# Halogenated Ketenes. 31. Cycloaddition of Dichloroketene with Hindered Olefins

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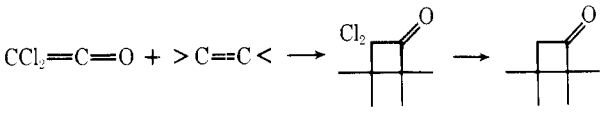
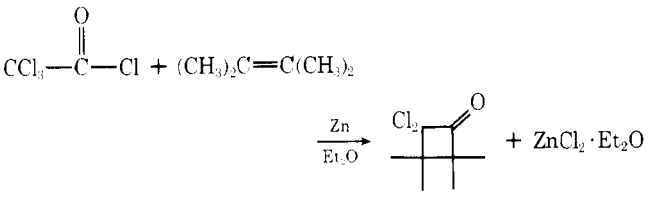
The cycloaddition of dichloroketene with tri- and tetrasubstituted ethylenes and other unreactive olefins utilizing an improved procedure has been accomplished. This procedure involves the preparation of dichloroketene by the zinc dechlorination of trichloroacetyl chloride in the presence of the olefins. The reactive ketene is formed so as to deter polymerization of the ketene in favor of cycloaddition. Dichloroketene has been added to 2,3-dimethyl-2-butene, 1-methylcyclohexene, 2-methyl-2-butene, 2,5-dimethyl-2,4-hexadiene, α-pinene, and 5-methylene-2-norbornene. The yields for the cycloaddition of dichloroketene with cyclohexene, 1-pentene, and norbornene have been significantly improved. The cycloaddition of chloroketene with 2-methyl-2-butene and 2,3-dimethyl-2-butene has been accomplished in a similar manner. The reductive removal of the chlorine atoms from several of the 2,2-dichlorocyclobutanones with tri-*n*-butyltin hydride or zinc and acetic acid is also reported.

In recent years the cycloaddition of dichloroketene with olefins has been used as a key step in a variety of syntheses.[1-11] The reactivity of dichloroketene and the ease of removal of the chlorine atoms by zinc in acetic acid or tri-*n*-butyltin hydride in good yield provide an elegant synthesis of cyclobutanone derivatives.[12-14] However, almost all of these reports are with mono- and disubstituted ethylenes. Tri- and tetrasubstituted ethylenes either yield no cycloaddition product or very low yields.[12]



We now wish to report the cycloaddition of dichloroketene with tri- and tetrasubstituted ethylenes and other unreactive olefins utilizing an improved procedure for the in situ cycloaddition. This procedure involves the preparation of the ketene by the zinc dehalogenation method in the presence of the olefins. The essential factors involve formation of the reactive dichloroketene so as to deter polymerization of the ketene in favor of the cycloaddition process. This is accomplished by effecting the in situ cycloadditions at a higher dilution and a slower rate of addition of the acid halide to the zinc slurry.

The in situ cycloaddition of dichloroketene, prepared by the zinc dechlorination of trichloroacetyl chloride, with an olefin to yield the 2,2-dichlorocyclobutanone is illustrated with 2,3-dimethyl-2-butene. The 2,2-dichlorocyclobutanones and

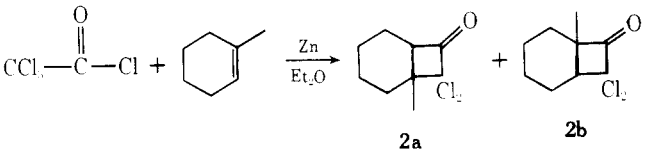


the yields of the preparations are shown in Table I. The infrared spectra of the cycloadducts revealed that the carbonyl absorptions range from 1798 to 1808 $cm^{-1}$.

