Anal. Calcd. for $C_{10}H_7K_4N_5O_2$: K, 37.46. Found: K, 39.2.

To a solution of this material in 0.12 *N* sodium hydroxide (20 ml.), 0.1 *N* potassium permanganate (12.5 ml.) was added slowly with stirring during a period of 30 min. After removal of the manganese dioxide by filtration, the solution was neutralized with dilute hydrochloric acid. Evaporation to a small volume *in vacuo* gave an orange precipitate of crude 5,7-diamino-3-methylpyrido[3,4-*b*]pyrazine (XVII, 90 mg.). Recrystallization of the crude product from water (5 ml.) with charcoal gave orange plates which were collected and dried *in vacuo* over phosphorus pentoxide at 76° for 4 hr.; the yield was 50 mg. (14%); m.p. 222–223° dec. (tends to sublime around 210° to give needles); λ_{max} in mμ ($\epsilon \times 10^{-3}$): pH 1—244 (17.9) and 314 (16.8); pH 7—265 (22.6) and 312 (7.3); pH 13—266 (23.3) and 312 (7. 3); $\bar{\nu}_{max}$ in cm.$^{-1}$: 3435, 3350, 3300 (NH); 3140, 2960(CH); 1650 (NH); 1600, 1580, 1540 (C=C, C=N); 1440 (C–CH_3); 1200, 1170, 1050, 780 (ring CH); R_f values: A, 0.71; B, 0.66; C, 0.29; D, 0.59.

Anal. Calcd. for $C_8H_9N_5$: C, 54.84; H, 5.18; N, 39.98. Found: C, 54.94; H, 5.29; N, 40.04.

B.—Diethyl 3-methylpyrido[3,4-*b*]pyrazine-5,7-dicarbamate (XIII, 140 mg., 0.44 mmole) was dissolved in a solution of potassium hydroxide (310 mg., 5.5 mmoles) in ethanol (5 ml.) to give an orange-red solution. On refluxing, the orange-red precipitate which first appeared gradually changed to orange-yellow. After 7 hr. the solution was allowed to cool to room temperature and the precipitate was collected by filtration. A solution of this precipitate in water (1 ml.) was neutralized with 3 *N* hydrochloric acid to give an orange precipitate of the crude product which was collected by filtration and washed with water; the yield was 59 mg. (77%), m.p. 226°. A second run using 5 g. of XIII gave 2.48 g. (91%) of pure XVIII, m.p. 226°.

Action of Methanolic Ammonia on Diethyl 3-Methylpyrido[3,4-*b*]pyrazine-5,7-dicarbamate (XIII).—The dicarbamate (XIII, 50 mg.) was dissolved in methanol (5 ml.), saturated with ammonia at 0°, and the solution was sealed in a Parr bomb. At intervals, samples of the solution were examined by paper chromatography. After 15 hr., the reaction mixture was found to contain a very complex mixture of derivatives, none of which appeared to be 5,7-diamino-3-methylpyrido[3,4-*b*]pyrazine (XVII). Only one component appeared yellow in daylight and gave a yellow fluorescence under ultraviolet light, and this material corresponded in R_f values (A, 0.89; B, 0.85; C, 0.30; D, 0.84) and appearance to XIV (or XV). After 36 hr., only two components were present in the reaction mixture; on standing for a further 3 days no more significant changes were noted. One component (R_f: C, 0.15) exhibited a green-blue fluorescence under ultraviolet light, but was invisible in daylight, while the other (R_f: C, 0.25) gave a yellow fluorescence under ultraviolet light and appeared yellow in daylight. This material was identified as XIV (or XV).

Action of *N*-Bromosuccinimide on Diethyl 8-Bromo-3-methylpyrido[3,4-*b*]pyrazine-5,7-dicarbamate (XI).—*N*-Bromosuccinimide (75 mg.), dibenzoyl peroxide (4 mg.), and XI (160 mg.) were refluxed in chloroform (3 ml.) for 11 hr. After standing at room temperature for several days, the solution was evaporated to dryness *in vacuo*. The residue was washed with boiling water and recrystallized from ethanol (30 ml.) to give pale yellow needles which weighed 119 mg. The melting point and infrared spectrum of the product were identical with those given by the starting material.

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and the members of the Analytical Section of Southern Research Institute who performed the spectral and microanalytical determinations reported, and to Dr. W. C. Coburn and Mrs. Martha Thorpe for their interpretation of the p.m.r. spectra. The authors also wish to thank Dr. C. Temple, Jr. for his help in the identification of the bromination product of XVII.

