Nuclear Magnetic Resonance Experiments on Acetals. Part LVIII.[1] Conformational Studies of 4-Methylene-1,3-dioxan

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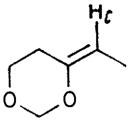
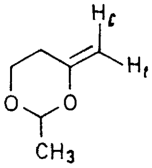
Complete analysis of the ^1H n.m.r. spectra of 4-methylene- (1), 2-methyl-4-methylene- (2), and 6-methyl-4-methylene-1,3-dioxan (3) clearly discloses substantial flattening in the C(2)–O(3)–C(4)–C(5)–C(6) region, but not in the C(6)–O(1)–C(2) region. A typical torsion angle set is proposed. The barrier to ring inversion in (1) is found to be 5.4 ± 0.3 kcal mol^{-1} (T_c = −161 ° in Freon-21).

RECENTLY, we reported that the conformations of 5-alkylidene-1,3-dioxans are markedly flattened chairs.[1] 1,3-Dioxans with sp^2 hybridised C(4) have been little investigated except for 4-oxo-derivatives for which data have been recently presented.[2] The C(2)–O(3) monoplanar (half-chair) form was proposed from ^1H n.m.r. parameters for the 2,6-*cis*-dialkyl derivatives, while the corresponding *trans*-derivatives would occupy twist-boat conformations. We are interested in the related 4-alkylidene-1,3-dioxans, and this system offers some further spectroscopic advantages lacking in the oxo-derivatives studied by Pihlaja:[2] (i) the presence of possible long range allylic coupling phenomena,[3] (ii) the evaluation of the Lambert–Buys criterion allowing [4–6] a description of ring shape, and (iii) the possibility of detecting ^2J parallel effects.[7] Also, because of the anancomeric nature of the models chosen for the oxo-compounds no information was gained about the barrier to topomerization.



(1)



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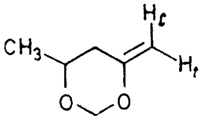

(3)

Together with the parent unsubstituted 4-methylene-1,3-dioxan (1) we have studied the 2- (2), and 6-methyl-substituted derivatives (3). The methyl groups will anchor the ring to a major extent.

RESULTS AND DISCUSSION

300 MHz Spectral data are in Tables 1 and 2. The assignment of the protons is straightforward, except for H$_c$ and H$_t$, because it proved impossible to assign these on an absolute basis or with the aid of INDOR, as for the others. To complete the assignment we used empirical shift-correction rules,[8] and compared the results with data obtained for ethers[9] and 1,3-dioxens[10] (see Appendix).

TABLE 1

Shift values δ (from Me_4Si internal standard at 300 MHz; 5 vol %) of 2-(2) and 6-methyl-4-methylene-1,3-dioxan (3) and 4-methylene-1,3-dioxan (1)

Compound (solvent)	(1) CS$_2$		(2)		(3)	
	R.t.[b]	−95°	CDCl$_3$	C$_6$D$_6$	CCl$_4$	C$_6$D$_6$
H(2a)	4.78	4.74	4.78	4.59	4.66	4.52
H(2e) [Me(2)]			(1.39)	(1.33)	5.03	5.02
H$_c$	4.06	4.13	4.16	4.02	4.03	4.02
H$_t$	4.33	4.34	4.44	4.57	4.34	4.58
H(5a)	2.27	2.26	2.56_5	2.30	2.15[a]	2.01
H(5e)			2.11_5	1.52	2.15[a]	1.71
H(6a)	3.73	3.74	3.72_5	3.29	3.66_5	3.29
H(6e) [Me(6)]			4.10	3.68	(1.22_5)	(0.97)

[a] Isochronous (degenerated). [b] R.t. = room temperature.

