B. In Methanol.—1-Methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic, 2.0 g) was solvolyzed in 25 ml of absolute methanol at 25° for 15 hr. The material was worked up as before and analysis by glpc (columns A, B, and C) revealed a single product peak with a retention time identical with that of authentic methyl 1-methylcyclobutyl ether (III).

C. In Acetic Acid.—1-Methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic, 5.1 g) was solvolyzed in 50 ml of acetic acid solvent (prepared as before[2] and containing 26 mmoles of sodium acetate) at 25° for 15 hr. The material was diluted with 200 ml of ice–water and extracted with three 75-ml portions of ether. Neutralization of the combined extracts with saturated aqueous sodium carbonate and concentration by flash distillation was followed by treatment with 25 ml of 5% aqueous sodium hydroxide for 4 hr at room temperature. The mixture was extracted with three 30-ml portions of ether and dried over anhydrous sodium sulfate; most of the solvent was removed by distillation. Analysis by glpc (columns A and C) revealed a single product peak with a retention time identical with that of authentic 1-methylcyclobutanol.

The Rearrangement of Chloroalkyl Thionocarbonates

D. L. GARMAISE AND G. Y. PARIS

Research Department, Abbott Laboratories Ltd., Montreal, Quebec, Canada

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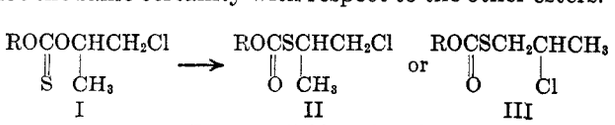
The observation that 2-chloroethyl 3,4-dichlorophenyl thionocarbonate rearranges spontaneously to the S-(2-chloroethyl) thiolcarbonate ester[1] led to an investigation of the behavior of some related chloroalkyl thionocarbonates. The thionocarbonates were prepared by the reaction of 3,4-dichlorophenyl chlorothionoformate with chloro alcohols and pyridine in chloroform at 0°. The rearrangement of the thionocarbonate to the S-chloroalkyl thiolcarbonate was indicated by the appearance of a carbonyl band at 1725–1727 cm^{-1}, and in the nmr spectrum, by replacement of the OCH_2 peak at τ 5.34–5.42 by the SCH_2 peak at τ 6.78–6.89 or by the SCH peak at about τ 6.30.

All of the 2- and 3-chloroalkyl esters that were investigated could be converted to the thiolcarbonate, the relative ease of rearrangement being in the order CH_2CH_2Cl> $CH(CH_3)CH_2Cl$ > $CH_2CHClCH_3$ > $CH_2CH_2CH_2Cl$ > $CH_2CH_2CHClCH_3$. The 4-chlorobutyl thionocarbonate was resistant to rearrangement, showing very slight conversion to the thiolcarbonate after being heated at 200° for 2 hr.

Although it was apparent that the rearrangement product from the 3-chloropropyl thionocarbonate must be the S-(3-chloropropyl) thiolcarbonate, there was not the same certainty with respect to the other esters.



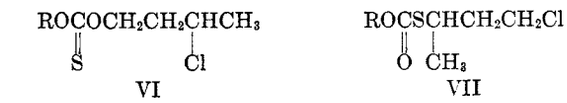
R = 3,4-dichlorophenyl

Thus the rearrangement of the 1-chloro-2-propyl ester I could conceivably lead to either II or III, depending on whether the reaction proceeded *via* a four-membered cyclic intermediate as in the Schönberg rearrangement of diaryl thionocarbonates,[2] or by displacement of chlorine by sulfur with consequent migration of the chlorine atom. The nmr spectrum was found to be in accord with structure III (Table I).

Examination of the spectra of compounds VIII, IX, and X, which are of unequivocal structure, permitted the identification of the chemical shifts. Assignment of τ 6.30–6.36 to the CH_2Cl group was indicated because it is the only methylene group which all these compounds have in common. It then follows that the signal at τ 5.34–5.42 is due to the OCH_2 group, and the one at τ 6.89 is due to the SCH_2 group. The rearrangement product obtained from I must correspond to the structure III, because it has a signal at τ 6.78 corresponding to two hydrogens (SCH_2) and a single hydrogen peak at τ 5.82, which must be due to CHCl. Structure II is excluded because it would be expected to give a peak at τ 6.30–6.36 for the CH_2Cl group.

