20–40° and a 3–8 s delay time. All spectra were recorded on a Varian Associates XL-100 spectrometer equipped with a Nicolet TT-100 Data System and an NT-440 Multinuclear Probe. Slight deviations of the ^{13}C–H couplings for compounds **1–3** from earlier reported values[10] obtained from ^{13}C satellites in the ^{1}H NMR spectra are well within the range of experimental error.

Molecular Orbital Calculations were carried out using the CNDO/2 program (No. 141) from the Quantum Chemistry Program Exchange, Chemistry Department, Indiana University.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We would also like to thank Mr. Steven Silber for his assistance in obtaining NMR spectra. The Varian XL-100 NMR spectrometer was obtained with a major equipment grant from the National Science Foundation.

Registry No.—**12,** 1120-56-5; **13,** 1528-30-9; **14,** 1192-37-6.

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Addition of Dichloroketene to Silyl Enol Ethers. Synthesis of Functionalized Cyclobutanones[1]

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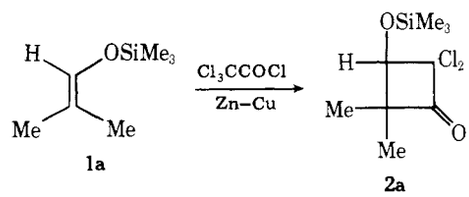
Dichloroketene, generated from trichloroacetyl chloride and activated zinc, has been found to react readily with silyl enol ethers. In most cases, good yields of 3-siloxy-substituted dichlorocyclobutanones could be isolated. The reaction appears to be both regio- and stereospecific. Mild acid hydrolysis of the siloxycyclobutanones afforded the corresponding 3-hydroxydichlorocyclobutanones. In some cases, cyclobutane ring opening or elimination to generate a dichlorocyclobutenone was observed. The silyl enol ethers derived from acetophenone and pinacolone, on the other hand, afforded only acyclic products from the dichloroketene. The possibility that these acyclic products may result from ring opening of initially formed cyclobutanones is discussed.

General Reaction Scheme. The cycloaddition of dichloroketene[2] to reactive olefins constitutes a convenient synthesis of cyclobutanones.[3] In view of the considerable synthetic utility of silyl enol ethers[4] as masked enols and our[5] own interest in these species, we investigated the reaction of dichloroketene with silyl enol ethers as a possible route to functionalized cyclobutanones.

When trichloroacetyl chloride was slowly added to a stirred mixture of the trimethylsilyl enol ether **1a** and activated zinc in dry ether, a mildly exothermic reaction occurred and a one to one adduct was obtained in 92% yield after workup. A strong high-frequency (1805 cm^{-1}) carbonyl absorption in the IR spectrum indicated cyclobutanone **2a** as the product of this cycloaddition (eq 1). Regiochemistry was assigned in accord with known examples of diphenylketene cycloadditions with enol ethers.[6] Several other silyl enol ethers were found to react smoothly with dichloroketene to afford good yields of substituted cyclobutanones (see Table I). The yields are generally higher than in cycloadditions of dichloroketene to simple olefins.



1a **2a** (1)

Hydrolysis of the trimethylsilyl group of the cycloadducts was readily accomplished by treating a tetrahydrofuran or methanol solution of the siloxycyclobutanone with dilute hydrochloric acid. As indicated in Table I, this afforded high yields of the hydroxy-substituted cyclobutanones (**3a–f**).

Generation of dichloroketene by the triethylamine dehydrohalogenation of dichloroacetyl chloride in the presence of silyl enol ethers did not lead to cycloadducts. For instance, in the case of **1b,** conversion to cyclopentanone appeared to be the major reaction, accompanied by minor amounts of **4** (eq

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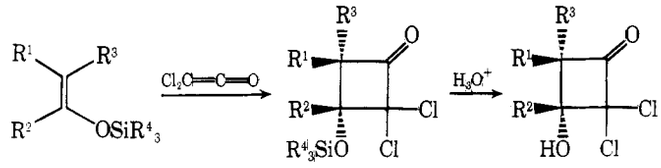
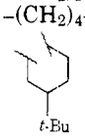
Table I

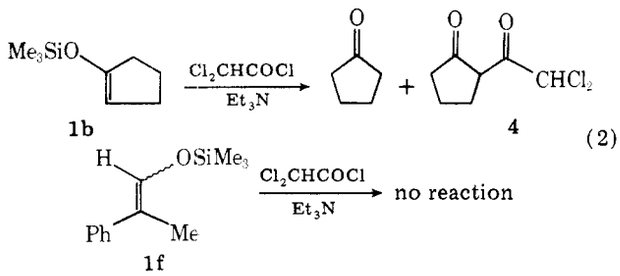


1 2 3

	R¹	R²	R³	R⁴	Registry no.	Yield of 2,[a] %	Registry no.	Yield of 3,[a] %	Registry no.
1a	Me	H	Me	Me	6651-34-9	92[b]	66324-00-3	83	66324-05-8
1b	$-(CH_2)_3-$		H	Me	19980-43-9	79	66324-01-4	88	66324-06-9
1c	$-(CH_2)_4-$		H	Me	6651-36-1	81	66402-59-3	85	66324-07-0
1d			H	Me	19980-19-9	95[b]	66402-60-6	73	66324-08-1
1e			H	*t*-Bu(Me)$_2$	66323-98-6	92	66324-02-5	*c*	
1f[d]	Ph	H	Me	Me		86[b,e]	66324-03-6	85[e]	66324-09-2
1g[f]	H	Ph	Me	Me	66323-99-7	94[f,g]	66324-04-7	*h*	
(*E*)-**1h**	Ph	Me	H	Me	19980-25-7	59[i,j]		*k*	
(*Z*)-**1h**	H	Me	Ph	Me	19980-24-6				

[a] Yield after distillation. [b] Crude yield; attempted distillation led to partial hydrolysis of the trimethylsilyl group. [c] Not hydrolyzed. [d] *E*/*Z* ratio was 70:30. [e] Stereochemistry unknown. [f] Apparently stereochemically homogeneous by NMR and GC. [g] Crude yield; attempted distillation led to partial conversion to the ring-opened product **7** (see text). [h] Hydrolysis afforded cyclobutenone **9** (see text) in 78% yield. [i] Adducts are thermally sensitive (see Experimental Section). [j] Ratio of cyclobutanones is identical to *E*/*Z* ratio of **1h**. [k] Hydrolysis afforded cyclobutenone **10** (see text) in 81% yield.

2). The silyl enol ether **1f** was found to be completely unreactive toward dichloroacetyl chloride and triethylamine.

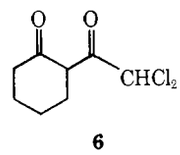


(2)

Therefore, we used the zinc dehalogenation procedure to generate dichloroketene, and in addition we found it advantageous to use the trichloroacetyl chloride within 2 to 3 days of its distillation and zinc within 1 week of its activation. Reactions were conveniently carried out in dry ether. Under these conditions, undesirable partial hydrolysis of silyl enol ethers to the parent carbonyl compounds was avoided. The reactions of dichloroketene with silyl enol ethers were followed by either GC or NMR spectroscopy and were usually complete within 2 to 3 h after addition of the acid chloride. The disappearance of acid chloride and silyl enol ether was monitored by GC; however, nearly all of the siloxycyclobutanone products **2** were found to decompose readily on gas chromatography. Attempted chromatography of **2** on silica gel or neutral alumina also led to extensive decomposition, but purification was achieved by bulb to bulb distillation at reduced pressure. Even under these conditions, however, several of the siloxycyclobutanones suffered partial conversion to the corresponding hydroxycyclobutanones (see Experimental Section).

