CYCLOADDITIONS OF KETENES WITH ALLENES

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The principle objective of this study is to conduct a
definitive investigation into the cycloaddition of allenes
and ketenes, with particular emphasis on halogenated ketenes.

Halogenated ketenes, alkylaldoketenes, and phenylalkyl-
ketenes undergo 1,2-cycloaddition reactions with reactive
allenes to yield α,β-unsaturated cyclobutanones. Tetra-
methylallene and 1,2-cyclononadiene exhibit unusual reactivity
in these cycloaddition reactions, unlike other allenes invest-
igated, such as 1,2-nonadiene, phenylallene, and 1,1-dimethyl-
allene. Apparently the cycloadducts prepared indicate
sufficient reactivity to warrant further study.

CYCLOADDITIONS OF KETENES WITH ALLENES

THESIS

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For the Degree of

MASTER OF SCIENCE

By

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CHAPTER I

INTRODUCTION
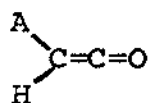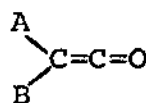
Ketenes have been known since Staudinger synthesized diphenylketene in 1905 (12). Ketene is structurally the simplest member of this family of organic compounds. A monosubstituted ketene is unsymmetrical and is known as an aldoketene, and a disubstituted ketene is referred to as a ketoketene. Ketoketenes may be symmetrical or unsymmetrical, depending on whether the substituents are identical. Halogenated ketenes have a halogen atom
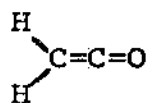
$$\begin{array}{cccc}
\overset{H}{\underset{H}{>}}C=C=O & \overset{A}{\underset{H}{>}}C=C=O & \overset{A}{\underset{B}{>}}C=C=O & \overset{}{\underset{X}{>}}C=C=O \\
\text{ketene} & \text{an aldoketene} & \text{a ketoketene} & \text{a halogenated} \\
& & & \text{ketene}
\end{array}$$
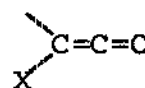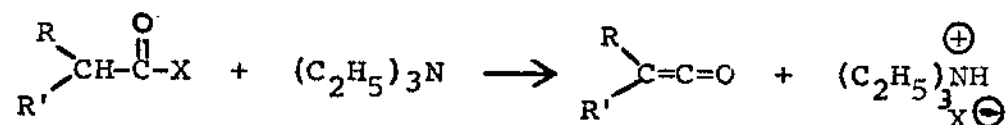
directly attached to the ketene functionality. Numerous reports have appeared in recent years on halogenated ketenes (4). Halogenated ketenes are quite reactive but have not been isolated to date.

Ketenes undergo two important types of reactions: nucleophilic addition and 2 + 2 cycloaddition reactions. The latter has received a great deal of attention in
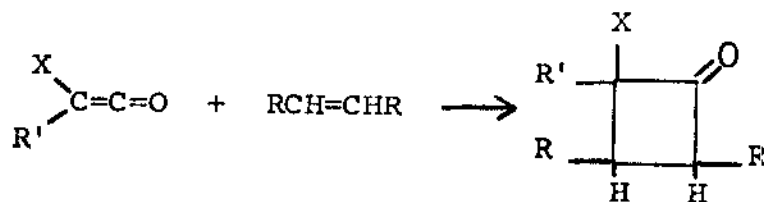
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recent years and has been established to be a concerted

$\pi 2s + \pi 2a$ process (15). This 1,2-cycloaddition process

is an excellent method for the preparation of cyclobuta-

nones (4,10).

Ketenes may be prepared by several different methods,

and the method of choice usually depends on the partic-

ular ketene desired. One of the oldest and most widely

employed methods is the dehydrohalogenation of an acid

chloride or bromide with triethylamine. An acid halide

possessing at least one α-hydrogen is dehydrohalogenated

in an inert solvent such as hexane. The triethylamine

salt precipitates from the reaction solution, thus leaving

a hexane solution of the ketene (8,9).

$$\underset{R'}{\overset{R}{\diagdown}}CH-\overset{\overset{O}{\|}}{C}-X \ + \ (C_2H_5)_3N \ \longrightarrow \ \underset{R'}{\overset{R}{\diagdown}}C=C=O \ + \ (C_2H_5)_3\overset{\oplus}{N}H \ X^{\ominus}$$

The instability of halogenated ketenes dictates that

reactions involving these ketenes be _in situ_ reactions;

e.g., the ketene is generated in the presence of some

reactive substance which traps the ketene. Usually the

halogenated ketene is trapped with an olefinic compound,

which results in the formation of a halogenated cyclo-

butanone. This is an excellent method for the prep-

aration of α-halo- and α, α -dihalocyclobutanones (3,5).

$$\begin{array}{c} X \\ \diagdown \\ \diagup \\ R' \end{array} C=C=O \quad + \quad RCH=CHR \quad \longrightarrow \quad \text{(cyclobutanone structure)}$$

These halogenated cycloadducts differ from other ketene

cycloadducts in that a good leaving group is present.

Consequently, such compounds have been demonstrated to

undergo various types of rearrangement reactions (6,13).

(reaction scheme with NaOAc / HOAc)

