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SUCROCHEMISTRY

PART IX[1]. MONO-, DI-, TRI-, AND TETRA-SUBSTITUTED DERIVATIVES PREPARED FROM SUCROSE OCTAMETHANESULPHONATE

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ABSTRACT

Treatment of sucrose octamethanesulphonate (**1**) with either sodium chloride or mesyl chloride in *N*,*N*-dimethylformamide gave a mixture of 6- and 6′-monochloro-monodeoxysucrose heptamethanesulphonates (**6**) and 6,6′-dichloro-6,6′-dideoxysucrose hexamethanesulphonate (**7**). A crystalline mixture of 6- and 6′-monoiodo derivatives **8** was obtained when **1** was treated with sodium iodide in butanone. Reaction of **1** with sodium bromide under various conditions gave a mixture of 6- and 6′-monobromo-monodeoxysucrose heptamethanesulphonates (**2**), 6,6′-dibromo-6,6′-dideoxysucrose hexamethanesulphonate (**3**), and, probably, 6-bromo-6-deoxy-1,3,4-tri-*O*-mesyl-*β*-D-fructofuranosyl 4,6-dibromo-4,6-dideoxy-2,3-di-*O*-mesyl-α-D-galactopyranoside (**4**). Reduction of mixture **2** afforded a crystalline monodeoxysucrose heptamethanesulphonate (**5**) containing equimolar amounts of the 6- and 6′-monodeoxy isomers. Similarly, **3** gave 6,6′-dideoxysucrose hexamethanesulphonate **9** which, on treatment with sodium azide in hexamethylphosphoric triamide, underwent selective nucleophilic substitution at C-4 to give 6-deoxy-*β*-D-fructofuranosyl 4-azido-4,6-dideoxy-α-D-galactopyranoside pentanesulphonate (**10**). Sodium azide reacted with the octasulphonate **1** in hexamethylphosphoric triamide to give the 4,6,6′-triazide **11** and 1′,4,6,6′-tetra-azide **12**. The triazide **11** was also obtained when 6,6′-dideoxy-6,6′-di-iodosucrose hexamethanesulphonate was treated with sodium azide in hexamethylphosphoric triamide. The secondary 4-mesyloxy substituent is therefore more reactive to nucleophilic substitution than that at the primary 1′-position in **1**.

INTRODUCTION

In Part VI[2], 6,6′-di-*O*-tosylsucrose hexa-acetate was observed to undergo nucleophilic substitution with chloride in hexamethylphosphoric triamide to give a

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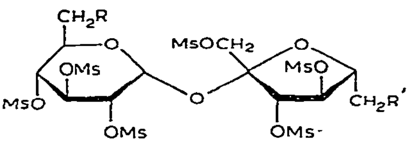
mixture from which 6-monochloro-6-monodeoxy and 6,6′-dichloro-6,6′-dideoxy derivatives were isolated. We have extended these studies to sucrose octamethanesulphonate (**1**) in order to explore further the comparative reactivities of the sulphonyloxy substituents at C-6 and C-6′, and at other positions. In this connection, a triazido-trideoxysucrose pentamethanesulphonate was isolated previously[3] from a reaction of **1** with azide, and consequently we have re-examined this reaction in order to gain a closer insight into the reactivity of the sucrose molecule[4,5].