Cyclic Imidocarbonate Hydrochlorides from the Reaction of Cyanogen Chloride with Dithiols and Diols

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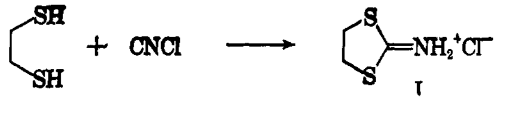
The reaction of ethanedithiol with cyanogen chloride in nonpolar solvents to give 2-imino-1,3-dithiolane hydrochloride is acid-catalyzed only in the presence of catalytic amounts of an alcohol. Hydrogen chloride accelerates the reaction of cyanogen chloride with mercaptoethanol to give 2-imino-1,3-oxathiolane hydrochloride and with ethylene glycol to give 2-imino-1,3-dioxolane hydrochloride. These reactions are quite general. Some physical properties of a number of cyclic imidocarbonate hydrochlorides and of 2-imino-1,3-dithiolane itself are described.

2-Imino-1,3-dithiolane hydrochloride (I) and its tin double salt were first characterized by Miolati.[1] The free imine was reported by Miolati to be an unstable oil.[1] His preferred synthesis of I involved a tin and hydrochloric acid partial reduction of ethylene thiocyanate followed by treatment of the tin–hydrochloride double salt with hydrogen sulfide.

Reaction of ethanedithiol with a cyanogen halide appeared to us to be a more attractive route to I. Formation of 2-imino-1,3-dithiolanes has been postulated as an intermediate step in the formation of thiocyanate ion in the quantitative estimation of *vic*-dithiols using cyanogen chloride in an aqueous system.[2,3] However, no iminodithiolane salts were actually isolated or identified from such a procedure.

Reaction of Dithiols, Mercapto Alcohols, and Diols with Cyanogen Chloride.—Reaction of ethanedithiol and cyanogen chloride (eq. 1) proceeded slowly in refluxing benzene. I precipitated in high purity but low yield. In subsequent reactions, using ethylene glycol dimethyl ether or acetonitrile as solvents, the yield was raised to as high as 66%. The reaction was still erratic, however, with long reaction times generally being required. When commercial chloroform saturated with hydrogen chloride was used, a rapid, exothermic reaction resulted. However, the reaction when run in toluene or in washed and dried chloroform



(1)

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[1] A. Miolati, *Ann.*, **262**, 61 (1891). The systematic name used by *Chemical Abstracts* for I is "cyclic ethylene dithioimidocarbonate hydrochloride."

[2] W. N. Aldridge, *Biochem. J.*, **42**, 52 (1948).

[3] J. R. Siegel and D. H. Rosenblatt, *J. Am. Chem. Soc.*, **80**, 1753 (1958).

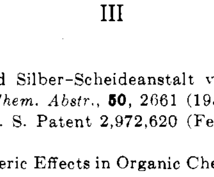
was not accelerated by adding hydrogen chloride. These results suggested that ethanol (as a preservative) in commercial chloroform was working in conjunction with hydrogen chloride to catalyze the reaction. This was confirmed by the adiabatic reaction described in the Experimental section and by the rapid reaction which occurred (91% yield of I) using the toluene–hydrogen chloride system with the addition of 1% of ethanol. Ethanol, by itself, was shown not to accelerate the reaction.

The procedure used with ethanedithiol was operable using a wide range of dithiols. 1,3-Propanedithiol gave a 64% yield of 2-imino-1,3-dithiane hydrochloride, a compound which Miolati[1] failed to obtain by reduction of 1,3-propane dithiocyanate. Free 2-imino-1,3-dithiolane was isolated as a crystalline solid after treatment of I with sodium bicarbonate solution. Some of its properties are described in the Experimental section.

The reaction of mercaptoethanol with cyanogen chloride was found to be markedly accelerated by hydrogen chloride (in the absence of an additional alcohol). Yields of 2-imino-1,3-oxathiolane hydrochloride (II) were no better than 60–65% due to side reactions attributed to water in the mercaptoethanol used. The by-products, each present in amounts of 15–20% depending upon the ratio of cyanogen chloride to mercaptoethanol used, were 2-mercaptoethyl carbamate and 2-thiocyanoethyl carbamate. High purity 1-mercapto-2-propanol on reaction with cyanogen chloride gave 2-imino-5-methyl-1,3-oxathiolane hydrochloride in 86% yield.

The acid-catalyzed reaction of ethylene glycol with cyanogen chloride at 0° afforded 2-imino-1,3-dioxolane hydrochloride for the first time. At room temperature, the exothermic reaction gave only 2-chloroethyl carbamate, the product previously reported from the uncatalyzed reaction of ethylene glycol and cyanogen chloride at 80–100°.[4] Recently, the formation of 2-chloroimino-1,3-dioxolane was reported by the low temperature reaction of ethylene glycol with potassium cyanide, chlorine, and sodium hydroxide in water.[5] The structure of 2-imino-1,3-dioxolane hydrochloride was supported by the determination of the available chloride ion, by its infrared spectrum which included a band at 1720 cm.$^{-1}$ attributable to the $>C{=}N-$ function for the compound, and by its complete rearrangement to 2-chloroethyl carbamate after several days at room temperature.

