162. *Spectra of Acetals. Part II.* The Infrared and Raman Spectra of Substituted* 1 : 3-*Dioxolans.*

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Assignments have been made for some of the frequencies of several substituted 1 : 3-dioxolans; a few of the vibrational modes were not identifiable. The hydroxyl group in 4-hydroxymethyl-2 : 2-dimethyldioxolan has been deuterated, enabling the frequencies associated with this group to be identified. Some assignments, based on this work, have been suggested for three hexitol ketals.

Ethylidene and *iso*propylidene acetals of ethylene and propylene glycol, which were all methyl-substituted dioxolans, were chosen for study since the effect, on the spectra, of substitution at each position in the dioxolan ring could then be observed since the methyl groups gave comparatively few and well-known characteristic frequencies. 4-Hydroxymethyl-2 : 2-dimethyldioxolan, together with its *O*-deutero-analogue and its methyl ether, were studied to observe the effect of the hydroxyl group, for correlation with the spectra of the sugar acetals and ketals.

Experimental

Preparation of Substituted Dioxolans.—2-Methyl-1 : 3-dioxolan, prepared by Hibbert and Timm's method,[1] had b. p. 82°/751 mm.

4-Methyl-1 : 3-dioxolan, obtained by condensation of propylene glycol and paraformaldehyde in the presence of syrupy orthophosphoric acid,[2] had b. p. 84°/736 mm.

An exchange reaction between acetaldehyde dipentyl acetal and propylene glycol, as performed by Lucas and Guthrie,[3] was used to afford the stereoisomers of 2 : 4-dimethyl-1 : 3-dioxolan. The separation of the isomers, their physical constants, and the assignment of configurations have been described elsewhere.[4]

2 : 2-Dimethyl-1 : 3-dioxolan, prepared by the method of Dworzak and Hermann,[5] had b. p. 92°.

2 : 2 : 4-Trimethyl-1 : 3-dioxolan, obtained [6] by condensing acetone with propylene glycol, had b. p. 101°.

Azeotropic distillation was utilised in the synthesis [7] of 4-hydroxymethyl-2 : 2-dimethyl-1 : 3-dioxolan, b. p. 85°/11 mm., n_D^{20} 1·4347. Reaction with methyl iodide and dry silver oxide [8] yielded 4-methoxymethyl-2 : 2-dimethyl-1 : 3-dioxolan, b. p. 50—51°/19 mm.

To 4-hydroxymethyl-2 : 2-dimethyldioxolan (13·2 g.) dissolved in ether (50 ml.), sodium wire (3 g.) was added. Then the excess of sodium was removed and the ether evaporated. The solid sodium salt was dissolved in deuterium oxide (2 g.), and the solution neutralised with dry carbon dioxide. 4-Deuteroxymethyl-2 : 2-dimethyl-1 : 3-dioxolan was obtained by distillation at 10^{-5} mm.

The spectra of these dioxolans, some of which were racemic mixtures, were measured as described in the preceding paper, and are recorded in the Tables.

Discussion

The assignments for the substituted dioxolans (Table 1) have been made by analogy with the assignments for dioxolan given in Part I. In assigning the internal vibrations of the methyl groups, use was made of the review by Sheppard and Simpson [9] on the spectra

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* Part I, preceding paper.

[1] Hibbert and Timm, *J. Amer. Chem. Soc.*, 1924, **46**, 1283.
[2] Clarke, *J.*, 1912, 1788.
[3] Lucas and Guthrie, *J. Amer. Chem. Soc.*, 1950, **72**, 5490.
[4] Barker, Bourne, Pinkard, Stacey, and Whiffen, *J.*, 1958,
[5] Dworzak and Herrmann, *Monatsh.*, 1930, **52**, 83.
[6] Boeseken and Hermans, *Rec. Trav. chim.*, 1923, **42**, 1104.
[7] Newmann and Renoll, *J. Amer. Chem. Soc.*, 1945, **67**, 162
[8] Baer and Fischer, *J. Biol. Chem.*, 1939, **128**, 463.
[9] Sheppard and Simpson, *Quart. Rev.*, 1953, **7**, 19.