Siloxycyclobutanone Ring Opening. In the dichloroketene reactions described thus far, the trimethylsilyl enol ether from cyclohexanone, **1c**, was found to be the most sensitive. For example, if trichloroacetyl chloride was not freshly distilled prior to reaction or if the acid chloride was added too rapidly to the suspension of zinc and **1c**, the reaction became quite vigorous and little, if any, cyclobutanone **2c** could be isolated. Instead, products **5** and **6** were formed in high yield. In addition, the hydrolysis of siloxycyclobutanone **2c** to the hydroxycyclobutanone **3c** was found to be extremely erratic. Often, even brief (1 min) treatment of a methanol or tetrahydrofuran solution of **2c** with dilute acid gave exclusively the ring-opened product **6**.

5

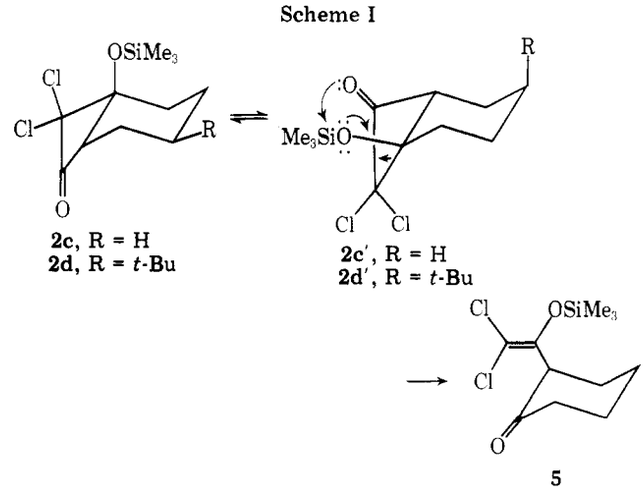


6

Enol ether **5** was readily hydrolyzed to **6** with dilute acid. For comparison, compound **6** was also synthesized by an alternative route[7] described by Murai, namely, the reaction of dichloroacetyl chloride with silyl enol ether **1c**.

As suggested in Scheme I, the flexibility of the cyclohexyl adduct **2c** may account for its relative instability. In one (**2c'**) of the possible conformations, the system appears to be well set up for a migration[8] of silicon from one oxygen to the other with consequent opening of the four-membered ring. This process may be catalyzed by zinc chloride present in the reaction mixture (see discussion below).

Scheme I



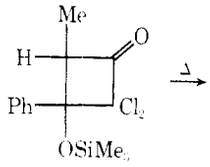
2c, R = H
2d, R = *t*-Bu

2c', R = H
2d', R = *t*-Bu

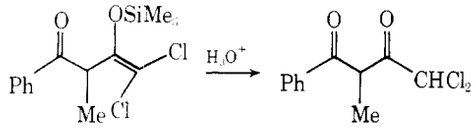
5

The less conformationally mobile 4-*tert*-butyl analogue **1d,** on the other hand, reacted smoothly with dichloroketene to afford the siloxycyclobutanone **2d.**[9] In no instances were any ring-opened products isolated in this reaction. In contrast to **2c,** the 4-*tert*-butyl analogue **2d** underwent clean hydrolysis to the hydroxycyclobutanone **3d,** a stable crystalline solid. This is attributable to the fact that conformation **2d′**, necessary for the ring-opening process, is unfavorable because of severe diaxial interactions. These results lend credence to the idea that a conformation such as **2c′** is involved in the ring-opening process.

Ring-opening reactions were also observed with the siloxycyclobutanone **2g.** Attempted distillation of **2g** led to partial conversion to the ring-opened product **7** (eq 3). Heating the



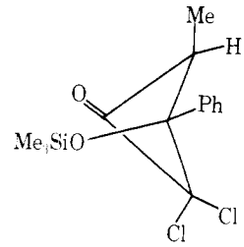
2g



(3)

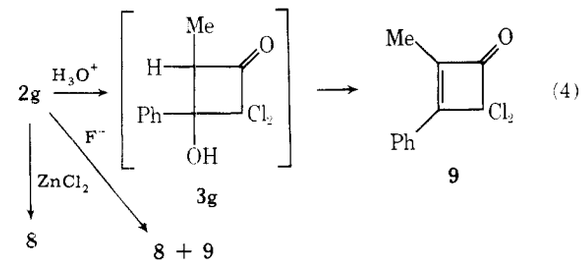
7 **8**

crude product **2g** or the distillate at 200 °C for 2 h led to complete ring opening to **7.** In this case, as for **2c′**, the favorable conformation has the siloxy group axial and the large phenyl substituent equatorial to the puckered cyclobutanone ring (**2g′**).



2g′

Although **7** was readily hydrolyzed to **8** with dilute acid, the siloxycyclobutanone **2g** proved to be resistant to conditions that completely hydrolyzed the other siloxycyclobutanones. Under more rigorous hydrolysis conditions (see Experimental Section), **2g** afforded cyclobutenone **9** in good yield (eq 4);



(4)

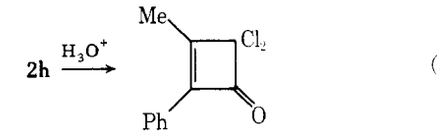
3g **9**

8 **8 + 9**

evidently, the hydroxy intermediate **3g** underwent loss of water (in a diaxial fashion from **2g′**).

Treatment of siloxycyclobutanone **2g** with tetrabutylammonium fluoride[10] in tetrahydrofuran solution at room temperature led to the rapid formation of the ring-opened product **8** and cyclobutenone **9.** Finally, complete ring opening of **2g** to afford **8** could be accomplished by stirring an ether solution of **2g** and zinc chloride at room temperature overnight.

In contrast to **2g,** a mixture of siloxycyclobutanones (*E*)- and (*Z*)-**2h** was readily hydrolyzed with dilute acid. Again in

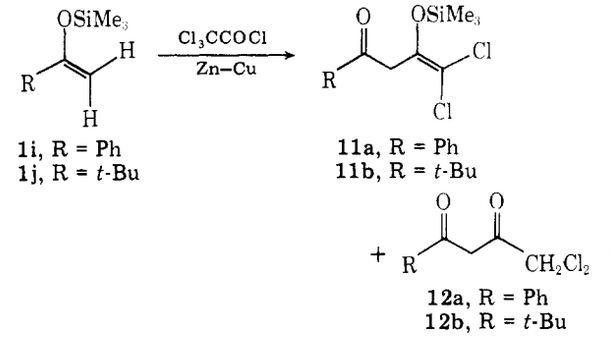


(5)

10

this case, however, hydroxycyclobutanones were not isolated, but rather the cyclobutenone **10**[12] (eq 5).

