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Dual Reactivity of 3,3-Dimethoxycyclopropene

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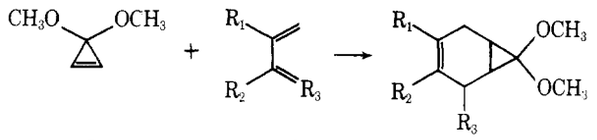
Charge transfer complex studies indicate that 3,3-dimethoxycyclopropene (I) is an electron-deficient olefin. Initial studies of its chemical reactivity were consistent with this conclusion. Diels–Alder reactions with electron-rich dienes (II) gave high yields of the postulated 7,7-dimethoxy-3-norcarenes (III) under mild conditions. Secondary amines (IV) reacted with I to give cyclopropylamines (V) and/or β-alanine derivatives (VI). Both products could arise from nucleophilic attack of the amine on the cyclopropene system. However, an alternative mechanism is also proposed. The reactions of I with tetracyclone (VII) and hexafluoroacetone (VIII) are best explained by nucleophilic attack of I on the carbonyl carbon of these compounds. The reaction with VII proceeds with cleavage of the cyclopropene ring and subsequent ring closure to a 2-furanone derivative (IXb). In the case of VIII, the adduct is a bicyclic oxetane (X). An improved synthesis of I is also reported. Also, cyclization of 1-bromo-3-chloro-2,2-ethylenedioxypropane (XII) to yield 3,3-ethylenedioxycyclopropene (XIII) along with 3,3-ethylenedioxycyclopropane (XIV) as a by-product is reported.

The synthesis of 3,3-dimethoxycyclopropene (I) in pure form was first accomplished in 1968.[2] Preliminary studies of its chemical reactivity indicated it to be a highly reactive species possessing a somewhat electron-deficient double bond. A study of charge transfer (CT) complexation using the NMR method now adds support to this conclusion. It was found that both styrene and divinyl ether, two electron-rich olefins, gave CT complexes with I. The equilibrium constants were 9.3×10^{-2} l. mol^{-1} for the styrene complex and 0.5×10^{-2} in the case of divinyl ether.

Diels–Alder Reactions of I. Diels–Alder reactions of I with electron-rich dienes (II) was therefore considered a favorable route to the unusual 7,7-dimethoxy-3-norcarenes. When I was mixed with an excess of IIa, IIb, or IIc and the solution allowed



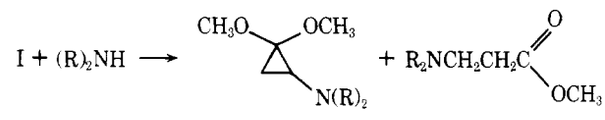
I IIa-d IIIa-d

R_1, R_2, R_3 = (a) H, H, H; (b) H, CH_3H; (c) CH_3, CH_3H; (d) H, H, OCH_3

to stand at room temperature for several days, the expected adducts were formed in high yield. Because of the symmetry of these systems, only one isomer was possible in each case. Pure samples were obtained by preparative gas chromatography (GC). Spectroscopy and elemental analysis (see Experimental Section) confirmed the predicted structures of IIIa–c. IIIa was hydrogenated to yield methyl cyclohexanecarboxylate.

When I and IId (threefold excess of diene) were mixed without solvent, high conversion to the adduct was observed. Analysis of the product after distillation (by GC) showed four components in the approximate ratio of 5:9:20:66. Isolation of the major component by preparative GC gave a product whose NMR, IR, and elemental analysis were completely consistent with the expected adduct, IIId. The second and third minor components were shown to consist largely of methyl benzoate. The first minor component was not identified (See supplementary material for further experimental details.)

Reactions of I with Secondary Amines. When I was added to excess diethylamine (IVa) and the mixture stored at room temperature for several days, the major product formed (60% by preparative GC) was 1,1-dimethoxy-2-diethylaminocyclopropane (Va). The NMR, IR, and mass spectra and elemental analysis gave data consistent with Va.

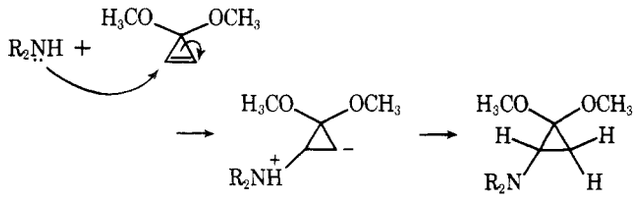


IVa-c Va-c VIa-c

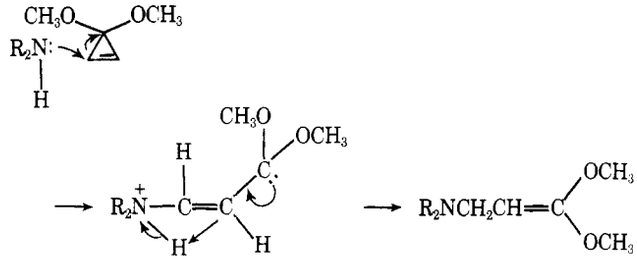
R = (a) C_2H_5; (b) C_3H_7; (c) C_6H_5

Addition of I to IVb gave a considerably more complex product. Analysis by GC indicated that two major components comprised about 85% of the mixture and that these components were present in a ratio of 40:60. Pure samples of each were then obtained by preparative GC.