TABLE 1. *Assignments (cm.$^{-1}$) for the substituted dioxolans.*

Assignment	2-Me	4-Me	*cis*-2 : 4-Me$_2$	*trans*-2 : 4-Me$_2$	2 : 2-Me$_2$	2 : 2 : 4-Me$_3$	4-HO·CH$_2$-2 : 2-Me$_2$	4-MeO·CH$_2$-2 : 2-Me$_2$	4-DO·CH$_2$-2 : 2-Me$_2$	
1st overtone of CH$_2$ scissors (C$_2$) 2 × 1506 cm.$^{-1}$		3019vw								IR
		3019w								R
1st overtone of Me antisym. band (2 × 1460 cm.$^{-1}$) perturbed by resonance with Me sym. C–H stretch	2946w	2939m	2940m	2939m	2943w	2939s	{ 2933m 2945m	2939s		IR
	2940vs P	2934s P	2934vs P	2934vs P	2936vs P	2936vs P	2938vs P	2937vs P		R
CH$_2$ (C$_2$) antisym. C–H Me (C$_2$) stretch	2997s	2982s *	2994s	2994s	2995vs	2995vs	2995vs	2995vs		IR
	2997vs b	2983vs b *	2982vs b *	2984vs b *	2991vs	2986vs b *	2991vs *	2991vs *		R
Me antisym. C–H stretch (C$_4$)		2982s *	2985s	2981s		2981s sh	2986sh	2987sh		IR
		1983sb *	2982vs b *	2984vs b *		2986vs b *	2991vs *	2991vs *		R
CH$_2$ antisym. C–H stretch (C$_4$, C$_5$)	2961w				2963w					IR
	—				—					R
Lone C–H stretch (C$_4$)		2898w	2902w sh	2902w sh		2898w	2899w sh	2899s		IR
		—	—	—		—	—	—		R
CH$_2$ (C$_4$, C$_5$) sym. C–H Me (C$_2$, C$_4$) stretch	2886s	2879s	2884s	2879s	2885vs	2878s	2888s	2886vs		IR
	2885s b P	2876s b P	2874vs b P	2872vs b P	2875vs b P	2868s P	*ca.* 2890vs vb P	2886vs vb P		R
CH$_2$ sym. C–H stretch (C$_2$)		2856s								IR
		?								R
OMe C–H stretch?								2820m		IR
								2815m P		R
								2841m		IR
								2835m P		R
CH$_2$ scissors (C$_2$)		1512s								IR
		1506s								R
CH$_2$ scissors (C$_4$, C$_5$)	1480vs	1477s	1480s sh	1477s sh	1477s sh	1479s sh	1482s sh	1480s sh	1482s	IR
	1480s	1480m	1481m	1478m	1482s	1483w	1480m	1480m		R
Me antisym. bend	1450vs	1457vs	1450vs	1448vs	1456vs	1456vs	1460vs	1458vs	1456vs	IR
	1455s	1456m	1451s	1448s	1461s	1460s	1459s	1459s		R
Me antisym. bend (*gem*-Me$_2$)					—	—	—	—		IR
					1428m	1432m	1437s	1436m		R
Lone C–H def. (C$_2$)	1408vs		1410vs	1408vs						IR
	—		—	—						R
Methyl sym. bend [lone C–H def (C$_4$)]	1381vs	1385vs	1382vs	1381vs	1374vs	1376vs	1375vs	1381vs	1377vs	IR
	—	—	—	—	1385vw	1377vw	1386vw	1380vw		R
CH$_2$ wag (C$_2$)		(1385m)								IR
		1397m								R
Sym. CH$_2$ wag (C$_4$, C$_5$)	1360vs				1342s *					IR
	1356w				1347w d *					R
CH$_2$ wag (C$_5$)		1336w	1339vs	1336s		1315vs	1318w	1320s	1318w	IR
		1335w	1342w	1334w—m		1314w	1331vw	1338vw		R
			1325w							