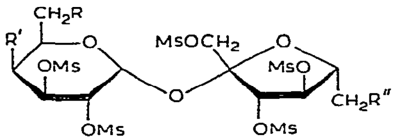
RESULTS AND DISCUSSION

Sucrose octamethanesulphonate (**1**) underwent selective reactions with sodium chloride, either in a mixture of *N*,*N*-dimethylformamide and butanone or in hexamethylphosphoric triamide, and with mesyl chloride in *N*,*N*-dimethylformamide[6], to give products containing predominantly mono- and di-chloro derivatives. They were separated on silica gel to give a crystalline monochloro-monodeoxysucrose heptamethanesulphonate (**6**, m.p. 182–186°) and 6,6′-dichloro-6,6′-dideoxysucrose hexamethanesulphonate (**7**). The former product (**6**) was an equimolar mixture of the 6- and 6′-chloro derivatives as revealed by co-chromatography with 6-chloro-6-deoxysucrose heptamethanesulphonate[2] (m.p. 99–101°), and by the p.m.r. spectrum which revealed a low-field triplet (τ 3.95, 1:2:1) due to overlapping doublets of H-1 in the 6- and 6′-monochlorides. Likewise, sodium bromide reacted with the octasulphonate **1** in butanone to give the 6,6′-dibromide **3**, and a crystalline mixture of 6- and 6′-monobromides **2** the p.m.r. spectrum of which also showed a low-field triplet (τ 3.96) arising from overlapping doublets. Reduction of the 6,6′-dibromide **3** gave the 6,6′-dideoxy derivative **9**, whereas the mixed monobromides **2** gave a crystalline, monodeoxy compound the p.m.r. spectrum of which provided unequivocal evidence for an equimolar mixture of 6- and 6′-monodeoxy derivatives (**5**). Thus, the H-1 signals appeared as a low-field triplet (1:2:1), arising from overlapping doublets, and the Me-5′ and Me-5 signals appeared as two doublets at higher field (τ 8.44 and 8.58; $J_{5,6}$ and $J_{5',6'}$ 6.0 Hz), which were equal in intensity and together integrated for 3 protons. Thus, the reactivities of the 6- and 6′-sulphonyloxy substituents in sucrose octamethanesulphonate (**1**) are comparable, in contrast to the selective reactivity[2] towards chloride of the 6-substituent in sucrose 6,6′-bis(toluene-*p*-sulphonate). The dibromide



1 R = R′ = OMs
2 R = Br, R′ = OMs
R = OMs, R′ = Br
3 R = R′ = Br
5 R = H, R′ = OMs
R = OMs, R′ = H

6 R = Cl, R′ = OMs
R = OMs, R′ = Cl
7 R = R′ = Cl
8 R = I, R′ = OMs
R = OMs, R′ = I
9 R = R′ = H



4 R = R′ = R″ = Br
10 R = R″ = H, R′ = N_3
11 R = R′ = R″ = N_3

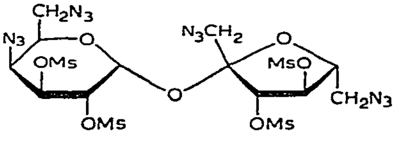
3 gave the expected[3] 6-deoxy-2,3,4-tri-*O*-mesyl-β-D-*xylo*-hex-5-enopyranosyl 6-deoxy-1,3,4-tri-*O*-mesyl-β-D-*threo*-hex-5-enofuranoside when treated with silver fluoride in pyridine.

Investigation of the reaction of 6,6′-dideoxysucrose hexamethanesulphonate (**9**) with sodium azide in hexamethylphosphoric triamide gave 6′-deoxy-β-D-fructofuranosyl 4-azido-4,6-dideoxy-α-D-galactopyranoside pentamethanesulphonate (**10**). Considerations of the most-favourable transition state for bimolecular nucleophilic substitution[7], together with the results of previous studies on glucopyranoid[8] and fructofuranoid[9] derivatives, favour C-4. The p.m.r. spectrum confirmed that substitution had not occurred at carbons 2, 3, 3′, and 4′, whilst the small value of $J_{3,4}$, due to axial H-4 and equatorial H-3 coupling[10], showed that inversion of configuration had occurred at C-4 to give the galactopyranoside derivative **10**.

