1,2-Cyclopropanediol Cyclic Carbonates. II.[1] Synthesis and Physical Properties

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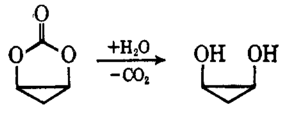
A series of 1,2-cyclopropanediol cyclic carbonates has been synthesized by carbene insertion on vinylene carbonate (**1**) and methylvinylene carbonate (**2**). Thus, *anti*-3-carbethoxy-1,2-cyclopropanediol carbonate (**4**) and the 1-methyl derivative **5** are obtained in low yield by heating **1** and **2** with ethyl diazoacetate at 80° in the presence of CuCN. Likewise, 1,2-cyclopropanediol carbonate (**10**) and the 1-methyl derivative **11** are obtained by passing diazomethane through **1** and **2** at 120°. 3,3-Dichloro-1,2-cyclopropanediol carbonate (**7**) and the 1-methyl derivative **8** are obtained by refluxing **1** and **2** in a benzene solution of phenyl(bromodichloromethyl)mercury. The nmr spectrum of **11** at 60 MHz is deceptively simple; however, at 100 MHz, the spectrum shows the expected ABX pattern in which the methyl hydrogens are coupled with the *syn* hydrogen (0.5 Hz) through a "W" arrangement of four σ bonds. The thermal stabilities of the cyclopropane carbonates vary considerably.

1,2-Cyclopropanediol, a simple glycol, has not been synthesized, although geminal cyclopropanediols and hemiketals are well known.[2-6] The intermediacy of 1,2-cyclopropanediols in the Clemmensen reduction of 1,3 diketones has been discussed by Staschewski[7] and Cusack and Davis.[8]

Among a number of potential precursors to 1,2-cyclopropanediols, 1,2-cyclopropanediol carbonates appear most promising. We therefore set out to synthesize a series of these carbonates with the hope that they could be converted into vicinal diols (eq 1). This



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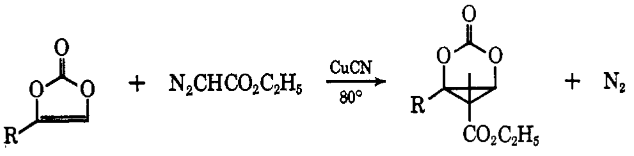
paper describes the synthesis and physical properties of six 1,2-cyclopropanediol cyclic carbonates. For a preliminary report on the synthesis of three of the compounds, see ref 1a.

The six compounds described herein have been obtained by carbene insertion on vinylene carbonate and methylvinylene carbonate using three different carbene precursors—ethyl diazoacetate (**3**), diazomethane (**9**), and phenyl(bromodichloromethyl)mercury (**6**). Vinylene and methylvinylene carbonates were prepared according to the procedures of Newman and Addor[9] and Moss,[10] respectively. On exposure to air or excessive heating, vinylene carbonates polymerize.

Ethyl Diazoacetate.—The insertion of carbethoxycarbene into double bonds has been extensively investigated.[11] Since carbethoxycarbene is considered electrophilic, yields of carbethoxycyclopropane derivatives are generally good when the carbene receptor is an electron-rich olefin (40–80%) but poorer when the olefin is electron deficient.

A 5.7% yield of *anti*-3-carbethoxy-1,2-cyclopropanediol cyclic carbonate (**4**) was obtained from **1** *via* eq 2.



