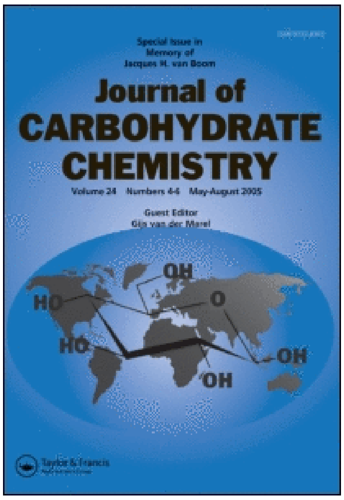


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Degradation of Some Octa-*O*-Benzoylaldobiononitriles: Studies of the Products by NMR Spectroscopy

Norma B. D'accorso[a]; Inge M. E. Thiel[a]
[a] Departamento de Quimica Orgánica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Buenos Aires, Argentina

To cite this Article D'accorso, Norma B. and Thiel, Inge M. E.(1989) 'Degradation of Some Octa-*O*-Benzoylaldobiononitriles: Studies of the Products by NMR Spectroscopy', Journal of Carbohydrate Chemistry, 8: 5, 743 — 751

To link to this Article: DOI: 10.1080/07328308908048036

URL: http://dx.doi.org/10.1080/07328308908048036

J. CARBOHYDRATE CHEMISTRY, 8(5), 743-751 (1989)

DEGRADATION OF SOME OCTA-O-BENZOYLALDOBIONONITRILES: STUDIES OF THE PRODUCTS BY NMR SPECTROSCOPY

Norma B. D'Accorso and Inge M. E. Thiel*

Departamento de Quimica Orgánica,
Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad
Universitaria, 1428 Buenos Aires, Argentina

Received July 6, 1988 - Final Form June 3, 1989

ABSTRACT

The Zemplén degradation of 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoylcellobiononitrile (**1**), -lactobiononitrile (**2**), and -maltobiononitrile (**3**) was carried out giving a mixture of the four 3-*O*-(D-hexopyranosyl)-D-arabinoses. Their reduction gave the 3-*O*-(D-hexopyranosyl)-D-arabinitols, and their benzoylation gave the 1, 2, 4, 5, 2', 3', 4', 6'-octa-*O*-benzoyl-(D-hexopyranosyl)-D-arabinitols. Their ^{1}H and ^{13}C NMR spectra are described, and their conformations are determined to be planar zig-zag for the acyclic moieties.

INTRODUCTION

The degradation of acylated aldononitriles with sodium methoxide is a potentially useful method for the synthesis of aldoses having one less carbon in their chain. The application of this reaction to peracylated aldobiononitriles gives rise to (hexopyranosyl)pentoses. This reaction was used by Zemplén with 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-acetylcellobiononitrile,[1] and a complex reaction mixture was obtained because the starting material was not pure. By acetylation of this mixture, 33% of 1, 2, 4, 2', 3', 4', 6'-hepta-*O*-acetyl-3-*O*-(β-D-glucopyranosyl)-α-D-arabinopyranose was separated, which was derived from the major product formed during the degradation, together with other minor acetylated products. Gelpi and Cadenas[2] repeated the reaction with pure octa-*O*-acetylcellobiononitrile and found a less complex mixture consisting of essentially four compounds, all of which could be separated as their peracetates.

Due to their structures, peracylated aldobiononitriles with 1-6 glycosidic bonds give by Zemplén degradation only two 5-*O*-(glycopyranosyl)furanose sugars. From 2, 3, 4, 5, 2', 3', 4', 6'-octa-*O*-acetylmelibiononitrile[3] and 2, 3, 4, 5, 2', 3', 4', 6'-octa-*O*-benzoylmelibiononitrile,[4] the free sugars were obtained crystalline in 72.8% and 82.2% yield, respectively. From 2, 3, 4, 5, 2', 3', 4', 6'-octa-*O*-acetylgentiobiononitrile,[5] 5-O-(β-D-glucopyranosyl)-α-D-arabinofuranose was obtained in 32% yield, and only traces of the β-anomer were observed.

