TRIMETHYLSILYLATED KETENE CYCLOADDITIONS

AND THE CHEMISTRY OF

CHLOROTRIALKYL-1,3-CYCLOBUTANEDIONE

DISSERTATION

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By

Theresa Chau-Ming Cheng, B. S., M. S.

Denton, Texas

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The purpose of this investigation is twofold: (1) to examine the trimethylsilyl substituent effect on the ketene functionality, (2) to study the chemistry of the novel unsymmetrical 1,3-cyclobutanediones, chlorotrialkyl-1,3-cyclobutanediones.

Trimethylsilylmethylketene was prepared by the triethyl-amine dehydrohalogenation of β-trimethylsilylpropionyl chloride. This ketene was not isolable but underwent cyclo-addition to produce the cyclobutanone derivatives and dimerized to yield a 2-oxetanone as expected for an aldoketene. Allyltrimethylsilane underwent cycloaddition with several different ketenes to form the cyclobutanones in good yield. However, the cycloaddition of vinyltrimethylsilane and ketenes were unsuccessful. This data is consistent with literature reports that the trimethylsilyl substituent is electron withdrawing at the vinyl position but is electron donating at the allylic position.

Phenyltrimethylsilylketene was prepared by the zinc dehalogenation of phenyltrimethylsilylbromoacetyl chloride. The stability of this ketene and the lack of reactivity in cycloaddition reactions and dimerization closely parallel that of trimethylsilylketene. Apparently, there is no

interaction of the carbon silicon bond with the α-substituted aromatic ring.

The lack of reactivity of trimethylsilylketene and phenyltrimethylsilylketene suggests that the trimethylsilyl substituent is electron donating to the ketene functionality. This electronic effect is considered to be a hyperconjugative phenomenon whereby the electrophilic character of the sp hydridized carbon is decreased as silicon accepts some positive character.

Chlorotrialkyl-1,3-cyclobutanediones are available by the dimerization of dialkylketenes and alkylchloroketenes. These diones react with sodium methoxide to yield the ring opened products, γ-chloro-β-keto esters and with peracetic acid to form α-chloro-β-keto γ-lactones. Both of these reactions are controlled by the C-Cl dipole effect which directs the nucleophilic attack from the rear side of the C-Cl bond. The reaction of chlorotrialkyl-1,3-cyclobutanediones with tri-n-butyltin hydride provides a good synthetic method for the corresponding trialkyl-1,3-cyclobutanediones. These diones exist predomenatly in the enolic form in solution and it is the enolic form which accounts for all the reactions of these diones. Trialkyl-1,3-cyclobutanediones do not undergo ring opening reaction and react with diazomethane to yield methoxy compounds.

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CHAPTER I

INTRODUCTION

Ketenes may be categorized into four different groups
depending upon the substituent(s) bonded to the ketene
functionality. Aldoketenes, (I), have hydrogen bonded to
the ketene functionality and ketoketenes, (II), have two
substituents other than hydrogen bonded to the sp^2 hybridized
carbon. Halogenated ketenes, (III), have a halogen directly
bonded to the sp^2 hybridized carbon and organometallic
ketenes, (IV), have a metal atom such as silicon, germanium
or tin bonded to this carbon.

$$\underset{\text{(I)}}{\overset{H}{\underset{}{>}}C=C=O,} \quad \underset{\text{(II)}}{\overset{R}{\underset{}{>}}C=C=O,} \quad \underset{\text{(III)}}{\overset{X}{\underset{}{>}}C=C=O,} \quad \underset{\text{(IV)}}{\overset{R_3M}{\underset{}{>}}C=C=O}$$
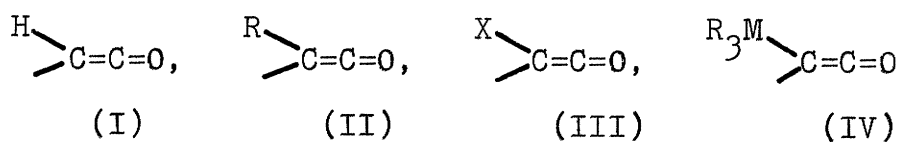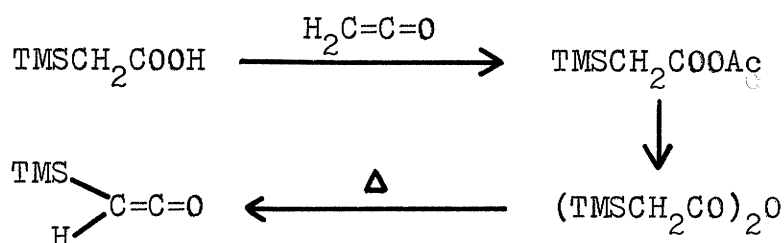
R = alkyl, aryl.

Ketene and a number of other substituted ketenes were
first synthesized by Staudinger at the begining of this
century.[1,2] The zinc dehalogenation of α-haloacid halides is

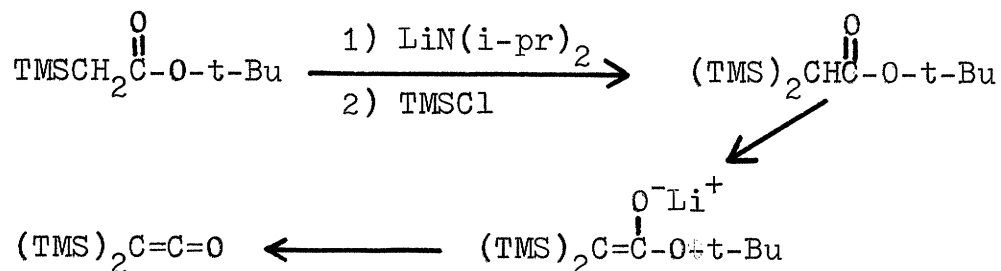$$-\overset{|}{\underset{|}{C}}-\overset{O}{\overset{||}{C}}-X \quad \xrightarrow{\text{Zn}} \quad {>}C=C=O \; + \; ZnCl_2$$
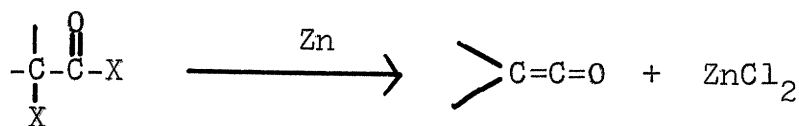
one of the oldest methods for the preparation of ketenes.[1,3,4]

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The most common preparative method is the triethylamine dehydrohalogenation of appropriately substituted acid halides.[5] A recent mechanistic study of this reaction

$$-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-C-X \quad \xrightarrow{\text{Et}_3\text{N}} \quad \overset{}{\underset{}{>}}C=C=O \quad + \quad \text{Et}_3\text{NH}^+\text{Cl}^-$$

indicates that nonhalogenated ketenes are formed from an acyl ammonium salt intermediate and the halogenated ketenes are derived from an enolate salt intermediate.[6-9]

$$\text{H}-\underset{\underset{|}{|}}{\overset{\overset{O}{\|}}{C}}-C-\text{NEt}_3{}^+\text{Cl}^- \qquad\qquad \underset{}{\overset{X}{>}}C=C\overset{O^-\overset{+}{H}\text{NEt}_3}{\underset{X}{<}}$$

The first organometallic ketene was reported in 1965 by Shchukouskaya and coworkers.[10] Trimethylsilylketene was prepared by the pyrolysis of trimethylsilylethoxyacetylene.

$$\text{EtO-C}\equiv\text{C-H} \quad \xrightarrow[\text{2) TMSCl}]{\text{1) MeLi}} \quad \text{EtO-C}\equiv\text{C-TMS} \quad \longrightarrow \quad \underset{\text{H}}{\overset{\text{TMS}}{>}}C=C=O$$

Many different substituted organometallic ketenes such as trichlorosilyl, triethylsilyl and bis-(trimethylsilyl)ketenes

$$\text{R}_3\text{M-X} \quad + \quad \text{R'O-C}\equiv\text{C-MgBr} \quad \xrightarrow{-\text{MgBrX}} \quad \text{R}_3\text{M-C}\equiv\text{C-OR'}$$

$$\underset{\text{R}_3\text{M'}}{\overset{\text{R}_3\text{M}}{>}}C=C=O \quad \xleftarrow{\text{R}_3\text{M'-X}}$$

have been prepared by this method. Bimetallic and mixed
bimetallic ketenes may be obtained by a modification of this
method.[11,12] Kostynk and coworkers have reported the
preparation of a number of different monometallic ketenes
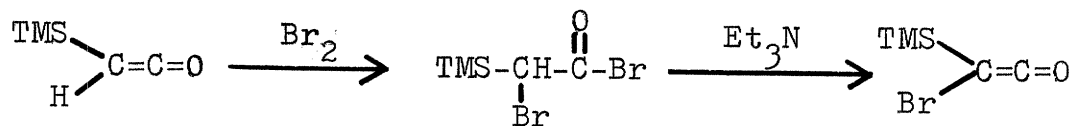by the pyrolysis of organometallic acetic anhydrides.[13] Also,

$$TMSCH_2COOH \xrightarrow{H_2C=C=O} TMSCH_2COOAc$$

$$\begin{array}{c} TMS \\ \diagdown \\ H \diagup \end{array} C=C=O \xleftarrow{\Delta} (TMSCH_2CO)_2O$$

Lustsenlo and Kostynk have reported that trimethylsilyl-,
triethylsilyl- and triphenylsilyl ketenes can be prepared by
the dehydrohalogenation of the appropriately substituted
silylacetyl chlorides.[14] Bis-(trimethylsilyl)ketene has been
obtained by the reaction of t-butyl bis-(trimethylsilyl)-
acetate with lithium diisopropylamide to yield the corres-
ponding enolate which when warmed to room temperature gives
the ketene.[15]

$$TMSCH_2\overset{O}{\overset{\|}{C}}-O-t-Bu \xrightarrow[2)\ TMSCl]{1)\ LiN(i-pr)_2} (TMS)_2CH\overset{O}{\overset{\|}{C}}-O-t-Bu$$

$$(TMS)_2C=C=O \xleftarrow{\quad\quad} (TMS)_2C=\overset{\overset{O^-Li^+}{|}}{C}-O-t-Bu$$

Brady and Owens have recently reported on the prepa-
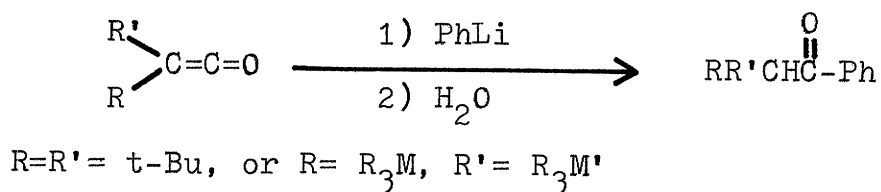ration of trimethylsilylbromoketene from trimethylsilylketene.

Bromine was added to trimethylsilylketene to yield the trimethylsilylbromoacetyl bromide which was dehydrobrominated with triethylamine to yield the trimethylsilylbromoketene.[16]

$$\underset{H}{\overset{TMS}{>}}C=C=O \xrightarrow{Br_2} TMS-\underset{Br}{\overset{}{CH}}-\overset{O}{\overset{\|}{C}}-Br \xrightarrow{Et_3N} \underset{Br}{\overset{TMS}{>}}C=C=O$$

All of the organometallic ketenes which have been reported in the literature are isolable and can be purified by distillation with the exception of trimethylsilylbromoketene. Aldoketenes and halogenated ketenes are usually not isolable and in situ reactions are effected whereby the ketenes are trapped. Halogenated ketenes have been observed in solution by infrared absorption near 2100 cm.$^{-1}$. The stability of ketenes is increased by increasing the size of the substituent(s) bonded to the sp^2 hybridized carbon.[7,9]

Ketenes undergo nucleophilic addition reactions with many different types of nucleophiles to yield the corresponding acyl derivatives.[17] In some recent developments Ruden has reported that the reaction rate of hindered amines and tertiary alcohols toward trimethylsilylketene can be catalyzed by BF$_3$ etherate solution.[18] Also, the treatment of di-butyl ketene and some bimetallic ketenes with organo-

$$\underset{R}{\overset{R'}{>}}C=C=O \xrightarrow[\text{2) } H_2O]{\text{1) PhLi}} RR'CH\overset{O}{\overset{\|}{C}}-Ph$$

R=R'= t-Bu, or R= R$_3$M, R'= R$_3$M'

lithium compounds and subsequent hydrolysis affords the corresponding ketones.[19,20]

The cycloaddition of non-metallic ketenes with olefins to yield cyclobutanones has received much attention in recent years. The olefinic compounds which have been studied include substituted olefins, conjugated dienes, vinyl ethers, methylenecycloalkanes and enamines.[21-25] It has been well
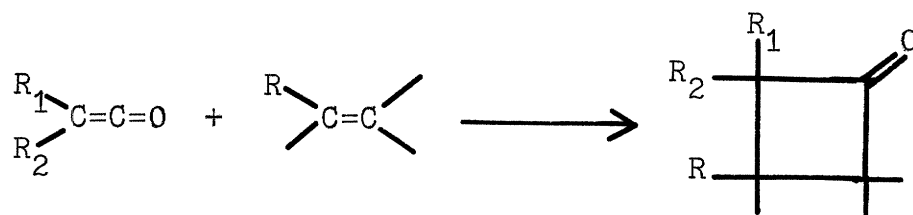

established that these olefinic cycloadditions occur by a ($\pi 2_a + \pi 2_s$) process whereby the ketene participates in an antarafacial role.[26-29] Ketenes also undergo cycloaddition with carbonyl compounds, imines, and carbodiimides to yield 2-oxetanones and 2-azetidinones respectively.[30-34] Cyclo-

additions to the carbon nitrogen double bond occur by a two step process which involves a dipolar intermediate.[35-38]

