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CHLOROTHIOFORMATES OF SUGARS FROM THE CORRESPONDING CHLOROMETHYLSULFENYL CHLORIDE DERIVATIVES*

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ABSTRACT

Reaction of bis[3-*O*-(chloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose] disulfide (**2**) with sodium iodide gave crystalline 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-chlorothioformate (**4**). With methanol in the presence of pyridine, **2** gave 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methoxythiocarbonyl)-α-D-glucofuranose (**5**), but in the presence of sodium carbonate **2** gave a mixture of **4**, **5**, and the corresponding methoxycarbonyl analog of **5**. With triethylamine, 3-*O*-diethylthiocarbamoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**6**) was obtained. Bis[6-*O*-(chloromethylsulfenyl chloride)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose] disulfide (**3**), in the presence of Silica Gel G or by titration with alkali, gave bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-(tetrathiobis[formate]) (**7**). With sodium iodide **3** gave either the corresponding chlorothioformate or a mixture of chlorothioformate together with what was assumed to be the iodothioformate.

INTRODUCTION

Reactions of chlorine with some thiocarbonyl derivatives of sugars have been previously reported[1]. Upon treating bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) 3,3′-[dithiobis(thioformate)] (**1**) with chlorine, a fairly stable, crystalline, sulfenyl chloride (**2**) derivative was obtained in almost quantitative yield. In general, sulfenyl chlorides are very reactive compounds. For example, at least 19 different reactions have been described for 2,4-dinitrobenzenesulfenyl chloride[2]. Some of the reactions of **2** and of bis[6-*O*-(chloromethylsulfenyl chloride)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose] disulfide (**3**) are reported here.

RESULTS AND DISCUSSION

*Reactions of bis[3-*O*-(chloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose] disulfide* (**2**). — Sulfenyl chlorides, such as 2-chloroethanesulfenyl chloride[3], are reduced by iodides to give the corresponding disulfides, whereas

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methoxydichloromethanesulfenyl chloride[4] is simultaneously reduced and hydrolyzed by such treatment to form bis(methoxycarbonyl) disulfide.

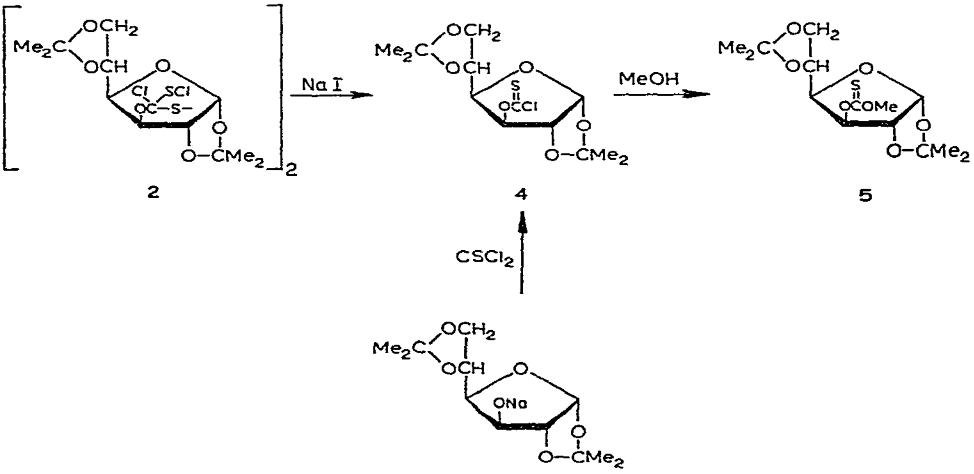
$$2\mathrm{ClCH_2CH_2SCl} + 2\mathrm{KI} \rightarrow (\mathrm{ClCH_2CH_2S})_2 + \mathrm{I_2} + 2\mathrm{KCl}$$

$$2\mathrm{CH_3OCCl_2SCl} + 2\mathrm{KI} + 2\mathrm{H_2O} \rightarrow (\mathrm{CH_3OCOS})_2 + \mathrm{I_2} + 2\mathrm{KCl} + 4\mathrm{HCl}$$