(reaction scheme with OH⁻)
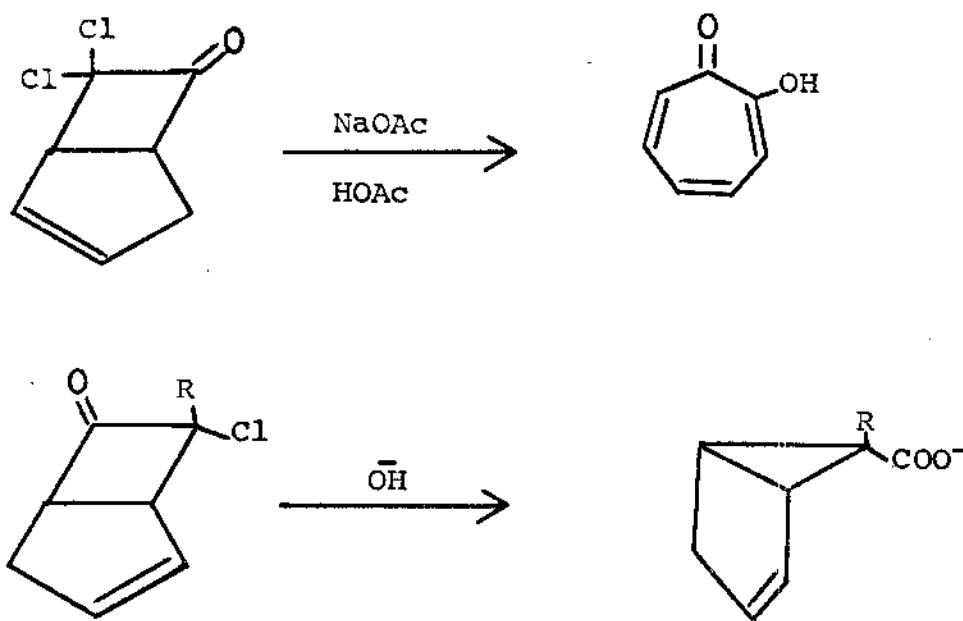
Although the cycloaddition of ketenes with olefins

has received a great deal of attention in recent years,

the cycloaddition of ketenes and allenes appears only

a few times in scattered reports in the literature. In 1965 Martin reported unexpected reactivity of 2,4-dimethyl-2,3-pentadiene (tetramethylallene) with diphenylketene and dimethylketene at room temperature (11). This presented a convenient means of preparing α, β-unsaturated cyclobutanones.

$$(CH_3)_2C=C=C(CH_3)_2 \ + \ R_2C=C=O$$
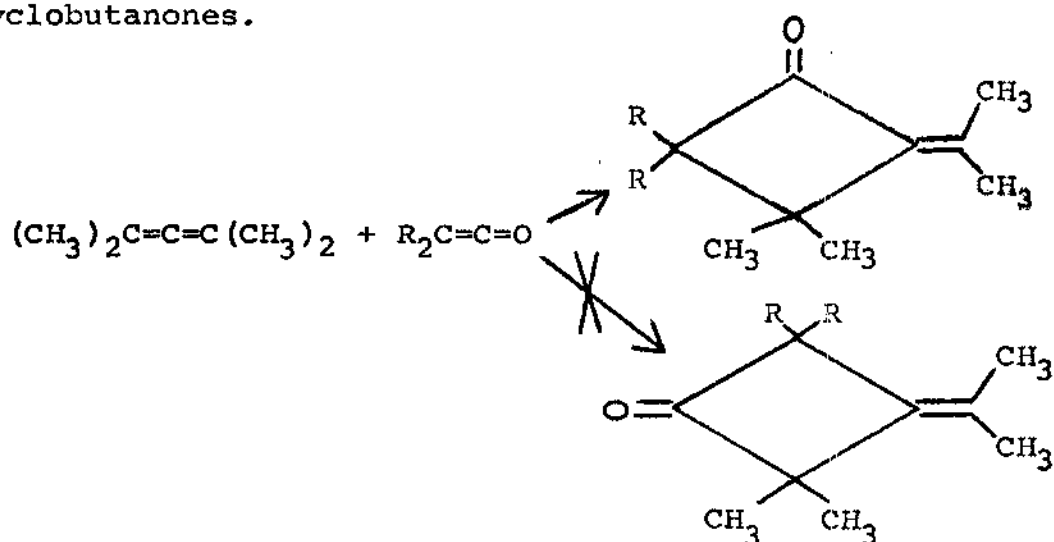
Moore and coworkers have prepared the cycloadduct of t-butylcyanoketene with 1,2-cyclononadiene and revealed that, when the allene is partially resolved, both epimers show optical activity (14). This type of stereo-

specificity has also been reported for the cycloadducts
of dimethylketene with 3-methyl-1,2-butadiene and 1,2-
cyclononadiene (1,2).
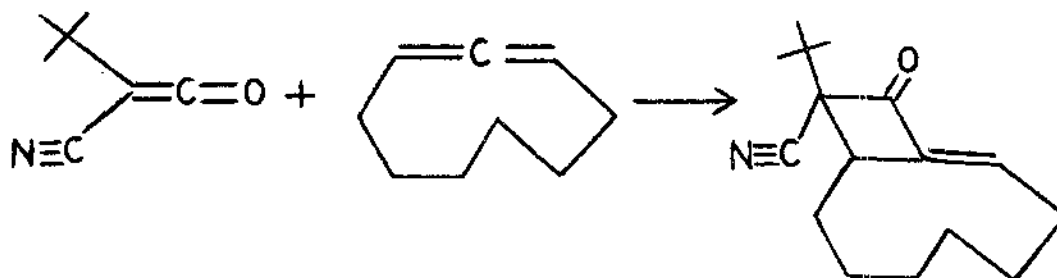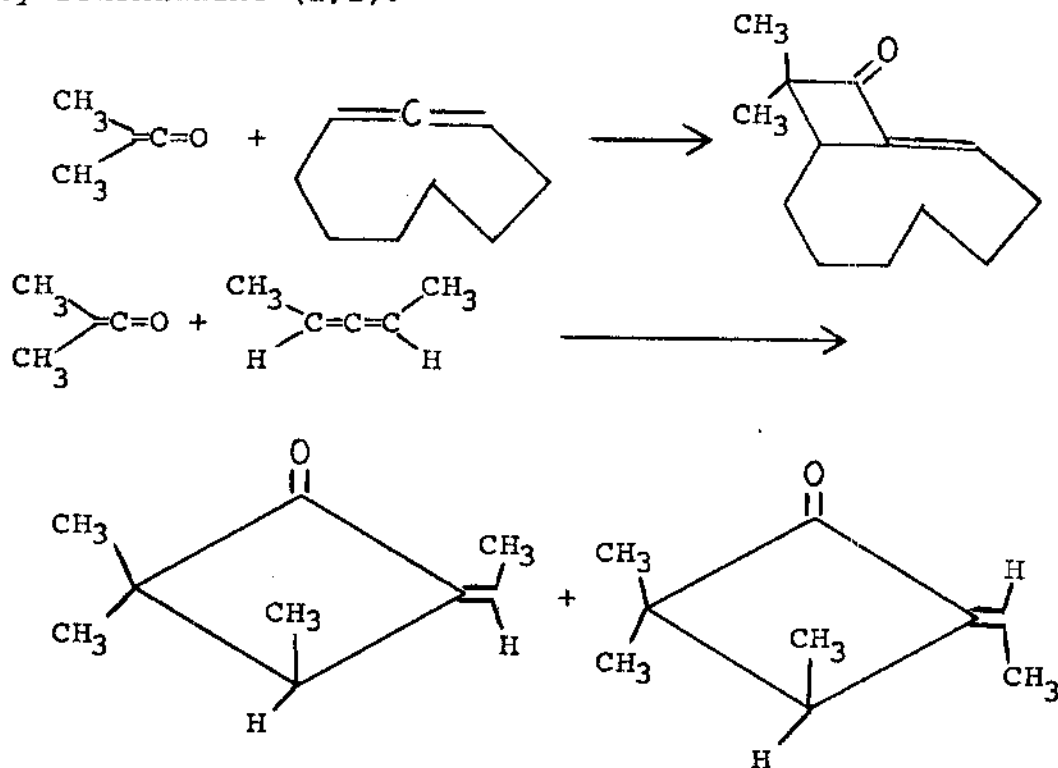
At 25°C: 95%   5%

