Halogenated Ketenes. 36. Reactions of Chloroketenes with Ketene Acetals

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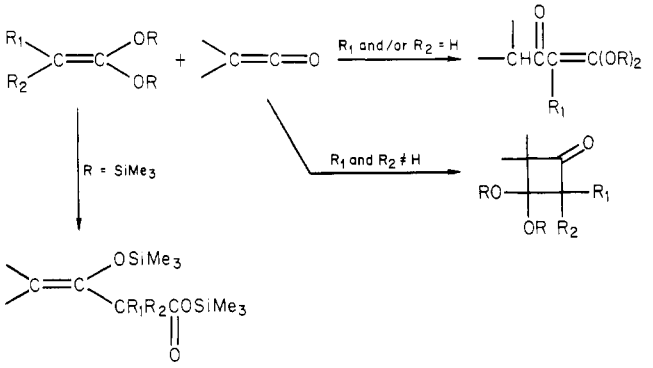
The products of the reactions of ketenes and ketene acetals are dependent upon substitution in the ketene acetals. Dichloroketene reacts with dimethylketene dimethyl acetal to regiospecifically yield the cyclobutanone. The reaction of methylchloroketene and ketene diethyl acetal yields an acyclic product, an acylketene acetal. Chloro-, dichloro-, and methylchloroketenes react with O-silylated ketene acetals to yield acyclic unsaturated esters. Dichloroketene reacts with the acylketene acetal, (α-chloropropionyl)ketene diethyl acetal, to yield a (4 + 2) cycloaddition product, a δ-lactone. All of these results are consistent with a two-step process involving a dipolar intermediate.

Ketene acetals are electron-rich olefins and well suited for cycloaddition reactions with ketenes. The scattered reports in the literature reveal that unsubstituted or monosubstituted ketene acetals usually yield acyclic products[1-3] and disubstituted ketene acetals yield the expected cyclobutanones in a regiospecific manner. Recently, O-silylated ketene acetals have been reported to yield acyclic products.[5,6]

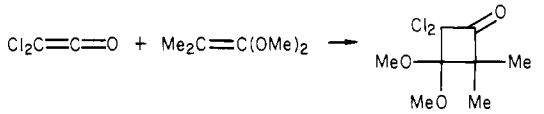


Certain ketenes react with ketene acetals in contrast to the above scheme. Ketene diethyl acetal reacts with ketene and (trimethylsilyl)ketene to yield an oxetane[7] and cyclobutanone,[8] respectively.

Ketenes react with the electron-rich tetraalkoxyethylenes in good yields to form tetraalkoxycyclobutanones. These cycloaddition products are intermediates in the synthesis of squaric acid,[9] semisquaric acid,[10] and 2-substituted semisquaric acids.[11,12] It is pertinent to realize that tetraalkoxyethylenes are disubstituted ketene acetals, i.e., acetals of dialkoxyketenes. Diphenylketene reportedly reacts with tetramethoxyethylene to yield an oxetane rather than the corresponding cyclobutanone.[13]

These varied results prompted us to investigate the reaction of the more reactive and synthetically versatile chloroketenes with ketene acetals in an effort to develop some new synthetic pathways and methodology.

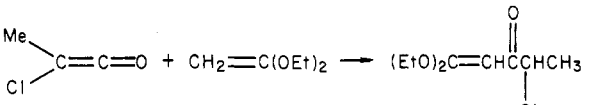
The in situ generation of dichloroketene from dichloroacetyl chloride and triethylamine in the presence of the dimethyl acetal of dimethylketene resulted in the formation of a single 1:1 adduct in an 82% yield. The



1

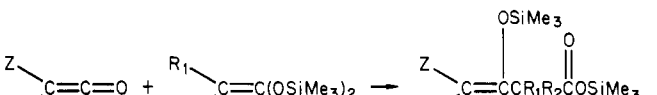
NMR spectrum of this product revealed two singlets of equal intensity appearing at δ 1.3 (2-CH_3) and 3.40 (2-O-CH_3) and a carbonyl band in the infrared at 1805 cm^{-1} characteristic of cyclobutanones. The structure of this particular regioisomer was assigned as 1 based on a comparison of the NMR data with the tetramethoxyethylene cycloadduct and known regiochemistry of ketene cycloadditions.[12]

The in situ generation of methylchloroketene from α-chloropropionyl chloride and triethylamine in the presence of ketene diethyl acetal resulted in the formation of an acyclic product, 4-chloro-1,1-diethoxy-1-penten-3-one (2), an acylketene acetal. The IR spectrum of 2 revealed a band at 1605 and 1595 cm^{-1}. The two ethoxy groups are nonequivalent as evidenced by the NMR spectrum and the vinyl proton appeared at δ 4.20.