The reaction of dichloroketene with silyl enol ethers **1i** and **1j,** from acetophenone and pinacolone, respectively, took a different course (eq 6). No cyclobutanone products could be



(6)

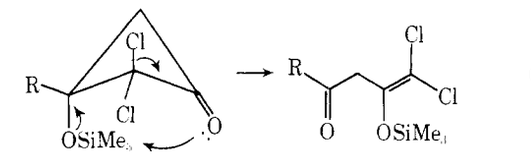
1i, R = Ph
1j, R = *t*-Bu

11a, R = Ph
11b, R = *t*-Bu

12a, R = Ph
12b, R = *t*-Bu

detected in either case. Instead, the acylic products **11** and **12** were isolated in high yields. That these products were not arising from the workup was demonstrated by NMR examination of the reaction mixtures prior to completion. Treatment of **11** with dilute acid led to **12.** Attempts to isolate cyclobutanones from the reaction of dichloroketene with **1i** at lower temperatures were to no avail.

One explanation for the formation of products **11** is a ring opening of an initially formed cyclobutanone species **13** (eq 7). The bulky substituent (R = Ph or *tert*-butyl) might prefer

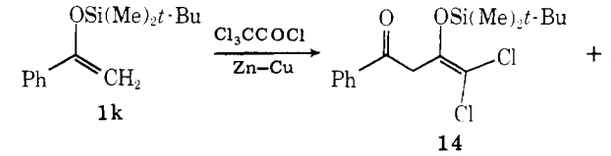


(7)

13 **11**

to occupy an equatorial conformation, forcing the trimethylsiloxy group into an axial conformation. Thus, a situation similar to that suggested for the cyclohexyl system **2c** might occur; attack of carbonyl oxygen on silicon might initiate ring opening to afford the observed products.

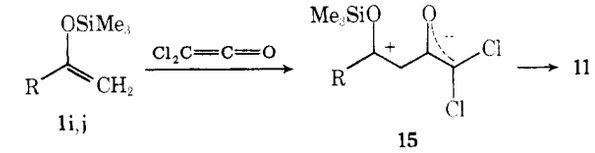
Since the *tert*-butyldimethylsilyl[10] group is much less susceptible to nucleophilic attack than the trimethylsilyl group, it was thought that enol ether **1k** might yield a stable cyclobutanone. However, this was found not to be the case (eq 8), and enol ether **1k** afforded only **14** and **12a** (R = Ph) under the usual reaction conditions.



(8)

1k **14** + **12a**

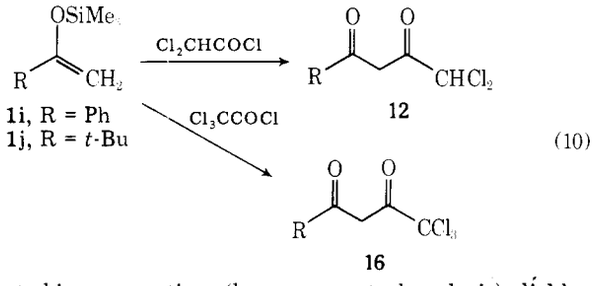
Another possibility for the generation of acyclic products in the reactions of **1i** and **1j** with dichloroketene is that cyclobutanone formation is not involved at all and that dichloroketene simply acylates the enol ether to give an initial zwitterionic species **15** which collapses to **11** (eq 9). The ste-



(9)

1i,j **15**

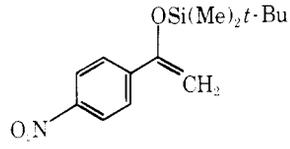
reospecificity of the cycloaddition observed for **1h** (see below) would speak against an ionic intermediate. On the other hand, Murai has reported[7] that silyl enol ethers **1i** and **1j** react with di- and trichloroacetyl chlorides to afford, after hydrolysis, fair (60–67%) yields of the 1,3-diketones **12** and **16,** respectively (eq 10). Although no products corresponding to **16** were



(10)

detected in our reactions (by mass spectral analysis), dichloroketene would of course be expected to be a much more reactive acylating reagent than either di- or trichloroacetyl chloride.

The possibility of destabilizing a zwitterionic species **15** with an electron-withdrawing substituent on the aromatic ring was investigated next. However, silyl enol ether **11** was unchanged

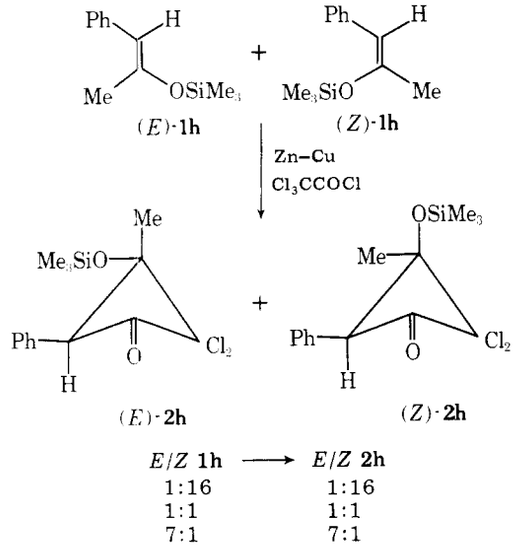


11

after a 3-day reaction with dichloroketene, as evidenced by NMR examination of aliquots from the reaction mixture, and therefore did not provide any positive evidence.

Stereochemistry. An opportunity to study the stereochemistry of the reaction of dichloroketene with silyl enol ethers was presented by the silyl enol ethers **1h,** derived from phenylacetone. The isomeric ratio is clearly evident from the NMR spectrum since the chemical shifts of the vinyl protons are distinct (δ 5.7 for the *E* isomer and δ 5.4 for the *Z* isomer).[11] Since the *E* and *Z* isomers could not be completely separated by either GC or spinning band distillation, various *E*/*Z* mixtures of **1h** were allowed to react with dichloroketene. This led to mixtures of cyclobutanones [(*E*)- and (*Z*)-**2h**] (Scheme II), the ratios of which were identical with the *E*/*Z* ratios of starting material (**1h**). These results suggest that an intermediate dipolar species capable of free rotation is not involved in the cycloadditions described thus far and that the reaction

Scheme II



E/*Z* 1h	*E*/*Z* 2h
1:16	1:16
1:1	1:1
7:1	7:1

of dichloroketene with these silyl enol ethers is a concerted stereospecific cycloaddition.

The siloxycyclobutanones (*E*)- and (*Z*)-**2h** were also found to be sensitive to heating, but ring-opened products, if formed, were not isolated. Thus, bulb to bulb distillation [120 °C (0.02 mm)] of a mixture of (*E*)- and (*Z*)-**2h** led to less than 70% recovery of material, although the IR and NMR spectra of crude and distilled products were superimposable; a dark tar remained in the distillation flask.

In summary, silyl enol ethers have been found to react readily with dichloroketene, affording in most cases good yields of cyclobutanones. Although the regiochemistry of the cyclobutanones suggests electronic control with the possibility of a dipolar intermediate, the stereochemical results indicate that such species do not have an appreciable lifetime.

