Synthetic Approaches to α-Methylene γ-Lactones via Cycloadditions of Ketenes[1]

Alfred Hassner,* Harold W. Pinnick, and Jay M. Ansell

Departments of Chemistry, State University of New York at Binghamton, Binghamton, New York, and University of Colorado, Boulder, Colorado

Received April 26, 1977

Methylchloroketene was cycloadded to several cycloalkenes and cycloalkadienes to produce fused substituted cyclobutanones which can be transformed by Baeyer–Villiger oxidation into lactones. Exocyclic elimination of HCl from the latter produces ring-fused α-methylene γ-lactones **4**. This route, adaptable to a larger scale, serves as a three-step fair-yield synthesis of **4** from cyclic olefins.

The α-methylene γ-butyrolactone unit is found in a number of biologically active, naturally occurring compounds.[2] Many of these natural products are antitumor agents,[3] and this has stimulated much of the recent research devoted to the development of new synthetic routes to α-methylene lactones. Consequently, there have been developed a variety of methods for the synthesis of this moiety.[4]

Most of these procedures involve the introduction of the α-methylene group into a preformed lactone. For example, Grieco and co-workers[5] have devised a route involving bromination, formation of the phosphonium salt and then ylide, and finally a Wittig reaction. Other methods using γ-lactones were recently described.[6]

In previous studies[7] we showed that cycloalkenes react readily and regioselectively with dichloroketene to produce fused cyclobutanones which can be oxidized to lactones.

Results

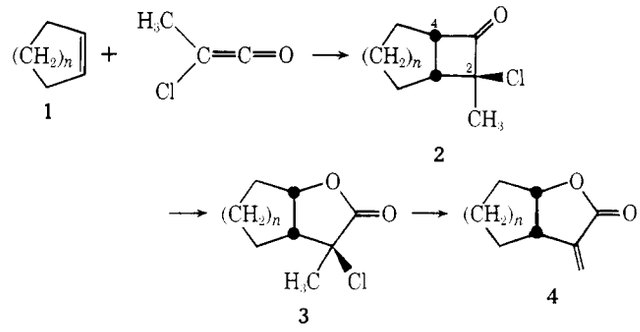
We report here a method for the facile transformation of cyclic olefins into cis-fused α-methylene γ-butyrolactones in three steps (Scheme I).[8] The overall results are summarized in Table I.

The cycloaddition step proceeded well with a variety of cyclic olefins by in situ generation[9] of a methylchloroketene from α-chloropropionyl chloride and triethylamine. The ketene cycloaddition appears to be highly stereoselective since only one chloro ketone isomer is isolated in each case. This is indicated by a methyl singlet in the NMR spectra of the adducts. Baeyer–Villiger oxidation of the cyclobutanones **2** led to lactones **3**. Among the different peroxidizing agents tried (*m*-chloroperbenzoic acid, acidic and basic hydrogen peroxide), the best results were obtained with hydrogen peroxide in acetic acid, producing lactones **3** in 65–90% yields. The α-methylene lactones are obtained in good yields after base-catalyzed dehydrochlorination (Table I). No extensive search for optimum yields has been carried out, but the best conditions of those examined for this step are the use of 1,4-diazabicyclo[2.2.2]octane (Dabco) and sodium iodide at 80 °C in dimethyl sulfoxide (Me_2SO). As a specific example, cyclooctene (**1d**, Table I) gives an 83% isolated yield of the ketene adduct **2d**, which is oxidized to the lactone **3d** in 87% yield. Elimination of the elements of HCl provides a 78% yield (40% after distillation) of the α-methylene lactone **4d**.

