616. *Aspects of Stereochemistry. Part XXI.*[1] *Absolute Configuration of Benzylidene Derivatives of Some Acyclic Polyhydric Alcohols*[2]

By N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall, and J. M. Webber

Each member of a series of 2-phenyl-1,3-dioxan derivatives with equatorial substituents at positions 4 and 6 showed a single signal for benzyl protons in the range τ 4·82—5·02 in n.m.r. spectroscopy. Each 4-alkyl-2-phenyl-1,3-dioxolan of a series prepared by vigorous, acid-catalysed benzylidenation of various 2-alkylethane-1,2-diols showed two benzyl proton signals of comparable intensity in the ranges 4·62—4·67 and 4·46—4·52 which are assigned to the *cis*- (IIa) and *trans*-isomers (IIb), respectively. Using this data and arguments based thereon, absolute configuration has been assigned to the various isomeric forms of 2,4:5,6-di-*O*-benzylidene-3-*O*-methyl-D-glucitol, 2-*O*-benzyl-1,3:4,5-di-*O*-benzylidene-D-arabitol, 1,6-di-*O*-benzoyl-2,3:4,5-di-*O*-benzylidenegalactitol, and to a di-*O*-benzylidene-*meso-glycero-gulo*-heptitol.

In Part XX,[1] two forms of 2,4:5,6-di-*O*-benzylidene-3-*O*-methyl-D-glucitol were described which differed only in the arrangement of the substituents at the acetal carbon atom in the 5,6-*O*-benzylidene group. The problem of assigning the absolute configuration to these compounds prompted an examination of the n.m.r. spectra of a range of benzylidene acetals. This Paper is concerned with derivatives of acyclic di- and poly-hydric alcohols containing isolated cyclic benzylidene acetal groups; fused ring systems are considered in the following Paper.

The signal (the τ scale is used throughout) for the proton on the acetal carbon atom in benzylidene derivatives is unsplit and occurs in a region of the spectrum (4·0—5·1 for *ca.* 10% solutions in dioxan) which is usually free from other signals. Assignment of the signal was based on a comparison of spectra of selected acetals prepared from Ph·CHO and Ph·CDO.[3] 2-Phenyl-1,3-dioxan had a single benzyl proton signal at 4·95, and the

[1] Part XX, preceding Paper.

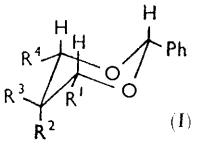
[2] Preliminary report of some of these results, N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall, and J. M. Webber, *Proc. Chem. Soc.*, 1964, 118.

[3] N. Baggett, B. Dobinson, A. B. Foster, J. Homer, and L. F. Thomas, *Chem. and Ind.*, 1961, 106; A. B. Foster, A. H. Haines, J. Homer, J. Lehmann, and L. F. Thomas, *J.*, 1961, 5005.

signals for a range of 4-, 5-, 4,5-, 4,6-, and 4,5,6-substituted compounds with the 4- and/or 6-substituents in equatorial positions were in the range 4·72—5·02 (see Table 1). The compounds in Table 1 may be allocated to one of two groups. First, those compounds

TABLE 1

Benzyl proton signals for some 2-phenyl-1,3-dioxan derivatives



(I)

