(4) D. W. Jones and G. Kneen, *J. Chem. Soc., Chem. Commun.*, 420 (1973).
(5) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 839 (1969).
(6) D. W. Jones and R. L. Wife, *J. Chem. Soc., Chem. Commun.*, 421 (1973).
(7) C. K. Bradsher, *Adv. Heterocycl. Chem.*, **16**, 289 (1974).
(8) C. K. Bradsher, F. H. Day, A. T. McPhail, and P. W. Wong, *J. Chem. Soc., Chem. Commun.*, 156 (1973).
(9) C. K. Bradsher and F. H. Day, *J. Heterocycl. Chem.*, **10**, 1031 (1973).
(10) C. K. Bradsher, F. H. Day, A. T. McPhail, and P. S. Wong, *Tetrahedron Lett.*, 4205 (1971).
(11) Throughout this paper the isomer referred to as syn is syn with reference to the phenylene ring.
(12) C. K. Bradsher, G. L. B. Carlson, N. A. Porter, and T. G. Wallis, *J. Org. Chem.*, **43**, 822 (1978).
(13) C. K. Bradsher and J. A. Stone, *J. Org. Chem.*, **33**, 519 (1968).
(14) C. K. Bradsher and D. J. Harvan, *J. Org. Chem.*, **36**, 3778 (1971).
(15) M. E. Parham, M. G. Frazer, and C. K. Bradsher, *J. Org. Chem.*, **37**, 358 (1972).
(16) Reference 7, p 317.
(17) D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968).
(18) I. J. Westerman and C. K. Bradsher, *J. Org. Chem.*, **43**, 3002 (1978).
(19) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **35**, 1874 (1970).
(20) Greater accuracy may be achieved by use of more careful integration procedures, cf. L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance in Organic Chemistry", 2nd ed., Pergamon Press, Elmsford, N.Y., 1969, p 52.
(21) S. J. Cristol and W. Linn, *J. Org. Chem.*, **34**, 1, (1969).
(22) D. M. Wieland A. J. McCarty, *J. Org. Chem.*, **37**, 4285 (1972).
(23) K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jpn.*, **43**, 3195 (1970).
(24) W. S. Burnham and C. K. Bradsher, *J. Org. Chem.*, **37**, 355 (1972).
(25) C. K. Bradsher, *Acc. Chem. Res.*, **2**, 181 (1969).
(26) J. C. Parham, Ph.D. Dissertation, Duke University, 1963.
(27) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **95**, 3902 (1973).
(28) P. Crews and J. Beard, *J. Org. Chem.*, **38**, 522 (1973).
(29) R. R. Schmidt and R. Machat, *Angew. Chem., Int. Ed. Engl.*, **9**, 311 (1970).
(30) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).
(31) J. N. Labows and D. Swern, *J. Org. Chem.*, **37**, 3004 (1972).
(32) C. K. Bradsher, J. P. Sherer, and J. C. Parham, *J. Chem. Eng. Data*, **10**, 180 (1965).
(33) C. K. Bradsher and L. E. Beavers, *J. Am. Chem. Soc.*, **78**, 2459 (1956).
(34) S. Winstein and L. L. Ingraham, *J. Am. Chem. Soc.*, **77**, 1741 (1955).
(35) The regiochemistry of the addition of 1,1,3-trideutereoindene to the acridizinium ion has been discussed earler (ref 18).

Trimethylsilylketene. Cycloadditions of Ketenes and Aldehydes

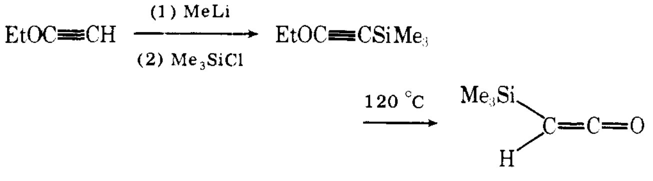
William T. Brady* and Kazem Saidi

Department of Chemistry, North Texas State University, Denton, Texas 76203

Received July 24, 1978

The cycloaddition of trimethylsilylketene with saturated aldehydes in the presence of a catalytic amount of $BF_3 \cdot Et_2O$ resulted in the formation of the *cis*- and *trans*-2-oxetanones. Trimethylsilylketene reacted with α,β-unsaturated aldehydes, cinnamaldehyde, crotonaldehyde, furfural, and α-methylcinnamaldehyde, in the presence of $BF_3 \cdot Et_2O$, to yield trimethylsilyl dienoate esters. These esters are derived from the 2-oxetanones which underwent a silicon migration from carbon to oxygen accompanied by a ring-opening reaction. Dichloroketene and diphenylketene reacted with cinnamaldehyde to yield the corresponding 2-oxetanones, which readily decarboxylated to the substituted 1,3-butadienes.

Trimethylsilylketene (**1**) was first reported in 1965 and was prepared by the pyrolysis of (trimethylsilyl)ethoxyacetylene.[1] The effect of the trimethylsilyl substituent on the properties and chemistry of this ketene is truly remarkable. This ketene is a colorless liquid which boils at 82 °C, is very stable (and yet an aldoketene, which is most unusual), does not dimerize upon heating, and can be stored for long periods of time.[2] Numerous efforts to effect cycloaddition of **1** with a variety of unsaturated compounds have been mostly unsuccessful.[2] Cycloaddition of **1** with dimethyl- and diethylketene acetals under rather vigorous conditions for a ketene cycloaddition has been reported.[3] Also, the cycloaddition of **1** with benzaldehyde gave *cis*- and *trans*-2-oxetanones, which decarboxylated upon distillation to yield both *cis*- and *trans*-trimethylsilylstyrenes.[4]



1

Me_3Si = trimethylsilyl

There are numerous reports in the literature on the cycloaddition of ketenes and carbonyl compounds to yield 2-oxetanones.[5] The cycloaddition of ketene with α,β-unsaturated carbonyl compounds has received considerable attention, primarily in the patent literature, but there is little to be found on the cycloaddition of other ketenes with these unsaturated compounds.

