the Reoplex, showed in both cases two overlapping peaks in the area ratio of 3:2 corresponding to **3a** and **3b**, respectively.

B. From 1.—To a stirred solution of 22.8 g (0.20 mol) of **1** in 300 ml of dry carbon tetrachloride at room temperature was added dropwise over a period of 1 hr 32 g (0.20 mol) of bromine dissolved in 50 ml of dry carbon tetrachloride. The reaction mixture became warm (~45°) and evolved hydrogen bromide profusely. When the bromine addition was completed, the mixture was freed from solvent in a rotary evaporator under vacuum during which time the temperature of the mixture was kept below 30°. The light brown oily residue was distilled in an apparatus equipped with two potassium hydroxide traps and gave 14.9 g (65%) of 4-bromo-6,8-dioxabicyclo[3.2.1]octane (**3**) boiling at 64° (0.5 mm). Glc on either or the two columns showed it to be identical in retention time with **3** obtained from **2** above and that it was an approximately 1:1 mixture of **3a** and **3b**.

Dehydrohalogenation of 4-Bromo-6,8-dioxabicyclo[3.2.1]octane (3). A. With a 1 or 2 *M* Excess of Potassium Hydroxide in 95% Ethyl Alcohol.—The published directions[2] were modified as follows. To a stirred solution of 56 g (1.0 mol) of potassium hydroxide in 900 ml of 95% ethyl alcohol was added 96.5 g (0.50 mol) of the cis–trans mixture **3ab**. The resulting solution was heated under reflux for 24 hr and then cooled and filtered. The solvent (700 ml) was removed by fractional distillation at atmospheric pressure. Water (200 ml) was added to the residual dark mass and the mixture was then continuously extracted with ether for 10 hr. The ether extract was dried ($MgSO_4$) and freed from solvent by fractional distillation. The remaining black oil was distilled under reduced pressure and gave 21.8 g (39%) of 6,8-dioxabicyclo[3.2.1]oct-3-ene (**4a**): bp 58° (15 mm); $n^{25}D$ 1.4775 [lit.[3] bp 83–84° (51.5 mm); $n^{22}D$ 1.4795]; 100-MHz pmr τ 4.18 (m, 2, vinyl), 4.52 (m, $W/2 \sim 5$ Hz, 1, anomeric H), 5.35 (m, 1, HCO), 6.06 (t, 1, HCO), 6.33 (d, 1, HCO), 7.22 (d, 1, CH aliphatic), and 8.13 (d, 1, CH aliphatic). Glc on both columns showed only one narrow symmetrical peak.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.04; H, 7.23.

The recovered bromide **3b** boiled at 71° (1.0 mm): $n^{27}D$ 1.5156 [lit.[2] of mixture **3a–b**, bp 68° (1 mm) or 90° (4.5 mm); $n^{27}D$ 1.5176]; glc analysis on either of the columns used showed only one narrow symmetrical peak; 100-MHz pmr τ 4.61 (s, 1, anomeric), 5.41 (m, 1, HCO), 6.05 (m, 3, CH_2O and HCBr), and 8.10 (m, 4, CH_2). Irradiation at τ 6.02 gave loss of coupling of ~6-7 Hz in the multiplet at τ 7.82 due to the two protons on C-3.

B. With Potassium *tert*-Butoxide in *tert*-Butyl Alcohol.—To a stirred solution of 0.75 mol of potassium *tert*-butoxide from 28.6 g of potassium metal slowly added to 750 ml of dry *tert*-butyl alcohol under N_2 was added 48.2 g (0.25 mol) of *cis,trans*-4-bromo-6,8-dioxabicyclo[3.2.1]octane (**3**). The mixture was kept at 80° for 24 hr and then half of the solvent was removed by fractional distillation. The dark residue was cooled and diluted with 250 ml of water. The resulting mixture was continuously extracted with ether for 12 hr. The ether extract was dried ($MgSO_4$) and freed from solvent by fractional distillation, and the residue distilled under vacuum to give 10 g (36%) of a 4:96 mixture (by glc) of the olefins **4a** and **4b**, respectively, bp 58–60° (16 mm), along with 12.3 g of **3b**, bp 72° (1.5 mm). The mixture of **4a** and **4b** was separated by distillation with a spinning-band column (50 cm): bp of **4b** 69–69.5° (41 mm); $n^{25}D$ 1.4750; 100-MHz pmr τ 4.14 (m, 2, vinyl), 4.34 (broad s, 1, anomeric H), 5.4 (t, 1, HCO), 6.02 (d, 1, HCO), 6.28 (t, 1, HCO), 7.47 (d, 1, CH aliphatic), and 8.03 (d, 1, CH aliphatic). Glc on both columns showed only one narrow symmetrical peak.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.24; 63.99; H, 7.31; 7.22.