Dichloroketene is unstable and very susceptible to polymerization. Trapping this ketene with olefins competes with this polymerization process. The rate of polymerization is concentration dependent, and dilution of the ketene results in a slower rate of polymerization and a more favorable condition for cycloaddition. The literature procedures indicate concentrations of 0.5–0.6 M acid halide and/or ketene in the reaction mixture.[12,15] Our improved procedure utilizes approximately a 0.05 M solution of acid halide and/or ketene in the reaction mixture.

The optimum conditions for these cycloadditions appear to be the addition of trichloroacetyl chloride in ether to a stirred mixture of the olefin in ether and the activated zinc at room temperature over a 4–6 h period. A faster rate of addition results in more polymerization of dichloroketene and lower yields of the cycloadducts. The formation of product begins to level off at about 10 h after completion of the addition with no apparent loss of product at even longer stirring times.

In the cycloaddition of dichloroketene and 1-methylcyclohexene, unlike a previous report,[16] we have observed both of the possible regioisomers, 8,8-dichloro-1-methylbicyclo[4.2.0]octan-7-one (**2a**) and 7,7-dichloro-1-methylbicyclo[4.2.0]octan-8-one (**2b**), which were formed in an approx-



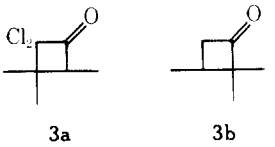
**2a** **2b**

imate ratio of 4:1 in favor of the expected **2a** based on VPC analysis of the dehalogenated isomer mixture.

This reaction was used to optimize the reaction conditions. The best yield of **2a** by published procedure[9] was 23%. Using the typical procedure amounts, four reactions with addition times of 2, 30, 90, and 230 min gave isolated yields of **2a** of 40, 50, 62, and 75%, respectively. No exotherm was observed with any of the additions using the present procedure.

The effect of additional stirring was determined by VPC analysis of the 230-min reaction. The amount of **2a** relative to the amount present at the end of the acid chloride addition was as follows: 30 min, 1.17; 1 h, 1.53; 2 h, 1.72; 4 h, 2.08; 8 h, 2.17; and 17 h, 2.22.

Two regioisomers are also possible in the cycloaddition of dichloroketene with 2-methyl-2-butene: 2,2-dichloro-3,3,4-trimethylcyclobutanone (**3a**) and 2,2-dichloro-3,4,4-trimethylcyclobutanone (**3b**). Only the expected former isomer,



**3a** **3b**

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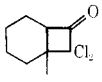
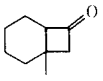
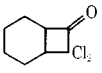
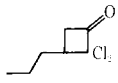
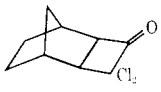
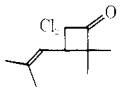
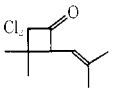
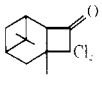
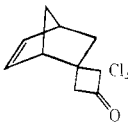
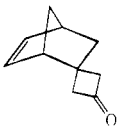
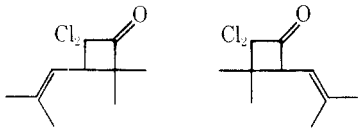
**Table I. Cycloadducts of Dichloroketene with Hindered and Unreactive Olefins**

| compd | olefin | registry no. | cycloadduct | registry no. | yield, % | reduction product | registry no. |
|---|---|---|---|---|---|---|---|
| 1 | 2,3-dimethyl-2-butene | 29416-06-4 |  | 66239-90-5 | 75 |  | 4070-14-8 |
| 2 | 1-methylcyclohexene | 591-49-1 |  | 68212-48-6 | 80 |  | 68212-54-4 |
| 3 | 2-methyl-2-butene | 513-35-9 |  | 68212-49-7 | 73 |  | 28290-01-9 |
| 4 | cyclohexene | 110-83-8 |  | 13866-27-8 | 90 (52[15]) | | |
| 5 | 1-pentene | 109-67-1 |  | 13866-29-0 | 58 (31[15]) | | |
| 6 | norbornene | 498-66-8 |  | 68295-68-1 | 64 (10[12]) | | |
| 7a | 2,5-dimethyl-2,4-hexadiene | 764-13-6 |  | 68212-50-0 | 30 | | |
| 7b | | |  | 68212-51-1 | 13 | | |
| 8 | α-pinene | 80-56-8 |  | 68212-52-2 | 16 | | |
| 9 | 5-methylene-2-norbornene | 694-91-7 |  | 68212-53-3 | 60 |  | 68212-55-5 |

