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(27) The standard deviation of this average calculates as ±0.017 Å when based upon the deviation of the individual observations from the average or ±0.005 Å when based on the standard deviations of the individual observations. Since the two observations differ by greater than twice the lower of these values (0.005 Å), the standard deviations of the individual observations must be slightly underestimated and the standard deviation of the average value probably lies somewhere between 0.006 and 0.017 Å.

γ-Alkylation of α,β-Unsaturated Carbonyl Compounds

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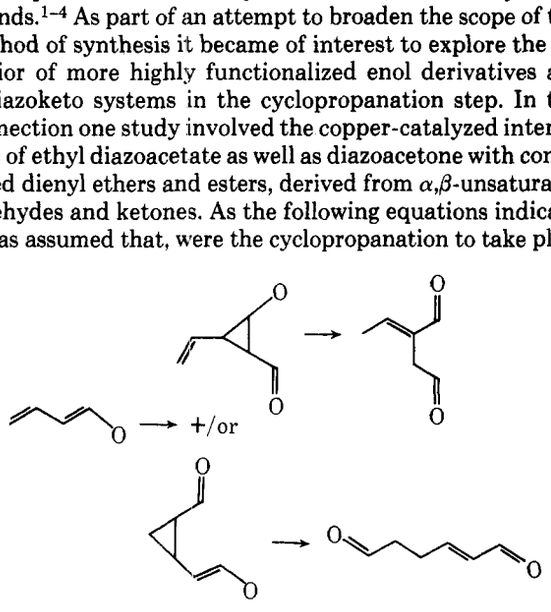
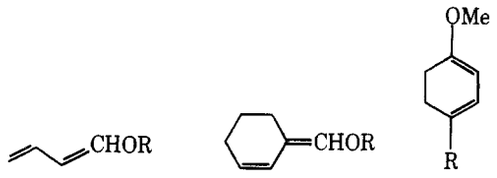
The copper-catalyzed reactions of ethyl diazoacetate and diazoacetone with the dienol derivatives 1-methoxy- and 1-trimethylsilyloxy-1,3-butadiene, 3-acetoxymethylene- and 3-trimethylsilyloxymethylenecyclohexene, and 1-methoxy-1,3-cyclohexadiene and its 4-methyl analogue are described. Hydrolysis of the olefinic cyclopropane adducts is shown to lead to α- and γ-alkylated α,β-unsaturated aldehydes and ketones.

The simple, three-step scheme of conversion of aldehydes or ketones into enol ethers or esters, cyclopropanation of these olefinic intermediates with α-diazocarbonyl reagents over copper, and aqueous acid cleavage of the resultant β-oxycyclopropylketo compounds has been shown to be the equivalent of α-alkylation of aldehydo and keto substances as well as a useful procedure for the synthesis of 1,4-dicarbonyl compounds.[1-4] As part of an attempt to broaden the scope of this method of synthesis it became of interest to explore the behavior of more highly functionalized enol derivatives and α-diazoketo systems in the cyclopropanation step. In this connection one study involved the copper-catalyzed interaction of ethyl diazoacetate as well as diazoacetone with conjugated dienyl ethers and esters, derived from α,β-unsaturated aldehydes and ketones. As the following equations indicate, it was assumed that, were the cyclopropanation to take place



on the unoxygenated double bond, the new three-step scheme would be the equivalent of a γ-alkylation of α,β-unsaturated keto systems,[5] leading to 1,6-dicarbonyl compounds.[6]

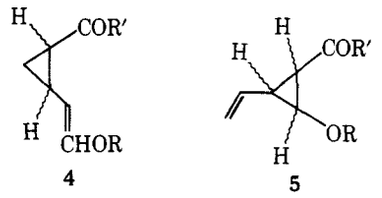
The crotonaldehyde-based dienyl ethers 1-methoxy-1,3-butadiene (**1a**) and 1-trimethylsilyloxy-1,3-butadiene (**1b**),[7,8] the enol acetate and trimethylsilyl ether from 1-cyclohexenecarboxaldehyde[9] (**2a** and **2b**, respectively), and the 1-methoxy-1,3-cyclohexadienes[10] **3a** and **3b** served as starting materials for this investigation. Diene **2a** was prepared by the acid-induced acetylation of 1-cyclohexenecarboxaldehyde with isopropenyl acetate, while diene **2b** was the result of the



1a, R = Me; **b**, R = $SiMe_3$ **2a**, R = Ac; **b**, R = $SiMe_3$ **3a**, R = H; **b**, R = Me

O-alkylation of the aldehyde with trimethylsilyl chloride in the presence of triethylamine.[7,11]

The decomposition of ethyl diazoacetate in cyclohexane or neat solutions of each of the six dienes over copper bronze at 65–85 °C led to 55–80% yields of stereo- and regioisomer mixtures of olefinic cyclopropanecarboxylates, i.e., **1a → 4a + 5a, 1b → 4b + 5b, 2a → 6a + 7a, 2b → 6b + 7b, 3a → 8a + 9a,** and **3b → 8b + 9b.** With the exception of the silyl ethers

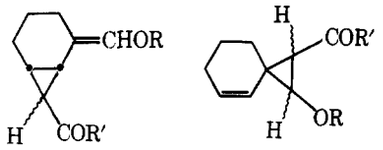


4 **5**

a, R = Me; R′ = OEt
b, R = $SiMe_3$; R′ = OEt
c, R = R′ = Me
d, R = $SiMe_3$; R′ = Me

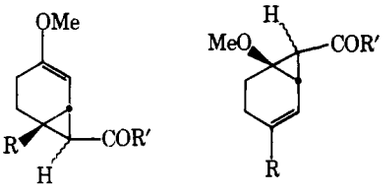
the regioisomers were separated into stereoisomer mixtures, no attempt having been made to fractionate the latter. Interaction of diazoacetone with each of the starting dienes under conditions similar to those of the diazoacetic ester reactions produced difficultly separable isomer mixtures of the ketone pairs **4c–5c, 4d–5d, 6c–7c, 6d–7d, 8c–9c,** and **8d–9d,** respectively.