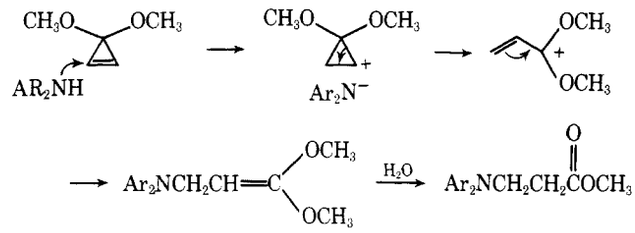
The first component was identified by spectroscopy as 1,1-dimethoxy-2-di-*n*-propylaminocyclopropene (Vb), the expected product. The second component was identified by spectroscopy as *N,N*-di-*n*-propyl-β-alanine methyl ester (VIb). Use of diphenylamine (IVc) in the reaction with I led predominantly to *N,N*-diphenyl-β-alanine methyl ester (VIc). Analysis of the crude reaction product by NMR revealed the absence of cyclopropyl protons; indicating only ring-opened product. Purification by silica gel chromatography yielded VIc in 65% recovery. NMR, IR, mass spectral, and elemental analyses were consistent with this structure. Mechanistically, the simple addition reaction may be considered as a nucleo-



philic attack at C-1 by the electron pair on nitrogen with production of negative charge at C-2, followed by proton transfer to complete the addition. Alternatively, 1,3 cleavage could occur followed by reorganization of the electron system and protonation at C-1 to give the ketene acetal. Hydrolysis



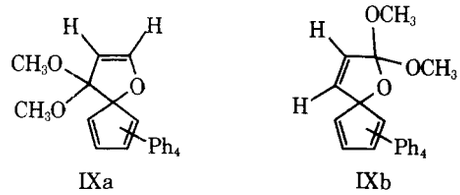
of the ketene acetal would then give the alanine esters observed. However, an alternative mechanism which may account for the increased degree of ring opening of I with acidity of the amine could involve initial proton attack followed by ring opening and amide addition to complete the process:



The order of reactivity here is consistent with the acidity constants for the amines (Ar_2NH, $pK_a = 23$; $EtNH_2$, $pK_a = 33$).

Reaction of I with Ketones. Reaction of I with tetracyclone (VII) might have been expected to give the Diels–Alder adduct. Such a reaction might serve as a convenient synthesis of substituted cycloheptatrienes through 1,4 cycloaddition and loss of carbon monoxide. However, NMR analysis of the product of this reaction was inconsistent with all of the expected structures and elemental analysis was consistent with a 1:1 adduct without the loss of carbon monoxide. Also, the IR spectrum was free of carbonyl absorption. Treating a sample of this adduct with aqueous acetone and a trace of acid resulted in the loss of methoxy signals in the NMR and the appearance of an intense carbonyl peak at 1780 cm^{-1} in the IR spectrum. The NMR spectrum also showed a widely separated AB quartet with a coupling constant, J_{AB}, of 5.5 Hz.

These observations are consistent with a structure in which a ring-opened cyclopropene has added across the carbonyl of VII. Two modes of addition appear possible, to give either IXa or IXb. Acid-catalyzed hydrolysis of these compounds should

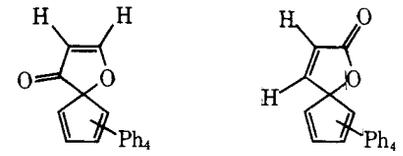


IXa IXb

give derivatives of a 3(2*H*)-furanone (IXc) and a 2(5*H*)-furanone (IXd), respectively. Spectral data for the unsubstituted furanones, available from the literature, are tabulated in Table I and compared with the data obtained for the hydrolysis product. On the basis of these comparisons, structure IXb was assigned to the adduct.

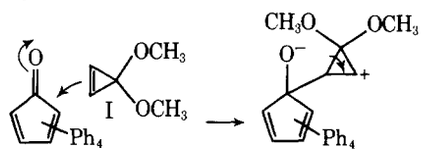
Table I. NMR Spectral Data for Certain Unsubstituted Furanones

Compd	IR, cm^{-1}	Chemical shift, δ A protons	B protons	J_{AB}, Hz
3(2*H*)-Furanone (IXc)[3]	1706	5.07	8.23	2.5
2(5*H*)-Furanone (IXd)[3]	1775, 1745[4]	7.63[5]	6.15	5.2
Hydrolyzed adduct	1780	7.45	6.10	5.5

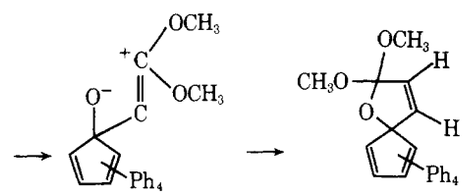


IXc IXd

Since VII has an electron-deficient carbonyl group, the mechanism can be viewed as nucleophilic attack by the olefin on that carbonyl carbon, followed by 1,3-bond cleavage and cyclization.

