[2 + 2], [4 + 1], and [4 + 2] Cycloaddition Reactions of Silylated Bisketenes

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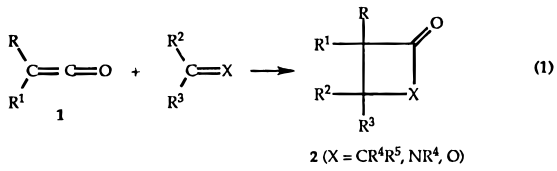
Cycloaddition reactions of the bisketenes O=C=C($SiMe_3$)CR=C=O (**15**, R = $SiMe_3$; **16**, R = Ph) include BF_3-catalyzed [2+2] cycloaddition of **15** with CH_3CHO to form an isolable β-lactone **18** adduct which undergoes thermal decarboxylation to the vinylketene **19**. Reactions of **15** and **16** with CH_2N_2 proceed by [4+1] cycloaddition to give mixtures of cyclopentene-1,3-diones **20** and methylenefuranones **21**, while Me_3SiCHN_2 and $PhCHN_2$ give only **20**. The reactions are interpreted in terms of a steric preference for nucleophilic attack by the substituted diazomethanes from the side of the ketene bearing the Me_3SiC=C=O substituent, leading to formation of **20**. With the less bulky CH_2N_2, attack occurs from both sides and approach from the side of the R group leads to formation of lactones **21**. Reaction of tetramethoxyethylene with **15** yields both a cyclopentene-1,3-dione **24** from net addition of dimethoxycarbene and a spirocyclopropylbutenolide **25**. Free dimethoxycarbene generated by heating an oxadiazoline precursor also reacted with **15** to give dione **24**. Various electrophilic dienophiles do not react with **15**, but nucleophilic alkynes react with **16** in thermal reactions to give spirocyclopropenylfuranones **33**−**36**, and Me_3SiC≡COEt and **16** react by net [4 + 2] cycloaddition to give the quinone **37** as the major product.

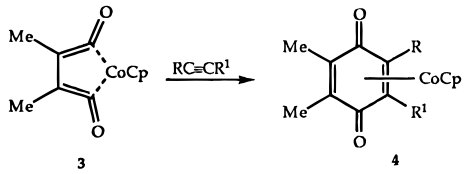
The [2+2] cycloaddition reactions of ketenes **1**, including dimerization and reactions with alkenes, imines, and aldehydes to form cyclobutenones, β-lactams, and β-lactones **2**, respectively (eq 1), are the most distinctive



(1)

reactions of these fascinating species.[1,2] There have been authoritative arguments for the concerted nature of these reactions[1f−h] and also strong arguments for stepwise processes.[3] These reactions are also the subject of intense theoretical study.[2] It is characteristic of monoketenes that they do not ordinarily give observed [4+2] cycloaddition products except in unusual circumstances.[4]

Bisketenes have been rare species, and only a few cycloaddition reactions of this family have been studied. The metal complex **3** reacts by a net [4+2] cycloaddition to form quinone complexes **4** (eq 2).[5a] Photolyses of



(2)

cyclobutene-1,2-diones such as **5** in the presence of cyclopentadiene were proposed to form bisketenes **6**

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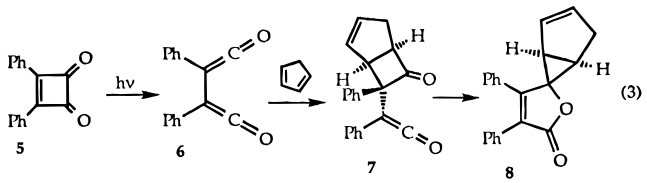
which underwent [2+2] cycloadditions to give the unobserved monoketenes **7** which rearranged to the spirocyclopropyl $\Delta^{\alpha,\beta}$-butenolide adducts **8** (eq 3).[5b] The bisketene



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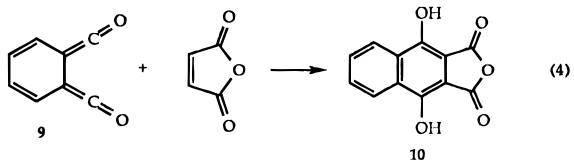
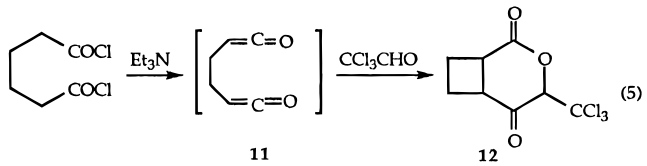
9 was reported to give a [4+2] cycloaddition to maleic anhydride (eq 4),[5c,d] and derivatives of **9** add to substituted



(4)

benzoquinones.[5f]

Reaction of adipyl chloride with triethylamine in the presence of chloral gave **12**, and this could have involved reaction of the bisketene **11**, but stepwise routes seem more likely (eq 5).[5g]



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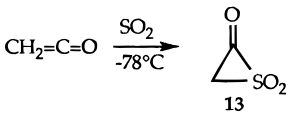
Ketenes react with diazomethanes by [2+1] cycloadditions to give cyclopropanones,[6a−d] and at −78 °C reaction with sulfur dioxide gives the adduct assigned the α-sultone structure **13** from [2+1] cycloaddition (eq 6).[6e]



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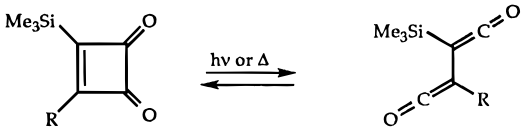
We have recently been engaged in the study of long-lived 1,2-bisketenes stabilized by the presence of trimethylsilyl groups.[7] These species are prepared by thermolysis or photolysis of the corresponding cyclobutene diones **14**, and the bisketene **15** (R = Me_3Si) is thermodynamically stable relative to the cyclobutenedione, whereas for **16** and **17** (R = Ph and Me, respectively) the bisketenes re-form **14** at measurable rates, but are sufficiently long-lived that their chemical reactivity can be studied (eq 7).[7c,d] The factors influencing the interconversion of these species have been studied by



