Reactions of Sulfonates with Sodium Ethylxanthate

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Various 6-*O*-tosyl- and 6-*O*-mesyl-α-D-glucopyranosides reacted with sodium ethylxanthate in either water or organic solvents to give 6-ethoxythiocarbonyl-6-thio derivatives. Methyl 6-ethoxythiocarbonyl-6-thio-α-D-glucopyranoside on treatment with sodium hydroxide yielded the 6-thiol, which on oxidation gave the 6,6′-disulfide. Cyclohexyl tosylates reacted with sodium ethylxanthate to give *S*-cyclohexyl-*O*-ethyl dithiocarbonates. Although the reaction of 1,2:3,4-di-*O*-isopropylidene-6-*O*-tosyl-α-D-galactopyranose with sodium ethylxanthate was negligible in solvents, in the dry state at 150° mainly bis(1,2:3,4-di-*O*-isopropylidene-6-deoxy-α-D-galactopyranose) 6,6′-sulfide resulted.

Displacements of sulfonyloxy groups by thiocyanate,[3] thiolacetate,[4] thiolbenzoate,[5] and thiosulfate[6] are well known, and the products resulting may be converted to thiols by saponification or reduction. Thiol groups have also been introduced into sugars and polysaccharides by transformations of various thiocarbonate esters.[7-11]

We displaced tosyloxy and mesyloxy groups of various blocked sugars and cycloaliphatic compounds with xanthate ion to produce dithiocarbonate esters from which we obtained thiols by treatment with such bases as sodium hydroxide or ammonia. Previously, such dithiocarbonates were formed by displacement of halides from 6-iodo sugars[12] and glycosyl bromides or chlorides.[13,14] Maki and Tejima[14] reported that sodium ethylxanthate displaced the bromide of 2-deoxy-3,4-di-*O*-acetyl-6-*O*-tosyl-α-D-glucopyranosyl bromide, but they did not report any displacement of the sulfonyloxy group by the xanthate.

The displacement of the sulfonyloxy groups with xanthate, followed by saponification, gives a facile procedure for achieving thiolation at primary positions in carbohydrates. The displacement takes place in aqueous media

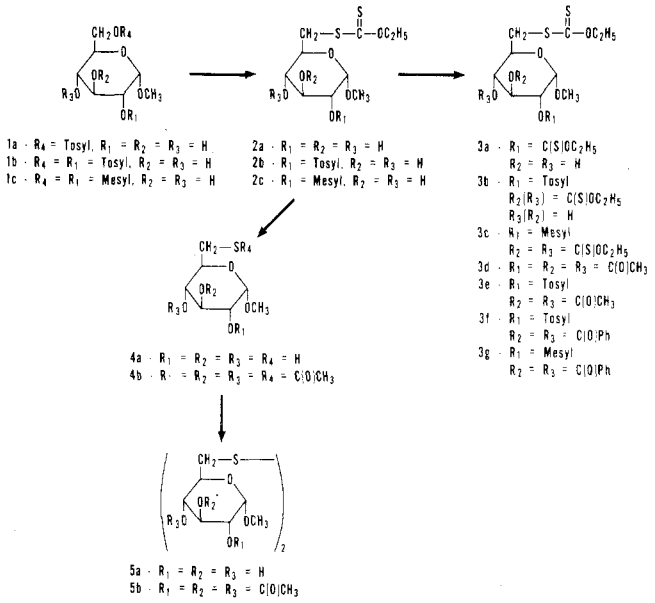
$$RCH_2OSO_2R' + C_2H_5OCS_2Na \longrightarrow RCH_2S_2COC_2H_5 + R'SO_2ONa \quad (1)$$

$$RCH_2S_2COC_2H_5 + H_2O \xrightarrow{NaOH} RCH_2SH + COS + C_2H_5OH \quad (2)$$

even where the starting compound is insoluble, as in reactions involving methyl 2,6-di-*O*-tosyl-α-D-glucopyranoside and tosylated starches. The displacements occur also in organic solvents, such as acetone, dimethyl sulfoxide, or *N,N*-dimethylformamide, either overnight at room temperature (25°) or within several hours at elevated temperatures (50–85°).

