Vicinal Electron Pairs and Conformation in Six-membered Rings. Some Evidence from the 1,3,2-Dioxathianes

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Barriers to ring reversal ($\Delta G^{\ddagger}$) at the n.m.r. coalescence temperature are reported for a series of 1,3,2-dioxathianes. The value for 1,3,2-dioxathiane-4,4,6,6-d_4 of 11.2 kcal/mol is compared with the corresponding values for cyclohexane and various six-membered rings with and without vicinal electron pairs. The 1,3,2-dioxathiane system is suggested as a model for trimethylene sulfites, where the strong preference of the exocyclic oxygen for the axial position interferes with barrier determination by n.m.r. techniques.

Les barrières d'inversion de cycle ($\Delta G^{\ddagger}$) à la température de coalescence r.m.n. sont rapportées pour une série de dioxathianes-1,3,2. La valeur obtenue, 11.2 kcal/mol pour le dioxathiane-1,3,2 d_4-4,4,6,6 est comparée avec les valeurs correspondantes pour le cyclohexane et divers systèmes cycliques à six membres avec ou sans paire d'électrons vicinale. Le système dioxathiane-1,3,2 est proposé comme modèle pour les sulfites de triméthylene, où la préférence marquée de l'oxygène exocyclique pour la position axiale gêne la détermination de la barrière par la technique du r.m.n. [Traduit par le journal]

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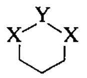
Introduction

There is now substantial evidence that the conformational properties of six-membered rings with two or more adjacent heteroatoms in the ring are significantly different from those of cyclohexane (1–3). This result is usually attributed to the presence of vicinal electron pairs which appear to increase the barrier to rotation about the connecting bond and at the same time displace, or even reverse (ref. 1*b*, p. 1205), the potential energy minima and maxima associated with rotation. Similar deviations exist in acyclic molecules (4) when ethane is considered the reference substance and their importance in six-membered ring behavior is a direct result of the importance of torsional barriers in determining conformational properties of rings.[1]

The work of Bushweller and co-workers (3) on the *s*-tetrathianes constitutes the most thorough study of this phenomenon to date. In addition to the expected high barriers to ring reversal, these workers have found changes in conformational energies dramatic enough to give rise to non-chair ground states and high barriers to pseudo-rotation between non-chair states.

Compounds with three adjacent oxygen and/or sulfur atoms (**1**–**4**) might be expected to demonstrate similar interesting properties. Experimental work on systems of this type has been limited so far to a determination of the ring reversal barrier of **1** and its 5,5-dimethyl derivative for which $\Delta G^{\ddagger}$ = 13.2 and 14.7 kcal/mol, respectively (7), in addition to rather extensive data collection on trimethylene sulfites (**2**) by such diverse techniques as dipole moments (1*b*, 8, 9), i.r. (9*a*, 10), n.m.r. (1*a*, 2, 10, 11), osmometry (12), and ultrasonic absorption (13). Although all of the data point to some novel conformational properties, uncertainties in interpretation of the more derivative forms of data, especially from ultrasonic absorption (14, 15) and the present lack of a trimethylene sulfite suitably substituted for direct measurement of chair ⇄ chair ring reversal by the n.m.r. technique have thus far prevented the emergence of a generally accepted conformational description for this molecule.



1 $\mathrm{X = S;\ Y = S}$
2 $\mathrm{X = O;\ Y = S{=}O}$
3 $\mathrm{X = O;\ Y = S}$
4 $\mathrm{X = O;\ Y = S\begin{smallmatrix}=O\\ =O\end{smallmatrix}}$

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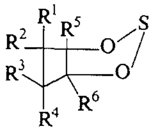
[1] This relationship is generally accepted (5, 6). However, successful application of this principle to estimate ring reversal barriers requires careful choice of acyclic models, as we will show.

This paper expands on our initial communication (16) of the magnitude of the barrier of ring reversal for some 1,3,2-dioxathianes (**3**). This system presents some synthetic difficulty, but its symmetry makes it ideal for n.m.r. study and its close structural resemblance to trimethylene sulfite confers on it some value as a model for the latter. Also, in this connection, **4** represents a closely related structure, the 5,5-dimethyl derivative of which has $\Delta G^{\ddagger} = 8.3$ kcal/mol (17). This result is in conformity with the fact that the ground state of this molecule has its energy increased by the location of a polar bond along the bisector of two electron pairs (4).