On the other hand, trichloromethanesulfenyl chloride gives thiophosgene[5] under such treatment.

$$\mathrm{Cl_3CSCl} + 2\mathrm{KI} \rightarrow \mathrm{ClCSCl} + \mathrm{I_2} + 2\mathrm{KCl}$$

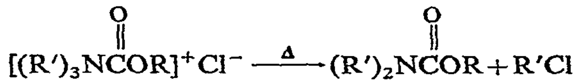
When compound **2** was treated with sodium iodide, 1 mole of iodine was released per mole of **2** in 5 min. T.l.c. of the reaction mixture showed one major product, which absorbed strongly under u.v. light (**2** did not absorb). This product was formulated as 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose 3-chlorothioformate (**4**). The structure of **4** was deduced from elemental analysis, by molecular-weight determination, from its reaction with methanol to give the known 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methoxythiocarbonyl)-α-D-glucofuranose (**5**), and by independent synthesis from the sodium salt of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and thiophosgene (see Scheme 1). We believe that **4** is the first sugar chlorothioformate to be reported.



SCHEME 1

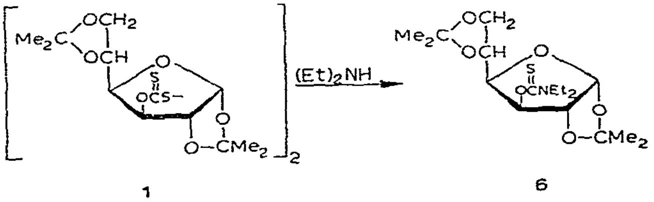
In a discussion concerning the mechanism of formation of thiophosgene from trichlorosulfenyl chloride, the $\mathrm{Cl_3CS^-}$ ion has been suggested as an intermediate that might be expected to expel chloride ion readily to form thiophosgene[6]. However, in the formation of the sugar chlorothioformate, the ion $\left[\mathrm{ROCS}\!-\!\overset{\mathrm{Cl}}{\underset{\mathrm{S^-}}{|}}\right]_2$ expels sulfur, not chloride. Some elemental sulfur was isolated from the reaction mixture.

Compound **2** was treated with a methanol–pyridine mixture and the thiocarbonate **5** was obtained in a fair yield. When pyridine was replaced by sodium carbonate, three major components were isolated; these were identified as **4**, **5**, and the previously reported[7] 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methoxycarbonyl)-α-D-glucofuranose. It has been reported[8] that trialkylamines react with chloroformates at high temperature to yield urethans; presumably the complex salts are intermediates.



$$[(R')_3N\overset{O}{\overset{\|}{C}}OR]^+Cl^- \xrightarrow{\Delta} (R')_2N\overset{O}{\overset{\|}{C}}OR + R'Cl$$

When **2** was refluxed with triethylamine in chloroform, 3-*O*-diethylaminothiocarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**6**), was isolated together with triethylamine hydrochloride. It is assumed that the complex salt of **4** with triethylamine is intermediate in this reaction. The structure of **6** was consistent with elemental analysis, i.r., u.v., and n.m.r. spectra (see Experimental). Compound **6** was independently synthesized by reaction of **1** with diethylamine (see Scheme 2).



