Table III. NMR Determination of the Equilibrium Constants of Charge Transfer Complexes

Complex	Solvent	Temp, °C	Δ^{A}_{AD}, Hz	K, l. M^{-1}
DVE–DMCP	Hexane	38	125.0	0.005
DVE–MA[10]	$CDCl_3$	24	33.5	0.036
St–DMCP	CCl_4	38	37.0	0.093
St–MA[10]	CCl_4	38	125.0	0.216

in uncomplexed form; $\Delta^{D}_{AD} = \delta^{A}_{AD} - \delta^{A}_{O}$, is the difference in the shift of the acceptor protons in pure complex; C_D is the concentration of the donor (which must always be much greater than the acceptor concentration in order that the quotient $\gamma_{AD}/\gamma_A\gamma_D$ remains constant over the range of solutions studied and thus $Q = K$, the equilibrium constant of complexation).

In these experiments the acceptor concentration was kept constant at 0.05 mol $l.^{-1}$, while the donor concentration was increased from 0.4 to 8.8 mol $l.^{-1}$. By plotting $1/\Delta^{A}_{obsd}$ as a function of $1/C_D$ a straight line was obtained in both cases. The slope of the line and its intersection with the ordinate permit a first approximation of the equilibrium constant of complexation and of the shift of acceptor protons in the pure complex. For a more exact determination of K and Δ^{A}_{AD}, the method of least squares was applied to eq 1, and the results obtained are shown in Table III. The data from the DVE study were subjected to a computer program for evaluation by the least-squares method. The results corroborated those obtained by a simple calculation, and further a correlation coefficient of 0.9995 was indicated. The corresponding values for maleic anhydride complexes are shown for comparison. The electron affinity of I thus appears to be considerably less than that of maleic anhydride. [See supplementary material (Tables IV and V) for additional experimental data.]

Acknowledgments. We gratefully acknowledge the support of this work in the form of financial support to one of us (R.M.A.) by the Glidden Organic Chemical Division of the SCM Corp. and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also gratefully acknowledge the many contributions by Dr. Richard L. Veazey during the course of this work.

Registry No.—I, 23529-83-1; IIa, 106-99-0; IIb, 78-79-5; IIc, 513-81-5; IId, 3036-66-6; IIIa, 60934-91-0; IIIb, 60934-92-1; IIIc, 60934-93-2; IIId, 60934-94-3; IVa, 109-89-7; IVb, 142-84-7; IVc, 122-39-4; Va, 60934-95-4; Vb, 60934-96-5; VIb, 27453-35-6; VIc, 52850-21-2; VII, 479-33-4; VIII, 684-16-2; IXb, 60934-97-6; X, 60934-98-7; XI, 22089-54-9; XII, 60934-99-8; XIV, 18552-96-0; St, 100-42-5; DVE, 109-93-3; DVE:DMCP, 60935-00-4; St:DMCP, 60935-01-5; ethylene glycol, 107-21-1; methyl cyclohexanecarboxylate, 4630-82-4.

Supplementary Material Available. Preparation, properties, and spectral data of IIIa, IIIb, and IIId and Tables IV and V (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) To whom correspondence should be addressed.
(2) (a) K. B. Baucom and G. B. Butler, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Texas, Feb. 1970, No. ORGN-139; (b) *J. Org. Chem.*, **37**, 1730 (1972).
(3) A. Hofman, W. Philipsborn, and C. H. Eugster, *Helv. Chim. Acta*, **48**, 1322 (1965).
(4) R. J. D. Smith and R. M. Jones, *Can. J. Chem.*, **37**, 2092 (1959).
(5) N. S. Bhacca, L. F. Johnson, and J. N. Shovlery, "Varian Associates NMR Spectra Catalog", National Press, New York, N.Y., 1962, Spectrum No. 51.
(6) M. J. Schlatter, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 223.
(7) H. Budzikiewiez, C. Djerani, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967, p 265.
(8) K. B. Baucom, Ph.D. Dissertation, University of Florida, 1971, p 36.
(9) M. . Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, **68**, 811 (1964).
(10) G. B. Butler and A. F. Campus, *J. Polym. Sci., Part A-1*, **8**, 545 (1970).

