Direct Conversion of 3,5,6-Tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucose into 4,5,6-Tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose Diethyl Dithioacetal

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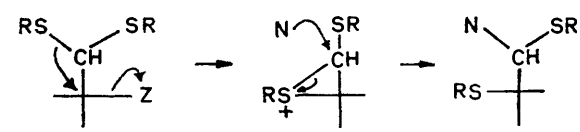
The reaction of 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucose with ethanethiol in the presence of hydrogen chloride gives a crystalline product in 60% yield as was first described in 1932. This product is now shown to be 4,5,6-tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-allose diethyl dithioacetal. A mechanistic outline for the reaction is proposed.

DURING investigations of the reaction of peracylated acyclic sugars in the carbonyl form with ethanethiol in the presence of acid catalysts we have observed replacement of acyloxy-groups in addition to diethyl dithioacetal formation, and, in an effort to understand the nature of the replacement processes, have studied the structure of the tetrathio-product (I) known to be formed on treatment of 3,5,6-tri-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (II) under the same conditions.[1] Although the tetrathio-derivative has been known for 40 years it has apparently not been subjected to full analysis despite the unlikely validity of the originally suggested structure (3,5,6-tri-*O*-benzoyl-2,4-di-*S*-ethyl-2,4-dithio-D-glucose diethyl dithioacetal). A considerable body of information reported in recent years indicates that ester migrations,[2] neighbouring group participations,[3,4] and configurational inversions might have been expected to occur during the reaction, and we now report justification for these expectations.

The n.m.r. spectrum of compound (I) showed it to contain three benzoyl groups, four ethylthio-groups, and seven chain protons, and therefore that the structure was at least isomeric with that originally suggested.[1] The acetal proton resonance was readily assignable as the only doublet in the spectrum, and the signals derived from the other two protons attached to sulphur-bonded carbon atoms were recognisable from their characteristic high-field positions.[5] From the observation that these resonances both exhibited 8·5 Hz splittings, which were unique in the spectrum, the non-acetal sulphur atoms could be concluded to be vicinally related, and their locations at C-2 and C-3 were established by the observation that irradiation at the frequency of the H-1 doublet caused decoupling of one of these high-field signals. In agreement with this, irradiation at the frequency of the signal assigned to H-4 caused collapse of the other of these resonances. It was concluded that the compound was a 4,5,6-tri-*O*-benzoyl-2,3-di-*S*-ethyl-2,3-dithio-D-hexose diethyl dithioacetal.

Thioether groups are known to participate readily as neighbouring groups in nucleophilic displacement reactions,[3] and when they are constituents of dithioacetal functions they can form cyclic sulphonium ions which may be opened by nucleophilic attack at the acetal centre. In consequence, the thio-groups can migrate to the carbon atom to which the leaving group was attached and Walden inversion occurs at this centre (see Scheme).[3d,4] Such neighbouring group participation is



SCHEME

extremely effective when three- and five-membered intermediate ions are involved,[3b] and several instances are recorded of migrations of thio-groups to positions

