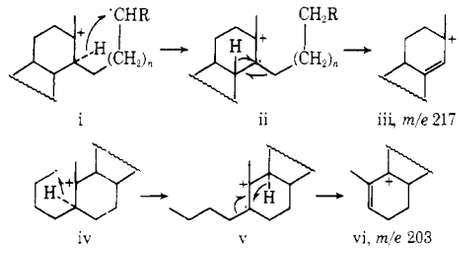

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The Effect of the Trimethylsilylmethyl Substituent on Ketene Cycloadditions

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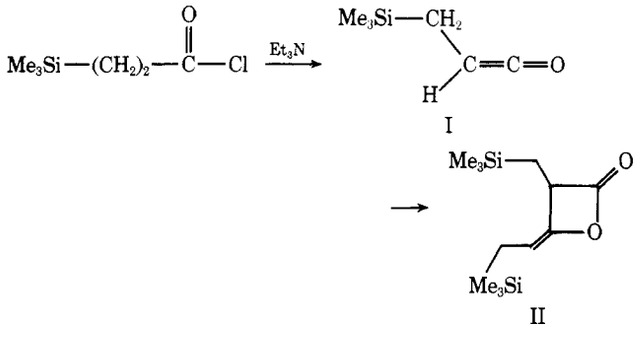
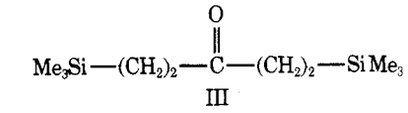
(Trimethylsilylmethyl)ketene is prepared by the dehydrochlorination of β-trimethylsilylpropionyl chloride. The 2-oxetanone dimer of the ketene is readily converted to 1,5-bis(trimethylsilyl)-3-pentanone. The ketene readily undergoes in situ cycloaddition to cyclopentadiene to yield only the *endo*-trimethylsilylmethylcyclobutanone and cycloaddition to ethyl vinyl ether yields only the trans cyclobutanone. Vinyltrimethylsilane would not undergo cycloaddition with a variety of ketenes. However, allyltrimethylsilane readily underwent cycloaddition with methylchloro- and dichloroketenes. An interpretation of these results is offered.

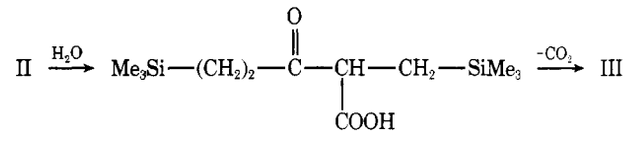
The effect of the trimethylsilyl substituent on the properties and chemistry of trimethylsilylketene is truly remarkable. This aldoketene is very stable, does not dimerize upon heating, and can be stored for long periods of time.[1,2] Numerous efforts to effect cycloaddition of trimethylsilylketene with a variety of unsaturated compounds have been mostly unsuccessful; the only cycloaddition which has been reported was with dimethyl and diethyl acetal of ketene under rather vigorous conditions for a ketene cycloaddition.[3] Also, condensation of trimethylsilylketene with benzaldehyde gave *cis*- and *trans*-trimethylsilylstyrene which presumably involved cycloaddition to form the 2-oxetanone which underwent decarboxylation to yield the olefins.[4] We have recently reported on the preparation and cycloaddition of trimethylsilylbromoketene and this ketene appears to be more reactive in cycloaddition reactions than trimethylsilylketene, although only cycloadducts with an imine and carbodiimide have been prepared.[5]

In this report we describe the effect of the trimethylsilylmethyl substituent on the properties and chemistry of (trimethylsilylmethyl)ketene and also describe the effect of the trimethylsilyl substituent and the trimethylsilylmethyl substituent on the reactivity of the olefin in ketene cycloaddition reactions.