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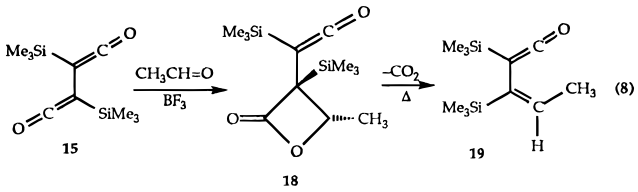
14a R = Me_3Si
14b R = Ph
14c R = Me

15 (R = Me_3Si); **16** (R = Ph); **17** (R = Me)

theoretical methods.[7e] We now report the study of the cycloaddition reactivity of bisketenes **15** and **16**.

Results and Discussion

Cycloaddition of ketenes with aldehydes is a major preparative route to β-lactones, and these latter compounds are prone to decarboxylation.[8] Reaction of **15** with acetaldehyde, catalyzed by $BF_3{\cdot}OEt_2$, leads to net [2+2] cycloaddition and formation and isolation as a solid of the novel ketenic β-lactone **18** (eq 8). The structure of



(8)

18 was established by its spectral properties, especially the distinctive features for ketenes summarized elsewhere,[1a] such as the IR band at 2084 cm^{-1}, and the ^{13}C signals for C_α and C_β of the silylketene at δ 178.6 and −3.7, respectively. The stereochemistry of **18** was determined by an NOE experiment in which irradiation of the ketenyl Me_3Si group resulted in 0.95% and 0.63% enhancement of the CH_3 and CH resonances, respectively, while irradiation of the lactone Me_3Si group resulted in 1.01% and 13.6% enhancement of the CH_3 and CH resonances, respectively.

The BF_3-catalyzed cycloaddition of $Me_3SiC(Hx\text{-}n)$=C=O with an aldehyde is reported to give a mixture of *E*/*Z* isomers,[8c] and cycloadditions of Me_3SiCH=C=O with aldehydes give a predominance of *E* or *Z* isomers depending upon the particular situation.[8b] Recent theoretical studies[8d] of the cycloaddition of chloroketene with acetaldehyde favor a transition state for the uncatalyzed reaction in which bond formation from the aldehyde oxygen to the ketenyl carbonyl carbon is most advanced and the *trans* cycloadduct is favored, whereas the transition state for the Lewis acid-catalyzed transition state involves predominant C−C bond formation with high zwitterionic character and favors *cis* products.[8d]

Upon heating of **18** decarboxylation occurred with formation of the vinylketene **19** (eq 8). The structural assignment of **19** is based on its spectral properties, including the distinctive ketenyl IR band at 2080 cm^{-1} and the ^{13}C NMR signals for C_α and C_β of the ketene at δ 176.6 and −1.3, respectively, and the stereochemical assignment shown is based on the assumed loss of CO_2 without change in the stereochemistry, as generally found in β-lactone decarboxylations.[8b] Although vinylketenes are ordinarily quite reactive,[1a] **19** is isolable with no apparent tendency for dimerization, in common with other silyl derivatives.[1a,9]

Reaction of the bisketenes **15** and **16** (which preferentially exist in the twisted conformations shown)[7a,e] with

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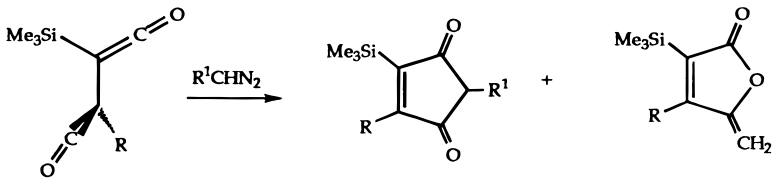


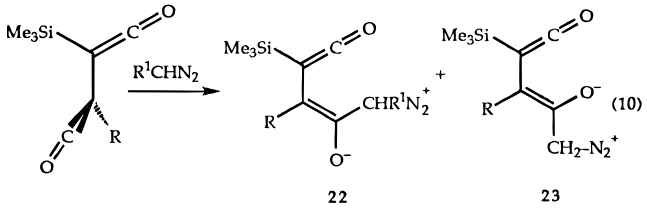
(9)

R		R, R^1			R		
Me_3Si	**15**	Me_3Si, H	**20a**	22%	Me_3Si	**21a**	63%
Ph	**16**	Ph, H	**20b**	49%	Ph	**21b**	16%
		Me_3Si, Me_3Si	**20c**	64%[a]			
		Ph, Me_3Si	**20d**	69%[a]	[a] After loss of Me_3Si		
		Me_3Si, Ph	**20e**	67%			

diazomethanes R^1CHN_2 led to two types of products, namely 2,5-disubstituted 4-(trimethylsily)-4-cyclopentene-1,3-diones (**20**) and 4-substituted 3-(trimethylsilyl)-5-methylene-2(5*H*)-furanones (**21**) (eq 9). However, the latter product was only observed for the reaction with CH_2N_2, while reactions of the bisketenes with Me_3SiCHN_2 and $PhCHN_2$ led only to **20**. No reaction was observed on treatment of the bisketenes with N_2CHCO_2Et, whereas *n*-$C_5H_{13}CHN_2$ led to a mixture of products from which no pure materials were isolated.

The derivatives **20c** and **20d** were not isolated, and their presence in the crude reaction product was only inferred from the initial ^1H NMR spectra. These compounds evidently undergo facile replacement of the group $R^1 = Me_3Si$ by hydrogen to form the isolated **20a** and **20b** because of the activation of the Me_3Si to nucleophilic displacement by the two adjacent carbonyl groups.

