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ASPECTS OF STEREOCHEMISTRY—II*

INTRAMOLECULAR HYDROGEN BONDING IN SOME MONOHYDROXY DERIVATIVES OF TETRAHYDROFURAN, TETRAHYDROPYRAN AND 1:3-DIOXAN

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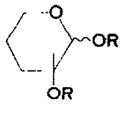
Abstract—The extent of intramolecular hydrogen bonding between hydroxyl groups and ring oxygens, as determined by infra-red spectroscopy in the hydroxyl stretching region, in a series of monohydroxy derivatives of tetrahydropyran, tetrahydrofuran and 1:3-dioxan provides direct experimental evidence for the stabilities of different conformations of certain of the alcohols. The synthesis of tetrahydropyran-3-ol is described and the mechanism of the reaction of perbenzoic acid with glycals is discussed.

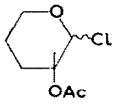
IN addition to the intramolecular hydrogen bonding (bonding), which may occur between hydroxyl groups in dihydroxy derivatives of tetrahydropyran, bonding between suitably located hydroxyl groups and the ring oxygen is also possible and, as a result, conformational stability may by influenced. Observations and comments on this effect were reported in Part I. Bonding may also occur between each ring oxygen and the hydroxyl group in derivatives of 1:3-dioxan-5-ol (1:3-O-methylene-glyceritol) and determination of the extent of bonding has permitted an allocation of configuration[1] to *cis*- and *trans*-1:3-O-benzylidene-glyceritol (2-phenyl-1:3-dioxan-5-ol).

The extent of intramolecular hydrogen bonding in these compounds may be determined from the infra-red spectra of their dilute solutions in carbon tetrachloride.[2,3] Below a concentration of 0·005 M intermolecular hydrogen bonding is negligible and absorptions at ca. 3590 cm^{-1} and ca. 3620 cm^{-1} may be associated[2] with bonded and free hydroxyl groups respectively. The respective proportions of free and bonded hydroxyl groups may be approximately assessed from the extinction coefficients (ϵ) for the relative absorptions.

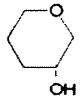
With the exception of tetrahydropyran-3-ol all the alcohols listed in Table 1 have been described in the literature. Tetrahydropyran-3-ol was prepared by the following route. Treatment of 2:3-dihydropyran with perbenzoic acid in wet ether furnished 2:3-dihydroxy-tetrahydropyran (I) which was isolated and purified as the diacetate (II). Reaction of the diacetate (II) with ethereal hydrogen chloride gave the chloro intermediate (III) which was converted to tetrahydropyran-3-ol (IV) by reduction with lithium aluminium hydride.



I, R=H
II, R=Ac



III



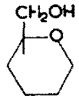
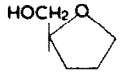
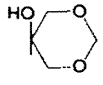
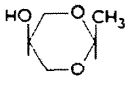
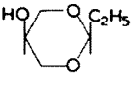
IV

* Part I, *Tetrahedron* **4**, 351 (1958).

[1] J. S. Brimacombe, A. B. Foster and M. Stacey, *Chem. & Ind.* 1228 (1958).
[2] L. P. Kuhn, *J. Amer. Chem. Soc.* **74**, 2492 (1952); *Chem. & Ind.* **76**, 4323 (1954).
[3] A. R. H. Cole and P. R. Jefferies, *J. Chem. Soc.* 4391 (1956).

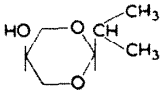
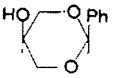
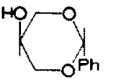
TABLE 1. INFRA-RED SPECTRAL DATA FOR CERTAIN ALCOHOLS

(Determined on solutions in carbon tetrachloride of concentration 0·005 M or less)

Alcohol	Structure[a]	Infra-red absorptions (cm^{-1})[b] Free OH(ε)	Bonded OH(ε)	$\Delta\nu$[c]	$\Delta\nu$[1,d]
Tetrahydropyran-2-ol (5-hydroxypentanal)		3620(40)	—		
Tetrahydropyran-3-ol		3620(40)	3604(50)	16	25
Tetrahydropyran-4-ol		3622(40)	—		
2-Hydroxymethyl-tetrahydropyran		—	3597(55)		
Tetrahydrofuran-2-ol (4-hydroxybutanal)		3619(40)	—		
Tetrahydrofuran-3-ol		3628(48)	—		
2-Hydroxymethyl-tetrahydrofuran (tetrahydrofurfuryl alcohol)		—	3600(47)		
1:3-Dioxan-5-ol (1:3-O-methylene glyceritol)		3635(21)	3594(100)	41	35
2-Methyl-1:3-dioxan-5-ol (1:3-O-ethylidene-glyceritol)		—	3593(50)		
2-Ethyl-1:3-dioxan-5-ol (1:3-O-propylidene-glyceritol)		—	3590(100)		