Mild treatment of cyclopropane **4a** with aqueous acid caused the hydrolysis of its enol ether moiety leading to the aldehydo ester **10,** whereas oxycyclopropane **5a** remains un-



6 7

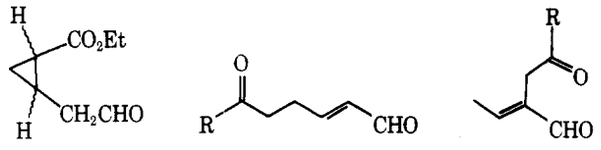
a, R = Ac; R′ = OEt
b, R = $SiMe_3$; R′ = OEt
c, R = Ac; R′ = Me
d, R = $SiMe_3$; R′ = Me



8 9

a, R = H; R′ = OEt
b, R = Me; R′ = OEt
c, R = H; R′ = Me
d, R = R′ = Me

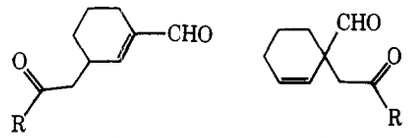
perturbed under these conditions. Hydrolyses of **4a** and **5a** at elevated temperature produced the acyclic substances **11a** and **12a**, respectively.[12] The same products result from the hydrolysis of the silyl ether mixture, **4b** and **5b**, on heating. Finally, mild, aqueous acid hydrolysis of either the ketone mixture **4c** and **5c** or the **4d–5d** mixture led to keto aldehydes **11b** and **12b**.



10 11 12

a, R = OEt
b, R = Me

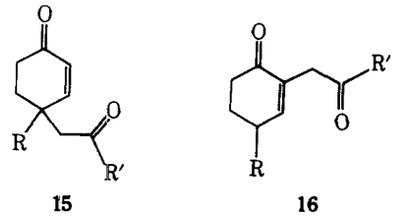
Cyclopropanes **6** and **7** were hydrolyzable in both acid and base. Cleavage of the three-membered rings of **6a** and **6b** with alcoholic base yielded ester **13a**, while **7a** and **7b** gave ester **14a**. Similarly, compounds **6c** and **6d** produced aldehydo ketone **13b**, while **7c** and **7d** led to **14b**.



13 14

a, R = OEt
b, R = Me

Acid hydrolysis of esters **8a**, **8b**, **9a**, and **9b** afforded cyclohexenone esters **15a**, **15b**, **16a**, and **16b**, respectively.



15 16

a, R = H; R′ = OEt
b, R = Me; R′ = OEt
c, R = H; R′ = Me
d, R = R′ = Me

Similar treatment of ketones **8c**, **8d**, **9c**, and **9d** produced diketones **15c**, **15d**, **16c**, and **16d** (in addition to its β,γ-unsaturated ketone isomer).

The isolation of 1,6-diketo compounds **11**, **13**, and **15** at the end of a two-step reaction scheme emanating from masked α,β-unsaturated keto systems makes the procedure a new γ-alkylation method. Furthermore, the ratios of cyclopropanation products (50–90% total yields) favoring nonoxygenated cyclopropanes (2:1 to 5:1) in most instances and the 1,6-diketo substances being the more preponderant, final products, irrespective of the O substituent of the initial conjugated diene, bodes well for this γ-alkylation concept. More work will be necessary to improve the regioselectivity of the cyclopropanation process.

Experimental Section

Boiling and melting points are uncorrected. Infrared spectra of neat liquids were recorded on a Perkin-Elmer 167 spectrophotometer and mass spectra obtained on a CEC 21-110 spectrometer. ^1H NMR spectra were run on $CDCl_3$ solutions with Me_4Si as internal standard (δ 0 ppm) on a Varian A-60 spectrometer and the ^{13}C NMR spectrum was recorded on a Varian XL-100-15 spectrometer operating at 25.02 MHz in the Fourier transform mode. GPC runs were performed on a 10-ft 20% Carbowax on Chromosorb W column in a Varian Autoprep A-700 chromatograph, while preparative TLC utilized Merck silica gel HF 254 as adsorbant.

3-Acetoxymethylenecyclohexene (2a). A stirring solution of 1.52 g of 1-cyclohexenecarboxaldehyde[9] [^1H NMR δ 1.65 (m, 4, methylenes), 2.21 (m, 4, allyl methylenes), 6.66 (m, 1, olefinic H), 9.35 (s, 1, CHO); ^{13}C NMR ($CDCl_3$) δ 21.06 (C-4, C-5), 21.78 (C-6), 26.19 (C-3), 141.12 (C-1), 150.95 (C-2), 193.72 (CO)] and 19 mg of *p*-toluenesulfonic acid in 12 mL of isopropenyl acetate was refluxed under nitrogen with slow removal of the solvent for 5.5 h. Fractional, vacuum distillation yielded 2.09 g of colorless, liquid diene **2a**: bp 55–58 °C (1.25 Torr); IR C=O 1752 cm^{-1} (s); ^1H NMR δ 1.61 (m, 2, CH_2), 2.06, 2.39 (m, 2 each, allyl methylenes), 2.12 (s, 3, Me) 5.68 (dt, 1, *J* = 10, 3 Hz, H-1), 5.93 (dt, 1, *J* = 10, 1 Hz, H-2), 6.92 (broad s, 1, OCH); mass spectrum *m/e* 152 (M^+), 110 (base), 95, 81, 79; exact mass *m/e* 152.0842 (calcd for $C_9H_{12}O_2$, 152.0836).

3-Trimethylsilyloxymethylenecyclohexene (2b). A stirring solution of 1.78 g of 1-cyclohexenecarboxaldehyde,[9] 2.71 g of trimethylsilyl chloride, and 3.28 g of triethylamine in 7 mL of dimethylformamide was refluxed under nitrogen for 21 h. After cooling the brown solution was diluted with 50 mL of hexane, washed with 30 mL of 5% sodium bicarbonate solution, 30 mL of water, and 30 mL of saturated brine solution, and dried (Na_2SO_4). Upon removal of the solvent the liquid was distilled, yielding 1.73 g of liquid diene **2b**: bp 33–34 °C (0.25 Torr); IR C=C 1643 (m), 1609 cm^{-1} (m); ^1H NMR δ 0.19 (s, 9 Me_3), 1.56 (m, 2, CH_2), 2.04, 2.35 (m, 2 each, allyl methylenes), 5.48 (dt, 1, *J* = 10, 4 Hz, H-1), 5.98 (dt, 1, *J* = 10, 2 Hz, H-2), 6.12 (broad s, 1, OCH); mass spectrum *m/e* 182 (M^+), 167, 93, 92, 75, 73 (base); exact mass *m/e* 182.1132 (calcd for $C_{10}H_{18}OSi$, 182.1126).

