Table III. Activation Parameters and Relative Rates Relevant to the Rearrangement[a]

substrate	rel rate (25 °C)	$\Delta H^{\ddagger}_{298}$, kcal mol	$\Delta S^{\ddagger}_{298}$, eu	$\Delta G^{\ddagger}_{298}$, kcal mol
1a[b]	1	16.6	−18.1	22.0
1b[b]	62	16.0	−11.5	19.4
1c[b]	83	15.4	−13.1	19.3
4[b]	1900	16.6	−1.2	17.0
1d	55	18.6	−3.0	19.5
1e	1680	21.3	12.9	17.5
1f	0			
1g	0			

[a] Activation parameters were calculated on the basis of k^{i}_{obsd} at various temperatures. [b] Cited from the previous work.[3]

fast as possible, the C^{β}–N–C^{α} plane (eq 2) in 8^- must be coplanar with the benzene ring (for the detailed discussion, refer to ref 3). The molecular model, however, shows that the plane is almost perpendicular to the benzene ring in 8^-, in the case of **1f** or **1g**.

On the other hand, the molecular model shows that in the case of **1f** or **1g** the C_1–O–CH_2 plane of **1** is appreciably perpendicular to the benzene ring because of the restricted rotation about the C_1–O bond owing to the two ortho substituents. Therefore, **1f** or **1g** more easily forms the stable complex, where the O–C_1–N plane of $\mathbf{2}^-$ is perpendicular to the benzene ring, the configuration releasing the steric strain at C_1 (sp^3) the most.[21]

Acknowledgments. We sincerely thank Assistant Professor Sadato Yabuki, Department of Liberal Arts, Gunma University, for the use of a rapid-reaction analyzer.

Registry No. **1d**, 70320-88-6; **1e**, 22404-13-3; **1f**, 70320-89-7; **1g**, 70320-90-0; $\mathbf{2f}^-$, 70343-40-7; $\mathbf{2g}^-$, 70343-41-8; **3d**, 70320-91-1; $\mathbf{3d}^-$, 70320-92-2; **3e**, 70320-93-3; $\mathbf{3e}^-$, 70320-94-4; MNFB, 455-88-9; NAEA, 142-26-7; PCDS, 38185-06-7; DNA, 606-22-4; DNCB, 606-21-3; DNFB, 573-55-7; *p*-nitrofluorobenzene, 350-46-9; 2,4-dinitro-6-methylfluorobenzene, 348-97-0; *p*-nitrochlorobenzene, 100-00-5; *N*-(β-hydroxy)ethyl-4-nitroaniline, 1965-54-4.

Supplementary Material Available: Table of NMR chemical shifts for **1f**, $\mathbf{2f}^-$, **1g**, $\mathbf{2g}^-$, $\mathbf{10}^-$, $\mathbf{11}^-$, $\mathbf{12}^-$, and **2a** (1 page). Ordering information is given on any current masthead page.

(21) The detailed kinetics of the formation of spiro complex 8^- including **1a–c**, **4**, **1f**, and **1g** are now in progress.

Halogenated Ketenes. 32. The Cycloaddition of Dichloroketene with Silyl Enol Ethers

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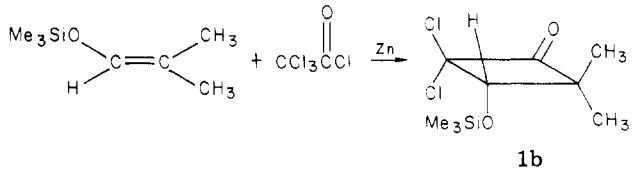
The generation of dichloroketene by the zinc dechlorination of trichloroacetyl chloride in the presence of silyl enol ethers results in good yields of 2,2-dichloro-3-siloxycyclobutanones. The silyl substituent is easily removed to yield the 3-hydroxycyclobutanones. Several of the siloxycyclobutanones and 3-hydroxycyclobutanones were thermally unstable and underwent a silicon migration and ring-opening reaction to yield 1,1-dichloro-2,4-diones. This thermal instability is related to conformational effects in the cyclobutanone ring. The chlorine atoms on the 2,2-dichloro-3-siloxycyclobutanones are readily removed by tri-*n*-butyltin hydride reduction.

The cycloaddition of several ketenes with alkyl enol ethers has been reported to form 3-alkoxycyclobutanones in good yield.[1-3] The analogous reaction of dichloroketene with trimethylsilyl enol ethers has only recently been reported.[4,5] We would like to report our findings on the cycloaddition of dichloroketene and a number of trimethylsily enol ethers and some chemistry of the resulting cyclobutanones.

The in situ cycloaddition of the trimethylsilyl enol ether from isobutyraldehyde, **1a**, with dichloroketene generated from trichloroacetyl chloride by activated zinc in dry ether under a nitrogen atmosphere resulted in a 1:1 cycloadduct in 89% yield. A strong carbonyl absorption in the infrared at 1805 cm^{-1} as well as other spectroscopic evidence supported the siloxycyclobutanone **1b** as the major product



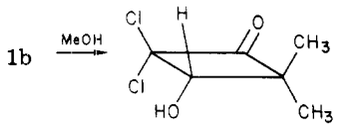
1b

of this reaction in accord with reported literature results.[5] A number of other trimethylsilyl enol ethers were found to react smoothly with dichloroketene to give the 2,2-dichloro-3-(trimethylsiloxy)cyclobutanones in good yield as revealed in Table I.

