Tellurocarbohydrates

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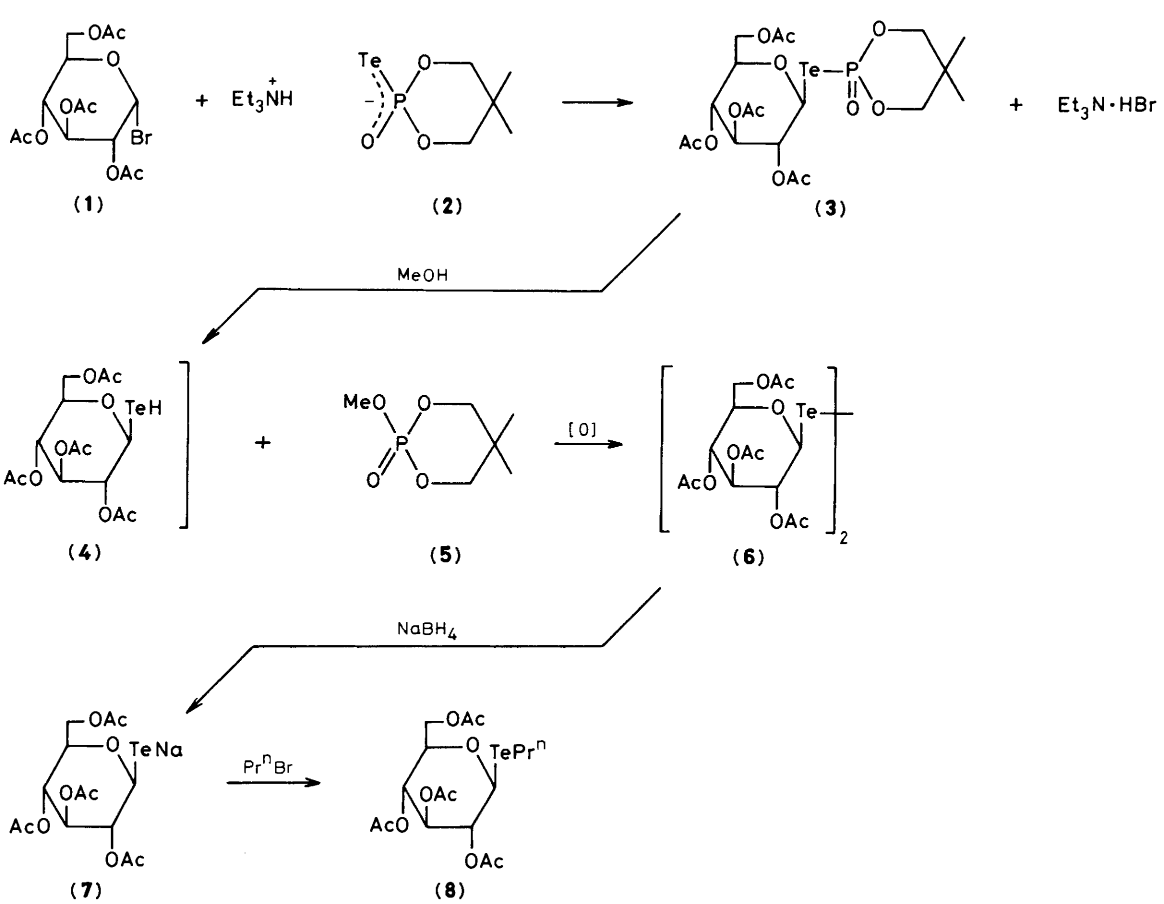
The 1-*Te*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucosyl) phosphorotelluroate (**3**) obtained by reaction of α-acetobromoglucose (**1**) with the triethylammonium phosphorotelluroate (**2**) gives on treatment with methanol bis(β-D-glucosyl) ditelluride (**6**) which on reduction with $NaBH_4$ is converted into sodium 1-telluro-β-D-glucoside (**7**), which was not isolated but in the presence of n-propyl bromide was alkylated *in situ* to give n-propyl 1-telluro-β-D-glucoside (**8**); compounds (**3**), (**6**), and (**8**) are the first representatives of their class.

