Reductive cleavage with metal in liquid ammonia. III. Olefin formation from the reaction of sodium metal with methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside dissolved in 1,2-dimethoxyethane[1]

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Methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside, when heated in refluxing 1,2-dimethoxyethane with an equimolar quantity of metallic sodium, gave approximately a 75% yield of a mixture of the three olefins, methyl 2,3-didehydro-3-deoxy-4,6-*O*-ethylidene-*S*-methyl-2-thio-α-D-altropyranoside (XI), 1,2-didehydro-1-deoxy-4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-D-*ribo*-hexopyranose (XII), and methyl 3,4-didehydro-3-deoxy-4,6-*O*-ethylidene-*S*-methyl-2-thio-α-D-*erythro*(or *threo*)-hexopyranoside (XIII) (tentative). Only compounds XI and XII could be separated and characterized. The structural assignments were based on a comparison with authentic samples and on nuclear magnetic resonance and infrared data, as well as on a comparison with the characteristics of analogous 4,6-*O*-benzylidene compounds previously reported (2).

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INTRODUCTION

It has been shown recently that the reaction of metallic sodium with methyl *S*-benzyl-4,6-*O*-benzylidene-2-thio-α-D-altropyranoside (I, R = H, R′ = $C_6H_5CH_2$) (Scheme 1) in the mixed solvent liquid ammonia–1,2-dimethoxyethane results in selective cleavage of the C—S bond, yielding the mercaptan II (R = H) (1). Under the same conditions, with I (R = CH_3, R′ = $C_6H_5CH_2$ or CH_3), the course of the reaction was altered drastically, yielding, by elimination of methyl alcohol, olefins III and IV (R′ = $C_6H_5CH_2$ or CH_3) (2). Under the alkaline conditions, a portion of III is isomerized to the 3,4-olefin V (R′ = $C_6H_5CH_2$ or CH_3). The same conversion of I (R = CH_3, R′ = $C_6H_5CH_2$ or CH_3) into olefins III–V is accomplished by refluxing a solution of I in 1,2-dimethoxyethane containing either metallic sodium or potassium or a base such as sodium methoxide or potassium hydroxide. On the other hand, treatment of I (R = CH_3, R′ = $C_6H_5CH_2$) with metallic sodium in liquid ammonia gave a high yield of the completely reduced substance VI (R = CH_3) (2).

As part of a study of this reaction we have applied certain of the above conditions to methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (X). This paper describes the results obtained.

RESULTS AND DISCUSSION

The reaction of sodium methyl mercaptide with methyl 2,3-anhydro-4,6-*O*-ethylidene-α-D-allopyranoside (VII) gave a 96% yield of methyl 4,6-*O*-ethylidene-*S*-methyl-2-thio-α-D-altropyranoside (VIII), along with a small amount (3.3%) of its isomer, methyl 4,6-*O*-ethylidene-*S*-methyl-3-thio-α-D-glucopyranoside (IX) (Scheme 2), both obtained as crystalline solids. The structural assignments are based on the identical elemental analyses of the two compounds VIII and IX and on the well-known mode of opening of the epoxide ring by nucleophilic agents, giving as the major product that compound arising from *trans*-diaxial ring opening (3–6). Support was also obtained from similar findings for the analogous 4,6-*O*-benzylidene analogue (2).

To corroborate the assignment of the configuration of X and, therefore, of VIII, the analogous methyl 4,6-*O*-benzylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (I,

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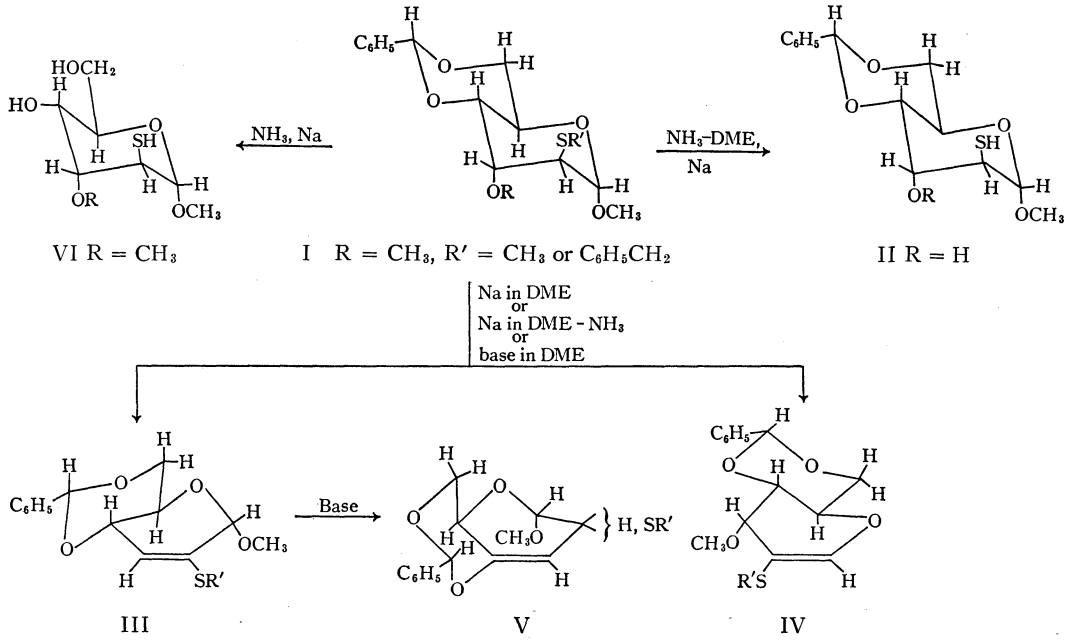


