# Chemistry of the S=O Bond. Part 6.[1] Infrared and Raman Spectra of Some Methyl-substituted Trimethylene Sulphites

By **Desmond G. Hellier** * and **Frederick J. Webb**, Department of Chemistry, Westfield College, University of London, London NW3 7ST

The i.r. and Raman spectra of twenty-five methyl-substituted trimethylene sulphites (1,3,2-dioxathian 2-oxides) have been examined in the 1 400—250 cm$^{-1}$ region. A number of bands have been assigned and appear to be characteristic of alkyl 1,3,2-dioxathians.

SIX-MEMBERED cyclic sulphites may have either a rigid chair conformation with an axial or equatorial S=O group or exist in equilibrium with non-chair (twist) forms. Previous investigations of the i.r. spectra of trimethylene sulphite and substituted trimethylene sulphites have concentrated on the stretching vibration, $\nu_{S=O}$, of the S=O bond.[2-4] A very strong absorption at *ca.* 1 190 cm$^{-1}$ is characteristic of a sulphite with an axial S=O group whereas a strong absorption at *ca.* 1 230 cm$^{-1}$ indicates an equatorial S=O group. Twist conformations apparently give intermediate values.[5-7]

We have examined the i.r. and Raman spectra (1 400—250 cm$^{-1}$) of some methyltrimethylene sulphites to obtain the principal vibrations in the alkyl-1,3,2-dioxa-

---

[1] Part 5, G. W. Buchanan and D. G. Hellier, *Canad. J. Chem.*, 1976, **54**, 1428.

[2] D. G. Hellier, J. G. Tillet, R. F. M. White, and H. F. van Woerden, *Chem. and Ind.*, 1963, 1956.

[3] E. Havinga and H. F. van Woerden, *Rec. Trav. chim.*, 1967, **86**, 341, 353.

[4] C. H. Green and D. G. Hellier, *J.C.S. Perkin II*, 1972, 458.

[5] W. Wucherpfennig, *Annalen*, 1970, **737**, 144.

[6] L. Cazaux and P. Maroni, *Compt. rend.*, 1971, **272**, 2065.

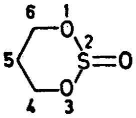
[7] P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 1963, 5307.

thian 2-oxide ring and to study the effect of conformational change on vibrational spectra.

*General Features*.—Each sulphite gives its own characteristic i.r. and Raman spectra, although the i.r. spectrum of isomeric sulphites tend to be very similar from 1 400 to 500 cm$^{-1}$. For all the sulphites examined the Raman spectrum contains more bands than the i.r. spectrum, particularly below 600 cm$^{-1}$. Table 1 contains the main assignments for the sulphites (1)—(25) together with the preferred conformations.

TABLE 1

Principal band assignments for 1,3,2-dioxathian 2-oxides in the 1 400—250 cm$^{-1}$ i.r. region *