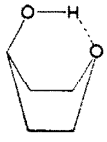
[a] Formula depicted to emphasize their relation with the carbohydrates.
[b] Values in parentheses are the relative extinction coefficients (ε).
[c] Arithmetical difference between free and bonded hydroxyl absorption frequencies.[2]
[d] Arithmetical difference between bonded and standard secondary hydroxyl (3629 cm^{-1}) absorption frequencies.[3]

TABLE 1 (*Cont.*)

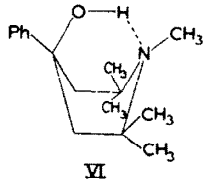
Alcohol	Structure[a]	Infra-red absorptions (cm^{-1})[b] Free OH(ϵ)	Bonded OH(ϵ)	$\Delta\nu$[c]	$\Delta\nu^{1/2}$[d]
2-Isopropyl-1:3-dioxan-5-ol (1:3-O-isobutylidene-glyceritol)		—	3589(55)		
cis-2-Phenyl-1:3-dioxan-5-ol (1:3-O-benzylidene-glyceritol)[e]		—	3593(78)		
trans-2-Phenyl-1:3-dioxan-5-ol[e]		3633(55)	3593(70)	40	36

[e] Data taken from ref. 1.

In Table 1 are recorded the infra-red absorption frequencies determined on solutions of 0·005 M or less of the alcohols in dry carbon tetrachloride. As would be expected from a consideration of accurate scale models, bonding does not occur in the tetrahydrofuran-2 and 3-ols or in the tetrahydropyran-2 and 4-ols. Intramolecular hydrogen bonding is theoretically possible in the boat conformation (V) of tetrahydropyran-4-ol but it appears that bonding is too weak to hold the molecule in such an unfavoured conformation. Bonding has been observed[4] in a related 6-membered ring compound in a boat conformation namely 4-hydroxy-1:2:2:6:6-pentamethyl-4-phenyl-piperidine (VI). In this case the alternative chair conformations are destabilized by the *gem*-dimethyl groups.



V



VI

Tetrahydrofuran-2-ol and tetrahydropyran-2-ol may be regarded as equilibrium mixtures of the cyclic forms and the respective acyclic structures 4-hydroxybutanal and 5-hydroxypentanal. The infra-red spectra of liquid films of the two alcohols showed weak carbonyl absorptions[5] at 1726 and 1724 cm^{-1} respectively, indicative of the presence of a small percentage of the acyclic forms. A similar inference could be drawn from the spectra of solutions of the two alcohols in carbon tetrachloride at concentrations of 10·0 mg/ml which showed the following absorptions: tetrahydrofuran-2-ol 1730 cm^{-1} ($\epsilon = 31$), tetrahydropyran-2-ol 1720 cm^{-1} ($\epsilon = 22$). Typical aliphatic aldehydes[5] show carbonyl absorption in the range 1720–1740 cm^{-1} and have[6] carbonyl extinction coefficients (ϵ) ca. 700 ± 100 so that in the present cases about 4 per cent of the alcohols are in the open chain form. This is the same

[4] R. E. Lyle, *J. Org. Chem.* **22**, 1280 (1957).
[5] L. J. Bellamy, *Infra-red Spectra of Complex Molecules* p. 133. Methuen (1956).
[6] R. E. Richards and W. R. Burton, *Trans. Faraday Soc.* **45**, 874 (1949).

order of magnitude as found by Hurd and Saunders[7] from ultra-violet measurements on solutions of the alcohols in aqueous dioxan.

In view of the low percentage of molecules of tetrahydrofuran-2-ol and tetrahydropyran-2-ol which exist in the open chain form, any bonding between the hydroxyl group and the carbonyl oxygen in the acyclic structures would be difficult to detect. However, it seems unlikely that such bonding would occur since the formation of seven or eight membered rings would be required.

