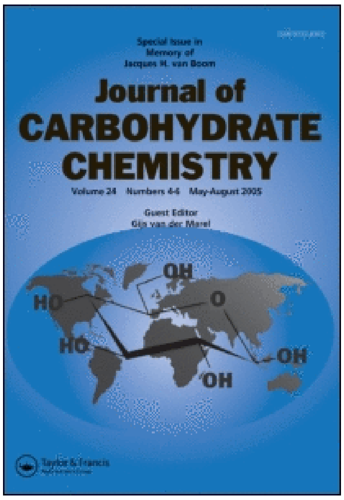


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

High-Pressure Approach to the Synthesis of Optically Pure Methyl 4-Deoxyheptosides

Janusz Jurczak[a]; Tomasz Bauer[a]; Jan Kihlberg[b]
[a] Institute of Organic Chemistry, Polish Academy of Sciences, Warszawa, Poland [b] Organic Chemistry 2, Chemical Center, The Lund Institute of Technology, Lunc 7, Sweden

To cite this Article Jurczak, Janusz , Bauer, Tomasz and Kihlberg, Jan(1985) 'High-Pressure Approach to the Synthesis of Optically Pure Methyl 4-Deoxyheptosides', Journal of Carbohydrate Chemistry, 4: 3, 447 — 450
To link to this Article: DOI: 10.1080/07328308508070195
URL: http://dx.doi.org/10.1080/07328308508070195

J. CARBOHYDRATE CHEMISTRY, 4(3), 447-450 (1985)

Communication

HIGH-PRESSURE APPROACH TO THE SYNTHESIS OF OPTICALLY PURE METHYL 4-DEOXYHEPTOSIDES

Janusz Jurczak* and Tomasz Bauer

Institute of Organic Chemistry,
Polish Academy of Sciences,
01-224 Warszawa, Poland

and

Jan Kihlberg

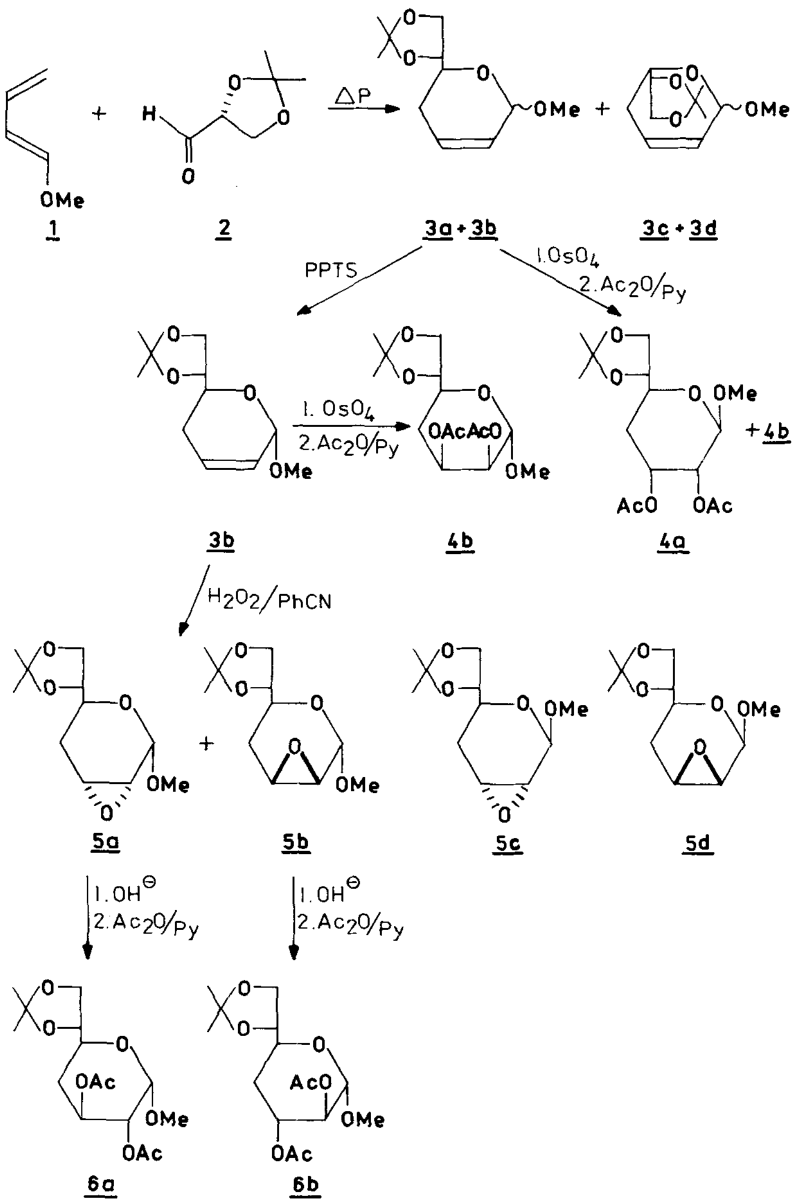
Organic Chemistry 2, Chemical Center,
The Lund Institute of Technology,
S-220 07 Lunc 7, Sweden

