PHOTOLYSIS OF SOME CARBOHYDRATE
DITHIOBIS (THIOFORMATES)

by

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I hereby recommend that this dissertation prepared under my
direction by Edward Irvin Stout
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ABSTRACT

The photolysis of several oxidatively coupled xanthates of model sugar compounds has been investigated. The photolysis of bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) dithiobis(thioformate) (XXXVIII) gave the xanthate ester, bis(6-deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) 6-O,6'-S-dithiocarbonate (LXX) in 78% yield. In concentrated solutions, bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) tetrathiobis(thioformate) (LXIX) was produced along with LXX. The photolysis of bis(1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) dithiobis(thioformate) (XIV) gave bis(3-deoxy-1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) 3-O,3'-S-dithiocarbonate (LXXVI), in which an oxygen atom on the sugar ring has been replaced with sulfur with retention of configuration. A cyclic mechanism in which either the excited thiocarbonyl sulfur or a sulfur of the disulfide linkage attacks the carbon giving a front side displacement of oxygen has been proposed to account for the observed results.

INTRODUCTION

The discovery of the viscose process (1) for the production of viscose rayon in 1892 by Cross and Bevin (2) initiated many studies on the complex xanthation reaction. The xanthation reaction was first reported by Zeise (3) in 1822, who reacted ethanol with carbon disulfide and sodium hydroxide.

The xanthate salt was found to undergo reaction with alkyl halides to form dithiocarbonates, which are also called xanthate esters (4). These xanthate esters react with amines to produce thiocarbamates (5). The formation of olefins by the pyrolysis of xanthate esters was discovered by Chugaev (6) in 1899. The xanthate salt was also readily oxidatively coupled (7,8) through the disulfide to give dimeric products.

Soon after their discovery of the xanthation of cellulose, Cross, Bevin, and Briggs extended the reaction to starch and other polysaccharides (9), thus establishing the general applicability of the xanthation reaction to carbohydrates. Lieser and Hackl (10) and Heuser and Schorsch (11) xanthated other polysaccharides.

The efficient reaction of simple alcohol xanthates with various metals resulted in the use of these reagents for the flotation of sulfide ores (12). Other uses of xanthates are as oil additives (13), as

adhesives for wood veneer (14), as textile sizing agents (15), as herbicides, insecticides, pesticides, and as fireproofing agents (13).

Starch xanthate, when oxidatively crosslinked or insolubilized with heavy metals, has been shown to be an effective wet strength agent for paper (16,17,18,19) and insulation board (20). It has also been shown to be an effective reinforcing agent in the preparation of starch reinforced rubbers when it is incorporated by latex master-batching procedures (21,22,23). These coprecipitated starch xanthate-latex mixtures have been dried and ground to give powdered elastomers that were readily compounded and fabricated into consumer goods by direct heat-compression molding. Products with good properties were obtained by direct extrusion of the compounded elastomer mixtures (24,25,26).

Several methods for preparing starch xanthates have been developed. Swanson et al. (27) have developed a rapid continuous process in which starch, sodium hydroxide, and carbon disulfide are mixed and extruded at 50% starch concentration in approximately two minutes to give uniformly substituted starch xanthates. Degrees of substitution from 0.03-0.7 were readily obtained. The xanthation method of Lancaster et al. (28) requires the gelatinization of a 10% starch slurry in sodium hydroxide and subsequent reaction with carbon disulfide. The potential use of starch xanthate as paper and rubber additives has led to the development of starch xanthate as a dry powder (29) and other useful forms (30,31,32,33).

Since the xanthation of cellulose requires several days in order to produce an acceptable viscose, considerable research has been

conducted to determine what reactions occur during this "ripening" period. The kinetics of the xanthation, dexanthation, and rexanthation have been studied by many research groups and these subjects have been reviewed by Rao (13) and Joedodibroto (34). The complexity of the xanthation mixture has caused a considerable variation of results which were dependent upon the reaction conditions. When xanthating simple alcohols, a two-phase liquid-liquid system is encountered: an aqueous sodium hydroxide-alcohol phase and a carbon disulfide phase. Xanthation of cellulose or some other polysaccharides, a three-phase system exists: solid cellulose, aqueous sodium hydroxide solution, and carbon disulfide. In addition, one has the side reactions of sodium hydroxide with carbon disulfide:

When working with the glucose polymers, cellulose and starch, there are three available hydroxyl groups of different reactivity, each of which is a potential site for xanthation (see Figure 1).

Kinetic studies on xanthation of cellulose and simple carbohydrates indicate that the reaction is pseudo-unimolecular following the rate expression, $k = \frac{2.3}{t} \log \frac{1}{1-X}$, where X is the amount of combined carbon disulfide (35). Recent work of Anderson, Samuelson, and Tornell

Figure 1. Repeating unit in starch molecule.

(36) have shown that xanthate formation is a second order reaction, determined by the concentration of carbon disulfide and sodium alcoholate. They have also shown that the ratio of the rate constants of the xanthation of the primary hydroxyl (C_6 -OH) versus that of the secondary hydroxyls (C_2 -OH, C_3 -OH) is not constant. Khurgina and Pakshver (37), Vermaas (38), Philipp and Fichte (39), and Dunbrant and Samuelson (40) have all shown that the decomposition of xanthate follows first order kinetics. The latter authors (39,40) have shown that the decomposition of cellulose xanthate occurs by two first order reactions: the slower one for the dexanthation of the primary xanthate group, and the faster one for the secondary xanthate. The uniformity of the emulsion xanthation of cellulose was studied by Cornell (41), who found that the higher molecular weight fraction was more highly xanthated. The location of the xanthate substituents in ripened viscose was determined by Willard and Pacsu (42) using a series of reactions which replaced the xanthate groups by methyl ether groups. Quantitative separation by paper chromatography after hydrolysis of the cellulose gave monomethyl ethers in

the ratio 37:20:43 for 6-O-methyl: 3-O-methyl:2-O-methyl, which indicates that under these conditions more substitution occurs at the primary position. Dunbrant and Samuelson (40) also determined the location of xanthation in viscose by studying the decomposition kinetics. Their results showed that during ripening the amount of secondary xanthate decreases, while the amount of primary xanthate passes through a maximum. Adamek and Purves (43) investigated the location of substitution in starch xanthate prepared by the emulsion technique. Their analysis differentiated only primary substitution from secondary. They found that during the initial stages of xanthation, considerably more substitution occurred on the secondary hydroxyls than on the primary, but as the xanthation progressed, a greater percentage of the xanthate groups were on the primary position.

Doane, Russell, and Rist (44, p. 77) have studied the uniformity of substitution of starch xanthate, which was prepared in a continuous screw-type mixer-reactor described by Swanson et al. (27). Their results showed no variation in the degree of substitution (D.S.) with molecular weight or between the amylose and amylopectin components of starch. Further investigation (44, p. 176; 45) as to the location of the xanthate groups showed that initially more substitution occurred on the secondary position. The rate of "inversion of substitution" was found to be concentration and temperature dependent. At 50% solids content and 25° the inversion had already occurred after 1 hr; initially, primary D.S. = 0.12, secondary D.S. = 0.17, and after 1 hr primary D.S. = 0.23, secondary D.S. = 0.18. When a similar reaction

mixture was kept at 11% solids and 5°, inversion was slower. Under these conditions, 67 hr were required to reach the maximum D.S. of 0.33, whereas at 50% solids, the maximum D.S. of 0.44 was achieved after 4 hr. On additional aging, the relative amount of secondary xanthate continued to decrease, while total D.S. changed only slightly. At 11% solids and 20° the rate of change was faster than at 5°.

