Use of Dimethoxydiphenylsilane, *NN*-Dimethylformamide, and Toluene-*p*-sulphonic Acid as a Novel Acetalating Reagent

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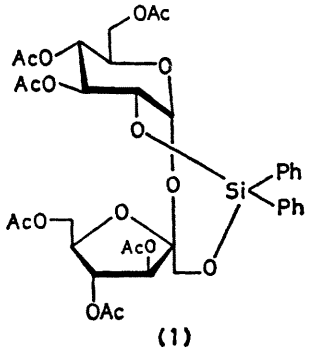
Summary Reaction of sucrose with a combination of dimethoxydiphenylsilane, *NN*-dimethylformamide, and toluene-*p*-sulphonic acid gave a mixture of 1′,2-*O*-(diphenylsilylene)sucrose and 1′,2:6,6′-di-*O*-(diphenylsilylene) sucrose, from which the 1′,2-silylene acetal has been isolated directly as its hexa-acetate (**1**) in 18% yield; the 1′,2:6,6′-disilylene acetal tetra-acetate (**2**) has been isolated after column chromatography.

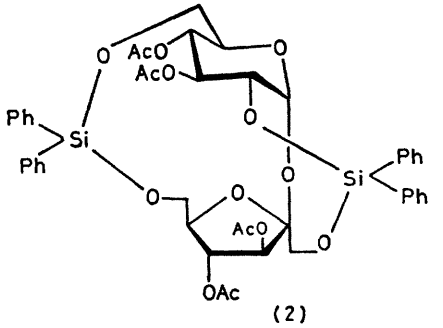
THE importance of cyclic acetal derivatives of carbohydrates as synthetic intermediates is well recognised, as is their value in conformational investigations.[1] In continuation of our studies on the synthesis of cyclic acetal derivatives of sucrose, we have used the combination of dimethoxydiphenylsilane, *NN*-dimethylformamide, and toluene-*p*-sulphonic acid (reagent *A*) as an acetalating reagent. Synthesis of cyclic acetals of sugars using this combination of reagents has hitherto not been reported. When sucrose was treated with reagent *A*, initially at 0 °C, and then for 4 h at room temperature, it gave, after acetylation with acetic anhydride and pyridine, 3,4,6,3′,4′,6′-hexa-*O*-acetyl-1′,2-*O*-(diphenylsilylene)sucrose (**1**, 18%), m.p. 142—144 °C, $[\alpha]_D$ + 60·6° (chloroform).† The resultant syrupy residue gave, after chromatographic fractionation, (**1**, 28%) and

† Satisfactory analyses were obtained for all compounds reported herein.

3,4,3′,4′-tetra-*O*-acetyl-1′,2:6,6′-di-*O*-(diphenylsilylene) sucrose (**2**, 4%), m.p. 234—236 °C, $[\alpha]_D$ + 9·7° ($CHCl_3$). It is of interest to note that the expected[2] 4,6-silylene acetal derivative was not detected in the reaction mixture. The structures of (**1**) and (**2**) were confirmed by ^{1}H-n.m.r. spectroscopy at 100 MHz, by mass spectrometry, and by chemical transformations. The 1′,2:6,6′-disilylene acetal (**2**) probably constitutes the first example in carbohydrate chemistry of a twelve-membered cyclic acetal ring.

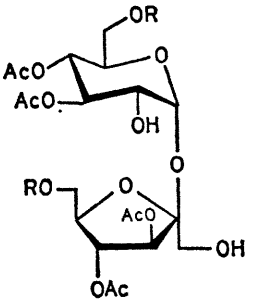


(1)



(2)

Treatment of (**1**) with boiling aqueous acetic acid gave the 1′,2-diol (**3**, 78%), m.p. 118—119 °C, $[\alpha]_D$ + 51° ($CHCl_3$). Similarly, the disilylene acetal (**2**) was transformed into the 1′,2,6,6′-tetraol (**4**, 68%), m.p. 154—156 °C, $[\alpha]_D$ + 46° ($CHCl_3$). The synthetic utility of these derivatives is illustrated by the conversion of (**3**) into 1-chloro-1-deoxy-β-D-fructofuranosyl 2-chloro-2-deoxy-α-D-mannopyranoside *via* the 1′,2-bis(chlorosulphate),[3] and by conversion of (**4**) into 1,6-dichloro-1,6-dideoxy-β-D-fructofuranosyl 2,6-dichloro-2,6-dideoxy-α-D-mannopyranoside,[4] by use of sulphuryl chloride reagent.



(3) R = Ac
(4) R = H

The reaction of sucrose with reagent *A* is a novel and potentially valuable method to give strained and otherwise inaccessible cyclic acetal derivatives.

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[1] A. N. De Belder, *Adv. Carbohydrate Chem.*, 1965, **20**, 219; *Adv. Carbohydrate Chem. Biochem.*, 1977, **34**, 179.
[2] R. Khan, *Carbohydrate Res.*, 1974, **32**, 375; R. Khan and K. S. Mufti, *ibid.*, 1975, **43**, 247; R. Khan, K. S. Mufti, and M. R. Jenner, *ibid.*, 1978, **65**, 109.
[3] R. Khan, M. R. Jenner, and H. Lindseth, *Carbohydrate Res.*, in the press.
[4] R. Khan and C. K. Lee, unpublished results.