In carbon tetrachloride solution the hydroxyl groups in 2-hydroxymethyl-tetrahydropyran and 2-hydroxymethyl-tetrahydrofuran appear to be completely bonded. In the latter case bonding involves the formation of a bicyclic system structurally related to *cis*-bicyclo [3.3.0] octane. A similar bicyclic system would be formed by bonding in 1:2-O-isopropylidene-glyceritol. However, in carbon tetrachloride solutions of this cyclic acetal, a significant percentage of the hydroxyl groups are not bonded as shown by the absorptions at 3647 cm^{-1} ($\epsilon = 25$, free hydroxyl) and 3608 cm^{-1} ($\epsilon = 49$, bonded hydroxyl). From a study of accurate scale models it appears that the *gem*-dimethyl groups in the isopropylidene residue may sterically hinder the approach of the hydroxyl group to the relevant ring oxygen and hence limit intramolecular hydrogen bonding.

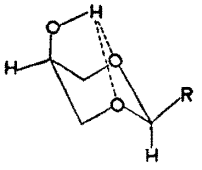
An examination of models also suggests that bonding could occur in both chair conformations of 2-hydroxymethyl tetrahydropyran. If the hydroxymethyl group is axial then the bicyclic system formed by bonding is structurally related to *cis*-hydrindane (*cis*-bicyclo [4.3.0] nonane) and if equatorial to *trans*-hydrindane. Although the available evidence does not indicate which configuration predominates, by analogy with the hydrindanes, for which combustion data indicates[8] the *trans*-form to be most stable, and on the basis of the principles of conformational analysis[9] 2-hydroxymethyl-tetrahydropyran would be expected to assume a chair conformation with the hydroxymethyl group in an equatorial position.

On the reasonable assumption[9,10] that the tetrahydropyran ring normally exists in the chair conformation then the presence of both free and bonded hydroxyl groups in carbon tetrachloride solutions of tetrahydropyran-3-ol may be interpreted as indicating the presence of an equilibrium of both chair conformations (Fig. 1). Bonding can occur only in the chair conformation with an axial hydroxyl group and the relative extinction coefficients (40 and 50) for free and bonded hydroxyl groups indicates approximately, equal proportions. Some stabilization of the conformation with an axial hydroxyl group must be conferred by bonding since, from the principles of conformational analysis,[9] the hydroxyl group would otherwise adopt predominantly an equatorial position. Pickering and Price[11] have concluded that for *cyclo*hexanol in carbon disulphide solution approximately 65 per cent of the molecule exists in the chair conformation with an equatorial hydroxyl group.

Introduction of a second ring oxygen as in 1:3-dioxan-5-ol permits more efficient bonding of an axially located hydroxyl group than in tetrahydropyran-3-ol (Fig 2). The relative extinction coefficients (21 and 100) for free and bonded hydroxyl groups in 1:3-dioxan-5-ol indicates that the equilibrium of chair conformations now strongly

[7] C. D. Hurd and W. H. Saunders, *J. Amer. Chem. Soc.* **74**, 5324 (1952).
[8] W. Hückel, *Liebigs Ann.* **533**, 1 (1938).
[9] D. H. R. Barton and R. C. Cookson, *Quart. Rev.* **10**, 44 (1956).
[10] J. A. Mills, *Adv. Carbohydrate Chem.* **10**, 1 (1955).
[11] R. A. Pickering and C. C. Price, *J. Amer. Chem. Soc.* **80**, 4931 (1958).

favours that with an axial hydroxyl group. Further, the introduction of a suitably oriented substituent on to C_2 in 1:3-dioxan-5-ol, as for example the phenyl group in *cis*-1:3-O-benzylidene-glyceritol (VII), effectively fixes the conformation and permits



VII, R=Ph
VIII, R=CH_3
IX, R=C_2H_5
X, R=iC_3H_7

complete bonding (Table 1). This is not the case with the *trans*-isomer[1] in which an appreciable percentage of the hydroxyl groups are not bonded (Table 1). By comparison with these results 1:3-O-ethylidene-glyceritol[12] (VIII), 1:3-O-propylidene-glyceritol[13] (X), and 1:3-O-isobutylidene-glyceritol[13] the spectra of which (Table 1) show absorptions for bonded hydroxyl groups only, may be tentatively assigned the *cis*-structures.[14]