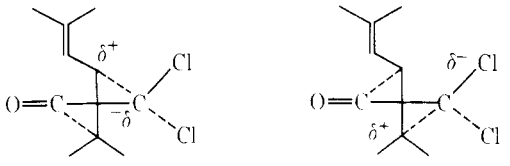
**3a,** was found. This is consistent with a recent report by Brook and co-workers on the cycloaddition of *tert*-butylcyanoketene and 2-methyl-2-butene in which only a single cyclobutanone was reported.[17]

The cycloaddition of dichloroketene with 2,5-dimethyl-2,4-hexadiene can also yield two regioisomers as illustrated. Both of these isomers were found in yields of 30 and 13%, with the expected 3-(2-methylpropenyl) isomer, **7a,** predominating. The formation of the 4-(2-methylpropenyl) isomer, **7b,** was



**7a** **7b**

unexpected since several other conjugated dienes (cyclic and noncyclic) have been reported to yield only the regioisomer which provides the greatest amount of stabilization of positive character on the β or 3-carbon atom in the transition state. Molecular models reveal that the best steric approach of the ketene to the transoid conformation of the diene positions the oxygen atom of the ketene cis to the vinyl group. This allows two dipolar transition states from the LUMO ketene–HOMO alkene model in which **7a** forms from an allylic cation-type transition state and **7b** forms from a tertiary carbocation-type transition state. Apparently the energy difference between these two transition states is not sufficient to eliminate one of the two pathways. With butadiene the allylic-type dipolar transition state would be much more stable than the primary

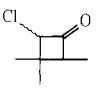
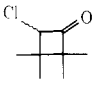


carbocation-type dipolar transition state; thus, only the 3-vinylcyclobutanone is observed.[12]

New regioisomer structures were assigned by interpretation of mass and NMR spectra. A major fragmentation process upon electron impact in a mass spectrometer for cyclobutane systems is ring splitting into two ethylene fragments.[18] The cyclobutanones of this work show a similar response in the mass spectrometer, allowing regioisomers to be assigned based on the major fragments present. Isomers **7a** and **7b** can be distinguished by the presence of major fragments with *m/e* values corresponding to $(CH_3)_2CCO^+$ in only one spectrum and $(CH_3)_2CCHCCO^+$ only in the other spectrum. Since only **7a** can fragment to $(CH_3)_2CCO^+$ and only **7b** can fragment to $(CH_3)_2CCHCCO^+$, identification of the regioisomers is made. NMR data is consistent with this assignment as the methine proton should experience more deshielding in **7b** (δ 4.22) due to the combined effect of the carbonyl and the vinyl groups than the methine proton in **7a** (δ 3.48) where it is removed from the carbonyl influence. Similar spectral interpretation was used to assign the structures of **2a** and **3.**

The cycloaddition of dichloroketene with 5-methylene-2-norbornene yielded only the spiro cycloadduct corresponding to addition across the exocyclic double bond even though the strain is much greater in the internal double bond.