Reaction of Cyclopropenone Ketals with Alcohols[1]

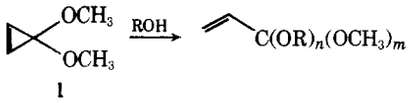
G. B. Butler,*[2] K. H. Herring, P. L. Lewis, V. V. Sharpe, III, and R. L. Veazey

Center for Macromolecular Science and Department of Chemistry, University of Florida, Gainesville, Florida 32611

Received August 5, 1976

3,3-Dimethoxycyclopropene (**1**), synthesized as previously described, undergoes a ring-opening reaction under mild conditions, with a variety of alcohols to give the corresponding monoalkyl dimethyl orthoacrylates. These results are consistent with a mechanism which involves initial protonation of **1** followed by solvolysis of the intermediate allyl oxonium cation. Less mild conditions result in exchange reactions between the alcohol and the methoxy groups of **1** giving the dialkyl methyl orthoacrylates and the trialkyl orthoacrylates. By a procedure similar to that used for **1**, 1,5-dioxaspiro[5.2]oct-7-ene (**5**), 1,5-dioxa-3,3-dimethylspiro[5.2]oct-7-ene (**6**) and 4,8,12,15-tetraoxatrispiro[2.2.2.2.2.2]pentadeca-1,10-diene (**7**) were prepared. These cyclic 3,3-dialkoxycyclopropenes were found to undergo reaction with alcohols in a manner similar to **1**. In addition, **5** was found to undergo an apparent thermal dimerization to yield the cyclobutane, dispiro[tricyclo[3.1.0.0^{2,4}]hexane-3,2′-(1′,3′-dioxane)-6,2″-(1″,3″-dioxane)] (**8**). The proposed structures were confirmed by NMR, IR, mass spectral, and elemental analyses.

In an attempt to prepare 1,1,2-trimethoxycyclopropane,[3a] a by-product in the preparation of 3,3-dimethoxycyclopropene (**1**),[3b] anhydrous methanol was reacted with **1**. Instead of the expected trimethoxycyclopropane, methyl orthoacrylate was obtained as the only product. To the best of our knowledge orthoacrylate esters have not been reported previously. We were interested in assessing the versatility of this reaction as a general synthetic route in substituted orthoacrylates.



1

$n = 1, m = 2$, R = CH_3 **2**
$n = 1, m = 2$, R = C_2H_5 **3**
$n = 2, m = 1$, R = C_2H_5 **3a**
$n = 3, m = 0$, R = C_2H_5 **3b**
$n = 1, m = 2$, R = $CH_3CH_2CH_2$ **4**
$n = 1, m = 2$, R = $(CH_3)_2CH$ **4a**
$n = 1, m = 2$, R = $(CH_3)_3C$ **4b**

Results and Discussion

Reaction with Alcohols. Optimum yields (73%) of methyl orthoacrylate (**2**) were obtained by treating **1** with anhydrous methanol at 0 °C for about 3 h. Higher temperatures, longer reaction times, and/or exposure to moisture gave rise to methyl β-methoxypropionate as a by-product. **2** prepared by this procedure had properties and spectra identical with those previously reported by Baucom.[4]

When 1 was treated with anhydrous ethanol under the same conditions as with methanol, ethyl dimethyl orthoacrylate (3) was obtained.

Should 3 or any mixed orthoacrylate not be isolated as soon as the reaction is complete, further exchange reactions are possible. For example, when 2 was allowed to react with ethanol at room temperature for several days, all three substituted orthoacrylates, 3, 3a, and 3b, were obtained.

The reaction of 1-propanol with 1 also yielded the monosubstituted product, 4. Anhydrous conditions must be employed or β-alkoxypropionate esters are obtained.

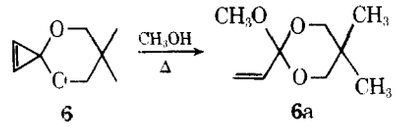
When 1 is treated with 2-propanol, the monosubstituted isopropyl dimethyl orthoacrylate (4a) is formed. A longer reaction time at 0 °C for 5 h was necessary.

tert-Butyl alcohol reacted even more slowly with 1. The reaction required about 22 h at 23 °C before cyclopropenyl hydrogens were no longer detectable in the NMR spectrum of the product mixture. The product, *tert*-butyl dimethyl orthoacrylate (4b), is unstable at temperature much above room temperature but could be purified by distillation under vacuum at room temperature or below.