Results and Discussion

We here report the synthesis and low temperature n.m.r. data for several 1,3,2-dioxathianes, including the barrier to ring reversal for 1,3,2-dioxathiane-4,4,6,6-d_4, (**3***b*), which probably provides the most reliable value for comparison with cyclohexane and other six-membered ring compounds.



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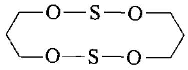
a —
b $R^1, R^2, R^5, R^6 = D$
c $R^3, R^4 = CH_3$
d $R^1, R^6 = CH_3$
e $R^1, R^6 = CH_3; R^2, R^3, R^4, R^5, = D$
f $R^2, R^6 = CH_3$
g $R^2, R^6 = CH_3; R^1, R^3, R^4, R^5 = D$

All unspecified R groups = H

Synthesis and Spectra of 1,3,2-Dioxathianes

The compound **3***a* was synthesized from 1,3-propanediol and sulfur dichloride according to the method of Thompson (18). The isolated liquid showed two peaks which could be separated readily by preparative g.l.c. The peak with lower retention time was found to be **3***a*. The retention time of the other liquid was identical to that for authentic trimethylene sulfite.

The i.r. spectrum of **3***a* showed no hydroxyl absorption. The ^1H n.m.r. spectrum at room temperature consisted of a triplet at δ 4.38 and a quintet at 1.98. Had the compound possessed a macrocyclic structure such as **5**, the same n.m.r. spectrum would have been observed. The



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mass spectrum showed a peak at *m/e* 106 which was assigned to the molecular ion. No peak at *m/e* 212 or higher was evident, nor was there any evidence of sulfite contamination (*m/e* 122).

In the low temperature n.m.r. experiment, the quintet at δ 1.98 broadened until at −70° two separate signals were obtained: δ 2.0–3.0 (multiplet) and 1.6 (broad doublet). These signals were assigned to axial and equatorial protons respectively. The C-5 proton signals sharpened at −85° and remained unchanged on further cooling. At −80° the doublet at δ 1.6 became a doublet of triplets ($J \simeq 2$ Hz).

These changes in the spectrum were shown to be reversible, and the coalescence temperature obtained was used to estimate the rate constant, k_c, for interconversion of the conformers from the equation

$$k_c = \Pi / \sqrt{2}\,\sqrt{(\nu_A - \nu_B)^2 + 6J_{AB}{}^2}$$

which reduces to

$$k_c = \Pi / \sqrt{2}(\nu_A - \nu_B)$$

when the signals are not coupled.[2] The value of $\Delta G^{\ddagger}$ was obtained from the Eyring equation,

$$k_c = k(K_B T/h)e^{-\Delta G^{\ddagger}/RT}$$

taking the transmission coefficient as unity. Both k_c and $\Delta G^{\ddagger}$ for the molecules studied are presented in Table 1.

The above procedure was repeated for 1,3,2-dioxathiane-4,4,6,6-d_4 (**3***b*) synthesized from labelled 1,3-propanediol and di-1-imidazolyl sulfide. The coalescence phenomenon of the simple AB spectrum provided a further check on the ring reversal barrier in this ring system and we consider the latter result of $\Delta G^{\ddagger} = 11.2$ kcal/mol at −42° to be the most reliable measure of ring reversal in 1,3,2-dioxathianes.

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[2] A recent comparative study of n.m.r. methods of determining free energies of activation has indicated the conditions under which this approximate method gives satisfactory results (19).

The 4,6-dimethyl derivatives were synthesized from 2,4-pentanediol (mixed isomers). G.l.c. of the product showed the presence of small amounts of all three 4,6-dimethyltrimethylene sulfites as well as racemic (**3***d*) and meso (**3***f*) 4,6-dimethyl-1,3,2-dioxathiane in a 56:44 ratio. I.r. and n.m.r. spectra for **3***f* were consistent with the assigned structure and the mass spectrum showed a peak at *m/e* 134 corresponding to the molecular ion. Proton n.m.r. spectra recorded in 1:1 CD_2Cl_2:C_2D_5Br showed no temperature dependence between +25 and −100°, a fact consistent with its expected adoption of a single chair conformation with both methyl groups equatorial.