(Trimethylsilylmethyl)ketene (I) was prepared by the triethylamine dehydrochlorination of β-trimethylsilylpropionyl chloride in hexane as evidenced by a band in the infrared at 2123 cm.$^{-1}$ The ketene was not isolable but underwent dimerization to yield the expected dimer, II. This dimer was accompanied by an unexpected product, 1,5-bis(trimethylsilyl)-3-pentanone (III). The formation of III was quite





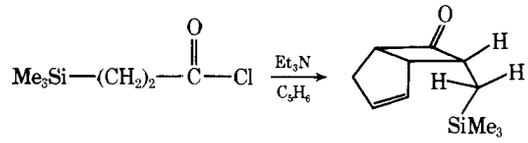


puzzling; however, it was established that this ketone was formed from the 2-oxetanone dimer. The dimer was hygroscopic and would slowly react with atmospheric moisture yielding the keto acid which decarboxylated to the ketone. Normal drying tube precautions were not sufficient to keep II from being hydrolyzed.

The β-trimethylsilylpropionyl chloride was prepared from vinyltrimethylsilane by the addition of hydrogen bromide in the presence of benzoyl peroxide, Grignard formation, carbonation, hydrolysis, and acid halide formation with thionyl chloride. In some original preparations, II and III were also accompanied by 1,4-bis(trimethylsilyl)butane. This was the result of a coupling reaction in the Grignard step and this coupled product codistilling with β-trimethylsilylpropionyl chloride. Careful distillation of the β-trimethylsilylpropionic acid eliminated this problem.

An alternate route to I would be the zinc dehalogenation of α-halo-β-trimethylsilylpropionyl chloride. Attempts to α-halogenate β-trimethylsilylpropionyl chloride were unsuccessful owing to cleavage of the carbon–silicon linkage.

The in situ cycloaddition of cyclopentadiene and (trimethylsilylmethyl)ketene occurred in 65% yield. The cyclobutanone structure was assigned on the basis of the infrared

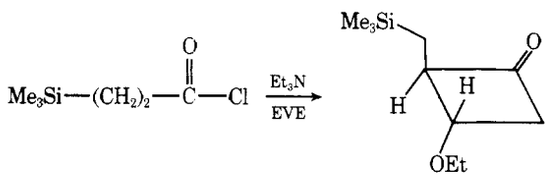


IV

band at 1785 cm^{-1} and also on NMR evidence. The vinyl protons appear as a multiplet and doublet. However, by decoupling the methylene protons in the cyclopentenyl ring, the olefinic protons clear up to a sharp double-doublet pattern.

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, this 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.

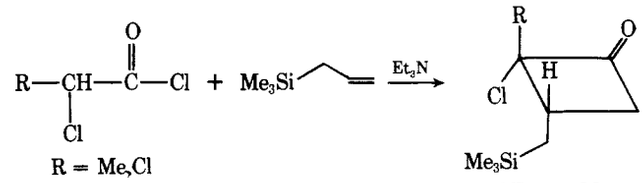
The in situ cycloaddition of ethyl vinyl ether and trimethylsilylmethylketene yielded the expected cyclobutanone in good yield. The methylene protons adjacent to the trimethylsilylmethyl substituent appeared as a doublet. In this case the methylene protons are not diastereotopic and it is likely that the only isomer which been found in this cycloaddition is the trans isomer.



V

The in situ cycloaddition of dichloro-, methylchloro-, and dimethylketenes with vinyltrimethylsilane were unsuccessful. Dimethylketene yielded only the dimer, methylchloroketene produced the vinyl ester, and the dichloroketene yielded only polymer. Apparently, the π electrons of the vinyl group interact with the empty d orbitals of the silicon atom resulting in a decreased nucleophilicity of the olefin. It is well known that the reactivity of olefins in ketene cycloaddition reactions strongly parallels the nucleophilicity of the olefin. Vinyltrichlorosilane and vinyltriethoxysilane have also been subjected to ketene cycloadditions and VPC and infrared data suggested only trace amounts of the cycloadducts. These vinylsilanes were also subjected to cycloaddition with diphenylketene with no success.

