Chlorination of Isothiocyanates. II. N-Aryl- and N-Alkyl-S-chloroisothiocarbamoyl Chlorides, a Novel Class of Sulfenyl Chlorides

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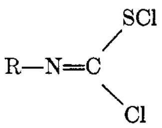
N-Aryl- and N-alkyl-S-chloroisothiocarbamoyl chlorides represent a novel class of sulfenyl chlorides and the true intermediates in the conversion of isothiocyanates to isocyanide dichlorides by chlorine. They are obtained in high to nearly quantitative yields by chlorination of the corresponding isothiocyanates as well as diisothiocyanates with 1 mole of chlorine for each isothiocyanato group. Some properties and the infrared absorption spectra of this new class of compounds are discussed.

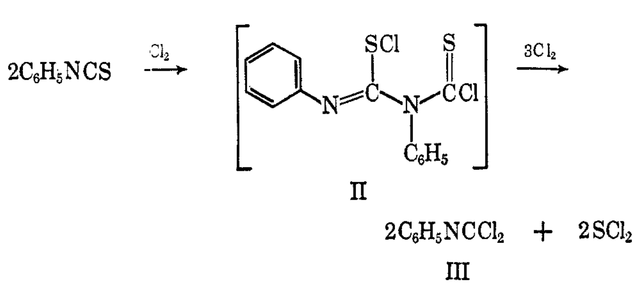
In a recent communication[1] we have described the first three representatives of N-aryl-S-chloroisothiocarbamoyl chlorides (I), a hitherto unknown class of



I

compounds. In the present paper we wish to report the preparation of both N-aryl and N-alkyl derivatives of I.

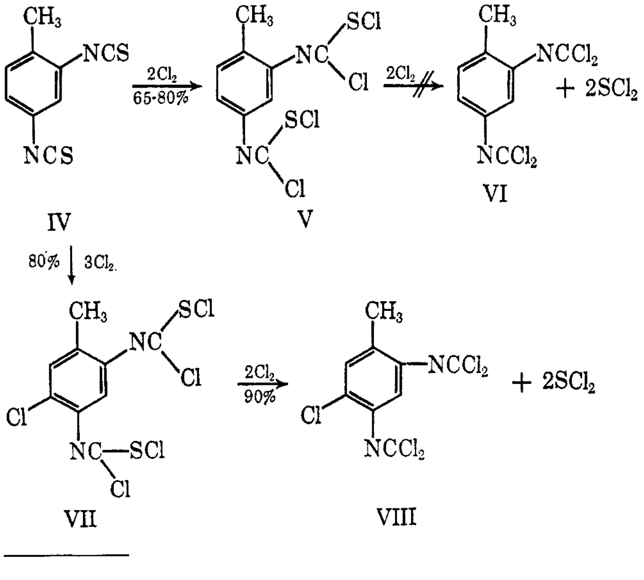
The chlorination of isothiocyanates is used as a preparative method for the synthesis of aromatic[2-5] and, in a few cases, of aliphatic isocyanide dichlorides.[6-8] Several attempts have been made to elucidate the reaction mechanism of the chlorination of isothiocyanates, particularly of phenyl isothiocyanate[3,9,10] but the results are not convincing.[11] The formation of highly sensitive chlorine adducts of ethyl and phenyl isothiocyanate of the empirical formula $(RNCS)_2Cl_2$ was reported in early work by Sell[9] and Helmers.[3] Some 50 years later, Dyson and Harrington[10] suggested the dimeric structure II for the labile phenyl compound and considered it a direct intermediate in the conversion of phenyl isothiocyanate to phenyl isocyanide dichloride (III).