| | ν/cm$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| | S=O | C–O | C–C | S–O(asym.) | S–O(sym.) | Conformation ‡ |
| Unsubst. (1) | 1 190vs | | 1 021s | 706m | 669s | A |
| 4-Methyl, isomer (a) (2) | 1 190vs | 1 061m | 1 015m | 722m | 686m | A |
| 4-Methyl, isomer (b) (3) | 1 192vs | 1 061m | 1 014m | 722m | 686m | A |
| 5-Methyl, isomer (a) (4) | 1 192vs | 1 083w | | 740s | 675s | A |
| 5-Methyl, isomer (b) (5) | 1 191vs | 1 083w | | 740s | 675s | A |
| 4,4-Dimethyl (6) | 1 194vs | | 1 023s | | 692s | A |
| 5,5-Dimethyl (7) | 1 190vs | | 1 033m | 737s | 676vs | A |
| 4,6-Dimethyl, isomer (a) (8) | 1 194s<br>1 234vs | 1 092w † | 1 011w † | 727m | 682w | B |
| 4,6-Dimethyl, isomer (b) (9) | 1 191vs | 1 078m † | | | | A |
| 4,6-Dimethyl, isomer (c) (10) | 1 196s<br>1 216w | 1 082m | | 728m | 682w | C |
| 5-Ethyl, isomer (a) (11) | 1 191vs | | 1 034w | 738vs | 680vs | A |
| 5-Ethyl, isomer (b) (12) | 1 190vs | 1 072w † | 1 032w | 737s | 679s | A |
| 5,5-Diethyl (13) | 1 192vs | 1 061w | 1 011w | 722w † | 679vs | A |
| 4,5,6-Trimethyl, isomer (a) (14) | 1 191vs | 1 099m | 1 032m | 727s | 679m | A |
| 4,5,6-Trimethyl, isomer (b) (15) | 1 194s | 1 066m<br>1 095m | | 716s<br>726w | | A |
| 4,4,6-Trimethyl, isomer (a) (16) | 1 189vs | 1 086w | 1 073w | 722m | 693m | A |
| 4,4,6-Trimethyl, isomer (b) (17) | 1 205s<br>1 238vs | 1 083w | 1 036m | 724w | 685m | B |
| 4,4,6,6-Tetramethyl (18) | 1 198s | 1 058w? | 1 042w | 720w | 689m | A |
| 4,5,5,6-Tetramethyl, isomer (a) 19) | 1 216s<br>1 229vs | 1 070m | 1 028w | 722vs | | B |
| 4,5,5,6-Tetramethyl, isomer (b) (20) | 1 199s | 1 077s | 1 010m | 726s | 678w | A |
| 4,5,5,6-Tetramethyl, isomer (c) (21) | 1 192vs<br>1 221s | 1 072m<br>1 084m | 1 046w | 724s | | C |
| 5-t-Butyl, isomer (a) (22) | 1 193vs | | 1 029m | 730s | 687vs | A |
| 5-t-Butyl, isomer (b) (23) | 1 195m<br>1 233s † | | 1 038m | 710m? | 675s | C |
| 5-Methyl-5-t-butyl, isomer (a) (24) | 1 192vs<br>1 222w | | 1 025w | | 687s | A |
| 5-Methyl-5-t-butyl, isomer (b) (25) | 1 191s<br>1 221s | | 1 024w | | 679s | C |

* Values obtained from 0.35M-solutions in carbon disulphide. Similar values were obtained in the Raman spectra. † Raman spectra value only. ‡ A, chair form, S=O axial; B, chair form, S=O equatorial; C, twist (non-chair) forms.

*The Region* 1 400—250 cm$^{-1}$.—For all the sulphites the vibrations in the range 1 400—1 250 cm$^{-1}$, in the i.r. and Raman spectra, may be assigned to C–H vibrations, which may include $CH_2$ wag, asymmetric $CH_3$ deformation, and $CH_3$ rock vibrations mixed with in-plane ring vibrations.[8-10] As previously indicated, a strong band at *ca.* 1 230 cm$^{-1}$ is usually an indication of the presence of an equatorial S=O bond [compounds (8), (17), and (19)]. All the methyltrimethylene sulphites characteristically exhibit weak bands at 1 230—1 250 cm$^{-1}$ in the i.r. (and occasionally in the Raman) which are probably due to C–C–H vibrations.[11,12] The four sulphites with twist conformations, (10), (21), (23), and (25), give a medium to strong band at *ca.* 1 220 cm$^{-1}$ in the i.r. and Raman. As expected all the other sulphites give a strong to very intense $\nu_{S=O}$ band at *ca.* 1 190 cm$^{-1}$ due to an axial S=O group.

Previous studies on related ring systems such as alkylcyclohexanes[13] and alkyl-1,3-dioxans[14] show medium-weak bands in the 1 100—1 180 cm$^{-1}$ region which have been assigned to C–H vibrations. Similar

---

[8] N. B. Colthup, L. H. Daly, and S. E. Wiberley, ' Introduction to Infra-red and Raman Spectroscopy,' Academic Press, New York, 1975, 2nd edn.

[9] F. F. Bentley, F. R. Dollish, and W. G. Fately, ' Characteristic Raman Frequencies of Organic Compounds,' Wiley–Interscience, New York, 1974.

[10] T. Shimanouchi and H. Takahashi, *J. Mol. Spectroscopy*, 1964, **13**, 43.