SCHEME 1. DME = 1,2-dimethoxyethane.

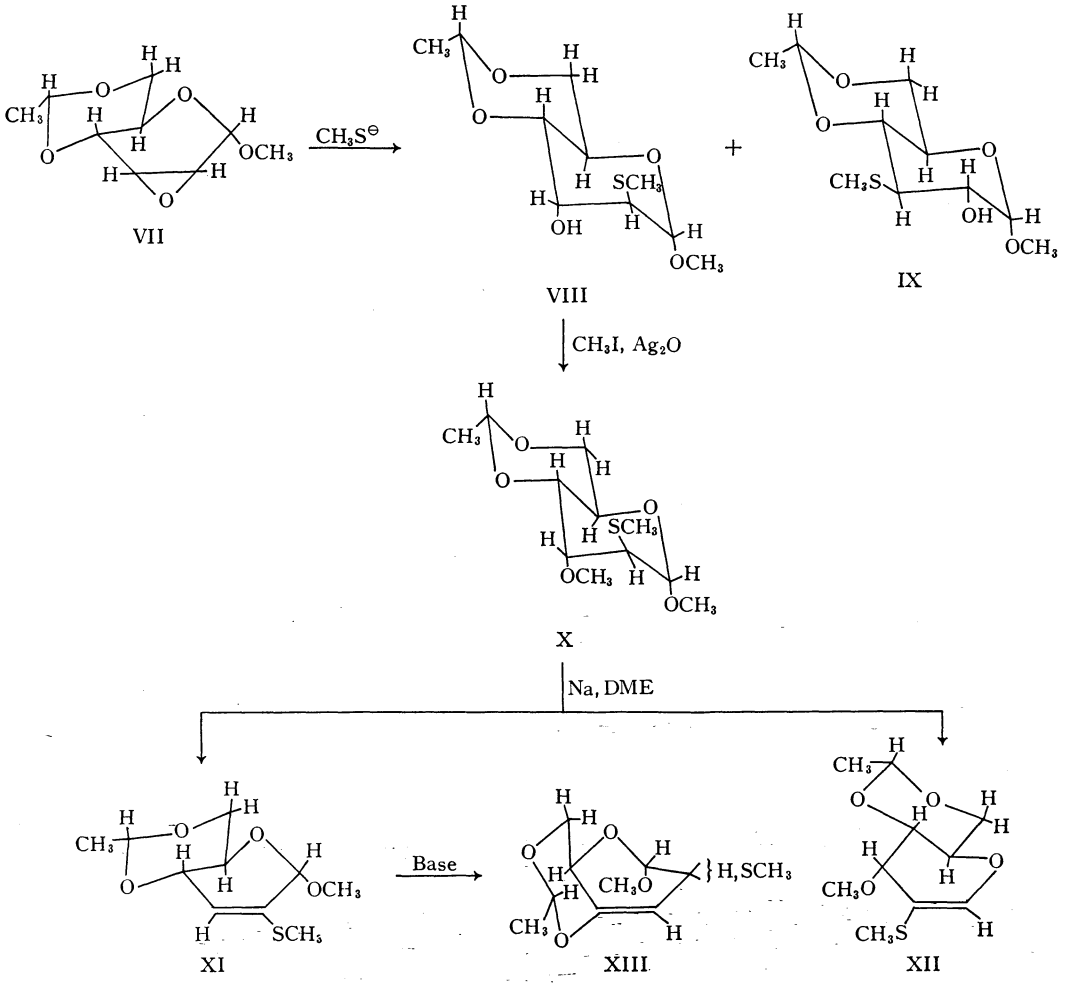
R = R′ = CH_3) (Scheme 1) was treated with 1,1-dimethoxyethane in the presence of some concentrated sulfuric acid to effect a *trans* acetalation to the 4,6-*O*-ethylidene compound (Scheme 3). The *trans* acetalation did occur[4] completely, as shown by the absence, in the nuclear magnetic resonance (n.m.r.) spectrum of the product, of aromatic proton signals in the region τ 2.5–3.5 and by the appearance of a quartet centered at τ 5.2 (J = 5 c.p.s.) characteristic of the 4,6-*O*-ethylidene group. The resulting product was a syrupy mixture containing the α and β anomers (as shown by the n.m.r. spectrum) which, when allowed to stand, deposited a 25% yield of the crystalline β anomer (m.p. 79–80°, $[\alpha]_D^{25}$ −60.8°). The same compound (β anomer) was obtained in a 35% yield when X (methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside, m.p. 56–57°, $[\alpha]_D^{25}$ +75°) was treated with 1,1-dimethoxyethane in the presence of sulfuric acid.