Compound **3***d* produced a peak at *m/e* 134 which was assigned to the molecular ion. A small peak at *m/e* 150 was presumably due to contamination from a related sulfite. The ^{1}H n.m.r. spectrum consisted of a multiplet at δ 4.60, a triplet at 1.80, and a doublet at 1.43, in agreement with a fast equilibrium between conformations. On cooling, the spectrum underwent the expected broadening with two methyl doublets appearing at −90°. Below −100° these doublets are sharp and no further change occurred to −110°. The coalescence temperature for these signals was estimated to be −83° which gives $\Delta G^{\neq} = 9.4$ kcal/mol. The methylene and methine protons in this compound did not give definable coalescence. As a further check on the ring reversal barrier in racemic-4,6-dimethyl-1,3,2-dioxathiane, the labelled derivative **3***e* was found to give $\Delta G^{\neq} = 9.75$ kcal/mol based on coalescence of the methyl signal (δ 1.40) at −79.[3]

Interpretation of Nuclear Magnetic Resonance Results and Comparison with Related Systems

The barriers determined in the present work are presented in Fig. 1 along with a variety of other determinations on related molecules.[4] The 1,3,2-dioxathiane barriers, like those for other six-membered ring systems with vicinal electron pairs, are generally higher than the comparable cyclohexane or 1,3-dioxane structure. Generally, the substitution of oxygen for sulfur in the ring appears to lower the barrier (tetramethyldithiane and -dioxane are exceptions). Removal of the vicinal electron pair interaction in 1,3,2-dioxathiane by conversion to trimethylene sulfate lowers the barrier to a value comparable to the similarly substituted 2,2,5,5-tetramethyl-1,3-dioxane.

If the analysis presented here has any relevance for the case of trimethylene sulfite barriers which are not amenable to direct n.m.r. measurement, then these compounds should have ring reversal barriers near those for the 1,3,2-dioxathianes and certainly higher than the trimethylene sulfates. It is unfortunate that the ultrasonic absorption method which appears to detect a barrier to conformational change in the trimethylene sulfite system (13, 21) gives no evidence as to the structure of either the low energy or high energy state which the barrier separates.[5] Clarification of the nature of the ultrasonic process must await comparative n.m.r. and ultrasonic data on representatives of each of the ring systems under discussion. In the meantime, it should be noted that although no experimental value exists for S—O bond rotation, the ring reversal barrier for 1,3,2-dioxathiane is consistent with a high rotation barrier, as has been found for related bond types.[6]

The effect of exocyclic oxygen in the axial position on a trimethylene sulfite in the chair form has often been discussed in terms of interaction with the axial substituents on C-4 and -6. Values of n.m.r. shifts for several 1,3,2-dioxathianes which lack this exocyclic oxygen make it possible to check for evidence of this interaction. When allowance is made for the averaging of n.m.r. signals caused by conformational interconversion in the 1,3,2-dioxathianes,

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[3] In spite of strenuous effort, complete purification of this compound was not achieved. Persistent n.m.r. signals appeared at δ 1.70, 1.50, and 1.18 p.p.m.

[4] These comparisons are presented in the format used by Kabuss and co-workers. References 20*a* and *c* contain additional data on six-membered ring reversal barriers.

[5] The difficulty with the low energy state is generally recognized (15) and in favorable cases this structure can be assigned from spectral data. The high energy state presents a much more formidable problem. Attempts to assign this structure and to attribute the measured barrier must of necessity rest on analogy with model compounds. In the case of trimethylene sulfites, lack of appreciation of the importance of vicinal electron pair effects led to inappropriate choice of acyclic models (13, 21) for estimation of the contribution of torsional barriers to the ring inversion barrier (1).

[6] Recent work has established a minimum value for S—S at 7.0 kcal/mol (22).

TABLE 1. Barriers to ring reversal for 1,3,2-dioxathianes

Compound 3	T_c(°C)*	$\Delta\nu_{AB'}$ (Hz)	J_{AB} (Hz)	K_c (s^{-1})	$\Delta G^{\ddagger}$∥ (kcal/mol)
a†	−38	56.1	15.1	147.5	11.3
b‡	−42	53.1	15.5	126.7	11.2
c†	−20	29.3	—	65.0	12.6
	−26	8.7	10.7	61.5	12.3
d§	−83	19.3	7.0	57.3	9.4
e§	−79	18.2	—	40.4	9.8

*Error in temperature measurement is ±2°.
†Measured in CD_2Cl_2 solution.
‡Measured in $CDCl_3$ solution.
§Measured in solution of CD_2Cl_2:C_2D_5Br (1:1).
∥Error estimated to be ±0.2 kcal/mol. Uncertainty in temperature is the major source of error (see ref. 19).