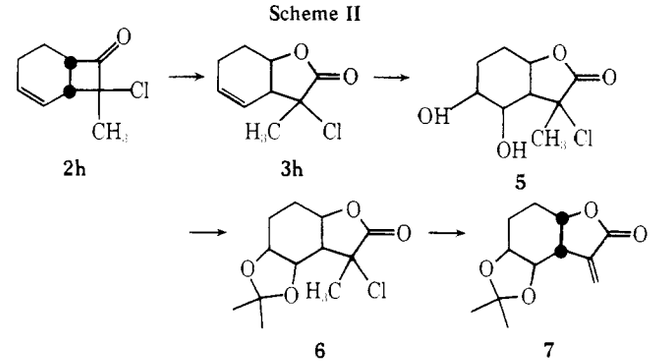
This method is not limited to small scale reactions (0.01 mol or less). For example, 0.08 mol of cyclooctene (**1d**) has been converted to the α-methylene lactone **4d** with percent yields in each step comparing favorably with small scale values (see Table I). It should be noted that distillation of α-methylene lactones often results in polymerization; about one-third of the crude product (pure by NMR) remained as a thick residue after distillation.

As a synthetic route to polyfunctional α-methylene lactones related to sesquiterpenes of plant origin, we examined the

Scheme I



Scheme II



reactions of the unsaturated chloro ketone **2h**. Baeyer–Villiger oxidation to **3h** was followed by OsO_4 oxidation of the residual double bond to the diol **5**. This was protected as the ketal **6** and converted to the α-methylene lactone **7** in good yields (see Scheme II).

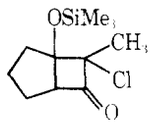
Discussion

The success of Scheme I depends largely on two factors: the preferential migration of C-4 over C-2 in the Baeyer–Villiger oxidation (**2** → **3**) and the preferential exocyclic vs. endocyclic elimination of HCl from **3**. The latter event is based on the stereochemical outcome of the cycloaddition step.

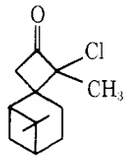
The first step in the scheme, the ketene cycloaddition, is presumably concerted and is known to be highly stereoselective.[9] Although two adducts have often been isolated, the major product has been shown to be the *exo*-chloro isomer.[9,10] This is precisely the stereochemistry necessary for placing the chlorine substituent cis to the ring junction proton, rendering endocyclic elimination of HCl energetically somewhat unfavorable.[11] The results of the base-catalyzed HCl elimination (exocyclic) suggest that the original adducts **2** indeed possess an *exo*-chlorine.

The high degree of regioselectivity observed,[12] i.e., exclusive isolation of **2h** and **8**, and the lack of rearrangement in the

0022-3263/78/1943-1774$01.00/0



8



2f

β-pinene adduct **2f** also point toward the concertedness of these cycloadditions.

In Baeyer–Villiger oxidations, the more substituted carbon (C-2 in ketone **2**) is usually found to migrate.[13a] However, we expected the presence of the electron-withdrawing chlorine substituent[13b] at C-2 to influence the migratory aptitudes and thus favor migration of the more electron-rich C-4. Indeed this led to the isolation of lactones **3**.

Finally, the synthesis of **7** indicates the usefulness of the overall reaction sequence as a route from readily available cycloalkenes to functionalized, fused α-methylene lactones.

Experimental Section[14]

Methylchloroketene Adducts 2 from Olefins.[15] General Procedure. Cyclopentene Adduct 2a. Cyclopentene (11.0 mL, 0.125 mol) and triethylamine (8.4 mL, 0.06 mol) in 60 mL of hexane were refluxed under nitrogen. α-Chloropropionyl chloride (4.8 mL, 0.05 mol) in 15 mL of hexane was added dropwise over 60 min. This was refluxed another 3.5 h and stirred at room temperature for 19 h. The reaction mixture was filtered, and the filtrate was washed with cold $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$) and concentrated to give 7.6 g of an oil which on distillation provided 6.1 g (77%) of adduct **2a:** bp 43–46 °C (0.7 mm) [lit.[9d] 48–58 °C (1.0 mm)]; NMR (CCl_4) δ 1.47 (s, 3, CH_3), 3.05 (m, 1, CH), 4.05 (m, 1, CH).