1-Dimethoxymethylcyclohexene. A stirring mixture of 1.20 g of 1-cyclohexenecarboxaldehyde,[9] 0.60 g of Amberlite IR-120-H ion exchange resin (medium porosity, washed three times with methanol), and 5 mL of trimethyl orthoformate in 5 mL of methanol was refluxed under nitrogen for 5 h. Sodium sulfate was added and the cooled mixture filtered through Celite and evaporated. An ether solution (50 mL) of the residue was washed with 100 mL of 5% sodium bicarbonate solution and 50 mL of brine solution, dried (Na_2SO_4), and evaporated. Distillation (0.2 Torr, bath temperature 31 °C) of the residue (1.45 g) on a Vigreux column (1.7 × 13 mm) yielded 1.21 g of colorless, liquid 1-cyclohexenecarboxaldehyde dimethyl acetal: ^1H NMR δ 1.58 (m, 4, methylenes), 1.96 (m, 4, allyl methylenes), 3.23 [s, 6, $(OMe)_2$], 4.40 (s, 1, O_2CH), 5.75 (broad s, 1, olefinic H); mass spectrum *m/e* 156 (M^+), 128 (base), 94, 78; exact mass *m/e* 156.1146 (calcd for $C_9H_{16}O_2$, 156.1149).

Ethyl 2-(β-Methoxyvinyl)cyclopropanecarboxylate (4a) and Ethyl 2-Methoxy-3-vinylcyclopropanecarboxylate (5a). All cyclopropanations followed an earlier procedure.[1,2] Ethyl diazoacetate (3.15 g) was added dropwise over a 4-h period to a stirring suspension of 300 mg of copper bronze[13] and 2.10 g of 1-methoxy-1,3-butadiene (**1a**) in 10 mL of cyclohexane kept at 80 °C under nitrogen. Thereafter the mixture was stirred at 80 °C for an additional 0.5 h and filtered. The catalyst was washed with 15 mL of ether and the combined filtrate and washings evaporated. Distillation of the residue gave 2.60

g of an ester mixture, bp 50–55 °C (0.1 Torr), which was separated by GPC (column temperature 120 °C) and led to two fractions of 10 and 20 min retention times. The first fraction consisted of 350 mg of **5a:** IR C=O 1730 (s), C=C 1640 cm^{-1} (m); ^1H NMR δ 1.25 (t, 3, J = 7 Hz, Me), 1.7–2.6 (m, 2, c-Pr H), 3.31 (s, 3, OMe), 3.4–3.6 (m, 1, OCH), 4.18 (q, 2, J = 7 Hz, OCH_2), 4.8–6.0 (m, 3, olefinic H); mass spectrum m/e 170 (M^+), 169, 131, 119, 97 (base), 69; exact mass m/e 170.0942 (calcd for $C_9H_{14}O_3$, 170.0943).

The second fraction contained 1.60 g of **4a:** IR C=O 1730 (s), C=C 1670 (s), 1655 cm^{-1} (s); ^1H NMR δ 0.7–2.1 (m, 4, c-Pr H), 1.22 (t, 3, J = 7 Hz, Me), 3.45, 3.59 (s, 3 total, OMe), 4.12 (q, 2, J = 7 Hz, OCH_2), 4.4–4.9 (m, 1, olefinic H), 6.41 (dd, 1, J = 13, 3 Hz, OCH); mass spectrum m/e 170 (M^+), 169, 131, 119, 97 (base), 69; exact mass m/e 170.0943 (calcd for $C_9H_{14}O_3$, 170.0943).

Ethyl 2-(β-Trimethylsilyloxyvinyl)cyclopropanecarboxylate (4b) and Ethyl 2-Trimethylsilyloxy-3-vinylcyclopropanecarboxylate (5b). A mixture of 2.25 g of ethyl diazoacetate, 500 mg of copper bronze, and 4.70 g of 1-trimethylsilyloxy-1,3-butadiene (**1b**) was treated and worked up as above. Distillation of the crude product yielded 3.00 g of starting diene (**1b**) and 2.80 g of a mixture of **4b** and **5b:** bp 57–62 °C (0.25 Torr); IR C=O 1730 (s), C=C 1695 (m), 1655 cm^{-1} (m); ^1H NMR δ 0.19 (s, 9, $SiMe_3$), 1.24, 1.29 (t, 3 total, J = 7 Hz, Me), 0.7–2.4 (m, 3–4, c-Pr H), 4.08, 4.13 (q, 2, J = 7 Hz, OCH_2), 4.3–6.5 (m, 2–3, olefinic H); exact mass m/e 228.1185 (calcd for $C_{11}H_{20}O_3Si$, 228.1181).

Ethyl 2-Acetoxymethylenebicyclo[4.1.0]heptane-7-carboxylate (6a) and Ethyl 2-Acetoxyspiro[2.5]oct-4-ene-1-carboxylate (7a). A mixture of 6.31 g of ethyl diazoacetate, 970 mg of copper bronze, and 4.27 g of dienol acetate **2a** in 20 mL of cyclohexane was treated and worked up as above. Distillation of the crude product yielded 4.76 g of a mixture of **6a** and **7a** (3.5:1 ratio by ^1H NMR spectral integration of the olefinic H peaks), bp 125–145 °C (0.35 Torr), and 751 mg of a mixture, bp >145 °C (0.5 Torr), predominating in the biscyclopropanation product: IR C=O 1760–1700 cm^{-1} (s); ^1H NMR δ 1.24 (t, 6, J = 7 Hz, Me_2), 2.03 (s, 3, COMe), 3.8–4.3 [m, 4, $(OCH_2)_2$], 4.48 (d, <1, J = 4 Hz, OCH); mass spectrum m/e 324 (M^+), 282, 238, 207, 196, 167, 123, 122, 121, 43 (base); exact mass m/e 324.1558 (calcd for $C_{17}H_{24}O_6$; 324.1571).

GPC of the ester mixture (**6a** and **7a**) on a 10-ft column of 10% SE-30 on Chromosorb W at 195 °C yielded **6a** [IR C=O 1720 (s), 1750 (s), C=C 1660 cm^{-1} (m); ^1H NMR δ 1.22 (t, 3, J = 7 Hz, Me), 2.08 (s, 3, COMe), 4.06 (dd, 2, J = 7 Hz, OCH_2), 6.96 (t, 1, J = 2 Hz, olefinic H); mass spectrum m/e 238 (M^+), 196 (base), 167, 150, 123, 122, 121; exact mass m/e 238.1217 (calcd for $C_{13}H_{18}O_4$, 238.1205)] and **7a** (1.2:1 mixture of trans and cis isomers, respectively) [IR C=O 1725 (s), 1755 (s), C=C 1640 cm^{-1} (m); ^1H NMR δ 1.23 (t, 6, Me_2), 2.05 (s, 3, trans COMe), 2.07 (s, 3, cis COMe), 4.02 (q, 2, J = 7 Hz, cis OCH_2), 4.06 (q, 2, J = 7 Hz, trans OCH_2), 4.45 (d, 1, J = 4 Hz, trans OCH), 4.84 (dt, 1, J = 10, 2 Hz, cis OCH), 5.3–6.2 (m, 4, olefinic H); mass spectrum m/e 238 (M^+), 196, 192, 178, 167, 151, 139, 123, 122, 121, 43 (base); exact mass m/e 238.1210 (calcd for $C_{13}H_{18}O_4$, 238.1205).

