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1,4-ANHYDRIDE FORMATION ON SOLVOLYSIS OF 1,6-DISUBSTITUTED DERIVATIVES OF 2,3,4,5-TETRA-*O*-ACETYLALLITOL

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ABSTRACT

The 6-*O*-mesyl, 6-*O*-tosyl, 6-bromo-6-deoxy, and 6-deoxy-6-iodo derivatives of 1,4-anhydro-DL-allitol were obtained by treatment of the corresponding 1,6-di-substituted derivatives (**2**, **3**, **6**, **4**) of 2,3,4,5-tetra-*O*-acetylallitol with hot, methanolic hydrogen chloride. Compounds **2** and **3** were prepared by the acetolysis of the 1,6-di-*O*-mesyl and 1,6-di-*O*-tosyl derivatives (**8** and **11**) of di-*O*-benzylideneallitol. Iodide displacement on **2** gave **4**, and detritylation–bromination of 2,3,4,5-tetra-*O*-acetyl-1,6-di-*O*-tritylallitol (**5**) gave **6**. The acetal residues of di-*O*-benzylideneallitol have been shown to span the secondary carbon atoms.

INTRODUCTION

Only two diacetals of allitol are readily accessible, namely the di-*O*-benzylidene derivative[1] and 2,4:3,5-di-*O*-methyleneallitol[2]. The former compound was selected as the precursor in a projected synthesis of 1,6-disubstituted derivatives of allitol, required for screening for anti-cancer activity, because of the known[3] greater ease of removal of benzylidene groups than methylene groups.

RESULTS AND DISCUSSION

The known di-*O*-benzylideneallitol has not been structurally characterised, although an application of the Hann–Hudson rules[4] enabled Barker and Bourne[3] to predict that the benzylidenation of allitol should afford the 2,4:3,5-diacetal. The chemical evidence presented below proves that the two benzylidene groups are located at the four secondary carbon positions (see **7**). Firstly, benzylidenation of allitol with subsequent mesylation yielded a product from which the sulphonyloxy groups could be readily displaced with sodium iodide to yield a di-*O*-benzylidenedideoxydi-iodo-allitol, a result to be expected for an α,ω-disulphonylated hexitol[5]. Secondly, reaction of the above di-*O*-mesyl derivative with acidified paraformaldehyde effected acetal

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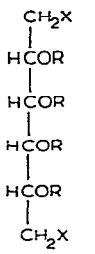
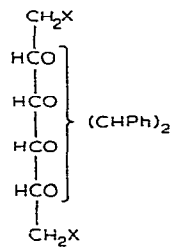
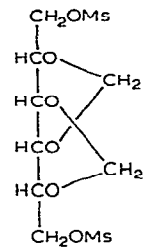
exchange[6] to give a product identical with the di-*O*-mesyl derivative (**12**) of the known 2,4:3,5-di-*O*-methyleneallitol. Thirdly, treatment of allitol with two molar equivalents of trityl chloride yielded a di-*O*-trityl derivative [predicted to be 1,6-di-*O*-tritylallitol (**1**) from the known preference of trityl groups for substitution at primary positions] which on benzylidenation gave a product identical with that obtained by tritylation of di-*O*-benzylideneallitol. Accordingly, the di-*O*-mesyl, di-iodo, and di-*O*-trityl derivatives of di-*O*-benzylideneallitol have been assigned the partial structures **8**, **9**, and **10**, respectively.



1 X = OTr, R = OH
2 X = OMs, R = Ac
3 X = OTs, R = Ac
4 X = I, R = Ac
5 X = OTr, R = Ac
6 X = Br, R = Ac



7 X = OH
8 X = OMs
9 X = I
10 X = OTr
11 X = OTs



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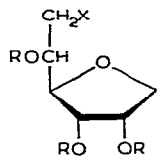
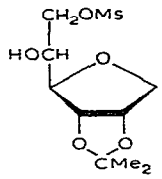
Acetolysis[7] of the 1,6-di-*O*-mesyl and 1,6-di-*O*-tosyl derivatives (**8** and **11**) of di-*O*-benzylideneallitol gave the 2,3,4,5-tetra-acetates (**2** and **3**, respectively). 2,3,4,5-Tetra-*O*-acetyl-1,6-dideoxy-1,6-di-iodoallitol (**4**) was prepared from **2** by an iodide displacement reaction, and 2,3,4,5-tetra-*O*-acetyl-1,6-dibromo-1,6-dideoxyallitol (**6**) was obtained by the detritylation–bromination of 2,3,4,5-tetra-*O*-acetyl-1,6-di-*O*-tritylallitol (**5**).

