Elimination, Oxidation, and Transposition Reactions in Conformationally Biased Carbohydrates: Methyl 4,6-*O*-Benzylidene-α-D-altropyranosides Containing the Phenylthio Group[1]

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The title compound containing a phenylthio group at C-3 and a methanesulfonate group at C-2 undergoes a quantitative transposition reaction in refluxing benzene to give the diequatorial isomer. In DMSO, a complex reaction takes place leading to elimination and oxidation at C-2. Oxidation of the title compound containing a phenylthio group at C-2, with acetic anhydride – DMSO gives the corresponding 3-uloside. With the isomeric 3-phenylthio derivative the enol acetate is formed. These results are rationalized based on mechanistic considerations.

Le composé ci-dessus nommé contenant les groupes phenylthio en C-3 et méthanesulfonate en C-2 subit une réaction de transposition quantitative par chauffage au reflux dans le benzène pour donner l'isomère diéquatorial. Dans le DMSO une réaction complexe a lieu conduisant aux composés résultant d'une élimination et d'une oxydation en position 2. L'oxydation du composé ci-dessus nommé contenant le groupe phenylthio en position 2 par le couple anhydride acétique – DMSO permet d'obtenir l'uloside-3 correspondant. Dans le cas du dérivé isomère phenlythio-3, on obtient l'acétate d'énol. L'étude du mécanisme de ces réactions permet d'interpréter les résultats obtenus.

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Introduction

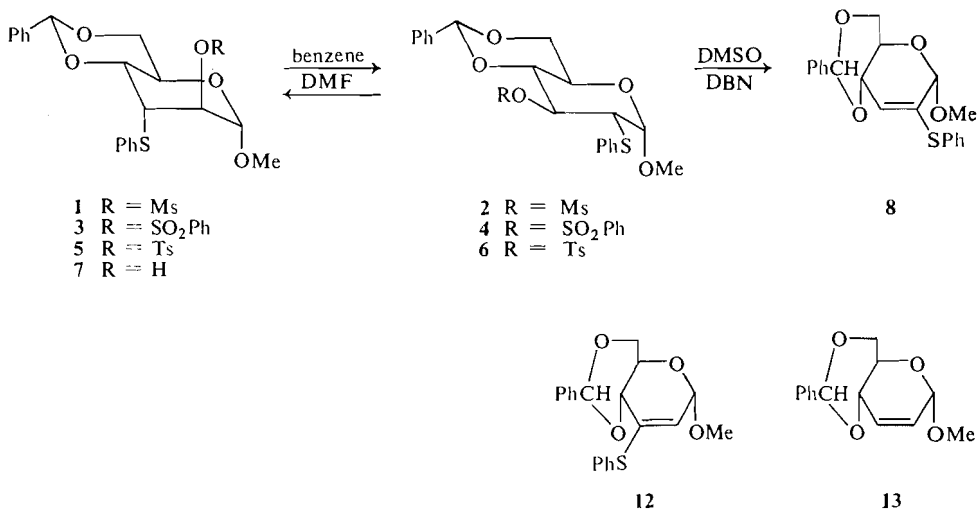
In a previous publication (1), we described the preparation of methyl 4,6-*O*-benzylidene-α-D-altropyranosides containing a phenylthio group at C-2 and -3, respectively, by the ring opening of appropriate epoxides with sodium thiophenoxide. The sulfonate esters of these compounds were found to undergo a variety of preparatively and mechanistically interesting reactions (2, 3) that seemed to depend on the location of the phenylthio and sulfonyloxy groups. Our rationale for investigating the chemistry of phenylthio ethers of polyfunctional compounds such as carbohydrates was based on the fact that the only proton α disposed to the sulfur atom was situated on the carbohydrate moiety. A primary objective was the exploration of reactions that might be triggered by the removal of a favorably disposed proton, the premise being that the sulfur atom in the phenylthio group would play an important role in stabilizing (4) incipient charged species in the transition state. Following our announced objective, we report the details of observations in the case of the conformationally and configurationally related methyl 4,6-*O*-benzylidene-2-*S*-phenyl-2-thio- and 3-*S*-phenyl-3-thio-α-D-altropyranoside sulfonates.