Received March 11, 1985 - Final Form June 19, 1985

Recently we have described[1] high pressure (4+2)cycloaddition of 1-methoxybuta-1,3-diene (1) to 2,3-*O*-isopropylidene-D-glyceraldehyde (2), which gives rise to chiral cycloadducts 3 (Scheme). When the reaction was carried out under high-pressure conditions (22 kbar, 50°C, diethyl ether as solvent, 20 h, 80% yield)[2] four diastereoisomeric adducts were formed in a ratio of 3a:3b:3c:3d=66:16:13:5. The reaction mixture was separated by column chromatography[3] yielding two fractions which contained diastereoisomeric mixtures (3a+3b) and (3c+3d), respectively. Absolute configuration at the C-5 carbon atom in both mixtures was established by chemical correlation.[1] These results prompted us to use a mixture (3a+3b), being stereochemically pure at C-5 chiral center, in the synthesis of optically active methyl 4-deoxyheptosides (Scheme).

The introduction of hydroxyl groups at carbon atoms C-3 and C-4, linked by a double bond, was carried out either by direct hydroxylation or by epoxidation and subsequent hydrolysis of the oxirane ring. *Cis*-hydroxylation of the diastereoisomeric mixture (3a:3b=8:2) was carried out using 4-methylmorpholine-4-oxide in the presence of osmium tetroxide,[4] to afford, after acetylation, two methyl 4-deoxyheptosides: D-*glycero*-β-D-*allo* (4a) and D-*glycero*-α-D-*manno* (4b) in a ratio of 8:2, respectively (overall yield 67%). Pure compounds 4a (52% yield) and 4b (11% yield) were isolated by column chromatography.[5,6] A diastereoisomeric mixture (3a+3b) was equilibrated using pyridinium p-toluenesulphonate (PPTS) in dry acetone,[7] to afford pure 3b in

0732-8303/85/0403-0447$3.50/0



Scheme

nearly quantitative yield. As expected, starting from 3b, methyl 4-deoxyheptoside 4b was obtained as the only product of cis-hydroxylation.

Epoxidation of the pure adduct 3b by the Payne method (benzonitrile - hydrogen peroxide - potassium carbonate)[8] afforded a mixture of two epoxides in a ratio of 5a:5b=3:7 (overall yield 79%).[9] This mixture was separated into pure components 5a (21% yield) and 5b (53% yield) by flash chromatography.[5,10]

Nucleophilic oxirane ring opening by aqueous potassium hydroxide, followed by acetylation, gave, from the α-ribo epoxide 5a, methyl 4-deoxyheptoside of α-gluco configuration (6a) as the major product. Under the same conditions, starting from α-lyxo epoxide 5b, compound 6b of α-altro configuration was formed as the single product.[5,11]

The present results offer a new possibility for the synthesis of optically pure methyl 4-deoxyheptosides and their derivatives.

