Tetrahedron, 1958, Vol. 4, pp. 351–360. Pergamon Press Ltd., London

# ASPECTS OF STEREOCHEMISTRY—I*

## PROPERTIES AND REACTIONS OF SOME DIOLS

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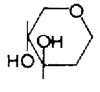
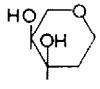
**Abstract**—The extent of intramolecular hydrogen-bonding, as determined by infra-red spectroscopy in the hydroxyl stretching region, in certain vicinal diols of *cyclo*hexane, *cyclo*pentane, tetrahydropyran and tetrahydrofuran and in related compounds provides evidence for the stabilities of different conformations. In certain compounds these stabilities can be affected by hydrogen bonding from a substituent hydroxyl group to a ring oxygen. Additional evidence is provided in the case of the tetrahydropyran diols by $[M]_D$ values. The rate of reaction of the vicinal diols of these cyclic systems with glycol splitting reagents, and their zone electrophoretic mobility in an alkaline borate buffer is influenced by the presence of a ring oxygen.

MUCH information is available concerning inter and intramolecular hydrogen bonding[1,2] in saturated carbocyclic vicinal diols and the reactivity of these compounds towards glycol splitting reagents.[1a,3] Little is known, however, of the effect, on these properties, of replacing a ring methylene group by oxygen to yield compounds derived from tetrahydropyran and tetrahydrofuran. Some consequences of this replacement are noted herein.

The diols studied are listed in Table 1. With the exception of *cyclo*hexane *trans*-1 : 2-diol (which was obtained *via* epoxidation[4] of *cyclo*hexene) the carbocyclic *trans*-diols were prepared by bromination of the corresponding olefins, solvolysis of the *trans*-dibromides with dry acetic acid and silver acetate and saponification of the resultant *trans*-diacetates. This reaction sequence which was used by Winstein and Roberts[5] for the synthesis of indan *trans*-1:2-diol appears to be a general method. The carbocyclic *cis*-diols were obtained by hydroxylation of the appropriate olefins with permanganate.[6] Evidence of the homogeneity of the carbocyclic diols, as prepared by these methods, was obtained by the application of zone electrophoresis (ionophoresis) in borate buffer (pH 10) using the enclosed strip technique[7] under




I




II

* A preliminary report of some of these results has been given Abstr. Papers Amer. Chem. Soc. Meeting, New York, September 1957, p. 2D.

[1a] L. P. Kuhn, *J. Amer. Chem. Soc.* **74**, 2492 (1952);[b] *Ibid.* **76**, 4323 (1954).

[2] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.* 4391 (1956).

[3] See H. H. Wasserman, *Steric Effects in Organic Chemistry* (Edited by M. S. NEWMAN) p. 378. Academic Press (1956). See also references cited therein.

[4] A. Roebuck and H. Adkins, *Organic Syntheses* Collective Vol. 3, p. 217.

[5] S. Winstein and R. M. Roberts, *J. Amer. Chem. Soc.* **75**, 2297 (1953).

[6] M. F. Clarke and L. N. Owen, *J. Chem. Soc.* 315 (1949).

[7a] H. G. Kunkel and A. Tiselius, *J. Gen. Physiol.* **35**, 89 (1951); [b] A. B. Foster, *Chem. & Ind* 1050 (1952).

standard conditions[7b] when, with one exception, each diol gave a single compact zone; *cyclo*pentane *cis*-1:2-diol appeared to contain a trace of the *trans*-isomer.

Synthesis of 1:5-anhydro 2-deoxy-D-*threo*pentitol* (I) [1:5-anhydro 4-deoxy-D-*threo*pentitol, (-)-tetrahydropyran 3/4-diol] was accomplished by platinum catalysed hydrogenation of 3:4-di-O-acetyl-D-xylal followed by saponification of the product. Alternatively 3:4-di-O-acetyl-D-xylal may be catalytically deacetylated (Zemplén) and the D-xylal so obtained hydrogenated to yield the diol (I). The *cis*-isomer 1:5-anhydro 2-deoxy-L-*erythro*pentitol [1:5-anhydro 4-deoxy-D-*erythro*pentitol, (+)-tetrahydropyran/3, 4-diol] was obtained by sequential application of platinum catalysed hydrogenation and saponification to 3:4-di-O-acetyl-L-arabinal. Racemic forms of the diols (II) and (I) have previously been obtained by *cis*- and *trans*-hydroxylation of 2:3-dihydropyran[8] and by hydrogenolysis of methyl β-L-arabinopyranoside.[9] Dehydration of L-threitol and erythritol with sulphuric acid gave respectively 1:4-anhydro-L-threitol (threitan) and 1:4-anhydro-erythritol (erythritan).