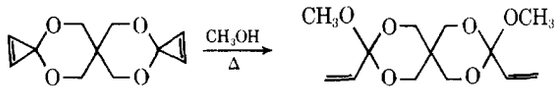
Reactivity of Cyclopropenone Cyclic Ketals with Alcohols. Since cyclic ketals are known to be more stable than their acyclic analogues,[5] we hoped that the cyclopropenone analogues would also be more thermally stable than 1. The desired cyclic ketals were prepared by first reacting 1-bromo-3-chloro-3,3-dimethoxypropane with the appropriate diol in the presence of a catalytic amount of sulfuric acid. The cyclic 2-bromomethyl-2-chloromethyl-1,3-dioxanes were obtained in yields up to 90%.

Cyclopropene ring formation was accomplished with potassium amide in liquid ammonia by employing the procedure reported by Albert and Butler.[6]

In a similar manner compounds 6 and 7 reacted with refluxing methanol to yield orthoacrylates (6a, 7a) in 59 and 55% yields, respectively.

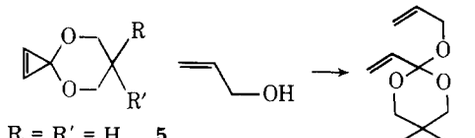


6 6a



7 7a

The addition of allyl alcohols to 5 and 6 should result in the formation of cyclopolymerizable diene monomers.[8] The dienes were prepared by reacting a 1:1 molar ratio of either 5 or 6 with

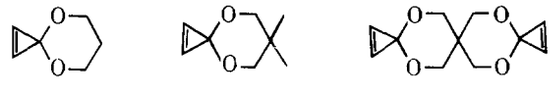


R = R' = H 5
R = R' = CH_3 6

10 11

allyl alcohol in methylene chloride. The reaction required several days at room temperature to go to completion. The dimer, 8, was obtained as a side product when 5 was the reactant.

Spectral Analysis. The nuclear magnetic resonance spectra (NMR) of the cyclopropenyl ketals show characteristic cyclopropenyl hydrogen absorptions as a singlet around δ 7.8–7.9.[9] The vinyl protons of the orthoacrylates appear as complex ABC multiplets between δ 5.1 and 5.8. Cyclic orthoacrylates show complex absorbances due to the complex

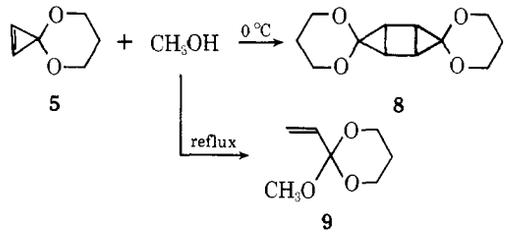


5 6 7

couplings of the ring protons. Further NMR studies are being carried out in this department on these compounds. In this manner 1,5-dioxaspiro[5.2]oct-7-ene (5), 1,5-dioxa-3,3-dimethylspiro[5.2]oct-7-ene (6), and 4,8,12,15-tetraoxatrispiro[2.2.2.2.2.2]pentadeca-1,10-diene (7) were prepared.

Albert and Butler prepared the ethylene ketal 1,4-dioxaspiro[4.2]hept-6-ene but were unable to separate it from side products.[7]

When 5 was treated with methanol under the same conditions as employed for 1, a quantitative yield of the dimer, dispiro[tricyclo[3.1.0.$0^{2,4}$]hexane-3,2'-(1',3'-dioxane)-6,2''-(1'',3''-dioxane)] (8) was obtained. None of the expected

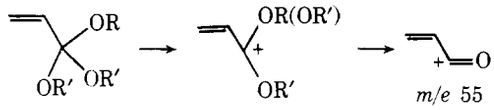


5 8 9

orthoacrylate, 9, was detected. However, under reflux conditions a moderate yield of 9 (65%) was obtained along with 9% of 8. No further reaction with methanol occurs as it does with the orthoacrylates of 1. In separate experiments it was found that neither the dimer of 1 nor 8 reacts with hot methanol.