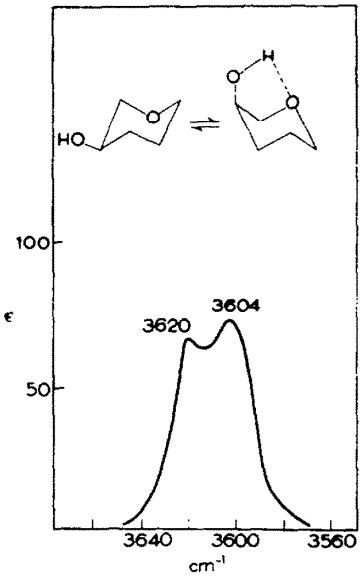


FIG. 1. Infra-red spectrum in CCl_4 solution at ca. 0·005 M concentration of tetrahydropyran-3-ol. The spectrum is consistent with the equilibria shown assuming that the molecules exist preferentially in the chair forms.[10]

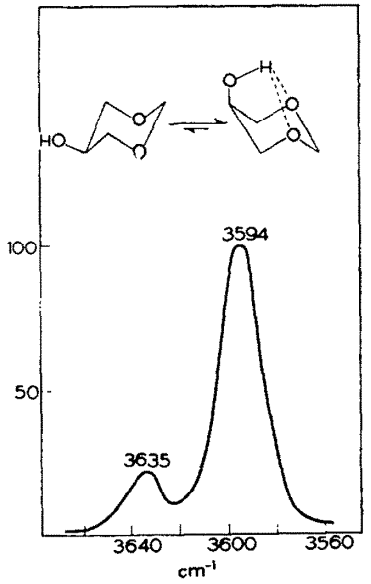
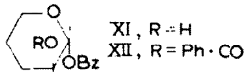


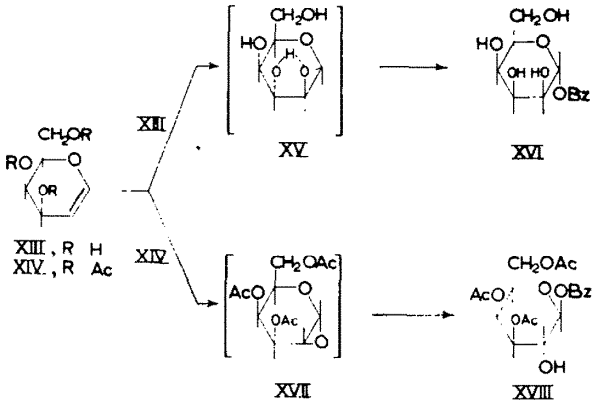
FIG. 2. Infra-red spectrum in CCl_4 solution at ca. 0·005 M concentration of 1:3 dioxan-5-ol. The spectrum is consistent with the equilibria shown assuming that the molecules exist preferentially in the chair forms.[10]

During the investigation of the synthesis of tetrahydropyran-3-ol a possible route via reduction of 2:3-epoxy-tetrahydropyran (2:7-dioxabicyclo [4.1.0] heptane) was examined but proved to be unsuitable since, under the experimental conditions used, the epoxide, if formed, underwent further reaction. For example, treatment of 2:3-dihydropyran with perbenzoic acid in dry chloroform gave a diol monobenzoate.

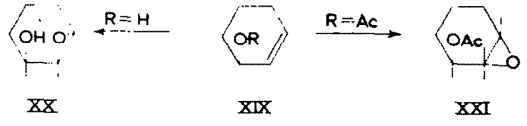
[12] H. S. Hill, A. C. Hill and H. Hibbert, *J. Amer. Chem. Soc.* **50**, 2243 (1928).
[13] S. M. Trister and H. Hibbert, *Canad. J. Res.* **14**[B], 415 (1939).
[14] N. Baggett and A. B. Foster, unpublished results.