Ethyl 2-Trimethylsilyloxymethylenebicyclo[4.1.0]heptane-7-carboxylate (6b) and Ethyl 2-Trimethylsilyloxyspiro[2.5]-oct-4-ene-1-carboxylate (7b). A mixture of 1.36 g of ethyl diazoacetate, 215 mg of copper bronze, and 1.12 g of dienol ether **2b** in 10 mL of cyclohexane was treated (2 h) and worked up as above. Distillation of the crude product [bp 83–100 °C (0.1 Torr)] yielded a 2.7:1 mixture of **6b** and **7b,** respectively: IR C=O 1722 (s), C=C 1655 cm^{-1} (m); ^1H NMR δ 0.18 (s, 9, $SiMe_3$), 1.23 (t, 3, J = 7 Hz, Me), 4.04 (q, 2, J = 7 Hz, OCH_2), 5.3–5.9 (m, <2, olefinic H), 6.18 (t, <1, J = 2 Hz, OCH of **6b**); exact mass m/e 268.1502 (calcd for $C_{14}H_{24}O_3Si$, 268.1494).

Ethyl 3-Methoxybicyclo[4.1.0]hept-2-ene-7-carboxylate (8a) and Ethyl 1-Methoxybicyclo[4.1.0]hept-4-ene-7-carboxylate (9a). A mixture of 2.28 g of ethyl diazoacetate, 500 mg of copper bronze, and 4.40 g of dienol ether **3a** was treated (3 h) and worked up as above. Distillation of the crude product gave 2.10 g of starting diene (**3a**) and 2.80 g of a mixture of **8a** and **9a,** bp 85 °C (0.5 Torr). Preparative TLC of the latter and elution with 4:1 hexane–ether yielded 1.70 g of **9a** [IR C=O 1730 (s), C=C 1650 cm^{-1} (m); ^1H NMR δ 1.25 (t, 3, J = 7 Hz, Me), 1.5–2.8 [m, 6, $(CH_2)_2$, $(CH)_2$], 3.29, 3.32 (s, 3 total, OMe), 4.15 (q, 2, J = 7 Hz, OCH_2), 5.4–6.1 (m, 2, olefinic H); mass spectrum m/e 196 (M^+), 123 (base), 91; exact mass m/e 196.1104 (calcd for $C_{11}H_{16}O_3$, 196.1099)] and 700 mg of **8a** [IR C=O 1725 (s), C=C 1658 cm^{-1} (m); ^1H NMR δ 0.8–2.5 [m, 7, $(CH_2)_2$, $(CH)_3$], 1.26 (t, 3, J = 7 Hz, Me), 3.48 (s, 3, OMe), 4.13 (q, 2, J = 7 Hz, OCH_2), 4.8–5.0 (m, 1, olefinic H); mass spectrum m/e 196 (M^+), 131, 119 (base); exact mass m/e 196.1103 (calcd for $C_{11}H_{16}O_3$, 196.1099)].

Ethyl 3-Methoxy-6-methylbicyclo[4.1.0]hept-2-ene-7-carboxylate (8b) and Ethyl 6-Methoxy-3-methylbicyclo[4.1.0]-hept-2-ene-7-carboxylate (9b). A mixture of 3.30 g of ethyl diazoacetate, 500 mg of copper bronze, and 6.30 g of dienol ether **3b** was treated and worked up as above. Distillation of the crude product gave 3.50 g of starting diene (**3b**) and 3.70 g of a mixture of **8b** and **9b,** bp 83–90 °C (0.4 Torr). Preparative TLC of the latter and elution with 3:1 hexane–ether led to 1.32 g of **9b** [IR C=O 1730 cm^{-1} (s); ^1H NMR δ 1.26 (t, 3, J = 7 Hz, Me of Et), 1.61 (d, 3, J = 1 Hz, olefinic Me), 1.7–2.4 [m, 6, $(CH_2)_2$, $(CH)_2$], 3.27 (s, 3, OMe), 4.13 (q, 2, J = 7 Hz, OCH_2), 5.63 (dd, 1, J = 5, 1 Hz, olefinic H); mass spectrum m/e 210 (M^+), 137 (base), 124, 105; exact mass m/e 210.1256 (calcd for $C_{12}H_{18}O_3$, 210.1256)] and 310 mg of **8b** [IR C=O 1725 (s), C=C 1658 cm^{-1} (m); ^1H NMR δ 1.25 (t, 3, J = 7 Hz, Me of Et), 1.30 (s, 3, Me), 1.5–2.5 [m, 6, $(CH_2)_2$, $(CH)_2$], 3.47 (s, 3, OMe), 4.12 (q, 2, J = 7 Hz, OCH_2), 4.7–5.0 (m, 1, olefinic H); mass spectrum m/e 210 (M^+), 132, 120, 69 (base); exact mass m/e 210.1254 (calcd for $C_{12}H_{18}O_3$, 210.1256)].

2-Acetyl-1-(β-methoxyvinyl)cyclopropane (4c) and 3-Acetyl-2-methoxy-1-vinylcyclopropane (5c). A mixture of 3.60 g of diazoacetone, 500 mg of copper bronze, and 3.60 g of dienol ether **1a** in 10 mL of cyclohexane was treated (70 °C) and worked up as above. Distillation of the crude product afforded 2.75 g of a mixture of **4c** and **5c:** bp 45–50 °C (0.25 Torr); IR C=O 1690 (s), C=C 1650 (m), 1640 cm^{-1} (m); ^1H NMR δ 0.7–2.0 (m, 3–4, CH_2, methines), 2.21, 2.22 (s, 3 total, Me), 3.45, 3.50 (s, 3 total, OMe), 4.4–5.4 (m, ca. 29% of 3, olefinic H of **5c**), 5.9–6.9 (m, ca. 71% of 2, olefinic H of **4c**); exact mass m/e 180.0838 (calcd for $C_8H_{12}O_2$, 180.0834).