One of the repetitions of this experiment gave a yield of 44% of a 21:79 ratio of **4a**:**4b** as the lowest proportion of **4b** obtained.

Isomerization of 4a and 4b. A. With Potassium *tert*-Butoxide in *tert*-Butyl Alcohol.—A solution of potassium *tert*-butoxide in *tert*-butyl alcohol [from 3.13 g (0.08 g-atom) of potassium added to 80 ml of dry *tert*-butyl alcohol] containing 4.88 g (0.04 mol) of **4a** was kept under N_2 at 80° for 24 hr. Subsequent treatment followed that described in B above. There was obtained 2.40 g (49%) of a 20:80 mixture of the olefins **4a** and **4b**, respectively (by glc), bp 59° (15 mm).

When 5.60 g (0.05 mol) of **4b** was treated similarly with 0.051 mol of potassium *tert*-butoxide in *tert*-butyl alcohol, there was obtained 3.50 g (63%) of a 15:85 mixture of the olefins **4a** and **4b**, respectively (by glc).

B. With Potassium Hydroxide in 95% Ethyl Alcohol.—A solution of 21 g (0.188 mol) of a 19:1 mixture of **4a** and **4b** and 36.8 g (0.65 mol) of potassium hydroxide in 180 ml of 95% ethyl alcohol was heated under reflux (N_2) for 24 hr. The solvent was then removed by fractional distillation. The residue, diluted with water, was extracted several times with ether. The combined ether extracts were dried (Na_2SO_4) and freed from solvent. Fractional distillation of the residue under vacuum gave 12.6 g (60%) of a colorless liquid, bp 58–62° (9 mm), $n^{23}D$ 1.4775. Glc analysis produced two well-separated narrow peaks which showed this to be a mixture of **4a** and **4b** in the ratio 2:3, respectively.

Registry No.—**4a**, 20583-51-1; **4b**, 27925-22-0.

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Conformational Analysis of Sulfur-Containing Heterocycles. A Dipolar Effect[1]

David N. Harpp* and John G. Gleason[2]

Department of Chemistry, McGill University,
Montreal, Canada

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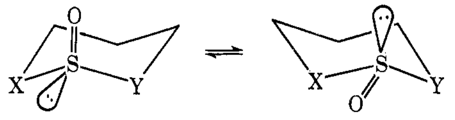
The conformational preferences for substituents on cyclohexane ring systems are well studied.[3] However, when heteroatoms containing nonbonded lone-pair electrons are present, conformational effects may be altered considerably.[4] The conformational preference for an axial disposition of a sulfoxide oxygen is very small (0.1–0.5 kcal).[5] It is therefore surprising that sulfoxides of the type **1** where X and Y are hetero-



1a, X = Y = O
b, X = O; Y = NH
c, X = Y = CH_2

atoms exhibit a remarkably high axial preference (3–5 kcal/mol).[6] The substitution of a heteroatom for a methylene group in such systems should lower the barrier to chair–chair interconversion by reducing 1–2 rotational interactions.[7] Moreover, Eliel[4a] has demonstrated that sulfur (presumably oxygen as well) with its lone pairs has a smaller space requirement than a methylene group. While there have been several explanations advanced[5] for the small preference for axial S=O in **1c**, the question remains open as to why

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[2] Holder of a NRCC Scholarship, 1968–1970.

[3] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, pp 36–126.

[4] See, for example, (a) E. L. Eliel and R. O. Hutchins, *J. Amer. Chem. Soc.*, **91**, 2703 (1969); (b) H. T. Kalff and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **85**, 467 (1966).

[5] (a) N. A. Allinger, J. A. Hirsh, M. A. Miller, and L. J. Tyminski, *J. Amer. Chem. Soc.*, **91**, 337 (1969); (b) J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).

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[7] E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959).

