$HCOOCH_3$), 165.0729 (28; $C_{13}H_9$, 165.0703, M - 2 $HCOOCH_3$ - H?), 153.0348 (31; $C_{11}H_5O$, 153.0340, M - CH_3OH - $COOCH_3$ - $C(CH_3)_2$, 152.0210 (32; $C_{11}H_4O$?, 152.0262, M - CH_3OH - $HCOOCH_3$ - $C(CH_3)_2$), 127.0648 (31; $C_{10}H_7$?, 127.0548, M - 2 $COOCH_3$ - C_3H_5); CI mass spectrum (NH_3 at 0.15 torr, normalized against spectrum minus reagent gas ions, 230 °C), negative ion spectrum, *m/e* (relative intensity > 0.4) 286.2 (100, m), 271.2 (1.9, M - CH_3), 255.0 (1.3, M - OCH_3), 240.2 (2.4, M - CH_3 - OCH_3); positive ion spectrum, *m/e* (relative intensity > 0.9) 304.1 (100, M + NH_4), 303.0 (5.7, M - 1 + NH_4), 288.2 (15, M - CH_4 + NH_4), 255.2 (51, M - OCH_3), 254.4 (15, M - CH_3OH), 227.1 (3.2, M - $COOCH_3$), 212.8 (1.0, M - OCH_3 - $C(CH_3)_2$).

Anal. Calcd for $C_{17}H_{18}O_4$ (mol wt 286.33): C, 71.31; H, 6.33. Found: C, 71.41; H, 6.22.

In order to look for the possible presence of small amounts of a solid 1:2 adduct, the reaction was repeated and worked up by preparative TLC on silica gel PF-254, but the only solid product isolated was again **5**, as white crystals, mp 116-116.5 °C.

Acknowledgment. It is a pleasure to acknowledge support of V.K. through teaching assistantships from the University of Minnesota (Sept-June of 1967-1968, 1968-1969, and 1970-1971), fellowships from the Shell Oil Co. (first summer session 1968), E. I. du Pont de Nemours and Co. (first summer session 1969), Union Carbide Corp. (Sept 1969 to Aug 1970), and the Eastman Kodak Co. (first summer session 1971), and a research assistantship granted by W.E.N. under U.S. Public Health Service Grant No. CA-04073-11 (July 15 to Sept 15, 1969). We are indebted to the National Science Foundation for equipment Grant CHE 77-28505, which aided in the purchase of an Enraf-Nonius X-ray diffractometer, and to Professor Louis H. Pignolet and Mr. Michael McGuiggan for the X-ray determination. We thank Professors J. Doyle Britton, Raymond M. Dodson, and J. Zanos Gougoutas for helpful discussions.

Registry No. 1d, 18636-55-0; **5a**, 76402-82-9; DMAD, 762-42-5; 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-one, 26465-81-6; 2,3-dihydro-3,3-dimethyl-1*H*-inden-1-ol, 38393-92-9.

Supplementary Material Available: Tables of bond distances (Table 3), bond angles (Table 4), final coordinates (Table 5), positional and thermal parameters and their estimated standard deviations, general temperature factor expressions, root-mean-square amplitudes of thermal vibration, weighted least-squares planes, and dihedral (torsional) angles (11 pages). Ordering information is given on any current masthead page.

Halogenated Ketenes. 34. Cycloaddition of Halogenated Ketenes and Conjugated Trimethylsilyl Enol Ethers

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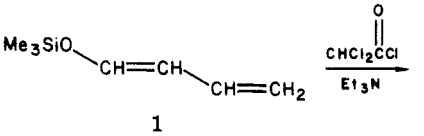
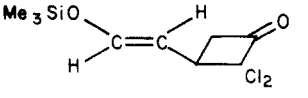
The generation of dichloroketene and methylchloroketene by the triethylamine dehydrohalogenation of the respective acid chlorides in the presence of conjugated trimethylsilyl enol ethers yields functionalized cyclobutanones with high regioselectivity. Both cross-conjugated and linear-conjugated trimethylsilyl enol ethers were found to yield [2 + 2] cycloaddition products in good yield.

The cycloaddition of dichloroketene and several mono- and disubstituted ketenes with a number of trimethylsilyl enol ethers to produce trimethylsiloxy- and hydroxy-functionalized cyclobutanones has recently been reported.[1-3] We now describe the reactions of dichloro- and methylchloroketene with several conjugated trimethylsilyl enol ethers. The conjugated trimethylsilyl enol ethers are readily prepared from α-enones by the procedure described by House.[4]

When dichloroacetyl chloride was slowly added to a dilute solution[5] of the trimethylsilyl enol ether from crotonaldehyde, **1**, and triethylamine, an exothermic reaction occured with the immediate precipitation of the triethylammonium salt. After the addition was complete, the reaction was stirred for several hours, and the salt was removed by filtration. The filtrate was concentrated and the residue vacuum distilled to yield a one to one adduct. A strong carbonyl absorption in the infrared at 1805 cm^{-1} as well as a strong vinyl absorption at 1655 cm^{-1} suggested that cyclobutanone **2** was the product of this cycloaddition.



