THE ACETOLYSIS OF SOME HYDROXYTETRAHYDRO-2-PYRANS[1]

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ABSTRACT

The reaction between acetic anhydride and several hydroxytetrahydropyrans in the presence of boron trifluoride has been studied. 2-Methyl-3-hydroxytetrahydropyran, 2-hydroxymethyl-4,5-dihydroxytetrahydropyran, and 3,4-dihydroxytetrahydropyran all underwent normal acetolysis to the expected straight-chain polyol acetates. Optically active forms of *cis*- and *trans*- 3,4-dihydroxytetrahydropyran gave the same, inactive pentanetetrol, showing that racemization of the active centers had accompanied ring cleavage. 2-Hydroxymethyltetrahydropyran gave 1,3,6-hexanetriol besides the expected 1,2,6-isomer. The reagent did not cleave 4-hydroxytetrahydropyran nor dihydro-D-galactal, but the latter underwent hydroxyl inversion to give dihydro-D-altral. 1,5-Anhydro-D-sorbitol (polygalitol) appeared to undergo both ring fission and inversion.

INTRODUCTION

The isolation of several hydroxylated derivatives of tetrahydro-2-pyran from the hydrogenolysis of methyl glycopyranosides (1, 2, 3) stimulated an interest in ring cleavage of this type of cyclic ether as a possible aid in determining their structure and configuration. Relatively few examples of this reaction are cited in the literature (4), in contrast to extensive studies on tetrahydrofurans (4, 5), but it is generally accepted that tetrahydropyrans are much more resistant to cleavage than are their five-membered ring analogues (4, 5). Of the reagents generally used to effect fission of cyclic ethers (4), those involving the use of acetic anhydride and an acid catalyst appeared most attractive, since the cleavage products could be deacetylated readily and the free polyols thus obtained conveniently examined by paper chromatography and periodic acid oxidation.

In preliminary experiments, several different catalysts were used to study the acetolysis of 2-hydroxymethyltetrahydropyran and 3,4-dihydroxytetrahydropyran. The cleavage of 2-hydroxymethyltetrahydropyran using zinc chloride and acetic anhydride for 8 hours at reflux temperature has been reported (6) to yield 1,2,6-hexanetriol triacetate. Re-examination of this reaction now showed that 85% of the starting material was recoverable as its acetate after 4 hours' refluxing and 75% with a reaction period of 28 hours. No trace of cleavage was detected when 3,4-dihydroxytetrahydropyran was subjected to the same conditions for 4 hours. Mixtures of sulphuric acid and acetic anhydride were found to cause some cleavage of 2-hydroxymethyltetrahydropyran but decomposition was extensive and the effect of these reagents on other tetrahydropyrans was not investigated. Trifluoroacetic anhydride promoted acetylation of each of these tetrahydropyrans but there was no evidence of ring opening. However, boron trifluoride was found to catalyze the cleavage without too much general decomposition and its use in the acetolysis of hydroxytetrahydropyrans was, therefore, examined in detail.

DL-*trans*-3,4-Dihydroxytetrahydropyran, treated with excess acetic anhydride saturated with boron trifluoride, split to an extent of 25% with a reaction time of 18 hours at room temperature and to 50% at 100° C for 1 hour, whereas at the higher temperature fission was virtually complete in 4 hours. The cleavage product, after deacetylation and purification, was the expected 1,2,3,5-pentanetetrol. D-*trans*-3,4-Dihydroxytetrahydropyran

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and L-*cis*-3,4-dihydroxytetrahydropyran were found to yield the same optically inactive pentanetetrol, showing that racemization of the optically active centers had accompanied ring fission. Under similar reaction conditions the triacetate of 2-hydroxymethyl-4,5-dihydroxytetrahydropyran gave a 25% yield of the expected 1,2,3,5,6-hexanepentol, which did not give a solid benzoate or *p*-nitrobenzoate and formed a sirupy pentaacetate.

