268.5° (lit.[3] m.p. 268–270°). Its structure was confirmed by infrared[7]: $\lambda_{max}^{HCCl_4}$ 3.50, 3.80, 6.90, 7.35, 9.05 10.30, and 12.50 μ.

Tricyclo[3.3.0.0^{3,7}]octane-1,3-dicarboxylic Acid.—To a solution of 1.0 g. KOH, 2 ml. of water, and 2 ml. of ethanol was added 430 mg., (1.33 mmoles) of 1,5-dibromoadamantane-2,6-dione. The resulting solution was refluxed for 4 hr. and acidified with dilute hydrochloric acid. The solution was concentrated to dryness and the residue was extracted with acetone. Tricyclo[3.3.0.0^{3,7}]octane-1,3-dicarboxylic acid (226 mg., 86% yield, m.p. 200–204°) was obtained. This was recrystallized from toluene–ethanol to get an analytical sample (m.p. 215–215.5°): λ_{max}^{KBr} 2.95, 3.33, 3.71, 3.85, 5.85, 6.75, 7.10, 7.60, 7.75, 8.20, 8.55, 9.16, 11.25, and 13.35 μ.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.18; neut. equiv., 98.1. Found: C, 61.29; H, 6.10; neut. equiv. 98.2.

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(7) We are indebted to V. Prelog, Swiss Federal Institute of Technology, Zurich, Switzerland, who provided a sample of adamantane for comparison purposes.

The Preparation and Nuclear Magnetic Resonance Spectrum of the Cyclic Sulfite of 1,1-Dimethylol-3-cyclopentene

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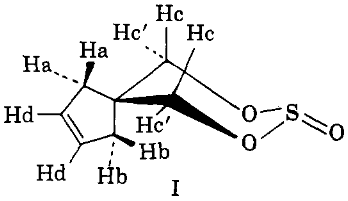
The pyramidal geometry of bonds attached to sulfur in organic sulfites has recently been confirmed by Lauterbur[1] and Pritchard.[2] In addition to the evidence obtained from the n.m.r. spectra of several cyclic sulfites they isolated two geometrical isomers of propylene sulfite[2] and three geometrical isomers of the cyclic sulfite derived from 2,4-pentanediol.[1] Hellier[3] has recently reported a study of trimethylene sulfite from which he draws the somewhat surprising conclusion that the sulfur–oxygen double bond assumes almost exclusively an axial conformation.

The pyramidal nature of the sulfite group imposes a magnetic asymmetry upon these molecules which is absent in the corresponding cyclic carbonates.[4] This may give rise to complex n.m.r. spectra.

As part of a study of small-ring spiran compounds the cyclic sulfite of 1,1-dimethylol-3-cyclopentene was prepared. This paper presents the evidence for its structure. Unequivocal proton assignments were made by employing isotopic substitution.

An isomeric mixture of diesters[5] containing 1,1-dicarbethoxy-3-cyclopentene was reduced with lithium aluminum hydride. From the reaction mixture 1,1-dimethylol-3-cyclopentene was isolated. The n.m.r. spectrum of the diol showed that double bond migration had not occurred during the reduction. It showed the following features given in τ-values (assignments shown in parentheses): 7.82, 4 protons (ring methylenes); 6.37, 4 protons (–CH_2OH); 6.24, broad, 2 protons (–OH); 4.40, 2 protons (vinyl hydrogen). The diol was converted to the cyclic sulfite (I) by treatment with thionyl chloride. The infrared spectrum showed a strong band at 1190 cm.$^{-1}$ attributed to the S=O bond. The n.m.r. spectrum of I shows the following features given in τ-values (assignments shown in parentheses): 8.62 and 7.57, partially resolved doublets, 2 protons each (hydrogens a and b); two doublets centered at 6.90 and 5.50, 2 protons each (hydrogens c and c′; and a complex multiplet centered at 4.77, 2 protons (d hydrogens). The coupling constant $J_{cc'}$ is 11 c.p.s.



I

In order to confirm that the doublets at τ 6.90 and 5.50 arise from the coupled protons c and c′, the corresponding cyclic sulfite with deuterium at c and c′ was prepared. A pure sample of 1,1-dicarbethoxy-3-cyclopentene was reduced with lithium aluminum deuteride to 1,1-dimethylol-d_4-3-cyclopentene. The n.m.r. spectrum shows, in addition to the broad hydroxyl absorption at τ 6.77[6] (2 protons), two singlets at τ 7.80 and 4.38 corresponding to the allyl and vinyl ring protons, respectively. The ratio of integrated areas for these two peaks is 2:1. Quantitative removal of the singlet at τ 6.37 confirms the assignments for the undeuterated diol. The deuterated diol was converted to the corresponding cyclic sulfite with thionyl chloride. The n.m.r. spectrum is identical with that for the undeuterated sulfite with the exception that the two doublets at τ 6.90 and 5.50 are quantitatively removed.