Geminal Couplings.—An overall flattening of the ring is obvious[10] from $|^2J(2)|$ 5.4 Hz which is lower than the chair value of 6.3 Hz in 1,3-dioxan, although resonance in the chair form between oxygen *p* electrons and the π orbitals may already have lowered the oxygen *p* electron density to some extend, and thus also the absolute value of $^2J(2)$.[11] The observed value however is almost that expected[10] for a half-chair form, while a 2,5 twist-boat would have resulted in −2.8 Hz.[12]

An estimate of the C(4)–C(5) torsion angle can be gained from $^2J(5)$, which is 0.9—1.2 Hz more negative than in the case in 1,3-dioxans (Table 2), as a result of the presence of the adjacent π-system. From the data of Barfield and Grant[13] we can conclude that the angle

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[1] Part LVII, M. Anteunis and R. Camerlynck, *Tetrahedron*, in the press.

[2] P. Äyräs and K. Pihlaja, *Tetrahedron*, 1973, **29**, 1311.

[3] (*a*) G. P. Newsoroff and S. Sternhell, *Austral. J. Chem.*, 1972, **25**, 1669; (*b*) R. J. Spear and S. Sternhell, personal communication.

[4] J. B. Lambert (*a*) *J. Amer. Chem. Soc.*, 1967, **89**, 1836; (*b*) *Accounts Chem. Res.*, 1971, **4**, 87.

[5] H. R. Buys, *Rec. Trav. chim.*, 1969, **88**, 1003.

[6] J. Gelan, G. Swaelens, and M. Anteunis, *Bull. Soc. chim. belges*, 1970, **79**, 321.

[7] D. Tavernier, Ph.D. Thesis, State University of Gent, 1972.

[8] U. E. Matter, C. Pascual, E. Pretch, A. Pross, W. Simon, and S. Sternhell, *Tetrahedron*, 1969, **25**, 691.

[9] J. Feeney, A. Ledwith, and L. H. Sutcliffe, *J. Chem. Soc.*, 1962, 2021; J. Feeney and L. H. Sutcliffe, *Spectrochim. Acta*, 1968, **24**, 1135.

[10] M. Anteunis, *Bull. Soc. chim. belges*, 1966, **75**, 413; M. Anteunis, G. Swaelens, and J. Gelan, *Tetrahedron*, 1971, **27**, 1917.

[11] M. Anteunis, G. Swaelens, F. Anteunis-De Ketelaere, and P. Dirinck, *Bull. Soc. chim. belges*, 1971, **80**, 409.

[12] M. Anteunis and G. Swaelens, *Org. Magnetic Resonance*, 1970, **2**, 389.

formed between the π-lobes and H(5a) is *ca.* 350° and between the lobes and H(5e) *ca.* 110° (Figure 1). This leads to a C(4)–C(5) torsion angle of *ca.* 35—40°.

TABLE 2

Spin coupling constants[a] of 4-methylene-1,3-dioxans (2) and (3) and comparative data for 2-alkyl-1,3-dioxan (A), 4-methyl-1,3-dioxan (B), *cis*-2,4-dimethyl-1,3-dioxan (C), [b] *cis*-4,6-dimethyl-1,3-dioxan (D), and *cis*-2,6-dimethyl-4-oxo-1,3-dioxan (E). [c]

	J/Hz							
	(2)		(3)	(A)	(B)	(C)	(D)	(E)
Coupling	−40°	+40°						
H_c, H_t	−0.8							
2a, 2c			−5.4		−6.1		−6.1	
5a, 5e	−14.1	−14.1	−13.8		−12.6	−13.2	−12.6	−17.8
6a, 6e	−10.9	−10.8		−11.5	−11.6	−11.2		
5a, 6a or (4a)	12.7_5	12.1_6	11.2	12.4	11.4	11.8	11.1	10.9
5a, 6e or (4e)	6.3	6.3		5.0	4.9	5.2		
5e, 6a or (4a)	2.8	3.18	2.8	12.6	2.6	2.9	2.3	4.44
5e, 6e or (4e)	1.2	1.78		1.3	1.7	1.7		
5a, H_c	-2.0_5	-1.9_5	-1.9_5					
5a, H_t	-2.0_5	-1.9_5	-1.9_5					
5e, H_c	-0.4_5	-0.2_5	−0.4					
5e, H_t	-0.4_5	-0.2_5	−0.4					
6e, H_c	−0.2							
6e, H_t	+0.5							
2a, H_c	0.1							
2a, H_t	0.1							
2e, H_c			0.7					
2e, H_t								
Me, H	5.0_5	5.0_4						

[a] For compounds (2) and (3) the analytical data were refined by SIMEQ 16/II simulations. [b] Ref. 7. [c] Ref. 2.

