

DETRITYLATION OF CARBOHYDRATE DERIVATIVES WITH SODIUM IN LIQUID AMMONIA

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The value of trityl ethers in carbohydrate synthesis lies in the fact that terminal hydroxyls may be selectively protected by this group (1). Trityl ethers may be cleaved by a number of methods, amongst the most common being by catalytic hydrogenation (2,3) by boiling with aqueous acetic acid (4) or treatment at room temperature with hydrogen chloride in chloroform (5) or hydrogen bromide in acetic acid (6). The use of silica gel for catalytic detritylation has also been reported (7). Previous use (8) of Birch reduction (9) for the cleavage of trityl ethers showed further value of the reaction (9) which has been widely used in carbohydrate field for removing protecting benzyl (10), benzylidene (11) and p-toluenesulfonyl (12) groups. Our results showed that detritylation of carbohydrate derivatives proceeds in a stoichiometric manner, two equivalents of sodium being necessary for a trityl group to be removed. The general applicability of the method for detritylation of carbohydrate derivatives greatly depends upon the solubility of the substrate in liquid ammonia which can be easily increased, as showed in a very recent work where this procedure was used in the detritylation of sucrose derivatives (13), by addition of an inert solvent into the reaction mixture. When the reaction is complete the detritylated carbohydrate is most conveniently isolated by partitioning the product between chloroform and water. The organic phase contains the noncarbohydrate reduction by-products and the water layer contains the sugar component.

Detritylation with sodium in liquid ammonia is of special advantage in one of the last steps of a synthesis since, as showed below, several protecting

groups may be simultaneously removed.

Methyl 2,3-di-O-benzyl-4-O-methyl-6-O-trityl- α -D-glucopyranoside (14) treated with sodium in a mixture of liquid ammonia and 1,2-dimethoxyethane (10:1) in the above described manner gave the expected methyl 4-O-methyl- α -D-glucopyranoside, m.p. 96-97°; lit. (14) m.p. 98°.

Methyl 4-O-acetyl-3-O-benzyl-2-O-methyl-6-O-trityl- α -D-glucopyranoside (15) treated as described above afforded methyl 2-O-methyl- α -D-glucopyranoside m.p. 147-148°; lit. (16) m.p. 147-148°.

Methyl 3-O-benzyl-2,4-di-O-methyl-6-O-trityl- α -D-glucopyranoside (15) treated in a similar manner yielded methyl 2,4-di-O-methyl- α -D-glucopyranoside m.p. 78-80°; lit. (17) m.p. 79°.

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