Results

When a solution of methyl 4,6-*O*-benzylidene-2-*O*-methanesulfonyl-3-*S*-phenyl-3-thio-α-D-altropyranoside (**1**) (1) was heated in dry benzene at reflux overnight, a new crystalline compound, isomeric with **1**, was isolated in quantitative yield. Nuclear magnetic resonance data revealed that the product was methyl 4,6-*O*-benzylidene-3-*O*-methanesulfonyl-2-*S*-phenyl-2-thio-α-D-glucopyranoside **2** (2). This assignment was corroborated by the transformation of **2** into the unsaturated derivative **8** in which the phenylthio group is situated at C-2 (*1*). The same type of transposition reaction was observed in the case of the 2-benzenesulfonate **3** and 2-*p*-toluenesulfonate **5** derivatives (Scheme 1). Under the same conditions, the configurationally related derivative **11** remained mostly unchanged.[2] In polar aprotic solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF) a reverse but partial transposition was observed with **2**, giving approximately equal amounts of **1** and **2**. A notable difference in the reactions that

[1]Part of a series on preparative and exploratory carbohydrate chemistry.

[2]Traces of elimination products are formed (1, 2).



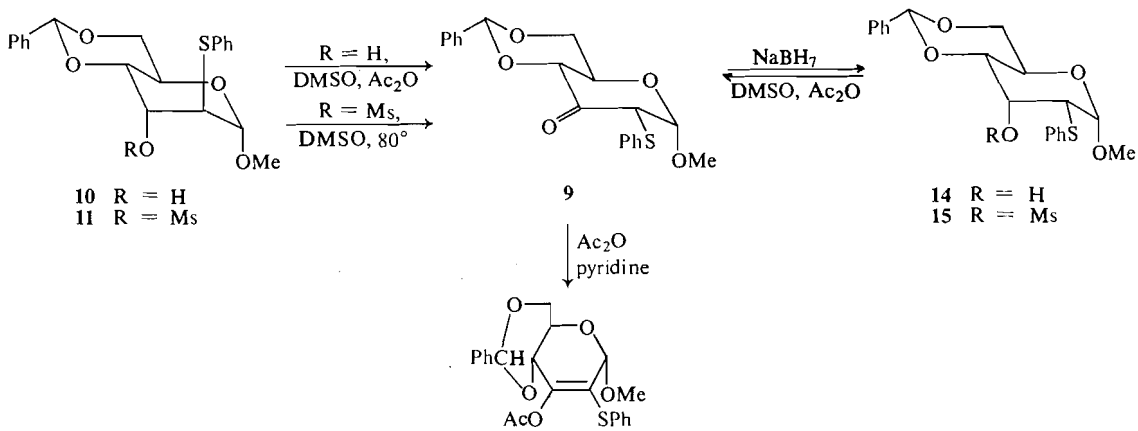
1 R = Ms
3 R = SO_2Ph
5 R = Ts
7 R = H

2 R = Ms
4 R = SO_2Ph
6 R = Ts

8

12 13

SCHEME 1



10 R = H
11 R = Ms

9

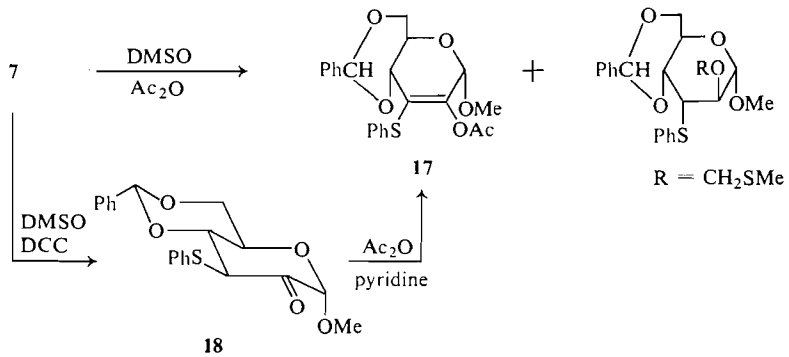
14 R = H
15 R = Ms

16

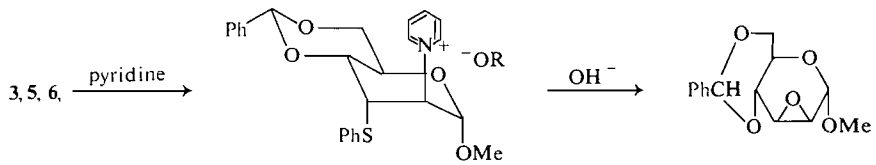
SCHEME 2

were conducted in DMSO, was the formation of a minor amount (~4%) of the 3-uloside **9**. The mechanistic significance of these results will be discussed in the following section. Heating a solution of **1** or **11** in DMSO alone (at 80°) gave the highly insoluble 3-uloside **9** in approximately 10–12% yield, in addition to the unsaturated products **8**, **12**, **13**, and a small amount of the transposed product **2** (Scheme 2). The uloside **9** was prepared independently by oxidation of methyl 4,6-*O*-benzylidene-2-*S*-phenyl-2-thio-α-D-altropyranoside **10** (1), in DMSO containing acetic anhydride. An excellent yield of the highly insoluble **9** was thus obtained. Reduction of **9** with sodium borohydride in a mixture of methanol and DMF gave the D-allo derivative **14**, as indicated by n.m.r. data. Oxidation of **14** with DMSO – acetic anhydride gave back the uloside **9**, thus confirming the epimerization at C-2 in the original oxidized product. Treatment of the uloside **9** with acetic anhydride in pyridine gave an 86% yield of the crystalline enol acetate derivative **16**.

When the 3-phenylthio derivative **7** was oxidized by the same procedure as described above, the major product was the enol acetate derivative **17**. A minor amount of the 2-methylthiomethyl ether was also formed. Oxidation of **7** to the