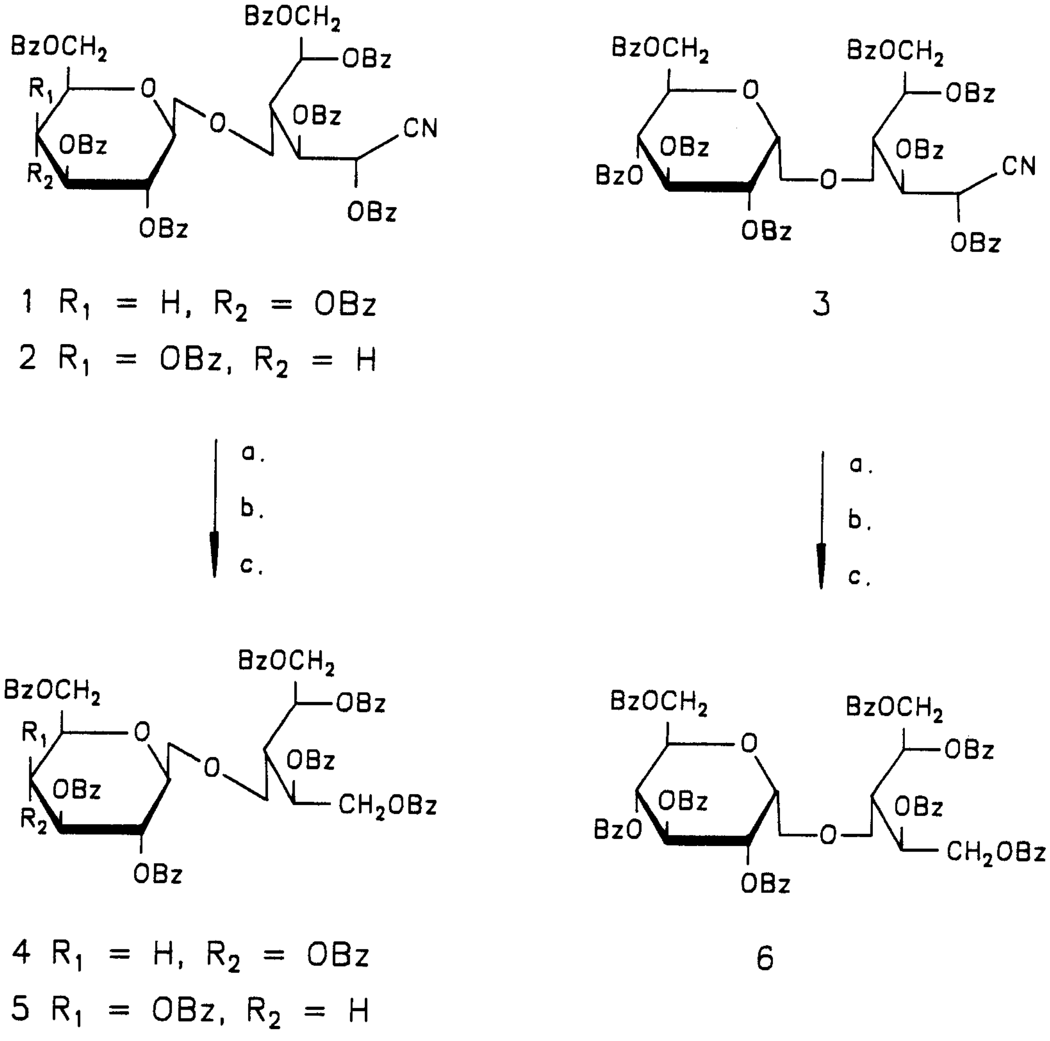
In comparison, the yield of free sugars formed by the classical Wohl degradation was found to be much lower: 1.9% for 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-acetyl-lactobiononitrile,[6] 2.3% for 2, 3, 4, 5, 2', 3', 4', 6'-octa-*O*-acetylmelibiononitrile,[4] and 2.3% for 2, 3, 4, 5, 2', 3', 4', 6'-octa-*O*-benzoylmelibiononitrile.[7]