The results of this study are in agreement with those reported by Arbuzov[4] regarding the structure of the sulfite derived from 2,2-dimethyl-1,3-propanediol. In calculating the effect of the electric field of the sulfite group on the various proton chemical shifts, he has assumed that the S=O group is in an equatorial conformation. Clearly, additional experimental work is needed to resolve the conformational uncertainty in six-membered ring cyclic sulfites.

Experimental[8]

1,1-Dimethylol-3-cyclopentene.—An isomeric mixture of diesters[9] (206 g., 0.971 mole) containing 1,1-dicarbethoxy-3-cyclopentene and 1,1-dicarbethoxy-2-vinylcyclopropane was dissolved in 500 ml. of anhydrous ether. This solution was added dropwise with stirring over a 5-hr. period to a suspension of 46.0 g. (1.21 moles) of lithium aluminum hydride in 600 ml. of an-

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(1) P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963).

(2) J. G. Pritchard and P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 2105 (1961).

(3) D. G. Hellier, J. G. Tillett, H. F. Van Woerden, and R. F. M. White, *Chem. Ind.* (London), **50**, 1956 (1963).

(4) B. A. Arbuzov, Y. Y. Samitov, and R. M. Mamina, *Proc. Acad. Sci. USSR*, **143**, 186 (1962).

(5) K. C. Murdock and R. B. Angier, *J. Org. Chem.*, **27**, 2395 (1962).

(6) Recent reports[7] indicate that substitution of deuterium for hydrogen at one position in a molecule can cause upfield shifts in resonance frequencies for the remaining hydrogens. Although we observe an upfield shift for the hydroxyl proton in the deuterated diol, the magnitude is much too large to be caused by a deuterium isotope effect and we attribute this shift to changes in concentration.

(7) (a) E. I. Snyder, *J. Phys. Chem.*, **67**, 2873 (1963); (b) G. V. D. Tiers, *J. Chem. Phys.*, **29**, 963 (1958); (c) H. S. Gutowsky, M. Karplus, and D. Grant, *ibid.*, **31**, 1278 (1959); (d) H. S. Gutowsky, *ibid.*, **31**, 1683 (1959).

(8) All melting points are corrected. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 321 infrared recording spectrophotometer unless otherwise noted. N.m.r. spectra were determined on a Varian Model A-60 spectrometer. Analyses were performed by West Coast Analytical Laboratories, Inc.

(9) K. C. Murdock and R. B. Angier, *J. Org. Chem.*, **27**, 2395 (1962).

hydrous ether. The mixture was boiled under reflux for 19 hr. under an atmosphere of nitrogen. The mixture was cooled and 100 ml. of water was carefully added. The resulting mixture was treated with 300 ml. of a 10% aqueous solution of sulfuric acid. The ether layer was separated and the aqueous phase was extracted with three 500-ml. portions of ether. The combined ether extract was dried over magnesium sulfate and concentrated. The residual oil was distilled, affording as the main fraction 101 g. of a colorless oil which solidified in the receiver, b.p. 99–110° (0.35 mm.). The crude diol was recrystallized from benzene to give 49.7 g. (40% based on total diester) of the pure diol as colorless needles, m.p. 76–77.5°.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44. Found: C, 65.80; H, 9.56.

The infrared spectrum (6% chloroform) shows a sharp band at 3610 cm.$^{-1}$ and a broad band centered at 3380 cm.$^{-1}$ attributed to free and associated O–H, respectively. The n.m.r. spectrum was determined as a 10% solution in chloroform containing tetramethylsilane.

1,1-Dimethylol-d_4-3-cyclopentene.—Difficulties were encountered in trying to separate the desired deuterated diol from side products in small-scale reductions of the diester mixture.[9] A sample of pure 1,1-dicarbethoxy-3-cyclopentene[10] was obtained in 55% yield by the action of thionyl chloride on pure 3-cyclopentene-1,1-dicarboxylic acid[8] followed by treatment of the diacid chloride with ethanol. The most notable difference between the properties of this pure diester and the mixture[9] previously reported is seen in the infrared spectra. The infrared spectrum[11] of the mixture of diesters shows a strong band at 918 and a shoulder at 993 cm.$^{-1}$ attributed to C–H deformation modes of a monosubstituted ethylene present in the contaminating 1,1-dicarbethoxy-2-vinylcyclopropane. The infrared spectrum[11] of pure 1,1-dicarbethoxy-3-cyclopentene shows a slight sharpening of the ester carbonyl band at 1740 and the bands at 918 and 993 cm.$^{-1}$ are removed. The pure diester (2.53 g., 0.0119 mole) was reduced with 0.500 g. (0.0119 mole) of lithium aluminum deuteride as described for the reduction using lithium aluminum hydride. The crude product was distilled and then recrystallized from benzene affording 0.505 g. (32%) of colorless needles, m.p. 74–75°. A mixture melting point with the undeuterated diol showed no depression below 74°. The infrared spectrum (7% in chloroform) is very similar to that of the undeuterated diol (identical in the 3-μ region) and shows two bands at 2105 and 2200 cm.$^{-1}$ attributed to the methylene C–D symmetric and antisymmetric stretching modes. The n.m.r. spectrum was determined as a 4% solution in chloroform containing tetramethylsilane.

