Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.5; H, 4.2; O, 26.3. Found: C, 69.7; H, 4.3; O, 26.0.

Lithium Aluminum Hydride Reduction of 4-Phenyl-1,3-Benzodioxan-4-ol-2-one (11).—A solution of 1.3 g (0.0054 mol) of 11 in 25 ml of dry tetrahydrofuran was added dropwise in about 0.5 hr to a stirred slurry of 2.0 g (0.05 mol) of lithium aluminum hydride in 50 ml of tetrahydrofuran. The mixture was blanketed with nitrogen and refluxed for 120 hr. After cooling in an ice bath the reactants were treated with 4.0 ml of 2 *N* sodium hydroxide, 6.0 ml of water, and 25 g of anhydrous sodium sulfate. The salts were filtered off and washed with tetrahydrofuran. The combined filtrates were concentrated to give 0.9 g (73%) of 4-phenyl-1,3-benzodioxan-4-ol (12): mp 73–75° (diethyl ether-pentane); ir (KBr), 2.29 (OH), 3.43, 6.72, 7.92, 8.05, 9.36, and 10.30 μ; uv, λ_{max} 230 mμ (ϵ 2955), 279 (shoulder, 3200), 283 (4220), and 289 (shoulder, 3210) in ethanol and λ_{max} 279 mμ (shoulder, ϵ 7050), 283 (7240), and 289 (shoulder, 5440) in 5% KOH–ethanol; nmr ($CDCl_3$), 2.43 (1 H, exchangeable, OH), 3.92 (2 H, broad singlet, O–CH_2O), 6.78 (4 H, singlet), and 7.20–7.78 ppm (5 H, multiplet). The mass spectrum exhibits a molecular ion peak at *m/e* 228 ($C_{14}H_{12}O_3$) with abundant fragment peaks at *m/e* 197 ($M^+ - CH_3O$), 105 ($C_6H_5CO^+$) and 77 ($C_6H_5^+$). The pK_{mcs}* value[17] was 9.5.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.7; H, 5.3; O, 21.0. Found: C, 73.6; H, 5.4; O, 21.2.

Registry No.—N-*p*-Chlorophenyl-DL-mandelamide, 10295-53-1; N-*p*-methoxyphenyl-DL-mandelamide, 15815-96-0; **6b**, 15815-97-1; **6c**, 15757-31-0; **8**, 15757-32-1; **11**, 15757-33-2; **12**, 15757-34-3.

Acknowledgment.—The authors express their appreciation to Mr. Urs Stoeckli and his associates for determining analytical and instrumental data.

The Synthesis and Desulfurization of 2,3,3-Trichloro- and 2,2,3-Trichlorothioxanes[1]

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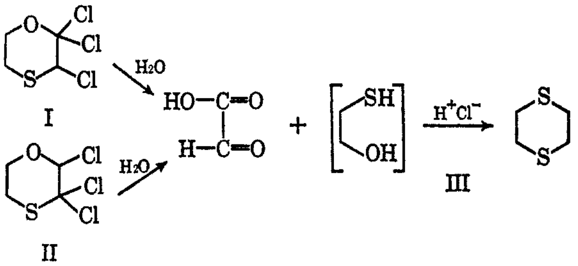
In the course of a research project on fluorinated derivatives of ethers and thioethers, it became of interest to synthesize some chlorinated derivatives of 1,4-thioxane as intermediates. We chose 1,4-thioxane because it contains both ether and thioether linkages in the ring.

Only a few references to the chlorinated derivatives of 1,4-thioxane are noted in the literature. Haubein[3,4] reported the preparation of several chlorothioxanes, among them a trichlorothioxane, but did not determine the positions of the chlorine atoms on the ring in the case of the trichlorothioxane. By a modification of the Haubein procedure[4] we have recently synthesized and identified two trichlorinated derivatives of 1,4-thioxane, $C_4H_5OSCl_3$. When 1,4-thioxane is chlorinated in a CCl_4 solution at 80° and 75 g/hr, a white crystalline compound, $C_4H_5OSiCl_3$, melting at 58° is isolated in 90% yield. If the rate is increased to 150 g/hr, a white crystalline compound melting at 53° is isolated in 93% yield. These compounds are stable when kept free of moisture but fume in moist air with the elimination of HCl and have a characteristic obnoxious odor. They impart slight irritation when in contact with the skin.

Aqueous hydrolysis of both compounds yields glyoxylic acid and β-mercaptoethanol which was isolated as dithiane under these conditions.[5] The hydrolysis products show that all three chlorine atoms were substituted on the same side of the thioxane ring.



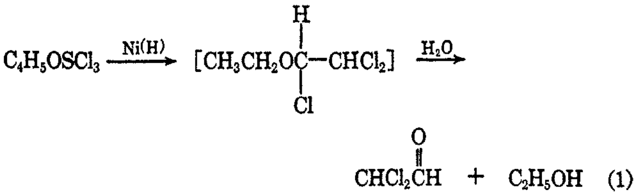
I

II

III

Since the instability of these compounds made structure determination difficult, desulfurization was decided upon as an unambiguous method.