The inter- and intra-molecular hydrogen bonding which may occur in dry carbon tetrachloride solutions of carbocyclic and acyclic diols has been intensively studied.[1,2] Intermolecular hydrogen bonding is critically dependent on the concentration of the diol and becomes negligible in solutions which are less than 0·005 M with respect to diol.[1] The infra-red spectral data in Table 1 were determined on solutions of the diols in dry carbon tetrachloride below this critical concentration. Under these conditions the absorption at ca. 3630 $cm^{-1}$ has been associated[1] with free hydroxyl groups and that at ca. 3580 $cm^{-1}$ with intra-molecularly hydrogen-bonded hydroxyl groups.† Kuhn[1] considers that the magnitude of $\Delta\nu$, the arithmetical difference between the free and bonded hydroxyl absorption frequencies for a given diol, is proportional to the strength of the hydrogen bond and hence an indication of the O-O distance in the diol. Cole and Jefferies[2] prefer to express $\Delta\nu$ as the difference between a standard secondary hydroxyl absorption frequency (3629 $cm^{-1}$) and the bonded hydroxyl absorption frequency. Both values of $\Delta\nu$ are recorded in Table 1. Further, as Cole and Jefferies have emphasised,[2] the extent of intramolecular hydrogen bonding may be approximately assessed from the relative extinction coefficients of the free and bonded hydroxyl groups and, together with $\Delta\nu$ values, this information constitutes direct experimental evidence on which the allocation of conformation to the diols in carbon tetrachloride solution may be based. The molecular extinction coefficients are included in parentheses in Table 1.

In considering six membered ring systems it is now accepted[11] that, in *cyclo*hexane derivatives at ordinary temperatures, the chair form will be preferred to other possible conformations. Further, in derivatives containing substituents of similar bulk, because of non-bonded interactions, the preferred chair forms will in general be those with the greatest possible number of equatorial substituents. It seems most probable[12] that similar considerations will apply to derivatives of tetrahydropyran and 1:3-dioxan.

* The orientation adopted for formulae (I) and (II), and hence the nomenclature, best illustrates the relationship of these compounds to the carbohydrate precursors.

† Subsequently referred to as bonded hydroxyl groups.

[8] O. Heuberger and L. N. Owen, *J. Chem. Soc.* 910 (1952).

[9] H. F. Bauer and D. E. Stuetz, *J. Amer. Chem. Soc.* **78**, 4097 (1956).

[10a] R. Montgomery and L. F. Wiggins, *J. Chem. Soc.* 390 (1946); [b]L. F. Wiggins, *Ibid.* 4 (1945); [c]*Ibid.* 1403 (1947).

[11] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* **10**, 44 (1956) and references cited therein.

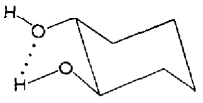
[12] J. A. Mills, *Adv. Carbohydrate Chem.* **10**, 1 (1955).