II

III

During attempts to prepare N,N'-(2,4-tolylene) bis-(isocyanide dichloride) (VI) by exhaustive chlorination of 2,4-tolylene diisothiocyanate (IV) in chloroform, we observed occasionally the temporary precipitation of small amounts of two yellow compounds of the empirical formulas $C_9H_6Cl_4N_2S_2$ (mp 75–75.5°) and $C_9H_5Cl_5N_2S_2$ (mp 105–106°), respectively. Both products were later obtained in substantial quantities by treating IV with 2 and 3 moles, respectively, of chlorine. The progress of the chlorination of IV was followed by changes in the infrared absorption spectrum. Particularly conspicuous was the intensity decrease of the -NCS absorption above 2000 cm^{-1}. Its total disappearance coincided with the consumption of 2 moles of chlorine for each mole of IV. This, and the results of the elemental analysis and molecular weight determination, suggested that the product from IV and 2 moles of chlorine was N,N'-(2,4-tolylene)bis-(S-chloroisothiocarbamoyl chloride) (V). Compound V, when further chlorinated, is attacked in the 5-position of the aromatic nucleus to afford N,N'-(5-chloro-2,4-tolylene)bis(S-chloroisothiocarbamoyl chloride) (VII)[12] before the C–SCl linkage is severed to form the $-N{=}CCl_2$ moiety. This particular reaction pattern explains why compound VI was never detected among the chlorination products of IV with 4 moles of chlorine, yet N,N'-(5-chloro-2,4-tolylene) bis(isocyanide



IV V VI VII VIII

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[9] E. Sell, *Ber.*, **6**, 322 (1873).

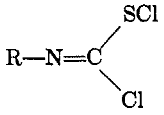
[10] G. M. Dyson and T. Harrington, *J. Chem. Soc.*, 191 (1940); 150 (1942).

[11] (a) Houben-Weyl, "Methoden der Organischen Chemie," Vol. IX, Georg Thieme Verlag, Stuttgart, 1955, p 882. (b) N. Kharasch, "Organic Sulfur Compounds," Vol. I, Pergamon Press Ltd., London, 1961, p 335.

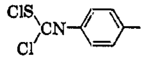
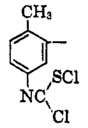
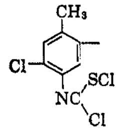
[12] The relative position of the chlorine atom attached to the aromatic ring was determined by nmr spectroscopy. The proton resonance spectrum (taken in $CDCl_3$ against tetramethylsilane as internal standard) consists of three peaks, representing one methyl group and two uncoupled aromatic protons. The methyl resonance is at 2.15 ppm, the low-field proton at 6.54 ppm, and the high-field proton at 7.32 ppm.

TABLE I

N-ARYL- AND N-ALKYL-S-CHLOROISOTHIOCARBAMOYL CHLORIDES

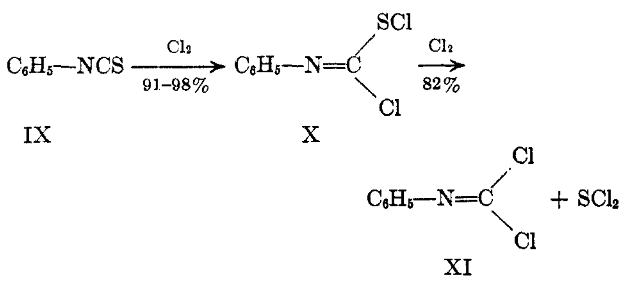


$R—N{=}C(SCl)Cl$

Compd	R	Mp, °C	n_D (°C)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % Cl	Calcd, % N	Calcd, % S	Found, % C	Found, % H	Found, % Cl	Found, % N	Found, % S	Mol wt Calcd	Mol wt Found
X	C_6H_5–	Liquid	1.6291 (25)	91–95	40.79	2.44	34.35	6.87	15.52	40.78	2.42	34.40	6.89	15.44	206.1	206.0
XII	p-ClC_6H_4–	41–42	...	69–90	34.94	1.68	44.26	5.83	13.30	35.11	1.63	44.10	5.89	13.49		
XIII	2,5-$Cl_2C_6H_3$–	31	...	71	30.56	1.10	51.61	5.10	11.60	30.87	1.35	51.10	5.03	11.28		
XIV	p-$NO_2C_6H_4$–	49	...	70	33.48	1.61	28.27	11.16	12.76	34.21	1.60	27.70	11.58	12.89	251.0	238.0
XVI	p-$CH_3OC_6H_4$-	Liquid	1.6251 (27)	46.5	40.70	2.99	30.06	5.94		42.27	3.12	30.00	5.73			
XV		82–83	...	67–97	28.75	1.21	42.49	8.38	19.15	28.99	1.30	42.60	8.36	19.24		
V		75–75.5	...	65–81	31.05	1.74	40.78	8.05	18.38	31.08	1.83	41.20	8.02	18.88	348.2	345.0
VII		105–106	...	55–83			46.38	7.32	16.72			46.10	7.35	16.72		
	CH_3–	Liquid		68	16.67	2.09	49.27	9.72	22.20	17.70	2.22	49.20	9.84	21.78		
	C_2H_5–	Liquid	1.5250 (24)	93	22.79	3.18	45.00	8.86		23.18	3.28	46.00	8.45			
	n-C_4H_9–	Liquid	1.5110 (24)	92	32.26	4.83	38.20	7.53		32.40	5.15	37.90	7.20		186.1	190.0
	n-C_7H_{15}–	Liquid	1.5000 (25)	94	42.12	6.62	31.11	6.14	14.02	42.66	6.67	31.20	5.81	14.42		
	C_6H_{11}–	Liquid	1.5410 (24)	98	39.61	5.22	33.45	6.60	15.08	40.15	5.22	33.40	6.43	14.82		