SCHEME 3



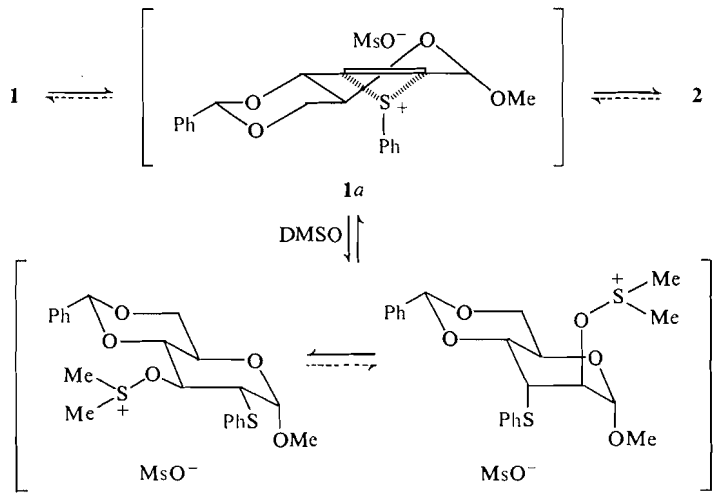
SCHEME 4

desired ketone was accomplished with the Pfitzner–Moffatt procedure (5) and a crude product corresponding to **18** was isolated in 71% yield. Treatment of the latter with acetic anhydride in pyridine effected a smooth transformation into the enol acetate **17**, in 87% yield (Scheme 3).

In an extension of our transposition studies, the tosylate and benzenesulfonates **5** and **3**, respectively, were heated in anhydrous pyridine. The products in both cases were the crystalline methyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-pyridinium-3-*S*-phenyl-3-thio-α-D-altropyranoside sulfonates **19** and **20**, respectively (Scheme 4). Formation of **19** was also observed when the diequatorial phenylthio tosylate **6** was heated in pyridine. Treatment of **19** with aqueous sodium benzoate or with sodium azide in methylcellosolve, at room temperature or at 80° gave unchanged starting material. However, in aqueous sodium hydroxide, or in aqueous sodium azide at 70°, a crystalline product was obtained in 90% yield that was identified as methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside **21** (6).

Discussion

The transformations of the sulfonate derivatives **1**, **3**, and **5** into their isomeric analogs **2**, **4**, and **6** involve double transposition of phenylthio and sulfonate groups with concomitant configurational inversion at the respective ring carbon atoms. While the intervention of 2,3-episulfonium ions is evident, the nature of the products seems to depend on the polarity of the solvent. In benzene, the reaction proceeds, in all probability, via a tight ion pair in which there is minimum separation of charged species and the product is the thermodynamically more stable diequatorial isomer. In such a diaxial–diequatorial rearrangement, steric decompression between the axial C-1 methoxyl and C-3 phenylthio group is an important driving force (Scheme 5). Although well known (7), the diaxial–diequatorial rearrangement has few precedents involving the phenylthio group (8, 9) and none, to our knowledge, in which the departing anionic species is a group of low nucleophilicity, such as alkyl and aryl sulfonates, and the assisting group is phenylthio. These results are of particular preparative significance since the rearrangement provides access to a selective and predetermined substitution pattern in the transposed products, which now comprise a vicinal diequatorial arrangement of substituents. Because of inherent structural and electronic properties, the participating ability of the sulfur atom in the phenylthio group is somewhat



