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# RING CONTRACTION BY CARBON PARTICIPATION IN A HEXOPYRANOSIDE RING: FORMATION OF BENZYL 2-O-BENZYL-3,5-DIDEOXY-3-C-BENZYLOXYMETHYL-α-L-LYXO-PENTOFURANOSIDE

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The title compound was formed in reaction of benzyl 2,4-di-O-benzyl-3-O-trifluoromethanesulfonyl-α-L-rhamnopyranoside and lithium triethylborohydride.

The powerful hydride transfer reagent, lithium triethylborohydride (1)[1] smoothly displaces both primary and secondary p-toluenesulfonyloxy (tosyloxy) groups in alicyclic systems[2] to yield deoxy derivatives in excellent yields. This reagent was successfully used also in carbohydrate chemistry to displace a primary tosyloxy group but failed to convert secondary tosylates to the deoxygenated analogues[3].
In our program aimed at synthesising constituents of microbial polysaccharides, we tried to prepare 3,6-dideoxy-L-arabino-hexopyranose (ascarylose) by deoxygenating at C-3 of benzyl 2,4-di-O-benzyl-α-L-rhamnopyranoside (2).
It was thought that a leaving group having leaving properties better than those of the tosyloxy group could be displaced by hydride ions derived from 1 even at a secondary position of a carbohydrate ring, and for this purpose the trifluoromethanesulfonyl (triflyl) group was selected. Thus, benzyl 2,4-di-O-benzyl-3-O-trifluoromethanesulfonyl-α-L-rhamnopyranoside (3) was treated with 1 under anhydrous conditions, in dioxane. Instead of the expected dideoxy-L-arabino-hexopyranoside derivative, however, formation of the parent alcohol (2) occurred[4] and, unexpectedly, the title compound (4) was formed in about 40 % yield ($\alpha_D$ -53°, c 0.4, $CHCl_3$). The structure of 4 was established by $^1$H n.m.r. at 100 MHz showing a one-proton line at $\delta$ = 5.1 ppm (H-1, $J_{1,2} < 1$ Hz), a one-proton doublet at 4.0 ppm (H-2, $J_{2,3}$ = 5.2 Hz), a one-proton multiplet at 2.8 ppm (H-3, $J_{3,6} = J_{3,6'} = 9.2$ Hz, $J_{3,4} \sim 9$ Hz), two doublets of doublets (each for one proton) at 3.6 and 3.7 ppm (H-6 and H-6', $J_{6,6'}$ = 16 Hz), a three-proton doublet ($CH_3$, $J_{4,5}$ = 6.6 Hz), in addition to a five-proton multiplet (for H-4 and the two $CH_2$-s) between 4.3 - 4.8ppm.

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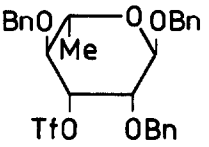


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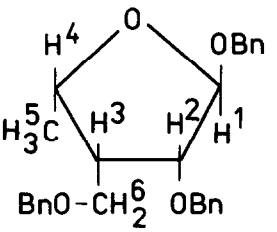


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The $^{13}C$ n.m.r. spectrum (at 25.3 MHz) of 4 showed lines at 104.0 ppm (C-1), 83.9 ppm (C-2), 43.8 ppm (C-3), 76.3 ppm (C-4), and 18.1 ppm (C-5), the $^{1}J_{C-1, H-1}$ coupling constant is 170 Hz.

The formation of 4 can be rationalized by a process initiated by removal of the triflyloxy group from C-3 and migration of the C-4 — C-5 bond electrons of the pyranoid ring, which in 3 lie in one plane with the C-4 — C-5 — OTf sequence, followed by addition of a hydride anion at the C-4 carbon of the hexopyranose ring.

This reaction is one of the rare cases of carbon participation in carbohydrate ring contraction processes[5] for which two previous examples (under solvolytic conditions) have been reported[6] in both of which stabilization was attained by loss of a proton to yield C-formyl derivatives. The different ways of stabilization of the rearranged carbocations in the present and the published processes are manifested in the different states of oxidation of the final products.

Investigations concerning the effect upon this reaction of other hydride sources and different leaving groups as well as the applicability of other nucleophiles are under way.

## References and notes

1 1 was obtained as a 1M solution in THF from FLUKA AG, Buchs, Switzerland

2 S. Krishnamurthy, H.C. Brown, J. Org. Chem., 41 3064 (1976)

3 V.K. Srivastava, L.M. Lerner, Carbohydr. Chem., 64 263 (1978)

4 This side reaction is well-documented in hydride reduction of tosylates, see Ref. 2 and references therein

5 For reviews on neighbouring-group participation in carbohydrate chemistry including also ring contraction reactions, see: L. Goodman, Adv. Carbohydr. Chem., 22 109 (1967), D.H. Ball, F.W. Parrish, Adv. Carbohydr. Chem. Biochem., 24 139 (1969)

6 P.W. Austin, J.G. Buchanan, and R.M. Saunders, J. Chem. Soc. (C) 1967 372., S. Inoue, H. Ogawa, Chem. and Pharm. Bull. (Japan) 8 79 (1960)

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