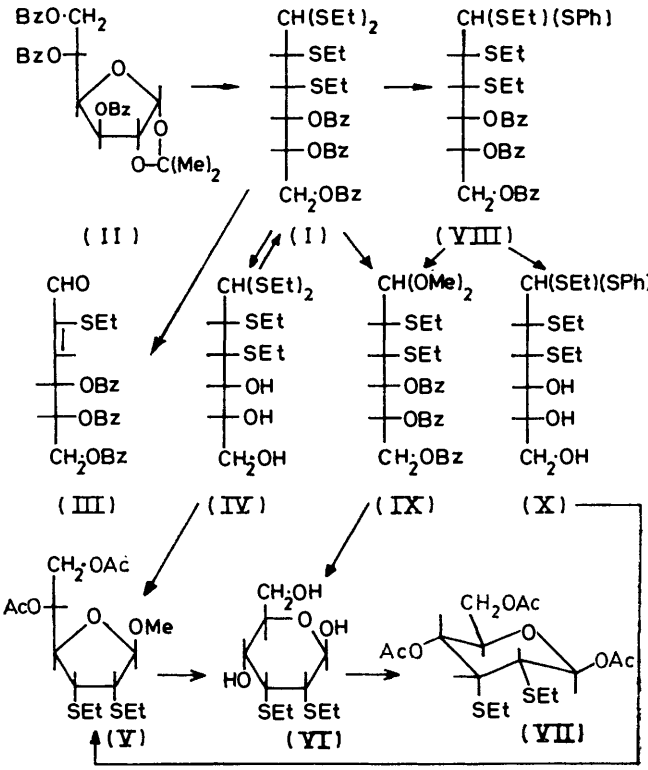
[1] P. Brigl and R. Schinle, *Ber.*, 1932, **65**, 1890.
[2] M. L. Wolfrom, S. W. Waisbrot, D. I. Weisblat, and A. Thompson, *J. Amer. Chem. Soc.*, 1944, **66**, 2063.
[3] (*a*) G. Gundermann, *Angew. Chem. Internat. Edn.*, 1963, **2**, 674; (*b*) B. Capon, *Quart. Rev.*, 1964, **18**, 45; (*c*) L. Goodman, *Adv. Carbohydrate Chem.*, 1967, **22**, 109; (*d*) J. S. Brimacombe. *Fortschr. chem. Forsch.*, 1970, **14**, 367; (*e*) K. J. Ryan, E. M. Acton, and L. Goodman, *J. Org. Chem.*, 1971, **36**, 2646.
[4] B. Berrang and D. Horton, *Chem. Comm.*, 1970, 1038.
[5] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, Oxford, 1969, p. 164.

2 [3c,4,6] and 4 [7] of aldose derivatives during solvolyses of dithioacetals. Migrations to position 5 by way of six-membered ionic intermediates are also known,[3d,7,8] but direct migrations to C-3 are apparently unknown, presumably in part because of the unfavourable nature of intermediates which would be involved.[3b] It was initially surprising therefore to find an ethylthio-group at this position and an ester group at C-4 in compound (I). Chemical confirmation of the presence of a C-3 *S*-ethyl group was obtained on treating the triester with mercury(II) salts in aqueous solution: hydrolysis to the free aldehyde occurred and was followed by a β-elimination of ethanethiol to give a syrupy enal product (III) which was shown by n.m.r. spectroscopy to contain one ethyl group and one formyl and one vinyl proton.

Base-catalysed debenzoylation of the tetrathio-compound (I) to give the triol (IV) occurred smoothly as evidenced by recovery of the starting material on rebenzoylation, and mercury-catalysed methanolysis of the debenzoylation product (IV) gave, after acetylation, methyl 5,6-di-*O*-acetyl-2,3-di-*S*-ethyl-2,3-dithio-β-D-allofuranoside (V). Although the 60 MHz n.m.r. spectrum of this product was difficult to analyse fully, the H-5 resonance was discernible, and from the low $J_{4,5}$ value and from its low-field position of resonance the proton was concluded to be attached to an exocyclic carbon atom of a furanoid ring rather than C-5 of a pyranoid ring in which case $J_{4,5}$ would be *ca.* 9 Hz (see later). This was to be expected, since methanolyses of aldose diethyl dithioacetals are used generally to produce methyl glycofuranosides,[9] and it is noteworthy that ring-closure occurred with high stereoselectivity, the *trans*-relationship of H-1 and H-2 being assignable from a low $J_{1,2}$ value.[10]

Deacetylation of the glycoside (V) followed by mild acid-catalysed hydrolysis gave a crystalline di-*S*-ethyl-dithioaldohexose (VI) which mutarotated in the positive sense, and which gave a syrupy triacetate (VII) on esterification with acetic anhydride in pyridine solution at 0°, conditions which give direct acylation.[11] N.m.r. spectroscopy allowed this compound to be readily characterised as the β-D-allopyranose derivative (VII). Spin-decoupling experiments confirmed the positions of the thio-groups, $J_{1,2}$ and $J_{4,5}$ values of *ca.* 9 Hz revealed the axial character of H-1, H-2, H-4, and H-5, and smaller coupling constants associated with H-3 ($J_{2,3} = J_{3,4} = ca.$ 4 Hz) revealed that H-3 was equatorial. From the direction of mutarotation of the free sugar (VI) it can be concluded that the glycosyl hydroxy-group is oriented ' upwards ' in the Haworth perspective formula (*i.e.* C-1 has the *R*-configuration), and for this to be the case, since H-1 and H-5 are *cis*-related, the compound must belong to the D-series.

