

TABLE II. EFFECT OF *o*-DINITROBENZENE ON THE RATE OF SEVERAL ETHERIFICATION REACTIONS

<i>o</i> -C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> ) <sub>2</sub> , moles	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H, moles	<i>k</i> , min. <sup>-1</sup> × 10 <sup>-4</sup>
Benzhydrol Self-Etherification		
0.000	0.001	101
0.0625	0.001	123
0.125	0.001	151
0.250	0.001	196
0.000	0.0015 <sup>a</sup>	155
0.125	0.0015 <sup>a</sup>	198
Anisyl Alcohol Self-Etherification		
0.000	0.002	192
0.125	0.002	256
Fluorenol Self-Etherification <sup>b</sup>		
0.000	0.016	130
0.125	0.016	161
Etherification of <i>n</i> -Butyl Alcohol by Triphenylcarbinol		
0.000	0.001	146
0.125	0.001	250

<sup>a</sup> Methanesulfonic acid replaced the *p*-toluenesulfonic acid.

<sup>b</sup> Total yield of water was 110–115% indicating that some alkylation of the benzene solvent occurred.

of the dipole moment of the added compounds,<sup>7–9</sup> on their effectiveness as electron acceptors in the formation of charge transfer complexes,<sup>10–12</sup> or on their ability to act as polyfunctional catalysts<sup>13</sup> met with only very limited success.

### Experimental Section

**Starting Materials.**—All constituents of the reaction mixtures were carefully purified by standard methods until their refractive indices or melting points agreed closely with the literature data except for diphenyl sulfone. Repeated recrystallization of it gave a product which melted at 124.5–125.5°, although the literature lists values as high as 128–129°.

**Experiments of Table I.**—The standard procedure employed for all the experiments of Table I was in all significant respects identical with that previously described<sup>6</sup> except the benzene solution of the benzhydrol and the compound being studied was adjusted to 990 ml. instead of 1000 ml. A volumetric flask recalibrated at 990 ml. was used for this and, after refluxing the solution 1 hr., 10 ml. of a 0.1 *M* solution of *p*-toluenesulfonic acid in benzene was added. This standard solution of acid was prepared by refluxing 0.1 mole of *p*-toluenesulfonic acid monohydrate in 995 ml. of benzene, in a flask fitted with a water separator, for 3 hr. during which the water of hydration was evolved and the acid was dissolved. Extreme care was taken during the storage and addition of this solution (from a 25-ml. buret) to keep it anhydrous. Adding the catalyst in this way circumvented difficulties encountered in accurately weighing small amounts of the very hygroscopic solid catalyst.

In the previously described procedure<sup>6</sup> it was necessary to insert a looped Chromel wire through the top of the condenser to displace any water droplets from its interior before each reading of the volume of water. This was found to be unnecessary if the condenser and water trap were scrubbed thoroughly first with detergent, then with scouring powder, and finally with both and then rinsed carefully.<sup>14</sup> This was done within 2 hr. of the time

they were to be used and during this period the apertures were closed with aluminum foil so that the inner surfaces remained wet.

All precautions of the earlier study<sup>6</sup> were taken. The benzhydrol used was recrystallized in a single batch. Five separate determinations of the rate constant for the control over a period of several months gave a value of 101.2 ± 1.1 min.<sup>-1</sup> × 10<sup>-4</sup>. Numerous repeat experiments showed the values in Table I were reproducible to within 2.3%. The temperature variation over the 20–80% portion of a given experiment was within ±0.1° in all but three cases. Among all the experiments the temperature was usually 82.1 ± 0.3° and almost invariably 82.1 ± 0.5°. The total yield of water was usually 100 ± 1%; in all except three cases for which it was 103% and one case (*m*-dimethoxybenzene) for which it was 110%, the yield of water was 100 ± 2%.

It was noted that the addition of benzhydrol to a solution of tetracyanoethylene in benzene deepens the color from lemon yellow to orange. The total yield of water in the tetracyanoethylene experiment (Table I) was 102% and at the end of the experiment the tetracyanoethylene was recovered in over 80% yield.

In most cases the plot of log  $a/(a-x)$  vs.  $t$  gave a straight line for approximately the 20–80% portion of the reaction. The slope of this line was multiplied by 2.303 to give the value of  $k$ .

**Supplementary Experiments.**—The modifications of the above standard procedure required for the experiments of Table II are readily apparent with the following exceptions.

In the experiments with fluorenol the catalyst was added as the solid. In spite of the excessive yields of water a straight line was obtained for the 10–70% portion of the reaction.

In the etherification of *n*-butyl alcohol by triphenylcarbinol 0.125 mole of each of the alcohols was used.

