from ethyl to isopropyl to *tert*-butyl, the amount of product with Markownikoff orientation decreases.

The addition to 4,4-dimethyl-2-pentyne forms small amounts of products with *Z*-Markownikoff and *Z*-anti-Markownikoff orientation. It is not yet clear if these products are the result of kinetic control or are the result of rapid isomerization of the major products of anti stereospecific addition.

Summary. The data presented clearly establish that alkyl groups have a different effect upon the rates than on the product composition of addition of 4-chlorobenzenesulfenyl chloride to alkynes. In the rate-determining transition state the effect of all of the alkyl groups, except *tert*-butyl, is predominantly polar. In the product-determining transition state, steric effects dominate.

Experimental Section

The alkynes were obtained commercially and their purity was verified by GLC and NMR.

4-Chlorobenzenesulfenyl chloride was prepared as previously described.[14]

1,1,2,2-Tetrachloroethane was purified as previously described.[14]

General Procedures. Ultraviolet Isomerization. A 2% solution of the *E* isomer, in benzene, was irradiated through Pyrex and copper sulfate filter for 40 h. The solvent was removed and the residue was dissolved in $CDCl_3$ and its proton and ^{13}C NMR spectrum recorded. The data are given in Tables IV–VII.

Acid-Catalyzed Isomerization. Anhydrous gaseous HCl was bubbled into a 1 M solution of the reaction mixture in benzene for approximately 1 min. Aliquots were taken from the solution, which was kept at room temperature. The solvent was removed, the residue was dissolved in $CDCl_3$, and its proton and ^{13}C NMR spectrum recorded. The data are given in Tables IV–VII. After several days the solutions began to darken and the NMR spectra indicated extensive decomposition.

Kinetics. Solutions for kinetic runs were prepared in general by direct weighing. The initial concentration of 4-chlorobenzenesulfenyl chloride was in the range $1 \pm 0.1 \times 10^{-3}$ M. The kinetic runs were carried out under pseudo-first-order conditions with a 20–80 times excess concentration of alkyne. When the alkyne was a gas at room temperature, the gas was bubbled into a given quantity of solvent and its concentration was determined by titration with a standard solution of 4-chlorobenzenesulfenyl chloride. The end point was taken as the appearance of the characteristic yellow of the slight excess of sulfenyl chloride. After the kinetic runs, the alkyne concentration was redetermined. No loss of alkyne by evaporation was ever detected.

All kinetic runs except for acetylene were carried out on a Durrum-Gibson stopped-flow spectrophotometer as previously described.[14] Rates of addition to acetylene were measured under pseudo-first-order conditions using the same concentrations of substrates as for the stopped-flow measurements, on a Cary 16 spectrophotometer with an external recorder by means of standard procedures.

Product Compositions. A solution of 0.12 g (0.001 mol) of 4-chlorobenzenesulfenyl chloride in 5 ml of 1,1,2,2-tetrachloroethane (TCE) was added dropwise to a solution containing 0.001 mol of alkyne in 3 ml of TCE at room temperature. The solvent was evaporated in a stream of dry nitrogen to constant weight. The residue, which corresponded to a quantitative yield, was dissolved in $CDCl_3$ and analyzed by NMR.

Analytical samples were prepared by adding a solution of 0.12 g (0.001 mol) of 4-chlorobenzenesulfenyl chloride in 5 ml of methylene chloride to 0.001 mol of alkyne in 3 ml of methylene chloride at room temperature. The solvent was evaporated in a stream of dry nitrogen to constant weight. Attempts to purify the residue by GLC or distillation led to decomposition. Satisfactory elemental analysis for **1–5, 8–10, 12** for C, H, Cl (±0.4%) were obtained directly upon removal of the solvent.

Acknowledgment. Continued financial support from the National Research Council of Canada is gratefully acknowledged. A University of Toronto Special Open Fellowship (1973–1974) and an NRC Postgraduate Scholarship (1974–1976) to Dennis G. Garratt are also very much appreciated.

Registry No.—4-Chlorobenzenesulfenyl chloride, 933-01-7; 1,1,2,2-tetrachloroethane, 630-20-6.