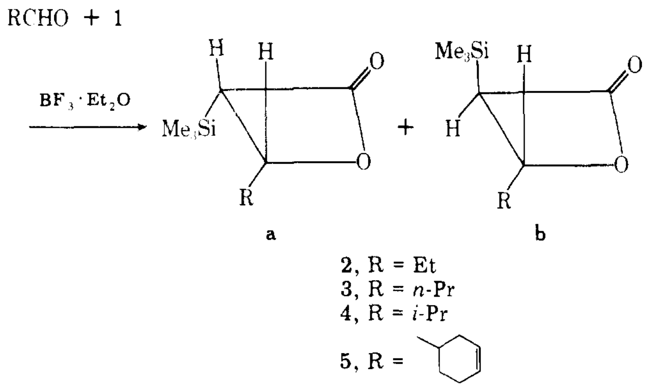
This report describes the cycloaddition of trimethylsilylketene with both saturated and α,β-unsaturated aldehydes. Also, we describe the cycloaddition of dichloroketene and diphenylketene with some α,β-unsaturated aldehydes and the reaction of trimethylsilylketene with ketene bis(trimethylsilyl) acetal.

Trimethylsilylketene was prepared by the pyrolysis of (trimethylsilyl)ethoxyacetylene and by the dehydrochlorination of (trimethylsilyl)acetyl chloride.[2,6] The former method gives a much better yield and was the method most often used.

The addition of equimolar quantities of **1** and simple aldehydes containing a few drops of $BF_3 \cdot Et_2O$ at 0 °C under a nitrogen atmosphere afforded the corresponding 2-oxetanones in 50–60% yields. The 2-oxetanones revealed the carbonyl band in the IR at 1805–1810 cm^{-1}. The cis and trans isomers were distinguished on the basis of the cis and trans coupling constants for the methinyl hydrogens in the NMR spectrum. The NMR spectrum of 4-ethyl-3-(trimethylsilyl)-2-oxetanones (**2a** and **2b**) revealed a doublet at δ 2.8 and a multiplet at δ 4.0 (J = 4 Hz) and a doublet at δ 3.2 and a multiplet at δ 4.3 (J = 6 Hz). The larger coupling constant was assigned to the cis isomer. The ratio of cis (**2a**)/trans (**2b**) was 55:45 based on the NMR and VPC data.

The 2-oxetanones did not undergo thermal decarboxylation

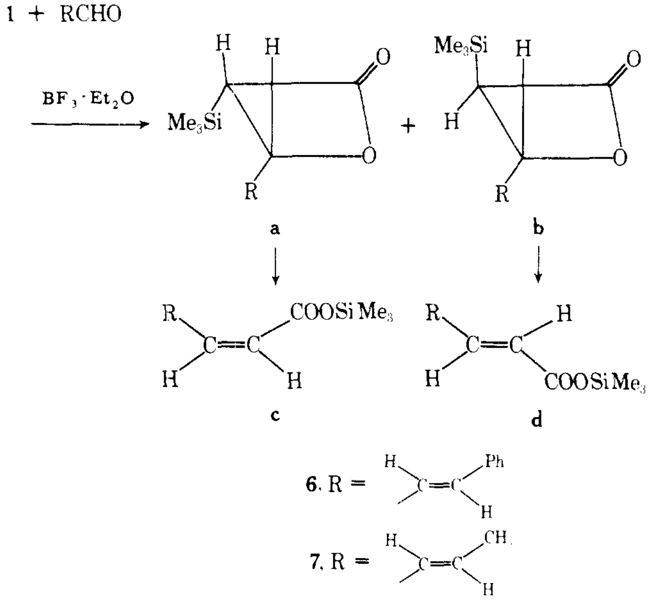
0022-3263/79/1944-0733$01.00/0 © 1979 American Chemical Society



when heated at 150 °C for 1 h. This is in contrast to most 2-oxetanones which readily decarboxylate upon heating.[5] It is noteworthy that these cycloadditions do not occur in the absence of the BF_3·Et_2O. This complex probably undergoes exchange with the aldehyde, resulting in activation of the carbonyl group to cycloaddition.

The reaction of equimolar quantities of 1 and α,β-unsaturated aldehydes containing a few drops of BF_3·Et_2O resulted in the formation of the corresponding 2-oxetanone as evidenced by an IR band at 1805–1810 cm^{-1} of the reaction mixture. However, during the distillation process the silyl substituent migrated from carbon to oxygen accompanied by a ring-opening reaction to yield the trimethylsilyl dienoate esters. The esters were isolated in 50–60% yields and revealed the carbonyl band in the IR at 1685 cm^{-1}.

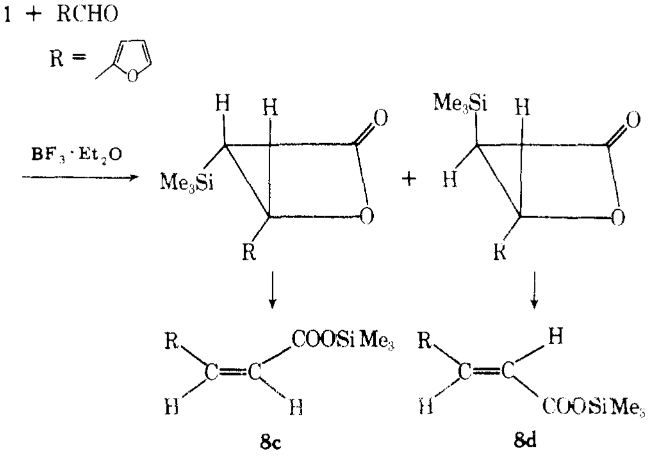
The cycloaddition of 1 with (*E*)-cinnamaldehyde and (*E*)-crotonaldehyde yields two silyl esters, **6c** and **6d** and **7c** and **7d**, respectively. These silyl esters were derived from the corresponding *cis*- and *trans*-2-oxetanones, which upon vacuum distillation resulted in the (*Z,E*)- and (*E,E*)-trimethylsilyl esters.