At 130°C: 80%   20%

Bis(trifluoromethyl)ketene has been reported to form
reaction products with 3-methyl-1,2-butadiene and tetra-
methylallene (7). This anomalous ketene underwent cyclo-
addition with the butadiene to yield not only the expected
α,β-unsaturated cyclobutanone but an oxetane as well.
Tetramethylallene combined with bis(trifluoromethyl)ketene

to form only open-chain products.

In conclusion, a literature survey at the time
this investigation was initiated revealed a very limited
amount of information on the cycloaddition of ketenes
and allenes and no examples of cycloadditions of halo-
genated ketenes with allenes.

The principle objective of this investigation is to
conduct a definitive investigation into the cycloaddition
of allenes and ketenes, with particular emphasis on
halogenated ketenes.

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CHAPTER II

EXPERIMENTAL

Proton nuclear magnetic resonance spectra were record-
ed at room temperature using Jeolco Minimar (60 mHZ) or
Jeolco PS-100 (100 mHZ) spectrophotometers. Carbon tetra-
chloride and chloroform were employed as solvents and
tetramethylsilane as the internal standard.

The infrared spectra were obtained using a Perkin-
Elmer Model 237 Grating Infrared spectrometer, using
both neat and solution samples. Sodium chloride discs
or fixed-thickness cells were employed.

·Vapor-phase chromatography was used for determining
the purity of products, monitoring reactions, and purify-
ing contaminated products by preparative chromatographic
separation techniques. The analytical instrument used
was an F & M Scientific Model 700 employing a thermal
conductivity detection system and a column of 5 feet x
0.25 inch packed with 3% SE. 30 on chromosorb W (AW-DMCS)
80/100 mesh. Chromatographic preparations were made on a
Varian Aerograph 1520 with a 20 feet x 0.4-inch column

with similar column-packing material.

Elemental analyses were performed by C. F. Geiger and Associates, Ontario, California, and by the Analytical Services Section of the Chemistry Department of North Texas State University, Denton, Texas.

Preparation of Reagents

All the solvents were commercially available and were distilled over sodium and stored over molecular sieves. Commercially available triethylamine was distilled over freshly cut sodium.

2-Phenylpropanoic acid was prepared in 52% yield by the silver oxide oxidation of commercially available hydratropaldehyde (2-phenylpropanal), having a boiling point of 145°C at 15 mm (10).

Propionyl chloride was used as received from Aldrich Chemical Company of Milwaukee, Wisconsin.

Bromochloroacetyl chloride was prepared from trichloroethylene in a two-step process (5). Trichloroethylene was treated with sodium ethoxide in ethanol to form α, β-dichlorovinyl ethyl ether in a 60% yield, bp 124-126°C. Bromine was then added to the ether to give bromochloroacetyl chloride in a 56% yield, bp 138-140°C.

Most of the acid chlorides were prepared from the corresponding commercially available acid by the following procedure: one mole of acid and 1.1 mole of thionyl chloride were refluxed at 100°C for 5-6 hours, and subsequent distillation afforded the acid chloride in 70+% yield. The acid halides prepared by this procedure are tabulated in Table I. The structure of these acid chlorides were confirmed by the nmr spectra and agreement of the observed boiling points with those found in the literature.

TABLE I

ACID CHLORIDES PREPARED FROM COMMERCIALLY AVAILABLE ACIDS

Acid Chloride	Boiling Range (°C)	Reference
Chloroacetyl chloride	105-106	13
2-Chloropropanoyl chloride	110-112	8
Dichloroacetyl chloride	108-110	4
2-Phenylbutanoyl chloride	83-85/4 mm	12
2-Phenylpropanoyl chloride	60-62/0.8 mm	9

General Procedure for Preparing Pure Ketenes. A solution of 0.2 mole of triethylamine in 50 ml of benzene was added dropwise to 0.2 mole of acid halide in 200 ml of dry

benzene at room temperature while stirring. After two hours of additional stirring, the salt was removed by filtration, the solvent evaporated, and the ketene distilled under vacuum as rapidly as possible. Once the ketene has been removed from the residual salt and polymer, it is reasonably stable if kept under refrigeration.

Phenylmethylketene (3)

A 70% yield of the ketene was prepared from 2-phenyl-propanoyl chloride and triethylamine; bp 58°C at 2.5 mm; ir, 2117 cm^{-1} (C=C=O); nmr, δ 1.9 (s, 3H) and 7.1 (m, 5H).