SCHEME 2

Reactions of bis[6-O-(chloromethylsulfenyl chloride)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose] disulfide (**3**). — Although **3** was crystalline and had a fairly sharp m.p., t.l.c. showed that it was contaminated with a minor component. Recrystallization from different solvents failed to remove the contaminant. When the minor component was separated by preparative t.l.c., its u.v. spectrum showed λ_{max} at 250 nm (same as **4**), indicating that a chlorothioformate group was present. The i.r. spectrum of the major component lacked the original absorptions at 9.0 and 13.8 μm (C–Cl), but absorbed at 5.7 and 5.8 μm (C=O). Apparently **3** decomposed on a t.l.c. plate, and simple mixing of the adsorbent (Silica Gel G)* with a solution of **3** verified this supposition. The release of acidic vapors during the mixing was noticeable. The major component recovered from the plate was formulated as bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-[tetrathiobis(formate)] (**7**) from elemental analysis and i.r. spectral data. Reaction of **7** with a mixture of methanol–pyridine–iodine gave 1,2:3,4-di-*O*-isopropylidene-6-*O*-(methoxycarbonyl)-α-D-galactopyranose; omission of methanol gave bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-carbonate. The structures were verified by independent synthesis of both compounds. Treatment of the sodium salt of 1,2:3,4-di-*O*-isopro-

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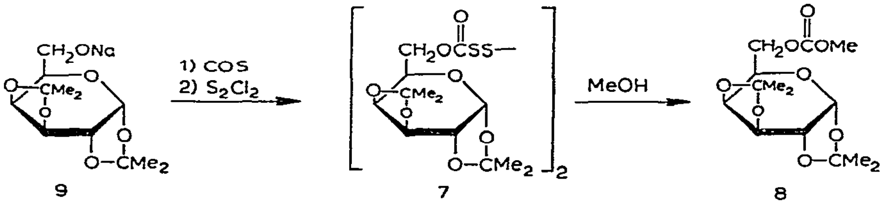
*Mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

pylidene-α-D-galactopyranose with carbonyl sulfide gave the corresponding monothiocarbonate (not isolated). Further reaction with sulfur monochloride gave **7** (see Scheme 3).



SCHEME 3

The first step in the formation of **7** from **3** probably is the removal of HCl to give an unstable intermediate $\left[\mathrm{ROCS}\overset{\mathrm{S^{+}OH^{-}}}{\underset{\mathrm{Cl}}{—}}\right]_2$ which upon loss of another mole of HCl rearranges to give **7**. In support of such a mechanism it was found that titration of **3** with alkali gave **7** with consumption of 4 moles per mole of alkali.

Automatic titration of **3** with alkali by means of a pH-Stat adjusted to pH 7.3 was complete in less than 2 min and no further addition of alkali occurred within one h. When the experiment was conducted with **2**, the rate of addition was slower (6 min) and alkali was consumed (although at a much lower rate) after initial consumption of 4 moles. An i.r. spectrum of the reaction products showed the same carbonyl absorption as in **7**.

When **3** was treated with sodium iodide, t.l.c. gave two somewhat overlapping spots, which both absorbed under u.v. light. The u.v. spectrum of the mixture showed one maximum (at 250 nm, same as **4**). Elemental analysis showed the presence of chlorine and iodine. Iodine percentages varied between 12 and 22% for several preparations. The compound that contained iodine had a slightly higher R_F value than the chloro derivative and was easily recognized by its brown color after brief irradiation of the plate with u.v. light. The product of lower R_F was identified as the corresponding chlorothioformate, and was prepared pure by reaction of **3** with about 2 moles of sodium iodide (instead of a large excess). The product of higher R_F apparently is the corresponding iodothioformate, although it was not isolated pure. The iodo product did not result from a reaction between the chlorothioformate derivative and excess sodium iodide. Presumably the intermediate $\left[\mathrm{ROCS}\overset{\mathrm{S^{-}}}{\underset{\mathrm{Cl}}{—}}\right]_2$ reacted with sodium iodide to give $\left[\mathrm{ROCS}\overset{\mathrm{S^{-}}}{\underset{\mathrm{I}}{—}}\right]_2$, which rearranged to give the iodo product.