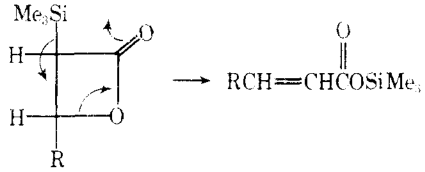


Furfural reacts in a similar manner with 1 to yield (*Z*)- and (*E*)-trimethylsilyl esters (**8c** and **8d**).

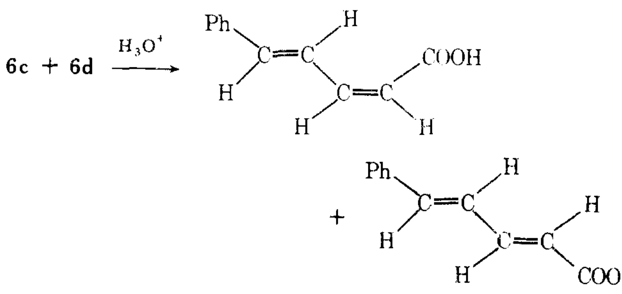
The cycloaddition of 1 and a mixture of (*E*)- and (*Z*)-α-methylcinnamaldehyde gave all four isomers in a ratio of 66:22:6.5:5.5 based on VPC. The parent peak in the mass spectrum for all four of these isomers was the same.

Apparently, these esters are formed from the corresponding 2-oxetanones by a silicon migration to oxygen and a ring-opening reaction. Similar migrations involving 1,3-shifts of organosilyl groups are well documented in the literature.[7] This is very similar to the result obtained upon cycloaddition of ketene and α,β-unsaturated ketones as reported by Young in 1949.[8] In this case it is proposed that a proton migrates to oxygen and the ring opening yields the corresponding dienoic acid.



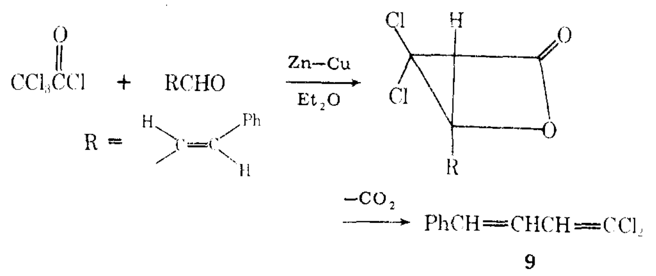


Further characterization and elucidation of the silyl esters were accomplished by hydrolysis and hydrogenation. The hydrolysis of the isomeric silyl ester mixtures resulted in the formation of the corresponding dienoic acids as illustrated with the dienoic silyl esters derived from trimethylsilylketene and cinnamaldehyde.



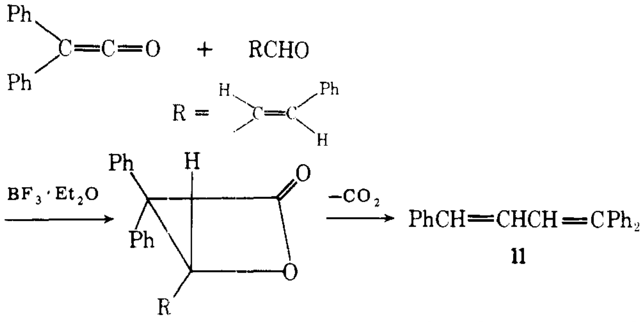
The hydrogenation of the isomeric silyl ester mixtures using platinum oxide in dry ether resulted in the saturated trimethylsilyl esters in near quantitative yield. Hydrolysis of the saturated esters yields the corresponding acids, which were identified by comparison with authentic samples.

The generation of dichloroketene by the zinc dechlorination of trichloroacetyl chloride in the presence of (*E*)-cinnamaldehyde and subsequent workup and distillation resulted in the formation of 1,1-dichloro-4-phenyl-1,3-butadiene (**9**). The in situ cycloaddition of dichloroketene and α-methylcinnamaldehyde gave a similar result, yielding 1,1-dichloro-3-methyl-4-phenyl-1,3-butadiene (**10**). The zinc halide etherate produced as a byproduct in the dehalogenation presumably

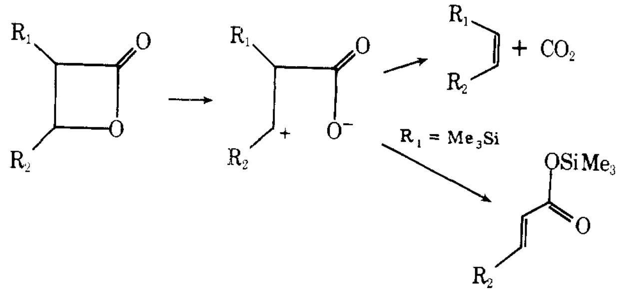


functions as the Lewis acid catalyst since no $BF_3 \cdot Et_2O$ is needed for these cycloadditions. We have previously observed the catalytic effect of zinc halide etherate in dichloroketene cycloadditions with simple ketones.[9] Apparently, in these cycloadditions with the cinnamaldehydes, the 2-oxetanones undergo decarboxylation during distillation to yield the highly conjugated systems.