In spite of growing interest in organic tellurium chemistry[1] it has not been possible to synthesize telluroglucosides,[2] analogues of well known O-, S-, and Se-glucosides or any other tellurium-containing sugar derivative. In our approach the carbon–tellurium bond was formed by employing *O,O*-dialkylphosphorotelluroates,[3] $(RO)_2P(Te)O^-$, which would be expected to be good nucleophiles towards four-co-ordinate carbon. The triethylammonium 2-tellurido-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane salt (**2**) was formed from 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinane and elemental tellurium in the presence of triethylamine in an oxygen-free atmosphere. The condensation of (**2**), prepared



in situ, with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**1**) led to the expected 2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)telluro-2-oxo-5,5-dimethyl-1,3,2λ^5-dioxaphosphorinane (**3**) [47%; colourless crystals, m.p. 155—156 °C; $\delta(^{31}P)$ −9.8 p.p.m.; J_{P-Te} 1245 Hz]† ‡ with inversion of configuration at the anomeric carbon atom. The proposed β-glycosyl structure of (**3**) was deduced from its ^1H n.m.r. spectrum which is almost identical with the spectra of β-S and β-Se analogues.[4] The lack of a characteristic α-anomeric proton signal (dd at δ *ca.* 6.0—6.8 in the S- and Se-analogues[4,5]) supports for the β-configuration. The glucosyl phosphorotelluroate (**3**) is sensitive towards oxygen and moisture. It can be kept, however, for 2—3 weeks without decomposition in a refrigerator under argon. On treatment with methanol in the presence of air compound (**3**) was transformed into the ditelluride (**6**) {30%;§ bright orange, odourless crystals;¶ m.p. 164—165 °C; $[\alpha]_D^{20}$ −164°; $\lambda_{max.}$ 380 nm; ^1H n.m.r. (CDCl$_3$) δ: 1.9, 2.0, 2.1, and 2.2 (4s, OAc); 3.6—3.8 (m, 5-H); 4.15—4.25 (m, 6-H$_2$); 5.15—5.25 (m, 1—4-H)}. It is most likely that the ditelluride (**6**) is formed in two steps: formation of acetylated telluroglucose (**4**) by nucleophilic displacement at phosphorus followed by immediate oxidation of (**4**) to the ditelluride (**6**). The presence of the dioxaphosphorinanone (**5**) was confirmed by ^{31}P n.m.r. spectroscopy (δ −6.4 p.p.m.). The ditelluride (**6**) is relatively stable towards oxygen; it was kept for several weeks *in vacuo* without decomposition. Reduction of (**6**) by sodium borohydride in the presence of excess of n-propyl bromide gave the telluro glucoside (**8**) as a syrup which readily decomposes on contact with air and moisture. The structure of (**8**) is evident from its ^1H n.m.r. spectrum (CDCl$_3$) δ: 0.85—1.15 (t, 3H, *Me*CH$_2$), 1.65—2.1 (m, 2H, MeC*H*$_2$), 2.7—2.8 (d, 2H, CH$_2$-Te), 3.55—3.8 (m, 1H, 5-H), 4.1—4.25 (m, 2H, 6-H$_2$), and 5.05—5.25 (m, 4H, 1—4-H).

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† All new compounds gave analytical data consistent with the proposed structures.

‡ This is the first example of a compound with a P–Te–C bond containing a four-co-ordinate P atom.

§ The actual yield of the tellurium-containing derivatives was considerably higher than the yield of isolated, pure compounds, as shown by spectroscopic data.

¶ The orange-red colour is characteristic of all ditellurides known,[1] which in aliphatic series usually possess a persistent odour.

References

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