When deacetylation of **2**, **3**, **4**, and **6** was attempted using hydrogen chloride in hot methanol, a reagent previously used[7] in the preparation of 1,6-di-*O*-mesyl-D-mannitol from its tetra-acetate, the corresponding 6-substituted derivative (**13**, **14**, **18**, and **16**) of 1,4-anhydro-DL-allitol was obtained. Crystalline compounds **14** and **18** showed an intense peak at *m/e* 103 in their mass spectra due to the oxycarbonium ion **21**, as did 1,4-anhydro-DL-allitol, thus indicating the presence of a 1,4-anhydro ring[8]. 1,4-Anhydro-6-bromo-6-deoxy-DL-allitol (**16**) was a syrup, but **14**, **16**, and **18** afforded crystalline 2,3,5-triacetates (**15**, **17**, and **19**) identical with authentic samples prepared from 1,4-anhydro-DL-allitol by selective tosylation and acetylation with subsequent halide-ion displacement of the tosyloxy group. The mass spectrum of **17** exhibited an intense peak at *m/e* 187 which could be attributed to the stable oxycarbonium ion **22** formed by characteristic cleavage[8] of the C-4–C-5 bond. The identification of 1,4-anhydro-6-*O*-mesyl-DL-allitol (**13**) is based on the consumption of only 1 mol. of periodate and the ready formation of a mono-*O*-isopropylidene derivative (**20**). In the mass spectrum of **13**, the base peak occurred at *m/e* 104 and the signal at *m/e* 103 was

of very low intensity, in contrast to the spectra of **14** and **18**. The signal at *m/e* 104 is probably due to the presence of the methanesulphonyl group since the peak at *m/e* 104 is of low intensity in the spectra of **14** and **18**.



13 X = OMs, R = H
14 X = OTs, R = H
15 X = OTs, R = Ac
16 X = Br, R = H
17 X = Br, R = Ac
18 X = I, R = H
19 X = I, R = Ac



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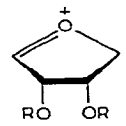

21 R = H, *m/e* 103
22 R = Ac, *m/e* 187

Although sulphonic esters are usually thought[5] to be resistant to solvolysis under acid conditions, recent results[9] indicate that the formation of anhydro-alditols from partially sulphonylated alditols is to be expected, especially at high temperatures. Examples include the conversion[10] of 3,4-di-*O*-mesyl-D-mannitol into 1,4-anhydro-3-*O*-mesyl-D-talitol and the formation[11] of 2,5-anhydro-1,6-dibromo-1,6-dideoxy-4-*O*-mesyl-D-glucitol from 3,5-di-*O*-acetyl-1,6-dibromo-1,6-dideoxy-2,4-di-*O*-mesyl-D-mannitol; however, the latter compound could be deacetylated with methanolic hydrogen chloride at room temperature without anhydro ring formation[11]. Brown and Timmis[7] obtained a product believed to be 1,4-anhydro-6-*O*-mesyl-DL-galactitol by the acid hydrolysis of 2,3:4,5-di-*O*-isopropylidene-1,6-di-*O*-mesylgalactitol, and the isolation of 1,6-di-*O*-mesyl-D-mannitol by vigorous deacetylation of the tetra-acetate was probably due to fortuitous quenching of the reaction before cyclisation could occur. A recent kinetic study[12] of the acid-catalysed dehydration of the hexitols has shown that allitol has the greatest rate of anhydro ring formation and D-mannitol the lowest, the relative rates being ~60:1 in 2–4M hydrochloric acid at 100°. The present results indicate that the relative ease of cyclisation of 1,6-disubstituted derivatives of allitol and D-mannitol also follows this order.