1, R = H
2, R = CH_3

4, R = H
5, R = CH_3 (2)

It distilled as a colorless liquid under reduced pressure but crystallized on standing. Spectral and elemental analyses establishes the structure as indicated. The infrared spectrum (dilute CCl_4) shows strong bands at 1848 and 1729 cm^{-1}, characteristic of the carbonate[12] and ester carbonyl-stretching vibrations. The nmr spectrum (neat, TMS standard) shows a coupled triplet and doublet at 2.22 and 4.93 ppm, respectively ($J = 1.3$ Hz), integrating 1:2. These are due to the cyclopropane hydrogens. Carbethoxycarbene insertion on **1** can lead to *syn* and *anti* isomer. As indicated by eq 2 the major product is the *anti* isomer, which is reasonable on a steric basis. Previous workers have shown that carbalkoxycarbenes, generated catalytically with copper-bronze[13,14] or cuprous cyanide,[15,16] add to olefins to produce the least-hindered double-bond insertion product. Further evidence for the stereochemical assignment is gleaned from the cyclopropane–hydrogens coupling constant. The value reported here is close to that reported by Sauer and Sonnet[15,16] for the *trans*-cyclopropane–hydrogen coupling constant in ethyl 6-*exo*-tricyclo[3.2.1.0^{2,4}]octene-3-*anti*-carboxylate ($J = 2.5$ Hz), *i.e.*, *trans* insertion of carbethoxycarbene in norbornadiene. Although the gas–liquid partition chromatogram of the distilled carbonate showed a single component, the nmr spectrum indicates that as much as 5% *syn* isomer may be present since the carbethoxymethylene quartet exhibits small shoulders. *anti*-3-Carbethoxy-1,2-cyclopropanediol carbonate is thermally stable to at least 180°, but the 1-methyl derivative noticeably decarboxylates at 140°.

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[1] (a) Part I: F. W. Breitbeil, J. J. McDonnell, T. A. Marolewski, and D. T. Dennerlein, *Tetrahedron Lett.*, 4627 (1965). (b) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts, p O175.

[2] O. Lipp and P. Koster, *Chem. Ber.*, **45**, 1799 (1912).

[3] R. Grewe and A. Struve, *ibid.*, **96**, 2819 (1963).

[4] H. G. Richey, Jr., J. M. Richey, and D. C. Clagett, *J. Amer. Chem. Soc.*, **86**, 3906 (1964).

[5] S. E. Schaafsura, H. Steinberg, and J. DeBoer, *Rec. Trav. Chim.*, **84**, 113 (1965).

[6] N. J. Turro, W. B. Hammond, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **87**, 2774 (1965).

[7] D. Staschewski, *Angew. Chem.*, **71**, 726 (1959).

[8] N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).

[9] M. S. Newman and R. W. Addor, *J. Amer. Chem. Soc.*, **77**, 3789 (1955).

[10] P. H. Moss, U. S. Patent 3,020,290 (1962); *Chem. Abstr.*, **56**, 12904*d* (1962).

[11] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 95–111.

[12] J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957). These authors report that ethylene and vinylene carbonates show strong infrared absorptions at 1817 and 1833 cm^{-1} (CCl_4 solution), respectively.

[13] P. S. Skell and R. M. Cetter, *Proc. Chem. Soc.*, 443 (1961).

[14] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

[15] R. R. Sauers and P. E. Sonnet, *Tetrahedron*, 1029 (1964).

[16] R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963).

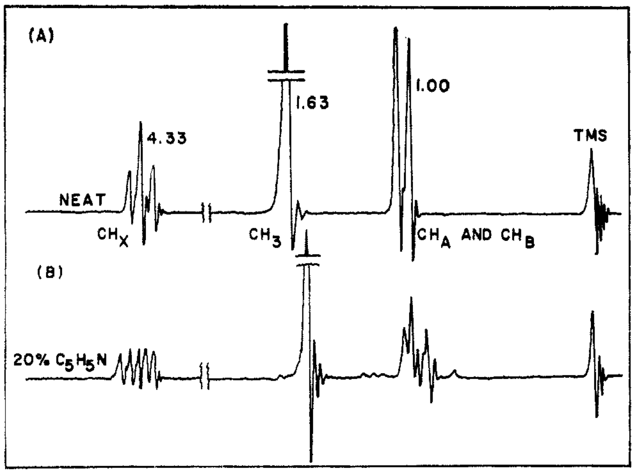
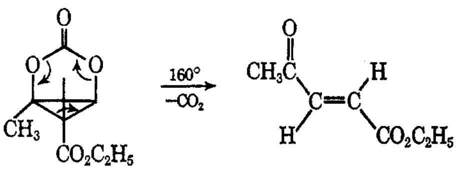


Figure 1.—60-MHz nmr spectra of **11** (500-Hz sweep width): A, neat, TMS standard; B, 20% pyridine solution, TMS standard.