TABLE 1. INFRA-RED SPECTRAL, GLYCOL CLEAVAGE AND IONOPHORETIC DATA ON CERTAIN DIOLS AND RELATED COMPOUNDS

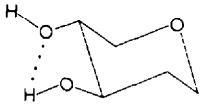
| Compound | Infra-red absorption ($cm^{-1}$)[a] | | $\Delta\nu$[b] | $\Delta\nu$[c] | Periodate oxidation ($t\frac{1}{2}$) | Lead tetra-acetate oxidation ($t\frac{1}{2}$) | $M_G$ |
|---|---|---|---|---|---|---|---|
| | Free OH | Bonded OH | | | | | |
| *cyclo*Hexane *trans*-1:2-diol | 3633 (55)[d] | 3602 (70)[d] | 31 | 27 | rapid | 1·9 hr | 0·00 |
| 1:5-Anhydro 2-deoxy-D-*threo*pentitol (I) | 3633 (56) | 3608 (52) | 25 | 21 | 20 min | 5hr | 0·00 |
| *cyclo*Hexane *cis*-1:2-diol | 3632 (58)[e] | 3592 (62)[e] | 40 | 37 | rapid | 5 min | 0·07 |
| 1:5-Anhydro 2-deoxy-L-*erythro*pentitol (II) | 3633 (25) | 3583 (58) | 50 | 46 | rapid | 9 min | 0·23 |
| *cyclo*Pentane *trans*-1 : 2-diol | 3624 | — | | | 5 min | 10 min | 0·00 |
| 1:4-Anhydro-L-threitol (L-threitan) | 3624 | — | | | | 11 hr | 0·00 |
| *cyclo*Pentane *cis*-1 : 2-diol | 3624 (50) | 3579 (50) | 45 | 50 | rapid | rapid | 0·69 |
| 1:4-Anhydroerythritol (erythritan) | 3624 (40) | 3585 (40) | 39 | 44 | | rapid | 0·88 |
| 1:4-3 : 6-Dianhydro-D-glucitol[f] (XII) | 3624 | 3540 | 84 | 89 | | | |
| 1:4-3 : 6-Dianhydro-D-mannitol[f] (XIII) | — | 3540 | | 89 | | | |
| 1:4-3 : 6-Dianhydro-L-iditol[f,g] (XIV) | 3624 | — | | | | | |
| Indan *trans*-1:2-diol | 3624 | — | | | 60 min | | 0·00 |
| Indan *cis*-1:2-diol | 3620 (43) | 3579 (60) | 41 | 50 | rapid | | 0·72 |
| *cyclo*Heptane *trans*-1:2-diol | 3626[h] | 3589[h] | 37 | 40 | rapid | | 0·53 |
| *cyclo*Heptane *cis*-1:2-diol | 3632[h] | 3588[h] | 44 | 41 | rapid | | 0·69 |
| 1:3-Dioxan-5-ol (1:3-O-methylidene glyceritol) | 3635 (25) | 3593 (100) | 42 | 36 | | | |

[a] Figures in parentheses refer to maximum extinction coefficients ($\varepsilon$).
[b] Arithmetical difference between absorption frequencies of free and bonded hydroxyl groups.
[c] Arithmetical difference[8] between absorption frequencies of standard secondary (3629 $cm^{-1}$) and bonded hydroxyl groups.
[d] Cole and Jefferies[8] record 3631 (62) and 3600 (75).
[e] Cole and Jefferies[8] record 3626 (60) and 3588 (60).
[f] These compounds are described in the literature.[10]
[g] Reported[10c] as a hemihydrate; obtained anhydrous by distillation.
[h] Data taken from ref. 2.

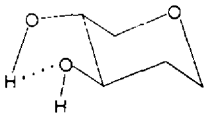
*cyclo*Hexane *trans*-1:2-diol and 1:5-anhydro-2-deoxy-D-*threo*pentitol (I) showed absorption for free hydroxyl groups at 3633 $cm^{-1}$ and bonded hydroxyl groups at 3602 $cm^{-1}$ and 3608 $cm^{-1}$ respectively. The extinction coefficients indicate that, in each diol, essentially one hydroxyl group is free and one is bonded.



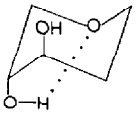
III



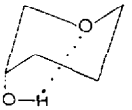
IVa



IVb



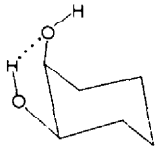
V



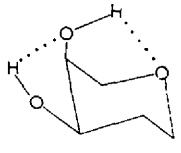
VI

Thus for *cyclo*hexane *trans*-1:2-diol the conformation (III) (and also the enantiomorphous structure) with both hydroxyl groups in equatorial positions must predominate as expected on theoretical grounds,[11] since bonding would not be possible in the alternative chair conformation, which has both hydroxyl groups in axial positions. The situation is more complex for 1:5-anhydro-2-deoxy-D-*threo*pentitol (I) which may exist in the chair conformations (IVa), (IVb) and (V) in each of which one hydroxyl group may be free and one bonded. On theoretical grounds[11] the conformations (IV) should be preferred to conformation (V). Although one hydroxyl group may be bonded in each case, adverse non-bonded interactions would be lower in the conformations (IV) (equatorial hydroxyl groups) than in conformation (V) (axial hydroxyl groups).

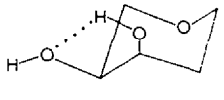
Some support for this view follows from the observation[13] that, in carbon tetrachloride solution, an appreciable percentage of the hydroxyl group in tetrahydropyran-3-ol is not bonded to the ring oxygen indicating that the intramolecular hydrogen bonding is not strong enough to fix the conformation. Intramolecular hydrogen



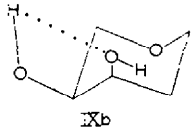
VII



VIII



IXa



IXb

[13] S. A. Barker, A. B. Foster, D. H. Whiffen and G. Zweifel, Unpublished results.

bonding in the conformation (VI) of tetrahydropyran-3-ol would be expected to be less sterically hindered than in conformation (V) of 1:5-anhydro-2-deoxy-D-*threo*pentitol.