Antisym. CH_2 wag (C_4, C_5)	1309w *	1307m	1300s	1303m	1342s *					IR
? Lone C–H def. (C_2, C_4)	1320w—m	1309m	1300w	1301m	1347w d *					R
Sym. CH_2 twist (C_4, C_5)	1309w *				?					IR
	—									R
CH_2 twist (C_2)		1246w sh								IR
		1250w								R
gem-Me_2 rock					1245s	1243s	1251s	1250s	1251vs	IR
					—	1249w	1240w—m	1259w		R
gem-Me_2 rock					1218vs *	1216vs	1212vs	1212vs	1213vs	IR
					1222m *	1220m d	1210m—s	1212w—m		R
Antisym. CH_2 twist (C_4, C_5)	1217s	1214m sh	1220s	1224s	1218vs *					IR
? Me rock (C_2, C_4) ? CH_2 twist (C_5)	1219w—m	1216w—m	1218w	1225m	1220m *					R
Ring antisym. stretch	1150vs	1162vs	1162vs 1141vs	1153vs	1148vs	1169vs	1158vs	1157vs 1141vs	1159vs	IR
	1151w	1149w P	1164w—m 1144w—m	1153m	—	—	1165vw	1164vw 1139vw		R
? Me rock (C_2)	1118vs	—	1117vs	1115vs						IR
	1120w		1116w	1117w—m						R
C–O stretch (OH)							1074vs		990s *	IR
							1079w d			R
Ring sym. stretch	1087vs	1092vs	1083vs	1084vs	1061vs	1096vs	1050vs	1052vs	1052vs	IR
	—	1077w P	1085w	1083m	1064w	1095vw	1051w	1050vw		R
Ring sym. stretch	1024vs	1008vs	1022vs	1036vs	1034s	1052vs	1025sh	1032s sh	1023s sh	IR
	1026m	1008wm d	1021w—m	1035m	1040vw	1056vw	—	—		R
? Ring antisym. stretch	?	?	947vs	943s	—	977vs	987vw	973s	990s *	IR
			947w	942w	955m	979w—m	967m	972mw		R
Ring breathing	947vs	939vs	935vs	926vs	947vs	945s	971m	953m 933w	972m	IR
	947? vs	938m—s P	932w	923w	946? vs	947w	955m	951w		R
? *gem*-Me_2 rock					916s	920vs	927vw	919w	919m	IR
					919w	919m	917m	915w—m		R
? *gem*-Me_2 rock					893s	873s	877m	890w	879m	IR
					889vw	876w	865w P	868w P		R
? CH_2 rock (C_4, C_5)	863vs	897s	858vs	858vs						IR
	—	901w	855w	858w						R
gem-Me_2 antisym. C–C stretch					837vs	841vs	843vs	843vs	839vs *	IR
					840w	843vw	—	836vw		R
Me–Ring (C_2, C_4) C–C stretch	838m	825s	830s	822s		841? vs *	833vs	843? vs	839vs *	IR
	838vs P	830vs P	826s P	822s P						R
gem-Me_2 sym. C–C stretch					782vs	788vs	791s	790s	791s	IR
					784vs P	789vs P	792s P	791s P		R

TABLE 1. (*Continued.*)

Assignment	2-Me	4-Me	*cis*-2 : 4-Me_2	*trans*-2 : 4-Me_2	2 : 2-Me_2	2 : 2 : 4-Me_3	4-HO·CH_2-2 : 2-Me_2	4-MeO·CH_2-2 : 2-Me_2	4-DO·CH_2-2 : 2-Me_2	
? CH_2 rock (C_2)		725m								IR
		726m								R
In-plane ring def.	692s	721? m	695s	693s	—	—		—		IR
	695m	—	695w—m	694w—m	675vw	692vw		692vw		R
In-plane ring def.		614m	609m		647s	644m				IR
	637vw	619vw	622w	639w	638s P	640s P	648m P 635m P	646m P 633m P		R
gem-Me_2 antisym. C–C def.					509vs	514vs				IR
					512vw	516w	513w	514vw		R
Me–ring (C_2) C–C def.	513m P		504w	517m						IR
			504m P	525w P						R
Me–ring (C_4) C–C def.			473w	440m						IR
		472vw	467w	445m		471vw	473w	456vw		R
gem-Me_2, sym. C–C def.					353vw	351vw	347w	344vw		R
Unassigned	IR 603w	IR 652w sh	IR 458w	IR 608m	IR 527w sh	IR 600s	IR 567vs	IR 735w	IR 731w	
	R 738vw	835s	518w	879s sh	1105vw	765w	608w	1077vs	825vw	
	784vw	R 334vw d	527w	R 283vw	R 133vw	R 145vw	~691m	1110vs	957vw	
	890vw	779vw	777vw	385vw	252vw	166vw	731w	1200vs	1107m	
		1111vw	793vw	609wd PP?	565vw	~248vw	908vw	1237s	2840vs	
			1244vw sh	715vw PP?	735vw	286vw	1117m	2820m		
			R 245vw	764w shp PP?	1120vw	422vw	3430vs	2841m		
			294vw	880w	1173vw	600wm d	R 316w	R 291wm PP		
			374vw	1172w		732vw	381vw	327wb		
			726vw	1364vw		815vw	420vw	372vw		
			770vw			1122vw d	600w PP?	~578vw		
			881w d			1143vw	735w P	~594vw		
			1366vw shp			2916w P	1121vw	665vw		
							1291vw	735w PP?		
							3450vw	1082vw		
								1107vw d		
								1289vw		
								2835m P		