Because, as has been noted, the debenzoylation of the tetrathio-compound (I) occurred without rearrangement, and because the hydrolysis of the glycoside (V) presumably also took place without complication, the characterisation of (I) depends upon the configurational inter-relationship of the sequence intermediates (IV) and (V). Most directly, the ring closure of the former could



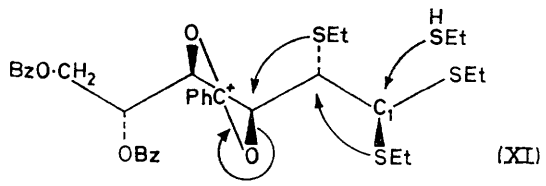
occur by two mercury-assisted nucleophilic displacements at C-1, one intramolecular and the other solvolytic, but the possibility is also open that either or both of these steps could have involved participation by a thioacetal group in the displacement of the C-2 sulphur-containing group and attack by the nucleophiles at C-1.[3c,4] The net effect of the displacement of one ethylthio-group by this pathway would be inversion at C-2, and so some doubt is cast on the validity of assigning the *allo*-configuration of compounds (VI) and (V) to compound (IV) and hence to compound (I). It therefore became necessary to determine whether the displacement reactions at C-1 occurred directly or indirectly, or whether they occurred by the different available pathways.

In an attempt to resolve this point an effort was made to prepare the diphenyl dithioacetal analogue of compound (I) with the intention of examining whether phenylthio-groups were introduced at C-2 during sub-

[6] D. Horton and D. H. Hutson, *Adv. Carbohydrate Chem.*, 1963, **18**, 123.
[7] N. A. Hughes, R. Robson, and S. A. Saeed, *Chem. Comm.*, 1968, 1381.
[8] N. A. Hughes and R. Robson, *Chem. Comm.*, 1968, 1383; J. Harness and N. A. Hughes, *ibid.*, 1971, 811.
[9] E. Pacsu, *Methods Carbohydrate Chem.*, 1963, **2**, 354; J. W. Green, *Adv. Carbohydrate Chem.*, 1966, **21**, 95.
[10] R. U. Lemieux and D. R. Lineback, *Ann. Rev. Biochem.*, 1963, **32**, 155.
[11] L. Hough and A. C. Richardson in ' Rodd's Chemistry of Carbon Compounds,' vol. 1F, ed. S. Coffey, Elsevier, Amsterdam, 1967, p. 380.

sequent mercury-catalysed nucleophilic displacement reactions. All attempts to prepare the desired compound were unsuccessful; however on treatment of compound (I) with benzenethiol and hydrogen chloride a crystalline mixture of diastereoisomeric ethyl phenyl thioacetals (VIII) was obtained in high yield in a reaction related in part to that by which Berrang and Horton [4] obtained 3,4,5,6-tetra-*O*-benzoyl-2-*S*-ethyl-2-thio-D-mannose ethyl phenyl dithioacetal from 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl dithioacetal. N.m.r. spectroscopy showed that the diethyl (I) and the ethyl phenyl (VIII) compounds were conformationally (and, it is concluded, configurationally) identical, and hence no inversion occurred during the synthesis of the latter from the former. In addition, the two acetals (I) and (VIII) afforded the same dimethyl acetal (IX) on methanolysis in the presence of mercury(II) chloride, which further establishes their configurational identity, and since the dimethyl compound (IX) after de-esterification was readily hydrolysed to the free sugar (VI) with mild acid, it is assigned the *allo*-configuration. The dimethyl acetal (IX) cannot have been formed from the phenylthio-compound (VIII) by a double inversion process at C-2 since the product was devoid of phenylthio-groups, and a process involving one direct and one indirect displacement can presumably be ruled out since a C-1 thio-group would be expected to have the same relative propensities to be displaced directly and be transferred to C-2 in a dithioacetal and in a methoxythio-acetal intermediate. It is therefore concluded that the compounds (I), (VIII), and (IX) have the same configuration at C-2. In addition, both dithioacetals were convertible into the furanoside derivative (V), and no product containing a phenylthio-group was obtained from the mixed thioacetal (X).

