ABSTRACT

Although acetal blocking groups are widely used in synthetic carbohydrate chemistry, there is a large degree of conservatism in choice of acetal groups. When used for protection, the acetal groups traditionally employed simply block the hydroxyl functions. No attempt has been made to employ an acetal protecting group which could mediate the subsequent transformations performed on the substrate.

In this work, a variety of approaches to effecting selective transformations of carbohydrate substrates are described. These approaches involve the use of acetal blocking groups which incorporate specific features which could direct subsequent transformations.

Part I presents a review on the formation, structure and stability of the cyclic acetals of the D-aldohexopyranoses and their glycosides. Acetal systems with the bicyclo[3.2.1]octane and the bicyclo[2.2.2]octane structures are also discussed.

The preparation of a series of 2-methoxybenzylidene acetals of some D-aldohexoses and D-aldohexopyranosides is described in part II. The hydrolysis and selective oxidation and reductive cleavages of the acetal groups in these compounds are also discussed. Some observations on the mechanism of these cleavages are made and rationalizations are tendered. Studies of methods of preparing glycosides by alkylation of O_1 of 4,6-protected aldohexopyranoses are also described.

In part III a study of the effect which a phenacyloxy group in the 2-position of the phenyl group of 4,6-O-arylidene acetals of D-glucopyranosides

and D-galactopyranosides has on the selective esterification of O_3 of these substrates is described. The selective pivaloylation of O_3 of a 4,6-protected D-glucopyranoside by anchoring a base to the 4,6-acetal group is also described. Refinements to this method which could make it invaluable in sucrochemistry are suggested.

In the final part, some approaches to the preparation of 3,6,8-trioxabicyclo[3.2.1] - and 2,5,7-trioxabicyclo[2.2.2]octanes from acyclic carbohydrate derivatives are described. These compounds have valuable potential in the chemical manipulation of acyclic polyols.