N, 2.57; O, 20.56; Cl, 19.53. Found: C, 52.88; H, 4.51; N, 2.66; O, 20.57; Cl, 19.32.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-(ethoxycarbonyl)amino-β-D-glucopyranoside (XVII).—Ethyl chloroformate (0.33 g) was added dropwise with stirring to a solution of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (VII, 1 g, 0.0027 mol) in 20 ml of absolute pyridine. The resulting mixture was stirred for 1 hr, kept overnight at 0°, and poured into ice–water. After 3 hr at 0° the precipitate was collected by filtration, washed with cold water, and recrystallized from absolute methanol to give 1.02 g (0.0026 mol, 96.2% yield) of XVII melting at 233–233.5°, $[\alpha]^{23}\text{D}$ −87° (*c* 1.26, pyridine).

Anal. Calcd for $C_{23}H_{27}NO_7$ (429.4): C, 64.33; H, 6.34; N, 3.27; O, 26.08. Found: C, 64.25; H, 6.57; N, 3.37; O, 26.33.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-phenoxycarbonylamino-β-D-glucopyranoside (XVIII).—Benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (VII, 1.07 g, 0.003 mol) in absolute pyridine (40 ml) was cooled to −5°, and phenyl chloroformate (0.52 g) was added dropwise with exclusion of moisture. The mixture was stirred 1 day at −5°. Pyridine was then removed by evaporation *in vacuo* until the volume was 15 ml and the mixture was poured into ice–water. The precipitate was collected by filtration, washed with cold water, and dried. Two recrystallizations from dioxane–hexane and absolute methanol gave 1.2 g (0.0025 mol, 87.5% yield) of XVIII melting at 247–247.5°, $[\alpha]^{27}\text{D}$ −84.5° (*c* 1.28, pyridine).

Anal. Calcd for $C_{27}H_{27}NO_7$ (477.5): C, 67.91; H, 5.70; N, 2.93; O, 23.46. Found: C, 67.46; H, 5.77; N, 3.28; O, 23.54.

Treatment of Benzyl 4,6-*O*-Benzylidene-D-glucopyranosido-[2,3:4′,5′]-2′-oxazolidinones (XIa and XI) with Alcoholic Potassium Hydroxide. Regeneration of Starting Compounds VIIa and VII.—A solution of benzyl 4,6-*O*-benzylidene-D-glucopyranosido[2,3:4′,5′]-2′-oxazolidinone (XIa or XI, 0.5 g, 0.00133 mol) in a hot mixture of potassium hydroxide (1 g) and 95% ethanol (60 ml) was refluxed for 5 hr at 85°. The mixture was then diluted with hot water (150 ml), allowed to cool, and kept at 0° to complete precipitation. The product was collected by filtration, washed with cold water, and dried. Recrystallization from absolute methanol gave 0.499 g (0.00126 mol, 95% yield) of benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-D-glucopyranoside (VIIa or VII).

Catalytic Hydrogenation of *trans*-Oxazolidinone XI.—Palladium black (1 g) was suspended in ethyl acetate (125 ml) in a hydrogenation flask. Benzyl 4,6-*O*-benzylidene-β-D-glucopyranosido-[2,3:4′5′]-2′-oxazolidinone (XI, 0.8138 g, 0.0021 mol) was then introduced, followed by hydrogen at atmospheric pressure. The hydrogen uptake started immediately and the hydrogenation was stopped after 30 min. The catalyst was removed by filtration and the filtrate was concentrated *in vacuo*. The remaining syrup was taken up in dioxane–acetone–petroleum ether and the mixture was kept at 0° for 2 weeks. Compound XIII, giving a characteristic carbonyl absorption at 1750 cm^{-1} and a positive test with Benedict reagent, was obtained.

Registry No.—II, 19358-93-1; III, 19358-94-2; IX, 19358-95-3; X, 19358-96-4; XI, 19358-97-5; XIa, 19358-98-6; XII, 19358-99-7; XIV, 19359-00-3; XIVa, 19359-01-4; XV, 19359-02-5; XVI, 19359-03-6; XVII, 19359-04-7; XVII, 13347-81-4.

