multiplet between τ 4.5 and 4.8, thus verifying that reaction had occurred exclusively at the terminal sites.

Anal. Calcd for $C_{20}H_{16}Cl_{12}$: C, 35.23; H, 2.37. Found: C, 35.4; H, 2.4.

Registry No.—**4**, 28861-35-0; **5**, 28861-36-1; **6**, 28861-37-2; **7**, 28861-38-3; *cis*-**8**, 28861-39-4; *trans*-**8**, 28861-40-7; *cis*-**9**, 28861-41-8; *trans*-**9**, 28861-42-9; **10**, 28861-43-0; **11**, 28861-44-1; **12**, 28861-45-2; **13**, 28861-46-3; **14**, 28861-47-4; **15**, 28861-48-5; **16**, 28861-49-6; *cis*-**17**, 28861-50-9; *trans*-**17**, 28861-51-0; *trans*-1,4,9-decatriene diadduct with hexachlorocyclopentadiene, 28861-52-1.

Acknowledgment.—The author is grateful to Mr. B. L. Martin and Mr. Paul Ciavolella for technical assistance.

Halogenated Ketenes. XXI. Cycloadditions with Carbonyl Compounds[1,2]

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The cycloaddition of methyl-, chloro-, isopropyl-, and phenoxyketenes with chloral has been accomplished. Both *cis*- and *trans*-2-oxetanones were obtained in approximately equal amounts. The generation of dichloroketene by the dehalogenation of trichloroacetyl chloride in the presence of acetone and cyclohexanone, respectively, afforded these cycloadducts. Zinc appears to activate the carbonyl group, thus increasing the reactivity with dichloroketene. However, chloroketene forms only α,β-dichlorovinyl dichloroacetate under these conditions.

The cycloaddition of ketenes and carbonyl compounds to produce 2-oxetanones (β actones) dates back to the early investigations of Staudinger.[3] Most of the early work was with diphenylketene, and it was found that the addition of simple carbonyl compounds to diphenylketene did not normally proceed unless elevated temperatures were employed. Since the high temperatures required for cycloadditions polymerized aldoketenes and lower ketoketenes, early investigation were mostly limited to diphenylketene.[4]

Later the cycloaddition of ketene to aldehydes was found to proceed smoothly in ether in the presence of mild Friedel–Crafts type catalysts.[5] Ketones, however, required much stronger catalysts and more vigorous conditions to react with ketene.[6]

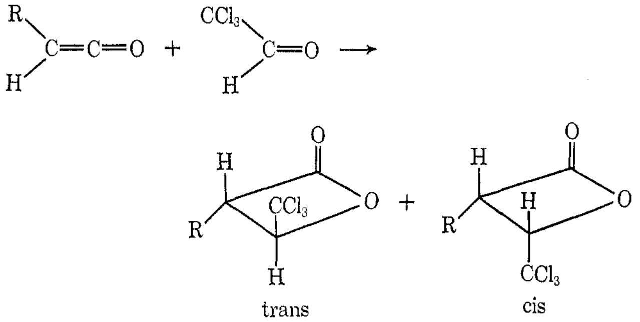
Borrmann and Wegler have recently reported that the cycloaddition of simple ketoketenes and carbonyl compounds is possible when the carbonyl compound is activated by electronegative substituents on the α carbon.[7] Thus, the cycloaddition of several ketenes to chloral were accomplished. The cycloadduct of dichloroketene and chloral was prepared by the *in situ* preparation of dichloroketene and subsequent trapping of this elusive ketene with chloral.[8] However, under these conditions it was found that dichloroketene would not react with simple ketones such as acetone, cyclohexanone, and acetophenone.

In the few literature reports where ketene–carbonyl cycloadditions could produce geometrical isomers, the stereochemical course of the cycloadditions has not been reported.[7,9,10] Borrmann and Wegler, in the only report of aldoketene–carbonyl cycloadditions, described the cycloaddition of phenoxy- and ring-substituted phenoxyketenes to chloral but did not describe the stereochemistry of the products.[5]

We wish now to describe the cycloaddition of several aldoketenes with chloral and report the stereochemistry of these cycloadditions.[11] Also, we describe a method for the cycloaddition of dichloroketene with some simple ketones.