In most instances, the trimethylsilyl substituent was readily removed by dissolving the siloxycyclobutanone in methanol and stirring the solution for several hours. The methanol was evaporated and the 3-hydroxycyclobutanones were conveniently vacuum distilled. In this manner **1b** gave **1c** in 88% yield. In those instances where the removal of the trimethylsilyl substituent did not proceed readily, the addition of several drops of dilute acid

(1) R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, **102**, 3405 (1969).
(2) R. Huisgen, L. A. Feiler, and G. Binsch, *Chem. Ber.*, **102**, 3460 (1969).
(3) R. Huisgen, L. Feiler, and G. Binsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 753 (1964).
(4) L. R. Krepski and A. Hassner, *J. Org. Chem.*, **43**, 3173 (1978).
(5) A. Hassner, H. W. Pinnick, and J. M. Ansell, *J. Org. Chem.*, **43**, 1774 (1978).

0022-3263/79/1944-2560$01.00/0

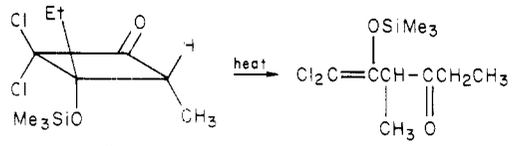


1c

was usually sufficient to effect this removal.

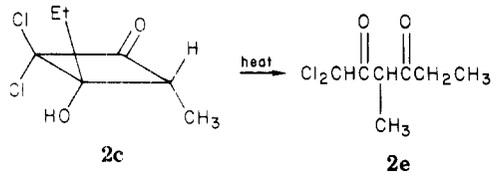
Many of the 3-(trimethylsiloxy)cyclobutanones and the 3-hydroxy derivatives were unstable at room temperature and showed some darkening on standing. Elemental analyses were obtained where possible, but in many cases the products were too unstable for satisfactory results. Relatively few of the cyclobutanones could be analyzed by gas chromatography due to extensive rearrangement and decomposition.

When an equal mixture of the *E* and *Z* isomers of the silyl enol ether derived from 3-pentanone **2a** was reacted with dichloroketene, siloxycyclobutanone **2b** was the major product. This cyclobutanone was found to rearrange in the gas chromatograph to yield an acyclic product, **2d**.



2b 2d

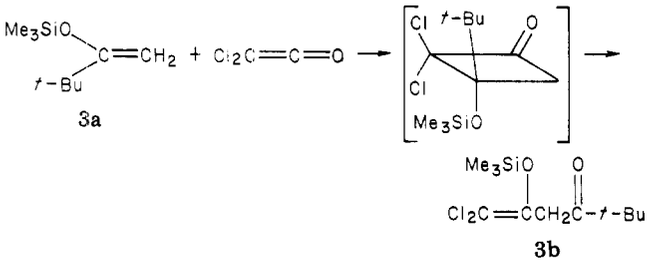
This compound was also formed in near quantitative yield when **2b** was heated in a sealed vial for 3 h at 130 °C. Likewise, the hydroxy derivative **2c** was also found to be thermally labile and underwent a ring-opening reaction to give the dione **2e**. When the siloxycyclobutanone **2b** was



2c 2e

treated with methanol in the presence of dilute acid, **2e** was the only product isolated.

The reaction of the silyl enol ether derived from pinacolone **3a** with dichloroketene gave an acyclic product **3b**. Possibly, **3b** could have resulted from an initially



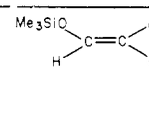
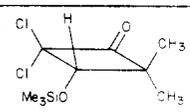
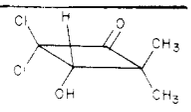
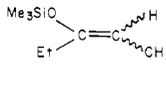
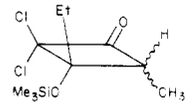
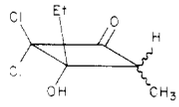
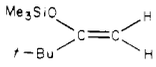
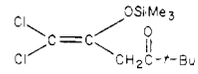
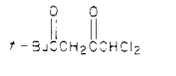
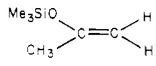
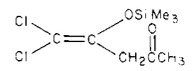
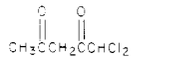
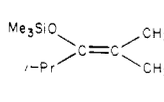
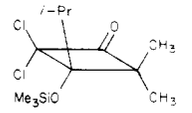
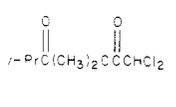
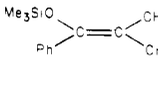
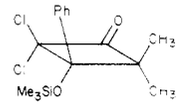
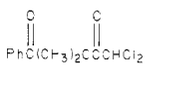
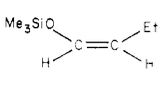
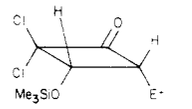
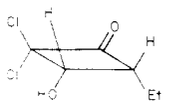
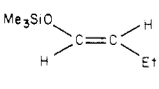
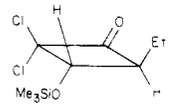
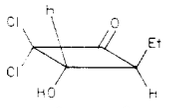
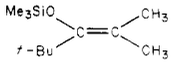
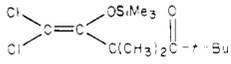
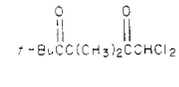
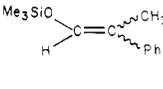
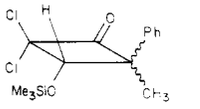
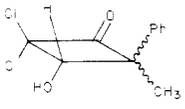
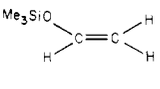
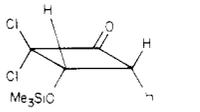
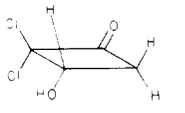
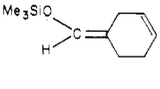
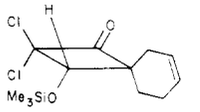
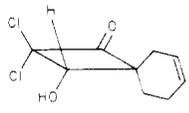
3a 3b

formed cyclobutanone followed by a ring-opening reaction analogous to that observed with **2b**.