Trimnell et al. (46,47) have studied the mechanism of this reaction by preparing selectively substituted methyl glucosides by chromatographic separation of the S-benzyl xanthate esters ($\text{R-O-C-S-CH}_2\text{-C}_6\text{H}_5$). These esters were then converted to the sodium xanthate salts by treatment with sodium hydrosulfide in DMSO and isolated by precipitation with ether. Rebenzylation of the xanthate salt showed only a small amount of other isomers formed during the workup. Aging the selected isomers in 18% sodium hydroxide for 30 min followed by rebenzylation gave the following results. Starting with the 2-isomer, the isomer distribution was 3% 2-isomer, 1% 3-isomer, 85% 6-isomer, and 8% polyxanthates. The 3-isomer gave 11% 2-isomer, 8% 3-isomer, 77% 6-isomer, and 4% polyxanthates. The 6-isomer gave 4% 2-isomer, 5% 3-isomer, 88% 6-isomer, and 3% polyxanthates. In all cases a xanthate mixture was obtained in which the 6-isomer predominated. Data were obtained on the rate of migration of the 2-isomer at 5°. After 30 min the xanthate distribution was 43% 2-isomer, 19% 3-isomer, 20% 6-isomer, and 18% polyxanthates; after 60 min 13% 2-isomer, 14% 3-isomer, 62% 6-isomer, and 11% polyxanthates; after 90 min 7% 2-isomer, 12% 3-isomer, 56% 6-isomer, and 25% polyxanthates. In order to determine if the

migration occurred by dexanthation followed by rexanthation, N_2 was passed through the reaction solution to remove carbon disulfide as it formed. Under these conditions no significant difference in the substituent distribution was observed when these samples were compared to samples which were not treated with N_2 . Evidence for an intramolecular xanthation was obtained when methyl 3-O-methyl- α -D-glucopyranoside 2-(S-benzyl-xanthate) was converted to the sodium salt and treated for 2 hr in 18% sodium hydroxide. Rebenzylation followed by tlc indicated no migration had occurred to give the 6-isomer, whereas, under similar reaction conditions extensive migration occurred when the 3-position was hydroxyl. Selectively blocking the C_4 hydroxyl as the methyl ether effectively stopped migration of the xanthate to the 6-position. From these results it was concluded that the migration of the xanthate from the 2-isomer to the 6-isomer of methyl glucoside proceeds via the hydroxyl group at C_4 and direct migration across the ring from either the 2- or 3-position was negligible. There still remains the unanswered question of what happens in starch and cellulose xanthates, in which the C_4 hydroxyl is blocked in the acetal linkage.

Pyrolysis of xanthate esters was first reported by Chugaev (6) in 1899. He found that the thermal degradation of the xanthate esters produced an olefin, a mercaptan, and carbonyl sulfide.

Because of the ease of xanthation of carbohydrates with relatively inexpensive reagents, the potential of the Chugaev reaction for

the introduction of new functionality into carbohydrates is of considerable interest. Nace (48) has reviewed most of the literature up to 1962 and the data have indicated that this reaction proceeds by a cis- β -elimination mechanism. Cram (49) and Barton (50) have suggested that the reaction is completely concerted and occurs by attack of the carbonyl sulfur on the β -hydrogen, which gives a six-membered cyclic transition state. This produces an unstable dithiolcarbonic acid which rapidly decomposes to the mercaptan and carbonyl sulfide.

Some cases of trans-elimination have been reported but in these cases the purity of the substrate has been questioned.

Xanthate esters which have no β -hydrogen or "unreactive" β -hydrogens undergo isomerization to give dithiolcarbonates (51-58). Carbohydrates which have an oxygen directly bonded to the carbon adjacent to the xanthate-bearing carbon give the dithiolcarbonate structure or remain unchanged (59). Freudenberg and Wolf (57) reported that the thermal isomerization of the 3-S-methyl xanthate ester (I) of 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose proceeded with retention of configuration although no proof of structure was given. Heap and Owen (60) have given support for the proposed structure by thermal rearrangement of the xanthate ester to give the dithiolcarbonate (II) which was reduced with LiAlH_4 to yield the mercaptan (III). Air

VII

The formation of the 3,6-epithio derivative indicated that the pyrolysis had occurred with retention of configuration because molecular models indicated that the corresponding allose derivative could not form the 3,6-epithio derivative. This was confirmed by the preparation of the same epithio compound from the S_N2 displacement of the 6-tosyl group from the 3,6-di-tosyl-1,2-O-isopropylidene- α -D-allofuranose with potassium thiobenzoate, followed by treatment with sodium methoxide in methanol. However, none of the 3,6-epithio-allose derivative could be detected when 1,2-O-isopropylidene-6-thiobenzoate-3-tosyl-glucofuranose was treated with sodium methoxide under similar conditions. Therefore, the pyrolysis of the xanthate ester did indeed proceed with retention of configuration. This isomerization presumably occurs by an S_Ni mechanism through a front-side displacement by the thiocarbonyl sulfur (59).

Wolfson and Foster (61) subjected several sugar xanthates to pyrolytic conditions. These sugar derivatives did not give carbonyl sulfide or mercaptan by products, and examination of the residues indicated no reaction had taken place. In the one case of methyl 3,4-O-isopropylidene- β -D-arabinopyranoside 2-O-(S-methyl dithiocarbonate), reduction of the pyrolysis product with Raney nickel gave methyl 2-deoxy-3,4-O-isopropylidene- β -D-erythro-aldopentose, which indicated an isomerization to a dithiolcarbonate had occurred. The preparation of unsaturated cellulose derivatives by thermal decomposition of

xanthate esters was reported by Polyakov, Rogovin, and Derevitskaya (62). Recently Descotes (63) obtained similar products by xanthate pyrolysis. The structures of these products, however, have not been proven.

The potential use of the coupled xanthate as paper (16,17,18, 19) and rubber (20-26) additives has led to an investigation of the chemistry of the oxidatively coupled xanthate, referred to hereafter as xanthide. Other names for this structure: dixanthogens, O-alkylthiocarbonic acid disulfide, bisalkyl xanthogen, and O-O-dialkyl ester of bithioformic acid. Oxidative coupling the xanthate to xanthide with I_2 or Cl_2 was reported by Debus (7,8) in 1852.

Other oxidants have been used for this oxidation reaction, such as sodium tetrathionate, sodium hypochlorite, sodium chlorate, nitrous acid, chloramine T, and others (64-67). Recently Shasha et al. (66) reported the quantitative preparation of 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose xanthide when dimethyl sulfoxide was added to the reaction mixture. Xanthides of the polysaccharides, cellulose (67), starch (68), and others have been prepared as insoluble solids.

The xanthide group reacts with cyanide to form a xanthoanhydride and thiocyanate (69). This reaction has been used for the quantitative determination of xanthides and polysulfides (70,71).

Shasha et al. (72) studied the reactions of xanthides of 1,2-; 1,4-; 1,5-; and 1,6-dihydroxyalkanes. They found that the monoxanthide derivative (VIII) of 1,2-propanediol decomposed to give a cyclic thio-carbonate (IX) when pyridine was added.

