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# Halogenated Ketenes. XXV. Cycloadditions with Allenes[1]

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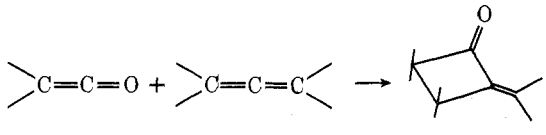
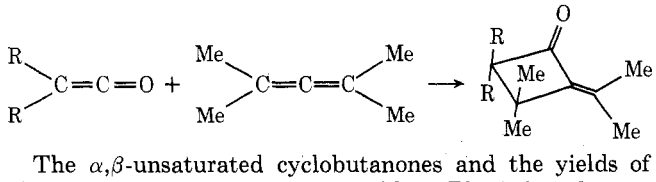
The cycloaddition of variously substituted ketenes with tetramethylallene, 1,2-cyclononadiene, and 1-methyl-1,2-cyclononadiene to give $\alpha,\beta$-unsaturated cyclobutanones is described. Tetramethylallene and 1,2-cyclononadiene exhibit unusual reactivity in such cycloadditions. Several other allenes investigated were very unreactive.

Allenes undergo cycloaddition reactions with ketenes to yield $\alpha,\beta$-unsaturated cyclobutanones. Tetramethylallene exhibited unexpected reactivity in cycloadditions with dimethyl- and diphenylketenes as reported by Hasek and coworkers in 1965.[2] Moore and coworkers have reported the cycloaddition of *tert*-butylcyanoketene and 1,2-cyclononadiene and revealed that, when the diene is partially resolved, both epimers show appreciable optical activity.[3] This type of stereospecificity has also been reported for the cycloaddition of dimethylketene with 1,3-dimethylallene and 1,2-cyclononadiene.[4,5] We now report on an investigation into the general nature of the cycloaddition of ketenes and allenes with particular emphasis on halogenated ketenes.



The reaction of ketenes with tetramethylallene is a 1,2-cycloaddition reaction and can be generally represented as follows.



The $\alpha,\beta$-unsaturated cyclobutanones and the yields of the preparations are shown in Table I. The infrared spectra of the cycloadducts revealed the carbonyl absorptions at 1740–1760 $cm^{-1}$ and the C=C absorptions at 1660 $cm^{-1}$.

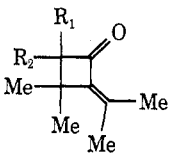
The cycloadditions of the halogenated ketenes and tetramethylallene were effected whereby the ketene was generated in the presence of the diene. This was accomplished by the triethylamine dehydrohalogenation of an appropriately substituted acid halide in refluxing hexane containing tetramethylallene. The order of addition of acid halide and amine was very critical. If the acid halide is added to a refluxing solution of hexane, tetramethylallene, and triethylamine, in some cases no cycloadduct can be isolated and in others a very small amount. This is the result of the amine reacting with the cycloadduct as it is formed. Conversely, the addition of triethylamine to the acid halide, hexane, and the diene results in a much improved yield in spite of the fact that this order of addition is desirable for the formation of $\alpha$-halovinyl esters.[6] Unfortunately, some of the $\alpha$-halovinyl ester is produced and is difficult to separate from the cycloadduct.

The cycloadducts of phenylmethyl- and phenylethylketenes with tetramethylallene were prepared by combining tion of the amine at −78° prior to the addition of the allene. Subsequent warming to room temperature produces a 25% yield of the cycloadduct.

The cycloadducts of phenylmethyl- and phenylethylketenes with tetramethylallene were prepared by combining equimolar amounts of the insolable ketene and the allene at room temperature.