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Halogenated Ketenes. 29. Further Studies on Mixed Dimerizations[1]

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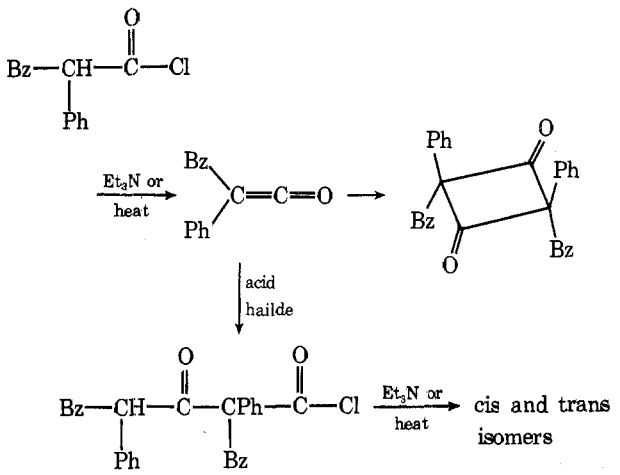
The mixed dimerizations of methylchloro- and *tert*-butylchloroketenes with methyl-*n*-propyl- and methylisopropylketenes resulted in equal amounts of the isomeric cyclobutanediones. *tert*-Butylketene codimerized with methylchloro-, methylbromo-, *tert*-butylchloro-, and *tert*-butylbromoketenes to yield only 2-oxetanone dimers. The β-keto acid chlorides prepared by the addition of α-chloropropionyl chloride and dichloroacetyl chloride to dimethylketene reacted with triethylamine to yield only the corresponding 2-oxetanones.

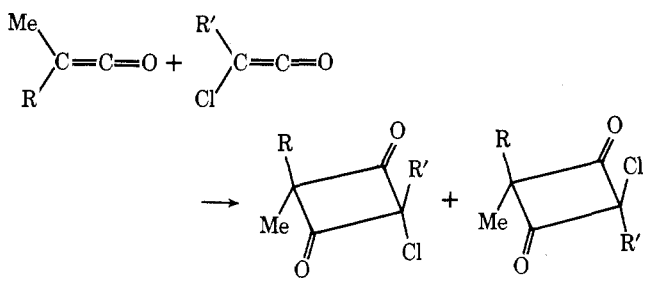
The dimerization of ketenes is regarded as a $[_\pi2_s + _\pi2_a]$ concerted process with a high negative entropy of activation and little solvent polarity dependence.[2] One of the ketene molecules participates as a $_\pi2_s$ component, while the other acts in a normal $_\pi2_a$ fashion, whereby the transition state involves an orthogonal approach of the reactant molecules.[3]

Dehmlow has recently reported that the thermal dimerization of some isolated unsymmetrical ketoketenes such as phenylmethyl-, benzylmethyl-, and benzylphenylketenes produced *cis*-cyclobutanediones. The same dimerization of benzylphenylketene by the dehydrochlorination of 2,3-diphenylpropanoyl chloride with either triethylamine or by heating above 230 °C produced both *cis*- and *trans*-cyclobutanediones. The proposed mechanism to produce the trans isomer was considered to be through the β-keto acid chloride, 2-benzyl-3-keto-2,4,5-triphenylpentanoyl chloride.[4]



We have previously reported on the mixed dimerizations of halogenated ketenes and nonhalogenated ketenes and would now like to describe some studies concerning the mechanism of formation of these unsymmetrical halogenated cyclobutanediones.[5] A fundamental question to consider was whether or not a concerted cycloaddition was occurring from the two respective ketenes as is the case for isolated ketoketenes or whether the ketenes did not dimerize but rather the cyclobutanediones were formed by the cyclization of an intermediate β-keto acid halide.

The codimerization of certain unsymmetrical dialkylketenes with some haloketenes yielded isomer diones in equal amounts as illustrated. These isomers were distinguished on



I, R = *n*-Pr; R′ = Me
II, R = *i*-Pr; R′ = Me
III, R = *n*-Pr; R′ = *t*-Bu

the basis of the NMR signal in the range of δ 1.48–1.60 for the protons of the methyl group cis to the chloro substituent and δ 1.28–1.36 for the methyl group trans to the chloro substituent (Table I).

Mixed dimerizations of isopropylmethylketene with isopropylchloro- and *tert*-butylchloroketenes were investigated and no evidence of dione or 2-oxetanone was detected. Apparently, the larger substituent retards the dimerization and polymerization predominates. Unfortunately, the stereochemistry in these systems was not as revealing as expected.