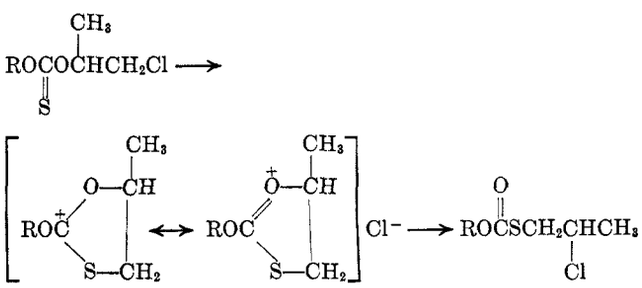
The 1-chloro-2-propyl ester was completely rearranged by heating at 140° for 30 min, but similar treatment of the 2-chloro-1-propyl ester (IV) gave an approximately equal mixture of unchanged thiono ester and the S-(1-chloro-2-propyl) thiol ester (V).

The rearrangement of the 3-chloro-1-butyl ester VI, brought to completion by heating at 200° for 2 hr, gave the S-(4-chloro-2-butyl) thiol ester VII. The

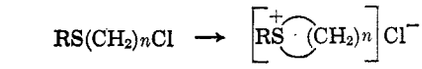


product gave a multiplet at τ 6.30 corresponding to three hydrogens which include the CH_2Cl and the SCH groups. The possible alternative structure, $ROC(O)SCH_2CH_2CHClCH_3$, is excluded because it would be expected to give a SCH_2 signal at τ 6.78–6.89 and a CHCl signal at τ 5.82.

These results indicate that the rearrangement occurs *via* a cyclic intermediate arising from nucleophilic displacement of chlorine by sulfur.



It has been shown that 2-chloroalkyl groups react more or less readily, 3-chloroalkyl groups relatively slowly, and the 4-chlorobutyl group very slowly. This order of reactivity, which corresponds to the relative ease of ring formation, is similar to that observed for the formation of cyclic sulfonium salts from ω-chloro sulfides.[3]



The five-membered ring was found to be formed bout 75 times as fast as the six-membered ring, with a

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TABLE I

Compd	Structure	Nmr, τ: OCH_2	CHCl	CH_2Cl	CH_2S	CH_2	CH_2CH_2	CH_3
VIII	$ROCO(CH_2)_4Cl$ ‖ S	5.42		6.36			8.01	
IX	$ROCO(CH_2)_3Cl$ ‖ S	5.34		6.30		7.73		
X	$ROCS(CH_2)_3Cl$ ‖ O			6.30	6.89	7.82		
III	$ROCSCH_2CHCH_3$ ‖ O Cl		5.82		6.78			8.45
VII	$ROCSCHCH_2CH_2Cl$ ‖ O CH_3			6.30		7.77		8.49

similar ratio of rate of formation for the six- and seven-membered rings.

The reduced SN2 reactivity of the secondary chlorine accounts for the relative inactivity of the 2-chloropropyl and 3-chlorobutyl esters as compared with the 1-chloro-2-propyl and 3-chloropropyl esters, respectively. It has previously been noted[1] that the 2,2-dichloroethyl and 2,2,2-trichloroethyl esters show no tendency to rearrange, due to the mutual deactivation of the chlorine atoms on the same carbon atom.[4]

Experimental Section[5]

3-Chloropropyl 3,4-Dichlorophenyl Thionocarbonate (IX) and S-(3-Chloropropyl) O-(3,4-Dichlorophenyl) Thiolcarbonate (X).—A solution of 3,4-dichlorophenyl chlorothionoformate (prepared from 3,4-dichlorophenol and thiophosgene as previously described[1]) (4.83 g, 0.02 mole) in 15 ml of chloroform was added dropwise to a stirred solution of 3-chloro-1-propanol (2.83 g, 0.03 mole) and pyridine (1.7 ml) in 15 ml of chloroform at 0–5°. The solution was washed with 1 *N* sodium hydroxide and with water, and was then dried and evaporated at room temperature. The residue consisted of the thionocarbonate IX (no carbonyl absorption; OCH_2 peak in the nmr spectrum at τ 5.34). The product rearranged partially on distillation at 171° (0.6 mm); after heating at 170° for 1 hr it rearranged completely to the thiolcarbonate X (carbonyl band at 1727 cm^{-1}; SCH_2 peak in the nmr spectrum at τ 6.89), yield 5.6 g (93%).

Anal. Calcd for $C_{10}H_9Cl_3O_2S$: C, 40.09; H, 3.03; Cl, 35.50; S, 10.70. Found: C, 40.20; H, 3.02; Cl, 34.64; S, 10.15.

