Pergamon

Tetrahedron Letters, Vol. 37, No. 3, pp. 415-416, 1996

0040-4039/96 $15.00 + 0.00

0040-4039(95)02173-6

A Versatile Route to 2,3-Unsaturated Sugar Derivatives *via* Corresponding 3-Acetoxy-1-Nitro-1-Alkenes

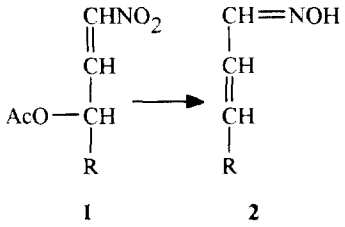
Miroslav Kóóš

Institute of Chemistry, Slovak Academy of Sciences, SK-84238 Bratislava, Slovak Republic

Abstract: Reduction of 3-*O*-acetylated sugar 1-nitro-1-alkenes with zinc and acetic acid afforded corresponding 2,3-unsaturated sugar oximes in high yields from which either free deprotected sugars or further useful 2,3-unsaturated sugar derivatives can be prepared.

Zinc in acetic acid has proven to be a very effective reducing agent for converting nitroalkenes into oximinoalkanes. This reducing agent was successfully applied to aliphatic nitroalkenes, to produce saturated ketoximes[1]. When 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-hex-2-enopyranosides were used as a starting material, corresponding 2,3-dideoxy-3-oximino-hexopyranosides resulted, exclusively[2]. Similar reactions were utilised in the synthesis of sinefungin[3]. However, the described syntheses involving carbohydrate substrates do not deal with *O*-acetyl protected sugars or with the preparation of aldoximes.

We now wish to report that when this reducing agent is applied to *O*-acetylated sugar 1-nitro-1-alkenes **1**, corresponding 2,3-unsaturated sugar oximes **2** (Scheme 1) are formed directly in high yields. The presence of an acetyl group at 3-*O*-position in starting compounds **1** is essential. If it is not present, corresponding 2-deoxy sugar oximes are produced, as expected.



1 **2**

R in **1a** and **2a**:	R in **1b** and **2b**:	R in **1c** and **2c**:	R in **1d** and **2d**:
HC(OAc) HC(OAc) H_2C(OAc)	AcO—CH AcO—CH H_2C(OAc)	AcO—CH HC(OAc) H_2C(OAc)	AcO—CH HC(OAc) HC(OAc) H_2C(OAc)

Scheme 1

Preparation of 2,3-dideoxy-4,5,6-tri-*O*-acetyl-D-*erythro*-hex-2-enose oxime **2a** from D-*arabino*-3,4,5,6-tetraacetoxy-1-nitro-1-hexene[4] **1a** is representative. Analogous L-*erythro*- and D-*threo*-hex-2-enose oximes (**2b** and **2c**) and D-*arabino*-hept-2-enose oxime (**2d**) were obtained in about 90 % yields under essentially the same reaction conditions starting from peracetoxy-1-nitro-1-alkenes prepared from L-arabinose[4], D-xylose[4], and D-mannose[5]. Deacetylation and deoximation[6] of **2a** gave known 2,3-dideoxy-D-*erythro*-hex-2-enopyranose[7,8].

Similarly, deprotection of **2c** afforded 2,3-dideoxy-D-*threo*-hex-2-enopyranose characterized as 1,4,6-tri-*O*-acetate[7,9].

Synthesis of 2a : To a magnetically well-stirred mixture of **1a** (1.59 g, 4.4 mmol) and zinc dust (freshly activated with 2N HCl) (1.0 g, 17.6 mmol) in ether (40 mL), 4N acetic acid (2.5 mL) was added dropwise at such a rate that ether refluxed gently. After addition had been completed, the reaction mixture was heated under reflux for an additional 4 h, then cooled to room temperature. The zinc acetate which separated was filtered off, washed thoroughly with ether and ethyl acetate, and the combined filtrates were dried (Na_2SO_4) and then concentrated *in vacuo*. The crude product was purified by chromatography on silica gel using hexane-ethyl acetate (50 : 20) as an eluent to give the less polar isomer [7,10] (530 mg, 42 % yield) followed by the more polar isomer[7,11] (573 mg, 46 % yield), identified[12] as *anti*- and *syn*-oxime **2a**.