[11] A. B. Remizov, *Zhur. priklad. Spectroskopii*, 1971, **14**, 425.

[12] A. I. Gren, *Vop. Stereokhim.*, 1972, **2**, 76.

[13] H. A. Szymanski, ' Interpreted Infra-red Spectra,' vol. 1, Plenum, New York, 1964.

[14] H. Wunderlich, *Z. analyt. Chem.*, 1968, 241, 234.

assignments may probably be made for this characteristic band in these alkyl cyclic sulphites. Further, it is apparent from six-membered cyclic compounds containing C–C and C–O bonds the $\nu_{C-O}$ is higher than $\nu_{C-C}$; both are normally found between 950 and 1 150 cm$^{-1}$ in heterocyclic compounds.[8,9,15] The majority of sulphites give a weak-medium band in the range 1 060—1 100 cm$^{-1}$ and this is assigned mainly to $\nu_{C-O}$. Similarly, the weak-medium band in the range 1 010—1 050 cm$^{-1}$ in the i.r. and Raman spectra may be assigned principally to $\nu_{C-C}$. Remizov has made a similar assignment for trimethylene sulphite.[11] There is no apparent relationship between conformation and $\nu_{C-O}$ and $\nu_{C-C}$.

A characteristic of 1,3,2-dioxathan 2-oxides mono- or di-substituted at C-5 is a medium to intense i.r. band at 970 cm$^{-1}$. At slightly lower frequency, between 900 and 950 cm$^{-1}$, medium to strong bands in the i.r. and often in the Raman are found for nearly all the compounds and probably arise from ring stretching modes.[8,11] Likewise, a series of bands at 850—890 cm$^{-1}$ are also found in the i.r. and Raman spectra of all the sulphites. Tentative i.r. and Raman spectral analyses of trimethylene,[11,16] ethylene,[17,18] and acyclic alkyl sulphites [19,20] suggest that this region may be assigned to the asymmetric S–O–C vibration.

A distinctive feature of sulphites, cyclic and acyclic, is the bands due to symmetric and asymmetric $\nu_{S-O}$ between 670—750 cm$^{-1}$. The data in Table 1 allow three observations in this connection; (*a*) simple isomeric sulphites give very similar values; (*b*) the sulphites which are only substituted at C-5 give the highest values for $\nu_{S-O}$ (asym.) at *ca.* 740 cm$^{-1}$ and the lowest values of $\nu_{S-O}$ (sym.) at 670—680 cm$^{-1}$; and (*c*) sulphites substituted at C-4 and C-6 have $\nu_{S-O}$ (sym.) values between 680 and 690 cm$^{-1}$. Another characteristic strong bond appears in the 750—800 cm$^{-1}$ region of the Raman spectrum of the majority of sulphites and may be assigned to a ring ' breathing ' vibration due to alkyl substitution of the ring. Alkylcyclohexanes [13] and alkyl-1,3-dioxans [12,21] give similar vibrations in this region.

The S=O bond deformation frequency is not obvious. Simon [22] has assigned a weak band at 612 cm$^{-1}$ in the Raman spectrum of ethylene sulphite to $\delta_{S=O}$ whereas Remizov [11] assigns a band at 460 cm$^{-1}$ in the Raman spectrum of trimethylene sulphite to this mode. Our results suggest that a weak band at 520—540 cm$^{-1}$ in the Raman spectra of all sulphites is due to S=O deformation. Remizov assigns this region in the spectrum of trimethylene sulphite to mixed $\nu_{SOC}$, $\nu_{CCC}$, and $\nu_{CCH}$.