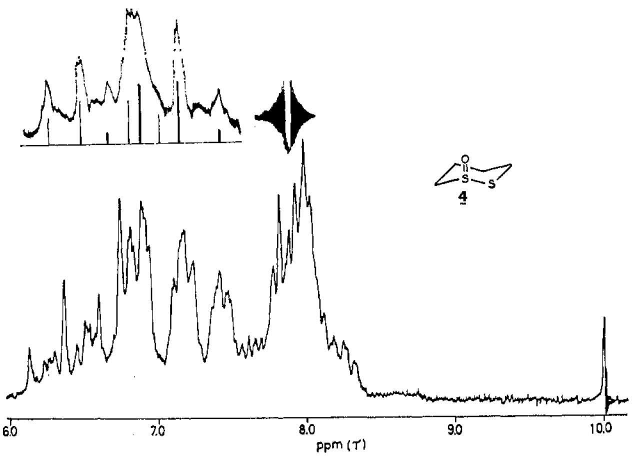
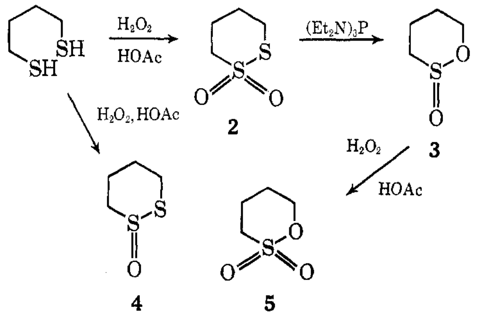


Figure 1.—60-MHz nmr spectrum of 1,2-dithiane 1-oxide (**4**).

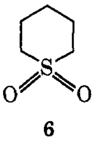
the introduction of the oxygen atoms into the ring (*e.g.*, **1a,b**) so markedly increases this axial preference. As outlined above, these heteroatoms should decrease the conformational stability of such molecules. We felt that further insight might be gained by an analysis of other similar heterocycles.

We have recently developed simple syntheses of some missing members of this series, 1,2-dithane 1,1-dioxide (**2**), 1,2-oxathiane 2-oxide (**3**),[8] its thio analog,



1,2-dithiane 1-oxide (**4**), and 1,2-oxathiane 2,2-dioxide (**5**), and have undertaken a detailed analysis of the nmr spectra of these compounds to further investigate this conformational preference.

The low temperature nmr spectra of both sultone **5** and thiosultone **2** indicated that these compounds undergo very rapid chair–chair interconversion as low as −90°. In contrast, the conformational isomers of thiane 1,1-dioxide (**6**) are observable at −60°.[5b] The



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second heteroatom, as expected, significantly lowers the barrier to chair–chair interconversion.

The spectrum of 1,2-dithiane 1-oxide (**4**) (Figure 1) was extremely complex; however, irradiation of the high-field multiplet caused the collapse of the low-field lines to two AB quartets thus indicating the nonequivalence of the pairs of protons α to the S and S=O groups. While it was not possible to definitively assign the configuration of the S=O bond in this molecule, clearly this ring is not undergoing interconversion.

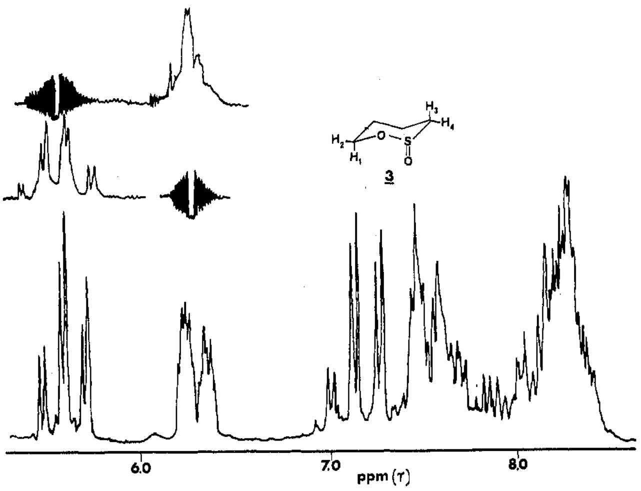

Figure 2.—100-MHz nmr spectrum of 1,2-oxathiane 2-oxide (**3**).

The 100-MHz nmr spectrum of 1,2-oxathiane 2-oxide (**3**) (Figure 2) was interpretable only in terms of a single conformational isomer. The multiplet at τ 5.58 may be assigned to the axial proton H_1 adjacent to the ring oxygen on the basis of the observed 11.5-Hz coupling which is consistent with a trans diaxial relationship to the adjacent proton.[9] The multiplet at τ 6.28 was assigned to the corresponding equatorial proton H_2. This assignment was confirmed by double resonance. Similarly, the multiplet at τ 7.13 was assigned to the axial proton H_3.