Experimental Section[13]

General. The silyl enol ether adducts **2** were either partially hydrolyzed to the alcohols upon attempted purification or underwent partial ring opening or elimination during attempted distillation. Hence, they were not submitted to elemental analysis but were identified by consistent IR, NMR, and mass spectra and hydrolysis to **3.**

Trichloroacetyl Chloride. This procedure is a slight modification of the literature procedure.[14]

To a stirred mixture of 97.0 g (0.59 mol) of Cl_3CCO_2H and 3.0 mL of DMF at 85 °C was added 51.0 mL (84.5 g, 0.71 mol) of thionyl chloride dropwise. When addition was complete, heating at this temperature was continued for 2 h. The bath temperature was lowered to 60–65 °C, and the product was distilled (40–45 °C at 20–25 mm) and collected in an ice-cooled receiver. The first few milliliters were discarded. The product was distilled one more time at reduced pressure and finally at atmospheric (625 mm) pressure (collected at 108–110 °C) to yield 74.3 g (70%) of trichloroacetyl chloride.

Activation of Zinc. This procedure is a slight modification of the procedure of Brady.[2a]

A stirred suspension of 10.0 g (0.15 mol) of zinc dust in 40 mL of water was degassed by bubbling N_2 through it for 15 min. Then 750 mg (4.7 mmol) of $CuSO_4$ was added at once. The black suspension was stirred while N_2 bubbled through it for 45 min more. The Zn–Cu couple was collected on a sintered glass funnel under a stream of N_2 and washed successively with 100 mL of degassed water and acetone. The Zn–Cu couple was transferred to a small flask under a stream of N_2 and dried at reduced pressure (0.2 mm) for 2 h. Nitrogen was admitted to the system when the vacuum was broken, and the Zn–Cu couple was stored under N_2 in a tightly stoppered flask.

General Procedure for the Addition of Dichloroketene to Silyl Enol Ethers. The trimethylsilyl enol ethers were prepared by House's procedure[11] and have been previously described. Trichloroacetyl chloride was used within 2 to 3 days of its distillation and zinc within 1 week of its activation.

A 100-mL three-neck flask equipped with a condensor, addition funnel, magnetic stirrer, and N_2 inlet was flame dried while being purged with N_2. When cool, the flask was charged with 5.0 mmol of the silyl enol ether, 7.5 mmol of activated zinc, and 40 mL of anhydrous ether. The mixture was stirred under N_2, and a solution of 6.5 mmol of Cl_3CCOCl in 15 mL of anhydrous ether was added dropwise over a 45-min period. Stirring at room temperature was continued until NMR or GC (a 5 ft × 0.25 in, 10% DC-550 column was used) analysis of aliquots indicated that the silyl enol ether had been consumed. The reaction mixture was then filtered through a pad of Celite and the unreacted zinc washed with a few milliliters of ether. The solution was concentrated in vacuo to ca. 25% of its original volume, an equal volume of pentane was added, and the solution was stirred for a few minutes to precipitate the zinc salts. The solution was decanted from the residue, washed with a cold saturated $NaHCO_3$ solution and brine, and dried over K_2CO_3, and the solvent was removed in vacuo to afford the crude product, which was purified by bulb distillation at reduced pressure.

General Procedure for the Hydrolysis of the Trimethylsilyl Group of the Dichloroketene Adducts. Hydrolysis of the trimethylsilyl group was accomplished by dissolving the dichloroketene adduct in methanol or THF (ca. 1 mmol/10 mL), adding a few drops of a 5% HCl solution, and stirring at room temperature for 1 h. The solvent was removed in vacuo, the residue was dissolved in ether, and the solution was washed with water and brine and dried over K_2CO_3.

The solvent was removed in vacuo and the product purified by bulb to bulb distillation at reduced pressure or by recrystallization.

2,2-Dichloro-3-trimethylsiloxy-4,4-dimethylcyclobutanone (2a). The reaction of 2.0 g (13.8 mmol) of trimethylsilyl enol ether **1a** by the general procedure (9 h) afforded 3.25 g (92%) of **2a** as a yellow oil. Attempted distillation of **2a** led to partial hydrolysis of the trimethylsilyl group. Siloxycyclobutanone **2a:** IR (neat) 1805, 1270, and 860 cm^{-1}; NMR (CCl_4) δ 4.22 (s, 1 H), 1.27 (s, 3 H), 1.17 (s, 1 H), and 0.17 (s, 9 H); MS *m/e* (%) 256 (M + 2, 1.1), 254 (M^+, 1.7), 241 (2.2), 239 (3.2), 193 (4.0), 191 (12.3), 144 (27.2), 129 (14.3), 75 (62.3), 73 (100), and 70 (71.2).

2,2-Dichloro-3-hydroxy-4,4-dimethylcyclobutanone (3a). Hydrolysis of 1.0 g (3.9 mmol) of siloxycyclobutanone **2a** afforded 0.71 g (99%) of a yellow oil which was purified by bulb to bulb distillation (oven 60 °C, 5 mm) to afford 0.59 g (83%) of **3a:** IR (neat) 3600–3350, 1799, 1470, 1130, and 860 cm^{-1}; NMR (CCl_4) δ 4.40 (s, 1 H), 3.9 (broad, OH, 1 H), 1.41 (s, 3 H), and 1.31 (s, 3 H); MS *m/e* (no M^+) 119 (3.1), 114 (1.4), 112 (2.3), 109 (6.8), 72 (17.8), 71 (10.3), 70 (100), 57 (13.3), 44 (7.3), 43 (17.8), 42 (35.7), and 41 (20.6).

Anal. Calcd for $C_6H_8O_2Cl_2$: C, 39.37; H, 4.40. Found: C, 39.28; H, 4.39.

7,7-Dichloro-1-trimethylsiloxybicyclo[3.2.0]heptan-6-one (2b). The reaction of 5.0 g (32 mmol) of trimethylsilyl enol ether **1b** by the general procedure (2 h) afforded 7.2 g (85%) of **2b** as a viscous orange oil. Bulb to bulb distillation (oven 95 °C, 0.02 mm) afforded 6.7 g (79%) of **2b** as a colorless oil which solidified upon refrigeration: IR (neat) 1805 cm^{-1}; NMR (CCl_4) δ 3.6 (broad, 1 H), 2.77–1.43 (6 H), and 0.25 (s, 9 H); MS *m/e* 268 (M + 2, 2.4), 266 (M^+, 3.6), 253 (3.5), 251 (5.4), 225 (4.7), 223 (7.1), 205 (7/[(= 2]3 (23.2), 156 (30.4), 95 (16.1), 93 (32.1), 79 (46.4), 75 (32.1), and 73 (100).

7,7-Dichloro-1-hydroxybicyclo[3.2.0]heptan-6-one (3b). Hydrolysis of 66.0 g (22.6 mmol) of siloxycyclobutanone **2b** afforded 3.87 g (88%) of **3b** which was recrystallized from hexane to afford 3.0 g (68%) of **3b:** mp 57–58 °C; IR (CCl_4) 3560, 1800, 1330, and 110 cm^{-1}; NMR (CCl_4) δ 3.60 (broad, 1 H), 3.23 (broad, OH, 1 H), and 2.8–1.0 (6 H); MS *m/e* 196 (M + 2, 1.4), 194 (M^+, 2.1), 160 (11.6), 158 (17.6), 151 (15.5), 149 (23.5), 133 (6.10), 131 (93.0), 115 (17.6), 113 (52.9), 110 (73.2), 95 (64.7), 85 (88.2), 84 (70.6), 67 (76.5), and 55 (100).

Anal. Calcd for $C_7H_8Cl_2O_2$: C, 43.10; H, 4.13. Found: C, 43.50; H, 4.11.

