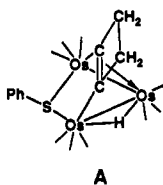


**Figure 2.** An ORTEP diagram of  $\text{Os}_3(\text{CO})_9(\mu\text{-}\eta^2\text{-C}_2\text{CH}_2\text{CH}_2)(\mu\text{-SPh})(\mu\text{-H})$ , **3**. Selected interatomic distances (Å) are  $\text{Os}(1)\text{-Os}(2) = 2.830(1)$ ,  $\text{Os}(1)\text{-Os}(3) = 2.940(1)$ ,  $\text{Os}(1)\text{-C}(1) = 2.22(1)$ ,  $\text{Os}(3)\text{-C}(1) = 2.12(2)$ ,  $\text{Os}(1)\text{-C}(2) = 2.26(2)$ ,  $\text{Os}(2)\text{-C}(2) = 2.06(2)$ ,  $\text{C}(1)\text{-C}(2) = 1.37(2)$ ,  $\text{C}(1)\text{-C}(4) = 1.54(2)$ ,  $\text{C}(2)\text{-C}(3) = 1.51(2)$ , and  $\text{C}(3)\text{-C}(4) = 1.52(2)$ .

$(\mu_3\text{-}\eta^2\text{-C}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})$ , **3**, were formed in the yields 21% and 35%, respectively.<sup>8</sup> Compound **3** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2.<sup>9</sup> This complex also consists of an open trismium cluster with a benzenthioato ligand bridging the open edge as in **2**, but it also has a "cyclobutene" ligand that serves as a four-electron donor coordinated to all three metal atoms. The transformation of hydrogen-substituted  $\mu_3\text{-}\eta^2$ -alkenyl ligands to alkyne ligands is a well-established process.<sup>10</sup> The  $\text{C}_4$  ring is completely planar and is inclined  $73.7^\circ$  from the  $\text{Os}_3$  plane. The ligand has adopted a  $\mu_3\text{-}\eta^2$  coordination mode that is characteristic of alkynes bonded to trimetallic centers.<sup>11</sup> The length of the unsaturated C–C bond,  $\text{C}(1)\text{-C}(2)$ , is  $1.37(2)$  Å and is also typical of alkynes coordinated to trimetallic sites.<sup>11</sup> The other C–C bonds in the ligand are equal in length within experimental error,  $1.51(2)$ – $1.54(2)$  Å, and are typical of C–C single bonds. The hydrogen atom that was shifted to the metal atoms bridges the elongated  $\text{Os}(1)\text{-Os}(3)$  bond,  $\delta = -17.41$  ppm. It is rapidly exchanging between the two metal–metal bonds on the NMR time scale at  $27^\circ\text{C}$ ,  $\Delta G^\ddagger_{273} = 13.2$  kcal/mol; thus the methylene groups are equivalent although the protons on each group are inequivalent,  $\delta = 4.34$  (2 H, d,  $^2J = 10$  Hz),  $3.66$  (2 H, d,  $^2J = 10$  Hz). Due to the dynamics the resonances of the alkyne carbons are not observed at  $27^\circ\text{C}$ ; however, they are clearly displayed at 156.9 and 193.9 ppm at  $-68^\circ\text{C}$ . These values are also typical of alkynes coordinated to clusters of three metal atoms.<sup>12</sup>

The bonding of alkynes to trimetallic centers can be viewed as a combination of the  $\sigma$ -donation and  $\pi$ -acceptance that leads to a substantial reduction of the  $\text{C}\equiv\text{C}$  bond order.<sup>13</sup> In the limit, a resonance structure **A** can be drawn in which the cyclobutene ligand in **3** is represented as a dimetalated cyclobutene with the C–C  $\pi$ -bond acting as a donor to the third metal atom. It is



believed that it is the stabilization provided by such coordination that has made the isolation of complex **3** possible. It is expected

(10) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

(11) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(12) (a) Aime, S.; Gobetto, R.; Milone, L.; Osella, D.; Violano, L.; Arce, A. J.; De Sanctis, Y. *Organometallics* **1991**, *10*, 2854. (b) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, F. G. A.; Woodward, P. J. *Chem. Soc., Dalton Trans.* **1981**, 162. (c) Evan, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

(13) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

that studies of the complexed form of cyclobutene will reveal some of its reactivity properties and might help to explain its curious absence in the free state.

**Acknowledgment.** This research was supported by the Office of Basic Energy Science of the U.S. Department of Energy.

**Supplementary Material Available:** An ORTEP diagram of **1** and tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **1–3** (30 pages); tables of observed and calculated structure factors for **1–3** (52 pages). Ordering information is given on any current masthead page.