The 3-(trimethylsiloxy)cyclobutanone resulting from the cycloaddition of dichloroketene and the silyl enol ether derived from acetone, **4a**, could not be isolated. However, this cyclobutanone was observed in the infrared as evidenced by a strong band at 1800 cm^{-1}, but a gentle warming of the reaction mixture resulted in the complete loss of the 1800 cm^{-1} band in the infrared and a concurrent increase in the intensity of the acyclic bands due to the formation of **4c** in 77% yield.

It is likely that in both of the above instances the acylic product is derived from the 3-siloxycyclobutanones.

Table I. 2,2-Dichloro-3-(trimethylsiloxy)cyclobutanones and Hydrolysis Products

compd	silyl enol ether (a)	siloxy product (b)	hydrolysis product (c)
1			
2			
3			
4			
5			
6			
(*Z*)-7			
(*E*)-7			
8			
9			
10			
11			

Silicon migration and ring opening requires a proximity of the silyl substituent to the carbonyl oxygen. A puckered conformation of the cyclobutanone ring with the silyl substituent occupying an axial position provides the necessary proximity of the silyl group and the carbonyl oxygen.[5]

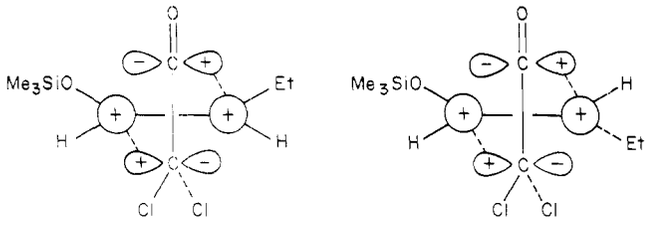
Silyl enol ethers **5a** and **6a** represent the first reported cycloadditions of tetrasubstituted enol ethers with ketenes. Dichloroketene cycloadditions with tetrasubstituted olefins have only recently been reported in the literature.[6,7] Removal of the trimethylsilyl substituent from **5b** and **6b** required acidic conditions which resulted in ring opening

(6) L. R. Krepski and A. Hassner, *J. Org. Chem.*, **43**, 2879 (1978).
(7) D. A. Bak and W. T. Brady, *J. Org. Chem.*, **44**, 107 (1979).

to the corresponding diones, **5c** and **6c**, respectively.

The preparation of the silyl enol ether from *n*-butyraldehyde resulted in an equal mixture of the *Z* and *E* isomers. The reaction of a 40% excess of this mixture with dichloroketene gave the 3-siloxycyclobutanones in a ratio of 2:1. The predominate isomer was the *Z* isomer, (*Z*)-**7b**, as determined by NMR. Fortunately, the C-3 proton was quite distinct in the NMR for the (*Z*)- and (*E*)-cyclobutanones and in agreement with the analogous couplings reported in the literature for alkoxycyclobutanones.[1,2] The reaction of a twofold excess of the silyl enol ether mixture with dichloroketene resulted in less than 5% of the (*E*)-siloxycyclobutanone, (*E*)-**7b**. Finally, an excess of dichloroketene gave an equal mixture of the two siloxycyclobutanones, (*Z*)-**7b** and (*E*)-**7b**. Clearly, the *E* isomer was not lost in the reaction workup. The removal of the trimethylsilyl substituent with methanol gave the respective 3-hydroxycyclobutanones without rearrangement.

The above results clearly suggest that dichloroketene reacts faster with the *Z* isomer of the silyl enol ethers. This is consistent with results reported for the alkyl enol ethers. This preference for the *Z* isomer is very consistent with the ($_\pi2_s$ + $_\pi2_a$) mechanistic pathway which requires an orthogonal approach of the ketene and olefin.[8] There is a steric interaction between a chlorine atom and the ethyl substituent in the *E* isomer which is not present in the *Z* isomer as illustrated below.



The sterically crowded silyl enol ether of 2,2,4-trimethyl-3-pentanone, **8a**, underwent cycloaddition with dichloroketene to form a 66% yield of the acyclic product **8b**. The silyl enol ethers of α-phenylpropionaldehyde and acetaldehyde, **9a** and **10a**, respectively, yield the 3-siloxycyclobutanones **9b** and **10b** as expected and were converted in good yield to the 3-hydroxycyclobutanones **9c** and **10c**.

The silyl enol ether of 3-cyclohexenecarboxaldehyde **11a** underwent cycloaddition with dichloroketene in good yield to the expected spirosiloxycyclobutanone **11b** and hydrolysis to the spirohydroxycyclobutanone **11c**.

The reductive removal of the chlorine atoms from the 2,2-dichloro-3-(trimethylsiloxy)cyclobutanones with tri-*n*-butyltin hydride is readily accomplished to give the 3-(trimethylsiloxy)cyclobutanones.[9-11] Some representative examples are give in Table II.

Experimental Section

Proton NMR were recorded on a Perkin-Elmer R-24B nuclear magnetic resonance spectrometer employing CCl_4 as the solvent and either $CHCl_3$ or tetramethylsilane as the internal standard. Analytical and spectroscopic samples were obtained where possible by VPC on a Perkin-Elmer Model 3920-B gas chromatograph with a 6 ft. × 0.25 in. column packed with 10% Qf-1 on acid washed Chromosorb W (80–100) support. The infrared spectra were obtained on a Perkin-Elmer Model 621 grating infrared spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double focusing spectrometer.