1



2

The NMR spectrum of the product prior to distillation and after distillation supported **2** as the major product of this reaction. A coupling constant of J = 12.1 Hz for the vinyl protons confirms the trans geometry. Less than 5% hydrolysis of the parent compound **2** to yield the aldehyde was indicated by the infrared and NMR spectra. Although cycloaddition may have occurred at the 1,2 double bond of silyl enol ether **1**, we were unable to confirm the presence of this product in any of the spectra. When the reaction was repeated, using the zinc dehalogenation of trichloroacetyl chloride in ether to produce dichloroketene,[1] the same product was observed. Reaction of **2** with anhydrous

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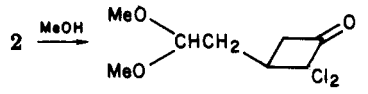
methanol resulted in the dimethyl acetal **3** in 82% yield.

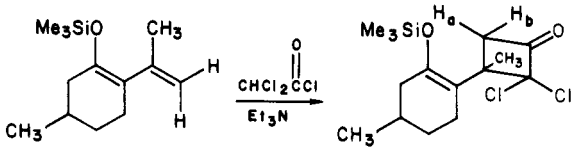


3

The reaction of methylchloroketene with trimethylsilyl enol ether **1** resulted in a mixture of isomers with the same regiochemistry observed with dichloroketene. Again, no 1,2-cycloaddition was observed with this silyl enol ether and methylchloroketene. Reaction of this cycloadduct with anhydrous methanol yielded the dimethyl acetal mixture.

Several other conjugated silyl enol ethers were found to give [2 + 2] cycloadducts with dichloro- and methylchloroketene in good yield. While the yields were quite good for the reactions, the purification of these highly reactive products was difficult. When possible the cycloadducts were distilled, but in some cases chromatography on silica gel was used to purify the products.[6]

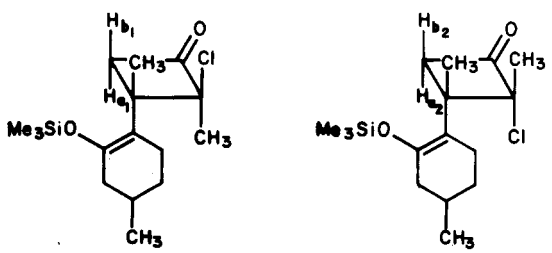
The reaction of dichloroketene with the trimethylsilyl enol ether of pulegone, **4**, gave the [2 + 2] cycloadduct with the same regiochemistry observed with silyl enol ether **1**. The NMR spectrum of the cycloadduct **5** was particularly



4 **5**

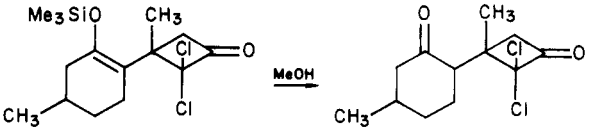
interesting. Two doublets in the spectrum with a coupling constant of J = 16.8 Hz at 3.92 and 2.77 ppm for the cyclobutanone ring protons supported the structure **5**. Although this is a remarkable difference in the chemical shift for the methylene protons H_a and H_b, the size of the geminal coupling and the *anisotropy* of the chemical shift for H_a and H_b have been observed in other related systems.[7]

The cycloadduct of methylchloroketene and silyl enol ether **4** was similar to that observed with dichloroketene except that two sets of doublets were found in the NMR spectrum. Integration of the spectrum revealed that one isomer was formed preferentially by a 1.7:1 margin. The isomer with the *trans*-methyl groups was determined to be the major isomer based on chemical shift of the methylene protons of the cyclobutanone ring. The methylene proton, H_{a_2}, periplanar to the chlorine atom appeared further downfield than the H_{a_1} proton[8] in **6**. This result is also in accordance with known ketene–olefin cycloadditions where bulky groups in the reactants appear cis in the products.[9]



6, major **6**, minor

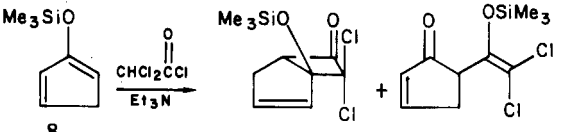
Methanolysis of **5** and **6** gave the respective ketones as illustrated with **5**.



5 **7**

Notably, the cycloadditions of methylchloro- and dichloroketene with the trimethylsilyl enol ethers **1** and **4** yielded only the 3,4-adducts. Apparently, the activation of the double bonds by the trimethylsiloxy substituent extends to the 3,4-position.[10] The regiochemistry observed for the cycloadditions of methylchloro- and dichloroketene with two linearly conjugated silyl enol ethers is likely a consequence of steric interactions. Ketene cycloadditions with trimethylsilyl enol ethers[2,3] and alkyl enol ethers[11] have been shown to be sensitive to steric considerations. Cycloaddition of dichloro- and methylchloroketene with silyl enol ether **1** occurs at the 3,4 double bond apparently because of monosubstitution, while the 1,2 double bond is disubstituted. The same reasoning could account for the regiochemistry observed with silyl enol ether **4**.