2

Some readily available bis(trimethylsilyl)ketene acetals were reacted with dichloro-, methylchloro-, and chloroketenes by the in situ generation of the ketenes in the presence of the ketene acetals. Acylic products were



3, Z = Me; R_1 = H; R_2 = OMe
4, Z = Cl; R_1 = H; R_2 = OMe
5, Z = H; R_1 = H; R_2 = OMe
6, Z = Me; R_1 = H; R_2 = $OSiMe_3$
7, Z = Cl; R_1 = H; R_2 = $OSiMe_3$
8, Z = H; R_1 = H; R_2 = $OSiMe_3$
9, Z = Me; R_1 = Me; R_2 = Me
10, Z = Cl; R_1 = Me; R_2 = Me
11, Z = H; R_1 = Me; R_2 = Me

formed in yields of at least 80% and were liquids that distilled under reduced pressure. The IR spectra of the unsaturated esters revealed the carbonyl absorption at

(1) Scarpati, R.; Sica, D.; Santacroce, C. *Tetrahedron* **1964**, *20*, 2735.
(2) Scharf, H. D.; Sporrer, E. *Synthesis* **1975**, 733.
(3) Scarpati, R.; Sica, D. *Rend. Acad. Sci. Fis. Mat. Naples* [IV], **1961**, *27*, 70.
(4) Scarpati, R.; Sica, D. *Gazz. Chim. Ital.* **1962**, *92*, 1073.
(5) Burlachenko, G. S.; Baukov, Y. I.; Lutsenko, I. F. *J. Gen. Chem. USSR, (Engl. Trans.)* **1970**, *40*, 88.
(6) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1979**, *44*, 733.
(7) Kato, T.; Yamamoto, Y.; Takeda, S. *Yakugaku Zasshi* **1974**, *94*, 884.
(8) Zaitseva, G. S.; Baukov, Y. I.; Maltsev, V. V.; Lutsenko, I. F. *Zh. Obshch. Khim.* **1974**, *44*, 1415 (Engl. Ed., p 1389).
(9) Bellus, D. *J. Org. Chem.* **1979**, *44*, 1208.
(10) Brady, W. T.; Saidi, K. *J. Org. Chem.* **1980**, *45*, 727.
(11) Bellus, D. *J. Am. Chem. Soc.* **1978**, *100*, 8026.
(12) Brady, W. T.; Watts, R. D. *J. Org. Chem.* **1980**, *45*, 3525.
(13) Hoffman, R. W., Bressel, U.; Gehlhause, J.; Hauser, H. *Chem. Ber.* **1971**, *104*, 873.

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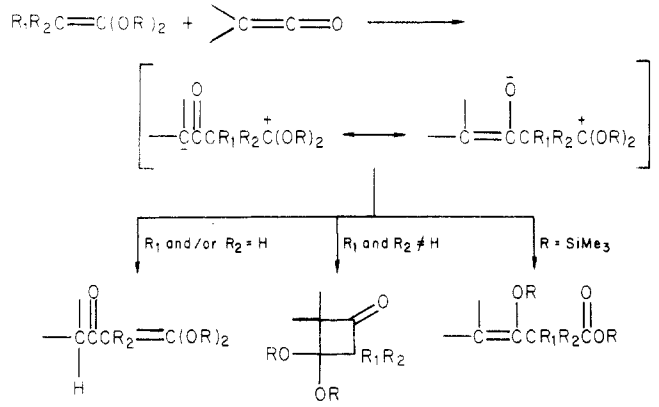
1720–1750 cm^{-1} and the carbon–carbon unsaturation at 1615–1670 cm^{-1}.

The NMR spectra revealed that the reaction of methylchloroketene and the bis(trimethylsilyl)ketene acetals yielded an equal mixture of the geometrical isomers.