On the available evidence the two arrangements (IVa) and (IVb) cannot be distinguished.

The similar extinction coefficients of free and bonded hydroxyl groups in *cyclo*hexane-*cis*-1:2-diol indicates the presence of one free and one bonded hydroxyl group as in conformation (VII). The two possible chair conformations of *cyclo*hexane-*cis*-1:2-diol are enantiomorphous and will occur to an equal extent in carbon tetrachloride solution. Conformation (VII) has a bonded equatorial hydroxyl group but it should be noted that the alternative arrangement with a bonded axial hydroxyl group is also feasible. A distinction between these possibilities is not permitted on the available data.

The extinction coefficients for 1 : 5-anhydro-2-deoxy-L-*erythro*pentitol of 25 and 58 respectively for free and bonded hydroxyl groups suggest that both hydroxyl groups are simultaneously hydrogen bonded to an appreciable extent. 1:5-Anhydro-2-deoxy-L-*erythro*pentitol (II) may exist in the chair conformations (VIII) and (IX) each of which contain one axial and one equatorial hydroxyl group. Hydrogen bonding is possible between the hydroxyl groups in each conformation but in conformation (VIII) an additional hydrogen bond may be formed between the axial $C_{(4)}$-hydroxyl group and the ring oxygen. The infra-red data are consistent with the predominance of the chair form (VIII) in the conformational equilibrium. The possible close proximity of the hydrogen of the $C_{(4)}$-hydroxyl group in conformations (VI) and (VIII) and the ring oxygen may be clearly seen in accurate scale models. The presence of some absorption associated with free hydroxyl groups in the spectrum of 1:5-anhydro-2-deoxy-L-*erythro*pentitol (II) may be due either to incomplete hydrogen bonding in conformation (VIII) or to the existence of a part of the diol in the alternative chair conformations (IX) where the ring oxygen cannot participate in intramolecular hydrogen bonding.

TABLE 2. OBSERVED AND CALCULATED $[M]_D$ VALUES FOR CERTAIN PYRAN DERIVATIVES

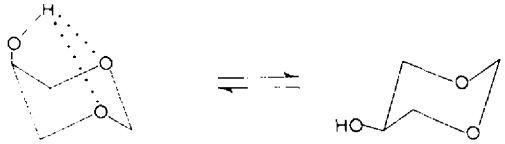
| Diol | Conformation | $[M]_D$ Calc. (parameters)[a] | Obs. |
|---|---|---|---|
| 1:5-Anhydro-2-deoxy-D-*threo*pentitol (I) | HO-groups axial (V)<br>HO-groups equatorial (IV) | −43° (−I)<br>−45° (−F) | −35° |
| 1:5-Anhydro-2-deoxy-L-*erythro*pentitol (II) | $C_{(3)}$-HO-group axial (IX)<br>$C_{(4)}$-HO-group axial (VIII) | −45°(−F)<br>+88° (+I + F) | +75° |

[a] Parameters are those evaluated by Whiffen.[14]

Using the parameters evaluated by Whiffen,[14] the molecular rotations ($[M]_D$) in aqueous solution of the possible chair conformations of 1:5-anhydro-2-deoxy-D-*threo*pentitol (I) and 1:5-anhydro-2-deoxy-L-*erythro*pentitol (II) may be calculated (Table II). In the case of the *trans*-diol (II) the calculated values for the conformations

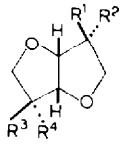
[14] D. H. Whiffen, *Chem. & Ind.* 964 (1956).

(IV) and (V) are $-45°$ and $-43°$ respectively (observed $-35°$); their similarity precludes the use of optical rotation measurements as a means of estimating the percentage of the respective chair forms in the conformational equilibrium. However the observed $[M]_D$ value of $+75°$ for the *cis*-diol (II) indicates that the conformation (VIII) (calc. $[M]_D$ $+88°$) predominates over conformation (IX) (calc. $[M]_D$ $-45°$) in the conformational equilibrium.