A crystalline tribromo derivative was isolated in 39% yield, in addition to the 6,6′-dibromide **3**, when the octasulphonate **1** was treated with sodium bromide in hexamethylphosphoric triamide. Unfortunately, the H-3 and H-4 signals could not be located in the p.m.r. spectrum, but the coupling constants did reveal that substitution had not occurred at carbons 2, 3, 3′, or 4′, and this, together with the above evidence on azide displacement, suggests that the tribromide is probably the 6′-bromo-6′-deoxy-β-D-fructofuranosyl 4,6-dibromo-4,6-dideoxy-α-D-galactopyranoside pentamethanesulphonate (**4**). This structural assignment is supported by the observation that the substitution reactions of 1′,4,6′-tri-*O*-mesylsucrose penta-acetate proceed most readily at C-4 and C-6′, for example by a selective reaction with sodium benzoate to give a derivative of 1′-*O*-mesyl-β-D-fructofuranosyl α-D-galactopyranoside[11].

Crystalline triazido and tetra-azido derivatives were isolated in 60 and 10% yield, respectively, when the octasulphonate **1** was treated with sodium azide in hexamethylphosphoric triamide. The triazide was identical with that isolated previously[3] and with the product obtained from a similar reaction with 6,6′-dideoxy-6,6′-di-iodosucrose hexamethanesulphonate.

By analogy with the previous substitution reactions, the triazide is identified as 6′-azido-6′-deoxy-β-D-fructofuranosyl 4,6-diazido-4,6-dideoxy-α-D-galactopyranoside pentamethanesulphonate (**11**). This structural assignment is supported by the p.m.r. spectrum and physical constants which are different from those of 1′,6,6′-triazido-1′,6,6′-trideoxysucrose[12] and 1′,6′-diazido-1′,6′-dideoxy-β-D-fructofuranosyl 4-azido-4-deoxy-α-D-galactopyranoside[11]. The p.m.r. spectrum of the tetra-azide supported the expected structure, namely, 1′,6′-diazido-1′,6′-dideoxy-β-D-fructofuranosyl 4,6-diazido-4,6-dideoxy-α-D-galactopyranoside tetramethanesulphonate (**12**).



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EXPERIMENTAL

General. — For procedures, see Part VI[2].

Preparation of chloro derivatives from sucrose octamethanesulphonate (**1**). — (*a*) *By reaction with sodium chloride in* N,N-*dimethylformamide–butanone.* A solution of **1** (10.0 g) in *N,N*-dimethylformamide and butanone (240 ml, 5:1) containing sodium chloride (5.0 g) was heated at 90° with stirring for 70 h. T.l.c. (chloroform–acetone, 4:1) showed two products. The reaction mixture was cooled to 40° and then poured into ice–water. The precipitate formed was filtered off, washed well with water, and then dried over phosphoric oxide in a vacuum oven at 50° overnight. The mixture was then eluted from silica gel (400 g) with chloroform–acetone (6:1), to give the following fractions. (*i*) 6,6′-Dichloro-6,6′-dideoxysucrose hexamethanesulphonate (**7**; 4 g, 43%) had m.p. 139–140° (from acetone–methanol), $[\alpha]_D^{25}$ +52.5° (*c* 1.0, acetone). N.m.r. data: τ 4.0 (1-proton doublet, $J_{1,2}$ 3.25 Hz, H-1), 5.1 (1-proton quartet, $J_{2,3}$ 9.0 Hz, H-2), 4.84 (1-proton quartet, $J_{3,4}$ 8.0 Hz, H-3), 4.94 (1-proton triplet, $J_{4,5}$ 8.0 Hz, H-4), 4.48 (1-proton doublet, $J_{3',4'}$ 7.5 Hz, H-3′), 4.46 (1-proton triplet, $J_{4',5'}$ 7.5 Hz, H-4′), 6.5–6.84 (18-proton multiplet, 6Ms).

Anal. Calc. for $C_{18}H_{32}Cl_2O_{21}S_6$: C, 25.5; H, 3.9; Cl, 7.9. Found: C, 25.4; H, 3.7; Cl, 8.4.

(*ii*) 6- And 6′-monochloro-monodeoxysucrose heptamethanesulphonate (**6**; 2.3 g, 23.0%) had m.p. 182–186° (from methanol).

