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Note

The chemical shift of the anomeric proton of some sugar perbenzoates

JORGE O. DEFERRARI, INGE M. E. THIEL

Departamento de Química Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires (Argentina)

AND RAÚL A. CADENAS

Departamento de Química, Facultad de Agronomia y Veterinaria, Universidad de Buenos Aires (Argentina)

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The present work reports some observations on the H-1 resonance of known perbenzoylated aldohexopyranoses (D-galactose, D-mannose, and D-glucose), perbenzoylated disaccharides (maltose, cellobiose, and lactose), and the nonabenzoates of maltitol, cellobiitol, and lactitol. Table I lists chemical-shift data and first-order spacings for H-1 of these sugar perbenzoates in chloroform-*d*.

TABLE I

CHEMICAL-SHIFT DATA AND FIRST-ORDER SPACINGS FOR H-1 OF SOME SUGAR PERBENZOATES IN CHLOROFORM-*d* AT 20° AND 60 MHz

Compound	*Chemical shift of H-1 doublet* (τ)	*Splitting of H-1 signal* (*Hz*)
Pentabenzoate of:		
α-D-galactopyranose	3.00	2.5
β-D-galactopyranose	3.10	4.5
α-D-mannopyranose	3.36	1.5
β-D-mannopyranose	3.55	0
α-D-glucopyranose	3.06	4.0
β-D-glucopyranose	~3.62	—
Octabenzoate of:		
α-maltose	3.18	3.5
α-cellobiose	3.21	3.5
α-lactose	3.22	3.5

The anomeric pair of penta-*O*-benzoyl-D-galactopyranoses shows the H-1 chemical-shifts displaced to lower field (0.64 p.p.m. for the α and 1.16 p.p.m. for the β anomer) compared with those of the corresponding acetates[1], probably owing to the electron-withdrawing ability of the benzoyl group. Analogous deshielding has been recorded for pentopyranose benzoates[2].

In the p.m.r. spectra of the anomeric penta-*O*-benzoyl-D-mannopyranoses, the H-1*e* signal (α anomer) appeared at lower field by 0.55 p.p.m., and the H-1*a* signal (β anomer) by 0.52 p.p.m., than the corresponding values for the acetates[1].

Penta-*O*-benzoyl-α-D-glucopyranose showed its H-1*e* signal at lower field by 0.60 p.p.m. than that of the corresponding acetate[1]. The β anomer showed a resonance signal centered at τ 3.62 attributable to H-1*a* superimposed on that of another proton (probably H-3, on the basis that both protons are in *syn*-diaxial orientation on the pyranose ring[1]). The difference in chemical shifts, H-1*a*−H-1*e*, for this anomeric pair of perbenzoates is 0.56 p.p.m. Similar differences have been reported for the anomers of D-glucopyranose[3–5] (0.58 p.p.m.), and penta-*O*-acetyl-D-glucopyranose[1,3] (0.58 p.p.m.), and for disaccharides having a D-glucopyranose residue as the reducing moiety[4], as in maltose (0.57 p.p.m.), lactose (0.58 p.p.m.), and cellobiose (0.57 p.p.m.).

On comparing the shifts of the H-1*a* signals for the perbenzoates of β-D-mannopyranose and β-D-glucopyranose, only a 0.07 p.p.m. shift to lower field is observed, occasioned by the influence of the axial 2-benzoyloxy group in the former compound. This is negligible compared to the deshielding of 0.20 p.p.m. in the corresponding acetates[1].

The small influence of the axial 2-benzoyloxy groups upon H-1*a* makes noteworthy the strong deshielding effect observed (0.52 p.p.m.) on passing from β-D-glucopyranose pentabenzoate to the β-D-galactopyranose pentabenzoate, attributable to the axial 4-benzoyloxy group in the β-D-*galacto* derivative.