The same β anomer was also prepared by treating methyl 2,3-anhydro-4,6-*O*-ethylidene-β-D-allopyranoside (7) with sodium methylmercaptide to obtain methyl 4,6-*O*-ethylidene-*S*-methyl-2-thio-β-D-altropyranoside (Scheme 3). Methylation with sodium hydride – methyl iodide in 1,2-dimethoxyethane (8) gave methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-β-D-altropyranoside, m.p. 79–80°, $[\alpha]_D^{25}$ −62.2°.

That anomerization of the α isomer occurred quite readily in the 2-thio compound is due, no doubt, to the *trans* stereochemistry of the substituents on carbon atoms 1 and 2, permitting participation of the methylthio group, via an episulfonium intermediate, in facilitating the breaking of the *trans* C_1—OCH_3 bond. This participation does not occur in the β anomer; hence it will accumulate.

We have not corroborated the structure of what we assume to be the isomer methyl 4,6-*O*-ethylidene-*S*-methyl-3-thio-α-D-glucopyranoside (IX). However, from the results obtained for the 4,6-*O*-benzylidene analogue

[4]The *trans* acetalation from methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (I, R = R′ = CH_3) (Scheme 1) to methyl 4,6-*O*-benzylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside did not occur, since no incorporation of the aromatic nucleus was found in the crude product, as shown by the n.m.r. spectrum.

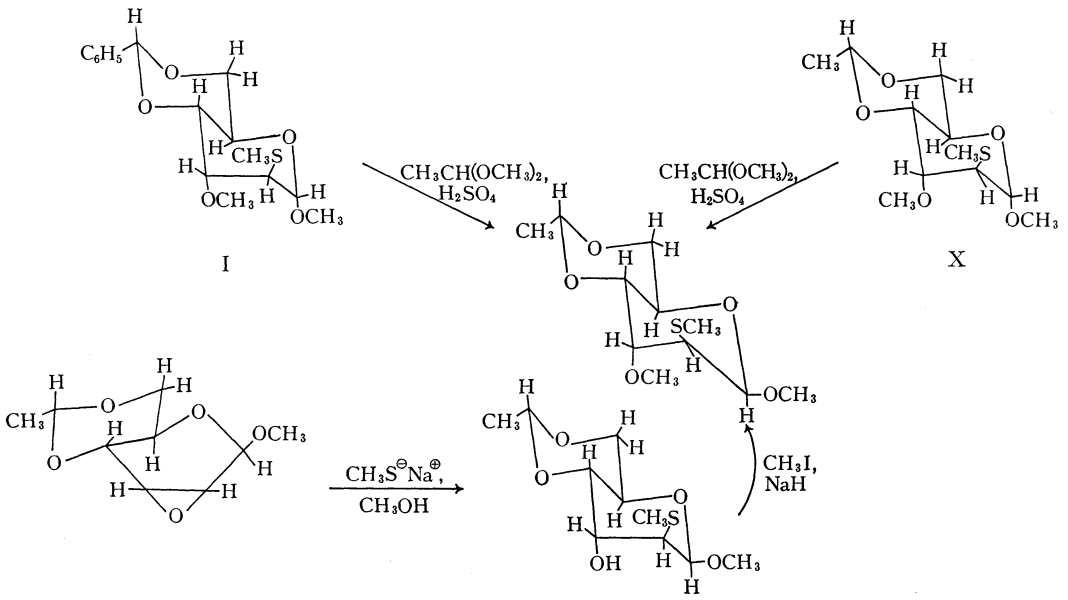


SCHEME 2. DME = 1,2-dimethoxyethane.

(2), we believe the structure to be as indicated.

When a mixture of methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (X) and an equimolar amount of metallic sodium was heated in refluxing 1,2-dimethoxyethane (previously dried and distilled from potassium), a solid was obtained in a 78% yield. This was shown by gas–liquid chromatography to be a mixture of apparently five components. The bulk of it (90%) was composed of the olefins XI–XIII (see Scheme 2). The gas–liquid chromatographic spectrum showed a well-resolved peak for XII, but XI and XIII had nearly the same retention time. The remaining 10% of the product (three peaks in the spectrum) consisted of starting material and two compounds which had lost the methylthio group but possessed vinylic protons. Difficulties with their isolation prevented a further investigation of these latter substances.