This compound may be tentatively allocated the structure *trans*-2-benzoyloxy-3-hydroxy-tetrahydropyran (XI) on the basis of a close parallel with the results of Wood and Fletcher[15] who showed that oxidation of D-galactal (XIII) with perbenzoic acid gave 1-O-benzoyl-α-D-talopyranose (XVI). It is of interest that, in the latter reaction, D-galactose derivatives are not formed so that if the reaction proceeds via the intermediate epoxide (XV) it is highly stereospecific. On the other hand perbenzoic acid





reacts[16] with 3:4:6-tri-O-acetyl-D-galactal (XIV) to yield 3:4:6-tri-O-acetyl-1-O-benzoyl-β-D-galactopyranose (XVIII) presumably via the intermediate epoxide (XVII). Henbest and Wilson[17] have shown that peracids oxidize cyclohex-2-enol (XIX, R = H) to the *cis*-epoxide (XX) whereas the acetate (XIX, R = Ac) reacts more slowly but



yields mainly the *trans*-epoxide (XXI). The stereospecificity of the former reaction is considered to be due to intramolecular hydrogen bonding in the transition state whereas in the latter reaction the bulk of the acetoxy group may block one side of the double bond. The parallelism between the reactions in the respective D-galactal and cyclohex-2-enol series is clear if the former proceed through the intermediate epoxides (XV) and (XVII). Since, in the D-galactal series an enol ether not an olefin is initially involved, then the occurrence of further reaction is not surprising. A similar reaction sequence occurs in the D-glucal series. Thus D-mannose is the main product[18] of the reaction of D-glucal and perbenzoic acid in the presence of water

[15] H. B. Wood and H. G. Fletcher, *J. Amer. Chem. Soc.* **79**, 3234 (1957).
[16] P. A. Levene and R. S. Tipson, *J. Biol. Chem.* **93**, 631 (1931).
[17] H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.* 1958 (1957).
[18] M. Bergmann and H. Schotte, *Ber.* **54**, 440 (1921); B. Helferich, *Adv. Carbohydrate Chem.* **7**, 209 (1952).

whereas the peracid reacts with 3:4:6-tri-O-acetyl-D-glucal to yield[19] predominantly 3:4:6-tri-O-acetyl-1-O-benzoyl-D-glucose. D-Glucose derivatives predominate when either 3-O-methyl or 3:4:6-tri-O-methyl-D-glucal is treated with perbenzoic acid in the presence of water.[19] In conflict with this general pattern of reactions is the observation[19] that mainly D-mannose derivatives result from the action of perbenzoic acid on 3:4:6-tri-O-acetyl-D-glucal in the presence of water. The epoxide (XVII) [3:4:6-tri-O-acetyl-1:2-anhydro-α-D-glucopyranose (Brigl's anhydride)] postulated as an intermediate in the reaction of 3:4:6-tri-O-acetyl-D-galactal (XIV) with perbenzoic acid has been obtained[20] by another route.

Benzoylation of the monobenzoate (XI) gave a dibenzoate with the possible structure *trans*-1:2-dibenzoyloxy-tetrahydropyran (XII). Treatment of the dibenzoate with ethereal hydrogen chloride followed by reduction with lithium aluminium hydride gave an inseparable mixture of benzyl alcohol and, presumably, tetrahydropyran-3-ol.

EXPERIMENTAL

With the exception of tetrahydropyran-3-ol the alcohols used in this paper are described in the literature. Table 2 contains the physical constants of and other data about the alcohols.

Actions of perbenzoic acid on 2:3-*dihydropyran.* 2:3-Dihydropyran (6 g) was added to a solution of perbenzoic acid (10 g) in dry chloroform (200 ml) at −5°. After 10 min the solution was extracted