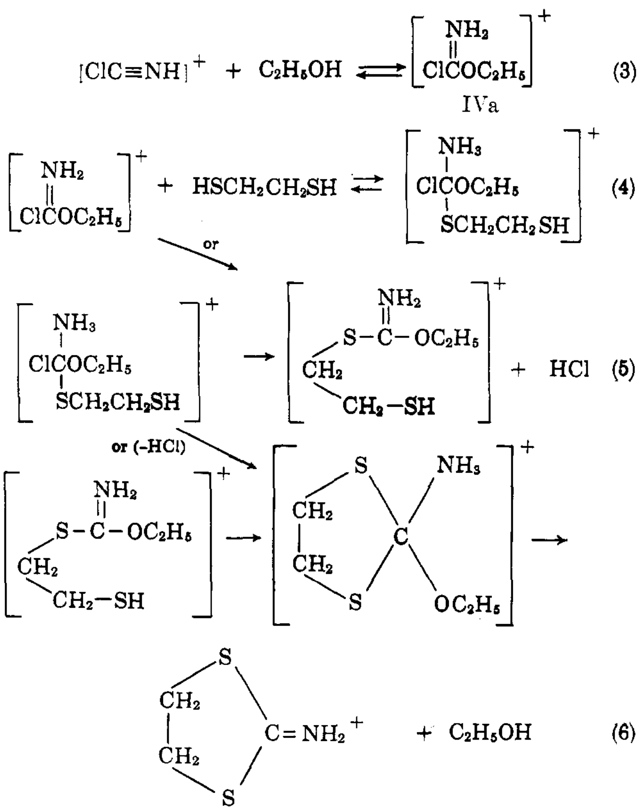
It was of interest to see if a more stable cyclic iminocarbonate (III) could be made by starting with neopentyl glycol. Not only would ring-closure be facilitated in this case by the *gem*-dimethyl effect,[6,7] but nucleophilic attack at the 4- or 6- carbon atoms would be somewhat hindered by the methyl groups in the 5-position. The reaction proceeded readily at 0° to give the product in 69% yield. III proved much more stable to rearrangement than 2-imino-1,3-dioxolane hydrochloride and, in fact, in a comparison at 100° rearranged more slowly than 2-imino-1,3-oxathiolane hydrochloride. Hydrolysis was rapid even at room temperature in ethanol solution.



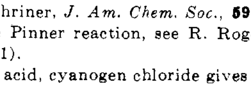
III

Reaction Mechanism.—Since mercaptans are reported to react rapidly with alkyl and aryl nitriles at 0° in the presence of hydrogen chloride, and in the apparent absence of an alcohol,[8] the results described for cyanogen chloride in this work are unusual. The following sequence is offered as an explanation for the ethanedithiol–cyanogen chloride case. The ionic species shown are recognized as being oversimplified for the solvent systems used.

$$ClC{\equiv}N + H^+ \rightleftharpoons [ClC{\equiv}NH]^+ \qquad (2)$$



In support of eq. 3, we have shown that, with hydrogen chloride present, cyanogen chloride reacts rapidly with alcohols as represented by ethylene glycol and mercaptoethanol.[9] In the latter case, if water is present, 2-mercaptoethyl carbamate is a by-product. Its formation is most easily explained by hydrolysis of the intermediate (IVb), analogous to IVa, and presumably


$$\left[HSCH_2CH_2O\overset{NH_2}{\overset{\|}{C}}Cl\right]^+$$

IVb

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[4] Deutsche Gold und Silber-Scheideanstalt vormals Roessler, British Patent 722,676 (1955); *Chem. Abstr.*, **50**, 2661 (1956).

[5] I. E. Simmons, U. S. Patent 2,972,620 (February 21, 1961); *Chem. Abstr.*, **55**, 14,481 (1961).

[6] G. S. Hammon, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 458.

[7] M. S. Newman and R. J. Harper, Jr., *J. Am. Chem. Soc.*, **80**, 6350 (1958)

[8] (a) H. Bader, J. D. Downer, and P. Driver, *J. Chem. Soc.*, 2775 (1950); (b) W. Autenrieth and A. Brüning, *Ber.*, **36**, 3464 (1903); (c) A. Pinner and F. Klein, *ibid.*, **11**, 1825 (1878); (d) F. E. Condo, E. T. Hinkel, A. Fassero, and R. L. Shriner, *J. Am. Chem. Soc.*, **59**, 230 (1937); (e) for a general review of the Pinner reaction, see R. Roger and D. G. Neilson, *Chem. Rev.*, **61**, 179 (1961).