Cleavage of 2-hydroxymethyltetrahydropyran was complete in 2 hours at room temperature, whilst at 100° C decomposition was extensive. The product from the reaction at room temperature, or lower, was an oil which could not be separated into more than one component by counter-current distribution (210 transfers). The deacetylated product was shown to be a sirupy hexanetriol. However, when oxidized with periodic acid, the material consumed only 0.4 moles of oxidant with the release of 0.4 moles of formaldehyde, indicating that it was a mixture of the expected 1,2,6-hexanetriol and an isomer having no vicinal hydroxyl groups. This mixture of isomers could not be resolved by column chromatography, nor by counter-current distribution (120 transfers), but the isomeric triol was isolated from the mixture by decomposition of the 1,2,6-isomer with periodate. The sirupy product had an infrared spectrum which was similar to that of the 1,2,6-isomer and formed a crystalline tris-*p*-nitrobenzoate having similar spectral properties to those of the 1,2,6-derivative. These data, together with the results from C-methyl determinations, suggested that the compound was most likely 1,3,6-hexanetriol. 1,3,6-Triacetoxyhexane was prepared from tetrahydrofuran-2-acetic acid (7) by lithium aluminum hydride reduction to tetrahydrofuran-2-ethanol and subsequent ring cleavage (8). The triol obtained on deacetylation was shown to be identical with that obtained from 2-hydroxymethyltetrahydropyran. The formation of 1,3,6-hexanetriol besides the 1,2,6-isomer is unexpected, since tetrahydrofuranyl carbinols have given rise to only one triacetate on acetolysis with zinc chloride as catalyst (5). Since the starting material was found to be pure, it could not have been derived from a major impurity, such as tetrahydrofuran-2-ethanol.

Cleavage of a fraction isolated from the hydrogenolysis of α-methyl-D-glucopyranoside and thought to be a hydroxytetrahydropyran derivative (2) was readily effected with the reagent at room temperature in 18 hours. The product, after deacetylation, was 1,4,5-hexanetriol, since it consumed 1.0 mole of periodic acid with the production of 1.0 mole of acetaldehyde, and yielded a tris-*p*-nitrobenzoate. Thus, if no rearrangement had taken place during acetolysis (this assumption is justified, since no isomeric products were isolated) the starting material must have been 2-methyl-3-hydroxytetrahydropyran, a product not unexpected from the hydrogenolysis reaction. The ready cleavage of this 2-alkyl derivative is in accord with the findings on 2-alkyl tetrahydrofurans by Paul (5). The formation of olefinic intermediates presumably was suppressed by the 3-hydroxyl substituent.

4-Hydroxytetrahydropyran was not cleaved to any extent at room temperature, at 65° C, or at 100° C, charring being extensive at the latter temperature. This result was unexpected and cannot be explained by the proposed mechanisms of ether cleavage (4). Similar results were obtained with dihydro-D-galactal and dihydro-D-glucal. When dihydro-D-galactal was first acetylated and then treated with excess reagent at 100° C ring cleavage was also not obtained, showing that the formation of acetic acid in the initial acetylation of the free polyol is not the cause of this failure to cleave the ether. However, after a 10-hour treatment at 100° C dihydro-D-galactal yielded a small amount of dihydro-D-altral. Paper chromatographic analysis of the deacetylated product obtained from dihydro-D-glucal showed the presence of compounds with R_f values corre-

sponding to dihydrogalactal and dihydroaltral. A similar examination of the reaction product from a small amount of 1,5-anhydro-D-sorbitol (polygalitol) indicated the presence of both fission products (hexitols) and inversion products, besides unreacted starting material.

