We have also studied the isotope effect on these reactions by competitively nitrating mixtures of bromobenzene and chlorobenzene, bromobenzene and *p*-chlorobenzene-*d* (88.2%), and bromobenzene and *m*-chlorobenzene-*d* (91%). The results are shown in Table II.

TABLE II
ISOTOPE EFFECTS ON THE NITRATION OF CHLOROBENZENE WITH NITRONIUM TETRAFLUOBORATE IN TETRAMETHYLENESULFONE SOLUTION AT 25.0°

Rate ratio	Value
p-Chlorobenzene-*d*-chlorobenzene[a]	1.05 ± 0.03[b]
(*para–ortho*)$_{p\text{-D}}$–(*para–ortho*)$_{p\text{-H}}$	1.06 ± 0.03[b]
m-Chlorobenzene-*d*-chlorobenzene	1.00 ± 0.02[b]
(*para–ortho*)$_{m\text{-D}}$–(*para–ortho*)$_{m\text{-H}}$	1.00 ± 0.03[b]

[a] Values are corrected for deuterium content. [b] The error reported is the maximum error found in five separate parallel determinations.

The isotope effects reported here are smaller than those reported for fluorobenzene and toluene nitrations.[1]

Since our data indicate that these reactions may not be well behaved kinetically, and since our primary interests are not in this field, we are discontinuing our investigations of these systems.

Conformational Analysis of a Disultone

J. HODGE MARKGRAF[1] AND ROY W. KING

Departments of Chemistry, Williams College, Williamstown, Massachusetts, and Iowa State University, Ames, Iowa

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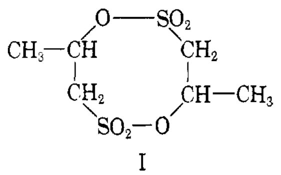
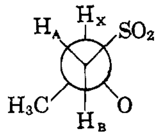
In a previous paper[2] the identification of 4,8-dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-tetraoxide (I) from the reaction of 1-propanol with sulfuryl chloride was reported. The assignment of structure was based on chemical shifts in n.m.r. spectra and was confirmed by chemical degradation. It was observed that diastereomeric configurations are possible for I.



I

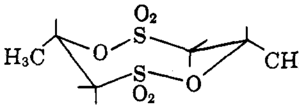
Although the utility of n.m.r. spectroscopy in conformational analysis of cyclic systems is well recognized, eight-membered rings have received scant attention.[3] Previous papers on this particular ring size have involved theoretical calculations, dipole moments, infrared and Raman spectra, and equilibration methods. It has been concluded that the preferred conformation of cyclooctane and its derivatives is a stretched crown.[4]

In our earlier work, the n.m.r. spectrum of the disultone (I) was discussed in terms of chemical shifts, which permitted differentiation between structural isomers. In that case coupling between protons was not germane to the identification of isomers. With the correct structure of the disultone established, it was of interest to consider the conformation of I. The spin-decoupling method permitted the protons to be analyzed as an ABX system, giving $J_{AB} = 14.8$ c.p.s., $J_{AX} = \pm 1.3$ c.p.s., and $J_{BX} = \pm 9.5$ c.p.s. Regarding the coupling constants, J_{BX} is fairly large and indicates that one methylene proton and the methine proton are *anti* most of the time. The J_{AX} value is consistent with a dihedral angle of about 60°.[5] It thus seems that the disultone shows a strong preference for one conformation. That eight-membered rings exist predominantly in one conformation has been concluded by others.[4,6] Such an interpretation with respect to the *anti* relationship of the methine and methylene protons is consistent with the chemical degradations of I reported previously. It was established that hydride ion effected a facile E2 elimination to produce derivatives of *trans*-1-propene-1-sulfonic acid.[2] It is known that such concerted, bimolecular eliminations proceed most readily when the atoms to be eliminated, hydrogen and sulfonate in the present case, are *anti*.[7] This favorable conformation for the elimination process is a corollary of the methine–methylene arrangement mentioned above. These relationships are represented in the Newman projection (II) along the C-5–C-4 bond.