TABLE 2. PHYSICAL CONSTANTS OF AND OTHER DATA ABOUT CERTAIN ALCOHOLS

Alcohol[a]	Physical constants			
	b.p.	n (temp.)	b.p.[a]	n[a] (temp)
Tetrahydropyran-2-ol (5-hydroxy-pentanal)[b,21]	50–52°/1 mm	1·4530 (22)	54–55°/3 mm[21]	1·4514 (25)[21]
Tetrahydropyran-3-ol	92–95° (bath)/ 12–15 mm	1·4571 (21)	—	—
Tetrahydropyran-4-ol[22]	85–88°/12 mm	1·4580 (20)	84–85°/12 mm[22]	1·4580 (20)[22]
2-Hydroxymethyl-tetrahydropyran[23]	95–96°/25 mm	1·4570 (20)	73–74·5°/11 mm[23b]	1·4582 (17)[23b]
Tetrahydrofuran-2-ol (4-hydroxy-butanal)[b,24,25]	70–72°/15 mm	1·4420 (22)	65°/12 mm[25]	1·4403 (20)[25]
Tetrahydrofuran-3-ol[26]	84–88°/24 mm	1·4507 (20)	82–88°/24 mm[26]	1·4497 (25)[26]
2-Hydroxymethyl-tetrahydrofuran (tetrahydrofurfuryl alcohol)	178–180°	1·4504 (20)		
1:3-Dioxan-5-ol (1:3-O-methylene-glyceritol)[27]	82°/11 mm	1·4533 (20)	82°/11 mm[27]	1·4533[27]
2-Methyl-1:3-dioxan-5-ol (1:3-O-ethylidene-glyceritol)[13]	40–45°/0·05 mm	1·5152 (21)	52°/2 mm[13]	1·4532 (17)[13]
2-Ethyl-1:3-dioxan-5-ol (1:3-O-propylidene-glyceritol)[13]	48°/0·01 mm	1·4490 (21)	50–51°/2 mm[13]	1·4448 (25)[13]
2-Isopropyl-1:3-dioxan-5-ol (1:3-O-isobutylidene-glyceritol)[13]	51–54°/ 0·01 mm	1·4785 (19)	55–56°/2 mm[13]	—

[a] Literature values.
[b] Reducing toward's Fehling's solution.

[19] P. A. Levene and A. L. Raymond, *J. Biol. Chem.* **88**, 513 (1930); C. Tanaka, *Bull. Chem. Soc. Japan* **5**, 214, (1930); *Chem. Zentr.* 2765 (1930, II).
[20] P. Brigl, *Z. Physiol. Chem.* **116**, 1 (1921); **122**, 245 (1922).
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thrice with cold 2 N NaOH and finally with water. Evaporation of the dried (Na_2SO_4) chloroform solution and recrystallization of the residue from ether–light petroleum (60–80°) gave *trans* (?)-2-benzoyloxy-tetrahydropyran-3-ol m.p. 85–87°. (Found: C, 64·5; H, 6·0. $C_{12}H_{14}O_4$ requires: C, 64·8; H, 6·3%). The infra-red spectrum (Nujol mull) showed absorptions at 1703 and 1720 cm^{-1} (carbonyl) and at 3460 cm^{-1} (hydroxyl).

A solution of benzoyl chloride (4 g) in dry pyridine (20 ml) was added to a solution of the preceding monobenzoate (3·5 g) also in dry pyridine (20 ml) at 0°. After 30 hr at room temp the mixture was diluted with chloroform, and the chloroform solution washed successively with dilute hydrochloric acid, water, aqueous cadmium chloride (10%, w/v), water and aqueous sodium hydrogen carbonate. Evaporation of the dried (Na_2SO_4) chloroform solution and recrystallization of the residue from methanol gave *trans* (?)-2:3-dibenzoyloxy-tetrahydropyran (5 g) m.p. 70–75°. (Found: C, 69·9; H, 5·4. $C_{19}H_{16}O_5$ requires: C, 69·9; H, 5·5%). The infra-red spectrum (Nujol mull) showed absorptions at 1721 and 1736 cm^{-1} (carbonyl) but no absorption for free hydroxyl groups.

Tetrahydropyran-3-ol. 2:3-Dihydropyran (9 g) was added to a solution of perbenzoic acid (15 g) in aqueous saturated ether (200 ml) at 0°. After 24 hr the mixture was extracted with water and the aqueous extract was washed with a small amount of ether to remove benzoic acid and then evaporated at 40°/12–15 mm to yield crude 2:3-dihydroxy-tetrahydropyran. The diol was acetylated by treatment with dry pyridine (30 ml) and acetic anhydride (15 ml) at room temp for 48 hr. The mixture was poured into water and the solution extracted with chloroform. The combined extracts were washed successively with N HCl, aqueous cadmium chloride, and dilute aqueous sodium hydrogen carbonate. Evaporation of the dried (Na_2SO_4) chloroform solution and distillation of the residue gave 2:3-diacetoxy-tetrahydropyran as a colourless liquid b.p. 70–72° (bath)/0·1 mm, n^{20} 1·4458 (Found: C, 53·2; H, 7·0. $C_9H_{14}O_5$ requires: C, 53·5; H, 7·0%).