[9] In the absence of acid, cyanogen chloride gives no immediate reaction with ethanol at 25°; A. Wurtz, *Ann.*, **79**, 280 (1851).

formed directly from protonated cyanogen chloride and mercaptoethanol.

The mechanism shown assumes that the thiol reacts rapidly with the chloroimidate (IVa) of eq. 3 but not with the protonated nitrile in eq. 2. High reactivity towards species IVa would not be surprising since mercaptans react rapidly with acid chlorides[10] and with aldehydes and ketones,[11] but lack of reactivity towards the protonated cyanogen chloride proposed by eq. 2 is not easily explained.

Frequency of the >C=N– Group.—An absorption band assignable to the >C=N– group of 2-imino-1,3-dithiolane falls at 1560 cm.$^{-1}$ (solid and solution). This value is low in comparison to that found for most >C=N– groups[12]; however, it is not unexpected. The carbonyl frequency of ethylene dithiolcarbonate at 1638 falls 134 cm.$^{-1}$ below that of cyclopentanone at 1772 cm.$^{-1}$.[13] The >C=N– frequency of cyclopentanone oxime at 1684[14] is some 88 cm.$^{-1}$ below that of the carbonyl group for cyclopentanone. A comparable reduction in frequency going from the carbonyl group of ethylene dithiolcarbonate to the >C=N– group of 2-imino-1,3-dithiolane would place the latter absorption in the range where it is actually found. Protonation of the imine to give I shifts the >C=N– frequency to 1570, reduces its intensity, and introduces a strong band at 1488 cm.$^{-1}$ assigned to the –NH_2 bending vibrations.[15]

As shown in Table I, in those hydrochlorides containing two sulfur atoms adjacent to the >C=N– group (I, VI, VII), the frequency increases slightly in this order: open chain < five-membered ring < six-membered ring. Large increases in the >C=N– frequency are found in going from the hydrochlorides of the dithiolane (I), to the oxathiolane (II), and to the dioxolane (IX). These changes are the net result of differences in the mesomeric and inductive capabilities of oxygen and sulfur in these systems as well as of probable differences in ring strain which have already been discussed for analogous carbonyl compounds.[13]

TABLE I

THE FREQUENCY OF THE >C=N– GROUP OF IMIDOCARBONATE HYDROCHLORIDES

Compound	Structure	>C=N– frequency,[a] cm.$^{-1}$
I	2-Imino-1,3-dithiolane hydrochloride	1570[b]
V	2-Imino-1,3-dithiolane	1560[b]
VI	2-Imino-1,3-dithiane hydrochloride	1580[b]
VII	Dimethyldithioimidocarbonate hydrochloride	1555[b]
II	2-Imino-1,3-oxathiolane hydrochloride	1678[c]
IX	2-Imino-1,3-dioxolane hydrochloride	1720[c]
III	2-Imino-5,5-dimethyl-1,3-dioxane hydrochloride	1690[c]

[a] Run as mulls in Nujol and in hexachlorobutadiene. [b] Perkin-Elmer Model 421 spectrophotometer. [c] Perkin-Elmer Model 137 Infracord.

Experimental[16]

Dithiols.—*trans*-1,2-Cyclohexanedithiol, *threo*-2,3-butanedithiol, and phenyl-1,2-ethanedithiol were prepared in 63, 28, and 43% over-all yields, respectively, from the corresponding epoxides *via* conversion to the trithiocarbonates and reduction of the latter with lithium aluminum hydride.[17,18] 1,2-Butanedithiol and 1,2-hexanedithiol were prepared from the corresponding dibromides in 43 and 53% yields, respectively, by the method of Zinner.[19] Methyl 1,2-dimercaptopropionate was prepared in 38% yield from methyl α-chloroacrylate.[20] Other dithiols were obtained commercially.

2-Imino-1,3-dithiolane Hydrochloride (I).—Hydrogen chloride was added to 210 ml. of toluene and 2.0 ml. of ethanol to make a 0.117 *M* solution. Ethanedithiol (108.6 g., 1.15 moles) was added, and cyanogen chloride (76 g., 1.24 moles) was passed over the stirred reaction mixture for 3.33 hr. with the temperature maintained at 40–50° by external cooling. After the reaction mixture had been kept at about 40° an additional 90 min., the precipitate was filtered and washed with toluene and ether. Vacuum drying gave 179.3 g. (91.2%) of I, m.p. 212–216° dec., lit.[1,21] m.p. 202°, 212° dec.; $\lambda_{\max}^{\text{MeOH}}$ 242 mμ (log ε 4.04) and 268 (3.81).

