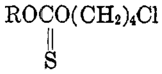
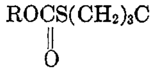
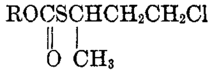
Table I

Compd	Structure	Nmr, τ						
		OCH$_2$	CHCl	CH$_2$Cl	CH$_2$S	CH$_2$	CH$_2$CH$_2$	CH$_3$
VIII	 $\mathrm{RO\underset{S}{\underset{\|}{C}}O(CH_2)_4Cl}$	5.42		6.36			8.01	
IX	 $\mathrm{RO\underset{S}{\underset{\|}{C}}O(CH_2)_3Cl}$	5.34		6.30		7.73		
X	 $\mathrm{RO\underset{O}{\underset{\|}{C}}S(CH_2)_3Cl}$			6.30	6.89	7.82		
III	 $\mathrm{RO\underset{O}{\underset{\|}{C}}SCH_2\underset{Cl}{\underset{\|}{C}}HCH_3}$		5.82		6.78			8.45
VII	 $\mathrm{RO\underset{O}{\underset{\|}{C}}S\underset{CH_3}{\underset{\|}{C}}HCH_2CH_2Cl}$			6.30		7.77		8.49

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

The reduced S$_N$2 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$_2$Cl 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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Reactions of Alkanediols with Triphosphonitrilic Chloride[1]

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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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polymers through polycondensation of cyclic phosphonitriles with selected diols. However, three different reaction schemes were observed depending upon reaction conditions and the diol used, resulting in the formation of (1) compounds believed to be spiro derivatives obtained by the reaction of each $PNCl_2$ group with a molecule of diol, (2) cyclic ethers by way of a dehydration reaction, and (3) polymeric substances.

Reactions of triphosphonitrilic chloride were first carried out with ethylene glycol and 2,2-bis(nitroxymethyl)-1,3-propanediol. The reaction with ethylene glycol yielded a product believed to be the five-membered ring phosphonitrilate spiro compound, tris-1,1:3,3:5,5-ethylene triphosphonitrilate. The elemental analysis and infrared spectrum were consistent with this structure. However, owing to its insolubility and noncrystalline character further identification of the product was not attempted. We previously reported the product of the reaction with 2,2-bis(nitroxymethyl)-1,3-propanediol to be the six-membered ring spiro compound, tris-1,1:3,3:5,5-[β,β-bis(nitroxymethyl)trimethylene]triphosphonitrilate.[3] Similar spiro compounds from reactions of triphosphonitrilic chloride with 1,4-tetrafluorobutanediol and 1,5-hexafluoropentanediol were reported by Rätz and co-workers;[4] Allcock reported the formation of spiro compounds with aromatic diols.[5]

With 1,3-propanediol, 1,4-butanediol, and 1,5-pentanediol, in the absence of solvent or acid acceptor, triphosphonitrilic chloride acted as a dehydrating agent to form the cyclic ethers trimethylene oxide, tetrahydrofuran, and tetrahydropyran, respectively. The evolution of large amounts of hydrogen chloride was observed at about 110° accompanied by an exothermic reaction which brought the temperature in the reaction flask to slightly above 200°.

The dehydrating action of phosphonitrilic chloride was previously noted by Bezman and Reed in their reported conversion of carboxylic acid salts to nitriles.[6] Also, we found that cyanuric chloride, whose reactions are in many ways similar to those of triphosphonitrilic chloride, reacts with 1,4-butanediol and with 1,5-pentanediol to form tetrahydrofuran and tetrahydropyran.[7] More recently Traynelis and co-workers[8] reported the formation of cyclic ethers in reactions of diols with dimethyl sulfoxide.

The reactions of triphosphonitrilic chloride with the longer chain 1,6-hexanediol, regardless of reaction conditions, gave polymeric materials which were insoluble in water or common organic solvents making it difficult to obtain a pure product for identification.

Experimental Section

Reaction of Triphosphonitrilic Chloride with Ethylene Glycol.—A solution of 0.75 g (0.012 mole) of ethylene glycol in 10 ml of pyridine was mixed with 0.7 g (0.002 mole) of triphosphonitrilic chloride. The mixture was shaken until the solid dissolved and then allowed to stand at room temperature for 24 hr. The solid was filtered and washed with water, alcohol, ether, and finally with methylene chloride. It turned brown at about 280° and melted above 300°: yield 0.67 g (33%). The infrared spectrum showed absorption peaks at 1250 cm^{-1} (trimeric P_3N_3 ring)[9] and 1040 cm^{-1} (P–O–R).[10] This compound is believed to be tris-1,1:3, 3:5,5-ethylene triphosphonitrilate.

Anal. Calcd for $C_6H_{12}N_3O_6P_3$: C, 22.85; H, 3.80; N, 13.33; P, 29.52. Found: C, 22.66; H, 4.11; Cl, negative; N, 13.08; P, 28.66.

Owing to the insolubility of this compound in common organic solvents a molecular weight was not obtained.

General Procedure for Reactions of Triphosphonitrilic Chloride in Excess of Diol.—A mixture of 1.75 g (0.005 mole) of triphosphonitrilic chloride and 10 ml of 1,4-butanediol was placed in a small flask with an attached distilling outfit and slowly heated in an oil bath. When the oil-bath temperature reached 110°, a rapid evolution of hydrogen chloride was observed and the flask temperature rose to 200–210°. The heating was continued when the evolution of gas had subsided and a liquid was collected distilling at 60–63°. The heating was stopped when no more liquid distilled. Fractional distillation resulted in a major portion of the liquid boiling at 63–65°, $n^{25}D$ 1.4049 (tetrahydrofuran bp 64–66°, $n^{25}D$ 1.4040). An unidentified solid containing no carbon remained in the distilling flask.

The reactions of triphosphonitrilic chloride with 1,3-propanediol and 1,5-pentanediol under the same conditions gave 33% yield of trimethylene oxide (bp 48°, $n^{25}D$ 1.3842; lit. bp 47.8°, $n^{25}D$ 1.3897) and 30% yield of tetrahydropyran (bp 82–84°, $n^{25}D$ 1.4193; lit. bp 81–82°, $n^{25}D$ 1.4195), respectively, based on complete hydrolysis of $(PNCl_2)_3$. In both of these reactions, an unidentified solid similar to the one noted above was obtained.

A Reaction of 1,6-Hexanediol with Triphosphonitrilic Chloride.—A solution containing 2.3 g of 1,6-hexanediol in 15 ml of pyridine was added to 3.5 g of triphosphonitrilic chloride. The reaction was exothermic. After the reaction had subsided, the mixture was allowed to stand at room temperature for 6 hr. The solid was separated by filtration and washed with alcohol, water, ether, and benzene, leaving 4.1 g of polymeric material melting at *ca.* 220°. Infrared spectra showed strong absorption at 1250 cm^{-1} indicating retention of the trimeric P_3N_3 ring structure.[9]

Anal. Found: C, 28.50, 28.76; H, 5.03, 5.01; Cl, positive; N, 12.25; P, 23.37, 23.56.

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Redetermination of the Hammett σ Value for the *m*-N,N-Dimethylamino Group[1]

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The σ value for the *m*-dimethylamino substituent was originally calculated to be −0.211 by Hammett,[2] using previously reported[3] rate constants for the reaction of substituted phenoxide ions with propylene oxide in 98% ethanol at 70.4°. The ρ value for this reaction was found to be −0.771 with a probable error of 0.046. Unfortunately it was later found that σ values calculated by similar indirect methods often

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[1] Supported in part by grant GM 11408 from the National Institutes of Health.

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