The 6-*O*-tosyl (**1a**),[15] 2,6-di-*O*-tosyl (**1b**),[16] and 2,6-di-*O*-mesyl (**1c**)[17] derivatives of methyl α-D-glucopyranoside have been treated with sodium ethylxanthate to give the corresponding 6-dithiocarbonates (**2a–c**) by selective displacement of sulfonyloxy groups at the 6 position. Minor products of the reaction were identified as ethoxythionocarbonate derivatives, such as **3b**, and thiols, similar to **4a** (Scheme I). The inactivity of the 2 position toward displacement in **1b** and **1c** was consistent with the inactivity of methyl 2-*O*-tosyl-α-D-glucopyranoside[18] toward sodium ethylxanthate under these conditions. The 6-dithiocarbonates, **2a–c**, were further characterized as acetates **3d,e** and benzoates **3f,g**. When **1a** was treated in water with stoichiometric amounts of sodium ethylxanthate at 65° for 3.5 hr, **2a** crystallized in 74% yield from the cooled reaction

Scheme I



mixture. Similarly, **1b** was transformed to **2b** (23%) and **1c** to **2c** (60%). Structures of these products and related derivatives were determined by elemental analyses and by uv, ir, and NMR spectra.

When **2a** was treated with sodium hydroxide, methyl 6-thio-α-D-glucopyranoside (**4a**) was obtained crystalline, and converted to the known peracetate **4b**.[19]

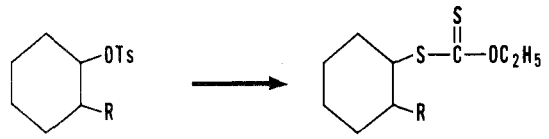
Compound **4a** was oxidized to disulfide **5a** by using diethyl dithiobis(thioformate) in pyridine.[20] Amorphous **5a** was converted to the fully acetylated derivative (**5b**).

Cyclohexyl tosylates **6a**[21] and **6b** underwent reaction with sodium ethylxanthate in acetone to give *S*-cyclohexyl-*O*-ethyl dithiocarbonates **7a** and **7b** and demonstrated that displacement was possible with certain secondary sulfonate positions in ring systems. NMR spectra did not clearly indicate stereochemical changes in going from **6b** to **7b** (Scheme II).

1,2:3,4-Di-*O*-isopropylidene-6-*O*-tosyl-α-D-galactopyranose (**8**)[22] did not readily react with sodium ethylxanthate in organic solvents. When the reactants were mixed in the dry state and kept under vacuum at 150° for 1 hr, **8** was transformed to a mixture of persubstituted sugars. The major component was identified as the crystalline monosulfide **9**. None of the expected dithiocarbonate was obtained in this reaction (Scheme III).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-tosyl-α-D-glucofuran-

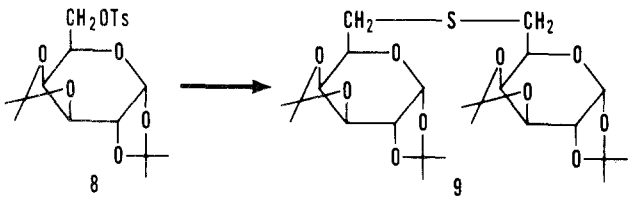
Scheme II



6a · R = H
6b · R = OH

7a · R = H
7b · R = OH

Scheme III



8 9

ose (**10**)[23] likewise did not react with sodium ethylxanthate in acetone at 25–65°, but in *N,N*-dimethylformamide at 130° compound **10** was converted to the known 3,4 olefin **11**.[23] Similarly, **11** was the only product identified on vacuum pyrolysis of **10** with sodium ethylxanthate under conditions used to convert **8** to **9**.

Experimental Section

The sulfonate esters were prepared by known methods. Melting points were determined in a Büchi apparatus and are uncorrected. Optical rotations were read with a Rudolph polarimeter. Ir and uv spectra were recorded with Perkin-Elmer 137 and 202 spectrometers, respectively. NMR spectra were determined with a Varian HA-100 spectrometer in pyridine d_5, chloroform-*d*, and/or carbon tetrachloride using tetramethylsilane (τ 10.00) as internal reference standard and a Model 200 AB Hewlett-Packard audiofrequency oscillator for decoupling experiments. Silica gel G was used for TLC, and sulfuric acid (5%) in methanol was the spraying agent. Silicic acid (Mallinckrodt, 100 mesh) was selected for larger scale separations.

Acetylations of **2a, 2b, 4a,** and **5a** were carried out in acetic anhydride and pyridine for 3 hr at 25°. Reaction mixtures were precipitated in water, and the resulting products were crystallized from alcohol or hexane. Products difficult to crystallize were precipitated from ether–hexane mixtures at 5°.