Adiabatic Reaction of Ethanedithiol and Cyanogen Chloride.—A 0.106 *M* solution of hydrogen chloride in chloroform (purified by washing with sulfuric acid, water, and followed by passing through one-tenth its weight of high activity alumina) was prepared. A 50-ml. sample was pipeted into a 350-ml. dewar flask equipped with a magnetic stirring bar and a rubber stopper having a thermometer, ice condenser, and an addition tube. Gaseous cyanogen chloride (5.1 g., 0.083 mole) was added over a 140-min. period (10° temperature rise). With an initial temperature of 30.5°, 1.0 ml. (0.012 mole) of ethanedithiol was added; no heat was evolved. The addition of a second 1.0 ml. of ethanedithiol had no effect and g.l.c. analysis showed that no reaction had occurred. The addition of 0.1 ml. of absolute alcohol led to a rapid and exothermic reaction. On the following day, the addition of 1.0 ml. of ethanedithiol had little effect, but another 0.1 ml. of ethanol led to reaction. The isolated 2-imino-1,3-dithiolane hydrochloride amounted to 5.35 g. (72%).

When a 0.0224 *M* solution of hydrogen chloride was used, no exothermic reaction was noted even in the presence of ethanol.

Other Cyclic Esters of Dithioimidocarbonic Acid.—Table II gives yield, analytical, and some spectral data for other iminodithiolane and dithiane analogs prepared. Reactions were run in the same way as for I; the solvent used in most cases was chloroform or toluene to which 1% ethanol was added. Hydrogen chloride was used as cocatalyst in each case. Products generally precipitated as colorless crystals and, in most cases, were vacuum sublimed at about 100° (0.05 mm.) for analyses.

2-Imino-1,3-dithiolane (V).—Two extractions with 25-ml. portions of ether of a mixture of 5.00 g. of I in 50 ml. of saturated sodium bicarbonate solution gave 2.08 g. (54.2%) of the free imine as colorless crystals, m.p. 63.8–64.8° (clear colorless melt); $\lambda_{\max}^{\text{water}}$ 239 mμ (log ε 3.949), 267 (3.551), maxima in aqueous solution reduced no more than 2% after 46 hr. at 24.4°; $\lambda_{\max}^{\text{Nujo}}$ 3110 (N–H), 1560 (C=N), 1285, 1243, 818 cm.$^{-1}$.

A 0.2894-g. sample in water gave a neutralization equivalent of 122.6 (calculated for $C_3H_5NS_2$, 119.2). The pH at the half-neutralization point was 5.85. Air evaporation of the water and

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(10) T. C. Bruice, "Organic Sulfur Compounds," Vol. I, N. Kharasch Ed., Pergamon Press, New York, N. Y., 1961, pp. 421–442.

(11) E. Campaigne, *ibid.*, pp. 134–145.

(12) For a discussion of the >C=N– stretching vibrations, see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 267–271.

(13) R. Mecke, R. Mecke, and A. Luttringhaus, *Ber.*, **90**, 975 (1957).

(14) Ref. 12, p. 268.

(15) These assignments were based on deuterium oxide exchange reactions.

(16) Melting points were run in capillary tubes and are uncorrected. Infrared curves were run on a Perkin-Elmer Model 137 Infracord unless stated otherwise. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer. Gas-liquid chromatography (g.l.c.) was done on an Aerograph Model A-100C instrument on a silicone-impregnated carrier. Analyses were by the Galbraith Laboratories, Inc., Knoxville, Tenn.

(17) C. C. J. Culvenor, W. Davies, and K. Pausacker, *J. Chem. Soc.*, 1050 (1946).

(18) S. M. Iqbal and L. N. Owen, *ibid.*, 1030 (1960).

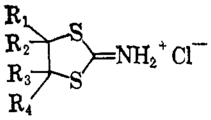
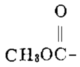
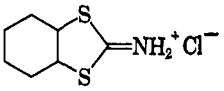
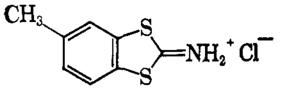
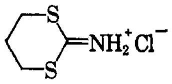
(19) H. Zinner, *Ber.*, **86**, 825 (1953).

(20) W. A. Lazier, A. P. Pavlic, and W. J. Peppel, U. S. Patent 2,422,246 (June 17, 1947); *Chem. Abstr.*, **41**, 6277 (1947).

(21) H. L. Wheeler and H. F. Merriam, *J. Am. Chem. Soc.*, **24**, 439 (1902).