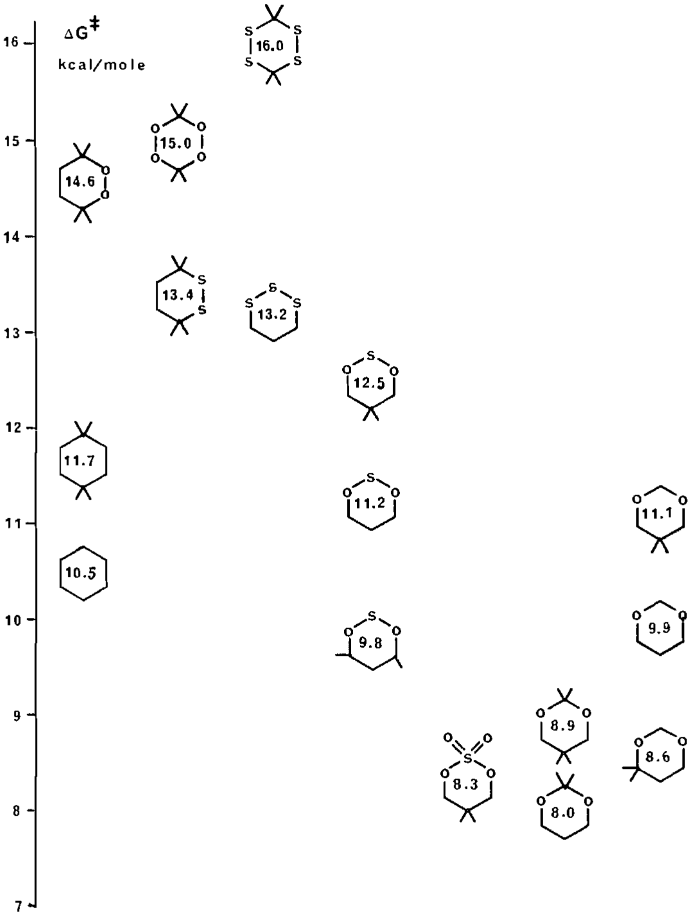

FIG. 1. Barriers to ring reversal ($\Delta G^{\ddagger}$ at T_c) for 1,3,2-dioxathianes and other six-membered rings.

most of the shifts observed for these compounds are within 0.1 p.p.m. of the value for the corresponding trimethylene sulfite (ref. 1*a*, p. 522). The most clear-cut exception arises from the meso-4,6-dimethyl-1,3,2-dioxathiane which, like its sulfite analog, is assumed to be fixed in the chair conformation with methyl groups equatorial. The axial 4,6-protons in the former appear at δ 4.25 p.p.m. which is 0.7 p.p.m. upfield from the corresponding proton in the trimethylene sulfite. This puts a quantitative estimate on the magnitude of S=O axial deshielding.

With the latter effect removed, the difference in chemical shift between axial and equatorial protons at C-4 and -6 in the dioxathianes (estimated from low temperature spectra) becomes smaller than typical cyclohexane values of 0.3–0.5 p.p.m. (*e.g.* $\Delta\nu$ = 8.7 Hz for **3***c*, Table 1), but it is not possible from the present data to determine which proton appears at higher field.

The protons at C-5 generally show the same shifts as the corresponding sulfites. The axial proton of the parent compounds (δ 2.5 p.p.m.) is almost 1 p.p.m. toward lower field than the equatorial one, a phenomenon common to 1,3-dioxanes and other compounds with oxygens at positions 1 and 3.

Throughout this paper possible non-chair forms of 1,3,2-dioxathianes have been ignored. The data discussed here appear to be consistent with this assumption, but the evidence is in no sense compelling. The presence of vicinal electron pairs should at least reduce the energy of non-chair forms relative to cyclohexane, for reasons previously discussed (1*b*).

Summary and Conclusions

The synthesis and n.m.r. study of a series of 1,3,2-dioxathianes has extended the available data on six-membered ring compounds with vicinal electron pairs. In conformity with previous findings for systems of this general type, ring reversal barriers are found to be higher than for similar compounds lacking vicinal electron pairs. The results support the general conclusion that electron pairs on adjacent atoms in a ring increase the barrier to rotation about the bond joining them, and in this way increase the barrier to ring reversal.