Benzoylations of **2b** and **2c** were conducted with benzoyl chloride and pyridine overnight at 25°. Reaction mixtures were diluted with chloroform and the solutions were washed with 5% HCl, 5% $NaHCO_3$, and water. After the solutions were dried and the solvent was evaporated, the benzoate esters were extracted from the residues with hexane or were precipitated from ether solution by hexane at 5°.

Reaction of Methyl 6-*O*-Tosyl-α-D-glucopyranoside (1a) with Sodium Ethylxanthate. A solution of **1a** (3.5 g, 10 mmol) and sodium ethylxanthate (1.5 g, 10 mmol) in water (10 ml) was kept at 65° for 3.5 hr. When the solution was diluted to 20 ml and cooled to room temperature, crystals formed. After 3 hr the mixture was filtered, and the crystals were washed with water and hexane. A second crop of crystals was obtained upon concentrating the filtrate and cooling: total yield 2.20 g (74%). The product, identified as methyl 6-*S*-ethoxythiocarbonyl-6-thio-α-D-glucopyranoside (**2a**), was recrystallized twice from water and vacuum dried at 55° for 1 hr: mp 110–112°; $[\alpha]^{21}D$ +158° (*c* 0.87, ethanol); ir (KBr) 8.05, 9.60 μ (OCS_2); uv max (ethanol) 358–362 nm (ε 57), 280–282 (11,520); NMR (C_5D_5N) τ 5.00 (d, H-1), 6.1–6.6 (m, 2 H, H-6, H-6′), 6.59 (s, 3 H, OCH_3), 5.42 (q, 2 H, OCH_2CH_3), 8.77 (t, 3 H, OCH_2CH_3).

Anal. Calcd for $C_{10}H_{18}O_6S_2$: C, 40.3; H, 6.08; S, 21.5. Found: C, 40.1; H, 5.91; S, 21.5.

When **1a** was treated with sodium ethylxanthate in organic solvents (acetone, dimethyl sulfoxide), yields of **2a** were similar. In addition several minor less polar by-products were separated by chromatography. Ir and uv of the major by-product suggested that both dithiocarbonate and thionocarbonate groups (7.7–8.2 μ, 230 and 280 nm) were present. NMR (C_5D_5N) indicated methyl 2-*O*-ethoxythiocarbonyl-6-*S*-ethoxythiocarbonyl-6-thio-α-D-glucopyranoside (**3a**): τ 4.70 (d, H-1), 4.38 (dd, H-2), 6.1–6.6 (m, 2 H, H-6, H-6′), 6.73 (s, 3 H, OCH_3), 5.43 (q, 2 H, OCH_2CH_3), 5.70 (q, 2 H, OCH_2CH_3), 8.81 (t, 3 H, OCH_2CH_3), 8.95 (t, 3 H, OCH_2CH_3).

Methyl 2,3,4-Tri-*O*-acetyl-6-*S*-ethoxythiocarbonyl-6-thio-α-D-glucopyranoside (3d). Acetylation of **2a** (0.160 g, 0.54 mmol) gave the known **3d** (0.228 g, 89%), which was recrystallized from ethanol or hexane: mp 57–60°; $[\alpha]^{23}D$ +116.8° (*c* 0.43, methanol) [reported mp 61–62°, $[\alpha]^{27}D$ +117.7° (methanol)].[12] We found NMR (C_5D_5N) τ 4.94 (d, H-1), 4.83 (dd, H-2), 4.18 (t, H-3), 4.74 (t, H-4), 5.86 (m, H-5), 6.24 (dd, H-6), 6.68 (dd, H-6′), 6.72 (s, 3 H, OCH_3), 5.46 (q, 2 H, OCH_2CH_3), 8.80 (t, 3 H, OCH_2CH_3), 7.92, 8.03, 8.09 (3 s, 9 H, OAc).