The cycloaddition of dichloroketene with the trimethylsilyl enol ether of 2-cyclopentenone, **8**, is interesting because this silyl enol ether is the 2-trimethylsiloxy derivative of cyclopentadiene.[12] As might be expected this silyl enol ether was found to be very reactive in ketene cycloadditions. The reaction of dichloroketene and silyl enol ether **8** gave two products in a 4:1 ratio. The major product was the adduct **9**, and the minor product was determined to be the acyclic isomer **10**. The IR and NMR spectra of the bridgehead hydrogen in **9** were consistent with reported results for similar cycloaddition products.[3,13]



8 **9** **10**

The cross-conjugated silyl enol ether **8** gave cycloaddition exclusively at the 1,2-bond with no evidence of reaction at the 3,4 double bond of this cyclopentadiene derivative. The regiochemistry observed with dichloroketene was also observed with methylcholoroketene. Although a thermal ring opening, as has been observed in other systems, is possible,[2] it is unlikely that the minor acyclic product **10** was derived from **9**. At no time during the reaction, or the reaction workup, was the reaction mixture heated. When the mixture was distilled, there was no evidence of further ring opening to **10**, and the same ratio of products was observed in the NMR spectrum. It is possible that an acylation-type mechanism is the source of **10**.[14] Alternatively, a dipolar intermediate could account for both products **9** and **10**.

Hydrolysis of the trimethylsilyl substituent was very difficult, and we were unable to isolate the hydroxy-

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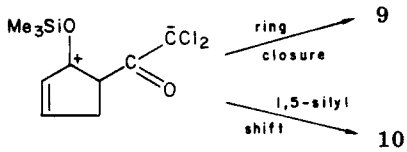
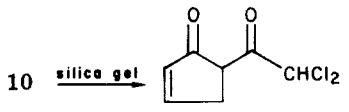


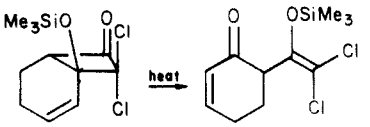
cyclobutanone in the rapidly polymerizing mixture. When a mixture of **9** and **10** was chromatographed on silica gel **9** was recovered in a pure form, and the acyclic isomer **10** underwent hydrolysis to give the highly reactive dione **11**.



11

When methylchloroketene was generated in the presence of trimethylsilyl enol ether **8**, a product analogous to **10** was not observed in the crude reaction mixture or in the distilled product. A mixture of the *endo*-methyl and the *exo*-methylsiloxycyclobutanones was formed with an isomer distribution of 1,2-(*endo*-methyl/*exo*-methyl). This assignment is in accord with known alkylhaloketene–cyclopentadiene cycloadduct isomer distributions[15] and with the closely related cycloadducts of ketenes and 1-(trimethylsiloxy)cyclopentene.[3] Methanolysis afforded the corresponding hydroxycyclobutanone.

The cycloaddition of dichloroketene and the trimethylsilyl enol ether from 2-cyclohexenone was very erratic and a difficult reaction with which to work. Although it was not possible to isolate the cycloadduct, **12** was observed as evidenced by NMR and IR spectra of the reaction mixture. When the crude reaction product was distilled, partial rearrangement to the acyclic product **13** was

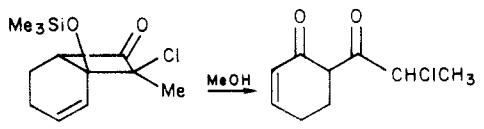


12 13

observed. Prolonged heating of **12** gave **13** and polymeric material. Column chromatography on silica gel of a mixture of **12** and **13** resulted in hydrolysis to the dione of **13**.

A similar difficulty has been reported with the dichloroketene adduct with the trimethylsiloxy enol ether of cyclohexanone. The instability of **12** appears to be related to conformational effects in the cyclobutanone ring allowed by the fused cyclohexene.[1] This tendency for ring opening is not observed by the more rigid cycloadducts of 1-(trimethylsiloxy)cyclopentene[2] and 2-(trimethylsiloxy)-cyclopentadiene reported here.

In contrast to what is observed with **12**, the methylchloroketene cycloadduct **14** was found to be much more stable and could be isolated by distillation, and a product corresponding to **13** was not observed with this ketene. An isomer ratio of 3:2 was observed, with the *endo*-methyl predominating.[16] Hydrolysis of the trimethylsilyl substituent did not yield the alcohol but gave ring opening to the dione **15**.