	τ	R^1	R^2	R^3	R^4
2-Phenyl-1,3-dioxan (I)	4·95	H	H	H	H
cis-4-Hydroxymethyl- [13]	4·90	CH_2·OH	H	H	H
cis-4-Methoxymethyl- [13]	4·90	CH_2·OMe	H	H	H
cis,cis-4,6-Dimethyl- [8]	4·91	Me	H	H	Me
cis-5-Hydroxy- [17]	4·90	H	OH	H	H
trans-5-Hydroxy- [17]	5·02	H	H	OH	H
cis-5-Benzoyloxy- [a]	4·82	H	OBz	H	H
trans-5-Benzoyloxy- [a]	4·90	H	H	OBz	H
cis-5-Acetoxy- [b]	4·88	H	OAc	H	H
trans-5-Acetoxy- [b]	4·95	H	H	OAc	H
cis-5-Methanesulphonyloxy- [a]	4·84	H	OMs	H	H
trans-5-Methanesulphonyloxy- [a]	4·93	H	H	OMs	H
Di-*O*-benzylidenepentaerythritol [c]	4·96	H	CH_2·O·CHPh·O·CH_2		H
2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-erythritol [3]	4·86	H	H	OAc	CH_2·OAc
1,3-*O*-Benzylidene-4-deoxy-L-erythritol [3]	4·92	H	H	OH	Me
2-*O*-Acetyl-1,3-*O*-benzylidene-4-deoxy-L-erythritol [3]	4·90	H	H	OAc	Me
1,2,3,5-Tetra-*O*-acetyl-4,6-*O*-benzylidene-D-glucitol [d]	4·89	H	H	OAc	CH_2·OAc | (CH·OAc)$_2$
2,4-Di-*O*-acetyl-1,3-*O*-benzylidene-L-threitol [3]	4·81	H	OAc	H	CH_2·OAc
2,4,5-Tri-*O*-acetyl-1,3-*O*-benzylidene-L-arabitol [3]	4·81	H	OAc	H	CH_2·OAc | CH·OAc
1,3,5-Tri-*O*-acetyl-2,4-*O*-benzylidenexylitol [e]	4·73	CH_2·OAc	OAc	H	CH_2OAc
1,3,5,6-Tetra-*O*-acetyl-2,4-*O*-benzylidene-D-glucitol [f]	4·72	CH_2·OAc | CH·OAc	OAc	H	CH_2OAc
2,4-*O*-Benzylidene-3-*O*-methyl-D-glucitol [1]	4·73	CH_2·OH | CH·OH	OMe	H	CH_2·OH
2,4-*O*-Benzylidene-1,3,5,6-tetra-*O*-methyl-D-glucitol [1]	4·72	CH_2·OMe | CH·OMe	OMe	H	CH_2·OMe

[a] N. Baggett, M. A. Bukhari, A. B. Foster, J. Lehmann, and J. M. Webber, *J.*, 1963, 4157. [b] N. Baggett, J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *J.*, 1960, 2574. [c] J. Böeseken and B. B. C. Felix, *Ber.*, 1928, **61**, 787. [d] M. p. 164—169°, $[\alpha]_D$ +13° (*c* 2·5 in $CHCl_3$) (Found: C, 57·55; H, 6·0. $C_{21}H_{26}O_{10}$ requires C, 57·5; H, 6·0%). [e] R. M. Hann, A. T. Ness, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1946, **68**, 1769. [f] L. von Vargha, *Ber.*, 1935, **68**, 18, 1377.

with various combinations of R^1, R^3, and R^4 substituents [formula (I)] which exist predominantly, if not exclusively, at normal temperatures, in a conformation containing a chair form of the 1,3-dioxan ring with equatorial substituents; evidence in support of this statement has been presented for some of the compounds.[3] With one exception (*trans*-5-hydroxy-2-phenyl-1,3-dioxan, τ 5·02) the signals for the compounds in this group are in the range 4·86—4·96 (cf. benzaldehyde diethyl acetal, τ 4·89). The position of the signal

in more complex molecules will be influenced by the types and numbers of substituents attached to the 1,3-dioxan ring.

The second group contains compounds which have an R^2 substituent [formula (I)]; the conformational instability of several of these compounds has been demonstrated,[3] and the benzyl proton occupies a position intermediate between axial and equatorial. The signals for compounds of this type were in the range 4·82—4·90 not significantly different from those of the first group. For a particular *cis–trans*-pair of 5-substituted 2-phenyl-1,3-dioxan derivatives, the benzyl proton signal for the *cis*-isomer appeared at lower field (cf. results for 4-alkylcyclohexanols [4]).