Results

The cycloaddition of aldoketenes to chloral produces *cis*- and *trans*-4-trichloromethyl-2-oxetanones.



The aldoketenes were generated *in situ* by the dehydrochlorination of the appropriately substituted acyl chlorides and/or by dehalogenation of appropriately substituted α-haloacyl halides with zinc.

As England and Krespan found in the generation of difluoroketene by *in situ* dehalogenation, the α-bromoacyl chloride is the preferred acid halide.[12] 2-Bromopropanoyl chloride consistently dehalogenated with greater ease, as evidenced by the amount of zinc consumed, than did the bromo bromide, the chloro bromide, or the chloro chloride.

The isomeric β lactones were isolated and separated by fractional distillation, preparative vpc, or column chromatography and identified by ir and nmr spectra.

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(1) Support of this investigation by the Robert A. Welch Foundation, the National Science Foundation, and a North Texas State University Faculty Research Grant is gratefully acknowledged.

(2) Paper XX: W. T. Brady and J. P. Hieble, *J. Org. Chem.*, submitted for publication.

(3) H. Staudinger, *Chem. Ber.*, **41**, 1493 (1908).

(4) R. N. Lacey in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1968.

(5) F. E. Kung, U. S. Patent 2,356,459 (1944); *Chem. Abstr.*, **39**, 88 (1945).

(6) H. E. Zaugg, *Org. React.*, **8**, 314 (1954).

(7) D. Borrmann and R. Wegler, *Chem. Ber.*, **99**, 1245 (1966).

(8) D. Borrmann and R. Wegler, *ibid.*, **102**, 64 (1969).

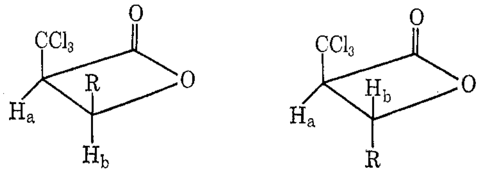
(9) D. Borrmann and R. Wegler, *ibid.*, **100**, 1575 (1967).

(10) R. H. Hasek and E. U. Elam, U. S. Patent 3,004,989 (1961); *Chem. Abstr.*, **56**, 4623 (1962).

(11) A preliminary report of a portion of this work has appeared: W. T. Brady and L. Smith, *Tetrahedron Lett.*, 2963 (1970).

(12) D. C. England and C. G. Krespan, *J. Org. Chem.*, **33**, 816 (1968).

Configurational assignments were made on the basis of the nmr coupling constants of the methinyl protons.



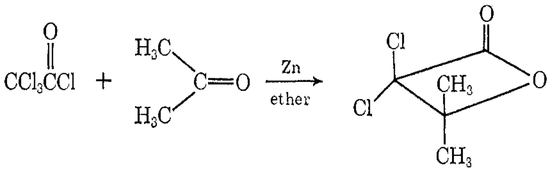
J_{ab} (cis) = 6 cps J_{ab} (trans) = 3 cps

The doublet for H_a appears downfield from the resonance of H_b by 25–75 cps.

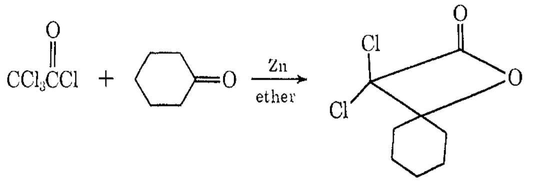
The isomer distributions were determined as ratios of integrated peak areas on gas chromatograms of the reaction solutions with the exception of the phenoxyketene–chloral system. The ratio, *cis-/trans*-IV, was obtained by nmr integration of the methinyl region.

The vpc and nmr methods were compared by making an artifical mixture of *cis-* and *trans*-3-methyl-2-oxetanone (I). The ratio, *cis-/trans*-I, in the mixture was 1.10 by weight. An average of several integrations of the *cis-* and *trans*-methinyl doublets in the nmr spectrum (30% in $CDCl_3$) of the mixture yielded *cis-/trans*-I = 1.12. The average integration of the peak areas in several chromatograms from the nmr solution yielded *cis-/trans*-I = 1.06. The experimentally determined distributions for compounds I–IV are summarized in Table I.