Reaction of Methyl 2,6-Di-*O*-tosyl-α-D-glucopyranoside (1b) with Sodium Ethylxanthate. A suspension of **1b** (5.0 g, 10.0 mmol) was agitated in water (5 ml) with sodium ethylxanthate (2.0 g, 14.0 mmol) and kept at 75–85° for 4 hr. The mixture was cooled and extracted with chloroform (70 ml). The extract was washed with water and dried. After filtration the chloroform solution was mixed with an equal volume of hexane and adsorbed onto silicic acid (200 g). Elution with ethyl acetate–hexane (1:7) desorbed a multicomponent minor fraction (0.21 g) from which was separated chromatographically methyl 3(4)-*O*-ethoxythiocarbonyl-6-*S*-ethoxythiocarbonyl-2-*O*-tosyl-α-D-glucopyranoside (**3b**).

Anal. Calcd for $C_{20}H_{28}O_9S_4$: C, 44.4; H, 5.22; S, 23.7. Found: C, 44.6; H, 5.17; S, 23.5.

Subsequent elution with ethyl acetate–hexane (1:3) desorbed a fraction (1.41 g) containing methyl 6-*S*-ethoxythiocarbonyl-6-thio-2-*O*-tosyl-α-D-glucopyranoside (**2b**), a syrup, which was purified by further chromatography: 1.01 g (23%); $[\alpha]^{24}D$ +129° (*c* 0.75, ethanol); uv max (ethanol) 280–282 nm (ε 10,210), 225–226 (15,950); ir (film) 8.4, 8.5 (OTs), 8.25 μ (OCS_2); NMR (C_5D_5N) τ 5.02 (d, H-1), 5.22 (dd, H-2), 6.1–6.7 (m, 2 H, H-6, H-6′), 6.79 (s, OCH_3), 7.85 (d, CH_3 of tosyl), 5.47 (q, OCH_2CH_3), 8.82 (t, OCH_2CH_3).

Anal. Calcd for $C_{17}H_{24}O_8S_3$: C, 45.1; H, 5.35; S, 21.3. Found: C, 45.2; H, 5.55; S, 20.8.

The yield of **2b** was slightly better if acetone was used as the solvent with a large excess of sodium ethylxanthate. A solution of **1b** (1.5 g, 3.0 mmol) and sodium ethylxanthate (5.0 g, 34.6 mmol) in acetone (30 ml) was kept at 25° for 28 hr and poured into ice water (500 ml). The mixture was acidified (1 *N* HCl) and extracted with ethyl acetate. The organic layer was washed with $NaHCO_3$ solution, then with water, and dried. Evaporation of solvent left a yellow syrup from which **2b** was obtained pure by desorption chromatography on silicic acid with ethyl acetate–hexane, 0.39 g (29%).

Methyl 3,4-Di-*O*-acetyl-6-*S*-ethoxythiocarbonyl-6-thio-2-*O*-tosyl-α-D-glucopyranoside (3e). Acetylation of **2b** (0.92 g, 2.0 mmol) gave **3e** as a syrup (0.65 g, 60%). After vacuum drying at 70° for 2 hr: $[\alpha]^{22}D$ +92.3° (*c* 0.81, ethanol); uv (ethanol) 280 nm (ε 10, 730), 227 (18,158); ir (film) 5.7 (C=O), 8.4 (OTs), 8.2, 9.6 μ (ester); NMR (C_5D_5N) τ 4.98 (d, H-1), 4.23 (t, H-3), 4.78 (t, H-4), 5.02 (dd, H-2), 5.88 (m, H-5), 6.30 (m, H-6), 6.70 (m, H-6′), 6.78 (s, 3 H, OCH_3), 7.81 (s, 3 H, OTs), 7.93, 8.21 (2 s, 6 H, OAc), 8.82 (t, 3 H, OCH_2CH_3), 5.46 (q, 2 H, OCH_2CH_3).

Anal. Calcd for $C_{21}H_{28}O_{10}S_3$: C, 47.0; H, 5.26; S, 17.9. Found: C, 47.4; H, 5.23; S, 17.3.

Methyl 3,4-Di-*O*-benzoyl-6-*S*-ethoxythiocarbonyl-6-thio-2-*O*-tosyl-α-D-glucopyranoside (3f). Benzoylation of **2b** (0.12 g, 0.27 mmol) gave **3f:** 0.11 g (64%); mp 167–168° (ethanol); ir (film) 5.78 (C=O), 7.92 (ester), 8.4, 8.5 (OTs), 8.2, 9.6 μ (OCS_2).

Anal. Calcd for $C_{31}H_{32}O_{10}S_3$: C, 56.4; H, 4.88; S, 14.6. Found: C, 56.6; H, 4.95; S, 14.9.