Anal. Calc. for $C_{19}H_{35}ClO_{24}S_7$: C, 25.1; H, 3.9; Cl, 3.9. Found: C, 25.1; H, 3.9; Cl, 3.9.

(*b*) *By reaction with mesyl chloride in* N,N-*dimethylformamide.* A solution of **1** (3.0 g) in *N,N*-dimethylformamide (20 ml) containing mesyl chloride (12.5 ml) was heated at 80° with stirring for 16 h. T.l.c. (chloroform–acetone, 4:1) showed one major product and a slow-moving minor component. The solution was cooled to 50° and the solvent was removed by rotary evaporation and co-distillation with toluene. The residual, brown syrup was dried for 16 h at 50° *in vacuo*, and then dissolved in acetone, decolourised, and concentrated to a small volume. Chromatography on silica gel (200 g) with chloroform–acetone (6:1) gave the following fractions. (*iii*) Compound **7** (1.1 g, 41.8%), m.p. and mixed m.p. 139–140° (from acetone–methanol), $[\alpha]_D^{26}$ +53.2° (*c* 0.46, acetone).

Anal. Calc. for $C_{18}H_{32}Cl_2O_{21}S_6$: C, 25.5; H, 3.9; Cl, 7.9. Found: C, 26.1; H, 3.9; Cl, 7.8.

(*iv*) Mixture **6** (70 mg, 2.8%), m.p. 182–186° (from acetone–methanol), mixed m.p. 182–185°, $[\alpha]_D^{26}$ +47.1° (*c* 0.28, acetone). The yield of the monochloro derivative was increased to 53% when, in a similar reaction, the time was reduced to 6.5 h.

Anal. Calc. for $C_{19}H_{35}ClO_{24}S_7$: C, 25.1; H, 3.9; Cl, 3.9. Found: C, 25.1; H, 3.9; Cl, 3.8.

(*c*) *By reaction with sodium chloride in hexamethylphosphoric triamide.* Sodium chloride (3.0 g) was added to a solution of **1** (3.0 g) in $(Me_2N)_3PO$ (15.0 ml) and the mixture was heated at 85° for 80 min with stirring. T.l.c. (chloroform–acetone, 4:1) showed one major product which had an R_F value similar to that of an authentic sample of monochloro derivative. The reaction mixture was worked up in the usual way, and the resulting dried material was chromatographed on a column of silica gel (200 g) with chloroform–acetone (6:1), to give the following fractions. (*v*) Compound **7** (0.4 g, 15%), m.p. and mixed m.p. 139–140° (from acetone–methanol), $[\alpha]_D^{24}$ +51.5° (*c* 1.0, acetone).

(*vi*) Mixture **6** (2.3 g, 80%), m.p. and mixed m.p. 182–186° (from acetone–methanol), $[\alpha]_D^{26}$ +48° (*c* 1.0, acetone).

The reaction of sucrose octamethanesulphonate (**1**) *with iodide.* — Sodium iodide (1.0 g) was added to a solution of **1** (2.0 g) in butanone (20 ml), and the mixture was refluxed with stirring for 90 min. When t.l.c. indicated that the yield of mono-iodide was optimal, the reaction was stopped. Sodium methanesulphonate and unreacted sodium iodide were filtered off and washed with ice-cold butanone, and the filtrate was concentrated to a syrup which was chromatographed on silica gel (150 g) with chloroform–acetone (12:1). This gave two fractions. (*i*) 6,6′-Dideoxy-6,6′-di-iodo-sucrose hexamethanesulphonate (0.4 g, 37.5%), m.p. and mixed m.p. 215–217° (from acetone–light petroleum). The i.r. spectrum was identical with that of an authentic sample[3]

(*ii*) Monodeoxy-monoiodosucrose heptamethanesulphonate (**8**; 0.58 g, 59%), m.p. 205–209° (from cold methanol), $[\alpha]_D^{29}$ +44.8° (*c* 0.44, acetone).