II

The question of the configuration of I remains unresolved; the methyl groups may be *cis* or *trans*. From Dreiding models it is evident that, when the preferred conformation (II) about the C-3–C-4 bond is satisfied, then the most reasonable molecular conformations (in terms of transannular repulsions and dihedral angles) are a stretched crown (III) for the *cis* isomer and a skewed chair[9] (IV) for the *trans* isomer. In both cases the methyl groups can be in comfortable "equatorial" positions. Although the *cis* isomer (III) is analogous to the preferred stretched-crown conformation for cyclooctane and derivatives,[4] it is not possible to infer the more stable configuration of the disultone



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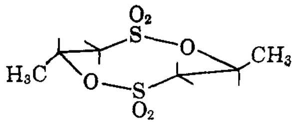

IV

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(1) To whom inquiries should be addressed at Williams College.

(2) J. H. Markgraf, B. A. Hess, Jr., C. W. Nichols, and R. W. King, *J. Org. Chem.*, **29**, 1499 (1964).

(3) F. A. L. Anet and J. S. Hartman, *J. Am. Chem. Soc.*, **85**, 1204 (1963).

(4) N. L. Allinger, S. P. Jindal, and M. A. DaRooge [*J. Org. Chem.*, **27**, 4290 (1962)] critically review the literature relevant to such a conclusion.

(5) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(6) (a) N. L. Allinger and S.-E. Hu, *J. Am. Chem. Soc.*, **83**, 1664 (1961); (b) H. E. Bellis and E. J. Slowinski, Jr., *Spectrochim. Acta*, **15**, 1103 (1959); (c) G. Chiurdoglu, T. Doehaerd, and B. Tursch, *Chem. Ind.* (London), 1453 (1959); (d) R. Kolinski, H. Piotrowska, and T. Urbanski, *J. Chem. Soc.*, 2319 (1958).

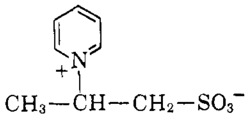
(7) It is recognized, however, that ground-state conformations cannot necessarily be inferred from the products; *cf.* Eliel's discussion of the Curtin–Hammett principle.[8]

(8) E. L. Eliel, "*Stereochemistry of Carbon Compounds*," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 149–152.

(9) R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960).

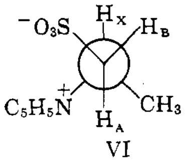
(III or IV) because a carbocyclic system is not necessarily a good model for a similar ring with four hetero atoms.

In the original report of the disultone[10] the reaction with pyridine was postulated to give a zwitterionic product, the correct structure of which must be V. Since the conformational analysis of ethane derivatives has been studied successfully by n.m.r. techniques, it is of interest to report the spectrum of V. In particular, comment on the question of internal rotation is afforded by the nonequivalence of the methylene protons in compounds such as V. The observed chemical shifts (in c.p.s. from internal acetonitrile) and coupling constants (in c.p.s.) are $\nu_A = -95.2$, $\nu_B = -91.8$, $\nu_X = -192.5$, and $\nu_{CH_3} = +15.5$; $J_{AB} = 15.2$, $J_{AX} = \pm 11.3$, $J_{BX} = \pm 2.7$, and $J_{CH_3X} = 6.9$. The methylene–methine coupling constants are of the same sign, but differ significantly in magnitude. One is larger than normal for a vicinal acyclic system, but any error in the assumption that the single line in the AB spectrum is completely degenerate would tend to decrease this. Nevertheless it strongly indicates an *anti*-type coupling in a conformation that is practically locked (VI). One would expect the sulfonate group to be near the pyridinium ring to minimize charge separation and *anti* to the methyl group to avoid steric interaction. The above conformation (VI) satisfies both this and the values of the coupling. The large difference between J_{AX} and J_{BX} indicates that other conformations play only a small part in the weighted mean.



$CH_3-\underset{}{\overset{\overset{+}{N}C_5H_5}{CH}}-CH_2-SO_3^-$

V



VI

Experimental

Melting points are uncorrected. Analyses were made by Galbraith Laboratories, Inc., Knoxville 21, Tenn.