Generation of Dichloroketene from Dichloroacetyl Chloride in the Presence of 1b. To a stirred solution of 1.0 g (6.4 mmol) of silyl enol ether **1b** and 0.96 mL (1.47 g, 10 mmol) of $Cl_2CHCOCl$ in 30 mL of anhydrous ether was added dropwise a solution of 2.05 mL (1.5 g, 15 mmol) of triethylamine in 15 mL of anhydrous ether. The mixture was stirred for 12 h after addition of the solution was completed and then washed with a 5% HCl solution, a saturated $NaHCO_3$ solution, and brine. The solution was dried over K_2CO_3 and the solvent removed in vacuo to afford 0.62 g of a dark oil, shown to contain mainly (>60%) cyclopentanone by coinjection with an authentic sample into the GC instrument (a 10 ft × 3/8 in, 15% DC-550 column was used for this analysis). At least three minor products were present in the mixture. The presence of **4** in the mixture was implicated by the spectra of the mixture: IR (neat) 3500 tailing to 2500, 1740, 1650–1550, and 1220 cm^{-1}; NMR (CCl_4) δ 12.4 (broad), 6.0 (s), and 3.0–1.2; MS *m/e* 196 and 194. (Compare spectra of **6** below.)

8,8-Dichloro-1-trimethylsiloxybicyclo[4.2.0]octan-7-one (2c). The reaction of 2.0 g (11.7 mmol) of trimethylsilyl enol ether **1c** by the general procedure at 0 °C (3 h) afforded 3.0 g (91%) of **2c** as a viscous yellow oil. Bulb to bulb distillation (oven 110 °C, 0.02 mm) afforded 2.7 g (81%) of **2c** as a slightly yellow oil: IR (neat) 1805, 1270, 1235, and 865 cm^{-1}; NMR (CCl_4) δ 3.7 (broad, 1 H), 2.7–1.2 (8 H), and 0.28 (s, 9 H); MS *m/e* 282 (M + 2, 1.6), 280 (M^+, 2.7), 267 (2.5), 265 (4.1), 219 (5.5), 217 (17.8), 170 (30.1), 155 (15.1), 109 (16.4), 75 (45.2) and 73 (100).

8,8-Dichloro-1-hydroxybicyclo[4.2.0]octan-7-one (3c). Hydroxycyclobutanone **3c** was obtained by a short (45 s) hydrolysis of siloxycyclobutanone **2c** in methanol: IR (CCl_4) 3600–3250, 1805, 1305, 1265, 1230, and 860 cm^{-1}; NMR (CCl_4) δ 3.70 (broad, 1 H), 3.15 (broad, 1 H), and 2.8–1.0 (8 H).

2-(2′,2′-Dichloro-1′-trimethylsiloxyvinyl)cyclohexanone (5). Compound **5** was formed when the Cl_3CCOCl was added too rapidly to a suspension of silyl enol ether **1c** and zinc or when Cl_3CCOCl was used without previous distillation. Compound **5:** IR (neat) 1710, 1620, 1260, 1130, 1050, 980, and 860 cm^{-1}; NMR (CCl_4) δ 3.6 (broad, 1 H), 2.7–1.5 (8 H), and 0.27 (s, 9 H); MS *m/e* 282 (M + 2, 4.3), 280 (M^+, 6.5), 267 (5.8), 265 (9.3), 217 (9.7), 171 (25.8), 155 (9.7), 127 (11.3), 125 (21.0), 95 (6.5), 93 (19.8), 75 (19.4), and 73 (100).

2-Dichloroacetylcyclohexanone (6). Hydrolysis of 1.0 g (3.6 mmol) of **5** afforded 0.72 g (96%) of **6:** IR (CCl_4) 3500 tailing to 2600, 1650–1550, 1270, 1180, 820, and 750 cm^{-1}; NMR (CCl_4) δ 14.6 (broad, 1 H), 6.22 (s, 1 H), and 3.0–1.2 (8 H); MS *m/e* 210 (M + 2, 2.9), 208 (M^+, 4.3), 192 (2.8), 190 (4.1), 165 (12.9), 163 (18.4), 147 (12.2), 145 (36.7), 98 (49.0), 92 (38.8), 91 (32.7), 70 (24.5), and 55 (100).

Preparation of 6 from 1c and Dichloroacetyl Chloride. A solution of 0.5 g (2.9 mmol) of silyl enol ether **1c** and 0.28 mL (0.43 g, 2.9 mmol) of $Cl_2CHCOCl$ in 15 mL of methylene chloride was stirred for 3 days, and then the solvent was removed in vacuo, 10 mL of methanol and 2 drops of a 5% HCl solution were added, and the solution was refluxed for 1 h. The solvent was removed in vacuo to afford 0.53 g of a brown oil, a mixture (ca. 1:1) of cyclohexanone and **6** which was not separated. The spectra of the mixture had absorptions identical with those reported above for **6.**

8,8-Dichloro-1-trimethylsiloxy-4-*tert*-butylbicyclo[4.2.0]-octan-7-one (2d). The reaction of 1.0 g (4.4 mmol) of silyl enol ether **1d** by the general procedure (2 h) afforded 1.4 g of a yellow oil which was purified by bulb to bulb distillation (oven 100 °C, 0.02 mm) to afford 1.25 g of a mixture (ca. 4:1) of **2d** and **3d.** Siloxycyclobutanone **2d:** IR (neat) 1805, 1377, 1270, and 860 cm^{-1}; NMR (CCl_4) δ 3.90–3.40 (1 H), 2.25–0.90 (7 H), 0.93 (s, 9 H), and 0.30 (9 H).

8,8-Dichloro-1-hydroxy-4-*tert*-butylbicyclo[4.2.0]octan-7-one (3d). Hydrolysis of 0.20 g of a mixture of **2d** and **3d** afforded 0.15 g of **3d,** which was recrystallized from hexane to afford 0.12 g of **3d:** mp 118–119 °C; IR (CCl_4) 3550, 1805, and 1377 cm^{-1}; NMR (CCl_4) δ 4.0–3.3 (1 H), 2.90 (broad, OH, 1 H), 2.3–1.2 (7 H), and 1.0 (s, 9 H); MS *m/e* 266 (M + 2, 3.3), 264 (M^+, 5.2), 251 (2.2), 249 (3.3), 203 (8.2), 201 (11.7), 137 (25.2), 69 (23.3), and 57 (100).

Anal. Calcd for $C_{12}H_{18}Cl_2O_2$: C, 54.35; H, 6.84. Found: C, 54.21; H, 6.93.

1-*tert*-Butyldimethylsiloxy-4-*tert*-butylcyclohexene (1e). A solution of 10.0 g (65 mmol) of 4-*tert*-butylcyclohexanone in 40 mL of anhydrous THF was added dropwise to a stirred suspension of 4.0 g (0.1 mol) of potassium hydride in 100 mL of anhydrous THF under N_2. After stirring for 1 h, a solution of 10.6 g (70 mmol) of *tert*-butyldimethylsilyl chloride in 80 mL of anhydrous THF was added dropwise. Stirring was continued for 12 h, excess potassium was destroyed by the cautious addition of a few milliliters of *tert*-butyl alcohol, and the solvent was removed in vacuo. The residue was taken up in 150 mL of ether, and the solution was washed with a 5% HCl solution, a saturated $NaHCO_3$ solution, and brine and dried over K_2CO_3. The solvent was removed in vacuo. Distillation of the residue afforded 10.3 g (59%) of **1e:** bp 100–104 °C (0.7 mm); IR (neat) 1600, 1475, 1375, 1270, 1210, and 900 cm^{-1}; NMR ($CDCl_3$) δ 4.65 (m, 1 H), 2.15–−0.88 (7 H), 0.90 and 0.87 (2 s, 18 H), and 0.08 (s, 6 H).