A solution of the solid (obtained in a 78% yield) in pentane deposited crystalline XI in a 42% yield. Chromatogrpahy of the residue on neutral alumina gave XII in a 17% yield. All attempts to separate XIII from the rest of the residue failed, although evidence for its presence was obtained from the infrared spectra as well as the n.m.r. spectra. That XIII arises from the isom-



SCHEME 3.

erization of XI (2) was shown by heating the latter in 1,2-dimethoxyethane with dry, powdered potassium hydroxide for 5 h. The n.m.r. and infrared spectra of the resulting product showed signals and absorption bands characteristic of both XI and what is believed to be XIII. The configuration about carbon atom 2 is not certain, but it is likely that XIII is actually a mixture of the *erythro* and *threo* isomers (2). This point is under investigation.

Scheme 4 shows a comparison of the characteristic n.m.r. and infrared absorption peaks for compounds XI–XIII of this work with those for the analogous 4,6-*O*-benzylidene compounds IX*a*, X*a*, and XI*a* described in ref. 2. The close similarity of these data supports the assignments of structures in the present work.

Table I contains the analytical, n.m.r., and infrared data characteristic of compounds X–XIII.

EXPERIMENTAL

All melting points are uncorrected.

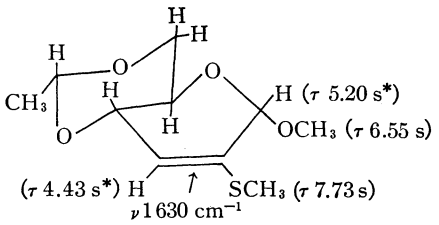
Rotations were determined with a Rudolph polarimeter, model 80. Elemental analyses were performed by Dr. C. Daesslé, Organic Microanalysis, 5757 Decelles Avenue, Montreal, and by Miss Darlene Roberts, Department of Chemistry, University of Alberta, Edmonton. Nuclear magnetic resonance spectra were obtained with a Varian Associates A-60 instrument. Infrared spectra were obtained with a Perkin–Elmer model 337 grating Infracord and a Perkin–Elmer model 421 grating spectrophotometer.

1,2-Dimethoxyethane, of commercial reagent grade, was dried with potassium metal and distilled from potassium.

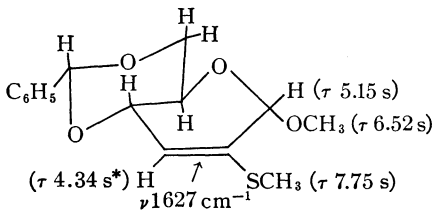
Methyl 4,6-O-Ethylidene-2,3-di-O-p-toluenesulfonyl-α-D-glucopyranoside

The following modifications of a published procedure (9) gave much better yields.

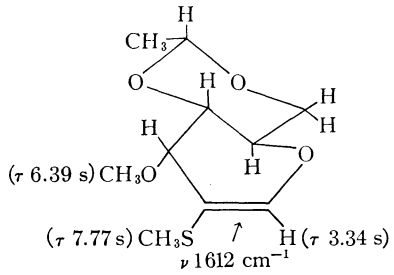
To a solution of 77 g (0.35 mole) of crude methyl 4,6-*O*-ethylidene-α-D-glucopyranoside (9) (obtained from 65 g of methyl α-D-glucopyranoside) in 450 ml of dry pyridine at room temperature was added 200 g (1.05 moles) of *p*-toluenesulfonyl chloride. The mixture was shaken until complete solution occurred; it then was set aside for 10 days at room temperature, and shaken vigorously twice daily as had been done for the ditosylation of the analogous 4,6-*O*-benzylidene glycoside (10). The solution was then poured into 3 l of ice water, whereupon a viscous oil appeared and solidified when left for 1 h. The brownish solid was crushed, filtered off, washed with water, and dissolved in chloroform. The chloroform solution was washed with water, decolorized with charcoal, and dried (Na_2SO_4). Removal of the solvent gave a brownish syrup (210 g) which was dissolved in 1 l of dry ether. When cooled in ice, the ether solution deposited 189 g of a solid which was then dissolved in 5 l of absolute hot ethanol. When cooled to room temperature, the solution gave 123 g of product. Concentration of the mother liquor gave additional