The formation of these products may be explained by a process involving initial attack of the diazomethane on the more activated of the ketenyl groupings, which is the phenyl-substituted moiety for **16** (R = Ph),[7c,d] to form the stereoisomeric zwitterions **22** or **23**, depending upon whether the diazomethane attacks the ketenyl group *anti* or *syn* to the substituent R (eqs 10, 11). In previous



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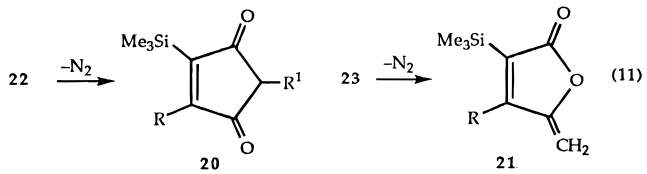
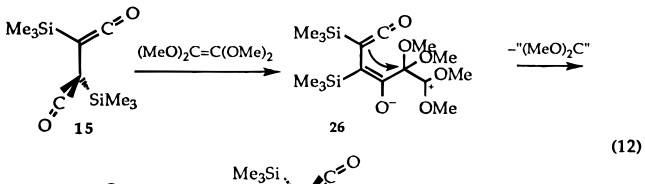


(11)

studies, we have analyzed such nucleophilic additions to ketenes as occurring in the ketene plane *syn* to the smaller group.[10] In the present case, inspection of the structures suggests that approach of the nucleophilic diazoalkane may be more facile *syn* to the ketenyl group $Me_3SiC{=}C{=}O$. Ring closure of the zwitterions **22** and **23** would lead to the cyclopentenediones **20** or the methylenefuranones **21**, respectively. When the diazomethane bears a bulky Me_3Si or Ph substituent; the size of the reagent evidently permits only attack *anti* to the group R (Me_3Si or Ph) by the less hindered approach *syn* to the $Me_3SiC{=}C{=}O$ substituent. Only for CH_2N_2 is some attack *syn* to the R groups feasible, leading to some formation of **21**. Consistent with this interpretation, it has been previously proposed[5b] that attack on **6** occurs preferentially from the side of the $PhC{=}C{=}O$ group.

Reaction of **15** with $(MeO)_2C{=}C(OMe)_2$[11b,c] yielded the cyclopentenedione **24** and the spirocyclopropylbutenolide **25**. The structures of **24** and **25** follow from their distinctive spectral properties, including the simple ^1H and ^{13}C NMR spectra of **24** and comparison of the data for **25** to those of other 5-spirocyclopropylbutenolides.[5b,12a] The formation of these products can be rationalized as resulting from attack on **15** *anti* or *syn*, respectively, to the Me_3Si groups (eqs 12, 13). Attack *anti* to the Me_3Si



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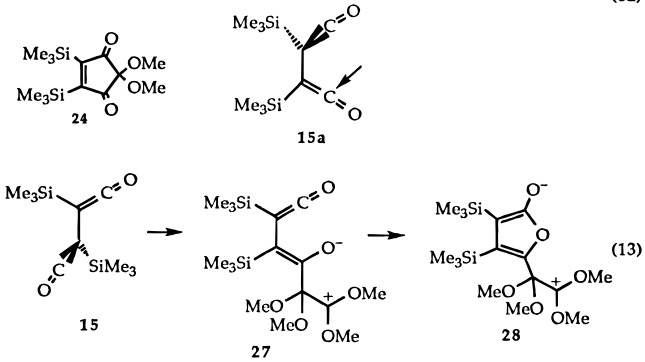

(13)

on the in-plane C=O π-system, illustrated for clarity by **15a**, would give the zwitterion **26**, and this could expel $(MeO)_2C$ (or its equivalent) as shown, perhaps by transfer to another molecule of **15**. As shown in eq 13 the initial zwitterion **27** formed from attack *syn* to the Me_3Si group can cyclize first to the zwitterion **28**, which can form **25**

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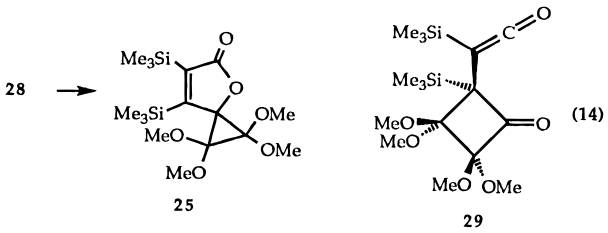
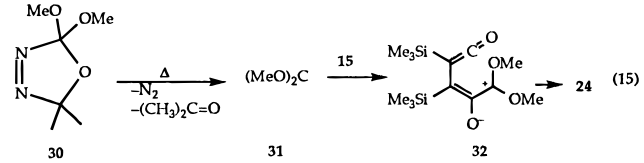
(eq 14), or alternatively [2+2] cycloaddition to form **29**



viaeither **26** or **27** can occur, and then **29** could form **25**, as has been proposed for other α-ketenylcyclobutanones.[5b,12a]

Although the reaction of bisketenes with cyclopentadiene has been interpreted[5b] as occurring by an initial concerted [2+2] cycloaddition, our review of the literature[1a] suggests that stepwise processes also merit consideration. The highly nucleophilic $(MeO)_2C{=}C(OMe)_2$ is expected to favor zwitterionic pathways, and a zwitterionic pathway has been proposed for the reaction of **9** with methanol.[12b]