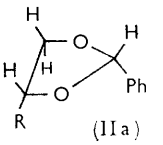
The above examples comprise β- and βC-benzylidene derivatives (using Barker and Bourne's terminology [5]); βT-acetals are encountered only in fused ring systems [6] and not as isolated cyclic acetals formed directly from acyclic polyhydric alcohols. Two simple diols which form βT-acetals are DL-pentane-2,4-diol and 2-methylpentane-2,4-diol; the benzyl proton signals (4·58 and 4·66, respectively) for the benzylidene acetals (III) and (IV) were at much lower field than those for the β- and βC-acetals in Table 1. The shift to lower field is probably due, at least in part, to deshielding [7] caused by the proximity of the methyl group axial and on the same side of the 1,3-dioxan ring as the benzyl proton [see formula (III)]; likewise, the signal for the methyl group is also displaced to lower field. Thus, the benzylidene derivative of *meso*-pentane-2,4-diol (Table 1) had a doublet at 8·98 (J 6 c./sec.) for the protons of two equivalent methyl groups whereas the corresponding derivative (III) of DL-pentane-2,4-diol had doublets at 9·01 and 8·79 (J 6—7 c./sec. in each case). These signal patterns provide a simple means of configurational identification of the pentane-2,4-diols [8] (cf. ref. 9).

Although only one of the two theoretically possible diastereoisomers is formed [10] when tetritols and higher polyhydric alcohols react with benzaldehyde under acid catalysis to give 2-phenyl-1,3-dioxan derivatives, comparable amounts of both diastereoisomers are formed in the case of 2-phenyl-1,3-dioxolan compounds which must therefore have similar thermodynamic stabilities.[6] The benzyl proton signals for a series of 2-phenyl-1,3-dioxolan derivatives (α-acetals) are shown in Table 2, and it can be seen that they occur at lower field than those for β- and βC-actals. The parent compound, 2-phenyl-1,3-dioxolan, had a single signal at 4·66 characteristic of a benzyl proton *cis* to hydrogen atoms at the 4- and 5-positions in the 1,3-dioxolan ring. The 4-substituted derivatives in Table 2 are undoubtedly equilibrium mixtures of diastereoisomers (both α-acetals) since they were formed under conditions of vigorous acid catalysis and, with the exception of the 4-phenyl derivative, each showed two benzyl proton signals of comparable intensity (integrated area) in the ranges 4·62—4·67 and 4·46—4·52. The former signals, which have a similar chemical shift to that for the parent compound, may be assigned to the isomer (IIa) (DL-pair) with hydrogen atoms in *cis* relationship at the 2-, 4-, and 5-positions, whereas the latter signals may be assigned to the isomer (IIb) (DL-pair) with the benzyl proton *cis* to the 4-substituent. The displacement of the benzyl proton signal to lower field in the latter isomers may be attributed [7] to deshielding arising from the expansion of the electron clouds of the benzyl proton and the 4-substituent because of their proximity (cf. the configurational assignments made by Perlin [11]). The displacement is not markedly different for the range of 4-alkyl derivatives in Table 2. However, in the 4-phenyl derivative, the signal for each isomer is displaced to lower field although the arithmetical difference (0·20) between the signals is of similar magnitude to that (0·12—0·21) for the 4-alkyl

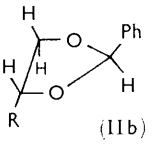
[4] A. H. Lewin and S. Winstein, *J. Amer. Chem. Soc.*, 1962, **84**, 2464.
[5] S. A. Barker and E. J. Bourne, *J.*, 1952, 905.
[6] J. A. Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 1.
[7] R. J. Abraham and J. S. E. Holker, *J.*, 1963, 806.
[8] A. Labib, Ph.D. Thesis, Birmingham, 1964.
[9] J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, 1963, **28**, 1545.
[10] B. Dobinson, A. B. Foster, and M. Stacey, *Tetrahedron Letters*, 1959, No. 1, p. 1.
[11] A. S. Perlin, *Canad. J. Chem.*, 1963, **41**, 399.

TABLE 2

Benzyl proton signals for some 2-phenyl-1,3-dioxolan derivatives



(IIa) +



(IIb)

	τ (IIb)	τ (IIa)	R
2-Phenyl-1,3-dioxolan [a]	—	4·66	H
4-Methyl- [b]	4·52	4·63	Me
4-Hydroxymethyl- [c]	4·52	4·64	CH_2·OH
4-Acetoxymethyl- [c]	4·49	4·62	CH_2·OAc
4-Isopropyl- [d]	4·50	4·63	Pr^i
4-(3-Hydroxypropyl)- [14]	4·50	4·64	$CH_2(OH)\cdot[CH_2]_2$
4-t-Butyl- [e]	4·46	4·67	Bu^t
4-Phenyl- [f]	4·24	4·44	Ph