We suggest that the D-*allo*-compound (I) could have been derived from the isopropylidene tribenzoate (II) by initial thiolysis to give 3,5,6-tri-*O*-benzoyl-D-glucose diethyl dithioacetal, from which the *manno*-carbonium ion (XI) could readily have been derived by ethylthio-incorporation at C-2 with Walden inversion (see before), and acid-catalysed cyclic ion formation from the geometrically *cis*-benzoyloxy–hydroxy system at C-3 and C-4. The suggested intermediate is ideally oriented for

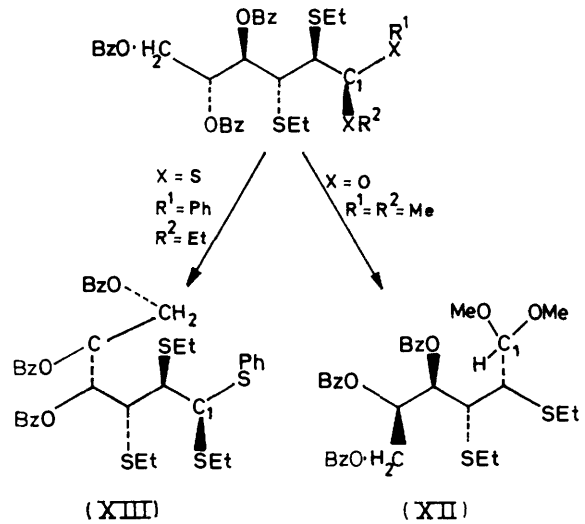


(XI)

solvent attack at C-1 and displacement of a C-1 ethylthio-group which can concurrently attack C-2 causing configurational inversion at this centre. The displaced C-2 group is then suitably oriented to attack the rear side of C-3, to which is attached a good leaving group. Configurational inversion therefore occurs at C-3 also. Additively, therefore, the high solvent nucleophilicity, the high propensity of ethylthio-groups to form episulphonium ions, and the electron-attracting properties of the carbonium ion (XI) drive the reaction to yield the product (I), which was isolated in 60% yield but which was shown by n.m.r. spectroscopy of the non-crystalline fraction of the products to have been formed almost exclusively.

Experiments are under way to test the validity of the suggested reaction route.

Although the dithioacetals (I) and (VIII) and the dimethyl acetal (IX) are all assigned the same configuration, the last of these adopts a different conformation from the others. In the fully extended zig-zag form *allo*-aldohexose derivatives have eclipsing interactions between the substituents at C-2 and C-4 and at C-3 and C-5, and would, in consequence, be expected to prefer distorted conformations in which these non-bonded interactions are relieved.[12] N.m.r. coupling constants (see Table) can be interpreted as indicating that in the case of the dimethyl acetal (IX) rotations about the C(2)–C(3) and C(4)–C(5) bonds occur as shown (XII), and the C-1 oxygen atoms are oriented away from the C-3 ethylthio-group. In the cases of the dithio-



(XIII) (XII)

acetals, [*e.g.* (XIII)] apparently the interaction between the bulky C-1 substituents and C-4 is sufficient to destabilise this orientation in favour of conformations formed from the regular zig-zag by rotations about the C(3)–C(4) and C(4)–C(5) bonds. Since the mixed ethyl phenyl diastereoisomers (VIII) gave only one n.m.r. doublet for H-1 it can be concluded that the C(1)–C(2) rotamer state is unaffected by exchange of the sulphur substituents; however each diastereoisomer gives a separate H-2, H-6, and H-6′ resonance, which indicates that these protons are affected by this change and therefore that the molecules are distorted in such a way as to bring C-6 within the magnetic influence of the C-1 sulphur substituents [see (XIII).

[12] W. W. Binkley, D. R. Diehl, and R. W. Binkley, *Carbohydrate Res.*, 1971, **18**, 459, and reference cited therein.

EXPERIMENTAL

N.m.r. spectra were measured on a Perkin-Elmer–Hitachi R-20 instrument (tetramethylsilane as internal reference). All reactions were followed by t.l.c. methods. No elemental analyses were performed on syrupy products; in all cases appropriate n.m.r. spectra were used for characterisation purposes.

