viously synthesized in 50% yield using an alkali metal coupling reaction,[13] was obtained in 95% yield from the reaction of **1** with bis(allyldimethylsilyl) ether (**10**). This very high yield was unexpected as the Thorpe–Ingold effect should be weaker for *gem*-dialkyl groups attached to silicon, where the bond lengths are longer. MM2 calculations failed to give correct predictions when the formation of five-membered rings was possible. Diallylmalonate **12** gave only linear oligomers; however, phenyl 1,1-diallylethyl ketone (**13**) cyclized in 55% yield to five-membered ring **14**. To investigate the possibility of an electronic effect on cyclization due to the phenyl group, it was replaced by a *tert*-butyl group (**15**), whereupon mostly linear oligomers were detected, with only a trace of cyclized material (by ^{1}H NMR and GC/MS). Substituent effects on the phenyl ring are the subject of further investigation.

These reactions represent the first examples in metathesis chemistry where *gem*-dialkyl groups affect the product distribution. Presently we are investigating the predictive power of calculations of ring stability for the synthesis of other systems, especially novel bi- and tricyclic molecules, as well as exploring the generality of catalysts and dienes that will carry out this remarkable reaction.

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Supplementary Material Available: ^{1}H and ^{13}C NMR, IR, and mass spectral and analytical data for **3**, **8**, **11**, and **14** (1 page). Ordering information is given on any current masthead page.

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(13) Weyenberg, D. R.; Torporcer, L. H.; Nelson, L. E. *J. Org. Chem.* **1968**, *33*, 1975.

A Stable and Persistent Bisketene: 2,3-Bis(trimethylsilyl)-1,3-butadiene-1,4-dione

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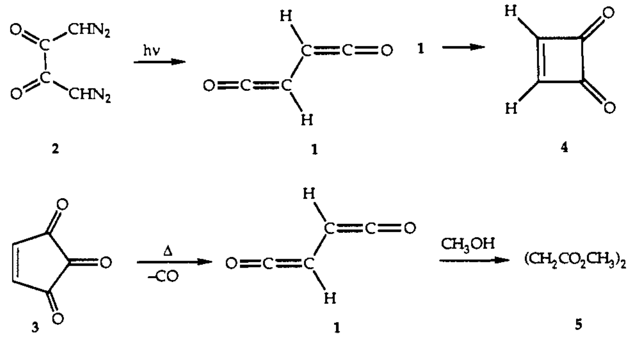
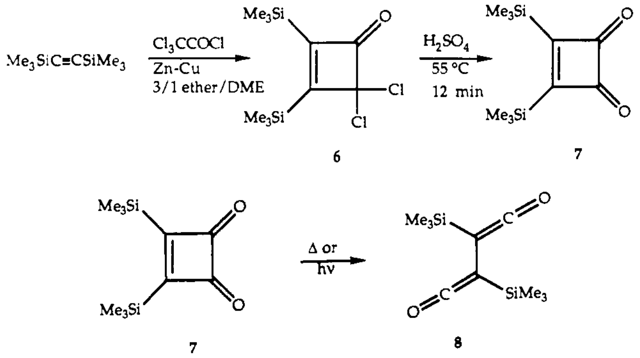
Bisketenes have long been the targets of chemical investigations.[1,2] The parent 1,3-butadiene-1,4-dione (**1**)[2a,b] is a reactive species that when formed by photolysis of the bis(diazo) diketone **2** in an Ar matrix at 10 K could be identified[2a] by its IR band at 2125 cm^{-1}. Pyrolysis of **3** at 430 °C also gave **1** as evidenced by cyclization to **4** and trapping with CH_3OH to give dimethyl succinate (**5**).[2b] While other bisketenes have been directly observed,[1d,g,2d] no free derivative of **1** has been reported that is stable toward cyclization.