Reactions of Chlorine with Some Thiocarbonyl Sugar Derivatives[1a]

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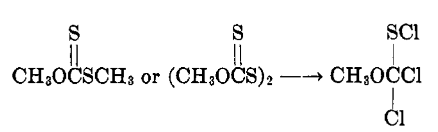
The reactions between chlorine and some thiocarbonyl sugar derivatives were investigated. In each reaction the major product(s) was (were) isolated and identified. Both bis(1,2:5,6-di-*O*-isopropylidene-3-*O*-thiocarbonyl-α-D-glucofuranose) disulfide (**1**) and bis[methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-thiocarbonyl-α-D-glucopyranoside] disulfide (**3**) added four chlorine atoms (two chlorine atoms to each carbon–sulfur double bond) to yield corresponding chloromethylsulfenyl chloride derivatives **2** and **4**. 1,2:5,6-Di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl-α-D-glucofuranose (**5**) reacted in a similar fashion to give **6**. On further reaction with chlorine, **6** lost the methylthio group and gave a dichloromethanesulfenyl chloride derivative (**7**). 1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-thionocarbonate (**8**), methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate (**10**), and 3-*O*-ethoxythiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**12**) yielded the corresponding carbonates **9**, **11**, and **13**. Conversion of **8** → **9** in the presence of $H_2{}^{18}O$ established the origin of the carbonyl oxygen atom. A dithiocarbonate derivative (**17**) was obtained from 1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose 5,6-trithiocarbonate (**16**). Two major reaction products from methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-[(1-piperidyl)thiocarbonyl]-α-D-glucopyranoside (**14**) were identified as the corresponding carbonyl compound **15** and the cyclic carbonate **11**.

The formation of sulfenyl chlorides by reaction of chlorine with certain organic disulfides and dithio esters has been reported.[2] Douglas and Osborne[3] studied the action of anhydrous chlorine at low temperature on some simple thio esters. Such dithio esters as the methyl ester of methyl xanthate undergo chlorinolysis with removal of the methylthio group as methylsulfur trichloride and with formation of methoxydichloromethanesulfenyl chloride. This product is also formed during chlorinolysis of bis(methoxythiocarbonyl) disulfide. Although this reaction has been conducted with a number of organic sulfur derivatives,



$$CH_3O\overset{\overset{S}{\|}}{C}SCH_3 \text{ or } (CH_3O\overset{\overset{S}{\|}}{C}S)_2 \longrightarrow CH_3O\underset{\underset{Cl}{|}}{\overset{\overset{SCl}{|}}{C}}Cl$$

no information is available on such a reaction with similar sulfur derivatives of carbohydrates. We have now extended our studies[4] on the preparation and reactions of thiocarbonyl derivatives of carbohydrates to the reaction of these derivatives with chlorine. We examined the behavior of carbohydrate bis(*O*-thiocarbonyl)disulfides, (alkylthio)dithiocarbonates, cyclic

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[1] (a) Presented before the Division of Carbohydrate Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968. (b) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article is not copyrighted.

[2] I. B. Douglass in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp 350–360.

[3] I. B. Douglass and C. E. Osborne, *J. Amer. Chem. Soc.*, **75**, 4582 (1953).

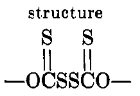
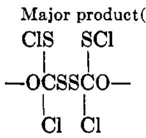
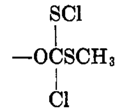
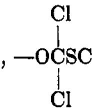
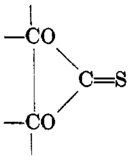
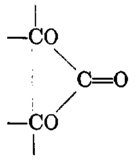
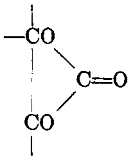
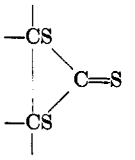
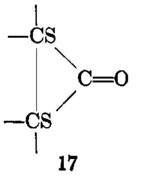
[4] W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, **30**, 3071 (1965); **32**, 1080 (1967); references cited therein.

and acyclic thionocarbonates, thiocarbamates, and trithiocarbonates upon treatment with chlorine at room temperature and without special precautions to exclude moisture.

Bis(*O*-thiocarbonyl) disulfide and (methylthio)-thiocarbonyl derivatives chlorinate readily under these conditions, the initial reaction being addition of chlorine to the carbon–sulfur double bond. Bis(1,2:5,6-di-*O*-isopropylidene-3-*O*-thiocarbonyl-α-D-glucofuranose) disulfide (**1**) and bis[methyl 4,6-*O*-benzylidene-2 (and 3-) *O*-thiocarbonyl-α-D-glucopyranoside] disulfide (**3**) each added four atoms of chlorine and gave bis[3-*O*-(chloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose] disulfide (**2**) and bis[methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-(chloromethylsulfenyl chloride)-α-D-glucopyranoside] disulfide (**4**) (Table I).