4,5,6-*Tri*-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose Diethyl Dithioacetal* (I).—(a) *From* 3,5,6-*tri*-O-*benzoyl*-1,2-O-*isopropylidene*-D-*glucose* (II). The isopropylidene tribenzoate (50 g) was dissolved in dry chloroform (200 ml)–ethanethiol (150 ml) and dry hydrogen chloride was passed into the solution continuously for 8 h at room temperature. T.l.c. then indicated that the reaction was complete. The solution was diluted with chloroform (200 ml), washed with saturated aqueous sodium hydrogen carbonate, and dried (Na_2SO_4). Removal of the solvents gave the tetrathio-derivative (I) (40 g, 62%) (from ethanol). Recrystallised from the same solvent it had m.p. 91·5—92·5°, $[\alpha]_D$ +0·5° (*c* 1·8 in Me_2CO) {lit.,[1] m.p. 92°, $[\alpha]_D$ −1·2° (Me_2CO)}.

2,3-*Di*-S-*ethyl*-2,3-*dithio*-D-*allose Diethyl Dithioacetal* (IV).—The tribenzoate (I) (20 g) was de-esterified with catalytic amounts of sodium methoxide in methanol; on completion of the reaction the sodium ions were removed with acid resin. The solvent was distilled off under reduced pressure and methyl benzoate was removed by co-distillation under reduced pressure with water. The *product* (10·2 g, 94%), $[\alpha]_D$ −2° (*c* 1·0 in EtOH), failed to crystallise even after preparative t.l.c. On rebenzoylation (see before) it was reconverted into the crystalline triester (I).

Methyl 5,6-*Di*-O-*acetyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-β-D-*allofuranoside* (V).—(a) *From* 2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose diethyl dithioacetal.* The triol (IV) (8·0 g) was dissolved in dry methanol (100 ml) and yellow mercury(II) oxide (10·0 g) was added, followed by a saturated solution of mercury(II) chloride (11·6 g, 2·1 mol. equiv.) in dry methanol during 0·25 h. The mixture was stirred for 1 h; t.l.c. then indicated complete conversion into a new product. The solids were removed and dry pyridine (20 ml) was added to the filtrate. Methanol was removed under reduced pressure,

N.m.r. parameters (60 MHz)

Compound	Chemical shifts (τ) H-1	H-2	H-3	H-4	H-5	H-6	Other H-thio-I protons		Coupling constants (Hz) $J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
(I) [a]	5·42(d)	6·85(q)	6·31(q)	3·59(t)	3·88(o)	4·98(q)	5·46(q)	15 Bz, 20 Et	4·5	8·5	4·8	4·8	3·0	6·0	12·5
(III) [b]	0·70(s)		3·21(d)	3·50(q)	4·20(o)	5·20(q)	5·53(q)	15 Bz, 5 Et			8·4	4·8	4·5	6·0	12·0
(V) [b]	5·13(s)	6·10(d)	6·3—6·75 [d]		4·87(sext)	6·00(q)	5·55(q)	6 Ac, 10 Et, 3 Me	<1	6·0	6·0	6·0	3·0	6·0	12·0
(VII) [a]	4·30(d)	6·93(q)	6·40(t)	5·10(q)		5·5—6·1		9 Ac, 10 Et	9·0	4·3	4·0	8·0			
(VIII) [a]	4·91(d)	6·77 / 6·52(q)	6·30(q)	3·50(t)	3·83(o)	5·02 / 4·94(q)	5·50 / 5·43(q)	15 Bz, 15 Et, 5 Ph	4·5	8·5	4·5	4·5	3·5	5·5	12·5
(IX) [b,c]	5·50(d)	6·91(q)	5·60(q)	4·20(q)	4·00(o)	5·10(q)	5·46(q)	15 Bz, 10 Et, 6 Me	7·5	3·0	9·4	2·6	3·2	7·0	12·0

[a] Solutions in deuteriochloroform. [b] Solutions in carbon tetrachloride. [c] The spectrum of a solution in deuteriochloroform was not significantly different but resolution of certain features was poorer. [d] These signals were resolved but were not specifically assigned.