Attempted hydrogenolysis of the benzylidene residues from **8** under mild conditions resulted in a virtually quantitative recovery of the starting material; a very small amount of 1,4-anhydro-6-*O*-mesyl-DL-allitol[13] was obtained. 1,4-Anhydro ring formation is an indication of the instability of 1,6-disubstituted derivatives of allitol and may have been caused by traces of acid in the reaction mixture, possibly derived from the catalyst.

EXPERIMENTAL

General. — Organic solutions were dried over anhydrous sodium sulphate and concentrated below 40° under reduced pressure. Melting points were determined on a

Kofler block and are uncorrected. Thin-layer chromatography (t.l.c) was performed on Kieselgel G (Merck) with (*A*) ethyl acetate–light petroleum (3:1), (*B*) ethyl acetate–ethanol–water (10:3:2), or (*C*) ethyl acetate–ethanol–water (45:5:3). Infrared spectra were obtained for Nujol mulls on a Perkin–Elmer Model 237 spectrometer. Mass spectra were recorded by P.C.M.U., Harwell, with an A.E.I. MS-9 instrument at 70 eV, and intensities are expressed as a percentage of the base peak.

1,6-Di-O-tritylallitol (**1**). — A mixture of allitol (2.5 g) and trityl chloride (8.0 g, 2.0 equiv.) in pyridine (15 ml) was shaken at room temperature for 100 h. Trituration with ice–water gave a white precipitate; recrystallisation from ether–light petroleum gave **1** (4.1 g, 45%), m.p. 74–80°; ν_{max} 3380 (broad, OH), 1600 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{44}H_{42}O_6$: C, 79.3; H, 6.3. Found: C, 79.7; H, 6.6.

2,3,4,5-Di-O-benzylidene-1,6-di-O-tritylallitol (**10**). — (*a*) A mixture of **1** (1.85 g), benzaldehyde (6 ml), and anhydrous zinc chloride (2.2 g) was shaken at room temperature for 63 h and then poured into a 1:1 mixture of water–light petroleum (100 ml); the precipitate was separated and dissolved in chloroform. The organic solution was washed with water, dried, and concentrated to a solid residue. Recrystallisation from *p*-dioxane gave a product (460 mg, 20%), m.p. 290–293°, corresponding to **10** with one mole of *p*-dioxane of crystallisation.

Anal. Calc. for $C_{58}H_{50}O_6 \cdot C_4H_8O_2$: C, 80.0; H, 6.2. Found: C, 79.7; H, 6.45.

Drying at 180° (3 h) yielded **10**, m.p. 290–293°. The i.r. spectrum showed no hydroxyl absorption.

Anal. Calc. for $C_{58}H_{50}O_6$: C, 82.6; H, 6.0. Found: C, 82.7; H, 6.2.

(*b*) A mixture of 2,3,4,5-di-*O*-benzylideneallitol[1] (1.0 g), trityl chloride (1.63 g, 2.1 equiv.), and pyridine (15 ml) was shaken for 63 h at room temperature. Trituration with ice–water gave a crude product (2.5 g) shown by t.l.c. to be a mixture of the starting materials and **10**. The product was dissolved in chloroform, di-*O*-benzylideneallitol (100 mg) was filtered off, and the filtrate was processed by preparative layer chromatography to yield a purified product (1.36 g) that was extracted with boiling ethanol. The residue was twice recrystallised from *p*-dioxane and dried at 180° to give **10** (370 mg, 15%), m.p. 290–293°. The i.r. spectrum was identical with that of the product described in (*a*).

2,3,4,5-Di-O-benzylidene-1,6-di-O-mesylallitol (**8**). — 2,3,4,5-Di-*O*-benzylideneallitol (12.0 g) was dissolved in pyridine (200 ml) by warming to 40–50°, and methanesulphonyl chloride (9.1 g, 2.2 equiv.) was added dropwise. After standing for 15 h at room temperature, the crude product was precipitated by addition of excess ice–water. Recrystallisation from pyridine–ethanol gave **8** (12.8 g, 76%), m.p. 190–191°, ν_{max} 1345, 1170 cm^{-1} (S=O).