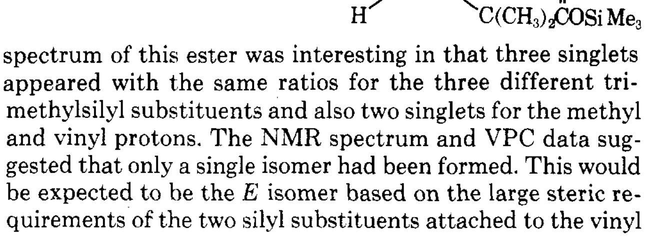
The cycloaddition of diphenylketene with (*E*)-cinnamaldehyde resulted in the formation of 1,1,4-triphenyl-1,3-butadiene (**11**). This butadiene is a solid and was isolated from the reaction mixture. Apparently, decarboxylation occurred spontaneously to yield this completely conjugated system. These decarboxylations are analogous to the cycloadduct decarboxylations of diphenylketene and benzoquinone, which readily lose carbon dioxide to yield the highly conjugated system.[10]



It is pertinent to note that the thermal stability of the 2-oxetanones containing a 4-vinyl substituent was distinctly diminished. The 3-silyl-4-vinyl-2-oxetanones readily underwent silyl migration and ring opening, and the 3,3-dichloro- and 3,3-diphenyl-4-vinyl-2-oxetanones readily decarboxylated. These data are suggestive of a BF_3-catalyzed dipolar ring opening in which the 4-vinyl substituent provides stabilization to the incipient carbonium ion.



The cycloaddition of **1** with the electron-rich diethyl acetal of ketene yielded the corresponding cyclobutanone.[3] This report prompted us to investigate the cycloaddition of trimethylsilylketene with dimethylketene bis(trimethylsilyl) acetal. Under the same reaction conditions, this ketene acetal reacted with the ketene to yield an open-chain product in good yield which was identified as trimethylsilyl 2,2-dimethyl-3-(trimethylsiloxy)-4-(trimethylsilyl)-3-butenoate. The NMR spectrum of this ester was interesting in that three singlets appeared with the same ratios for the three different trimethylsilyl substituents and also two singlets for the methyl and vinyl protons. The NMR spectrum and VPC data suggested that only a single isomer had been formed. This would be expected to be the *E* isomer based on the large steric requirements of the two silyl substituents attached to the vinyl system. This ester is apparently the product of a nucleophilic attack on trimethylsilylketene rather than a cycloaddition with concurrent or subsequent silicon migration from the oxygen of the acetal to the oxygen of the ketene. A similar product has been reported for the reaction of ketene bis(trimethylsilyl) acetals and nonsilylated ketenes.[11] Apparently, this sterically crowded electron-rich tetrasubstituted ethylene has a lower energy pathway to the open-chain product than the cycloadduct.



Experimental Section

The proton NMR spectra were recorded on a Perkin-Elmer R-12B nuclear magnetic resonance spectrometer employing CCl_4 as the solvent and either CH_2Cl_2 or $CHCl_3$ as the internal standard. Analytical and spectroscopic samples were obtained by VPC on a Perkin-Elmer Model 3920-B gas chromatograph using either a 6 ft × 0.25 in. column packed with 10% SE-30 on acid-washed Chromosorb W (80–100) support or a 10 ft × 0.25 in. column packed with 10% QF-1 on acid-washed Chromosorb W (80–100) support. The IR spectra were recorded on a Beckman IR 33 or on a Perkin-Elmer Model 621 grating infrared spectrometer. Spectra were obtained using neat samples and in CCl_4 solutions. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer and on a Finnigan GC/MS 3200 with a data system 6100.

Commercially available ether, benzene, and triethylamine were dried and purified by distillation from potassium–sodium alloy prior to each run. Ethoxyacetylene was commercially available and also was prepared by bromination of ethyl vinyl ether and dehydrobromination with *n*-butylamine and KOH, respectively.[12] The zinc was activated by a procedure described by one of us and was always stored and used under a nitrogen atmosphere.[13] Trichloroacetyl chloride was prepared from the corresponding acid and thionyl chloride. This acid halide was freshly distilled prior to each dichloroketene preparation. The commercially available aldehydes were distilled prior to use.

Trimethylsilylketene was prepared by a procedure similar to that of Ruden.[2] To a stirred solution of ethoxyacetylene in dry ether at 0 °C under a nitrogen atmosphere was added methyllithium dropwise, followed by the addition of trimethylchlorosilane. The stirring was continued overnight at room temperature. The ether was evaporated, the residue was then subjected to a vacuum, and the ethoxy(trimethylsilyl)acetylene was collected in a vacuum trap. This acetylenic compound was heated to 120 °C, and trimethylsilylketene distilled at 82 °C in 65% yield.

Diphenylketene was prepared by the triethylamine dehydrochlorination of diphenylacetyl chloride.[14]

Dimethylketene bis(trimethylsilyl) acetal was prepared from isobutyric acid by reaction with lithium diisopropylamide at 0 °C followed by the addition of trimethylchlorosilane.[11]

Typical Procedure for Trimethylsilylketene Cycloadditions with Saturated Aldehydes. A 17.5-mmol (2-g) portion of **1** was added dropwise to a stirred solution of 17.5 mmol of aldehyde containing a few drops of $BF_3 \cdot Et_2O$ at 0 °C under a nitrogen atmosphere. When the addition was complete (30–45 min), the reaction mixture was allowed to warm to room temperature and stirring was continued until the ketene had been consumed as evidenced by the disappearance of the ketene band in the IR at 2080 cm^{-1} and the formation of a strong band at 1805–1810 cm^{-1} (C=O of 2-oxetanone). The 2-oxetanones were purified by vacuum distillation through a short-path distillation apparatus and further characterized.