14 15

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Experimental Section

Proton NMR spectra were recorded on a Perkin-Elmer R-24B nuclear magnetic resonance spectrometer, employing carbon tetrachloride or deuteriochloroform as the solvent with tetramethylsilane or chloroform as the internal standard. Infrared spectra were obtained with a Beckman IR 33, and mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E double-focusing mass spectrometer.

Hexane and triethylamine were distilled from sodium–potassium alloy prior to use. Acid halides were obtained by treatment of the acid with thionyl chloride and redistilled prior to use for best results. The trimethylsilyl enol ethers used in this study were prepared by the procedure of House[4] and were redistilled prior to use. It was most difficult to obtain acceptable elemental analyses on the siloxycyclobutanones due to the ease of hydrolysis. However, the hydrolysis or methanolysis products usually gave acceptable elemental analyses. NMR, IR, and mass spectral data are reported for all the cycloaddition products as well as the hydrolysis or methanolysis products.

Typical Procedure for Ketene Cycloadditions with Trimethylsilyl Enol Ethers. A solution 0.03 mol of fresh distilled acid chloride in 250 mL of dry hexane was added over 4 h to a stirred solution of 0.06 mol of trimethylsilyl enol ether and 0.032 mol of triethylamine in 250 mL of dry hexane under a nitrogen atmosphere. The reaction was stirred for 4 h after the addition was complete. The triethylammonium salt was removed by filtration, and the reaction solution concentrated. The residue was vacuum distilled or isolated by column chromatography on silica gel when possible.[6]

2,2-Dichloro-3-[2-(trimethylsiloxy)ethenyl]cyclobutanone, 2. From 5.88 g (0.04 mol) of dichloroacetyl chloride, 5.68 g (0.04 mol) of silyl enol ether **1**, and 4.3 g (0.043 mol) of triethylamine was isolated 7.16 g (71%) of **2** after distillation at 82–87 °C (0.05 mm). Some hydrolysis of the trimethylsilyl group was evident: IR 1805, 1655, 1390, 1245, 1055, 840 cm^{-1}; NMR δ 6.31 (d, 1 H, J = 12.1 Hz), 4.92 (m, 1 H), 3.2 (m, 3 H), 0.24 (s, 9 H); mass spectrum, m/e (%), 254 (M + 2, 3.0), 252 (4.6), 212 (12.0), 210 (18.2), 142 (33.3), 127 (6.1), 95 (13.6), 93 (36.4), 73 (100).

When 4.9 g (0.027 mol) of trichloroacetyl chloride, 4.97 g (0.035 mol) of trimethylsilyl enol ether **1**, and 6.2 g of zinc were reacted according to a procedure previously described,[2] 5.03 g (74%) of **2** was isolated.

2,2-Dichloro-3-(2,2-dimethoxyethyl)cyclobutanone, 3. From 3.35 g (0.013 mol) of **2** in 20 mL of anhydrous methanol stirred for 8 h was isolated 2.5 g (82%) of the acetal **3** as a clear colorless oil after distillation of 83–85 °C (0.05 mm): IR 1803, 1455, 1390, 1215, 1125, 1060, 790 cm^{-1}; NMR δ 4.41 (t, 1 H), 3.19 (s, 6 H), 3.05 (m, 2 H), 2.2–1.9 (m, 3 H); mass spectrum, m/e (%), 228 (M + 2, 1.0), 226 (1.4), 1.97 (3.6), 1.95 (5.5), 138 (2.7), 136 (3.7), 111 (3.2), 109 (4.5), 75 (59.1), 58 (100), 47 (7.3).

Anal. Calcd for $C_8H_{12}Cl_2O_3$: C, 42.31; H, 5.33. Found: C, 42.09; H, 5.33.

2-Chloro-2-methyl-3-[2-(trimethylsiloxy)ethenyl]cyclobutanone. From 7.1 g (0.05 mol) of silyl enol ether **1**, 3.03 g (0.03 mol) of triethylamine, and 3.18 g (0.025 mol) of 2-chloropropanoyl chloride was isolated 3.83 g (66%) of cycloadduct as a pale yellow oil after distillation at 72–78 °C (0.05 mm). Some hydrolysis to the aldehyde was indicated in the IR and NMR spectra: IR 1792, 1660, 1450, 1255, 1170, 845 cm^{-1}; NMR δ 6.2 (m, 1 H), 4.8 (m, 1 H), 3.1 (m, 3 H), 1.66, 1.52 (s, s, 3 H), 0.18 (s, 9 H); mass spectrum m/e (%), 234 (M + 2, 4.5), 232 (11.4), 192 (12.2), 190 (32.5), 142 (22.8), 127 (27.6), 95 (15.5), 93 (45.5), 73 (100).