The increased yield in the synthesis of I by dehalogenation as opposed to dehydrochlorination may be seen in Table I. To further explore the effect of the method of ketene generation on the cycloaddition, dehalogenations of trichloroacetyl chloride in the presence of acetone and cyclohexanone were investigated and found to produce VI and VII.



VI



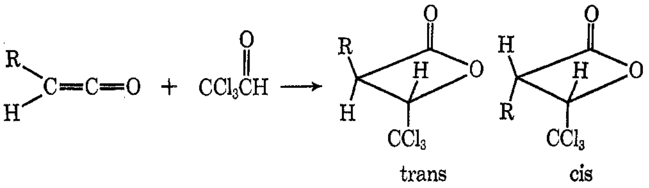
VII

As a comparison of the two methods, dimethylketene, when prepared by *in situ* dehydrochlorination of isobutyryl chloride with triethylamine in the presence of chloral, yielded 15% V. Debromination of 2-bromo-2-methylpropanoyl bromide with zinc in the presence of chloral produced 60% V.

When dimethylketene was prepared by pyrolysis of the dimer, tetramethyl-1,3-cyclobutadione, and combined with chloral in ether, V was produced in 10% yield. An identical sample containing zinc yielded 65% of V. Oshe and coworkers have reported that V is obtained in 65% yield when the cycloaddition is catalyzed by boron trifluoride etherate.[13]

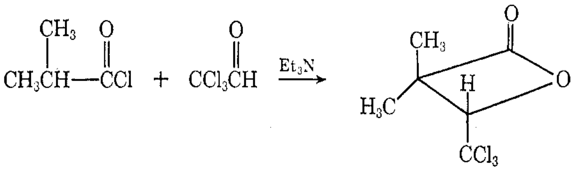
Table I

Aldoketene–Chloral Cycloadditions

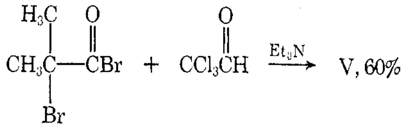


Compd	R	Method[a]	cis/trans	Yield, %
I	CH_3	DHX	1.4	43
I	CH_3	DX	1.4–2.0	95
II	Cl	DHX	1.6	40
III	*i*-Pr	DX	0.9	25
IV	PhO	DHX	1.7	61

[a] DHX = dehydrohalogenation; DX = dehalogenation.

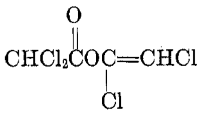


V, 15%



$$CH_3\overset{H_3C}{\underset{Br}{C}}-\overset{O}{\overset{\|}{C}}Br + CCl_3\overset{O}{\overset{\|}{C}}H \xrightarrow{Et_3N} V, 60\%$$

In an attempt to produce chloroketene and effect the *in situ* cycloaddition to chloral by dehalogenation, dichloroacetyl chloride and chloral were treated in the usual manner with zinc. The product isolated, however, was concluded to be α,β-dichlorovinyl dichloroacetate (VIII) from the spectral data and elemental analysis.



$$CHCl_2\overset{O}{\overset{\|}{C}}O\underset{Cl}{C}=CHCl$$

VIII

Diphenyl-, phenylmethyl-, phenylethyl-, and phenylketenes exhibited very little reactivity toward chloral under a wide variety of conditions.

β lactones normally eliminate carbon dioxide and produce olefins when heated.[14] However, when heated at 160° for 6–12 hr, I and II were recovered unaltered. The unusual thermal stability of 4-trichloromethyl-2-oxetanones has been reported by Ohse and coworkers for 3,3-dimethyl-4-trichloromethyl-2-oxetanone (V).[13] When heated, 3,3-dichloro-4,4-dimethyl-2-oxetanone (VI) decarboxylated in the expected manner to produce 1,1-dichloro-2-methylpropene.

Discussion

The isomer distributions obtained from the cycloaddition of several different aldoketenes with chloral

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[13] H. Oshe, R. Palm, and H. Cherdron, *Monatsh. Chem.*, **98**, 2138 (1967).

