116. *A Bisglycerol Tricarbonate.*

By L. HOUGH and J. E. PRIDDLE.

Examination of the infrared spectrum of a crystalline bisglycerol tricarbonate has shown it to be bis(glycerol 1,2-carbonate) 3,3′-carbonate (I). A quantitative evaluation of the relative intensities of the two C=O stretching absorptions of the compound is described. The apparent C=O stretching absorption intensities of propylene carbonate, propane-1,3-diol carbonate, dimethyl carbonate, and diethyl carbonate have also been calculated.

PREPARATIONS of a crystalline glycerol carbonate, $(C_9H_{10}O_9)_x$, were patented in 1911 and 1912 by Scheuble and Hochstetter.[1] Of the two methods cited, namely, the reaction of carbonyl chloride with glycerol in an organic base such as pyridine, and the ester-exchange of glycerol with an organic carbonate, the latter was the more convenient. In 1935, similar preparations of the glycerol carbonate were patented.[2] Bruson and Riener[3] re-investigated the ester-exchange by altering the molar ratio of the reagents and, with an excess of glycerol, resinous polycarbonates were obtained.

The only attempt to elucidate the structure of Scheuble and Hochstetter's glycerol carbonate was made by Contardi and Ercoli,[4] who assumed the molecular formula to be $C_9H_{10}O_9$. (This molecular formula has now been verified.) On this basis, they considered only two structures, namely, bis(glycerol 1,2-carbonate) 3,3′-carbonate (I), and the rather crowded, cage-like bisglycerol 1,1′:2,2′:3,3′-tricarbonate (II). By comparison with the structure of the known 3-chloropropane-1,2-diol carbonate (III), they preferred the former. They did not, however, consider other isomeric structures such as (IV) and (V). A recent

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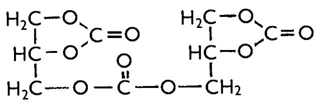
[1] Scheuble and Hochstetter, B.P. 19,924/1911; *Chem. Zentr.*, 1912, **83**, II, 1756.

[2] Soc. industrielle Vator, F.P. 779,342/1935; *Chem. Abs.*, 1935, **29**, 5460.

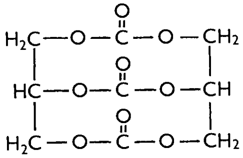
[3] Bruson and Riener, *J. Amer. Chem. Soc.*, 1952, **74**, 2100.

[4] Contardi and Ercoli, *Gazzetta*, 1934, **64**, 522.

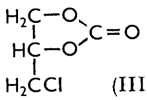
examination[5] of the formation of carbonate derivatives of methyl glycopyranosides has revealed that five-membered cyclic carbonates are formed in preference to six-membered cyclic carbonates because of the more favourable situation of a trigonal carbon atom in a five- rather than in a six-membered ring. By analogy, glycerol would be expected to give a carbonate of structure (I) in preference to (IV) and (V).



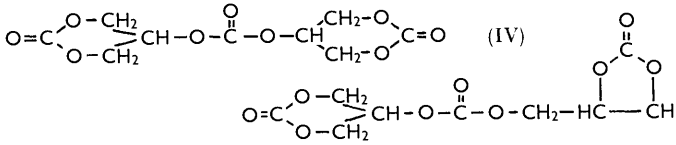
(I)



(II)



(III)



(IV)

(V)

Studies of the infrared absorption spectra of some carbohydrate carbonates[6] and other simpler organic carbonates[7] have revealed the usefulness of the C=O stretching frequency in structural work. Thus five-membered organic cyclic carbonates showed a C=O vibration absorption maximum near 1800 cm.$^{-1}$, whereas with linear carbonates the maximum appeared close to 1760 cm.$^{-1}$. As expected by comparison with cyclic lactones and ketones, the six-membered propane-1,3-diol carbonate also showed a C=O vibration maximum at 1760 cm.$^{-1}$.

The infrared absorption spectrum of bisglycerol tricarbonate (potassium bromide disc) showed C=O stretching absorptions at 1800 and 1760 cm.$^{-1}$, the former being the more intense. This ruled out structures (II) and (IV) since they do not contain five-membered cyclic carbonate groups. In order to establish the ratio of open to cyclic carbonate groups and so distinguish between structures (I) and (V), the C=O stretching intensities at 1800 and 1760 cm.$^{-1}$ were examined quantitatively.

Methods have been given for calculating the difference between the true integrated absorption intensity and the experimentally determined value;[8] an increment of 2—3% was involved. R. N. Jones and his co-workers[9] have shown that the C=O stretching absorption intensities of similar carbonyl groups in different steroid environments are approximately the same. Antia[10] has used this principle to prove the structure of 1,3,4-tri-*O*-acetyl-α-D-xylopyranose.

It was appropriate therefore to examine the infrared spectra of propylene carbonate and diethyl carbonate as model compounds in order to determine the ratio of apparent integrated C=O stretching absorption intensities of the five-membered cyclic-carbonate and open-carbonate groups.

The apparent integrated C=O stretching absorption intensity of propylene carbonate was 4·7 intensity units (*c* 1·61 in $CHCl_3$) (one intensity unit $= 1 \times 10^4$ mole^{-1} l. cm.$^{-2}$), and the value for diethyl carbonate was 4·0 intensity units (*c* 1·4 in $CHCl_3$). The ratio of these intensities is 1·2 : 1. For bisglycerol tricarbonate, the ratio of the intensity of the 1800 cm.$^{-1}$ peak to that of the 1760 cm.$^{-1}$ peak was 2·39 : 1. Hence the presence of

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[5] Hough and Priddle, *Chem. and Ind.*, 1959, 1600.