The infrared spectra of the orthoacrylates exhibit very weak and sometimes no peaks around 1625 cm^{-1} for the vinyl protons.[10] This was attributed to a combination of both steric and electron-withdrawing effects of the ortho ester group.[11]

Predominant peaks in the mass spectra of orthoacrylates are those due to the loss of alkoxy groups. The resulting allyl oxonium ions usually give rise to the vinyl carbonyl ion as the base peak at *m/e* 55. Only the trimethyl derivative, 2, shows



m/e 55

a parent ion and then only at 0.02% of the base peak. The ion fragmentation patterns are similar to those of other ortho esters.[12] The dimer, 8, shows a prominent parent ion as well as a P − 1 ion. The stabilities of these ions can be attributed to their electronic isomeric structures.[12]

Experimental Section

All temperatures are reported uncorrected in °C. All pressures are expressed in millimeters of mercury. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60A spectrometer. The chemical shift data are reported relative to an internal reference tetramethylsilane using the parameter δ. The solvent used was deuteriochloroform. Mass spectral data were obtained from a Hitachi Perkin-Elmer RMU mass spectrometer using an ionization voltage of 70 eV unless otherwise stated. Infrared spectra were recorded with a Beckman IR8 infrared spectrophotometer. The IR8 scan is linear with respect to wavenumber and data are reported in units of reciprocal centimeters (cm^{-1}). Gas chromatography (GC) was conducted on a Hewlett-Packard 700 laboratory chromatograph. The column used was stainless steel, 12 ft × 0.5 in. o.d. The solid support was Chromosorb G* (60–80 mesh); the liquid phase was loaded 30% w/w Carbowax*. Injection port and column temperatures were 120–140 °C; detector temperature was 150 °C. All solvents and chemicals used as reactants were commercial grade and were used as received unless otherwise noted. The alcohols used were dried carefully by standard procedures immediately prior to use.

Preparation of 1. The procedure developed by Albert and Butler was used without revision.[6,7]

Reaction of 1 with Anhydrous Methanol. A clean, dry, 50-ml round-bottom flask was equipped with a stirring bar and rubber septum, and dried by passing nitrogen through it for 45 min. This flask was then charged with 25.0 ml of anhydrous methanol, and the system was cooled to 0 °C in an ice bath. Then 2.11 g (2.11×10^{-2} mol) of 1 was injected with a small syringe into the stirring methanol. The system was stirred for approximately 3 h and the ice bath was allowed to warm to room temperature. At the end of 3 h, GC analysis showed methanol and a single product peak. The product was recovered by distillation of the methanol and vacuum distillation (25 °C, 1.0 mm) of the methyl orthoacrylate (2). A total of 2.04 g (73.2% yield) of product was recovered.

The NMR spectrum showed peaks at δ 3.23 (9 H, s) and 5.53 (3 H, m). The IR spectrum exhibited absorbances at 2960 (s), 1625 (w), 1440 (m), 1411 (m), 1240 (m), 1180 (s), 1080 (s), 1040 (s), 994 (m), and 948 cm^{-1} (m). Mass spectral analysis revealed major ion peaks at *m/e* (rel intensity) 132 (0.02), 131 (0.04), 117 (8.2), 105 (30.2), 102 (9.2), 101 (100), 59 (23.4), 55 (97.4), 45 (21.3), 27 (42.1); metastable ion (reaction), 29.9 (101 → 55). Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.17. Found: C, 54.55; H, 9.25.

Reaction of 1 with Other Alcohols. 1 was treated with anhydrous ethanol by a procedure analogous to that reported for the reaction with methanol. Dimethyl ethyl orthoacrylate (3) was recovered by vacuum distillation of the ethanol at 25 °C (25 mm); 3 distilled at 35 °C (0.025 mm), yield 29.5%.

The reaction of 1 with anhydrous 1-propanol was accomplished by the same procedure. The product, dimethyl propyl orthoacrylate (4), was recovered by vacuum distillation of propanol at 25 °C (25 mm); 4 distilled at 45 °C (0.75 mm) and was further purified by GC.

The reaction of 1 with anhydrous 2-propanol was accomplished by the same procedure except that a reaction time of 5 h was necessary before the NMR absorbances of the vinyl protons were no longer detectable. A single product, dimethyl isopropyl orthoacrylate (**4a**), was recovered after vacuum distillation of 2-propanol at approximately 25 °C (25 mm), followed by preparative GC.

The reaction of 1 with *tert*-butyl alcohol was accomplished by the same procedure except that a reaction time of about 22 h at room temperature (23 °C) was necessary for complete reaction. The product, dimethyl *tert*-butyl orthoacrylate (**4b**), was recovered from the remaining, decomposed 1 by vacuum distillation at 20 °C (0.5 mm), yield 3.69 g (68%).