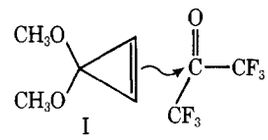


VII

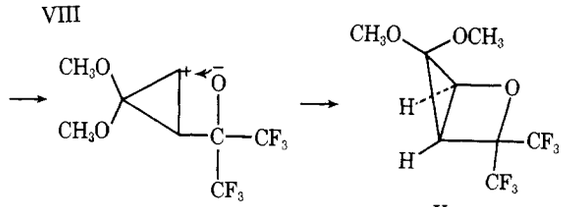


IXb

Hexafluoroacetone (VIII) is electrophilic in nature and two modes of addition to I could be postulated. The first is analogous to the reaction with VII, involving ring opening of the cyclopropene. Alternatively, the product could retain the three-membered ring by closure at C-2 to give the bicyclic system, 3,3-bis(trifluoromethyl)-5,5-dimethoxy-2-oxabicyclo[2.1.0]pentane (X).



I VIII



X

When I and excess VIII were mixed and allowed to stand for 3 days at room temperature there was smooth and complete conversion to a single compound which was readily purified by use of a silica gel 60 column (EM Reagents, 70–230 mesh).

^1H and ^{19}F NMR, IR, mass spectral, and elemental analysis are consistent with the assignment of structure X to this compound. In contrast to IXb, X was resistant to hydrolysis.

Table II. Mass Spectral Fragments from 3,3-Ethylenedioxycyclopropane

m/e	Rel intensity	Mol formula	Fragment lost
100	74	$C_5H_8O_2^+$	Molecular ion
56	62	$C_3H_4O^+$	C_2H_4O
44	48	$C_2H_4O^+$	C_3H_4O
99	100	$C_5H_7O_2^+$	H
55	92	$C_3H_3O^+$	C_2H_4O
43	90	$C_2H_3O^+$	C_3H_4O
40	42	$C_3H_4^+$	$C_2H_4O_2$

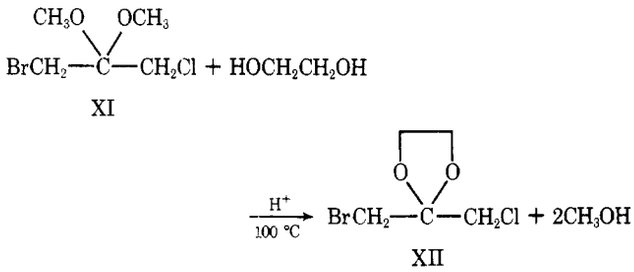
After 17 h in refluxing aqueous dioxane containing a trace of acid, X was recovered unchanged.

Improved Synthesis of I. Cyclization of 1-bromo-3-chloro-3,3-dimethoxypropane (XI) with potassium amide in liquid ammonia was accomplished[2] by addition to the potassium amide solution. Yields were reported to be 30–50%; however, in this work, this procedure gave inconsistent yields of 0–50% with 10–15% being the most frequent results.

Significant improvement was realized by reversing the order of addition of reactants in the cyclization process. Yields in the range of 40–58% were consistently obtained. This modification also results in a safer process which permitted scaling up to five times the original 0.1 M quantities.

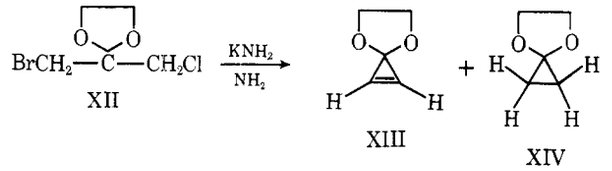
The apparatus used was similar to that of Schlatter,[6] which consisted of two flasks arranged side by side with appropriate connecting tubes and provisions for pressurizing one of the flasks. The potassium amide was prepared in the usual fashion and then transferred by means of nitrogen pressure to the other flask which contained XI in excess ammonia. A relatively short reaction time at the temperature of refluxing ammonia was required to complete the cyclization and excess amide was destroyed with ammonium chloride. Isolation of the product then followed the established process.