The monoxanthide derivative (X) of 2,2-dimethyl-1,3-propanediol decomposed similarly to the 1,3-cyclic thionocarbonate (XI). The dioxanthide (XII), however, underwent a different decomposition, which produced a cyclic xanthate ester (XIII).

The monoxanthides of 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol all rearranged to yield xanthate ester products.

The formation of the thionocarbonate apparently arises from a nucleophilic displacement on the thiocarbonyl carbon by the oxygen of the unsubstituted hydroxyl group.

Presumably, the formation of the xanthate ester product could occur by a nucleophilic displacement on the carbon carrying the xanthate group by the polarized thiocarbonyl sulfur or by one of the sulfur atoms of the sulfur atoms of the disulfide bond:

However, the stereochemistry and the mechanism of this reaction have not been investigated.

The 3,3'-xanthide (XV) of 1,2-isopropylidene- α -D-glucofuranose has been subjected to similar reaction conditions. It gave the 5,6-thionocarbonate (XVI) in good yield (73). The thionocarbonate (XVI) was readily converted to the carbonate (XVII) by treatment with

silver nitrate. On methylation of the thionocarbonate a unique ortho-ester (XVIII) was formed (74).

Methyl 4,6-O-benzylidene- α -D-glucopyranoside 2,3-thionocarbonate (XIX) was prepared from the rearrangement of the monoxanthide (XX) of methyl 4,6-O-benzylidene- α -D-glucopyranoside (75). This carbonate was the first example of a 5-membered trans-fused ring on a pyranose sugar.

This decomposition of xanthides has been shown to be quite general for the formation of cyclic thionocarbonates of carbohydrates (76). The xanthide group also reacts with alcohols to give acyclic thionocarbonates (77).

A mixture of two symmetrical xanthides readily undergo an exchange reaction in polar solvents to form the unsymmetrical xanthide. In this way ethyl 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose xanthide (XXII) was prepared (78).

An attempted transesterification between 1,2-O-isopropylidene- α -D-glucofuranose (XXIV) and ethyl xanthide (XXIII) did not give the expected 5,6-thionocarbonate (XVI) but gave the 5,6-carbonate (XVII) (79). Subsequent reactions showed that the thionocarbonate was not an intermediate and, therefore, neither was the mixed xanthide.

The formation of a sulfenyl iodide (XXV) has been proven in the crosslinking reaction of sodium 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose xanthate (XXVI) with iodine. The sulfenyl iodide (XXV) is unstable and further reacts to form the xanthide (XIV) (80).

Xanthide (XIV) consumes two moles of chlorine to produce a bis(chlorosulfonyl chloride) derivative (XXVII) (81).

This sulfonyl chloride reacted with sodium iodide to give the chloro-thioformate (82,83).

Xanthides also react with trimethyl phosphite to give a dithiocarbonate anhydrosulfide with 0,0'-dimethyl phosphorothionate derivative (84), which in the presence of pyridine gives a bis(thiocarbonyl)monosulfide, also referred to as xanthogen monosulfide or xanthoanhydride.

Schonberg et al. (85) have reported an insertion reaction occurs between a diaryldiazomethane and xanthide, but not with dialkyl-diazomethane.

XXIII

Shasha, Doane, and Russell (81) also found no reaction occurs between diazomethane and xanthide.

The xanthides of several carbohydrates have been decomposed in the presence of pyridine by Trimmell, Doane and Russell (86). They found that only when xanthides were on primary positions would rearrangement occur to give dithiocarbonate. Thionocarbonates were obtained when the xanthide groups were on secondary positions. Some primary xanthides also gave thionocarbonates.

XXIX

XXX

Recently, however, Trimnell and coworkers (87) have reported the formation of cyclic dithiocarbonates from methyl α -D-xylopyranoside and methyl 4,6-O-benzylidene- α -D-glucopyranoside xanthides both of which can only have xanthides in secondary positions.

Xanthation of 2,3:5,6-di-O-isopropylidene-D-mannose (XXXIV) (88) followed by treatment with iodine gave the expected xanthide (XL) in low yield. However, prolonged xanthation gave bis(1-S-carbonyl-2,3:5,6-di-O-isopropylidene-1-thio-D-mannofuranose) disulfide (XLI) and none of the xanthide. This product was readily converted to bis(2,3:5,6-di-O-isopropylidene- α -D-mannofuranosyl) disulfide (XLII). In these products the oxygen atom at C-1 has been replaced with sulfur. This unexpected isomerization led to an investigation of the behavior of the xanthide (XLIII) of 2,3:5,6-di-O-isopropylidene-D-mannitol. The nmr spectrum of the xanthide showed that xanthation occurred at C-1 to give a 1,1-xanthide. On treatment with pyridine the xanthide produced the bis(2,3:5,6-di-O-isopropylidene-D-mannitol) orthocarbonate (XLIV) (89).

For the past several years there has been considerable interest in the use of photochemistry as a method for introducing new functional groups into carbohydrates and as a new route to important carbohydrate derivatives. Horton and Jewell (90) reported the photochemical transformation of a dithiol acetal (XLV). A sulfide (XLVI) was obtained in 60% yield which could be further transformed photochemically into the deoxy-sugar (XLVII).

The photolysis of a diazo-sugar (XLVIII) (91) in methanol gave the unsaturated sugar (XLIX), but in isopropanol it was converted to the deoxy derivative (L).

The primary azides of hexopyranosides are readily converted to C-6 aldehyde carbohydrates by photolysis (92-97). Irradiation of 6-deoxy-6-iodo-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose with added base gives 6-deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (98). Galactose azine is converted to a mixture of lyxose and galactose when subjected to uv light (99). Decarboxylation of 2-deoxy-(2',4'-dinitroaniline)-D-gluconic acid by irradiation has been reported (100).

Binkley and Binkley (101) studied the photolysis of D-galactose oxime and found the major product to be an unstable nitrogen-containing compound, which spontaneously decomposed to D-lyxose. Deoxy sugars have also been prepared by photodecomposition of dimethyl thiocarbamate derivatives (102). Sulfur-containing sugars have been prepared by the photo-addition of mercaptans to unsaturated sugars (103-104).

The relatively high efficiency with which sulfur compounds absorb light (105,106), especially compounds which contain the thiocarbonyl group, has resulted in a large number of reports on the photochemistry of organic sulfur compounds (105,107,108). The xanthate group and derivatives thereof exhibit a very strong absorbance of ultraviolet light and, therefore, have the potential of photochemical transformations by direct irradiation. The photolyses of some xanthate esters have been reported. Okawara and coworkers subjected O-ethyl S-benzyl xanthate (LI) to uv irradiation and found benzyl mercaptan (LII) and carbonyl sulfide (LIII) as major products, which were obtained in low yield (109-111). When styrene or methyl methacrylate was added to the reaction mixture polymerization occurred, indicating

a free radical mechanism for the photodecomposition of the xanthate ester.

Photolysis of O-benzyl S-methyl xanthate (LIII) in the presence of cyclohexene gave methyl mercaptan (LIV), carbonyl sulfide, 3-benzylcyclohexene (LV), and a dimer of cyclohexene (LVIII). The xanthate ester, O-diphenylmethyl S-methyl xanthate (LVI), gave 1,1,2,2-tetraphenylethane (LVII) and LVIII. These results suggested the formation of a carbene intermediate.