Phenylethylketene (2)

The isolable ketene was prepared in a 64% yield from 2-phenylbutanoyl chloride and triethylamine; bp 62°C at 0.1 mm; ir, 2110 cm^{-1} (C=C=O); nmr, δ 1.2 (t, 3H), 2.4 (q, 2H), and 7.1 (m, 5H).

Preparation of Tetramethylallene (6,7). A 500-g portion of the symmetrical dimer (2,2,4,4-tetramethyl-1,3-cyclobutadione) of dimethylketene was placed in a 2-liter distilling flask and melted (115°C). One gram of dry aluminum chloride was added, and the mixture was heated to a gentle reflux for one hour. Distillation with a water aspirator yielded 453 g (91%) of the

β-lactone dimer, 4-isopropylidene-3,3-dimethyl-2-oxetanone, bp 170°C.

The β-lactone was heated in a distilling flask until the vapors passed into a pyrolysis tube heated to 450-550°C, whereupon the resulting vapors passed through a condenser and into a dry ice trap. The resulting solution was distilled to yield tetramethylallene (94%); bp 87°C; nmr, δ 1.5 (s).

Preparation of 3-Methyl-1,2-butadiene (1). A 0.8-mole portion of 3-methyl-1-butyne-3-ol and 0.25 liters of concentrated hydrochloric acid were shaken in a separatory funnel for 10 minutes at room temperature. The organic layer was dried overnight at 0°C with magnesium sulfate. The mixture was filtered, and the resulting filtrate was added dropwise over a 2-hour period to a solution of 0.44 mole of lithium aluminum hydride in 300 ml of tetrahydrofuran contained in a distilling flask equipped with stirrer, addition funnel, and condenser. To prevent loss of the volatile product during reduction, a dry ice trap was connected to the top of the condenser. After the addition was completed, the reaction mixture was stirred and heated under reflux for an additional 18 hours. The

condenser was then exchanged for a 12-inch Vigreaux

column, and crude allene and some tetrahydrofuran was

removed by distillation through the column. Fractionation

produced a 51% yield of the allene.

General Procedure for Allene Preparation by the

Skattebøl Method (11). A. 1,1-Dihalocyclopropanes: Equi-

molar amounts of olefin and bromoform and a slight excess

of potassium t-butoxide were employed. The bromoform was

slowly added to a stirred slurry of potassium t-butoxide,

the olefin, and dry pentane (50-100 ml per mole of olefin),

at 0° to $-10^O C$. The addition time was usually 6 to 8

hours. The reaction mixture was allowed to stir at room

temperature overnight. After the addition of 250 ml of

water, the product was extracted with ether. The ether

extract was then concentrated after drying over magnesium

sulfate and distilled to yield the dihalocyclopropane.

B. Allenes: A 0.1-mole portion of the 1,1-dihalo-

cyclopropane derivative was diluted with 25 ml of dry

ether and cooled in a dry ice/acetone bath. An ethereal

solution of methyllithium (0.12 mole) was added dropwise

with stirring during 30 minutes. The reaction mixture was

further stirred for 30 minutes and then water was added.

The ether layer was separated, and the aqueous phase extracted with a small amount of ether. The combined ether extracts were washed with water until neutral and dried over magnesium sulfate. After filtration the product was distilled to yield the pure allene.

1-Phenyl-1,2-propadiene

A. A 37% yield of 1,1-dibromo-2-phenylcyclopropane was prepared from styrene and bromoform, bp 90-91°C at 0.1 mm.

B. The allene was prepared from the above cyclopropane and methyllithium in an 82% yield, bp 64-65°C at 11 mm.

1,2-Cyclononadiene

A. A 50% yield of 9,9-dibromobicyclo [6.1.0] nonane was made from cyclooctene and bromoform, bp 80-82°C at 0.1 mm.

B. The cyclic allene was prepared from the above cyclopropane derivative and methyllithium in a 93% yield, bp 63°C at 16 mm.

1,2-Nonadiene

A. A 40% yield of 1,1-dibromo-2-hexylcyclopropane was made from 1-octene and bromoform, bp 70°C at 0.1 mm.

B. The allene was prepared from the above cyclopropane and methyllithium in an 85% yield, bp 45°C at 15 mm.

General Procedure for Ketene-Allene Cycloadditions by Dehydrohalogenation. A 0.075-mole portion of triethylamine in 20 ml of dry pentane or hexane was added dropwise with stirring to a refluxing solution of 0.075 mole of acid halide and 0.10 mole of allene in 150 ml of dry pentane or hexane. After the addition was complete, the mixture was stirred another hour at reflux and then stirred at room temperature overnight. The mixture was filtered and the solvent evaporated. Vacuum distillation of the filtrate provided the α, β-unsaturated cyclobutanone.

2-Chloro-4-isopropylidene-2,3,3-trimethylcyclobutanone

The cycloadduct of methylchloroketene and tetramethylallene was prepared in a 72% yield; bp 70°C at 0.10 mm; ir, 1740 cm^{-1} (C=O) and 1660 cm^{-1} (C=C); nmr, δ1.4 (s, 6H), 1.5 (s, 3H), 1.8 (s, 3H), and 2.0 (s, 3H); mol wt (theory), 186.5; mass spec, parent peaks at 186 (Cl^{35}) and 188 (Cl^{37}).

Analysis calculated for $C_{10}H_{15}ClO$: Cl, 19.03. Found: Cl, 19.03.

2,2-Dichloro-4-isopropylidene-3,3-dimethylcyclobutanone

The cycloadduct of dichloroketene and tetramethyl-allene was prepared in a 55% yield; bp 80°C at 0.10 mm; ir, 1750 cm^{-1} (C=O) and 1660 cm^{-1} (C=C); nmr, δ 1.5 (s, 6H), 1.9 (s, 3H), and 2.0 (s, 3H); mol wt (theory), 207; mass spec, parent peaks at 206 (Cl^{35},Cl^{35}), 208 (Cl^{35},Cl^{37}), and 210 (Cl^{37},Cl^{37}).

Analysis calculated for C$_9$H$_{12}$Cl$_2$O: C, 51.7; H, 5.79. Found: C, 51.52; H, 5.73.