SCHEME 5

curtailed when compared to alkylthio and benzylthio analogs (10). The significance of this comparison can be appreciated if it is recalled that mesylation or tosylation of vicinally disposed alkylthio and alcohol groups frequently leads to the corresponding chlorides, rather than the sulfonates, as a result of the intervention of episulfonium ions and subsequent attack by chloride ion (11). The phenylthio group offers the advantage of having a sulfur atom that is of reduced nucleophilicity under normal conditions, allowing such reactions as sulfonylation to take place; yet, its participating ability can be called into play in polar solvents, or in nonpolar solvents, but at moderately elevated temperatures. The partial transposition of groups from the stable diequatorial, to the diaxial orientation in polar solvents such as DMSO and DMF denotes a certain separation of charges rendering the return to diequatorial orientation not as favored a pathway as in benzene. The intervention of DMSO as a competing nucleophile in these reactions seems evident in the formation of the uloside **9** from **1**, **2**, or **11**. The episulfonium ion, common to all three, can be attacked by the solvent to give two possible oxydimethylsulfonium ions (Scheme 5), that have the necessary structural features for oxidation to **9** by the generally accepted ylid pathway (5). The absence of the uloside **18** in these reactions demonstrates a certain preference for the equatorial oxydimethylsulfonium ion intermediate (Scheme 5). In view of the favorable dispositions of the phenylthio group for episulfonium ion formation in **1**, **2**, and **11**, a direct displacement of the 3-methanesulfonate group by DMSO can be excluded. In support of the above suggested intervention by the solvent as a reactant, it is of interest that no ulosides were formed when DMF was the solvent. The major product (~50%) was the diequatorial derivative **2**.

The formation of the unsaturated compounds **8** and **12** by the treatment of appropriate sulfonate esters with bases or by heating in aprotic solvents alone, represents an interesting example of *syn*-elimination (12–14). To the best of our knowledge, there are no precedents to this type of elimination reaction with *trans* vicinally-oriented phenylthio and sulfonate groups. Base-catalyzed eliminations are well known in the corresponding sulfones in the cyclohexane series (12, 15). Although the precise mechanism of *syn*-eliminations (concerted or carbanionic) is not known with certainty (13) it would appear that the acquisition of carbanionic character of the C-2 and -3 ring carbon atoms bearing the phenylthio group in the respective derivatives would be favored in the transition state of these elimination reactions. Attempts to incorporate a deuterium atom on the ring carbon atom α to the phenylthio group in the elimination of **11** were not successful. This is not surprising, since it is known that elimination in such cases can proceed at much faster rates than incorporation of deuterium (15, 16).

Alternatively, it is interesting to speculate that the unsaturated compounds arise, in part, from a common episulfonium ion intermediate such as **1***a* (Scheme 5). For example, the formation of **8**, among other products, in the DMSO-mediated elimination reaction of **1**, necessitates a pre-

liminary rearrangement to **2** followed by a *syn*-elimination, or an abstraction of a proton at the episulfonium ion stage. The unexpected formation of **13** from **11** during base treatment in DMSO, could be explained on the basis of a seemingly favored extrusion of the phenylthio group from an intermediate such as **1***a* or a concerted-type elimination of the mesyloxy and phenylthio groups. The latter possibility is reminiscent of the formation of olefins in the base-catalyzed eliminations of aliphatic phenylthio ethers (17*a*), and in the formation of unsaturated compounds from episulfonium ions (17*b*).

Irrespective of the actual mechanistic pathway (s), it appears that the underlying reasons for the different behavior of **1** relative to the configurationally related **11** in these and other reactions (1), are steric in nature. A projection along the C_2—C_3 bond in both derivatives reveals a severe interaction between the diaxial substituents at C-1 and -3 in **1**, which is presumably relieved in the transposed product **2** or the unsaturated products **12** and **13**. The same factors can be operative in the case of **11** insofar as some elimination reactions are concerned, steric relief being derived from loss of the axial mesyloxy group. The formation of unsaturated derivatives may also depend on the relative acidities of the protons situated on C-2 and -3 in **11** and **1**, respectively, in the presence of bases.