In ethanol no decomposition of O-benzyl S-methyl xanthate (LVI) occurred. However, addition of triethylamine gave methyl benzyl thioether, S-benzyl ethyl thiocarbonate, dibenzyl thioether, and dibenzyl disulfide (112).

Acyl xanthate esters (LIX) have been photolyzed and produced acyl radicals (LX) and xanthate radicals (LXI) (113). The acyl radical then loses carbon monoxide and a recombination reaction occurs between the new alkyl radical and the xanthate radical to give a xanthate ester (LXII), which is stable to Pyrex-filtered light.

Shah, Singh, and George (114,115) observed that the photolytic decomposition of a dixanthate (LXIII) gave a mixture of dimeric compounds (LXIV, LXV) which appeared to be formed from a carbene intermediate.

Another similar xanthate ester (LXVI) was prepared by Schonberg and Sodtke (116) and was photolyzed to produce a coupled product (LXVII).

Xanthates have been used as photoinitiators in polymerization reactions (109,111,117-120) and incorporated in polymers for grafting sites (119,120).

Because of the strong absorption of light of the xanthide group (106), the photoreactivity of xanthate derivatives, and the chemical reactivity of the xanthide group, a study of the photochemistry of some carbohydrate xanthides was undertaken.

RESULTS

Photolysis of Bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) Dithiobis(thioformate) (XXXIII)

Compound XXXIII was photolyzed in methanol (0.016 M) for 3 hr under N_2 with a high pressure Hg arc lamp (450 watt) using a quartz immersion well. The insoluble white solid (LXIX) which had formed was removed by filtration. Column chromatography of the filtrate afforded unreacted XXXIII, 1,2:3,4-di-O-isopropylidene- α -D-galactopyranose (LXVIII), sulfur, and a component (LXX) of R_f intermediate to that of XXXIII and LXVIII. The uv spectrum of LXX showed absorption characteristic of a xanthate ester (106).

From elemental analysis LXX was formulated as bis(6-deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) 6-O,6'-S-dithiocarbonate, which was isolated in 35% yield. The nmr spectrum showed a 2-proton absorption centered at τ 6.68, which is in the expected range for thio-methylene protons (87).

Additional evidence for the structure of LXX was obtained by reductive cleavage with $LiAlH_4$ (60) to give LXVIII and 1,2:3,4-di-O-isopropylidene-6-thio- α -D-galactopyranose (LXXI).

The structure of LXXI was confirmed by nmr and elemental analysis. The nmr of this sample showed a one-proton doublet at τ 8.37, which slowly disappeared when kept with D_2O for 18 hr. The slow exchange and the position of the peak is indicative of a thiol group (87). A two-proton multiplet centered at τ 7.31, assigned to the protons of the thiol substituted methylene group, collapsed to a broad doublet when the deuterium exchange was complete.

The mass spectrum of LXX showed a high mass peak at 563 which corresponds to M-15. Other mass peaks supporting the structure appeared at 319, 303, and 275, which corresponds to $M-CH_3-C_{12}H_{20}O_5$,

The insoluble solid LXIX showed a strong continuous absorption from 350-220 nm with an ill-defined shoulder at approximately 315 nm. From the nmr and elemental analysis, LXIX was formulated as bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) tetrathio-bis(thioformate). Although this compound had a fairly wide mp range, 160-164°, its physical properties were the same as those of an authentic sample prepared from the sodium xanthate salt of LXVIII and sulfur monochloride. Attempted recrystallization from methanol gave XXXIII, free sulfur, and a component of melting point of 149-151° identified as bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) trithio-bis(thioformate)

(LXXII). This decomposition might be expected since polysulfides are known to readily lose sulfur to form disulfides (121). The wide melting point range of LXIX may be due to thermal decomposition as the melting point was approached or from the presence of a small quantity of other polysulfides, such as trisulfides and pentasulfides. Evidence that other sulfides were present in the reaction mixture was obtained when LXIX, obtained from a large-scale preparation, was fractionally crystallized from a large volume of methanol by slow evaporation of the solvent at room temperature. The first fraction had a melting point range of 160-163°, while later fractions gave melting point ranges of 153-160°, 148-156°, and 130-145°. Elemental analysis of these later fractions indicated they were mixtures of di-, tri-, and tetrasulfides, but the first fraction was pure LXIX.

Nitrogen was flushed through the reaction mixture (methanol solvent) during photolysis and the effluent gases were bubbled into a hexane solution which contained piperidine. During the first 2 hr, uv analysis showed only absorbance due to the reaction product of piperidine and COS (λ_{max} 240 nm). However, after 3 hr, detectable amounts of the reaction product of piperidine and CS₂ were present (122).

Using cyclohexane solvent and similar reaction conditions, the same products were obtained in nearly the same yields when XXXIII was photolyzed. Longer irradiation in either solvent gave more complex mixtures, because LXX also undergoes photodecomposition under these reaction conditions. The yield of LXIX was increased by photolyzing at 5° in methanol. When Corex-filtered light was used LXX did not react

to any significant extent. Therefore, a cyclohexane solution (0.064 M) of XXXIII was irradiated for 22 hr with Corex-filtered light to yield LXIX (37%), LXX (35%), and LXVIII (13%). A more dilute solution (0.003 M) gave LXX in 74% yield and LXIX could not be detected after 5.5 hr. However, when irradiation was stopped after 2 hr an apparent mixture of polysulfides was obtained, based on mp 145-153° and elemental analysis.

The photolysis of the tetrasulfide (LXIX) in cyclohexane resulted in the formation of the xanthate ester (LXX), but at a slower rate than XXXIII. Under similar conditions a 9.2% yield of LXX was obtained from LXIX compared to 35% from XXXIII.

The effect of solvent on the reaction mixture is shown in Table 1. The results show that the yield of LXX is highest in cyclohexane and that in the alcohol solvents more LXVIII is produced along with CS₂. In all cases some 6-deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactose (LXXIII) was obtained.

Table 1. Solvent effect on products of irradiation of XXXIII.

Irrad. time	Product yield in moles/mole XXXIII					
	Pyrex					Corex
	Cyclohexane		Methanol	Isopropanol		Cyclohexane
	13 hr	23 hr	19 hr	13 hr		5.5 hr
Sulfur	0.80	0.75	0.88	0.34	0.34	0.33
LXXIII	0.11	0.2	0.09	< 0.2	0.16	< 0.23
LXX	0.74	0.5	0.57	0.31	0.27	0.74
LXVIII	0.15	0.21	0.55	0.80	1.07	0.25
COS	0.34	-	0.25	-	0.81	-
CS ₂	0.0	-	0.27	-	0.81	-

The photolysis of a solution of XXXIII and ethyl xanthide (XXIII) in cyclohexane rapidly gave the mixed xanthide (LXXIV). After 15-20 min an apparent photostationary state of the three xanthides was established.

Compound XXXIII was found to react readily with methyl radicals generated by the thermal decomposition of acetyl peroxide. Using approximately 2 moles of acetyl peroxide per mole of XXXIII, of the S-methyl xanthate ester LXXV of LXVIII was obtained.

The structure of LXXV was confirmed by comparison of its properties to that of an authentic sample prepared from the sodium xanthate salt of LXVIII and methyl iodide.