2-Acetyl-1-(β-trimethylsilyloxyvinyl)cyclopropane (4d) and 3-Acetyl-2-trimethylsilyloxy-1-vinylcyclopropane (5d). A mixture of 2.10 g of diazoacetone, 500 mg of copper bronze, and 7.00 g of dienol ether **1b** was treated (70 °C) and worked up as above. The crude product was distilled yielding 4.30 g of starting diene (**1b**) and 2.15 g of a liquid mixture of **4d** and **5d:** bp 50–54 °C (0.25 Torr); IR C=O 1695 (s), C=C 1640 cm^{-1} (m); ^1H NMR δ 0.19 (s, 9, $SiMe_3$), 2.21, 2.18 (s, 3 total, Me); exact mass m/e 198.1058 (calcd for $C_{10}H_{18}O_2Si$, 198.1054).

7-Acetyl-2-acetoxymethylenebicyclo[4.1.0]heptane (6c) and 1-Acetoxy-2-acetylspiro[2.5]oct-4-ene (7c). A mixture of 3.95 g of diazoacetone, 1.30 g of copper bronze, and 6.68 g of dienol acetate **2a** in 50 mL of cyclohexane was treated (5 h) and worked up as above. Distillation of the crude product provided 5.00 g of starting diene (**2a**) and 2.40 g of a 3.2:1 mixture (by integration of the olefinic hydrogen NMR signals) of **6c** and **7c,** respectively, bp 108–130 °C (0.35–0.40 Torr). Redistillation afforded 2.09 g of the mixture: IR C=O 1755 (s), 1695 cm^{-1} (s); ^1H NMR δ 2.08, 2.18 (s, 6 total, Me), 4.49 (d, <1, J = 4 Hz, c-Pr H of *trans*-**7c**), 5.2–5.9 (m, <2, olefinic H of **7c**), 6.93 (t, <1, J = 2 Hz, olefinic H of **6c**); exact mass m/e 208.1091 (calcd for $C_{12}H_{16}O_3$, 208.1099).

7-Acetyl-2-trimethylsilyloxymethylenebicyclo[4.1.0]heptane (6d) and 2-Acetyl-1-trimethylsilyloxyspiro[2.5]oct-4-ene (7d). A mixture of 1.32 g of diazoacetone, 370 mg of copper bronze, and 1.91 g of dienol ether **2b** in 10 mL of cyclohexane was treated (2 h) and worked up as above. Distillation of the crude product gave 1.26 g of a 1.7:1 mixture of starting diene (**2b**) and 3-hexene-2,5-dione [bp 26–40 °C (0.25–0.35 Torr)], respectively, and 825 mg of a 2.3:1.8:1 mixture of **6d, 7d,** and **13b,** respectively. Redistillation of the latter gave an oil: bp 65–79 °C (0.1–0.15 Torr); IR C=O 1720 (s), 1688 cm^{-1} (s); ^1H NMR δ 0.18 (s, 9, $SiMe_3$), 2.15 (s, 3, Me), 3.92 (d, <1, J = 4 Hz, OCH of *trans*-**7d**), 5.2–5.9 (m, <2, olefinic H of **7d**), 6.19 (t, <1, J = 2 Hz, olefinic H of **6d**); exact mass m/e 238.1399 (calcd for $C_{13}H_{22}O_2Si$, 238.1388).

7-Acetyl-3-methoxybicyclo[4.1.0]hept-2-ene (8c) and 7-Acetyl-6-methoxybicyclo[4.1.0]hept-2-ene (9c). A mixture of 1.68 g of diazoacetone, 500 mg of copper bronze, and 4.40 g of dienol ether **3a** was treated (2 h) and worked up as above. Distillation of the crude product yielded 2.20 g of starting diene (**3a**) and 2.20 g of a colorless, liquid mixture of **8c** and **9c:** bp 61–65 °C (0.15 Torr); IR C=O 1690 (s), C=C 1655 (m), 1604 (w), 1585 cm^{-1} (w); ^1H NMR δ 2.15, 2.20 (s, 3 total, Me), 3.35, 3.51, 3.54 (s, 3 total, OMe), 4.89 (t, <1, J = 2 Hz, olefinic H of **8c**), 5.6–6.0 (m, <2, olefinic H of **9c**).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.34; H, 8.28.

7-Acetyl-3-methoxy-6-methylbicyclo[4.1.0]hept-2-ene (8d) and 7-Acetyl-6-methoxy-3-methylbicyclo[4.1.0]hept-2-ene (9d). A mixture of 2.20 g of diazoacetone, 500 mg of copper bronze, and 8.80 g of dienol ether **3b** was treated (3 h) and worked up as above. Distillation of the crude product yielded 7.90 g of starting diene (**3b**) and 1.17 g of a colorless, liquid mixture of **8d** and **9d:** bp 50–60 °C (0.1 Torr); IR C=O 1685 (s), C=C 1650 (m), 1605 cm^{-1} (w); ^1H NMR δ 1.67 (m, <3, olefinic Me of **9d**), 1.78, 1.81 (s, <3, Me of **8d**), 2.09, 2.18 (s, 3 total, Me of Ac), 3.29 (s, <3, OMe of **9d**), 3.48 (s, <3, OMe of **8d**),

4.58 (m, <1, olefinic H of **8d**), 5.25 (m, <1, olefinic H of **9d**).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.12; H, 8.81.

Ethyl 2-(β-Oxoethyl)-1-cyclopropanecarboxylate (10). A mixture of 100 mg of ester **4a** and 10 mL of 2 N hydrochloric acid was stirred under nitrogen at room temperature for 4 h. It was diluted with 15 mL of water, saturated with sodium chloride, and extracted with 75 mL of ether. The extract was washed with 5% sodium bicarbonate solution and brine, dried (Na_2SO_4), and evaporated, leaving 70 mg of colorless, liquid aldehydo ester **10:** IR aldehyde CH 2725 (w), C=O 1725 cm^{-1} (s); ^1H NMR δ 1.27 (t, 3, J = 7 Hz, Me), 2.46 (dd, <2, J = 6, 2 Hz, $COCH_2$ of one isomer), 2.82 (dd, <2, J = 6, 1 Hz, $COCH_2$ of other isomer), 4.15 (q, 2, J = 7 Hz, OCH_2), 9.76 (t, 1, J = 2 Hz, CHO); exact mass m/e 156.0790 (calcd for $C_8H_{12}O_3$, 156.0786).

Ethyl 6-Oxo-4-hexenoate (11a). A solution of 430 mg of ester **4a** and 4 mL of 5 N hydrochloric acid in 12 mL of ethanol was refluxed for 1.5 h. Workup as for aldehyde **10** (vide supra) led to 300 mg of product whose preparative TLC yielded liquid aldehydo ester **11a:** IR aldehyde CH 2725 (w), C=O 1731 (s), 1688 (s), C=C 1631 cm^{-1} (m); ^1H NMR δ 1.30 (t, 3, J = 7 Hz, Me), 2.3–3.0 [m, 4, $(CH_2)_2$], 4.20 (q, 2, J = 7 Hz, OCH_2), 6.18 (dd, 1, J = 15, 7 Hz, H-5), 6.93 (dt, 1, J = 15, 8 Hz, H-4), 9.52 (d, 1, J = 7 Hz, H-6); mass spectrum m/e 156 (M^+), 83 (base); exact mass m/e 156.0790 (calcd for $C_8H_{12}O_3$, 156.0786).