Comparison of the spectral data in the region 1 400—550 cm$^{-1}$ for all the sulphites clearly show that, with the exception of the $\nu_{S=O}$ band, the positions of the main bands are not a function of conformation, and no correlation between the appearance of the spectra and the three possible conformations, as in (9A), (8B), and (10C), is apparent. Below 550 cm$^{-1}$ there are major differences between the i.r. and Raman spectra of isomeric sulphites, with usually more distinctive bands in the Raman spectrum. Although the 250—500 cm$^{-1}$ region may be assigned to a combination of ring deformation vibrations (bending and twisting modes) it is not yet possible to identify individual vibrations, although some tentative assignments have been made by Remizov.[17]

## EXPERIMENTAL

The i.r. spectra were recorded on a Perkin-Elmer 521 spectrometer as previously described.[4] The i.r. region 1 400—250 cm$^{-1}$ was recorded for solutions in carbon disulphide (0.35M) with a caesium iodide variable path-length cell set at 0.05 mm. The spectra were recorded on a linearly expanded, calibrated scale and the absorption frequencies could be quoted to $\pm 1$ cm$^{-1}$ except where peak broadening occurred. The Raman spectra were recorded by the University of London Intercollegiate Research Service at Imperial College with a Cary 81 Raman spectrometer equipped with a krypton laser operating at 5 862 Å. In all cases the 1 400—250 cm$^{-1}$ region was recorded for the neat liquid or solid, with frequencies quotable to $\pm 3$ cm$^{-1}$. In a number of instances, high fluorescence was encountered resulting in poorly resolved peaks.

*Preparation of Sulphites*.—All sulphites were prepared by the method and techniques previously described.[4] The preparations of the sulphites (1),[4] (7),[23] (8)—(10),[5] (22), and (23) [24] have already been described in detail. Elemental analyses for new compounds are in Table 2, and purity was in all cases greater than 96% by g.l.c.

TABLE 2

Elemental analyses

| | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|
| Compound | C | H | S | C | H | S |
| (2), (3) † | 35.5 | 5.7 | 23.3 | 35.3 | 5.9 | 23.5 |
| (4), (5) † | 35.2 | 5.8 | 23.4 | 35.3 | 5.9 | 23.5 |
| (6) | 39.8 | 6.6 | 21.2 | 40.0 | 6.7 | 21.3 |
| (11), (12) † | 40.1 | 6.7 | 21.1 | 40.0 | 6.7 | 21.3 |
| (13) | 47.0 | 8.1 | 17.8 | 47.2 | 7.9 | 18.0 |
| (14), (15) † | 43.7 | 7.2 | 19.3 | 43.9 | 7.3 | 19.5 |
| (16), (17) † | 43.8 | 7.2 | 19.3 | 43.9 | 7.3 | 19.5 |
| (18) | 47.1 | 7.8 | 17.8 | 47.2 | 7.9 | 18.0 |
| (19)—(21) † | 47.0 | 7.9 | 17.8 | 47.2 | 7.9 | 18.0 |
| (24), (25) | 49.9 | 8.2 | 16.5 | 50.0 | 8.3 | 16.7 |

† Isomeric mixture.

4-*Methyl*-1,3,2-*dioxathian* 2-*Oxide*, *Isomers* (*a*) *and* (*b*).—By the standard procedure commercial butane-1,3-diol (Koch–Light) in anhydrous ether gave the crude sulphite (71%), b.p. 120—150 °C at 25 mmHg; ratio of isomer 1 to isomer 2 *ca.* 4 : 1 by $^1$H n.m.r. Fractional distillation through a 6 × 0.5 in unrestricted column gave two fractions:

---

[15] L. J. Bellamy, 'Advances in Infra-red Group Frequencies,' Methuen, London, 1968.

[16] A. B. Remizov, *Zhur. priklad. Spektroskopii*, 1975, **22**, 252.

[17] G. Heintz and A. Simon, *Chem. Ber.*, 1962, **95**, 2333.

[18] R. I. Kozlova, T. G. Mannafov, A. B. Remizov, and N. N. Vakhrusheva, *Zhur. priklad. Spektroskopii*, 1973, **19**, 109.

[19] S. Detoni and D. Hadzi, *Spectrochim. Acta*, 1957, **11**, 601.

[20] P. Klaeboe, *Acta Chem. Scand.*, 1968, **22**, 2817.

[21] H. M. Pickett and H. L. Strauss, *J. Chem. Phys.*, 1970, **53**, 276.

[22] H. Kriegsmann and A. Simon, *Z. phys. Chem.* (*Leipzig*), 1955, **204**, 369; H. Dutz, H. Kriegsmann, and A. Simon, *Chem. Ber.*, 1956, **89**, 2390.