### Solvent-Free Cyclization of Linear Dienes Using Olefin Metathesis and the Thorpe–Ingold Effect

Malcolm D. E. Forbes,\*<sup>†</sup> Jasson T. Patton,<sup>†</sup>  
Tanya L. Myers,<sup>†</sup> Heather D. Maynard,<sup>†</sup>  
Dennis W. Smith, Jr.,<sup>‡</sup> Gregory R. Schulz,<sup>†</sup> and  
Kenneth B. Wagener<sup>‡</sup>

Department of Chemistry, CB# 3290  
University of North Carolina,  
Chapel Hill, North Carolina 27599  
Department of Chemistry  
University of Florida  
Gainesville, Florida 32611  
Received January 27, 1992

The olefin metathesis reaction is of great synthetic utility in polymer chemistry.<sup>1</sup> The recent development of ring-opening (ROMP)<sup>2</sup> and acyclic diene (ADMET)<sup>3</sup> metathesis polymerization reactions has opened new avenues for the synthesis of novel polymeric materials. Recently we used ADMET to synthesize several photochemically active poly(keto olefins)<sup>4</sup> using the catalyst  $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{OCMe}(\text{CF}_3)_2)_2$  ( $\text{Ar} = 2,6$ -diisopropylphenyl) (**1**) developed by Schrock and co-workers in 1990.<sup>2a–i</sup> In the course of that work, we discovered that neat samples of highly substituted dienes will cyclize quantitatively via metathesis to give difunctional five- and seven-membered rings instead of the expected linear polymer. Examples of substituted diene cyclizations by metathesis even in the presence of a solvent are rare. Their systematic exploitation in organic synthesis has therefore been limited to two recent studies by Fu and Grubbs, who cyclized

<sup>†</sup> University of North Carolina.

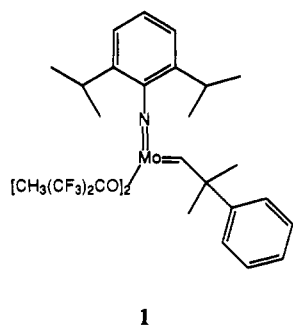
<sup>‡</sup> University of Florida.

(1) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: New York, 1982. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, 1982; Vol. 8, pp 499–551.

(2) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) Swager, T. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 894. (c) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169. (d) Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1488. (e) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 450. (f) Krouse, S. A.; Schrock, R. R. *Macromolecules* **1988**, *21*, 1885. (g) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875. (h) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899. (i) Bazan, G. C.; Kosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

(3) (a) Wagener, K. B.; Boncella, J. M.; Nel, J. G.; Duttweiler, R. P.; Hillmyer, M. A. *Makromol. Chem.* **1990**, *191*, 365. (b) Wagener, K. B.; Matayabas, J. R. *Macromolecules* **1991**, *24*, 618; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31* (1), 464. (c) Nel, J. G.; Wagener, K. B.; Boncella, J. M. *Macromolecules* **1990**, *23*, 5155; *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 130. (d) Lindmark-Hamberg, M.; Wagener, K. B. *Macromolecules* **1987**, *20*, 2949. (e) Wagener, K. B.; Brzezinska, K. *Macromolecules* **1991**, *24*, 5273. (f) Wagener, K. B.; Smith, D. W. *Macromolecules* **1991**, *24*, 6073. (g) Patton, J. T.; Boncella, J. M.; Wagener, K. B. *Macromolecules* **1992**, *25*, 3862.