TABLE I

PRODUCTS OF REACTION OF CARBOHYDRATE THIOCARBONYL DERIVATIVES WITH CHLORINE

Compd	Thiocarbonyl structure	Major product(s)
1, 3	 $-O\overset{S}{\overset{\|}{C}}SS\overset{S}{\overset{\|}{C}}O-$	 $-O\underset{Cl}{\overset{ClS}{C}}SS\underset{Cl}{\overset{SCl}{C}}O-$ **2, 4**
5	 $-O\overset{S}{\overset{\|}{C}}SCH_3$	 $-O\underset{Cl}{\overset{SCl}{C}}SCH_3$, **6**  $-O\underset{Cl}{\overset{Cl}{C}}SCl$ **7**
8, 10, 12		 **9, 11, 13**
14	 $-O\overset{S}{\overset{\|}{C}}NC_5H_{10}$	 $-O\overset{O}{\overset{\|}{C}}NC_5H_{10}$, **15**  **11**
16		 **17**

Compound **2** was isolated as a white crystalline product in nearly quantitative yield.

The proposed structure of **2** was consistent with its elemental analysis, ir spectrum, and mass spectrum. While the mass spectrum did not reveal a molecular ion peak at 810, it did exhibit a peak at M − 15 which is characteristic[5] for *O*-isopropylidene derivatives. In addition the five mass peaks present in the spectrum at 795, 797, 799, 801, and 803 were in the proper ratios expected for the presence of four chlorine atoms in the molecule.

Product **4** was recovered as a white partly crystalline compound in about 30% yield. Analyses of **4** were consistent with the proposed structure.

Sulfenyl chloride **2** was stable during storage at room temperature for several weeks Under similar storage conditions, sulfenyl chloride **4** gradually decomposed and evolved acidic vapors. Instability of **4** is largely attributed to the presence of the hydroxyl group in the molecule. Sulfenyl chlorides react with alcohols and form hydrogen chloride and carbonyl-containing compounds along with other products.[2] Such a reaction might also explain the lower yield for **4** compared with that of **2** since the residue remaining after removal of **4** showed strong carbonyl absorption in the 5.6–5.9-μ region.

When bis(methoxythiocarbonyl) disulfide was treated with chlorine under our conditions, the tetrachloro derivative was obtained as a syrup in a quantitative yield.

We also examined bis(*O*-thiocarbonyl) disulfide derivatives of starch (starch xanthide) and 6-*O*-tritylstarch (*O*-tritylstarch xanthide). Powdered starch xanthide rapidly consumed gaseous chlorine with the evolution of heat. Exposure of the xanthide to chlorine gas for 10 min or for several hours gave essentially the same product based on sulfur and chlorine content. The ratio of chlorine to sulfur in the product was about 2:1 and not 1:1 as it would if chlorine were added to the carbon–sulfur double bond. Treatment of *O*-tritylstarch xanthide with chlorine caused detritylation and gave a chlorinated product with a chlorine–sulfur ratio of 0.6:1. Both the product from starch xanthide and from *O*-tritylstarch xanthide had strong carbonyl absorptions near 5.7 μ. Upon storage, both products lost much of their sulfur and chlorine.

Addition of chlorine to the carbon–sulfur double bond appeared also to be the initial reaction when 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methylthio)thiocarbonyl-α-D-glucofuranose (**5**) was treated with chlorine. Careful addition of a solution of chlorine in ether to **5**, while the progress of the reaction was monitored spectroscopically, permitted the isolation of 1,2:5,6-di-*O*-isopropylidene-3-*O*-[(methylthio)chloromethanesulfenyl chloride]-α-D-glucofuranose (**6**) as a yellow unstable syrup, which gave off acidic vapors upon standing. Sulfur and chlorine values and nmr data acquired soon after isolation of **6** were consistent with the proposed structure.

When the addition of chlorine to **5** was continued beyond that required for formation of **6**, the major compound formed was 3-*O*-(dichloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropyidene-α-D-glucofuranose (**7**). This product also decomposed on standing.