[a] A. Reiche, E. Schmitz, and E. Beyer, *Chem. Ber.*, 1958, **91**, 1935. [b] C. Pientadosi, C. E. Anderson, E. A. Brecht, and C. L. Yarbro, *J. Amer. Chem. Soc.*, 1958, **80**, 6613. [c] Components of the equilibrium *O*-benzylideneglycerol mixture (ref. 16) and of the acetylated mixture. [d] B. p. 124—125°/12 mm. (Found: C, 75·1; H, 8·4. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%). [e] B. p. 130—140° (bath)/12 mm. [f] B. p. 140° (bath)/12 mm. (Found: C, 78·9; H, 6·2. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%).

derivatives. Depending on its orientation,[12] a second phenyl group in a benzylidene derivative could shield or deshield the benzyl proton. Only deshielding effects with consequent shifts to lower field have so far been encountered; for example, 1,2,5,6-tetra-*O*-benzoyl-3,4-*O*-benzylidene-D-mannitol, which contains a symmetrical αT-acetal, had a benzyl proton signal at 4·23.

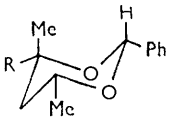
The seven-membered benzylidene derivative (γ-acetal) 2-phenyl-1,3-dioxepan had a single benzyl proton signal at 4·74 which is similar in chemical shift to those for the range of 2-phenyl-1,3-dioxan derivatives in Table 1. However, γ-benzylidene derivatives have been encountered only as parts of fused ring systems [6] and not as isolated cyclic acetals formed directly from acyclic polyhydric alcohols. That their formation is unlikely when α- or β-acetals can be formed as alternatives is illustrated by the conversion of butane-1,2,4-triol on benzylidenation into *cis*-4-hydroxymethyl-2-phenyl-1,3-dioxan together with only a small amount of 4-(2-hydroxyethyl)-2-phenyl-1,3-dioxolan, and no detectable formation of a seven-membered acetal.[13]

Benzylidenation of 3,4-*O*-isopropylidene-L-rhamnitol catalysed by zinc chloride gave a liquid product [14] with benzyl proton signals at 4·47 and 4·63. These signals fall within the ranges for the 4-alkyl-2-phenyl-1,3-dioxolan derivatives in Table 2 and they indicate the benzylidene acetal to be in the 1,2-position (α-acetal) and, since the signals had comparable integrated areas, that a near equimolar mixture of diastereoisomers was formed.

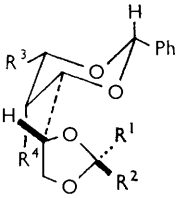
On the basis of the preceding results and argument, absolute configuration may be assigned to the 2,4:5,6-di-*O*-benzylidene derivatives of 3-*O*-methyl-D-glucitol described in Part XX.[1] Isomer *C* (m. p. 143—144°, $[\alpha]_D$ +26·5° in $CHCl_3$) had benzyl proton signals at 4·45 and 4·77, and isomer *D* (m. p. 112—116°, $[\alpha]_D$ +25° in $CHCl_3$) at 4·58 and 4·77. The signal at 4·77 for each isomer may be assigned (cf. compounds in Table 1) to the 2,4-*O*-benzylidene group (βC-acetal), and the signals at 4·45 and 4·58 (cf. compounds in Table 2) to the 5,6-*O*-benzylidene ring (α-acetal) with the benzyl proton *cis* and *trans*, respectively, to C4, *i.e.*, structures (V) and (VI).

[12] L. M. Jackman in "Physical Methods in Organic Chemistry," ed. J. C. P. Schwarz, Oliver, and Boyd, London, 1964, p. 181.
[13] A. B. Foster, A. H. Haines, and M. Stacey, *Tetrahedron*, 1961, **16**, 177.
[14] A. B. Foster, T. D. Inch, and J. M. Webber, unpublished results.