**Table II. Cycloadducts of Chloroketene with Hindered and Unreactive Olefins**

| compd | olefin | cycloadduct | registry no. | yield, % |
|---|---|---|---|---|
| 10 | 2-methyl-2-butene |  | 59528-57-3 | 33 |
| 11 | 2,3-dimethyl-2-butene |  | 59528-44-8 | 55[21] |

As we have stated in a previous report on the cycloaddition of methylchloroketene with 5-methylene-2-norbornene, this is a further indication that ketene–olefin cycloadditions are sterically controlled.[19] A recent report on the cycloaddition of diphenylketene with methylenenorbornenes also reveals this much greater reactivity of the exocyclic double bond.[20]

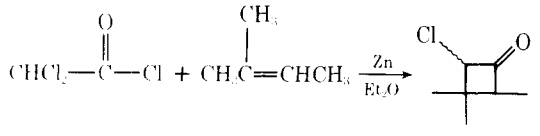
The improved cycloaddition procedure which we have described also provides significantly better yields for the cycloaddition of dichloroketene with mono- and disubstituted ethylenes as indicated in Table I for cyclohexene, norbornene, and 1-pentene.

Another distinctive advantage of this improved procedure enables the ratio of olefin/acid halide to be reduced to 1. In previous literature procedures a large excess of olefin was thought to be necessary to successfully compete with the polymerization process. This consideration becomes increasingly important when expensive or limited quantities of olefin are available.

Another convenient method for the preparation of dichloroketene is the dehydrochlorination of dichloroacetyl chloride with triethylamine. This method has also been widely used for the in situ cycloaddition of dichloroketene to a variety of unsaturated compounds. Polymerization of the ketene is also a troublesome competing reaction in this process. We made an effort to improve this procedure over established descriptions in the literature by focusing attention on the concentration of ketene and/or acid halide and also the order and rate of addition. The in situ cycloaddition of 2-methyl-2-butene with dichloroketene at a molar concentration of 0.05 resulted in a yield of the 2,2-dichloro-3,3,4-trimethylcyclobutanone of 31%. As can be seen from Table I, this contrasts with a yield of 73% when the in situ cycloaddition is done by the dehalogenation method.

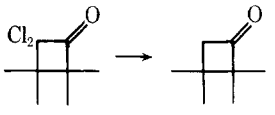
Attempted cycloadditions of dichloroketene with several other olefins utilizing our improved procedure were either unsuccessful or gave very low yields (<10%) of cyclobutanones. These olefins included trichloroethylene, allyl acetate, isopropenyl acetate, and the dimethyl acetal of acrolein. However, these unsuccessful cycloadditions with dichloroketene are the result of electronic effects rather than steric problems.

The in situ cycloaddition of chloroketene with some hindered olefins has also been accomplished in a similar manner as illustrated with 2-methyl-2-butene. The 2-chlorocyclobu-



tanones and the yields of the preparations are shown in Table II. Dichloroketene is much superior to chloroketene in olefin cycloadditions in terms of yields of cycloadducts even though chloroketene has a less hindered transition state for the cycloaddition than dichloroketene. In the chloroketene cycloadditions the polymerization of chloroketene is also the competing reaction as significant amounts of dark nonvolatile tars are produced. Consequently, if the synthesis of a cyclobutanone derivative involved the reductive removal of the chlorine atom(s), the ketene of choice would certainly be dichloroketene as compared to chloroketene due to the significantly better yields.

The reductive removal of the chlorine atoms from 2,2-dichlorocyclobutanones with tri-*n*-butyltin hydride or zinc and acetic acid is easily accomplished. The resultant nonhalocyclobutanones possess the same structure as would be obtained



by the cycloaddition of ketene itself with the olefin. The advantage of dichloroketene over ketene is of course the much greater reactivity of this ketene. Several of the 2,2-dichlorocyclobutanones described in this paper were reduced with tri-*n*-butyltin hydride and/or zinc and acetic acid. The results of these reductions are tabulated in Table I.

The zinc–acetic acid reduction of 2,2-dichloro-3,3,4-trimethylcyclobutanone (**3**) resulted in ring opening.

## Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer R-12B nuclear magnetic resonance spectrometer employing carbon tetrachloride as the solvent and either chloroform or tetramethylsilane as an internal standard. Analytical and spectroscopic samples were obtained by VPC on a Perkin-Elmer Model 3920-B gas chromatograph with a 6 ft × 0.25 in column packed with 10% SE-30 on acid-washed Chromosorb W (80/100) support or a 10 ft × 0.25 in. column packed with 10% QF-1 on acid-washed Chromosorb W (80/100) support. The infrared spectra were recorded on a Beckman IR 33 and a Perkin-Elmer Model 621 grating infrared spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer.

Ether was dried and purified by distillation from potassium sodium alloy prior to use. The zinc was activated by a procedure described by one of us and was always kept and used under a nitrogen atmosphere.[2] Triethylamine was commercially available and was dried over sodium metal and distilled prior to use. Trichloroacetyl chloride was also commercially available but was distilled prior to use. Dichloroacetyl chloride was prepared from dichloroacetic acid using thionyl chloride and distilled prior to each run.

**Typical Procedure for Dichloroketene Cycloadditions.** A solution of 0.025 mol of freshly distilled trichloroacetyl chloride in 250 mL of dry ether was added over 4 h to a stirred, refluxing mixture of 0.025 mol of olefin in 250 mL of dry ether and 5 g of activated zinc under a nitrogen atmosphere. The reaction mixture was stirred at reflux for an additional 16 h after the addition was complete. The excess zinc was filtered, washed, dried, and usually revealed a loss of about 0.025 g-atom. The reaction solution was concentrated to about 50 mL and then stirred with 100 mL of pentane. The pentane solution was decanted from the zinc salts and evaporated, and the residue was vacuum distilled to yield the cycloadduct.

**2,2-Dichloro-3,3,4,4-tetramethylcyclobutanone (1).** From 0.025 mol of trichloroacetyl chloride, 0.025 mol of 2,3-dimethyl-2-butene, and 10.76 g of zinc in 450 mL of ether was obtained 3.64 g (75%) of **1**, bp 68–72 °C (0.55 mm), which solidified. The solid was sublimed at 50 °C (3 mm): mp 91–98 °C with decomposition; IR 1800 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 1.34 (s, 6 H), 1.28 (s, 6 H); mass spectrum, *m/e* 194 (parent).

Anal. Calcd for $C_8H_{12}Cl_2O$: C, 49.25; H, 6.20. Found: C, 49.34; H, 6.12.

**8,8-Dichloro-1-methylbicyclo[4.2.0]octan-7-one (2a).** From 0.011 mol of trichloroacetyl chloride, 0.010 mol of 1-methylcyclohexene, and 4.70 g of zinc in 150 mL of ether was obtained 1.65 g (80%) of **2a**: bp 60 °C (0.14 mm); IR 1798 $cm^{-1}$ (C=O); $^1H$ NMR ($CHCl_3$ reference) $\delta$ 3.45 (m, 1 H), 1.05–1.9 (m, 8 H), 1.28 (s, 3 H); mass spectrum, *m/e* 206 (parent).

Anal. Calcd for $C_9H_{12}Cl_2O$: C, 52.20; H, 5.84. Found: C, 51.96; H, 5.84.

**2,2-Dichloro-3,3,4-trimethylcyclobutanone (3).** From 0.05 mol of trichloroacetyl chloride, 0.052 mol of 2-methyl-2-butene, and 4.63 g of zinc in 750 mL of ether was obtained 6.58 g (73%) of **3**: bp 60 °C (0.65 mm); IR 1805 $cm^{-1}$ (C=O); $^1H$ NMR $\delta$ 3.32 (q, 1 H), 1.32 (s, 3

H), 1.00 (s, 3 H), 0.94 (d, 3 H); mass spectrum, *m/e* (relative intensity) (no parent peak) 180, 152 (4, P − CO), 124 (30, P − $CH_3CHCO$), 89 (26, P − $CH_3CHCO$, Cl), 70 (51, P − $Cl_2CCO$), 56 (100).

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.44; H, 5.57. Found: C, 46.51; H, 5.68.