Compounds that possess thiocarbonyl groups flanked on either side by oxygen gave no isolable sulfenyl chloride derivative. 1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-thionocarbonate (**8**), methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate (**10**), and 3-*O*-ethoxythiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**12**) reacted with chlorine and gave their respective carbonate derivatives 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (**9**), methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-

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(5) D. C. DeJongh and K. Biemann, *J. Amer. Chem. Soc.*, **86**, 67 (1964).

carbonate (**11**), and 3-*O*-ethoxycarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**13**). Each reaction was followed by observing the disappearance of the absorption maxima for the thiocarbonyl group near 230–238 mμ. Yields of carbonate ranged from 50 to 70% when the reaction was conducted in the presence of aqueous sodium carbonate or when the reaction mixtures were treated with aqueous sodium carbonate upon completion of the chlorine treatment. Omission of the sodium carbonate permitted hydrolysis of the isopropylidene group in compounds **8** and **12** and the benzylidene group in compound **10** and resulted in lower yields of **9**, **11**, and **13**. Thionocarbonate has been oxidized to carbonate with other reagents, such as silver nitrate, silver carbonate, and lead tetraacetate.[4]

The thiocarbonyl sulfur atom in thiocarbamates and trithiocarbonates is likewise replaced by oxygen upon treatment with chlorine. Methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-[(1-piperidyl)thiocarbonyl]-α-D-glucopyranoside (**14**) gave two major chlorinolysis products in almost equal amounts as shown by tlc. Separation and isolation of the two components by preparative tlc gave the cyclic carbonate **11** and methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-[(1-piperidyl)carbonyl]-α-D-glucopyranoside (**15**). Cyclic carbonate **11** was obtained in somewhat higher amount than **15**. The mechanism for the formation of **11** is not clear. That **15** is not intermediate was demonstrated when reaction of **15** under the conditions used for **14** gave none of the cyclic product.

Chlorine treatment of 1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose 5,6-trithiocarbonate (**16**) afforded a 47% yield of crystalline 1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose 5,6-dithiocarbonate (**17**). Compound **17** was prepared independently from **16** upon oxidation with potassium permanganate.

The precise mechanism involved in replacement of the thiocarbonyl sulfur atom in **8**, **10**, **12**, **14**, and **16** by oxygen is not clear. The reaction might proceed *via* addition of a molecule of chlorine to form a chlorosulfenyl chloride intermediate, which is then hydrolyzed by water. Although water was not intentionally added to some of the reaction solutions, the solvents used were not dried and the reactions were often conducted in open flasks.

That the carbonyl oxygen atom is indeed provided by water was shown when the conversion **8** → **9** was performed in the presence of a small amount of water which contained 5% $H_2{}^{18}O$. The mass spectrum of **9** prepared in the presence of $H_2{}^{18}O$-enriched water showed 4.54% more ^{18}O than the spectrum of **9** prepared without added $H_2{}^{18}O$. The calculation was made from the intensities of the mass peaks at 233 mass units which correspond to M − 15 plus two mass units for the ^{18}O isotope.

Experimental Section

Melting points were determined with a Fisher-Johns[6] apparatus and are uncorrected. Optical rotations were measured in a 1-dm tube with a Rudolph polarimeter. Ultraviolet and infrared spectra were recorded by Perkin-Elmer Models 202 and 137 spectrophotometers, respectively. Nmr spectra were recorded in deuterated chloroform by a Varian A-60 nmr spectrometer with tetramethylsilane as internal reference. Tlc was performed with silica gel as the adsorbent in the solvents indicated. Components were detected by sulfuric acid. Mass spectra were obtained with a Nuclide 12-90-G mass spectrometer equipped with a probe inlet. Water enriched (5%) with $H_2{}^{18}O$ was a product of Yeda Research and Development Co., Rehovoth, Israel.