In hexane, *tert*-butylketene was generated by the triethylamine dehydrochlorination of 3,3-dimethylbutanoyl chloride. This ketene was unusually stable in the reaction mixture at room temperature, lasting for 2 or 3 days as evidenced by the infrared absorption at 2119 cm^{-1}. Attempts to isolate the ketene were unsuccessful owing to the equilibrium between the ketene and the acid halide and the polymerization of the ketene. Refluxing the reaction mixture for 3 days resulted in a 30% yield of the 2-oxetanone homodimer of *tert*-butylketene.

Codimerization of *tert*-butylketene with halogenated ketenes in situ yielded only 2-oxetanone dimers in moderate to poor yields. Two such 2-oxetanones are possible depending

Table I. Chemical Shifts (δ) of Methyl Protons of Cyclobutanediones

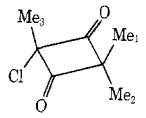
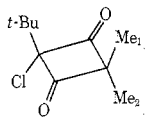
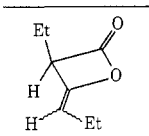
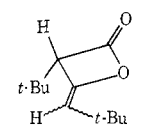
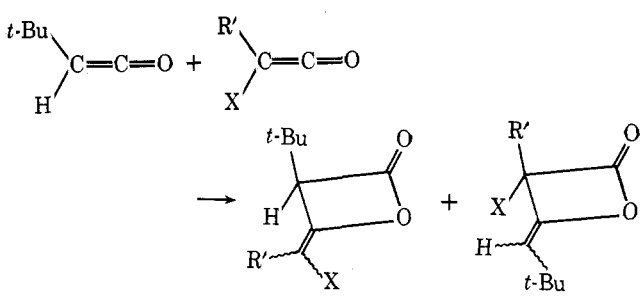
Compd	Me_1 (trans to Cl)	Me_2 (cis to Cl)	Me_3 (gem. to Cl)
	1.36	1.52	1.70
	1.28	1.60	
I	1.36	1.52	1.64, 1.72
II	1.27	1.46	1.60, 1.66
III	1.28	1.56	

Table II. Methyl and Proton Chemical Shifts (δ) of the 2-Oxetanones

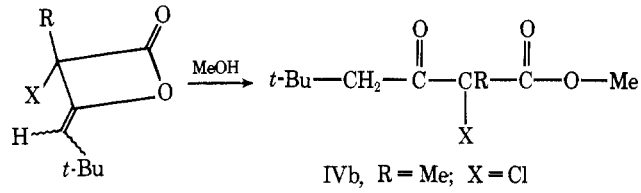
Compd	H(α)	H(vinyl)
	3.88	4.64
	3.74	4.64
IVa		4.84
VIa	3.86	
VIIa	3.80	

upon whether cycloaddition occurs across the carbon–oxygen double bond of the halogenated ketene or the *tert*-butylketene as illustrated. Only one 2-oxetanone was produced in each



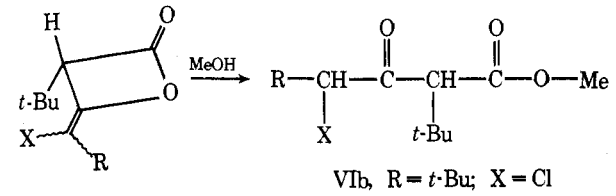
system, but the structure of the dimer was dependent upon the particular alkylhaloketene. The 2-oxetanone exhibited bands in the infrared at 1887–1900, 1828–1835 (C=O), and 1710–1742 cm^{-1} (C=C). The assignment of structure of the 2-oxetanone could be made on the basis of the α proton and the vinyl proton in the NMR. The α protons appeared in the range δ 3.80–3.86 and the vinyl protons in the range δ 4.80–4.85; a comparison of these values with the α proton and vinyl proton of the homodimers of ethyl- and *tert*-butylketenes allowed assignment to be made (Table II).