The in situ cycloaddition of dichloro- and methylchloroketenes with allyltrimethylsilane resulted in the expected cyclobutanones in 50–60% yield. Only the β-trimethylsilylmethylcyclobutanones were found in each case as evidenced by the NMR data. The chemical shift of the methylene protons of the cyclobutanone ring occur near δ 3.0, indicating that this downfield shift is due to being adjacent to the carbonyl group. Two isomers are possible in the cycloaddition of

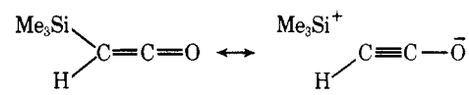


VI, R = Me
VII, R = Cl

methylchloroketene and allyltrimethylsilane. The ratio is 6:1 as evidenced by the integration of the two methyl singlets and it is believed that isomer predominates which has the methyl group cis to the trimethylsilylmethyl substituent (upfield chemical shift).

The vinyltrimethylsilane is unreactive in a ketene cycloaddition because of the electron-withdrawing effect of the trimethylsilyl substituent. The trimethylsilylmethyl substituent appears to be electron donating and thus activating based on the ease of cycloaddition of allyltrimethylsilane. This is consistent with reports in the literature on the electronic effects of these two silyl substituents.[7] However, the effect of the trimethylsilylmethyl substituent on ketene reactivity is not very pronounced. The chemistry of this aldoketene is about what would be expected from an aldoketene with a large substituent such as the trimethylsilylmethyl group assuming no electronic effects.

The spearhead of ketene reactions, both nucleophilic addition and cycloaddition, is the electrophilicity of the sp-hybridized carbon. Since the trimethylsilyl substituent is usually an electron-withdrawing substituent, the lack of reactivity of trimethylsilylketene seems inconsistent with these facts. Although we have suggested above that the trimethylsilyl substituent is electron withdrawing in the case of vinyltrimethylsilane, we now offer that this substituent is electron donating in this particular environment in trimethylsilylketene. This effect can be ascribed to hyperconjugation as illustrated below.



Experimental Section

^1H NMR spectra were recorded on a Jeolco PS-100 nuclear magnetic resonance spectrometer employing chloroform as the solvent and as the internal standard. VPC was performed on an F & M Scientific Model 700 gas chromatograph with a 10 ft × 0.25 in. column packed with 10% SE-30 on an acid-washed Chromosorb W (80/100). The infrared spectra were recorded on a Beckman 320 spectrometer.

Hexane was distilled from sodium prior to use. β-Trimethylsilylpropionic acid was prepared from vinyltrimethylsilane and converted to the acid chloride by a standard procedure.[8,9]

3-Trimethylsilylmethyl-4-(2-trimethylsilyl)ethylidene-2-oxetanone (II). To a solution of 0.2 mol of triethylamine in 150 ml of dry hexane was added dropwise 0.1 mol of β-trimethylsilylpropionyl chloride in 20 ml of hexane under a dry nitrogen atmosphere at room temperature over a 0.5-h period.[10] At the completion of the addition, the reaction mixture was refluxed for about 2 h. 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 rotatory evaporator, residual salt removed by filtration, and vacuum distillation afforded the dimer at 71–73 °C (0.05 mm) (85%): IR 1850 and 1710 cm^{-1}; NMR, δ 0.1 (s, 9 H), 0.18 (s, 9 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 (III). 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 °C (0.05 mm): IR 1720 cm^{-1}; NMR δ 0.10 (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 isolated from the reaction mixture described above unless the β-trimethylsilylpropionic acid was carefully distilled. 1,4-Bis(trimethylsilyl)butane is a product from a Grignard coupling reaction in the preparation of the acid and vacuum distills at 36–38 °C (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 Cycloadditions. To a solution of 0.2 mol of triethylamine and 0.2 mol of olefin in 150 ml of dry hexane at room temperature was added 0.1 mol of acid halide in 20 ml of hexane dropwise over a 0.5-h period.[10] After the addition was complete, the reaction mixture was stirred and refluxed for 2 h. 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 (IV).** This cycloadduct of (trimethylsilylmethyl)ketene and cyclopentadiene was obtained at 65 °C (0.05 mm) (65%): IR 1800 and 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 (dm, 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, 67.96; H, 9.52.

