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CYCLOPROPANEDIOL CYCLIC CARBONATES

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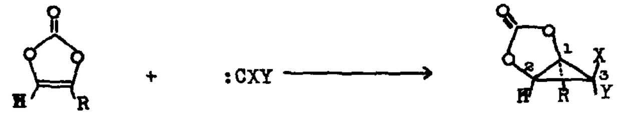
In the course of conducting another investigation it became necessary to synthesize cyclopropanediol cyclic carbonates. A literature search revealed that this class of compound has not yet been synthesized. The synthesis of these compounds is the subject of this communication.

To us the most obvious route to these materials is by carbene insertion on vinylene carbonate or its derivatives (eq. 1).



(1)

Ia) R=H

Ib) $R=CH_3$

IIa) $R=H, X=H, Y=CO_2C_2H_5$

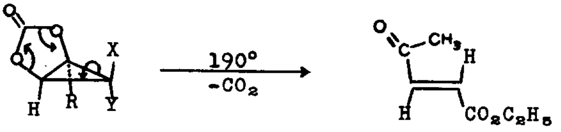
IIb) $R=CH_3, X=H, Y=CO_2C_2H_5$

IIc) R=H, X=H, Y=H

Vinylene carbonate was prepared according to the procedure of Newman and Addor[2] and with suitable modifications, methylvinylene carbonate was also synthesized. Ethyl diazoacetate (14.4 g., 0.126 mole) in 15.0 g. of Ia was added dropwise to a suspension of 2.0 g. cuprous cyanide in 16.8 g. Ia at 80°. Instantaneous evolution of nitrogen was noted with the addition of each drop and the heat of reaction was more than sufficient to maintain the reaction temperature at 80°. A distillation was carried out directly on the contents of the reaction flask. The forerun was largely Ia (b.p., 29° at 0.30 mm.). The middle cut was largely a mixture of diethyl maleate and fumarate (b.p. 55-75° at 0.25 mm.). The last two fractions (b.p. 92-97° at 0.25 mm.) contained at least four components as determined by GPC (5% SE-30 on 60/80 chromosorb W). Two of the components were the maleate and fumarate esters; a minor component, not present in lower boiling fractions, eluted from the column first. The fourth component had the longest retention time and was purified by GPC on a prep-scale. Collectively, the following evidence proves that the highest boiling component was 3-carbethoxy-cyclopropanediol cyclic carbonate (IIa), which amounted to about 5.0 g. (23% yield). The purified colorless liquid crystallized on standing and, when recrystallized from CCl_4, melted at 38-39°. An IR spectrum (CCl_4) showed absorption at 1812 cm^{-1}(s) and 1706 cm^{-1}(s) due respectively to the carbonate and ester carbonyl stretching bands. An NMR[3] spectrum (CCl_4, TMS standard) showed a coupled triplet and doublet at 128.8 c/s and 296.0 c/s respectively (J=1.6 c/s) integrating 1:2. These absorptions are due to the cyclopropane hydrogens, the downfield doublet being assigned to the hydrogens on the carbons bearing the carbonate group. In addition the typical ethyl group triplet and quartet was observed. A carbon-hydrogen analysis[4] agreed with the proposed structure.

This synthesis was extended using methylvinylene carbonate

(Ib) with similar results. In one experiment, a 17% yield of 1-methyl-3carbethoxy-1,2-cyclopropanediol cyclic carbonate (IIb) was obtained. Compound IIb (b.p. 115-118° at 0.60 mm.) was purified by prep-scale GPC and submitted to elemental[5] and spectroscopic analysis. An IR spectrum (CCl_4) showed absorption at 1818 cm^{-1} (s), 1709 cm^{-1} (s), and 1422 cm^{-1} (m) due respectively to the carbonate and ester carbonyl stretching bands and the methy group. An NMR spectrum (CCl_4, TMS standard) showed a singlet at 109.9 c/s and coupled doublets at 131.5 c/s and 291.1 c/s (J=1.6 c/s) integrating 3:1:1. The downfield absorption is due to the cyclopropane hydrogen on the carbon bonded to an oxygen of the carbonate group. The typical ethyl triplet and quartet was also noted. In purifying IIb by prep-scale GPC, a low boiling liquid was collected which eluted before fumarate and maleate esters and which was not present in lower boiling fractions from the distillation conducted prior to GPC purification. Recall that a low boiling material such as in this instance was also observed in the distillation of IIa. The low boiling liquid from IIb was identified as ethyl trans-4-oxo-2-pentenoate (III) by comparison with the NMR and IR spectra, and the GPC retention time of an authentic sample. Compound IIb did not decompose under GPC conditions and is a result of pyrolysis of IIb under distillation conditions (eq. 2).



(2)

IIb III

Finally methylene was inserted into Ia by bubbling a mixture of diazomethane (0.4 mole) entrained in nitrogen through Ia (0.18 mole) at 120° in which was stirred 0.5 g. of cuprous chloride. The reaction product was concentrated by distilling off unreacted Ia. The pot residue was shown by GPC to contain only two substances, Ia and a higher boiling material, which was obtained as a pure liquid by simple distillation (0.26 g., yield 3%). The IR and NMR spectra, the GPC retention time and the method of synthesis are very strong indications that the product is 1,2-cyclopropanediol cyclic carbonate. The IR spectrum showed absorptions at 1795 cm^{-1} (s), 3050 cm^{-1} (w), 874 cm^{-1} (m) and a doublet at 1045 cm^{-1} (m), the latter three bands being generally associated with a cyclopropane methylene[6]. These bands were not observed in the spectrum of Ia. The NMR spectrum (CCl_4, TMS internal standard) showed two complex multiplets centered at 288.5 c/s and 66.0 c/s integrating 1:1. The NMR spectrum of ethylene carbonate shows a singlet at 274.0 c/s (neat, TMS standard).

The mechanism for the formation of the cyclopropanediol cyclic carbonates is unknown at this time.

Stereochemical assignments for IIa and IIb (carbethoxy group anti to carbonate group) were made on the basis of previous investigations. It has been shown that the elements of carbalkoxy carbene generated either photolytically[7] or catalytically with copper-bronze[8,9] or cuprous cyanide[10,11] add to olefins to produce the least hindered double bond insertion product. Further evidence in support of this assignment was obtained from NMR coupling constants. The coupled cyclopropane hydrogens in IIa and IIb exhibited J values of 1.6 c/s. Sauers and Sonnet[10,11] reported that the *tran* cyclopropane hydrogens in ethyl 6-exo-tricyclo $[3.2.1.0^{2,4}]$ octene-3-anti-carboxylic acid had a J value of 2.5 c/s (carbethoxy carbene addition to norbornadiene).

The syntheses reported herein are being extended to other substituted vinylene carbonates and carbene sources and a systematic study of reaction variables is being conducted in an effort to increase yields. The pyrolytic and chemical reactivities of compounds IIa and IIb are also under investigation.

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3. NMR Spectra were obtained at 60 mc with a Varian A-60 spectrometer.
4. Anal. Calcd. for $C_7H_8O_5$: C, 48.8; H, 4.7.
   Found : C, 48.3; H, 4.6.
5. Anal. Calcd. for $C_8H_{10}O_5$: C, 51.6;H, 5.4.
   Found : C, 51.2;H, 5.4.
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