When the considerable evidence now available to reinforce this generalization is applied to the relatively intractable trimethylene sulfite problem, it becomes apparent that the latter compounds must be in some sense anomalous. Perhaps the chair ⇄ chair interconversion in these molecules occurs across a barrier very much lower than that measured for any other similar ring (to accomodate one interpretation of ultrasonic absorption results). Alternately, the chair ⇄ chair interconversion may have a barrier which is comparable to that for structurally similar molecules, but which is not amenable to n.m.r. measurement because the sulfite ring system is strongly biased toward one chair form. Weighing these possibilities against each other, we find that uncertainties in conformational assignments for the higher energy state in ultrasonic absorption studies remove the necessity for the former interpretation. The latter situation appears to us particularly likely since it can readily incorporate the ultrasonic results on the basis of chair ⇄ non-chair interconversions.

Experimental

Elemental analyses were obtained from Midwest Microlab, Ltd., Indianapolis, Indiana.

Proton n.m.r. spectra were measured on a JEOL C60HL spectrometer using TMS as internal reference.

Mass spectra were taken by Dr. Larry Dusold, Chemistry Department, Wayne State University, Detroit, on an AEI MS902B spectrometer.

G.l.c. analyses were made with an F & M Model 720 instrument using columns packed with 10% diethyleneglycol succinate (LAC728) on chromosorb W and at a flow rate of carrier gas (helium) of 60 ml/min. Analytical work was done on a 1/4 in. × 5 1/2 ft column (70–90°) and collections on a 3/4 in. × 8 ft column (135°). Dioxathianes were prepared essentially by the method of Thompson (18). For the preparation of 4,6-dimethyl-1,3,2-dioxathianes, the reaction was carried out under a nitrogen atmosphere to reduce the formation of sulfites. The deuterated parent compound, **3***b* was prepared in better yield by substituting di-1-imidazolyl sulfide for sulfur dichloride.

1,3,2-Dioxathiane (3a)

From 38.0 g (0.5 mol) of 1,3-propanediol and 51.5 g (0.5 mol) of sulfur dichloride there was obtained an oil which after distillation afforded 4.5 g of light yellow liquid, b.p. 38–48° at 12–13 mm. G.l.c. of this liquid showed two peaks. The component of lower retention time was identified as 1,3,2-dioxathiane by spectral means although the index of refraction, $n_D^{25.5}$ 1.4750, differed from the reported value, n_D^{23} 1.4948 (18).

The i.r. spectrum of the pure liquid showed no hydroxyl absorption. The n.m.r. spectrum in CD_2Cl_2 consisted of a triplet at δ 4.38 p.p.m. (J = 5.0 Hz) and a quintet at 1.98 p.p.m. (J = 5.0 Hz). The low temperature n.m.r. results have been described. A peak at m/e 106 in the mass spectrum was assigned to the molecular ion.

Authentic trimethylene sulfite possessed the same retention time as the second product from the reaction.

1,1,3,3-Tetradeuterio-1,3-propanediol (23)

A solution of 5.0 g of $LiAlD_4$ in 200 ml of anhydrous tetrahydrofuran was placed under a nitrogen atmosphere in a 500 ml three-necked flask equipped with a reflux condenser, dropping funnel, and magnetic stirrer. Dimethyl malonate (13.2 g) diluted to 25 ml with anhydrous tetrahydrofuran was introduced with stirring at a rate sufficient to maintain gentle reflux. The mixture was then heated and stirred under reflux for 20 h. Decomposition was accomplished by the careful addition of water (50 ml), 15% NaOH (5.0 ml), and water (150 ml). The mixture was filtered and the precipitate washed with six 50-ml portions of boiling tetrahydrofuran. Evaporation of solvent from the dried ($MgSO_4$) filtrate and washings yielded 4.4 g of a clear, light yellow oil.

I.r. analysis showed the usual hydroxyl absorption as well as C—D stretching at 2100 and 2200 cm^{-1}. A singlet at 1.7 p.p.m. in the n.m.r. spectrum was assigned to C-2 protons and the hydroxyl protons appeared at 3.89 p.p.m.

Di-1-imidazolyl Sulfide

Following the procedure of Walter and Radke (24), 36.0 g of imidazole was reacted with sulfur dichloride (13.5 g) to yield 16.2 g of product, m.p. 78–83° (lit. (24) m.p. 80–85°).