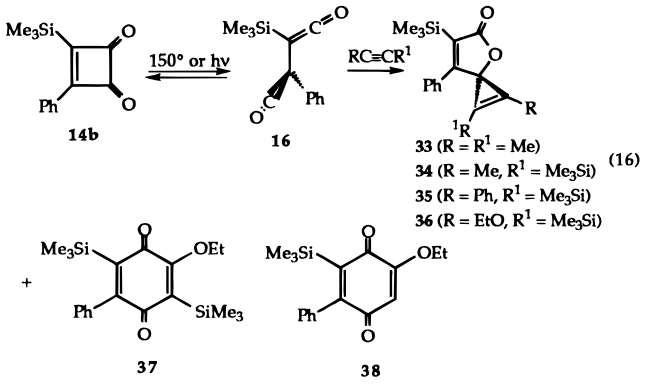
The cyclopentenedione **24** also forms from the reaction of bisketene **15** with dimethoxycarbene (**31**) as generated from the oxadiazoline precursor **30** (eq 15).[13] The bisketene **15** and the carbene were both generated in situ from the thermolysis of the cyclobutenedione **14a** and **30**, respectively, in benzene, and **24** was obtained in 62% yield. Tetramethoxyethylene is formed from dimethoxycarbene under the conditions of eq 15,[13] and this suggests that the formation of **24** from bisketene **15** and $(MeO)_2C{=}C(OMe)_2$ described above does not involve a dissociation of the latter to form dimethoxycarbene, which reacts with **15** as in eq 15.



The nucleophilic dimethoxycarbene **31** generated from **30** would be expected to react with the bisketene **15** by in-plane nucleophilic attack at the carbonyl carbon from the face opposite the Me_3Si group to form intermediate **32** (eq 15), analogous to the formation of **26** in eq 12. No product analogous to **21**, which would result from attack on the opposite face of the ketene (eqs 10, 11), was detected. A concerted reaction in which the in-plane HOMO of the carbene attacks one ketenyl group while the out-of-plane LUMO of the carbene undergoes simultaneous bonding to the other carbonyl carbon is also conceivable, but the present evidence does not establish this point.

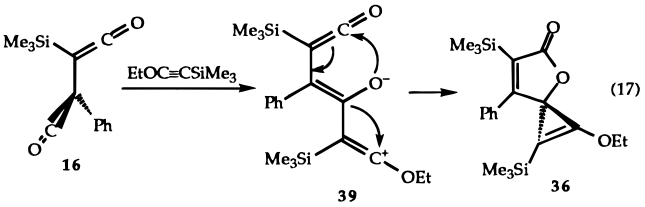
To examine the reactivity of silyl-substituted bisketenes with electron-deficient dieneophiles, **15** was heated with maleic anhydride, dimethyl acetylenedicarboxylate, and 4-phenyl-1,2,4-triazoline-3,5-dione, but these procedures uniformly gave no observed reaction. This failure of the bisketene to react with electrophiles is consistent with the known behavior of monoketenes.[1]

The bisketene **16** with one phenyl-substituted ketene moiety may be generated photochemically from the corresponding cyclobutenedione **14b** in high yield, or may be generated in a low equilibrium concentration by heating of **14b** (eq 7), and has been found to be much more reactive than **15**.[7c,d] Heating of **14b** in the presence of 2-butyne led to no observed reaction, but photolysis of **14b** with 350 nm light at 5 °C for 1 week in the presence of 2-butyne or 1-(trimethylsilyl)propyne led to formation of 1:1 adducts, which on the basis of their spectral properties were assigned the spirocyclopropenylbutenolide structures **33** and **34** (eq 16). The formation of such



spirocyclopropenylbutenolides was previously observed in the reactions of **9**.[5e] When **14b** was heated with the more reactive dienophile 1-phenyl-2-(trimethylsilyl)-acetylene, a 1:1 adduct was formed and was assigned the analogous structure **35**. This was also obtained by photolysis of **14b** in the presence of the alkyne. Photochemically generated bisketene **16** reacted upon addition of the even more reactive 1-ethoxy-2-(trimethylsilyl)-acetylene at −25 °C to give the adduct **36** and also the unstable [4+2] cycloadduct **37** in yields of 8% and 64%, respectively (eq 16). Upon chromatography, **37** tended to undergo desilylation to **38**, which was also rather unstable.

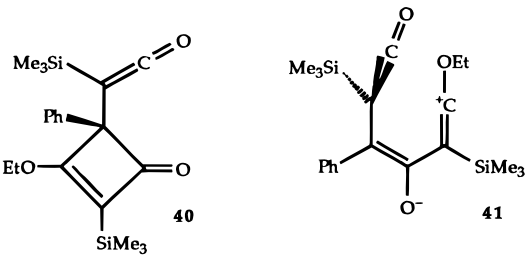
The formation of the spirocyclopropenylbutenolides **33**−**36** could occur by a stepwise process with attack *syn* to the phenyl group forming a zwitterionic intermediate such as **39** as shown in eq 17 for the example forming **36**. This mechanism is consistent with the observed greater reactivity with increasing nucleophilicity of the different alkynes in the formation of **33**−**36** and is also in accord with the pattern of eqs 10, 12, and 15.



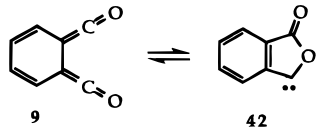
Alternatively there could be initial attack *anti* to the phenyl with formation of cyclobutenones such as **40** which rearrange to **33**−**36** in a process analogous to that proposed[5b] for initial formation of cyclobutanones (eq 3). Formation of the [4+2] cycloadduct **37** could also occur from **40** or alternatively could involve the intermediate **41** formed from **16** by approach of the alkyne to the PhC=C=O moiety *anti* to the phenyl. A twisted geometry for **41** is shown, but the question of the electronic nature of this reaction has not been examined in detail, and alternatives may be envisaged.