Burwell (4) proposed as the first step in the catalytic acetolysis of aliphatic ethers the addition of an acetyl cation to the ether oxygen. Presumably this mechanism is also operative in the acetolysis of tetrahydropyrans in the presence of boron trifluoride. The subsequent cleavage of a carbon–oxygen bond of the ether linkage and addition of an acetyl anion to the residual carbonium ion is more difficult to reconcile with the divergent results obtained. An intermediate cation, having the positive charge distributed between the oxygen atom and the carbon atoms in positions 2 and 3, analogous to the cation proposed in the acid-catalyzed cyclization of terpenes (11), would explain, for example, the formation of 1,3,6-hexanetriol in addition to the 1,2,6-isomer from 2-hydroxymethyltetrahydropyran. Such a cation could either cleave directly to such end products, or produce an intermediate olefin, analogous to those isolated by Paul (5) from 2-alkyl tetrahydrofurans. The olefinic diacetate could then be acetylated in the presence of boron trifluoride (12), or might recyclize to tetrahydrofuran-2-ethanol, which would undergo readily ring fission to 1,3,6-hexanetriol. Hydroxyl groups in the 3 position would prevent the formation of such intermediates and lead only to a single, expected product, which is in agreement with the present findings. However, such a mechanism would not explain the resistance to cleavage of the dihydroglycals and 4-hydroxytetrahydropyran. The failure of the former compounds to undergo ring fission may be explained (9) by boron complex formation of the type reported by Angyal and McHugh (10). Aliphatic ethers are known to form stable complexes with boron trifluoride (4) and it is conceivable that complex formation of one type or another prevents the cleavage reaction with some hydroxytetrahydropyrans.

It is concluded that although boron trifluoride is an excellent catalyst for the acetolysis of some tetrahydropyrans, the unexpected results obtained in other cases show that its action is not of a general nature.

EXPERIMENTAL

Paper chromatography was carried out using Whatman No. 1 paper and 1-butanol – ethanol – water (40:11:19, v/v) as solvent. The chromatograms were developed with ammoniacal silver nitrate spray reagent (13) and the distances travelled by compounds relative to rhamnose (R_{Rh}) were measured. Column chromatography was carried out on cellulose using benzene–ethanol–water (500:50:1, v/v) (A), 1-butanol (B), or 1-butanol $\frac{1}{4}$ saturated with water (C) as solvents. In counter-current distribution, a modified 100-tube E.C. Apparatus Co. fractionator was used (14). Deacetylation of polyol acetates was carried out in the manner previously described (2).

3,4-Dihydroxytetrahydropyran

(*a*) DL-*trans-3,4-Dihydroxytetrahydropyran* (*Dihydro*-DL-*xylal*)

A mixture of the diol (1.1 g) and acetic anhydride (10 ml) was saturated with boron trifluoride at such a rate that the internal temperature did not exceed 60° C. The reaction mixture was then heated on a steam bath for 4 hours, cooled, and poured into an ice-cold excess of saturated aqueous sodium carbonate or bicarbonate solution. The mixture was filtered and the residue and filtrate were extracted thoroughly with chloroform which was washed once with water, dried over calcium chloride, and evaporated. After distillation at 170–180° C and 0.5 mm, the cleavage product (2.05 g) was deacetylated.

Paper chromatography of the residue indicated a major component, R_{Rh} 1.14, and a minor component, R_{Rh} 1.73, the latter corresponding to unchanged starting material. The mixture was resolved by column chromatography using solvent B, and the cleavage product was thus obtained as a colorless sirup (0.9 g, 72%), b.p. 175–185° C (air bath) at 0.1 mm. Calculated for $C_5H_{12}O_4$: C, 44.11%; H, 8.88%. Found: C, 44.18%; H, 8.83%. The tetrol consumed 2.0 moles of periodic acid with the liberation of 1.0 mole of formaldehyde (15). The tetraacetate of the tetrol, prepared with sodium acetate and acetic anhydride, was a colorless oil, b.p. 175–180° C (air bath) at 0.5 mm; n_D^{20} 1.4442. Calculated for $C_5H_8(OCOCH_3)_4$: C, 51.31%; H, 6.63%; $COCH_3$, 56.6%. Found: C, 51.64%; H, 6.77%; $COCH_3$, 57.1%. The derived tetra-*p*-nitrobenzoate separated as light yellow crystals, m.p. 187° C, from acetone – ethyl acetate. Calculated for $C_{33}H_{24}N_4O_{16}$: C, 54.10%; H, 3.30%; N, 7.65%. Found: C, 54.47%; H, 3.54%; N, 7.68%.