2-Bromo-2-chloro-4-isopropylidene-3,3-dimethylcyclobutanone

The cycloadduct of bromochloroketene and tetramethyl-allene was prepared in a 25% yield; bp 85°C at 0.10 mm; ir, 1760 cm^{-1} (C=O) and 1660 cm^{-1} (C=C); nmr, δ 1.5 (s, 3H), 1.6 (s, 3H), 1.9 (s, 3H), and 2.1 (s, 3H); mol wt (theory), 251.5; mass spec, parent peaks at 250 (Cl^{35},Br^{79}), 252 (Cl^{35},Br^{81}; Cl^{37},Br^{79}), and 254 (Cl^{37},Br^{81}).

4-Isopropylidene-2,3,3-trimethylcyclobutanone

The cycloadduct of methylketene and tetramethylallene was prepared in a 20% yield; bp 40°C at 0.25 mm; ir, 1740 cm^{-1} (C=O) and 1660 cm^{-1} (C=C); nmr, δ 1.0 (d, 3H), 1.2 (s, 3H), 1.4 (s, 3H), 1.7 (s, 3H), 1.95 (s, 3H), and 2.5 (q, 1H); mol wt (theory), 152; mass spec, parent peak at 152.

10,10-Dichlorobicyclo [7.2.0] undeca-1-en-11-one

The cycloadduct of dichloroketene and 1,2-cyclonona-diene was prepared in a 75% yield; bp 108°C at 0.005 mm; ir, 1770 cm^{-1} (C=O) and 1670 cm^{-1} (C=C); nmr, δ 1.5 (m, 8H), 2.35 (m, 4H), 3.3 (m, 1H), and 6.7 (m, 1H).

Analysis calculated for $C_{11}H_{14}Cl_2O$: Cl, 30.47. Found: Cl, 30.64.

10-Chloro-10-methylbicyclo [7.2.0] undeca-1-en-11-one

The methylchloroketene and 1,2-cyclononadiene cyclo-adduct was prepared in a 72% yield; bp 98-100°C at 0.005 mm; ir, 1770 cm^{-1}(C=O) and 1670 cm^{-1} (C=C); nmr, δ 1.5 (m, 9H), 2.0 (m, 4H), 2.3 (m, 2H), 2.85 (2d, 1H), and 6.4 (m, 1H).

2-Chloro-4-isopropylidene-3,3-dimethylcyclobutanone

A 0.075-mole portion of chloroacetyl chloride was added with stirring to a solution of 0.075 mole of tri-ethylamine in 100 ml of dry pentane at -70°C. After the addition was complete, a pentane solution of 0.10 mole 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°C at 0.15 mm; ir, 1750 cm^{-1} (C=O) and 1660 cm^{-1} (C=C);
nmr, δ 1.3 (s, 3H), 1.45 (s, 3H), 1.8 (s, 3H), 2.0 (s, 3H),
and 4.1 (s, 1H); mol wt (theory), 172.5; mass spec,
parent peaks at 172 (Cl^{35}) and 174 (Cl^{37}).

4-Isopropylidene-2,3,3-trimethyl-2-phenylcyclobutanone

Equimolar amounts of phenylmethylketene and tetra-
methylallene were combined, neat, and stirred for 30 hours
at 50°C. A near quantitative yield was obtained of the
cycloadduct; bp 92°C at 0.05 mm; ir, 1740 cm^{-1} (C=O)
and 1660 cm^{-1} (C=C); nmr, δ 0.9 (s, 3H), 1.4 (s, 3H),
1.5 (s, 3H), 1.8 (s, 3H), 2.1 (s, 3H),and 7.2 (m, 5H).

2-Ethyl-4-isopropylidene-3,3-dimethyl-2-phenylcyclobutanone

Equimolar amounts of phenylethylketene and tetra-
methylallene were combined, neat, and stirred for 30 hours
at 50°C. A near quantitative yield was obtained of the
cycloadduct; bp 105°C at 0.05 mm; ir, 1740 cm^{-1} (C=O)
and 1660 cm^{-1} (C=C); nmr, δ 0.75 (t, 3H), 0.9 (s, 3H),
1.5 (s, 3H), 1.8 (s, 3H), 1.95 (q, 2H), 2.1 (s, 3H),
and 7.2 (m, 5H).

4-Methoxyisopropylidene-2,3,3-trimethylcyclobutanone

Four grams of the cycloadduct of methylchloroketene
and tetramethylallene was added dropwise with stirring to

a distilling flask containing two grams of freshly cut

sodium in methanol. The mixture was stirred an additional

3 hours before 50 ml of water was added. The organic

layer was extracted with chloroform, dried over magnesium

sulfate, concentrated, and distilled. An 80% yield of

the methoxy derivative was obtained; bp 60°C at 0.50 mm;

ir, 1740 cm^{-1} (C=O) and 1670 cm^{-1} (C=C); nmr, δ1.2

(m, 8H), 1.7 (m, 1H), 1.8 (s, 3H), 2.0 (s, 3H), and

3.4 (s, 3H).

Note--The analysis for carbon was consistantly low on all

samples of the cycloadducts and their derivatives. Re-

peated efforts to purify samples were made; and even-

though the gas chromatograph indicated extremely pure

products, the carbon analyses were low. However, the

hydrogen and chlorine analyses were good as compared with

the theoretical percentages. A possible explanation for the

poor carbon analyses could be that carbon monoxide was in-

adequately converted to carbon dioxide during combustion

to give accurate carbon percentages.