S-(2-Chloro-1-propyl) O-(3,4-Dichlorophenyl) Thiolcarbonate (III).—1-Chloro-2-propanol was treated with 3,4-dichlorophenyl chlorothionoformate as described above. The undistilled residue was a mixture of the thiono and thiol esters containing about 10% of the latter. The product was heated at 140° for 30 min and then distilled to give the pure thiol ester, bp 134–136° (0.25 mm), $n^{25}D$ 1.5675, yield 84%.

Anal. Calcd for $C_{10}H_9Cl_3O_2S$: C, 40.09; H, 3.03; Cl, 35.50; S, 10.70. Found: C, 39.62; H, 2.87; Cl, 35.17; S, 10.46.

The Rearrangement of 2-Chloro-1-propyl 3,4-Dichlorophenyl Thionocarbonate (IV).—2-Chloro-1-propanol (prepared by lithium aluminum hydride reduction of 2-chloropropionic acid[6]) gave, on esterification with 3,4-dichlorophenyl chlorothionoformate, the thiono ester IV uncontaminated with the thiol isomer. The product was heated at 140° for 30 min and distilled at 144° (0.4 mm), giving an 83% recovery of a mixture of 45% IV and 55% S-(1-chloro-2-propyl) O-(3,4-dichlorophenyl) thiolcarbonate (V) (the nmr spectrum contained both OCH_2 and CH_2Cl signals, at τ 5.41 and 6.28, respectively).

Anal. Calcd for $C_{10}H_9Cl_3O_2S$: C, 40.09; H, 3.03; Cl, 35.50; S, 10.70. Found: C, 40.38; H, 2.50; Cl, 34.83; S, 11.09.

3-Chloro-1-butyl 3,4-Dichlorophenyl Thionocarbonate (VI) and S-(4-Chloro-2-butyl) O-(3,4-Dichlorophenyl) Thiolcarbonate (VII).—3,4-Dichlorophenyl chlorothionoformate (7.25 g, 0.03 mole) in 20 ml of chloroform was added dropwise at 0–5° to a solution of 3-chloro-1-butanol (prepared by the lithium aluminum hydride reduction of 3-chlorobutyric acid[7]) (4.35 g, 0.04 mole) and pyridine (2.0 ml) in 20 ml of chloroform. The reaction mixture was worked up in the usual way, giving the pure thiono ester VI, bp 154–156° (0.25 mm), $n^{25}D$ 1.5642, yield 6.2 g (67%). The product was heated at 200° for 2 hr, the progress of the rearrangement being followed by the appearance of the carbonyl band at 1725 cm^{-1}. Distillation in a collar flask at 0.5 mm (bath temperature 170°) yielded the pure thiol isomer VII, $n^{25}D$ 1.5638.

Anal. Calcd for $C_{11}H_{11}Cl_3O_2S$: C, 42.12; H, 3.54; Cl, 33.92; S, 10.22. Found: C, 42.38; H, 3.48; Cl, 33.71; S, 10.40.

S-(4-Chlorobutyl) O-(3,4-Dichlorophenyl) Thionocarbonate (VIII).—4-Chloro-1-butanol (3.26 g, 0.03 mole) was treated with 3,4-dichlorophenyl chlorothionoformate (4.83 g, 0.02 mole) as described above to give the product, bp 172–174° (0.2 mm), yield 3.9 g (63%). After being heated at 200° for 2 hr, the product gave a small peak at 1725 cm^{-1}.

Anal. Calcd for $C_{11}H_{11}Cl_3O_2S$: C, 42.12; H, 3.54; Cl, 33.92; S, 10.22. Found: C, 42.21; H, 3.58; Cl, 33.75; S, 9.98.

Acknowledgment.—The authors are indebted to Dr. Z. Valenta for valuable discussions.

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(5) Analyses were performed by Dr. C. Daessle, Montreal, Quebec, and by the Microanalytical Laboratory of Abbott Laboratories, North Chicago, Ill.

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Reactions of Alkanediols with Triphosphonitrilic Chloride[1]

A. J. MATUSZKO[2] AND M. S. CHANG

Research and Development Department, U. S. Naval Propellant Plant, Indian Head, Maryland

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The chlorine atoms on cyclic phosphonitrilic chlorides are capable of being replaced by a number of electronegative substituents with retention of the ring structure. As part of a study of substitution reactions undertaken in this laboratory, trimeric phosphonitrilic chloride, $(PNCl_2)_3$, was treated with a series of alkanediols. Our objective in this work was to synthesize

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(2) To whom correspondence should be addressed: Air Force Office of Scientific Research, Washington, D. C. 20333.