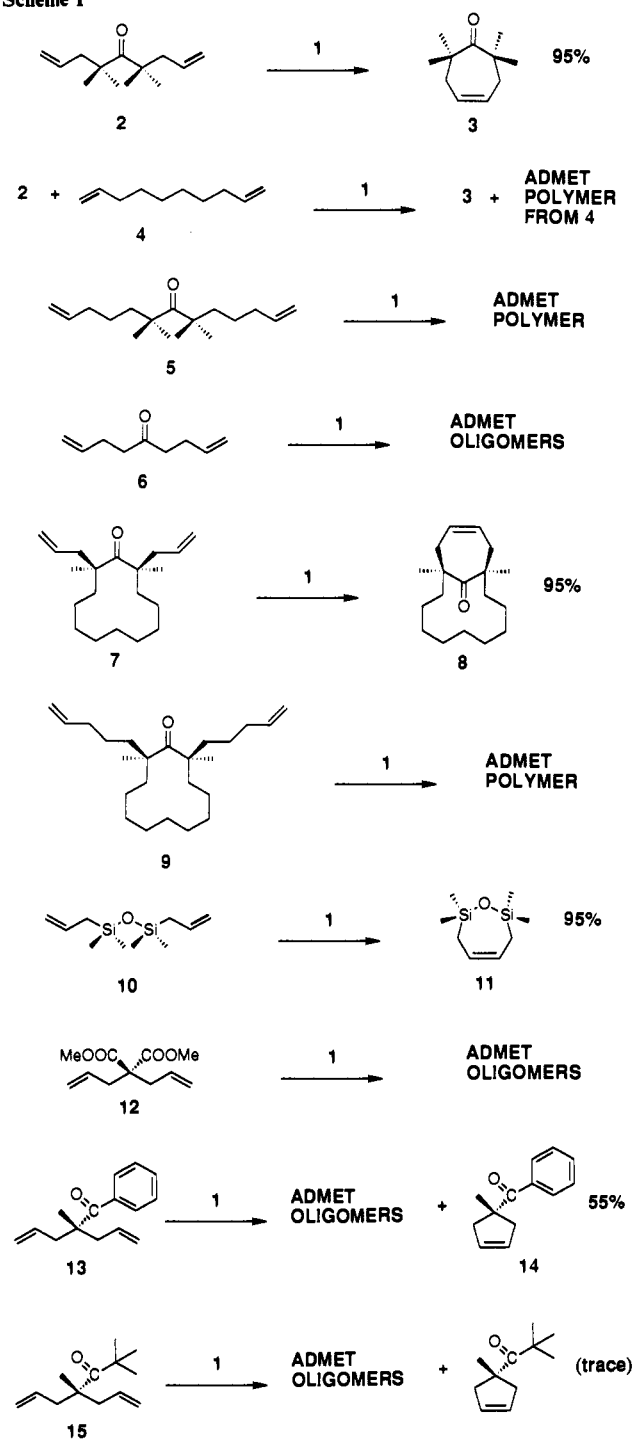
(4) (a) Patton, J. T.; Wagener, K. B.; Forbes, M. D. E.; Myers, T. L.; Maynard, H. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 1070. (b) Forbes, M. D. E.; Myers, T. L.; Patton, J. T.; Wagener, K. B.; Maynard, H. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 883.



several substituted diene ethers, amines, and amides to unsaturated oxygen and nitrogen heterocycles.<sup>5</sup> Cyclization of unsubstituted dienes in various solvents has been reported,<sup>6</sup> but complete conversion occurred in only a few cases.<sup>7</sup> Formation of cyclic alkene oligomers from back-biting during the ROMP reaction is also known.<sup>8</sup> The reactions we report here are unusual in that they are intermolecular between catalyst and substrate, yet can give 100% yield of product solely from the monomer *in the absence of solvent*.

The reactions are summarized in Scheme I. Keto diene **2**<sup>9</sup> cyclized in 95% isolated yield to tetramethylcycloheptenone **3** in 1 h total reaction time.<sup>10</sup> An attempt to copolymerize **2** with 1,9-decadiene (**4**) (1:1 ratio, no solvent) resulted in complete cyclization of **2**, while all of **4** underwent ADMET homopolymerization. The polymer could be separated from **3** by precipitation into methanol. The longer diene **5** gave only polymer, indicating that certain chain lengths and/or conformations of the diene are necessary for high-yield cyclizations. The unsubstituted keto diene **6** gave only a mixture of linear oligomers in an NMR tube reaction. These two results strongly suggest that the cyclization is brought about by the Thorpe-Ingold effect,<sup>11</sup> i.e., the *gem*-dimethyl groups on each side of the carbonyl are contributing substantially to the thermodynamic stability of the ensuing ring and/or the transition state leading to ring closure. We have performed MM2 calculations on the cyclized product **3** and, as

Scheme I



(5) (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324.

(6) (a) Finkel'shtein, E. Sh.; Portnykh, E. B.; Ushakov, N. V.; Vdovin, V. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *3*, 641. (b) Alvarez, C.; Pacreau, A.; Parlier, A.; Rudler, H.; Daran, J.-C. *Organometallics* **1987**, *6*, 1057. (c) Plugge, M. F. C.; Mol, J. C. *Synlett* **1991**, 507. (d) Tsuji, J.; Hashiguchi, S. *Tetrahedron Lett.* **1980**, 2955. (e) Tsuji, J.; Hashiguchi, S. *J. Organomet. Chem.* **1981**, *218*, 69.

