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Note

Hydration of acetates of *aldehydo*-aldoses*

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The reversible hydration of aldehyde groups has received scant attention in carbohydrate chemistry[1,2]. It has been established[3,4] that the aldehydo and aldehydrol forms present in this equilibrium can be readily and unequivocally differentiated by n.m.r. spectroscopy.

In the course of a recent study[5] of the conformations of tetra-*O*-acetyl-*aldehydo*-pentoses and 6-deoxy-*aldehydo*-L-galactose tetraacetate by n.m.r. spectroscopy, a few drops of deuterium oxide were added to solutions of these aldehydes in chloroform-*d* to permit examination of the hydration process. The aldehydrol of 6-deoxy-*aldehydo*-L-galactose 2,3,4,5-tetraacetate was, however, found to be insoluble in this medium**. Other solvents commonly used in n.m.r spectroscopy proved also to be unsuitable for this study.

Tetrahydrofuran was found to be a suitable, water-miscible solvent for the tetraacetylated *aldehydo*-aldoses (**1**–**5**) derived from D-ribose, L-arabinose, D-xylose, D-lyxose, and L-fucose, as well as for the corresponding aldehydrols. Accordingly, the spectra of the five derivatives were first measured in tetrahydrofuran alone, and then deuterium oxide was added to give a 7:3 solvent system. The rate and extent of formation of the aldehydrol was determined by n.m.r. spectroscopy of the resultant, clear solutions. The H-1 signals of the aldehydo forms were observed several p.p.m. to lower field of the H-1 signals of the aldehydrol forms, and the latter signals were situated among, but not obscured by, signals of certain methine protons on carbon atoms of the chain. The solvent resonances, which obliterated the high-field portion of the spectra, were situated ~ 1.5 p.p.m. to higher field of the H-1 signals of the aldehydrol forms.

Table I records the equilibrium compositions observed for the five examples mentioned, together with n.m.r. spectral data for the H-1 signals of the aldehydo and aldehydrol forms. Also included are approximate estimates of the half-lives of the

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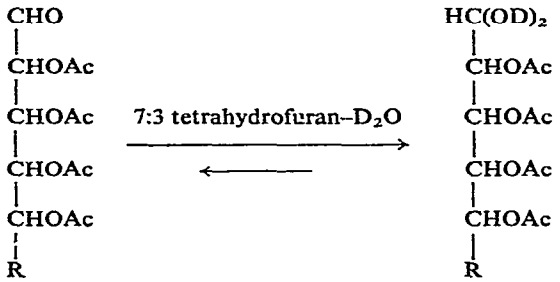
**Micheel and Suckfüll[6] and Wolfrom and Orsino[1] have noted the exceptional insolubility of certain derivatives of 2,3,4,5-tetra-*O*-acetyl-*aldehydo*-D(or L)-galactose in common solvents.

equilibration reactions. In each case, equilibrium had proceeded half way to completion in 10–20 min at 28° in the 7:3 tetrahydrofuran–deuterium oxide mixture, and was essentially complete in 3 h.



1 D-*ribo*, R = H
2 L-*arabino*, R = H
3 D-*xylo*, R = H
4 D-*lyxo*, R = H
5 L-*galacto*, R = Me

TABLE I

PROPORTIONS OF COMPONENTS AT EQUILIBRIUM, HALF-LIVES FOR ATTAINMENT OF EQUILIBRIUM, AND N.M.R. SPECTRAL DATA FOR THE H-1 SIGNALS OF THE ALDEHYDO AND ALDEHYDROL FORMS OF SOME *aldehydo*-ALDOSE TETRAACETATES, MEASURED AT 100 MHz IN 7:3 TETRAHYDROFURAN–DEUTERIUM OXIDE

2,3,4,5-Tetra-O-acetyl-aldehydo *derivative of*	*CHO*[a] *at equilibrium, %*	K_{eq}^{a} ([*CH*(*OD*)$_2$]/[*CHO*])	*Half-life*[a] *(min)*	*Chemical shift* (τ) [$J_{1,2}$ *(Hz)*] *for H-1 of*	
				CHO	*CH(OD)*$_2$
D-Ribose (1)	8	11	9	0.40 [~0]	4.97 [2]
L-Arabinose (2)	10	9	14	0.45 [~0]	5.08 [6.5]
D-Xylose (3)	7	13	19	0.39 [~0]	4.88 [2]
D-Lyxose (4)	10	10	7	0.42 [~0]	5.00 [<1]
L-Fucose (5)	27	3	21	0.36 [~0]	4.94 [2]

[a] ±5%.

It is noteworthy that the proportion of free aldehydo form at equilibrium for the aldopentose derivatives **1**–**4** is less than 10% (27% for the deoxyaldohexose derivative **5**), even in a medium composed mainly of a non-hydroxylic solvent. In hydroxylic solvents, the aldehydrol form is undoubtedly favored overwhelmingly over the free aldehyde form.

These data indicate the need for caution in ascribing a major role to free aldehyde forms as principal species, or as intermediates in reactions, for aldoses and their derivatives in hydroxylic solvents, even when structural features preclude the formation of cyclic hemiacetals.

EXPERIMENTAL

*N.m.r. spectral observation of the equilibration of some tetra-*O*-acetyl-*aldehydo*-aldoses in 7:3 tetrahydrofuran–deuterium oxide.* — After initial determination, at ~ 28°, of the 100-MHz n.m.r. spectrum (Varian HA-100 spectrometer) of a 15% (w/v) solution (0.35 ml) of each of the aldehydo derivatives **1**–**5** (see Ref. 5 for details of preparation) in tetrahydrofuran, deuterium oxide (3 drops, 0.15 ml) was added, and the mixture was shaken to produce homogeneity. Spectra of the solutions were then recorded (at ~28°) after the elapse of various times up to 24 h. Relative areas of the H-1 signals of the aldehydo and aldehydrol forms were determined by planimetry and verified by triangulation. The results are presented in Table I.

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