Cyclohexene Adduct 2b. Similarly, from 0.05 mL of acid chloride was obtained 1.9 g (22%) of colorless liquid: bp 75–80 °C (1.8 mm) [lit.[9c] 55–67 °C (1.0 mm)]; NMR (CCl_4) δ 1.53 (s, 3, CH_3), 2.68 (m, 1, CH), 4.0 (m, 1, CH); IR (neat) 1785 (C=O) cm^{-1}.

Cycloheptene Adduct 2c. From 0.01 mol of acid chloride was obtained 1.23 g (66%) of colorless liquid: bp 65–70 °C (0.4 mm); NMR (CCl_4) δ 1.5 (s, 3, CH_3), 2.8 (m, 1, CH), 3.95 (m, 1, CH).

Cyclooctene Adduct 2d. From 0.01 mol of cyclooctene was obtained 1.65 g (83%) of colorless liquid: bp 95–100 °C (0.1 mm) [lit.[9c] 122–129 °C (0.5 mm)]; NMR (CCl_4) δ 1.47 (s, 3, CH_3), 2.64 (m, 1, CH), 3.57 (m, 1, CH). In an eightfold scale the yield of **2d** was 11.3 g (71%).

Methylenecyclohexane Adduct 2e. From 0.01 mol of acid chloride was obtained 0.93 g (50%) of colorless liquid: bp 69–74 °C (0.5 mm) [lit.[12f] 67–70 °C (0.6 mm)]; NMR (CCl_4) δ 1.6 (s, 3, CH_3), 2.85 (s, 2, CH_2).

β-Pinene Adduct 2f. From 0.01 mol of acid chloride was obtained 1.65 g (73%) of colorless liquid: bp 95–101 °C (0.4 mm) [lit.[12f] 95–98 °C (0.25 mm)]; NMR (CCl_4) δ 1.6 (s, 3, CH_3), 2.95 (s, 2, CH_2).

1,5-Cyclooctadiene Adduct 2i. From 0.01 mol of olefin was obtained 1.0 g (50%) of colorless liquid: bp 94–97 °C (0.4 mm); NMR (CCl_4) δ 1.55 (s, 3, CH_3), 2.8 (m, 1, CH), 3.75 (m, 1, CH); IR (neat) 1785 (C=O), 1650 (C=C) cm^{-1}.

Cyclopentadiene Adduct 2g. From 0.03 mol of acid chloride at room temperature was obtained 4.0 g (85%) of colorless liquid: bp 36–42 °C (0.04 mm) [lit.[12f] 70–72 °C (5.0 mm)]; NMR (CCl_4) δ 1.45 (s, 3, CH_3), 2.65 (m, 2, CH_2), 3.7 (m, 1, CH), 4.3 (m, 1, CH), 5.9 (m, 2, CH=CH).

1,3-Cyclohexadiene Adduct 2h. From 0.01 mol of acid chloride at room temperature was obtained 1.1 g (65%) of colorless liquid: bp 65–70 °C (0.4 mm); IR 1800 (C=O) cm^{-1}; NMR (CCl_4) δ 1.5 (s, 3, CH_3), 3.15 (m, 1, CH), 4.2 (m, 1, CH), 5.95 (m, 2, CH=CH). Its identity was proven by comparison with published spectra.[9c]

Trimethylsiloxycyclopentene Adduct 2j. From 0.01 mol of the silyl enol ether at room temperature was obtained 1.9 g (71%) of colorless liquid: bp 70–80 °C (0.06 mm); NMR (CCl_4) δ 0.2 (s, 9, $SiMe_3$), 1.47 (s, 3, CH_3), 3.4 (m, 1, CH); IR (neat) 1780 (C=O) cm^{-1}.

Trimethylsiloxycyclohexene Adduct 2k. From 0.01 mol of the silyl enol ether at room temperature was obtained 0.51 g (20%) of colorless liquid: bp 125–135 °C (0.4 mm); NMR (CCl_4) δ 0.2 (s, 9, $SiMe_3$), 1.7 (s, 3, CH_3), 3.35 (m, 1, CH); IR (neat) 1788 (C=O) cm^{-1}.