The effect of the trimethylsilyl substituent on the properties and chemistry of trimethylsilylketene is truly remarkable. Numerous efforts to effect cycloaddition with

the usual olefinic compounds have been unsuccessful. The only cycloaddition which has been reported was with dimethyl- and diethyl ketals of dimethylketene under rather vigorous condition.[39] Also, condensation of trimethylsilylketene with
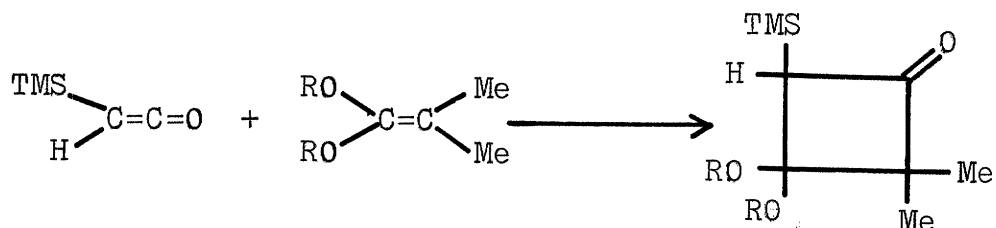
benzaldehyde gave _cis_ and _trans_ trimethylsilylstyrene which presumably involved cycloaddition to from the 2-oxetanone which underwent decarboxylation to yield the olefins.[40] Tri-


methylsilylbromoketene readily undergoes cycloaddition with an imine and carbodiimide to yield the corresponding 2-aze-tidinones.[14] It has also been reported that trimethylsilyl-ketene reacts with phosphoranes to yield silylallenes which undergo rearrangement to form the acetylene isomers.[41]
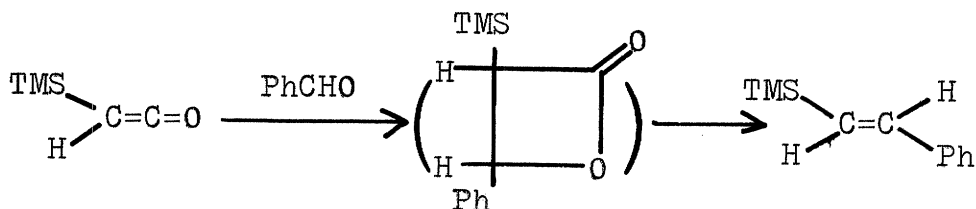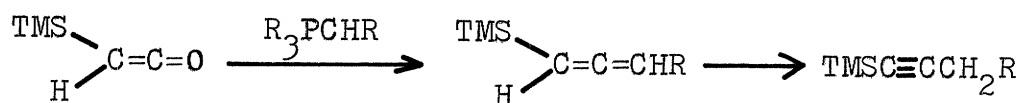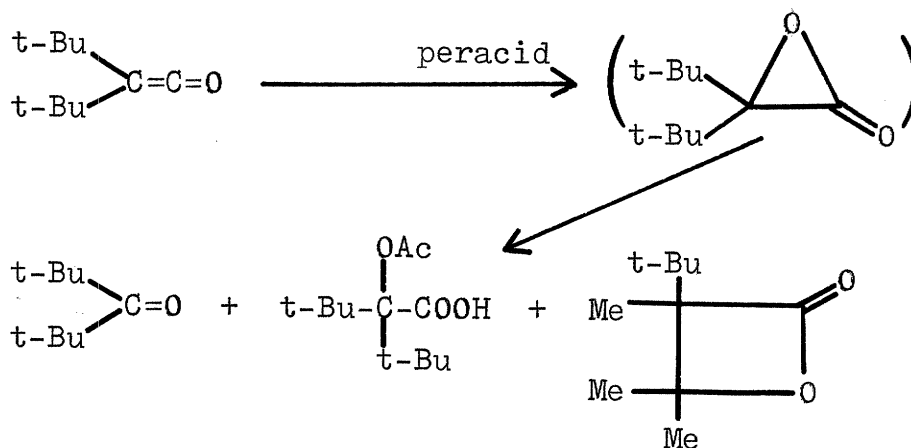

Lipp and Buckremer reported in 1932 that diazomethane added to ketene to yield the unstable cyclopropanone as a

transient intermediate.[42] Turro and Hammond have more re-
cently studied the reaction of methylketene and dimethyl-
ketene with diazomethane and found that at - 78° the cyclo-
propanones were formed in high yield and that the unsymmet-
rical dimethylcyclopropanone was moderately stable at room

$$\text{(Me) H}\diagdown\atop\text{Me}\diagup\text{C=C=O} \xrightarrow{\text{CH}_2\text{N}_2} \triangle\text{H (Me)}$$
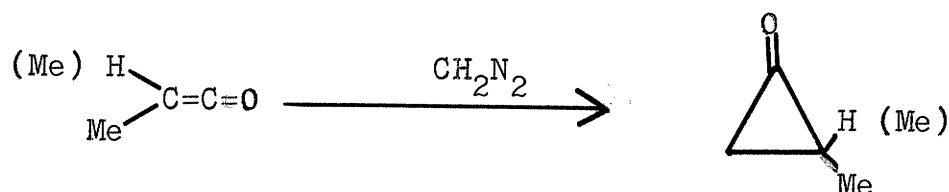
temperature.[43,44] The peracid oxidation of some hindered
ketenes, di-t-butyl ketene and diphenyl ketene, occurs
through an α-lactone intermediate which has been detected
spectroscopically. The products which are produced from
this α-lactone include a 2-oxetanone, a ketone and an α-
acetoxyacid.[45, 46]

$$\text{t-Bu}\diagdown\atop\text{t-Bu}\diagup\text{C=C=O} \xrightarrow{\text{peracid}} \left(\text{t-Bu}\diagdown\atop\text{t-Bu}\diagup\right)$$

$$\text{t-Bu}\diagdown\atop\text{t-Bu}\diagup\text{C=O} \; + \; \text{t-Bu-}\overset{\text{OAc}}{\underset{\text{t-Bu}}{\text{C}}}\text{-COOH} \; + \;$$

Ketenes are well known to undergo dimerization and
polymerization reactions. Aldoketenes are most susceptable

to dimerization forming 2-oxetanones. However, the more stable ketoketenes dimerize to produce the 1,3-cyclobutane-diones.[47-52]

The symmetrical diones obtained from dimethylketene and diphenylketene can be converted to the 2-oxetanone dimer by the addition of a catalytic amount of sodium methoxide or aluminum chloride.[53-55] No dimers of halogenated ketenes or organometallic ketenes have been reported. The only isolable products from the dehydrohalogenation reaction of α-haloacid halides with triethylamine have been α-halovinyl esters.[7]
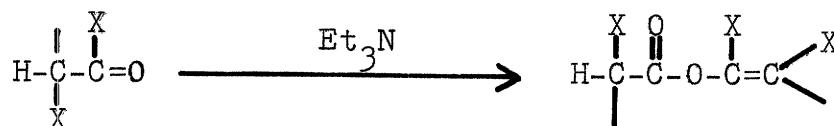
Mixed dimerizations of ketenes have rarely been studied, because, in addition to the low yield of mixed dimers, the two monodimers are produced. However, Brady and Ting recently described the mixed dimerization of ketoketenes and halogenated ketenes. The structure of the mixed dimers have been established as halotrialkyl-1,3-cyclobutanediones.[56]

The dimethylketene and pentamethyleneketene dimers are the only 1,3-cyclobutanediones whose chemistry have been

studied. Tetramethyl-1,3-cyclobutanedione slowly undergoes nucleophilic attack to yield the ring opened products.[57] This reaction can be catalyzed by adding a small amount of strong base.

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-C(CH_3)_2-\overset{\overset{O}{||}}{C}-Nu$$
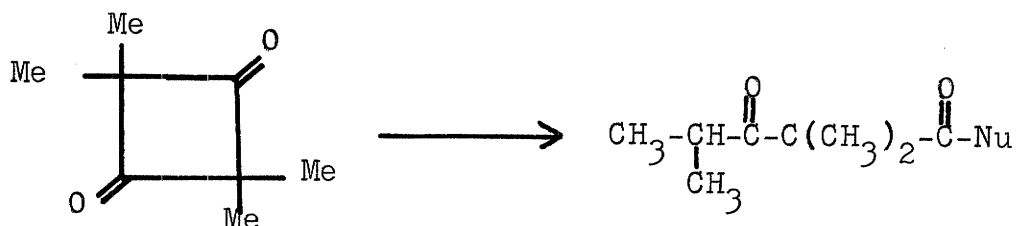
The hydrogenation of tetramethyl-1,3-cyclobutanedione with a ruthenium catalyst yields the corresponding _cis_ and _trans_ glycols in excellent yield.[58] These symmetrical diones also react with diazomethane to yield the ring expanded product in quantitative yield.[59]
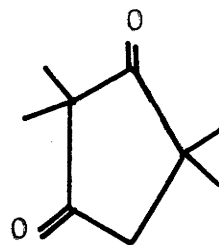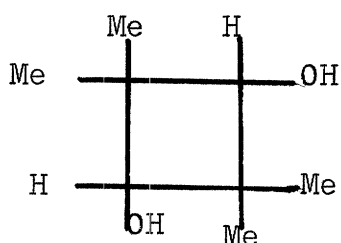
The peracid oxidation of tetramethyl-1,3-cyclobutane-dione occurred smoothly to yield the expected lactone, with no further ring expansion products being formed.[60, 61]
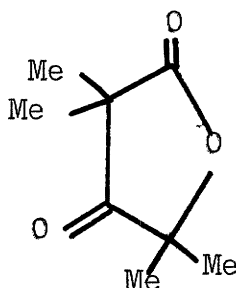
The reaction of some symmetrical diones with methylene-triphenylphosphorane leads to ring opened products. In the case of the pentamethyleneketene dimer, the expected diene is formed but the major product is the ring opened dione.[62,63]
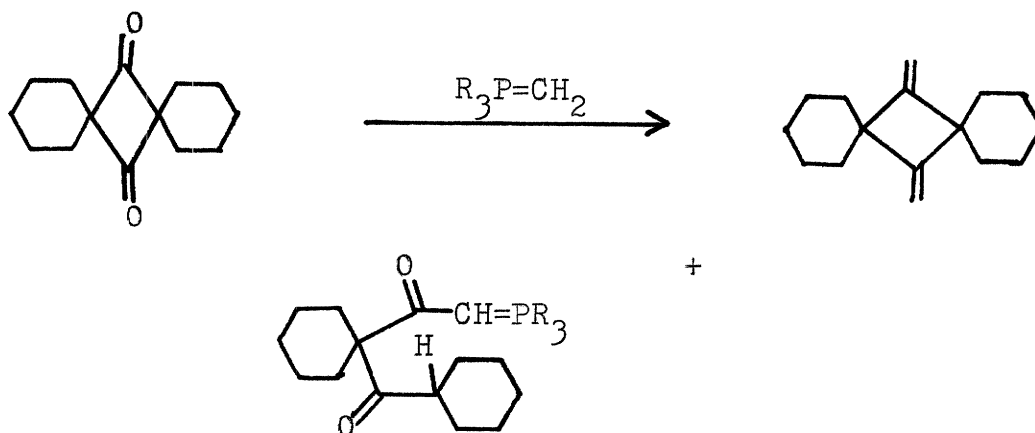
This dissertation is concerned with two different types of investigations. The first study is an examination into the effect that the trimethylsilyl substitutent has on the chemistry of trimethylsilylketene. This study was approached by the synthesis of trimethylsilylmethylketene and phenyl-trimethylsilylketene and a subsequent investigation of these novel ketenes in an effort to learn more about this effect. The second study is an investigation into the chemistry of the mixed dimers of dialkylketenes and halogenated ketenes, chlorotrialkyl-1,3-cyclobutanediones. Various reactions of these mixed dimers were studied in an effort to explore some new chemistry of cyclobutanediones.

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CHAPTER II

EXPERIMENTAL

Proton nuclear magnetic resonance (n.m.r.) spectra were recorded on Jeolco PS-100 and Hitachi Perkin-Elmer 60 Spectrometers employing tetramethylsilane or chloroform as an internal standard. Vapor phase chromatography was performed on an F. & W. Scientific Model 700 instrument with a 10 ft x $\frac{1}{4}$ in. column packed with 10% SE 30 or Carbowax 20 M on an acid washed Chromosorb W (80/100). The infrared spectra were obtained on a Beckman 320 and Perkin-Elmer Model 237 Grating Infrared Spectrometers. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E Focusing Double Mass Spectrometer. Elemental analyses were performed by Midwest Microlab. Ltd., 6000 East 46th Street, Indianapolis, Ind. 46226.

Preparation of Reagents

Solvents were dried and purified by distillation from potassium-sodium alloy or metallic sodium prior to use. Triethylamine was commercially available and was dried over sodium metal and distilled prior to use.