Methanolysis of the 2-oxetanones was used to confirm the NMR assignments. The distinction was made on the basis of the hydrogen in the NMR. Methyl 2-*tert*-butyl-3-keto-5,5-dimethylhexanoate was synthesized from the 2-oxetanone dimer of *tert*-butylketene with methanol for comparison purposes, and it was found that the γ hydrogen was revealed in the NMR at δ 2.30. Since the β-keto esters produced had values of 2.5 and 4.0, it was apparent that those with a chemical shift of δ 2.5 were derived from a 2-oxetanone which resulted from cycloaddition across the carbon–carbon double bond of the halogenated ketenes. Those β-keto esters with a



IVa, R = Me; X = Cl
Va, R = Et; X = Cl

IVb, R = Me; X = Cl
Vb, R = Et; X = Cl

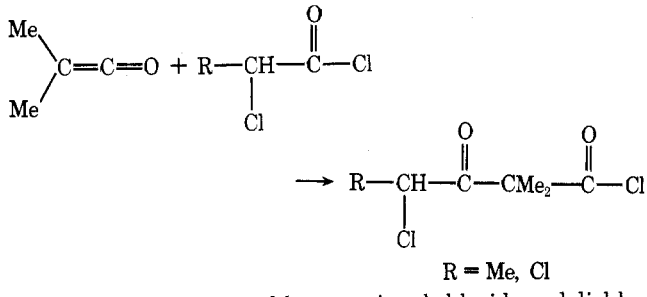


VIa, R = *t*-Bu; X = Cl
VIIa, R = *t*-Bu; X = Br

VIb, R = *t*-Bu; X = Cl
VIIb, R = *t*-Bu; X = Br

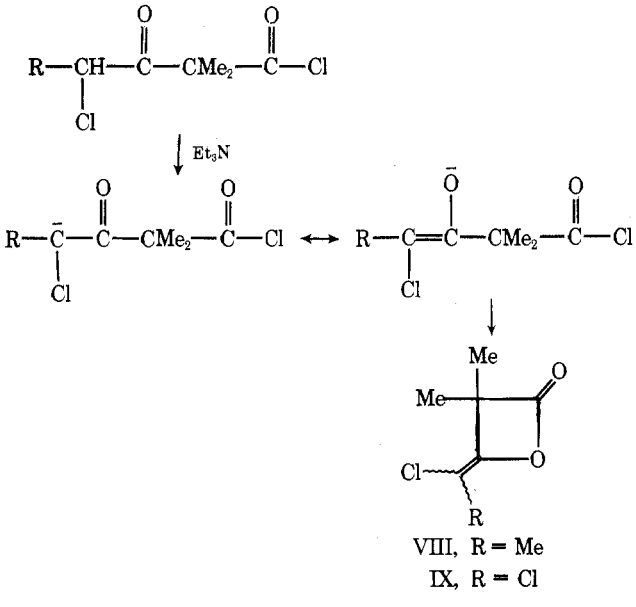
chemical shift of δ 4.0 were derived from the 2-oxetanone which resulted from cycloaddition across the carbon–carbon double bond of the *tert*-butylketene. It was found that for mixed dimerizations of *tert*-butylketene with methylchloro- or ethylchloroketenes, cycloaddition occurred only across the carbon–carbon double bond of the haloketenes. However, for *tert*-butylbromo- and *tert*-butylchloroketenes, cycloaddition occurred only across the carbon–carbon double bond of *tert*-butylketenes.

Since it is known that ketenes will react with acid halides to form β-keto acid halides and that these acid halides can cyclize to form cyclobutanediones, it seemed highly desirable to synthesize some β-keto acid halides. 4,4-Dichloro-3-keto-2,2-dimethylbutanoyl chloride and 4-chloro-3-keto-2,2-dimethylpentanoyl chloride were synthesized by the addition



R = Me, Cl

of dimethylketene to α-chloropropionyl chloride and dichloroacetyl chloride, respectively.[6] These β-keto acid chlorides



VIII, R = Me
IX, R = Cl

were treated separately with triethylamine in benzene under the same conditions as the mixed dimerizations. The 2-oxetanones were produced in both cases with no evidence of the dione dimer. The two 2-oxetanones were characterized by infrared, NMR, mass spectroscopy, and elemental analysis. Apparently, triethylamine abstracts the γ hydrogen to form an enolate anion which can then undergo an intramolecular nucleophilic displacement to form the 2-oxetanone.

Several attempts to synthesize the β-keto acid halide from dimethylketene and 2-chloro-3,3-dimethylbutanoyl chloride were unsuccessful. Also, attempts to isolate the β-keto acid chloride from the reaction mixture of equal molar amounts of α-chloropropionyl chloride, isobutyryl chloride, and triethylamine in benzene resulted in formation of only the α-chlorovinyl ester and the mixed dimer. No evidence of the β-keto acid chloride could be found. Furthermore, the addition of α-chloropropionyl chloride to a solution of *n*-propylmethylketene and triethylamine in benzene resulted in only the formation of the α-chlorovinyl ester and the mixed dimer. No evidence of any β-keto acid chloride could be found.