The photochemical transformation of XXXIII to LXIX and LXX is in contrast to the pyrolysis reaction reported by Trimmell et al. (86) in which XXXIII gave only bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranose) 6,6'-thionocarbonate (XXXIV). However, on pyrolysis bis(methyl 2,3,4-tri-O-methyl- α -D-glucopyranoside) 6,6'-dithiobis(thioformate) (XXXI) rearranged to the corresponding dithiocarbonate (XXXII) (86). They also reported that dithiocarbonates were not formed when xanthides attached to secondary positions were pyrolyzed.

Photolysis of Bis(methyl 2,3,4-tri-O-methyl- α -D-glucopyranoside) 6,6'-Dithiobis(thioformate) (XXXI)

The photolysis of XXXI in cyclohexane resulted in the formation of XXXII in 47% yield. No attempt was made to identify any polysulfides similar to LXIX and products having disulfide bonds were destroyed by reaction with thiophenol or p-chlorothiophenol (123).

Photolysis of Bis(1,2:5,6-di-O-isopropylidene- α -D-glucofuranose) 3,3'-Dithiobis(thioformate) (XIV)

The photolysis of XIV with Corex-filtered light gave the xanthate ester, bis(3-deoxy-1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) 3-O,3'-S-dithiocarbonate (LXXVI), as a white crystalline solid in 34% yield. Analysis of the original reaction mixture by measurement of the absorption at 283 nm showed that the total xanthate ester formed was 37%. Therefore, the xanthate ester formation occurred with at least 92% retention of configuration.

This xanthate ester, LXXVI, was reduced with LiAlH_4 to give 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose (LXXVII) and 1,2:5,6-di-O-isopropylidene-3-thio- α -D-glucofuranose (III). The nmr spectrum of III was identical to that of the known III prepared by the method of

Heap and Owen (60). The thiol was also converted to the S-acetyl derivative (LXXVIII) and exhibited properties identical to those previously reported for this compound (60).

The xanthate ester, LXXVI, was independently synthesized by reaction of the 3-thio (III), prepared by the method of Heap and Owen (60), with the 3-chlorothioformate XXVIII of LXXVII, described by Shasha et al. (83).

The xanthate ester prepared by this procedure had the same properties as the product obtained from the photolysis of XIV. A mixture of the two showed no depression of the melting point.

Examination of the minor components of the reaction mixture showed no components which could be identified as the xanthate ester in which the inversion had occurred.

DISCUSSION OF RESULTS

To account for the products of the photolysis of XXXIII, two mechanisms are proposed. The first mechanism describes the reaction process as being initiated by the homolytic cleavage between the thiocarbonyl carbon and sulfur (-C--S , see scheme 1). The thiocarbonyl radical (LXXIX) was assumed to readily eliminate carbonyl sulfide to produce the 6-deoxy-1,2:3,4-di-O-isopropylidene- α -D-galactopyranose radical (LXXX) which could then attack XXXIII at the disulfide bond producing LXX and the xanthate radical (LXXXI). This radical (LXXXI) may dimerize, couple with the xanthate disulfide radical (LXXXII) produced from the initial cleavage, or initiate a chain displacement reaction (121) at any of the disulfide bonds until a termination reaction occurs, such as shown in equations 4-6.

Scheme 1

The polysulfides, LXIX and LXXII, may be formed by the radical combination reactions 4 and 6, which are similar to the reactions proposed by Byers et al. (124) for the formation of tetrasulfides from disulfides.

The second mechanism proposed is shown in scheme 2. This mechanism involves the attack of an excited sulfur atom on the methylene carbon, which requires a seven-membered cyclic transition state if it involves the thiocarbonyl sulfur, or a five-membered transition state if it involves a sulfur of the disulfide linkage. The reaction then proceeds with the elimination of carbonyl sulfide and free sulfur. This molecular sulfur may insert into a disulfide bond (125-127) or possibly abstract another atom of sulfur to form S_2 (128), which could insert into a disulfide bond (129). These insertion reactions would account for the formation of the trisulfide and tetrasulfide products.

Scheme 2

Neither of the proposed mechanisms accounts for the apparent preference of tetrasulfide formation. However, Hoffmeister and Tarbell (130, p. 35) found a similar preferential formation of a hexasulfide on pyrolysis of benzoyl cyclopentamethylene thiocarbamyl disulfide. The photolysis of benzoic-pyrrolidine dithiocarbamic anhydride gave a hexasulfide, while photolysis of benzoic-morpholine dithiocarbamic anhydride gave a tridecasulfide (130, p. 2857). They suggested that the selective formation of the polysulfides is due to the lower solubilities of these polysulfides. This appears to be the most plausible explanation of the results presented here, for in the mechanism presented in scheme 1 disulfide exchange would be expected to occur very rapidly to form many polysulfides based on the rapid exchange of ethyl xanthide and XXXIII. In scheme 2 one would expect insertion to occur in all polysulfides.

The rapid exchange reaction of ethyl xanthide with XXXIII is assumed to proceed by a radical mechanism based on results of Siebert (117), who has shown that photolysis of xanthide will catalyze the polymerization of butyl acrylate, and on results of Walling (in 131) which showed that disulfides photolyze to thiyl radicals. The above results indicate the xanthate radical is relatively stable and does not readily

abstract hydrogen atoms from cyclohexane since LXVIII was obtained in low yield and carbon disulfide could not be detected in the reaction mixture.

However, methanol or isopropanol appears to serve as a hydrogen source for the xanthate radical in dilute solution since carbon disulfide and LXVIII are produced in larger quantities at the expense of LXX when photolysis is carried out in these solvents.

Although methyl radicals readily attacked the disulfide bond of the xanthide which supports the mechanism in scheme 1, the stereoselectivity in the formation of LXXVI, the low yield of LXX from the tetrasulfide LXIX, the high yield of LXX in dilute solution, and the low yield of the 6-deoxy derivative, LXXIII, in isopropanol, strongly favor the cyclic mechanism shown in scheme 2. If a free radical were formed on C₃ of the glucose (LXXXIII), one would expect to obtain both the allo (LXXXIV) and the gluco (LXXVI) configuration in the 3-thiosugar.

An initial isomerization similar to the thermal rearrangement of xanthate esters was considered unlikely since, under the reaction conditions, no carbonyl-containing products could be detected by infra-red analysis of the reaction mixture.

The photolysis of either the mono- or the dixanthide of methyl 4,6-O-benzylidene- α -D-glucopyranoside under similar reaction conditions did not give a xanthate ester. Likewise, the monoxanthide of trans-1,2-cyclohexanediol did not give a xanthate ester product.

EXPERIMENTAL

Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Optical rotations were determined in a 1-dm tube with a Rudolph polarimeter. Infrared spectra were recorded with a Beckman IR-33 spectrophotometer. Nuclear magnetic resonance spectra of CDCl_3 solutions were recorded on a Varian HA-100 spectrometer with tetramethylsilane as internal reference standard (τ -10.0). A Perkin-Elmer Model 202 spectrophotometer was used to record uv spectra. For tlc, Silica Gel G was used as the adsorbent and 19:1 (v/v) methanol-sulfuric acid as the spray reagent. Mallinckrodt silicic acid (100 mesh) was used for large-scale chromatography. All reagents were reagent grade and were used without further purification. The light source was a Hanovia high pressure mercury arc lamp (450 watt, #679A) in a quartz immersion well, with or without additional filters.