Reaction of Bis(*O*-thiocarbonyl) Disulfides with Chlorine. A.—A solution of bis(1,2:5,6-di-*O*-isopropylidene-3-*O*-thiocarbonyl-α-D-glucofuranose) disulfide[7] (**1**, 1.0 g) in ether (50 ml) was treated with a slow stream of chlorine. Within a few minutes white crystals deposited from the solution and the chlorine stream was stopped. The contents of the flask were kept at 5° for 1 hr and then filtered. The solid material was washed with ether and dried. The yield of product characterized as bis[3-*O*-(chloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose] disulfide (**2**) was nearly quantitative, mp 168–169° (recrystallized from ether–hexane), $[\alpha]^{23}\mathrm{D}$ +52° (*c* 1, chloroform). Comparison of the infrared spectra (films) of **1** and **2** revealed that the characteristic absorption[7] for the bis(*O*-thiocarbonyl) disulfide group near 8.0 and 9.7 μ was lacking in compound **2** and instead there was strong absorption at 9.0 and 13.8 μ (C–Cl). Mass spectrum showed peaks at 795, 797, 799, 801, and 803 mass units, which correspond to M − 15 for the various distributions of ^{35}Cl and ^{37}Cl. Intensities of the five peaks were in the ratios expected for the presence of four chlorine atoms.

Anal. Calcd for $C_{26}H_{38}Cl_4O_{12}S_4$: C, 38.4; H, 4.7; Cl, 17.5; S, 15.8. Found: C, 38.7; H, 5.0; Cl, 17.4; S, 15.6.

B.—Bis[methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-thiocarbonyl-α-D-glucopyranoside] disulfide[8] (**3**, 1.0 g) was treated with ether (5 ml) that contained excess chlorine. Yellow solid **3** readily dissolved and within several seconds a white precipitate was deposited from the solution. The liquid layer was decanted and the precipitate was washed three times with ether (3 ml each) and dried. Yield of the white solid, which was characterized as bis[methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-(chloromethylsulfenyl chloride)-α-D-glucopyranoside] disulfide (**4**), was 350 mg: mp 108–112°; infrared spectrum (Nujol), 2.86 (OH), 9.1, 13.3 (phenyl), 13.8 (C–Cl), and 14.3 μ (phenyl).

Anal. Calcd for $C_{30}H_{34}Cl_4O_{12}S_4$: C, 42.1; H, 4.0; Cl, 16.6; S, 15.0. Found: C, 41.8; H, 4.3; Cl, 16.5; S, 14.9.

C.—Bis(methoxythiocarbonyl) disulfide (0.5 g) in ether (20 ml) was treated with a slow stream of chlorine for 5 min and then the ether and excess chlorine were removed under reduced pressure. The syrup, which remained, weighed 0.8 g: infrared spectrum (film), 8.4, 9.0, 10.6, 12.0, and 13.9 μ. A spectrum (film) of the starting material showed 8.0, 8.6, 9.7, and 10.8 μ.

Anal. Calcd for $C_4H_6Cl_4O_2S_4$: Cl, 40.0; S, 36.0. Found: Cl, 39.4; S, 35.6.

D.—Starch, sodium hydroxide, and carbon disulfide (1:1:1 molar ratio) were mixed in a reactor as described previously.[9] A 2% aqueous dispersion of this starch xanthate was adjusted to pH 6, and aqueous iodine was added to convert the xanthate into xanthide. The insoluble xanthide was washed with water, ethanol, and ether and then air equilibrated for several hours. Sulfur content of the product was 14.7%. A portion (200 mg) of the product was placed in a 50-ml flask and the flask was then filled with chlorine gas. The xanthide was agitated for 10 min by means of a magnetic stirring bar. After excess chlorine was removed by evacuation, benzene (20 ml) was added to the flask and distilled off at 40° under reduced pressure. Extraction with benzene was repeated until the distillate was neutral to pH test paper. The starch product was then washed with ether and carbon disulfide and dried to constant weight. Sulfur and chlorine contents of the product were 5.5 and 13.6%, respectively. Analyses were similar for a product (200 mg) kept 16 hr in a flask (500 ml) filled with chlorine. Infrared spectrum (KBr) revealed carbonyl absorption near 5.7–5.8 μ.

E.—6-*O*-Tritylstarch xanthide was prepared as previously described[8] for the corresponding amylose derivative. Sulfur in the product amounted to 15.7%. After reaction of the air dried

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[6] The 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.

[7] W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.*, **30**, 162 (1965).

[8] E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, **3**, 354 (1967).