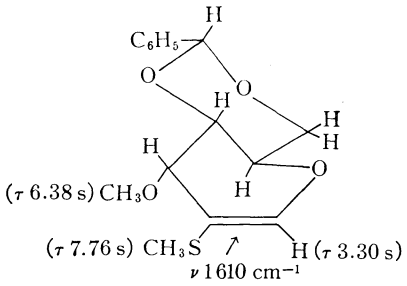
XI



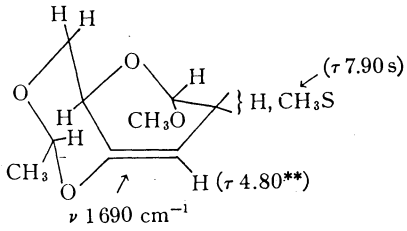
IX*a*



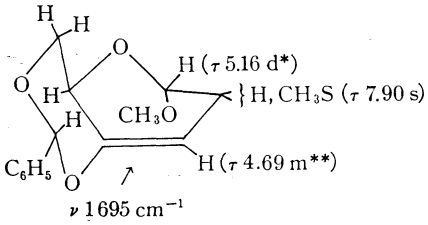
XII



X*a*



XIII



XI*a*

SCHEME 4. The asterisk indicates signals that are not sharp, but are resolvable at high resolution. The double asterisk indicates a closely spaced multiplet. s = singlet, d = doublet, and m = multiplet.

material. The total yield was 131 g (74.4% overall yield based on the 65 g of methyl α-D-glucoside used), m.p. 156–157° (lit. m.p. 156–157°, yield 47.4% (9)).

Methyl 2,3-Anhydro-4,6-O-ethylidene-α-D-allopyranoside (VII)

The following modifications, based upon the analogous reaction with methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-toluenesulfonyl-α-D-glucopyranoside (11), were less stringent than those frequently recommended (7, 9) and gave nearly quantitative yields of the anhydro compound.

To an ice-cold solution of methyl 4,6-*O*-ethylidene-2,3-di-*O*-*p*-toluenesulfonyl-α-D-glucopyranoside (120 g, 0.227 mole) in 1 250 ml of reagent-grade chloroform was added a 2.7 *N* solution of sodium methoxide in methanol (prepared from 26.1 g of sodium in 420 ml of methanol). The flask and contents were left for 4 h in ice water to prevent the loss of solvent as a result of the exothermic reaction. It then was left at room temperature for 6 days. The mixture was poured into 2.5 l of ice water, the chloroform layer separated, and the aqueous layer extracted with chloroform (2 × 500 ml). The combined chloroform solutions were washed free of alkali with water, dried (Na_2SO_4), and freed from solvent in a rotary evaporator. The residual solid (50 g) showed weak absorption in the region 3 300 – 3 600 cm^{-1} (Nujol) indicative of OH and at 1 600 cm^{-1} (aromatic); hence it was further purified by sublimation (9) at 100° and 1 mm to yield 42.3 g (92%) of a colorless sublimate. The residue gave 4.5 g of unchanged ditosylate. The sublimate, crystallized from 2 l of hot petroleum ether (b.p. 60–80°), gave VII as glistening needles, m.p. 129°, yield 41 g (84%) (lit. m.p. 126–129°, yield 65.3% (9)).

Methyl 4,6-O-Ethylidene-S-methyl-2-thio-α-D-altropyranoside (VIII) and Methyl 4,6-O-Ethylidene-S-methyl-3-thio-α-D-glucopyranoside (IX)

To an ice-cold solution of sodium methoxide

TABLE I

Nuclear magnetic resonance, infrared, and analytical characteristics of olefinic compounds obtained from the reaction of sodium in 1,2-dimethoxyethane with methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (X) (n.m.r. spectra* in $CDCl_3$ referred to tetramethylsilane; infrared spectra in $CHCl_3$ (2%) calibrated with polystyrene (1 601 cm^{-1}))

Compound	Ethylidene methine proton (τ)	Vinyl proton (τ)	Anomeric proton (τ)	C_3O-methyl protons	Anomeric methyl protons (τ)	*S*-Methyl protons (τ)	Ethylidene methyl protons (τ)	Absorption† in olefinic region (cm^{-1})	Melting or boiling point	$[\alpha]_D^{25}$ (*c*, 1 in $CHCl_3$)	Yield (%)
VIII	5.16 (q) J = 5 c.p.s.	—	5.30 (s)	—	6.60 (s)	7.78 (s)	8.62 (d) J = 5 c.p.s.	—	126–127°	+100°	96
X	5.27 (q) J = 5 c.p.s.	—	5.32 (s)	6.50 (s)	6.65 (s)	7.78 (s)	8.64 (d) J = 5 c.p.s.	—	56–57°	+75°	96
XI	5.22 (q) J = 5 c.p.s.	4.43 (s)‡	5.20 (s)‡	—	6.55 (s)	7.73 (s)	8.65 (d) J = 5 c.p.s.	1 630 (m)	99–100°	+36°	42
XII	5.30 (q) J = 5 c.p.s.	3.34 (s)		6.39 (s)	—	7.77 (s)	8.62 (d) J = 5 c.p.s.	1 612 (st)	94° at 0.8 mm (η_D^{25} 1.5046)	+226.5°	17
XIII (?)	?	4.80§	—	—	?	7.90 (s)	8.62 (d) J = 5 c.p.s.	1 690 (st)	?	?	?

