The Synthesis of Carbohydrate C-Phosphine Oxides

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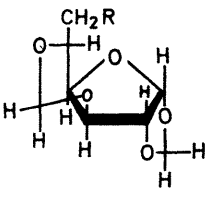
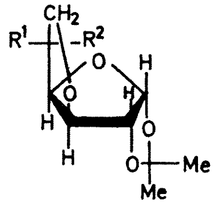
Summary Carbohydrate derivatives bearing a *C*-phosphine oxide substituent can be prepared by the reaction of lithium diphenylphosphine with suitably blocked sulphonate ester or epoxide derivatives.

A CONTINUING[1] interest in carbohydrate derivatives bearing a phosphorus substituent attached *via* a carbon–phosphorus linkage,[2] prompted us to investigate the reaction of lithium diphenylphosphine[3] (**1**) with a variety of carbohydrate substrates, including primary and secondary sulphonate ester and epoxide derivatives. Three examples are given to illustrate that such reactions provide a general route to carbohydrate-*C*-phosphine oxides.

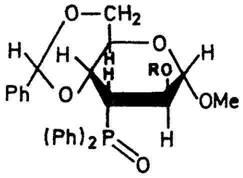
Treatment of (**1**) with 1,2 : 3,5-di-*O*-methylene-6-*O*-tosyl-α-D-glucofuranose[4] (**2**) in anhydrous tetrahydrofuran solution at 0° for 3 h afforded, after conventional work-up and recrystallisation from benzene–light petroleum, diphenyl-(1,2 : 3,5-di-*O*-methylene-α-D-glucofuranose)-3-*C*-phosphine oxide (**3**),† m.p. 164—166°, $[\alpha]_D^{25}$ +27°, (*c* 1·07), in 63% yield.



(2) R = OTs
(3) R = $P(O)(Ph)_2$



(4) R^1 = OMs; R^2 = H
(5) R^1 = H; R^2 = $P(O)(Ph)_2$



(7) R = H
(8) R = Ac

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† All derivatives reported here had n.m.r. spectra in accord with the assigned structures; with the exception of (**5**), all compounds had the correct elemental microanalyses. Optical rotations were measured for chloroform solutions.

Similarly, 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-mesyl-α-D-glucofuranose[5] (**4**) reacted with (**1**) at 20° for 24 h to give, after work-up and vacuum sublimation, a 38% yield of diphenyl-(3,6-anhydro-1,2-*O*-isopropylidene-α-L-idofuranose)-5-*C*-phosphine oxide (**5**), m.p. 208—209°, $[\alpha]_D^{25}$ +37° (*c* 0·95).

Methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside[6] (**6**) reacted with (**1**) for 12 h at 20° to give, in 72% yield, diphenyl(methyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside)-3-*C*-phosphine oxide (**7**), m.p. 280° (decomp.). This product was acetylated to give a quantitative yield of diphenyl(methyl-3-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-α-D-altropyranoside)-3-*C*-phosphine oxide (**8**), m.p. 222—225°, $[\alpha]_D^{25}$ +88° (*c* 0·89).

The assignment of the phosphine oxide, rather than the phosphine structure to (**3**), (**5**), (**7**), and (**8**) was based on ^{31}P chemical shift data.[7] The configurational assignments were based on the known stereospecific dependencies of *vicinal* H–H couplings.[8]

(**1**) reacts with a variety of other carbohydrate derivatives to give phosphine oxide derivatives in yields varying from 60—75%; the yield reported for the conversion of (**4**) into (**5**) is the lowest of any reaction we have studied so far and typifies the poor conversions obtained for secondary sulphonate esters.

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