Preparation of 1-Bromo-3-chloro-2,2-ethylenedioxypropane (XII). Successful preparation of XII was achieved

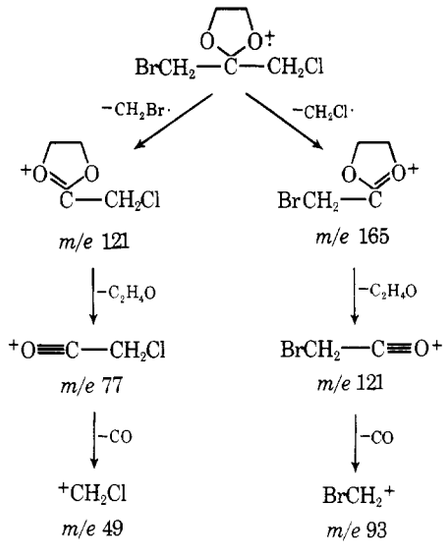


in essentially quantitative yield by acid-catalyzed exchange of ethylene glycol on XI. The NMR, IR, and elemental analysis are consistent with the proposed structure. The mass spectrum shows no parent peak, which is characteristic of ethylene ketals.[7] The base peak at *m/e* 121 shows an unusual isotopic abundance ratio of 1.65:1 since it can arise from two sources, one with bromine and one with chlorine. The ions are at *m/e* 49 and 93 and correspond to CH_2Cl^+ and CH_2Br^+, respectively, but the expected metastable peaks are not observed to confirm that they arise from the oxonium ion species as indicated in Scheme I.

Synthesis of 3,3-Ethylenedioxycyclopropene (XIII). Cyclization of XII was accomplished via the original procedure,[2] to yield XIII, identified by spectroscopy. However, an

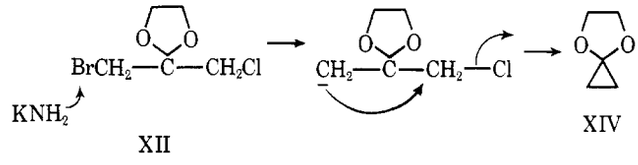


Scheme I. Mass Spectral Fragmentation Pattern for 1-Bromo-3-chloro-2,2-ethylenedioxypropane (XII)



unexpected product, 4,7-dioxaspiro[2.4]heptane (XIV), was obtained as the major component in this cyclization, the ratio of XIII:XIV being 20:80.

Formation of XIV is difficult to rationalize. The preparation of the potassium amide was carefully conducted to ensure that no unreacted metal remained. Thus, when the bromochloro ketal was added, the reaction medium should not have been a reducing system; thus, it is unlikely that the cyclopropene derivative is being hydrogenated. Likewise, a dehalogenation reaction involving the free metal is not possible. Baucom[8] obtained a similarly unexpected product which retained all four methylene protons from the reaction of XI with lithium hydride in the presence of VII. The reaction scheme postulated to account for that product could apply in this case although the amide displacement on bromine does not have compelling precedence. Both the mass and IR spectra of XIV



exhibited some unexpected characteristics. The mass spectrum showed an abundant molecular ion at *m/e* 100 which had 74% of the intensity of the base peak at *m/e* 99. This is not a usual characteristic of ethylene ketals.[7] Each of these ions, then, apparently experiences a similar fragmentation pattern as indicated by Table II.

The appearance of ions at *m/e* 44 and 43 by loss of C_3H_4O from the molecular ion and the base peak ion, respectively, suggests rupture of the dioxolane ring and extrusion of the elements of cyclopropane. Such involvement of the dioxolane ring is unusual and reflects the structural peculiarity of this spiro ketal.[7] Support for this process is found in the metastable peaks produced. The transition *m/e* 99 to 55 by loss of C_2H_4O is a common reaction of ethylene ketals and gives an observable metastable peak at 30.6. A metastable peak at 18.7 is only slightly less intense and corresponds to the transition *m/e* 99 to 43 by loss of C_3H_4O.

A characteristic feature of the IR spectra of dioxolane derivatives is a group of four or five peaks between 1000 and 1200 cm^{-1}. This pattern is prominent in the spectrum of XII with peaks at 1030, 1095, 1130, and 1140 cm^{-1}. The spectrum of the cyclization product, however, does not have this characteristic pattern. In the region of interest there are only two strong peaks at 1030 and 1185 cm^{-1}. Apparently the molecular vi-

brations responsible for absorptions at these frequencies are constrained by the small ring attached as a spiro derivative to the dioxolane ring.

Experimental Section

General Methods. All temperatures are reported uncorrected. Melting points were determined in open capillary tubes using a Thomas-Hoover melting point apparatus. All pressures are expressed in millimeters of mercury. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga., or PCR, Inc., Gainesville, Fla. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian A-60 spectrometer. The chemical shift data are reported relative to the internal reference tetramethylsilane using the parameter δ. Unless otherwise noted the solvent was deuteriochloroform. Mass spectral data were obtained from a Hitachi Perkin-Elmer RMU mass spectrometer using an ionization voltage of 70 eV. Infrared (IR) spectra were recorded with either a Beckman IR8 infrared spectrophotometer or a Perkin-Elmer 137 sodium chloride spectrophotometer. The data are reported in units of reciprocal centimeters (cm^{-1}).

Gas chromatography (GC) was conducted on a Hewlett-Packard 700 laboratory chromatograph or on an Aerograph Hy-Fi Model 600-D. Refractive indices were measured on a Bausch and Lomb ABBE-3L refractometer. Dimethoxycyclopropene was prepared either by the previously published procedure[2] or by the improved procedure reported in this paper. All other chemical reactants were purified according to standard practices.