(b) *From* 2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose diethyl dithioacetal* (IV). The trihydroxy-compound (IV) (0·5 g) was dissolved in dry pyridine at 0° and benzoyl chloride (0·47 ml, 3·3 mol. equiv.) was added; the mixture was left at 0° for 0·5 h and at room temperature for 24 h. Crushed ice (10 g) was added and the product crystallised (0·59 g, 64% after filtration and washing with cold ethanol). Recrystallised from ethanol it had m.p. and mixed m.p. 91·5—92·5°, $[\alpha]_D$ −1·4° (*c* 1·2 in Me_2CO); for n.m.r. spectrum see Table. Irradiation at τ 5·42 caused removal of the 4·5 Hz splitting in the quartet at τ 6·85, and irradiation at τ 3·59 removed the 4·8 Hz splitting in the quartet at τ 6·31.

4,5,6-*Tri*-O-*benzoyl*-3-*deoxy*-2-S-*ethyl*-2-*thio*-D-*erythro*-*hex*-2-*enose* (III).—The diethyl dithioacetal (I) (0·2 g) was dissolved in aqueous acetone (1 : 1; 3 ml) and was stirred with yellow mercury(II) oxide (0·2 g). Saturated aqueous mercury(II) chloride (0·16 g, 2·1 mol. equiv.) was added slowly during 15 min and the mixture was stirred for a further 2 h. Conversion into a chromatographically homogeneous product was then complete. After removal of the solids, the solution was extracted with chloroform (20 ml), and after washing and drying, the extract yielded the *aldehydo*-compound (0·12 g, 79%), $[\alpha]_D$ −38° (*c* 1·7 in EtOH) as a syrup. The n.m.r. spectrum (Table) revealed the presence of one free aldehydic proton, one vinylic proton, one *S*-ethyl group, and three benzoyl ester groups.

the residue was diluted to 40 ml with dry pyridine, and acetic anhydride (12 ml) was added at 0°. After 12 h acetylation was complete (t.l.c.); the solution was poured on crushed ice and set aside for 5 h. Hydrogen sulphide was then passed in to precipitate mercury(II) sulphide. Solids were removed and the filtrate was shaken with chloroform; the chloroform solution was extracted with dilute sulphuric acid and washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give a chromatographically homogeneous pale yellow syrupy *furanoside diacetate* (6·3 g, 77%), $[\alpha]_D$ +54° (*c* 1·6 in EtOH), which was shown to be a discrete product by n.m.r. spectroscopy (see Table).

(b) *From* 4,5,6-*tri*-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose ethyl phenyl dithioacetal* (VIII). The mixed dithioacetal (0·3 g) was debenzoylated in the usual manner and was converted into the methyl glycofuranoside derivative as described in (a) with mercury(II) oxide and mercury(II) chloride (2·1 mol. equiv.). Acetylation as before gave a syrup (0·1 g, 66%), $[\alpha]_D$ +47° (*c* 1·0 in EtOH), n.m.r. spectrum identical with that of the first sample (see Table).

2,3-*Di*-S-*ethyl*-2,3-*dithio*-β-D-*allopyranose* (VI).—(a) *From the methyl furanoside derivative* (V). The acetylated furanoside derivative (0·5 g) was deacetylated in the usual way with sodium methoxide in methanol and the product was hydrolysed at room temperature in acetone–aqueous sul-

phuric acid (N) (1 : 1; 10 ml) for 24 h. In this time the compound was converted into a main product and a small amount of a chromatographically more mobile product. The acid was neutralised with sodium hydrogen carbonate, the mixture was filtered, and the filtrate was taken to dryness under reduced pressure. Extraction of the residue with chloroform (20 ml) and drying and evaporation of the extract gave the *free sugar* (0·22 g, 60%), m.p. 116—118° [from chloroform–light petroleum (b.p. 40—60°)], $[\alpha]_D$ −27° ⟶ −0·8° (2 h, constant) [*c* 1·2 in H_2O–Me_2CO (1 : 1)] (Found: C, 44·7; H, 7·6; S, 23·8. $C_{10}H_{20}O_4S_2$ requires C, 44·7; H, 7·5; S, 23·9%).