Anal. Calc. for $C_{19}H_{35}IO_{24}S_7$: C, 22.8; H, 3.8; I, 12.7. Found: C, 22.5; H, 3.8; I, 13.5.

Reaction of sucrose octamethanesulphonate (**1**) *with sodium bromide.* — (*a*) *In butanone.* Compound **1** (1.0 g) was added to a suspension of sodium bromide (1.0 g) in butanone (50 ml) and the mixture was heated at 105° for 20 h with stirring. T.l.c. (chloroform–acetone, 2:1) showed three spots, the faster-moving corresponding to the 6,6′-dibromide **3** and the slower to the starting material. Sodium methanesulphonate and unreacted sodium bromide were filtered off and washed with cold butanone, and the filtrate was concentrated. The residual syrup was eluted from a column of silica gel (200 g) with chloroform–acetone (16:1) to give the following two fractions. (*i*) 6,6′-Dibromo-6,6′-dideoxysucrose hexamethanesulphonate (**3**; 0.2 g, 21%), m.p. 171–173° (from methanol), $[\alpha]_D^{26}$ +39.5° (*c* 0.89, acetone). N.m.r. data: τ 4.0 (1-proton doublet, $J_{1,2}$ 3.0 Hz, H-1), 5.04 (1-proton quartet, $J_{2,3}$ 11 Hz, H-2), 4.9 (1-proton triplet, $J_{3,4}$ 8.5 Hz, $J_{4,5}$ 8.5 Hz, H-4), 4.46 (1-proton doublet, $J_{3',4'}$ 7.5 Hz, H-3′), 4.64 (1-proton triplet, $J_{4',5'}$ 7.5 Hz, H-4′), 5.62–6.82 (18-proton multiplet, 6Ms). The remaining protons could not be interpreted due to overlapping.

Anal. Calc. for $C_{18}H_{32}Br_2O_{21}S_6$: C, 23.2; H, 3.7; Br, 16.4; S, 20.5. Found: C, 23.8; H, 3.8; Br, 17.0; S, 20.5.

(*ii*) 6- And 6′-monobromo-monodeoxysucrose heptamethanesulphonate (**2**; (0.6 g, 61%), m.p. 189–193° (from methanol), $[\alpha]_D^{30}$ +32° (*c* 1.0, acetone).

Anal. Calc. for $C_{19}H_{35}BrO_{24}S_7$: C, 24.0; H, 3.7; Br, 8.5; S, 23.6. Found: C, 24.5; H, 4.0; Br, 8.2; S, 24.0.

(*b*) *In hexamethylphosphoric triamide.* Sodium bromide (2.5 g) was added to a solution of **1** (4.0 g) in $(Me_2N)_3PO$ (14 ml) and the mixture heated at 85° with stirring. After 2 h, t.l.c. (chloroform–acetone, 2:1) showed two faster-moving products and the reaction mixture was worked up as usual. The precipitate was dissolved in acetone, dried ($MgSO_4$), and concentrated to a syrup which was eluted from a column of silica gel (300 g) with chloroform–acetone (16:1). The following two fractions were obtained. (*iii*) 6′-Bromo-6′-deoxy-β-D-fructofuranosyl 4,6-dibromo-4,6-dideoxy-α-D-galactopyranoside (**4**; 1.5 g, 39%), m.p. 140–141° (from methanol), $[\alpha]_D^{26}$ +54.8° (*c* 0.75, acetone). N.m.r. data: τ 4.02 (1-proton doublet, $J_{1,2}$ 3.5 Hz, H-1), 5.0 (1-proton quartet, $J_{2,3}$ 10 Hz, H-2), 4.46 (1-proton doublet, $J_{3',4'}$ 7.5 Hz, H-3′), 4.66 (1-proton triplet, $J_{4',5'}$ 7.5 Hz, H-4′), 6.1–6.6 (15-proton multiplet, 5-Ms).