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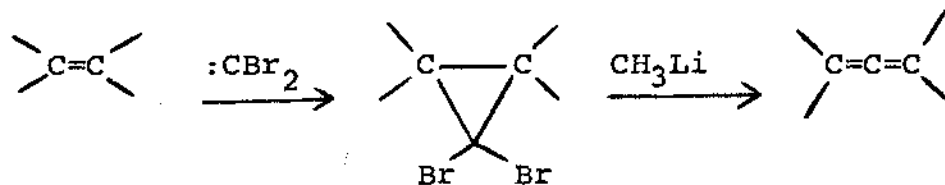
CHAPTER III

RESULTS AND DISCUSSION

Tetramethylallene was prepared in two steps from the cyclobutadione dimer of dimethylketene. Rearrangement of 2,2,4,4-tetramethyl-1,3-cyclobutadione in the presence of aluminum chloride produced the β-lactone dimer of dimethylketene, 4-isopropylidene-3,3-dimethyl-2-oxetanone, in 91% yield (5). This β-lactone was then refluxed over a hot wire to yield tetramethylallene in 94% yield (7).
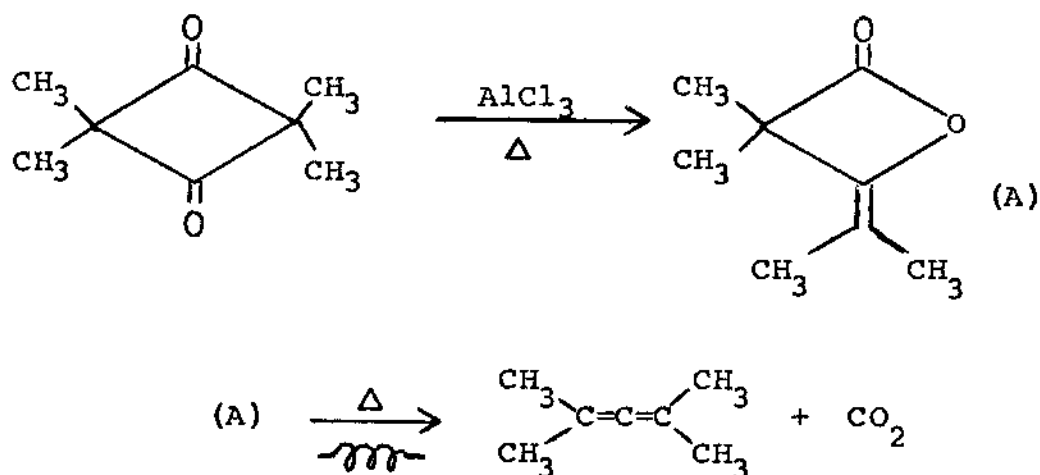
Commercially available 3-methyl-1-butyn-3-ol was the source of 3-methyl-1,2-butadiene, and this conversion was accomplished in a 51% yield (1). The acetylenic

alcohol was converted to 3-chloro-3-methyl-1-butyne by
shaking the alcohol with concentrated hydrochloric acid
for 10 minutes at room temperature. The acetylenic chlor-
ide was reduced with lithium aluminum hydride thus yielding
the allene. The volatility of this allene made it dif-
ficult to use or isolate from its solvent.

A general procedure for allene preparation was employ-
ed for phenylallene, 1,2-cyclononadiene, and 1,2-nona-
diene (8). Dibromocarbene was generated in the presence of
an appropriate olefin and an addition reaction produced
the corresponding dibromocyclopropane derivative, which
was converted to the desired allene by treatment with
methyllithium. Styrene was converted to 1,1-dibromo-
2-phenylcyclopropane in a 37% yield and subsequent

$$\ce{>C=C<} \quad \xrightarrow{\ce{:CBr2}} \quad \underset{\underset{Br \quad Br}{\diagdown}}{\ce{>C\!-\!-\!C<}} \quad \xrightarrow{\ce{CH3Li}} \quad \ce{>C=C=C<}$$

reaction with methyllithium produced an 82% yield of
1-phenyl-1,2-propadiene. The second step in this syn-
thesis required low temperature and that contact of the
product with base be as short as possible because the
aryl group facilitates base-catalyzed allene-acetylene

rearrangement. 1-Octene was converted to 1,1-dibromo-2-hexylcyclopropane in a 40% yield and reacted with methyllithium to produce an 85% yield of 1,2-nonadiene. Cyclooctene reacted with dibromocarbene to yield the dibromo derivative in 50% yield and 1,2-cyclononadiene was produced in a 93% yield.
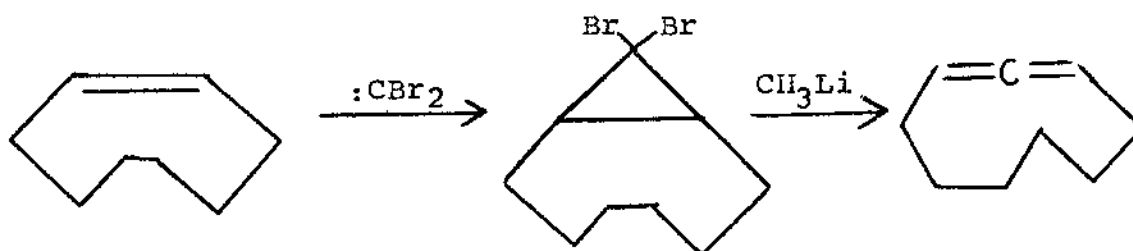
The two isolable ketenes, phenylmethylketene and phenylethylketene, were prepared by dehydrohalogenation of the appropriate acid chloride with triethylamine at room temperature (3,4). Phenylmethylketene was prepared from 2-phenylpropanoyl chloride in a 70% yield and phenyl-ethylketene from 2-phenylbutanoyl chloride in a 64% yield.
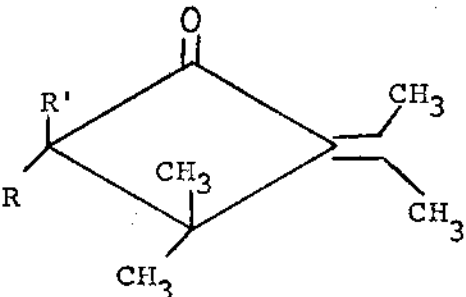
The 1,2-cycloaddition reaction of ketenes with tetramethylallene can be generally illustrated as follows:
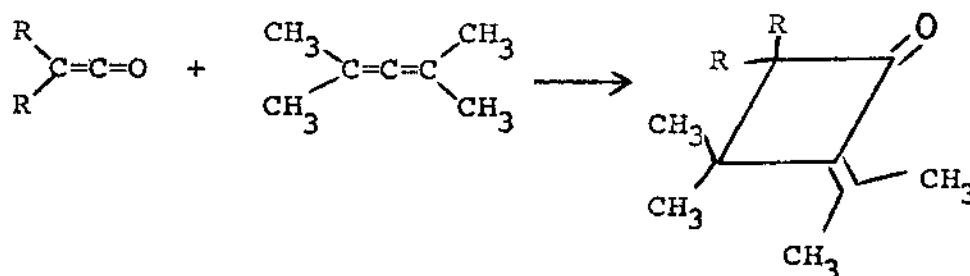
The α,β-unsaturated cyclobutanones and the yields of these preparations are shown in Table II. The infrared spectra revealed carbonyl absorptions at 1740-1760 cm^{-1} and the C=C absorption at 1660 cm^{-1}. The carbonyl absorptions for cyclobutanones is 1800 cm^{-1} (2).