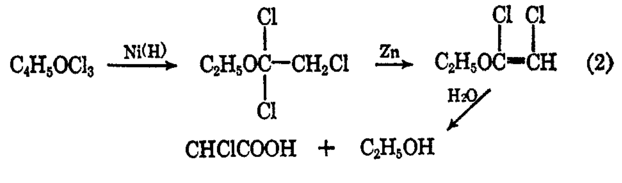
It was found that an active preparation of Raney nickel, Raney nickel "C,"[6] could be used to desulfurize the trichlorinated compounds without causing hydrogenolysis of the chlorine atoms. The compound melting at 53° was desulfurized according to the reaction in eq 1.



$$C_4H_5OSCl_3 \xrightarrow{Ni(H)} [CH_3CH_2O\overset{H}{\underset{Cl}{C}}-CHCl_2] \xrightarrow{H_2O} CHCl_2\overset{O}{\overset{\|}{C}}H + C_2H_5OH \quad (1)$$

The α,α,β-trichloroethyl ether was not isolated but was hydrolyzed in solution. Identification of the hydrolysis products dichloroacetaldehyde and ethanol was taken as proof that the compound melting at 53° was 2,3,3-trichlorothioxane.

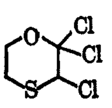
Desulfurization of the compound melting at 58° took place according to eq 2. In this case the heretofore



$$C_4H_5OCl_3 \xrightarrow{Ni(H)} C_2H_5O\overset{Cl}{\underset{Cl}{C}}-CH_2Cl \xrightarrow{Zn} C_2H_5O\overset{Cl}{C}=\overset{Cl}{C}H \quad (2)$$

$$\xrightarrow{H_2O} CHClCOOH + C_2H_5OH$$

unknown α,α,β-trichloroethyl ether was hydrolyzed to monochloroacetic acid in solution. The desulfurization products confirmed that the compound melting at 58° is 2,2,3-trichlorothioxane.



The chlorination of 1,4-thioxane at 145° to give 2,3,3-trichlorothioxane is consistent with the chlorination

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[2] All inquiries should be addressed to this author at General Electric Silicone Products Department, Waterford, N. Y.

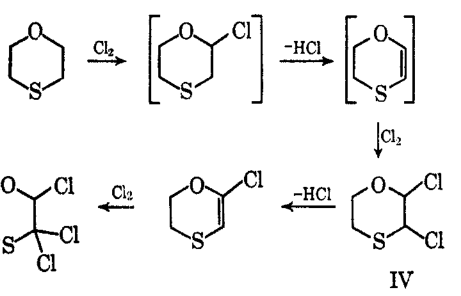
[3] A. H. Haubein, U. S. Patent 2,766,169 (1956).

[4] A. H. Haubein, *J. Amer. Chem. Soc.*, **81**, 144 (1959).

[5] E. Swistak, *Comp. Rend.*, **240**, 1544 (1955).

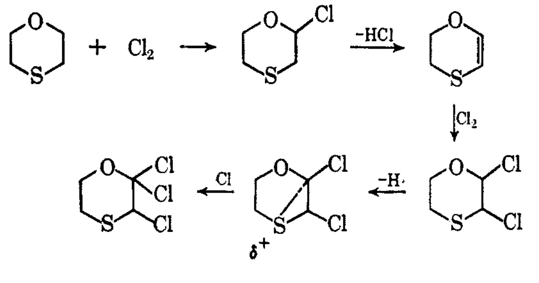
[6] C. D. Hurd and B. Rudner, *J. Amer. Chem. Soc.*, **73**, 5157 (1951).

SCHEME I



and thermal dehydrohalogenation of ethyl ether[7] (Scheme I). However, an entirely different mechanism must be postulated for the chlorination at 80° to give 2,2,3-trichlorothioxane. The dichloride IV is known to be stable at 80°[8] and it is highly unlikely that the chlorine atoms α to the sulfur atom would be removed in preference to the more active one in the β position (α to the ether linkage). Instead, it is more probable that the last step in this reaction is a free-radical process with no olefin being formed. Theoretically, the homolytic cleavage of the hydrogen α to oxygen could be anchimerically assisted and the resulting radical stabilized by a sulfur bridge (Scheme II). This theory is supported by the work of Kwart

SCHEME II



and Evans,[9] which suggests that sulfur is able to perform this function with greater facility than oxygen and thus causes the radical formed in the position β to sulfur to be more stable.

Experimental Section

Chemicals.—The 1,4-thioxane used in this study was donated by the New Product Division of the Thiokol Chemical Corp. This compound was freed of peroxides by known procedures and distilled. The fraction boiling at 147–150° was used. The Raney nickel used in this study was obtained from the E. H. Sargent Co. as a 50% nickel, 50% aluminum alloy. It was converted into Raney nickel "C" by the method of Hurd.[7] The solvent methyl Cellosolve (ethylene glycol monomethyl ether) was obtained from Fisher Chemical Co. and purified by distillation. Chlorine gas was obtained from the Matheson Co. in cylinders.