When the cleavage reaction was carried out at 0° C for 18 hours and at room temperature for 24 hours, the product contained about 25% and 50%, respectively, of the tetrol.

(*b*) D-*trans-3,4-Dihydroxytetrahydropyran* (*Dihydro*-D-*xylal*)

Diacetyldihydro-D-xylal (2.0 g) was treated with acetic anhydride (7.5 ml) and boron trifluoride and the resulting tetrol (0.9 g, 67%) was isolated and purified as described above. Periodic acid oxidation of the polyol and analyses of the free polyol and its tetraacetate were consistent with a 1,2,3,5-pentanetetrol structure. The tetrol had no optical rotation in saturated aqueous sodium borate and its derived tetra-*p*-nitrobenzoate was shown by melting point, mixed melting point, and X-ray powder diagram comparison to be identical with that of the tetrol from dihydro-DL-xylal.

(*c*) L-*cis-3,4-Dihydroxytetrahydropyran* (*Dihydro*-L-*arabinal*)

Dihydro-L-arabinal (0.5 g) was cleaved and the derived tetrol (0.3 g, 52%) isolated and purified as described above. The tetrol had no optical rotation in saturated aqueous sodium borate and its tetra-*p*-nitrobenzoate derivative was identical with those of the tetrols from dihydro-D- and dihydro-DL-xylal (melting point, mixed melting point, infrared spectrum, and X-ray powder diagram).

2-Hydroxymethyl-4,5-dihydroxytetrahydropyran

The triacetate of this triol (3.8 g) was treated with acetic anhydride (5 ml) and boron trifluoride at 100° C for 4 hours and the product isolated and purified in the usual way. Paper chromatography of the product indicated that it was a mixture of the starting material and a hexanepentol (R_{Rh} 0.66). The pentol was isolated by column chromatography using solvent C and was a colorless sirup (0.58 g, 25%), n_D^{20} 1.4860. Calculated for $C_6H_{14}O_5$: C, 43.36%; H, 8.49%. Found: C, 43.60%; H, 8.48%. The substance consumed 3.2 moles of periodic acid with the production of 1.8 moles of formaldehyde showing that it was essentially 1,2,3,5,6-hexanepentol. It failed to give a solid benzoate or *p*-nitrobenzoate. The pentaacetate, prepared with sodium acetate and acetic anhydride, was a pale yellow sirup, n_D^{20} 1.4488. Calculated for $C_6H_9(OCOCH_3)_5$: C, 51.06%; H, 6.43%; $COCH_3$, 57.1%. Found: C, 51.08%; H, 6.80%; $COCH_3$, 57.4%.

2-Methyl-3-hydroxytetrahydropyran

One gram of a tetrahydropyran fraction obtained from hydrogenolysis of α-methyl-D-glucopyranoside (2) was treated with acetic anhydride (6 ml) and boron trifluoride at room temperature for 18 hours. The crude product was distilled at 160–170° C (air bath) and 12 mm and was then deacetylated. Paper chromatography of the product indicated that cleavage was complete and that the product was a hexanetriol (R_{Rh} 1.73). The triol was purified by column chromatography in solvent A and by distillation at

130–135° C (air bath) and 0.1 mm giving a colorless sirup (0.64 g, 55%), n_D^{20} 1.4738. Calculated for $C_6H_{14}O_3$: C, 53.71%; H, 10.52%; C-methyl, 20.2%. Found: C, 53.43%; H, 10.50%; C-methyl, 20.2%. The triol consumed 1.0 mole of periodic acid and yielded 1.0 mole of acetaldehyde (16).