4-Ethyl-3-(trimethylsilyl)-2-oxetanone (2a and 2b). A 17.5-mmol (2-g) portion of **1** and 17.5 mmol (1.02 g) of propionaldehyde containing a few drops of $BF_3 \cdot Et_2O$ were reacted to give 1.8 g (60%) of **2a** and **2b**: bp 78 °C (0.5 mm); IR 1810 cm^{-1} (C=O); NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.18 (trans isomer), 0.2 (cis isomer) (two s, 9 H), 2.8 (trans isomer, J = 4 Hz), 3.2 (cis isomer, J = 6 Hz) (two d, 1 H), 4.0 (trans isomer, J = 4 Hz), 4.3 (cis isomer, J = 6 Hz) (two m, 1 H); methyl and methylene groups of the cis and trans isomers were multiplets at δ 1.0 and 1.70, respectively; mass spectrum, parent peak *m/e* 172, found for both isomers *m/e* 157 (loss of a methyl group).

Anal. Calcd for $C_8H_{16}O_2Si$: C, 55.8; H, 9.30. Found: C, 56.16; H, 9.58.

4-*n*-Propyl-3-(trimethylsilyl)-2-oxetanone (3a and 3b). A 17.5-mmol (2-g) portion of **1** and 17.5 mmol (1.26 g) of *n*-butyraldehyde containing a few drops at $BF_3 \cdot Et_2O$ were reacted to give 1.76 g (54%) of **3a** and **3b**: bp 56–60 °C (0.025 mm); IR 1810 cm^{-1} (C=O); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 0.18 (trans isomer), 0.2 (cis isomer) (two s, 9 H), 2.85 (trans isomer, J = 4 Hz), 3.28 (cis isomer, J = 6 Hz) (two d, 1 H), 4.15 (trans isomer, J = 4 Hz), 4.7 (cis isomer, J = 6 Hz) (two m, 1 H); methyl and methylene protons of the cis and trans isomers were multiplets at δ 1.0 and 1.55, respectively; mass spectrum, parent peak *m/e* 186, found for both isomers *m/e* 171 (loss of a methyl).

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.00; H, 9.73. Found: C, 57.50; H, 9.94.

4-Isopropyl-3-(trimethylsilyl)-2-oxetanone (4a and 4b). A 17.5-mmol (2-g) portion of 1 and 17.5 mmol (1.26 g) of isobutyraldehyde containing a few drops of BF_3·Et_2O were reacted to give 1.82 g (56%) of **4a** and **4b:** bp 67 °C (0.025 mm); IR 1810 cm^{-1} (C=O); NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.20 (trans isomer), 0.25 (cis isomer) (two s, 9 H), 2.90 (trans isomer, J = 4 Hz), 3.25 (cis isomer, J = 6 Hz) (two d, 1 H), 3.85 (trans isomer, J = 4 Hz), 4.10 (cis isomer, J = 6 Hz) (two m, 1 H); methyl and methinyl protons of the cis and trans isomers were a d of d and a multiplet at δ 1.0 and 1.80, respectively; mass spectrum, parent peak *m/e* 186, found for both isomers *m/e* 171 (loss of a methyl).

Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.0; H, 9.73. Found: C, 58.25; H, 9.79.

4-(3-Cyclohexenyl)-3-(trimethylsilyl)-2-oxetanone (5a and 5b). A 17.5-mmol (2-g) portion of 1 and 17.5 mmol (1.02 g) of 3-cyclohexenecarboxaldehyde containing a few drops of BF_3·Et_2O were reacted to give 2.5 g (65%) of **5a** and **5b:** bp 95–100 °C (0.15 mm); IR 1805–1810 cm^{-1} (C=O); NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.21 (trans isomer), 0.23 (cis isomer) (two s, 9 H), 2.05 (m, 7 H), 3.0 (trans isomer), 3.3 (cis isomer) (two d, 1 H), 4.0 (m, 1 H), 5.6 (s, 2 H); mass spectrum, parent peak *m/e* 224, found *m/e* 224.

Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.31; H, 8.92. Found: C, 64.83; H, 9.19.

Typical Procedure for the Cycloaddition of Trimethylsilylketene with α,β-Unsaturated Aldehydes. A 17.5-mmol (2-g) portion of 1 was added dropwise to a stirred solution of 17.5 mmol of an α,β-unsaturated aldehyde containing a few drops of BF_3·Et_2O at 0 °C under a nitrogen atmosphere. When the addition was complete (30–45 min), the reaction mixture was allowed to warm to room temperature and stirring was continued until the ketene had been consumed as evidenced by the disappearance of the ketene band in the IR at 2080 cm^{-1}. This stirring period was from 2 h to overnight, depending on the aldehyde. The silyl esters were purified by vacuum distillation through a short-path distillation apparatus.

Typical Procedure for Hydrolysis of the Trimethylsilyl Dienoate Esters. To 0.5 g of the silyl ester was added 2 mL of 5% HCl, and this mixture was stirred for 30 min at room temperature. The dienoic acid was filtered in near quantitative yield and purified by sublimation.

Typical Procedure for Hydrogenation of the Trimethylsilyl Dienoate Esters. A 0.5-g portion of the silyl ester in 15–20 mL of dry ether containing a catalytic amount of platinum oxide catalyst was hydrogenated for 12–15 h. The catalyst was removed by filtration, the ether was evaporated, and the residue was vacuum distilled to yield the saturated silyl ester in near quantitative yield.

Typical Procedure for Hydrolysis of the Saturated Trimethylsilyl Esters. To 0.5 g of saturated silyl ester was added about 2 mL of 5% HCl, and this reaction mixture was stirred for 30 min at room temperature. The saturated acid was purified by distillation or sublimation.

