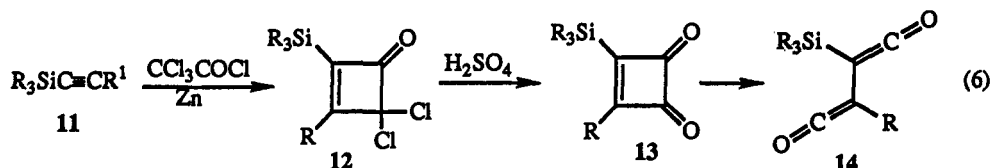
between the substituent lone pair and the in-plane p orbital of the carbonyl carbon of the ketene. Evidence against this attraction being the major factor causing this conformational preference includes the fact that the *anti*-lone pair conformation is also more stable than the coplanar arrangement by 40.2 kJ/mol, and is only 8.4 kJ/mol less stable than the *syn* conformation (3a,b).



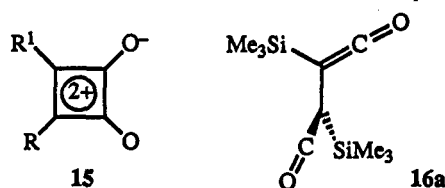
The thermal and photochemical ring opening of cyclobutenediones **3** to form 1,2-bis(ketenes) has long been studied, and evidence has been obtained for the formation of **4–10**, as well as others with bis EtO, AcO, and EtS substituents (4,5). Some of these were trapped in cycloaddition reactions or with nucleophiles, and in some cases these were detected spectroscopically by IR or UV at low temperatures, often in matrices or by the use of fast detection techniques (4,5). Comparison of the calculated 31.8 kJ/mol stabilizing influence of the SiH<sub>3</sub> group on ketene relative to hydrogen (eq. 5) and the fact that the *anti* conformation of the parent bis(ketene) **8** is calculated to be only 28.9 kJ/mol less stable than the corresponding cyclobutenedione **3** (3a) suggested that silylated bis(ketenes) substituted with silyl groups should be observable intermediates.



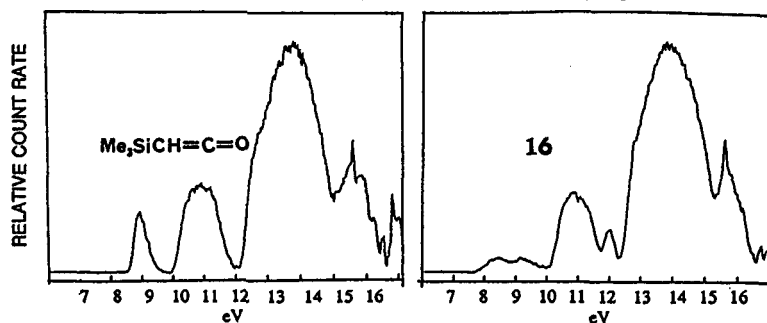
To test this prediction silylated cyclobutenediones **13** have been prepared by reaction of trialkylsilyl substituted alkynes **11** with dichloroketene to give the dichlorocyclobutenediones **12** followed by hydrolysis (eq. 6). In confirmation of the prediction when R is also a trialkylsilyl group thermolysis of **13** proceeds to give the more stable bis(ketene) **14** as the only observable product, and these are stable indefinitely in the absence of O<sub>2</sub>, H<sub>2</sub>O, or other reactive materials (6a).



The effect of substituents on the ring opening of cyclobutenediones **3** has been examined by ab initio molecular orbital calculations, and it has been found that while the substituent effects determined for monoketenes by eq. 1 are still manifested in the bisketenes these are significantly attenuated, so that only about half the effect is observed (7a). A substituent effect on the cyclobutenediones is also observed, as these appear to be stabilized by electron donor groups, and destabilized by electron acceptors. This is in accord with the positive charge induced in the ring by its 2π electron aromatic character (**15**). Calculations (7a,b), and experimental photoelectron and dipole moment studies (7b) also indicate that the favored structure of the 1,2-bis(ketene) is not a planar form, but rather is a twisted almost perpendicular structure, as indicated by **16a** for the bis(Me<sub>3</sub>Si) substituted derivative.