The triacetate was a colorless oil, b.p. 105° C (air bath) and 0.1 mm with n_D^{20} 1.4366 (Paul (5) reported n_D^{10} 1.44029; found n_D^{10} 1.4403). Calculated for $C_6H_{11}(OCOCH_3)_3$: C, 55.37%; H, 7.75%; $COCH_3$, 49.6%. Found: C, 54.97%; H, 7.90%; $COCH_3$, 50.7%.

The derived tris-*p*-nitrobenzoate, after several recrystallizations from methanol–acetone, had m.p. 149–150° C. Calculated for $C_{27}H_{23}O_{12}N_3$: C, 55.77%; H, 3.99%; N, 7.23%. Found: C, 55.95%; H, 3.90%; N, 7.24%.

4-Hydroxytetrahydropyran

γ-Pyrone (12.5 g) was hydrogenated in ethanol (75 ml) with Raney nickel (0.6 g) at 100° C and 80 atmospheres pressure for 10 hours. The residual oil, after evaporation of the solvent, was fractionally distilled, yielding 4-hydroxytetrahydropyran (8.5 g), b.p. 90–92° C at 12 mm, n_D^{20} 1.4590. This tetrahydropyran was recovered unchanged from the reaction with boron trifluoride and acetic anhydride at room temperature for 18 hours, at 65° C and at 100° C for 2 hours. At the elevated temperatures charring took place and at 100° C a very small amount of an oil, b.p. 125–130° C (air bath) and 0.1 mm was obtained. The deacetylated product had R_{Rh} 1.62, corresponding to a hexanetriol. The amount obtained was too small for further identification.

Dihydro-D-galactal

Dihydro-D-galactal (0.5 g) was treated with acetic anhydride (5.0 ml) and boron trifluoride at 100° C for 10 hours. The crude product, after deacetylation, showed two major spots, R_{Rh} 1.12 and 1.37, and a weak spot, R_{Rh} 0.74, on paper chromatography. Unchanged dihydrogalactal (0.15 g, R_{Rh} 1.12) was removed from the reaction product by crystallization from methanol – ethyl acetate and the residue was then chromatographed using solvent A. By this means, the material with R_{Rh} 1.37 was isolated and after crystallization from ethyl acetate was identified as dihydro-D-altral by means of mixed m.p. 101–103° C, and by comparison of its X-ray powder diagram with that of an authentic specimen (3). A similar result was obtained using triacetyldihydro-D-galactal and a large excess of acetic anhydride and boron trifluoride.

Dihydro-D-glucal and 1,5-Anhydro-D-sorbitol (Polygalitol)

The product from the reaction of dihydro-D-glucal (R_{Rh} 1.24) with excess acetic anhydride and boron trifluoride at 100° C for 4 hours was deacetylated and paper chromatography of the product showed two major components having R_{Rh} 1.37 and 1.12 and a trace component, R_{Rh} 0.76.

Polygalitol (R_{Rh} 0.74), when similarly treated, yielded a mixture of substances having R_{Rh} values of 0.85, 0.74, 0.45, corresponding to an isomerization product, unchanged starting material, and a hexitol respectively.

2-Hydroxymethyltetrahydropyran

The reaction between 2-hydroxymethyltetrahydropyran (5 g) and acetic anhydride (15 ml) and boron trifluoride was complete in 2 hours at room temperature. The crude acetate mixture was distilled at 117–128° C and 0.5 mm to give a pale yellow oil (6.4 g, 57%) n_D^{20} 1.4472, which failed to separate into more than one component when subjected to counter-current distribution between 70% acetone/petrol (b.p. 60–70° C) when 210 transfers were applied (14). The same oil resulted when the reaction was carried out at

room temperature for 24 hours and also when the acetate of the starting material (6.5 g) was similarly reacted with acetic anhydride (9 ml) and boron trifluoride. At 100° C, decomposition was extensive and only a small amount of the oil was isolated. Calculated for $C_6H_{11}(OCOCH_3)_3$: C, 55.37%; H, 7.75%. Found: C, 55.40%; H, 7.85%.