*Signals are indicated as s, singlet; d, doublet; and q, quartet.
†Olefinic absorption bands are indicated as m, medium; and st, strong.
‡Signals not sharp, apparently resolvable at high resolution.
§Narrow multiplet.

(prepared from 2 g (0.26 mole) of sodium in 180 ml of methanol) was added ice-cold methanethiol (25 g, 0.52 mole) under an atmosphere of dry, purified nitrogen. After the solution had been stirred for 15 min, 27 g (0.133 mole) of VII was added and the reaction mixture refluxed for 18 h. The solution was cooled in ice, neutralized to pH 7 by the dropwise addition of glacial acetic acid (~15 g), and then poured into 2 l of ice water. The combined chloroform extracts (3 × 250 ml) of this cold solution were washed with 10% brine solution until neutral (VIII is somewhat soluble in water), dried (Na_2SO_4), and freed from solvent. The solid residue (34 g) was dissolved in 1 l of hot ether. When cooled in a refrigerator overnight, the ether solution deposited VIII as long needles, yield 32 g (96%), m.p. 126–127°, $[\alpha]_D^{25}$ +100° (*c*, 1 in $CHCl_3$). The infrared spectrum in Nujol showed a band at 3 520 cm^{-1} (OH). The integrated n.m.r. spectrum in $CDCl_3$ showed signals in agreement with structure VIII. These are shown in Table I.

Anal. Calcd. for $C_{10}H_{18}O_5S$: C, 47.98; H, 7.25; S, 12.81. Found: C, 47.78; H, 7.08; S, 12.51.

Removal of the ether from the mother liquor obtained from the separation of VIII, and subsequent crystallization of the residue from Skellysolve B (commercial hexane), gave small needles (1.1 g, 3.3%) melting at 75–76°, $[\alpha]_D^{25}$ +112.5° (*c*, 1 in $CHCl_3$). The infrared spectrum in Nujol showed absorption at 3 425 cm^{-1} (OH). The integrated n.m.r. spectrum in $CDCl_3$ agreed with the assignment of this compound as methyl 4,6-*O*-ethylidene-*S*-methyl-3-thio-α-D-glucopyranoside (IX). Resonance signals appeared at τ 5.25 (quartet for the ethylidene methine proton, J = 5 c.p.s.), τ 8.61 (doublet for the ethylidene methyl protons, J = 5 c.p.s.), τ 5.2 (anomeric proton, singlet), τ 7.76 (*S*-methyl protons, singlet), and τ 6.63 (anomeric methyl protons, singlet).

Anal. Calcd. for $C_{10}H_{18}O_5S$: C, 47.98; H, 7.25; S, 12.81. Found: C, 48.05; H, 7.34; S, 12.50.

Methyl 4,6-O-Ethylidene-3-O,S-dimethyl-2-thio-α-D-altropyranoside (X)

Methylation of VIII (31 g) was carried out by a modification (5) of Purdie's procedure (12). The crude methylated product (32 g) showed evidence of free hydroxyl groups in the infrared spectrum; hence it was purified by chromatography on neutral alumina. The eluting solvent (benzene–hexane (1:1)) removed the methylated product X, giving 29.5 g (91%) of a material melting at 56–57°, $[\alpha]_D^{25}$ +75° (*c*, 1 in $CHCl_3$). The infrared spectrum in Nujol showed no absorption in the region 3 600 – 3 300 cm^{-1} (OH). The integrated n.m.r. spectrum in $CDCl_3$ agreed with structure X. The significant n.m.r. signals and analytical data are shown in Table I.

Anal. Calcd. for $C_{11}H_{20}O_5S$: C, 49.98; H, 7.63; S, 12.13. Found: C, 50.05; H, 7.51; S, 12.16.

Further elution of the column of neutral alumina with ether gave 2 g of unchanged starting material, thus raising the yield of fully methylated product to 96.4%.

Methyl 4,6-O-Ethylidene-S-methyl-2-thio-β-D-altropyranoside

A solution of sodium methoxide (prepared from sodium (0.2 g) and methanol (18 ml)) was cooled in an ice bath; to this was added 3 g of methyl mercaptan. The mixture was stirred for 20 min, after which 2.5 g of methyl 2,3-anhydro-4,6-*O*-ethylidene-β-D-allopyranoside (7) was added under a nitrogen atmosphere. Ten minutes later the mixture was heated under reflux for 18 h, cooled, and neutralized with glacial acetic acid. The solution was then poured into ice water (200 ml) and the cloudy solution extracted with chloroform (6 × 50 ml). The combined chloroform solutions were washed with brine (10%), dried (Na_2SO_4), and filtered; then the filtrate was freed from solvent in a rotary evaporator. The syrupy residue (3.7 g) was crystallized from ether–pentane, giving needles (2.1 g) melting at 104–105°. The mother liquor was evaporated and the residue chromatographed on neutral alumina (grade 2, 30 g). Elution with benzene and ether (1:1) gave a colorless syrup which crystallized from ether–hexane, giving 750 mg of a material melting at 104–105°, total yield 2.85 g (88%), $[\alpha]_D^{25}$ −57.6° (*c*, 1 in $CHCl_3$). The infrared spectrum in Nujol showed a broad band at 3 445 cm^{-1} (OH).