Trimethylsilyl β-Styrylacrylate (6c and 6d). A 52.6-mmol (6-g) portion of 1 and 52.6 mmol (6.94 g) of (*E*)-cinnamaldehyde containing a few drops of BF_3·Et_2O resulted in 8 g (62%) of **6c** and **6d:** bp 90 °C (0.025 mm); IR 1625 (C=C) and 1685 (C=O) cm^{-1}; NMR (CCl_4 with CH_2Cl_2 as a reference) δ 0.5 (s, 9 H), 5.8 (two d, 1 H), 6.6 (m, 2 H), 8.0 (d of d, 1 H); mass spectrum, parent peak *m/e* 246, found *m/e* 246.

Anal. Calcd for $C_{14}H_{18}O_2Si$: C, 68.30; H, 7.32. Found: C, 68.65; H, 7.35.

β-Styrylacrylic acid was obtained by hydrolysis of **6c** and **6d,** mp 164–165 °C (lit.[15] mp 165 °C).

Trimethylsilyl 5-phenylpentanoate was obtained in near quantitative yield by hydrogenation of 0.5 g of **6c** and **6d:** IR 1712 cm^{-1} (C=O); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 0.4 (s, 9 H), 1.75 (m, 4 H), 2.35 (t, 2 H), 2.7 (t, 2 H), 7.1 (s, 5 H); mass spectrum, parent peak *m/e* 250, found *m/e* 250.

Hydrolysis of trimethylsilyl 5-phenylpentanoate yielded 5-phenylpentanoic acid, mp 58 °C (lit.[16] mp 58–59 °C).

Trimethylsilyl 2,4-Hexadienoate (7c and 7d). A 45-mmol (5.13-g) portion of 1 and 45 mmol (3.15 g) of (*E*)-crotonaldehyde containing a few drops of BF_3·Et_2O yielded 3.9 g (48%) of **7c** and **7d:** bp 35–40 °C (0.25 mm); IR (before distillation) 1805–1810 cm^{-1} (C=O); IR (after distillation) 1640 (C=C) and 1690 (C=O, conjugated to double bond) cm^{-1}; NMR (CCl_4 with CH_2Cl_2 as a reference) δ 0.3 (*E,E* isomer), 0.35 (*Z,E* isomer) (two s, 9 H), 1.0 (d, 3 H), 5.7–7.5 (m, 4 H); mass spectrum, parent peak *m/e* 184, found *m/e* 184.

Sorbic acid was obtained by hydrolysis of **7c** and **7d,** mp 122–127 °C (lit.[17] mp 124 °C).

Trimethylsilyl hexanoate was obtained by hydrogenation of **7c** and **7d:** bp 50–55 °C (0.5 mm); IR 1705 cm^{-1} (C=O); NMR (CCl_4 and CH_2Cl_2 as a reference) δ 0.2 (s, 9 H), 0.9 (d, 3 H), 1.4 (m, 6 H), 2.2 (t, 2 H); mass spectrum, parent peak *m/e* 188, found *m/e* 188.

Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.4; H, 10.64. Found: C, 57.62; H, 10.52.

n-Caproic acid was obtained by hydrolysis of trimethylsilyl hexanoate, bp 204–205 °C (lit.[18] bp 204–206 °C).

Trimethylsilyl β-Furylacrylate (8c and 8d). A 17.5-mmol (2-g) portion of 1 and 17.5 mmol (1.7 g) of furfural containing a few drops of BF_3·Et_2O gave 1.9 g (50%) of **8c** and **8d:** bp 58–62 °C at 0.2 mm; IR 1690 cm^{-1} (C=O); NMR (CCl_4 with Me_2SO as a reference) δ 0.4 (s, 9 H), 5.5–7.7 (m, 5 H); mass spectrum, parent peak *m/e* 210, found *m/e* 210.

Anal. Calcd for $C_{10}H_{14}O_3Si$: C, 57.14; H, 6.66. Found: C, 57.40; H, 6.74.

Trimethylsilyl 4-Methyl-5-phenyl-2,4-pentadienoate. A 17.5-mmol (2-g) portion of 1 and 17.5 mmol (2.6 g) of a mixture of both (*E*)- and (*Z*)-α-methylcinnamaldehyde containing a few drops of BF_3·Et_2O gave 2.5 g (55%) of a mixture of all four isomers, *E,Z*, *E,E*, *Z,E*, and *Z,Z*: bp 95 °C (0.25 mm); IR 1625 (C=C), 1680 (C=O) cm^{-1}; NMR (CCl_4, CH_2Cl_2 as a reference) δ 0.3 (s, 9 H), 2.0 (s, 1 H), 5.8 (d, 1 H), 6.7 (s, 1 H), 7.2 (s, 5 H), 7.3 (d, 1 H); mass spectrum, parent peak *m/e* 260, found *m/e* 260.

4-Methyl-5-phenyl-2,4-pentadienoic acid was obtained by hydrolysis of 0.5 g of the trimethylsilyl ester, which was purified by sublimation, mp 100–107 °C (lit.[19] mp 109–110 °C).

Trimethylsilyl 5-phenyl-4-methylpentanoate was obtained by hydrogenation of the trimethylsilyl dienoate ester: bp 75–80 °C (0.005 mm); IR 1710 cm^{-1} (C=O); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 0.3 (s, 9 H), 0.95 (d, 3 H), 1.7 (m, 3 H), 2.35 (t, 2 H), 2.65 (d, 2 H), 7.2 (s, 5 H); mass spectrum, parent peak *m/e* 264, found *m/e* 264.

Anal. Calcd for $C_{15}H_{24}O_2Si$: C, 68.23; H, 9.09. Found: C, 68.54; H, 8.73.

Hydrolysis of this saturated ester yielded 4-methyl-5-phenylpentanoic acid, which was further purified by sublimation, mp 52–56 °C (lit.[20] mp 55–56 °C).