An 8.6% yield of *anti*-1-methyl-3-carbethoxy-1,2-cyclopropanediol cyclic carbonate (**5**) was obtained from **2**. It distilled as a colorless liquid under reduced pressure. The ir spectrum (dilute CCl_4) shows strong absorption at 1848 and 1736 cm^{-1}. The nmr spectrum (heat, TMS standard) shows a singlet at 1.77 ppm and coupled doublets at 2.20 and 4.79 ppm (J = 1.8 Hz) integrating 3:1:1 along with an ethyl triplet and quartet at 1.25 and 4.19 ppm (J = 7.0 Hz). Pronounced shoulders on the ethyl bands indicate the presence of some *syn* isomer, although no other distinctive peaks were present. A gas–liquid partition chromotogram shows, in addition to some decomposition product, two components with similar retention times in a ratio of 9:1 due, presumably, to **5** and the corresponding *syn* isomer. Carbonate **5** is thermally labile. Decomposition becomes noticeable at 140° (loss of vacuum on distillation) and rapid at 160°. Distillation of **5** should not be attempted unless a vacuum of at least 0.30 mm can be maintained. The decomposition product, a result of decarboxylation, is ethyl *trans*-4-oxo-2-pentenoate (eq 3) as established by comparison of the nmr and infrared spectrum and gas–liquid phase chromatogram of a sample isolated by preparative scale gas–liquid partition chromatography with those of an authentic sample.



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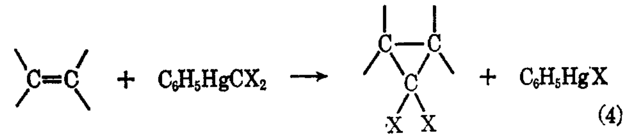
(3)

Phenyl(bromodichloromethyl)mercury.—Recently, Seyferth and coworkers[17] developed a new method for synthesizing *gem*-dihalocyclopropane compounds in which an olefin is refluxed in benzene with a phenyl(trihalomethyl)mercury compound, usually phenyl(bromodichloromethyl)mercury (**6**). The phenylmercuric halide that forms (eq 4) is insoluble in benzene and serves as an indicator of reaction. Previous efforts to synthesize *gem*-dihalocyclopropanes from electron-deficient olefins have usually resulted in low yields or no reaction at all.[18] However, Seyferth and coworkers[17] report the synthesis of hexachlorocyclopropane in 74% yield using **6**. Accordingly, excess **1** and **2** were each refluxed in benzene with **6** for 2 hr (eq 5). In both cases, the reaction appeared to be complete in 15 min. Phenylmercuric bromide was isolated in high yield, and the desired products were obtained by distillation. The yields of **7** and **8** were 95 and 86%, respectively. The nmr spectrum of **7** shows a singlet at 4.53 ppm, that of **8**, singlets at 1.88 and 4.42 ppm integrating 3:1. The infrared spectra of **7** and **8** (dilute CCl_4) show strong carbonate carbonyl-stretching bands at 1828 and 1855 cm^{-1}, respectively.