Reaction of Methyl 2,6-Di-*O*-mesyl-α-D-glucopyranoside (1c) with Sodium Ethylxanthate. A solution of **1c** (3.5 g, 10.0 mmol) in water (20 ml) containing sodium ethylxanthate (2.0 g, 14.0 mmol) was kept at 75–85° for 2.5 hr. The clear solution was cooled and extracted with chloroform (100 ml). The chloroform extract was dried, the solvent was evaporated, the residue was taken up in ether (15 ml), and the ether solution was added dropwise to hexane (300 ml) cooled to 5°. A solid precipitated which was filtered after 1 hr and identified as methyl 6-*S*-ethoxythiocarbonyl-2-*O*-mesyl-6-thio-α-D-glucopyranoside (**2c**): 2.25 g (60%); mp 71–73° (crystallized from ether–hexane); $[\alpha]^{24}D$ +135° (*c* 1.04, ethanol); uv max (ethanol) 280 nm (ε 10,480), 224 (5430); ir (film) 2.8 (OH), 7.4, 8.5 (OMs), 8.2, 9.6 μ (OCS_2); NMR (C_5D_5N) τ 4.83 (d, H-1), 5.15 (dd, H-2), 6.1–6.6 (m, 2 H, H-6, H-6′), 6.63, 6.70 (2 s, 6 H, OCH_3, OMs).

Anal. Calcd for $C_{11}H_{20}O_8S_3$: C, 35.1; H, 5.36; S, 25.6. Found: C, 35.2; H, 5.47; S, 25.9.

The filtrate from the initial precipitation of **2c** contained a persubstituted compound (0.015 g) tentatively identified as methyl

3,4-di-*O*-ethoxythiocarbonyl-6-*S*-ethoxythiocarbonyl-2-*O*-mesyl-6-thio-α-D-glucopyranoside (**3c**): ir (film) 7.3, 8.5 (OMs), 7.7 (OCSO), 8.1, 9.6 μ (OCS_2); NMR (CCl_4) τ 5.10 (d, H-1), 4.02 (t, H-3), 4.41 (t, H-4), 6.52 (s, 3 H, OCH_3), 7.10 (s, 3 H, OMs), 8.4–8.8 (m, OCH_2CH_3), 5.3–5.6 (m, OCH_2CH_3).

Methyl 3,4-Di-*O*-benzoyl-6-*S*-ethoxythiocarbonyl-2-*O*-mesyl-6-thio-α-D-glucopyranoside (3g). Benzoylation of **2c** (0.43 g, 1.14 mmol) gave **3g:** 0.20 g (30%); mp 60–70° (amorphous); ir (film) 5.77 (C=O), 7.4, 8.5 (OMs), 7.9 (ester), 8.2 μ (OCS_2).

Anal. Calcd for $C_{25}H_{28}O_{10}S_3$: C, 51.4; H, 4.84; S, 16.5. Found: C, 51.4; H, 5.05; S, 16.3.

Methyl 6-Thio-α-D-glucopyranoside (4a). A mixture of **2a** (0.298 g, 1.0 mmol) and 1 *N* sodium hydroxide (10 ml) was stirred at 50° for 10 min. The resulting clear solution was cooled, neutralized with 1 *N* hydrochloric acid (10 ml), and flushed with nitrogen for 2 min. The solvent was evaporated and the residue was extracted with four 25-ml portions of chloroform. The extracts were combined and dried. Evaporation of chloroform left a syrup which was kept under vacuum at 60° for 1 hr. Compound **4a** crystallized upon evacuation at room temperature: 0.168 g (80%); mp 100–102°; $[\alpha]^{24}D$ +145° (*c* 0.4, ethanol); ir (film) 3.88 μ (SH); NMR ($CDCl_3$) τ 8.33 (t, SH), 5.28 (d, H-1), 7.0–7.4 (m, 2 H, H-6, H-6′), 6.58 (s, 3 H, OCH_3).

Anal. Calcd for $C_7H_{14}O_5S$: C, 40.0; H, 6.7; S, 15.2. Found: C, 39.5; H, 6.6; S, 14.9.

This compound has been reported[19] as a syrup, $[\alpha]^{20}D$ +181° (*c* 0.5, ethanol), ir 2550 cm^{-1} (3.92 μ) for SH. We found that ion exchange resins used in desalting the reaction mixture caused some oxidation to the disulfide, which may account for the higher rotation reported (see preparation of **5a**).