Consideration of the pentabenzoates of α-D-glucopyranose and α-D-galactopyranose revealed that the change of the configuration of C-4 led to a small deshielding of H-1*e* (0.06 p.p.m.), suggesting that the axial 4-benzoyloxy group has little influence upon equatorially attached, anomeric protons. On the other hand, the shielding observed on passing from the α-D-*gluco* to the α-D-*manno* configuration (0.36 p.p.m.) could be mainly ascribable to the influence of the axial 2-benzoyloxy group in the latter. In the acetates[1], the effect has the same direction, but by 0.20 p.p.m. It is concluded that regularities observed for acetates are not valid for these monosaccharide perbenzoates. If it is true that an axial, neighboring, benzoyloxy group shields an equatorial proton (by a higher value than in acetates), its effect on an axial, antiparallel proton is not predictable, and seems to be dependent on other features of the molecule.

In the α-octabenzoates of maltose, cellobiose, and lactose, a low-field signal for H-1*e* was observed (see Table I), but, for the corresponding β anomers (H-1*a*), a signal between τ 3.00 and 3.50 was absent. Accepting, for these disaccharide benzoates, a shift of 0.57 p.p.m. to higher field from H-1*e* to H-1*a* (as already indicated for sugars possessing the D-*gluco* configuration), in the β-benzoates of maltose, cellobiose, and lactose the H-1*a* signal would appear at about τ 3.75, 3.78, and 3.79, respectively, superimposed on the signals for the rest of the protons.

The correctness of the assignment for the H-1*e* signal was confirmed by its absence from the spectra of the corresponding nonabenzoates of the 4-*O*-D-glycopyranosyl-D-glucitols synthesized by reduction of the appropriate, free disaccharide

with sodium borohydride, and subsequent benzoylation. These nonabenzoates have only H-1′ as the more deshielded proton; however, no signal appeared between τ 3.00 and 3.50 in the spectra of the nona-*O*-benzoyl derivatives of maltitol (H-1′*e*), cellobiitol (H-1′*a*), and lactitol (H-1′*a*). The free aldobioses maltose and cellobiose[4,5] showed a distinct signal for that glycosidic proton that was not apparent in the p.m.r. spectra of their octabenzoates and of the corresponding nona-*O*-benzoylated aldobiitols.

EXPERIMENTAL

The benzoates of D-galactopyranose[6,7], D-mannopyranose[8,9], D-glucopyranose[10,11], maltose[12], cellobiose[13], and lactose[14] were prepared, and purified until their physical constants agreed with those in the literature. The p.m.r. spectra were recorded at 60 MHz, in chloroform-*d* at 20°, with a Varian A-60 n.m.r. spectrometer. Tetramethylsilane was used as the internal standard. First-order spacings for the H-1 signals (see Table I) were read directly from the spectra.

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REFERENCES

1 R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, 43 (1965) 2059.
2 P. L. Durette and D. Horton, *J. Org. Chem.*, 36 (1971) 2658.
3 L. D. Hall, *Tetrahedron Lett.*, 23 (1964) 1457.
4 J. M. van der Veen, *J. Org. Chem.*, 28 (1963) 564.
5 V. S. R. Rao and J. F. Foster, *J. Phys. Chem.*, 67 (1963) 951.
6 M. L. Wolfrom and C. C. Christman, *J. Amer. Chem. Soc.*, 58 (1936) 39.
7 R. M. de Lederkremer and J. O. Deferrari, *J. Org. Chem.*, 27 (1962) 2561.
8 E. Fischer and R. Oetker, *Ber.*, 46 (1913) 4029.
9 R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *J. Amer. Chem. Soc.*, 72 (1950) 2200.
10 P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, 76 (1928) 513.
11 E. Fischer and K. Freudenberg, *Ber.*, 45 (1912) 2709.
12 I. M. E. Thiel, J. O. Deferrari, and R. A. Cadenas, *J. Org. Chem.*, 31 (1966) 3704.
13 J. O. Deferrari, I. M. E. Thiel, and R. A. Cadenas, *J. Org. Chem.*, 30 (1965) 3053.
14 J. O. Deferrari, I. M. E. Thiel, and R. A. Cadenas, unpublished results.