Lactones 3 from Cyclobutanones 2.[6] Cyclopentane Lactone 3a. The cyclobutanone from cyclopentene (0.79 g, 5.0 mmol) was dissolved in 5 mL of 90% HOAc and cooled to 0 °C. A solution of 2.5 g of 30% H_2O_2 in 3 mL of 90% HOAc was added. This was maintained at 0 °C for 24 h, poured into H_2O, and extracted with Skellysolve F. The organic extract was washed with $NaHSO_3$ solution and H_2O, dried ($MgSO_4$), and concentrated to give 0.57 g (65%) of colorless liquid: NMR (CCl_4) δ 1.75 (s, 3, CH_3), 3.0 (m, 1, CH), 5.1 (m, 1, CH).

Table I. Conversion of Olefins into α-Methylene Lactones

Registry no.	Olefin 1	Cyclobutanone 2[a]	Lactone 3[b]	α-Methylene lactone 4
142-29-0	Cyclopentene (**a**)	77	65	73,[b] 40[a]
110-83-8	Cyclohexene (**b**)	22	90	
628-92-2	Cycloheptene (**c**)	66	77	50[a]
931-88-4	Cyclooctene (**d**)	83	87	78,[b] 40[a]
		71[c]	80[c]	63,[b,c] 44[a,c]
1192-37-6	Methylenecyclohexane (**e**)	50		
127-91-3	β-Pinene (**f**)	73		
542-92-7	Cyclopentadiene (**g**)	85	27	
592-57-4	1,3-Cyclohexadiene (**h**)	65	67	
111-78-4	1,5-Cyclooctadiene (**i**)	50		
19980-43-9	1-Cyclopentenyl trimethylsilyl ether (**j**)	71		
6651-36-1	1-Cyclohexenyl trimethylsilyl ether (**k**)	20		

[a] Yield in percent of distilled product. [b] Yield in percent of crude product. [c] Large scale.

Cyclohexane Lactone 3b. From 0.17 g (1.0 mmol) of ketene adduct was obtained 0.17 g (90%) of pale yellow liquid: NMR (CCl_4) δ 1.7 (s, 3, CH_3), 4.9 (m, 1, CH); IR (neat) 1780 (C=O) cm^{-1}.

Cycloheptane Lactone 3c. From 0.93 g (5.0 mmol) of ketene adduct was obtained 0.78 g (77%) of colorless liquid: NMR (CCl_4) δ 1.7 (s, 3, CH_3), 2.7 (m, 1, CH), 4.95 (m, 1, CH).

Cyclooctane Lactone 3d. From 0.80 g (4.0 mmol) of ketene adduct was obtained 0.76 g (87%) of pale yellow liquid: NMR (CCl_4) δ 1.7 (s, 3, CH_3), 2.7 (m, 1, CH), 4.8 (m, 1, CH).

Cyclopentadiene Lactone 3g. From 3.6 g (23 mmol) of ketene adduct was obtained 1.07 g (27%) of pale yellow liquid: NMR (CCl_4) δ 1.75 (s, 3, CH_3), 2.7 (m, 2, CH_2), 3.7 (m, 1, CH), 5.2 (m, 1, CH), 5.7 (m, 1, CH=C), 5.9 (m, 1, CH=C).

