Tetrahedron Letters, Vol.32, No.37, pp 4963-4964, 1991
Printed in Great Britain

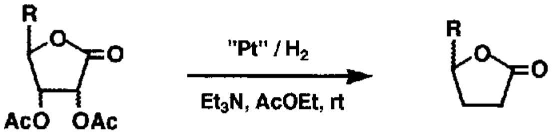
0040-4039/91 $3.00 + .00
Pergamon Press plc

ONE-POT CONVERSION OF O-ACETYLSUGAR LACTONES INTO 2,3-DIDEOXYSUGAR DERIVATIVES VIA PLATINUM-CATALYZED HYDROGENOLYSIS

Junko Katsuki and Junji Inanaga*
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Summary: O-Acetylsugar lactones were cleanly converted into the corresponding 2,3-dideoxysugar derivatives at room temperature under an atmospheric pressure of hydrogen in the presence of triethylamine and platinum catalysts.

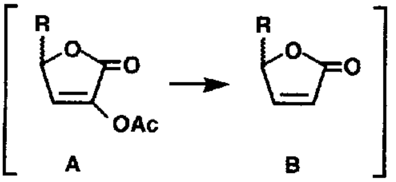
It has been reported that acetylated aldono-1,4-lactones, when treated with hydrogen in the presence of triethylamine and palladium on carbon, form acetylated 3-deoxyaldono-1,4-lactones through elimination of the 3-acetoxyl group and subsequent stereospecific hydrogenation of the unsaturated intermediate.[1] On the other hand, we happened to find that the use of "platinum" catalysts in place of "palladium" brought about the additional hydrogenolysis of the 2-acetoxyl group thus affording the corresponding 2,3-dideoxysugar lactones. (Eq. 1)

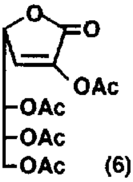


(1)

Tri-*O*-acetyl-D-ribono-1,4-lactone (**1**), tetra-*O*-acetyl-L-mannono-1,4-lactone (**2**), tetra-*O*-acetyl-D-gulono-1,4-lactone (**3**), penta-*O*-acetyl-D-glucoheptono-1,4-lactone (**4**), and tetra-*O*-acetyl-D-glucono-1,5-lactone (**5**)[2] were deacetoxylated highly selectively. (Table 1) Surprisingly, the corresponding mono-deacetoxy derivatives were not produced at all under the conditions.

The reaction seems to proceed through i) elimination of the 3-acetoxyl group by triethylamine to give the 2-acetoxybutenolide (**A**), ii) platinum-catalyzed hydrogenolysis of the 2-acetoxyl group leading to the butenolide (**B**), and iii) hydrogenation of the remaining double bond.





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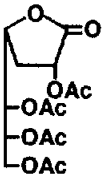
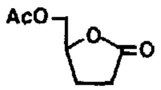
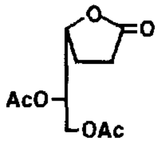
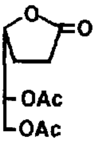
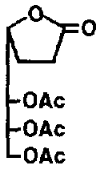
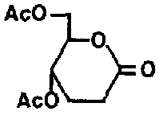


(7)

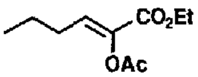
In fact, when 2-acetoxybutenolide (**6**) was once isolated[3] and then subjected to the platinum-catalyzed hydrogenation, the 2,3-dideoxy derivative was obtained in high yield as a sole product, while palladium-catalyzed[4] reaction of **6** afforded 3-deoxy lactone (**7**) exclusively.

Table 1. One-Pot Conversion of *O*-acetylsugar Lactones (**1**-**5**) to 2,3-Dideoxysugar Lactones[a)]

Catalyst	Product[b)] / Yield[c)]				
					
PtO_2	64 %	84 %	98 %	88 %	<10 %
Pt-C	73 %	99 %	99 %	86 %	58 %

a) A mixture of an *O*-acetylsugar lactone (1 eq), triethylamine (2 eq), and a catalytic amount of PtO_2 or Pt-C in ethyl acetate was vigorously stirred at room temperature for 2 days under an atmospher of hydrogen (1 atm. pressure). b) A single isomer determined by ^1H NMR (400 MHz) analysis. All products gave satisfactory ^1H NMR and mass (CI) spectra, which are identical with those of the compounds prepared from the same substrates via an alternative process (Pd-C, H_2, Et_3N;SmI_2) [J. Inanaga, J. Katsuki, and M. Yamaguchi, *Chem. Lett.*, **1991**, 1025]. c) Isolated yield.

No reaction took place in a comparative experiment without triethylamine, indicating that the present platinum-catalyzed hydrogenolysis of 2-acetoxyl group occurs through the butenolide intermediate (**A**) but not through the saturated derivatives (**1**-**5**).



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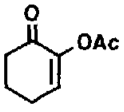

(9)

The present hydrogenolysis seems, however, peculiar to cyclic lactones since neither an open chain substrate (**8**) nor a cyclic enone system (**9**) gave the corresponding deacetoxylated products under the conditions.[5]

2,3-Dideoxysugar lactones thus obtained would be useful for natural product synthesis not only as chiral synthons but also as templates for the preparation of other types of chiral non-racemic intermediates.[6]

References and Notes

1. K. Bock, I. Lundt, and C. Pedersen, *Acta Chem. Scand.*, B, **35**, 155 (1981).
2. These were prepared from the corresponding sugar lactones (commercially available) by heating in acetic anhydride containing a few drops of concentrated sulfuric acid. See also reference 1.
3. Treatment of **4** with triethylamine afforded butenolide (**6**) in low yield. It has been pointed out that the initially formed 2,3-unsaturated lactones (e.g., **6**) are sensitive to base and readily undergo further elimination: a) C. R. Nelson and J. S. Gratzl, *Carbohydr. Res.*, **60**, 267 (1978); b) O. J. Varela, A. F. Cirelli, and R. M. D. Lederkremer, *ibid.*, **79**, 219 (1980); c) S. V. Attwood and A. G. M. Barrett, *J. Chem. Soc., Perkin Trans. 1*, 1315 (1984).
4. Palladium on carbon and palladium hydroxide were examined as catalysts.
5. In the latter case, a diastereomeric mixture of 1,2-diol monoacetates was produced.
6. a) S. Hanessian, *Total Synthesis of Natural Products: The 'Chiron' Approach* in Organic Chemistry Series, Vol. 3, ed by J. E. Baldwin, Pergamon Press (1983); b) S. Hanessian, *Aldrichimica Acta*, **22**, 3 (1989).

(Received in Japan 17 June 1991)