[23] W. Emerson and H. H. Szmant, *J. Amer. Chem. Soc.*, 1956, **78**, 454.

[24] H. F. van Woerden, Ph.D. Thesis, Leiden, 1964.

(i) b.p. 119—120 °C at 25 mmHg, pure isomer (a) (99%), and (ii), b.p. 148—149 °C at 25 mmHg, mainly isomer (b) (75%), with *ca.* 20% unchanged diol (by $^1$H n.m.r.). Isomer (b) was purified from the second fraction by preparative g.l.c. [15 ft column of 27% Montan Wax on Phase Sep P1; gas flow 135 ml min$^{-1}$; 180 °C; $t_R$ (a) 13.5 and (b) 22.0 min; injection sample sizes 45 μl]. Isomer (a) showed $n_D^{21}$ 1.445 1 and (b) $n_D^{21}$ 1.457 6.

5-*Methyl*-1,3,2-*dioxathian* 2-*Oxide*, *Isomers* (*a*) *and* (*b*).—2-Methylpropane-1,3-diol was prepared as follows (in a system kept under a stream of dry nitrogen). To a stirred suspension of lithium aluminium hydride (10 g, 0.27 mol) in dry ether (400 ml) at 0 °C was added dropwise a dry ethereal solution (200 ml) of diethyl methylmalonate (0.26 mol) (Ralph Emmanuel). On attaining room temperature the mixture was refluxed for ½ h, then cooled again to below 0 °C. The aluminium complex was destroyed by very slow addition of water (20 ml) and 10% w/v sodium hydroxide (16 ml).[25] The precipitate coagulated on stirring for a further 2 h and was filtered off and washed several times with ether. The washings were added to the main solution, which was then dried ($MgSO_4$) for 12 h. Removal of the solvent gave the diol (0.88 mol, 34%), b.p. 100—102 °C at 10 mmHg (lit.,[26] 111—114 °C at 17 mmHg). A 68% yield of crude sulphite, b.p. 62—64 °C at 2 mmHg, was obtained from the diol. The isomers [(a) : (b) 3.2 : 1] were separated by preparative g.l.c. [15 ft column of 25% Carbowax 20M on Chromosorb P (30—60 mesh); gas flow 83 ml min$^{-1}$; 166 °C; $t_R$ (a) 17.1 min and (b) 21.0 min. Peak resolution was excellent for injection sample sizes of 50 μl and the isomers were obtained >99% pure: (a) $n_D^{21}$ 1.4467; (b) $n_D^{21}$ 1.4507.

4,4-*Dimethyl*-1,3,2-*dioxathian* 2-*Oxide*.—By the standard procedure 3-methylpentane-1,3-diol (0.1 mol) (B.A.S.F.) with benzene as solvent gave the sulphite (0.059 mol, 59%), b.p. 34—36 °C at 1.5 mmHg. Redistillation gave >99% pure sulphite, b.p. 32—33 °C at 1.0 mmHg, $n_D^{25}$ 1.4516 (lit.,[27] b.p. 79—80 °C at 13 mmHg, $n_D^{14}$ 1.4548).

5-*Ethyl*-1,3,2-*dioxathian* 2-*Oxide*, *Isomers* (*a*) *and* (*b*).—Diethyl ethylmalonate (0.24 mol) was reduced by lithium aluminium hydride (0.27 mol) to give pure 2-ethylpropane-1,3-diol (0.13 mol, 55%), b.p. 126—127 °C at 20 mmHg (lit.,[26] 119—121 °C at 17 mmHg). By the standard procedure, the diol (0.096 mol) with benzene as solvent gave >90% pure sulphite (0.053 mol, 55%), b.p. 85—87 °C at 1 mmHg. The isomers [(a) : (b) 3.5 : 1] were separated by preparative g.l.c. [7 ft column of 22% Carbowax 20 M on Chromosorb P (60—85 mesh); gas flow 55 ml min$^{-1}$; 152 °C; $t_R$ (a) 23.2 (b) 26.8 min; injection sample sizes 30 μl]. Both isomers were obtained 99% pure: (a) $n_D^{25}$ 1.4478; (b), $n_D^{25}$ 1.4527.