Exchange Reaction between 2 and Ethanol. A clean, dry, 25-ml round-bottom flask was equipped with a stirring bar and rubber septum, and dried by passing nitrogen through it for 35 min. Into the vessel were injected 10.0 ml of anhydrous ethanol and 1.44 g (1.09×10^{-2} mol) of **2.** After 4 days at room temperature with stirring, the ethanol was vacuum distilled at 25 °C (25 mm). The product mixture was analyzed by GC. Temperatures and column parameters were as follows: oven, 95 °C; detector, 190 °C; injection port, 170 °C; 0.25 in. o.d. × 8 ft loaded 10% w/w Carbowax on Chromosorb P*. Four fractions were collected and analyzed. The first fraction (F1) constituted 11.8% of the product mixture and was identified by retention time as **2.** The second fraction (F2) constituted 20.6% of the product mixture and was identified by NMR, IR, and mass spectral analysis to be **3.** The third fraction (F3) was identified as diethyl methyl orthoacrylate (**3a**) which constituted 25.9% of the product mixture. The fourth fraction (F4) was identified as ethyl orthoacrylate (**3b**). It constituted 31.7% of the product mixture.

Preparation of 2-Bromomethyl-2-chloromethyl-1,3-dioxane. A mixture of 108.7 g (0.5000 mol) 1-bromo-3-chloro-2,2-dimethoxypropane and 38.0 g (0.5000 mol) of 1,3-propanediol was heated to about 95 °C in the presence of 4 drops of sulfuric acid. The mixture was maintained at 95 °C for 2 h while methanol distilled. The temperature of the reaction mixture was then increased to 130 °C and maintained there for 2 h to ensure complete reaction. The product was crystallized from ether/pentane to yield 57.8 g of a white, crystalline solid product. The combined filtrates were concentrated to a light yellow oil. An NMR analysis of this oil revealed that it was mostly the starting ketal. To it was added 20.0 g (0.263 mol) of 1,3-propanediol, and the mixture was heated to 110–130 °C for 8 h. After cooling, the yellow-brown oil was crystallized from ether/pentane to yield an additional 23.0 g of product. The combined yield of the product was 80.8 g (77.5%). The product was recrystallized from ether/pentane to give white crystals which melted at 59–60 °C. The NMR spectrum showed peaks at δ 1.78 (2 H, p, J = 5.6 Hz), 3.70 (2 H, s), 3.81 (2 H, s), and 3.96 (4 H, t, J = 5.6 Hz). The IR spectrum (KBr) showed absorbances at 2997 (m), 2887 (m), 2807 (m), 1478 (m), 1469 (m), 1425 (s), 1246 (s), 1207 (s), 1096 (s), 1017 (s), 930 (m), 851 (m), 738 (m), and 674 cm^{-1} (m). The mass spectrum showed major ions at *m/e* (rel intensity) 181 (46.2), 179 (47.7), 153 (7.7), 151 (7.7), 137 (35.4), 135 (100.0), 123 (38.5), 121 (41.5), 109 (6.2), 107 (16.9), 95 (9.2), 93 (9.2), 79 (23.1), 77 (69.2), 59 (13.8), 51 (7.7), 49 (20.0), 43 (9.2), 42 (23.1), 41 (26.2), 39 (12.3), 29 (13.8), and 27 (24.6). Anal. Calcd for $C_6H_{10}O_2ClBr$: C, 31.40; H, 4.40; Cl, 15.45; Br, 34.82. Found: C, 31.53; H, 4.40; Cl, 15.32; Br, 35.00.

Preparation of 2-Bromomethyl-2-chloromethyl-5,5-dimethyl-1,3-dioxane. This compound was prepared in 86% yield according to the procedure described for 2-bromomethyl-2-chloromethyl-1,3-dioxane. The compound distilled as a colorless liquid, bp 98 °C (0.04 mm).

Preparation of 2,4,8,10-Tetraoxaspiro[5.5]-3,9-di(bromomethyl)-3,9-di(chloromethyl)undecane. This compound was prepared in 92% yield by the same procedure as reported for 2-bromomethyl-2-chloromethyl-1,3-dioxane. Pentaerythritol was the starting alcohol. The compound is a white solid, mp 157.5–158.5 °C.

