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NEW METHOD FOR THE 1-DEACETYLATION OF PERACETATES OF AMINOSUGARS

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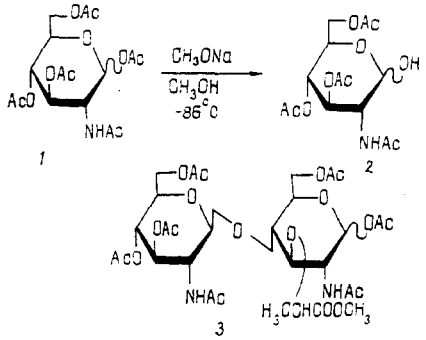
A method for the selective O-deacetylation at the glycosidic centers of aminosugar peracetates is proposed.

Incomplete acetates of amino sugars containing free hemiacetal hydroxyls are important intermediates used widely in the synthetic chemistry of glycosaminides. They are used to obtain "aglycon" components and glycosylating reagents — glycosyl halides and oxazoline derivatives of aminosugars where the initial substance used are acid-labile compounds [2, 3].

Because of differences in the reactivities of an acyloxy group at a glycosidic center and other acyloxy groups [1], 1-deacetylation in pyridine can be achieved with the aid of traditional mild nucleophilic agents. However, a deficient selectivity of all reagents, particularly in the completing stages of the process, is common, because of which 1-deacetylation cannot be carried to completion without a substantial fall in yield through the formation of more highly deacetylated products. The most selective reagent is hydrazine acetate in DMF [2].

Sometimes the use of hydrazine acetate is accompanied by the occurrence of side reactions — for example, in the case where activated carbonyl and carboxy functions are present in the molecule. Thus, the deacetylation by this method of compound (**3**) takes place with an accumulation of unregenerable products. This is apparently connected with the formation of a hydrazide at the carboxy group of the lactyl residue [2].



We have established that the selectivity of deacetylation depends not so much on the reagent as on the temperature. Thus, at −86°C even such a strong nucleophile as sodium methanolate in methanol deblocks a glycosidic hydroxyl with high selectivity. For example, according to the results of HPLC, the yield of 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranoside by reaction 1b amounted to 83%. At the same time, the amount of peracetate that had not reacted was 8%. The yield of product (**2**) by reaction 1a was 86%, and the amount of peracetate in the reaction mixture was 7%. Under the reaction conditions no formation of products of the migration of the acetyl group was observed.

This method of 1-deacetylation, like the similar Zemplen procedure [4], which is used for complete deacetylation, is distinguished by simplicity of performance. Furthermore, the use of sodium methanolate in methanol permits working up to be simplified and the lowering of the yield connected with the washing out of an excess of hydrazine hydrate and with unavoidable losses of water-soluble deacetylation products to be avoided. On the other hand, in some cases the insignificant amount of highly deacetylated derivatives present in the mixture obtained and also the absence of substances of noncarbohydrate nature permits the use of the product without chromatographic purification.

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EXPERIMENTAL

HPLC was conducted on a Bio-Rad 1330 instrument with an Erbasil C-18 (10 μm) (4.6 × 250 mm) column. The substances were revealed with the aid of a UV detector at a wavelength of 210 nm. Systems: isopropanol–water (93:7) and (94:6). TLC on Silufol UV-254 plates in the chloroform–ethanol (10:1) (A) and chloroform–benzene–ethanol (10:1:1) (B) systems, the zones being detected by carbonization at 300°C. Column chromatography was conducted on silica gel L-100/250.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranose (2). Method a. A solution of sodium methanolate obtained by dissolving 0.25 g of Na in 10 ml of MeOH was added to a solution of 3.26 g of D-glucosamine peracetate in 45 ml of absolute methanol cooled to −86°C. Monitoring was carried out periodically by TLC. After the end of the reaction (disappearance of the spot of the full acetate from the chromatogram) the mixture was neutralized by the addition of a methanolic solution of H_3PO_4 and it was then heated to room temperature and, after the precipitate of sodium phosphate had been removed, it was evaporated. The mixture was separated with the aid of CC in the chloroform–ethanol (100:1)→(100:3) system. Yield 86%.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranose (2). Method b. A solution of 0.5 g of D-glucosamine in 5 ml of DMF was treated with 0.175 g of hydrazine acetate. Monitoring was carried out periodically by TLC. After the end of the reaction, the mixture was neutralized with 2 ml of CH_3COOH and was evaporated. The residue was dissolved in 100 ml of chloroform and was washed three times with saturated NaCl solution. After drying and evaporation of the chloroform fraction, the mixture was separated by CC in the chloroform–ethanol (100:1)→(100:3) system. Yield 83%.

2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-mannopyranose. The synthesis was analogous to that of 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranose by method **a**. Yield 80%.

2-Acetamido-4-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-6-O-acetyl-3-O-[D-1-(methoxycarbonyl)ethyl]-2-deoxy-D-glucopyranose (3). The synthesis was analogous to that of 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-D-glucopyranose by method **a**. Yield 70%.

REFERENCES

1. N. K. Kochetkov, A. F. Bochkov, B. A. Dmitriev, A. I. Usov, O. S. Chizhov, and V. N. Shibaev, Chemistry of the Carbohydrates [in Russian], Khimiya, Moscow (1967), p. 190.
2. N. V. Bonin, S. É. Zurabyan, and A. Ya. Khorlin, Izv. Akad. Nauk SSSR, Ser. Khim., 2806 (1981).
3. S. É. Zurabyan and A. Ya. Khorlin, Usp. Khim., **43**, 1874 (1974).
4. G. Zemplen and E. Racsu, Ber., No. 62, 1613 (1929).