Recently the prediction was made by this laboratory[3a] that with an appropriate choice of substituents bisketenes may become more stable than the isomeric cyclobutenediones. The basis of this prediction was ab initio calculations that indicate that **1** is only 6.9 kcal/mol less stable than **4**, and that electropositive substituents exert large stabilizing influences on ketenes and could favor the acyclic structure.[3a] For example, the SiH_3 group has a calculated isodesmic ketene stabilizing energy of 7.6 kcal/mol.[3a,b] We have now confirmed this prediction, using the ketene stabilizing effect of silicon substitution.[3]



Cycloaddition of dichloroketene[4a,b] with bis(trimethylsilyl)acetylene at 25 °C gave **6** (88%),[4c,d,5a,b] which on reaction with concentrated H_2SO_4 gave **7** (73%).[5a,c] Heating of **7** in $CDCl_3$ at 100 °C in a sealed tube for 1 h gave complete conversion to **8**[5a,d] as the only observable product by ^{1}H NMR. Photolysis of **7** in $CDCl_3$ (0.04 M) for 12 min at 350 nm also formed **8** in 70% yield as estimated by NMR, but some **7** remained and further photoreaction of **8** occurred. Pure **8** was isolated as a yellow oil (mp 10 °C) from the photoreaction by preparative VPC (OV-17 column, 130 °C).[5e] The identification of **8** follows from its strong IR band at 2084 cm^{-1} and the characteristic[6] ^{13}C signal of the C_β at δ 5.6.



The kinetics of the conversion of **7** to **8** on heating in $CDCl_3$ in a sealed tube were monitored by the change in the ^{1}H NMR absorption at intervals over 3 half-lives, leading to $E_{act} = 29.4 \pm 0.8$ kcal/mol.[5f] The reactivity of **7** is within the ranges reported

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(1) (a) Hatchard, W. R.; Schneider, A. K. *J. Am. Chem. Soc.* **1957**, *79*, 6261–6263. (b) Blomquist, A. T.; Meinwald, Y. C. *J. Am. Chem. Soc.* **1957**, *79*, 2021–2022. (c) Blomquist, A. T.; Spencer, R. D. *J. Am. Chem. Soc.* **1948**, *70*, 30–33. (d) Boate, D. R.; Johnson, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858–8863. (e) Jewell, C. F., Jr.; Liebeskind, L. S.; Williamson, M. *J. Am. Chem. Soc.* **1985**, *107*, 6715–6716. (f) Baldwin, J. E. *J. Org. Chem.* **1963**, *28*, 3112–3114. (g) Obata, N.; Takizawa, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2017–2020.

(2) (a) Maier, G.; Reisenauer, H. P.; Sayrac, T. *Chem. Ber.* **1982**, *115*, 2192–2201. (b) Kasai, M.; Oda, M.; Kitahara, Y. *Chem. Lett.* **1978**, 217–218. (c) Hochstrasser, R.; Wirz, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 181–183. (d) Tomioka, H.; Fukao, H.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 540–543. (e) Miller, R. D.; Kirchmeyer, S. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society, Washington, DC, 1992; ORGN 281.

(3) (a) Gong, L.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1991**, *113*, 6021–6028. (b) The reaction $SiH_3CH{=}C{=}O + CH_2{=}CH_2 \rightarrow SiH_3CH{=}CH_2 + CH_2{=}C{=}O$ has $\Delta E = 7.6$ kcal/mol. (c) Allen, A. D.; Tidwell, T. T. *Tetrahedron Lett.* **1991**, *32*, 847–850. (d) Ruden, R. A. *J. Org. Chem.* **1974**, *39*, 3607–3608. (e) Danheiser, R. L.; Sard, H. *J. Org. Chem.* **1980**, *45*, 4810–4812.

(4) (a) Danheiser, R. L.; Savariar, S.; Cha, D. D. *Org. Synth.* **1989**, *68*, 32–40. (b) Deprés, J.-P.; Greene, A. E. *Org. Synth.* **1989**, *68*, 41–48. (c) Garratt, P. J.; Tsotinis, A. *J. Org. Chem.* **1990**, *55*, 84–88. (d) A compound previously prepared and assigned the structure **6** is now assigned a different, unknown structure based on its method of preparation and spectral characteristics (Dr. P. J. Garratt, private communication).