RESULTS AND DISCUSSION

Wohl degradation of perbenzoylated 1-4 linked aldobiononitriles[8] gave the free 3-*O*-(D-hexopyranosyl)-D-arabinoses in less than 32% yield. In order to get higher yields of these free sugars, we used the Zemplén degradation. Zemplén degradation of aldobiononitriles with 1-4 glycosidic linkages was carried out with 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoylcellobiononitrile (**1**), 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoyllactobiononitrile (**2**), and 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoylmaltobiononitrile (**3**), all giving the expected four 3-*O*-(D-hexopyranosyl)-D-arabinoses in over 85% yield. In these examples the position of the glycosidic linkage permits the formation of both furanose and pyranose cyclic forms, in contrast to 1-6 glycosidically linked compounds in which only the furanose cyclic form is possible.

Separation of the free sugars of the reaction mixture was carried out by preparative paper chromatography. The extracts from the individual spots on the paper chromatograms were dried and weighed. A chromatographic analysis of each zone showed that an equilibrium mixture of products was again formed. In order to determine the relative proportions, the intensity of the ^{13}C NMR signals of C-1 were used, as has been described for analysis of the Wohl degradation products of these compounds,[8] and these results indicated proportions similar to those determined by weight.

The mixtures of products obtained from the Zemplén degradation of **1**, **2**, and **3** with sodium methoxide were directly treated with sodium



1 R_1 = H, R_2 = OBz

2 R_1 = OBz, R_2 = H

3

4 R_1 = H, R_2 = OBz

5 R_1 = OBz, R_2 = H

6

Reagents: a. CH_3ONa/CH_3OH; b. $NaBH_4$; c. BzCl/Pyridine

SCHEME 1

Table 1. ^{1}H NMR Data for 3-*O*-(D-Hexopyranosyl)-D-arabinitol Perbenzoates (4-6).[a]

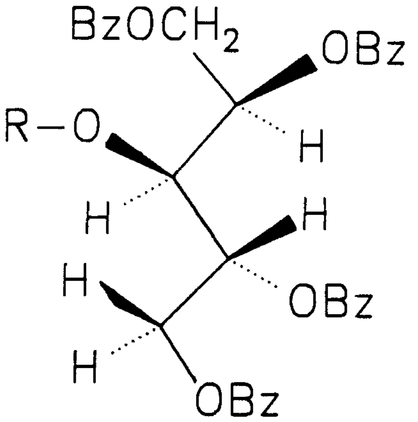
Acyclic Part Compound	H-1a ($J_{1a,2}$)[b]	H-1b ($J_{1b,2}$)	($J_{1a,1b}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5a}$)	H-5a ($J_{4,5b}$)	H-5b ($J_{5a,5b}$)
4	4.58 dd (3.9)	4.41 dd (6.8)	(12.5)	5.88 ddd (3.1)	5.93 dd (7.3)	4.16 ddd (6.9)	4.74 dd (3.9)	4.39 dd (12.3)
5	4.37 dd (6.2)	4.30 dd (6.3)	(12.8)	5.70 ddd (3.7)	5.98 dd (7.5)	4.74 ddd (3.9)	4.72 dd (5.4)	4.47 dd (12.2)
6	4.29 dd (3.7)	4.22 dd (7.1)	(12.4)	5.71 ddd (3.6)	6.22 dd (7.5)	4.71 ddd (4.2)	4.65 dd (6.3)	4.43 dd (12.3)

Cyclic Part Compound	H-1' ($J_{1',2'}$)	H-2' ($J_{2',3'}$)	H-3' (3',4')	H-4' ($J_{4',5'}$)	H-5' ($J_{5',6'a}$)	H-6'a ($J_{5',6'b}$)	H-6'b ($J_{6'a,6'b}$)
4	5.24 d (7.8)	5.68 dd (10.6)	5.64 dd (9.5)	5.92 dd (9.3)	4.43 ddd (4.1)	4.88 dd (8.6)	4.69 dd (12.5)
5	5.53 d (7.9)	5.92 dd (10.4)	5.61 dd (3.4)	5.97 dd (1.0)	4.51 ddd (5.4)	4.95 dd (4.2)	4.47 dd (11.9)
6	5.74 d (3.5)	5.79 dd (10.1)	6.12 t (10.1)	5.65 dd (9.3)	4.73 ddd (3.1)	4.64 dd (6.8)	4.50 dd (11.8)

[a] Determined at 300 MHz in $CDCl_3$ solution, relative to Me_4Si. Chemical shifts are in δ-units. Aromatic protons were observed between δ 7.1 - 8.1.