All of the above results are consistent with a two-step mechanistic pathway involving a dipolar intermediate as originally proposed by Scarpati and co-workers.[1] If the



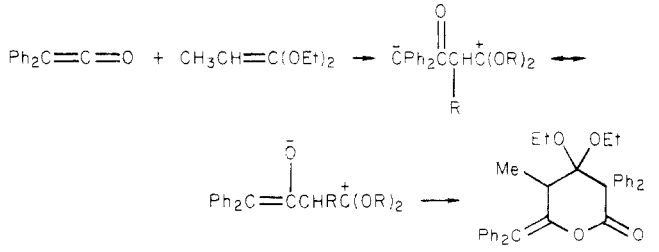
ketene acetal is unsubstituted or monosubstituted there is a hydrogen α to the carbon containing a positive charge and the loss of this hydrogen as a proton yields the acylketene acetal. This is what we observed in the reaction of methylchloroketene with the diethyl acetal of ketene and is consistent with literature reports.[1,2]

The dipolar intermediate from a disubstituted ketene acetal and a ketene undergoes ring closure to the cyclobutanone derivative. This is what we observed with dichloroketene and the dimethyl acetal of dimethylketene and is consistent with the literature report.[4]

The dipolar intermediate from a ketene and an O-silylated ketene acetal achieves stabilization by a 1,5-silyl migration to yield the unsaturated ester. This unexpected result was a disappointment because the readily available O-silylated ketene acetals appear to be not useful in reactions with ketenes to yield desirable synthetic products.

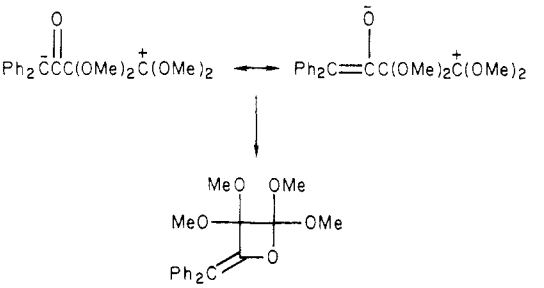
The following observations are also offered in support of the above described mechanism.

1. In the original report by Scarpati and co-workers,[1] the dipolar intermediate was inadvertently trapped by the reaction of 2 equiv of diphenylketene with 1 equiv of methylketene diethyl acetal although it apparently was not recognized as a trapping of this intermediate.



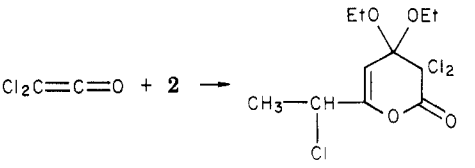
2. A more recent report describes the reaction of methylketene with triethoxy(trimethylsiloxy)ethylene to yield both the unsaturated ester and the cyclobutanone.[14] Both products are consistent with the dipolar intermediate.

3. The anomalous results observed in the reaction of diphenylketene and tetramethoxyethylene are consistent with the dipolar intermediate. Conjugation with the two phenyl substituents is retained if ring closure occurs from the enolate.



Although a recent report[5] on the reaction of diphenylketene with *O*-(trimethylsilyl)-*O*-methyl ketene acetal of ketene proposes a cyclic six-membered transition state, we feel the evidence we have presented and an examination of the literature strongly support the dipolar intermediate even in reactions with O-silylated ketene acetals.

(α-Chloropropionyl)ketene diethyl acetal (**2**) reacted with dichloroketene, generated by the triethylamine dehydrochlorination of dichloroacetyl chloride, to yield a (4 + 2) product rather than the (2 + 2) adduct. The δ-lac-

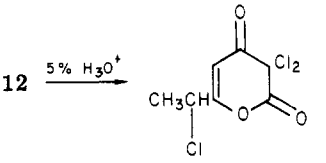


12

tone, 6-(1-chloroethyl)-3,3-dichloro-4,4-diethoxy-3,4-dihydro-2*H*-pyran-2-one (**13**) was formed in 25% yield. The remaining acylketene acetal was recovered. Numerous attempts at varying the reaction conditions did not improve the yield. Apparently, the electron-withdrawing ability of the acyl group decreases the electron density of the π-system such that the dichloroketene polymerization favorably competes with the cycloaddition process.