This interpretation has placed both axial protons H_1 and H_3 to low field relative to their equatorial counterparts H_2 and H_4. In alicyclic systems, axial protons are normally displaced to high field relative to equatorial protons.[9] Previous studies have shown that protons in a 1,3 diaxial relationship to a sulfinyl oxygen experience a deshielding effect[10] (the so-called syn-axial effect)[10e,f] due to a proximity effect[10f,11] and/or an acetylene-like anisotropy[10,f,g,12] of the S=O bond. Thus, the deshielding of H_1 relative to H_2 would imply that H_1 is in a 1,3 cis-diaxial relationship to the S=O bond as illustrated. In addition, deshielding of proton H_3 relative to H_4 is consistent with that observed for other sulfoxide systems.[13,14]

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(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 193.

(10) (a) For a review, see J. G. Tillett, *Quart. Rep. Sulfur Chem.*, **2**, 227 (1967); see also (b) C. R. Johnson, and W. O. Sigel, *J. Amer. Chem. Soc.*, **91**, 2796 (1969); (c) E. T. Strom, B. S. Snowden, and P. A. Toldan, *Chem. Commun.*, 50 (1969); (d) C. R. Johnson, *Tetrahedron Lett.*, 1879 (1969); (e) A. B. Foster, J. M. Durbury, T. D. Inch, and J. M. Webber, *Chem. Commun.*, 881 (1967); (f) K. W. Buck, A. B. Foster, W. D. Pardoe, M. H. Qadir, and J. M. Webber, *ibid.*, 759 (1966); (g) J. G. Pritchard and P. C. Lauterbur, *J. Chem. Soc.*, 2105 (1961), and references cited therein.

(11) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Fransico, Calif., 1964, p 51.

(12) R. D. F. Copper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *J. Amer. Chem. Soc.*, **91**, 1408 (1969).

(13) M. Nishio, *Chem. Commun.*, 560 (1969); see also R. S. Edmondson, *Tetrahedron Lett.*, 1649 (1965).

(14) This deshielding of H_3 relative to H_4 is not, however, consistent with assumed acetylenic anisotropy of the S=O bond.[10g] Using an anisotropy constant as -22.6×10^{-30} cm^3 molecule^{-1}, in good agreement with that calculated for an S=O bond in sulfites[10g] and acetylenes,[12] and applying the McConnell point dipole approximation[15] predicts that the signal for H_3 should occur 0.66 ppm upfield from H_4. Such is not the case; the resonance for H_3 is 0.4 ppm *downfield* from H_4. The shift difference of −0.4 ppm is much closer to that which would be expected if the S=O bond anisotropy resembled that of a carbonyl bond and not an acetylenic bone, an assumption for which there is some precedent.[13] However, a more quantitative description of this anisotropy should take into account contributions resulting from the presence of other heteroatoms and bonds in the molecule.

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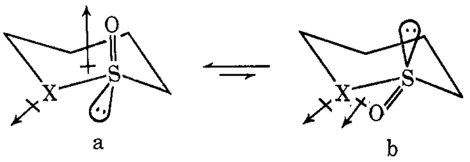
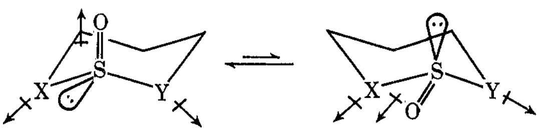
Since the nmr spectra of both **3a** and **4** are unchanged over a wide temperature range (-90 to $+150$°), it may be concluded that both these compounds are conformationally pure. Thus **3** (and presumably **4**) adopt the same axial sulfoxide conformation as do the sulfites. Since only one isomer is observed at room temperature for sulfite **1a**, the oxides of oxathiane **3**, oxathiazine **1b**, and dithiane **4** under conditions where less than 5% of the minor isomer would be detectable, a conformational barrier in excess of 2000 cal exists for these compounds. This is more than 1800 cal greater than the barrier observed for sulfoxide **1c** (X = Y = CH_2).

We suggest that this strong preference for an axial S=O configuration results from a dipolar interaction analogous to the anomeric effect observed in carbohydrate systems.[16] The conformation in which the S=O bond is in an equatorial position possesses an unfavorable dipolar arrangement, since the net dipole resulting from the nonbonded lone-pair electrons of oxygen is nearly parallel to that of the S=O bond. This unfavorable arrangement is relieved with the S=O bond adopting an axial configuration. Such a dipolar effect has been used to explain the conformational preference (500 cal) of the trans-diaxial conformation of *trans*-1,2-dibromocyclohexane over the corresponding diequatorial isomer.[17] For methyl glycosides, the dipolar or anomeric effect is approximately 1.5 kcal;[18] for a highly polar group as a sulfoxide, this effect should be even greater.