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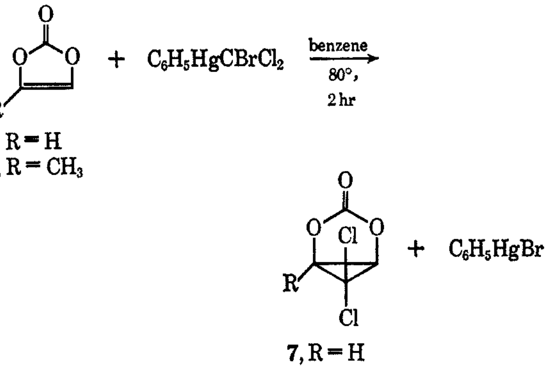


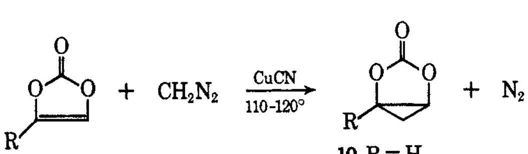
1, R = H
2, R = CH$_3$

(5)

7, R = H
8, R = CH$_3$

Diazomethane.—The practical and theoretical aspects of methylene insertion into double bonds have been the subject of hundreds of publications.[19] Our object here was to synthesize the carbonate precursor of 1,2-cyclopropanediol in sufficient quantity to permit the study of methods for converting the carbonate into the diol. The carbonates discussed above, owing to their difunctionality, will present problems in their convertion into the diols.

Catalytic decomposition of diazomethane (**9**) in the presence of **1** or **2** gave 1,2-cyclopropanediol cyclic carbonates (**10**) and (**11**) in low yields (eq 6). Distillation at reduced pressure provided only starting material plus **10** or **11**.



(6)

1, R = H
2, R = CH$_3$

10, R = H
11, R = CH$_3$

1,2-Cyclopropanediol cyclic carbonate thus synthesized was obtained in 28% yield based on the amount

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[17] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y-P. Mui, H. D. Simmons, Jr., A. J.-H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[18] For example, S. W. Tobey and R. West [*ibid.*, **86**, 56 (1964)] found that only a 5% yield of hexachlorocyclopropane could be obtained by treating tetrachloroethylene with many of the older well-known dichlorocarbene precursors.

[19] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

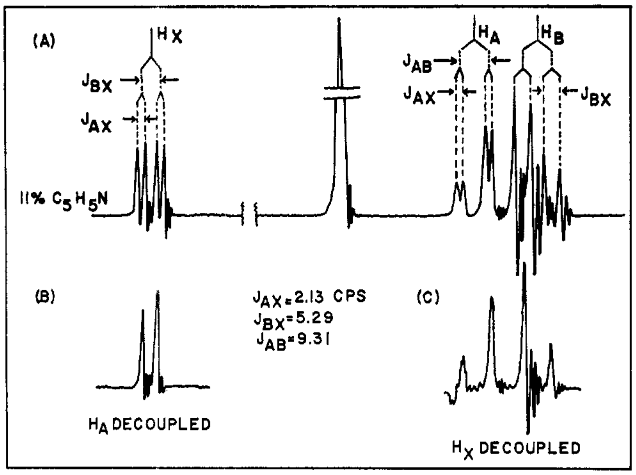


Figure 2.—100-MHz nmr spectra of **11** in 11% pyridine solution (500-Hz cps sweep width): A, upfield and downfield multiplets; B, H_A decoupled; C, H_X decoupled.

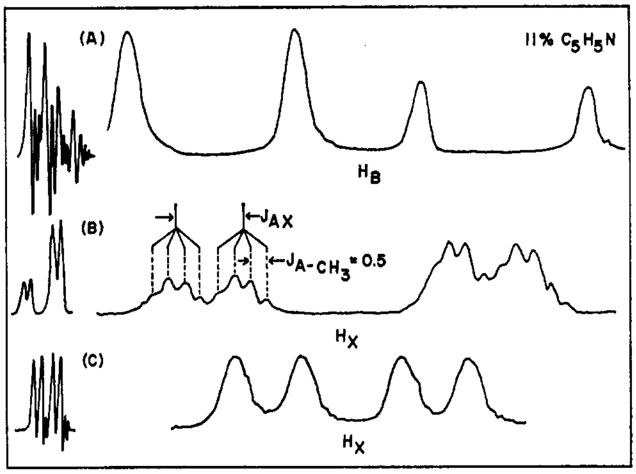
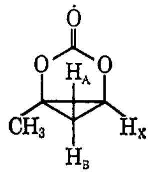