1,1-Dimethylol-3-cyclopentene Sulfite.—A solution of 35.1 g. (0.274 mole) of the diol in 150 ml. of dry ether and 44 ml. of anhydrous pyridine was cooled by means of an ice bath. The cooled solution was stirred as 98.0 g. (0.823 mole) of thionyl chloride was added, dropwise, over a period of 30 min. The mixture was stirred for 1 hr. and, after allowing it to warm to room temperature, it was stirred an additional 4 hr. It was then carefully poured onto ice and extracted with three 30-ml. portions of ether. The ether extract was washed with aqueous sodium bicarbonate and then with water, dried over magnesium sulfate, and concentrated. The crude sulfite was distilled affording 28.3 g. (59%) of a colorless oil which solidified in the receiver, b.p. 117–119° (8 mm.), m.p. 47.5–49.0°. One recrystallization from anhydrous ether raised the melting point to 49–50°.

Anal. Calcd. for $C_7H_{10}O_3S$: C, 48.26; H, 5.78; S, 18.40. Found: C, 48.00; H,5.86; S, 17.90.

The infrared spectrum (10% in carbon disulfide) showed a strong band at 1190 cm.$^{-1}$ (S═O). The n.m.r. spectrum was determined as a 9% solution in benzene containing tetramethylsilane.

1,1-Dimethylol-d_4-3-cyclopentene Sulfite.—The deuterated diol (0.200 g., 0.00152) was converted to the corresponding cyclic sulfite by the procedure described for the undeuterated compound. The product was distilled through a Hickman still followed by crystallization from ether to yield 0.037 g. (14%) of colorless crystals, m.p. 47–48.5°. A mixture melting point determination with undeuterated sulfite showed no depression below 47°. The infrared spectrum (5% in chloroform) shows bands at 2120 and 2240 with a shoulder at 2160 cm.$^{-1}$ (C–D stretch). The spectrum in carbon disulfide is similar to that for the undeuterated sulfite. The n.m.r. spectrum was determined as a 6% solution in benzene containing tetramethylsilane.

Acknowledgment.—The authors wish to thank Dr. G. E. Maciel for the determination of preliminary n.m.r. spectra and to acknowledge the support of this work by Research Corporation (Frederick Gardner Cottrell Grant).

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[10] J. Meinwold, P. G. Gassman, and J. K. Crandall [*J. Org. Chem.*, **27**, 3366 (1962)] report the preparation of the pure diester by cycloalkylation of malonic ester with *cis*-1,4-dibromobutene-2.

[11] Determined as a pure liquid with a Perkin-Elmer Infracord spectrophotometer.

Proton Magnetic Resonance and Stereochemistry of 2-*o*-Tolyl-3-(2-hydroxyethyl)cyclohexanol and Related Compounds[1]

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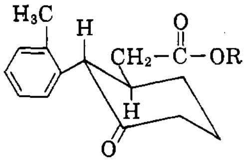
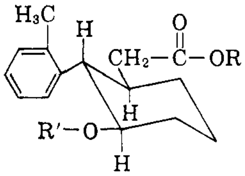
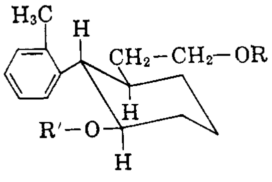
As part of an investigation dealing with the stereospecificity on biological activity of certain aryl-substituted cyclohexanols, several compounds of known stereochemistry were required. In a previous publication[3] we have reported and discussed the n.m.r. spectra and stereochemistry 1-(2-hydroxyethyl)-2-*o*-tolylcyclohexanols and related compounds. The present report treats the n.m.r. spectra of *trans*-2-*o*-tolyl-*cis*-3-(2-hydroxyethyl)cyclohexanol (VII), related intermediates, and derivatives (compounds I through VIII).



I, R = H
II, R = CH_3
III, R = CH_2–CH_3



IV, R = R′ = H
V, R = CH_3; R′ = H
VI, R = CH_3; R′ = $COCH_3$



VII, R = R′ = H
VIII, R = R′ = $COCH_3$

The diol VII was obtained from lithium aluminum hydride reduction of the hydroxy acid IV, the acetoxy methyl ester VI, and the keto ester II. No change in stereochemistry will result in the reduction of IV and VI, but the reduction of the keto ester II could yield diastereoisomeric diols. Only the all-equatorial compound VII was isolated from lithium aluminum hydride re-

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[1] This investigation was supported by research grants, HE-03843-(04 and 05), from the National Heart Institute, Public Health Service. The n.m.r. spectra were determined by B. J. Nist, Department of Chemistry, University of Washington.

[2] Fellow of the American Foundation for Pharmaceutical Education, 1962-1963.

[3] D. C. Staiff and A. C. Huitric, *J. Org. Chem.*, **28**, 3531 (1963).