The dimerization of *tert*-butylketene with methylchloro- or ethylchloroketene resulted in the formation of a 2-oxetanone (IVa and Va) which is the result of cycloaddition across the carbon–carbon double bond of the halogenated ketene. The formation of these 2-oxetanones from the corresponding β-keto acid halide is very unlikely because it would require the haloketene adding to 3,3-dimethylbutanoyl chloride. This is quite unlikely for steric reasons but more importantly because acid halides normally require activation to add to ketenes. Conversely, this aldoketene with *tert*-butylchloro- or *tert*-butylbromoketene formed the 2-oxetanone (VIa and VIIa) whereby the addition occurred across the carbon–carbon double bond of *tert*-butylketene. An examination of the orthogonal [2 + 2] process with molecular models reveals a prohibitive steric interaction between the large *tert*-butyl groups in going from the orthogonal state to the 2-oxetanone. However, the formation of the necessary β-keto acid halides seems quite likely. Consequently, the most likely route to the 2-oxetanone mixed dimer is through the β-keto acid halide intermediate. The mixed dimerizations of *tert*-butylketene appear to be quite sensitive to steric effects, but the [2 + 2] process seems more sensitive than the β-keto acid halide pathway.

Since it is known that 2-oxetanone dimers of ketenes can isomerize to the 1,3-cyclobutanedione dimers, and vice versa, it seemed necessary to demonstrate whether isomerization of any kind was occurring in the reaction mixtures. The 2-oxetanone dimers of the *tert*-butylketene with *tert*-butylchloro- or methylchloroketenes in benzene containing triethylamine, upon refluxing for 24 h, underwent no change. Likewise, the dione dimer of methylchloroketene and *n*-propylmethylketene upon refluxing in benzene containing triethylamine revealed no change. Also, the dimerization was run both with a stoichiometric amount of triethylamine and with an excess of amine. The results were the same in both cases; only 2-oxetanone dimer was produced. Furthermore, the 2-oxetanone dimers in heptane or hexane containing a catalytic amount of sodium methoxide, upon refluxing for 24 h, underwent no change. Consequently, it is concluded that no isomerization occurred under the reaction conditions, and the results obtained actually represent the cycloaddition results.

In conclusion studies with alkylhaloketenes and dialkylketenes revealed only mixed dimers with the dione structure which are believed to be the result of cycloaddition of the two different ketenes. These mixed dimerizations are sensitive to steric effects, as no dimers were obtained when the substituents on the ketenes were bulky such as isopropyl and *tert*-butyl. Conversely, studies with the aldoketene, *tert*-butyl-

ketene, yielded only 2-oxetanone mixed dimers with the alkylhaloketenes with no evidence of the diones. Two different β-keto acid halides were prepared and shown to undergo conversion to the corresponding 2-oxetanones upon treatment with triethylamine. Consequently, it seems that even in the mixed dimerizations, if the two ketenes are ketoketenes the resultant dimers will be of the dione structure, and if one of the ketenes is an aldoketene, then only the 2-oxetanone is produced.

Experimental Section

^{1}H NMR spectra were recorded on a Jeolco PS-100 NMR spectrometer employing tetramethylsilane as an internal standard and CCl_4 as the solvent. All solvents and triethylamine were dried by distillation from sodium. VPC was performed on an F & M Scientific Model 700 gas chromatograph with 10 ft × 0.25 in. columns packed with 10% SE-30 and Carbowax 20M on an acid-washed Chromosorb W (80.000). Dimethylketene was prepared by the pyrolysis of tetramethylcyclobutanedione. The β-keto acid halides were prepared as previously described.[6]

General Procedure for Mixed Dimerizations. To a refluxing solution of 0.1 mol of α-halo acid chloride and 0.1 mol of 2-methylpentanoyl chloride, 2,3-dimethylbutanoyl chloride, or 3,3-dimethylbutanoyl chloride in 150 ml of benzene was added dropwise with stirring 0.25 mol of triethylamine in 20 ml of benzene. The reaction mixture was stirred for 8 h to 2 days and the salt removed by filtration, and then the filtrate was concentrated under vacuum and vacuum distilled.