TABLE II

HYDROCHLORIDES OF SOME CYCLIC ESTERS OF DITHIOIMIDOCARBONIC ACID

Structure				Yield, %	M.p., °C.[a]	$C=NH_2^+$ stretch, cm.$^{-1}$	λ_{max}^{MeOH}, mμ	(log ε)	Analysis, %									
									Calcd.					Found				
									C	H	N	S	Cl	C	H	N	S	Cl
																		
R_1	R_2	R_3	R_4															
CH_3	H	H	H	91	168-170[b]	1570			28.3	4.8				28.2	5.0			
CH_3	H	H	CH_3	59[c]	176-177				32.7	5.5		34.9	19.3	32.9	5.9		35.0	19.2
CH_3	CH_3	H	H	62	184-186	1560			32.7	5.5		34.9	19.3	32.9	5.8		34.8	19.6
C_2H_5	H	H	H	94	161-163	1570							19.3					19.3
n-C_4H_9	H	H	H	83	96-99	1570							16.7					16.8
C_6H_5	H	H	H	91	195-200	1560			46.6	4.4	6.0	27.7	15.3	46.7	4.3	6.0	27.9	15.0
 $CH_3O\overset{\overset{O}{\|}}{C}-$	H	H	H	80	127-128				28.1	3.8	6.6	30.0	16.6	27.9	3.9	6.6	30.0	16.8
				83[d]	243-246	1580			40.0	5.8		30.6	16.9	40.3	6.0		30.8	16.9
				87	260-265	1560	233 240 274 s 303 s	(4.030) (3.782) (3.625) (3.891)	44.1	3.7		29.5	16.3	43.9	3.7		29.2	16.0
				64	176-178	1580	258	(4.196)	28.3	4.8			20.9	28.0 27.8	5.3 5.2			20.9 20.8

[a] Melting points were usually accompanied by decomposition. [b] Miolati reported m.p. 172–175° (ref. 1). [c] After washing with 3:1 ether–methanol; *trans* isomer. [d] *trans* isomer.

vacuum drying of the residue afforded 0.3604 g. (95.3% recovery) of I (by infrared).

Pure V shows slight decomposition at room temperature after 3 days and moderate decomposition after a week. Impure samples decompose more rapidly to give insoluble polymers. Decomposition is accompanied by depletion of the >C=N– absorption peak at 1560 cm.$^{-1}$ and the appearance of an –SCN band at 2050 cm.$^{-1}$. Breakdown is probably initiated by abstraction of the imino hydrogen atom in a manner analogous to that demonstrated for iminooxathiolane salts.[22] In water, decomposition is rapid above pH 7; in nonaqueous systems, triethylamine effects rapid build-up of the –SCN peak in the infrared.

Solution spectra in carbon tetrachloride failed to show either the presence of an –SH or an –SCN group indicating a lack of tautomeric equilibrium with 2-mercaptoethyl thiocyanate.

2-Imino-1,3-oxathiolane Hydrochloride (II).—Mercaptoethanol (89.4 g., 1.15 moles) which had been fractionated through a short packed column (b.p. 59° at 11–12 mm., but which still showed the apparent presence of water by g.l.c.) was added to 300 ml. of dry chloroform 0.36 *M* in hydrogen chloride. Addition of 83.5 g. (1.36 moles) of cyanogen chloride was completed over 3 hr. with the reaction temperature maintained at 35–45° by external cooling. The following morning the precipitate was filtered and washed with chloroform and with ether. Dry II amounted to 97.7 g. (60.6%), m.p. 115–117°, but suspended solids remained even to 240° and recrystallization from acetic acid–ether gave no improvement, lit.[23] m.p. 114–115°, infrared curve same as that published,[23] λ_{max}^{MeOH} 223 mμ (log ε 3.76).

Addition of petroleum ether (b.p. 30–60°) to the mother liquor precipitated 25.4 g. of colorless plates, m.p. 66.0–67.8°, with an apparent crystal transition at 58° after recrystallization from water (lit.[24] m.p. 64–69° for 2-thiocyanoethyl carbamate); λ_{max}^{Nujol} 2140 (SCN), 1680 and 1620 ($CONH_2$) cm.$^{-1}$. The 25.4 g. is 15.2% of mercaptoethanol used.

Anal. Calcd. for $C_4H_6N_2O_2S$: C, 32.9; H, 4.1. Found: C, 32.8, 32.9; H, 4.6, 4.8.