Vinyltrimethylsilane was commercially available and also prepared by the reaction of methylmagnesium bromide and vinyltrichlorosilane in ether.[1]

β-Trimethylsilylpropionic acid was prepared from vinyl-

trimethylsilane by the addition of hydrogen bromide in the presence of benzoyl peroxide at 0°, Grignard formation, carboxylation, and hydrolysis to form the acid.[2]

Phenyltrimethylsilylmethane was obtained from the coupling reaction of benzyl magnesium chloride and trimethylchlorosilane.[3]

N-tert-Butylbenzylimine was prepared from benzaldehyde and t-butylamine.[4]

Chlorotrimethylsilylphenylmethane was obtained by the reaction of sulfuryl chloride and phenyltrimethylsilylmethane.[5]

Phenylethylketene was prepared by the dehydrohalogenation of 2-phenylbutanoyl chloride with triethylamine in benzene solution.[6]

t-Butyl phenylacetate, t-butyl phenylchloroacetate and methyl phenylchloroacetate were prepared from the corresponding acid halides and alcohols in the presence of N,N-dimethylaniline in ether solution.[7]

3,3-Dimethylbutanoic acid was prepared by the reaction of t-butyl alcohol with 1,1-dichloroethene in the presence of sulfuric acid.[8]

The acid halides employed in this investigation were prepared from the appropriate carboxylic acids and thionyl chloride or phosphorous pentachloride and are listed in Table I. The α-haloacid chlorides were obtained by reaction of the acid chloride with sulfuryl chloride. All of the acid

halides were confirmed by a comparision of boiling points in the literature and also by ir and nmr spectra.

TABLE I

ACID CHLORIDES PREPARED FROM THE CORRESPONDING ACIDS

ACID CHLORIDE	BOILING POINT
Trimethylsilylpropanoyl chloride[9]	90°/55 mm.
2-Phenylbutanoyl chloride	60-62°/0.05 mm.
2-Chloropropanoyl chloride[10]	110-112°
Phenylacetyl chloride[11]	110-112°/30 mm.
Phenylchloroacetyl chloride[12]	65-68°/0.05 mm.
2-Chlorobutanoyl chloride[13]	129-131°
2-Chloro-3-methylbutanoyl chloride[10]	149-150°
Dichloroacetyl chloride[14]	108-110°
Isobutyryl chloride[15]	92°
3,3-Dimethylbutanoyl chloride[16]	128-130°
2-Chloro-3,3-dimethylbutanoyl chloride[17]	90-92°/30 mm.

Preparation of trimethylsilylketene[18]

To a stirred solution of 7.0 g (0.1 mole) of ethoxy-acetylene in 250 ml of anhydrous ether under nitrogen 62 ml of 1.7 M (0.105 mole) methyllithium at -78° was added over a period of 1 hour. After the additional hour and 11 g (0.101 mole) of trimethylchlorosilane was added. The mixture was stirred at room temperature overnight and the ether removed by rotary evaporation. The residue was separated from the salt under vacuum and collected in the cold

trap (-78°). Trimethylsilylketene was obtained by a slow distillation of the condensate at 80-82° (the temperature of the oil bath was 120°) to yield 7 g (60%); ir, 2060 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), 1.6 (s, 1 H).

3-Trimethylsilylmethyl-4-(2-trimethylsilyl)-ethylidene-2-oxetanone

To a solution of 0.2 mole of triethylamine in 150 ml of dry hexane was added dropwise 0.1 mole of β-trimethyl-silylpropionyl chloride in 20 ml of hexane under a dry nitrogen atmosphere at room temperature over a ½ hour period. At the completion of the addition, the reaction mixture was refluxed for about 2 hours. The ketene was very short-lived as evidenced by the disappearance of the band in the infrared at 2123 cm.$^{-1}$. The solvent was evaporated on a rotary evaporator, residual salt removed by filtration, and vacuum distillation afforded the dimer at 71-73° at 0.05 mm (85%); ir; 1805, 1710 cm.$^{-1}$; nmr, δ, 0.1 (s, 18 H), 1.40 (d, 2 H), 1.42 (d, 2 H), 3.80 (t, 1 H), and 4.54 (t, 1 H); mass spectrum parent peak at m/e 256 (theory 256).

Anal. Calcd. for $C_{12}H_{24}O_2Si_2$: C, 56.25; H, 9.37. Found: C, 56.20; H, 9.41.

1,5-Bis(trimethylsilyl)-3-pentanone

This disilylated ketone was also isolated from the dimerization reaction mixture unless the reaction was run under a dry nitrogen atmosphere and strict precautions were

taken to keep atmospheric moisture from the system. All of
the 2-oxetanone dimer could be converted to this ketone by
the addition of water to the dimer. This ketone distilled
at 55-56° at 0.05 mm; ir, 1720 cm.$^{-1}$; nmr, δ, 0.01 (s, 18 H),
0.70 (t, 4 H), 2.26 (t, 4 H); mass spectrum parent peak at
m/e 230 (theory 230).

1,4-Bis(trimethylsilyl)butane

This disilylated compound was also isolated from the
reaction mixture described above unless the β-trimethylsilyl-
propionic acid is carefully distilled. 1,4-Bis(trimethyl-
silyl)butane is a product from a Grignard coupling reaction
in the preparation of the acid and vacuum distills at 36-38°
at 0.05 mm; nmr, δ, -0.10 (s, 18 H), 0.48 (m, 4 H), and 1.18
(m, 4 H).

Anal. Calcd. for $C_{10}H_{26}Si_2$: C, 59.41; H, 12.87. Found:
C, 59.67; H, 13.05.

General Procedure for Ketene-Olefin Cycloaddition

A solution containing 0.2 mole of triethylamine, and
0.2 mole of olefin in 200 ml of dry hexane was placed in a
500 ml three-necked flask, equipped with a mechanical stirrer
and a dropping funnel. Under a nitrogen atmosphere, a solu-
tion of 0.1 mole of acid chloride in 20 ml of dry hexane was
added dropwise at room temperature over a ½ hour period.
After the addition was completed, the reaction mixture was
stirred and refluxed for 2 hours. The reaction was monitored

by vpc analysis, and upon completion of the reaction, the salt was removed by filtration and the solvent by rotary evaporation. The residue was vacuum distilled.

Endo-7-trimethylsilylmethylbicyclo(3.2.0)-hept-2-en-6-one

The cycloadduct of trimethylsilylmethylketene and cyclopentadiene was obtained at 65° at 0.05 mm (65%); ir, 1800, 1610 cm.$^{-1}$; nmr, δ, 0.20 (s, 9 H), 0.84 (8 lines, 2 H), 2.64 (m, 2 H), 3.80 (m, 3 H), and 5.98 (d-m, 2 H); mass spectrum parent peak at m/e 194 (theory 194).

Anal. Calcd. for $C_{11}H_{18}OSi$: C, 68.04; H, 9.28. Found: C, 67.69; H, 9.52.

Trans-3-ethoxy-2-trimethylsilylmethylcyclobutanone

This cycloadduct of trimethylsilylmethylketene and ethyl vinyl ether was distilled at $40-42^\circ$ at 0.05 mm (60%); ir, 1780 cm.$^{-1}$; nmr, δ, 0.10 (s, 9 H), 0.88 (d, 2 H), 1.22 (t, 3 H), 2.94-3.90 (m, 5 H), and 4.27 (m, 1 H); mass spectrum parent peak at m/e 200 (theory 200).

Anal. Calcd. for $C_{10}H_{20}O_2Si$: C, 60.00; H, 10.00. Found: C, 59.51; H, 10.82.

2-Chloro-2-methyl-3-trimethylsilylmethylcyclobutanone

The cycloadduct of methylchloroketene and allytrimethylsilane distilled at $68-70^\circ$ at 0.025 mm (62%); ir, 1780 cm.$^{-1}$; nmr, δ, 0.24 (s, 9 H), 1.04 (8 lines, 2 H), 1.68 and 1.80

(two singlets, ratio 6:1, 3 H), 2.84 (m, 2 H), and 3.40 (m, 1 H).

Anal. Calcd. for $C_9H_{17}ClOSi$: C, 52.81; H, 8.31. Found: C, 52.39; H, 8.26.

2,2-Dichloro-3-trimethylsilylmethylcyclobutanone

This cycloadduct of dichloroketene and allyltrimethylsilane was vacuum distilled at 65-66° at 0.025 mm (54%); ir, 1785 cm.$^{-1}$; nmr, δ, 0.12 (s, 9 H), 1.20 (8 lines, 2 H), 2.98 (m, 2 H), and 3.40 (m, 1 H).

Anal. Calcd. for $C_8H_{14}ClOSi$: C, 42.67; H, 6.22. Found: C, 42.89; H, 6.11.

Phenyltrimethylsilylacetic acid

To a solution of 0.1 mole of phenyltrimethylsilylmethane in 200 ml of anhydrous ether was added 75 ml of 1.6 M (0.12 mole) n-butyl lithium dropwise over an hour period at 0° under a nitrogen atmosphere. After the addition was complete, the reaction mixture was stirred at room temperature for 20 hours. The solution which had turned to an orange-brown color was slowly poured over crushed dry ice with stirring. When all the dry ice had evaporated, a 5% hydrochloric acid solution was added with stirring to acidify the solution. The ether layer was separated and the aqueous solution extracted with ether and combined with the original ether solution. This solution was dried over anhydrous magnesium sulfate and then the ether removed by evaporation. Upon standing overnight

in the refrigerator the acid crystallized from the residue and was purified by sublimation to yield 7 g (34%); Mp., 117-118°; ir, 1688, 3000 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), 3.30 (s, 1 H), 7.10 (s, 5 H), and 12.30 (s, 1 H); mass spectrum parent peak at m/e 208 (theory 208).

Anal. Calcd. for $C_{11}H_{16}O_2Si$: C, 63.46; H, 7.69. Found: C, 63.18; H, 7.83.

Phenyltrimethylsilylacetyl chloride

To a solution of 3 g (0.014 mole) of phenyltrimethylsilylacetic acid in 30 ml of carbon tetrachloride was added 3.5 g (0.028 mole) of oxalyl chloride with stirring at room temperature. The reaction mixture was stirred for an additional 2 hours until gas ceased to be evolved. Attempts to isolate this compound were unsuccessful due to thermal decomposition, but nmr and ir spectra were obtained on the reaction solution; ir, 1785 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), 3.76 (s, 1 H), and 6.96 (s, 5 H).

Phenyltrimethylsilylbromoacetyl chloride

To the phenyltrimethylsilylacetyl chloride solution was added 2 g (0.012 mole) of bromine and the reaction solution was stirred at room temperature for 10 hours. This compound was not isolated but ir and nmr data were obtained; ir, 1790 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), and 7.10 (s, 5 H).

Phenyltrimethylsilyl ketene

The phenyltrimethylsilylbromoacetyl chloride solution

described above was concentrated by rotary evaporation and added to a stirred mixture which contained 1 g of activated zinc and 30 ml of dry tetrahydrofuran. After the completion of the addition, the reaction mixture was stirred under nitrogen at room temperature for an additional 2 hours. The solvent was removed by evaporation and the residue washed with dry hexane. The zinc salt was removed by filtration, and the hexane was evaporated. The ketene was distilled at 60° at 2 mm, yielded 1.1 g (41% based on 3 g of phenyltrimethylsilylacetic acid); ir, 2085 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), and 7.10 (s, 5 H); mass spectrum parent peak at m/e 190 (theory 190).

The Reaction of Phenyltrimethylsilylacetyl Chloride and N-t-Butyl benzylimine

A solution containing 3.2 g (0.02 mole) of N-t-butyl-benzylimine, 0.02 mole of phenyltrimethylsilylacetyl chloride and 2 g (0.02 mole) of triethylamine in 60 ml of carbon tetrachloride was refluxed for 2 hours. The amine salt was removed by filtration and the solvent was evaporated on a rotary evaporator. The residue was distilled at 110° at 0.1 mm and on standing crystallized to give 2.5 g (46%) of the nonsilated cycloadduct which was a mixture of cis and trans N-t-butyl-3,4-diphenyl-2-azetidinones. Purification was accomplished by sublimation but only the trans isomer sublimed, Mp, 104°

(<u>trans</u> isomer); ir, 1790 cm.$^{-1}$; nmr (<u>trans</u> isomer), δ, 1.30 (s, 9 H), 4.55 (d, 1 H, J (trans)= 3 Hz), 4.9 (d, 1 H, J = 3 Hz), and 6.87 (s, 5 H), 6.92 (s, 5 H); nmr (cis isomer), δ, 1.3 (s, 9 H), 3.84 (d, 1 H, J (cis)= 7 Hz), 4.38 (d, 1 H, J = 7 Hz), 7.14 (s, 5 H), and 7.26 (s, 5 H); mass spectrum parent peak at m/e 279 (theory 279).

Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.73; H, 7.63. Found: C, 81.74; H, 7.64.

Preparation of Diazomethane[19]

To a mixture of 100 ml methylene chloride and 30 ml of 40% potassium hydroxide at 5° was added 10 g of finely pow-dered <u>N</u>-nitrosomethylurea in small portions over a period of one to two minutes with stirring. The deep yellow methylene chloride layer was separated and dried over potassium hy-droxide pellets in the refrigerator overnight. This solution contained about 2.8 g (0.66 mole) of diazomethane as reported in the literature.