Typical Procedure for the Cycloaddition of Dichloroketene with α,β-Unsaturated Aldehydes. A solution of 25 mmol of freshly distilled trichloroacetyl chloride in 150 mL of dry ether was added very slowly (3–4 h) to a stirred mixture of 25 mmol of aldehyde in 150 mL of dry ether and 7 g of activated zinc under a nitrogen atmosphere. This reaction mixture was stirred overnight. The excess zinc was filtered, washed, and dried, revealing a stoichiometric loss. The reaction solution was concentrated to about 50 mL and stirred with 50 mL of hexane. The hexane solution was decanted from the zinc salts and evaporated, and the residue was vacuum distilled to yield the diene.

1,1-Dichloro-4-phenyl-1,3-butadiene (9). A 25-mmol portion of trichloroacetyl chloride was reacted with 25 mmol of (*E*)-cinnamaldehyde containing 7 g of zinc in 300 mL of ether to give 1.74 g (35%) of the diene: bp 61–65 °C (0.05 mm); IR 1590 cm^{-1} (C=C); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 6.65 (m, 3 H), 7.3 (s, 5 H); mass spectrum, parent peak *m/e* 198, found *m/e* 198, base peak at *m/e* 128 (loss of two Cl atoms).

Anal. Calcd for $C_{10}H_8Cl_2$: C, 60.30; H, 4.02. Found: C, 60.11; H, 4.06.

1,1-Dichloro-3-methyl-4-phenyl-1,3-butadiene (10). A 25-mmol portion of trichloroacetyl chloride was reacted with 25 mmol of α-methylcinnamaldehyde (both isomers) to give 1.7 g (32%) of the diene: bp 69 °C at 0.05 mm; IR 1590 cm^{-1} (C=C); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 2.35 (s, 3 H), 6.6 (s, 1 H), 6.7 (s, 1 H), 7.3 (s, 5 H); mass spectrum, parent peak *m/e* 212, found *m/e* 212, base peak at *m/e* 142 (loss of two Cl atoms).

Anal. Calcd for $C_{11}H_{10}Cl_2$: C, 61.98; H, 4.70. Found: C, 61.72; H, 4.75.

1,1,4-Triphenyl-1,3-butadiene (11). A 51.5-mmol (10-g) portion of diphenylketene was added dropwise to a stirred solution of 51.5 mmol (6.8 g) of (*E*)-cinnamaldehyde containing a few drops of BF_3·Et_2O at room temperature under a nitrogen atmosphere. When the addition was complete, the reaction mixture was stirred overnight. Addition of methanol to the reaction solution caused the product to precipitate, yielding 7.5 g (52%) of the diene: mp 98–99 °C (purified by sublimation); IR 1607 cm^{-1} (C=C); NMR (CCl_4 with CH_2Cl_2 as a reference) δ 6.8 (m, 3 H), 7.3 (m, 15 H); mass spectrum, parent peak *m/e* 282, found *m/e* 282, base peak at *m/e* 166 (due to Ph_2C^+).

Anal. Calcd for $C_{22}H_{18}$: C, 93.62; H, 6.38. Found: C, 93.37; H, 6.41.

Trimethylsilyl 2,2-Dimethyl-3-(trimethylsiloxy)-4-(trimethylsilyl)-4-butenoate (12). A 17.5-mmol (2-g) portion of 1 was added dropwise to a stirred solution of 17.5 mmol (4.07 g) of dimethylketene bis(trimethylsilyl) acetal at 110 °C under a nitrogen atmosphere. The reaction solution was stirred at this temperature until the ketene had been consumed as evidenced by the disappearance of the ketene band in the IR (~36 h). Vacuum distillation resulted in 4.5 g (75%) of **12**: bp 68 °C at 0.025 mm; IR 1615 (C=C), 1720 (C=O) cm^{-1}; NMR (CCl_4 with $CHCl_3$ as a reference) δ 0.15 (s, 9 H), 0.27 (s, 9 H), 0.33 (s, 9 H), 1.35 (s, 6 H), 4.45 (s, 1 H); mass spectrum, parent peak at *m/e* 346, found *m/e* 346.

Anal. Calcd for $C_{15}H_{34}O_3Si_3$: C, 52.02; H, 9.83. Found: C, 51.92; H, 9.83.

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

Registry No.—1, 4071-85-6; **2a**, 67354-22-7; **2b**, 67354-14-7; **3a**, 67354-23-8; **3b**, 67354-15-8; **4a**, 67354-24-9; **4b**, 67354-16-9; **5a**, 68781-92-0; **6c**, 68781-93-1; **6d**, 68781-94-2; **7c**, 68781-95-3; **7d**, 68781-96-4; **8c**, 68781-97-5; **8d**, 68781-98-6; **9**, 56772-77-1; **10**, 68781-99-7; **11**, 18720-11-1; **12**, 68782-00-3; trimethylsilyl 5-phenylpentanoate, 68782-01-4; trimethylsilyl hexanoate, 14246-15-2; (*E,Z*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-02-5; (*E,E*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-03-6; (*Z,E*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-04-7; (*Z,Z*)-trimethylsilyl 4-methyl-5-phenyl-2,4-pentadienoate, 68782-05-8; trimethylsilyl 4-methyl-5-phenylpentanoate, 68782-06-9; propionaldehyde, 123-38-6; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2; 3-cylohexenecarboxaldehyde, 100-50-5; (*E*)-cinnamaldehyde, 14371-10-9; (*E*)-crotonaldehyde, 123-73-9; furfural, 98-01-1; (*E*)-α-methylcinnamaldehyde, 15174-47-7; (*Z*)-α-methylcinnamaldehyde, 66051-14-7; dichloroketene, 4591-28-0; trichloroacetyl chloride, 76-02-8; diphenylketene, 525-06-4; dimethylketene bis(trimethylsilyl) acetal, 31469-25-7; ethoxyacetylene, 927-80-0; trimethylchlorosilane, 75-77-4.