Figure 3.—100-MHz nmr spectra of **11** in 11% pyridine solution (50-Hz cps sweep width): A, H_B multiplet; B, H_A multiplet; C, H_X multiplet.

of **9** consumed. The infrared spectrum (dilute CCl_4) shows strong absorptions at 1859, 1844, and 1822 cm^{-1}, due to the carbonate carbonyl group.[20] The nmr spectrum (neat, TMS standard) shows two complex multiplets centered at 1.03 and 4.55 ppm integrating 1:1. Carbonate **10** shows unusual thermal stability, being unchanged on heating to 280°.

Similarly, **11** was obtained in 19% yield. The infrared spectrum (dilute CCl_4) shows strong absorption at 1846 and 1826 cm^{-1}. The 60-MHz nmr spectrum of **11** as shown in Figure 1a is deceptively simple. A complex ABX pattern was expected. Line spacings in the triplet and doublet were identical (3.5 Hz), indicating the presence of a $>CH-CH_2-$ grouping, which would be incompatible with the expected structure. One explanation could be the doubly fortuitous occurrence of identical chemical shifts for H_A and H_B and identical coupling constants, J_{AX} and J_{AB}, in **12**. However, this seemed unlikely.



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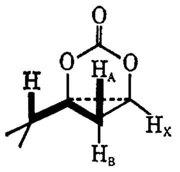
A spectrum in pyridine confirmed our convictions (Figure 1b). Pyridine is a solvent known to enhance chemical shifts. The complex pattern in pyridine is that expected, but not easily interpretable.

At 100 MHz, the nmr spectrum of **11** in pyridine becomes entirely intelligible and indirectly offers proof of structure for **4** and **5**. The simplified spectrum allows a first-order analysis to be carried out. The upfield and downfield multiplets are depicted in Figure 2a along with their assigned splittings and coupling constants. These multiplets were expanded (sweep width, 50 Hz) to obtain accurate coupling constants and chemical shifts. The assignments were verified by decoupling experiments. On decoupling H_X, the geminally coupled H_A and H_B exhibit a typical AB pattern (Figure 2c). Likewise, irradiation of the low-field quartet of the AB multiplet produces a doublet for H_X with the appropriate J_{BX} value (Figure 2b). The chemical-shift assignments for H_A and H_B can be made with a large degree of certainty from the following evidence. In Figure 3b, the expanded portion of H_A shows that each peak is further split into quartets (0.5 Hz), while the multiplets due to H_B and H_X show no such splitting (Figures 3a, 3c). This can most reasonably be ascribed to long-range coupling (four σ bonds) of H_A with the methyl group protons. Preferential long-range coupling between protons in a "W" arrangement is well established (**13**).[21] The observed J_{AX} coupling of 2.13 Hz in **13** provides strong support for the *anti* assignment indicated for **4** and **5**.



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The cyclopropane–hydrogen coupling constants for **4** and **5** are 1.8 and 1.3 Hz, respectively. If the carbethoxy groups were *syn* in **4** and **5**, a *cis* coupling constant of about 5.0 Hz would be expected for the cyclopropane hydrogens.

Experimental Section[22]

1-Methyl-3-carbethoxy-1,2-cyclopropanediol Cyclic Carbonate (5).—A flask charged with 91.7 g (0.917 mol) of **2** and 11.0 g of copper(I) cyanide was heated to 80° with magnetic stirring and 91.0 g (0.910 mol) of **2** mixed with 114.0 g (1.00 mol) of ethyl diazoacetate was added dropwise. External heating (oil

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[20] The authors in ref 12 report that the strong carbonate carbonyl bands in the infrared spectra of ethylene and vinylene carbonates exhibit shoulders, and they cite references that offer possible explanations for these observations.