General Procedure for Diazomethane Reaction with Ketenes

To 0.01 mole of ketene in 30 ml of methylene chloride was added 0.03 mole of diazomethane in methylene chloride at -78° with stirring. Upon warming to room temperature, the reaction solution was stirred overnight. The solvent was removed under reduced pressure and the product vacuum dis-tilled.

Reaction of Phenylethylketene with Diazomethane

Approximately an equal mixture of cyclobutanones were obtained from this reaction in 84% yield at 65-70° at 0.05 mm. Separation by vapor phase chromatography revealed 2-ethyl-2-phenylcyclobutanone; ir, 1795 cm.$^{-1}$; nmr, δ, 0.8 (t, 3 H), 1.9 (1, 2 H), 2.1-2.5 (two sets of t, 2 H), 2.9-3.2 (m, 2 H), and 7.10 (s, 5 H); mass spectrum parent peak at m/e 174 (theory 174).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.76; H, 8.05. Found: C, 82.70; H, 8.15.

The other cyclobutanone was also purified by collection from vapor phase chromatography and identified as 3-ethyl-3-phenylcyclobutanone; ir, 1795 cm.$^{-1}$; nmr, δ, 0.75 (t, 3 H), 1.85 (q, 2 H), 2.80-3.50 (m, 4 H), and 7.15 (s, 5 H); mass spectrum parent peak at m/e 174 (theory 174).

Reaction of Phenyltrimethylsilylketene with Diazomethane

Vapor phase chromatography analysis of the vacuum distillate revealed two major components. 3-Phenyl-3-trimethylsilylcyclobutanone was collected by vpc and estimated to be produced in 20% yield; ir, 1780 cm.$^{-1}$; nmr, δ, 0.00 (s, 9 H), 3.33 (s, 4 H), and 7.10 (s, 5 H); mass spectrum parent peak at m/e 268 (theory 268).

A nonsilylated ketone, 2-phenylcyclobutanone, was also purified by collection from the vpc and estimated to be

produced in a 20% yield; ir, 1790 cm.$^{-1}$; nmr, δ, 1.8-2.7 (m, 2 H), 2.7-3.3 (m, 2 H), 4.3 (d-d, 1 H), and 7.12 (s, 5 H); mass spectrum parent peak at m/e 146 (theory 146).

Reaction of Trimethylsilylketene with Diazomethane

3-Trimethylsilylcyclobutanone was obtained from this reaction; ir, 1790 cm.$^{-1}$; nmr, δ, 0.0 (s, 9 H), 1.1-1.8 (m, 1 H), and 2.7-3.3 (m, 4 H); mass spectrum peak at m/e 142 (theory 142).

Reactions of Unsymmetrical 1,3-Cyclobutanediones

The chlorotrialkyl-1,3-cyclobutanediones that were em-ployed in this investigation are listed in Table II. Chloro-trialkyl-1,3-cyclobutanediones were prepared by the mixed

TABLE II

CHLOROTRIALKYL-1,3-CYCLOBUTANEDIONES

Chlorotrialkyl-1,3-cyclobutanediones[20]	Boiling Point
2-Chloro-2-methyl-4,4-dimethyl-1,3-cyclobutanedione	70°/0.025 mm.
2-Chloro-2-ethyl-4,4-dimethyl-1,3-cyclobutanedione	55°/0.025 mm.
2-Chloro-4,4-dimethyl-2-isopropyl-1,3-cyclobutanedione	42°/0.05 mm.
2-Chloro-2-t-butyl-4,4-dimethyl-1,3-cyclobutanedione	39°/0.025 mm.

dimerization a halogenated ketene and dialkylketenes.[21] The α-chloroacid chloride and disubstituted acid chlorides were treated with triethylamine in benzene solution to afford the mixed dimers.

Preparation of tri-n-butyltin hydride[22]

A 6 g (0.15 mole) portion of lithium aluminum hydride was suspended in 250 ml of anhydrous ether in a one liter three necked flask, provided with a stirrer, reflux condenser, gas inlet tube and a dropping funnel. After purging the system with nitrogen, 49 g (0.15 mole) of commercially available tri-n-butyltin chloride in 100 ml of ether were added gradually with stirring. The reaction mixture was refluxed for $2\frac{1}{2}$ hours and then cooled to room temperature. A 0.5 g portion of hydroquinone was added and the mixture cooled by an ice bath. A 12 ml portion of water was added dropwise, and then 300 ml of a 20 % aqueous solution of sodium potassium tartrate added to dissolve the precipitated alumina. Etheral extracts of this solution were dried with anhydrous sodium sulfate. The ether was removed by a rotary evaporator and the product collected by vacuum distillation at 77-78° at 0.5 mm in 70% yield.

General Procedure for Conversion of Chlorotrialkyl-1,3-cyalobutanediones to Trialkyl-1,3-cyclobutanediones

To a 0.05 mole of chlorotrialkyl-1,3-cyclobutanedione in 150 ml of cold hexane containing 0.1 g of aza-bisisobutyronitrile was added dropwise 0.06 mole of freshly distilled

tri-n-butyltin hydride. This mixture was stirred in the ice bath for an additional two hours. The crude product was separated from the reaction solution by filtration, washed with ether, and recrystallized from methanol.

Trimethyl-1,3-cyclobutanedione

An 80% yield of this dione was obtained with a Mp at 165-166°; ir (DMSO), 1620, 1753 and 3444 cm.$^{-1}$; nmr (DMSO), δ, 1.12 (s, 6 H), 1.40 (s, 3 H), and 2.52 (s, 1 H); mass spectrum parent peak at m/e 126 (theory 126).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.66; H, 7.94. Found: C, 66.82; H, 8.46.

4-Ethyl-2,2-dimethyl-1,3-cyclobutanedione

An 85% yield of this dione was obtained; Mp, 143-145°; ir (DMSO), 1612, 1739, and 2444 cm.$^{-1}$; nmr, δ, 1.02 (t, 3 H), 1.16 (s, 6 H), 1.92 (q, 2 H), and 2.58 (s, 1 H); mass spectrum parent peak at m/e 140 (theory 140).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.96; H, 8.76.

2,2-Dimethyl-4-isopropyl-1,3-cyclobutanedione

This dione was obtained in 80% yield, Mp, 138-140°; ir (DMSO), 1612, 1742, and 3444 cm.$^{-1}$; ir (KBr), 1759 cm.$^{-1}$; nmr (DMSO), δ, 0.98 (d, 6 H), 1.06 (s, 6 H), 2.24 (sep., 1 H) and 2.44 (s, 1 H); mass spectrum parent peak at m/e 154 theory 154).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.13; H, 9.09. Found: C, 70.03; H, 9.54.

4-t-Butyl-2,2-dimethyl-1,3-cyclobutanedione

This dione was obtained in 90% yield, Mp, 217° ; ir (DMSO), 1633, 1739, and 3444 cm.$^{-1}$; ir (KBr), 1724 cm.$^{-1}$; nmr (DMSO), δ, 1.12 (s, 15 H), and 2.54 (s, 1 H); mass spectrum parent peak at m/e 168 (theory 168).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.43; H, 9.52. Found: C, 71.66; H, 9.70.

General Procedure for Treatment of Substituted 1,3-Cyclobutanediones with Sodium Methoxide in Methanol

To 50 ml of methanol containing 0.5 g of sodium methoxide was added 0.015 mole of 1,3-cyclobutanedione, and the solution was heated to reflux. The reaction was monitored by vpc as a two to seven day refluxing time was required for disappearance of all the cyclobutanedione. Upon cooling, the reaction solution was concentrated on a rotary evaporator and neutralized with dilute acid in an ice bath and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate, and the solvent removed, and the residue vacuum distilled.

Methyl 4-chloro-2,2-dimethyl-3-ketopentanoate

The reaction of 2-chloro-2,4,4-trimethyl-1,3-cyclobutanedione with sodium methoxide in methanol was complete in two days as evidenced by vpc, and the ester was obtained in

82% yield, Bp 42-44°at 0.05 mm; ir, 1718, 1748 cm.$^{-1}$; nmr,
δ, 1.40 (s, 3 H), 1.49 (s, 3 H), 1.58 (d, 3 H), 3.37 (s, 3 H)
and 4.65 (q, 1 H); mass spectrum parent peak at m/e 192
(theory 192).

Methyl 4-Chloro-2,2-dimethyl-3-ketohexanoate

The reaction of 2-chloro-ethyl-4,4-dimethyl-1,3-cyclo-
butanedione with sodium methoxide in methanol was complete
in five days in 75% yield at 50-52° at 0.05 mm; ir, 1718,
1748 cm.$^{-1}$; nmr, δ, 0.90 (t, 3 H), 1.26 (s, 3 H), 1.36 (s,
3 H),1.90 (m, 2 H), 3.52 (s, 3 H), and 4.12 (t, 1 H); mass
spectrum parent peak at m/e 206 (theory 206).

Methyl 4-Chloro-2,2,5-trimethyl-3-ketohexanoate

The ketoester was obtained from the reaction of 2-chloro-
4,4-dimethyl-2-isopropyl-1,3-cyclobutanedione and sodium
methoxide in 60% yield, reaction was not complete for seven
days; Bp 58-60° at 0.05 mm; ir, 1718, 1748 cm.$^{-1}$; nmr, δ,
1.0 (2 sets of d, 6 H), 1.44 (s, 3 H), 1.52 (s, 3 H), 2.40
(m, 1 H), 3.83 (s, 3 H), and 4.40 (d, 1 H); mass spectrum
parent peak at m/e 220 (theory 220).

Anal. Calcd. For $C_{10}H_{17}ClO_3$: C, 54.42; H, 7.71. Found:
C, 54.65; H, 7.80.

Preparation of Peracetic Acid [23]

A concentrated solution of peracetic acid was prepared
by cautiously adding 9.1 g of 90% hydrogen peroxide to a
stirred solution of 10 g of acetic acid and 0.11 ml of

concentrated sulfuric acid contained in a flask immersed in a water bath at 22-23° . The mixture was stirred for 12 hours and the peracetic acid content of the solution was reported to be about 45%.

General Procedure for Baeyer Villiger Oxidation

To a 50 ml solution of chloroform containing 0.015 mole of substituted 1,3-cyclobutanedione was added dropwise at room temperature 0.05 mole of peracetic acid. The solution was stirred and the reaction monitored by vpc. After the disappearance of all the dione, the organic layer was separated and washed with dilute sodium carbonate solution and then dried over magnesium sulfate. The chloroform was removed under reduced pressure and the lactone distilled.

α-Chloro-α,γ-dimethyl-β-keto-γ-valerolactone

This lactone was obtained by the reaction of peracetic acid with 2-chloro-2,4,4-trimethyl-1,3-cyclobutanedione in 70% yield at 53-56° at 0.05 mm; ir, 1770, 1809 cm.$^{-1}$; nmr, δ, 1.52 (s, 3 H), 1.84 (s, 6 H); mass spectrum parent peak at m/e 176 (theory 176).

Anal. Calcd. for $C_7H_9ClO_3$: C, 47.60; H, 5.14. Found: C, 47.33; H, 5.01.

α-Chloro-α-ethyl-γ-methyl-β-keto-γ-valerolactone

This lactone was obtained from the reaction of peracetic acid and 2-chloro-2-ethyl-4,4-dimethyl-1,3-cyclobutanedione

in 55% yield at 61-63° at 0.05 mm; ir, 1770, 1809 cm.$^{-1}$; nmr, δ, 0.99 (t, 3 H), 1.56 (s, 3 H), 1.72 (s, 3 H), and 2.18 (q, 2 H); mass spectrum parent peak at m/e 190 (theory 190).

Anal. Calcd. for $C_8H_{11}ClO_3$: C, 50.40; H, 5.82. Found: C, 50.79; H, 5.62.

α,α,δ,δ-Tetramethyl-β-keto-γ-caprolactone

This lactone was obtained from the reaction of peracetic acid and 4-t-butyl-2,2-dimethyl-1,3-cyclobutanedione in 15% yield at 66-67° at 0.05 mm; ir, 1739, 1802 cm.$^{-1}$; nmr, δ, 1.06 (s, 9 H), 1.20 (s, 3 H), 1.26 (s, 3 H), and 4.42 (s, 1 H); mass spectrum parent peak at m/e 184 (theory 184).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.22; H, 8.69. Found: C, 65.32; H, 8.99.

General Procedure for Diazomethane Reaction with 1,3-Cyclobutanediones

To 0.01 mole of 1,3-cyclobutanedione in 50 ml of ether was added 0.03 mole of diazomethane in ether at petroleum ether dry ice temperature. Upon warming to room temperature, the reaction solution was stirred for three days. The solvent was removed under reduced pressure and the product vacuum distilled.

4-Chloromethyl-2,2,4-trimethyl-1,3-cyclobutanedione

The product of diazomethane and 4-chloro-2,2,4-trimethyl-1,3-cyclobutanedione was distilled at 44-46° at 0.025 mm in 20 % yield; ir, 1777 cm.$^{-1}$; nmr, δ, 1.36 (s, 6 H), 2.00

(s, 3 H), and 4.24 (s, 2 H); mass spectrum parent peak at m/e 174 (theory 174).