8,8-Dichloro-1-*tert*-butyldimethylsiloxy-4-*tert*-butylbicyclo[4.2.0]octan-7-one (2e). The reaction of 1.0 g (3.7 mmol) of silyl enol ether **1e** by the general procedure (2 h) afforded 1.4 g of a yellow oil which was purified by bulb to bulb distillation (oven 130 °C, 0.02 mmol) to afford 1.28 g (92%) of **2e:** IR (neat) 1805, 1475, 1375, 1270, 860, and 800 cm^{-1}; NMR (CCl_4) δ 3.92–3.37 (1 H), 2.25–1.1 (7 H), 0.98 (s, 9 H), 0.92 and 0.88 (2 s, 9 H), 0.28 (s, 3 H), and 0.23 (s, 3 H).

2,2-Dichloro-3-trimethylsiloxy-4-methyl-4-phenylcyclobutanone (2f). The reaction of 0.50 g (2.43 mmol) of silyl enol ether **1f** (*E*/*Z* = 70:30)[11] by the general procedure (3 h) afforded 0.66 g (86%) of **2f.** Attempted distillation of **2f** led to partial hydrolysis of the trimethylsilyl group. Siloxycyclobutanone **2f:** IR (neat) 1805, 1265, 1200, 910, 860, 780, and 720 cm^{-1}; NMR (CCl_4) δ 7.32 (s, 5 H), 4.80 (s, 1 H), 1.57 (s, 3 H), and 0.33 (s, 9 H); MS *m/e* (no M^+) 255 (1.7), 235 (2.5), 240 (1.8), 238 (2.8), 208 (18.0), 165 (5.7), 163 (8.3), 134 (23.6), 133 (100), 105 (52.8), 93 (12.5), and 73 (65.3).

2,2-Dichloro-3-hydroxy-4-methyl-4-phenylcyclobutanone (3f). Hydrolysis of 0.50 g (1.58 mmol) of siloxycyclobutanone **2f** followed by bulb to bulb distillation (oven 120 °C, 0.02 mm) afforded 0.33 g (85%) of **3f:** IR (neat) 3600–3300, 1800, 1500, 1450, 1170, 860, 775, and 715 cm^{-1}; NMR (CCl_4) δ 7.38 (s, 5 H), 4.90 (s, 1 H), 3.57 (broad s, 1 H), and 1.62 (s, 3 H); MS *m/e* (no M^+) 183 (3.1), 181 (9.4), 165 (6.3), 163 (14.1), 133 (100), 105 (32.8), and 77 (57.8).

2,2-Dichloro-3-phenyl-3-trimethylsiloxy-4-methylcyclobutanone (2g). The reaction of 2.0 g (9.7 mmol) of silyl enol ether **1g** by the general procedure (2 h) afforded 2.88 g (94%) of **2g.** Attempted distillation (120 °C, 0.02 mm) of **2g** led to partial ring opening. Siloxycyclobutanone **2g:** IR (neat) 1810, 1450, 1260, 1160, 1040, 910, 860, and 710 cm^{-1}; NMR (CCl_4) δ 7.42 (s, 5H); 4.25 (q, J = 7 Hz, 1 H), 1.38 (d, J = 7 Hz, 3 H), and −0.013 (s, 9 H); MS *m/e* (no M^+) 284 (2.1), 282 (5.4), 262 (4.4), 260 (7.0), 129 (10.4), 122 (10.0), 117 (8.6), 106 (8.8), 105 (100), 93 (8.0), 77 (26.2), 75 (8.5), and 73 (35.7).

1,1-Dichloro-2-trimethylsiloxy-3-methyl-4-phenylbut-1-en-4-one (7). Heating 1.4 g (4.4 mmol) of siloxycyclobutanone **2g** for 2 h at 200 °C followed by bulb to bulb distillation (oven 115 °C, 0.02 mm) afforded 0.96 g of a mixture (ca. 1:1) of **7** and **8.** Compound **7:** IR

(neat) 1690 cm^{-1}; NMR (CCl_4) δ 7.9–7.5 (5 H), 4.65 (q, J = 7 Hz, 1 H), 1.32 (d, J = 7 Hz, 3 H), and 0.08 (s, 9 H). The spectral properties of **8** are reported below.

1,1-Dichloro-3-methyl-4-phenylbutane-2,4-dione (8). A solution of 0.20 g (0.63 mmol) of siloxycyclobutanone **2g** and 0.20 g (1.5 mmol) of zinc chloride in 15 mL of ether was stirred for 15 h. It was then poured into 25 mL of pentane, the solution was washed with a saturated $NaHCO_3$ solution and dried over K_2CO_3, and the solvents were removed in vacuo to afford 144 mg (94%) of **8:** IR (neat) 1740, 1675, 1450, 1280, 975, and 710 cm^{-1}; NMR (CCl_4) δ 8.07 (m, 2 H), 7.60 (m, 3 H), 6.08 (s, 1 H), 5.13 (q, J = 7 Hz, 1 H), and 1.50 (d, $J \approx 7$ Hz, 3 H); MS m/e (no M^+) 210 (1.4), 208 (4), 174 (10.4), 161 (4.0), 134 (4.0), 117 (15.0), 116 (13.0), 115 (4.0), 105 (100), and 77 (42.0).

2,2-Dichloro-3-phenyl-4-methylcyclobutenone (9). A solution of 0.50 g (1.5 mmol) of siloxycyclobutanone **2g** and 3 drops of concentrated HCl in 15 mL of THF was refluxed for 15 h. The solvent was removed in vacuo, 25 mL of ether was added to the residue, and the solution was washed with a saturated $NaHCO_3$ solution. The solution was dried over K_2CO_3 and the solvent removed in vacuo to afford 0.34 g of a yellow oil which was purified by bulb to bulb distillation (oven 120 °C, 0.02 mm) to afford 0.28 g (78%) of **9:** IR (CCl_4) 1780, 1610, 1450, 1350, and 860 cm^{-1}; NMR (CCl_4) δ 8.0 (m, 2 H), 7.67 (m, 3 H), and 2.20 (s, 3 H); MS m/e 228 (M + 2, 7.8), 226 (M^+, 12.3), 165 (7.6), 163 (22.7), 161 (7.2), 128 (8.2), 127 (6.3), 122 (9.6), 77 (100), and 51 (17.1).

Reaction of 2g with Fluoride Ion. A solution of 0.50 g (1.6 mmol) of siloxycyclobutanone **2g** and 0.42 g (1.6 mmol) of tetrabutylammonium fluoride in 15 mL of THF was stirred for 1 h, the solvent was removed in vacuo, and 40 mL of hexane was added to the residue. The solution was washed with water and dried over K_2CO_3, and the solvent was removed in vacuo to afford 0.35 g of a mixture (ca. 2:1) of **8** and **9** as determined by NMR spectroscopy.