The formation of butenolide-type products is commonplace in the reactions of 1,2-bisketenes[5b,e,12] and, for example in the case of bisketene **9**, has been taken as

(13) (a) El-Saidi, M.; Kassam, K.; Pole, D. L.; Tadey, T.; Warkentin, J. *J. Am. Chem. Soc.* **1992**, *114*, 8751−8752. (b) Pole, D. L.; Warkentin, J. *Liebigs Ann. Chem.* **1995**, 1907.



evidence for the intervention of the cyclic carbene structure **42** (eq 18).[14]



(18)

However, as noted above, it is not necessary to invoke carbene-like structures to explain the reaction products in these bisketene reactions, and the same conclusion has been reached by others.[12] Thus bisketene **16** is generated in high yield and is directly observed by NMR, and no direct evidence for the presence of carbene structures analogous to **42** has been found. Similarly in our previous study of the generation and ring closure of **9** using detection by time-resolved infrared spectroscopy, no evidence for **42** was seen, and the data could be explained without its intervention.[7f] Thus while the existence of **42** and related carbenes cannot be disproven, direct evidence for them is lacking, and these appear to be unnecessary.

In summary bisketenes **15** and **16** have been shown to undergo cycloaddition reactions by a diversity of pathways to yield products resulting from net [2+2], [4+1], and [4+2] processes and also tandem processes forming spiro products. The pathways followed are determined both by the structures of the bisketenes and of the ketenophilic reagents.

Experimental Section

General Procedures. All glassware was oven-dried at 120 °C overnight and allowed to cool in a dessicator before use. Air and moisture sensitive reactions were carried out under an atmosphere of nitrogen. DME and ether were distilled from sodium/benzophenone directly before use. All other reagents were used as received from commercial sources, unless noted.

***(E)*-2-(Trimethylsilyl)-2-(1′-trimethylsilyl)-2′-oxoethenyl)-3-methylpropiolactone (18).** Bisketene **15** (156 mg, 0.69 mmol) was dissolved in 1 mL of $CHCl_3$, and freshly distilled acetaldehyde (200 μL, 160 mg, 3.6 mmol) and $BF_3{\cdot}Et_2O$ (10 μL, 12 mg, 0.08 mmol) were added. The solution was left for 1 h at 25 °C, the solvent evaporated, and the residue recrystallized from ether to give **18** (153 mg, 0.57 mmol, 82%): mp 64.5−65.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 9), 0.29 (s, 9), 1.51 (d, 3, J = 6.2 Hz), 4.55 (q, 1, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ −3.66, 0.35, 11.4, 18.1, 48.2, 73.6, 171.4, 178.6; IR ($CDCl_3$) 2084 (s), 1796 (s) cm^{-1}; EIMS m/z 270 (M^+, 31), 255 ($M^+ - CH_3$, 22), 227 ($M^+ - CO, CH_3$, 33), 199 (30), 171 (44), 155 (46), 147 (68), 73 (Me_3Si^+, 100); HRMS m/z calcd for $C_{12}H_{22}O_3Si_2$ 270.1108, found 270.1086.

2,3-Bis(trimethylsilyl)-1,3(*Z*)-pentadien-1-one (19). The ketenyl β-lactone **18** (30.0 mg, 0.111 mmol) dissolved in anhydrous ether (200 μL) was injected into a gas chromatograph (column O.V. 17, injector 250 °C, column 100 °C, rt 22 min), to give **19** as a colorless oil (8.8 mg, 0.039 mmol, 35%): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9), 0.18 (s, 9), 1.75 (d, 3, $J_{1,2}$ = 6.6 Hz), 6.05 (q, 1, $J_{1,2}$ = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ −1.26, 0.15, 17.2, 29.7, 129.3, 139.1, 176.6; IR ($CDCl_3$) 2080 (s), 1793 (s) cm^{-1}; EIMS m/z 226 (M^+, 24), 198 ($M^+ - CO$, 12), 171 (36), 110 ($M^+ - Me_3Si, CH_3, CO$, 76), 73 (Me_3Si^+, 100); HRMS m/z calcd for $C_{11}H_{22}OSi_2$ 226.1209, found 226.1212.

4,5-Bis(trimethylsilyl)-4-cyclopentene-1,3-dione (20a). Bisketene **15** (63.2 mg, 0.279 mol) was dissolved in 10 mL of anhydrous ether in a 25-mL three-necked round bottomed flask under N_2 flow, Me_3SiCHN_2 (31.9 mg, 0.279 mmol) was added dropwise, and the solution was stirred overnight. The ether solution was washed twice with H_2O (10 mL), dried over anhydrous $MgSO_4$, and evaporated to give a yellow liquid/brownish-red solid mixture. This mixture was chromatographed, using a 1/9 EtOAc/hexane solvent to give yellow crystals of **20a** (43 mg, 0.18 mmol, 64%); mp 38.0−38.5 °C; ^{1}H NMR δ 0.34 (s, 18), 2.76 (s, 2); ^{13}C NMR ($CDCl_3$) δ 0.51, 41.2, 175.5, 205.8; IR ($CDCl_3$) 1730, 1690 (s) cm^{-1}; UV λ_{max} (hexanes) 434 nm (ϵ = 50), 250 nm (shoulder); EIMS m/z 240 (M^+, 24), 225 ($M^+ - CH_3$, 50), 197 ($M^+ - CO, CH_3$, 51), 155 ($M^+ - CH_2$-CO, CO, CH_3, 100), 73 (Me_3Si^+, 74); HRMS m/z calcd for $C_{11}H_{20}O_2Si_2$ 240.1002, found 240.0994. Anal. Calcd: C, 54.95; H, 8.38. Found: C, 54.58; H, 8.61.