$|^2J(6)|$ Is somewhat smaller than the corresponding 1,3-dioxan values. This also points to a deviation in the O(1)–C(6) torsion angle. Although the protons involved are less sensitive to torsional relationships in an OCH_2C than in an OCH_2O system,[7] the decrease is almost equal to that observed in 1,4-dioxen [$^2J(5)$ −10.8 Hz][14] where a deformation (flattening) is certainly present (*cf.* ref. 15).

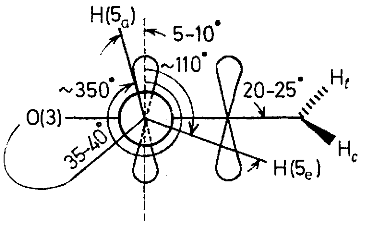
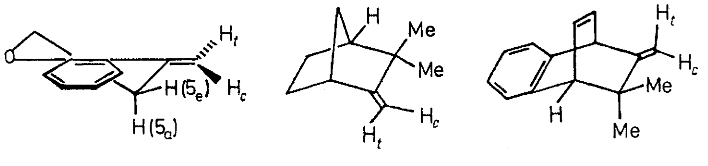


FIGURE 1

Allylic Couplings (*Figure* 1).—With dihedral angles of ϕ *ca.* 110 and *ca.* 350°, one would expect[3a] allylic couplings of, respectively, −0.2 to −1.0 Hz [$^4J(5e,H_c)$ and $^4J(5e,H_t)$] and −2.0 to −2.5 Hz [$|^4J(5a,H_c)| \leqslant |^4J(5a,H_t)|$]. The observed values are in satisfactory agreement. The somewhat less negative values (-1.9_5 to -2.0_5 Hz) than expected for the latter may be compared with those observed for the chroman (4),*,[3b] which presumably is a half-chair, with ϕ values *ca.* 360 and 120° (Figure 2).



(4) (5) (6)

FIGURE 2

Vicinal Couplings.—From the ratio $R = J^c/J^t$ (the Lambert–Buys criterion),[4,6] one may obtain a good approximation of torsion angle values in XCH_2CH_2Y groups, even when unsaturation is present.[5] From $R = 1.5$ in the present 4-methylene derivatives, one computes[5] a C(5)–C(6) torsion angle of *ca.* 52°, a value almost identical with that found in methylenecyclohexane,[16] and to be compared with a value of 54—55° in 1,3-dioxans.[5,6,17] It is noteworthy that the individual values for J(5a,6a) and J(5e,6e) are almost equal to those observed for chair 1,3-dioxans. This is expected, even for flattening, because the former is not very sensitive to torsional changes, and the latter has already been diminished in the chair form by the spatial orientation of the oxygen *p*-lobes,[10,18] a factor which compensates for the intrinsic decrease expected for the flattened 4-methylene derivatives. On the other hand, the tendency towards

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* $^4J(5e, H_c)$ −0.85 Hz; $^4J(5e, H_c)$ −0.48 Hz; $^4J(5a, H_c)$ −2.19 Hz, and $^4J(5a, H_t)$ −2.17 Hz.

[13] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

[14] G. P. Pfundt and S. Farid, *Tetrahedron*, 1966, **22**, 2237.

[15] M. Anteunis and R. Camerlynck, *Tetrahedron*, in the press.

[16] R. Bucourt, *Topics in Stereochem.*, 1974, **8**, 161.

[17] R. J. de Kok and C. Romers, *Rec. Trav. chim.*, 1970, **89**, 313.

[18] M. Anteunis, D. Tavernier, and F. Borremans, *Bull. Soc. chim. belges*, 1966, **75**, 396.

increase of both ${}^3J$(5a,6e) and ${}^3J$(5e,6a) indicates the decrease in the C(5)–C(6) torsion angle, but the increase in J values is not pronounced enough to fit the possibility of twist-boat forms. For 2,5-twist-boats for instance, ΣJ *ca.* 31 Hz [19] and here this value is only 23—24 Hz.