2-Chloro-2-methyl-3-(2,2-dimethoxyethyl)cyclobutanone. From 2.55 g (0.011 mol) of the above described cyclobutanone in 15 mL of anhydrous methanol was isolated 1.72 g (76%) of the methanolysis product as a yellow oil after distillation at 71–76 °C (0.05 mm); IR 1795, 1460, 1390, 1135, 1075 cm^{-1}; NMR δ 4.32 (t, 1 H), 3.24 (s, 6 H), 3.05 (m, 2 H), 2.3–1.8 (m, 3 H), 1.65, 1.58 (s, s, 3 H); mass spectrum m/e (%) 208 (M + 2, 0.5), 206 (1.4), 177 (2.2), 175 (7.3), 113 (12.3), 90 (40.6), 75 (85.5), 63 (61.6), 58 (100).

Anal. Calcd for $C_9H_{15}ClO_3$: C, 52.31; H, 7.32. Found: C, 51.93; H, 7.52.

2,2-Dichloro-3-methyl-3-[4-methyl-2-(trimethylsiloxy)-cyclohexenyl]cyclobutanone, 5. From 11.2 g (0.05 mol) of silyl

enol ether 4, 3.54 (0.035 mol) of triethylamine, and 4.41 g (0.03 mol) of dichloroacetyl chloride was isolated 14.7 g of crude reaction product. Column chromatography[6] of 2.1 g of this material gave 0.83 g (58%) of 5 as a pale yellow oil: IR 1808, 1675, 1465, 1265, 835 cm^{-1}; NMR δ 3.92 (d, 1 H, J = 16.8 Hz), 2.77 (d, 1 H, J = 16.8 Hz), 2.3–1.4 (m, 7 H), 1.42 (s, 3 H), 1.12 (d, 2 H), 0.33 (s, 9 H); mass spectrum, m/e (%) 336 (0.2), 334 (0.3), 308 (0.6), 306 (0.8), 281 (3.5), 240 (2.6), 225 (5.3), 187 (3.7), 185 (6.4), 152 (33.3), 143 (31.6), 95 (24.6), 93 (36.8), 73 (100).

2,2-Dichloro-3-(2-oxo-4-methylcyclohexyl)cyclobutanone, 7. Reaction of 0.56 g (0.0017 mol) of 5 with 5 mL of methanol gave a pale yellow oil which solidified on standing. Sublimation gave 0.41 g (91%) of 7 as a white crystalline material: mp 58–60 °C; IR 1805, 1712, 1460, 1388, 995, 775 cm^{-1}; NMR δ 3.08 (br m, 2 H), 2.5–1.5 (m, 8 H), 1.47 (m, 3 H), 1.11 (d, 3 H); mass spectrum, m/e (%) 264 (M + 2, 0.8), 262 (1.3), 211 (0.6) 209 (1.6), 187 (2.5), 185 (7.1), 152 (26.7), 112 (19.3), 109 (23.3), 81 (64.2), 57 (100).

Anal. Calcd for $C_{12}H_{16}Cl_2O_2$: C, 54.77; H, 6.13. Found: C, 54.82; H, 6.21.

2-Chloro-2,3-dimethyl-3-[4-methyl-2-(trimethylsiloxy)-cyclohexenyl]cyclobutanone, 6. From 11.4 g (0.051 mol) of silyl enol ether 4, 3.81 g (0.03 mol) of 2-chloropropanoyl chloride, and 3.23 g (0.032 mol) of triethylamine was isolated 13.3 g of crude reaction mixture. Column chromatography on silica gel[6] of 2.7 g gave 0.94 g (49%) of 6 as a mixture of two isomers in a ratio of 1.7:1: IR 1787, 1670, 1455, 1240, 1110, 810 cm^{-1}; NMR δ (Z isomer) 3.95, (d, 1 H, J = 16.3 Hz): (E isomer) 3.84 (d, 1 H, J = 16.3 Hz); (both isomers) 2.6 (m, 1 H), 1.62 (m, 3 H), 1.37 (m, 3 H), 1.11 (m, 3 H), 0.31 (s, 9 H); mass spectrum m/e (%) 316 (M + 2, 0.2), 314 (0.5), 225 (2.4), 171 (1.2), 169 (4.0), 152 (31.3), 138 (33.7), 112 (28.2), 109 (28.6), 81 (100), 73 (53.4).

2-Chloro-2,3-dimethyl-3-(2-oxo-4-methylcyclohexyl)-cyclobutanone. Column chromatography (0.0016 mol) of 6 gave 0.26 g (67%) of the ketone as a pale yellow oil which slowly darkened upon standing at room temperature: IR 1798, 1715, 1455, 1385, 1090 cm^{-1}; NMR δ 2.9 (br m, 2 H), 2.6–1.6 (m, 11 H), 1.4 (m, 3 H), 1.1 (m, 3 H); mass spectrum, m/e (%) 244 (M + 2, 1.5), 242 (2.7), 207 (1.6), 1.65 (12.3), 152 (34.8), 138 (39.1), 112 (30.4), 109 (34.8), 95 (82.6), 81 (100), 69 (60.9).

Anal. Calcd for $C_{13}H_{19}ClO_2$: C, 64.32; H, 5.01. Found: C, 64.66; H, 7.91.