Preparation of 3,4-Dimethyl-7,7-dimethoxy-3-norcarene (IIIc). A mixture of 0.8 g (8 mmol) of I and 1.0 g (12 mmol) of IIc was charged to a 5-ml round-bottomed flask and stored at room temperature for 4 weeks. At the end of this time the excess diene was evaporated in a stream of nitrogen and NMR analysis of the residue indicated almost quantitative conversion to the expected adduct (IIIc). Analysis by gas chromatography on a 12-ft column of Carbowax 30 at 150 °C indicated that the mixture consisted of 90–95% of the major component. A pure sample was obtained by preparative GC under the same conditions.

The NMR spectrum showed the following absorptions: δ 3.38 (s, 3, OCH_3), 3.28 (s, 3, OCH_3), 2.10 (m, 4, ring CH_2), 1.58 (s, 6, CH_3), and a multiplet centered at 1.30 (m, 2, bridgehead H).

The IR spectrum (neat) gave absorbances at 2900 (s), 1445 (s), 1410 (m), 1385 (w), 1325 (m), 1270 (s), 1230 (m), 1205 (m), 1125 (s), 1080 (s), 1020 (w), 980 (w), 935 (m), 895 (w), and 815 cm^{-1} (w).

Mass spectral analysis gave an abundant molecular ion at *m/e* 182 (63% of base peak) and other fragments at *m/e* 167, 135, 108, 107 (base peak), 105, 94, 93, 91, and 59. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.43; H, 9.95. Found: C, 72.54; H, 9.72.

For preparation, properties, spectral data, and analysis of structures IIIa, IIIb, and IIId, see supplementary material.

Preparation of 1,1-Dimethoxy-2-diethylaminocyclopropane (Va). A mixture of 1.5 g (15 mmol) of I and 25 ml of IVa was stored at room temperature for 3 weeks. Excess amine was evaporated in a stream of nitrogen and the residue was distilled bulb to bulb at 1 mm pressure. Analysis by GC indicated one major and two minor components. The major component constituted about 60% of the mixture and was isolated by preparative GC (8-ft column of 10% Carbowax at 160 °C).

The NMR spectrum of the major component (Va) gave absorbances at δ 3.42 (s, 3, OCH_3), 3.32 (s, 3, OCH_3), 2.89–2.51 (q, 4, $-CH_2H$), 2.14–1.90 (m, 1, ring CH), 1.18–0.94 (t, 6, CH_3), and 1.05–0.75 (m, 2, ring CH_3).

The IR spectrum (neat) showed peaks at 2960 (s), 2840 (m), 2205 (w), 1750 (w), 1625 (w), 1450 (s), 1390 (m), 1370 (m), 1280 (s), 1220 (s), 1170 (s), 1095 (s), 1065 (s), 1045 (s), 1015 (m), 990 (m), 920 (m), 895 (m), 875 (m), and 765 cm^{-1} (s).

Mass spectral analysis showed a trace of the parent peak and a peak at P − 1 for loss of hydrogen. The base peak occurred at *m/e* 158 corresponding to the loss of methyl radical. Other fragments were observed at *m/e* 142, 126, 116, 101, 98, 84, and 56. The peak at *m/e* 56 is prominent (64% of base peak) but it is difficult to rationalize.

Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.15; H, 11.00; N, 7.89.

Preparation of 1,1-Dimethoxy-2-di-*n*-propylaminocyclopropane (Vb) and *N,N*-Di-*n*-dipropyl-β-alanine Methyl Ester (VIb). Freshly distilled IVb (22 ml) and 1.0 g (10 mmol) of I were mixed and the solution was stored at room temperature for 3 weeks. Distillation under reduced pressure gave one fraction [bp 50 °C (0.5 mm), 1.5 g] whose NMR spectrum indicated some of the expected cyclopropylamine. GC (8-ft Carbowax, 190 °C) showed two major components in the approximate ratio of 40:60 in the order of elution time. These two components were isolated by preparative GC.

The first component (0.6 g) (Vb) gave an IR spectrum almost superimposable on that of Va. The NMR spectrum showed absorbances at δ 3.45 (s, 3, OCH_3), 3.35 (s, 3, CH_3), 2.85–2.40 (m, 7, $-CH_2N$), 2.22–1.90 (d of s, 1, ring CH), 1.80–1.19 (m, 4, CCH_2C), and 1.10–0.65 (m, 8, CH_3 and ring CH_2).

The second component (0.9 g) (VIb) gave an NMR spectrum showing absorptions at δ 3.65 (s, 3, CH_3), 2.97–2.62 (m, 3, $-CH_2C{=}O$), 2.56–2.17 (m, 6, $-CH_2N$), 1.78–1.17 (m, 4, CCH_2C), and 1.07–0.66 (m, 6, CCH_3).

The IR spectrum gave absorbances at 2940 (s), 2875 (w), 2800 (m), 1750 (s), 1460 (m), 1440 (m), 1250 (m), 1205 (s), 1080 (w), and 1060 cm^{-1} (w).