EXPERIMENTAL

General. — N.m.r. spectra were recorded by a Varian A-60 n.m.r. spectrometer with chloroform-*d* as solvent and tetramethylsilane as internal reference standard (τ = 10.00). Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured with a Rudolph polarimeter. O.r.d. curves were recorded with a Cary Model 60 spectropolarimeter (26°, 0.1 dm). I.r. spectra were determined with a Perkin–Elmer Model 137 spectrophotometer as Nujol mulls or films cast onto silver chloride plates. U.v. spectra were recorded with a Perkin–Elmer Model 202 spectrophotometer. Automatic titration was performed with a Radiometer Type SBR$_2$, Electronic Measuring Instruments, Copenhagen, Denmark. Silica Gel G was used as the adsorbent for t.l.c. The eluent was 9:1 (v/v) carbon disulfide–ethyl acetate and the spray reagent was 19:1 (v/v) methanol–sulfuric acid. Microscope slides served for qualitative tests and 10×20 cm glass plates were used for preparative t.l.c.

Bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) 3,3′-[dithiobis(thioformate)][9] (**1**), bis[3-*O*-(chloromethylsulfenyl chloride)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose] disulfide[1] (**2**), and bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-[dithiobis(thioformate)][10] were prepared as described previously.

Bis[6-*O*-(chloromethylsulfenyl chloride)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose] disulfide (**3**) was prepared in yields exceeding 90% by a procedure similar to that for **2**; m.p. 133–136° (carbon disulfide), $[\alpha]_D$ −54° (*c* 1.0, *p*-dioxane), i.r. 9.0 and 13.8 μm (C–Cl).

Anal. Calc. for $C_{26}H_{38}Cl_4O_{12}S_4$: Cl, 17.5; S, 15.8. Found: Cl, 17.4; S, 15.8.

Silica Gel G caused decomposition of **2** and **3** and could not be used for t.l.c. of these compounds.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose 3-chlorothioformate (**4**). — (*a*) Sodium iodide (1.5 g) in acetone (15 ml) was added to a solution of **2** (1 g) in chloroform (10 ml). The solution, which turned dark brown immediately owing to release of iodine, was kept for 10 min. Upon addition of *n*-hexane (50 ml) a dark-green solid precipitated and was removed by filtration. The solvent was evaporated and the syrup was dissolved in a small volume of acetone to remove free sulfur. T.l.c. showed one major component (**4**). Upon evaporation of the acetone slow crystallization occurred. Compound **4** was purified by preparative t.l.c., yield 440 mg (53%), m.p. 63–64° (ether); λ_{max}^{ether} 250 (ε 7,000); R_F 0.55, $[\alpha]_D$ −23° (*c* 3.0, *p*-dioxane); $[\alpha]_{400}^{26}$ +333°, $[\alpha]_{378}^{26}$ 0°, $[\alpha]_{339}^{26}$ −640° (*c* 0.18, dioxane).

Anal. Calc. for $C_{13}H_{19}ClO_6S$: C, 46.0; H, 5.6; Cl, 10.6; S, 9.4. Found: C, 45.5; H, 5.7; Cl, 10.3; S, 9.4.

Molecular-weight determination (Rast) indicated a monomeric structure. In a separate experiment the iodine released was titrated according to the procedure of Kharasch and Wald[11] for the determination of sulfenyl chlorides. Each mole of **4** produced 1 mole of iodine within 5 min.

(*b*) A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (0.5 g) in methyl sulfoxide (0.5 ml) and sodium hydroxide (0.5 ml, 5M) was cooled to 5° and treated with thiophosgene (0.3 ml). The mixture was kept for 5 min and then extracted with ether. T.l.c. of the extract revealed three components, in similar proportions. The component of highest R_F was extracted from the plate and identified as **4** (t.l.c.

and u.v. and i.r. spectra), the slowest component corresponded to the starting sugar (t.l.c.), and the third one to the expected bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose) 3-3′-thionocarbonate. The thionocarbonate product has been characterized previously[10].

Reaction of **2** *with methanol.* — (*a*) To a suspension of **2** (220 mg) in methanol (5 ml), pyridine (0.5 ml) was added. The mixture was refluxed for 30 min and, after evaporation of excess solvent, was extracted with ether to give 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methoxythiocarbonyl)-α-D-glucofuranose (**5**), 120 mg (66%); R_F 0.47. The compound was identical with an authentic sample[7] by t.l.c. and comparison of u.v. and i.r. spectra.