Key: IR, infrared; R, Raman; v, very; s, strong; m, medium; w, weak; d, diffuse; b, broad; sh, shoulder; shp, sharp; P, polarised; PP, partly polarised.

* Frequency used twice.

of paraffin hydrocarbons since the arrangement of methyl groups in paraffins containing an internal tertiary carbon atom is analogous to that in methyldioxolans. In paraffins containing an internal quaternary carbon atom it is analogous to that in the *gem*-dimethyldioxolans.

Vibrations involving Methylene Groups.—Assignments for these were made by strict analogy with those for dioxolan, and many have been discussed in Part I.

Vibrations involving Methyl Substituents.—(a) *Bending.* The strong infrared band and Raman line at 1450—1460 cm.$^{-1}$ shown by all methyldioxolans has been assigned to the internal antisymmetrical methyl bending vibration. 2 : 2-Dimethyldioxolans show an additional strong Raman line at *ca.* 1430 cm.$^{-1}$ (corresponding infrared band absent), presumably due to splitting of the antisymmetrical methyl bending frequency of the *gem*-dimethyl group. The very strong infrared band at *ca.* 1380 cm.$^{-1}$ in all the methyldioxolans has been attributed to the symmetrical methyl bending vibration.

(b) *Rocking.* In contrast to the internal methyl bending vibrations the rocking modes of the methyl groups often couple strongly with the skeletal vibrations. The *gem*-dimethyl rocking vibrations have been assigned to the strong infrared bands near 1250 and 1220 cm.$^{-1}$; the corresponding Raman lines are of weak or medium intensity. These frequencies are higher than those (1210 and 1190 cm.$^{-1}$) found by Sheppard and Simpson [9] for paraffins with an internal quaternary carbon atom. The frequency near 1250 cm.$^{-1}$ is only present in 2 : 2-dimethyldioxolans. A frequency near 1220 cm.$^{-1}$ is present in all the substituted dioxolans and can be assigned to a methylene twisting vibration or methyl rocking mode in the compound where there are no *gem*-dimethyl groups. Further methyl rocking vibrations may be assigned to two of the strong infrared bands at 800—1000 cm.$^{-1}$, shown by 2 : 2-dimethyldioxolans. The most probable frequencies are *ca.* 880, *ca.* 920, and *ca.* 980 cm.$^{-1}$, if the band at *ca.* 840 cm.$^{-1}$ is assigned to the antisymmetrical carbon–carbon stretching vibration of the *gem*-dimethyl group (see below).

(c) *Stretching.* The symmetrical stretching vibration of the 2 : 2-*gem*-dimethyl group has been assigned to the very strong polarised Raman line and intense infrared band at *ca.* 790 cm.$^{-1}$. This is to be compared with a strong polarised Raman line at 685—750 cm.$^{-1}$ for the corresponding vibration in the paraffins.[9] The band at 790 cm.$^{-1}$ is only present in the spectra of 2 : 2-dimethyldioxolans, in agreement with this assignment. The corresponding antisymmetrical stretching vibration of the *gem*-dimethyl group has been assigned to the very strong infrared band at *ca.* 840 cm.$^{-1}$ (absent in the other substituted dioxolans), but could alternatively be attributed to a rocking mode with one of the other bands between 800 and 1000 cm.$^{-1}$ assigned to the stretching vibration.

