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SYNTHESIS OF SOME COBALT DERIVATIVES OF CARBOHYDRATES

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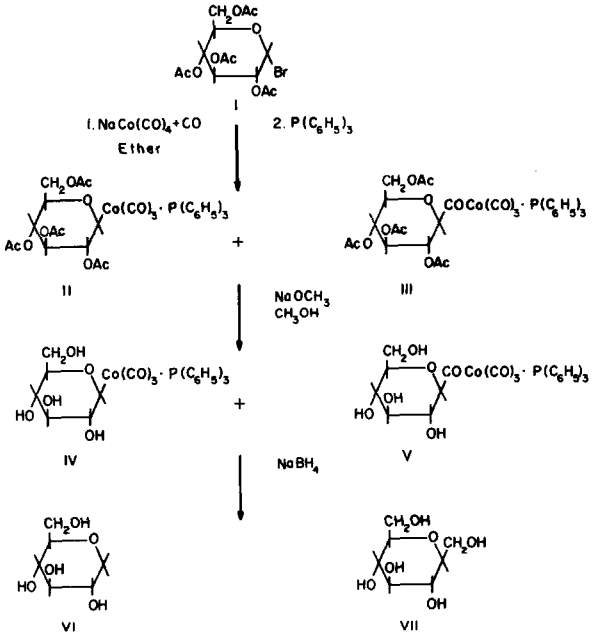
Very few metallic derivatives of carbohydrates in which the metal is linked by a σ-bond to the carbon of the carbohydrate are known (1-3). In this communication we wish to report the conversion of 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide (I) into cobalt derivatives II and III using cobalt tetracarbonyl anion to displace the bromide ion.



The general procedure used is a modification of the method used by other workers (4,5) for the synthesis of alkyl and acyl tricarbonyl triphenylphosphine complexes. The equipment

previously used in the application of the oxo reaction to the unsaturated carbohydrates (6,7) has been modified as described below. A separate inlet fitted with an injector septum (from an Aerograph v.p.c. instrument) was attached to the head of the Aminco autoclave. Ether solutions of the reactants were injected through the septum by means of a Hamilton syringe. The first part of the experiment was carried out under nitrogen in a dry box. 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide (5 g.) was placed in a glass liner which was then inserted in an autoclave of 200 ml. internal capacity. After the autoclave was sealed, it was removed from the dry box, flushed three times with 9 atm. of Matheson C.P. carbon monoxide (gas passed through gas purifier) and finally pressurized with 1 atm. of carbon monoxide. An ether solution of sodium cobalt tetracarbonyl (8,9) (100 ml. of ca. 0.2N) was then injected, through the septum. After the autoclave was again flushed with carbon monoxide, it was pressurized with 10 atm. of carbon monoxide and then rocked at room temperature for about 2 days (about 40 p.s.i. gas absorbed). The gas was then vented until the residual gas pressure was about 1 atm. and the autoclave then cooled to 0°. After a solution of triphenylphosphine (4 g.) in anhydrous ether (50 ml.) was injected, the autoclave was again rocked for about 9 hr. at room temperature or until no further increase in gas pressure was obtained. After the carbon monoxide was vented from the autoclave, the sodium bromide was removed from the reaction mixture by filtration under nitrogen (sodium bromide washed with ether). Slow addition of purified methyl iodide (10 ml.) precipitated excess triphenylphosphine as the salt which was then removed by filtration under nitrogen. After the filtrate was evaporated under reduced pressure at room temperature, the residual yellow syrup (5.6 g.) was extracted under nitrogen with 250 ml. of anhydrous petroleum ether (30-60°) and stored over-night at 0° to give a yellow solid A. An amount of 3 g. of A was chromatographed under nitrogen on a column (50 x 4.5 cm. D) of air-dried deactivated silica gel G using a 1:1 mixture of anhydrous ether-petroleum ether (30-60°) as developer. The faster moving zone on the column was eluted and on evaporation of the solvent gave compound II which was recrystallized from ether-petroleum ether (1:20); m.p. 79-80°; $[\alpha]_D^{20}$ -19° (c 3, benzene). [Found: C, 57.30; H, 4.90; Calcd. for $C_{35}H_{34}O_{12}CoP$: C, 57.05; H, 4.65]. Compound II gave a p.m.r. spectrum (multiplet at 8 τ equal to 12 hydrogens, multiplets at 4.3 to 6.5 τ equal to 7 hydrogens and unequal doublet at 2.5 τ equal to 15 aromatic hydrogens) in agreement with the assigned structure. Compound II (0.16 g.) was then de-O-acetylated with 0.01N sodium methoxide in methanol (15 ml.) at 0° for 14 hr. to afford a water soluble fairly unstable cobalt derivative IV which was subsequently reduced

with sodium borohydride in water. Acetylation of the reduced product with acetic anhydride and pyridine afforded a crystalline compound which was identical (m.p., I.R. and p.m.r.) with an authentic sample of 2,3,4,6-tetra-O-acetyl-1,5-anhydro-D-glucitol (10). Therefore compound II is 2,3,4,6-tetra-O-acetyl-β-D-glucosyl cobalt tricarbonyl triphenylphosphine.

Similar deacetylation, reduction and acetylation of the slower moving zone as that performed on compound II gave a mixture of acetates which were separated readily by v.p.c. at 220° on a column of 10 % SE-52 on 60/80 mesh chromosorb W. The major component had identical properties (m.p., no depression in mixed m.p., I.R. and p.m.r.) to those of an authentic sample of 1,3,4,5,7-penta-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptitol (11), whereas the minor component was identical with the acetate of compound VI. Therefore compound III is 2,3,4,6-tetra-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptosoyl cobalt tricarbonyl triphenylphosphine.

When product A was reduced with sodium borohydride and then acetylated a mixture of acetates of compounds VI and VII in the ratio of 1:8 was obtained (determined by v.p.c.). On standing in air (or in contact with silica gel) compound III slowly converted into compound II.

Treatment of tri-O-acetyl-3-deoxy-α-D-erythro-hex-2-enopyranosyl chloride (12) with sodium cobalt tetracarbonyl and triphenylphosphine gave a red compound; methyl-2-deoxy-2-iodo-α-D-manno (and gluco) pyranoside (13) have also been allowed to react with cobalt tetracarbonyl anion. The nature of these products (in addition to those from 5,6- and 1,2-carbohydrate epoxides will be the subject of a future communication (14).

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