Ethyl 3-Formyl-3-pentenoate (12a). A solution of 100 mg of ester **5a** and 1 mL of concentrated hydrochloric acid in 8 mL of ethanol was refluxed under nitrogen for 2 h. Upon workup as for **10** (vide supra) there was obtained 80 mg of oil whose microdistillation gave liquid aldehydo ester **12a:** IR aldehyde CH 2770 (w), C=O 1730 (s), 1685 (s), C=C 1646 cm^{-1} (m); ^1H NMR δ 1.23 (t, 3, J = 7 Hz, Me of Et), 2.01 (d, 3, J = 7 Hz, Me), 3.33 (s, 2, CH_2), 4.15 (q, 2, J = 7 Hz, OCH_2), 6.82 (q, 1, J = 7 Hz, H-4), 9.48 (s, 1, CHO); mass spectrum m/e 156 (M^+), 111, 110, 83, 55, 45, 43, 29, 27 (base), 26, 25; exact mass m/e 156.0791 (calcd for $C_8H_{12}O_3$, 156.0786).

Hydrolysis of 4b and 5b. A 3.00-g mixture of **4b** and **5b** was poured onto a silica gel column, 40 g, and kept thereon for 24 h. Elution with benzene and evaporation gave 1.80 g of colorless oil whose preparative TLC separated the 2:2:1 mixture of aldehydes **10, 11a,** and **12a,** respectively.

A solution of 890 mg of a **4b–5b** mixture and 1 mL of concentrated hydrochloric acid in 10 mL of ethanol was refluxed under nitrogen for 2 h. Workup as for 10 (vide supra) gave 492 mg of an oil whose preparative TLC separated the 4:1 mixture of **11a** and **12a,** respectively.

6-Oxo-2-heptenal (11b) and 4-Formyl-4-hexen-2-one (12b). A mixture of 500 mg of the **4c–5c** mixture and 30 mL of 1 N hydrochloric acid was stirred under nitrogen at room temperature for 2 h. Workup as for **10** above gave 350 mg of oil whose GPC separation (135 °C) led to 195 mg of **11b** [4 min retention time; IR aldehyde CH 2720 (w), C=O 1715 (s), 1685 (s), C=C 1632 cm^{-1} (m); ^1H NMR δ 2.19 (s, 3, Me), 2.58 (m, 2, H_2-4), 2.68 (s, 2, H_2-5), 6.08 (dd, 1, J = 15, 7 Hz, H-2), 6.88 (dt, 1, J = 15, 6 Hz, H-3), 9.48 (d, 1, J = 7 Hz, H-1); mass spectrum m/e 126 (M^+), 83, 68, 57, 55, 44 (base), 42, 40; exact mass m/e 126.0676 (calcd for $C_7H_{10}O_2$, 126.0680)] and to 80 mg of **12b** [11 min retention time; IR aldehyde CH 2720 (w), C=O 1715 (s), 1680 (s), C=C 1644 cm^{-1} (m); ^1H NMR δ 1.95 (d, 3, J = 7 Hz, Me), 2.18 (s, 3, COMe), 3.38 (s, 2, $COCH_2$), 6.80 (q, 1, J = 7 Hz, olefinic H), 9.46 (s, 1, CHO); mass spectrum m/e 126 (M^+), 83, 55, 43 (base); exact mass m/e 126.0683 (calcd for $C_7H_{10}O_2$, 126.0680).

Keeping 1.90 g of a **4c–5c** mixture on a silica gel column (30 g) and elution with benzene led to 1.40 g of a 2.5:1 mixture of **11b** and **12b,** respectively.

Hydrolysis of 4d and 5d. A 1.00-g mixture of **4d** and **5d** was kept on a silica column, 20 g, for 24 h and then eluted with benzene. The eluates yielded 700 mg of colorless oil whose GPC separated it into keto aldehydes **11b** and **12b** in 2.5:1 ratio.

A mixture of 1.20 g of the **4d–5d** mixture and 10 mL of 1 N hydrochloric acid in 20 mL of ether was stirred under nitrogen at room temperature for 1 h. Workup as for **10** above gave 900 mg of a 2.5:1 mixture of **11b** and **12b,** respectively, separated by GPC.

Ethyl (3-Formyl-2-cyclohexenyl)acetate (13a). A mixture of 103 mg of ester **6a** and 30 mg of anhydrous potassium carbonate in 3 mL of ethanol was stirred at 27 °C for 4 h. It then was diluted with 30 mL of brine solution and extracted with 40 mL of chloroform. The extract was dried ($MgSO_4$) and evaporated. Distillation [81–83 °C (0.2 Torr)] of the residue, 77 mg, yielded the ester **13a:** IR aldehyde CH 2710 (w), C=O 1730 (s), 1682 (s), C=C 1642 cm^{-1} (m); ^1H NMR δ 1.28 (t, 3, J = 7 Hz, Me), 2.26 (d, 1, J = 2 Hz, H of $COCH_2$), 2.39 (s, 1, other H of $COCH_2$), 4.08 (q, 2, J = 7 Hz, OCH_2), 6.52 (m, 1, olefinic H), 9.21 (s, 1, CHO); mass spectrum m/e 196 (M^+, base), 151, 123, 122, 109; exact mass m/e 196.1092 (calcd for $C_{11}H_{16}O_3$, 196.1099); semicarbazone mp 148–149 °C (crystallized from aqueous ethanol).

Anal. Calcd for $C_{12}H_{19}O_3N_3$: C, 56.90; H, 7.56; N, 16.59. Found: C, 57.05; H, 7.54; N, 16.48.