Since the oxime group and double bond in the products **2** may be modified through a variety of reactions, our synthesis may be of use for preparing further interesting and not so readily available sugar derivatives. The limiting factor is, of course, the availability of starting 3-*O*-acetylated sugar 1-nitroalkenes **1**.

REFERENCES AND NOTES:

1. Nightingale, D. V.; Janes, J. R. *J. Am. Chem. Soc.* **1944**, *66*, 352-354.
2. Baer, H. H.; Rank, W. *Can. J. Chem.* **1972**, *50*, 1292-1295.
3. Maguire, M. P.; Feldman, P. L.; Rapoport, H. *J. Org. Chem.* **1990**, *55*, 948-955.
4. a) Sowden, J. C. *Methods Carbohydr. Chem.* **1962**, *1*, 132-135; b) Sowden, J. C.; Oftedahl, M. L. *Methods Carbohydr. Chem.* **1962**, *1*, 235-237; c) Sowden, J. C.; Fischer, H. O. L. *J. Am. Chem. Soc.* **1947**, *69*, 1048-1050.
5. Sowden, J. C.; Schaffer, R. *J. Am. Chem. Soc.* **1951**, *73*, 4662-4664.
6. a) Acid-catalyzed exchange method using levullinic acid; DePuy, C. H.; Ponder, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 4629-4631; b) oxidative method using ceric ammonium nitrate; Bird, J. W.; Diaper, D. G. M. *Can. J. Chem.* **1969**, *47*, 145-150.
7. All compounds gave satisfactory spectral and elemental analyses.
8. Ferrier, R. J.; Prasad, N. *J. Chem. Soc. (C)* **1969**, 581-586.
9. Ciment, D. M.; Ferrier, R. J. *J. Chem. Soc. (C)* **1966**, 441-445.
10. Data of **2a** (less polar isomer): colourless oil, $[\alpha]_D$ +18° (c 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.75 (dd, 1H, H-1, $J_{1,2}$ = 9.7 Hz, $J_{1,3}$ = 0.5 Hz), 6.41 (ddd, 1H, H-2, $J_{2,3}$ = 15.8 Hz, $J_{2,4}$ = 1.3 Hz), 5.96 (ddd, 1H, H-3, $J_{3,4}$ = 6.6 Hz), 5.60 (ddd, 1H, H-4, $J_{4,5}$ = 4.7 Hz), 5.25 (ddd, 1H, H-5, $J_{5,6}$ = 3.8 Hz, $J_{5,6'}$ = 6.6 Hz), 4.27 (dd, 1H, H-6, $J_{6,6'}$ = 12.2 Hz), 4.18 (dd, 1H, H-6'), 2.11, 2.08 and 2.06 (3s, 3OAc); ^{13}C NMR ($CDCl_3$): δ 149.5 (C-1), 131.9 (C-3), 127.8 (C-2), 71.3 (C-4), 71.0 (C-5), 61.4 (C-6), 170.5, 170.0 and 169.4 (3C=O), 20.5 ($2CH_3$) and 20.4 (CH_3).
11. Data of **2a** (more polar isomer): colourless oil $[\alpha]_D$ +18° (c 1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.09 (d, 1H, H-1, $J_{1,2}$ = 9.5 Hz), 6.99 (ddd, 1H, H-2, $J_{2,3}$ = 15.6 Hz, $J_{2,4}$ = 1.3 Hz), 6.02 (dd, 1H, H-3, $J_{3,4}$ = 6.4 Hz), 5.63 (ddd, 1H, H-4, $J_{4,5}$ = 4.8 Hz), 5.26 (ddd, 1H, H-5, $J_{5,6}$ = 3.8 Hz, $J_{5,6'}$ = 6.6 Hz), 4.26 (dd, 1H, H-6, $J_{6,6'}$ = 12.2 Hz), 4.19 (dd, 1H, H-6'), 2.12, 2.10 and 2.07 (3s, 3OAc); ^{13}C NMR ($CDCl_3$): δ 146.8 (C-1), 134.0 (C-3), 121.4 (C-2), 71.4 (C-4), 71.2 (C-5), 61.6 (C-6), 170.6, 170.0 and 169.5 (3C=O), 20.7 ($2CH_3$) and 20.6 (CH_3).
12. Lamchen, M. *Carbohydr. Res.* **1971**, *16*, 309-316.

(*Received in UK* 12 *September* 1995; *revised* 14 *November* 1995; *accepted* 17 *November* 1995)