*Carbohydrate Research*, 113 (1983) 336–338
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

## Note

# 2-Haloethylidene acetals of some alditols

SHAUL YANAI*
*Plastics Research Department, The Weizmann Institute of Science, Rehovot (Israel)*
(Received August 24th, 1982; accepted for publication, September 22nd, 1982)

Diethoxyphosphinylethylidene acetals of D-glucitol, D-mannitol, and galactitol have been prepared[1,2] by transacetalation reactions between diethyl 2,2-di(ethoxyethyl)phosphonate and the respective alditol. Apparent deviations from the Barker and Bourne rules were attributed to electronic influence by the phosphorus atom[1]. Preparation of haloethylidene acetals under similar conditions of reaction could constitute a proof for this assumption. Furthermore, these compounds provide an alternative route to dialkoxyphosphinylethylidene acetals, through the well known, Michaelis–Arbusov reaction, by reacting with trialkyl phosphites. Various methods of preparing cyclic chloroacetals have been published[3]; however, we preferred the transacetalation procedure described by Sinclair and Wheadon[4].

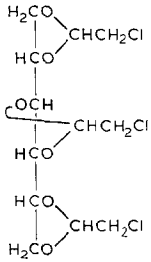
Chloroacetaldehyde diethyl acetal reacted with D-glucitol in the presence of conc. hydrochloric acid, to give a viscous, colorless, distillable syrup (**1**). The compound consumed practically no periodate, no free hydroxyl groups were detected, and microanalysis confirmed it to have the composition of a tri-acetal. A syrupy, monoacetal derivative (**2**) was obtained in shorter reaction-times. Compound **2** contained a terminal, vicinal-diol grouping (formaldehyde release, 0.78 and 0.82 mol), and consumed ~3 mol of periodate (2.81 and 2.82 mol). Having four adjacent hydroxyl groups, compound **2** is 1,2(5,6)-*O*-(2-chloroethylidene)-D-glucitol.

Reaction of chloroacetaldehyde diethyl acetal on D-mannitol yielded a crystalline diacetal (**3**). One mol of this compound consumes 1 mol of periodate, and practically no formaldehyde is released during periodate oxidation. The chemical shifts of the acetal protons ($\delta$ 5.24) in its n.m.r. spectrum are characteristic of 1,3-dioxolane systems[5]. Thus, acetal **3** must be the 1,2:5,6-diacetal. On performing a similar reaction with diethyl 2,2-di(ethoxyethyl)phosphonate[2], the 1,3:4,6-diacetal derivative was obtained. Using bromoacetaldehyde diethyl acetal as the reagent, a multi-component, inseparable syrup was obtained. However, the same reagent

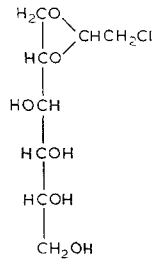
*Present address: Department of Macromolecular Science, Case Western Reserve University, Cleveland, OH 44106, U.S.A

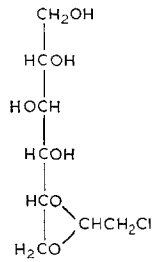
reacted with galactitol to give a high yield of a single, crystalline product whose $^{13}C$-n.m.r. spectrum was identical with that of the phosphonated derivative, and which is therefore assigned the 1,3:4,6-diacetal structure (**4**).

Steric effects therefore control the nature of the product to the same extent as the electronic effects exerted by phosphinyl substituents[1].

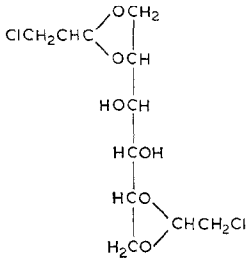


1

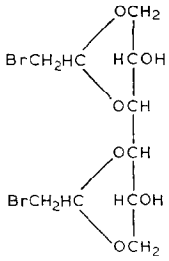




2



3



4

EXPERIMENTAL

Instrumentation and analytical procedures employed have been described[1].