Ethyl (1-Formyl-2-cyclohexenyl)acetate (14a). A mixture of 86 mg of ester **7a** and 24 mg of anhydrous potassium carbonate in 2 mL of ethanol was stirred at 27 °C for 4 h. Workup as for **13a** above led to 66 mg of a liquid mixture of aldehydo ester **14a** (minor component) [IR aldehyde CH 2720 (w), C=O 1750 (s), 1730 (s), C=C 1635 cm^{-1} (w); ^1H NMR δ 9.33 (s, 1, CHO)] and its isomer, the ethyl lactol ether of (1-formyl-2-cyclohexenyl)acetic acid [IR C=O 1790 (s), C=C 1610 cm^{-1} (w); ^1H NMR δ 1.23 (t, 3, J = 7 Hz, Me), 4.06 (q, 2, J = 7 Hz, OCH_2), 4.95 (s, <1, OCH of one isomer), 5.01 (s, <1, OCH of the other isomer), 5.42 (d, 1, J = 10 Hz, c-hex H-2), 5.82 (dt, 1, J = 10, 3 Hz, c-hex H-3); mass spectrum m/e 196 (M^+)].

A mixture of 107 mg of the **6b–7b** mixture and 25 mg of anhydrous potassium carbonate in 2.5 mL of ethanol was stirred at 25 °C for 4 h. Workup as above gave 79 mg of a mixture of **13a, 14a,** and the lactol ethyl ether isomer of the latter.

3-Acetonyl-1-cyclohexenecarboxaldehyde (13b) and 1-Acetonyl-2-cyclohexenecarboxaldehyde (14b). A mixture of 1.27 g of a 1.6:1 **6c–7c** mixture and 318 mg of anhydrous potassium carbonate in 35 mL of ethanol was stirred at room temperature for 3 h. Workup as for **14a** above gave 920 mg of oil whose distillation [75–85 °C (0.15 Torr)] yielded 637 mg of a 4:1 mixture of **13b** and **14b,** respectively, which was separated by GPC (180 °C) into **13b** [IR aldehyde CH 2730 (w), C=O 1712 (s), 1680 (s), C=C 1640 cm^{-1} (m); ^1H NMR δ 2.08 (s, 3, Me), 2.48 (d, 1, J = 2 Hz, H of $COCH_2$), 2.58 (s, 1, other H of $COCH_2$), 6.53 (m, 1, olefinic H), 9.26 (s, 1, CHO); mass spectrum m/e 166 (M^+), 124, 123 (base), 79, 43; exact mass m/e 166.1000 (calcd for $C_{10}H_{14}O_2$, 166.0993); bissemicarbazone (from aqueous ethanol), mp 218–226 °C (Anal. Calcd for $C_{12}H_{20}O_2N_6$: C, 51.41; H, 7.19; N, 29.98. Found: C, 51.47; H, 7.21; N, 29.94)] and **14b** [IR aldehyde CH 2740 (w), C=O 1725 (s), 1715 (s), C=C 1605 cm^{-1} (w); ^1H NMR δ 2.11 (s, 3, Me), 2.80 (s, 2, $COCH_2$), 5.42 (dt, 1, J = 10, 2 Hz, olefinic H), 5.88 (dt, 1, J = 10, 3 Hz, olefinic H), 9.45 (s, 1, CHO); mass spectrum m/e 166 (M^+), 138, 137, 123, 95, 81, 80, 79, 77, 69, 67, 43 (base); exact mass m/e 166.0997 (calcd for $C_{10}H_{14}O_2$, 166.0993).

A combination of 584 mg of the **6d–7d** mixture and 157 mg of anhydrous potassium carbonate in 10 mL of ethanol was stirred at 25 °C for 4 h. Workup as for **14a** above yielded 446 mg of an oil, identified by ^1H NMR spectral analysis as a mixture of **13b** and **14b.**

Ethyl (4-Oxo-2-cyclohexenyl)acetate (15a). A solution of 350 mg of ester **8a** and 1.5 mL of concentrated hydrochloric acid in 15 mL of ethanol was refluxed under nitrogen for 2 h. It then was diluted with 100 mL of water, saturated with sodium chloride, and extracted with 100 mL of ether. The extract was washed with 35 mL of 5% sodium bicarbonate solution and 20 mL of saturated brine solution, dried (Na_2SO_4), and evaporated. Microdistillation of the residue, 300 mg, yielded **15a:** IR C=O 1727 (s), 1679 (s), C=C 1606 cm^{-1} (w); ^1H NMR δ 1.27 (t, 3, J = 7 Hz, Me), 4.16 (q, 2, J = 7 Hz, OCH_2), 5.95 (dd, 1, J = 10, 2 Hz, H-3), 6.82 (ddd, 1, J = 10, 3, 1 Hz, H-2). [The substance contains a minor amount of the β,γ-unsaturated isomer, as revealed by the extra signals at 1.25 (t, 3, J = 7 Hz, Me), 4.14 (q, 2, J = 7 Hz, OCH_2), 5.60 (m, 1, olefinic H).]

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.78; H, 7.68.

Ethyl (1-Methyl-4-oxo-2-cyclohexenyl)acetate (15b). A solution of 125 mg of ester **8b** and 0.5 mL of concentrated hydrochloric acid in 8 mL of ethanol was refluxed under nitrogen for 2 h. Workup as for **15a** above yielded 95 mg of liquid **15b:** IR C=O 1735 (s), 1675 (s), C=C 1605 cm^{-1} (w); ^1H NMR δ 1.25 (t, 3, J = 7 Hz, Me), 2.45 (s, 2, $COCH_2$), 4.15 (q, 2, J = 7 Hz, OCH_2), 5.90 (d, 1, J = 10 Hz, H-3), 6.85 (dd, 1, J = 10, 1 Hz, H-2).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.21.

Ethyl (6-Oxo-1-cyclohexenyl)acetate (16a). A solution of 150 mg of ester **9a** and 0.5 mL of concentrated hydrochloric acid in 8 mL of ethanol was refluxed under nitrogen for 2 h. Workup as for **15a** above yielded 120 mg of liquid **16a:** IR C=O 1735 (s), 1670 cm^{-1} (s); ^1H NMR δ 1.25 (t, 3, J = 7 Hz, Me), 3.28 (broad s, 2, $COCH_2$), 4.13 (q, 2, J = 7 Hz, OCH_2), 6.85 (t, 1, J = 4 Hz, olefinic H).

Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.77; H, 7.58.

Ethyl (3-Methyl-6-oxo-1-cyclohexenyl)acetate (16b). A solution of 150 mg of ester **9b** and 0.6 mL of concentrated hydrochloric acid in 10 mL of ethanol was refluxed under nitrogen for 2 h. Workup as for **15a** above afforded 120 mg of oily **16b:** IR C=O 1735 (s), 1675 (s), C=C 1608 cm^{-1} (w); ^1H NMR δ 1.20 (d, 3, J = 6 Hz, Me), 1.25 (t, 3, J = 7 Hz, Me of Et), 3.20 (broad s, 2, $COCH_2$), 4.15 (q, 2, J = 7 Hz,

OCH_2), 6.70 (m, 1, olefinic H).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.11; H, 8.26.