(*b*) Compound **2** (100 mg) was dissolved in chloroform (1 ml) and treated with methanol (1 ml). The pH of the solution became very low on standing and some precipitation of elemental sulfur occurred. When the experiment was repeated, but with added sodium carbonate, t.l.c. showed three major spots. All three components were isolated and identified by means of i.r. and u.v. spectra and by t.l.c. The product having the highest R_F value was identified as **4**, the second as **5**, and the third as 1,2:5,6-di-*O*-isopropylidene-3-*O*-(methoxycarbonyl)-α-D-glucofuranose. Characterization of the third product has been previously reported[7]. Stirring a methanol–chloroform solution of **5** in the presence of excess sodium carbonate did not give the corresponding methoxycarbonyl derivative.

*3-*O*-Diethylthiocarbamoyl-1,2:5,6-di-*O*-isopropylidene-α-*D*-glucofuranose* (**6**). — (*a*) Triethylamine (0.5 ml) was added to a solution of **2** (300 mg) in chloroform (5 ml). The mixture was refluxed for 2 h, during which time the solution turned dark and some precipitation occurred. The solvents were evaporated and the mixture was extracted with ether. The residue (102 mg) was characterized as triethylamine hydrochloride (i.r.). T.l.c. of the extract showed mainly one component corresponding to the title compound **6**. The yield of **6** after purification by preparative t.l.c. was 60 mg (22%), m.p. 51–53°, $[\alpha]_D$ $-38°$ (*c* 2.7, *p*-dioxane); $\lambda_{\max}^{\text{film}}$ 6.65 μm (thiocarbamoyl); R_F 0.49; $\lambda_{\max}^{\text{EtOH}}$ 253 nm (ε 14,000) compared with $\lambda_{\max}^{\text{EtOH}}$ 249 (ε 14,000) for 3-*O*-dimethylthiocarbamoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[12]. N.m.r. data: multiplet (18 protons) centered at τ 8.7 (6 methyl groups) and two partly overlapped quartets (4 protons) centered at τ 5.8.

Anal. Calc. for $C_{17}H_{29}NO_6S$: C, 54.4; H, 7.7; S, 8.5. Found: C, 54.1; H, 7.9; S, 8.6.

(*b*) To a solution of **1** (670 mg) in ether (5 ml), diethylamine (140 mg) in ether (2 ml) was added. After the mixture had been kept for about 5 min, some precipitate formed (presumably the diethylamine xanthate of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose), which was filtered off. The filtrate was concentrated to a thick syrup, dissolved in a small volume of alcohol to remove some free sulfur, and reconcentrated to yield 322 mg (86%) of product identified as **6** by t.l.c., sulfur analysis (8.5%), and by u.v. and i.r. spectra.

*Bis(1,2:3,4-di-*O*-isopropylidene-α-*D*-galactopyranose) 6,6′-[tetrathiobis(formate)]* (**7**). — (*a*) A solution of **3** (600 mg) in a mixture of *p*-dioxane (3 ml) and chloroform

(3 ml) was titrated with an aqueous solution of sodium hydroxide; phenolphthalein served (in *p*-dioxane) as indicator. By the end of the titration the uptake of alkali was 4 moles per mole of **3**. The mixture was extracted with ether and the extract washed with water and dried (Na_2SO_4) to yield mainly the title compound, which was purified by preparative t.l.c. to yield 330 mg (63%); R_F 0.37. The i.r. spectrum showed peaks in the carbonyl region at 5.7 and 5.8 μm in a ratio about 3:2, respectively.

Anal. Calc. for $C_{26}H_{38}O_{14}S_4$: C, 44.4; H, 5.4; S, 18.2. Found: C, 44.4; H, 5.4; S, 17.9.