Preparation of 5. This compound was prepared in 73.8% yield from 2-bromomethyl-2-chloromethyl-1,3-dioxane according to the procedure described by Albert and Butler.[6,7] The product distilled at 35–40 °C (0.3–0.4 mm) as a colorless liquid. The NMR spectrum showed peaks at δ 1.81 (2 H, p, J = 5.6 Hz), 3.97 (4 H, t, J = 5.6 Hz), and 7.83 (2 H, s). The IR spectrum (neat) showed absorbances at 3138 (m), 3108 (s), 2980 (s), 2868 (s), 1598 (s), 1483 (m), 1458 (m), 1428 (m), 1364 (m), 1297 (s), 1272 (s), 1242 (s), 1150 (s), 1082 (s), 1023 (s), 923 (s), 900 (s), 856 (m), and 728 cm^{-1} (m). The mass spectrum showed major ion fragments at *m/e* (rel intensity) 112 (19.2), 111 (3.8), 86 (9.6), 82 (7.6), 55 (40.4), 54 (100.0), 53 (13.5), 42 (13.5), 41 (11.5), 32 (13.5), 29 (11.5), 28 (55.8), and 26 (32.7). Metastable ion (reactions) occur at 110.01 (112 → 111) and 66.74 (112 → 86). Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.10; H, 7.19.

Preparation of 6. The preparation of this compound was accomplished in 70% yield by using the procedure described by Albert and Butler,[6,7] bp 40–55 °C (0.015 mm) (colorless liquid).

Preparation of 7. This compound was prepared in 95% yield from 2,4,8,10-tetraoxaspiro[5.5]-3,9-di(bromomethyl)-3,9-di(chloromethyl)undecane according to the procedure reported by Albert and Butler.[6,7] The product is a white solid which explodes above 130 °C. The compound was recrystallized from a mixture of ethyl acetate and hexane.

Reaction of 5 with Methanol at 0 °C. The procedure described for the reaction of 1 and methanol was repeated with **5.** A white precipitate immediately began to form, and at the conclusion of the 3-h reaction time a 95% yield of a white solid, mp 158–160 °C, was obtained. The compound was identified as the dimer, **8,** based upon spectral examination. The NMR spectrum showed absorbances at δ 1.86 (4 H, p, J = 5.6 Hz), 1.91 (4 H, s), 3.94 (4 H, t, J = 5.6 Hz), and 4.03 (4 H, t, J = 5.6 Hz). The IR spectrum (KBr) showed peaks at 3058 (m), 2990 (s), 2970 (m), 2933 (m), 2859 (w), 1472 (m), 1461 (w), 1397 (s), 1376 (s), 1285 (m), 1248 (s), 1197 (s), 1154 (s), 1101 (s), 1074 (s), 996 (m), 944 (m), 908 (m), and 871 cm^{-1} (s). The mass spectrum showed major ion fragments at *m/e* (rel intensity) 224 (10.9), 223 (5.5), 195 (25.5), 194 (5.5), 167 (9.1), 166 (49.1), 165 (9.1), 153 (16.4), 152 (90.1), 139 (12.7), 138 (36.2), 137 (14.5), 126 (12.7), 112 (18.2), 96 (18.2), 95 (10.9), 94 (54.5), 82 (20.0), 54 (20.0), 52 (54.5), 42 (54.5), and 41 (63.6). Metastable ion peaks appear (reaction) at 169.8 (224 → 195), 114.7 (166 → 138), and 87.8 (138 → 110). Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.38; H, 7.11.

Reaction of 5 with Refluxing Methanol. To 20 ml of refluxing freshly distilled anhydrous methanol was added 2.16 g (0.0193 mol) of **5.** The solution was gently refluxed for 4 h, cooled, and analyzed by NMR spectroscopy. The NMR showed that cyclopropenyl hydrogens were absent. The methanol was distilled at room temperature and reduced pressure to yield a light straw colored oil. Distillation at 38–44 °C (0.04 mm) yielded 1.80 g (64.7%) of the cyclic orthoacrylate (**9**) and 0.19 g (8.8%) of the dimer, **8.** The NMR spectrum of the adduct showed absorbances at δ 1.24–2.56 (2 H, m), 3.23 (3 H, s), 3.57–4.47 (4 H, m), and 5.20–5.81 (3 H, m). The IR spectrum (neat) showed peaks at 2989 (m), 2903 (w), 2848 (w), 1416 (m), 1257 (m), 1247 (m), 1149 (w), 1117 (s), 1078 (s), 1054 (s), and 967 cm^{-1} (m). The mass spectrum showed major ion fragments at *m/e* (rel intensity) 113 (3.7), 99 (5.5), 89 (15.7), 87 (5.5), 73 (14.8), 72 (88.8), 71 (24.1), 59 (14.8), 57 (13.0), 55 (100.0), 45 (92,5), 44 (7.4), 43 (5.5), 42 (14.8), 41 (13.0), 32 (16.7), 31 (24.1), 29 (18.5), and 27 (24.1). Anal. Calcd for $C_7H_{12}O_3$: C, 63.51; H, 8.29. Found: C, 63.34; H, 8.26.