[14] H. C. Gilch, *J. Org. Chem.*, **30**, 4392 (1965).

(Table I) reveal that the reaction is not stereoselective. Aldoketene–olefin cycloadditions are concerted processes and stereoselectively produce *cis*- or *endo*-cyclobutanones.[15–17] In contrast, aldoketene–imine cycloadditions occur *via* a dipolar intermediate stereoselectively to yield *trans*-2-azetidinones.[18]

That the isomer distributions for the aldoketene–chloral cycloadditions are approximately the same regardless of the nature of (a) the substituent on the ketene, (b) the reaction solvent, or (c) the method of *in situ* preparation of the ketene suggests a concerted process. The lack of reactivity of the phenylketenes was very unexpected but suggests that a dipolar intermediate is not involved since phenyl groups would be very stabilizing.

If the cycloaddition of the aldoketenes to chloral is a concerted process, the conservation of orbital symmetry considerations should predict the steric route of the cycloaddition. A consideration of the four possible orthogonal approaches leads to the conclusion that both isomers would be expected with perhaps a predominance of the cis isomer.[16]

The cycloaddition of dichloroketene with acetone and cyclohexanone when the ketene is generated *in situ* by dehalogenation suggested a catalytic effect by zinc and/or zinc halides. This was confirmed by the cycloaddition of dimethylketene with chloral in the presence and absence of activated zinc. The role of the zinc is probably activation of the carbonyl functionality since ketene–olefin cycloadditions are not catalyzed by zinc under identical conditions. Although zinc enhances the reaction of both dichloro- and methylketenes with chloral, the reactivities of dichloroketene and methylketene differ markedly. When methylketene was generated *in situ* by dehalogenation, no evidence of cycloaddition with benzaldehyde, acetone, 2-butanone, or cyclohexanone could be found.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were recorded on a Jeolco Minimar 60-Mcps or Jeolco NMR PS 100-Mcps spectrometer. Mass spectra were obtained with a Hitachi RMU-6E mass spectrometer. An F & M Scientific Model 700 was used for analytical gas chromatography and an Aerograph 90A was used for small scale preparative purposes. Columns of 4, 6, and 8 ft by 0.25 in. packed with 10% SE-30 on Chromosorb W (DMSC) 60–80 mesh were used on both instruments.

All of the solvents were dried with calcium or lithium aluminum hydrides, distilled, and stored over molecular sieves, 4A, prior to use. The acid halides were prepared from the corresponding acids by classical procedures. The isolable ketenes were prepared by standard procedures found in the literature. Chloral was vacuum distilled and stored under nitrogen in brown glass bottles with septum caps at 0–5°. Portions were removed with a syringe as needed. Other aldehydes and ketones were distilled and stored in the same manner.

Activation of Zinc.—Granular zinc (15 g, 20 mesh) was rinsed in 75 ml of 5% aqueous HCl containing 0.1 g of $HgCl_2$/50 ml until the surface was bright. The zinc was separated by filtration, washed with distilled water and with acetone, and dried with a stream of nitrogen. The zinc was transferred to the reaction flask under nitrogen and covered with ether.

Cycloaddition of Methylketene and Chloral to Give 3-Methyl-4-trichloromethyl-2-oxetanone (I). Method A.—Triethylamine, 32 ml (230 mmol), in 75 ml of ether was added to a vigorously stirred solution of propionyl chloride, 20 ml (230 mmol), and chloral, 20 ml (204 mmol), in 300 ml of ether at room temperature. Filtration of the reaction mixture after 4 hr revealed a theoretical amount of salt. Concentration of the filtrate and distillation of the residue yielded a crude mixture of *cis*- and *trans*-I, 43% based on chloral. Fractional distillation gave three fractions, 51–54°, 54–55°, and 56° (0.2 mm). The first two fractions were shown to be mixtures of *cis*- and *trans*-I: ir 1870 cm^{-1} (C=O); nmr ($CDCl_3$) (*cis*-I) δ 1.55 (d), 4.2 (m), and 5.08 (d, J = 6.8 cps); nmr (*trans*-I) δ 1.55 (d), 3.81 (m), and 4.77 (d, J = 3.2 cps). Fraction three was found to be pure *cis*-I: nmr (CCl_4) δ 1.53 (d, 3 H), 4.08 (m, 1 H), and 4.98 (d, J = 6.8 cps, 1 H). Spin decoupling of the methyl resonane at δ 1.53 reduced the quintet at 4.08 to a doublet, J = 6.8 cps. Spin decoupling of the quintet reduced the methyl doublet to a singlet.