[b] Spin-spin coupling (J-values) are first-order values reported in hertz (Hz). Multiplicities are d, doublet; dd, doublet of doublets; ddd, double doublet of doublets; t, triplet.

borohydride, and the 3-*O*-(D-hexopyranosyl)-D-arabinitols thus formed were subsequently benzoylated. 1, 2, 4, 5, 2', 3', 4', 6'-Octa-*O*-benzoyl-3-*O*-(β-D-glucopyranosyl)-D-arabinitol (**4**) (67.6%), 1, 2, 4, 5, 2', 3', 4', 6'-octa-*O*-benzoyl-3-*O*-(β-D-galactopyranosyl)-D-arabinitol (**5**) (82.7%), and 1, 2, 4, 5, 2', 3', 4', 6'-octa-*O*-benzoyl-3-*O*-(α-D-glucopyranosyl)-D-arabinitol (**6**) (60.0%) were obtained (See SCHEME 1). Their 300-MHz ^{1}H NMR spectra could be interpreted on a first-order basis, and the data are presented in Table 1. From these values, using the methods of Angyal[9] and Horton,[10] the conformations of the acyclic chains in



4 R = 2', 3', 4', 6'-Tetra-*O*-benzoyl-β-D-glucopyranosyl-

5 R = 2', 3', 4', 6'-Tetra-*O*-benzoyl-β-D-galactopyranosyl-

6 R = 2', 3', 4', 6'-Tetra-*O*-benzoyl-α-D-glucopyranosyl-

FIG. 1. Conformation of **4** - **6**.

solution were determined to be planar zig-zag and extended. For the benzoylated derivatives, coupling constants of 7.4 - 10.7 Hz correspond to diaxial vicinal protons, and couplings of 3.0 - 4.4 Hz correspond to vicinal gauche protons.[11] In compounds **4**, **5**, and **6**, $J_{2,3}$ ranges from 3.1 to 3.7 Hz and corresponds to protons with a gauche relation, while $J_{3,4}$ is 7.3 to 7.5 Hz and is attributed to trans diaxial protons. Based on these data, the acyclic portion is determined to be in the extended, planar zig-zag conformation generally described for acyclic benzoylated derivatives having the *arabino* configuration.[12] The cyclic pyranoside, as expected, is in the $^4C_1$ conformation. The conformations of these compounds are shown in Figure 1.

The ^{13}C NMR spectra were assigned by comparison with the signals of benzoylated monosaccharides[13] and disaccharides[14] and with penta-*O*-benzoyl-D-arabinitol.[15] These data are listed in Table 2.

A comparison of the ^{13}C NMR signals of compounds **4**, **5**, and **6** show differences of less than 0.7 ppm in the acyclic part. This result confirms the similar conformation deduced from the ^1H NMR coupling constants. In the cyclic part the expected differences of the chemical shifts for C-1' appear to be due to the change from β to α in the D-*gluco* configuration in compounds **4** and **6** and the resulting influence on C-3' and C-5'. Inversion of C-4' in the β-linked compounds **4** and **5** results in the expected differences in chemical shift for C-4' and C-2' but less of a difference is observed for the hexocyclic C-6'.