Ether was dried and purified by distillation from sodium–potassium alloy prior to use. Zinc was activated by a procedure previously described and stored under nitrogen.[11] Trichloroacetyl chloride was prepared from trichloroacetic acid and thionyl chloride and distilled prior to each cycloaddition. Silyl enol ethers were prepared according to literature procedures and distilled prior to use for best results.[18]

Typical Procedure for Dichloroketene Cycloadditions.[7] A solution of 0.025 mol of freshly distilled trichloroacetyl chloride in 250 mL of dry ether was added slowly over a period of 4–6 h to a stirred mixture of 5.0 g of activated zinc and 0.035 mol of silyl enol ether in 250 mL of ether under a nitrogen atmosphere. The reaction was stirred for several hours after the addition was complete. The excess zinc was filtered, and the reaction solution was concentrated to about 50 mL and then stirred with 100 mL of pentane. The pentane solution was decanted from the zinc salts and evaporated, and the residue was vacuum distilled.

The excess silyl enol ether was found to improve the yields of the cycloadducts, limit polymerization of dichloroketene, and in general provide for a cleaner workup.

Typical Procedure for the Hydrolysis of 2,2-Dichloro-3-(trimethylsiloxy)cyclobutanones. A 2.0-g portion of the 2,2-dichloro-3-(trimethylsiloxy)cyclobutanone was dissolved in 10 mL of methanol and stirred at room temperature for 2–16 h depending on the cyclobutanone.

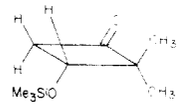
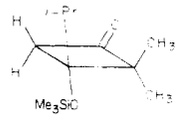
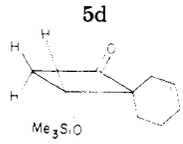
2,2-Dichloro-3-(trimethylsiloxy)-4,4-dimethylcyclobutanone (1b).[4] A 0.027-mol portion of trichloroacetyl chloride, 5.3 g of activated zinc, and 0.035 mol of silyl enol ether **1a** in 450 mL of dry ether yielded 6.15 g (89%) of a pale yellow liquid after distillation at 40–45 °C (0.05 mm): IR 1801, 1260, 1140, and 850 cm^{-1}; NMR δ 4.28 (s, 1 H), 1.39 (s, 3 H), 1.28 (s, 3 H), 0.31 (s, 9 H); mass spectrum, *m/e* (M + 2) 256 (0.9), (M) 254 (1.5), 241 (2.2), 239 (3.3), 186 (21.0), 184 (31.0), 144 (12.1), 129 (11.2), 73 (100), 70 (43.0).

2,2-Dichloro-3-hydroxy-4,4-dimethylcyclobutanone (1c).[4] The hydrolysis of 5.2 g of **1b** gave 3.3 g (88%) of **1c** after distillation at 54–58 °C (0.05 mm) as a clear colorless oil: IR 3600–3300, 1801, 1460, 1140, 855 cm^{-1}; NMR δ 4.45 (s, 1 H), 1.43 (s, 3 H), 1.32 (s, 3 H); mass spectrum, *m/e* (no M) 121 (1.6), 119 (4.6), 114 (2.4), 112 (4.0), 99 (6.4), 72 (23.2), 70 (100), 57 (21.6).

Anal. Calcd for $C_6H_8Cl_2O_2$: C, 39.37; H, 4.41. Found: C, 39.13; H, 4.67.

2,2-Dichloro-3-ethyl-3-(trimethylsiloxy)-4-methylcyclobutanone (2b). From 0.027 mol of trichloroacetyl chloride, 0.35 mol of silyl enol ether **2a**, and 4.8 g of zinc was isolated 5.8 g of **2b** (80%) after distillation at 65–71 °C (0.05 mm): IR 1802, 1455, 1265, 1050, 845 cm^{-1}; NMR δ 3.34 (m, 1 H), 1.89 (q, 2 H), 1.11 (m, 6 H), 0.21 (s, 9 H); mass spectrum, *m/e* (M + 2) 270 (1.2), (M) 268 (1.8), 214 (7.3), 212 (10.9), 199 (1.2), 197 (3.5), 158 (2.7), 143 (4.3), 95 (11.0), 93 (34.0), 73 (68.0), 57 (100).

Table II. Reductions of 2,2-Dichloro-3-(trimethylsiloxy)cyclobutanones

dichloro compd	reduction product (% yield)
1b	 (61)
	1d
5b	 (67)
	5d
11b	 (62)
	11d

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970.
(9) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).
(10) M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968).
(11) W. T. Brady, E. F. Hoff, Jr., R. Roe, Jr., and F. H. Parry, III, *J. Am. Chem. Soc.*, **91**, 5679 (1969).

2,2-Dichloro-3-ethyl-3-hydroxy-4-methylcyclobutanone (2c). The hydrolysis of 2.15 g (0.008 mol) of **2b** gave 1.24 g (79%) of **2c** as a yellow oil after distillation at 38–44 °C (0.01 mm): IR 3600–3350, 1798, 1448, 1250, 1055, 835 cm^{-1}; NMR δ 3.82 (s, 1 H), 3.52 (m, 1 H), 1.95 (m, 2 H), 1.05 (m, 6 H); mass spectrum, *m/e* (M + 2) 198 (1.0), 196 (1.4), 169 (2.2), 167 (2.9), 142 (3.6), 140 (5.4), 113 (24.2), 57 (100), 43 (2.2).

6,6-Dichloro-5-(trimethylsiloxy)-4-methyl-5-hexen-3-one (2d). A 1.95-g (0.0073 mol) portion of **2b** was heated at 120 °C for 3 h to yield after distillation 1.5 g (78%) of **2d** at 60–63 °C (0.05 mm): IR 1708, 1602, 1445, 1250, 1065, 835 cm^{-1}; NMR δ 3.82 (q, 1 H), 2.31 (q, 2 H), 1.11 (m, 6 H), 0.25 (s, 9 H); mass spectrum, *m/e* (M + 2) 270 (1.0), (M) 268 (1.5), 235 (2.2), 233 (6.8), 147 (3.8), 95 (3.0), 93 (7.5), 75 (7.5), 73 (21.2), 57 (100).