The catalyst (0.001 mole) was also added as a solid in the experiments using cyclohexane in place of benzene as the solvent. In these experiments the kinetics shifted toward zero order and the reproducibility of the rates was poor. For the fastest of three controls the time required for the evolution of a 50% yield of water was 101 min., while with 0.05 mole of *s*-trinitrobenzene present the time was only 49 min. Only 0.05 mole instead of the standard 0.125 mole of *s*-trinitrobenzene was added to 1 l. of reaction mixture because of the limited solubility of the nitro compound in cyclohexane. The cyclohexane was purified by washing it with concentrated sulfuric acid and then with water and distilling it as for benzene. The temperature for the experiments in cyclohexane was 82.2 ± 0.2° and the total yield of water was 100%.

## Temperature Dependence of the Conformational Equilibria of Cyclic Sulfites

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*Received June 24, 1965*

Hellier, *et al.*,<sup>1</sup> suggested that the S=O group in six-membered cyclic sulfites is more stable in the axial rather than the equatorial conformation. They have identified the 1190-cm.<sup>-1</sup> band with an axial S=O and the 1230-cm.<sup>-1</sup> band with an equatorial S=O. Two geometric isomers of *meso*-2,4-pentanediol cyclic sulfite were isolated by Pritchard, *et al.*<sup>2,3</sup> The more stable one, isomer I, had the S=O band at *ca.* 1190 cm.<sup>-1</sup>, and the less stable one, isomer II, had the main S=O absorption at 1230 cm.<sup>-1</sup>. Thermal equilibration of the isomers yields mainly I. Pritchard, *et al.*,<sup>3</sup>

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

(2) J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

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

(7) "Dipole Moments," Appendix, compiled by N. U. Sidgwick, published for the Faraday Society, Gurney and Jackson, London, 1940.

(8) C. J. LeFevre and R. J. LeFevre, *J. Chem. Soc.*, 957 (1935).

(9) G. Briegleb and J. Kambeitz, *Z. Physik. Chem. (Frankfurt)*, **B25**, 253 (1934).

(10) R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

(11) L. J. Andrews, *Chem. Rev.*, **54**, 713 (1954).

(12) W. Brackmann, *Rec. trav. chim.*, **68**, 147 (1949).

(13) C. G. Swain and J. F. Brown, *J. Am. Chem. Soc.*, **74**, 2538 (1952).

(14) E. F. Pratt and J. F. Van de Castle, *J. Org. Chem.*, **26**, 2973 (1961).

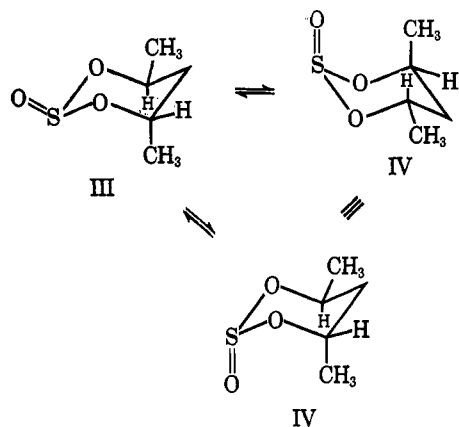


Figure 1.—Identity of sulfite pyramid inversion and chair interconversion for racemic 2,4-pentanediol cyclic sulfite.

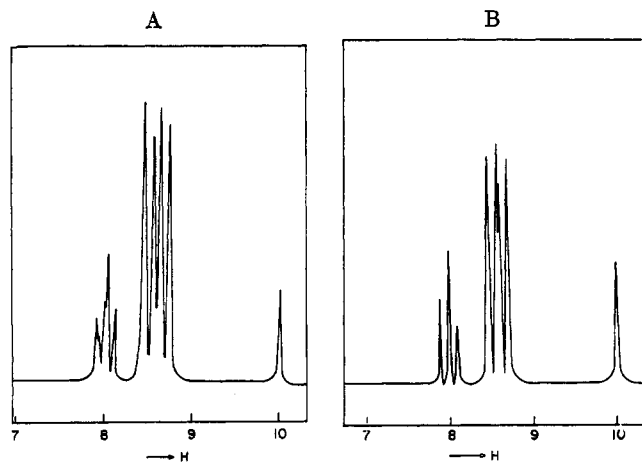


Figure 2.—Methyl and methylene protons resonance for racemic 2,4-pentanediol cyclic sulfite: (A) at 27°, (B) at 190°.

converted II almost completely into I by heating it at 200° for 15 min. Our attempts to convert I into II, by heating I for 12 hr. at 160° or 1 hr. at 200°, could not reveal the presence of even less than 1% of II (*via* n.m.r.). Longer heating periods at 200° resulted in partial decomposition of I to olefinic products. These results indicate that for the conversion  $I \rightleftharpoons II$ ,  $\Delta F > 4.4$  kcal./mole.<sup>4</sup> Since the *cis*-2,4-dimethyl groups must be stable in the equatorial conformation, Hellier's suggestions imply that isomer I is Me(e) Me(e) S=O(a) and isomer II is Me(e) Me(e) S=O(e).