The stretching of the methyl–ring bond ($Me-C_{(2)}$ or $Me-C_{(4)}$) has been assigned to the very strong polarised line at *ca.* 830 cm.$^{-1}$. The corresponding vibration in the paraffins [9] occurs near 815 cm.$^{-1}$.

(d) *Deformations involving methyl groups.* As with the stretching vibrations, these deformations can be expected at higher frequencies than corresponding vibrations in the paraffins, *e.g.*, antisymmetrical deformation of the *gem.*-dimethyl group in dioxolans, weak Raman line at *ca.* 515 cm.$^{-1}$ (corresponding vibration in paraffins,[9] weak Raman line at 480—490 cm.$^{-1}$). Similarly, the symmetrical deformation of the *gem.*-dimethyl group in dioxolans has been assigned to the weak Raman line at *ca.* 350 cm.$^{-1}$, compared with 350—305 cm.$^{-1}$ in paraffins.[9]

The polarised Raman line of medium intensity near 515 cm.$^{-1}$ in 2-methyldioxolan and *cis*- and *trans*-2 : 4-dimethyldioxolan has been assigned to the C–C deformation of a 2-methyl group. This compares with a medium-intensity Raman line at 415—450 cm.$^{-1}$, assigned to the corresponding vibration in the paraffins.[9] When the methyl group is on a carbon atom (position 4) attached to one oxygen atom rather than two, the deformation vibration in the dioxolans drops to *ca.* 470 cm.$^{-1}$. This frequency is absent in 2-methyl- and 2 : 2-dimethyl-dioxolans, in agreement with this assignment.

C–H *Deformations.*—The deformation of the single hydrogen on a tertiary carbon does not usually give rise to strong features in either the Raman or infrared spectra of paraffin hydrocarbons, where they occur at 1330—1360 cm.$^{-1}$ and *ca.* 1380 cm.$^{-1}$. The very strong infrared band at *ca.* 1408 cm.$^{-1}$ has been assigned to one of the deformation modes of the lone C–H group in position 2 of dioxolans. The intensity of this band is considerably enhanced and the frequency increased by the adjacent oxygen atoms. This band is only present in 2-methyl- and *cis*- and *trans*-2 : 4-dimethyl-dioxolans. The other C–H deformation vibration can probably be given the frequency near 1300 cm.$^{-1}$ although this also occurs in the 4-substituted dioxolans and might alternatively be assigned to a twisting vibration. However, the lower-frequency vibration is perhaps less affected by the oxygen atoms and occurs at a similar frequency for 2- and 4-substituted dioxolans. The higher-frequency C–H deformation (position 4) has not beeen observed, presumably because it is overlaid by the symmetrical methyl bending vibration at 1380 cm.$^{-1}$.

Vibrations involving a Hydroxymethyl Substituent.—Assignments for the O–H deformation and the C–O stretching vibration of hydroxyl groups have been discussed by Stuart and Sutherland,[10] who suggested the assignment of a band at 950 cm.$^{-1}$ to the out-of-plane O–H deformation, a band at 1370 cm.$^{-1}$ to the in-plane deformation, and a band at 1110 cm.$^{-1}$ to the C–O stretching vibration coupled with other skeletal vibrations.

Comparison of the spectra of 4-hydroxymethyl- and 4-deuteroxymethyl-2 : 2-dimethyldioxolan showed that the band at 1074 cm.$^{-1}$ disappeared from the spectra of the former and was replaced by a band at 990 cm.$^{-1}$ in 4-deuteroxymethyl-2 : 2-dimethyldioxolan. The band at 1074 cm.$^{-1}$ has therefore been assigned to the C–O stretching vibration. That this frequency is somewhat lower than that observed by Stuart and Sutherland[10] may be due to hydrogen-bonding to the ring-oxygen atoms. The bands found by them at *ca.* 1370 and 950 cm.$^{-1}$ were very broad, extending over *ca.* 200 cm.$^{-1}$ and so have not been detected with the single-beam instrument used in our work.