(b) *From the dimethyl acetal derivative* (IX). The benzoylated dimethyl acetal derivative (1 g) was de-esterified in the usual manner with sodium methoxide in methanol, sodium ions were removed with acid resin, and the solvent and methyl benzoate were removed by repeated evaporation under reduced pressure in the presence of added water. The remaining syrup was dissolved in water (20 ml) and stirred with acid resin (Dowex 50W–X8; 5 g) at room temperature for 24 h; hydrolysis was then complete to give a major product and a small amount of a chromatographically more mobile product. Removal of the resin and the solvent gave a crystalline product. Recrystallisation from chloroform–light petroleum (b.p. 40—60°) gave the free sugar (0·16 g, 37%), m.p. and mixed m.p. 114—118°, $[\alpha]_D$ −23° ⟶ −2° (2 h, constant), [*c* 1·1 in H_2O–Me_2CO (1 : 1)].

1,4,6-*Tri*-O-*acetyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-β-D-*allopyranose* (VII).—The free sugar (0·1 g) was dissolved in dry pyridine (1·5 ml) at 0°, acetic anhydride (0·6 ml) was added, and the solution was kept at 0° for 12 h. Ice–water was added and after a further 5 h the solution was extracted with chloroform. The organic phase was dried and evaporated under reduced pressure in the presence of added ethanol. The *product* (0·12 g, 82%), $[\alpha]_D$ +7° (*c* 1·1 in EtOH) was homogeneous (t.l.c.), and the n.m.r. spectrum was consistent with the assigned structure (see Table) but indicated the presence of about 20% of the α-anomer (anomeric proton resonance at low field).

Irradiation of the doublet at τ 4·3 caused decoupling of the quartet at τ 6·93, which was therefore assigned to H-2. Similar irradiation of the triplet at τ 6·40 also caused collapse of the quartet at τ 6·93 and also of the quartet at τ 5·1 in agreement with expectations based on the assigned structure.

4,5,6-*Tri*-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose Ethyl Phenyl Dithioacetal* (VIII).—The dithioacetal (I) (1 g) was dissolved in dry chloroform–benzenethiol (1 : 1; 8 ml) and dry hydrogen chloride was passed through at room temperature for 1 h; t.l.c. then indicated complete conversion into a new compound. Chloroform (20 ml) was added and the solution was extracted with aqueous sodium hydroxide (2N), washed with water, dried, and taken to dryness to afford a product which crystallised on trituration with ethanol. Recrystallisation from ethanol gave the C-1 diastereoisomeric *ethyl phenyl dithioacetals* (0·85 g, 80%), m.p. 71—83°, $[\alpha]_D$ +8° (*c* 1·3 in Me_2CO) (Found: C, 63·6; H, 5·7; S, 17·3. $C_{39}H_{42}O_6S_4$ requires C, 63·8; H, 5·8; S, 17·5%); for n.m.r. data see Table; the relative intensities of the resonances indicated that the diastereoisomers were present in the approximate ratio 3 : 2.

4,5,6-*Tri*-O-*benzoyl*-2,3-*di*-S-*ethyl*-2,3-*dithio*-D-*allose Dimethyl Acetal* (IX).—(a) *From the diethyl dithioacetal* (I). The dithioacetal (I) (2 g) was dissolved in dry chloroform–methanol (1 : 2; 30 ml) and yellow mercury(II) oxide (1·4 g) and a saturated methanolic solution of mercury(II) chloride (1·6 g, 2·1 mol. equiv.) were added during 15 min. After 3 h stirring at room temperature the reaction was complete. Pyridine (5 ml) was added, the solids were removed, hydrogen sulphide was passed into the filtrate, the solids were again removed, and the new filtrate was diluted with chloroform and extracted with water. The organic phase was dried and the solvent was removed in the presence of ethanol added to facilitate distillation of the pyridine. The *dimethyl acetal* (1·47 g, 80%), $[\alpha]_D$ +29° (*c* 1 : 1 in EtOH) was shown to be pure by t.l.c. and n.m.r. spectroscopy (see Table).

(b) *From the ethyl phenyl dithioacetal* (VIII). By a similar procedure involving the use of mercury(II) chloride (2·1 mol. equiv.), the ethyl phenyl dithioacetal (VIII) (0·15 g) was converted into the dimethyl acetal (0·1 g, 76%), $[\alpha]_D$ +31° (*c* 1·2 in EtOH), n.m.r. spectrum identical with that of the acetal derived from compound (I).

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