2,2-Dichloro-3-methyl-3-trimethylsiloxy-4-phenylcyclobutanone [(*E*)- and (*Z*)-2h]. The reaction of 1.0 g (4.85 mmol) of a mixture (*E*/*Z*, 1:16)[12] of silyl enol ethers **1h** by the general procedure (3 h) afforded 1.4 g of a mixture (1:16 by NMR spectroscopy) of (*E*)- and (*Z*)-**2h.** Bulb to bulb distillation (oven 100 °C, 0.02 mm) afforded 0.9 g (59%) of an identical mixture. The spectra of the crude and distilled mixtures were identical. The mixture: IR (neat) 1805, 1260, 1210, 1030, 860, and 710 cm^{-1}; MS m/e (no M^+) 282 (4.4), 280 (6.7), 228 (5.5), 226 (8.3), 165 (3.3), 163 (11.7), 149 (20.0), 148 (40.0), 147 (100), 105 (21.7), 95 (5.8), 93 (15.0), 77 (20.2), 75 (22.2), and 73 (61.7). Siloxycyclobutanone (*E*)-**2h:** NMR (CCl_4) δ 7.2 (broad s, 5 H), 5.02 (s, 1 H), 1.23 (s, 3 H), and 0.28 (s, 9 H). Siloxycyclobutanone (*Z*)-**2h:** NMR (CCl_4) δ 7.2 (broad s, 5 H), 4.75 (s, 1 H), 1.82 (s, 3 H), and −0.12 (s, 9 H).

The reaction of a 7:1 *E*/*Z* mixture of silyl enol ethers **1h** afforded (*E*)-**2h** and (*Z*)-**2h** in a ratio of 7:1. The reaction of other *E*/*Z* mixtures also yielded (*E*)- and (*Z*)-**2h** in ratios identical with those of the starting silyl enol ether.

2,2-Dichloro-3-methyl-4-phenylcyclobutenone (10). Hydrolysis of 0.50 g (1.58 mmol) of a mixture of siloxycyclobutanones (*E*)- and (*Z*)-**2h** afforded 0.34 g of a yellow oil which was purified by bulb to bulb distillation (oven 110 °C, 0.02 mm) to afford 0.29 g (81%) of **10:** IR (CCl_4) 1780, 1620, 1380, 930, 850, and 700 cm^{-1}; NMR (CCl_4) δ 7.7 (m, 2 H), 7.5 (m, 3 H), and 2.55 (s, 3 H); MS m/e 228 (M + 2, 8.3), 226 (M^+, 12.7), 163 (27.3), 161 (9.0), and 77 (100).

1,1-Dichloro-2-trimethylsiloxy-4-phenylbut-1-en-4-one (11a). The reaction of 5.0 g (26 mmol) of silyl enol ether **1i** by the general procedure (2 h) afforded 7.5 g of a yellow oil as a 4:1 mixture of **11a** and **12a.** Distillation (90–95 °C, 0.02 mm) led to a 2.5:1 mixture of **11a** and **12a.** Compound **11a:** IR (neat) 1690, 1270, 1040, 1000, 870, 780, and 710 cm^{-1}; NMR (CCl_4) δ 7.9 (m, 2 H), 7.4 (m, 3 H), 3.9 (s, 2 H), and 0.15 (s, 9 H).

1,1-Dichloro-4-phenylbutane-2,4-dione (12a). Hydrolysis of 2.0 g of a mixture of **11a** and **12a** afforded, after bulb to bulb distillation (oven 110 °C, 0.02 mm), 1.3 g of **12a:** IR (neat) 3400 tailing to 2600, 1650–1550, 1270, 775, and 720 cm^{-1}; NMR (CCl_4) δ 14.3 (broad, 1 H), 7.9 (m, 2 H), 7.4 (m, 3 H), 6.58 (s, 1 H), and 5.93 (s, 1 H); MS m/e 232 (M + 2, 4.3), 230 (M^+, 6.3), 196 (2.7), 194 (4.2), 168 (8.3), 147 (100), 105 (33.3), 77 (47.9), and 69 (74.8).

1,1-Dichloro-2-trimethylsiloxy-5,5-dimethylhex-1-en-4-one (11b). The reaction of 2.0 g (11.6 mmol) of silyl enol ether **1j** by the general procedure (7 h) afforded 3.0 g of a mixture (ca. 4:1) of **11b** and **12b.** Compound **11b:** IR (neat) 1720, 1630, 1470, 1300, 1270, 1040, 1020, and 870 cm^{-1}; NMR (CCl_4) δ 3.42 (s, 2 H), 1.12 (s, 9 H), and 0.17 (s, 9 H).

1,1-Dichloro-5,5-dimethylhexane-2,4-dione (12b). Hydrolysis of 0.50 g of a mixture of **11b** and **12b** followed by bulb to bulb distillation (oven 90 °C, 0.02 mm) afforded 0.31 g of **12b:** IR (neat) 1650–1550, 1375, 1320, 1235, 1150, and 800 cm^{-1}; NMR (CCl_4) δ 14.3 (broad, 1 H), 5.96 (s, 1 H), 5.76 (s, 1 H), and 1.18 (s, 9 H); MS m/e 212 (M + 2, 10.4), 210 (M^+, 15.3), 155 (45.4), 153 (73.7), 127 (100), 120 (34.0), 118 (63.8), and 57 (70.3).

1-*tert*-Butyldimethylsiloxy-1-phenylethylene (1k). Silyl enol ether **1k** was prepared by a reaction analogous to that described for **1e.** Distillation afforded a 35% yield of **1k:** bp 95–100 °C (3 mm); IR (neat) 1600 cm^{-1}; NMR (CCl_4) δ 7.6–7.0 (m, 5 H), 4.75 (broad s, 1 H), 4.27 (broad s, 1 H), 0.95 (s, 9 H), and 0.12 (s, 6 H).

1,1-Dichloro-2-*tert*-butyldimethylsiloxy-4-phenylbut-1-en-4-one (14). The reaction of 0.50 g of silyl enol ether **1k** by the general procedure (1 h) afforded 0.66 g of a mixture (ca. 2.5:1) of **14** and **12a.** Compound **14:** IR (neat) 1690 cm^{-1}; NMR (CCl_4) δ 7.92 (m, 2 H), 7.45 (m, 3 H), 3.92 (s, 2 H), 0.85 (s, 9 H), and 0.15 (s, 6 H).

1-*tert*-Butyldimethylsiloxy-1-(4-nitrophenyl)ethylene (1l). Silyl enol ether **1l** was prepared by a reaction analogous to that described above for **1e.** Distillation afforded a 22% yield of **1l:** bp 125–128 °C (0.1 mm); IR (neat) 1590, 1520, 1350, 1320, 1260, 1110, 1020, 850, and 800 cm^{-1}; NMR (CCl_4) δ 8.27 (d, J = 8 Hz, 2 H), 7.73 (d, J = 8 Hz, 2 H), 5.0 (d, J = 2 Hz, 1 H), 4.55 (d, J = 2 Hz, 1 H), 1.0 (s, 9 H), and 0.22 (s, 6 H).