Long Range Couplings involving H(2).—We have observed long range couplings (Table 2) between both H(2a) and H(2e) with H_c and H_t in (2) and (3). Feeney has shown [9] that for vinyl ethers long range phenomena of this kind are observed only through p(O)–π overlap. It is therefore concluded that overlap exists in the 4-methylenedioxans.

Pseudo-homoallylic Couplings ${}^5J$(C*H*=C–C–C*H*).—We found (Table 2) ${}^5J$(6e,H$_t$) +0.5 Hz and ${}^5J$(6a,H$_c$) —0.2 Hz for compound (2). Such patterns have, to our knowledge, been reported only for camphene (5) [20] and in (6) [3c] (Figure 2). It was originally observed in cyclopentane derivatives.[21] It seems reasonable that $|{}^5J(6a,H_c)| < |{}^5J(6e,H_t|$,[3c] as found for (6) (i.e. coupling between the bridge-head proton and H$_t$ and H$_c$).

Low Temperature Studies.—We could not determine at 60 MHz the value of peak separation $\Delta\nu_{\text{max.}}$ between axial and equatorial protons for the frozen conformers of (1) with enough precision. The lowest temperature we could reach was −163°, just sufficient to observe the coalescence temperature T_c at −161°. For sufficiently low temperatures, however, model calculations for $\Delta G^{\ddagger}$ of topomerization show that fluctuations in $\Delta\nu_{\text{max.}}$ have but little influence on the final value of $\Delta G^{\ddagger}$, and computation at $-161 \pm 2°$ (and $\Delta\nu_{\text{max.}}$ *ca.* 40 Hz *) (in Freon-21 at 60 MHz) gives a value for $\Delta G^{\ddagger}$ of 5.4 ± 0.3 kcal mol^{-1}. This is an appreciable lowering by comparison with 1,3-dioxan (9.7 kcal mol^{-1})[23] and lower than the value obtained for 1,3-dioxen (7.1 kcal mol^{-1}),[24] but almost identical with the value for 5-methylene-1,3-dioxan (5.5 kcal mol^{-1}).[24]

Conformation of 4-*Methylene*-1,3-*dioxan.*—All the criteria we have detailed point to typical features, from which we are able to deduce the basic conformation of the system. Figure 1 depicts the partial conformation around O(3)–C(4)–(C)5 system deduced from ${}^2J$(5) and the observed allylic couplings. From ${}^2J$(6) a substantial deviation in the O(1)–C(6) region from the basic value of 59° in 1,3-dioxan [17] is revealed, and the R value gives a good indication that the torsion around C(5)–C(6) is *ca.* 52°. From ${}^2J$(2) we know that the mean angles around C(2)–O(3) and C(2)–O(1) are certainly not 63°, as is the case in 1,3-dioxan,[17] and a pair of values, one *ca.* 40° and the other *ca.* 55°, agree best [11] with ${}^2J$(2) −5.4 Hz. Finally we must account for a possible overlap between O(3) and the C(4) π bond, which will be maximal if the ring torsion angle around this bond is *ca.* 30°. This leads us to Figure 3A.

The torsion values ϕ_1—ϕ_6 may be approximately derived on an entirely different basis according to the principle of distribution patterns for deformation in ring systems, as developed by Bucourt [16] and which we had occasion to apply previously with success in the case of 5-methylene-1,3-dioxan.[24] Strictly speaking, the method is only valid for cyclohexanes, as it is based on results obtained by model calculations on the saturated hydrocarbon. If ultimate refinement can be done by the introduction of known torsion angles, as deduced from our earlier criteria, the method gives an excellent semi-quantitative result. It is based upon the recognition that deformation of certain torsion angles cannot remain local to the bond involved and that they are reflected in other bonds according to a certain pattern. The original deformation being taken as 100%, the torsions of the bonds next to this experience the same deformation but to only *ca.* 60% extent, the subsequent bonds remain almost unchanged (small reverse deformation of *ca.* 10%), but the bond opposite to the original site of change will be deformed in the reverse direction to the extent of *ca.* 30% (Figure 3B).