Preparation of Bis(1,2:3,4-di-O-isopropylidene-6-O-thiocarbonyl- α -D-galactopyranose) Disulfide (XXXIII)

This compound was prepared analogous to XIV with properties as reported by Doane et al. (73, p. 3071).

Photolysis of XXXIII

Quartz, Methanol (0.016 M)

A solution of XXXIII (2.5 g) in methanol (230 ml) was sparged with nitrogen for 10 min. The light yellow solution was then irradiated for 3 hr, while the flow of nitrogen continued. The insoluble

solid present in the reaction mixture was collected to yield LXIX (0.247 g), mp 160-164°, $[\alpha]_D^{23}$ 0.0° (c 1, CHCl₃), $\lambda_{\max}^{\text{ether}}$ 315 nm (ϵ 7150) and 240 nm (ϵ 21000), $\lambda_{\max}^{\text{film}}$ 1250 cm⁻¹ (OC(S)SS), nmr: τ 4.49 (doublet, J_{1,2} 7 cps-H₁), τ 5.20-5.44 (multiplet), τ 5.60-5.84 (multiplet), τ 8.43, 3.57, 8.68 (singlets-CMe₂).

Anal. Calcd for C₂₆H₃₈O₁₂S₆: C, 42.5; H, 5.3; S, 26.2; mol wt 738. Found: C, 42.3; H, 5.5; S, 26.4; mol wt 778 (vapor pressure osmometry, CHCl₃).

The methanol filtrate was concentrated and kept in an ice bath for 4 hr to yield a white precipitate. Recrystallization from methanol gave XXXIII (0.777 g), mp 130-134°.

Combining the methanol filtrates and evaporation of the solvent at 40° under reduced pressure gave a yellow syrup, which was chromatographed on silicic acid. The column was eluted with acetone:hexane (1:50). The first component eluted was free sulfur (0.005 g). Next eluted was a mixture of XXXIII and LXX (0.078 g) determined by tlc. Continued elution gave LXX (0.578 g, 27%) as a yellow syrup, $[\alpha]_D^{23}$ -55° (c 1, CHCl₃), $\lambda_{\max}^{\text{MeOH}}$ 283 nm (ϵ 8200); nmr: τ 4.50 (2-proton, 4-line multiplet, H₁), τ 5.1-5.5 (4-proton multiplet), τ 5.6-6.1 (6-proton multiplet), τ 6.68 (2-proton multiplet), τ 8.51, 8.59, 8.66 (24-protons, singlets, CMe₂).

Anal. Calcd for C₂₅H₃₈O₁₁S₂: C, 51.9; H, 6.6; S, 11.1; mol wt 578. Found: C, 51.6; H, 6.6; S, 11.4; mol wt 586 (vapor pressure osmometry, CHCl₃).

Next eluted was LXVIII (0.227 g). Compound LXX was recrystallized from hexane at -20° on long standing to give a crystalline solid of mp $107-110^{\circ}$.

Quartz, Isopropanol (0.016 M)

A solution of XXXIII (2.5 g) in isopropanol (230 ml) was irradiated under N_2 for 3 hr using the quartz immersion well. The reaction mixture was filtered and the solvent evaporated at 40° under reduced pressure. Thin layer chromatography of the resulting light yellow syrup showed three components; one of R_f equal to the R_f of XXXIII, one of R_f equal to the R_f of LXX, and the other of R_f equal to the R_f of LXVIII. The syrup was dissolved in methanol (50 ml) and kept for 1.5 hr. A white precipitate (0.39 g) formed of mp $149-151^{\circ}$, which was formulated from elemental analysis as bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) trithiobis(thioformate) (LXXII).

Anal. Calcd for $C_{26}H_{38}O_{12}S_5$: C, 44.6; H, 5.32; S, 22.8. Found: C, 44.3; H, 5.4; S, 22.2.

The filtrate was kept for 72 hr at -20° and a second precipitate (0.50 g) formed of mp $130-152^{\circ}$. This precipitate was assumed to be a mixture of XXXIII and LXXII, since tlc showed only one component. The methanol was evaporated and the remaining syrup was chromatographed to give free sulfur (0.024 g), XXXIII (0.25 g), LXX (0.30 g), and LXVIII (0.60 g).

Quartz, Cyclohexane (0.016 M)

A solution of XXXIII (2.5 g) in cyclohexane (230 ml) was irradiated for 3 hr under N_2 using the quartz immersion well. The reaction

mixture was concentrated at 40° under reduced pressure. The resulting syrup was dissolved in methanol (50 ml) and kept at -20° . A white ppt formed, which was collected, washed with methanol, and dried (0.9 g), mp $130-162^{\circ}$, assumed to be a mixture of XXXIII, LXIX, and other polysulfides. The methanol was evaporated and the resulting syrup chromatographed to give XXXIII (0.2 g), LXX (0.75 g), LXVIII (0.41 g), and sulfur (0.035 g).

Corex, Cyclohexane (0.064 M)

A solution of XXXIII (10.0 g) in cyclohexane (230 ml) was irradiated under a continuous flow of N_2 for 24 hr using Corex-filtered light. The reaction mixture was filtered to remove the insoluble LXIX (0.448 g), which had formed. The volatile components were then removed at room temperature. The resulting yellow syrup was dissolved in methanol (500 ml) and the methanol was slowly evaporated. As the solvent evaporated a white ppt formed (2.8 g, mp $152-158^{\circ}$). Recrystallization from methanol (250 ml) gave LXIX (mp $159-163^{\circ}$). The remaining original methanol solution was kept at 5° for 18 hr to give XXXIII (2.8 g) as a white ppt. Filtration of the supernatant liquid and concentration of the solvent at 40° under reduced pressure gave a yellow syrup which was chromatographed on silica gel to give XXXIII (0.27 g), LXX (3.2 g), and LXVIII (0.53 g).

Pyrex, Cyclohexane (0.003 M)

A solution of XXXIII (0.5 g) in cyclohexane (230 ml) was irradiated under a continuous flow of N_2 for 14 hr using Pyrex-filtered

light. The volatile components were evaporated at room temperature. The resulting light yellow syrup was chromatographed to give sulfur (0.019 g), LXXIII (0.040 g), LXX (0.320 g), and LXVIII (0.030 g). No CS_2 could be detected in the effluent gases, but COS was found as a diethylamine complex in an ethanol (1 L):diethylamine (4.0 ml) solution by uv analysis (0.25 mmol).

Pyrex, Isopropanol (0.003 M)

A solution of XXXIII (0.5 g) in isopropanol (230 ml) was irradiated under a continuous flow of N_2 for 23 hr. The volatiles were evaporated at room temperature. The resulting syrup was chromatographed to yield sulfur (0.008 g), LXX (0.14 g), and LXVIII (0.15 g). A mixture of CS_2 (0.62 mmol) and COS (0.60 mmol) was detected in the effluent gases by uv analysis of an ethanol (1 L):diethylamine (4.0 ml) solution into which the gases had been sparged. Compound LXXIII was obtained as a mixture (0.040 g).