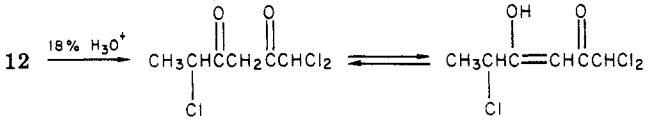
The δ-lactone revealed a band in the IR at 1794 cm^{-1} (C=O) and 1695 cm^{-1} (C=C). The frequency of these bands are consistent with the 3,3-dichloroenolic δ-lactones.[15,16] The NMR spectrum revealed that the two geminal ethoxy groups are equivalent.

Mild acid-catalyzed hydrolysis of **12** led to the formation of the expected β-keto δ-lactone, **13**. The NMR spectrum



revealed the loss of the two ethoxy substituents and a downfield shift of the vinyl proton from δ 5.35 to 6.70. The IR spectrum showed two carbonyl groups at 1760 and 1680 cm^{-1} and a shift to a lower frequency of the carbon-carbon double bond at 1620 cm^{-1}.

A more vigorous hydrolysis of **12** led to the formation of a ring-opened product, 1,1,5-trichloro-2,4-hexanedione (**14**) through the loss of carbon monoxide. The IR spec-



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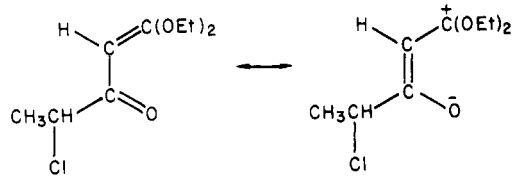
(14) Bellus, D. "Oxocarbons"; West, R., Ed.; Academic Press: New York, 1980.

(15) Bargagna, A.; Evangelisti, F.; Schenone, P. *J. Heterocycl. Chem.* **1979**, *16*, 93.

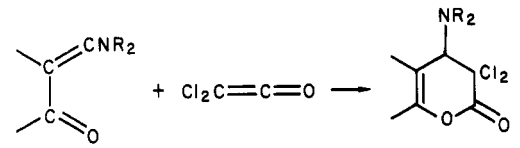
(16) Mosti, L.; Schenone, P.; Menozzi, G. *J. Heterocycl. Chem.* **1978**, *15*, 181.

trum of the tautomers revealed absorptions at 3500 (OH), 1765 (C=O), and 1610 cm^{-1} (C=C). The NMR spectrum indicated an enolic proton at δ 13.5 and one of equal intensity at δ 6.10. This spectrum revealed a equal mixture of the two tautomers based on integrations of these protons.

The polar 1,4-cycloaddition of dichloroketene to **2** arises from the nucleophilic nature of the oxygen of the acyl group of the ketene acetal. The increased electron density on this oxygen is due to the α,β-unsaturation and the electron-releasing ability of the geminal alkoxy groups β to the carbonyl. The nucleophilic oxygen atom attacks the electron deficient sp-hybridized carbon of the ketene to form the dipolar intermediate which subsequently undergoes ring closure to yield the δ-lactone.

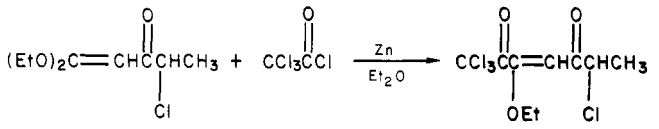


Scarpati and co-workers[1] reported an analogous (4 + 2) adduct as being formed in the reaction of diphenylketene with an acylketene. Shenone and co-workers[15,16] have reported on several examples of (4 + 2) cycloadditions of dichloroketene with N,N-disubstituted vinyl ketones to yield δ-lactones or 2-pyrone derivatives.



We observed that dichloroketene undergoes a similar (4 + 2) cycloaddition with acetylketene diethyl acetal and chloroacetylketene diethyl acetal.

In an effort to improve the yield of **12**, the ketene was generated from trichloroacetyl chloride and zinc in ether. A 90% yield of an acyclic dione, **15**, was isolated rather than the expected δ-lactone. The acid chloride adds to the carbon–carbon double bond of the acylketene and then apparently a Boord elimination occurs to yield the dione.