2-(*cis*-2-Hydroxy-5-cyclohexenyl)-2-chloropropanoic Acid Lactone (3h). From 8.5 g (50 mmol) of ketene adduct **2h** was obtained 5.46 g (59%) of white crystalline solid: mp 45–47 °C; IR 1795 (C=O) cm^{-1}; NMR (CCl_4) δ 1.5 (s, 3), 1.6–2.3 (m, 4), 2.95 (m, 1), 4.8 (m, 1), 5.25 (m, 1), 5.8 (m, 1); MS 187 (M^+).[18]

2-(*cis*-2,5,6-Trihydroxycyclohexyl)-2-chloropropanoic Acid 2-Lactone (5).[16] To 12.2 g (65.5 mmol) of lactone **3h** in 220 mL of THF and 150 mL of H_2O were added 3.84 g (36 mmol) $NaClO_3$ and 80 mg of OsO_4. This was stirred at room temperature for 80 h and then poured into 150 mL of saturated NaCl. The aqueous phase was extracted with ether (2 × 100 mL). The organic phase was dried and, after the solvent was removed, placed under vacuum (0.5 mm) for 2 h. The resultant oil was crystallized by adding a minimal amount of petroleum ether and allowing the mixture to stand overnight. The crystals were filtered and washed with cold petroleum ether, yielding 4.4 g (30.6%) of crystals: mp 138–140 °C; IR (Nujol) 3500, 3450–3220 (OH free and bonded), 1785 (C=O) cm^{-1}; NMR (acetone-d_6) δ 1.85 (s, 3), 1.9 (m, 4), 2.5 (dd, 1), 3.35 (m, 1), 3.95 [m, 3 (20)], 4.9 (m, 1); MS 221 (M^+).

Anal. Calcd for $C_9H_{13}O_4Cl$: C, 49.0; H, 5.90; Cl, 16.04. Found: C, 48.89; H, 5.93; Cl, 15.99.

2-(*cis*-2-Hydroxy-5,6-isopropylidenedioxycyclohexyl)-2-chloropropanoic Acid Lactone (6). A solution of 4.0 g (18.4 mmol) of glycol **5**, 2.85 g (27.2 mmol) of 2,2-dimethoxypropane, 75 mL of dry benzene, and a trace of *p*-toluenesulfonic acid was refluxed overnight. The cooled solution was neutralized with ~1 mL of Et_3N and washed three times with 30 mL of saturated $NaHCO_3$, and the resultant

washes were extracted with 30 mL of Et_2O. The organic phase was dried and the solvent stripped. Placing the resultant product under vacuum (0.5 mm) gave 4.29 g (90%) of a white crystalline solid: mp 99–100 °C; IR (Nujol) 1775 (C=O) cm^{-1}; NMR (CCl_4) δ 1.15 (s, 3), 1.35 (s, 3), 1.75 (s, 3), 1.8 (m, 4), 2.35 (m, 1), 3.7 (m, 1), 4.2 (m, 1), 4.8 (m, 1); MS 261 (M^+).

Anal. Calcd for $C_{12}H_{17}O_4Cl$: C, 55.3; H, 6.53; Cl, 13.59. Found: C, 55.15; H, 6.53; Cl, 13.51.

α-Methylene Lactones 4. General Procedure. (THF is added for homogeneity if necessary). **Cyclopentane α-Methylene Lactone 4a.** The α-chloro-α-methyl lactone from cyclopentene (0.08 g, 0.5 mmol) was mixed with Dabco (0.22 g, 2.0 mmol), NaI (0.30 g, 2.0 mmol), and 1 mL of Me_2SO at 80 °C for 24–70 h. The cooled reaction mixture was poured into Skellysolve F/dilute HCl and extracted. The organic extract was washed with H_2O, dried ($MgSO_4$), and concentrated to give 0.05 g (73%) of yellow liquid.

Similarly, from 0.44 g (2.5 mmol) of lactone was obtained 0.14 g (40%) of colorless liquid: bp 85–90 °C (0.24 mm); NMR (CCl_4) δ 4.9 (m, 1, CH), 5.55 (d, 1, CH=C), 6.1 (d, 1, CH=C); IR (neat) 1755 (C=O), 1660 (C=C) cm^{-1}.