Pyrex, Methanol (0.003 M)

A solution of XXXIII (0.5 g) in methanol (230 ml) was irradiated under a continuous flow of N_2 for 19 hr using Pyrex-filtered light. The cloudy reaction mixture was kept at room temperature and the volatiles were allowed to evaporate. The resulting syrup was chromatographed to yield sulfur (0.021 g), a mixture containing mostly LXXIII (0.016 g), LXX (0.25 g), and LXVIII (0.107 g). Analysis of the effluent gases showed a mixture of COS (0.185 mmol) and CS_2 (0.205 mmol), determined by uv analysis after reaction with diethylamine.

Corex, Cyclohexane (0.003 M)

A solution of XXXVIII (0.5 g) in cyclohexane (230 ml) was irradiated with Corex-filtered light under a continuous flow of N_2 for 5.5 hr. The volatiles were removed at room temperature and the resulting syrup was chromatographed to yield sulfur (0.008 g), LXX (0.32 g), and LXVIII (0.087 g). Only COS could be detected in the effluent gases by uv analysis after reaction with diethylamine in ethanol.

Irradiation of Bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) Tetrathiobis(thioformate) (LXIX)

A methanol (230 ml) suspension of LXIX (2.4 g) was irradiated for 3 hr under N_2 using quartz-filtered light. The reaction mixture was filtered and unreacted LXIX (1.3 g) was recovered. The solvent was removed from the filtrate and the resulting syrup was treated with pyridine (5 ml) and p-chlorothiophenol (1 g). After 30 min the pyridine was evaporated and the sample was chromatographed to give LXX (0.197 g) and LXVIII (0.540 g).

Preparation of 1,2:3,4-Di-O-isopropylidene-6-thio- α -D-galactopyranose (LXXI) from LXX

Compound LXX (0.5 g) was dissolved in ether (20 ml) and $LiAlH_4$ (0.25 g) was added in portions over a 5-min period. The resulting black-gray mixture was then refluxed for 1 hr. Thin layer chromatography of the reaction mixture showed two components, one of R_f equal to that of LXVIII and the other of R_f greater than that of LXX. "Newcell" thiol spray reagent indicated the component of higher R_f was a thiol. After the excess $LiAlH_4$ was destroyed by adding ethyl acetate, the

reaction mixture was poured into 5% aqueous acetic acid (50 ml). The reaction flask was rinsed with acetic acid (2 ml) and the combined acetic acid solutions extracted three times with ether (50 ml portions). The ether solution was kept over sodium bicarbonate until neutral, then washed with water and dried over sodium sulfate. Evaporation of the ether gave a colorless syrup, which was chromatographed on silica gel. Elution with hexane:CHCl₃ (4:1) gave LXXI (0.165 g), nmr: τ 4.51 (1-proton doublet, $J_{1,2}$ 5 cps, H-1), τ 5.40 (1-proton quartet, $J_{2,3}$ 8 cps, $J_{3,4}$ 3 cps, H-3), τ 5.70 (2-proton multiplet, H-2,4), τ 6.25 (1-proton sextet, $J_{4,5}$ 2 cps, $J_{5,6}$ 6 cps, H-5), τ 7.31 (2-proton multiplet, H-6), τ 8.37 (1-proton doublet, J 9 cps, H-thiol), τ 8.49, 8.60, 8.69, 8.76 (12-protons, singlets, CMe₂). The signal at τ 8.37 disappeared when kept with D₂O for 18 hr and the signal at τ 7.31 became a broad doublet.

Photolysis of XXXIII and Ethyl Xanthide

A solution of XXXIII (2.5 g) and ethyl xanthide (XXII) (2.5 g) in cyclohexane (230 ml) was photolyzed under nitrogen (quartz). After 5 min a new component was detected by tlc. This component had an R_f identical to that of an authentic sample of the mixed xanthide (LXXIV) (78). After 30 min LXXIV became a major component. Carbonyl sulfide was detected in the effluent gases by uv analysis of an ethanol solution containing piperidine.

Reaction of XXXIII with Acetyl Peroxide

Cyclohexane (50 ml) containing XXXIII (1.0 g) was warmed to 70° and acetyl peroxide (0.2 ml) was added (132). After 1 hr of gentle reflux more acetyl peroxide (0.4 ml) was added. The reaction mixture was refluxed for 1 hr. After cooling, the solvent was removed by evaporation at 50° under reduced pressure to yield a light yellow syrup.

Chromatography gave a major component (0.58 g), which was identified as 1,2:3,4-di-O-isopropylidene-6-O-[methylthio(thiocarbonyl)]- α -D-galactopyranose (LXXV). The uv, nmr, and mass spectra were identical to those of an authentic sample.

Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 48.0; H, 6.2; S, 18.3. Found: C, 47.9; H, 6.5; S, 17.8.

Preparation of 1,2:3,4-Di-O-isopropylidene-6-O-[methylthio(thiocarbonyl)]- α -D-galactopyranose (LXXV)

Dimethyl sulfoxide (5.0 ml), LXVIII (5.0 g), 5 N sodium hydroxide (5.0 ml), and carbon disulfide (7.5 ml) were stirred 10 min. The reaction mixture was cooled to 5° and methyl iodide (5.0 ml) was added. After 1 min a ppt formed; the mixture was kept for 15 min. Then water (100 ml) and $CHCl_3$ (50 ml) were added to the brown mixture and the two phases were separated. The $CHCl_3$ solution was washed three times with H_2O (100 ml), dried with Na_2SO_4 and the solvent removed. The resulting dark brown syrup was dissolved in 1:1 hexane:chloroform and filtered through silica gel. Evaporation of the solvent gave a bright yellow syrup. This syrup was dissolved in methanol and treated with charcoal.

The solvent was removed at 50° under reduced pressure to give a nearly colorless syrup.

Anal. Calcd for $C_{14}H_{22}O_6S_2$: C, 48.0; H, 6.3; S, 18.3.

Found: C, 47.9; H, 6.2; S, 18.6.

Preparation of Bis(1,2:3,4-di-O-isopropylidene- α -D-galactopyranos-6-yl) Tetrathiobis(thioformate) (LXIX)

A mixture of LXVIII (4.5 g), DMSO (5 ml), 5 N NaOH (5.0 ml), and carbon disulfide (5 ml) was stirred for 10 min. After addition of acetic acid (0.6 ml), sulfur monochloride (1.0 ml) was added. A precipitate formed, which was collected and washed with acetone (30 ml) and ether (150 ml). The sample was dried and suspended in acetone (50 ml). The mixture was filtered and the filtrate was evaporated to give an off-white solid, mp 158-162°. The nmr of this sample was identical to that of LXIX from the photolysis of XXXIII.

Anal. Calcd for $C_{26}H_{38}O_{12}S_6$: C, 42.6; H, 5.2; S, 26.2.

Found: C, 42.0; H, 5.2; S, 25.8.

Preparation of Bis(1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) 3,3'-Dithiobis(thioformate) (XIV)

This compound was prepared according to the method of Shasha et al. (66).

Photolysis of Bis(1,2:5,6-di-O-isopropylidene- α -D-glucofuranos-3-yl) 3,3'-Dithiobis(thioformate) (XIV)

Corex, Cyclohexane (0.064 M)

A solution of XIV (10.0 g) in cyclohexane (230 ml) was irradiated under N_2 for 27 hr using Corex-filtered light. The solution was

kept at room temperature and the volatile components evaporated. Hexane was added to the syrup and the resulting solution was filtered. The hexane filtrate was seeded with crystalline LXXVI and kept at 5°. A crystalline ppt of LXXVI formed, which was collected and washed with cold hexane (2.02 g). Thin layer chromatography of the supernatant showed considerable LXXVI in solution along with unreacted XIV and LXXVII.