The regiospecific formation of the 2-pyridinium salts **19** and **20** follows other well-established patterns of ring-opening reactions in the analogous episulfonium ions (10). It was hoped that these salts would lend themselves to nucleophilic displacement reactions via 2,3-episulfonium ions, much the same way as they were formed, in the presence of pyridine as a nucleophile. The insolubility of these salts, even in aprotic solvents, precluded such a study. The unexpected formation of the epoxide **21** in the presence of aqueous sodium azide or aqueous base is reminiscent of the formation of **21** in the attempted methylation of **7** with methyl iodide and silver oxide (1). Although the two reactions are unrelated insofar as the reagents are concerned, it appears that the phenylthio group is somehow activated and is lost by intramolecular attack by an hydroxyl group at C-2. It is of interest that the displacement of an equatorially disposed pyridinium group in a compound related to **19**, but containing an oximino group at C-3 instead of the phenylthio group, could be effected with sodium benzoate in DMF at room temperature (18).

The transformations of **10** and **11** into **9** with DMSO–Ac_2O and DMSO, respectively, are accompanied by an epimerization at C-2. The same process takes place during the oxidation of **7** into **18** with DMSO–DCC. The corresponding enolic forms are therefore protonated from the least hindered β-side, so as to give the thermodynamically more stable equatorial epimers.

Epimerization has also been observed in the oxidation of other carbohydrate derivatives containing an axially-oriented azide or amide function, vicinal to an alcohol group (21, 22). The formation of an enol acetate in the oxidation of **7**, but not of **10**, with DMSO–Ac_2O can be rationalized on the basis of a more favorable stereoelectronic protonation (19, 20) of the enol **A** compared to that of enol **B**, in which the approach of the proton from the "α"- side is hindered (Scheme 6). The latter is consequently trapped as the enol acetate **17**. In the presence of acetic anhydride and pyridine, the enols derived from **9** and **18**, respectively, are much more susceptible to acetylation compared to the same process in DMSO as solvent, where the effective concentration of hydrogen ions is greater.

Experimental

General

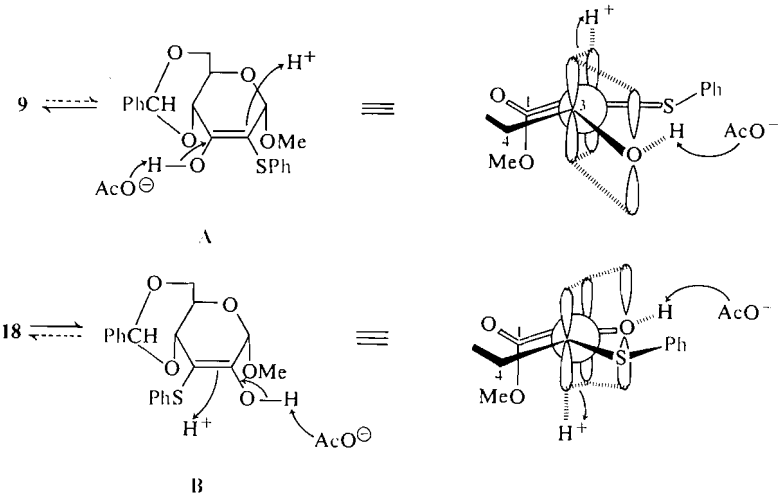
Melting points are uncorrected. Nuclear magnetic resonance spectra were recorded for solutions in chloroform-*d* (unless otherwise stated) at 60 or 100 MHz, with tetramethylsilane as the internal standard. Infrared spectra were recorded with a Beckman IR-8 spectrometer. Optical rotation were measured with a Perkin-Elmer Model 141 automatic polarimeter. Thin-layer chromatography (t.l.c.) was performed with plates coated with silica gel GF_{254} and the spots were detected with a sulfuric acid spray and with the acidic ammonium molybdate spray (23). Conventional processing or processing in the usual manner signifies drying organic solutions with anhydrous sodium sulfate, filtration and evaporation of the filtrate under diminished pressure.

Methyl 4,6-O-Benzylidene-3-O-methylsulfonyl-2-S-phenyl-2-thio-α-D-glucopyranoside (2)

A solution of **1**, m.p. 101–102° (1.137 g, 2.5 mmol), in 25 ml of dry benzene was heated under reflux for 18 h. Removal of the solvent afforded 1.10 g (99%) of the title compound, which could be distinguished from **1** by t.l.c. ($CHCl_3$–2,2,4-trimethylpentane–MeOH, 10:5:0.6). Recrystallization from absolute ethanol gave an analytical sample, m.p. 142–143°; $[\alpha]_D^{25}$ −66.4° (*c*, 1.78 $CHCl_3$); n.m.r.: 5.51 (s, C*H*Ph), 5.07 (dd, $J_{3,2}$ = 10.6 Hz; $J_{3,4}$ = 9.4 Hz, H-3), 4.91 (d, $J_{1,2}$ = 3.1 Hz, H-1), 5.41 (s, OCH_3), 5.28 (q, $J_{2,3}$ = 10.6 Hz; $J_{2,1}$ = 3.1 Hz, H-2), 2.89 p.p.m. (s, OSO_2CH_3) etc.

