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REACTIONS OF CARBOHYDRATE TRANS-FUSED CYCLIC CARBONATES

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We recently described methods to prepare five-membered cyclic carbonates (1) and thionocarbonates (2) from vicinal trans hydroxyl groups in pyranoside rings. By such methods, methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-carbonate (I) and methyl 4,6-O-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate were prepared as crystalline compounds in good yields.

We now wish to report that ring opening of the trans-fused cyclic carbonate occurs readily when I is treated with either an alcohol, a thiol, or an amine. Under similar reaction conditions, the epimeric cis-fused compound methyl 4,6-O-benzylidene-α-D-mannopyranoside 2,3-carbonate (II) undergoes little or no ring opening.

When I was refluxed in methanol for 100 minutes, there occurred an 80% conversion to a mixture of the 2- and 3-O-methoxycarbonyl derivatives of I. Under the same conditions the cis-fused carbonate (II) was recovered unchanged. Triethylamine catalyzes the conversion of I into the methoxycarbonyl derivatives. When triethylamine is added to the methanolic solution of I, the reaction is immediate and quantitative. The 2- and 3-O-methoxycarbonyl derivatives of I were purified by fractional crystallization and gave the correct melting points (3). Some ring opening of cis-fused carbonate II also occurred when triethylamine was present in the refluxing solution.

When a chloroform solution of I was treated with one equivalent of α-toluenethiol under reflux, no opening of the cyclic carbonate ring was evident. Upon addition of triethylamine to the refluxing solution, however, there was complete conversion to an isomeric mixture of the 2- and 3-O-(α-toluenethio)carbonyl products within 4 hours. The mixture was separated by thin-layer chromatography into individual crystalline isomers, which had correct sulfur values. Treatment under similar conditions of cis-fused carbonate II gave no reaction.

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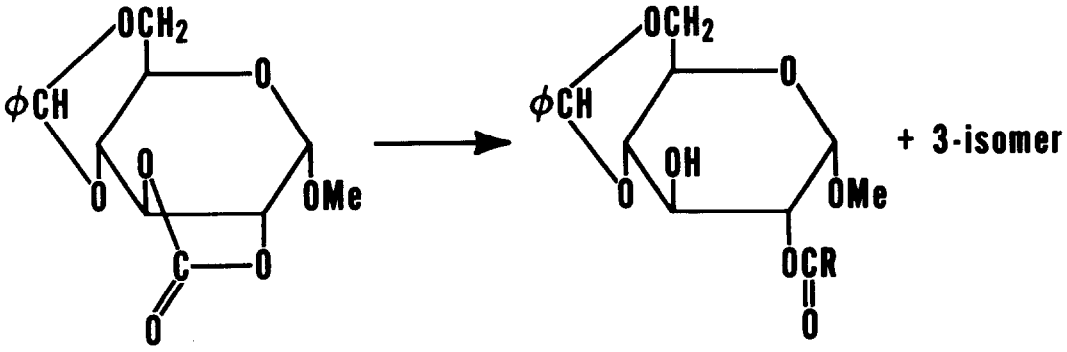
The trans-fused cyclic carbonate I also was opened more readily by piperidine than was the cis-fused cyclic carbonate II. When chloroform solutions of I and II were treated with two equivalents of piperidine at 43° for 24 hours, I was completely converted to the corresponding 2- and 3-O-(1-piperidyl)carbonyl derivatives, whereas II was recovered unchanged. Again, the isomers were recovered by fractional crystallization from ether-hexane and gave correct elemental analyses. When I and II were dissolved in piperidine, both were converted to the (1-piperidyl)carbonyl derivatives.

The reactions described were conveniently monitored by thin-layer chromatography and by carbonyl absorption (1) in the infrared region.

The new derivatives reported here are being more fully characterized. Also, work is underway to explore other reactions of the cyclic carbonate group and to extend the reactions to the analogous thionocarbonate group.



I

R = OMe; $SCH_2\phi$; NC_5H_{10}

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