3-Methoxy-2,4,4-trimethylcyclobutenone

The product of diazomethane and trimethyl-1,3-cyclobutanedione was obtained at 38-39° at 0.05 mm in 87 % yield; ir, 1616, 1750 cm.$^{-1}$; nmr, δ, 1.11 (s, 6 H), 1.60 (s, 3 H), and 4.11 (s, 3 H); mass spectrum parent peak at m/e 140 (theory 140).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 67.94; H, 8.74.

2-Ethyl-3-methoxy-4,4-dimethylcyclobutenone

The product from the reaction of 4-ethyl-2,2,4-trimethyl-1,3-cyclobutanedione and diazomethane was obtained at 45-47° at 0.05 mm in 85% yield; ir, 1616, 1750 cm.$^{-1}$; nmr, δ, 1.14 (s, 6 H), 2.20 (q, 2 H), and 3.94 (s, 3 H); mass spectrum parent peak at m/e 154 (theory 154).

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.02; H, 9.09. Found: C, 69.82; H, 9.11.

3-Methoxy-4,4-dimethyl-2-isopropyl-cyclobutenone

The product from the reaction of 2,2-dimethyl-isopropyl-1,3-cyclobutanedione and diazomethane was obtained at 52-54° at 0.05 mm in 80% yield; ir, 1616, 1750 cm.$^{-1}$; nmr, δ, 0.92 (s, 6 H), 1.40 (s, 6 H), 2.28 (s, 1 H), and 3.96 (s, 3 H); mass spectrum parent peak at m/e 168 (theory 168).

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found:
C, 71.19; H, 9.99.

<div align="center">

**2-t-Butyl-3-methoxy-4,4-dimethyl-
cyclobutenone**

</div>

This compound was obtained from the reaction of 2,2-
dimethyl-4-t-butyl-1,3-cyclobutanedione and diazomethane and
was distilled at 45-47° at 0.025 mm in 90% yield; ir, 1616,
1752 cm.$^{-1}$; nmr, δ, 1.10 (s, 9 H), 1.3 (s, 6 H), and 4.0 (s,
3 H); mass spectrum parent peak at m/e 182 (theory 182).

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.49; H, 9.89. Found:
C, 71.81; H, 9.97.

<div align="center">

General Procedure for Sodium Borohydride
Reduction

</div>

To a stirred solution of 0.015 mole of cyclobutenone in
100 ml of methanol was slowly added sodium borohydride until
the reduction was complete as evidenced by vpc. The solvent
was removed and the saturate alcohol vacuum distilled.

<div align="center">

3-Methoxy-2,2,4-trimethylcyclobutanol

</div>

This alcohol was obtained from the reaction of trimethyl-
1,3-cyclobutanedione and sodium borohydride at 35-37° at
0.025 mm in near quantitative yield; ir, 3334 cm.$^{-1}$; nmr,
δ, 0.90 (d, 3 H), 1.08 (s, 3 H), 1.12 (s, 3 H), 1.78 (q, 1 H),
2.41 (s, 1 H), 2.54 (d, 1 H, J_{trans}= 7 Hz), and 2.82 (d, 1 H,
J_{trans}= 7 Hz), 3.12 (s, 3 H).

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found:
C, 66.84; H, 11.29.

4-t-Butyl-3-methoxy-2,2-dimethyl-cyclobutanol

This alcohol was obtained from the reaction of 2,2-dimethyl-4-t-butyl-1,3-cyclobutanedione and sodium borohydride at 62-63° at 0.05 mm in quantitative yield; ir, 3334 cm.$^{-1}$; nmr, δ, 0.96 (s, 9 H), 0.98 (s, 3 H), 1.40 (s, 3 H), 1.64 (s, 1 H), 1.90 (d-d, 1 H), 3.22 (s, 3 H), 3.47 (d, 1 H, J_{cis}= 10Hz), and 3.76 (d, 1 H, J_{trans}= 7 Hz).

Anal. Calcd. for $C_{11}H_{22}O_2$: C, 70.86; H, 11.83. Found: C, 71.22; H, 11.97.

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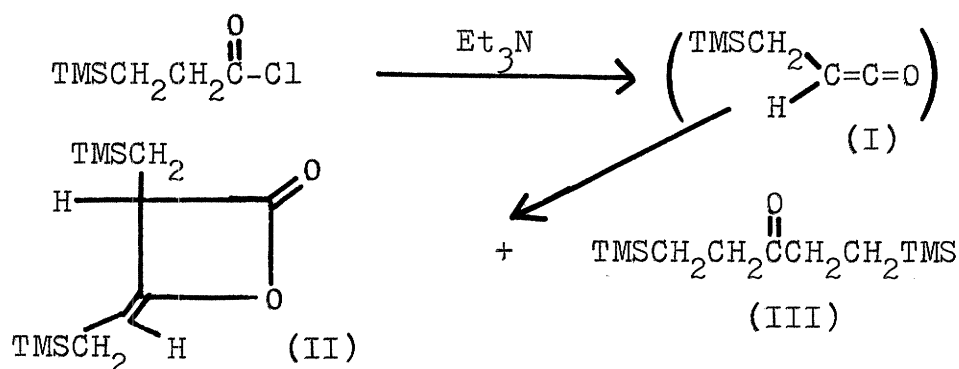16. Traynham, J. G., and Battiste, M. A., J. Org. Chem., 22, 1551 (1956).

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RESULTS AND DISCUSSION

The Effect of Trimethylsilyl
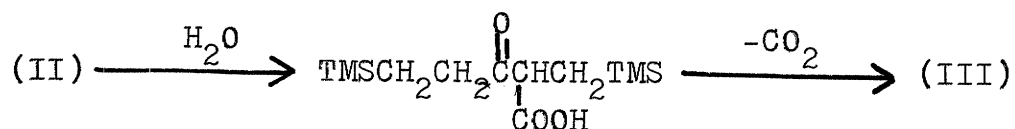### Substituent on Ketene

The properties and chemistry of trimethylsilylketene are very unusual for an aldoketene. The carbon analogue, t-butyl-ketene, although detectable in solution but not isolable, undergoes cycloaddition and dimerization as expected for a hindered aldoketene. Apparently, the steric effect of the trimethylsilyl substituent on the ketene functionality is not the reason for the remarkable character of the trimethyl-silylketene. The electronic effect of the trimethylsilyl substituent must be the determining factor for the unusual properties of trimethylsilylketene. Consequently, the purpose of this investigation was to study the nature of the tri-methylsilyl substituent on the ketene functionality.

Trimethylsilylmethylketene, (I), was prepared by the

$$TMSCH_2CH_2\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\ Et_3N\ } \left(\begin{matrix} TMSCH_2 \\ H \end{matrix} C=C=O \right) \text{(I)}$$

$$+ \quad TMSCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2TMS \\ \text{(III)}$$

(II)

triethylamine dehydrohalogenation of β-trimethylsilylpro-pionyl chloride in hexane. The ketene band was observed in

the infrared at 2123 cm.$^{-1}$ but had a very short life time
and was not isolable but underwent dimerization to yield the
expected 2-oxetanone (II). This dimer was accompanied by an
unexpected product, 1,5-bis-(trimethylsilyl)-3-pentanone
(III). This ketone was formed from the dimer. The dimer is
hygroscopic and will slowly react with atmospheric moisture
to yield the ketoacid which readily decarboxylates to the
ketone. Normal drying tube precautions were not sufficient

$$(II) \xrightarrow{\text{H}_2\text{O}} \text{TMSCH}_2\text{CH}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\underset{\underset{\text{COOH}}{|}}{\text{CH}}\text{CH}_2\text{TMS} \xrightarrow{-\text{CO}_2} (III)$$

to keep the dimer from being hydrolyzed. It is necessary to
effect the dehydrohalogenation under a dry nitrogen atmosphere
to prevent the formation of the ketone. Conversely, if water
is added to the reaction mixture after the dehydrohalogenation
is complete, carbon dioxide can be observed to be evolved.
The ketone is formed exclusively as no dimer can be detected.

The β-trimethylsilylpropionic acid was prepared from
vinyltrimethylsilane by the addition of hydrogen bromide,

$$\text{TMSCH}=\text{CH}_2 \xrightarrow{\text{HBr}} \text{TMSCH}_2\text{CH}_2\text{Br} \xrightarrow{\text{Mg}} \text{TMS}(\text{CH}_2)_4\text{TMS}$$
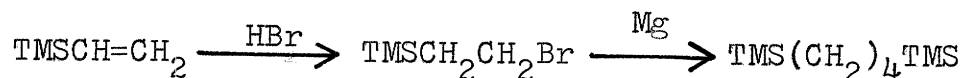
Grignard formation, carboxylation and hydrolysis. In the
process of Grignard formation, 1,4-bis-(trimethylsilyl)-
butane was formed as a coupling product, the formation of
which depended upon the concentration of the Grignard reagent

in ether solution. This product could be eliminated by
careful distillation of the acid.

An alternate route to trimethylsilylmethylketene would
be the zinc dehalogenation of α-halo-β-trimethylsilylpro-
pionyl chloride. However the α-halogenation of β-trimethyl-
silylpropionyl chloride with sulfuryl chloride or bromine
were unsuccessful due to the cleavage of the carbon-silicon
bond.

The *in situ* cycloaddition of cyclopentadiene and tri-
methylsilylmethylketene occurred in 65% yield. It was
recognized that a (4+2) cycloadduct could occur as a possible
consequence of secondary orbital interaction of the empty d-
orbital in silicon and the π system of the diene. However,
the (2+2) cycloadduct was assigned on the basis of the
infrared band at 1785 cm.$^{-1}$ and also on nmr evidence. The
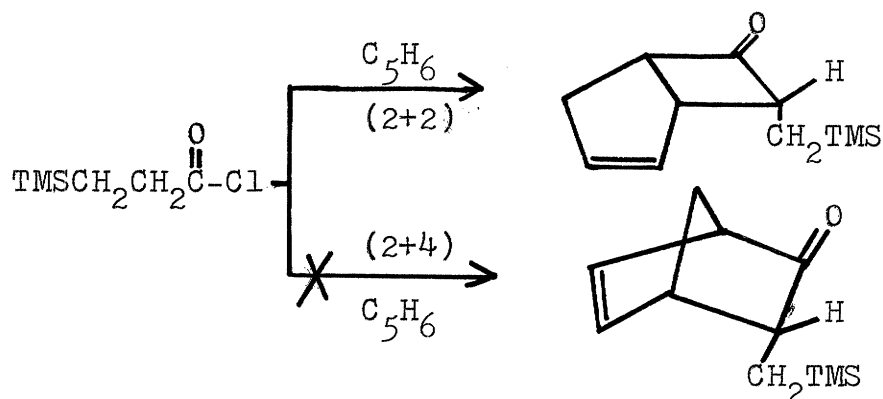
nmr spectrum revealed that upon decoupling the vinyl protons
from the methylene protons, a dramatic change was observed.
The vinyl protons in the (4+2) cycloadduct would not be
expected to reveal much change upon decoupling. Furthermore,

the nmr spectrum of this trimethylsilylmethylketene cyclo-
pentadiene adduct is very consistent with many other ketene
cyclopentadiene adducts prepared in this laboratory.

Two isomeric cyclobutanone structures are possible
depending on whether the trimethylsilylmethyl substituent
is _endo_, or _exo_. Only one isomer is formed from the reaction
of trimethylsilylmethylketene with cyclopentadiene. The
methylene protons adjacent to the trimethylsilylmethyl
substituent appeared as an eight line pattern in the nmr.
This indicates that the methylene protons are diastereotopic.
Each methylene proton from this isomer appears as a doublet-
doublet, thus accounting for the eight lines. It has been
well established that in (2+2) concerted ketene olefin
cycloadditions the large substituent on the ketene occurs
in the _endo_ position owing to less steric hindrance in the
transition state. If there is a large difference in the
size of the substituents on the ketene, only that isomer is
formed where the largest substituent is _endo_. Consequently,
it is suggested that the _endo_-trimethylsilylmethyl substituted
isomer is the one found in this cycloaddition.

The _in situ_ cycloaddition of ethyl vinyl ether and
trimethylsilylmethylketene yielded the expected cyclobutanone
in good yield. The methylene protons adjacent to the
trimethylsilylmethyl substituent appeared as a doublet.

In this case the methylene protons are not diastereotopic
and it is likely that the only isomer which been found in
this cycloaddition is the <u>trans</u> isomer.

$$TMSCH_2CH_2\overset{O}{\overset{\|}{C}}-Cl \quad \xrightarrow[\text{EtOCH=CH}_2]{\text{Et}_3\text{N}}$$
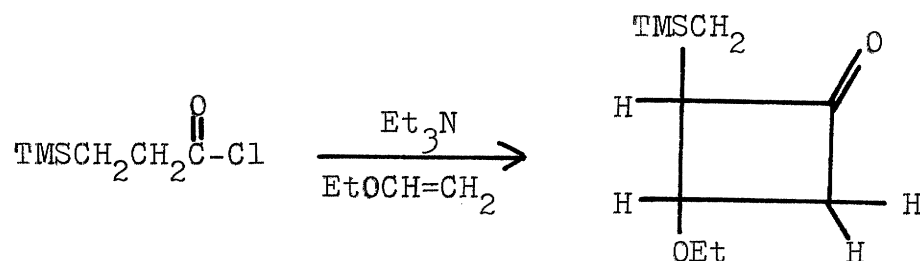
The cycloaddition of nonsilated ketenes and silated
olefins was also investigated to learn more about the effect
of the trimethylsilyl substituent on the ketene olefin
cycloaddition.