***trans*-3-Ethoxy-2-trimethylsilylmethylcyclobutanone (V).** This cycloadduct of (trimethylsilylmethyl)ketene and ethyl vinyl ether was distilled at 40–42 °C (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 (VI). The cycloadduct of methylchloroketene and allyltrimethylsilane distilled at 68–70 °C (0.025 mm) (62%): IR 1780 cm^{-1}; NMR (both isomers) 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 (VII). This cycloadduct of dichloroketene and allyltrimethylsilane was vacuum distilled at 65–66 °C (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 $C_8H_{14}Cl_2OSi$: C, 42.67; H, 6.22. Found: C, 42.89; H, 6.11.

Acknowledgments. The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—I, 61063-48-7; II, 61063-49-8; III, 18053-95-7; IV, 61063-50-1; V, 61063-51-2; *cis*-VI, 61063-52-3; *trans*-VI, 61063-53-4; VII, 61063-54-5; β-trimethylsilylpropionyl chloride 18187-31-0; 1,4-bis(trimethylsilyl)butane, 18001-81-5; cyclopentadiene, 542-92-7; ethyl vinyl ether, 106-98-9; methylchloroketene, 13363-86-5; allyltrimethylsilane, 762-72-1; dichloroketene, 4591-28-0.

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(10) The use of a stoichiometric amount of triethylamine resulted in the same distribution of products but a lower yield.

Synthesis of 4,5-Dihydroxy-1,3,6,8-tetramethylphenanthrene[1]

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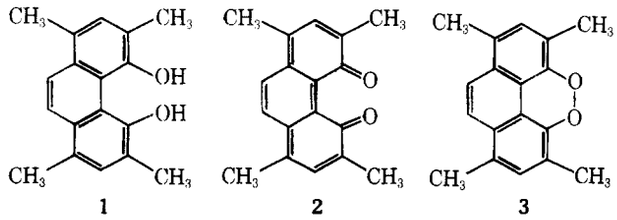
Received July 12, 1976

Bromination of 4,6-dimethyl-3-hydroxybenzoic acid (**4**) yielded exclusively 2-bromo-4,6-dimethyl-3-hydroxybenzoic acid (**5**), which was methylated to yield methyl 2-bromo-4,6-dimethyl-3-methoxybenzoate (**6**). Ullman coupling of **6** afforded dimethyl 6,6′-dimethoxy-3,3′,5,5′-tetramethyldiphenate (**7**). Reduction of **7** with $LiAlH_4$ yielded 2,2′-di(hydroxymethyl)-6,6′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl (**8**), which was converted into 2,2′-di(chloromethyl)-6,6′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl (**9**) via the dimesylate of **8**. A new phenanthrene synthesis which involved treatment of **9** with sodamide in ammonia afforded 4,5-dimethoxy-1,3,6,8-tetramethylphenanthrene (**11**) in almost quantitative yield. Demethylation of **11** by heating with pyridine hydrochloride or with anhydrous sodium sulfide yielded 4,5-dihydroxy-1,3,6,8-tetramethylphenanthrene (**1**), which could not be oxidized to a monomeric quinone.

The main objective of this work was to synthesize 4,5-dihydroxy-1,3,6,8-tetramethylphenanthrene (**1**), to see if it could be oxidized to the corresponding quinone, **2**, whose stability with respect to the tautomeric cyclic peroxide, **3**, would be of interest. It was hoped that the methyl groups would decrease the nuclear oxidation encountered in a previous attempt to synthesize 4,5-phenanthrenequinone from 4,5-dihydroxyphenanthrene.[3]



The synthesis of **1** was carried out as outlined in Scheme I. 4,6-Dimethyl-3-hydroxybenzoic acid (**4**), prepared as described[4] except that diethyl acetylenedicarboxylate, made by an improved procedure, was used in place of dimethyl acetylenedicarboxylate, was brominated cleanly to 2-bromo-4,6-dimethyl-3-hydroxybenzoic acid (**5**). This structure is supported by analysis and the fact that acid-catalyzed esterification failed. Hence a highly hindered acid, namely **5**, was at hand.