1,1-Dichloro-3-methyl-2,4-hexanedione (2e). Hydrolysis of 1.4 g (0.0052 mol) of **2e** with methanol gave 0.87 g (85%) of **2e** after distillation at 55–62 °C (0.1 mm): IR 1730, 1710, 1600, 1555, 1345, 1228, 1090, 795 cm^{-1}; NMR δ 5.97 (s, 1 H), 4.23 (q, 1 H), 2.56 (q, 2 H), 1.47 (d, 3 H), 1.11 (t, 3 H); mass spectrum, *m/e* (M + 2) 198 (1.2), (M) 196 (1.4), 180 (1.8), 178 (2.4), 169 (3.5), 167 (5.9), 169 (5.7), 149 (3.5), 114 (43.5), 86 (2.9), 84 (4.1), 57 (100).

Heating 1.2 g (0.0006 mol) of **2c** for 2 h at 140 °C gave 0.92 g (77%) of **2e** after distillation.

6,6-Dichloro-5-(trimethylsiloxy)-2,2-dimethyl-5-hexen-3-one (3b).[4] From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **4a**, and 5.2 g of zinc was isolated 5.8 g (82%) of **3b** after distillation at 75–81 °C (0.01 mm). Some hydrolysis to **3c** was observed: IR 1722, 1635, 1460, 1295, 855 cm^{-1}; NMR δ 3.49 (s, 2 H), 1.14 (s, 9 H), 0.21 (s, 9 H).

1,1-Dichloro-5,5-dimethylhexane-2,4-dione (3c).[4] **Hydrolysis** of 2.0 g (0.0007 mol) of **3b** gave 1.33 g (89%) of **3c** after distillation at 68–74 °C (0.01 mm) as a yellow oil which readily darkened at room temperature: IR 1655–1545, 1445, 1360, 1310, 1211, 795 cm^{-1}; NMR δ 14.58 (s, 1 H), 5.92 (s, 1 H), 5.86 (s, 1 H), 1.19 (s, 9 H); mass spectrum, *m/e* (M + 2) 211 (3.0), (M) 210 (4.5), 155 (23), 153 (35.0), 127 (100), 120 (16.1), 118 (48.3), 85 (12.0), 57 (80.1).

5,5-Dichloro-4-(trimethylsiloxy)-4-penten-2-one (4b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **4a**, and 4.7 g of zinc was isolated 4.74 g (79%) of **4b** after distillation at 35–41 °C (0.05 mm): IR 1720, 1610, 1250, 1020, 845 cm^{-1}; NMR δ 3.34 (s, 2 H), 2.15 (s, 3 H), 0.12 (s, 9 H); mass spectrum, *m/e* (M + 2) 242 (8.2), (M) 240 (12.3), 227 (11.3), 225 (16.4), 147 (13.2), 95 (13.6), 93 (34.5), 85 (60.9), 73 (80.5), 43 (110).

1,1-Dichloro-2,4-pentanedione (4c). Hydrolysis of 2.9 g (0.012 mol) of **4b** with methanol gave 1.56 g (77%) of **4c** as a pale yellow oil after distillation at 36–40 °C (0.1 mm): IR 1625–1575, 1415, 1320, 795 cm^{-1}; NMR δ 13.87 (s, 1 H), 5.88 (s, 1 H), 5.82 (s, 1 H), 2.13 (s, 3 H); mass spectrum, *m/e* (M + 2) 170 (7.3), (M) 168 (12.2), 107 (3.3), 105 (9.8), 86 (15.5), 85 (100), 43 (99).

Anal. Calcd for $C_5H_6Cl_2O_2$: C, 35.53; H, 3.58. Found: C, 35.82; H, 3.65.

2,2-Dichloro-3-isopropyl-3-(trimethylsiloxy)-4,4-dimethylcyclobutanone (5b). From 0.035 mol of silyl enol ether **5a**, 0.025 mol of trichloroacetyl chloride, and 5.1 g of activated zinc was isolated 6.54 g (88%) of **5b** as a pale green oil after distillation at 76–82 °C (0.05 mm): IR 1801, 1468, 1255, 1152, 1095, 885, 838 cm^{-1}; NMR δ 2.61 (m, 1 H), 1.13 (m, 6 H), 0.96 (d, 6 H), 0.22 (s, 9 H); mass spectrum, *m/e* (no M) 283 (0.9), 281 (1.4), 263 (11.7), 261 (33.3), 228 (34.2), 226 (50.0), 226 (50.0), 188 (9.0), 186 (9.9), 171 (6.3), 148 (16.2), 95 (13.5), 93 (35.1), 73 (100), 71 (71.2), 43 (71.6).

Anal. Calcd. for $C_{12}H_{22}Cl_2O_2Si$: C, 48.48; H, 7.46. Found: C, 47.97; H, 7.23.

1,1-Dichloro-3,3,5-trimethyl-2,4-hexanedione (5c). A 2.3-g (0.0078 mol) portion of siloxycyclobutanone **5b** was dissolved in 10 mL of methanol containing several drops of concentrated HCl and heated at reflux. Upon removing the solvent, there was obtained 1.63 g (93%) of a low-melting solid **5c**. Sublimation provided an analytical sample with mp 47–49 °C: IR 1730, 1700, 1462, 1390, 1315, 1010, 935 cm^{-1}; NMR δ 6.16 (s, 1 H), 2.95 (m, 1 H), 1.49 (s, 6 H), 1.05 (d, 6 H); mass spectrum, *m/e* (no M) 191 (1.8), 189 (4.4), 156 (3.0), 154 (3.9), 141 (5.4), 121 (8.9), 119 (19.2), 71 (100), 43 (76.5).

Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.02; H, 6.27. Found: C, 47.95; H, 6.27.

2,2-Dichloro-3-phenyl-3-(trimethylsiloxy)-4,4-dimethylcyclobutanone (6b). From 0.035 mol of trichloroacetyl chloride and 0.025 mol of silyl enol ether **6a** was isolated 5.86 g (71%) of **6b** after distillation at 95–104 °C (0.05 mm): IR 1802, 1680, 1448, 1252, 1125, 880, 845 cm^{-1}; NMR δ 7.49 (m, 5 H), 1.61 (s, 3 H), 1.49 (s, 3 H), −0.05 (s, 9 H); mass spectrum, *m/e* (M + 2) 332 (0.8), (M) 330 (1.2), 297 (3.6), 295 (9.7), 2.62 (10.5), 260 (13.7), 220 (11.3), 179 (4.4), 177 (6.5), 143 (73.4), 105 (93.5), 95 (13.7), 93 (26.0), 77 (41.1), 73 (100).

4,4-Dichloro-2,2-dimethyl-1-phenyl-1,3-butanedione (6c). Hydrolysis of 2.1 g (0.0064 mol) of 6b with methanol containing a few drops of dilute HCl and removal of the solvent afforded a white solid. Sublimation gave 1.49 g (91%) of **6c**: mp 51–53 °C; IR 1738, 1675, 1465, 1452, 1268, 970 cm^{-1}; NMR δ 7.4 (m, 5 H), 6.06 (s, 1 H), 1.59 (s, 6 H); mass spectrum, *m/e* (no M) 223 (3.3), 175 (2.0), 151 (1.6), 149 (2.5), 105 (100), 77 (37.7), 51 (34.4).

Anal. Calcd for $C_{12}H_{12}Cl_2O_2$: C, 55.62; H, 4.67. Found: C, 55.52; H, 4.76.

2,2-Dichloro-3-(trimethylsiloxy)-4-ethylcyclobutanone (7b). From 0.025 mol of trichloroacetyl chloride and 0.035 mol of an equal mixture of silyl enol ethers (*Z*)-**7a** and (*E*)-**7a** was obtained 5.23 g (82%) of a 2:1 mixture of the (*Z*)- and (*E*)-siloxycyclobutanones, respectively, after distillation at 66–72 °C (0.1 mm): IR 1797, 1455, 1248, 1155, 1045, 840 cm^{-1}; NMR (*Z* isomer) δ 4.57 (d, 1 H, J = 7.9 Hz), 3.66 (m, 1 H), 1.59 (m, 2 H), 1.08 (t, 3 H), 0.21 (s, 9 H), (*E* isomer) 4.23 (d, 1 H, J = 7.1 Hz); mass spectrum, *m/e* (no M) 241 (2.0), 239 (3.2), 186 (34.8), 184 (50.1), 144 (15.2), 129 (17.7), 95 (30.4), 93 (30.5), 73 (100), 70 (19.6), 55 (34.8).

From 0.025 mol of trichloroacetyl chloride and 0.06 mol of an equal mixture of silyl enol ethers (*Z*)-**7a** and (*E*)-**7a** was obtained 5.36 g (84%) of the (*Z*)-siloxycyclobutanone after distillation. Less than 5% of the product was the *E* isomer as determined by NMR.

From 0.035 mol of trichloroacetyl chloride and 0.025 mol of an equal mixture of silyl enol ethers (*Z*)-**7a** and (*E*)-**7a** was obtained 5.19 g (81%) of a 1:1 mixture of the *Z* and *E* isomers after workup.

2,2-Dichloro-3-hydroxy-4-ethylcyclobutanone (7c). The hydrolysis of 2.0 g (0.008 mol) of an equal mixture of (*Z*)-**7a** and (*E*)-**7a** resulted in 1.23 g (84%) of a 1:1 mixture of the (*Z*)- and (*E*)-hydroxycyclobutanones after distillation at 60–65 °C (0.1 mm): IR 3600–3250, 1794, 1451, 1245, 1130, 840 cm^{-1}; NMR (*Z* isomer) δ 5.35 (s, broad, 1 H), 4.61 (d, 1 H, J = 7.9 Hz), 3.71 (m, 1 H), 1.75 (m, 2 H), 1.08 (t, 3 H), (*E* isomer) 4.41 (d, 1 H, J = 7.2 Hz); mass spectrum, *m/e* (M + 2) 184 (0.4), 182 (0.7), 169 (32.0), 167 (48.1), 154 (11.9), 152 (35.7), 132 (67.5), 104 (83.3), 88 (63.5), 73 (100), 58 (95.2).

The hydrolysis of 2.1 g (0.0084 mol) of the (*Z*)-siloxycyclobutanone gave 1.22 g (82%) of the (*Z*)-hydroxycyclobutanone.

6,6-Dichloro-5-(trimethylsiloxy)-2,2,4,4-tetramethyl-5-hexen-3-one (8b). From 0.025 mol of trichloroacetyl chloride and 0.035 mol of silyl enol ether **8a** was isolated 5.11 g (66%) of **8b** at 70 °C (0.1 mm): IR 1745, 1695, 1455, 1260, 840 cm^{-1}; NMR δ 1.48 (s, 6 H), 1.04 (s, 9 H), 0.21 (s, 9 H); mass spectrum, *m/e* (M + 2) 312 (1.1), (M) 310 (1.5), 277 (2.9), 275 (8.1), 190 (4.0), 188 (4.8), 147 (6.6), 119 (3.7), 117 (3.8), 85 (27.2), 73 (31.6), 57 (100).