7,7-Dichloro-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one, 9. From 6.16 g (0.04 mol) of 8, 5.05 g (0.05 mol) of triethylamine, and 6.62 g (0.045 mol) of dichloroacetyl chloride was isolated 9.22 g (87%) of a mixture of 9 and 10 in a ratio of 4:1. Chromatography on silica gel of 2.1 g of the mixture yielded 1.51 g of cyclobutanone 9: IR 1805, 1618, 1450, 1238, 1169, 1080, 900 cm^{-1}; NMR δ 6.1 (m, 1 H), 5.84 (m, 1 H), 3.8 (t, 1 H), 2.75 (m, 2 H), 0.29 (s, 9 H); mass spectrum, m/e (%) 266 (M + 2, 4.0), 264 (6.0), 251 (1.6), 249 (2.4), 203 (13.5), 201 (34.1), 187 (8.0), 185 (23.0), 154 (42.9), 139 (64.0), 114 (8.0), 112 (24.6), 95 (10.3), 93 (50.8), 73 (100).

Anal. Calcd for $C_{10}H_{14}Cl_2O_2Si$: C, 45.29; H, 5.32. Found: C, 45.61; H, 5.44.

5-[2,2-Dichloro-1-(trimethylsiloxy)ethenyl]cyclopent-2-enone, 10. The minor product observed in the reaction of dichloroketene and 8 was determined to be 10: IR 1728, 1640, 1445, 1265, 845 cm^{-1}; NMR δ 7.4 (m, 1 H), 6.9 (m, 1 H), 4.5 (m, 1 H), 2.7 (m, 2 H), 0.21 (s, 9 H); GC/MS m/e (%) 266 (M + 2, 19.0), 264 (26.5), 231 (4.1), 229 (11.6), 203 (14.5), 201 (31.4), 187 (17.4), 185 (48.8), 155 (40.5), 139 (46.3), 111 (24.0), 75 (62.0), 73 (100).

5-(2,2-Dichloroacetyl)cyclopent-2-enone, 11. Chromatography on silica gel of 2.1 g of the mixture of 9 and 10 gave 0.36 g (86%) of 11 as a white crystalline solid, mp 81–82 °C, along with 1.54 g of 9. Dione 11: IR 1735, 1688, 1610, 1412, 1390, 810 cm^{-1}; NMR δ 7.2 (m, 1 H), 6.4 (m, 1 H), 5.97 (s, 1 H), 4.2 (m, 1 H), 3.4 (m, 2 H); mass spectrum, m/e (%) 192 (M + 2, 5.1), 192 (8.2), 131 (2.0), 129 (6.1), 109 (100), 81 (62.2), 58 (13.3).

7-Chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one. From 6.18 g of 8, 4.55 g (0.045 mol) of triethylamine, and 5.08 g (0.04 mol) of 2-chloropropanoyl chloride was isolated 8.03 g (82%) of a clear colorless oil after distillation at 61–66 °C (0.05 mm) with an isomer distribution of 1.2 (*endo*-methyl/*exo*-methyl). An analytical sample was prepared by silica gel chromatography: IR 1795, 1623, 1453, 1352, 1255, 1238, 850 cm^{-1}; NMR δ (*endo*-methyl isomer) 3.48 (t, 1 H), 1.47 (s, 3 H; (*exo*-methyl isomer) 3.81 (t, 1 H), 1.69 (s, 3 H); (both isomers) 5.8 (m, 2 H), 2.57 (m, 2 H), 0.16 (s, 9 H); mass spectrum, m/e (%) 246 (M + 2, 1.4), 244 (2.7), 231 (1.0), 229 (1.4), 181 (57.7), 165 (28.8), 154 (65.8), 91 (20.7), 73 (100).

Anal. Calcd for $C_{11}H_{17}ClO_2Si$: C, 53.97; H, 700. Found: C, 54.13; H, 7.19.

7-Chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-2-en-6-one. Methanolysis of 2.6 g (0.011 mol) of the above described cyclobutanone gave 1.43 g (78%) of the corresponding hydroxy compound after distillation at 55–60 °C (0.05 mm) with an isomer distribution of 1.2 (*endo*-methyl/*exo*-methyl): IR 3600–3300, 1790, 1620, 1445, 1348, 1210, 1145, 845 cm^{-1}; NMR δ (*endo*-methyl isomer) 3.51 (t, 1 H), 1.47 (s, 3 H); (*exo*-methyl isomer) 3.81 (t, 1 H), 1.68 (s, 3 H); (both isomers) 5.8 (m, 2 H), 5.25 (s, 1 H, OH), 2.5 (m, 2 H); mass spectrum, m/e (%) 174 (M + 2, 1.7), 172 (5.6), 109 (100), 91 (31.5), 82 (79.8), 81 (37.6), 63 (29.3), 55 (50.6).

Anal. Calcd for $C_8H_9ClO_2$: C, 55.67; H, 5.26. Found: C, 55.91; H, 5.53.