(7) (a) Doyle, G. J. *Catal.* **1973**, *30*, 118. (b) Faron, M. F.; Greenlee, W. S. *J. Chem. Soc., Chem. Commun.* **1975**, 759.

(8) Reif, L.; Höcker, H. *Macromolecules* **1984**, *17*, 952.

(9) All starting materials were obtained from Aldrich and used as received. Compounds **2**, **5**, **7**, **9**, **13**, and **15** were synthesized by alkylation of the appropriate starting ketone using lithium diisopropylamide in THF at or below  $-40^{\circ}\text{C}$  followed by either methyl iodide, allyl iodide, or 5-iodopentene (from 5-bromopentene, Aldrich). Dimethyl malonate was diallylated in a similar fashion at  $-65^{\circ}\text{C}$  to give **12**. Unmethylated ketone **6** was synthesized by reaction of 2 equiv of the Grignard of 4-bromo-1-butene with methyl formate, followed by oxidation to the ketone using Jones' reagent. Diene **10** was synthesized by reaction of 2 equiv of allylmagnesium bromide with dichlorotetramethyldisiloxane.

(10) In a typical bulk reaction, 0.5 g of neat, dry diene was stirred under dry, oxygen-free nitrogen at  $25^{\circ}\text{C}$ . Five milligrams of catalyst was added, and the evolution of ethylene, often vigorous, was immediately observed. The flask was stirred for 0.5–1 h and then placed under a 1-mm vacuum with stirring for an additional 0.5 h. The flask was then exposed to air whereupon the catalyst was destroyed. Metal salts were removed by adding hexanes and washing successively with  $\text{NaHCO}_3$ , 10% HCl, and brine. After filtration through Celite and drying over  $\text{Na}_2\text{SO}_4$ , evaporation of the solvent gave either cyclized products as colorless oils or polymeric materials as pale yellow solids. For products **3** and **11** it was possible to vacuum distill to dryness from the crude reaction mixture, sometimes leading to isolated yields greater than 95%. If the amount of diene available was too small to run as above (**6**), the diene and catalyst were added to an NMR tube with diene- $d_8$  as solvent. The presence of symmetric *cis* internal olefin peaks in the  $^1\text{H}$  NMR spectrum (triplets at 5.7–5.9 ppm) was used to confirm whether or not the compound had cyclized.

(11) (a) Eliel, E. L. *Stereochemistry of Carbon Compounds*; McGraw-Hill: New York, 1962; pp 197–202. (b) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224. (c) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.

a model for the polymer, on the dimer expected from a single metathesis turnover during the reaction of catalyst **1** with keto diene **2**. Over all the conformations of the dimer investigated, significant stabilization ( $>10\text{ kcal mol}^{-1}$ ) of the cyclic molecule was found. In the case of un-methylated ketone **6**, the dimer was found to be stabilized by  $3\text{ kcal mol}^{-1}$  over the cyclic ketone, matching the experimental findings at room temperature.<sup>12</sup>

Neat cyclic keto diene **7** (*cis* isomer) also cyclized in 95% yield to the unusual bicyclic ketoalkene **8** in 1 h. As in the linear case, the longer diene **9** (*cis* isomer) gave only polymeric material under the same conditions. The seven-membered heterocycle **11**, pre-

(12) At lower temperatures ( $-60^{\circ}\text{C}$ ), competition between cyclization and oligomerization of **2** was observed. This observation is consistent with there being a large, negative  $\Delta S^{\ddagger}$  for the intermolecular reaction and a small  $\Delta S^{\ddagger}$  for the intramolecular cyclization. This can be a major factor controlling monodispersity in living polymerizations.

viously synthesized in 50% yield using an alkali metal coupling reaction,<sup>13</sup> 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. Di-allylmalonate **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 <sup>1</sup>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.

**Acknowledgment.** This work was supported in part by the Petroleum Research Fund through Grant ACS-PRF 23636-G6.4. We thank W. D. Wulff for helpful discussions and for bringing ref 6b to our attention, and we thank one of the reviewers for many critical comments and suggestions.

**Supplementary Material Available:** <sup>1</sup>H and <sup>13</sup>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.