Treatment of **7** with a mixture of methanol, pyridine, and iodine [under conditions previously used[7] for the preparation of alkyloxythiocarbonyl derivatives from the corresponding dithiobis(thioformates)] gave mostly (t.l.c.) 1,2:3,4-di-*O*-isopropylidene-6-*O*-(methoxycarbonyl)-α-D-galactopyranose (**8**), which was crystallized from *n*-hexane (m.p. 93°) and characterized by comparison (t.l.c. and i.r. spectrum and mixed m.p.) with an authentic sample. The authentic sample was prepared by treatment of a pyridine solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose with methyl chloroformate[13]. When the experiment was repeated, but with omission of methanol, bis(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose) 6,6′-carbonate was obtained, which also was identified by spectral comparison with an authentic sample*. In both experiments some carbonyl sulfide was detected.

(*b*) A solution of **3** (2.2 g) in acetone was applied to preparative t.l.c plates. The major component was extracted from the plate with ether to yield **7**, 1.2 g (63%).

(*c*) Metallic sodium (about 0.5 g) was added to a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (1 g) in ether (15 ml). After 16 h, the ether solution containing the 6-alcoholate (**9**) was decanted from excess sodium and was treated with carbonyl sulfide. The monothiocarbonate so obtained was not isolated, but was treated directly with sulfur monochloride (0.2 ml). After 15 min, t.l.c. showed a major component having the same R_F as **7**. I.r. spectra of preparations (*a*), (*b*), and (*c*) were superposable. No yield was recorded in preparation (*c*).

1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose 6-chlorothioformate (**10**). — (*a*) A solution of sodium iodide (240 mg) in acetone (6 ml) was added dropwise with stirring to a solution of **3** (0.6 g) in chloroform (5 ml). The mixture was kept for 10 min and the product was isolated either with the use of *n*-hexane as described for **4** or by extraction with ether. The extract was washed with sodium thiosulfate solution, followed by water, and dried (Na_2SO_4). The product crystallized out slowly on evaporation of ether to yield 380 mg (76%) of crystalline product, m.p. 78–82°. The product was essentially pure at this stage (t.l.c.) except for traces of elemental sulfur.

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*This sample was prepared by reaction of 1,2.3,4-di-*O*-isopropylidene-α-D-galactopyranose in pyridine with phosgene in hexane according to the procedure of Baggett *et al.*[14] When the pyridine was replaced by triethylamine, a compound was isolated that from i.r. and elemental analysis appears to be  $RO\overset{\overset{O}{\|}}{C}NEt_2$, where R represents the di-*O*-isopropylidene-D-galactose moiety.

It was purified by means of preparative t.l.c., m.p. 84–86° (ether); $\lambda_{\max}^{\text{ether}}$ 250 nm (ε 7,000); R_F 0.62, $[\alpha]_D$ $-50°$ (*c* 2.7, *p*-dioxane).

Anal. Calc. for $C_{13}H_{19}ClO_6S$: Cl, 10.6; S, 9.4. Found: Cl, 10.4; S, 9.4.

(*b*) A solution of sodium iodide (1.5 g) in acetone (6 ml) was added in one portion to a solution of 3 (1 g) in chloroform (5 ml). The mixture was kept for 10 min and the product was isolated by extraction with ether. The extract was washed with thiosulfate solution, followed by water, and dried (Na_2SO_4). On evaporation of the ether a crystalline mass was obtained. The different preparations (m.p. 68–70° up to 80–84°) contained besides chlorine, variable proportions of iodine (12–22%). T.l.c. showed two somewhat overlapping spots that absorbed under u.v. light. The compound that contained iodine had a slightly higher R_F value than the chloro derivative (**10**) and was easily recognized by its brown color after irradiation of the plate with u.v. light.

No change (t.l.c.) was observed when a solution of **10** was treated with sodium iodide. Thus the iodo product did not result from a reaction between the chlorothioformate derivative and excess sodium iodide.

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