Closely parallel results were obtained with 2-*O*-benzyl-D-arabitol which, on zinc chloride-catalysed benzylidenation, gave a moderate yield of a product which could be fractionated into two di-*O*-benzylidene derivatives, *E* (m. p. 123—124°, $[\alpha]_D$ +10·8° in $CHCl_3$, benzyl proton signals at 4·42 and 4·73) and *F* (m. p. 96—97°, $[\alpha]_D$ −4·5° in $CHCl_3$, τ 4·51 and 4·71);



(III) R = H
(IV) R = Me



(V) R^1 = H, R^2 = Ph, R^3 = CH_2·OH, R^4 = OMe
(VI) R^1 = Ph, R^2 = H, R^3 = CH_2·OH, R^4 = OMe
(VII) R^1 = H, R^2 = Ph, R^3 = H, R^4 = O·CH_2Ph
(VIII) R^1 = Ph, R^2 = H, R^3 = H, R^4 = O·CH_2Ph

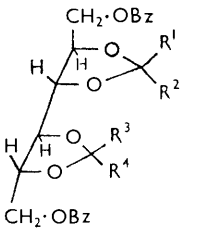
the former isomer was first obtained by Dr. A. H. Haines.[15] The signals at 4·73 and 4·71 may be assigned to six-membered acetal rings, and those at 4·42 and 4·51 to the isomeric forms of a five-membered acetal. Only a 1,3:5,6-distribution of the benzylidene groups (β- and α-acetals) accords with this data, and the structures (VII) and (VIII) may be assigned to isomers *E* and *F*. A 1,3:5,6-distribution of the benzylidene acetal rings would be predicted on conformational grounds.[6] The slight displacement of the benzyl proton signals for isomers *E* and *F* to lower field compared with those for the relevant mono-*O*-benzylidene derivatives in Tables 1 and 2 again illustrates the effect of two phenyl groups in the same molecule.

Unlike the tetritols and higher polyhydric alcohols, glycerol reacts with benzaldehyde under acid catalysis to give preferentially, but not exclusively, 2-phenyl-1,3-dioxolan derivatives (1,2-*O*-benzylideneglycerols). Using differential solubilities, Hibbert and his co-workers [16] were able to fractionate the equilibrium mixture into 2-phenyl-1,3-dioxan and 2-phenyl-1,3-dioxolan derivatives, and to demonstrate that, for a mixture obtained by sulphuric acid catalysis, the ratio of five- to six-membered acetals was *ca.* 3 : 1. A more complete analysis of equilibrium mixtures of *O*-benzylideneglycerols can be effected on the basis of the benzyl proton signals. The equilibrium mixture obtained by vigorous acid catalysis (toluene-*p*-sulphonic acid and azeotropic removal of water) had signals at 4·52, 4·64, 4·90, and 5·02 with integrated areas in the approximate ratios 2·15 : 2·3 : 1·3 : 1·0. The signals at 4·90 and 5·02 may be assigned to the *cis*- and *trans*-forms of 5-hydroxy-2-phenyl-1,3-dioxan, both of which are known crystalline,[17] and the signals at 4·52 and 4·64 to *trans*- and *cis*-forms of 4-hydroxymethyl-2-phenyl-1,3-dioxolan. The latter isomers are not known crystalline or separately pure. The ratio of five- to six-membered acetals for the above mixture was *ca.* 1·9 : 1.

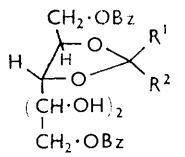
1,6-Di-*O*-benzoylgalactitol should [6] react with benzaldehyde to give a 2,3:4,5-di-*O*-benzylidene derivative. Catalysis of the reaction with zinc chloride [18,19] gave two di-*O*-benzylidene derivatives, *G* (m. p. 119—120°) and *H* (m. p. 146—147°) which on graded acidic hydrolysis [19] afforded the same 1,6-di-*O*-benzoyl-2,3-*O*-benzylidenegalactitol (m. p. 137—141°) thereby establishing the original 2,3:4,5-distribution of the benzylidene groups in isomers *G* and *H*. Four isomers are possible for 1,6-di-*O*-benzoyl-2,3:4,5-di-*O*-benzylidenegalactitol: with both benzyl protons *cis* (IX) or *trans* (X) to CH_2·OBz, and with one benzyl proton *cis* and one *trans* to a CH_2·OBz group [(XI) and (XII)]. Isomers (IX) and (X) are *meso*-forms, and isomers (XI) and (XII) comprise a DL-pair. Since the