Cycloheptane α-Methylene Lactone 4c. From the cycloheptane lactone (0.78 g, 3.8 mmol) was obtained 0.32 g (50%) of colorless liquid: bp 110–115 °C (0.07 mm); NMR (CCl_4) δ 4.7 (m, 1, CH), 5.5 (d, 1, CH=C), 6.15 (d, 1, CH=C); IR (neat) 1755 (C=O), 1665 (C=C) cm^{-1}. Its identity was proved by comparison with published spectra.[17]

Cyclooctane α-Methylene Lactone 4d. From 0.11 g (0.5 mmol) of lactone was obtained 0.07 g (78%) of yellow oil.

Similarly, from 0.65 g (3.0 mmol) of lactone was obtained 0.21 g (40%) of colorless liquid: bp 120–130 °C (0.2 mm); NMR (CCl_4) δ 4.65 (m, 1, CH), 5.5 (d, 1, CH=C), 6.15 (d, 1, CH=C); IR (neat) 1755 (C=O), 1660 (C=C) cm^{-1}.

Cyclooctane α-Methylene Lactone 4d. From 9.05 g (41.8 mmol) of lactone was obtained 4.73 g (63%) of orange liquid, which was distilled to give 3.32 g (44%) of colorless liquid, bp 108–112 °C (0.4 mm).

2-(*cis*-2-Hydroxy-5,6-isopropylidenedioxycyclohexyl)-2-propenoic Acid Lactone (7). A solution of 0.7 g (2.72 mmol) of acetal lactone **6**, 1.21 g (10.8 mmol) of diazabicyclo[2.2.2]octane, 1.64 g (10.8 mmol) of sodium iodide, and 30 mL of Me_2SO was warmed to 80 °C for 4 days. The cooled solution was then extracted with petroleum ether (4 × 50 mL) followed by extraction with 1:1 petroleum ether/ether (2 × 50 mL). The combined extracts were washed with cold 0.1 N HCl (2 × 50 mL), saturated $NaHCO_3$ (1 × 25 mL), and H_2O (1 × 25 mL). The organic layer was dried and the solvent stripped to yield 263 mg (51.8%) of white crystalline solid: mp 89–91 °C; IR (CCl_4) 1770 (C=O) cm^{-1}; NMR δ 1.3–1.85 [m, 10: 1.30 (s), 1.43 (s)], 3.45 (m, 1), 4.32 (m, 2), 4.76 (m, 1), 5.6 (d, 1), 6.2 (d, 1); MS 225 (M^+).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.28; H, 7.14. Found: C, 64.06; H, 7.17.

Acknowledgment. Support of this research by Grant CA 19203 from the National Cancer Institute of the National Institutes of Health is gratefully acknowledged.

Registry No.—**2a,** 25370-65-4; **2b,** 65337-65-7; **2c,** 65277-03-4; **2d,** 65277-04-5; **2e,** 42200-05-5; **2f,** 42077-49-6; **2g,** 13363-87-6; **2h,** 56084-87-8; **2i,** 65277-05-6; **2j,** 65277-06-7; **2k,** 65277-07-8; **3a,** 61769-60-6; **3b,** 65277-08-9; **3c,** 65277-09-0; **3d,** 65277-10-3; **3g,** 61769-65-1; **3h,** 65277-11-4; **4a,** 61747-55-5; **4c,** 3725-04-0; **4d,** 65277-12-5; **5,** 65277-13-6; **6,** 65277-14-7; **7,** 65277-15-8; α-chloropropionyl chloride, 13363-86-5; 2,2-dimethoxypropane, 77-76-9.