1,1-Dichloro-3,3,5,5-tetramethyl-2,4-hexanedione (8c). Hydrolysis of 3.1 g of **8b** gave 2.15 g (91%) of the dione as a crystalline solid with mp 37–38 °C after sublimation: IR 1735, 1695, 1465, 980, 820 cm^{-1}; NMR δ 6.12 (s, 1 H), 1.56 (s, 6 H), 1.19 (s, 9 H); mass spectrum, *m/e* (no M) (M − 35) 203 (1.3), 190 (6.6), 188 (6.6), 156 (21.1), 154 (30.3), 121 (10.3), 119 (28.8), 85 (73.7), 57 (100).

Anal. Calcd for $C_{10}H_{16}Cl_2O_2$: C, 50.2; H, 6.75. Found: C, 49.86; H, 6.71.

2,2-Dichloro-3-(trimethylsiloxy)-4-methyl-4-phenylcyclobutanone (9b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **9a**, and 4.1 g of zinc was obtained 6.2 g (78%) of **9b** at 95–100 °C (0.07 mm). The two isomers were inseparable by VPC and a ratio of products could not be determined: IR 1804, 1610, 1500, 1455, 1260, 1190, 850 cm^{-1}; NMR δ 7.26 (m, 5 H), 4.88 (m, 1 H), 1.67 (m, 3 H), 0.37 (s, 9 H); mass spectrum, *m/e* (no M) 303, (0.1), 301 (0.1), 255 (0.0), 253 (2.7), 206 (7.3), 163 (3.2), 147 (14.5), 132 (100), 105 (10), 104 (12.7), 73 (30.1).

Anal. Calcd for $C_{14}H_{18}Cl_2O_2Si$: C, 53.0; H, 5.72. Found: C, 53.61; H, 5.77.

2,2-Dichloro-3-hydroxy-4-methyl-4-phenylcyclobutanone (9c). The hydrolysis of 2.0 g (0.0063 mol) of **9b** afforded 1.34 g (87%) of **9c** as a yellow oil at 95–99 °C (0.1 mm): IR 3600–3350, 1797, 1610, 1498, 1450, 1265, 840 cm^{-1}; NMR δ 7.25 (m, 5 H), 6.2 (s, 1 H), 4.90 (m, 1 H), 1.64 (m, 3 H); mass spectrum, *m/e* (no M) 247 (0.02), 245 (0.03), 232 (0.02), 230 (0.03), 165 (2.2), 163 (3.3), 147 (9.8), 132 (100), 105 (34.8), 104 (43.5), 79 (18.5), 77 (19.6).

2,2-Dichloro-3-(trimethylsiloxy)cyclobutanone (10b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **10a**, and 4.8 g of activated zinc was attained 4.8 g (84%) of **10b** as a yellow oil at 45–50 °C (0.2 mm): IR 1808, 1260, 845 cm^{-1}; NMR δ 4.61 (m, 1 H), 3.31 (m, 2 H), 0.37 (s, 9 H); mass spectrum, *m/e* (no M) 213 (4.5), 211 (6.5), 186 (64.9), 184 (100), 171 (32.5), 169 (46.8), 101 (92.0), 75 (77.9), 74 (76.6), 59 (62.3).

2,2-Dichloro-3-hydroxycyclobutanone (10c). Hydrolysis of 2.0 g (0.0088 mol) of **10b** afforded 1.1 g (81%) of **10c** as a clear colorless oil at 35–40 °C (0.02 mm): IR 3600–3300, 1802, 1370, 1190, 855 cm^{-1}; NMR δ 4.79 (m, 1 H), 4.6 (s, 1 H), 3.44 (m, 2 H); mass spectrum, *m/e* (M + 2) 156 (4.9), (M) 154 (7.4), 128 (5.5), 126 (9.1), 114 (5.9), 112 (100), 110 (29.6), 71 (85.0), 43 (72.0).

3-Cyclohexenespiro[3′,3′]dichloro-4′-(trimethylsiloxy)-cyclobutan-2′-one (11b). From 0.025 mol of trichloroacetyl chloride, 0.035 mol of silyl enol ether **11a**, and 5.1 g of zinc was obtained 6.13 g (84%) of **11b** as an oil at 80–85 °C (0.025 mm): IR 1801, 1440, 1375, 1260, 1190, 875, 845 cm^{-1}; NMR δ 5.61 (m, 2 H), 4.29 (s, 1 H), 2.31–1.95 (m, 6 H), 0.25 (s, 9 H); mass spectrum, *m/e* (no M) 259 (2.4), 257 (3.6), 186 (8.4), 184 (13.1), 182 (7.1), 169 (3.6), 167 (5.5), 147 (64.3), 108 (52.4), 80 (25.8), 79 (23.8), 73 (100).

3-Cyclohexenespiro[3′,3′]dichloro-4′-hydroxycyclobutan-2′-one (11c). From 2.05 g (0.007 mol) of **11b** was isolated 1.32 g (85%) of **11c** as an oil at 79–85 °C (0.05 mm): IR 3600–3350, 1795, 1650, 1435, 1152, 845 cm^{-1}; NMR δ 5.62 (m, 2 H), 4.39 (s, 1 H), 4.02 (s, 1 H), 2.29–1.95 (m, 6 H); mass spectrum, *m/e* (no M) 202 (2.6), 152 (3.9), 111 (100), 84 (15.3), 83 (23.1), 82 (46.2).