15

It would appear that all ketene reactions with electron-rich olefins occur through a two-step dipolar intermediate. The determining factor between a concerted and two-step process seems to be the ability of electron-donating substituents to stabilize the positive charge in the dipolar intermediate. If there is not sufficient stabilization such as in simple olefins, a concerted process with some charge separation in the transition state occurs which is responsible for the regiochemistry. However, if there are substituents in the olefin capable of stabilizing the positive charge, then the process is not concerted but two-step, i.e., imines, carbodiimides, ketene acetals, enamines, etc. It is even likely that vinyl ethers and silyl enol ethers undergo cycloaddition with ketenes through a dipolar intermediate.

Experimental Section

Proton NMR were recorded on a Perkin-Elmer R-24B NMR spectrometer employing CCl_4 as the solvent and chloroform or tetramethylsilane as the internal standard. The infrared spectra were obtained on a Beckman IR 33 spectrometer. Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6E double focusing spectrometer and a Finnigan GC/MS 3200 with a 6100 Data System.

Hexane, ether, and triethylamine were dried and purified by distillation from sodium potassium alloy prior to use. α-Chloropropionyl chloride was prepared from the corresponding acid and thionyl chloride. Chloroacetyl chloride, dichloroacetyl chloride, trichloroacetyl chloride, isobutyric acid, methoxyacetic acid, and glycolic acid were purchased from Aldrich Chemical Company, Inc.

Zinc was activated by a standard procedure.[17]

Ketene diethyl acetal was prepared by the dehydrobromination of α-bromoacetaldehyde diethyl acetal with potassium *tert*-butoxide.[18]

Dimethylketene bis(trimethylsilyl) acetal was prepared from isobutyric acid by reaction with lithium diisopropylamide at 0 °C followed by the addition of trimethylchlorosilane.[19] Tris(trimethylsiloxy)ethylene and 2-methoxy-1,1-bis(trimethylsiloxy)ethylene were prepared according to a procedure described by Wissner.[20]

Dimethylketene dimethyl acetal was prepared by the dealcoholation of methyl orthoisobutyrate.[21,22]

The halogenated ketenes were generated in situ and trapped with the appropriate ketene acetal. Methylchloro-, dichloro-, and chloroketene were generated via the dehydrochlorination of α-chloropropionyl chloride, dichloroacetyl chloride, and chloroacetyl chloride, respectively.

2,2-Dichloro-3,3-dimethoxy-4,4-dimethylcyclobutanone (1). A 3.7-g (0.025 mol) portion of dichloroacetyl chloride in 100 mL of dry hexane was added over a 2-h period at 22–24 °C to 200 mL of dry hexane containing 2.9 g (0.025 mol) of dimethylketene dimethyl acetal and 2.8 g (0.0275 mol) of triethylamine. The solution was stirred overnight. The amine salt was removed by filtration and the filtrate concentrated and the residue vacuum distilled at 39–40 °C (0.05 mm) to yield 4.65 g (82%): Ir (neat) 1805 cm^{-1}; NMR δ 1.30 (s, 6 H), 3.40 (s, 6 H); mass spectrum, *m/e* (M) 226.

Anal. Calcd for $C_8H_{12}O_3Cl_2$: C, 42.31; H, 5.28. Found: C, 42.19; H, 5.23.

(α-Chloropropionyl)ketene Diethyl Acetal (2). A solution of 3.15 g (0.025 mol) freshly distilled α-chloropropionyl chloride in 100 mL of dry hexane was added over 2 h to a stirred mixture of 2.9 g (0.025 mol) of ketene diethyl acetal and 2.8 g (0.0275 mol) of triethylamine in 200 mL of dry hexane at 22–24 °C under a nitrogen atmosphere. After the addition was complete the mixture was stirred overnight. The amine salt was removed by filtration and the filtrate was concentrated on a rotatory evaporator. The residue was vacuum distilled to yield the acylketene acetal, which distilled at 87–89 °C (0.05 mm) to give 4.39 g (85%): IR (neat) 1605, 1580 cm^{-1}; NMR δ 0.70–1.05 (m, 9 H), 3.35–4.10 (m, 5 H), 4.20 (s, 1 H); mass spectrum, *m/e* (M) 206.

Anal. Calcd for $C_9H_{15}O_3Cl$: C, 52.31; H, 7.26. Found: C, 52.63; H, 7.18.