(5) (a) All new compounds were isolated in >98% purity as measured by ^{1}H NMR and were characterized by ^{1}H and ^{13}C NMR, IR, UV, and HRMS. (b) **6**: obtained in 88% yield after chromatography on silica gel, mp 35.0–35.5 °C after recrystallization from pentane; ^{1}H NMR ($CDCl_3$) δ 0.278, 0.421; ^{13}C NMR ($CDCl_3$) δ −1.64, −1.06, 96.8, 169.1, 184.1, 196.7; IR (film) 1776 cm^{-1}. (c) **7**: obtained in 73% yield after chromatography on silica gel, yellow solid, mp 50–52 °C after recrystallization from pentane; ^{1}H NMR ($CDCl_3$) δ 0.370; ^{13}C NMR ($CDCl_3$) δ −1.57, 201.97, 217.09; IR (solid film) 1769 cm^{-1}; UV (pentane) λ_{max} 222 (ϵ 14 000), 268 (sh), 354 nm (ϵ 37). (d) **8**: ^{1}H NMR ($CDCl_3$) δ 0.206; ^{13}C NMR δ ($CDCl_3$) −0.94 (Me_3Si), 5.62 (sp^2 C), 181.8 (sp C); IR (film) 2084 cm^{-1}; UV λ_{max} 376 (ϵ 110), 325 (ϵ 250), 248 (sh, ϵ 770). (e) Unpublished calculations by M. A. McAllister in this laboratory indicate that **8** prefers a nonplanar conformation. (f) Rate constants (10^4 s^{-1}) and temperatures (°C): 9.47 (99.7), 9.45 (99.0), 2.61 (87.8), 2.52 (87.5), 1.17 (81.0), 1.11 (80.0).

(6) (a) Grishin, Yu. K.; Ponomarev, S. V.; Lebedev, S. A. *Zh. Org. Khim.* **1974**, 404–405. (b) Firl, J.; Runge, W. *Z. Naturforsch.* **1974**, *29B*, 393–398.

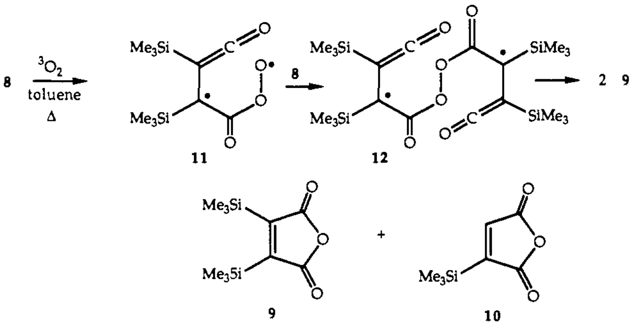
0002-7863/92/1514-10980$03.00/0

for ring opening of variously substituted cyclobutenes to 1,3-butadienes,[7] and of cyclobutenones to vinylketenes.[8] Theoretical studies of these latter reactions have appeared.[9,10]

Thus **8** is thermodynamically stable and persistent in the pure state at room temperature, as predicted,[3a] due to the effect of silyl substitution. The bisketene structure **1** is, however, calculated to be destabilized relative to ketene and butadiene; thus the isodesmic reaction of eq 1 has a calculated ΔE of −11.9 kcal/mol, based on the published[3a] energies of the individual species.

$$\underset{\mathbf{1}}{(\mathrm{CH{=}C{=}O})_2} + 2\mathrm{CH_2{=}CH_2} \xrightarrow{\Delta E\,=\,11.9\ \mathrm{kcal/mol}} 2\mathrm{CH_2{=}C{=}O} + (\mathrm{CH{=}CH_2})_2 \quad (1)$$

A degassed sample of **8** in $CDCl_3$ was unchanged after standing for 45 days at 2 °C, but bubbling O_2 into a refluxing solution of **8** in toluene gave bis(trimethylsilyl)maleic anhydride (**9**),[11] (trimethylsilyl)maleic anhydride (**10**),[11] and small amounts of other unidentified products. Previous reactions of ketenes[12] and strained alkenes[13] with O_2 have been interpreted as involving perepoxide and diradical intermediates.[12] A diradical pathway for reaction of **8** with $^3O_2$ could involve an initial triplet diradical **11** followed by reaction of a second molecule of **8** to give **12**, which could lead to **9** after intersystem crossing.



Various mono- and difunctional nucleophiles also react with **8** by unique pathways which will be reported shortly.