[15] A. H. Haines, Ph.D. Thesis, Birmingham, 1961.
[16] H. S. Hill, M. S. Whelen, and H. Hibbert, *J. Amer. Chem. Soc.*, 1928, **50**, 2235.
[17] B. Dobinson and A. B. Foster, *J.*, 1961, 2338.
[18] W. T. Haskins, R. M. Hann, and C. S. Hudson, *J. Amer. Chem. Soc.*, 1942, **64**, 136, 137.
[19] H. Zinner and W. Thielebeule, *Chem. Ber.*, 1960, **93**, 2791.

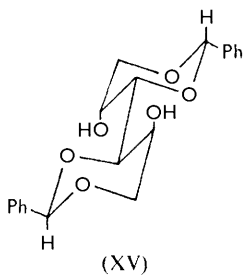
benzyl protons in isomer (IX) have identical environments they should have the same chemical shift, and the same considerations apply to isomer (X). On the other hand, isomer (XI) [or (XII)] has benzyl protons with slightly different environment, and discrete signals might be expected. Samples of isomers *G* and *H* were kindly provided by Professor H. Zinner. Isomer *G* had benzyl proton signals with similar integrated areas at 4·20 and 4·24, and is clearly the DL-form [(XI) + (XII)], whereas isomer *H* had a single signal at 4·20 and is therefore a pure *meso*-form; the available evidence does not permit a distinction between the structures (IX) and (X). The 1,6-di-*O*-benzoyl-2,3-*O*-benzylidenegalactitol obtained [19] on graded acidic hydrolysis of isomers *G* and *H* had a single benzyl proton signal at 4·20 and is therefore most probably a pure diastereoisomer with structure (XIII) or (XIV).



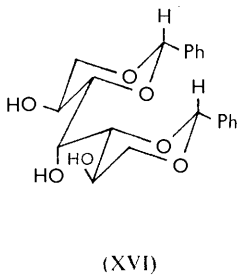
(IX) $R^1 = R^4 = H$, $R^2 = R^3 = Ph$
(X) $R^1 = R^4 = Ph$, $R^2 = R^3 = H$
(XI) $R^1 = R^3 = H$, $R^2 = R^4 = Ph$
(XII) $R^1 = R^3 = Ph$, $R^2 = R^4 = H$



(XIII) $R^1 = H$, $R^2 = Ph$
(XIV) $R^1 = Ph$, $R^2 = H$



(XV)



(XVI)

meso-glycero-gulo-Heptitol (α-glucoheptitol) affords, on zinc chloride-catalysed benzylidenation, a di-*O*-benzylidene derivative [20] (m. p. 149°) which had a single benzyl proton signal at 4·84 indicative of six-membered acetals and a symmetrical structure. Only a 1,3:5,7-distribution of the benzylidene groups accords with these requirements, and such a structure would have 1,3-dioxan rings with equatorial substituents (XVI) and hence is analogous to the conformationally rigid *trans*-5-substituted derivatives of 2-phenyl-1,3-dioxan in Table 1. On the other hand, 1,3:4,6-di-*O*-benzylidenegalactitol (τ 4·78) will have 1,3-dioxan rings with one axial and two equatorial substituents (XV) and hence is analogous to the conformationally unstable *cis*-5-substituted 2-phenyl-1,3-dioxan derivatives and the *O*-benzylidene derivatives of L-threitol and L-arabitol in Table 1. For a particular pair of 5-substituted derivatives of 2-phenyl-1,3-dioxan, the benzyl proton for the conformationally rigid *trans*-isomer is at higher field than that for the *cis*-derivative. A parallel signal relationship (4·84 and 4·78) may be noted for the heptitol (XVI) and galactitol derivative (XV) thus providing further support for the assigned structures.