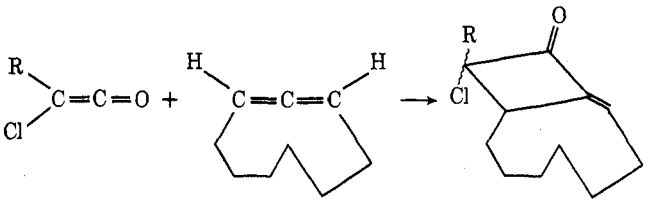
The nmr data for the tetramethylallene cycloadducts are recorded in Table II. The two methyl groups of the isopropylidene substituent are in different environments and thus are revealed as two singlets in the spectra ($\delta$ 1.7–1.9 and 1.95–2.1). The methyl protons closest to the carbonyl are expected to be further downfield. The two methyl groups attached to the 3 carbon of the cyclobutanone are above and below the plane of the ring and will be in identical environments only when the substituents on the ketene are identical (a symmetrical ketene). This is evident in the dichloroketene (IV) and bromochloroketene (V) cycloadducts in that IV shows only one singlet at $\delta$ 1.5 for the two methyl groups and V reveals two singlets at $\delta$ 1.5 and 1.6; yet it is interesting to note that, in the ethylchloroketene adduct (III), these methyl groups occur at identical chemical shifts. The spectrum of the methylbromoketene adduct (II) revealed five singlets with equivalent areas as expected. However, the methylchloroketene adduct (I) revealed only four singlets in a ratio of 2:1:1:1. Apparently, the methyl of the ketene functionality and the methyl trans to the chloro substituent overlap at $\delta$ 1.4.

**Table I**
**Cycloadducts from Halogenated Ketenes and Tetramethylallenes**



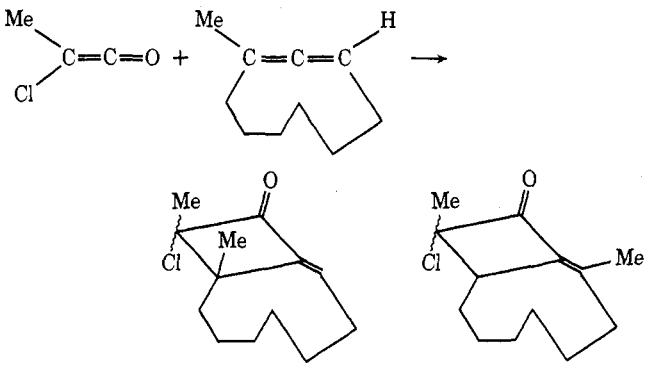
| Compd | $R_1$ | $R_2$ | Yield, % |
|---|---|---|---|
| I | Me | Cl | 72 |
| II | Me | Br | 65 |
| III | Et | Cl | 70 |
| IV | Cl | Cl | 55 |
| V | Cl | Br | 45 |
| VI | Cl | H | 25 |
| VII | Me | H | 20 |
| VIII | Me | Ph | 90 |
| IX | Et | Ph | 90 |

The *in situ* cycloaddition of 1,2-cyclononadiene with methylchloroketene and dichloroketene occurred smoothly and in good yield (72 and 75%, respectively). The infrared spectra revealed C=C absorptions at 1670 $cm^{-1}$ and carbonyl absorptions at 1770 $cm^{-1}$. The carbonyl absorptions are higher than those observed for the tetramethylallene adducts, but this is probably to be expected because of the strain imposed by the rigid cyclic system.



X, R = Cl
XI, R = Me

Likewise the cycloaddition of methylchloroketene and 1-methyl-1,2-cyclononadiene occurred readily to yield the expected adduct in 70% yield. The nmr spectrum revealed that both isomers were produced with a predominance of that isomer resulting from cycloaddition with the least substituted double bond.

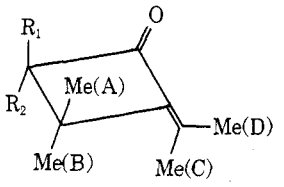


XII

Several of the other allenes which were investigated included phenylallene, 1,2-nonadiene, 1,1-dimethylallene, allene, and trichloromethylallene. In all of these cases, either no cycloadduct could be detected or a very small amount was produced.

Cyclopentadiene is one of the most reactive olefinic compounds in ketene cycloaddition reactions, and tetramethylallene appears to closely parallel this diene in reactivity. In an effort to compare the two dienes a competitive experiment was performed and it was found that a ratio of the two cycloadducts was 5:1 in favor of the cyclopentadiene.