8,8-Dichloro-1-(trimethylsiloxy)bicyclo[4.2.0]oct-2-en-7-one, 12. From 6.72 g (0.04 mol) of the silyl enol ether from 2-cyclohexenone, 7.4 g (0.05 mol) of dichloroacetyl chloride, and 6.1 g (0.06 mol) of triethylamine was isolated 7.45 g (68%) of a yellow oil after distillation at 82–88 °C (0.05 mm). The NMR indicated two products in a 3:1 ratio. The minor isomer was determined to be 13. Major isomer 12: IR 1802, 1635; NMR δ 6.1 (m, 2 H), 3.95 (m, 1 H), 2.6 (m, 2 H), 1.9 (m, 2 H), 0.28 (s, 9 H); GC/MS m/e (%) 280 (M + 2, 1.9), 278 (2.7), 263 (1.6), 217 (2.2), 215 (3.5), 168 (19.1), 151 (12.7), 123 (20.6), 95 (23.8), 93 (28.6), 73 (100).

6-[2,2-Dichloro-1-(trimethylsiloxy)ethenyl]cyclohex-2-enone, 13. Prolonged heating at 120 °C of the mixture of 12 and 13 isolated previously gave 13 and some polymeric material: IR 1680, 1645; NMR δ 6.9 (m, 1 H), 5.5 (m, 1 H), 3.6 (m, 1 H), 2.3-1.6 (m, 4 H), 0.13 (s, 9 H); GC/MS, m/e (%) 280 (M + 2, 2.2), 278 (3.3), 245 (2.7), 243 (7.9), 169 (12.8), 168 (16.9), 151 (6.3), 96 (19.6), 73 (100).

6-(2,2-Dichloroacetyl)cyclohex-2-enone. Column chromatography of 1.4 g (0.005 mol) of a mixture of 12 and 13 resulted in hydrolysis to the dione. Recovered was 0.7 g (67%) of an oil which darkened upon standing at room temperature: IR 1730, 1625, 1450, 1390, 810 cm^{-1}; NMR δ 13.6 (br s, 1 H), 6.8 (m, 1 H), 6.1 (m, 1 H), 5.96 (s, 1 H), 2.6–1.7 (m, 4 H); mass spectrum, m/e (%) 208 (M + 2, 0.6), 206 (0.9), 173 (0.7), 171 (2.3), 123 (79.3), 79 (17.8), 68 (43.7), 55 (100).

Anal. Calcd for $C_8H_8Cl_2O_2$: C, 46.41; H, 3.59. Found: C, 46.52; H, 4.02.

8-Chloro-8-methyl-1-(trimethylsiloxy)bicyclo[4.2.0]oct-2-en-7-one, 14. From 8.4 g (0.05 mol) of silyl enol ether from 2-cyclohexenone, 3.54 g (0.035 mol) of triethylamine, and 3.81 g (0.03 mol) of 2-chloropropanoyl chloride was isolated 7.74 g of crude product after distillation at 76–83 °C (0.05 mm). Column chromatography of 2.1 g gave 1.53 g (73%) of 14 as a mixture of isomers with a isomer distribution of 1.5 (*endo*-methyl/*exo*-methyl) based upon integration of the NMR spectrum: IR 1795, 1645, 1455, 1265, 1155, 848 cm^{-1}; NMR δ (*exo*-methyl isomer) 3.9 (m, 1 H), 1.69 (s, 3 H); (*endo*-methyl isomer) 3.5 (m, 1 H), 1.48 (s, 3 H); (both isomers) 6.1 (m, 2 H), 2.6–1.7 (m, 4 H), 0.29 (s, 9 H); mass spectrum, m/e (%) 260 (M + 2, 4.2), 258 (11.8), 245 (1.2), 243 (3.5), 222 (14.4), 195 (25.0), 168 (100), 153 (5.6), 151 (14.6), 123 (13.9), 105 (12.5), 73 (68.1).

6-(2-Chloropropanoyl)cyclohex-2-enone, 15. Hydrolysis of 1.1 g (0.0043 mol) of 14 with methanol gave 0.47 g (59%) of 15 as a pale yellow oil which rapidly darkened after distillation at 68–71 °C (0.05 mm); IR 3600–3300, 1745, 1680, 1625, 1405, 1230, 1060 cm^{-1}; NMR δ 15.4 (br s, 1 H), 6.7 (m, 1 H), 5.8 (m, 1 H), 4.55 (q, 1 H), 2.5–1.8 (m, 4 H), 1.45 (d, 3 H); mass spectrum, m/e (%) 188 (M + 2, 3.9), 186 (10.7), 151 (5.6), 150 (7.1), 123 (100), 95 (39.7), 67 (19.2), 55 (21.4).

Anal. Calcd for $C_9H_{11}Cl_1O_2$: C, 62.71; H, 5.26. Found: C, 62.58; H, 5.11.