Anal. Calcd. for $C_{10}H_{18}O_5S$: C, 47.98; H, 7.25; S, 12.80. Found: C, 47.99; H, 7.03; S, 12.88.

Methyl 4,6-O-Ethylidene-3-O,S-dimethyl-2-thio-β-D-altropyranoside

Methylation was carried out by a modification of the published directions (8).

To a solution of methyl 4,6-*O*-ethylidene-*S*-methyl-2-thio-β-D-altropyranoside (1.25 g) in 1,2-dimethoxyethane (18 ml, distilled from potassium) and methyl iodide (5 g), cooled in ice, was added sodium hydride in small portions (0.26 g, obtained from a mineral oil dispersion of the hydride from which the oil had been washed with dry hexane). The mixture was then stirred at room temperature for 2 h. The cloudy solution was freed from solvent under reduced pressure, water was carefully added to the residue, the mixture was extracted with ether, and the ether solution was washed, dried (Na_2SO_4), and freed from solvent. The oily residue, crystallized from ether–hexane, gave 1.0 g (77%) of a material melting at 79–80°, $[\alpha]_D^{25}$ −62.2° (*c*, 1 in $CHCl_3$). No absorption for OH was found in the infrared spectrum.

Anal. Calcd. for $C_{11}H_{20}O_5S$: C, 49.99; H, 7.63; S, 12.12. Found: C, 49.92; H, 7.61; S, 12.50.

Anomerization of Methyl 4,6-O-Ethylidene-3-O,S-dimethyl-2-thio-α-D-altropyranoside (X)

A mixture of 250 mg of methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (X), 1,1-dimethoxyethane (5 ml), and concentrated sulfuric acid (0.03 ml) was stirred at room temperature for 24 h. The mixture, dissolved in dichloromethane (20 ml), was washed with aqueous sodium bicarbonate (10%) and water, and then dried (Na_2SO_4). Removal of the solvent left an oil which crystallized slowly from cold ether–hexane, crude m.p. 72–74°.

Recrystallization from ether–hexane gave 80 mg (35%) of a material melting at 78–79°, $[\alpha]_D^{25}$ −61° (*c*, 1 in $CHCl_3$). A mixture melting point with methyl 4,6-*O*-ethylidene-3-*O*,*S*-dimethyl-2-thio-β-D-altropyranoside (above) was undepressed.

Conversion of Methyl 4,6-O-Benzylidene-3-O,S-dimethyl-2-thio-α-D-altropyranoside into Methyl 4,6-O-Ethylidene-3-O,S-dimethyl-β-D-altropyranoside

A solution of methyl 4,6-*O*-benzylidene-3-*O*,*S*-dimethyl-2-thio-α-D-altropyranoside (250 mg) in 1,1-dimethoxyethane (5 ml) containing 0.03 ml of concentrated sulfuric acid was stirred at room temperature for 24 h. Dichloromethane (20 ml) was added, and the solution was washed with 10% aqueous sodium bicarbonate and with water, and then dried (Na_2SO_4). Removal of the volatile solvent gave a yellow oil (200 mg) which was chromatographed on neutral alumina, with ether–hexane (1:1) as eluent. A colorless oil was obtained whose n.m.r. spectrum in $CDCl_3$ showed signals for the ethylidene group (quartet at τ 5.2 (J = 5 c.p.s.) and doublet at τ 8.66 (J = 5 c.p.s.)), but none in the region of τ 2.5–3.5 for aromatic protons. On storage in the refrigerator, the ether–hexane solution deposited a cluster of needles (75 mg, 30%) melting at 77–78°. Recrystallization from ether–hexane raised the melting point to 79–80°, $[\alpha]_D^{25}$ −60.8° (*c*, 1 in $CHCl_3$). A mixture melting point with authentic β isomer (above) was undepressed.

The Reaction of Methyl 4,6-O-Ethylidene-3-O,S-dimethyl-2-thio-α-D-altropyranoside (X) with Sodium in 1,2-Dimethoxyethane