Anal. Calcd for $C_5H_5Cl_3O_2$: C, 29.52; H, 2.48. Found: C, 29.66; H, 2.46.

The *cis*-/*trans*-I in the reaction mixture was 1.39 as determined by vpc.

The dehydrochlorination of propionyl chloride in the presence of chloral was also carried out in hexane, tetrahydrofuran, and acetonitrile with approximately the same yields and isomer distributions of I.

Method B.—A solution of 2-bromopropanoyl chloride, 10 ml (98.5 mmol), in 25 ml of ether was added dropwise to rapidly stirred zinc, 12 g, in 150 ml of ether containing chloral, 15 ml (153 mmol). The reaction temperature was maintained below the boiling point of ether by cooling the reaction flask with a water bath. Filtration of the reaction mixture after 4 hr revealed that a theoretical amount of zinc had been consumed. The filtrate was concentrated and extracted with hexane. Distillation of the concentrated hexane extracts produced I in 95% yield. The isomer distribution in the reaction mixture during the reaction was 2.1 as determined by vpc.

Cycloaddition of Chloroketene and Chloral to Give 3-Chloro-4-trichloromethyl-2-oxetanone (II).—Triethylamine, 19 ml (132 mmol), in 50 ml of hexane was slowly added to a rapidly stirred solution of chloroacetyl chloride, 10 ml (132 mmol), and chloral, 15 ml 153 mmol), in 150 ml of hexane at room temperature. After the addition was complete, stirring was continued for 2 hr. Filtration resulted in a theoretical amount of salt. Concentration of the filtrate and distillation of the residue yielded (40%) a mixture of *cis*- and *trans*-II: ir 1870 cm^{-1} (C=O); nmr ($CDCl_3$) (*cis*-II) pair of doublets centered at δ 5.58 and 5.18 (J = 6.0 cps); nmr (*trans*-II) pair of doublets centered at δ 5.25 and 5.04 (J = 3.0 cps). Fractional distillation at 0.1 mm gave *trans*-II (bp 56–58°), several fractions containing both isomers, and *cis*-II (bp 78–80°): nmr (CCl_4) (*trans*-II) δ 5.44 (d, J = 3.0 cps, 1 H) and 5.17 (d, J = 6.0 cps, 1 H).

Anal. Calcd for $C_4H_2Cl_4O_2$: C, 21.46; H, 0.90. Found: C, 21.48; H, 1.02.

The *cis*-/*trans*-II in the reaction mixture was 1.64 as determined by vpc.

The dehydrochlorination of chloroacetyl chloride in the presence of chloral was also conducted in ether, tetrahydrofuran, and acetone and produced approximately the same isomer ratio. The yield in acetone was lower while the ethers produced a slightly higher yield than hexane.

Dehalogenation of Dichloroacetyl Chloride in the Presence of Chloral to Give α,β-Dichlorovinyl Dichloroacetate (VIII).—Dichloroacetyl chloride, 5 ml (52 mmol), in 10 ml of ether was added to zinc, 10 g, in 50 ml of ether containing chloral, 6 ml (61 mmol), with rapid stirring and warming with a water bath. Ir spectra of the reaction solution showed only a very low concentration of II and strong C=O absorption at 1785 cm^{-1}. Filtration revealed that less than a theoretical amount of zinc had been consumed. The filtrate was concentrated and extracted with hexane. The hexane extract was concentrated *in vacuo* and the residue distilled: yield 4.1 g (60%); bp 38–39° (0.15 mm); ir 1785 (C=O) and 1650 cm^{-1} (C=C); nmr ($CDCl_3$) δ 6.20 (s, 1 H) and 7.56 (s, 1 H).