2-Chloro-2,4-dimethyl-4-*n*-propyl-1,3-cyclobutanedione (I). The mixed dimer of methylchloroketene and *n*-propylmethylketene was obtained after refluxing for 1.5 days in a 57% yield at bp 42–45 °C (0.05 mm); ir 1761 cm^{-1} (C=O); NMR a multiplet centered at δ 1.60 out of which there were four singlets at 1.36, 1.52, 1.64, and 1.72.

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.29; H, 6.90; Cl, 18.83. Found: C, 57.23; H, 6.87; Cl, 18.62.

2-Chloro-2,4-dimethyl-4-isopropyl-1,3-cyclobutanedione (II). The reaction mixture was refluxed for 2 days and afforded a 42% yield of the mixed dimer of methylchloroketene and isopropylmethylketene: bp 47–50 °C (0.8 mm); ir 1754 cm^{-1} (C=O); NMR four singlets at δ 1.27, 1.46, 1.60, and 1.66 and a multiplet at δ 2.40; mass spectrum parent peak at *m/e* 188.

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.29; H, 6.70. Found: C, 57.52; H, 6.92.

2-Chloro-2-*tert*-butyl-4-methyl-4-*n*-propyl-1,3-cyclobutanedione (III). The mixed dimer of *tert*-butylchloroketene and *n*-propylmethylketene was obtained after refluxing for 2 days in a 48% yield: bp 64–65 °C (0.25 mm); ir 1754 cm^{-1} (C=O); NMR δ 0.95 (m), 1.15 (s, 9 H), 1.28 (s), and 1.56 (s) out of multiplet, 1.85; mass spectrum parent peak at *m/e* 230.

Anal. Calcd for $C_{12}H_{19}ClO_2$: C, 62.47; H, 8.24; Cl, 15.40. Found: C, 62.67; H, 8.69; Cl, 15.99.

3-Chloro-3-methyl-4-(2,2-dimethylpropylidene)-2-oxetanone (IVa). The mixed dimer of *tert*-butylketene and methylchloroketene was isolated after refluxing for 8 h (32% yield): bp 45–48 °C (0.08 mm); ir, 1887, 1818 (C=O), and 1724 cm^{-1} (C=C); NMR δ 1.18 (s, 9 H), 1.88 (s, 3 H), and 4.84 (s, 1 H).

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.29; H, 6.90; Cl, 18.83. Found: C, 56.72; H, 6.91; Cl, 18.74.

3-Chloro-3-ethyl-4-(2,2-dimethylpropylidene)-2-oxetanone (Va). The mixed dimer of *tert*-butylketene and ethylchloroketene was obtained by refluxing for 24 h (10% yield). This compound was characterized by ir at 1887, 1773 (C=O), and 1724 cm^{-1} (C=C) and conversion to the methyl keto ester (Vb).

3-*tert*-Butyl-4-(1-chloro-2,2-dimethylpropylidine)-2-oxetanone (VIa). The mixed dimer of *tert*-butylketene and *tert*-butylchlorotene was obtained by refluxing for 2 days (20% yield): bp 54–57 °C (0.1 mm); ir 1923–1852 (broad, C=O) and 1695 cm^{-1} (C=C); NMR δ 1.16 (s, 9 H), 1.32 (s, 9 H), and 3.86 (s, 1 H). This compound was further characterized by conversion to the methyl keto ester (VIb).

3-*tert*-Butyl-4-(1-bromo-2,2-dimethylpropylidene)-2-oxetanone (VIIa). This cycloadduct of *tert*-butylketene and *tert*-butylbromoketene was obtained after refluxing for 2 days (10% yield): bp 77–80 °C (0.15 mm); ir, 1908, 1852 (C=O), and 1681 cm^{-1} (C=C); NMR δ 1.23 (s, 9 H), 1.32 (s, 9 H), and 3.80 (s, 1 H).

Anal. Calcd for $C_{12}H_{19}BrO_2$: C, 52.36; H, 6.91; Br, 29.09. Found: C, 52.10; H, 7.19; Br, 29.14.

General Procedures for Methanolysis of 2-Oxetanones. Methanolysis of the 2-oxetanones from the mixed dimerizations of halogenated ketenes and *tert*-butylketene was accomplished by refluxing for 6–8 h in methanol to give a quantitative yield of the β-keto esters. The esters revealed bands in the ir at 1748 and 1718 cm^{-1} (C=O).