A solution of 8.8 g (0.033 mole) of X in 600 ml of dry 1,2-dimethoxyethane containing finely divided metallic sodium[5] (500 mg, 0.0348 mole) was refluxed for 24 h in a nitrogen atmosphere. The solution became deep yellow within 1 h, and then turned slowly to brownish black. The cold solution was decanted from any residual unreacted sodium and from precipitated sodium methoxide, and the solvent was removed under vacuum in a rotary evaporator. The reddish-brown solid residue was dissolved in 10 ml of ethanol to destroy traces of unreacted metal, and the resulting mixture was diluted with 200 ml of 10% brine. The mixture was extracted with ether (2 × 200 ml), and the ether layer was washed with 10% brine solution and dried ($MgSO_4$). Removal of the solvent gave 7 g (90%) of a solid residue. This was fractionated by chromatography on neutral alumina. Benzene–hexane (1:1) elution followed by benzene elution gave a total of 6 g (78%) of a material containing no free hydroxyl group. The infrared spectrum in Nujol showed absorption at 1 690, 1 630, and 1 612 cm^{-1} (strong) indicative of three olefinic compounds. Analysis of a portion of this material by gas–liquid chromatography on a column of 25% silicone rubber on Gas Chrom P[6] (60–80 mesh), with a helium flow rate of 100 ml/min, showed the presence of five peaks, two of which were the major components (90%) in a ratio of 1:2.

Further elution of the alumina column gave 500 mg of a dark-yellow oil showing infrared absorption indicative of enolic and keto functions. This was not investigated further.

The nonhydroxyl-containing fraction above (6 g) was dissolved in pentane, from which was obtained a crystalline compound considered to be the 2,3-olefin XI, yield 3.2 g (42%). The integrated n.m.r. spectrum and resonance signals agreed with structure XI. The characteristic analytical data are shown in Table I. The assignment of structure XI to this compound was based on considerations employed for the structural assignment of the analogous 4,6-*O*-benzylidene 2,3-olefin (2). The infrared spectrum showed olefinic absorption at 1 630 cm^{-1}. The n.m.r. spectrum showed signals for one vinyl proton at τ 4.43 (singlet) and for one anomeric proton at τ 5.20 (singlet). Both of these singlets appear to be resolvable under high resolution, with a coupling constant of <0.5 c.p.s. characteristic of allylic proton coupling.

Anal. Calcd. for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.99; H, 6.82; S, 14.08.

The solid residue (2.8 g) obtained by removal of the solvent from the mother liquor after XI had been separated was fractionated on a column of neutral alumina. Elution with pentane gave 1.3 g (17%) of pure 1,2-olefin XII. This was not obtained as a crystalline compound, but distilled at 94° and 0.8 mm, η_D^{25} 1.5046, $[\alpha]_D^{25}$ +226.5° (*c*, 1 in $CHCl_3$). The strong absorption in the infrared at 1 612 cm^{-1} is in agreement with the structural feature —O—C=C—S— (2). The integrated n.m.r. spectrum and its characteristic signals agreed with structure XII and are shown in Table I.

Anal. Calcd. for $C_{10}H_{16}O_4S$: C, 51.70; H, 6.94; S, 13.80. Found: C, 51.70; H, 6.88; S, 13.57.

The olefins XI and XII, when subjected separately or together to gas–liquid chromatographic analysis, each gave a single peak and emerged unchanged.

Further elution of the neutral alumina column (above) with benzene–hexane (1:1) gave a material which was a mixture of the 2,3-olefin XI, the 1,2-olefin XII, and a third olefinic material which is believed to be the 3,4-olefin XIII, since the infrared spectrum showed absorption at 1 690 cm^{-1} (strong) as well as the characteristic absorption of the 2,3-olefin and 1,2-olefin at 1 630 and 1 612 cm^{-1}, respectively. The n.m.r. spectrum showed olefinic proton signals at τ 4.43 (2,3-olefin), τ 3.34 (1,2-olefin), and τ 4.70 (3,4-olefin (?)). The correspondence of the infrared absorption at 1 690 cm^{-1} and n.m.r. olefinic proton absorption at τ 4.80 to those for the

[5]Sodium was heated in xylene until just molten, the stoppered flask was shaken vigorously until the metal solidified, and the xylene was decanted and replaced with 1,2-dimethoxyethane.

[6]Diatomaceous silica product (Applied Science Laboratories, Inc., 140 North Barnard St., State College, Pennsylvania).

analogous compound methyl 4,6-*O*-benzylidene-3,4-didehydro-3-deoxy-*S*-methyl-2-thio-α-D-*erythro*(or *threo*)-hexopyranoside (2) supports the tentative assignment of structure XIII to this compound. All attempts to isolate XIII have so far been fruitless. Analysis of this mixture of the three olefins by gas–liquid chromatography on a column of 25% silicone rubber on Gas Chrom P showed only two peaks, the one with the lower retention time being the 1,2-olefin, and that with the greater retention time possessing a slight shoulder and being obviously a mixture of the 2,3- and 3,4-olefins. The characteristic n.m.r. and infrared absorptions for XIII are shown in Table I.

Isomerization of XI to XIII

In agreement with previous observations on analogous compounds (2), a 5 h treatment of pure XI in refluxing 1,2-dimethoxyethane with KOH produced a mixture, after removal of the 1,2-dimethoxyethane, which showed n.m.r. signals and infrared absorption peaks characteristic of both the 2,3- and 3,4-olefins.

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