**2,2-Dichloro-4,4-dimethyl-3-(2-methylpropenyl)cyclobutanone (7a) and 2,2-Dichloro-3,3-dimethyl-4-(2-methylpropenyl)cyclobutanone (7b).** A 0.025-mol portion of trichloroacetyl chloride, 0.025 mol of 2,5-dimethyl-2,4-hexadiene, and 6.37 g of zinc in 500 mL of ether yielded 1.47 g (30%) of **7a** and 0.65 g (13%) of **7b**, bp 60 °C (0.5 mm). **7a:** IR 1805 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 5.30 (d, $J$ = 9 Hz, 1 H), 3.48 (d, $J$ = 9 Hz, 1 H), 1.82 (s, 3 H), 1.72 (s, 3 H), 1.30 (s, 3 H), 1.20 (s, 3 H); mass spectrum, *m/e* (relative intensity) (no parent) 220, 157 (2.9, P − CO, Cl), 150 (100, P − $Me_2CCO$), 110 (25.5, P − $Cl_2CCO$), 70 (97, P − $C_6H_8Cl_2$).

Anal. Calcd for $C_{10}H_{14}Cl_2O$: C, 54.32; H, 6.38. Found: C, 54.54; H, 6.51.

**7b:** IR 1805 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 5.09 (d, $J$ = 8 Hz, 1 H), 4.22 (d, $J$ = 8 Hz, 1 H), 1.79 (s, 3 H), 1.65 (s, 3 H), 1.50 (s, 3 H), 1.14 (s, 3 H); mass spectrum, *m/e* (relative intensity) (no parent) 220, 157 (5.4, P − CO, Cl), 110 (11.8, P − $Cl_2CCO$), 96 (100, P − $Me_2CCl_2$), 41 (40, CHCO).

Anal. Calcd for $C_{10}H_{14}Cl_2O$: C, 54.32; H, 6.38. Found: C, 54.58; H, 6.43.

**4,4-Dichloro-2,8,8-trimethyltricyclo[5.1.1.0$^{2,5}$]nonan-3-one (8).** From 0.025 mol of trichloroacetyl chloride, 0.032 mol of $\alpha$-pinene, and 8.77 g of zinc in 500 mL of ether was obtained 0.99 g (16%) of **8**: bp 76 °C (0.35 mm); IR 1807 $cm^{-1}$ (C=O).

**2-Bicyclo[2.2.1]heptene-5-spiro-2,2-dichlorocyclobutan-3-one (9).** A 0.025-mol portion of trichloroacetyl chloride, 0.025 mol of 5-methylene-2-norbornene, and 8.95 g of zinc in 500 mL of ether yielded 2.74 g (60%) of **9** which was isolated by preparative VPC on the SE-30 column at 190 °C: IR 1808 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 6.1–6.9 (m, 2 H), 1.1–3.7 (m, 8 H); mass spectrum, *m/e* 216 (1.3, parent peak), 174 (58.7, P − $CH_2CO$), 66 (100, $C_5H_6$).

Anal. Calcd for $C_{10}H_{10}Cl_2O$: C, 55.33; H, 4.64. Found: C, 55.63; H, 4.71.

**Chloroketene Cycloadditions.** The chloroketene cycloadditions were accomplished in exactly the same manner as described for the dichloroketene cycloadditions except dichloroacetyl chloride was substituted for trichloroacetyl chloride and the temperature was at ether reflux.

**2-Chloro-3,3,4-trimethylcyclobutanone (10).** From 0.025 mol of dichloroacetyl chloride, 0.25 mol of 2-methyl-2-butene, and 10.76 g of zinc in 450 mL of ether was obtained 2.53 g (33%) of **10:** bp 84 °C (4 mm); IR 1785 $cm^{-1}$ (C=O); $^1H$ NMR ($CHCl_3$) $\delta$ 4.7 (d, $J$ = 2.3 Hz, 1 H), 3.15 (qd, $J$ = 6.5, 2.3 Hz, 1 H), 1.55 (s, 3 H), 1.15 (d, $J$ = 6.5 Hz, 3 H), 1.09 (s, 3 H); mass spectrum, *m/e* (relative intensity) (no parent peak) 131 (3.5, P − $CH_3$), 111 (6.1, P − CL), 90 (57, P − $CH_3CHCO$), 70 (79.8, P − ClCHCO), 56 (100, P − $ClCHCMe_2$).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.34; H, 7.56. Found: C, 57.24; H, 7.52.