Anal. Calc. for $C_{22}H_{26}O_{10}S_2$: C, 51.3; H, 5.1; S, 12.5. Found: C, 51.5; H, 5.1; S, 12.0.

2,3,4,5-Di-O-benzylidene-1,6-dideoxy-1,6-di-iodoallitol (**9**). — A solution of **8** (600 mg) and sodium iodide (610 mg) in acetic anhydride (25 ml) was heated under reflux for 1 h; the cooled reaction mixture was treated with ice–water, and the

precipitate was separated and dried. Recrystallisation from acetic anhydride gave **9** (368 mg, 55%), m.p. 269–271°.

Anal. Calc. for $C_{20}H_{20}I_2O_4$: C, 41.5; H, 3.5; I, 43.9. Found: C, 41.7; H, 3.4; I, 43.7.

1,6-Di-O-mesyl-2,4:3,5-di-O-methyleneallitol (**12**). — (*a*) Reaction of 2,4:3,5-di-*O*-methyleneallitol[2] (700 mg) with methanesulphonyl chloride (940 mg) in pyridine (10 ml) overnight, followed by addition of ice–water, gave a crude product that was recrystallised from ethanol to give **12** (593 mg, 48%), m.p. 198–199°, ν_{max} 1345, 1170 cm^{-1} (S=O).

Anal. Calc. for $C_{10}H_{18}O_{10}S_2$: C, 33.2; H, 5.0; S, 17.7. Found: C, 33.0; H, 5.0; S, 17.4.

(*b*) A mixture of **8** (2.0 g), paraformaldehyde (2.5 g), glacial acetic acid (10 ml), and conc. sulphuric acid (0.7 ml) was heated on a steam bath for 2 h[6]. Trituration with ice–water then gave a crude product that was twice recrystallised from pyridine–methanol to yield **12** (761 mg, 52%), m.p. 195–199°. The i.r. spectrum was identical with that of the product described in (*a*).

2,3,4,5-Di-O-benzylidene-1,6-di-O-tosylallitol (**11**). — Toluene-*p*-sulphonyl chloride (4.7 g, 2.2 equiv.) was added in portions to a solution of 2,3,4,5-di-*O*-benzylideneallitol (4.0 g) in pyridine (80 ml). Addition of ice–water after 20 h precipitated the crude product. Recrystallisation from pyridine–ethanol gave **11** (4.77 g, 64%), m.p. 183–185°, ν_{max} 1600 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{34}H_{34}O_{10}S_2$: C, 61.2; H, 5.1; S, 9.6. Found: C, 61.4; H, 5.1; S, 9.5.

2,3,4,5-Tetra-O-acetyl-1,6-di-O-tosylallitol (**3**). — Acetal **11** (4.0 g) was stirred with an ice-cold mixture of acetic anhydride (70 ml), acetic acid (30 ml), and conc. sulphuric acid (2 ml) for 48 h; at no time was a clear solution obtained. After treatment with ice, the mixture was filtered to yield a crude product that was recrystallised from ethanol to give **3** (1.80 g, 45%), m.p. 167–169°, ν_{max} 1743, 1735 (C=O), 1600 cm^{-1} (C=C, aromatic).

Anal. Calc. for $C_{28}H_{34}O_{14}S_2$: C, 51.0; H, 5.2; S, 9.7. Found: C, 51.3; H, 5.2; S, 9.8.

The residue, which was insoluble in hot ethanol, was recrystallised from acetic anhydride to yield **11** (575 mg), m.p. 183–185°.

2,3,4,5-Tetra-O-acetyl-1,6-di-O-mesylallitol (**2**). — Acetal **8** (12.0 g) was stirred with ice-cold acetic anhydride (250 ml), acetic acid (200 ml), and conc. sulphuric acid (7 ml). The clear solution obtained after 36 h was poured on to ice and stored at 0° for 60 h, whereupon the crude product crystallised. Recrystallisation from ethanol gave **2** (6.15 g, 51%), m.p. 100–103°, ν_{max} 1750 cm^{-1} (C=O).

Anal. Calc. for $C_{16}H_{26}O_{14}S_2$: C, 37.9; H, 5.2; S, 12.7. Found: C, 37.7; H, 5.1; S, 13.0.