Corex, Cyclohexane (0.016 M)

A solution of XIV (2.5 g) in cyclohexane (230 ml) was irradiated under N₂ for 20 hr using Corex-filtered light. The volatile components were evaporated at room temperature and the yellow syrup was chromatographed to give: sulfur (0.10 g), XIV (0.25 g), XIV and LXXVI (0.36 g), LXXVI (0.92 g), and LXXVII (0.56 g).

Compound LXXVI was recrystallized from hexane and exhibited the following properties: mp 133-135°, $[\alpha]_D^{23} - 56^\circ$ (c 1, acetone), $\lambda_{\max}^{\text{EtOH}}$ 282 nm (ϵ 9600).

Anal. Calcd for C₂₅H₃₈O₁₁S₂: C, 52.0; H, 6.5; S, 11.1, mol wt 578. Found: C, 51.6; H, 6.7, S, 11.6, mol wt 550 (vapor pressure osmometry in CHCl₃).

Nuclear magnetic resonance spectrum shows the following: τ 4.15 (3-proton multiplet, H-1, H-1', H-3'), τ 5.31 (2-proton doublet, H-2) τ 5.6-6.1 (9-proton multiplet), τ 8.48, 8.60, 8.70 (24-protons, singlets, CMe₂).

Pyrex, Cyclohexane (0.003 M)

A solution of XIV (0.5 g) in cyclohexane (230 ml) was irradiated under N_2 for 13.5 hr using Pyrex-filtered light. The volatile components of the reaction mixture were evaporated at room temperature and the remaining syrup was chromatographed to give: sulfur (0.013 g), 1,2:5,6-di-O-isopropylidene-3-O-[cyclohexylthio(thiocarbonyl)]- α -D-glucofuranose (LXXXV) (0.044 g), XIV (0.080 g), LXXVI (0.250 g), and LXXVII (0.066 g).

Reduction of LXXVI with $LiAlH_4$

Compound LXXVI (0.5 g) was dissolved in ether (20 ml) and $LiAlH_4$ (0.25 g) was added in small portions over a 5-min period. The resulting gray-black mixture was then refluxed for 1 hr. After destroying the excess $LiAlH_4$ with ethyl acetate, the reaction mixture was poured into 5% acetic acid (50 ml). The mixture was transferred to a separatory funnel, and the flask was rinsed with acetic acid (2.0 ml). The ether layer was separated and the water layer was washed twice with ether (50 ml). The ether extracts were combined and washed with $NaHCO_3$ solution and with water. The ether layer was dried with Na_2SO_4 . Evaporation of the ether and addition of hexane to the colorless syrup gave a crystalline precipitate, identified as LXXVII (0.291 g) by comparison with an authentic sample. The hexane solution was concentrated to a colorless syrup, which was purified by chromatography on silica gel. Elution with $CHCl_3$ gave a colorless syrup (0.188 g), which was identified as 1,2:5,6-di-O-isopropylidene-3-thiol- α -D-glucofuranose (III).

The nmr spectrum of this sample was identical to that of an authentic sample prepared by the method of Heap and Owen (60).

Anal. Calcd for $C_{12}H_{20}O_5S$: C, 52.2; H, 7.3; S, 11.6; mol wt 276.

Found: C, 52.1; H, 7.4; S, 11.5; mol wt 312 (vapor pressure osmometry in $CHCl_3$).

Preparation of Bis[3-O-(chloromethylsulfenyl
chloride)-1,2:5,6-di-O-isopropylidene- α -
D-glucofuranose] Disulfide (XXVII)

A slow stream of chlorine was bubbled through an ether solution (100 ml) of XIV (2.0 g) for 5 min. The ether was then evaporated at room temperature. The resulting mixture, which consisted of a white crystalline solid and a syrup, was redissolved in ether (50 ml) and chlorine was bubbled through the solution for 10 min. The ether was evaporated and the white solid was washed with three portions of ether (25 ml), then dried at 50° for 10 min. The product was identical to an authentic sample.

Preparation of 1,2:5,6-Di-O-isopropylidene- α -D-
glucofuranose 3-Chlorothioformate (XXVIII)

To a solution of XXVII (2 g) in chloroform (10 ml) was added a solution of sodium iodide (1.5 g) in acetone (15 ml). After 10 min, hexane (50 ml) was added to the dark brown solution, which gave a dark green ppt. The mixture was filtered and the filtrate concentrated at 40° under reduced pressure to yield a dark syrup. The syrup was dissolved in ether (75 ml) and the solution extracted with sodium thiosulfate solution. After extracting the ether solution with water,

drying with sodium sulfate, and treating with activated charcoal, the ether was evaporated to yield a yellow syrup which partially crystallized. The product was used without further purification.

Preparation of Bis(1,2:5,6-di-O-isopropylidene-
 α -D-glucofuranos-3-yl) 3-O,3'-S-Dithio-
carbonate (LXXVI) from III and XXVIII

To a solution of III (1.0 g) in ether (10 ml) was added XXVIII (1.2 g). Triethylamine (0.5 ml) was added dropwise to produce immediately a white ppt. Thin layer chromatography indicated nearly all III and XXVIII had reacted and gave a product of R_f equal to that of LXXVI. The white ppt was removed by filtration. After evaporation of the ether, the syrup was dissolved in chloroform and washed with water, dried with sodium sulfate, and the solvent evaporated. After ten days the sample was chromatographed to give LXXVI, which crystallized from hexane, mp 133-134°. A portion of the product was mixed with LXXVI obtained from the photolysis of XIV and gave mp 132-134°; nmr, uv, and ir of both products were identical.

Preparation of 3-S-Acetyl-1,2:5,6-di-O-
isopropylidene- α -D-glucofuranose
(LXXVIII) from III

An ether solution (10 ml) containing III (0.125 g) was treated with acetic anhydride (2.5 ml) and pyridine (3.0 ml). The solution was kept three days. The excess reagents were evaporated at room temperature (72 hr). The resulting syrup was dissolved in ether (20 ml) and the solution was extracted twice with water (10 ml). The ether

solution was dried with sodium sulfate and the solvent was evaporated to give a colorless syrup (0.075 g), $[\alpha]_D^{23} - 47^\circ$ (c 1, CHCl_3); lit.

$[\alpha]_D^{23} - 46^\circ$.

Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_6\text{S}$: C, 52.7; H, 6.95; S, 10.0.

Found: C, 52.9; H, 7.19; S, 9.9.

Photolysis of Bis(methyl 2,3,4-tri-O-
methyl- α -D-glucopyranoside)
6,6'-Dithiobis(thioformate) (XXXI)

A solution of XXXI (2.5 g) in methanol (230 ml) was irradiated under N_2 for 3 hr using a quartz immersion well. The solution was concentrated at 50° under reduced pressure to yield a yellow syrup. This syrup was treated with p-chlorothiophenol and pyridine to destroy unreacted XXXI and polysulfides. The pyridine was evaporated and the remaining syrup was chromatographed to give XXXII (0.970 g, 46%) and methyl 2,3,4-tri-O-methyl- α -D-glucopyranoside.

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