Anal. Calcd for $C_4H_2Cl_4O_2$: C, 21.5; H, 0.90; mol wt (theoretical), 222. Found: C, 21.53; H, 0.97; mol wt (mass spectrum), 222.

Cycloaddition of Isopropylketene and Chloral to Give 3-(2-Propyl)-4-trichloromethyl-2-oxetanone (III).—A solution of 2-bromo-3-methylbutanoyl chloride, 25 ml (215 mmol), in 50 ml of ether was added dropwise to rapidly stirred zinc, 20 g, in 300 ml of ether containing chloral, 30 ml (306 mmol). Filtration after 4 hr revealed that a theoretical amount of zinc had been

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[15] W. T. Brady, E. F. Hoff, Jr., R. Roe, Jr., and F. H. Parry, III' *J. Amer. Chem. Soc.*, **91**, 5679 (1969).

[16] W. T. Brady and R. Roe, Jr., *ibid.*, **92**, 4618 (1970).

[17] T. DoMinh and O. P. Strausz, *ibid.*, **92**, 1766 (1970).

[18] J. L. Luche and H. B. Kagan, *Bull. Soc. Chim. Fr.*, **6**, 2450 (1969).

consumed. The filtrate was concentrated and extracted with hexane. The hexane was removed from the extracts *in vacuo* and the residue distilled yielding 25% III. Separation of *cis*- and *trans*-III and other components was not possible by fractional distillation. *cis*-III was obtained by preparative vpc of the crude residue from the hexane extracts: ir 1860 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.27 (t, 6 H), 2.73 (m, 1 H), 3.95 (m, 1 H), and 5.30 (d, J = 6.0 cps, 1 H).

Anal. Calcd for $C_7H_9Cl_3O_2$: C, 36.3; H, 3.92. Found: C, 36.5; H, 3.84.

trans-III was separated from the other components by elution from a 18 × 300 mm silica gel column with 70:30 cyclohexane-benzene: nmr ($CDCl_3$) δ 1.25 (d, 6 H), 2.37 (m, 1 H), 3.72 (m, 1 H), and 5.0 (d, J = 3.5 cps, 1 H).

The isomer distribution in the reaction mixture was 0.9 as determined by vpc.

Cycloaddition of Phenoxyketene and Chloral to Give 3-Phenxoy-4-trichloro-2-oxetanone (IV).—Triethylamine, 15.5 ml (110 mmol), in 25 ml of tetrahydrofuran was added dropwise to a rapidly stirred solution of phenoxyacetyl chloride, 15 ml (110 mmol), and chloral, 15 ml (153 mmol), in 200 ml of tetrahydrofuran at room temperature. After 2 hr, filtration yielded a theoretical amount of salt. Distillation of the concentrated filtrate produced two main fractions of IV (61%), bp 140 and 157° (0.2 mm). The second fraction solidified and was purified sublimation at 70° (0.05 mm), mp 70–72°. *cis*-IV: ir 1870 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.10 (d, J = 6.0 cps, 1 H), 5.62 (d, J = 6.0 cps, 1 H), and 7.2 (m, 5 H). *trans*-IV: bp 140° (0.2 mm) [lit. bp 128° (0.1 mm[7])]; nmr ($CDCl_3$) δ 5.17 (d, J = 3.0 cps, 1 H), 5.62 (d, J = 3.0 cps, 1 H), and 7.2 (m, 5 H).

The isomer distribution was determined by integration of the methinyl region of the nmr spectrum of the reaction solution. In these samples the downfield doublets of the two isomers were used since the upfield doublets of the isomers were superimposed. *cis*-/*trans*-IV = 1.7.

Cycloaddition of Dimethylketene and Chloral to Give 3,3-Dimethyl-4-trichloromethyl-2-oxetanone (V). Method A.—2-Bromo-2-methylpropanoyl bromide, 10 ml (83 mmol), in 20 ml of ether was added to rapidly stirred zinc, 15 g, in 200 ml of ether containing chloral, 15 ml (153 mmol), at room temperature. Filtration of the reaction mixture after 8 hr revealed that a theoretical amount of zinc had reacted. The filtrate was concentrated and extracted with hexane. The hexane extracts were concentrated to yield crystalline V (60%). V was further purified by sublimation at 45° (0.1 mm): mp 62–63° (lit.[13] mp 65°); nmr ($CDCl_3$) δ 1.60 (d, 6 H) and 4.74 (s, 1 H).