**2-Chloro-3,3,4,4-tetramethylcyclobutanone (11).** A 0.025-mol portion of dichloroacetyl chloride, 0.125 mol of 2,3-dimethyl-2-butene, and 3.28 g of zinc in 500 mL of ether yielded 2.18 g (55%) of **11:** bp 55 °C (0.25 mm); IR 1782 $cm^{-1}$ (C=O); $^1H$ NMR ($CHCl_3$) $\delta$ 4.67 (s, 1 H), 1.08 (s, 3 H), 1.01 (s, 3 H), 0.8 (s, 6 H); mass spectrum, *m/e* 160 (parent).

Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.16. Found: C, 59.79; H, 8.21.

**2,2,3,3-Tetramethylcyclobutanone (12).** A 2.5-g (0.013-mol) portion of 2,2-dichloro-3,3,4,4-tetramethylcyclobutanone in 10 mL of cyclohexane saturated with azobis(isobutyronitrile) was added dropwise over 20 min to 15.25 g (0.052 mol) of tri-*n*-butyltin hydride in 20 mL of cyclohexane under a nitrogen atmosphere. The solution was heated at reflux for an additional 90 min. Vacuum distillation afforded 0.6 g (37%) of **12** at 24 °C (2 mm). Preparative VPC gave a solid: mp 56–58 °C; IR 1770 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 2.69 (s, 2 H), 1.18 (s, 6 H), 1.03 (s, 6 H); mass spectrum, *m/e* 126 (parent peak).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.93; H, 10.96.

From 1.35 g (6.9 mol) of **1** and 3 g of zinc in 25 mL of acetic acid refluxed for 17 h was obtained 0.58 g (66%) of **12.**

**2,3,3-Trimethylcyclobutanone (13).** This reduction was accomplished exactly as described above for **12.** From 3.31 g (0.018 mol) of 2,2-dichloro-3,3,4-trimethylcyclobutanone and 10.64 g (0.037 mol) of tri-*n*-butyltin hydride was obtained 0.54 g (27%) of 2,3,3-trimethylcyclobutanone and a 25% yield of 2-chloro-3,3,4-trimethylcyclobutanone. **13:** IR 1774 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 0.98 (d, $J$ = 7 Hz, 3 H), 1.09 (s, 3 H), 1.38 (s, 3 H), 2.53–3.28 (m, 3 H); mass spectrum, *m/e* 112 (parent peak).

Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 75.13; H, 11.00.

**1-Methylbicyclo[4.2.0]octan-7-one and 1-Methylbicyclo[4.2.0]octan-8-one (14a and 14b).** A 2-g (0.097-mol) portion of **2a** and **2b** was refluxed with 5 g of zinc in 25 mL of acetic acid for 16 h, and there was obtained 1.2 g (90%) of a mixture containing 70% **14a,** 21% of **14b,** and 9% of the monochloro derivative of **14a. 14a:** IR 1780 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 2.52–2.88 (m, 3 H), 1.22–1.7 (m, 11 H); mass spectrum, *m/e* 138 (parent peak).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.22; H, 10.51.