Table 2. ^{13}C NMR Data for 3-*O*-(D-Hexopyranosyl)-D-arabinitol Perbenzoates 4-6.[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'
4	63.40	70.29	76.04	70.26	62.39	101.09	71.69	72.74	69.44	72.65	62.76
5	63.46	70.32	75.75	70.41	62.40	101.18	69.91	71.76	67.89	71.63	61.83
6	62.80	70.63	76.39	70.63	62.41	96.58	71.16	69.37	68.96	68.96	62.61

[a] Measured at 75.52 MHz for solutions in $CDCl_3$ with Me_4Si as internal standard. Aromatic carbons appeared in the region δ128.22 - 133.58.

EXPERIMENTAL

General Procedures. Melting points are uncorrected. Optical rotations were determined at 20 °C with a Perkin-Elmer 141 Polarimeter. TLC was performed on plates coated with silica gel G (E. Merck, Darmstadt) with 9:1 benzene-ethyl acetate as the eluent and iodine vapor for detection. Paper chromatography was performed on Whatman No. 1 paper by the descending technique using D-glucose as reference standard and 10:4:4 (v/v) butanol-ethanol-water as solvent. The detection reagents used were $AgNO_3$-CH_3ONa/CH_3OH-NH_3[16] and aniline hydrogen phthalate.[17] Solutions were concentrated under diminished pressure below 50 °C. ^{1}H NMR spectra were recorded at 300 MHz on a Bruker EM 360A instrument for solutions in $CDCl_3$ with Me_4Si as internal standard. The spectra were amenable to first-order analysis. ^{13}C NMR spectra were recorded at 75.52 MHz on the same instrument with wide-band proton decoupling and Me_4Si as internal standard.

2, 3, 5, 6, 2', 3', 4', 6'-Octa-*O*-benzoylcellobiononitrile (**1**),[18] 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoyllactobiononitrile (**2**),[18] and 2, 3, 5, 6, 2', 3', 4', 6'-octa-*O*-benzoylmaltobiononitrile (**3**)[18] were prepared as described in literature.

Degradation of compounds 1, 2 and 3. General Procedure. Octa-*O*-benzoylaldobiononitrile[18] (2 g) was dissolved in 4 mL of chloroform, the solution was cooled in a water-ice bath, and a 2% solution of sodium methoxide in methanol was added until pH 8 was reached. After 10 min shaking, a gelatinous mass was obtained which was kept for 10 min at 5 °C. Water (10 mL) was added, and the chloroform layer was separated and washed several times with water. The water layers were neutralized with Zeo Karb 225 [H^+] resin, and the

Table 3. Yields and Physical Constants of the Mixture From the Degradation of Compounds 1, 2, and 3.

Compounds formed from 2 g of compound:		Yield g	% by weight	$[\alpha]_D$	R_f
1	3-*O*-β-D-glucopyranosyl-D-arabinoses (4 spots)	0.486	90.0	-7.8°	0.42, 0.52, 0.89, 0.99
2	3-*O*-β-D-galactopyranosyl-D-arabinoses (4 spots)	0.459	85.6	-25.4°	0.63, 0.91, 1.00, 1.04
3	3-*O*-α-D-glucopyranosyl-D-arabinoses (4 spots)	0.500	92.0	+39.6°	0.59, 0.63, 0.86, 0.99

Table 4. Yields and Physical Constants of Compounds 4-6.

Compound formed:	g	%	mp	$[\alpha]_D$	Anal. Calc. for $C_{67}H_{54}O_{18}$ C, 70.16; H, 4.74
1,2,4,5,2',3',4',6'-octa-*O*-benzoyl-3-*O*-(β-D-glucopyranosyl)-D-arabinitol (4)	0.98	67.6	99-101°	+31.0°	found: C, 70.43; H, 4.74.
1,2,4,5,2',3',4',6'-octa-*O*-benzoyl-3-*O*-(β-D-galactopyranosyl)-D-arabinitol (5)	1.20	82.7	114-116°	+54.3°	found: C, 70.74; H, 4.53.
1,2,4,5,2',3',4',6'-octa-*O*-benzoyl-3-*O*-(α-D-glucopyranosyl)-D-arabinitol (6)	0.87	60.0	115-117°	+85.3°	found: C, 70.22; H, 4.80.

solution was concentrated. The reaction mixture was analyzed by paper chromatography with 10:4:4 butanol-ethanol-water as solvent, and the spots were detected with both the silver nitrate and aniline hydrogen phthalate reagents. The weight and yield of the dried products, the R_f values, and $[\alpha]_D$ values are given in Table 3.