References and Notes

(1) Cycloadditions 23. For the previous paper in this series, see A. Hassner, R. M. Cory, and N. Sartoris, *J. Am. Chem. Soc.*, **98,** 7698 (1976).
(2) See, for example, W. Parker, J. S. Robert, and R. Ramage, *Q. Rev., Chem. Soc.*, **21,** 331 (1967).
(3) For several examples, see S. M. Kupchan, *Trans. N.Y. Acad. Sci.*, **32,** 85 (1970); S. M. Kupchan, M. A. Eakin, and A. M. Thomas, *J. Med. Chem.*, **14,** 1147 (1971).
(4) P. A. Grieco, *Synthesis*, 67 (1975), and references cited therein; R. B. Gamill, C. A. Wilson, and T. A. Bryson, *Synth. Commun.*, **5,** 245 (1975).
(5) (a) P. A. Grieco and C. S. Pogonowski, *J. Org. Chem.*, **39,** 1958 (1974). (b) An improved yield in the first step can be realized by bromination of the enol silyl ether: R. H. Reuss and A. Hassner, *Ibid.*, **39,** 1785 (1974).
(6) See, for instance, P. A. Grieco, M. Nishizama, S. D. Burke, and N. Marinovic, *J. Am. Chem. Soc.*, **98,** 1612 (1976); S. Danishefsky, T. Kitahara, R. McKee, and P. F. Schuda, *Ibid.*, **98,** 6715 (1976).
(7) V. R. Fletcher and A. Hassner, *Tetrahedron Lett.*, 1071 (1970); A. Hassner, V. R. Fletcher, and D. P. G. Hamon, *J. Am. Chem. Soc.*, **93,** 264 (1971).
(8) (a) These results were reported by the authors at the First Chemical Congress of the North American Continent, Mexico City, November 1975, Abstracts, ORG 122. (b) While this work was essentially completed, a similar sequence of reactions was reported by S. M. Ali and S. M. Roberts, *J. Chem. Soc., Chem. Commun.*, 887 (1975).
(9) (a) W. T. Brady, *Synthesis*, 415 (1971); (b) W. T. Brady and R. Roe, Jr., *J. Am. Chem. Soc.*, **92,** 4618 (1970); (c) **93,** 1662 (1971); (d) **92,** 146 (1970).
(10) M. Rey, S. Roberts, A. Dieffenbacker, and A. S. Dreiding, *Helv. Chim. Acta*, **53,** 417 (1970).
(11) A. E. Greene, J. C. Muller, and G. Ourisson, *J. Org. Chem.*, **39,** 186 (1974).
(12) Regiochemistry has been determined for silyl enol ethers: (a) L. R. Krepski and A. Hassner, unpublished results. For dienes: (b) W. T. Brady and B. M. Holifield, *Tetrahedron Lett.*, 5511 (1966); (c) W. T. Brady and B. M. Holifield, *Tetrahedron*, **23,** 4251 (1967); (d) W. T. Brady, F. H. Perry III, R. Roe, Jr., and E. F. Hoff, Jr., *Tetrahedron Lett.*, 819 (1970); (e) W. T. Brady and R. Roe, Jr., *J. Am. Chem. Soc.*, **92,** 4618 (1970). For β-pinene: (f) W. T. Brady and A. D. Patel, *J. Org. Chem.*, **38,** 4106 (1973).
(13) (a) C. H. Hassall, *Org. React.*, **9,** 73 (1957); (b) E. E. Smissman and J. V. Bergen, *J. Org. Chem.*, **27,** 2316 (1962).
(14) NMR spectra were obtained using a Varian EM-360 spectrometer with Me_4Si as an internal standard and were consistent with the proposed structures or with spectra previously reported (ref 9). IR spectra were run on either a Perkin-Elmer 337 or 451 spectrometer. Mass spectral data (run on a CH5 spectrometer) were obtained for most compounds and were consistent with the proposed structures.
(15) For valuable or nonvolatile olefins, an excess of α-chloropropionyl chloride (10–15%) is used. Otherwise, the olefin is in excess (10–100%).
(16) For a similar conversion, see L. Gruber, I. Tomoskozi, E. Major, and G. Kovacs, *Tetrahedron Lett.*, 3729 (1974).
(17) J. A. Marshall and N. Cohen, *J. Org. Chem.*, **30,** 3475 (1965).
(18) The mass spectra of these compounds exhibit a M + 1 peak rather than the expected M^+ peak; however, the fragment ions are consistent with their structures.