X XI

In only one (X) of the chair conformations (X) and (XI) of 1:3-dioxan-5-ol (1:3-O-methylidene glyceritol) can the hydroxyl group participate in intramolecular hydrogen bonding with the ring oxygens. The data in Table 1 show that, in carbon tetrachloride solution, not only does intramolecular hydrogen bonding occur but that most of the hydroxyl groups are bonded. Clearly, determination of the extent of intramolecular hydrogen bonding may be of potential value in the allocation of structure to *cis*- and *trans*-forms of 2-C-substituted 1:3-dioxan-5-ol (e.g. 1:3-O-alkylidene and 1:3-O-arylidene glyceritols) since bonding will be sterically hindered in the *trans*-form. Structures have been allocated in this way to the *cis*- and *trans*-forms of 2-C-phenyl 1:3-dioxan-5-ol (1:3-O-benzylidene glyceritols) and will be discussed in detail elsewhere.[15]



XII $R^2 = R^3 = OH$, $R^1 = R^4 = H$

XIII $R^2 = R^4 = OH$, $R^1 = R^3 = H$

XIV $R^1 = R^3 = OH$, $R^2 = R^4 = H$

The infra-red spectrum data (Table 1) for *cyclo*pentane *cis*-1:2-diol and 1:4-anhydro-L-threitol (L-threitan) are closely similar as are those of *cyclo*pentane *trans*-1:2-diol and 1:4-anhydroerythritol (erythritan). Intramolecular hydrogen bonding is possible only in the *cis*-diols. The high $\Delta\nu$ values reflect the close proximity of the hydroxyl groups although they are not in truly eclipsed positions.[16] The series of 1:4-3:6-dianhydrohexitols illustrates the influence of structure on intramolecular hydrogen bonding and emphasises the potential value of these observations in structural determination. The $C_{(2)}$- and $C_{(3)}$-, $C_{(4)}$- and $C_{(5)}$-oxygen bonds in 1:4-3:6-dianhydro-L-iditol (XIV) are *trans*-related as in L-threitan so that intramolecular hydrogen bonding is precluded. A *cis*-relation of the $C_{(2)}$- and $C_{(3)}$-oxygen bonds

[15] J. S. Brimacombe, A. B. Foster and M. Stacey, *Chem. & Ind.* 1228 (1958).
[16] H. Kwart and W. G. Vosburgh, *J. Amer. Chem. Soc.* **76**, 5400 (1954).

exists in the D-mannitol analogue (XIII) permitting a single intramolecular hydrogen bond. In the D-glucitol compound (XII) two intramolecular hydrogen bonds may occur and the absence of detectable absorption for free hydroxyl groups indicates the completeness of the hydrogen bonding.

The influence of structure on the rate of reaction of carbocyclic vicinal diols with lead tetra-acetate has been studied in detail.[3] A comparison of the rates of attack, by lead tetra-acetate, and sodium metaperiodate on the five and six membered cyclic diols is recorded in Table 1. In those cases where the rate of oxidation was sufficiently slow to follow kinetically, replacement of a ring methylene group by oxygen was observed to retard the rate of attack by the glycol splitting reagents. The effect was especially marked in 1:4-anhydro-L-threitol.

The $M_G$ values (relative mobilities[17]) recorded in Table 1 were obtained by zone electrophoresis (ionophoresis) of the diols in borate buffer at pH 10 using the enclosed strip technique.[7] With one exception all the vicinal *trans*-diols showed zero mobility; the high $M_G$ value of *cyclo*heptane *trans*-1:2-diol indicates an extensive reaction with borate ions to form the negatively charged complex[18] which migrates in the electric field. Complex formation is most likely permitted by the flexibility of the seven membered ring. This flexibility, also enables *cyclo*heptane *trans*-1:2-diol to form an *iso*propylidene derivative[19] and an osmate complex.[20]

All the vicinal *cis*-diols so far studied show a definite mobility under the adopted experimental conditions. Replacement of a ring methylene group by oxygen appears to facilitate complex formation and confers a higher $M_G$ value. This effect is most noticeable in 1:5-anhydro 2-deoxy-L-*erythro*pentitol which has an $M_G$ value (0·23) much higher than the carbocyclic analogue, *cyclo*hexane *cis*-1:2-diol (0·07).

## EXPERIMENTAL

*cyclo*Heptane trans-1 : 2-*diol*

Bromine was added slowly to a cooled (0°) solution of *cyclo*heptene (12 g) in ether (40 ml) until the bromine colour persisted. After washing successively with 0·01N-sodium hydroxide and water the dried ($MgSO_4$) ethereal solution was concentrated. From the residue *cyclo*heptane *trans*-1:2-dibromide[21] (25·4 g, 79·4%) was obtained as a colourless liquid b.p. 138–140° (bath)/20–25 mm, $n^{23·5}$ 1·5532.