Preparation of 1, 2, 4, 5, 2', 3', 4', 6'-octa-O-benzoyl-3-O-(D-hexopyranosyl)-D-arabinitols (4, 5, and 6). The mixture of 3-*O*-(D-hexopyranosyl)-D-arabinoses (0.4 g) obtained in the previous reactions was dissolved in 5 mL of water and reduced with a solution of sodium borohydride (150 mg) in water (3 mL). The mixture was neutralized with Zeo Karb 225 [H^+] resin, filtered, and concentrated. The vacuum-dried residue was dissolved in pyridine (10 mL), and benzoyl chloride (10 mL) was added in small portions, keeping the temperature 70 - 90 °C. The syrup which formed was treated with ice water until a solid was obtained. The products were recrystallized from 2-propanol. For yield and physicochemical data, see Table 4. For ^{1}H NMR data, see Table 1; for ^{13}C NMR data, see Table 2.

ACKNOWLEDGMENTS

The authors thank the Consejo Nacional de Investigaciones Cientificas y Técnicas and the Universidad de Buenos Aires for partial financial support. They are grateful to Prof. Dr. T. N. Mitchell and Prof. Dr. W. P. Neumann, Universität Dortmund, West Germany, for the NMR spectra, and UMYMFOR (CONICET - FCEyN UBA) for the microanalyses.

REFERENCES

1. G. Zemplén, *Ber.*, **59**, 1254 (1926).
2. M. E. Gelpi and R. A. Cadenas, *Carbohydr. Res.*, **88**, 277 (1981).
3. M. E. Gelpi, B. N. Zuazo, and J. O. Deferrari, *An. Asoc. Quim. Argent.*, **62**, 35 (1974).
4. B. N. Zuazo and I. M. E. Thiel, *Carbohydr. Res.*, **172**, 156 (1988).
5. N. S. MacDonald and W. L. Evans, *J. Am. Chem. Soc.*, **64**, 2731 (1942).
6. M. E. Gelpi, J. O. Deferrari, and R. A. Cadenas, *J. Org. Chem.*, **30**, 4064 (1965).
7. J. O. Deferrari, B. N. Zuazo, and M. E. Gelpi, *Carbohydr. Res.*, **30**, 313 (1973).
8. N. B. D'Accorso and I. M. E. Thiel, *An. Asoc. Quim. Argent.*, submitted.
9. S. J. Angyal, R. Le Fur, and D. Gagnaire, *Carbohydr. Res.*, **23**, 121 (1972).
10. D. Horton and J. D. Wander, *J. Org. Chem.*, **39**, 1859 (1964).
11. I. M. Vazquez, N. B. D'Accorso, I. M. E. Thiel, and A. M. Schüller, *An. Asoc. Quim. Argent.*, **72**, 583 (1984).
12. N. B. D'Accorso and I. M. E. Thiel, *Rev. Latinoamer. Quim.*, **17**, 36 (1986); N. B. D'Accorso and I. M. E. Thiel, *Carbohydr. Res.*, **167**, 301 (1987).

13. N. B. D'Accorso, I. M. E. Thiel, and M. Schüller, *Carbohydr. Res.*, **124**, 177 (1984).

14. N. B. D'Accorso, I. M. Vazquez, and I. M. E. Thiel, *Carbohydr. Res.*, **156**, 207 (1986).

15. N. B. D'Accorso and I. M. E. Thiel, *Carbohydr. Res.*, **167**, 19 (1987).

16. R. A. Cadenas and J. O. Deferrari, *Analyst.*, **86**, 132 (1961).

17. S. M. Partridge, *Nature* (London), **164**, 443 (1949).

18. N. B. D'Accorso, B. N. Zuazo, and I. M. E. Thiel, *Carbohydr. Res.*, **172**, 147 (1988).