General.—All melting points were uncorrected and determined on a Fisher-Johns melting point apparatus. Elemental analyses were by Galbraith Laboratories in Knoxville, Tenn. All reactions were carried out in light.

2,3,3-Trichlorothioxane.—To a 1-l. flask fitted with a mechanical stirrer, Friedrich's reflux condenser, thermometer, and coarse fritted-glass dispersing device were added 208 g (2.0 mol) of 1,4-thioxane and 350 ml of carbon tetrachloride. The mixture was stirred and heated to reflux. The heating was discontinued and chlorine gas was introduced at approximately 150 g/hr. When approximately 6 mol of chlorine had been added, the reaction mixture was kept at −5° until complete precipitation occurred. This required 20–24 hr. The white crystalline material was filtered and washed with cold ligroin. One recrystallization from a 1:5 ethyl ether–ligroin mixture and decolorizing charcoal gave 290 g (93% yield) of pure trichlorothioxane, mp 53°. *Anal.* Calcd for $C_4H_5OSCl_3$: Cl, 51.25; S, 15.45. Found: Cl, 51.29; S, 15.46.

2,2,3-Trichlorothioxane.—In a procedure similar to the one above, 104 g (1.0 mol) of 1,4-thioxane in 300 ml of carbon tetrachloride was chlorinated as 80° with 225 g of chlorine at a rate of 75 g/hr. The reaction mixture worked up in the above manner gave 185 g (90%) of white crystals melting at 58°. *Anal.* Calcd for $C_4H_5OSCl_3$: Cl, 51.25; S, 15.45. Found: S, 51.60; Cl, 15.30.

Hydrolysis of Trichlorothioxane Melting at 53°.—A 10-g sample of the trichlorothioxane in 50 ml of water was heated to boiling, stoppered, and shaken for 1 hr. Glyoxylic acid was isolated from the solution as the 2,4-dinitrophenylhydrazone, mp 191–192° (lit.[10] mp 190° dec), and did not depress the melting point of an authentic sample of glyoxylic acid, 2,4-dinitrophenylhydrazone. The 1,4-dithiane (mp 110–111°) was sublimed from the solution and did not depress the melting point of dithiane prepared by an unambiquous route.

The hydrolysis of trichlorothioxane melting at 58° was accomplished by the above procedure with the same products being isolated.

Desulfurization of 2,3,3-Trichlorothioxane in Methyl Cellosolve.—To a stirred solution of 35 g (0.336 mol) of trichlorothioxane (mp 53°) in 500 ml of dry methyl Cellosolve was added 150 g of Raney nickel "C." An ice bath was applied to keep the spontaneous reaction mixture at 10°. After the exothermic period was over, the reaction mixture was gradually heated to 60° and kept at this temperature for 12 hr. The Raney nickel was decanted and centrifuged in a clinical centrifuge to separate the remainder of the nickel. It was observed that the obnoxious odor of the trichlorothioxane had disappeared and the product had a pleasant odor.

The resulting α,β,β-trichloroethyl ether was hydrolyzed to give dichloroacetaldehyde and ethanol. The dichloroacetaldehyde was isolated as the 2,4-dinitrophenylhydrazone mp 146–150° (lit.[11] mp 146°). Further hydrolysis converted the dichloroacetaldehyde into glyoxal which was isolated as the 2,4-dinitrophenylosazone, mp 317° (lit.[12] mp 318° dec), and the bissemicarbazone, mp 270° (lit.[13] mp 270°).

Desulfurization of 2,2,3-Trichlorothioxane in Diethylcarbitol.—Diethylcarbitol (250 ml) was made anhydrous by predrying with sodium sulfate and distilling from sodium ribbon. To this was added 100 g of Raney nickel "C" and 10 g of 2,2,3-trichlorothioxane (mp 58°). The reaction mixture was stirred with a mechanical stirrer and let react for 7 days at room temperature. The reaction mixture was separated from the Raney nickel as above. The desulfurized mixture (50 g) was added to 2 g of mossy zinc and refluxed for 1 hr. The zinc chloride was filtered off and the filtrated distilled through a Vigreux column. The fraction boiling at 120–130° was collected. This fraction fumed in moist air, gave positive tests for unsaturation, and was assumed to be $CH_3CH_2OCCl{=}CHCl$. Hydrolysis of the above distillate by refluxing 10 g of it in 10 g of H_2O for 1 hr gave monochloroacetic acid. This was identified as the *p*-phenylphenacyl ester, mp 115° (lit.[14] 116°), and did not depress the melting point of an authentic sample of the *p*-phenylphenacyl ester of monochloroacetic acid.

Acknowledgment.—We gratefully acknowledge the help of Fred Jones, Clyde Bishop, and Curtis Harper who prepared the trichlorothioxanes while graduate students at the Carver Research Foundation.

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[8] A. H. Haubein, U. S. Patent 2,725,331 (1955).

[9] H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 (1966).

[10] "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1965, p 1543.

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[12] See ref 10, p 1542.

[13] "Chemical Rubber Handbook of Tables for Organic Compounds," 3rd ed, Chemical Rubber Co. Press, Cleveland, Ohio.

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