ACKNOWLEDGMENT

This work was supported by the Polish Academy of Sciences MR-I-12 grant.

REFERENCES AND FOOTNOTES

1. J. Jurczak, T. Bauer, S. Filipek, M. Tkacz, and K. Zygo, J. Chem. Soc., Chem. Commun., 540(1983).

2. For the high-pressure experiments we used the piston-cylinder type apparatus described earlier: J. Jurczak, M. Chmielewski, and S. Filipek, Synthesis, 41(1979).

3. Kieselgel Merck 60 (230-400 mesh), hexane-ethyl acetate 9:1 v/v as eluent.

4. V. Van Rheenen, R. C. Kelly, and D. Y. Cha, Tetrahedron Lett., 1973 (1976).

5. Satisfactory analyses and spectral data were obtained for all new compounds.

6. Selected ^{1}H NMR data (360MHz, $CDCl_3$,δ), 4a: 5.61(m,1H,H-3,ΣJ=9.4Hz), 4.99(m,1H,H-2,ΣJ=11.2Hz), 4.71(d,1H,H-1,J_{12}=8.3Hz), 3.76(m,1H,H-5,ΣJ=20.5Hz), 3.26(s,3H,OMe); 4b: 5.47(m,1H,H-3, ΣJ=20.5Hz), 5.37(m,1H,H-2,ΣJ=1.8Hz) 4.58(d,1H,H-1,J_{12}=1.4Hz), 3.72(m,1H,H-5,ΣJ=20.9Hz), 3.00(s,3H,OMe).

7. J. Jurczak, T. Bauer, and A. Golebiowski, Bull. Pol. Ac.: Chem., in press.

8. G. B. Payne, P. H. Deming, and P. H. Williams, J. Org. Chem., 26, 659(1961).

9. When epoxidation of the diastereoisomeric mixture (3a+3b) is carried out under the same conditions, a mixture of four epoxides (5a+5b+5c+5d) is formed (overall yield 83%). This mixture was also separated by flash chromatography into pure components: 5a (10% yield), 5b (45% yield), 5c (13% yield), and 5d (6% yield).[10]

10. Selected ^{1}H NMR data (360MHz, $CDCl_3$,δ), 5a: 4.94(d,1H,H-1, J_{12}=3.6Hz), 3.76(m,1H,H-5,ΣJ=23.8Hz), 3.45(s,3H,OMe), 3.43(m,1H, H-3), 3.38(dd,1H,H-2,J_{23}=3.9Hz); 5b: 4.79(s,1H,H-1), 3.54(s,3H,OMe), 3.38(m,2H,H-3,H-5), 3.13(d,1H,H-2,J_{23}=4.0Hz); 5c: 4.78(s,1H,H-1), 3.55(s,3H,OMe), 3.45(m,2H,H-3,H-5), 3.18(d,1H,H-2,J_{23}=4.2Hz); 5d: 4.88(s,1H,H-1), 3.66(m,1H,H-5.ΣJ=22.7Hz), 3.46(s,3H,OMe), 3.37(m,1H,H-3,ΣJ=9.7Hz), 2.99(d,1H,H-2,J_{23}=3.6Hz).

11. Selected ^{1}H NMR data (360MHz, $CDCl_3$, δ), 6a: 5.30(m,1H,H-3,ΣJ=26.6Hz), 4.90(d,1H,H-1,$J_{1 2}$=3.6Hz), 4.85(m,1H,H-2,ΣJ=13.7Hz), 3.37(s,3H,OMe); 6b: 5.12(m,1H,H-3,ΣJ=10.1Hz), 4.93(m,1H,H-2,ΣJ=6.0Hz), 4.70(d,1H,H-1,$J_{1 2}$=1.0Hz), 3.68(m,1H,H-5,ΣJ=20.9Hz), 3.50(s,3H,OMe).