Preliminary results [21] with pentafluorobenzylidene derivatives reveal a parallel with the

[20] A. B. Foster, D. I. Stephens, and J. M. Webber, unpublished results.
[21] N. Baggett, A. B. Foster, R. Stephens, (the late) E. V. Arosker, and J. M. Webber, unpublished results.

benzylidene analogues. Thus, the following benzyl proton signals were observed: 2-pentafluorophenyl-1,3-dioxan (4·43); 2-pentafluorophenyl-1,3-dioxolan (4·09); *cis,trans*-4-methyl-2-pentafluorophenyl-1,3-dioxolan (4·00, 4·15). Compared with the phenyl group, the larger inductive effect of the pentafluorophenyl group, with consequent greater deshielding, probably accounts for the shift to lower field of the acetal proton signals in the pentafluorobenzylidene derivatives.

Experimental

The n.m.r. spectra were measured on a Varian A60 instrument at normal working temperature on *ca.* 10% solutions of the benzylidene derivatives in dioxan. Tetramethylsilane (6%) and benzyl alcohol (10%), separately in chloroform, were used as external references. The τ values recorded are those directly observed, and they were reproducible to less than $\pm 0{\cdot}02$ p.p.m. Some of the benzylidene derivatives were poorly soluble in dioxan.

2-O-*Benzyl*-D-*arabitol*. A solution of 2-*O*-benzyl-4-*O*-formyl-D-arabinose [22] (7·3 g.) and sodium borohydride (2 g.) in water (300 ml.) was stored at room temperature for 18 hr., the pH was adjusted to 7·0 with acetic acid, sodium ions were removed with Amberlite IR-120 (H^+ form), and the solution was evaporated at reduced temperature and pressure. Acetic and boric acids were removed by repeated distillation of methanol from the residue which was then crystallised from ethyl acetate to give the *product* (5·2 g., 74%), m. p. 66—69° (Found: C, 59·8; H, 7·8. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·5%). The m. p. could not be obtained sharp, and the range varied with the conditions of crystallisation; *e.g.*, from benzene–ethanol the product had m. p. 73—78°, $[\alpha]_D$ −4·5° (*c* 2·7 in MeOH) (Found: C, 59·8; H, 7·4%).

Benzylidenation of 2-O-*Benzyl*-D-*arabitol*.—A mixture of this compound (2 g.), zinc chloride (4 g.), and benzaldehyde (10 ml.) was stirred at room temperature for 3 days and then shaken with a mixture of water (100 ml.) and light petroleum (100 ml.; b. p. 60—80°). The organic layer was separated from the filtered mixture, washed with aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Evaporation gave a residue (1 g.), $[\alpha]_D$ +4·4° (*c* 1·1 in $CHCl_3$), which after three recrystallisations from ethanol gave 2-O-*benzyl*-1,3:4,5-*di*-O-*benzylidene*-D-*arabitol*-E (0·12 g.), m. p. 123—124°, $[\alpha]_D$ +10·8° (*c* 0·8 in $CHCl_3$) (Found: C, 74·1; H, 6·6. $C_{26}H_{26}O_5$ requires C, 74·6; H, 6·3%).

Evaporation of the mother-liquor from the first recrystallisation described above gave a residue, m. p. 80—85°, $[\alpha]_D$ *ca.* 0° (*c* 1·4 in $CHCl_3$), which on recrystallisation three times from methanol gave 2-O-*benzyl*-1,3:4,5-*di*-O-*benzylidene*-D-*arabitol*-F (63 mg.), m. p. 96—97°, $[\alpha]_D$ −4·5° (*c* 0·07 in $CHCl_3$) (Found: C, 74·7; H, 6·2%).

2-*Phenyl*-1,3-*dioxepan*.—A mixture of butane-1,4-diol (50 g.), benzaldehyde (100 ml.), toluene-*p*-sulphonic acid (1 g.), and toluene (400 ml.) was boiled under reflux using a device for collection of the water removed azeotropically (*ca.* 12 ml.). The cooled mixture was washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated. Distillation of the residue gave the *product* (19 g., 20%), b. p. 110—120°/*ca.* 15 mm. (Found: C, 73·8; H, 7·7. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%).

The 4-alkyl-2-phenyl-1,3-dioxolan derivatives in Table 2 were re-prepared using the above general method.

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Edgbaston, Birmingham 15. [*Received, November 25th,* 1964.]

[22] J. C. P. Schwarz and M. MacDougall, *J.*, 1956, 3065.