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Registry No.—(*E*)-**1f,** 51425-64-0; **1i,** 13735-81-4; **1j,** 17510-46-2; **1k,** 66324-10-5; **1l,** 64600-20-0; (*E*)-**2h,** 66323-87-3; (*Z*)-**2h,** 66323-88-4; **4,** 66323-95-3; **5,** 66323-89-5; **6,** 66323-90-8; **7,** 66323-91-9; **8,** 66323-92-0; **9,** 66323-93-1; **10,** 34647-96-6; **11a,** 66323-94-2; **11b,** 66323-97-5; **12a,** 37471-43-5; **12b,** 26709-24-0; **14,** 66323-96-4; Cl_3CCO_2H, 76-03-9; Cl_3CCOCl, 76-02-8; $Cl_2C{=}C{=}O$, 4591-28-0; $Cl_2CHCOCl$, 79-36-7; 4-*tert*-butycyclohexanone, 98-53-3; *tert*-butyldimethylsilyl chloride, 18162-48-6.

References and Notes

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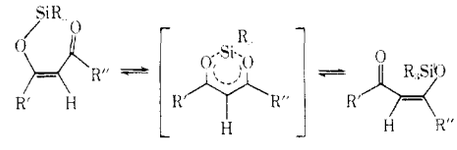
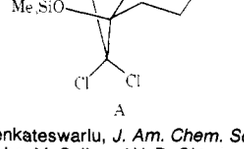


(9) The cycloaddition of dichloroketene to cyclohexene systems has been demonstrated [A. Hassner, V. R. Fletcher, and D. P. G. Hamon, *J. Am. Chem. Soc.,* **93,** 264 (1971)] to be highly regioselective; that is, the newly formed bond of the carbonyl carbon will prefer to be axial with respect to the six-membered ring. On this basis, the cycloaddition of dichloroketene to silyl enol ether **1d** is assumed to generate siloxycyclobutanone **2d** rather than the other possible isomer, A (*tert*-butyl and siloxy trans).



A

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(13) Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra were obtained of liquid films or carbon tetrachloride solutions as noted on a Perkin-Elmer 457 instrument. NMR spectra were recorded on Varian A-60A or EM-360 spectrometers with Me_4Si as an internal standard. GC data were recorded on a Varian Aerograph A90-P3 instrument with a thermal conductivity detector. Mass spectra were recorded on a Varian MAT CH5 instrument. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga.

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Synthesis of 2-Substituted 4-Oxahomoadamantanes

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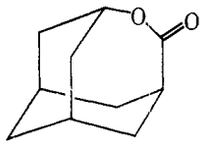
An entry into 2-substituted 4-oxahomoadamantanes has been developed. Treatment of bicyclo[3.3.1]non-6-ene-3-*endo*-methanol with *m*-chloroperbenzoic acid gives 2-*exo*-hydroxy-4-oxahomoadamantane (**8**). Jones oxidation of **8** provides the corresponding ketone, which undergoes reduction with sodium borohydride to give exclusively 2-*endo*-hydroxy-4-oxahomoadamantane. Extensions of this reaction permit the preparation of 2,5-disubstituted and 2,5,5-trisubstituted 4-oxahomoadamantanes. An improved synthesis of 4-oxahomoadamantane is also noted, and its ^{13}C NMR spectrum is reported.

The synthesis, chemistry, and pharmacology of heteroadamantanes and related cage compounds have attracted considerable attention.[2] With the exception of 4-oxahomoadamantan-5-one[3,4] (**1**) and its derivatives,[5] the only substituted 4-oxahomoadamantanes which are known are compounds **2–6**.[6] We now wish to report the stereoselective



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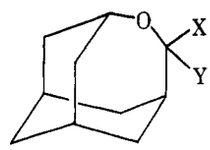
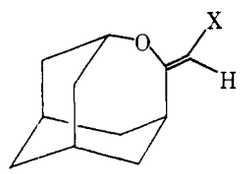


2, X = OH; Y = CH_3
3, X = OH; Y = CH_2Cl
4, X = I; Y = CH_2I



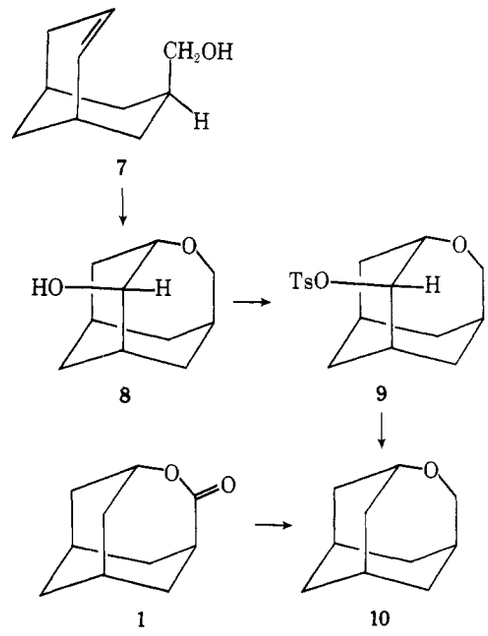
5, X = H
6, X = I

synthesis of both 2-*exo*-hydroxy- and 2-*endo*-hydroxy-4-oxahomoadamantane.[7] Extensions of the reactions employed to prepare these compounds permit the synthesis of 2,5-disubstituted and 2,5,5-trisubstituted 4-oxahomoadamantanes.

Results and Discussion

Treatment of bicyclo[3.3.1]non-6-ene-3-*endo*-methanol[3a,4a] (**7**) with *m*-chloroperbenzoic acid affords 2-*exo*-hydroxy-4-oxahomoadamantane (**8**) in ca. 70% yield. The skeletal framework of **8** follows from its conversion to the known ether,[3a,8] 4-oxahomoadamantane (**10**). Reaction of **8** with *p*-toluenesulfonyl chloride in pyridine gives exo tosylate **9**. Subsequent treatment of **9** with lithium aluminum hydride provides **10**. Owing to some minor discrepancies between the ^1H NMR parameters observed for **10** and those previously reported for this compound,[9] ether **10** was also synthesized by an independent route. Treatment of lactone **1** with boron trifluoride etherate and lithium aluminum hydride provides **10** in 95% yield. The physical and spectral properties of **10** prepared by these independent routes are identical. Moreover, consistent with the presence of a plane of symmetry in **10**, the ^{13}C NMR spectrum of **10** contains only seven signals and three of these signals are twice as intense as the others.[10] Since the reported syntheses of **10** all either proceed in low yield and/or give mixtures of reaction products[3a,8] and since **1** can readily be prepared from commercially available 2-adamantanone[3] (**11**), the route **11** → **1** → **10** appears to be the method of choice for the synthesis of 4-oxahomoadamantane.

The assigned skeletal position and stereochemistry of the hydroxyl substituent in **8** follow in part from its mode of synthesis. Thus, **7** → **8** is rationalized as occurring by initial epoxidation of **7** from the less sterically encumbered face of the carbon–carbon double bond to give **12**, which then undergoes intramolecular nucleophilic attack by the hydroxylic oxygen to provide **8**. In order to firmly establish the stereochemistry at C-2 in **8**, the C-2 epimer of **8** was also prepared. Oxidation of **8** with Jones reagent gives 4-oxahomoadamantan-2-one (**13**), and sodium borohydride reduction of **13** provides 2-*endo*-hydroxy-4-oxahomoadamantane (**14**). In an earlier study we were not able to devise GLC conditions



7

8

9

1

10

0022-3263/78/1943-3179$01.00/0