Typical Procedure for the in Situ Addition of Chloroketenes with Ketene Bis(trimethylsilyl) Acetals. A solution of 0.025 mol of the freshly distilled acid chloride in 100 mL of dry hexane was added over 2 h to a stirred mixture of 0.025 mol of ketene bis(trimethylsilyl) acetal and 0.0275 mol of triethylamine in 200 mL of dry hexane at 22–24 °C under a nitrogen atmosphere. After the addition was complete the mixture was stirred overnight. The amine salt was removed by filtration, the filtrate was concentrated on a rotatory evaporator, and the residue was vacuum distilled to yield the adduct.

Trimethylsilyl 4-Chloro-2-methoxy-3-(trimethylsiloxy)-3-pentenoate (3). This adduct, obtained from methylchloroketene and 2-methoxy-1,1-bis(trimethylsilyl)ethylene, was isolated

(17) Brady, W. T.; Liddell, H. G.; Vaughn, W. L. *J. Org. Chem.* **1966**, *31*, 626.
(18) McElvain, S. M.; Kundiger, D. "Organic Syntheses", Wiley: New York, 1955; Collect. Vol. 3, p 506.
(19) Ainsworth, C.; Kuo, Y. *J. Organomet. Chem.* **1972**, *46*, 73.
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(22) McElvain, S. M., Davie, W. R. *J. Am. Chem. Soc.* **1951**, *73*, 1400.

as a 1:1 mixture of the cis/trans isomers which distilled at 60–64 °C (0.05 mm) to give 6.90 g (85%): IR (neat) 1745, 1660 cm^{-1}; NMR δ 0.25 (s, 9 H), 0.35 (s, 9 H), 2.05 (s, 1.5 H), 2.15 (s, 1.5 H), 2.35 (s, 1.5 H), 3.40 (s, 1.5 H), 4.35 (s, 0.5 H); mass spectrum, *m/e* (M) 324.

Anal. Calcd for $C_{12}H_{25}ClO_4Si_2$: C, 44.36; H, 7.75. Found: C, 43.84; H, 8.35.

Trimethylsilyl 4,4-Dichloro-2-methoxy-3-(trimethylsiloxy)-3-butenoate (4). Dichloroketene reacted with 2-methoxy-1,1-bis(trimethylsiloxy)ethylene to yield **4** which distilled at 55–56 °C (0.025 mm) to give 7.50 g (87%); Ir (neat) 1740, 1620 cm^{-1}; NMR δ 0.10 (s, 9 H), 0.20 (s, 9 H), 3.35 (s, 3 H), 4.62 (s, 1 H); mass spectrum, *m/e* (M) 344.

Anal. Calcd for $C_{11}H_{22}Cl_2O_4Si_2$: C, 38.26; H, 6.42. Found: C, 38.02; H, 6.53.

Trimethylsilyl 4-Chloro-2-methoxy-3-(trimethylsiloxy)-3-butenoate (5). Chloroketene reacted with 2-methoxy-1,1-bis(trimethylsiloxy)ethylene to yield **5**, which distilled at 63–64 °C (0.075 mm) to give 6.21 g (80%): IR (neat) 1735, 1635 cm^{-1}; NMR δ 0.18 (s, 9 H), 0.25 (s, 9 H), 3.28 (s, 3 H), 3.90 (s, 1 H), 5.50 (s, 1 H); mass spectrum, *m/e* (M) 310.

Anal. Calcd for $C_{11}H_{23}ClO_4Si_2$: C, 42.48; H, 7.40. Found: C, 42.07; H, 7.29.

Trimethylsilyl 4-Chloro-2,3-bis(trimethylsiloxy)-3-pentenoate (6). Reaction of methylchloroketene and tris(trimethylsiloxy)ethylene yielded this unsaturated ester, isolated as a 1:1 mixture of isomers, which distilled at 70–75 °C (0.05 mm) to give 8.13 g (85%): IR (neat) 1750, 1670, cm^{-1}; NMR δ 0.15–0.25 (m, 27 H), 2.00 (s, 1.5 H), 2.10 (s, 1.5 H), 4.75 (s, 0.5 H), 5.20 (s, 0.5 H); mass spectrum, *m/e* (M) 382.

Anal. Calcd for $C_{14}H_{31}ClO_4Si_3$: C, 43.90; H, 8.10. Found: C, 43.75; H, 8.37.