Reaction of 6 with Methanol. The procedure described for the reaction of **5** with refluxing anhydrous methanol was followed for **6.** A 59% yield of a colorless liquid which distilled at 30 °C (0.01 mm) was obtained as the only product (**6a**).

Reaction of 7 with Methanol. The procedure described for the reaction of **5** with refluxing anhydrous methanol was repeated with

7. Distillation at 120 °C (0.03 mm) gave a 54.7% yield of a colorless liquid which solidified upon standing. The compound was further purified by sublimation at 90 °C (0.03 mm) to give **7a**, a white solid, mp 53–54 °C.

Reaction of 1-Dimer[3b] or 8 with Refluxing Anhydrous Methanol. Approximately 0.5 g of the appropriate dimer was placed in 50 ml of methanol, and the solution was heated to reflux for 30 min. Upon cooling, the respective dimer crystallized and was identified by comparing its melting point and NMR spectrum to those of the authentic compound. No other products were detected.

Reaction of 5 with Allyl Alcohol. To a clean, dry, 25-ml round-bottom flask flushed with dry nitrogen and capped with a rubber septum were added 2.11 g (0.0188 mol) of **5** and 5 ml of dry methylene chloride by means of a syringe. After the contents of the flask were stirred to ensure solution, 1.17 g (0.0200 mol) of anhydrous allyl alcohol was added in one portion by means of a syringe. The sample was stirred and allowed to stand at room temperature for 7 days, at which time an NMR spectrum of the solution showed no cyclopropenyl hydrogens present. The sample was diluted with 25 ml of ether, and 0.74 g (35.0% yield) of a white solid was recovered. This compound was identified as the dimer, **8**, by comparing its melting point, IR, and NMR spectra to that of the authentic compound. The ether–methylene chloride solution was concentrated to about 1 ml in volume by distillation at room temperature and reduced pressure. High vacuum distillation yielded 0.91 g (28% yield) of a colorless liquid which boiled at 38–42 °C (0.1 mm). This compound was identified as the allyl alcohol adduct, **10**, on the basis of IR, NMR, and mass spectral analysis. The NMR spectrum gave peaks at δ 1.15–2.28 (2 H, m), 3.28–4.05 (6 H, m), and 4.53–5.74 (6 H, m). The IR spectrum (neat) gave absorbances at 3108 (m), 3093 (m), 2971 (s), 2936 (s), 2892 (s), 1647 (m), 1468 (m), 1407 (s), 1367 (m), 1292 (m), 1238 (s), 1117 (s), 1063 (s), 1027 (s), 969 (m), 922 (m), and 856 cm^{-1} (w). The mass spectrum gave major ion fragments at *m/e* (rel abundance) 143 (1.2), 129 (1.2), 114 (3.8), 113 (42.2), 100 (1.9), 87 (2.5), 86 (5.0), 85 (6.3), 73 (6.9), 71 (2.3), 69 (2.3), 58 (12.0), 57 (39.0), 56 (10.7), 55 (100.0), 43 (5.0), 42 (6.3), 41 (40.8), 39 (15.7), 31 (18.9), 29 (13.8), 28 (25.2), and 27 (28.3). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.34; H, 8.26.

Reaction of 6 with Allyl Alcohol. This compound was treated with allyl alcohol by employing the same procedure as reported for **5** and allyl alcohol. No dimeric product was obtained upon the addition of ether. After the ether and methylene chloride were removed at reduced pressure and room temperature, several milliliters of a light straw colored oil remained. Distillation at 38 °C (0.04 mm) gave a 40% yield of a colorless liquid which was identified as the allyl alcohol adduct, **11**, by analysis of its spectra.