Allyltrimethylsilane underwent cycloaddition with di-
chloroketene and methylchloroketene to form the expected

$$TMSCH_2CH=CH_2 \quad + \quad R-\underset{\underset{Cl}{|}}{CH}-\overset{O}{\overset{\|}{C}}-Cl \quad \xrightarrow{\text{Et}_3\text{N}}$$
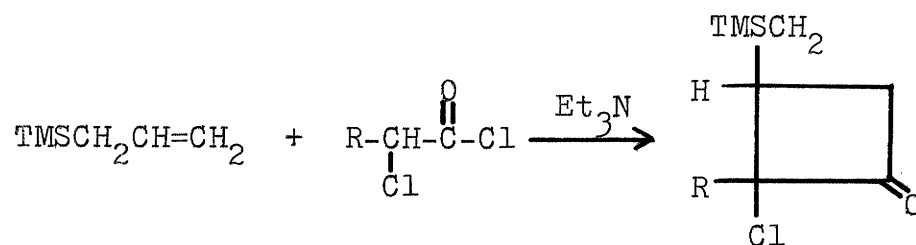
R = Cl, Me.

cyclobutanones in 50-60% yield. Only the α-trimethylsilyl-
methylcyclobutanones were formed in each case due to the

charge separation in the transition state of the cyclo-
addition.[3] Two isomers are possible in the cycloaddition of
methylchloroketene and allyltrimethylsilane. The ratio was
6:1 as evidenced by the integration of the two methyl singlets
from the nmr spectrum. It is believed that the isomer
predominated which had the methyl group cis to the trimethyl-
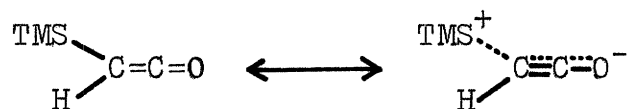silyl substituent because of the up field chemical shift of
these protons.

The *in situ* cycloaddition of dichloro-, methylchloro-.
and dimethyl- ketenes with vinyltrimethylsilane were unsuc-
cessful. Dichloroketene yielded only polymer, methylchloro-
ketene produced the α-halo vinyl ester and dimethylketene
yielded only dimer. Apparently, the π-electrons of the
vinyl group interact either with the empty d-orbital of the
silicon or with the orbital of the silicon-carbon bond
which results in a decreased nucleophilicity of the olefin.[2]
It is well known that the reactivity of olefins in ketene
cycloaddition reactions strongly parallels the nucleo-
philicity of the olefins. Vinyltrichlorosilane and vinyl-
triethoxysilane have been also subjected to ketene cyclo-
additions. Vpc and infrared data suggest the formation of
only trace amounts of the cycloadducts. These vinylsilanes
are also subjected to cycloaddition with diphenylketene with
no success.

It has been indicated that trimethylsilylmethylketene underwent cycloaddition and dimerization as expected for an aldoketene. The trimethylsilyl substituent effect in trimethylsilylketene does not appear in trimethylsilylmethylketene where the trimethylsilyl substituent is removed by one carbon from the ketene functionality. Allyltrimethylsilane cycloadded with ketenes to form the cyclobutanones in rather high yields compared to most monosubstituted olefins. This indicates an increasing nucleophilicity of the carbon-carbon double bond of allyltrimethylsilane, which is the result of the electron donating ability of the trimethylsilylmethyl substituent. However, the low reactivity of vinyltrimethylsilane in cycloadditions with ketenes indicates the electron withdrawing nature of the trimethylsilyl substituent.
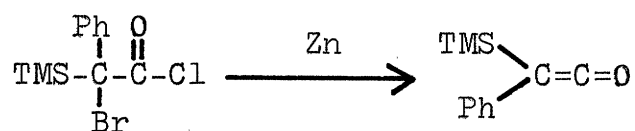
It is well known that the electrophilicity of the sp hybridized carbon in the ketene functionality is the spearhead of ketene reactions, both for nucleophilic addition and cycloadditions. The interaction of the π-electrons of the carbon-carbon double bond or trimethylsilylketene and the empty d-orbitals of the silicon atom would be expected to increase the reactivity of the ketene. Conversely, if the trimethylsilyl substituent is electron donating, the reactivity of the ketene would be expected to be decreased. Consequently, the lack of reactivity of trimethylsilylketene suggests that the trimethylsilyl substituent is electron donating in this particular situation. This electronic effect is considered

to be a hyperconjugative phenomenon whereby the electro-
philic character of the sp hydridized carbon is decreased
as silicon accepts some positive character. This hypothesis

$$\text{TMS}{\diagdown}\atop{H\diagup}\!\!\!\!>\!\!C\!=\!C\!=\!O \quad \longleftrightarrow \quad \text{TMS}^{+}{\diagdown}\atop{H\diagup}\!\!\!\!>\!\!C\!\equiv\!C\!=\!O^{-}$$

is supported by some spectroscopic data. The infrared and
raman spectra of trimethylsilylketene reveal an increasing
bond order for the carbon-carbon double bond and a decreasing
bond order for the carbon-oxygen double bond as compared to
ketene.[4] The C-13 nmr data of some organometallic ketenes
have been studied and the rehybridization of the sp^2 and sp
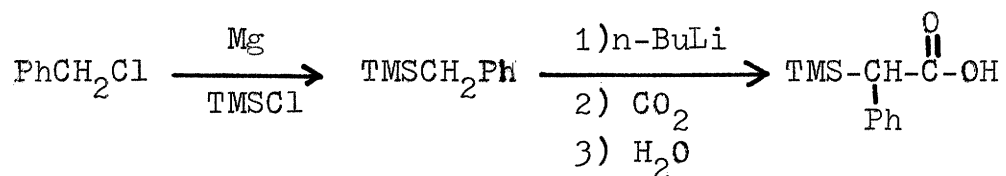carbon atoms of the trimethylsilylketene is suggested.[5]

Phenyltrimethylsilylketene was prepared by the zinc
dehalogenation of phenyltrimethylbromoacetyl chloride in
tetrahydrofuran. The ketene was isolable and vacuum dis-
tilled at 60 at 2 mm.

$$\text{TMS-}\!\!\underset{\underset{Br}{|}}{\overset{\overset{Ph}{|}}{C}}\!\!-\!\!\overset{\overset{O}{\|}}{C}\!\!-\!\!\text{Cl} \quad \xrightarrow{\quad Zn \quad} \quad \text{TMS}{\diagdown}\atop{Ph\diagup}\!\!\!\!>\!\!C\!=\!C\!=\!O$$

Phenyltrimethylsilylbromoacetyl chloride was prepared
from the reaction of phenyltrimethylsilylacetic acid with
oxalyl chloride, and subsequent bromination with bromine.
Attempts to isolate either of the acid chlorides were unsuc-
cessful due to thermal decomposition.

$$\text{TMS-CH-C-OH} \xrightarrow{\text{(COCl)}_2} \text{TMS-CH-C-Cl} \xrightarrow{\text{Br}_2} \text{TMS-C-C-Cl}$$
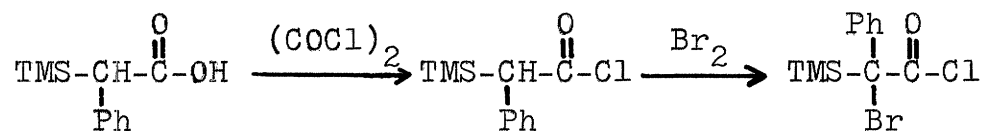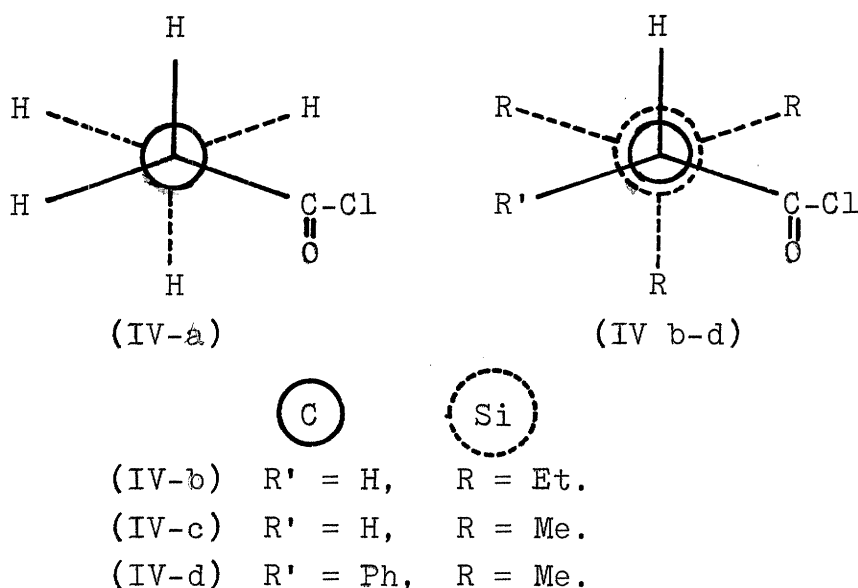
Phenyltrimethylsilylacetic acid was prepared from phenyltrimethylsilylmethane by treatment with n-butyl lithium, carboxylation and hydrolysis. Phenyltrimethylsilylmethane was obtained by the coupling reaction of benzyl magnesium chloride with trimethylchlorosilane.

$$\text{PhCH}_2\text{Cl} \xrightarrow[\text{TMSCl}]{\text{Mg}} \text{TMSCH}_2\text{Ph} \xrightarrow[\substack{2)\ \text{CO}_2 \\ 3)\ \text{H}_2\text{O}}]{1)\text{n-BuLi}} \text{TMS-CH-C-OH}$$
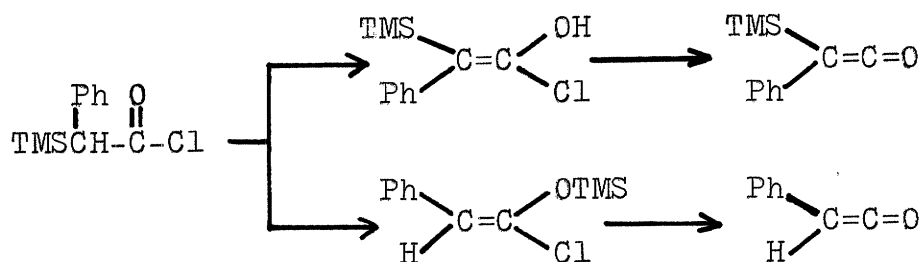
The attempted triethylamine dehydrohalogenation of phenyltrimethylsilylacetyl chloride in hexane was unsuccessful. The carbon-silicon bond was cleaved in this elimination reaction as evidenced by nmr data. Apparently, the amine attacks the d-orbitals on the silicon atom thus resulting in cleavage of the carbon-silicon bond. It is known that the initial step in the dehydrohalogenation reaction of nonhaloacid halides involves the formation of an acyl ammonium halide which occurs by the nucleophilic attack of the amine at the carbonyl carbon center.[7] However, in silylacid halides the silicon can also act as an electrophilic center due to the availability of the empty d-orbitals. Therefore in the dehydrohalogenation of silylacid halides, the nucleophilic attack by the amine could occur at either electrophilic

center. The steric conditions around the two electrophilic centers will determine which site prevails. In (IV-a) and (IV-b), less hindrance is around the carbonyl, so that the preferential attack at the carbonyl to yield acyl ammonium chloride is consistent with the high yield of the trimethyl-silylmethylketene cyclopentadiene cycloadduct and the tri-ethylsilylketene formation.[6] In (IV-c) and (IV-d), a certain amount of hindrance is around the carbonyl carbon, so, the competing nucleophilic attack at silicon accounts for the low yield of trimethylsilylketene[6] and the cleavage of carbon silicon bond in the dehydrohalogenation of phenyltrimethyl-silylacetyl chloride. The zinc dehalogenation method provided

(IV-a)   (IV b-d)

(IV-b)   R' = H,   R = Et.
(IV-c)   R' = H,   R = Me.
(IV-d)   R' = Ph,   R = Me.

a better route for the preparation of the substituted tri-methylsilylketenes with the advantage that no nucleophile is present in the reaction mixture.
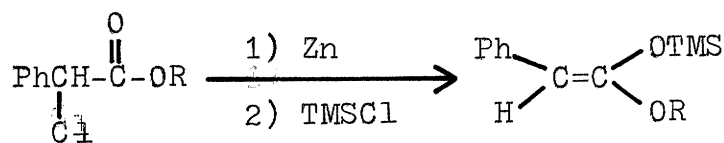
Phenyltrimethylsilylacetyl chloride decomposed upon heating to two ketenes as evidenced by the bands in the ir at 2040 and 2053 cm.$^{-1}$ and after distillation only phenyl-trimethylsilylketene remained in the distillation vessel.

$$
\begin{array}{c}
\text{Ph} \quad \text{O} \\
\overset{|}{\text{TMSCH}}\overset{\|}{-\text{C}}\text{-Cl}
\end{array}
\quad
\underset{\text{Ph}}{\overset{\text{TMS}}{\diagdown}}\text{C=C}\underset{\text{Cl}}{\overset{\text{OH}}{\diagup}}
\longrightarrow
\underset{\text{Ph}}{\overset{\text{TMS}}{\diagdown}}\text{C=C=O}
$$

$$
\underset{\text{H}}{\overset{\text{Ph}}{\diagdown}}\text{C=C}\underset{\text{Cl}}{\overset{\text{OTMS}}{\diagup}}
\longrightarrow
\underset{\text{H}}{\overset{\text{Ph}}{\diagdown}}\text{C=C=O}
$$

Trimethylchlorosilane was found in the cold trap. Apparently, the phenyl substituent favors the enol tautomers from which elimination yields the ketenes.