Trimethylsilyl 4,4-Dichloro-2,3-bis(trimethylsiloxy)-3-butenoate (7). The reaction of dichloroketene and tris(trimethylsiloxy)ethylene yielded this ester, which distilled at 65–66 °C (0.025 mm) to give 8.57 g (85%): IR (neat) 1775, 1635 cm^{-1}; NMR δ 0.15–0.25 (m, 27 H), 5.08 (s,, 1 H); mass spectrum, *m/e* (M) 402.

Anal. Calcd for $C_{13}H_{28}Cl_2O_4Si_3$: C, 38.69; H, 6.94. Found: C, 38.39; H, 7.14.

Trimethylsilyl 4-Chloro-2,3-bis(trimethylsiloxy)-3-butenoate (8). This adduct, obtained from the reaction of chloroketene and tris(trimethylsiloxy)ethylene, distilled at 59–60 °C (0.025 mm) to give 7.38 g (80%): IR (neat) 1750, 1650 cm^{-1}; NMR δ 0.10–0.25 (m, 27 H), 4.30 (s, 1 H), 5.45 (s, 1 H); mass spectrum, *m/e* (M) 368.

Anal. Calcd for $C_{13}H_{29}ClO_4Si_3$: C, 42.35; H, 7.86. Found: C, 42.14; H, 7.80.

Trimethylsilyl 4-Chloro-2,2-dimethyl-3-(trimethylsiloxy)-3-pentenoate (9). Methylchloroketene reacted with dimethylketene bis(trimethylsilyl) acetal to yield **9** isolated as a mixture of 1:1 cis/trans isomers which distilled at 60–64 °C (0.025 mm) to give 6.61 g (82%): IR (neat) 1730, 1655 cm^{-1}; NMR δ 0.40 (s, 18 H), 1.40 (s, 6 H), 2.00 (s, 1.5 H), 2.10 (s, 1.5 H); mass spectrum, *m/e* (M) 322.

Anal. Calcd for $C_{13}H_{27}ClO_3Si_2$: C, 48.35; H, 8.37. Found: C, 48.08; H, 8.51.

Trimethylsilyl 4,4-Dichloro-2,2-dimethyl-3-(trimethylsiloxy)-3-butenoate (10). Reaction of dichloroketene and dimethylketene bis(trimethylsilyl) acetal yielded **10**, which distilled at 70–71 °C (0.10 mm) to give 6.06 g (80%): Ir (neat) 1735, 1610 cm^{-1}; NMR δ 0.30–0.35 (m, 18 H), 1.35 (s, 6 H); mass spectrum, *m/e* (M) 342.

Anal. Calcd for $C_{12}H_{24}Cl_2O_3Si_2$: C, 41.97; H, 6.70. Found: C, 41.63; H, 7.01.

Trimethylsilyl 4-Chloro-2,2-dimethyl-3-(trimethylsiloxy)-3-butenoate (11). The ester obtained from the reaction of chloroketene and dimethylketene bis(trimethylsilyl) acetal, distilled at 51–52 °C (0.025 mm) to yield 6.32 g (82%): IR (neat) 1730, 1635 cm^{-1}; NMR δ 0.40–0.45 (m, 18 H), 1.40 (s, 6 H), 5.38 (s, 1 H); mass spectrum, *m/e* (M) 308.

Anal. Calcd for $C_{12}H_{25}ClO_3Si_2$: C, 46.66; H, 8.10. Found: C, 46.43; H, 8.16.

6-(1-Chloroethyl)-3,3-dichloro-4,4-diethoxy-3,4-dihydro-2*H*-pyran-2-one (12). A 3.7-g (0.025 mol) portion of dichloroacetyl chloride in 100 mL of dry hexane was added over 2 h to a stirred solution of 5.2 g (0.025 mol) of **2** and 2.8 g (0.0275 mol) of triethylamine in 200 mL of dry hexane at 22–24 °C under nitrogen. After the addition was complete, the mixture was stirred overnight. The amine salt was removed by filtration, the filtrate was concentrated on a rotatory evaporator, and the δ-lactone was distilled under vacuum at 100 °C (0.05 mm) to give 1.98 g (25%): IR (neat) 1795, 1695 cm^{-1}; NMR δ 1.20 (t, 6 H, 8 Hz), 1.65 (d, 3 H, J = 6 Hz), 3.70 (q, 4 H, J = 8 Hz), 4.35 (q, 1 H, J = 6 Hz), 5.35 (s, 1 H); mass spec trum, *m/e* (M − 45) 271.

