

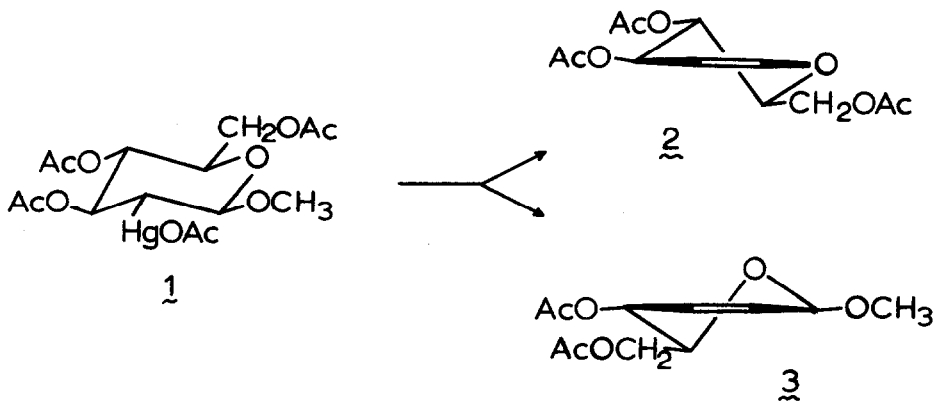
A CONVENIENT PREPARATION OF METHYL 4,6-DI-O-ACETYL-2,3-DIDEOXY-  
 $\beta$ -D-ERYTHRO-HEX-2-ENOPYRANOSIDE<sup>1</sup>

Andrew DeBoer, Christopher J. Thanel\*, and Greg A. Wilson\*

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82070

(Received in USA 16 October 1972; received in UK for publication 13 November 1972)

We have been studying iodide ion catalyzed deoxymercuration reactions under a variety of reaction conditions in an attempt to exploit this reaction particularly with the intent of using it in multifunctional molecules.<sup>2</sup> We have found that trans-2-acetoxycyclohexyl-mercuric acetate undergoes deoxymercuration rapidly relative to several related compounds. We have then been able to use this information to predict the course of deoxymercuration in cases where more than one option exists. As a result, we have carried out the deoxymercuration of methyl 3,4,6-tri-O-acetyl-2-acetoxymercuri-2-deoxy- $\beta$ -D-glucopyranoside (1) from which two products can be formed, namely, 3,4,6-tri-O-acetyl-D-glucal (2) and methyl 4,6-di-O-acetyl-2,3-dideoxy- $\beta$ -D-erythro-hex-2-enopyranoside (3). The acetoxymercuri compound 1 can



\* NSF Undergraduate Research Participant.

be prepared by the oxymercuration of 2,<sup>3,4</sup>

The iodide ion catalyzed deoxymercuration of 1 gave only 3 and was carried out as follows:

A 0.4 M solution (25 ml) of NaI in 75% aqueous ethanol was added to a solution of 1 g of 1 in 25 ml of 75% aqueous ethanol at room temperature. After 30 min, 4 ml of 0.5 M aqueous Na<sub>2</sub>S was added and the HgS was removed by filtration. The filtrate was concentrated on the rotary-evaporator to a volume of 15 ml and then diluted with water to a volume of 100 ml. The product was extracted from this solution with ether. The organic extracts yielded 0.36 g (80%) of a pale yellow syrup whose nmr spectrum matched that previously reported for 3 and did not indicate the presence of any impurities. The product was distilled (oil bath 100°, 0.01 mm and showed  $[\alpha]_{589}^{25} = 126^\circ$  (c 0.135, CHCl<sub>3</sub>).

Because of the previously reported<sup>5</sup> difficulty in determining the ratio of  $\alpha$ -3 to  $\beta$ -3, due to their similar nmr spectra, 3 was hydrogenated over 5% Pd/C in ethyl acetate and gave only methyl 2,3-dideoxy- $\beta$ -D-erythro-hexopyranoside as determined from the nmr spectrum. The deoxymercuration reaction does not affect the stereochemistry at the anomeric carbon atom.

The  $\alpha$  anomer of 3 can be synthesized by the method of Ferrier.<sup>6</sup> An alternate method for the preparation of  $\alpha$ -3 and  $\beta$ -3 has also been reported.<sup>7</sup>

#### REFERENCES

1. Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.
2. A. DeBoer and G. A. Wilson, unpublished results.
3. P. T. Manolopoulos, M. Mednick, and N. N. Lichtin, *J. Amer. Chem. Soc.*, 84, 2203 (1962).
4. G. R. Inglis, J. C. P. Schwarz, and L. McLaren, *J. Chem. Soc.*, 1014 (1962).
5. R. J. Ferrier, *J. Chem. Soc.*, 5443 (1964).
6. R. J. Ferrier and N. Prasad, *J. Chem. Soc. (C)*, 570 (1969).
7. A. Rosenthal and J. N. C. Whyte, *Can. J. Chem.*, 46, 2245 (1968).