4,8-Dimethyl-1,5-dioxa-2,6-dithiacyclooctane 2,2,6,6-Tetraoxide (I).—Samples of the disultone described previously were used.[2]

2-(N-Pyridinium)propane 1-Sulfonate (V).—A solution of the disultone (0.476 g., 0.00195 mole) in dry pyridine (5 ml.) was refluxed for 2.5 hr. Turbidity developed within 15 min.; white solid was present after 0.5 hr. The solid was collected, washed four times with acetone, and dried in a vacuum desiccator to give 0.347 g. (44.3%) of product, sintering at 278°, m.p. 297.5–298.5° dec. (lit.[10] m.p. 278° dec).

Anal. Calcd. for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96; S, 15.93. Found: C, 47.73; H, 5.54; N, 6.73; S, 16.06.

N.m.r. Spectra.—Measurements were obtained with a Varian HR-60 instrument at 60 Mc. Conditions for the spectrum of I were described earlier.[2] For the spectrum of V the solvent was deuterium oxide and the internal standard was acetonitrile. It was not possible to attain as good resolution in deuterium oxide as in the case of the disultone. The errors in the derived constants are therefore likely to be higher.

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[10] G. Manecke, *Chem. Ber.*, **85**, 160 (1952).

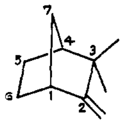
Monochloro Products from Camphene. Identification of Camphenol as 6-Hydroxycamphene[1,2]

Herman G. Richey, Jr., Theodore J. Garbacik,
David L. Dull, and James E. Grant

Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania

Received March 30, 1964

Camphenol, a crystalline alcohol, was prepared from camphene (**1**) by Tishchenko.[3] The structure of camphenol is the subject of this paper. Tishchenko obtained from reaction of camphene (**1**) and chlorine in carbon tetrachloride solution a monochloride fraction that he concluded must consist of **2** (*cis* and *trans*), **3**, and **4**. This monochloride mixture was treated with potassium acetate under conditions that caused only partial reaction, yielding a chloride fraction, thought to contain recovered **2** and **3**, and an acetate fraction. Saponification of the acetate fraction gave camphenol. Structure **6** was assigned to camphenol on the basis of oxidation and rearrangement reactions, and it was assumed that its acetate and chloride precursors had the related structures **5** and **4**.



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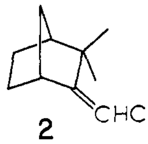

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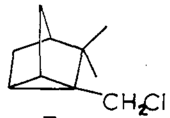

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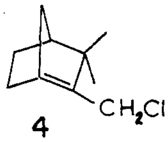

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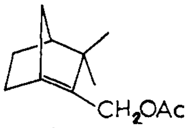

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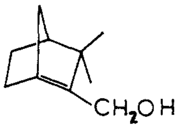

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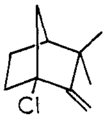

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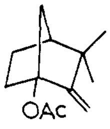

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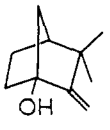

9

Chiurdoglu, Goldenberg, and Geeraerts reported later that camphenol had structure **9**.[4] They concluded on the basis of infrared spectra that the monochloride fraction consisted of **2**, **3**, and **7**, and that, on treatment of this fraction with potassium acetate, **7** reacted to form **8**, which on saponification gave **9**. More recent publications by Tishchenko[5] and by Chiur-

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[1] This work was supported in part by a grant from the Central Fund for Research of the Pennsylvania State University. Grateful acknowledgement is hereby made of this support. We are also pleased to acknowledge the assistance of the National Science Foundation in providing funds to aid in the purchase of the Varian A-60 n.m.r. spectrometer which was used in this research.

[2] Much of this work is contained in the senior theses of T. J. G. (June, 1962) and D. L. D. (June, 1963), The Pennsylvania State University.

[3] D. Tishchenko, *J. Gen. Chem. USSR*, **23**, 1051 (1953).

[4] G. Chiurdoglu, Ch. Goldenberg, and J. Geeraerts, *Bull. soc. chim. Belges*, **66**, 200 (1957).

[5] D. V. Tishchenko, *J. Gen. Chem. USSR*, **27**, 2943 (1957).