4,5-Bis(trimethylsily)-4-cyclopentene-1,3-dione (20a) and 3,4-Bis(trimethylsilyl)-5-methylene-2(5*H*)-furanone (21a). The bisketene **15** (27.8 mg, 0.123 mmol) was dissolved in anhydrous ether (2 mL), diazomethane (0.63 mmol in 5 mL of ether solution) was added, and the solution was stirred at rt under nitrogen for 2 h. The solvent was then evaporated to give crude product which was further purified by thin layer chromatography (on silica gel eluted by 3% ethyl acetate in hexane) to give **20a** (vide supra) (6.5 mg, 0.027 mmol, 22%) and the colorless oil **21a** (18.5 mg, 0.077 mmol, 63%): ^{1}H NMR ($CDCl_3$) 0.35 (s, 9), 0.39 (s, 9), 4.98 and 5.19 (ea 1, d, $J_{1,2}$ = 2.5 Hz); ^{13}C NMR ($CDCl_3$) δ 0.53, 1.60, 97.0, 144.2, 159.6, 165.8, 173.0; IR ($CDCl_3$) 1744, 1628 cm^{-1}; EIMS m/z 240 (M^+, 22), 225 ($M^+ - CH_3$, 65), 197 ($M^+ - CH_3, CO$, 46), 181 ($M^+ - Me, CO_2$, 54), 155 ($Me_3SiC{\equiv}CSiMe_2^+$, 100), 73 (Me_3Si^+, 60); HRMS m/z calcd for $C_{11}H_{20}O_2Si_2$ 240.1002, found 240.1000.

4-(Trimethylsilyl)-5-phenyl-4-cyclopentene-1,3-dione (20b). A solution of 3-(trimethylsilyl)-4-phenyl-3-cyclobutene-1,2-dione (**14b**), (17.2 mg, 0.075 mmol) in $CDCl_3$ (0.5 mL) was photolyzed for 2 h using 350 nm light at 6 °C to give the bisketene 2-(trimethylsilyl)-3-phenyl-1,3-butadiene-1,4-dione (**16**)[7c] in 99% yield as measured by ^{1}H NMR. The bisketene was then added to Me_3SiCHN_2 (15 mg, 0.132 mmol) in hexane (2 mL), and the solution was stirred under nitrogen for 16 h at rt. The solvent was evaporated to give a crude solid product which was further purified by thin layer chromatography (on silica gel eluted by 5% ethyl acetate in hexane) to give **20b** as a yellow-green solid product (12.6 mg, 0.052 mmol, 69%): mp 98.5−99.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9), 3.02 (s, 2), 7.20−7.50 (m, 5); ^{13}C NMR ($CDCl_3$) δ −0.72, 42.0, 128.1, 129.0, 129.8, 131.0, 161.5, 168.4, 200.7, 204.0; IR ($CDCl_3$) 1733 (s), 1696 (s) cm^{-1}; EIMS m/z 244 (M^+, 53), 229 ($M^+ - CH_3$, 58), 201 ($M^+ - CH_3, CO$, 23), 159 ($PhC{\equiv}CTMS^+ - CH_3$, 100), 73 (Me_3Si^+, 7); HRMS m/z calcd for $C_{14}H_{16}O_2Si$ 244.0919, found 244.0915.

3-(Trimethylsilyl)-4-phenyl-5-methylene-2(5*H*)-furanone (21b). A solution of **14b** (51.0 mg, 0.222 mmol) in $CDCl_3$ (1 mL) was photolyzed as above for 1.5 h to give the bisketene **16** (87%, monitored by ^{1}H NMR). The solution was cooled to 0 °C, diazomethane (0.3 mmol) in ether (1.1 mL) was added over 5 min, and the solution was kept at 0 °C for 1 h and then at rt overnight. The solvent was evaporated, and the crude product was further purified by thin layer chromatography (on silica gel eluted using 5% ethyl acetate in hexane) to give **20b** (vide supra) as a yellow-green solid (26.5 mg, 0.11 mmol, 49%) and **21b** as a colorless oil (8.7 mg, 0.036 mmol, 16%): ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9), 5.01 and 5.31 (ea d, 1, $J_{1/2}$ = 2.6 Hz), 7.25−7.50 (m, 5); ^{13}C NMR ($CDCl_3$) δ 0.22, 98.2, 128.1, 128.4, 129.2, 129.5, 131.4, 142.9, 157.6, 169.4; IR ($CDCl_3$) 1746 (vs), 1630 (s) cm^{-1}; EIMS m/z 244 (M^+, 47), 229 ($M^+ - CH_3$, 26), 201 ($M^+ - CH_3, CO$, 18), 159 ($PhC{\equiv}CSiMe_2^+$, 100), 73 (Me_3Si^+, 15); HRMS m/z calcd for $C_{14}H_{16}O_2Si$ 244.0919, found 244.0916.

4,5-Bis(trimethylsilyl)-2-phenyl-4-cyclopentene-1,3-dione (20e). The bisketene **15** (32.6 mg, 0.144 mmol) dissolved in anhydrous ether (0.5 mL) was added to 2.5 equiv of

(14) (a) Tomioka, H.; Yamamoto, K. *J. Chem. Soc., Chem. Commun.* **1995**, 1961−1962. (b) Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858−8863.

phenyldiazomethane[11a] (43 mg, 0.36 mmol) in anhydrous ether under nitrogen, and the mixture was stirred 16 h at rt. The solvent was evaporated to give the crude solid product which was further purified by thin layer chromatography (on silica gel eluted using 5% ethyl acetate in hexane) to give **20e** as a yellow solid (30.5 mg, 0.097 mmol, 67%): mp 87.6−88.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.38 (s, 18), 3.76 (s, 1), 7.00−7.35 (m, 5); ^{13}C NMR ($CDCl_3$) δ 0.51, 56.4, 127.4, 128.4, 128.9, 133.5, 175.3, 205.8; IR ($CDCl_3$) 1689 (s) cm^{-1}; EIMS *m/z* 316 (M^+, 37), 301 ($M^+ - CH_3$, 6), 183 (9), 155 ($Me_3SiC{\equiv}CSiMe_2^+$, 13), 118 ($PhCHCO^+$, 100), 73 (Me_3Si^+, 42); HRMS *m/z* for $C_{17}H_{24}O_2Si_2$ 316.1315, found 316.1315.