5,5-*Diethyl*-1,3,2-*dioxathian* 2-*Oxide*.—The sulphite was prepared from 2,2-diethylpropane-1,3-diol (Eastman Kodak) with ether as solvent; b.p. 70 °C at 1 mmHg $n_D^{20}$ 1.4579 (lit.,[28] b.p. 66 °C at 0.5 mmHg).

4,5,6-*Trimethyl*-1,3,2-*dioxan* 2-*Oxide*, *Isomers* (*a*) *and* (*b*).—By the standard procedure 3-methylpentane-2,4-diol (Koch–Light) (0.33 mol) in ether gave the sulphite (0.215 mol, 65%), b.p. 102—107 °C at mmHg, found by g.l.c. to be *ca.* 95% pure but consisting of at least five isomers. Two of the isomers [(a) : (b) 3 : 1] were separated on a 15 ft column of 27% Montan Wax on Phase Sep P1; gas flow 135 ml min$^{-1}$; 180 °C $t_R$ (a) 30.1 (b) 30.9 min; injection sample sizes 20 μl. Peak resolution was poor, requiring vigorous ' topping and tailing '. Isomers (a) and (b) were obtained >95% pure; (a) $n_D^{20}$ 1.4483; (b) $n_D^{20}$ 1.4489.

4,4,6-*Trimethyl*-1,3,2-*dioxathian* 2-*Oxide*, *Isomers* (*a*) *and* (*b*).—2-Methylpentane-2,4-diol (Koch–Light) (0.31 mol) with ether as solvent gave 98% pure sulphite (0.175 mol, 58%), b.p. 130—140 °C at 40 mmHg (lit.,[29] b.p. 71—73 °C at 3.5 mmHg). The isomers [(a) : (b) 6.8 : 1] were separated by preparative g.l.c. [7 ft column of 20% Apiezon L on Chromosorb P (60—85 mesh); gas flow 68 ml min$^{-1}$; 174 °C; $t_R$ (a) 10.6 and (b) 15.3 min]. Peak resolution was excellent for injection sample sizes of 40 μl; isomer (a) $n_D^{19}$ 1.4474; isomer (b) m.p. 39—40 °C (lit.,[30] 40 °C).

4,4,6,6-*Tetramethyl*-1,3,2-*dioxathian* 2-*Oxide*.—1,1,3,3-Tetramethylpropane-1,3-diol was prepared by dropwise addition of diacetone alcohol (0.15 mol) in dry ether (100 ml) to the Grignard reagent prepared from magnesium turnings (0.30 mol) and methyl iodide (0.30 mol) in anhydrous ether (500 ml). The reactants were stirred until the solid complex dissolved and then added to acetic acid (0.50 mol) in crushed ice (150 g). After neutralising with potassium carbonate the ether layer was distilled to give the diol (0.042 mol, 28%), b.p. 100—102 °C at 20 mmHg (lit.,[31] 102 °C at 18 mmHg), purity >95% by $^1$H n.m.r. By the standard procedure, the diol (0.042 mol) in ether gave the sulphite (0.028 mol, 67%), b.p. 120—125 °C at 20 mmHg (lit.,[32] 77.5 °C at 5 mmHg), purified by preparative g.l.c. [3 ft column of 25% Montan Wax on Chromosorb P (60—85 mesh); gas flow 180 ml min$^{-1}$; 150 °C; $t_R$ 11.7 min for injection sample sizes of 40 μl]; $n_D^{19}$ 1.4518 (lit.,[32] $n_D^{25}$ 1.4490).