Acknowledgment. Financial support of this work by the Natural Sciences and Engineering Research Council of Canada and technical assistance by Annette D. Allen are gratefully acknowledged.

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(7) (a) Cooper, W.; Walters, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 4220–4224. (b) Pomerantz, M.; Hartman, P. H. *Tetrahedron Lett.* **1968**, 991–993. (c) Frey, H. M.; Pope, B. M.; Skinner, R. F. *Trans. Faraday Soc.* **1967**, *63*, 1166–1170. (d) Brauman, J. I.; Archie, W. C., Jr. *Tetrahedron* **1971**, *27*, 1275–1280.

(8) (a) Huisgen, R.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1976**, 55–56. (b) Mayr, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun.* **1976**, 57–58.

(9) (a) Breulet, J.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1984**, *106*, 1221–1226. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099–2111. (c) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708–3710. (d) Bachrach, S. M.; Liu, M. *J. Org. Chem.* **1992**, *57*, 2040–2047.

(10) (a) Seidl, E. T.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 1493–1499. (b) Seidl, E. T.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1991**, *113*, 5195–5200. (c) Nguyen, M. T.; Ha, T.; More O'Ferrall, R. A. *J. Org. Chem.* **1990**, *55*, 3251–3256.

(11) Isolated yields of **9** and **10** after radial chromatography were 14 and 7%, respectively. **9**: mp 58–59.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.390; ^{13}C NMR ($CDCl_3$) δ 0.03, 161.6, 168.5; IR ($CDCl_3$) 1830 (w), 1814 (w), 1752, 1747 (d, s) cm^{-1}; CIMS *m/z* 243 ($M^+ + 1$); EIMS *m/z* 227 ($M^+ - CH_3$, 11), 155 (100), 73 (Me_3Si^+, 47); HRMS *m/z* calcd for $C_{10}H_{18}O_3Si_2 - CH_3$ ($M^+ - CH_3$) 227.0560, found 227.0567. **10**: oil; ^{1}H NMR ($CDCl_3$) δ 0.345, 6.985; ^{13}C NMR ($CDCl_3$) δ −2.3, 142.8, 155.6, 164.7, 167.5; IR ($CDCl_3$) 1855 (w), 1816 (w), 1764 (s) cm^{-1}; CIMS *m/z* 171 ($M^+ + 1$, 100), 155 ($M^+ - CH_3$, 72); HRMS *m/z* calcd for $C_6H_7O_3Si$ ($M^+ - CH_3$) 155.0164, found 155.0152.

(12) (a) Bartlett, P. D.; McCluney, R. E. *J. Org. Chem.* **1983**, *48*, 4165–4168. (b) Wheland, R.; Bartlett, P. D. *J. Am. Chem. Soc.* **1970**, *92*, 6057–6058. (c) Turro, N. J.; Ito, Y.; Chow, M.; Adam, W.; Rodriquez, O.; Yang, F. *J. Am. Chem. Soc.* **1977**, *99*, 5836–5838. (d) Turro, N. J.; Chow, M.; Ito, Y. *J. Am. Chem. Soc.* **1978**, *100*, 5580–5582. (e) Turro, N. J.; Chow, M. *J. Am. Chem. Soc.* **1980**, *102*, 5058–5064. (f) Majerski, Z.; Vinkovic, V. *Synthesis* **1989**, 559–560.

(13) (a) Bartlett, P. D.; Banavali, R. *J. Org. Chem.* **1991**, *56*, 6043–6050. (b) Pasto, D. J.; Yang, S.; Muellerleile, J. A. *J. Org. Chem.* **1992**, *57*, 2976–2978.