Anal. Calcd. for $C_{21}H_{24}O_7S_2$: C, 55.73; H, 5.34; S, 14.17. Found: C, 55.40; H, 5.62; S, 13.87.

Treatment of **2** with 1,5-diazabicyclo[5.3.0]nonene (24) in DMSO at 80° gave the known crystalline **8** (m.p. and



SCHEME 6

mixture m.p.) (1). When a solution of **2** (0.1 g, 0.21 mmol) was heated in 3 ml of DMSO at 80° during 24 h, a 1:1 mixture of **1** and **2** resulted. Separation by preparative t.l.c. gave 40 mg of **1** (m.p. and mixture m.p.). A small amount (4.1%) of the uloside **9**, as well as traces of the unsaturated derivatives **8**, **12**, and **13** were also formed. When the reaction was done in DMF, a 1:1 mixture of **1** and **2** (80%) was formed, as well as traces of **8**, **12**, and **13**, which were isolated and characterized. When **1** was heated in DMF (75°; 12 h), the major product was **2** (~50%).

Methyl 2-O-Benzenesulfonyl-4,6-O-benzylidene-3-S-phenyl-3-thio-α-D-altropyranoside (3)

To a solution of **7** (3.74 g, 10 mmol) in 15 ml of pyridine were added 3.6 ml (5.3 g, 30 mmol) of benzenesulfonyl chloride with cooling and stirring. After stirring at room temperature overnight, the solution was poured into ice water, the precipitate was filtered, washed and dried to give the title compound (4.2 g, 81%). Thin-layer chromatography ($CHCl_3$–2,2,4-trimethylpentane–MeOH, 10:5:1) indicated a slight contamination with the transposed product **4**. Recrystallization in ether–dichloromethane gave 3.9 g (75% of pure product, m.p. 114–115° (dec.); $[\alpha]_D^{25}$ +10.50 (*c*, 2.01 $CHCl_3$).

Anal. Calcd. for $C_{20}H_{26}O_7S_2$: S, 12.46. Found: 12.46.

Methyl 3-O-Benzenesulfonyl-4,6-O-benzylidene-2-S-phenyl-2-thio-α-D-glucopyranoside (4)

A solution containing 0.3 g (0.583 mmol) of **3**, m.p. 114–115°, in 5 ml of benzene was refluxed for 2 days. Evaporation of the solvent gave 0.298 g (99%) of the transposed product **4**, which was recrystallized from hot methanol, m.p. 120–121° (dec.); $[\alpha]_D^{25}$ −77.33° (*c*, 1.31 $CHCl_3$).

Anal. Calcd. for $C_{26}H_{26}O_7S_2$: C, 60.68; H, 5.09; S, 12.46. Found: C, 60.44; H, 5.13; S, 12.61.

Methyl 4,6-O-Benzylidene-2-S-phenyl-2-thio-α-D-ribo-hexopyranoside-3-ulose (9)

To a solution of **10** (1.55 g, 3.09 mmol) (1) in 4 ml of DMSO was slowly added 3 ml of acetic anhydride. After stirring at room temperature for 12 h, the thick slurry was poured into ice water (30 ml) and the pale-yellow solid was filtered, washed well with water, then with warm hexane. The highly insoluble colorless product (**9**) (1.06 g, 92%) was analytically pure, m.p. 204–205° (dec.); λ_{max}^{KBr} 1735 cm^{-1} (C=O).

Anal. Calcd. for $C_{20}H_{20}O_5S$: C, 64.50; H, 5.41; S, 8.61. Found: C, 64.30; H, 5.38; S, 8.60.

Methyl 3-Acetoxy-4,6-O-benzylidene-2-S-phenyl-2-thio-α-D-erythro-hex-2-enopyranoside (16)

Acetic anhydride (1.8 ml) was added to a cold suspension of **9** (0.575 g, 1.54 mmol) in 6 ml of pyridine. The suspension became homogeneous after 6 h and after stirring for a total of 24 h, the solution was poured into ice water, the crystalline product was filtered and washed with water to give the title compound (0.55 g, 86%). Recrystallization from hot ethanol gave an analytical sample, m.p. 113–114°; $[\alpha]_D^{25}$ −89.3° (*c*, 2.30 chloroform); λ_{max}^{KBr} 1760 cm^{-1} (enol acetate); n.m.r.: 5.55 (s, CHPh), 4.74 (s, H-1), 3.50 (s, OCH_3), 2.11 p.p.m. (s, $OCOCH_3$), etc.