A suspension of silver acetate (40 g) in glacial acetic acid (80 ml) was treated with acetic anhydride (25 ml) at 110° for 2 hr. The dibromide (25·4 g) was then added to this mixture and the temperature maintained at 110° for 15 hr. Thereafter insoluble material was removed, the filtrate evaporated and *cyclo*heptane *trans* 1:2-diacetate (8·2 g, 40·4%) was obtained as a colourless liquid b.p. 99–101° (bath)/0·5 mm, $n^{23}$ 1·4530.

The diacetate (4 g) was saponified by treatment for 2 hr with a boiling mixture of ethanol (8 ml) and aqueous sodium hydroxide (8 ml, 35% w/v). After dilution with water (8 ml) the reaction solution was extracted with ether continuously during 1 day. Evaporation of the extract yielded *cyclo*heptane *trans* 1 : 2-diol (1·43 g, 74%) after

[17] A. B. Foster, *J. Chem. Soc.* 982 (1953).
[18] H. S. Isbell, J. F. Brewster, N. B. Holt and H. L. Frush, *J. Res. Nat. Bur. Stand.* **40**, 129 (1948).
[19] H. G. Derx, *Rec. Trav. Chim.* **41**, 312 (1922).
[20] R. Criegee, B. Marchand and H. Wannowius, *Liebigs Ann.* **550**, 111 (1942).
[21] R. Willstatter, *Liebigs Ann.* **317**, 204 (1901).

isolation as a colourless liquid b.p. 100° (vapour)/0·50 mm which solidified on cooling, m.p. 60–62° without recrystallisation.[18]

Indan *trans*-1:2-diol,[5] m.p. 156–157° and *cyclo*pentane trans-1:2-diol[5] b.p. 131°/15–20 mm were prepared from the appropriate olefins by the above general procedure. *cyclo*Hexane *trans*-1:2-diol, m.p. 102–103° was prepared by the method of Roebuck and Adkins.[4]

*Preparation of* cis-*diols*

The general method described by Clarke and Owen[6] when applied to the appropriate olefins gave *cyclo*hexane *cis*-1:2-diol[6] (14%), m.p. 93–94°, *cyclo*heptane cis-1 : 2-diol[18] (11%) m.p. 45–46°, *cyclo*pentane *cis*-1:2-diol[18] (11%) b.p. 133° (vapour)/29 mm, and indan *cis*-1:2-diol[5] (10·8–14·5%), m.p. 96–98°. The m.p.'s are in good agreement with those reported in the literature.

3:4-*Di*-O-*acetyl* 1:5-*anhydro* 2-*deoxy*-D-threo*pentitol*

A solution of 3:4-di-O-acetyl-D-xylal [3 g, m.p. 36–38°, $[\alpha]_D^{20}$ −288°(*c*, 1·0 in water), prepared according to the method of Overend, Shafizadeh and Stacey[22]] in aqueous alcohol (100 ml, 1:1 v/v) in which was suspended platinum oxide (100 mg) was shaken in an atmosphere of hydrogen at a slight over pressure at room temperature. Absorption of hydrogen was complete within 30 min and after removal of catalyst and solvents the *product* (1·3 g, 43%) was isolated as a colourless liquid b.p. 102° (vapour)/0·5 mm, $[\alpha]_D^{20}$ −38°(*c*, 0·85 in $CHCl_3$), $[M]_D$ −77° (Found: C, 54·1; H, 6·6. $C_9H_{14}O_5$ requires C, 53·4; H, 6·9%).

1:5-*Anhydro*-2-*deoxy*-D-threo*pentitol*

A solution of 3:4-di-O-acetyl 1:5-anhydro-2-deoxy-D-*threo*pentitol (1·4 g) in 6 N-sodium hydroxide (8 ml) and ethanol (8 ml) was boiled under reflux for 2 hr. After removal of sodium ions by Amberlite [IR-120 ($H^+$)] and evaporation of the solvents the product was isolated as a colourless liquid b.p. 75–80° (vapour)/0·5 mm which crystallised on storage to yield a very hygroscopic solid (0·5 g, 60·7%) m.p. 69° (without recrystallisation), $[\alpha]_D^{20}$ −29·6° (*c*, 2·5 in water), $[M]_D$ −35° (Found: C, 50·6; H, 8·6. $C_5H_{10}O_3$ requires C, 50·8; H, 8·5%).