Acknowledgments. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, for which we are grateful. One of us (P.L.L.) also received financial support from the National Science Foundation Undergraduate Research Participation Program, summer 1973.

Registry No.—**1**, 60935-33-3; **2**, 60935-34-4; **3**, 60935-35-5; **3a**, 60935-36-6; **3b**, 42216-96-6; **4**, 60967-61-5; **4a**, 60935-37-7; **4b**, 60935-20-8; **5**, 60935-21-9; **6**, 60935-22-0; **6a**, 60935-23-1; **7**, 60935-24-2; **7a**, 60935-25-3; **8**, 60935-26-4; **9**, 60935-27-5; **10**, 60935-28-6; **11**, 60935-29-7; methanol, 67-56-1; ethanol, 64-17-5; propanol, 71-23-8; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; 2-bromomethyl-2-chloromethyl-1,3-dioxane, 60935-30-0; 1-bromo-3-chloro-2,2-dimethoxypropane, 22089-54-9; 1,3-propanediol, 504-63-2; 2-bromomethyl-2-chloromethyl-5,5-dimethyl-1,3-dioxane, 60935-31-1; 2,4,8,10-tetraoxaspiro[5.5]-3,9-di(bromomethyl)-3,9-di(chloromethyl)undecane, 60935-32-2; pentaerythritol, 115-77-5; allyl alcohol, 107-18-6; 2,2-dimethyl-1,3-propanediol, 126-30-7.

Supplementary Material Available. Mass spectra of orthoacrylates and additional NMR and mass spectral data (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented in part as paper no. 227 before the Organic Division, Southeastern Regional Meeting, American Chemical Society, Norfolk, Va., Oct 1974.
(2) To whom correspondence should be addressed.
(3) (a) Unreported results, G. B. Butler and R. L. Veazey; (b) K. B. Baucom and G. B. Butler, *J. Org. Chem.*, **37**, 1730 (1972).
(4) K. B. Baucom, Ph.D. Dissertation, University of Florida, 1971.
(5) J. F. W. McOmie, *Adv. Org. Chem.*, **3**, 191 (1963).
(6) G. B. Butler and R. M. Albert, Abstracts, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974, No. ORGN-125.
(7) R. M. Albert and G. B. Butler, *J. Org. Chem.*, preceding paper in this issue.
(8) G. B. Butler, G. C. Corfield, and C. Aso, *Prog. Polym. Sci.* **4**, 71 (1975).
(9) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1967.
(10) K. Nakanishi, "Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif., 1962.
(11) L. J. Bellamy, "The Infra-red Spectra of Complex Organic Molecules", 2d ed, Wiley, New York, N.Y., 1958.
(12) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, Calif., 1967.

Direct Oxidation of Tertiary Allylic Alcohols. A Simple and Effective Method for Alkylative Carbonyl Transposition[1]

William G. Dauben* and Drake M. Michno

Department of Chemistry, University of California, Berkeley, California 94720

Received July 6, 1976

The oxidation of cyclic tertiary allylic alcohols, generated by the 1,2 addition of organometallic reagents to α,β-unsaturated cyclic ketones, with pyridinium chlorochromate (PCC) affords transposed 3-alkyl α,β-unsaturated ketones in excellent yield. Acyclic tertiary allylic alcohols also undergo this rearrangement in fair to good yields. Tertiary allylic alcohols generated by the addition of vinylmagnesium bromide to saturated ketones can be oxidized to the corresponding α,β-unsaturated aldehydes in good to excellent yield with PCC.

The ability to transpose a functional group efficiently from one carbon to another, as in 1,3-carbonyl transposition of α,β-unsaturated ketones, offers a wide degree of latitude in synthetic design of many naturally occurring compounds. In recent years a number of synthetic methods and reagents have become available for effecting this type of functional exchange. Among the methods commonly employed are included allylic interconversion of oxygen with selenoxide,[2] sulfoxide,[3] and amine oxides[4] via 2,3-sigmatropic rearrangements and the Wharton epoxy ketone rearrangement.[5] The formation and subsequent rearrangement of isoxazoles[6] has also been used to accomplish this exchange of functionality. In general, however, these methods suffer from inferior yields and/or multistep manipulation of delicate intermediates.

In a variation on this theme, Trost[7] has recently developed a procedure by which tertiary allylic alcohols, generated by the 1,2 addition of an organometallic reagent to an α,β-unsaturated ketone, are converted in several steps to new,