4,5,5,6-*Tetramethyl*-1,3,2-*dioxathian* 2-*Oxide*.—To a stirred mixture of isopropyl methyl ketone and methanolic 2N-sodium methoxide (20 ml) (4 : 1 molar ratio) was added dropwise, during 2½ h, a mixture of acetaldehyde (1.15 mol) and isopropyl methyl ketone (0.58 mol), with the temperature maintained at 15 °C. After stirring for a further ½ h the mixture was neutralised with powdered oxalic acid and the precipitate filtered off. The excess of ketone was recovered by distillation and the residue fractionated to give 4-hydroxy-3,3-dimethylpentan-2-one (0.38 mol), b.p. 80—83 °C at 25 mmHg (lit.,[33] 65 °C at 2.5 mmHg). The ketone (0.58 mol) was reduced with lithium aluminium hydride (0.265 mol) to give the 3,4-diol (0.315 mol, 54%), b.p. 105—110 °C at 25 mmHg (lit.,[33] 80—83 °C at 2 mmHg). By the standard procedure, the diol (0.315 mol) in ether gave the sulphite (0.24 mol, 77%), b.p. 98—102 °C at 25 mmHg, found by g.l.c. to contain four isomers and *ca.* 5% impurity. Three isomers were separated [30 ft column of 20% Carbowax 20 M on Chromosorb P (30—60 mesh), gas flow 20 ml min$^{-1}$; 203 °C; using injection sample sizes 15 μl; $t_R$ (a) 31.8, (b) 34.6, and (c) 44.2 min]. Even under optimised conditions peak separation was poor, necessitating rigorous ' topping and tailing '. Isomers (a)—(c) were obtained >95% pure: (a), m.p. 68 °C (lit.,[34] 66—69 °C); (b) $n_D^{20}$ 1.4564 (lit.,[34] $n_D^{25}$ 1.4540); (c), $n_D^{20}$ 1.4589 (lit.,[34] $n_D^{25}$ 1.4568).

---

[25] N. Anderson, A. Hochsteller, and J. Marshall, *J. Org. Chem.*, 1967, **32**, 113.

[26] E. Eliel and Sr. M. C. Knoeber, *J. Amer. Chem. Soc.*, 1968, **90**, 3444.

[27] T. Halsall and A. Hands, *J. Chem. Soc.*, 1961, 3251.

[28] M. Ehrenstein and P. Th. Herzig, *J. Org. Chem.*, 1952, **17**, 724.

[29] U.S.P., 2,465,915/1949.

[30] S. Sarel and V. Usieli, *Israel J. Chem.*, 1968, **6**, 885.

[31] A. Franke and M. Kohn, *Monatsh.*, 1907, **28**, 1001.

[32] R. P. Arshinova, Yu. Yu. Samitov, and L. K. Yuldasheva, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 2461.

[33] B. Bachler, E. Cherbuliez, J. Rabinowitz, and A. Sussman, *Helv. Chim. Acta*, 1961, **44**, 1808.

[34] L. Cazeaux and P. Maroni, *Compt. rend.*, 1971, **273**, 156.

*5-Methyl-5-t-butyl-*1,3,2-*dioxathian* 2-*Oxide, Isomers* (*a*) *and* (*b*).—Diethyl t-butylmalonate [24] (0.15 mol) was added dropwise to a stirred solution of sodium hydride (0.17 mol) dispersed in toluene followed by methyl iodide (0.18 mol). The mixture was refluxed for 1.5 h and on cooling precipitated sodium iodide. After filtering, distillation gave diethyl methyl-t-butylmalonate (0.11 mol, 73%), b.p. 118—125 °C at 20 mmHg (lit.,[26] 104 °C 10 mmHg). The ester (0.125 mol; in diethyl ether) was reduced with lithium aluminium hydride (0.265 mol) to give the crude diol. Recrystallisation from diethyl ether gave 2-methyl-2-t-butylpropane-1,3-diol (0.085 mol 68%), m.p. 184—185 °C. By the standard procedure the diol (0.062 mol) in diethyl ether gave the sulphite (0.044 mol, 71%), b.p. 115—118 °C at 20 mmHg. The isomers [(a) : (b) 6.6 : 1] were separated and purified by preparative g.l.c. [3 ft column of 20% Apiezon L on Chromosorb P (60—85 mesh); gas flow 72 ml min$^{-1}$; 152 °C; $t_R$ (a) 14.1 and (b) 16.8 min; injection sample sizes 25 µl]. ' Topping and tailing ' of the peaks was required to effect separation, giving >99% purity for both isomers: (a), m.p. 34 °C; (b), $n_D^{20}$ 1.4707.

One of us (F. J. W.) thanks the S.R.C. for a research studentship.

[6/1449 *Received*, 23*rd July*, 1976]