3:4-*Di*-O-*acetyl*-1:5-*anhydro*-2-*deoxy*-L-erythro*pentitol*

A solution of 3:4-di-O-acetyl-L-arabinal [3·2 g, b.p. 110–140° (vapour)/0·01 mm, $[\alpha]_D^{20}$ −236° (*c*, 1·12 in $CHCl_3$), prepared according to the method of Deriaz *et al.*[23]] was hydrogenated and isolated as for the *threo* isomer to yield the product (2·2 g, 67%), b.p. 86–90° (vapour)/0·2 mm, $[\alpha]_D^{20}$ +75° (*c*, 1·0 in $H_2O$) $[M]_D$ +151°. (Found; C, 53·6; H, 6·9. $C_9H_{14}O_5$ requires C, 53·4; H, 6·9%).

1:5-*Anhydro*-2-*deoxy*-L-erythro*pentitol*

(*a*) 3:4-Di-O-acetyl-1:5-anhydro-2-deoxy-L-*erythro*pentitol (1·4 g) was saponified as for the *threo* isomer and the product (0·5 g, 60·7%) isolated as a colourless liquid b.p. 120° (vapour)/0·2–0·3 mm, $[\alpha]_D^{20}$ +64° (*c*, 1·5 in water), $[M]_D$ +75°. (Found: C, 51·2; H, 8·9. $C_5H_{10}O_3$ requires C, 50·8; H, 8·5%).

[22] W. G. Overend, F. Shafizadeh and M. Stacey, *J. Chem. Soc.* 671 (1950).
[23] R. E. Deriaz. W. G. Overend, M. Stacey, E. G. Teece and L. F. Wiggins, *J. Chem. Soc.* 1879 (1949).

(*b*) A solution of L-arabinal [0·8 g, m.p. 80–82°, $[\alpha]_D^{20}$ −202° (*c*, 3·0 in water) prepared according to the method of Deriaz *et al.*[23]] in aqueous ethanol (20 ml, 1:1 v/v) was shaken at room temperature in an atmosphere of hydrogen at slight over pressure and in the presence of platinum oxide (50 mg). Hydrogen absorption was complete within 1 hr and after removal of catalyst and evaporation of the solvents 1:5-anhydro-2-deoxy-L-*erythro*pentitol (0·57 g, 70·4%) was isolated as a colourless liquid b.p. 118–120° (vapour)/0·2–0·3 mm with physical constants identical to those of the product from (*a*).

1:4-*Anhydro*-L-*threitol*

A solution of butyl L-tartrate (10 g, $n^{16·5}$1·4450, $[\alpha]_D^{20}$ +10·2°) in dry tetrahydrofuran (50 ml) was slowly added to a well stirred mixture of lithium aluminium hydride (6 g) in tetrahydrofuran (150 ml) and ether (75 ml) and the final solution boiled under reflux for 1·5 hr. Thereafter the mixture was decomposed by the addition of water (200 ml) the precipitate removed by centrifugation, washed with water and the combined supernatants evaporated. The residue was dissolved in aqueous methanol (200 ml, 1 : 1 v/v) and the solution neutralised with $CO_2$. After removal of insoluble inorganic material and evaporation of the filtrate L-threitol was obtained as a colourless glass which failed to crystallise. It was therefore dissolved in aqueous sulphuric acid (20 ml, 1 : 1 v/v) and shaken during 1 hr with benzaldehyde (15 ml). After dilution of the reaction mixture with water, the crystalline precipitate was collected, washed with water and recrystallised from toluene to yield 1:2:3:4-di-O-benzylidene-L-threitol[24] (2·2 g), m.p. 215–217°, $[\alpha]_D^{25}$ +81° (*c*, 0·5 in $CHCl_3$).

The dibenzylidene derivative (2·2 g) was hydrolysed by treatment with a boiling mixture of N-sulphuric acid (10 ml) and ethanol (30 ml) for 30 min. The hydrolysate was concentrated, extracted with ether and freed from anions with Amberlite IRA–400 ($HO^-$) and concentrated. Recrystallisation of the residue gave L-threitol[24] (0·5 g) m.p. 88–89°, $[\alpha]_D^{20}$ −4° (*c*, 8·0 in water).