The mother liquor from separation of 2-thiocyanoethyl carbamate, concentrated *in vacuo*, left 22.7 g. of an oil, apparently a mixture of 2-thiocyanoethyl and 2-mercaptoethyl carbamates (by infrared). Distillation of a sample of this oil gave a fraction, b.p. 95–98° (1.3 mm.), which solidified and, after two recrystallizations from ether-petroleum ether, gave m.p. 42.0–43.0°; λ_{max}^{Nujol} 3400, 3300, 1680, and 1610 (–$CONH_2$), and 2565 cm.$^{-1}$ (weak, –SH); positive sodium azide-iodine test for mercaptan; soluble in dilute sodium hydroxide but soon gave a precipitate for which the carbamyl group is intact (by infrared), presumably the disulfide.

Anal. Calcd. for 2-mercaptoethyl carbamate ($C_3H_7NO_2S$): C, 29.7; H, 5.8; S, 26.5. Found: C, 30.4, 30.5; H, 6.1, 5.9; S, 26.2, 26.4.

2-Imino-5-methyl-1,3-oxathiolane Hydrochloride.—The reaction of 104.3 g. (1.13 moles) of 1-mercapto-2-propanol (Jefferson Chemical, single peak by g.l.c.) with 74.8 g. (1.22 moles) of cyanogen chloride in 200 ml. of reagent grade toluene (0.02% water by label) containing dry hydrogen chloride afforded 149.8 g. (86.1%) of 2-imino-5-methyl-1,3-oxathiolane hydrochloride identical by infrared with a sample prepared from propylene oxide and thiocyanic acid.[12]

2-Imino-1,3-dioxolane Hydrochloride (IX).—Redistilled ethylene glycol (28.1 g., 0.45 mole) was mixed with 100 ml. of ethylene glycol dimethyl ether which had been dried over calcium chloride and passed through activated alumina directly into the reaction flask. After hydrogen chloride was passed in for 5 min., 27.8 g. (0.45 mole) of cyanogen chloride was passed in over a 1.5-hr. period at 0°. After stirring the mixture at 0° overnight, the precipitate was collected and washed with glyme and with ether. The colorless, free-flowing solids amounted to 18.8 g. (33.6%), m.p. 77–78° (some nonmelt even at 240°). Infrared shows distinctive absorption attributable to $=NH_2^+$ in the 1500–1600- and 2600–3200-cm.$^{-1}$ regions and at 1720 cm.$^{-1}$ (C=N).

Anal. Calcd. for $C_3H_6ClNO_2$: Cl, 28.7. Found: Cl, 28.5, 28.6 (by addition to excess silver nitrate solution and back titration).

Concentration of the mother liquor at 25° afforded only 2-chloroethyl carbamate, identical by infrared with a sample prepared by the above reaction run at 30–40°, m.p. 65–70°, lit.[4] m.p. 70.5°.

Using ether as solvent (at 2–3°, glycol partially miscible), a 62% yield of IX was isolated. It was tacky and smelled of hydrogen chloride even after careful washing with benzene and with ether and completely rearranged to 2-chloroethyl carbamate within 24 hr. (by infrared). A pure sample of IX at 23–24°

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[22] C. C. Price and P. F. Kirk, *J. Am. Chem. Soc.*, **75**, 2396 (1953).

[23] T. Wagner-Jauregg and M. Haring, *Helv. Chim. Acta*, **41**, 377 (1958).

[24] T. Wagner-Jauregg, *Ann.*, **561**, 87 (1948).

showed no change (infrared) after 5 hr., extensive rearrangement to 2-chloroethyl carbamate after 45 hr., and complete rearrangement after 6 days. There was no rearrangement after 6 days at 0°. IX appears as clear cylindrical rods under a binocular scope and becomes studded with flat prisms as rearrangement proceeds.

2-Imino-5,5-dimethyl-1,3-dioxane Hydrochloride (III).—The reaction was run at 0° as for IX using 50.0 g. (0.48 mole) of recrystallized neopentyl glycol and 30.8 g. (0.50 mole) of cyanogen chloride in 150 ml. of reagent grade chloroform, 0.284 *M* in hydrogen chloride. Solids were present within 1 hr. The product, collected the following morning, amounted to 54.9 g. (69.2%) of colorless solids after washing with chloroform and ether and vacuum drying. A sample in acetic acid was filtered, reprecipitated with benzene, and washed with ether for analyses, m.p. 135.5° (partial with capillary immersed at 132°, some nonmelt at 270°); $\lambda_{\max}^{\text{Nujol}}$ 2800–3300 (broad) and 1520 assigned to $=NH_2^+$, 1690 cm.$^{-1}$ (C=N).

Anal. Calcd. for $C_6H_{12}ClNO_2$: C, 43.5; H, 7.3; N, 8.5; Cl, 21.4. Found: C, 43.4, 43.4; H, 7.5, 7.6; N, 8.5, 8.7; Cl, 21.5, 21.6.

