NOTES.

Tetra-acetyl Aldehydophenylglucosides. By R. TECWYN WILLIAMS.

A COMPARATIVE study of the fate of phenols and their glucosides in the animal body necessitated the synthesis of certain phenolic glucosides. One of the methods of synthesis used was that of Helferich and Schmitz-Hillebrecht (*Ber.*, 1933, **66**, 378), which consists in condensing phenol with β-glucose penta-acetate in the presence of anhydrous zinc chloride or *p*-toluenesulphonic acid, whereby an α- or a β-glucoside is formed respectively. When this method is applied to the preparation of the glucosides of the hydroxybenzaldehydes, very poor yields are obtained. An interesting point, however, emerges in that, whilst no glucoside formation was detected when salicylaldehyde was condensed with glucose penta-acetate, *m*-hydroxybenzaldehyde gave an *α-glucoside*, and *p*-hydroxybenzaldehyde gave a β-glucoside, irrespective of the nature of the catalyst. It has been shown by Sisido (*J. Soc. Chem. Ind. Japan*, 1936, **39**, 217) that salicylaldehyde does condense with glucose penta-acetate in the presence of *p*-toluenesulphonic acid if a very high vacuum is used, whereby the acetic acid formed is removed, and the condensation facilitated. The product obtained, however, is tetra-acetyl salicylic acid β-*d*-glucoside (helicin tetra-acetate).

Melting points are corrected.

The condensations were carried out as follows: Equal weights of β-glucose penta-acetate and hydroxybenzaldehyde were melted together, and the catalyst (anhydrous zinc chloride, 10% of wt. of aldehyde; *p*-toluenesulphonic acid, 1% of wt. of aldehyde) added. The mixture was heated and stirred at 120—130° for 30 minutes. It was then partially cooled, and the tarry product extracted with benzene. The dark extract was washed with water, then with 5% sodium hydroxide solution until clear, and finally with water. The benzene solution was dried over anhydrous calcium chloride and evaporated to a syrup under diminished pressure. The syrup was triturated with light petroleum and then taken up in ethyl or methyl alcohol. The alcoholic solution deposited crystals of the tetra-acetyl glucoside after several days at room temperature.

(a) p-*Hydroxybenzaldehyde with* p-*toluenesulphonic acid as catalyst.* The syrup from this aldehyde (30 g.) deposited from ethyl alcohol 1—2 g. of tetra-acetyl *p*-aldehydophenyl-β-*d*-glucoside. Slow recrystallisation from ethyl alcohol gave thick plates, m. p. 145°, $[\alpha]_D^{19^\circ}$ $-28{\cdot}0^\circ$ in chloroform (*c*, 0·8) (Mauthner, *J. pr. Chem.*, 1912, **85**, 568, gives m. p. 144—145°, but does not record a rotation).

(b) p-*Hydroxybenzaldehyde with anhydrous zinc chloride.* Tetra-acetyl *p*-aldehydophenyl-β-glucoside was again isolated in similar yield, m. p. and mixed m. p. 145°, $[\alpha]_D^{18^\circ}$ $-27{\cdot}9^\circ$ in chloroform ($c = 2{\cdot}3$) (Found: C, 55·9; H, 5·4. Calc. for $C_{21}H_{24}O_{11}$: C, 55·7; H, 5·3%). The 2 : 4-*dinitrophenylhydrazone* formed a red jelly in ethyl alcohol. After it had been washed with water it crystallised from ethyl acetate–acetic acid in orange needles, m. p. 216—218° (Found: N, 8·8. $C_{27}H_{28}O_{14}N_4$ requires N, 8·7%).

(c) m-*Hydroxybenzaldehyde with* p-*toluenesulphonic acid.* The syrup deposited *tetra-acetyl* m-*aldehydophenyl*-α-d-*glucoside* from methyl alcohol. Crystallisation from 40% aqueous acetone gave a crystalline powder, m. p. 123—124°, $[\alpha]_D^{22°}$ + 153·9° in chloroform (*c*, 2).

(d) m-*Hydroxybenzaldehyde with anhydrous zinc chloride.* In this case 30 g. of the aldehyde yielded 6·5 g. of the tetra-acetyl α-glucoside, m. p. and mixed m. p. 123—124°, $[\alpha]_D^{22°}$ + 154·2° in chloroform ($c = 1$) (Found : C, 55·55; H, 5·5%). Its 2 : 4-*dinitrophenylhydrazone* was an orange-yellow powder (from alcohol), m. p. 170° (Found : N, 8·9%). The isomeric tetra-acetyl β-glucoside has been described by Bargellini and De Fazi (*Gazzetta*, 1915, **45**, II, 11), who record m. p. 105—107° and $[\alpha]_D$ −43·2° (in alcohol). These authors obtained a hard resin on deacetylating their tetra-acetate, and a similar result was obtained here on deacetylating tetra-acetyl *p*-aldehydophenyl-β- and *m*-aldehydophenyl-α-glucoside with sodium methoxide in methyl alcohol.