Anal. Calcd. for $C_{22}H_{22}O_6S$: C, 63.75; H, 5.35; S, 7.73. Found: C, 63.59; H, 5.18; S, 7.73.

Methyl 4,6-O-Benzylidene-2-S-phenyl-2-thio-α-D-allopyranoside (14)

A suspension of **9** (2.232 g, 6 mmol) in 300 ml of methanol and 5 ml of DMF was treated with sodium borohydride (3 g) over a period of 15 min. After stirring for 1.5 h, the solution was evaporated to dryness, the solid residue was partitioned between 200 ml of chloroform and 200 ml of water, and the organic phase was processed in the usual manner to give the title compound as colorless crystals (2.01 g, 92%). Recrystallization from hot ethanol gave an analytical sample, m.p. 167–169°; $[\alpha]_D^{25}$ −47.9° (*c*, 2.17 chloroform); λ_{max}^{KBr} 3480 cm^{-1} (hydroxyl); n.m.r.: 5.51 (s, C*H*Ph), 4.85 (d, $J_{1,2}$ = 3.75 Hz, H-1), 3.50 p.p.m. (s, OCH_3), etc.

Anal. Calcd. for $C_{20}H_{22}O_5S$: C, 64.15; H, 5.92; S, 8.56. Found: C, 64.17; H, 5.74; S, 8.44.

Oxidation of **14** with acetic anhydride in DMSO gave the ulose derivative **9**, in 57% yield (m.p., mixture m.p., i.r.).

*Methyl 4,6-O-Benzylidene-3-O-methylsulfonyl-2-S-phenyl-2-thio-α-D-allopyranoside (**15**)*

To a stirred solution containing **14** (0.117 g, 0.31 mmol) in 2 ml of anhydrous pyridine, was slowly added 0.08 ml (1 mmol) of methanesulfonyl chloride with cooling. After standing 36 h at 5°, the solution was poured into ice water and the resulting crystalline product was recovered by filtration. The solid was washed with aqueous sodium bicarbonate, then with water and dried to give the title compound (0.115 g, 82%), m.p. 76–78°. Recrystallization from ethanol gave material having, m.p. 77–78°; $[\alpha]_D^{25}$ −79.1° (*c*, 0.32 chloroform); n.m.r.: 5.52 (s, C*H*Ph), 5.19 (t, $J_{3,2} = J_{3,4} = 3$ Hz; H-3), 4.91 (d, $J_{1,2} = 3.75$ Hz, H-1), 3.42 (s, OCH_3), 3.35 (dd, $J_{2,1} = 3.75$ Hz, $J_{2,3} = 3$ Hz, H-2), 3.03 p.p.m. (s, OSO_2CH_3), etc.

Anal. Calcd. for $C_{21}H_{24}O_7S_2$: C, 55.73; H, 5.34; S, 14.17. Found: C, 55.74; H, 5.30; S, 14.27.

Treatment of **15** with 1,5-diazabicyclo[5.3.0]nonene (DBN) in DMSO gave the known (1) crystalline **8** (m.p. and mixture m.p.).

*Methyl 4,6-O-Benzylidene-3-S-phenyl-3-thio-α-D-arakinopyranoside-2-ulose (**18**)*

A solution of 7 (0.374 g, 1 mmol) (1) in a mixture of DMSO (1.5 ml) and anhydrous benzene (1.5 ml) was treated sequentially with 0.08 ml (1 mmol) of trifluoroacetic acid and 0.62 g (3 mmol) of *N,N*-dicyclohexylcarbodiimide. After stirring at room temperature for 24 h, the solution was diluted with ether (25 ml), washed with aqueous sodium bicarbonate and the organic phase was processed as usual to give a syrup that crystallized after trituration with cold ether; yield (0.268 g, 71%) of crude **18**, homogeneous on t.l.c. (chloroform–2,2,4-trimethylpentane–methanol, 30:15:0:3).