[9] C. L. Swanson, T. R. Naffziger, C. R. Russell, B. T. Hofreiter, and C. E. Rist, *Ind. Eng. Chem., Prod. Res. Dev.*, **3**, 22 (1964).

and pulverized product with chlorine for several minutes, the product had only 2% chlorine. When the reaction was repeated with freshly prepared, undried xanthide suspended in ether, a chlorine content of 8.8% was realized. Sulfur content of the chlorinated product was 13% and its infrared spectrum (KBr) showed carbonyl absorption near 5.7 μ but no phenyl absorption near 6.1 μ. That detritylation had occurred during chlorination was confirmed when no precipitate formed when the product was dissolved in concentrated sulfuric acid and diluted with water.

Reaction of (Alkylthio)dithiocarbonate with Chlorine.—A solution of 1,2:5,6-di-*O*-isopropylidene-3-*O*-[(methylthio)thiocarbonyl]-α-D-glucofuranose (**5**, 0.5 g) in ether (25 ml) was stirred while a solution of chlorine in ether was added dropwise. The progress of the reaction was followed by observing the decrease in the absorption maximum at 285 mμ for the starting material. Upon disappearance of the maximum at 285 mμ, the ether was removed under reduced pressure to yield a yellow syrup. Sulfur and chlorine analyses (14.9 and 16.8%, respectively) and nmr spectrum (signal at τ 7.36 for S–CH$_3$) were consistent with the proposed structure of 1,2:5,6-di-*O*-isopropylidene-3-*O*-[(methylthio)chloromethanesulfenyl chloride]-α-D-glucofuranose (**6**). When the addition of chlorine was continued after the 285-mμ maximum had disappeared, a different product was formed. Removal of the ether left a yellow syrup, which gave correct sulfur and chlorine analyses (7.8 and 26.3%, respectively) for 3-*O*-(dichloromethanesulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**7**). An nmr spectrum had no S–CH$_3$ signal.

Both chlorinated products **6** and **7** were unstable and decomposed when kept for several hours. The products were not amenable to tlc since chromatograms varied in the number of spots depending upon the length of time that elapsed between application of the components and immersion in the solvent.

Reaction of Thionocarbonates with Chlorine. A.—1,2-*O*-Isopropylidene-α-D-glucofuranose 5,6-thionocarbonate[7] (**8**, 260 mg) in tetrahydrofuran (15 ml) was treated with a solution of chlorine in ether by dropwise addition. The progress of the reaction was followed spectrometrically by observance of the decrease in thionocarbonate absorption near 235 mμ of periodically withdrawn samples. Addition of chlorine was stopped when there was no maximum at 235 mμ. Upon completion of the reaction a white compound crystallized from the solution. Yield of the product, identified as 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (**9**), was 200 mg, mp 230–231°, infrared spectrum (Nujol) identical with an authentic sample.

The experiment was repeated but with addition of 1 drop of water, which was enriched (5%) with $H_2{}^{18}O$, to the tetrahydrofuran solution. The product was isolated and gave the same melting point and infrared spectrum as **9**. Mass spectrum of the product had a M − 15 peak at 231 mass units. The intensity of the peak at 233 mass units (two units higher than the M − 15 peak due to the ^{18}O isotope) showed that there was 4.54% more ^{18}O in **9** isolated from the $H_2{}^{18}O$ treatment than in **9** prepared without such treatment.

B.—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate[8] (**10**, 300 mg) in chloroform (20 ml, spectroscopic grade) was stirred and sodium carbonate (2 g) in water (30 ml) was added. A solution of chlorine in chloroform was added slowly while progress of the reaction was monitored as in part A. Upon complete disappearance of the absorption maximum near 238 mμ for **10**, the mixture was stirred an additional 30 min. After the chloroform layer was separated and dried, the chloroform was removed under reduced pressure. Tlc (carbon disulfide–ethyl acetate 7:3) revealed a major component of R_f 0.3 and a minor spot at the origin. Separation of the major component from a preparative tlc plate afforded 132 mg of a crystalline product identified as methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (**11**). Infrared spectrum and melting point of this product were identical with those of authentic[8] **11**.

C.—3-*O*-Ethoxythiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**12**, 300 mg) was treated with chlorine by the procedure used in part B. Infrared spectrum (film) of the product was identical with a spectrum of 3-*O*-ethoxycarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**13**). Separation of the major product by preparative tlc (ethyl acetate–carbon disulfide 1:9) from a minor contaminant gave the known ethoxycarbonyl derivative, 195 mg, mp 71–73°.