Anal. Calc. for $C_{17}H_{29}Br_3O_{18}S_5$: C, 22.1; H, 3.1; Br, 26.1; S, 17.4. Found: C, 22.4; H, 3.4; Br, 26.8; S, 17.7.

(*iv*) The dibromide **3** (1.4 g, 36%), m.p. and mixed m.p. 171–172° (from methanol).

6- and 6′-Monodeoxysucrose heptamethanesulphonate (**5**). — A solution of the monobromide **2** (150 mg) in methanol–ethyl acetate (150 ml, 1:1) was mixed with barium carbonate (1.0 g) and heated to boiling with stirring. Raney nickel (150 mg) was then added to the mixture and, after 2 min, hydrazine hydrate (1 ml) was added dropwise. The reaction mixture was refluxed for 2 h until t.l.c. (acetone–chloroform, 1:2) showed one product. The hot reaction mixture was filtered through Hyflo Supercel, and the filtrate was concentrated to a syrup which crystallised from methanol to give **5** (0.76 g, 83%), m.p. 135–138°.

Anal. Calc. for $C_{19}H_{36}O_{25}S_7$: C, 26.1; H, 4.1; S, 25.6. Found: C, 26.4; H, 4.4; S, 25.5.

6,6′-Dideoxysucrose hexamethanesulphonate (**9**). — Barium carbonate (1.0 g) was added to a boiling solution of the dibromide **3** (200 mg) in methanol (150 ml). The addition of Raney nickel (1.0 g) was followed by the dropwise addition of hydrazine hydrate, and the mixture was refluxed with stirring for 45 min. T.l.c. (chloroform–acetone, 4:1) showed a product of different colour than, but the same R_F value as, the starting material. The hot solution was filtered through Hyflo Supercel, and the filtrate was concentrated to a syrup which crystallised from methanol to give **9** (150 mg, 90%), m.p. 189–190°, $[\alpha]_D^{25}$ +42.2° (*c* 1.0, acetone); lit.[3] m.p. 191–192°, $[\alpha]_D^{24}$ +44.4° (acetone).

*6-Deoxy-2,3,4-tri-O-mesyl-β-*D-xylo*-hex-5-enopyranosyl 6-deoxy-1,3,4-tri-O-mesyl-β-*D-threo*-hex-5-enofuranoside.* — Anhydrous silver fluoride (100 mg) was added to a solution of **3** (100 mg) in pyridine (10 ml). The mixture was stirred at room temperature for 4.5 h. T.l.c. (chloroform–acetone, 4:1) then showed a product that moved slightly faster than the starting material. The mixture was poured into ice–water and an acetone solution of the resulting precipitate was decolourised, dried ($MgSO_4$), and concentrated. Crystallisation of the residue from methanol gave the title diene (29 mg, 35%), m.p. 110–113°, $[\alpha]_D^{30}$ +15° (*c* 1.0, acetone); lit.[3] m.p. 110–111°, $[\alpha]_D^{26}$ +13.7° (acetone).

*6′-Deoxy-β-*D*-fructofuranosyl 4-azido-4,6-dideoxy-α-*D*-galactopyranoside penta-*

methanesulphonate (**10**). — The hexasulphonate **9** (1.0 g) in $(Me_2N)_3PO$ (4.0 ml) containing sodium azide (1.5 g) was heated at 85° with stirring for 16 h. T.l.c. (chloroform–acetone, 3:1) then showed one product with an R_F value slightly higher than that of the starting material. The reaction mixture was worked up as usual, and the product was dried over phosphoric oxide and crystallised from methanol to give **10** (0.7 g, 75%), m.p. 79–83°, $[\alpha]_D^{23}$ +39.6° (*c* 1.55, acetone). N.m.r. data: τ 4.4 (1-proton doublet, $J_{1,2}$ 3.5 Hz, H-1), 5.4 (1-proton quartet, $J_{2,3}$ 10 Hz, H-2), 4.84 (1-proton quartet, $J_{3,4}$ 3.5 Hz, H-3), 4.7 (1-proton doublet, $J_{3',4'}$ 7.5 Hz, H-3') 5.2 (1-proton triplet, $J_{4',5'}$ 7.5 Hz, H-4'), 6.8–6.96 (15-proton multiplet, 5Ms).