4,4,6,6-Tetradeuterio-1,3,2-dioxathiane

Under a nitrogen atmosphere 8.58 g of di-1-imidazolyl sulfide was dissolved in 250 ml of anhydrous tetrahydrofuran in a 500 ml three-necked flask equipped with an addition funnel and a magnetic stirrer. 1,1,3,3-Tetradeuterio-1,3-propanediol (4.35 g diluted to 15 ml with anhydrous tetrahydrofuran) was introduced rapidly with stirring. After 15 min of stirring, the tetrahydrofuran was removed on the rotary evaporator and the residue vacuum distilled. The product was contained in a fraction (2.24 g) with b.p. 29–33°/0.25 mm.

The peak of lower retention time on preparative g.l.c. (17% of total) was found to be the desired product (3*b*). The other major peak (83%) had a retention time corresponding to trimethylene sulfite.

5,5-Dimethyl-1,3,2-dioxathiane (3c)

Reaction of 52 g (0.5 mol) of 2,2-dimethyl-1,3-propanediol with sulfur dichloride gave a brown liquid which was separated by distillation into two fractions: (*i*) 1.65 g, b.p. 26–30°/2.0–2.2 mm and (*ii*). 14.7 g, b.p. 31–40°/1.2 mm. In addition to the desired product, these fractions contained 12 and 37%, respectively, of 5,5-dimethyltrimethylene sulfite.

Spectral results for this compound (3*c*) have been reported (16).

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H, 7.51; S, 23.89. Found: C, 45.0; H, 7.6; S, 23.6.

4,6-Dimethyl-1,3,2-dioxathianes (3d and f)

Sulfur dichloride (26.0 g, 0.25 mol) was reacted with 2,4-pentanediol (26.0 g, 0.25 mol, mixed isomers) under nitrogen to yield a crude oil. Distillation gave two fractions: (*i*) 13.8 g, b.p. 67–74°/13 mm and (*ii*). 4.23 g, b.p. 67–70°/1.25 mm. G.l.c. of fraction *i* showed five peaks, of which the two major peaks had the lowest retention times and n.m.r. spectra corresponding to the desired products.

The *trans*-4,6-dimethyl compound (3*d*) showed a multiplet at δ 4.60 p.p.m., a triplet at 1.8 p.p.m. (J = 5.3 Hz), and a doublet at 1.43 p.p.m. (J = 6.8 Hz).

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H, 7.51; S, 23.89. Found: C, 44.7; H, 7.5; S, 23.9.

The *cis*-compound (3*f*) showed a multiplet at δ 4.25 p.p.m., a five-line signal at 1.5–1.83 p.p.m., and a doublet at 1.33 p.p.m. (J = 6 Hz) in $CDCl_3$ solution.

Anal. Found: C, 44.5; H, 7.6; S, 23.8.

2,3,3,4-Tetradeuterio-2,4-pentanediol

The procedure of Pritchard and Vollmer for synthesis of 2,4-pentanediol (25) was adapted to make the tetradeuterio derivative. Sodium borodeuteride (5.0 g, 0.12 mol) was added to a three-necked 300 ml flask containing 50 ml of D_2O and 0.3 ml of a 40% solution of NaOD in D_2O. The reaction flask was cooled to 10° and 20.0 g (0.20 mol) of 2,4-pentanedione in 60 g of CH_3OD was added during 2 h while the temperature was maintained at 10–15°. Following an additional 2 h of stirring at room temperature, the solvent was removed under vacuum and glycerine (100 ml) was added. Fractional distillation yielded 18.2 g (84.3%) of a colorless liquid, b.p. 50–55°/0.1 mm; n_D^{25} 1.4314.

4,5,5,6-Tetradeuterio-4,6-dimethyl-1,3,2-dioxathianes (3e and g)

The procedure described for 3*d* and *f* was followed using tetradeuteriodiol, and preparative g.l.c. which provided the dioxathianes as before. The peak of lowest retention time showed an n.m.r. singlet (δ 1.32 p.p.m.) which was unchanged on cooling to −100° and this compound was therefore assigned the *cis*-structure (3*g*). The second g.l.c. peak also had as the most prominent feature of its n.m.r. spectrum a singlet (δ 1.40 p.p.m.), but cooling caused a broadening of the signal and separation into two singlets (δ 1.25, 1.55 p.p.m.) at −100°. This compound was assigned the *trans*-structure (3*e*). Weak signals at δ 1.2, 1.5, and 1.7 p.p.m. were also present and are probably due to contamination from the corresponding sulfites, which are also represented by the three smaller peaks of higher retention time in the crude product as before.

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