In the infrared spectra of the pure liquids the O–H stretching vibration in 4-hydroxymethyl-2 : 2-dimethyldioxolan gives a band at 3430 cm.$^{-1}$, while the O–D stretching vibration produced a band at 2480 cm.$^{-1}$. In each compound a weak diffuse Raman line is detectable near the frequency of the infrared band. The ratio (1 : 1·38) of the O–H to the O–D stretching frequency is in good agreement with the theoretical value of 1·41 for a pure stretch.

Ring Vibrations.—The ring vibrations at 1158 and 1087 cm.$^{-1}$ occur consistently in the substituted dioxolans. Those corresponding to the 1030 cm.$^{-1}$ symmetrical ring vibration in dioxolan itself show a large variation in frequency, presumably due to coupling of this ring vibration with the vibrations of the substituent groups.

In dioxolans substituted only in the 2-position, the ring breathing vibration is readily identifiable as a strong polarised Raman line near 940 cm.$^{-1}$. In the 4-substituted dioxolans, however, the intensity of the Raman line is considerably less and so can no longer be observed as polarised. The corresponding infrared band is strong for all but 4-hydroxymethyl- and 4-methoxymethyl-2 : 2-dimethyldioxolan, for which coupling prevents its identification. The variation of intensity of this vibration precludes its use in what might have been a promising method of differentiation of five- and six-membered acetal rings since Raman spectra of 1 : 3-dioxolan and 1 : 3-dioxan showed that the ring breathing frequency of each was the only strong polarised line below 1500 cm.$^{-1}$ (1 : 3-dioxolan, 939 cm.$^{-1}$; 1 : 3-dioxan, 834 cm.$^{-1}$). Moreover, another difficulty was that 2-methyl-1 : 3-dioxolan showed a strong polarised line at 837 cm.$^{-1}$ (due to methyl–ring bond stretching) in addition to the strong polarised Raman line at 947 cm.$^{-1}$ due to its ring breathing frequency.

The remaining ring stretching vibration (dioxolan, 962 cm.$^{-1}$) appears to couple strongly, rendering its assignment difficult in the substituted dioxolans.

Assignments for the in-plane ring deformations at *ca.* 690 and *ca.* 640 cm.$^{-1}$ are similar to that for dioxolan itself.

[10] Sutherland, *Discuss. Faraday Soc.*, 1950, **9**, 261; Stuart and Sutherland, *J. Chem. Phys.*,1952, **20**, 1977; 1956, **24**, 559.

TABLE 2. *Assignments (cm.$^{-1}$) for three hexitol ketals.*

		3 : 4-*O*-*iso*Propylidene-	
Assignment	iditol	mannitol	sorbitol
Me antisym. bend	1456s	1452s	1458s
Me sym. bend	1378s	1375s	1380s
Lone C–H def.	1336sh	1338m	1338w
gem-Me$_2$ rock sym.	1242s	1239s	1258m—s
gem-Me$_2$ rock antisym.	1214s	1218s	1207m—s
Ring antisym. stretch	1165s	1167s	1158m—s
? Skeletal stretch	1119s	1117s	1129m—s
C–O stretch (OH)	1077s	1073vs	1095m
Ring sym. stretch	1052s	?	1064sh, 1055sh
Ring sym. stretch	1029vs	1034vs	1045vs
Skeletal stretch	1002vs	1011s	1022s
? Ring stretch, *gem*-Me$_2$ rock	989s 952m—s	981m 934sh	994m 955m
? *gem*-Me$_2$ antisym. stretch	878s	876vs	870s
gem-Me$_2$ rock	856s		862s
gem-Me$_2$ sym. stretch	814s	814w	806s
?–CH(OH)·CH$_2$·OH rock	716m	713m—s	721w—m

Hexitol Ketals.—The infrared spectra of the 3 : 4-*O*-*iso*propylidene ketals of L-iditol, D-mannitol, and D-sorbitol were measured over the range 650—1500 cm.$^{-1}$; the partial assignments of frequencies shown in Table 2 were made by analogy with those for the substituted dioxolans.

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