Anal. Calc. for $C_{17}H_{21}N_3O_{18}S_5$: C, 28.15; H, 4.2; N, 5.9. Found: C, 29.0; H, 4.2; N, 6.5.

6'-Azido-6'-deoxy-β-D-fructofuranosyl 4,6-diazido-4,6-dideoxy-α-D-galactopyranoside pentamethanesulphonate (**11**). — A solution of 6,6'-dideoxy-6,6'-diiodosucrose hexamethanesulphonate (4.0 g) in $(Me_2N)_3PO$ (16 ml) containing sodium azide (4.0 g) was heated at 85° for 16 h with stirring. T.l.c. (chloroform–acetone, 2:1) then showed the presence of one fast-moving product. The reaction mixture was worked up in the usual way, and a solution of the brown precipitate in acetone was decolourised, dried ($MgSO_4$), and concentrated to a syrup which crystallised from acetone–ether to give the triazide **11** (2.5 g, 80%), m.p. 151–153°, $[\alpha]_D^{25}$ +45.2° (*c* 1.0, acetone). The n.m.r. and i.r. spectra corresponded to those of a previous sample[3]. N.m.r. data: τ 4.08 (1-proton doublet, $J_{1,2}$ 3.5 Hz, H-1), 5.06 (1-proton quartet, $J_{2,3}$ 10.5 Hz, H-2), 4.68 (1-proton quartet, $J_{3,4}$ 3.5 Hz, H-3), 4.50 (1-proton doublet, $J_{3',4'}$ 7.5 Hz, H-3'), 4.62 (1-proton triplet, $J_{4',5'}$ 7.5 Hz, H-4').

Anal. Calc. for $C_{17}H_{29}N_9O_{18}S_5$: C, 25.3; H, 3.3; N, 15.6. Found: C, 25.8; H, 3.5; N, 15.6.

Reaction of sucrose octamethanesulphonate (**1**) *with sodium azide in hexamethylphosphoric triamide.* — A solution of **1** (4.0 g) in $(Me_2N)_3PO$ (20 ml) containing sodium azide (3.0 g) was heated at 90° with stirring for 48 h. T.l.c. (chloroform–acetone, 3:1) then showed the presence of two products. The reaction mixture was worked up in the usual way, and a solution of the dark-brown syrup in acetone was decolourised, dried ($MgSO_4$), and concentrated. Elution of the syrupy product from silica gel (250 g) with chloroform–acetone (16:1) gave the following two fractions. (*i*) 1',6'-Diazido-1',6'-dideoxy-β-D-fructofuranosyl 4,6-diazido-4,6-dideoxy-α-D-galactopyranoside tetramethanesulphonate (**12**, 0.33 g, 10%), m.p. 171–173° (from methanol), $[\alpha]_D^{25}$ +45.7° (*c* 0.28, acetone). N.m.r. data: τ 4.08 (1-proton doublet, $J_{1,2}$ 3.5 Hz, H-1), 5.06 (1-proton quartet, $J_{2,3}$ 10 Hz, H-2), 4.72 (1-proton quartet, $J_{3,4}$ 3.5 Hz, H-3), 4.45 (1-proton doublet, $J_{3',4'}$ 8.0 Hz, H-3'), 4.72 (1-proton triplet, $J_{4',5'}$ 8.0 Hz, H-4'), 6.6–6.74 (12-proton multiplet, 4Ms).

Anal. Calc. for $C_{16}H_{26}N_{12}O_{15}S_4$: C, 25.5; H, 3.5; N, 22.3. Found: C, 25.9; H, 3.5; N, 21.9.

(*ii*) The triazide **11** (2.0 g, 60%) which had m.p. and an i.r. spectrum identical with those of the previous sample.

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