TABLE II

CYCLOADDUCTS FROM KETENES AND TETRAMETHYLALLENE

Compound	R	R'	Yield (%)
I	CH_3	Cl	72
II	Cl	Cl	55
III	Cl	Br	45
IV	Cl	H	25
V	CH_3	H	20
VI	CH_3	C_6H_5	90
VII	C_2H_5	C_6H_5	90

The ketene-tetramethylallene cycloadditions were performed in such a manner that the ketene was generated in the presence of the diene. This was accomplished by the triethylamine dehydrohalogenation of the appropriately substituted acid chloride in refluxing pentane or hexane containing tetramethylallene. The order of addition of acid halide and amine was very critical. If the acid halide is added to a solution of solvent, allene, and amine under temperature conditions varying from -70°C to reflux, in some cases no cycloadduct can be isolated and in others only 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 and diene in refluxing solvent results in a much improved yield inspite of the fact that this order of addition is desirable for the formation of ∝-halovinyl esters (6). Unfortunately, some of the ∝-halovinyl ester is produced and is difficult to separate from the cycloadduct.
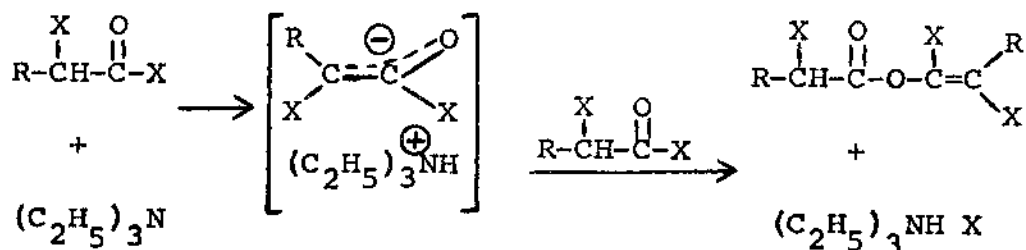
Chloroketene cycloadditions produce better yields when chloroacetyl chloride is added to a pentane solution of triethylamine at -70°C prior to the addition of tetramethylallene. Subsequent warming to room temperature and normal work-up gives a 25% yield of cycloadduct.

The cycloadducts of phenylmethylketene and phenylethylketene with tetramethylallene were prepared simply by combining equimolar portions of the isolable ketene with the allene, neat, giving near quantitative yields in both cases.

The nmr data for the ketene-tetramethylallene cycloadducts is recorded in Table III. The outstanding consistency of similar group locations aid in the proof-of-structure of these compounds. The two methyl groups of the isopropylidene substituent are in different environments and thus are revealed as two singlets in the nmr spectra (δ 1.7 - 1.9 and δ1.95 - 2.1). It is expected that the carbonyl is shifting the absorption of the methyl group nearer it 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

TABLE III

NMR DATA OF TETRAMETHYLALLENE CYCLOADDUCTS (δ VALUES)*

Adduct	A	B	C	D	R'	R
I	1.4	1.5	1.8	2.0	CH_3, 1.4	Cl,--
II	1.5	1.5	1.9	2.0	Cl,--	Cl,--
III	1.5	1.6	1.9	2.1	Cl,--	Br,--
IV	1.45	1.3	1.8	2.0	Cl,--	H, 4.1
V	1.4	1.2	1.7	1.95	CH_3, 1.0(d)	H, 2.5(q)
VI	1.5	0.9	1.8	2.1	CH_3, 1.4	C_6H_5, 7.2(m)
VII	1.5	0.9	1.8	2.1	CH_3, 0.75(t)	C_6H_5, 7.2(m)
					CH_2, 1.95(q)	

* All δ values are singlets unless otherwise noted.

the ketene are identical (a symmetrical ketene). This is

evident in the dichloroketene (II) and bromochloroketene

(III) cycloadducts in that II shows only one singlet at

δ 1.5 for the two methyl groups and III reveals two sin-

glets at δ 1.5 and δ 1.6. The spectrum of the methyl-

chloroketene 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 sub-

stituent overlap at δ 1.4.

The *in situ* cycloaddition of 1,2-cyclononadiene with

methylchloroketene and dichloroketene occurred smoothly

and in good yield (72 and 75%, respectively). The infrared

A = CH$_3$, Cl
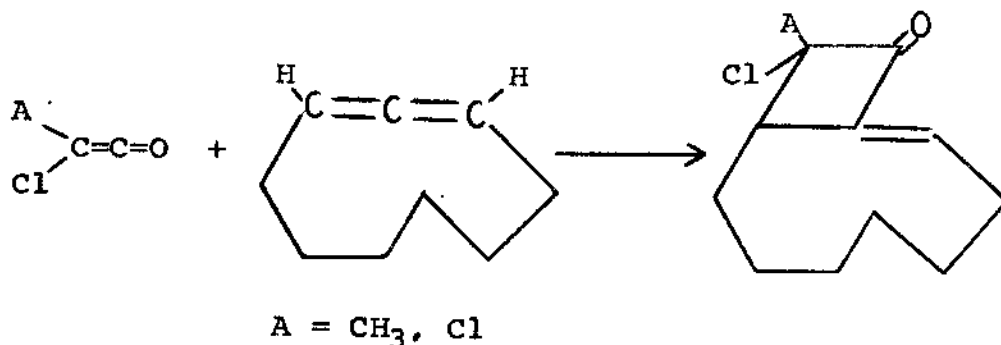
spectra revealed C=C absorptions at 1670 cm^{-1} and carbonyl

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.