**Table II**
**Nmr Data of Tetramethylallene Cycloadducts[a]**



| Compd | A | B | C | D | $R_1$ | $R_2$ |
|---|---|---|---|---|---|---|
| I | 1.4 | 1.5 | 1.8 | 2.0 | Me, 1.4 | Cl |
| II | 1.4 | 1.5 | 1.9 | 2.1 | Me, 1.7 | Br |
| III | 1.4 | 1.4 | 1.8 | 2.0 | Et, 1.85 (q), 1.1 (t) | Cl |
| IV | 1.5 | 1.5 | 1.9 | 2.0 | Cl | Cl |
| V | 1.5 | 1.6 | 1.9 | 2.1 | Cl | Br |
| VI | 1.45 | 1.3 | 1.8 | 2.0 | Cl | H, 4.1 |
| VII | 1.4 | 1.2 | 1.7 | 1.95 | Me, 1.0 (d) | H, 2.5 (q) |
| VIII | 1.5 | 0.9 | 1.8 | 2.1 | Me, 1.4 | Ph, 7.2 (m) |
| IX | 1.5 | 0.9 | 1.8 | 2.1 | Et, 1.95 (q), 0.75 (t) | Ph, 7.2 (m) |

[a] All $\delta$ values are singlets unless otherwise noted.

Tetramethylallene is obviously not typical of all the allenes regarding ketene cycloadditions. Of the allenes studied, only tetramethylallene and 1,2-cyclononadiene produced significant amounts of cycloadducts. The reactivity of the cyclononadiene is probably due to relieving the strain in the cyclic system. The tetramethylallene reactivity is apparently due to the presence of the four methyl groups which are electron releasing, thus increasing the electron density of the cumulative system. Generally, the more nucleophilic the diene, the more reactive is the diene in a ketene cycloaddition.

## Experimental Section

Proton nmr spectra were recorded on Jeolco Minimar 60-MHz and Jeolco PS-100 nmr spectrometers employing tetramethylsilane as an internal standard and $CCl_4$ as the solvent. Vpc was performed on an F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on acid-washed Chromosorb W (80–100). Solvents and triethylamine were distilled from sodium and stored over Linde type 4-A molecular sieve. Tetramethylallene was obtained by the $AlCl_3$-catalyzed rearrangement of the tetramethylcyclobutadione dimer of dimethylketene followed by pyrolysis over a hot wire. The other allenes were prepared by the Skattebøl method.[7]

**General Procedure for *in Situ* Ketene–Allene Cycloadditions.** A 0.075-mol portion of triethylamine in 20 ml of dry pentane or hexane was added dropwise with stirring to a refluxing solution of 0.075 mol of acid halide and 0.10 mol of allene in 150 ml of dry pentane or hexane. After the addition was complete, the mixture was stirred for another 1 hr at reflux and then stirred at room temperature overnight. The mixture was filtered and the solvent was evaporated. Vacuum distillation of the filtrate provided the $\alpha,\beta$-unsaturated cyclobutanone.

**2-Chloro-4-isopropylidene-2,3,3-trimethylcyclobutanone (I).** The cycloadduct of methylchloroketene and tetramethylallene was prepared in 72% yield at 70° (0.10 mm): mol wt (theory), 186.5; mass spectrum, parent peaks at *m/e* 186 ($^{35}Cl$) and 188 ($^{37}Cl$).

*Anal.* Calcd for $C_{10}H_{15}ClO$: Cl, 19.03. Found: Cl, 19.03.

**2-Bromo-4-isopropylidene-2,3,3-trimethylcyclobutanone (II).** Methylbromoketene and tetramethylallene cycloadded to produce a 65% yield, bp 93–95° (0.25 mm).

*Anal.* Calcd for $C_{10}H_{15}BrO$: Br, 34.63. Found: Br, 34.56.