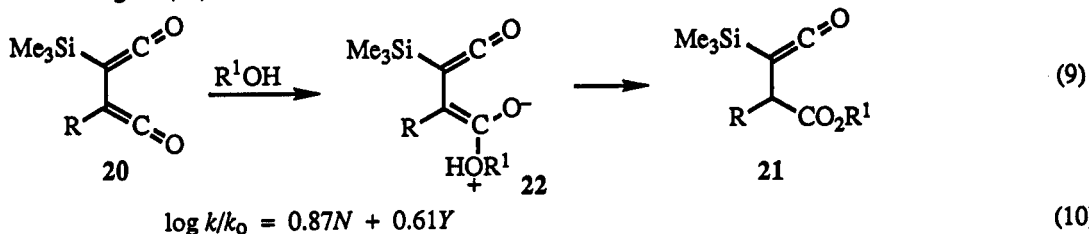
Thus the measured dipole moments of Me<sub>3</sub>SiCH=C=O and of the bisketene **16** are 1.8±0.3 and 2.7±0.3 Debye, respectively (7b). The greater dipole moment of **16** relative to the monoketene excludes an *anti* coplanar conformation, and while a simple calculation shows that this dipole moment corresponds to a dihedral angle of 80° the uncertainty in the measurement does not rule out dihedral angles of between 0° and 120°. The measured photoelectron spectrum of the bisketene **16** below 14 eV (Fig. 2) is accurately reproduced by the synthetic spectrum (Fig. 3), calculated using the HF/6-31G\*\*//HF/6-31G\*\* calculated torsional angle of 105° and the program PESPEC (7c). As is usually found the



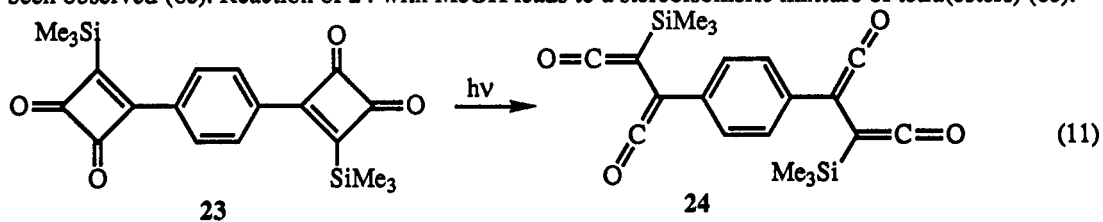
**Figure 2.**  
 Experimental photoelectron spectra of Me<sub>3</sub>SiCH=C=O and of bisketene **16**.



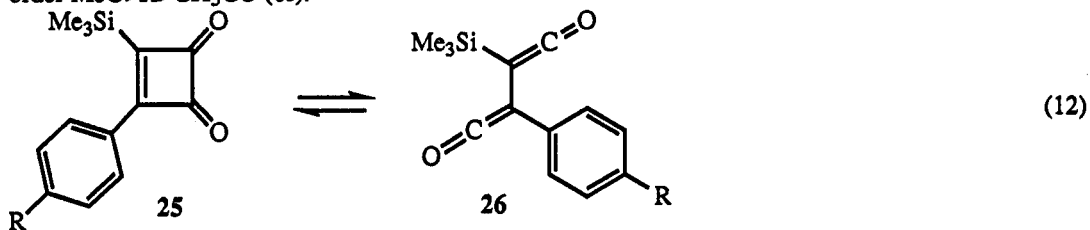
The reaction of bis(ketenes) **20** with alcohols leads to the mono(ketenyl) esters **21** (eq. 9), which have been characterized spectroscopically, and when R = Me or Ph these are quite stable, and can be purified by VPC (6a,b). The reactivity of **16** with alcohols has been correlated by the Winstein-Grunwald eq. 10, in which a dependence upon both the solvent ionizing power parameters  $Y_{OTs}$  and the solvent nucleophilicity parameters  $N_{OTs}$  are observed (6a). These parameters are defined for tosylate solvolysis, and are not optimized for nucleophilic additions, but the rather good correlation observed is supportive of a process proceeding through rate-limiting formation of a transition state resembling **22** (6a).



The bis(cyclobutenedione) **23** has also been prepared by a route analogous to that of eq. 6, and is converted by photolysis to the tetra(ketene) **24** (eq. 11), which has been characterized by IR and NMR (6e). The kinetics of the successive ring closure of **24** first to a bis(ketene) and then to **23** have also been observed (6e). Reaction of **24** with MeOH leads to a stereoisomeric mixture of tetra(esters) (6e).



A test of the importance of the positive charge on the cyclobutenedione ring as shown by structure **15** is provided by the effect of aryl substituents on the equilibrium between **25** and **26**, and the rates of conversion of **26** back to **25** (eq. 12). It is found that for an electron-withdrawing group R = CH<sub>3</sub>CO that the percentage of **26** in equilibrium with **25** is 4% at 100 °C, as opposed to 1% for R = H, and none observable for R = MeO. Similarly the effect of R on the rates of ring closure of **26** to **25** is in the order MeO > H > CH<sub>3</sub>CO (6f).



In conclusion the understanding gained from theoretical studies on substituent effects on ketene structures and stabilities (6a,b) and of the structures and interconversions of cyclobutenediones and bisketenes has permitted the rational synthesis of a variety of new 1,2-bis(ketenes) with a range of

predictable stabilities. These multi-functional species undergo a variety of interesting and useful reactions which are often not those anticipated on the basis of naive expectations.

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