2,2-Dimethyl-3-(trimethylsiloxy)cyclobutanone (1d). A 2.8-g (0.011 mol) portion of **1b** in 10 mL of cyclohexane saturated with azobis(isobutyronitrile) was added dropwise over 30 min to 12.2 g (0.041 mol) of tri-*n*-butyltin hydride in 20 mL of cyclohexane under a nitrogen atmosphere. The solution was heated at reflux for an additional 12 h. Removal of the solvent under reduced pressure and vacuum distillation afforded 1.24 g (61%) of **1d** at 40–45 °C (0.5 mm): IR 1782, 1451, 1258, 906 cm^{-1}; NMR δ 4.11 (m, 1 H), 3.05 (m, 2 H), 1.01 (s, 3 H), 0.99 (s, 3 H); mass spectrum, *m/e* (M) 186 (4.5), 171 (64.3), 158 (41.6), 130 (93.5), 128 (100), 116 (89.6), 76 (92.2), 71 (79.2), 58 (97.4).

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.00; H, 9.73. Found: C, 58.1; H, 9.62.

2,2-Dimethyl-3-isopropyl-3-(trimethylsiloxy)cyclobutanone (5d). From 4.65 g (0.016 mol) of dichlorocyclobutanone **5b**, 14.5 g (0.05 mol) of tri-*n*-butyltin hydride, and a catalytic amount of azobis(isobutyronitrile) was isolated 2.38 g (67%) of **5d** at 70–75 °C (0.5 mm): IR 1782, 1468, 1260, 1083, 845 cm^{-1}; NMR δ 2.78 (m, 2 H), 1.81 (m, 1 H), 1.1–0.75 (m, 12 H), –0.04 (s, 9 H); mass spectrum, *m/e* (M) 228 (7.8), 213 (9.1), 186 (48.1), 171 (20.8), 158 (44.2), 143 (54.5), 91 (18.2), 77 (84.4), 73 (100), 43 (61.0).

3-Cyclohexenespiro-4′-(trimethylsiloxy)cyclobutan-2′-one (11d). From 4.97 g of **11b**, 19.8 g (0.068 mol) of tri-*n*-butyltin hydride, and a catalytic amount of azobis(butyronitrile) was isolated 2.35 g (62%) of **11d** at 50–55 °C (0.15 mm): IR 1784, 1468, 1252, 1184, 1154, 887 cm^{-1}; NMR δ 5.4 (m, 2 H), 4.0 (d of d, 1 H), 2.84 (m, 2 H), 1.92 (m, 4 H), 1.53 (m, 2 H), –0.06 (s, 9 H); mass spectrum, *m/e* (M) 224 (8.8), 182 (100), 167 (10.3), 142 (14.7), 108 (70.6), 92 (44.1), 75 (47.1), 73 (76.5).

Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.99. Found: C, 64.36; H, 9.43.

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Registry No. **1a**, 6651-34-9; **1b**, 66324-00-3; **1c**, 66324-05-8; **1d**, 70320-48-8; (*Z*)-**2a**, 51425-54-8; (*E*)-**2a**, 70320-49-9; *cis*-**2b**, 70320-50-2; *trans*-**2b**, 70320-51-3; *cis*-**2c**, 70320-52-4; *trans*-**2c**, 70320-53-5; **2d**, 70320-54-6; **2e**, 70320-55-7; **3a**, 17510-46-2; **3b**, 66323-97-5; **3c**, 26709-24-0; **4a**, 1833-53-0; **4b**, 70320-56-8; **4c**, 53009-77-1; **5a**, 55339-64-5; **5b**, 70320-57-9; **5c**, 70320-58-0; **5d**, 70320-59-1; **6a**, 39158-85-5; **6b**, 70320-60-4; **6c**, 70320-61-5; (*Z*)-**7a**, 19980-22-4; (*E*)-**7a**, 19980-23-5; *cis*-**7b**, 70320-62-6; *trans*-**7b**, 70320-63-7; *cis*-**7c**, 70320-64-8; *trans*-**7c**, 70320-65-9; **8a**, 65102-17-2; **8b**, 70320-66-0; **8c**, 70320-67-1; (*Z*)-**9a**, 51425-65-1; (*E*)-**9a**, 51425-64-0; *cis*-**9b**, 70320-68-2; *trans*-**9b**, 70320-69-3; *cis*-**9c**, 70320-70-6; *trans*-**9c**, 70320-71-7; **10a**, 6213-94-1; **10b**, 70320-72-8; **10c**, 70320-73-9; **11a**, 51075-25-3; **11b**, 70320-74-0; **11c**, 70320-75-1; **11d**, 70320-76-2; trichloroacetyl chloride, 76-02-8; dichloroethenone, 4591-28-0.

Notes

A Novel Ring Enlargement Involving Electrophilic Attack on the Dienolate Anion Derived from 7,8-Bis(trimethylsilyloxy)-*cis*-bicyclo[4.2.0]octa-3,7-diene

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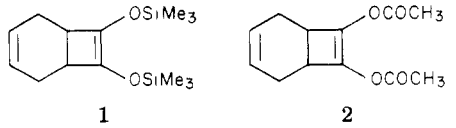
As a protecting group for the hydroxyl function the trimethylsilyl group is often too sensitive to be carried through a series of reactions without suffering premature deblocking.[1] We encountered an instance of this difficulty during attempts to dehydrogenate the readily available bis(trimethylsilyl) enol ether **1** to the corresponding cyclohexadiene.[2] For that reason we investigated the replacement of the trimethylsilyl groups of **1** by a more stable protective group, for example, acetyl, as in diacetate **2**. Although **2** was not obtained, the results led to the uncovering of a novel rearrangement which we wish to describe in the present note.



1 **2**

In view of the common technique of cleaving enol trimethylsilyl ethers with alkyl lithium reagents,[3] we sought

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