Method B.—Triethylamine, 13.5 ml (95.5 mmol), in 25 ml of tetrahydrofuran was added dropwise to a rapidly stirred solution of chloral, 15 ml (153 mmol), and isobutyryl chloride, 10 ml (95.5 mmol), in 200 ml of tetrahydrofuran at room temperature. The ir spectrum of the reaction solution indicated that V was formed. The yield of V was estimated to be about 15% by comparison of the gas chromatogram of the reaction solution to that of a standard solution of V. Isolation of the product was complicated by the presence of tetramethyl-1,3-cyclobutadione dimethylketene dimer.

Method C.—To 195 mmol of dimethylketene in 50 ml of ether was added 1 ml (102 mmol) of chloral. The resulting solution was transferred by a syringe to two septum bottles, one with 2 g of zinc and the other empty. After 1 hr, both solutions contained V as evidenced by vpc. During the next several hours the concentration of V, as estimated by comparison of vpc peak areas of sample and standard solutions of V, were 10 and 65% for the control and zinc sample respectively; ir (both solutions) 1850 cm^{-1} (C=O).

Cycloaddition of Dichloroketene and Acetone to Give 3,3-Dichloro-4,4-dimethyl-2-oxetanone (VI).—Trichloroacetyl chloride, 25 ml (228 mmol), in 50 ml of ether was added dropwise to rapidly stirred zinc, 18 g, in 100 ml of acetone and 500 ml of ether. The reaction temperature was maintained at 27° with a water bath. Filtration after 4 hr revealed that 86% of a theoretical amount of zinc had been consumed. The filtrate was concentrated and extracted with hexane. The hexane was removed from the extract *in vacuo*. Distillation of the residue yielded 30% of VI: bp 34° (0.5 mm); mp 24–25°; ir 1875 cm^{-1} (C=O); nmr (CCl_4) δ 1.79 (s),

Anal. Calcd for $C_5H_6Cl_2O_2$: C, 35.5; H, 3.58. Found: C, 35.7; H, 3.47.

Cycloaddition of Dichloroketene and Cyclohexanone to Give 3,3-Dichloro-1-oxaspiro[3.5]nonan-2-one (VII).—Trichloroacetyl chloride, 20 ml (182 mmol), in 50 ml of ether was added dropwise to rapidly stirred zinc, 15 g, in 200 ml of ether containing 25 ml of cyclohexanone. The reaction temperature was maintained at 30° with water bath. Filtration after 6 hr showed that 90% of the theoretical amount of zinc had been consumed. The filtrate was concentrated and extracted with hexane. Removal of the hexane and distillation of the residue afforded a 51% yield of VII: bp 62° (0.2 mm); ir 1850 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.8 (m).

Anal. Calcd for $C_8H_{10}Cl_2O_2$: C, 45.9; H, 4.82. Found: C, 45.7; H, 5.17.

Attempted Pyrolysis of *cis*-I.—A sample of *cis*-I was heated at 150° under nitrogen for 6 hr. Vacuum distillation afforded *cis*-I (90%) unchanged.

Attempted Pyrolysis of *trans*-II.—A sample of *trans*-II was heated at 160° for 12 hr. Vacuum distillation afforded *trans*-II unchanged.

Pyrolysis of VI.—A sample of VI was heated at 150° for 2 hr. Distillation yielded 50% of 1,1-dichloro-2-methylpropene, bp 106–107° (lit.[13] bp 108–110°).

Registry No.—*cis*-I, 28186-55-2; *trans*-I, 28186-56-3; *cis*-II, 28186-53-0; *trans*-II, 28186-54-1; *cis*-III, 29005-70-7; *trans*-III, 29005-71-8; *cis*-IV, 29005-72-9; *trans*-IV, 29005-73-0; V, 15347-83-8; VI, 28193-85-5; VII, 29005-76-3; VIII, 29005-77-4.