**2-Chloro-2-ethyl-4-isopropylidene-3,3-dimethylcyclobutanone (III).** The cycloadduct of ethylchloroketene and tetramethylallene was prepared in 70% yield, bp 75° (0.1 mm).

*Anal.* Calcd for $C_{11}H_{17}ClO$: Cl, 17.70. Found: Cl, 17.47.

**2,2-Dichloro-4-isopropylidene-3,3-dimethylcyclobutanone (IV).** The cycloadduct of dichloroketene and tetramethylallene was prepared in 55% yield at 80° (0.10 mm): mol wt (theory), 207;

mass spectrum, parent peaks at $m/e$ 206 ($^{35}Cl$, $^{35}Cl$), 208 ($^{35}Cl$, $^{37}Cl$), and 210 ($^{37}Cl$, $^{37}Cl$).

*Anal.* Calcd for $C_9H_{12}Cl_2O$: C, 51.1; H, 5.79. Found: C, 51.52; H, 5.73.

**2-Bromo-2-chloro-4-isopropylidene-3,3-dimethylcyclobutanone (V).** Bromochloroketene and tetramethylallene yielded the cycloadduct at 85° (0.10 mm): mol wt (theory), 251.5; mass spectrum, parent peaks at $m/e$ 250 ($^{35}Cl$, $^{79}Br$), 252 ($^{35}Cl$, $^{81}Br$; $^{37}Cl$, $^{79}Br$), and 254 ($^{37}Cl$, $^{81}Br$).

**4-Isopropylidene-2,3,3-trimethylcyclobutanone (VII).** The cycloadduct of methylketene and tetramethylallene was prepared in a 20% yield at 40° (0.25 mm): mol wt (theory), 152; mass spectrum, parent peak at $m/e$ 152.

*Anal.* Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.51. Found: C, 78.79; H, 10.54.

**10,10-Dichlorobicyclo[7.2.0]undec-1-en-11-one (X).** The cycloadduct of dichloroketene and 1,2-cyclononadiene was prepared in 75% yield at 108° (0.005 mm): nmr $\delta$ 1.5 (m, 8 H), 2.35 (m, 4 H), 3.3 (m, 1 H), and 6.7 (m, 1 H).

*Anal.* Calcd for $C_{11}H_{14}Cl_2O$: Cl, 30.47. Found: Cl, 30.64.

**10-Chloro-10-methylbicyclo[7.2.0]undec-1-en-11-one (XI).** The methylchloroketene and 1,2-cyclononadiene cycloadduct was prepared in 73% yield at 98–100° (0.005 mm): nmr $\delta$ 1.5 (m, 9 H), 2.0 (m, 4 H), 2.3 (m, 2 H), 2.85 (2 d, 1 H), and 6.4 (m, 1 H).

*Anal.* Calcd for $C_{12}H_{17}ClO$: Cl, 16.70. Found: Cl, 16.52.

**Cycloaddition of Methylchloroketene and 1-Methyl-1,2-cyclononadiene (XII).** The cycloaddition of this unsymmetrical allene with methylchloroketene produced both the isomers of the cycloadduct in a ratio of 2:1 with the least substituted cycloadduct predominating in a 70% yield: bp 105° (0.005 mm); ir 1770 (C=O) and 1670 $cm^{-1}$ (C=O); nmr $\delta$ 1.5 (m, 12 H), 2.05 (m, 4 H), 2.3 (m, 2 H, allyl protons), 2.85 [(2 d for methinyl proton of one isomer) and 6.4 (t for vinyl proton of second isomer)] (1 H). The ratio of methinyl proton to vinyl proton is 2:1.

*Anal.* Calcd for $C_{13}H_{19}ClO$: Cl, 15.68. Found: Cl, 16.01.

**2-Chloro-4-isopropylidene-3,3-dimethylcyclobutanone (VI).** A 0.075-mol portion of chloroacetyl chloride was added with stirring to a solution of 0.075 mol of triethylamine in 100 ml of dry pentane at −78°. After the addition was complete, a pentane solution of 0.10 mol of tetramethylallene was added. The mixture was allowed to warm slowly to room temperature overnight. After filtration and solvent evaporation, the filtrate was vacuum distilled to yield the cycloadduct (25%): bp 75° (0.15 mm); mol wt (theory), 172.5; mass spectrum, parent peaks at $m/e$ 172 ($^{35}Cl$) and 174 ($^{37}Cl$).