(e) *o*-Hydroxybenzaldehyde with either catalyst gave a syrup from which no crystalline glucoside was obtained. However, crystalline material (prismatic needles) was isolated which contained no carbohydrate. This material was optically inactive in chloroform, gave no hydrazone with 2 : 4-dinitrophenylhydrazine, no coloration with ferric chloride, and was insoluble in water and caustic soda solution. It gave a deep red coloration with concentrated sulphuric acid and after recrystallisation from alcohol had m. p. 130°. These properties showed it to be 3 : 4 : 7 : 8-dibenz-2 : 6 : 9-bisdioxan (disalicylaldehyde). This was confirmed by the fact that it did not depress the m. p. of authentic disalicylaldehyde, m. p. 130°, prepared according to Adams, Fogler, and Kleger (*J. Amer. Chem. Soc.*, 1922, **44**, 1126) by auto-condensation of salicylaldehyde in the presence of acetic anhydride and concentrated sulphuric acid at 0°.—MEDICAL SCHOOL, BIRMINGHAM. [*Received, August* 14*th*, 1940.]

Heat of Hydration of the Proton. By E. C. BAUGHAN.

APPLICATION of cycles of the Born–Haber type to acids and bases requires the heat of hydration of the proton. This may be obtained in various ways; the simplest is by the following cycle :

$$\begin{tikzcd}
& \mathrm{H_g} + \mathrm{X_g} \arrow[r, "-I", "+E_\mathrm{X}"'] & \mathrm{H_g^+} + \mathrm{X_g^-} \arrow[dl, "+S_\mathrm{H}+S_\mathrm{X}"] \\
\mathrm{HX_{gas}} \arrow[ur, "-B"] & & \\
& \mathrm{H^+_{aq.}} + \mathrm{X^-_{aq.}} \arrow[ul, "-Q"'] &
\end{tikzcd}$$

where B is the bond-strength, *i.e.*, the heat necessary to break HX into atoms, I the ionisation potential of hydrogen, and S_H, S_X, the heats of hydration of the proton and the halogen ion.

This cycle has been used before, but only, apparently, for hydrogen chloride (van Arkel and de Boer, " La Valence et l'Électrostatique," Alcan, Paris, 1936, Chap. 10). As modern accurate data have changed considerably the accepted values of some terms, particularly B and E_X, the electron affinity of the halogens, a recalculation of $S_\mathrm{H} + S_\mathrm{X}$ (and hence of S_H) is desirable for all four halogens. The values of Q, the exothermic heat of solution of the gas in water, in which hydrogen chloride, bromide, and iodide are completely ionised, were taken from Landolt–Börnstein's Tables, *viz.*, 17·8, 20·0, and 19·2 kg.-cals., respectively. That for hydrogen fluoride (11·6) comes from the value HF (monomeric gas) ⟶ $\mathrm{HF_{aq.}}$ + 11·6 kg.-cals. (von Wartenberg and Fitzner, *Z. anorg. Chem.*, 1936, **151**, 323), and the assumption that, as hydrogen fluoride has about the same acid strength as formic acid, whose heat of ionisation is only 0·013 kg.-cal. at 25°, that of hydrogen fluoride will be negligible [$K_{25°}$, HF = $3{\cdot}53 \times 10^{-4}$ (Fredenhagen and Wellmann, *Z. physikal. Chem.*, 1932, *A*, **162**, 458); $K_{25°}$, $\mathrm{H{\cdot}CO_2H} = 1{\cdot}75 \times 10^{-4}$]. The B values are due to Pauling (" The Nature of the Chemical Bond," 1939), *viz.*, HF, 147·5; HCl, 102·7; HBr, 87·3; HI, 71·4.

Values of the electron affinity of the halogens from Born–Haber cycles for the alkali halides have been obtained by Mayer and Helmholz (I) (*Z. Physik*, 1932, **75**, 19), and also by Verwey and de Boer (II) (*Rec. Trav. chim.*, 1936, **55**, 451); the difference is due to different estimates of the van der Waals terms. These results are : (I) F, 95·3; Cl, 86·5; Br, 81·5; I, 74·2; (II) F, 92·2; Cl, 83·0; Br, 77·2; I, 69·9. Hence we get for $S_\mathrm{H} + S_\mathrm{X}$: (I) 375·6, 345·8, 337·6, 328·2; (II) 378·7, 349·3, 341·9, 332·5 for the four halogens respectively. Taking the values for the $S_{\mathrm{X}'}$ terms given by Eley and Evans (*Trans. Faraday Soc.*, 1938, **34**, 1093), *viz.*, $\mathrm{F^-}$ 96; $\mathrm{Cl^-}$, 64; $\mathrm{Br^-}$, 58; $\mathrm{I^-}$, 46 (these are based on the assumption $S_{\mathrm{F}^-} = S_{\mathrm{K}^+}$), we obtain the following values of S_H : (I) 280, 282, 280, 282; (II) 283, 285, 284, 287. Mean $S_{\mathrm{H}^+} = 282{\cdot}5 \pm 3$ kg.-cals.—THE UNIVERSITY, MANCHESTER, 13. [*Received, August* 12*th*, 1940.]