4-Acetonyl-2-cyclohexenone (15c) and 2-Acetonyl-2-cyclohexenone (16c). A combination of 1.00 g of a **8c–9c** mixture and 15 mL of 2 N hydrochloric acid in 15 mL of ether was stirred at 25 °C for 1 h. The ether layer was separated, the aqueous solution saturated with sodium chloride and extracted with ether, and the combined organic solutions worked up as for **15a** above. Preparative TLC of the crude product, 750 mg, and elution with 4:1 ether–hexane yielded 110 mg of diketone **16c** [IR C=O 1710 (s), 1670 cm^{-1} (s); ^1H NMR δ 2.17 (s, 3, Me), 3.25 (broad s, 2, $COCH_2$), 6.78 (t, 1, J = 3 Hz, H-3); mass spectrum m/e 152 (M^+), 54, 37 (base); exact mass m/e 152.0837 (calcd for $C_9H_{12}O_2$, 152.0833)] and 565 mg of diketone **15c** [IR C=O 1715 (s), 1675 (s), C=C 1616 cm^{-1} (w); ^1H NMR δ 2.22 (s, 3, Me), 5.95 (dd, 1, J = 10, 2 Hz, H-2), 6.81 (ddd, 1, J = 10, 3, 1 Hz, H-3); mass spectrum m/e 152 (M^+), 95, 55, 43 (base); exact mass m/e 152.0830 (calcd for $C_9H_{12}O_2$, 152.0836)].

4-Acetonyl-4-methyl-2-cyclohexenone (15d) and 2-Acetonyl-4-methyl-2-cyclohexenone (16d). A combination of 1.30 g of a **8d–9d** mixture and 25 mL of 2 N hydrochloric acid in 25 mL of ether was stirred at 25 °C for 1 h. Workup as for **15c–16c** above yielded 850 mg of oil, bp 70 °C (0.15 Torr), whose preparative GPC (180 °C) yielded 477 mg of a mixture of **16d** and its isomer, **2-acetonyl-4-methyl-3-cyclohexenone (16d′)** [10 min retention time; IR C=O 1710 (s), 1675 cm^{-1} (s); ^1H NMR δ 1.16 (d, <3, J = 7 Hz, Me of **16d′**), 1.72 (broad s, <3, Me of **16d**), 2.15 (s, <3, COMe of **16d′**), 2.45 (s, <3, COMe of **16d**), 5.17 (m, <1, H-3 of **16d′**), 6.51 (m, <1, H-3 of **16d**); exact mass m/e 166.0989 (calcd for $C_{10}H_{14}O_2$, 166.0993)] and 190 mg of **15d** [14 min retention time; IR C=O 1720 (s), 1675 (s), C=C 1607 cm^{-1} (w); ^1H NMR δ 1.25 (s, 3, Me), 2.13 (s, 3, COMe), 2.58 (s, 2, $COCH_2$), 5.78 (d, 1, J = 10 Hz, H-2), 6.80 (broad d, 1, J = 10 Hz, H-3); mass spectrum m/e 166 (M^+), 109, 108 (base), 95, 43; exact mass m/e 166.0986 (calcd for $C_{10}H_{14}O_2$, 166.0993)].

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Registry No.—**1a,** 3036-66-6; **1b,** 6651-43-0; **2a,** 61967-78-0; **2a** biscyclopropanation product, 61967-79-1; **2b,** 61967-80-4; **3a,** 2161-90-2; **3b,** 2161-94-6; **4a,** 61967-81-5; **4b,** 61967-82-6; **4c,** 61967-83-7; **4d,** 61967-84-8; **5a,** 61967-85-9; **5b,** 61967-65-5; **5c,** 61967-66-6; **5d,** 61967-67-7; **6a,** 61967-68-8; **6b,** 61967-69-9; **6c,** 61967-70-2; **6d,** 61967-71-3; **7a,** 61967-72-4; **7b,** 61967-73-5; **7c,** 61967-74-6; **7d,** 61967-75-7; **8a,** 61967-76-8; **8b,** 61967-77-9; **8c,** 61967-31-5; **8d,** 61967-29-1; **9a,** 61967-30-4; **9b,** 61967-32-6; **9c,** 61967-33-7; **9d,** 61967-34-8; **10,** 61967-35-9; **11a,** 61967-36-0; **11b,** 61967-37-1; **12a,** 61967-38-2; **12b,** 61967-39-3; **13a,** 61967-40-6; **13a** semicarbazone, 61967-41-7; **13b,** 61967-42-8; **13b** bissemicarbazone, 61967-43-9; **14a,** 61967-44-0; **14a** ethyl ether lactol isomer, 61967-45-1; **14b,** 61967-46-2; **15a,** 16831-58-6; **15a** β,γ isomer, 61967-47-3; **15b,** 16831-59-7; **15c,** 56051-94-6; **15d,** 61967-48-4; **16a,** 24124-06-9; **16b,** 61967-49-5; **16c,** 33553-25-2; **16d,** 61967-19-9; **16d′,** 61967-20-2; 1-cyclohexenecarboxaldehyde, 1192-88-7; isopropenyl acetate, 108-22-5; trimethylsilyl chloride, 75-77-4; 1-dimethoxymethylcyclohexene, 61967-21-3; trimethyl orthoformate, 149-73-5; ethyl diazoacetate, 623-73-4; diazoacetone, 2684-62-0.

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Addition to 2,4-Dienes. Halogenation of Ethyl Sorbate

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The addition of chlorine and bromine to ethyl sorbate (**1a**) gave 1,2- and 1,4-dihalo products derived from attack of the halogen across the γ,δ double bond. Chlorination of **1a** under ionic conditions proceeds through a tightly bridged chloronium ion intermediate, as indicated by the stereospecific formation of *erythro*-1,2-dichloride **3a**. Stereospecificity in **3a** is lost when chlorine is added to **1a** under radical conditions, indicating a molecule-induced homolysis for this reaction. Even under ionic conditions, bromine reacts with **1a** by a radical process unless an efficient radical scavenger is used.

The loss of stereospecificity in the ionic halogenation[2] of conjugated olefins such as β-methylstyrenes[3] and dienes[4] is ascribed to weakly bridged halonium ion intermediates. Apparently bromine bridges more tightly than chlorine, since 1,2-addition of bromine to *trans,trans*-2,4-hexadiene (**1b**) is more stereospecific (80%) than the 1,2-addition of chlorine (60%).[4] Halogenations of these dienes and olefins under radical conditions[2] involve nonbridged radical intermediates resulting in nonstereospecific products.[5]

We undertook this study to determine what effect a con-