Methyl 2-Chloro-3-keto-2,5,5,-trimethylhexanoate (IVb). The 2-oxetanone derived from *tert*-butylketene and methylchloroketene (IVa) upon methanolysis distilled at 47–50 °C (0.25 mm): NMR δ 1.06 (s, 9 H), 1.52 (s, 3 H), 2.50 (2 s, 2 H), and 3.78 (s, 3 H).

Methyl 2-Chloro-2-ethyl-3-keto-5,5-dimethylhexanoate (Vb). The 2-oxetanone from ethylchloroketene and *tert*-butylketene (Va) gave the methyl ester at bp 65 °C (0.05 mm); NMR δ 0.96 (t) and 1.02 (s) total of 12 H, 2.28 (q, 2 H), 2.50 (2 s, 2 H), and 3.78 (s, 3 H).

Anal. Calcd for $C_{11}H_{19}ClO_3$: C, 56.29; H, 8.10; Cl, 15.14. Found: C, 55.92; H, 8.24; Cl, 15.03.

Methyl 2-*tert*-Butyl-4-chloro-3-keto-5,5-dimethylhexanoate (VIb). This methyl keto ester was derived from the 2-oxetanone from *tert*-butylketene and *tert*-butylchloroketene (VIa) and was obtained at 58–60 °C (0.05 mm): NMR δ 1.10 (s, 18 H), 3.64 (s, 1 H), 3.70 (s, 3 H), and 4.0 (s, 1 H); mass spectrum parent peak at *m/e* 262.

Anal. Calcd for $C_{13}H_{23}ClO_3$: Cl, 13.52. Found: Cl, 13.35.

Methyl 4-Bromo-2-*tert*-butyl-3-keto-5,5-dimethylhexanoate (VIIb). This ester was derived from the 2-oxetanone from *tert*-butylketene and *tert*-butylbromoketene (VIIa) and was obtained at 60–65 °C (0.025 mm): NMR δ 1.08 (s, 9 H), 1.12 (s, 9 H), 3.68 (s) and 3.70 (s) total of 4 H, and 4.04 (s, 1 H); mass spectrum parent peak at *m/e* 274.

General Procedure for the Dehydrochlorination of β-Keto Acid Chlorides. To 0.06 mol of triethylamine in 20 ml of benzene was added 0.03 mol of β-keto acid chloride (4-chloro-3-keto-2,2-dimethylpentanoyl chloride or 4,4-dichloro-3-keto-2,2-dimethylbutanoyl chloride) in 5 ml of benzene. After the addition, the reaction mixture was refluxed for about 5 h. The amine salt was removed by filtration and washed with benzene. The solvent was removed by evaporation and the residue vacuum distilled.

3,3-Dimethyl-4-(1-chloroethylidene)-2-oxetanone (VIII). This compound appeared to undergo some decomposition during the distillation. The crude product was characterized by ir, 1887, 1818 (C=O), and 1754 cm^{-1} (C=C); NMR δ 1.48 (so, 6 H) and 2.02 (s, 3 H); mass spectrum parent peak at *m/e* 160.

3,3-Dimethyl-4-(dichloromethylene)-2-oxetanone (IX). This 2-oxetanone was distilled at 37–39 °C (0.24 mm): ir 1890, 1818 (C=O), and 1695 cm^{-1} (C=C); NMR δ 1.52 (s); mass spectrum parent peak at *m/e* 180.

Anal. Calcd for $C_6H_6Cl_2O_2$: C, 39.78; H, 3.31; Cl, 39.23. Found: C, 39.85; H, 3.42; Cl, 38.95.

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Registry No.—*trans*-I, 59005-14-0; *cis*-I, 59005-15-1; *trans*-II, 59005-16-2; *cis*-II, 59005-17-3; *trans*-III, 59005-18-4; *cis*-III, 59005-19-5; IVa, 59005-20-8; IVb, 59005-21-9; Va, 59005-22-0; Vb, 59005-23-1; VIa, 59005-24-2; VIb, 59005-25-3; VIIa, 59005-26-4; VIIb, 59005-27-5; VIII, 59005-28-6; IX, 59005-29-7; methylchloroketene, 13363-86-5; propylmethylketene, 29336-29-6; isopropylmethylketene, 59005-30-0; *tert*-butylchloroketene, 52920-17-9; *tert*-butylketene, 59005-31-1; ethylchloroketene, 29264-44-6; *tert*-butylbromoketene, 29264-48-0.

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