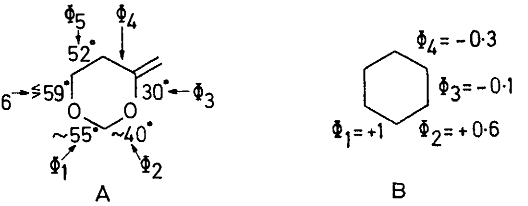

FIGURE 3

These principles may be used to predict the final distribution of distortions given certain torsion angles and a knowledge of the original undisturbed values. In order to obtain convergence, one may start from two sets of model compounds, either carbocyclic or heterocyclic. This compensates for deviations because the pattern of torsional deformations along the bonds in the ring will certainly be somewhat different depending on the system under consideration. The flow of changes is illustrated in Figure 4. Starting from the torsion value of 56° in cyclohexane,[25] a new distribution pattern b will be obtained when changing one of the angles, *e.g.* ϕ_3 from 56 to 30° [as deduced earlier for the O(3)–C(4) bond]. Typically, the values ϕ_1 and ϕ_5 have not been changed.[26]

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* This value is substantiated by a shift study of 6-methyl-4-methylene-1,3-dioxan (3) and the known influence of alkyl substitution on the shifts of ring protons.[22]

[19] D. Tavernier and M. Anteunis, *Bull. Soc. chim. belges*, 1967, **76**, 157.

[20] S. H. Grover and J. B. Stothers, *J. Amer. Chem. Soc.*, 1969, **91**, 4331.

[21] M. Anteunis and F. Compernolle, *Bull. Soc. chim. belges*, 1967, **76**, 482.

[22] D. Tavernier and M. Anteunis, *J. Magnetic Resonance*, 1974, **13**, 181.

[23] E. Coene and M. Anteunis, *Bull. Soc. chim. belges*, 1970, **79**, 37; *cf.* D. Tavernier, M. Anteunis, and E. Bernaert, *ibid.*, in the press; H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org Magnetic Resonance*, 1969, **1**, 67; H. Friebolin, S. Kabuss, W. Maier, and A. Lüttringhaus, *Tetrahedron Letters*, 1962, 683.

[24] M. Anteunis and R. Camerlynck, *Tetrahedron*, in the press.

[25] H. G. Schmid, A. Jaeschke, H. Friebolin, S. Kabuss, and R. Mecke; *Org. Magnetic Resonance*, 1969, **1**, 263; C. Altona and M. Sundaralingan, *Tetrahedron*, 1970, **26**, 925; N. L. Allinger and F. Wu; *ibid.*, 1971, **27**, 5093.

[26] R. Bucourt and D. Hainaut, *Bull. Soc. chim. France*, 6519, 1366.

We have argued however that ϕ_5 must be close to 52° and so a second change for ϕ_5 is introduced, resulting in the values illustrated in *c*. The same 'factorisation flow' may be introduced, starting from typical values in 1,3-dioxan, resulting in the values of *f*. Except for ϕ_1, the two sets *c* and *f* resemble each other sufficiently closely to take these final values for granted. While inspecting *f* we know that some deformation must still be allowed with respect to ϕ_1, because the values of 63 and 47° are not in satisfactory agreement with $^2J(2)$ −5.4 Hz. Therefore, *c* seems to represent the best set. One notes that ϕ_6 now explains the observed $^2J(6)$ value as previously discussed.