8-Endo Cyclization of (Alkoxycarbonyl)methyl Radicals Generated from Bromoacetates

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The radical cyclization reactions developed in the last decade are now firmly established as indispensable tools in synthetic chemistry. These reactions exhibit useful regio- and stereoselectivity employing a variety of functional groups as radical acceptors.[1]

Initial attempts to cyclize (alkoxycarbonyl)alkyl radical species from α-haloalkanoate esters under standard radical-generating conditions with tributylstannane and AIBN led only to simple reduction products, and the results were attributed to the relative stability of these carbonyl conjugated radicals. Stork[2] and Ueno[3] solved this problem by developing tin hydride-mediated cyclization of α-halo acetals as an indirect route to γ- and δ-lactones. Another practical solution to this problem has been devised by Curran[4] based on the halogen atom transfer reactions. More recently, however, direct syntheses of γ- and δ-lactones via 5-exo or 6-exo radical cyclizations using α-haloalkanoates as substrates were reported.[5]

We report herein that (alkoxycarbonyl)methyl radicals generated from bromoacetates under standard high-dilution conditions undergo intramolecular cyclization in a regioselective 8-endo mode[6] to yield eight-membered-ring heptanolactones. This 8-endo cyclization is preferred over 5-exo cyclization as proved in competition experiments.

Slow addition (via a syringe pump) of a solution of tributylstannane (1.4 equiv) in benzene containing AIBN (0.1 equiv) over 5 h into a benzene solution (0.015 M) of the bromoacetate **2a** under reflux gave the acetate **2b** (24%) and the lactone **2c** (52%) (Scheme I). Further examples of 8-endo cyclization are presented in Table I.[7] On the contrary, lower and higher homologues **5a** and **6a** were transformed mainly into the corresponding acetates **5b** and **6b**, and cyclization products (6-exo or 7-endo mode for **5a** and 8-exo or 9-endo mode for **6a**) were not isolated.[8] These results indicate that the 8-endo mode of cyclization is the in-

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(1) For reviews, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Hart, D. J. *Science* **1984**, *223*, 883. (c) Neumann, W. P. *Synthesis* **1987**, 665. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Curran, D. P. *Synthesis* **1988**, 417 and 489. (f) Curran, D. P. *Chem. Rev.* **1991**, *91*, 1237.

(2) (a) Stork, G.; Mook, R., Jr.; Biller, S. A.; Rychnovsky, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 3741. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765. (c) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 303. (d) Stork, G.; Sher, P. M.; Chen, H. L. *J. Am. Chem. Soc.* **1986**, *108*, 6384. (e) Stork, G. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 149.

(3) (a) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *J. Am. Chem. Soc.* **1982**, *104*, 5564. (b) Ueno, Y.; Moriya, O.; Chino, K.; Watanabe, M.; Okawara, M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1351.

(4) (a) Curran, D. P.; Chang, C. T. *Tetrahedron Lett.* **1987**, *28*, 2477. (b) Curran, D. P.; Chang, C. T. *J. Org. Chem.* **1989**, *54*, 3140. (c) Curran, D. P.; Chang, C. T. *Tetrahedron Lett.* **1990**, *31*, 933.

(5) (a) Belletire, J. L.; Mahmoodi, N. O. *Tetrahedron Lett.* **1989**, *30*, 4363. (b) Clough, J. M.; Pattenden, G.; Wight, P. G. *Tetrahedron Lett.* **1989**, *30*, 7469. (c) Hannesian, S.; Di Fabio, R.; Marcoux, J. F.; Prud'homme, M. *J. Org. Chem.* **1990**, *55*, 3436.

(6) For prior observations of 8-endo cyclizations of different radical systems, see: (a) Snider, B. B.; Merritt, J. E. *Tetrahedron Lett.* **1991**, *47*, 8663. (b) Sato, T.; Ishida, S.; Ishibashi, H.; Ikeda, M. *J. Chem. Soc., Perkin Trans. 1* **1991**, 353.

(7) All products in Tables I and II were separated by silica gel column chromatography, and the specified yields are *isolated* yields. In every case, separation was easily achieved even though products were isomeric compounds. For example, product (**8b–e**) from **8a** exhibited four well-separated spots on a silica gel TLC plate. Spectroscopic data for heptanolactone **1c** were reported in Matsubara, S.; Takai, K.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2029 and ref 15. Structural determination of other products is supported by a full set of spectroscopic data.

(8) The reaction of **5a** produced a complex product mixture from which **5b** was isolated in 42% yield. The conversion of **6a** into **6b** was accompanied by one major byproduct, which appeared to be a dimeric species formed by the intermolecular attack of the (alkoxycarbonyl)methyl radical and subsequent reduction.