6-(1-Chloroethyl)-3,3-dichloro-3,4-dihydro-2*H*-pyran-2,4-dione (13). One gram of **12** was stirred at 60 °C for 1 h with 10 mL of 5% HCl/dioxane solution to yield a quantitative amount of the lactone which distilled at 82–83 °C (0.01 mm): IR (neat) 1760, 1680, 1620 cm^{-1}; NMR δ 1.35 (d, 3 H, J = 6 Hz), 3.75 (q, 1 H, J = 6 Hz), 6.70 (s, 1 H); mass spectrum, *m/e* (M) 242.

Anal. Calcd for $C_7H_5Cl_3O_3$: C, 34.51; H, 2.05. Found C, 34.77; H, 2.26.

1,1,5-Trichlorohexane-2,4-dione (14). One gram of **12** was stirred at 60 °C for 2 h with 10 mL of 18% HCl/dioxane solution to yield a quantitative amount of the dione which distilled at 64–65 °C (0.10 mm). This product existed in the keto enol form in a 1:1 ratio: IR (neat) 3500, 1765, 1750, 1610 cm^{-1}; NMR δ 1.75 (d, 3 H, J = 6 Hz), 3.45 (s, 2 H), 4.20 (q, 1 H, J = 6 Hz), 5.8 (s, 1 H), 6.10 (s, 0.5 H), 13.5 (s, 0.5 H); mass spectrum, *m/e* (M) 216.

Anal. Calcd for $C_6H_7Cl_3O_2$: C, 33.12; H, 3.22. Found: C, 33.38; H, 3.42.

3-Ethoxy-1,1,1,6-tetrachloro-3-heptene-2,5-dione (15). A solution of 20 mL of dry ether, 0.69 g (10.5 mmol) of activated zinc, and 2 g (9.6 mmol) of **2** was brought to reflux under nitrogen, and then 1.1 mL (1.83 g, 10.0 mmol) of trichloroacetyl chloride in 10 mL of dry ether was added dropwise over 1 h. The mixture was refluxed for an additional 2 h and then filtered through a pad of Celite, and the unreacted zinc was washed with 25 mL of ether. The filtrate was concentrated to about 25% of its original volume, and then an equal volume of hexane was added followed by filtration to remove the zinc salts. After removal of the solvent, the crude reaction mixture was distilled under vacuum. This adduct was isolated as a 2:1 mixture of cis/trans isomers which distilled at 89–92 °C (0.025 mm) to yield 2.65 g (90%): IR (neat) 1800, 1740, 1680 cm^{-1}; NMR δ 1.22 (m, 3 H, J = 8 Hz), 1.65 (m, 3 H, J = 6 Hz), 4.00 (m, 2 H, J = 8 Hz), 4.40 (q, 1 H, J = 6 Hz), 5.78 (s, 1/3 H), 5.88 (s, 2/3 H); mass spectrum, *m/e* (M − 29) 277.

Anal. Calcd for $C_9H_{10}Cl_4O_3$: C, 35.08; H, 3.25. Found: C, 34.85; H, 3.42.

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Registry No. 1, 78550-00-2; **2**, 78550-01-3; *cis*-**3**, 78550-02-4; *trans*-**3**, 78550-03-5; **4**, 78550-04-6; **5**, 78550-05-7; *cis*-**6**, 78550-06-8; *trans*-**6**, 78550-07-9; **7**, 78550-08-0; **8**, 78550-09-1; *cis*-**9**, 78550-10-4; *trans*-**9**, 78550-11-5; **10**, 78550-12-6; **11**, 78550-13-7; **12**, 78550-14-8; **13**, 78550-15-9; **14**, 78550-16-0; *cis*-**15**, 78550-17-1; *trans*-**15**, 78550-18-2; dichloroacetyl chloride, 79-36-7; dimethylketene dimethyl acetal, 5634-54-8; α-chloropropionyl chloride, 7623-09-8; ketene diethyl acetal, 2678-54-8; methylchloroketene, 13363-86-5; 2-methoxy-1,1-bis(trimethylsilyl)ethylene, 71616-97-2; dichloroketene, 4591-28-0; chloroketene, 29804-89-5; tris(trimethylsiloxy)ethylene, 69097-20-7; dimethylketene bis(trimethylsilyl)acetal, 62618-96-6.