A solution of the diacetate (5 g) in ether (50 ml) which had been saturated with hydrogen chloride at 0° was kept at the same temp for 48 hr. The solution was then evaporated under diminished pressure and the remaining traces of hydrogen chloride were removed by repeated distillation of benzene from the residue. A solution of the syrupy product in ether containing lithium aluminium hydride (7·5 g) was boiled under reflux for 4 hr. Excess of lithium aluminium hydride was destroyed by the addition of water and the resultant precipitate was dissolved by the addition of a saturated aqueous solution of Rochelle salt. Exhaustive extraction of the solution with ether followed by evaporation of the extract and distillation of the residue gave tetrahydropyran-3-ol as a colourless liquid b.p. 92–95° (bath)/12–15 mm, n^{21} 1·4571 which was non-reducing towards Fehling's solution (Found: C, 58·95; H, 9·0. $C_5H_{10}O_2$ requires: C, 58·8; H, 9·8). Toluene-*p*-sulphonylation in the usual manner gave syrupy 3-toluene-*p*-sulphonyloxy-tetrahydropyran. (Found: C, 56·1; H, 6·4; S, 12·3. $C_{12}H_{16}O_4S$ requires: C, 56·2; H, 6·2; S, 12·5%). The infra-red spectrum (liquid film) was quite distinct from those of the isomeric tetrahydropyran-2- and 4-ols.

1:3-O-*Methylene-glyceritol* (1:3-*dioxan-5-ol*). A solution of 2-O-benzoyl-1:3-O-methylene-glyceritol (3 g, prepared according to the method of Hibbert and Carter[27]) in chloroform (20 ml) was treated with dry methanol (5 ml) to which a trace of metallic sodium had been added. After 24 hr at room temp neutralization was effected with solid carbon dioxide and the solution was evaporated. A solution of the residue in water was extracted firstly with light petroleum (60–80°) and then exhaustively with ether. Evaporation of the ether extract and distillation of the residue gave 1:3-O-methylene glyceritol, b.p. 80–85°/11 mm, n^{20} 1·4540. (Hibbert and Carter[27] quote b.p. 82°/11 mm, n^{20} 1·4533). Saponification of the benzoate using aqueous alkali according to the method of Hibbert and Carter[27] gave a product n^{20} 1·4541. The infra-red spectra (liquid film) of the two products were identical.

1:3-O-*Ethylidene-glyceritol* (2-*methyl*-1:3-*dioxan-5-ol*). Acetaldehyde (15 g) was passed into a mixture of glyceritol (34 g) and conc H_2SO_4 (1·0 ml). The mixture was neutralized with solid K_2CO_3 and excess acetaldehyde was removed by extraction with light petroleum (60–80°). The residue was dissolved in ether, the solution washed with water and then evaporated to yield a residue from which a mixture (29 g) of O-ethylidene-glyceritols was obtained with b.p. 45–48°/0·05 mm. Benzoyl chloride (26 g) was added to a solution of the mixed O-ethylidene-glyceritols (25 g) in dry pyridine (100 ml). After 10 hr at 0° the mixture was worked up in the usual way to yield 5-benzoyloxy-2-methyl-1:3-dioxan m.p. 86° (Hill, Hill and Hibbert[13] quote m.p. 86° for the same compound prepared in a different manner). The behaviour of the benzoate on chromatography on alumina indicated that it was homogeneous.

Debenzoylation was effected with sodium methoxide in methanol as described above for 5-benzoyloxy-1:3-dioxan to yield 2-methyl-1:3-dioxan-5-ol, b.p. 40–45°/0·05 mm, n^{21} 1·5152; (Hill, Hill and Hibbert[13] quote b.p. 52°/2 mm, n_D^{17} 1·4532).

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.[28] Concentration of the diol was always approximately 0·005 M; the extinction coefficients, ϵ, are maximum values and are equal to $(1/cl)\log_{10}(I_0/I)$ with l in cm and c in moles/litre and are accurate to ± 10. The results are recorded in Table 1. It would be unwise to asssume that the extinction coefficients of bonded and free hydroxyl groups are identical either in one molecule or between molecules and so accurate values are not available for the proportion of each form. The extinction coefficients per hydroxyl group lie in the range 40–125 for compounds with hydroxyl groups which are free, bonded or with a proportion of each. This means that the ratio of bonded to free hydroxyl groups is approximately the ratio of the extinction coefficients but the variations are such that accurate values for each form cannot be obtained.

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