3, X = O
4, X = S

A similar argument may be advanced for the conformational preference of an axial S=O bond in sulfite **1a** and the oxathiazine oxide **1b**. Thus, in all of these cases **1a**, **1b**, **3**, and **4**, the sulfoxide bond is adjacent to at least one heteroatom bearing lone-pair electrons and therefore should experience an electrostatic dipole repulsion when the S=O bond is in an equatorial conformation.[19]



1a, X = Y = O
b, X = O; Y = NH

Experimental Section

1,2-Dithiane, 1,1-Dioxide (2).—This compound was prepared as previously described,[20] mp 54–56°.

1,2-Oxathiane 2-Oxide (3).—Substance **3** was formed by desulfurization with tris(diethylamino)phosphine[21] as described in an earlier publication,[20] bp 60–61° (0.5 mm).

1,2-Oxathiane 2,2-Dioxide (5).—To a solution of 100 mg (0.84 mmol) of 1,2-oxathiane 2-oxide (**3**) in 5 ml of water was added an aqueous potassium permanganate solution until the permanganate color persisted. The solution was filtered and acidified with concentrated hydrochloric acid, and the solvent removed under vacuum; the residue was dissolved in ether and dried, and the ether removed under vacuum to provide a clear oil identical in its ir and nmr spectrum with an authentic sample.

1,2-Dithiane 1-Oxide (4).—A solution of 10.0 g (82 mmol) of 1,4-butanedithiol in 200 ml of acetic acid was cooled to 10° and 17 ml (175 mmol) of a 35% hydrogen peroxide solution was slowly added. To maintain solution, 25–40 ml of methylene chloride was added as necessary. After this stirred for 24 hr, the solvent was removed under vacuum, the residue diluted with water, extracted with ether, washed with water, and dried, and the solvent removed under vacuum to afford a viscous oil which on distillation provided a fraction, bp 100–105° (0.1 mm), which crystallized on cooling to yield 0.6 g (5%) of a wax-like material, mp 67–74°. This material could be sublimed *in vacuo* [70–90° (0.1 mm)] to provide pure product, mp 74–76°. This material was homogeneous by vpc analysis, ir (KBr) 1060 cm^{-1} (S=O). The mass spectrum of this material exhibits a parent ion at *m/e* 136.0007 (calcd for $C_4H_8OS_2$, *m/e* 136.0016).

Registry No.—**2**, 18321-15-8; **3**, 24308-29-0; **4**, 7153-76-6; **5**, 1633-83-6.

Acknowledgment.—We wish to thank the National Research Council of Canada for financial support of this work and Professors J. T. Edward and A. S. Perlin for helpful discussions.

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[16] Reference 3, p 375.

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[20] D. N. Harpp, J. G. Gleason, and D. K. Ash, *J. Org. Chem.*, **36**, 322 (1971).

[21] This phosphine has been used to desulfurize a wide variety of organosulfur compounds: see D. N. Harpp, J. G. Gleason, and J. P. Snyder, *J. Amer. Chem. Soc.*, **90**, 4181 (1968); D. N. Harpp and B. A. Orwig, *Tetrahedron Lett.*, 2691 (1970); D. N. Harpp and D. K. Ash, *Chem. Commun.*, 811 (1970).

Formation and Transannular Reactions of Cyclopropane Half-Cage Alcohols[1a]

ROBERT K. HOWE*[1b]

Monsanto Company, Agricultural Division,
Research and Development Department,
St. Louis, Missouri 63166

PETER CARTER AND S. WINSTEIN[1c]

Department of Chemistry, University of California
at Los Angeles, Los Angeles, California 90024

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Dechlorination of hexachloro half-cage alcohol **1** with lithium and *tert*-butyl alcohol in tetrahydrofuran[2] gave a solid alcohol mixture that consisted of 55% of the known[2,3] half-cage alcohol **2** and 45% of a new alcohol, cyclopropane half-cage alcohol **3**. In the nmr spec-

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[1] (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967. (b) Address inquiries to this author. (c) Deceased Nov 23, 1969.

[2] P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (*London*), 405 (1960).

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