**14b:** IR 1780 $cm^{-1}$ (C=O); $^1H$ NMR ($CHCl_3$) $\delta$ 2.42 (m), 1.2–2.3 (m).

**2-Bicyclo[2.2.1]heptene-5-spirocyclobutan-3-one (15).** From 1.25 g (0.057 mol) of **9,** 3.34 g (0.0114 mol) of tri-*n*-butyltin hydride, and 15 mL of cyclohexane saturated with azobis(isobutyronitrile) was obtained 0.57 g (68%) of **15:** bp 68 °C (0.4 mm); IR 1780 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 6.02 (broad s, 2 H), 3.02, 2.95, 2.78 (m, s, broad s, 6 H), 2.05 (d of d, $J$ = 3.5 Hz, 2 H), 1.52 (broad s, 2 H); mass spectrum, *m/e* 148 (parent peak).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.71; H, 8.39.

There was also obtained 0.14 g (13%) of the monochloro compound, bicyclo[2.2.1]heptane-5-spiro-2-chlorocyclobutan-3-one: IR 1790 $cm^{-1}$ (C=O); $^1H$ NMR ($CCl_4$) $\delta$ 6.20 (m, 2 H), 4.75 (d of d, 1 H), 1.23–3.20 (m, 8 H); mass spectrum, *m/e* 182 (parent peak).

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**Registry No.—2b,** 68212-56-6; **14b,** 68212-57-7; trichloroacetyl chloride, 76-02-8; dichloroacetyl chloride, 79-36-7; bicyclo[2.2.1]heptane-5-spiro-2-chlorocyclobutan-3-ane, 68212-58-8; dichloroketene, 4591-28-0; chloroketene, 29804-89-5.

## References and Notes[22]

(1) W. T. Brady, "The Chemistry of Ketenes and Allenes", S. Patai, Ed., Interscience, New York, in press.
(2) W. T. Brady, *Synthesis,* 415 (1971).
(3) S. M. Ali, T. V. Lee, and S. M. Roberts, *Synthesis,* 155 (1977).
(4) B. M. Jacobson and P. D. Bartlett, *J. Org. Chem.,* **38,** 1030 (1973).
(5) K. Tanaka and A. Yoshikoshi, *Tetrahedron,* **27,** 4889 (1971).
(6) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *J. Chem. Soc. D,* 89 (1970).
(7) E. J. Corey, K. C. Nicolaou, and D. J. Beames, *Tetrahedron Lett.,* 2439 (1974).
(8) P. A. Grieco, *J. Org. Chem.,* **37,** 2363 (1972).
(9) K. E. Harding, J. W. Trotter, and L. M. May, *J. Org. Chem.,* **42,** 2715 (1977).
(10) L. R. Smith, G. E. Gream, and J. Meinwald, *J. Org Chem.,* **42,** 927 (1977).
(11) A. D. Baker, D. Wong, S. Lo, M. Bloch, G. Horozoglu, N. L. Goldman, R. Engel, and D. C. Liotta, *Tetrahedron Lett.,* 215 (1978).
(12) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron,* **27,** 615 (1971).
(13) M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Lett.,* 3583 (1968).
(14) W. T. Brady, E. F. Hoff, Jr., R. Roe, Jr., and F. H. Parry, III, *J. Am. Chem. Soc.,* **91,** 5679 (1969).
(15) W. T. Brady and O. H. Waters, *J. Org. Chem.,* **32,** 3703 (1967).
(16) P. W. Jeffs and G. Molina, *J. Chem. Soc., Chem. Commun.,* 3 (1973).
(17) P. R. Brook, A. M. Eldeeb, K. Hunt, and W. S. McDonald, *J. Chem. Soc., Chem. Commun.,* 10 (1978).
(18) D. A. Bak and K. Conrow, *J. Org. Chem.,* **31,** 3608 (1966).
(19) W. T. Brady and A. D. Patel, *J. Org. Chem.,* **38,** 4106 (1973).
(20) J. Becherer and R. W. Hoffmann, *Tetrahedron,* **34,** 1193 (1978).
(21) This cycloadduct has been prepared by a similar procedure: M. J. van den Brink, H. Austermuhle-Bertola, and P. A. Kramer, U.S. Patent 4 028 418, June 7, 1977.