Attempts to synthesize this acid by several other methods were unsuccessful. The attempted Grignard formation of phenyl-trimethylsilylchloromethane followed by carboxylation and hydrolysis yielded mainly polymer. The Grignard reagent was formed with much difficulty and was unusually reactive. Also, treating phenyltrimethylsilylchloromethane with two equivalents of metallic lithium, carboxylation, and hydrolysis, yielded no acid, only polymer.
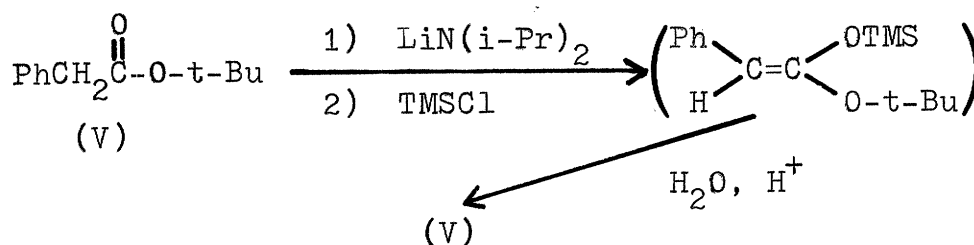
Trimethylchlorosilane was added to a suspension of zinc and methyl phenylchloroacetate in tetrahydrofuran in an

$$
\begin{array}{c}
\text{O} \\
\overset{\|}{\text{PhCH}-\text{C}-\text{OR}} \\
\overset{|}{\text{Cl}}
\end{array}
\quad
\xrightarrow[\text{2) TMSCl}]{\text{1) Zn}}
\quad
\underset{\text{H}}{\overset{\text{Ph}}{\diagdown}}\text{C=C}\underset{\text{OR}}{\overset{\text{OTMS}}{\diagup}}
$$

R = Me, t-Bu.

attempt to prepare methyl phenyltrimethylsilylacetate, but
the isolated product was methyl trimethylsilylacetal of phenyl
ketene. t-Butyl phenylchloroacetate was used in an attempt
to hinder O-silation to produce the desired C-silated ester
but still the ketal was the only isolated product. The α-
substituted phenyl group apparently favors the highly
conjugated enolic form which accounts for the formation of
the O-silated products.

Trimethylchlorosilane was added to an organolithium
solution which was generated at -78° in tetrahydrofuran by
the reaction of t-butyl phenylacetate and lithium diiso-
propylamine. After the completion of the reaction, the
solution was neutralized by adding dilute acetic acid. The
desired t-butyl phenyltrimethylsilylacetate was not obtained
but the initial nonsilated ester was recovered. This result

$$PhCH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-t-Bu \quad \xrightarrow[2)\ TMSCl]{1)\ LiN(i-Pr)_2} \quad \left(\underset{H}{\overset{Ph}{>}}C=C\underset{O-t-Bu}{\overset{OTMS}{<}}\right)$$

(V)

$$\xleftarrow{H_2O,\ H^+}$$

(V)

suggested the formation of O-silated acetal during the
reaction which hydrolyzed in the acid work up to form the
nonsilated ester.[8]

Phenyltrimethylsilylketene has a yellow color and is
very stable at room temperature. Numerous efforts to effect
the dimerization and cycloaddition with cyclopentadiene,

ethyl vinyl ether, diisopropylcarbodiimide and N-t-butyl
benzylimine were unsuccessful. The nonsilated cycloadduct,
N-t-butyl-3,4-diphenyl-2-azetidinone was obtained from the
reaction of phenyltrimethylsilylacetyl chloride and N-t-butyl
benzylimine in the presence of triethylamine. No evidence
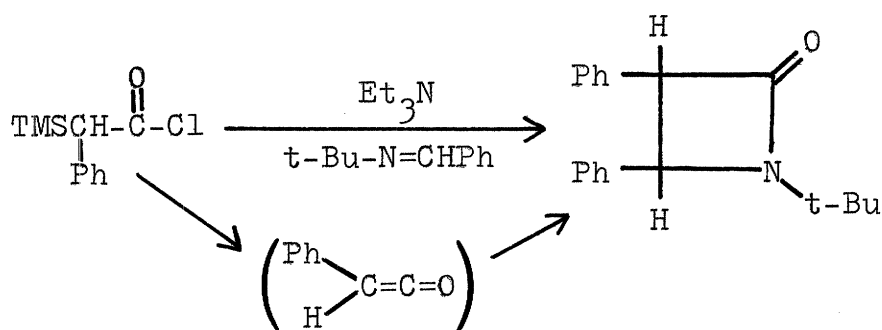
was found for the amide formation from the acid halide and
imine. This cycloadduct was formed by the phenylketene
cycloaddition with the imine. The cis and trans isomers were
separated by sublimation and structures were assigned on the
basis of coupling constants in the nmr spectrum. The coupling
constant for the trans isomer is 3 Hz, and 7 Hz for the cis
isomer.

Phenyltrimethylsilylketene and trimethylsilylketene
were separately treated with phenyl lithium in ether at -78°
and subsequently hydrolyzed. The ketene band in the infrared
disappeared prior to hydrolysis. There were no isolable
products from these reactions.

The reaction of phenylethylketene with diazomethane at
-78° in methylene chloride produced the 1:2 cycloadducts,
the cyclobutanones, in high yield. When either excess

phenylethylketene or diazomethane was employed, the same
products were obtained. This suggests that the intermediate
cyclopropanone is much more reactive with diazomethane than
phenylethylketene.
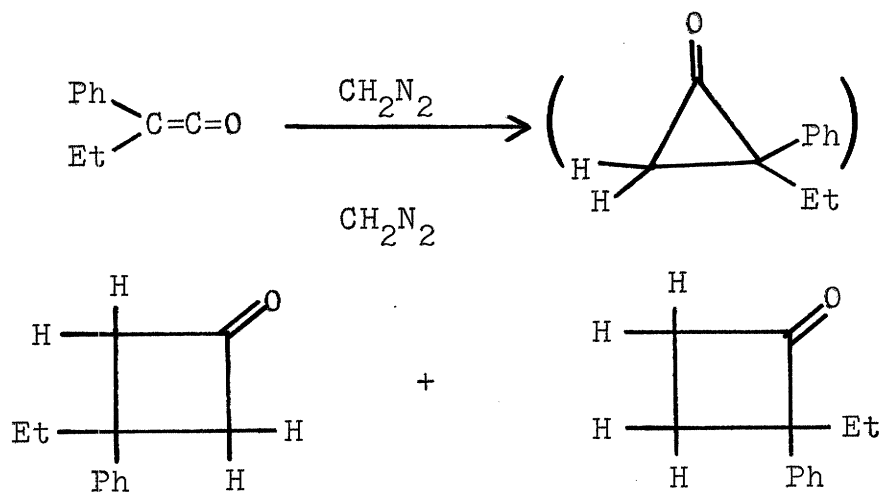
Phenyltrimethylsilylketene was treated with diazomethane
under the same conditions as described above for phenylethyl-
ketene. The infrared spectrum of the cold reaction solution
indicated that cyclobutanones were produced in good yield.
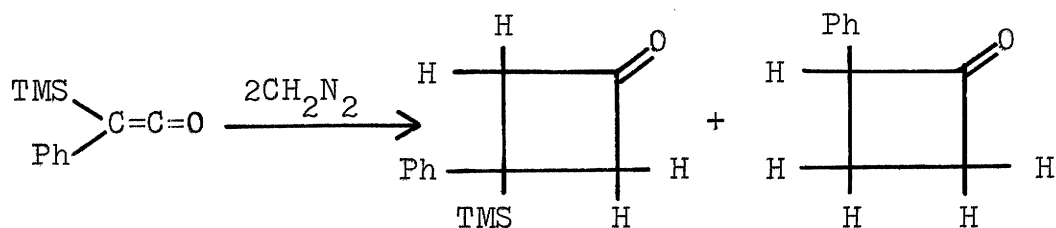
The products could not be isolated by distillation because
of decomposition upon heating. 3-Phenyl-3-trimethylsilyl-
cyclobutanone and 2-phenylcyclobutanone were produced in
approximate equal amounts and isolated by vpc. The loss of

the trimethylsilyl substituent is believed to be due to
thermal rearrangement to the O-silated isomer which is
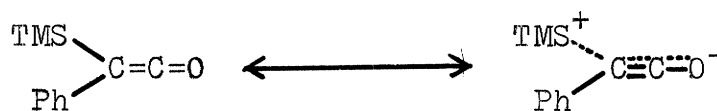highly hygroscopic and is hydrolyzed by atmospheric moisture
to 2-phenylcyclobutanone.

The reaction of trimethylsilylketene and diazomethane
yielded 3-trimethylsilylcyclobutanone. Thermal decomposition

$$\text{TMS}\underset{H}{\overset{}{>}}C=C=O \xrightarrow{CH_2N_2} \quad \xrightarrow{CH_2N_2}$$
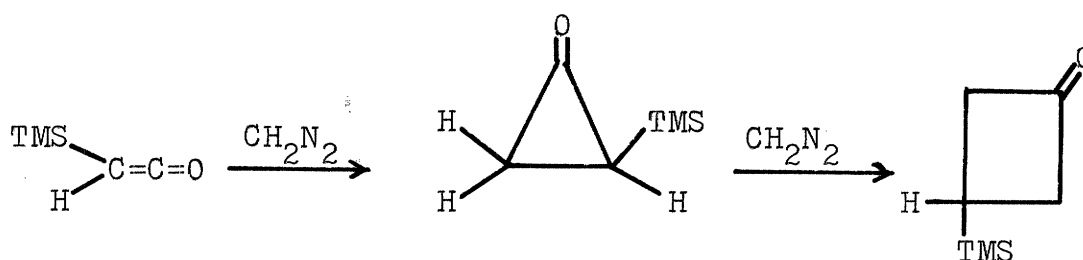
occurred during vpc analysis. The formation of the cyclo-
butanone strongly suggests a high reactivity of the substi-
tuted cyclopropanone intermediate. It has been found that
a trimethylsilyl substituent alpha to a carbonyl group is
thermally unstable and rearranges to form the trimethylsilyl-
vinyl ether which is easily hydrolyzed to lose the trimethyl-
silyl group. This would account for the lack of 2-trimethyl-
silylcyclobutanones from being isolated in the diazomethane
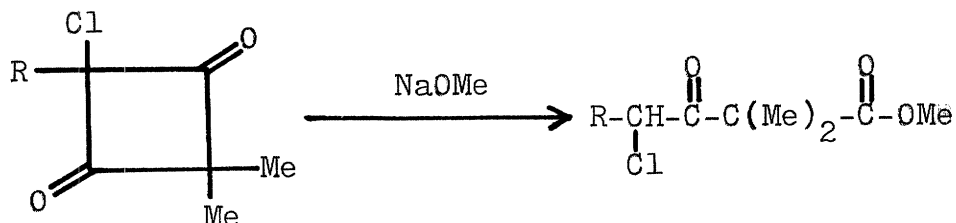reaction with both phenyltrimethylsilylketene and trimethyl-
silylketene.

The chemistry of phenyltrimethylsilylketene closely
parallels that of trimethylsilylketene such that the phenyl
group has no appreciable effect on the reactivity of the

ketene. Apparently, there is no interaction of the carbon
silicon bond orbital with the aromatic ring. It is well
known that the σ-π hyperconjugative effect exists in many
substituted benzyltrimethylsilanes.[16] However, the lack
of interaction of the trimethylsilyl substituent with the
benzene ring in phenyltrimethylsilylketene is not too
suprising because the Si-C bond is locked in the same plane
as that of the carbonyl π-bonding orbital and this orient-
ation provides the maximum overlapping of these orbitals.
In this particular system the aromatic orbitals do not
provide the maximum interaction with the carbon-silicon
orbitals.

$$\underset{Ph}{\overset{TMS}{>}}C=C=O \longleftrightarrow \underset{Ph}{\overset{TMS^+}{>}}C\equiv C = O^-$$

Some Reactions of Chlorotrialkyl-
1,3-cyclobutanediones

The base catalyzed ring contraction of α-halocyclo-
butanones to cyclopropyl derivatives is a very useful and
well documented reaction.[9, 10] Tetraalkyl-1,3-cyclobutane-
diones undergo ring opening reactions in the presence of base
to yield -keto esters. 1,2-Cyclobutanedione has been
prepared and shown to undergo ring contraction to hydroxy-
cyclopropanecarboxylic acid.[11] The view of these consider-
ations, the halotrialkyl-1,3-cyclobutanediones provide an
interesting system for study. It would appear that such
compounds could undergo a ring contraction reaction and/or
a ring opening reaction. The cyclopropanone would be expected
to undergo ring opening in the presence of base to yield a
succinic acid derivative.

