A Simple, Efficient Synthesis of Vinyl β-D-Glucopyranosides

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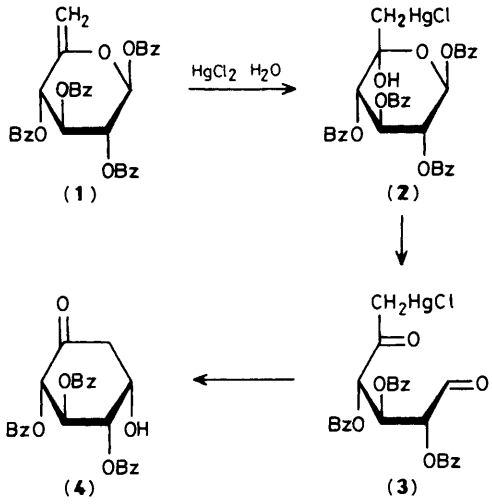
Reaction of tetra-*O*-acetyl-α-D-glucopyranosyl bromide with α-mercuriated carbonyl compounds provides simple and efficient access to acetylated vinyl and substituted vinyl β-D-glucopyranosides.

Because of the unavailability of the required alcohol, standard glycosidation methods cannot be applied to the synthesis of vinyl glycosides and no simple alternative procedure has been reported.

Transvinylation from isobutyl vinyl ether to 2,3,4,6-tetra-*O*-benzyl-D-gluco-[1] and -galacto-pyranose[2] with the aid of mercury(II) acetate has provided a means of obtaining the anomerically mixed vinyl glucosides and galactosides in moderate yields; the related reaction, however, of tetra-*O*-acetyl-D-glucose with ethyl vinyl ether in the presence of

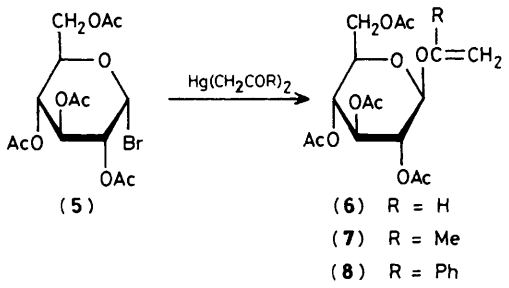


Scheme 1. Bz = benzoyl.

mercury(II) acetate and an acid catalyst gave a complex set of products.[3] Specific anomers are available by use of elimination reactions: Hofmann elimination applied to *N*-(2-β-D-glucopyranosyloxyethyl)trimethylammonium iodide gave the vinyl glycoside (29% as the tetra-acetate),[1] Norrish type II photochemical degradation of 4-oxopentyl glycosides gave the vinyl analogues in modest yields,[4] and oxidation of 2′-(phenylselenenyl)ethyl glycosides to the corresponding selenoxides followed by thermal elimination afforded the vinyl compounds in approximately 75% yield.[5] In the particular case of prop-1-enyl glycosides effective syntheses can be achieved by catalysed isomerisations of the analogous allyl compounds.[6]

In the course of investigating a reaction by which 6-deoxyhex-5-enopyranose derivatives are converted into 2-deoxyinososе compounds by way of mercuriated intermediates [*e.g.* (**1**) → (**4**), Scheme 1][7] we isolated the aldehydoketone (**3**) which readily ring closes in an aldol-like reaction to give the cyclohexanone product.[8] We have subsequently pursued the potential value of simpler α-mercuriated carbonyl compounds in synthesis in carbohydrate chemistry and now report their reaction with tetra-*O*-acetyl-α-D-glucopyranosyl bromide. The possibility that it might lead to a new approach to the important *C*-glycosides particularly interested us.

Treatment of the glycosyl halide (**5**) (7.6 g) with bis(formylmethyl)mercury[9] (10.0 g, 2 mol. equiv.) in refluxing chloroform (220 ml) for 22 h under nitrogen, removal of the mercury-containing compounds by washing with aqueous sodium thiocyanate solution and then water, and finally drying and evaporation of the solvent gave almost pure vinyl β-D-glucopyranoside tetra-acetate (**6**) in 92% yield. Recrystallisation gave the known compound in 80% yield.



Scheme 2

Analogous reaction carried out with bis(acetonyl)mercury[10] afforded the 1′-methyl-substituted glycoside (**7**), m.p. 107—108 °C, $[\alpha]_D$ −11° ($CHCl_3$) in 90% yield after recrystallisation, and bis(benzoylmethyl)mercury[11] (1 mol. equiv.) led to the 1-styryl compound (**8**), m.p. 105—107 °C, $[\alpha]_D$ −40° ($CHCl_3$), (70% after recrystallisation). In this case by-products were removed by filtration before the thiocyanate extraction.

These mercury-containing compounds therefore did not react as carbon nucleophiles as had occurred with the aldehydic group in the intramolecular reaction (Scheme 1), and as is the case with other aldehydes,[12] but behaved instead as oxygen nucleophiles (Scheme 2), as in their reaction with acyl halides to give enol esters.[11,13]

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