Carbohydrate Research, 33 (1974) C1—C3

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Preliminary communication

Sugar 2,3-diphenyl-2-cyclopropen-1-yl ethers and their glycosylation. A new route to oligosaccharides

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(Received January 9th, 1974; accepted February 6th, 1974)

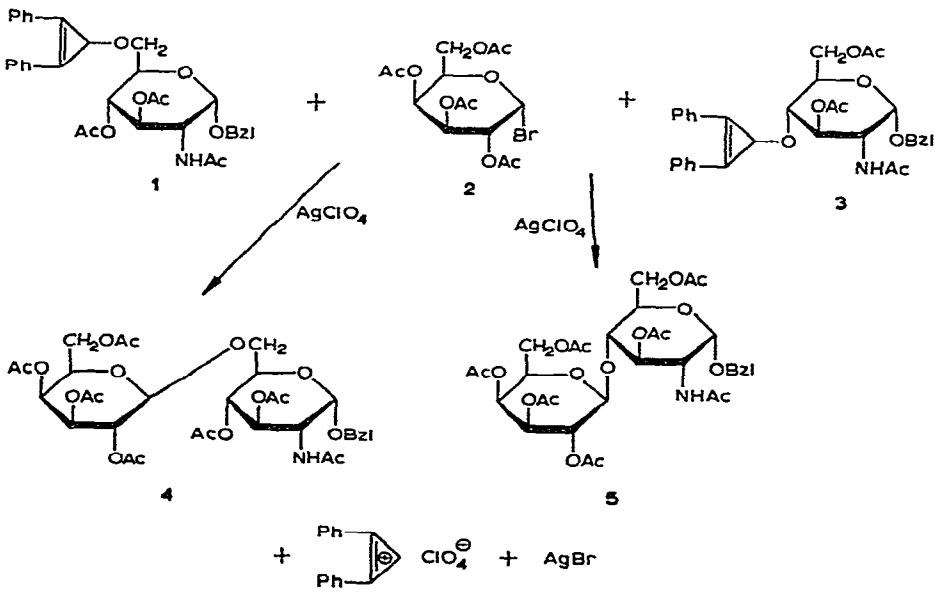
Bredereck *et al.*[1] have proposed a simplified synthesis of oligosaccharides involving the action of glycose 1-perchlorates on sugar trityl ethers. In this reaction, the leaving group was a trityl cation similar to the proton in the Koenigs–Knorr reaction. However, Bredereck's method is applicable only for glycosylation of a primary hydroxyl group of the sugar. The only other example of glycosylation of a protected, sugar hydroxyl group was that reported by Kochetkov *et al.*[2] in the synthesis of β,β-trehalose. This reaction, which was carried out under drastic conditions, is based on the treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with *tert*-butyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside in the presence of silver perchlorate.

The search for a leaving group which, like the trityl group, can form a stable cation, but in addition can etherify a secondary as well as a primary sugar hydroxyl group, brought us ultimately to the 2,3-diphenyl-2-cyclopropen-1-yl (DPC) group. This is the first example of the use of DPC ethers in carbohydrate chemistry. These ethers are obtained by treatment of the partially protected sugars having the appropriate hydroxyl group free with 2,3-diphenyl-2-cyclopropen-1-ylium perchlorate[3] in the presence of 2,4,6-trimethylpyridine.

In a typical experiment, the corresponding sugar derivatives in dry acetonitrile or benzene were treated with a slight excess of 2,3-diphenyl-1-cyclopropen-1-ylium perchlorate in the presence of an equivalent quantity of 2,4,6-trimethylpyridine for 1 h at room temperature. Thus, benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside[4] gave, in 80% yield, benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-(2,3-diphenyl-2-cyclopropen-1-yl)-α-D-glucopyranoside (**1**), m.p. 141—142° (from acetone–hexane), $[\alpha]_D^{25}$ +97° (*c* 1, acetone) and benzyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-α-D-glucopyranoside[5] gave, in 53% yield, benzyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3-diphenyl-2-cyclopropen-1-yl)-α-D-glucopyranoside (**3**), m.p. 170—171° (from acetone–hexane), $[\alpha]_D^{25}$ +118° (*c* 1, acetone); **1** and **2** were isolated by column chromatography on alumina and the proposed structures were in agreement with the results of elementary analysis and physical data;

n.m.r. (chloroform-*d*, tetramethylsilane as internal standard): δ 4.6 (s, 1 H, cyclopropenyl) and 7.3–7.9 (m, 10 H, 2 Ph); i.r. data: ν_{max}^{Nujol} 1800–1810 cm^{-1} (C=C, cyclopropenyl), and u.v.: $\lambda_{max}^{CH_3CN}$ 302 and 318 nm, and shoulder at 287 nm (see ref. 6). The DPC ethers obtained were extremely labile under acidic conditions; they decomposed during t.l.c. on silica gel. In contrast, they were stable to alkali; thus, they were not affected by treatment with aqueous ammonia and sodium methoxide or triethylamine in methanol.

The glycosylation of the ethers **1** and **3** was performed by treatment with a slight excess of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (**2**) and silver perchlorate in dry benzene at room temperature for 30 min. Chromatography on alumina gave, in 50% yield from **1**, benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-



galactopyranosyl)-α-D-glucopyranoside (**4**), amorphous, $[\alpha]_D^{25}$ +58° (*c* 1, chloroform), which was *O*-deacetylated into benzyl 2-acetamido-2-deoxy-6-*O*-β-D-galactopyranosyl-α-D-glucopyranoside, identical with an authentic sample[7], and, in 35% yield from **2**, benzyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranoside (**5**), m.p. 103–104° (from methanol), $[\alpha]_D^{25}$ +65° (*c* 1, chloroform); lit.[5] m.p. 107–108.5°, $[\alpha]_D$ +68°. The glycosylating procedure may be performed without separation of DPC intermediates.

These examples show that 2,3-diphenyl-2-cyclopropen-1-yl ethers are a promising reagent for oligosaccharide synthesis. The experimental details and the limits of application of this method will be published elsewhere.

ACKNOWLEDGMENT

The authors thank Drs. I. G. Bolesov and V. A. Novoselov (Moscow State University) for helpful discussions.

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