*1,2(5,6)-O-(2-Chloroethylidene)-D-glucitol* (**2**). — To D-glucitol (18.2 g) in an open, conical flask was added freshly distilled chloroacetaldehyde diethyl acetal (15.3 g); with continuous magnetic stirring at room temperature, concentrated hydrochloric acid (25 mL) was added at once, and complete dissolution of the alditol occurred within 30 min. After 10 h, the solution was poured into water (100 mL), made neutral with solid sodium hydrogencarbonate, and the suspension filtered. On addition of small portions of ethanol to the filtrate, a reddish-brown oil separated. A solution of the oil in ether was dried ($Na_2SO_4$), treated with charcoal, and evaporated; $\eta_D^{20}$ 1.4725; $R_F$ 0.43 in 6:3:1 1-butanol–acetic acid–water. Formaldehyde release: 0.78; 0.82. Periodate consumption: 2.81 (6 h) and 2.82 mol (24 h).

*Anal.* Calc. for $C_8H_{15}ClO_6$: C, 39.6; H, 6.2; Cl, 14.6. Found: C, 39.7; H, 6.6; Cl, 14.8.

On repeating the reaction for 18 h, but with double the quantity of chloroacetal, a heavy, colorless oil was obtained on diluting with water. The product was distilled, giving a very viscous syrup (compound **1**): b.p. 205–210° /0.9 torr (lit.[3] 219–220°/0.05 torr).

*Anal.* Calc. for $C_{12}H_{17}Cl_3O_6$: C, 39.6; H, 4.7; Cl, 29.3. Found: C, 39.5; H, 4.7; Cl, 28.4.

*1,2:5,6-Di-O-(2-chloroethylidene)-D-mannitol* (**3**). — To D-mannitol (3.2 g) were added chloroacetaldehyde diethyl acetal (6 g) and conc. hydrochloric acid (10 mL). After stirring magnetically for 14 h at room temperature, the solution was poured in water (50 mL). A white suspension was obtained, which changed to long, white needles (4.3 g) after 3 h in an ice bath; m.p. 88–92°; $R_F$ 0.62; $\nu_{max}^{KBr}$ 3330–3280 (OH), 1140 (acetal), and 750 (C–Cl); $^1$H-n.m.r. (60 MHz, in $CDCl_3$): $\delta$ 2.43 (s, 2 H, OH), 3.60 and 3.68 (dd, 4 H, $ClCH_2$), 3.85–4.45 (m, 8 H, sugar skeleton protons), and 5.24 (septet, 2 H, acetalic site); periodate consumption: 0.74 (3 h), 0.88 (6 h); no release of formaldehyde.

*Anal.* Calc. for $C_{10}H_{16}Cl_2O_6$: C, 39.6; H, 5.3; Cl, 23.4. Found: C, 39.6; H, 5.1; Cl, 23.2.

*1,3:4,6-Di-O-(2-bromoethylidene)galactitol* (**4**). — Bromoacetaldehyde diethyl acetal (7.75 g) was allowed to react with galactitol (3.2 g) as for compound **3**: yield 3.6 g (54%); m.p. 186–188° (70% ethanol); $R_F$ 0.42; $^{13}$C-n.m.r. (22.63 MHz): $\delta$ 45.54 ($CH_2Br$), 61.94 (C-2,5), 71.23 (C-1,6), 75.33 (C-3,4), and 98.91 (C acetal). periodate consumption: 0.07 (3 h), 0.03 (12 h).

*Anal.* Calc. for $C_{10}H_{16}Br_2O_6$: C, 30.6; H, 4.1; Br, 40.8. Found: C, 31.1; H, 4.0; Br, 39.8.

## REFERENCES

1 S. Yanai, M. Halmann, and D. Vofsi, *Carbohydr. Res.*, 83 (1980) 243–248.
2 S. Yanai, M. Halmann, and D. Vofsi, *Carbohydr. Res.*, 83 (1980) 379–382.
3 B. G. Yasnitskii, S. A. Sarkisyants, and E. G. Ivanyuk, *Zh. Obshch. Khim.*, 37 (1964) 1940–1945
4 H. B. Sinclair and W. J. Wheadon, *Carbohydr. Res.*, 4 (1967) 292–297
5 T. G. Bonner, E. J. Bourne, D. Lewis, and L. Yuceer, *J. Chem. Soc., Perkin Trans. 1*, (1975) 1323–1325.