4,5-Bis(trimethylsilyl)-2,2-dimethoxy-4-cyclopentene-1,3-dione (24) and 3′,4′-Bis(trimethylsilyl)-2,2,3,3-tetramethoxyspiro(cyclopropane-1,5′-2(5′*H*)-furanone) (25). Cyclobutenedione **14a** (252 mg, 1.11 mmol) and tetramethoxyethylene[11b−d] (1 mL, 6.4 mmol) were heated for 4 days in a 5-mL round bottomed flask at 90 °C, and then the solution was dissolved in ethyl acetate and washed three times with brine before being dried over $MgSO_4$. Filtration and evaporation of the solvent yielded a heterogeneous orange solid/oil. Radial chromatography (10% EtOAc/hexanes) yielded two fractions. The first was recrystallized from MeOH/H_2O to give **24** (orange prisms, 33.6 mg, 0.11 mmol, 10%): mp 48.5−51.9 °C; ^{1}H NMR ($CDCl_3$) δ 0.35 (s, 18, Me_3Si), 3.54 (s, 6, OCH_3); ^{13}C NMR ($CDCl_3$) δ 0.12, 51.3, 85.5, 173.4, 200.1; IR (vapor) 1714 cm^{-1} (C=O); EIMS *m/z* 300 (M^+, 18), 285 (24), 272 (20), 257 (34), 226 (24), 155 ($Me_3SiC{\equiv}CSiMe_2^+$, 100), 125 (58), 73 (Me_3Si^+, 92); CIMS, NH_3 *m/z* 318 ($M + NH_4^+$, 100); HRMS *m/z* calcd for $C_{13}H_{24}O_4Si_2$ 300.1213, found 300.1209. The second fraction, following recrystallization from MeOH/water, yielded **25** as bright yellow spars (49.4 mg, 0.13 mmol, 12%): mp 78.1−81.2 °C; ^{1}H NMR δ 0.28 (s, 9), 0.31 (s, 9), 3.37 (s, 6), 3.45 (s, 6); ^{13}C NMR ($CDCl_3$) δ 0.25, 0.84, 51.0, 52.0, 96.9, 108.4, 112.3, 156.5, 183.2; IR (KBr) 1722 cm^{-1}; UV (CH_3CN) λ_{max} 212 (very strong, enone K band), 369 (weak, enone R band) nm; EIMS *m/z* 374 (M^+, 3), 359 (13), 346 (35), 331 (89), 315 (38), 227 (99), 199 (37), 171 (55), 125 (60), 89 (72), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{16}H_{30}O_4Si_2$ 374.1581, found 374.1578.

Reaction of **14a** (80 mg, 0.35 mmol) and oxadiazoline **30**[13a] (60 mg, 0.37 mmol) in 12.5 mL of dry benzene in a sealed thermolysis tube at 110 °C for 20 h followed by evaporation of the solvent and chromatography on silica gel (10% EtOAc/hexanes) also gave **24**, in 62% yield.

General Procedure for the Cycloaddition of Photochemically Generated 16 with Alkynes. A solution of 3-phenyl-4-(trimethylsilyl)cyclobutenedione (**14b**) (46 mg, 0.2 mmol) and the appropriate alkyne (5 equiv) in chloroform (2 mL) was degassed by bubbling through argon for 30 min and was then irradiated with 350 nm light for 7 days at 5 °C. The solvent was evaporated, and the residue was purified by thin layer chromatography (5/95 ethyl acetate/hexane) to give the products as yellow oils.

3′-(Trimethylsilyl)-4′-phenyl-1,2-dimethylspiro(cyclopropene-3,5′-2′(5′*H*)-furanone) (33) (43%): ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9), 2.01 (s, 6), 6.9−7.4 (m, 5); ^{13}C NMR ($CDCl_3$) δ −0.92, 9.02, 115.5, 127.2, 127.9, 128.5, 131.2, 134.0, 174.6, 177.0; IR (CCl_4) 1728 (vs), 1585 (s) cm^{-1}; UV λ_{max} (CH_3CN) 248 nm (ϵ = 8800); EIMS *m/z* 284 (M^+, 14), 269 ($M^+ - CH_3$, 57), 241 ($M^+ - CH_3{-}CO$, 60), 174 ($Me_3SiC{\equiv}CPh^+$, 20), 159 ($PhC{\equiv}CSiMe_2^+$, 92), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{17}H_{20}O_2Si$ 284.1233, found 284.1232.

3′-(Trimethylsilyl)-4′-phenyl-1-methyl-2-(trimethylsilyl)spiro(cyclopropene-3,5′-2′(5′*H*)-furanone) (34) (35%): ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9), 0.25 (s, 9), 2.20 (s, 3), 7.2−7.5 (m, 5); ^{13}C NMR ($CDCl_3$) δ −1.24, −0.75, 11.6, 121.5, 127.7, 127.8, 128.6, 130.0, 133.8, 133.9, 174.8, 178.4 (one C not observed); IR (CCl_4) 1730 (vs), 1587 (s) cm^{-1}; EIMS *m/z* 342 (M^+, 6), 327 ($M^+ - CH_3$, 58), 299 ($M^+ - CH_3$, CO, 56), 159 ($PhC{\equiv}CSiMe_2^+$, 88), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{19}H_{26}O_2Si_2$ 342.1471, found 342.1469.