Chlorotrialkyl-1,3-cyclobutanediones (VI a-d) are
readily available from the mixed dimerization of dimethyl-
ketene and alkylhaloketenes. Treating the compounds (VI a-d)
with sodium methoxide in methanol yields the ring opened

products, β-keto esters. Although two β-keto esters are
possible due to whether the ring opens to the disubstituted


(VI a-d) a, R=Me; b, R=Et; c, R=i-Pr; d, R=t-Bu.

carbon or the chlorosubstituted carbon, only γ-chloro-β-keto
ester was found. There was no evidence of the cyclopropanone
derivative or the diester of succinic acid. Apparently, the
strain associated with the cyclopropanone ring system
prohibits this ring contraction pathway from being followed.
The formation of only the γ-chloro-β-keto ester is consistent
with the chloro substituent stabilizing the carbanionic
character in the transition state to a greater degree than
the methyl substituents. The ring opening reaction of tetra-
methyl-1,3-cyclobutanedione requires a much longer reaction
time than the chlorotrialkyl-1,3-cyclobutanediones. This
further supports the stabilizing influence of the chloro
substituent. The rate of the reaction decreased as the size
of the alkyl group increased from methyl to isopropyl. When
the alkyl group is t-butyl, ring opening does not occur after
seven days reaction time and the dione is completely recovered.
This is not too surprising since it is known that the carbon
chlorine bond dipole effect directs the nucleophilic attack

to the alkyl substituent side of the molecule.[12] Obviously,
when the alkyl group becomes larger the reaction is slowed
down by steric hindrance. For the bulky t-butyl substituent,
the nucleophilic attack is sterically retarded.

The chlorotrialkyl-1,3-cyclobutanediones (VI a-d) react
with freshly distilled tri-n-butyltin hydride to yield the
corresponding trialkyl-1,3-cyclobutanediones (VII a-d) which
exist as the dione in the solid state as evidence by infrared
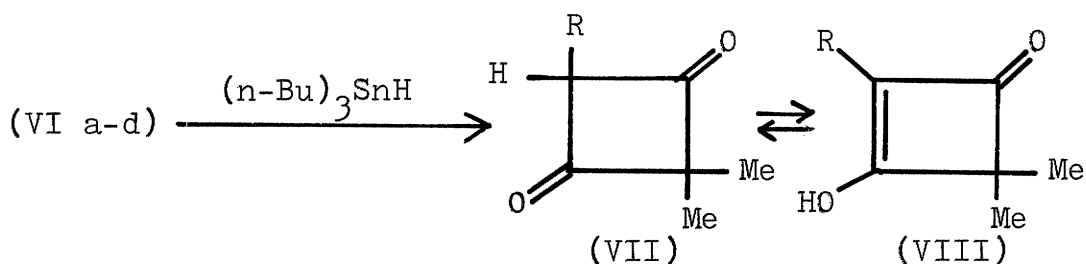
absorption at 1724-1753 cm.$^{-1}$. The enol form (VIII) is
the predominant structure in solution as evidenced by infrared
absorptions at 3444, 1739, and 1612 cm.$^{-1}$. Conversion of the
chlorotrialkyl-1,3-cyclobutanediones can also be accomplished
by treatment with sodium borohydride in methanol. This is a
high yield reaction and provides a good synthetic method for
trialkyl-1,3-cyclobutanediones.

The trialkyl-1,3-cyclobutanediones (VII a-d) did not
undergo ring opening reaction. Apparently, the well-delo-
calized enolate is immediately produced in the basic media,
and the reaction is terminated at this stage. This accounts

for the enol form in solution, which loses the acidic proton
easily in the presence of a base.

$$(VIII\ a\text{-}d) \xrightarrow{\text{NaOMe}}$$
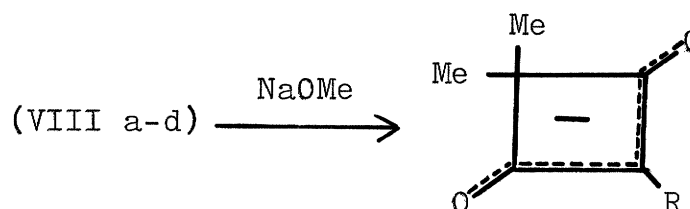
The peracid oxidation of chlorotrialkyl-1,3-cyclobutane-
diones gave the ring expansion β-keto γ-lactone in good
yield. Although two β-keto γ-lactones were possible depending
upon which carbon is bonded to the introduced oxygen, only
the α-chloro β-keto γ-lactone was observed. The structure

$$(VI\ a,b) \xrightarrow{\text{CH}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OOH}}$$
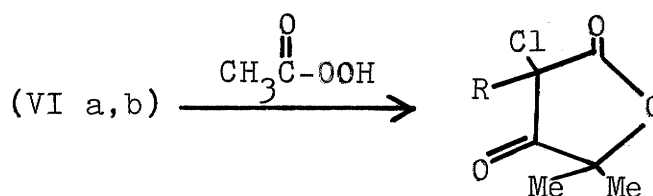
was assigned on the basis of nmr data, that is, the chemical
shift of the geminal methyl groups in these compounds is
comparatively downfield from the chemical shift of the geminal
methyl group in the cyclobutanediones. This is consistent
with the nature of Baeyer-Villiger oxidations in which the
migrating ability of the group reflects the electronic
character on the group.[13] Peracid oxidation of compounds
(VI c,d) did not occur, the diones were recovered unchanged.
This is probably due to the C-Cl dipole effect which directed

the nucleophilic attack to the alkyl group side of the
molecule, when the alkyl group was isopropyl or t-butyl the
oxidation was retarded.

The Baeger-Villiger oxidation of the trialkyl-1,3-cyclo-
butanediones yielded several products as evidenced by vpc
analysis. The only isolated and identified product was found
from the reaction of 4-t-butyl-2,2-dimethyl-1,3-cyclobutane-
dione and peracetic acid. The assignment of the structure
to the ring expanded γ-lactone was based on the downfield

$$(VIII\ d) \xrightarrow{\underset{\displaystyle CH_3\overset{O}{\overset{\|}{C}}-OOH}{}}$$
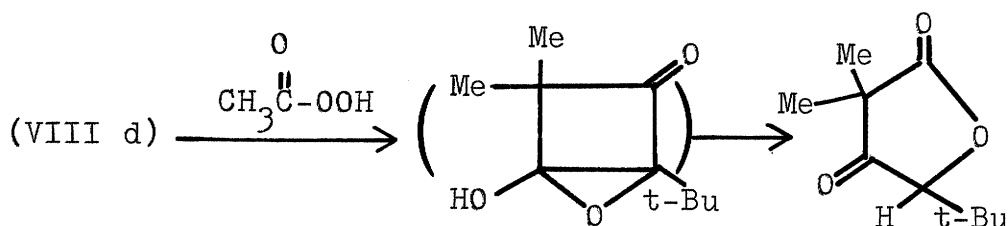
proton signal of the methinyl hydrogen in the nmr. This
lactone must come from the enol form of the trialkyl-1,3-
cyclobutanedione, otherwise the tertiary carbon migrating to
form the γ-lactone isomer is expected. The formation of an
epoxide is proposed in the oxidation reaction for this
particular compound, followed by rearrangement to yield the
more stable β-keto γ-lactone.

Diazomethane is a very strong ring enlargement reagent
for cyclic ketones.[14] However, the reaction of diazomethane
with chlorotrialkyl-1,3-cyclobutanediones yields a mixture
of products and nonvolatile polymeric material. The only
identifiable isolated product was from chlorotrimethyl-1,3-

cyclobutanedione whereby methylene insertion occured between the carbon-chlorine bond. This structure was assigned on the basis of the nmr downfield shift of the methylene protons

(VI a) $\xrightarrow{CH_2N_2}$
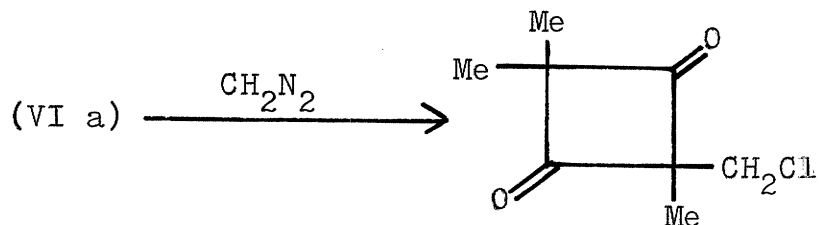
and also on mass spectrometry data. There were products formed by the dione reacting with two moles of diazomethane as evidenced by the mass spectrometry data.

The reaction of diazomethane with trialkyl-1,3-cyclo-butanediones (VIIIa-d) resulted in methylation of the hydroxy group of the enolic form. There was no evidence of ring

(VIII a-d) $\xrightarrow{CH_2N_2}$ (IX)
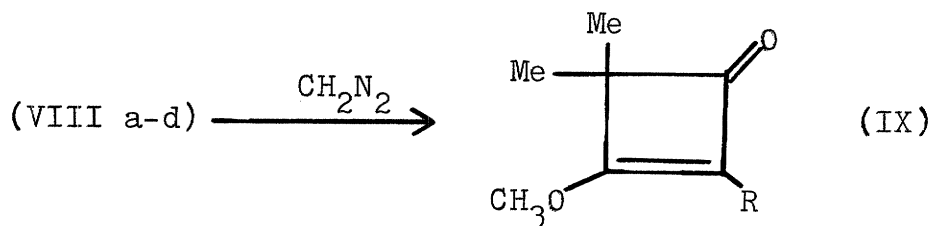
expanded products. It was very obvious that the enolic form was the reacting species which accounted for all the reaction of the trialkylcyclobutanediones.

Mayr has recently reported the ring opening of cyclo-butenones to vinylketenes in refluxing hexane.[15] Extended refluxing of the methoxycyclobutenones, compounds (IX a-d) resulted in no change. Tetraalkyl-1,3-cyclobutanediones

isomerize to the corresponding 2-oxetanones in the presence of aluminum chloride. This isomerization was not observed for either the chlorotrialkyl-1,3-cyclobutanediones or the trialkyl-1,3-cyclobutanediones.

The sodium borohydride reduction of the methylated tri-alkyl-1,3-cyclobutanediones (IX a, d) led to the corresponding saturated alcohols in quantitative yields. Of the four isomeric alcohols that are possible, only two were detected, and these were (X) and (XI) as evidenced by nmr analysis.

$$(IX)a,d \xrightarrow{NaBH_4}$$

(IX-a) R=Me.

(IX-b) R=t-Bu.

(X)   (XI)
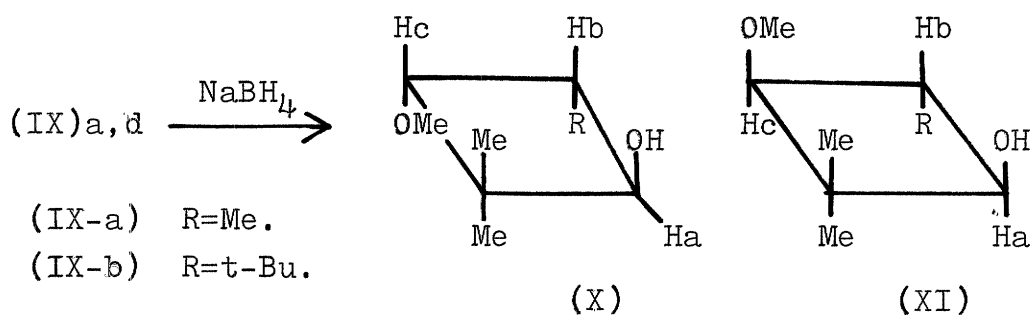
When R is methyl the ratio of (XI)/(X) is 2.2, and when R is t-butyl, the ratio of (XI)/(X) is 0.3. The alcohol (X-d) revealed Ha (d, 1 H, 3.76 ppm, J_{a-b} trans=7 Hz) and Hc (d, 1 H, 3.47 ppm, J_{b-c}cis= 10 Hz). Conversely, the isomer (XI-d) (the minor isomer) revealed Ha (d, 1 H, 3.11 ppm, J_{a-b}trans= 7 Hz) and Hc (d, 1 H, 2.76 ppm, J_{b-c}trans= 7 Hz). In (X), Ha is cis to the methoxy, and Hc is cis to the hydroxy group; consequently, the chemical shifts of these hydrogens are comparatively downfield relative to (XI) in which Ha is trans to the methoxy and Hc is trans to the hydroxy group.

In conclusion, it is proposed that the low reactivity of trimethylsilylketene is due to the electron releasing hyperconjugative effect of the trimethylsilyl substituent thus decreasing the electrophilicity of the sp hybridized carbon of the ketene functionality. This effect is also observed in phenyltrimethylsilylketene, thus indicating no appreciable electronic effect by the phenyl substituent. However, trimethylsilylmethylketene has the normal ketene reactivity, which is consistent with the above described effect since removing the trimethylsilyl substituent by one carbon atom would be expected no obvious change of the electrophilicity of the sp hybridized carbon of the ketene. Chlorotrialkyl-1,3-cyclobutanediones react with sodium methoxide in methanol to yield ring opened, γ-chloro-β-keto esters. However, the corresponding trialkyl-1,3-cyclobutanediones do not undergo ring opening reaction as these compounds exist predomenatly in the enolic form, and the enolic form is the reacting species which accounted for all the reaction of the trialkylcyclobutanediones.

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