The difference in free energy between the two pyramidal orientations of the cyclic sulfite of racemic 2,4-pentanediol, *viz.* Me(e) Me(a) S=O(e) (III) and Me(a) Me(e) S=O(a) (IV), could be expected to be smaller than for the two configurations of the *meso* compound, because the Me(a) S=O(a) repulsion may partly obliterate stabilization of the S=O group in the axial conformation. A mixture of both orientations may be expected at room temperature or higher. Equilibration between III and IV can be achieved either by isomerization (sulfite pyramidal inversion) or by conformational equilibration (chair-chair interconversion), which in this case lead to identical products (see Figure 1). A similar situation exists for the cyclic sulfite of 2,2-dimethyl-1,3-propanediol.

(4) Cf. H. B. Henbest and S. A. Kahn, *Proc. Chem. Soc.*, 56 (1964).

Heating 2,2-dimethyl-1,3-propanediol cyclic sulfite from room temperature to 190° did not reveal a noticeable change in the chemical shifts of the two methyl groups (singlets at  $\tau$  8.79 and 9.21) one *cis* and one *trans* to the S=O group. However, when the n.m.r. spectrum of racemic 2,4-pentanediol cyclic sulfite was followed as a function of temperature, a reversible change in the chemical shifts of the two methyls could be observed (Figure 2). The two methyl peaks approached each other gradually at elevated temperatures (two doublets centered at  $\tau$  8.53 and 8.66 at 190°) and separated back reversibly at low temperatures (two doublets centered at  $\tau$  8.52 and 8.70 at 27°). The chemical shifts must be time averages of the different conformations involved, therefore indicating the presence of either ring interconversion, such as in cyclohexane,<sup>5</sup> or sulfite pyramidal inversion, such as aziridines.<sup>6</sup> In analogy with these cases it is clear that the two methyls with increasing temperature secede from a nonequivalent magnetic environment to a more similar environment. The temperature range studied was enough to indicate this trend but not to define its limits such as to allow quantitative calculations.<sup>5-7</sup> A change from an equatorial to an axial S=O increases the relative difference in distance between each methyl and the oxygen atom. If we assume the difference in magnetic environment between the two methyls also increases with this change, the n.m.r. data probably indicate a conversion from Me(a) Me(e) S=O(a) (IV) to Me(e) Me(a) S=O(e) (III) with rising temperature. It is noteworthy that the multiplet centered at *ca.*  $\tau$  8, corresponding to the methylene protons, converges into a sharp triplet at 190°. This could also be an indication for conformational interconversion.

The infrared spectrum of the compound, dissolved in perchloroethylene or in the liquid state, revealed (among others) a strong peak at 1190 and a weak shoulder at 1230  $\text{cm}^{-1}$  at room temperature.<sup>8</sup> By increasing the temperature slowly to 120° the first peak diminished considerably ( $\sim 10\%$ ) while the second remained unchanged, which can point to an increase in the relative amount of the conformation that absorbs at 1230  $\text{cm}^{-1}$ .<sup>1,2</sup> In agreement with the assignments of Hellier, *et al.*,<sup>1</sup> the infrared changes indicate that the equatorial conformation of the S=O group increases in proportion with rising temperature.<sup>9</sup>

These results suggest a conformational mixture at room temperature in which the conformation with the axial S=O (IV) predominates, the amount of the conformer with the equatorial S=O (III) increasing with temperature.

Recently, Edmundson<sup>10</sup> concluded from n.m.r. data of 2,2-dimethyl-1,3-propanediol cyclic sulfite that the S=O group of this also exists in the axial position.

**Acknowledgment.**—The authors are indebted to Mr. H. Talts for the n.m.r. and infrared determinations.

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(7) E. W. Garbisch, *ibid.*, **86**, 1780 (1964).

(8) Resolution was better in solution rather than in the liquid state; Cf. ref. 3.

(9) Cf. K. Kozima and Y. Yamanouchi, *ibid.*, **81**, 4159 (1959).

(10) R. S. Edmundson, *Tetrahedron Letters*, 1649 (1965).