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# $SmI_2$-Promoted Deacetoxylation of *O*-Acetylsugar Lactones. An Easy Access to Deoxysugar Lactones

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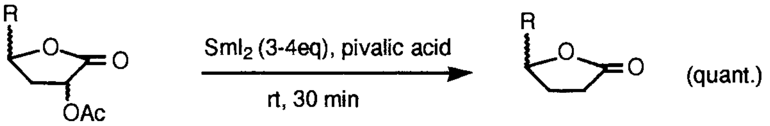
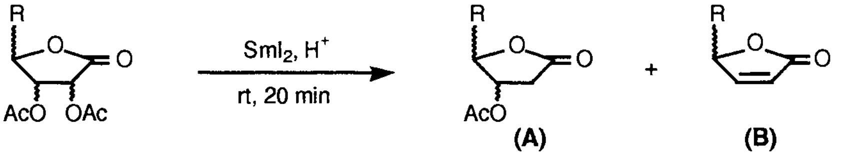
Selective deacetoxylation of *O*-acetylsugar lactones and *O*-acetyl-3-deoxysugar lactones was accomplished at room temperature with the aid of $SmI_2$ in the presence of pivalic acid or acetic acid to give the corresponding α,β-unsaturated lactones and saturated lactones (2,3-dideoxysugar derivatives), respectively.

Deoxysugars, especially deoxysugar lactones have recently been received much attention because of not only their interesting biological activities[1)] but also the usefulness in the natural product synthesis as chiral non-racemic intermediates with well-defined stereochemistry at numerous chiral centers.[2)]

We report here a convenient method to obtain 2,3-dideoxysugar lactones from natural carbohydrates via site-selective deacetoxylation of *O*-acetylsugar lactones by means of $SmI_2$-promoted electron transfer reaction.

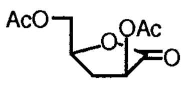


(1)



(2)

3-Deoxysugar lactones (**6**-**10**), prepared in good to excellent yields from the corresponding sugar lactones (**1**-**5**) by treating with hydrogen (1 atm) in the presence of triethylamine and $Pd(OH)_2$ catalyst,[3)] were cleanly reduced by $SmI_2$ to give the corresponding 2,3-dideoxy derivatives in quantitative yields. (Eq. 1)[4)]



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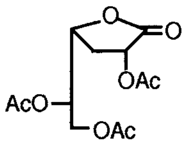

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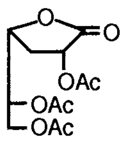

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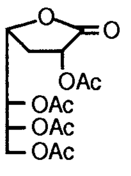

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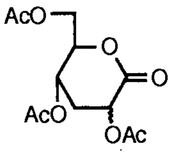
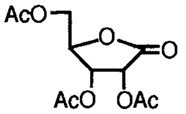
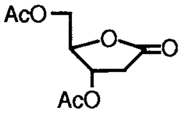
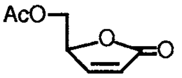
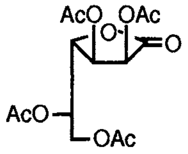
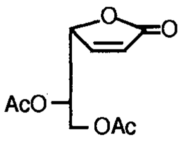
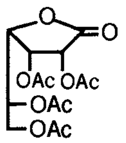
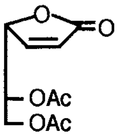
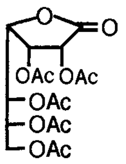
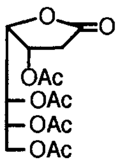
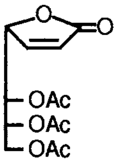
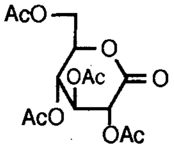
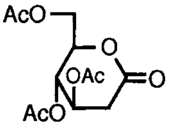
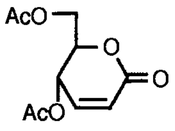


**10**

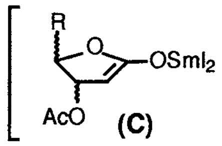
When *O*-acetylsugar lactones (**1**-**5**) were subjected to the present reduction conditions, the corresponding α,β-unsaturated lactones (**B**) were obtained as sole or major products with the concomitant formation of 2-deoxy derivatives (**A**). (Eq. 2)[4)] The results are summarized in Table 1.

The reaction seems to proceed through the formation of the lactone enolate intermediate (**C**) followed by

Table 1. $SmI_2$-Promoted Deacetoxylation of *O*-Acetylsugar Lactones (**1**-**5**)a)

| *O*-Acetylsugar lactone | | Proton source | Product A | Product B | Yield b)/% |
|---|---|---|---|---|---|
|  | **1** | pivalic acid<br>AcOH |  |  | 47 (54) c)<br>30 (63) d) |
|  | **2** | pivalic acid<br>AcOH | |  | 67 (72)<br>60 (64) |
|  | **3** | pivalic acid<br>AcOH | |  | 58 (93)<br>60 (70) |
|  | **4** | pivalic acid<br>AcOH |  |  | 54 (75) e)<br>67 (75) d) |
|  | **5** | pivalic acid<br>AcOH |  |  | 47 f)<br>68 d) |

a) To a solution of *O*-acetylsugar lactone (**1**-**5**, 0.1 mmol) and pivalic acid or acetic acid (0.25 mmol) in THF (2 ml) was added a $SmI_2$-THF solution (0.1 mol $dm^{-3}$, 3-4 ml) and the mixture was stirred at room temperature for 20 min. b) Combined isolated yield. The yield based on recovered starting material is indicated in parentheses. c) **A** / **B** = 36 / 64. d) The α,β-unsaturated lactone (**B**) was the only product. e) **A** / **B** = 42 / 58. f) **A** / **B** = 50 / 50.



**(C)**

elimination of its 3-acetoxyl group. To our surprise, however, the use of acetic acid to suppress the elimination process (**C**→**B**) by rapid protonation rather promoted the elimination thus yielding the butenolide and pentenolide derivatives exclusively. (See Table 1)

Although the present reduction did not give satisfactory results for the selective formation of 2-deoxysugar lactones, it is rather fruitful from the synthetic point of view that it offers a highly efficient route to sugar-derived conjugated lactones which are not so conveniently accessible by any other available methodologies.

References

1) For example, see O. Uchikawa, N. Okukado, T. Sakata, K. Arase, and K. Terada, *Bull. Chem. Soc. Jpn.*, **61**, 2025 (1988).
2) S. Hanessian, "*Total Synthesis of Natural Products: The 'Chiron' Approach*," in "Organic Chemistry Series, Vol. 3," ed by J. E. Baldwin, Pergamon Press (1983); S. Hanessian, *Aldrichimica Acta*, **22**, 3 (1989).
3) K. Bock, I. Lundt, and C. Pederson, *Acta Chem. Scand.*, B, **35**, 155 (1981); S. V. Attwood and A. G. M. Barrett, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 1315.
4) The addition of HMPA, which was essential for the deacetoxylation of α-acetoxyesters [K. Kusuda, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, **30**, 2945 (1989)], rather decreased the yield in this case.

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