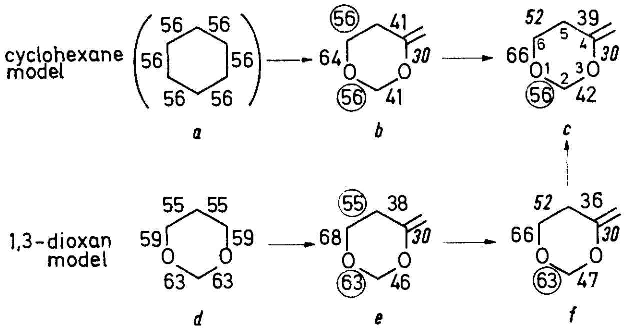

FIGURE 4

Comparison between 4-*Methylene*-, *and* 4-*Oxo*-1,3-*dioxan* (*Table* 2).—In *cis*-2,6-dimethyl-4-oxo-1,3-dioxans,[2] $^2J(5)$ is −17.8 Hz, and this reflects[13] the fact that τ [C(4) (=O)–C(5)] must be almost zero. The vicinal coupling values $^3J(5a,6a)$ 10.9 and $^3J(4a,5e)$ 4.44 Hz certainly disclose much more pronounced flattening than is the case in the 4-methylene derivatives. There are at least two good reasons for the difference between the two kinds of molecules. (i) In the 4-oxo-derivative there is more pronounced mesomeric overlap, $-\underset{\cdot\cdot}{\ddot{O}}-C=O \longleftrightarrow -\overset{+}{O}=C-O^{-}$, leading to the half-chair form as the basic conformation,[2] and (ii) the larger steric requirements of the methylene group prevents the molecule from reaching flattening as pronounced as in the oxo-derivative in the region of C(4). The latter feature may also be illustrated by the difference in the barrier to rotation that exists between 2-methylpropene (2.1 kcal mol^{-1}) and acetone (0.8 kcal mol^{-1}).[27]

Finally, it is interesting to note that whereas 5-methylene-1,3-dioxan prefers a flattened chair,[24] 4-methylene-1,3-dioxan has some more complex alterations as the result of possible p(O) lobe–π-lobe overlap.

EXPERIMENTAL

4-Methylene-1,3-dioxan derivatives are very unstable and were prepared immediately before use and stored at very low temperature. They cannot be purified by g.l.c. The preparation of 2,6-dimethyl-4-methylene-1,3-dioxan, as described below for 2-methyl-4-methylene-1,3-dioxan, failed in the acetalization step, even under the mild kinetically-controlled conditions which have recently been developed for the preparation of strained cyclic acetals.[28]

4-*Methylene*-1,3-*dioxan* (1).—4-Bromomethyl-1,3-dioxan (20 g),[29] b.p. 88—90° at 20 mmHg, was refluxed during 30 min over potassium hydroxide pellets (40 g), and the volatile fraction, distilled under low vacuum, was redistilled, yield 8.9 g (80%), b.p. 48—51° at 30 mmHg, (Found: C, 59.75; H, 7.95. Calc. for $C_5H_8O_2$: C, 60.0; H, 8.05%).

2-*Methyl*-4-*methylene*-1,3-*dioxan* (2).—This was prepared in five steps, starting from but-2-yne-1,4-diol (Aldrich) which was converted into 1,4-dihydroxybutan-2-one according to Reppe's hydration method.[30] Reduction of the ketone afforded butane-1,2,4-triol (48%), b.p. 151° at 1 mmHg. This was acetalized with depolymerized acetaldehyde by heating in 30 : 70 sulphuric acid–water, and 2-methyl-4-hydroxymethyl-1,3-dioxan, b.p. 93° at 11 mmHg, δ 4.58 (2-H), 1.65 (5a-H), and 1.25 (5e-H), was isolated in 27% yield from the chloroform extract. This was tosylated in 78% yield with tosyl chloride in pyridine, and the crude mixture was then treated in dry acetonitrile with a 20% excess of lithium bromide. (It is important to remove precipitated lithium tosylate every hour by filtration.) After 8 h the solution was evaporated to dryness (Rotavap) and 2-methyl-4-bromomethyl-1,3-dioxan was obtained in 64% yield, b.p. 79—82° at 13 mmHg [Found: C, 36.7; H, 5.75, Br (Schöniger), 40.55. Calculated for $C_6H_{11}BrO_2$: C, 36.95, H, 5.7; Br, 40.95%]. The bromide was further treated as for (1) to give the final product (2), yield 81%, b.p. 74—78° at 60 mmHg. (Found: C, 62.9; H, 8.8. Calc. for $C_6H_{10}O_2$: C, 63.15; H, 8.85%).