3′-(Trimethylsilyl)-4′-phenyl-1-phenyl-2-(trimethylsilyl)spiro(cyclopropene-3,5′-2′(5′*H*)-furanone) (35) (37%): ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9), 0.15 (s, 9), 6.9−7.6 (10, m); ^{13}C NMR ($CDCl_3$) δ −1.2, −0.7, 122.0, 126.9, 127.8, 128.0, 128.8, 129.1, 129.6, 130.7, 133.4, 133.7, 136.4, 174.8, 177.7 (one C not observed); IR (CCl_4) 1730 (vs), 1600 (s), 1587 (s) cm^{-1}; EIMS *m/z* 404 (M^+, 3), 389 ($M^+ - CH_3$, 58), 299 ($M^+ - CH_3$, CO, 56), 174 ($PhC{\equiv}CSiMe_3^+$, 65), 159 ($PhC{\equiv}CSiMe_2^+$, 94), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{24}H_{28}O_2Si_2$ 404.1628, found 404.1624.

Thermal Generation of 16 and Cycloaddition. A solution of 3-phenyl-4-(trimethylsilyl)cyclobutenedione (**14b**) (46 mg, 0.2 mmol) and 1-phenyl-2-(trimethylsilyl)acetylene (5 equiv) in $CHCl_3$ (2 mL) was degassed by bubbling with argon for 0.5 h, and then the container was sealed and heated at 120 °C for 24 h. The solvent was evaporated, and the resulting crude product was purified by thin layer chromatography (5/95 ethyl acetate/hexane) to give **35** in 42% yield.

Photochemical Generation of 16 and Cycloaddition. A solution of 3-phenyl-4-(trimethylsilyl)cyclobutenedione (46 mg, 0.2 mmol) in 2 mL of $CDCl_3$ was degassed by bubbling with argon for 30 min and was then irradiated for 1 h with 350 nm light at 6 °C to give the bisketene **16** in 88% conversion as determinated by ^{1}H NMR. The reaction mixture was cooled in a refrigerator at −25 °C, 1-ethoxy-2-(trimethylsilyl)acetylene (71 mg, 0.5 mmol) was added in one portion, and the yellow color of the reaction mixture turned immediately to orange. The reaction mixture was left for 16 h, and the solvent evaporated. Radial chromatography (5% EtOAc in hexane) gave the furanone **36** (5.2 mg, 0.014 mmol, 8%) and the desilylated 1,4-benzoquinone **38** (33.8 mg, 0.113 mmol, 64%). In one experiment the nondesilylated quinone **37** was also isolated by radial chromatography, but this compound was rather unstable and tended to form **38**.

3′-(Trimethylsilyl)-4′-phenyl-1-ethoxy-2-(trimethylsilyl)-spiro(cyclopropene-3,5′-2′(5′*H*)-furanone) (36): ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9), 0.09 (s, 9), 1.48 (t, 3, $J_{1,2}$ = 6.83 Hz), 4.15−4.20 (m, 2), 7.0−7.4 (m, 5); ^{13}C NMR δ −0.95, −0.81, 14.6, 70.2, 84.4, 127.9, 128.3, 128.9, 131.1, 133.6, 146.4, 175.5, 178.0 (one C not observed); IR (film) 1809, 1730, 1702 cm^{-1}; EIMS *m/z* 372 (M^+, 6), 343 (M^+ − Et, 100), 255 (38), 159 ($PhCCTMS^+ - CH_3$, 34), 73 (Me_3Si^+, 8); HRMS *m/z* calcd for $C_{20}H_{28}O_3Si_2$ 372.1577, found 372.1576.

2,5-Bis(trimethylsilyl)-3-phenyl-6-ethoxy-1,4-benzoquinone (37): ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9), 0.07 (s, 9), 1.47 (t, 3, $J_{1,2}$ = 7.0), 4.28 (q, 2, $J_{1,2}$ = 7.0), 7.10−7.35 (m, 5); ^{13}C NMR δ 0.28, 2.21, 15.0, 69.2, 93.2, 111.9, 127.5, 128.1, 130.0, 132.8, 148.4, 148.5, 191.5, 204.0; IR ($CDCl_3$) 1690, 1594 cm^{-1}; UV λ_{max} (CH_3CN) 239 ($\epsilon = 3.0 \times 10^5$), 293 (sh, $\epsilon = 5.9 \times 10^4$), 346 nm (sh, $\epsilon = 2.0 \times 10^4$); EIMS *m/z* 372 ($M^+$, 13), 344 ($M^+$ − CO, 33), 316 (M^+ − 2CO, 40), 271 (53), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{20}H_{28}O_3Si_2$ 372.1577, found 372.1573.

2-(Trimethylsilyl)-3-phenyl-6-ethoxy-1,4-benzoquinone (38): ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9), 1.47 (t, 3, J = 6.9 Hz), 4.14 (q, 2, J = 6.90 Hz), 4.69 (s, 1), 7.1−7.40 (m, 5); ^{13}C NMR δ 0.65, 14.7, 68.1, 86.7, 128.1, 128.8, 129.2, 130.4, 132.8, 145.7, 146.8, 187.3, 200.0; IR ($CDCl_3$) 1700, 1594 cm^{-1}; UV λ_{max} (CH_3CN) 235 ($\epsilon = 1.3 \times 10^5$), 273 nm (sh, $\epsilon = 3.5 \times 10^4$); EIMS *m/z* 272 ($M^+$ − CO, 95), 244 (M^+ − 2CO, 40), 229 (81), 159 (82), 73 (Me_3Si^+, 100); HRMS *m/z* calcd for $C_{16}H_{20}O_2Si$ (M^+ − CO) 272.1232, found 272.1230.

In an NOE experiment with **38**, saturation of the CH_2 gave a 15.7% increase of the 4.69 ppm proton with no NOE enhancement of the phenyl and trimethylsilyl groups, and saturation of the 4.69 ppm proton gave 4.1% NOE of the CH_2 group with no change in the phenyl and trimethylsilyl groups. Saturation of the TMS protons gave a 7.2% increase of the two ortho Ph protons at 7.15−7.25, with no change of the 4.69 ppm H and ethyl groups.

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Supporting Information Available: NMR spectra for compounds **18**−**20a,b,e, 21a,b, 24, 25,** and **33**−**38** (15 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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