Methyl 2,3,4-Tri-*O*-acetyl-6-*S*-acetyl-6-thio-α-D-glucopyranoside (4b). Acetylation of **4a** (0.159 g, 0.76 mmol) gave **4b** as a syrup: 0.279 g (97%); $[\alpha]^{26}D$ +119° (*c* 1.67, chloroform); $n^{20}D$ 1.4794; NMR (CCl_4) τ 7.72 (s, 3 H, SAc), 8.00, 8.03, 8.09 (3 s, 9 H, OAc).

Anal. Calcd for $C_{15}H_{22}O_9S$: S, 8.47. Found: S. 8.55. Reported[19] for this compound: $[\alpha]^{20}D$ +118° (*c* 1, chloroform), $n^{20}D$ 1.4792.

Bis(methyl 6-thio-α-D-glucopyranoside) 6,6′-Disulfide (5a). A solution of **4a** (0.189 g, 0.90 mmol) in pyridine (5 ml) was treated with diethyl dithiobis(thioformate) (0.109 g, 0.45 mmol). After 5 min the pyridine was evaporated and the residue was dissolved in ethanol (10 ml). Evaporation of the ethanol left a syrup which was vacuum dried at 70° for several hours: 0.189 g (quantitative); $[\alpha]^{23}D$ +347°; NMR (C_5D_5N) τ 4.96 (d, 2 H, H-1), 6.25 (dd, 2 H, H-6), 6.77 (dd, 2 H, H-6′), 6.58 (s, 6 H, OCH_2).

Anal. Calcd for $C_{14}H_{26}O_{10}S_2$: C, 40.2; H, 6.26; S, 15.3. Found: C, 39.9; H, 6.27; S, 15.3.

Bis(methyl 2,3,4-tri-*O*-acetyl-6-thio-α-D-glucopyranoside) 6,6′-Disulfide (5b). Acetylation of **5a** (0.084 g, 0.02 mmol) gave **5b:** 0.112 g (83%); mp 156° (ethanol); $[\alpha]^{26}D$ +259° (*c* 0.37, chloroform); NMR (C_5D_5N) τ 4.81 (d, 2 H, H-1), 4.74 (dd, 2 H, H-2), 4.13 (t, 2 H, H-3), 4.70 (t, 2 H, H-4), 5.78 (m, 2 H, H-5), 6.75 (dd, 2 H, H-6), 6.95 (dd, 2 H, H-6′), 6.59 (s, 6 H, OCH_3), 7.95, 8.02, 8.08 (3 s, 9 H, OAc).

Anal. Calcd for $C_{26}H_{38}O_{16}S_2$: C, 46.6; H, 5.71; S, 9.56. Found: C, 46.2; H, 5.49; S, 9.51.

***S*-Cyclohexyl-*O*-ethyl Dithiocarbonate (7a).** Cyclohexyl tosylate (**6a,** 1.0 g, 3.9 mmol) and sodium ethylxanthate (2.0 g, 14 mmol) in acetone (10 ml) were kept at 25° for 24 hr. Sodium tosylate (0.74 g) was removed by filtration and acetone by evaporation of the filtrate. The residue was extracted with hexane and the hexane was evaporated. The resulting colorless syrup was chromatographed with hexane as the eluent: 0.31 g (39%); uv (ethanol) 283 nm; NMR ($CHCl_3$) τ 5.47 (q, 2 H, OCH_2), 6.37 (m, CHS), 7.8–8.8 (13 H).

Anal. Calcd for $C_9H_{16}OS_2$: C, 52.9; H, 7.84; S, 31.3. Found: C, 53.1; H, 7.98; S, 30.8.

***trans*-Cyclohexyl-2-ol Tosylate (6b).** To a solution of *trans*-1,2-cyclohexanediol (12 g) in chloroform (200 ml) and pyridine (50 ml) was added a solution of *p*-toluenesulfonyl chloride (19 g) in benzene (130 ml) over a period of 45 min. The solution was stirred overnight and then warmed to 50° for 1 hr. The reaction mixture was extracted with H_2O (100 ml), hydrochloric acid (100 ml, 1 *N*), 5% sodium bicarbonate (50 ml), and H_2O (50 ml). The organic layer was dried and the solvent was evaporated. The resulting syrup was dissolved in $CHCl_3$ and hexane was added. The mixture was kept overnight at 5° to give a crystalline precipitate, 4.0 g, mp 85–95°. Recrystallization gave **6b:** mp 89–90°; NMR ($CDCl_3$) τ 2.2 (d, 2 H), 2.7 (m, 2 H), 5.74 (m, 1 H, CHOTs), 6.48 (m, 1 H, CHOH), 7.60 (s, 3 H, CH_3), 7.66–8.8 (8 H).