*Methyl 2-Acetoxy-4,6-O-benzylidene-3-S-phenyl-3-thio-α-D-erythro-hex-2-enopyranoside (**17**)*

A. From (7).

A solution containing 0.5 g (1.33 mmol) of 7 in 3 ml of DMSO was treated with 2 ml of acetic anhydride. After stirring at room temperature for 24 h, the solution was poured into ice water, and processing was continued by extraction with ether. Evaporation of the organic phase gave the title compound (0.410 g) contaminated with a small amount of the 2-methylthiomethyl ether derivative of 7. The crystalline mixture was separated by preparative t.l.c. (benzene – ethyl acetate, 15:1) to give the pure product **17**, m.p. 121.5–122.5°; $[\alpha]_D^{25}$ +45.3° (*c*, 2.35 chloroform); λ_{max}^{KBr} 1755 cm^{-1} (enol acetate); n.m.r.: 5.52 (s, H-1), 5.38 (s, C*H*Ph), 3.38 (s, OCH_3), 2.05 p.p.m. (s, $OCOCH_3$), etc.

Anal. Calcd. for $C_{22}H_{22}O_6S$: C, 63.75; H, 5.35; S, 7.73. Found: C, 63.48; H, 5.68; S, 7.69.

B. From (**18**).

Treatment of a solution of **18** (0.134 g, 0.34 mmol) in pyridine with acetic anhydride and processing as for compound **16** gave 0.112 (87%) of crystalline **17** (m.p. and mixture m.p.).

*Methyl 4,6-O-Benzylidene-2-deoxy-3-S-phenyl-2-N-pyridinium-3-thio-α-D-altropyranoside p-Toluenesulfonate (**19**)*

A solution of methyl 4,6-*O*-benzylidene-3-*S*-phenyl-3-thio-2-*O*-*p*-toluenesulfonyl-α-D-altropyranoside **5** (0.2 g, 0.38 mmol) (25) in 5 ml of anhydrous pyridine was heated with stirring at 80–90° for 24 h, whereupon a crystalline product had separated out of solution. Filtration and recrystallization from boiling methanol gave the title compound in the form of needles (0.15 g), m.p. 225° (dec.); $[\alpha]_D^{25}$ −23.77° (*c*, 0.53 MeOH).

Anal. Calcd. for $C_{32}H_{33}O_7S_2N$: C, 63.24; H, 5.47; S, 10.55; N, 2.30. Found: C, 63.49; H, 5.36; S, 10.88; N, 2.13.

Similar treatment of the 3-toluenesulfonate **6** and the 2-benzenesulfonate **4** gave the respective 2-pyridinium salts **19** (92%) and **20** (87%), m.p. 240° (dec.); $[\alpha]_D^{25}$ −24.24 (*c*, 0.66 MeOH).

Anal. Calcd. for $C_{31}H_{31}O_7S_2N$: C, 62.82; H, 5.10; S, 10.82; H, 2.36. Found: 62.49; H, 5.36; S, 10.88; N, 2.13.

*Treatment of Methyl 4,6-O-Benzylidene-2-deoxy-3-S-phenyl-2-N-pyridinium-3-thio-α-D-altropyranoside p-Toluenesulfonate **19** with Aqueous Sodium Azide*

A solution containing the title compound (60 mg, 0.1 mmol) and sodium azide (33 mg, 0.5 mmol) in 2 ml of water was heated at 70° overnight. The crystalline precipitate that resulted was filtered, washed with water, and dried to give 25 mg (90%) of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**21**) m.p. and mixture m.p. 144°. The product was identical (i.r., n.m.r., t.l.c.) to an authentic sample.

The same results were obtained in 0.1 *N* sodium hydroxide (25°; 12 h).

Treatment of **19** with aqueous sodium benzoate, sodium azide in methanol or in methylcellosolve (80°) gave unchanged starting material.

*Treatment of Methyl 4,6-O-Benzylidene-2-O-methanesulfonyl-3-S-phenyl-3-thio-α-D-altropyranoside **1** and the Isomeric **11** with Dimethyl Sulfoxide*

A solution of **1** (0.18 g, 0.4 mmol) in 5 ml of DMSO was heated at 80° until the disappearance (t.l.c.) of starting material (*ca.* 3.5 h). The solution was poured into 30 ml of ice water and the solution was extracted with chloroform and processed in the usual manner to give a syrup. Trituration with 95% ethanol gave crystalline **9** (10 mg, 10%); m.p. and mixture m.p. 203–204°. The mother liquors consisted of a complex mixture of products containing four major products, (t.l.c.), **8, 2, 12, 13.**

Treatment of the isomeric **11** under the same conditions gave the uloside **9** in 12% yield. The mother liquors consisted of the same mixture of products as above.

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