6-*Methyl*-4-*Methylene*-1,3-*dioxan* (3).—4-Hydroxypent-1-ene (61%), b.p. 120°, was prepared according to the literature[31] by adding a mixture of allyl bromide and depolymerized acetaldehyde (in slight excess) to previously activated (iodine and allyl bromide) magnesium in ether at −10°. Decomposition with sulphuric acid was executed below 10°. Pentane-1,2,4-triol was obtained from 4-hydroxypent-1-ene (60 g) in water (2 l) by oxidation with potassium permanganate (110 g) in water (3 l) at 5°. Manganese dioxide was discarded by centrifuging, and the solution evaporated under reduced pressure, yield 44.4 g (53%), b.p. 150—155° at 0.2 mmHg. *cis*-6-Hydroxymethyl-4-methyl-1,3-dioxan was obtained from reaction of the triol with formaldehyde, by analogy with the other methylene derivatives, yield 28%, b.p. 92—102° at 13 mmHg. N.m.r. analysis revealed [J (5,6) and J (4,5)] that no *trans*-derivative had been formed. The hydroxy derivative was tosylated (crude yield 71%) and treated with lithium bromide as previously described to yield (61%) *cis*-6-bromomethyl-4-methyl-1,3-dioxan, b.p. 76—78° at 12 mmHg (Found: C, 37.05; H, 5.65; Br, 40.6. Calc. for $C_6H_{11}BrO_2$: C, 36.95; H, 5.7; Br, 40.95%). 6-Methyl-4-methylene-1,3-dioxan was formed as for the other derivatives in 73% yield, b.p. 82—84° at 15 mmHg.

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[27] F. Morino and E. Hirota, *Ann. Rev. Phys. Chem.*, 1969, **20**, 139; J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 39.

[28] M. Anteunis and C. Becu, *Synthesis*, 1974, 23.

[29] C. C. Price and I. F. Krishnamurti, *J. Amer. Chem. Soc.*, 1950, **72**, 5335.

[30] W. Reppe, *Annalen*, 1955, **596**, 67.

[31] W. H. Janko, H. S. Mosher, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1945, **67**, 666; L. Stöhr, *Ber.*, 1939, **72**, 1138.

APPENDIX

Pascual *et al.* have developed [8] from data for over 4 000 literature cases equation (1) in order to predict shift values for olefinic protons in substituted ethylenes. The values of the increments that we need for the present study are given in Table 3. With the aid of equation (1) we compared a series of 1,3-dioxan derivatives possessing olefinic protons. As Table 4 shows the assignments of H_c and H_t in methylenedioxans become unambiguous.

$$\delta(\text{in p.p.m.}) = 5.25 + Z_{gem} + Z_{cis} + Z_{trans} \qquad \text{(i)}$$

TABLE 3

	H	Alkyl	Carbo-cyclic	$ROCH_2$	AlkylO	=C–C–O
Z_{gem}	0	0.45	0.69	0.64	1.22	1.21
Z_{cis}	0	−0.22	−0.25	−0.01	−1.07	−0.60
Z_{trans}	0	−0.28	−0.28	−0.01	−1.21	−1.00

TABLE 4

Comparison between calculated and experimental shift values in dioxan derivatives using Pascual's empirical increments [8]

Compound		Calc.	Obs.		Calc.	Obs.	Solvent
4-Methylene-1,3-dioxan	H_c	4.00	4.06	H_t	4.37	4.33	CS_2
6-Methyl-4-methylene-1,3-dioxan	H_c	4.00	4.03	H_t	4.37	4.34	CCl_4
2-Methyl-4-methylene-1,3-dioxan	H_c	4.00	4.16	H_t	4.37	4.44	$CDCl_3$
1,3-Dioxen	H(4)	6.44	6.43	H(5)	4.89	4.78	CS_2
5-Methyl-1,3-dioxen	H(4)	6.22	6.28				CCl_4
5-Methylene-1,3-dioxan	$=CH_2$	4.72 [a]	4.79				CCl_4
2-Methyl-5-methylene-1,3-dioxan	$=CH_2$	4.72 [a]	4.93				$CDCl_3$
4-Methyl-5-methylene-1,3-dioxan			4.85				$CDCl_3$

[a] These values become 5.22 if increments of non alkyl-ring substitution are taken.

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