Mass spectral analysis showed a molecular ion at *m/e* 187 (13% of base peak); the base peak was observed at *m/e* 158 (loss of ethyl radical). Another abundant fragment was recorded at *m/e* 114 (65% of base peak) and arises from the loss of a methyl acetate radical. Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13: H, 11.30; N, 7.48. Found: C, 64.25; H, 11.37; N, 7.39.

Preparation of *N,N*-Diphenyl-β-alanine Methyl Ester (VIc). To a 25-ml round-bottomed flask was added 1.0 g (10 mmol) of I, 1.8 g (11 mmol) of IVc (recrystallized from pentane), and 10 ml of methylene chloride which had been passed through a column of alumina. The solution was stored at room temperature for 4 weeks and then added dropwise to pentane to precipitate unreacted IVc. When all material was found to be soluble at 0 °C, the solvents were removed and the residue was analyzed by NMR. Adduct formation was indicated by two nonequivalent methoxy groups. A new compound giving a sharp singlet at δ 3.18 was also noted.

About half of this sample was placed on a silica gel column with pentane to attempt chromatographic separation of the mixture. A vigorous exothermic reaction occurred immediately. Development of the column gave 1.0 g of material which appeared to be largely a single compound. A second chromatography on silica gel gave this material in pure form (VIc).

The NMR analysis gave absorbances at δ 7.32–6.65 (m, 10, aromatic H), 4.15–3.80 (m, 2, $-CH_2N$), 3.51 (5, 3, OCH_3), and 2.75–2.38 (m, 2, $-CH_2C{=}O$).

In the IR there were absorbances at 3040 (m), 2960 (m), 1750 (s), 1600 (s), 1500 (s), 1465 (m), 1440 (m), 1365 (s), 1315 (s), 1280 to 1165 (three or four broad bands), 1100 (m), 1065 (s), 1035 (m), 995 (m), 895 (w), and 695 cm^{-1} (s).

The mass spectrum showed only two major peaks, an abundant (40% of base peak) molecular ion at *m/e* 255 and the base peak at *m/e* 182. The next most abundant fragment was *m/e* 77 (16% of the base peak). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.26; H, 6.71; N, 5.49. Found: C, 75.33; H, 6.76; N, 5.42.

Solvent separation techniques were applied to that portion of the original reaction mixture which was not chromatographed. First, it was dissolved in pentane and cooled in dry ice. No selective precipitation was achieved. The solvent was then evaporated and the material was dissolved in methanol. This solution was divided into two portions. One portion was allowed to slowly evaporate but no crystallization occurred. The oil which remained was found to be the same product as from the chromatography experiment (VIc).

The second half of the methanolic solution was treated with a few drops of water which caused an oil to separate. This oil was separated and dried under vacuum at room temperature. The NMR spectrum showed the expected absorptions for VIc. In addition there was a multiplet at δ 1.9–2.3, a singlet at δ 3.18, and increased absorptions in the aromatic region.

The IR (neat) of this sample gave absorbances at 3390 (w), 3030 (w), 2940 (m), 1740 (m), 1665 (w), 1590 (s), 1495 (s), 1460 (w), 1440 (w), 1360 (m), 1305 (m), 1265 (w), 1225 (s), 1190 (w), 1150 (m), 1125 (w), 1085 (m), 1060 (s) 990 (w), 950 (w), 915 (w), 870 (w), 750 (s), 740 (shoulder), and 695 cm^{-1} (s).

Further attempts to obtain this compound in pure state were unsuccessful as all manipulations resulted in conversion of the material to VIc.

Reaction of I with VII. To a solution of 0.5 g (5 mmol) of I in 25 ml of freshly distilled THF was added to a THF solution of 1.0 g (5 mmol) of VII. This mixture was heated to reflux and held for 8 h with no observed color change. GC analysis of a sample indicated decomposition of I and no reaction of the diene. Additional I (0.6 g) was added and the mixture was stored at room temperature. After 2 weeks the color had faded from the solution. Solvent was evaporated from the reaction mixture and methanol was added to the tan residue. A white solid separated which was recrystallized from acetone to yield 0.3 g (12.5%) of pure material, mp 213.5–215.0 °C.

The NMR spectrum (str. IXb) showed absorbances at δ 7.44–6.68 (m, 20, aromatic H), 6.35–5.96 (AB, 2, vinylic H), and 2.95 (s, 6, OCH_3).

The IR spectrum showed weak absorbances at 3100, 3070, 3050, 2990, 2960, and 2860 cm^{-1}. Other peaks were observed at 1630 (w), 1600 (w), 1495 (m), 1447 (m), 1345 (m), 1265 (m), 1240 (m), 1190 (m), 1160 (m), 1130 (s), 1105 (w), 1070 (s), 1045 (s), 1000 (s), 870 (m), 820 (m), 780 (m), 765 (m), 735 (m), and 700 cm^{-1} (s).

Mass spectral analysis gave a molecular ion at *m/e* 434 which was also the base peak. Other major fragments were observed for P − 15 and P − 28. Anal. Calcd for $C_{34}H_{28}O_3$: C, 84.27; H, 5.82. Found: C, 84.11; H, 5.79.