2,3,4,5-Tetra-O-acetyl-1,6-dideoxy-1,6-di-iodoallitol (**4**). — A solution of **2** (750 mg) and sodium iodide (750 mg) in acetic anhydride (30 ml) was heated under reflux for 2 h. Treatment of the cooled mixture with excess of ice–water gave a crude

product that was recrystallised from aqueous ethanol to yield **4** (605 mg, 72%), m.p. 103–106°, ν_{max} 1740 cm^{-1} (C=O).

Anal. Calc. for $C_{14}H_{20}I_2O_8$: C, 29.5; H, 3.5; I, 44.6. Found: C, 29.6; H, 3.4; I, 44.6.

*2,3,4,5-Tetra-*O*-acetyl-1,6-di-*O*-tritylallitol* (**5**). — A solution of allitol (1.82 g) and trityl chloride (5.57 g, 2.0 equiv.) in pyridine (10 ml) was stored at room temperature. After 48 h, the mass was broken up, diluted with pyridine (10 ml), and cooled to 0°. Acetic anhydride (15 ml) in pyridine (10 ml) was added slowly and, after 63 h at room temperature, treatment with ice–water gave a crude product. Recrystallisation from aqueous ethanol gave **5** (3.72 g, 20%), m.p. 180–190°; ν_{max} 1745 cm^{-1} (C=O). The product was homogeneous on t.l.c. and had R_F 0.70 (solvent *A*).

Anal. Calc. for $C_{52}H_{50}O_{10}$: C, 74.8; H, 6.0. Found: C, 74.8; H, 5.9.

*2,3,4,5-Tetra-*O*-acetyl-1,6-dibromo-1,6-dideoxyallitol* (**6**). — Hydrogen bromide was passed through a solution of **5** (2.0 g) in chloroform (30 ml) for 1.5 h; t.l.c. then indicated complete conversion of **5** into a slower-moving product. Concentration of the solution afforded a solid residue (2.17 g) that was fractionated by dry-column chromatography on silica gel. Elution with chloroform gave, as the first fraction, triphenylmethanol (730 mg). Next eluted was **6** (890 mg, 79%) which, after recrystallisation from ethanol, had m.p. 105–107.5°, ν_{max} 1740 cm^{-1} (C=O).

Anal. Calc. for $C_{14}H_{20}Br_2O_8$: C, 35.3; H, 4.2; Br, 33.3. Found: C, 35.5; H, 4.1; Br, 33.3.

*1,4-Anhydro-6-*O*-mesyl-*DL*-allitol* (**13**). — A solution of **2** (5.9 g) in 3% methanolic hydrogen chloride (230 ml) was heated under reflux for 2.5 h. Concentration of the solution gave an orange syrup that solidified on trituration with cold ethyl acetate. The crude product was recrystallised from ethyl acetate to give **13** (1.45 g, 52%), m.p. 90–91.5°; ν_{max} 3500 (sharp), 3310 (broad; OH), 1335, 1170 cm^{-1} (S=O). Mass spectrum: *m/e* 244 (0.3, M+2), 242 (0.2, M), 104 (100, **21**+1), 74 [98, (**21**+1)−30]. Periodate consumption: 0.25 h, 0.95 equiv.; 2 h, 0.99 equiv.

Anal. Calc. for $C_7H_{14}O_7S$: C, 34.7; H, 5.8; S, 13.2. Found: C, 34.6; H, 5.75; S, 13.1.

The product (150 mg) was heated under reflux in 2,2-dimethoxypropane (8 ml) containing toluene-*p*-sulphonic acid (10 mg). After 1 h, the cooled solution was neutralised (NaOMe) and partitioned between chloroform–water. Concentration of the dried, organic extract gave a syrup that partially crystallised on trituration with light petroleum. Recrystallisation from ethanol–light petroleum gave fine needles (12 mg) of the 2,3-*O*-isopropylidene derivative **20**, m.p. 113–114°; ν_{max} 3420 (broad, OH), 1375 (CMe_2), 1332, 1175 cm^{-1} (S=O).

Anal. Calc. for $C_{10}H_{18}O_7S$: C, 42.6; H, 6.4. Found: C, 43.0; H, 6.15.