At a temperature of 100°, III showed little change after 15 min., an estimated 23% conversion to 2,2-dimethyl-3-chloropropylcarbamate after 36 min., and essentially complete conversion after 58 min. (as estimated by disappearance of a strong infrared band at 1110 and appearance of a new band at 1080 cm.$^{-1}$). II, run simultaneously, was completely rearranged to 2-chloroethyl thiolcarbamate after 15 min. at 100°, the first point checked.

A sample of the rearranged product of III, recrystallized from hexane (colorless plates), vacuum sublimed at 70° (0.1 mm.), and melted at 79.0–80.4°; $\lambda_{\max}^{\text{Nujol}}$ 3400, 1680, 1605 cm.$^{-1}$ (all $CONH_2$).

Anal. Calcd. for $C_6H_{12}ClNO_2$ (2,2-dimethyl-3-chloropropyl carbamate): C, 43.5; H, 7.3; Cl, 21.4. Found: C, 43.4, 43.8; H, 6.7, 7.2; Cl, 21.0.

Dimethyldithioimidocarbonate Hydrochloride (VII).—Addition of hydrogen chloride to about equal amounts of methyl mercaptan and methyl isothiocyanate in chloroform at 0° afforded an 87% yield of the colorless crystalline hydrochloride, m.p. 158–159° dec. A vacuum-sublimed sample, m.p. 160.5–161.5°, was analyzed. The free base and the hydroiodide have been reported.[25]

Anal. Calcd. for $C_3H_8ClNS_2$: Cl, 22.5. Found: Cl, 22.2 (ionic).

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The Reaction of Primary and Secondary Alkylaryl and Alkyl Sulfonates with Potassium *t*-Butoxide in Dimethyl Sulfoxide[1]

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Sulfonate esters of primary and secondary alcohols react rapidly with potassium *t*-butoxide in dimethyl sulfoxide to give alkenes and alkyl *t*-butyl ethers. The reaction is complete within 30 min. at 20–25° for 0.5 *M* solutions of the ester. Esters of cyclic and secondary acyclic alcohols give about 80% yields of alkenes and no appreciable quantities of ethers. Esters of normal primary alcohols and of cyclohexylcarbinol give 20–25% alkenes and 60–70% ethers. Esters of primary alcohols containing α-alkyl substituents give 20–30% alkenes and 30–40% ethers. *n*-Octyl benzenesulfonate, *p*-tosylate, and *p*-brosylate give essentially identical yields. Although the *p*-nitrobenzenesulfonate gives exceptionally low yields of alkene and ether, the ether/alkene ratio for the series is nearly constant.

Dimethyl sulfoxide has been used widely as a solvent to facilitate base-promoted reactions.[2] Cyclohexyl and 1-octyl benzenesulfonates have been shown to react rapidly with potassium *t*-butoxide in this solvent at room temperature to give, respectively, cyclohexene (83%, gas chromatography), and a mixture of 1-octene (24%, g.c.) and octyl *t*-butyl ether (67%, g.c.).[3] Because of the potential synthetic importance of this facile reaction, the effects of structural variations in both the alkyl and sulfonate moieties upon the reaction products have been examined.

In the previous study[3] it was shown that a maximum yield of cyclohexene was obtained after 30 min. stirring at 20–25° of a solution 0.5 *M* in cyclohexyl benzenesulfonate and 1.0 *M* in potassium *t*-butoxide. Although decreases in alkoxide stoichiometry produced significant decreases in the yield of cyclohexene, a reaction time of only 10 min. still yielded 74% alkene. In the present study, therefore, a reaction time of 30 min. at 20–25° was used with solutions 0.5 *M* in ester and 1.0 *M* in alkoxide.

In Table I are presented the results of variations in the alkyl moiety of the benzenesulfonates. To examine effects of variations in the leaving group on relative and absolute yields, a number of sulfonates of 1-octanol and 1-hexanol were investigated and the results are presented in Table II. Each run was duplicated.

With the following exceptions, all alkenes were identified by boiling points, refractive indices, and g.c. comparison with authentic samples. 2-Methyl-1-butene was identified by g.c. comparison with an authentic sample; 2-ethyl-1-butene and 2-ethyl-1-hexene were identified by g.c. relative retention times.

Octyl *t*-butyl ether was identified by its boiling point, refractive index, chromatographic behavior, and infrared spectrum.[3] Hexyl *t*-butyl ether was identified similarly, with an elemental analysis also (see Experimental). Cyclohexylcarbinyl *t*-butyl ether was identified by g.c. comparison with material prepared by a Williamson synthesis. All other ethers were identified by relative g.c. retention times.

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(1) Presented before the Organic Division at the 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

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