Several other allenes were investigated as partners
for cycloadditions with halogenated ketenes which included
1-phenyl-1,2-propadiene, 1,2-nonadiene, and 3-methyl-1,2-
butadiene. In all cases, either no or very small amounts
of cycloadducts were produced.

Tetramethylallene is obviously not typical of all
the allenes regarding ketene cycloadditions. Of the
allenes studied, only 1,2-cyclononadiene and tetramethyl-
allene produced substantial yields of the α,β-unsaturated
cyclobutanones. The reactivity of the cyclononadiene can
probably be attributed to relieving the strain in the
cyclic system. Apparently the reactivity of tetramethyl-
allene is due to the four electron releasing methyl groups
which increases the electron density of the allene function-
ality. In general, the more nucleophilic the unsaturated
moiety, the more reactive it is in a ketene cycloaddition.
The reactivity of this allene parallels that of cyclo-
pentadiene, which is one of the most reactive olefins
in a ketene cycloaddition (2).

The cycloadduct of tetramethylallene and methyl-
chloroketene readily reacted with sodium methoxide in
methanol at room temperature. Sodium chloride precipitated

from the reaction mixture upon addition of the cycload-
duct to the basic reaction solution. The nmr spectrum
of the substituted product revealed that an allylic
substitution reaction had occurred through the enol
form of the cycloadduct.
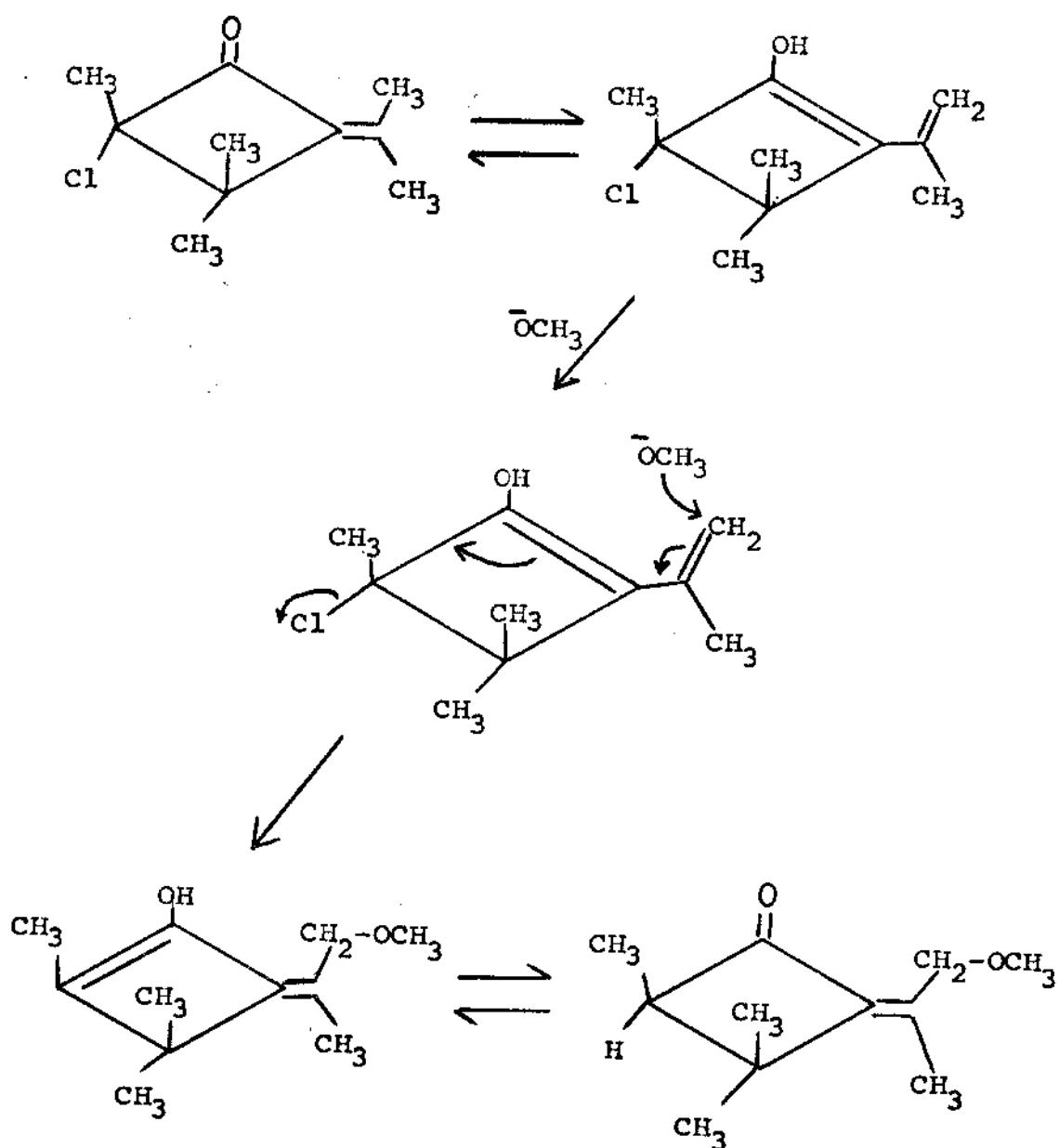
In conclusion, halogenated ketenes, alkylaldoketenes, and phenylalkylketenes undergo a 1,2-cycloaddition reaction with reactive allenes to yield α,β-unsaturated cyclobutanones. Tetramethylallene and 1,2-cyclononadiene exhibit unusual reactivity in these cycloaddition reactions unlike the other allenes investigated. Apparently the cycloadducts prepared indicate sufficient reactivity to warrant further study.

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