[21] N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 115–121.

[22] Nmr spectra were obtained using a Varian A-60 (except where noted) with tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded using a Perkin-Elmer Model 21 spectrometer. Gas-liquid partition chromatograms were obtained with an F & M Model 500 chromatograph equipped with a 6-ft copper column packed with 20% silicone gum rubber on 80 mesh Chromosorb W at 125°. Melting points were obtained using a circulating oil bath and are not corrected. Elemental analyses were carried out by Micro-Tech Laboratories, Inc., Skokie, Ill.

bath) was terminated, and the addition rate was adjusted to maintain a reaction temperature of 80°. After addition was complete heating at 80° was continued for 30 min. The reaction mixture was cooled and later vacuum distilled through a short column: fraction 1, 149.0 g, bp 90–95 (25 mm)—mainly **2**; fraction 2, 20.9 g, bp 70–72° (0.65 mm)—a mixture of diethyl maleate and fumarate; fraction 3, 18.5 g, bp 72–78° (0.30 mm)—a mixture of diethyl maleate and fumarate, ethyl *trans*-2-oxo-3-pentenoate (product decomposition), and desired product (**5**). A considerable amount of undistillable material remained. Redistillation of the third fraction at 0.25 mm gave a small amount of forerun and the desired product, bp 81°. Infrared absorptions (dilute CCl_4) were noted at 1848 (s), 1736 (s), 1098 (s), 1436 (m), 1373 (m), 1387 cm^{-1} (m). The nmr spectrum shows a singlet at 1.77 ppm, coupled doublets at 2.20 and 4.78 ppm (J = 1.8 Hz), and a coupled triplet and quartet at 1.25 and 4.18 ppm (J = 7.0 Hz) integrating 3:1:1:3:2.

Anal. Calcd for $C_8H_{10}O_5$: C, 51.6; H, 5.4. Found: C, 51.7; H, 5.6.

3-Carbethoxy-1,2-cyclopropanediol cyclic carbonate (4) was prepared in exactly the same manner as **5**. One distillation yielded **1**, bp 73° (29 mm), diethyl fumarate and maleate, bp 54–58° (0.30 mm), and **4**, bp 88–91° (0.35 mm), mp 38–39° (from CCl_4), yield 5.7%. Infrared absorptions (dilute CCl_4) were at 1848 (s), 1729 (s), 1310 (s), 1093 (s), 1409 (m), 1387 (m), 1408 cm^{-1} (m). The nmr spectrum (neat, TMS standard) showed a coupled triplet and doublet at 2.22 and 4.93 ppm, respectively (J = 1.30 Hz), and a coupled triplet and quartet at 1.30 and 4.13 ppm (J = 7.0 Hz), integrating 1:2:3:2.

Anal. Calcd for $C_7H_8O_5$: C, 49.1; H, 4.7. Found: C, 49.0; H, 5.3.

1-Methyl-3,3-dichloro-1,2-cyclopropanediol Cyclic Carbonate (8).—Methylvinylene carbonate (12.93 g, 0.129 mol) and 19.13 g (0.0434 mol) of **6** were heated to reflux in 25 ml of benzene with stirring. A white flaky precipitate of phenylmercuric bromide began to form at 80°, and in 15 min the reaction mixture became very thick. Refluxing was continued for 2 hr. The product mixture was cooled in ice and filtered. After air drying, 14.97 g (0.0419 mol) of phenylmercuric bromide was obtained (97%). The filtrate was distilled at reduced pressure: fraction 1, 9.33 g, bp 82–89° (17 mm), mostly **2**; fraction 2, 6.83 g of **8**, bp 70–71° (2.4 mm), mp 43.5–45.0° (CCl_4). Infrared absorptions (dilute CCl_4) were observed at 1855 (s), 1380 (w), 1134 (s), 930 cm^{-1} (s). The nmr spectrum (CCl_4, TMS standard) showed singlets at 1.88 and 4.42 ppm, integrating 3:1.