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Registry No. 1, 6651-43-0; 2, 76430-25-6; 3, 76430-26-7; 4, 76430-27-8; 5, 76430-28-9; 6, 76446-94-1; 7, 76430-29-0; 8, 63559-16-0; 9, 76430-30-3; 10, 76430-31-4; 11, 76430-32-5; 12, 76430-33-6; 13, 76430-34-7; 14 (isomer 1), 76430-35-8; 14 (isomer 2), 76496-33-8; 15, 76430-36-9; dichloroacetyl chloride, 79-36-7; methanol, 67-56-1; 2-chloro-2-methyl-3-[2-(trimethylsiloxy)ethenyl]cyclobutanone, 76430-37-0; 2-chloropropanoyl chloride, 7623-09-8; 2-chloro-2-methyl-3-(2,2-dimethoxyethyl)cyclobutanone, 76430-38-1; 2-chloro-2,3-dimethyl-3-(2-oxo-4-methylcyclohexyl)cyclobutanone, 76430-39-2; 7-chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one (isomer 1), 76430-40-5; 7-chloro-7-methyl-1-(trimethylsiloxy)bicyclo[3.2.0]hept-2-en-6-one (isomer 2), 76496-34-9; 7-chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (isomer 1), 76430-41-6; 7-chloro-1-hydroxy-7-methylbicyclo[3.2.0]hept-2-en-6-one (isomer 2), 76496-35-0; 2-cyclohexenone silyl enol ether, 54781-19-0; 6-(2,2-dichloroacetyl)cyclohex-2-enone, 76430-42-7.

Generation of Bicyclo[4.1.0]heptatrienes

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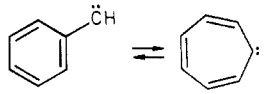
Derivatives of bicyclo[4.1.0]heptatriene have been generated in solution by the base-induced dehydrochlorination of *gem*-dichlorocyclopropanes. Reaction of 7,7-dichlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane with potassium *tert*-butoxide in tetrahydrofuran at 0 °C gives mainly products derived from solvent incorporation by carbene insertion. Evidence that the carbene results from rearrangement of the bicycloheptatriene derives from the successful interception of the bicycloheptatriene with nucleophile (MeS^-). *endo*-7-Chlorodibenzo[*a*,*c*]bicyclo[4.1.0]heptane failed to react with potassium *tert*-butoxide in tetrahydrofuran. Generation of benzobicyclo[4.1.0]heptatrienes was also accomplished via the base-induced dehydrochlorination of *gem*-dichlorocyclopropanes. 1-Methylbenzobicyclo[4.1.0]heptatriene gives products derived from multiple carbene–carbene rearrangements. In contrast, nonannelated methylbicycloheptatrienes generated by the dehydrochlorination route give only carbene-derived products resulting from the initially produced bicycloheptatriene.

The interconversion of phenyl carbene and its derivatives with bicycloheptatrienylidenes (eq 1) was first pos-



(1)

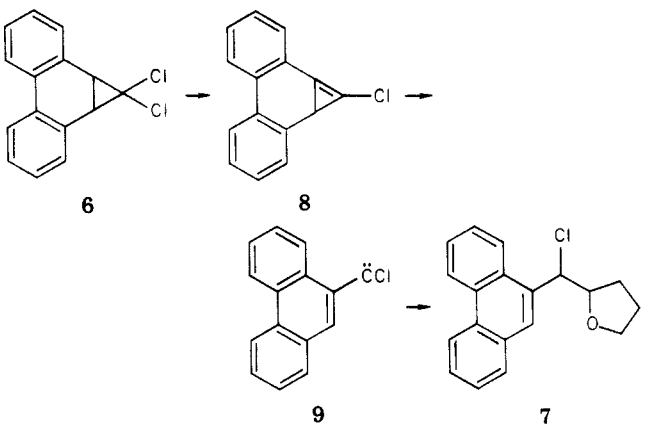
tulated by Shechter and Vander Stouw[1,2] to account for the formation of styrene in the gas-phase pyrolysis of *o*-tolylidiazomethane. On the basis of analogy with the well-known interconversion of vinylcarbene and cyclopropene,[2b] these workers suggested that the rearrangement depicted in eq 1 probably proceeds via bicyclo[4.1.0]heptatriene (1) as a reactive intermediate. Although other

1

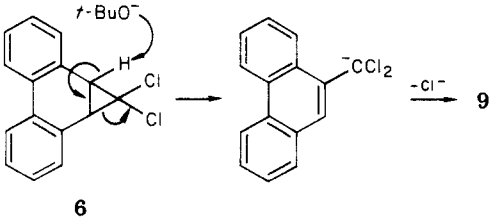
intermediates have been considered,[2-12] only 1 seems to be consistent with all of the experimental observations.

The discrete existence of bicyclo[4.1.0]heptatrienes 2 and 3 as intermediates in solution was established by their

Scheme I



Scheme II



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