[6] Hough, Priddle, Theobald, Barker, Douglas, and Spoors, *Chem. and Ind.*, 1960, 148.

[7] Angell, *Trans. Faraday Soc.*, 1956, **52**, 1178; Hales, Idris Jones, and Kynaston, *J.*, 1957, 618; Gatehouse, Livingstone, and Nyholm, *J.*, 1958, 3137; Sarel, Pohoryls, and BenShoshan, *J. Org. Chem.*, 1959, **24**, 1873.

[8] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72; Cabana and Sandorfy, *Spectrochim. Acta*, 1960, **16**, 335.

[9] R. N. Jones, Ramsay, Keir, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 80.

[10] Antia, *J. Amer. Chem. Soc.*, 1958, **80**, 6138.

five-membered cyclic groups and open-carbonate groups in the ratio of 2·0 : 1 was revealed, thus providing proof for the bis(glycerol 1,2-carbonate) 3,3′-carbonate structure (I).

The value of the integrated C=O absorption intensity of propane-1,3-diol carbonate was 5·3 intensity units (c 1·38 in $CHCl_3$), which clearly ruled out structure (V).

The validity of the method employed was confirmed by a similar calculation using data obtained for methyl 4,6-di-*O*-methoxycarbonyl-α-D-mannopyranoside 2,3-carbonate,[5] in which the ratio of the intensities of the 1800 and the 1760 cm.$^{-1}$ peak was 1 : 1·51. By using the C=O stretching intensity of propylene carbonate in conjunction with that of dimethyl carbonate [3·7 intensity units (c 1·65 in $CHCl_3$)], a ratio of 1·9 : 1 was found for the number of *O*-methoxycarbonyl groups to cyclic carbonate groups.

EXPERIMENTAL

Infrared Absorption Spectra.—The spectra were obtained by using a Unicam S.P. 100 double-beam infrared spectrometer with a rock-salt prism. A potassium bromide disc technique (0·5 mg. of compound in 500 mg. of KBr) was used for the glycerol carbonate, but in all other cases chloroform solutions were used.

Bis(glycerol 1,2-*carbonate)* 3,3′-*Carbonate.*[1, 2]—This was prepared by heating glycerol (20 g.) with diphenyl carbonate (17 g.) at 130°. The product (12 g.), crystallised from pyridine–ethanol and recrystallised from acetone, had m. p. 151—152°, $\nu_{max.}$ (C=O stretching) 1800 and 1760 cm.$^{-1}$ [Found: C, 41·0; H, 4·0%; M (Rast), 274. Calc. for $C_9H_{10}O_9$: C, 40·9; H, 4·0%; M, 262).

Propane-1,3-*diol Carbonate.*—The method of Carothers and Van Natta [11] was used. Metallic sodium (0·2 g.) was dissolved in a mixture of propane-1,3-diol (30·4 g.) and diethyl carbonate (57 ml.), and the solution heated at 120°, rising to 180° in 3 hr. The propane-1,3-diol carbonate (22 g.) obtained after recrystallisation from ether had m. p. 48°, $\nu_{max.}$ (C=O stretching) 1760 cm.$^{-1}$ (Found: C, 46·8; H, 5·9. Calc. for $C_4H_6O_3$: C, 47·1; H, 5·9%).

Commercial preparations of dimethyl carbonate, diethyl carbonate, and propylene carbonate were purified by fractional distillation. They had $\nu_{max.}$ (C=O) at 1760, 1760, and 1800 cm.$^{-1}$, respectively.

Calculation of Integrated Absorption Intensities.—The apparent integrated absorption intensity (A) of a peak is given by the equation:

$$A = \frac{1}{cl}\int \log_e \left(\frac{y_0}{y}\right)_\nu d\nu$$

where c is the concentration in mole l.$^{-1}$, l the path length in cm., and y_0 and y are the transmission of the solvent and of the compound plus solvent, respectively, at the required frequency ν.

In order to calculate the relative absorption intensities of the overlapping C=O peaks of the glycerol carbonate it was assumed that the peaks were symmetrical and that the frequencies of the two maxima were 1760 and 1800 cm.$^{-1}$. The movement of these maxima from their true frequencies by the overlapping of the peaks was insignificant. A graph of $\log_e y_0/y$ against ν was plotted, and the individual peak areas were calculated by correcting for the overlap. (Where the potassium bromide disc technique was used, y_0 was estimated from a horizontal portion of the infrared spectrum where the absorption due to the compound was very small over *ca.* 100 cm.$^{-1}$.)

The smaller peak did not extend significantly to frequencies greater than that of the maximum of the larger peak at 1800 cm.$^{-1}$; hence the area above this frequency was taken as the half-peak area. The values of $\log_e y_0/y$ for the larger peak at frequencies less than 1800 cm.$^{-1}$ were then plotted by using symmetry. Since $y_1 = y_0 + y - y_2$, where y, y_1 and y_2 represent approximately the transmissions at any particular frequency for the complete curve, the smaller peak, and the larger peak, respectively, values for y_1 below 1760 cm.$^{-1}$ could be calculated. A plot of these values against frequency enabled the half-peak area to be determined.

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[11] Carothers and Van Natta, *J. Amer. Chem. Soc.*, 1930, **52**, 314.

The ratio of the intensity of the peaks at 1800 cm.$^{-1}$ and 1760 cm.$^{-1}$ was therefore given by

$$2\int_{1800}^{\infty}\log_e\left(\frac{y_0}{y_2}\right)_\nu d\nu \Big/ 2\int_{0}^{1760}\log_e\left(\frac{y_0}{y_1}\right)_\nu d\nu$$

All integrals were evaluated graphically.

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