*1,4-Anhydro-6-*O*-tosyl-*DL*-allitol* (**14**). — A solution of **3** (1.8 g) in 3% methanolic hydrogen chloride (50 ml) was heated under reflux for 15 h. The filtered solution was concentrated and the syrupy residue was extracted with ether. Concentration of the ethereal extract gave a solid product that was recrystallised from ethanol-light petroleum to yield **14** (367 mg, 42%), m.p. 112–114°; ν_{max} 3530 (sharp,

OH), 3445 (sharp, OH), 3270 (broad, OH), 1600 cm^{-1} (C=C, aromatic). Mass spectrum: *m/e* 319 (0.1, M+1), 173 (25, M−145), 155 (21, p-$CH_3C_6H_4SO_2^+$), 103 (100, **21**), 91 (62, $C_7H_7^+$), 73 (28, **21**−30).

Anal. Calc. for $C_{13}H_{17}O_7S$: C, 49.2; H, 5.4; S, 10.1. Found: C, 48.8; H, 5.6; S, 10.3.

Acetylation of the product (210 mg) in the usual manner afforded, after crystallisation from ethanol, the 2,3,5-triacetate (**15**) (237 mg), m.p. 76–78°; lit.[14] m.p. 73–75°. The i.r. spectrum was identical with that of **15** obtained[14] previously.

Anal. Calc. for $C_{19}H_{24}O_{10}S$: C, 51.5; H, 5.4; S, 7.2. Found: C, 51.4; H, 5.45; S, 6.9.

1,4-Anhydro-6-bromo-6-deoxy-DL-*allitol* (**16**). — A solution of **6** (1.13 g) in 3% methanolic hydrogen chloride (50 ml) was heated under reflux for 2.5 h. Concentration then gave syrupy **16**, R_F 0.17 (solvent *A*). Acetylation in the usual manner, with recrystallisation of the product from aqueous ethanol, gave 2,3,5-tri-*O*-acetyl-1,4-anhydro-6-bromo-6-deoxy-DL-allitol (**17**) (560 mg, 67%), m.p. 84–86°; lit.[14] m.p. 81–83°. The i.r. spectrum was identical with that of **17** obtained[14] previously.

Anal. Calc. for $C_{12}H_{17}BrO_7$: C, 40.7; H, 4.8; Br, 22.6. Found: C, 40.9; H, 4.8; Br, 21.8.

1,4-Anhydro-6-deoxy-6-iodo-DL-*allitol* (**18**). — Methanolysis (as for **6**) of **4** (1.10 g) for 3.5 h gave a dark-red solution. Concentration, trituration of the residue with methanol–ether, and recrystallisation from ether gave **18** (280 mg, 37%), m.p. 83–85°; ν_{max} 3330 cm^{-1} (broad, OH). Mass spectrum; *m/e* 274 (0.3, M), 129 (13, M−145), 103 (100, **21**), 73 (17, **21**−30).

Anal. Calc. for $C_6H_{11}IO_4$: C, 26.3; H, 4.0; I, 46.3. Found: C, 26.5; H, 4.0; I, 44.5.

2,3,5-Tri-O-*acetyl-1,4-anhydro-6-deoxy-6-iodo*-DL-*allitol* (**19**). — (*a*) Acetylation of **18** (150 mg), in the usual manner, gave **19** (150 mg, 69%), m.p. 73–75° (from ethanol); ν_{max} 1750, 1734 cm^{-1} (OAc).

Anal. Calc. for $C_{12}H_{17}IO_7$: C, 36.0; H, 4.35; I, 31.8. Found: C, 36.0; H, 4.2; I, 31.7.

(*b*) A solution of 2,3,5-tri-*O*-acetyl-1,4-anhydro-6-*O*-tosyl-DL-allitol[14] (370 mg) and sodium iodide (410 mg) in acetic anhydride (10 ml) was heated under reflux for 2.5 h. The reaction was then quenched with water, and the product was isolated by chloroform extraction to give **19** (134 mg, 40%), m.p. 69–70° (from ethanol). The i.r. spectrum was identical with that of the product from (*a*).

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