Deacetylation of the above oil yielded a pale yellow sirup, n_D^{20} 1.4720, which did not separate into more than one component on column chromatography using solvent A or on counter-current distribution between water and *n*-butanol with 120 transfers. On paper chromatography it showed a single spot R_{Rh} 1.73, corresponding to a hexanetriol. Calculated for $C_6H_{14}O_3$: C, 53.71%; H, 10.52%. Found: C, 53.89%; H, 10.40%. Oxidation of the sirup with periodic acid resulted in the uptake of 0.4 mole of oxidant and the formation of 0.4 mole of formaldehyde.

The triol mixture (0.5 g) in water (20 ml) and periodic acid (0.5 g) in water (10 ml) was left to stand at room temperature for 2 hours and was then treated with Dowex-1 – bicarbonate until it gave a negative reaction to starch/KI paper. The mixture was filtered and evaporated and formaldehyde removed from the residue by steam distillation. The residue was then dissolved in water, extracted several times with ether, and recovered by evaporation of the aqueous solution. Distillation of the residual material afforded a colorless sirup (0.2 g), b.p. 135° C (air bath) at 0.1 mm, having R_{Rh} 1.73, n_D^{20} 1.4696, and low reducing power to the silver nitrate spray. C alculated for $C_6H_{14}O_3$: C, 53.71%; H, 10.50%. Found: C, 53.40%; H, 10.58%.

The derived tris-*p*-nitrobenzoate, m.p. 130–131° C, crystallized from ethyl acetate. Calculated for $C_{27}H_{23}O_{12}N_3$: C, 55.77%; H, 3.99%; N, 7.23%. Found: C, 56.09%; H, 3.89%; N, 7.23%.

Synthesis of Tetrahydrofuran-2-ethanol

A solution of tetrahydrofuran-2-acetic acid, prepared from tetrahydrofurfuryl bromide (17) by the method of Barger *et al.* (7), (10.5 g) in dry ether (200 ml) was added slowly with stirring to a mixture of lithium aluminum hydride (3.59 g) and dry ether (150 ml). When addition was complete, the mixture was stirred at room temperature for 18 hours and the excess lithium aluminum hydride was then decomposed by careful addition of water. The mixture was then shaken with excess dilute sulphuric acid and the ethereal phase was extracted with aqueous sodium bicarbonate and the aqueous phase again extracted with ether for 18 hours. The ethereal solution of the neutral products was evaporated and the residue distilled at 115–120° C (air bath) and 20 mm giving tetrahydrofuran-2-ethanol (8.0 g, 85%) as a colorless mobile oil n_D^{20} 1.4545. Calculated for $C_6H_{12}O_2$: C, 62.04%; H, 10.41%. Found: C, 61.66%; H, 10.56%.

1,3,6-Hexanetriol from Tetrahydrofuran-2-ethanol

Tetrahydrofuran-2-ethanol (4.06 g) in acetic anhydride (5 ml) was added slowly with stirring to a refluxing mixture of acetic anhydride (15 ml) and zinc chloride (0.3 g) (8). The mixture was refluxed for a further 18 hours and most of the excess anhydride was removed by distillation. The residue was cooled and poured into cold saturated aqueous sodium carbonate. The product was extracted into chloroform, which was washed once with water and dried over calcium chloride and evaporated. The residue was distilled at 120–130° C and 0.5 mm to give 6.5 g (71%) of an oil having n_D^{20} 1.4408. Calculated for $C_6H_{11}(OCOCH_3)_3$: C, 55.37%; H, 7.75%; $COCH_3$, 49.6%. Found: C, 55.58%; H, 7.52%; $COCH_3$, 49.5%.

The oil was deacetylated in the usual way and the triol was purified by column chromatography in solvent A and by distillation at 135° C (air bath) and 0.1 mm. The infrared

spectrum of the sirup, n_D^{20} 1.4753, was indistinguishable from that of the triol of 2-hydroxymethyltetrahydropyran. Confirmation of this identity was obtained by mixed melting point determination and infrared spectra comparison of the derived *p*-nitrobenzoate.

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