Preparation of 3,3-Bis(trifluoromethyl)-5,5-dimethoxy-2-oxabicyclo[2.1.0]pentane (X). Approximately 5 ml of VIII was condensed into a Fisher-Porter pressure bottle by cooling the bottle in a dry ice–2-propanol bath and also using a dry ice cooled condenser over it. To this was added 1 ml of I. The pressure bottle was then sealed and allowed to warm to room temperature. After 3 days, the excess VIII was allowed to evaporate and the residue was analyzed by NMR. The spectrum was very simple and showed a poorly resolved multiplet at δ 5.66 (one proton), a broad singlet at δ 4.86 (one proton), and sharp singlets at δ 3.81 and 3.50 (three protons each). There was also evidence for a small amount of impurity near δ 3.35, but this was easily removed by dissolving the sample in pentane and passing it through a column of silica gel.

The ^{19}F NMR spectrum revealed that the compound had two different trifluoromethyl groups which were coupled with each other. Additional coupling, probably to one or more protons, was indicated but no further information about the structure could be obtained from this spectrum.

The IR spectrum showed absorbances at 3150 (w), 2970 (m), 2865 (w), 2855 (w), 1725 (w), 1670 (s), 1465 (m), 1410 (m), 1358 (m), 1325 (s), 1290 (s), 1225 (s), 1115 (s), 1055 (s), 1008 (m), 962 (s), 945 (s), 828 (m), 775 (m), 746 (w), 736 (w), and 715 cm^{-1} (s).

The mass spectrum showed a small peak at *m/e* 266 for the molecular ion. The base peak occurred at *m/e* 197, corresponding to loss of trifluoromethyl radical. Other abundant fragments (greater than 20% of base peak) were observed at *m/e* 235 (loss of methoxy radical) and 69 (CF_3^+ ion). Anal. Calcd for $C_8H_8F_6O_3$: C, 36.10; H, 3.30. Found: C, 36.13; H, 3.02.

Improved Synthesis of I. An apparatus resembling that of Schlatter[6] was used. It consisted of two three-necked flasks arranged side by side. Each was equipped with a mechanical stirrer and an adequate dry ice cooled condenser which was protected from the atmosphere by a drying tube filled with soda lime. One 500-ml flask had a Hershberg stirrer of chromel wire and its third opening was fitted with a two-holed rubber stopper. One hole was for a nitrogen inlet tube which extended to just within the neck of the flask. The other hole contained a bent tube which reached to the very bottom. The other 1000-ml flask was also equipped with a two-holed rubber stopper. One hole was for a short section of tubing which reached just inside the neck of the flask and was connected to the longer tube of the first flask by a short section of rubber tubing. The second hole was for a nitrogen inlet. A Teflon stirrer was used in the second flask. Ammonia was collected in the first flask and potassium amide was prepared from 11.2 g (0.29 mol) of potassium metal as previously described.[2] The second flask was charged with 21.7 g (0.1 mol) of XI and about 400 ml of ammonia.

Transfer of the amide solution was made by closing the nitrogen line to the second flask, opening the line between the two flasks, and partially blocking the vent from the first flask with one finger. The stirring of the reaction mixture caused the flask to be filled when the addition was only two-thirds complete, so some ammonia was allowed to evaporate. As a result, the total addition time was 1.5 h. The color of the reaction mixture was bright yellow until near the end when it became dark green.

Stirring was continued for 4 h longer and then excess amide was destroyed by adding ammonium chloride. A marked color change from green to brown occurred when 4.5 g (0.08 mol) had been added. Ammonia was then allowed to evaporate under vigorous stirring and ethyl ether was added as replacement solvent. After 400 ml had been added, the mixture was stirred until the temperature rose to −25 °C. The solution was then filtered and the equipment and solid by-products were rinsed well with ether. The solid weighed 25.0 g (theory, 26.0 g) and gave an aqueous solution of pH 7 or 8 in which very little organic material was apparent.

Following overnight storage in the dry ice chest, the ether was distilled from the filtered solution under 80 mm pressure until the temperature of the flask rose to 0 °C. Receivers were then changed and the pressure was slowly reduced to 0.5 mm. Product was distilled until the pot temperature rose to 25 °C. The yield was 12.5 g of a 38% solution of dimethyoxycyclopropene in ether. This represents a yield of 4.9 g (49%) of pure product. Redistillation of the ether solvent at atmospheric pressure yielded an additional 0.9 g for a total recovery of 58%. Residue from the main product distillation weighed only 1.6 g and did not contain any unreacted starting material.

When scaled up to five times this size, the amide was prepared in a 2-l. flask and the reaction was conducted in a 3-l. flask. The yield from 108.5 g (0.5 mol) of bromochloro ketal was 32.4 g (65%) of pure dimethoxycyclopropene.