3,3-Dichloro-1,2-cyclopropanediol Cyclic Carbonate (7).—Using 11.00 g (0.128 mol) of **1**, 18.92 g of **6** (0.043 mol), and 25 ml of dry benzene, **7** was prepared exactly as described for **8**. Phenylmercuric bromide (13.75 g) was obtained in 89% yield. The filtrate was distilled at reduced pressure. After recovering unreacted **1**, 7.23 g (0.0428 mol) of **7** was obtained (95% yield): bp 77.5–81° (1.6 mm); mp 32.5–33.5° (2:3 $CHCl_3$–CCl_4). Infrared absorptions (dilute CCl_4) were observed at 1828 (s), 1380 (w), 1140 (m), and 1078 cm^{-1} (s). The nmr spectrum (CCl_4, TMS standard) showed a singlet at 4.53 ppm.

1-Methyl-1,2-cyclopropanediol Cyclic Carbonate (11).—Diazomethane[23] (0.187 mol) was prepared from N-methyl-N-nitroso-*p*-toluenesulfonamide (0.312 mol). A flask, charged with 24.0 g of **1** (0.240 mol) and 1.0 g of copper(I) cyanide, was equipped with a condenser, a magnetic stirrer, and a gas inlet tube leading below the surface of the carbonate. Diazomethane, entrained in ether, was passed through **1** at 110–120°. Nitrogen and ether passed through the condenser. After cooling, the reaction mixture was filtered and distilled at reduced pressure: fraction 1, 7.77 g (0.080 mol) of **1**, bp 82–85° (15 mm); fraction 2, 5.11 g of **11**, bp 85° (4 mm). This represents a 19% yield (based on diazomethane). Infrared absorptions (dilute CCl_4) were observed at 1846 (s), 1826 (s), 1293 (m), 1118 (s), 1063 cm^{-1} (m). The nmr spectrum (100 MHz, 10% pyridine) showed an eight-line multiplet centered at 0.92 ppm, a four-line multiplet centered at 4.34 ppm, and a singlet at 1.46 ppm integrating 2:1:3.

Anal. Calcd for $C_5H_6O_3$: C, 52.6; H, 5.3. Found: C, 52.7; H, 5.3.

1,2-Cyclopropanediol Cyclic Carbonate (10).—Using the same procedure described in the preparation of **11**, **10** was synthesized by treating 43.1 g of **1** (0.502 mol) and 2.0 g of copper(I) cyanide with 0.12 mol of diazomethane. Distillation at reduced pressure gave two fractions: fraction 1, 32.4 g **1** (0.377 mol), bp 73–75° (29 mm); fraction 2, 3.4 g of **10**, bp 81–83° (3 mm). The yield was 28% (based on diazomethane). Infrared absorptions (dilute CCl_4) were observed at 1859 (s), 1844 (s), 1822 (s), 1416 (w), 1331 (m), 1170 (m), 1124 (s), 1056 (m), 956 cm^{-1} (s). The nmr spectrum (neat, TMS standard) showed a complex multiplet at 1.03 and 4.55 ppm integrating 1:1.

Anal. Calcd for $C_4H_4O_3$: C, 48.0; H, 4.0. Found: C, 47.8, H, 4.1.

Registry No.—**4,** 17026-92-5; **5,** 17026-93-6; **7,** 17026-94-7; **8,** 17026-95-8; **10,** 5239-49-6; **11,** 17047-82-4.

Acknowledgment.—The authors wish to thank Mr. James Loo of the Chicago Medical Center for providing the 100-MHz nmr spectra.

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[23] "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., p 261. This reference quotes a 60% yield—we assumed the same in our synthesis.