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

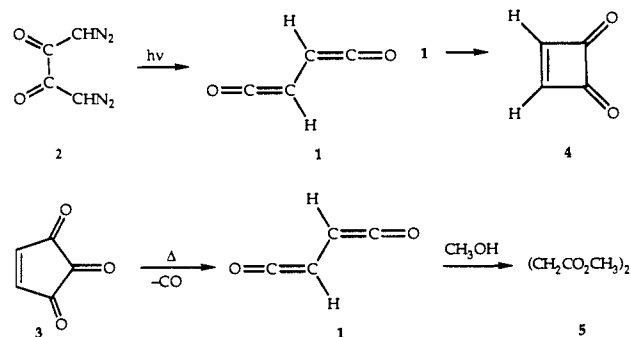
## A Stable and Persistent Bisketene: 2,3-Bis(trimethylsilyl)-1,3-butadiene-1,4-dione

Da-Chuan Zhao and Thomas T. Tidwell\*

Department of Chemistry, University of Toronto  
Toronto, Ontario, Canada M5S 1A1  
Received September 14, 1992

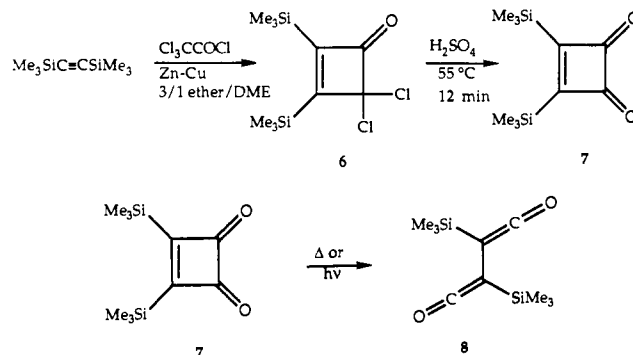
Bisketenes have long been the targets of chemical investigations.<sup>1,2</sup> The parent 1,3-butadiene-1,4-dione (**1**)<sup>2a,b</sup> is a reactive species that when formed by photolysis of the bis(diazo) diketene **2** in an Ar matrix at 10 K could be identified<sup>2a</sup> by its IR band at 2125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

Recently the prediction was made by this laboratory<sup>3a</sup> 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.<sup>3a</sup> For example, the SiH<sub>3</sub> group has a calculated isodesmic ketene stabilizing energy of 7.6 kcal/mol.<sup>3a,b</sup> We have now confirmed this prediction, using the ketene stabilizing effect of silicon substitution.<sup>3</sup>

Cycloaddition of dichloroketene<sup>4a,b</sup> with bis(trimethylsilyl)acetylene at 25 °C gave **6** (88%),<sup>4c,d,5a,b</sup> which on reaction with concentrated H<sub>2</sub>SO<sub>4</sub> gave **7** (73%).<sup>5a,c</sup> Heating of **7** in CDCl<sub>3</sub> at 100 °C in a sealed tube for 1 h gave complete conversion to **8**<sup>5a,d</sup> as the only observable product by <sup>1</sup>H NMR. Photolysis of **7** in CDCl<sub>3</sub> (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).<sup>5e</sup> The identification of **8** follows from its strong IR band at 2084 cm<sup>-1</sup> and the characteristic<sup>6</sup> <sup>13</sup>C signal of the C<sub>β</sub> at δ 5.6.



The kinetics of the conversion of **7** to **8** on heating in CDCl<sub>3</sub> in a sealed tube were monitored by the change in the <sup>1</sup>H NMR absorption at intervals over 3 half-lives, leading to *E*<sub>act</sub> = 29.4 ± 0.8 kcal/mol.<sup>5f</sup> The reactivity of **7** is within the ranges reported

(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<sub>3</sub>CH=C=O + CH<sub>2</sub>=CH<sub>2</sub> → SiH<sub>3</sub>CH=CH<sub>2</sub> + CH<sub>2</sub>=C=O has Δ*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.; Tsoinis, 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 <sup>1</sup>H NMR and were characterized by <sup>1</sup>H and <sup>13</sup>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; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.278, 0.421; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.64, -1.06, 96.8, 169.1, 184.1, 196.7; IR (film) 1776 cm<sup>-1</sup>. (c) **7**: obtained in 73% yield after chromatography on silica gel, yellow solid, mp 50-52 °C after recrystallization from pentane; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.370; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.57, 201.97, 217.09; IR (solid film) 1769 cm<sup>-1</sup>; UV (pentane) λ<sub>max</sub> 222 (ε 14 000), 268 (sh), 354 nm (ε 37). (d) **8**: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.206; <sup>13</sup>C NMR δ (CDCl<sub>3</sub>) -0.94 (Me<sub>3</sub>Si), 5.62 (sp<sup>2</sup> C), 181.8 (sp C); IR (film) 2084 cm<sup>-1</sup>; UV λ<sub>max</sub> 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<sup>4</sup> s<sup>-1</sup>) 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.