Anal. Calcd for $C_{13}H_{18}O_4S$: C, 57.8; H, 6.67; S, 11.8. Found: C, 57.5; H, 6.90; S, 11.5.

***S*-(Cyclohexyl-2-ol) *O*-Ethyl Dithiocarbonate (7b).** A solution of **6b** (1.0 g) in acetone (15 ml) was treated with sodium ethylxanthate (1.0 g). After the solution was heated for 4 hr at 50°, TLC (hexane–acetone, 4:1) showed that almost all the **6b** had reacted. The major product was isolated by chromatography and identified as *S*-(cyclohexyl-2-ol) *O*-ethyl dithiocarbonate (**7b**): ir (film) 2.8 μ (OH); uv (methanol) 283 nm; NMR ($CDCl_3$) τ 5.39 (q, 2 H, OCH_2CH_3), 5.92, 6.43 (m, 2 H, >CHOH, >CHS), 7.5–8.8 (m, 9 H).

Anal. Calcd for $C_9H_{16}O_2S_2$: C, 49.1; H, 7.27; S, 29.1. Found: C, 49.2; H, 7.33; S, 29.9.

Reaction of 1,2:3,4-Di-*O*-isopropylidene-6-*O*-tosyl-α-D-galactopyranose (8) with Sodium Ethylxanthate. A solution of **8** (4.15 g, 10 mmol) was mixed with sodium ethylxanthate in a beaker and kept in a heated desiccator at 150° for 2.5 hr under vacuum. After this mixture was cooled, the residue was extracted with chloroform (150 ml) and filtered. The chloroform solution was washed with water and dried. TLC (ethyl acetate–carbon disulfide 1:9) showed a multicomponent mixture of at least six components, R_f 0.14–0.46, the major one of which was R_f 0.14 (starting material, R_f 0.20 in this system). The chloroform was evaporated to a syrup (3.4 g), and the higher R_f components were removed by desorption from silicic acid (200 g) with 5–15% ethyl acetate in hexane. Subsequent elutions with 20–25% ethyl acetate in hexane yielded mixtures containing R_f 0.14 component and the pure R_f 0.14 component, identified as bis(1,2:3,4-di-*O*-isopropylidene-6-deoxy-α-D-galactopyranose) 6,6′-sulfide (**9**): 0.40 g (15%); mp 114–115° (hexane); NMR (C_5D_5N) τ 4.35 (d, 2 H, H-1), 5.4–5.6 (m, 4 H, H-2, H-4), 5.26 (dd, 2 H, H-3), 5.80 (t, 2 H, H-5), 6.7–7.1 (m, 4 H, H-6, H-6′), 8.4–8.8 (m, 24 H, isopropylidene).

Anal. Calcd for $C_{24}H_{38}O_{10}S$: C, 55.6; H, 7.39; S, 6.18. Found: C, 55.2; H, 7.56; S, 6.33.

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Registry No.—**1a,** 6619-09-6; **1b,** 54497-89-1; **1c,** 14257-63-7; **2a,** 54497-90-4; **2b,** 54497-91-5; **2c,** 54497-92-6; **3a,** 54497-93-7; **3b,** 54498-02-1; **3c,** 54497-94-8; **3d,** 24274-52-0; **3e,** 54497-95-9; **3f,** 54497-96-0; **3g,** 54497-97-1; **4a,** 40652-97-9; **4b,** 54497-98-2; **5a,** 54497-99-3; **5b,** 54498-00-9; **6a,** 953-91-3; **6b,** 15051-90-8; **7a,** 54497-82-4; **7b,** 54498-01-0; **8,** 4478-43-7; **9,** 54532-14-8; sodium ethylxanthate, 140-90-9; diethyl dithiobis(thioformate), 502-55-6; *trans*-1,2-cyclohexanediol, 1460-57-7; *p*-toluenesulfonyl chloride, 98-59-9.

References and Notes

(1) Agricultural Research Service, U. S. Department of Agriculture. Mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.
(2) Work conducted as a research project in an undergraduate organic chemistry course.
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