Preparation of 1-Bromo-3-chloro-2,2-ethylenedioxypropane (XII). A mixture of 21.7 g (0.1 mol) of XI and 7.6 g (0.12 mol) of ethylene glycol was placed in a 100-ml round-bottomed flask along with 2 drops of concentrated H_2SO_4 and heated on the steam bath for 6 h. Analysis of an aliquot indicated quantitative conversion to the ethylene ketal.

The crude product was dissolved in pentane and washed with water. After drying with Na_2SO_4, the solvent was removed on a rotary evaporator to yield 17.0 g (79%) of ketal. Distillation under reduced pressure [bp 70 °C (1.2 mm)] gave analyticaly pure material, mp 10 °C, $n^{26}D$ 1.5020.

The NMR spectrum showed a four-proton singlet at δ 4.05 and two two-proton singlets at δ 3.62 and 3.47. IR absorbances were observed at 2980 (s), 2905 (s), 1477 (s), 1422 (s), 1200–1020 (group of four strong bands), 1000 (s), 950 (s), 805 (m), 750 (s), and 660 cm^{-1} (m).

The mass spectral analysis showed no parent peak. Fragments were observed at *m/e* 165 (1:1), 121 (1.65:1) (base peak), 93 (1:1), 77 (3:1), and 49 (3:1). (The numbers in parentheses are the ratios of the indicated peak to the P + 2 peak.) Anal. Calcd for $C_5H_8O_2BrCl$: C, 27.87; H, 2.74; Br, 37.09; Cl, 16.45. Found: C, 28.01; H, 3.71; Br, 36.80; Cl, 16.32.

Cyclization of XII. This cyclization was accomplished by the published procedure[2] for synthesis of I from XI, yield 1.3 g (13%) as an 80% solution in ether. The NMR spectrum showed three singlets at δ 7.72, 4.01, and 0.90. When a sample was treated with D_2O, the signal at δ 7.72 disappeared and left the other two in equal intensities. Hydrolysis of the entire reaction mixture was then effected by stirring for 3 h with 17 ml of H_2O. Preparative GC on a 12-ft column of Carbowax 30 at 150 °C gave a pure sample of 4,7-dioxaspiro[2.4]heptane (XIV).

The IR spectrum gave absorbances at 3110 (w), 3030 (m), 2990 (m), 2910 (s), 1490 (m), 1460 (s), 1405 (w), 1335 (s), 1185 (s), 1030 (s), 1000 (s), 945 (w), 930 (w), 850 (m), 765 (w), and 755 cm^{-1} (w).

Mass spectral analysis showed a molecular ion at *m/e* 100, which was 74% as intense as the base peak (*m/e* 99). Other fragments were observed at *m/e* 56, 55, 44, 43, and 40. Anal. Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 59.85; H, 8.13.

Charge Transfer Complex Studies. I was purified by redistillation under reduced pressure [bp 36 °C (33 mm)]. The donor reagents styrene (St) and divinyl ether (DVE), as well as all solvents, were distilled just prior to use.

A stock solution (0.25 M) of I was used and Me_4Si was used as internal standard. One milliliter of the stock solution was transferred by pipet to each of a series of labeled 5-ml volumetric flasks. The concentration of acceptor was thus held constant for each series of solution. A varying quantity of donor was added to each flask from a buret and then each solution was diluted to volume with the solvent being used for that study. After dilution, each solution was mixed thoroughly and an aliquot was transferred to the appropriately labeled NMR tube.

The NMR spectra for each series were obtained without the intervention of other samples which might affect the instrument response. No special precautions were taken to maintain a constant temperature, but 5 min was allowed for each solution to equilibrate at the ambient operating temperature of the spectrometer (about 38 °C). Because of the large concentration difference between donor and acceptor, only the NMR signals for Me_4Si and the cyclopropene protons were recorded. The chemical shift of the acceptor protons (δ^A_{obsd}) was measured as cycles per second downfield from Me_4Si. Data and observations for the study using styrene as donor are shown in Table IV and those for the divinyl ether case are given in Table V.

The equilibrium constant for complex formation and the shift of acceptor protons in the pure complex were calculated by use of the Hanna–Ashbaugh equation:[9]

$$\frac{1}{\Delta^A_{obsd}} = \frac{1}{Q\Delta^A_{AD}}\frac{1}{C_D} + \frac{1}{\Delta^A_{AD}} \quad (1)$$

where $\Delta^A_{obsd} = \delta^A_{obsd} - \delta^A_{O'}$ is the difference between the shift of the acceptor protons in complexing media and the shift of the acceptor

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.]

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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.

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Reaction of Cyclopropenone Ketals with Alcohols[1]

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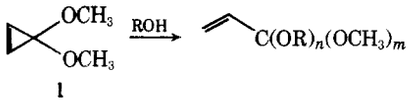
3,3-Dimethoxycyclopropene (**1**), synthesized as previously described, undergoes a ring-opening reaction under mild conditions, with a variety of alcohols to give the corresponding monoalkyl dimethyl orthoacrylates. These results are consistent with a mechanism which involves initial protonation of **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]