L-Threitol (2·17 g) was treated with a mixture of water (2·2 g) and sulphuric acid (2·2 g) in a sealed tube at 120° for 1 day. After dilution of the hydrolysate with water (75 ml) anions were removed with Amberlite IRA-400 ($HO^-$) and the solution concentrated. 1:4-Anhydro-L-threitol (L-threitan) was obtained from the residue as a hygroscopic colourless liquid (1·1 g) b.p. 120° (vapour)/15–17 mm which solidified on storage, m.p. 63–64° (without recrystallisation), $[\alpha]^{20}$ −4° (*c*, 7·2 in water). Klosterman and Smith[24] quote $[\alpha]_D^{25} = -5°$ (in water).

1:4-*Anhydro erythritol*

A solution of erythritol (3 g) in water (3 g) and sulphuric acid (3 g) was heated in a sealed tube for 2 days at 120°. 1:4-Anhydro erythritol (1·3 g) isolated as for the *threo*-isomer was obtained as a colourless hygroscopic liquid b.p. 144° (vapour)/2–3 mm $n^{20}$1·4767. Klosterman and Smith[24] quote $n_D^{24}$ 1·4370 for this compound.

*Zone electrophoresis of diols*

The zone electrophoretic (ionophoretic) mobility of the diols in Table 1 were determined using the apparatus and technique described by Foster[7b] with a borate buffer[25] of pH 10. The mobility is given as an $M_G$ value which is defined as the

[24] H. Kolsterman and F. Smith, *J. Amer. Chem. Soc.* **74**, 5336 (1952).
[25] A. B. Foster, P. A. Newton-Hearn and M. Stacey, *J. Chem. Soc.* 30 (1956).

mobility of a substance relative to that of D-glucose under standard conditions (see Foster[26] for a detailed discussion).

*Oxidation of diols*

(a) *With periodate.* A solution of the diol (0·43 m-mole, 50 mg) in water (5 ml) was treated with 0·05 M aqueous sodium metaperiodate (15 ml) and the volume rapidly adjusted to 100 ml, all solutions being kept at 0°. Aliquots were withdrawn at suitable time intervals and unchanged oxidant determined by the standard arsenite method.[27] In those cases where the rate of reaction was slow enough to follow the times ($t_{\frac{1}{2}}$) of half oxidation of the diols was determined and recorded in Table 1.

(b) *With lead tetra-acetate.* A solution of the diol (26 mg) in glacial acetic acid was adjusted to 20° and treated with a 0·1315 N-solution (49 ml) of lead tetra-acetate in glacial acetic acid also at 20°. The volume was rapidly adjusted to 50 ml. At suitable time intervals unconsumed oxidant was determined in aliquots (5 ml) by a standard procedure.[28] In those cases where oxidation was not too fast the time ($t_{\frac{1}{2}}$) of half oxidation was determined and recorded in Table 1.

1:3-*Dioxan*-5-*ol* (1:3-O-*methylidene glyceritol*)

This compound was obtained as a colourless liquid b.p. 82° (vapour)/11 mm, $n^{20}$ 1·4533 using the method of Hibbert and Carter[29] who quote similar physical constants.

Methylation of this compound as described by Hibbert and Carter[29] gave 5-O-methyl 1:3-dioxan-5-ol (2-O-methyl 1:3-O-methylidene glyceritol) b.p. 147° (vapour)/760 mm, $n^{25}$1·4230. Acidic hydrolysis of the methyl ether[29] gave 2-O-methyl b.p. 120° (vapour)/13 mm, $n^{23}$ 1·4476 which was completely resistant to attack by lead tetra-acetate under the conditions described above.

*Infra-red spectra.* These were measured in 2 cm layers in $CCl_4$ solution with a 2500 l.p.i. grating used in the fourth order on the spectrometer previously described.[30] Concentration of the diol was always $<0{\cdot}005$ M; the extinction coefficients, $\varepsilon$, are maximum values and are equal to $(1/cl)\log_{10}(I_0/I)$ with $l$ in cm and $c$ in moles/litre. The results are recorded in Table 1.

[26] A. B. Foster, *Adv. Carbohydrate Chem.* **12**, 81 (1957).
[27] J. M. Bobbitt, *Adv. Carbohydrate Chem.* **11**, 1 (1956).
[28] R. C. Hockett and W. S. McClenahan, *J. Amer. Chem. Soc.* **61**, 1667 (1939).
[29] H. Hibbert and N. M. Carter, *J. Amer. Chem. Soc.* **50**, 3120 (1928).
[30] H. Spedding and D. H. Whiffen, *Proc. Roy. Soc.* A **238**, 245 (1956).