**4-Isopropylidene-2,3,3-trimethyl-2-phenylcyclobutanone VIII).** Equimolar amounts of phenylmethylketene and tetramethylallene were combined and stirred for 30 hr at 50°, bp 92 (0.05 mm).

**2-Ethyl-4-isopropylidene-3,3-dimethyl-2-phenylcyclobutanone (IX).** Equimolar quantities of phenylethylketene and tetramethylallene were combined and stirred for 30 hr at 50°, bp 105° (0.05 mm).

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**Registry No.** I, 42915-13-9; II, 42915-14-0; III, 42915-15-1; IV, 42915-16-2; V, 42915-17-3; VI, 42915-18-4; VII, 42915-19-5; VIII, 42915-20-8; IX, 42915-21-9; X, 42915-22-0; XI, 42915-23-1; XIIA, 42915-24-2; XIIB, 42915-25-3; methylchloroketene, 13363-86-5; tetramethylallene, 1000-87-9, methylbromoketene, 29264-45-7; ethylchloroketene, 29264-44-6; dichloroketene, 4591-28-0; bromochloroketene, 42915-26-4; methylketene, 6004-44-0; 1,2-cyclononadiene, 1123-11-1; 1-methyl-1,2-cyclononadiene, 42915-27-5; chloroacetyl chloride, 79-04-9; phenylmethylketene, 3156-07-8; phenylethylketene, 20452-67-9.

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# Addition of Sulfonyl Iodides to Allenes[1]

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Sulfonyl iodides add rapidly to allenes to give 1:1 adducts. The addition of sulfonyl iodides to 1,2-propadiene yields a mixture of products, including the two 1:1 adducts resulting from attack by the sulfonyl radical on both the central and terminal positions of the allenic unit. Complete kinetic control has probably not been achieved under the conditions of these additions. In contrast, the addition of sulfonyl iodides to phenylallene and 3-methyl-1,2-butadiene proceeds rapidly and in excellent yield to give only the products resulting from central attack by the sulfonyl radical, *i.e.*, $R_1R_2C{=}C(SO_2R)CH_2I$. The addition of *p*-toluenesulfonyl iodide to 2,3-pentadiene behaves in a similar fashion, giving a moderate yield of 1:1 adduct resulting from central attack. The structures of the adducts were proven by zinc–acid reduction to the unsaturated sulfones.

Although the chemistry of sulfonyl halides has been extensively investigated, most of the work has concentrated on the chemistry of the readily available sulfonyl chlorides. Much less work has been done with the relatively stable, but less readily available sulfonyl bromides, and relatively few of the highly reactive, very unstable sulfonyl iodides have been prepared.

The sulfur–halogen bond of sulfonyl halides has been found to be particularly susceptible to homolytic cleavage; consequently, the free-radical reactions of sulfonyl halides comprise a large portion of their chemistry. Much of the work in this area of date has involved the free-radical addition of sulfonyl halides to olefins,[2-10] the following chain mechanism being generally accepted.

$$RSO_2X \xrightarrow{h\nu} RSO_2\cdot + X\cdot$$

or

$$RSO_2X + In\cdot \longrightarrow RSO_2\cdot + InX \quad (1)$$

$$RSO_2\cdot + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2SO_2R \quad (2)$$

$$R\dot{C}HCH_2SO_2R + RSO_2X \longrightarrow \underset{\displaystyle X}{\underset{|}{R}}CHCH_2SO_2R + RSO_2\cdot \quad (3)$$

Step 1 is the chain-initiating step, which may be effected by either irradiation or the addition of an initiator (In·) such as a peroxide.

Perhaps the most extensive work with sulfonyl iodides has been carried out by Truce and Wolf,[11] who prepared a