Reaction of Thiocarbamates with Chlorine.—A mixture of methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-[(1-piperidyl)thiocarbonyl]-α-D-glucopyranosides (**14**) was prepared by reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-thionocarbonate (**10**) with piperidine.[10] The mixture of 2- and 3-*O* isomers was used for reaction with chlorine. A solution of the thiocarbamates (180 mg) in ether (100 ml) was stirred while chlorine in ether was added dropwise. The addition of chlorine, which was accompanied by precipitation of piperidine hydrochloride, was continued until no more precipitate formed. The mass was then shaken with water (100 ml) that contained sodium carbonate (2 g). The ether layer was separated and evaporated to a syrup. Tlc (chloroform–acetone 9.5:0.5) revealed two spots. Separation of the components on a preparative tlc plate and isolation therefrom gave methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (**11**, 68 mg) and methyl 4,6-*O*-benzylidene-2- (and 3-) *O*-(1-piperidyl)carbonyl-α-D-glucopyranoside[11] (**15**, 50 mg). These products were identified by comparison with authentic samples.

Reaction of Trithiocarbonate with Chlorine.—1,2-*O*-Isopropylidene-5,6-dithio-β-L-idofuranose 5,6-trithiocarbonate[4] (**16**, 500 mg) in chloroform (50 ml of spectroscopic grade) was treated with chlorine by a procedure similar to that used for **10** except that the absorption maximum near 315 mμ was monitored. Tlc (chloroform–acetone 4:1) showed one major spot with R_f 0.5 and two minor spots with R_f 0.1 and 0.9. The major component was separated by preparative tlc and extracted from the plate with acetone. Evaporation of the acetone gave 220 mg of a crystalline compound (mp 144–146°) which upon recrystallization from chloroform–hexane had mp 152–154°, $[\alpha]^{23}$D +48° (*c* 1, chloroform). The product was identified as 1,2-*O*-isopropylidene-5,6-dithio-β-L-idofuranose 5,6-dithiocarbonate (**17**) by infrared (film) at 5.7 and 6.1 μ (carbonyl), by elemental analyses, and by independent synthesis from **10** (see following section).

Anal. Calcd for $C_{10}H_{14}O_5S_2$: C, 43.2; H, 5.0; S, 23.0. Found: C, 42.9; H, 5.2; S, 23.4.

When a chloroform solution of **16** was treated with a stream of chlorine gas at 25° or lower until the yellow solution became colorless, a major component of R_f 0.9 was observed by tlc. Evaporation of the reaction mixture to constant weight gave a syrup which, from several preparations, analyzed for 20–25% of chlorine.

Preparation of 1,2-*O*-Isopropylidene-5,6-dithio-β-L-idofuranose 5,6-Dithiocarbonate (17).—Potassium permanganate (4.0 g) in water (5 ml) and acetone (100 ml) was mixed with **16** (400 mg). After the mixture was refluxed for 45 min, ethanol (50 ml) was added and reflux was continued for another 15 min. Manganese dioxide thus formed was filtered off and the colorless filtrate was evaporated to dryness to yield 320 mg of a crystalline product, mp 142–146°, which was washed with water and recrystallized, mp 148–150° (chloroform–hexane) or 150–152° (acetone–hexane). Tlc of the product showed only one spot with an identical R_f as **17** and the infrared spectrum of the product was superimposable with **17**.

Registry No.—**1**, 2946-03-4; **2**, 19461-97-3; bis(methyl 4,6-*O*-benzylidene-2-*O*-thiocarbonyl-α-D-glucopyranoside) disulfide, 14419-71-7; bis(methyl 4,6-*O*-benzylidene-3-*O*-thiocarbonyl-α-D-glucopyranoside) disulfide, 19426-90-5; **5**, 16667-96-2; **8**, 2816-87-7 **10**, 14419-72-8; **12**, 19189-59-4; methyl 4,6-*O*-benzylidene-2-*O*-[(1-piperidyl)thiocarbonyl]-α-D-glucopyranoside, 19407-33-1; **16**, 19426-91-6; **17**, 19407-34-2; chlorine, 7782505; methyl 4,6-*O*-benzylidene-3-*O*-[(1-piperidyl)thiocarbonyl]-α-D-glucopyranoside, 19407-35-3.

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[10] Unpublished work.

[11] E. I. Stout, W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *Tetrahedron Lett.*, 4481 (1967).