References and Notes

(1) L. L. Shchukovskaya, R. I. Pal'chik, and A. N. Lazarev, *Dokl. Akad. Nauk SSSR*, **164**, 357 (1965); *Chem. Abstr.*, **63**, 18138 (1965).

(2) (a) R. A. Ruden, *J. Org. Chem.*, **39**, 3607 (1974). (b) We have attempted the cycloaddition of trimethylsilylketene with a wide variety of unsaturated compounds with very limited success.

(3) G. S. Zaitseva, Yu. I. Baukov, V. V. Mal'tsev, and I. F. Lutsenko, *Zh. Obshch. Khim.*, **44**, 1415 (1974); *Chem. Abstr.*, **81**, 105619 (1974).

(4) G. S. Zaitseva, N. G. Vinokurova, and Yu. I. Baukov, *Zh. Obshch. Khim.*, **45**, 1398 (1975); *Chem. Abstr.*, **83**, 114548 (1975).

(5) (a) L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions", Interscience, New York, 1967, p 139; (b) W. T. Brady, *Synthesis*, 415 (1971).

(6) I. F. Lutsenko, Yu. I. Baukov, A. S. Kostyuk, N. I. Savalyeva, and V. K. Krysina, *J. Organomet. Chem.*, **17**, 241 (1969).

(7) A. G. Brook, A. R. Bassindale, P. Chen, and J. Lennon, *J. Organomet. Chem.*, **94**, C21 (1975).

(8) F. G. Young, *J. Am. Chem. Soc.*, **71**, 1346 (1949).

(9) W. T. Brady and A. D. Patel, *J. Heterocycl. Chem.*, **8**, 739 (1971).

(10) (a) J. C. Martin, J. L. Chitwood, P. G. Gott, and J. J. Drutak, *J. Org. Chem.*, **36**, 2216 (1971); (b) J. Thiele and H. Balhorn, *Chem. Ber.*, **37**, 1463 (1904).

(11) C. Ainsworth and Y. N. Kuo, *J. Organomet. Chem.*, **46**, 73 (1972).

(12) K. S. Y. Lau and M. Schlosser, *J. Org. Chem.*, **43**, 1595 (1978).

(13) W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

(14) H. Staudinger, *Chem. Ber.*, **44**, 1619 (1911).

(15) J. Klein and E. D. Bergamann, *J. Am. Chem. Soc.*, **79**, 3452 (1957).

(16) R. V. Christian, Jr., *J. Am. Chem. Soc.*, **74**, 1591 (1952).

(17) P. R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, 417 (1953). The melting point of sorbic acid has also been reported at 134 °C.[15]

(18) E. R. Taylor and H. T. Clarke, *J. Am. Chem. Soc.*, **49**, 2831 (1927).

(19) P. D. Molho and M. Giraud, *Bull. Soc. Chim. Fr.*, 1143 (1970).

(20) S. I. Yamada and S. Terashima, *J. Chem. Soc. D*, 511 (1969).

Photoelectron Spectra of the 1,2,5,6-Tetramethyl-3,4,7,8-tetramethylene Derivatives of Tricyclo[3.3.0.0^{2,6}]octane and Tricyclo[4.2.0.0^{2,5}]octane

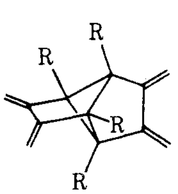
Weston Thatcher Borden,*[1a] Stanley D. Young,[1a] David C. Frost,[1b]
Nicholas P. C. Westwood,[1b] and William L. Jorgensen[1c]

Departments of Chemistry, University of Washington, Seattle, Washington 98195,
University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5, and
Purdue University, West Lafayette, Indiana 47907

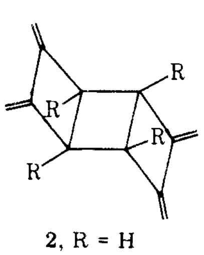
Received July 11, 1978

The photoelectron spectra of the title compounds, 4 and 5, are reported, along with assignments of the first three bands in each. Analysis within a ZDO model of the splitting between the first two bands in the spectrum of 4 requires that the b_1 orbital of the tetramethylcyclobutane ring have an energy of −9.3 eV. This finding is discussed in light of calculations on the effect of tetramethylation of cyclobutane and the approximations inherent in the ZDO model.

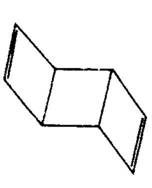
The magnitude of the through-bond splitting between different symmetry combinations of π orbitals localized on unsaturated groups depends on the extent to which one combination is destabilized relative to the other by interaction with adjacent σ orbitals of appropriate symmetry.[2] The bonds of small rings, by virtue of their high energy and large amounts of p character, are ideal candidates for producing substantial through-bond splittings.[3] In particular, cyclobutane rings have been shown by a variety of spectroscopic,[4] chemical,[5] and theoretical[6] studies to interact strongly with unsaturated bridging groups. Therefore, the through-bond splittings in 3,4,7,8-tetramethylenetricyclo[3.3.0.0^{2,6}]octane (1) and *anti*-3,4,7,8-tetramethylenetricyclo[4.2.0.0^{2,5}]octane (2) are expected to be significant.



1, R = H
4, R = CH_3



2, R = H
5, R = CH_3



3

More specifically, in 1 the b_1 and a_2 combinations of the butadiene highest occupied molecular orbitals (HOMO's) should be significantly split by their interactions with b_1 and a_2 orbitals of the cyclobutane ring.[7] The b_1 orbital of the ring

0022-3263/79/1944-0737$01.00/0