dichloride) was obtained in approximately 70% yield from IV and 5 moles of chlorine.

The results of the chlorination of IV prompted us to reinvestigate the chlorination of phenyl isothiocyanate. Again, the consumption of 1 mole of chlorine for each mole of phenyl isothiocyanate—dissolved in $CHCl_3$—coincided with the extinction of the absorption at 2080 cm^{-1}. The reaction mixture contained little of a moisture-sensitive, yellow solid which had slowly developed during the chlorination and which appears to be identical with that reported by Helmers[3] and other investigators.[10] The principal reaction product, however, is pure N-phenyl-S-chloroisothiocarbamoyl chloride (X) obtained in a 95% yield as a yellow liquid. Structure X is evidenced by elemental analysis, molecular weight determination, and by its conversion to phenyl isocyanide dichloride (XI) with 1 mole of chlorine. The formation of XI in more than 80% yield shows that, in contrast to compound V, X is attacked predominantly at the carbon–sulfur linkage while chlorination of the aromatic nucleus is not appreciable before the conversion to the $-N{=}CCl_2$ group is completed.



$$\underset{\text{IX}}{C_6H_5—NCS} \xrightarrow[91-98\%]{Cl_2} \underset{\text{X}}{C_6H_5—N{=}C(SCl)Cl} \xrightarrow[82\%]{Cl_2} \underset{\text{XI}}{C_6H_5—N{=}CCl_2} + SCl_2$$

The N-(4-chlorophenyl) (XII), N-(2,5-dichlorophenyl) (XIII), N-(4-nitrophenyl) (XIV), and N,N′-(1,4-phenylene) (XV) derivatives of I were synthesized accordingly in yields of between 70 and 90% (Table I). In contrast, N-(4-methoxyphenyl)-S-chloroisothiocarbamoyl chloride (XVI) was obtained in only 47% yield.

N-Alkyl- and N-cycloalkyl-S-chloroisothiocarbamoyl chlorides were prepared like the aromatic representatives by chlorination of the corresponding alkyl or cycloalkyl isothiocyanates in a low-boiling hydrocarbon such as n-pentane. They were obtained in a pure state in nearly quantitative yields. A lower yield was only experienced for the N-methyl derivative which was always accompanied by a white, moisture-sensitive solid of the empirical formula $(CH_3NCSCl)_2$.

The S-chloroisothiocarbamoyl chlorides are intensively yellow colored compounds. The aliphatic derivatives are liquids, while most of the aromatic derivatives are well crystallized. Sensitive to moisture and heat, they can be kept unchanged for a long time provided they are stored at subzero temperatures in a pure state or dissolved in an aliphatic hydrocarbon. At above 100°, both the aliphatic and aromatic S-chloroisothiocarbamoyl chlorides are swiftly converted to a mixture consisting of isocyanide dichloride, isothiocyanate, SCl_2, chlorine, and tar, with the first compound being the principal component. Distillation of the liquid representatives *in vacuo* at temperatures above 40° was always accompanied by partial dissociation into chlorine and the corresponding isothiocyanate. The reaction of S-chloroisothiocarbamoyl chlorides with water progresses only slowly owing to poor wetting but becomes very exothermic upon the addition of solvents which dissolve both water and the carbamoyl chlorides. Hydrolysis of N-phenyl-S-chloroisothiocarbamoyl chloride in water–dioxane afforded a yellow crystalline compound of the empirical formula $C_{14}H_{10}N_2S_2O$ in a 67% yield. Melting point and mass spectroscopical investigation suggest the identity of this product with 4-phenyl-5-phenylimino-1,2,4-dithi-

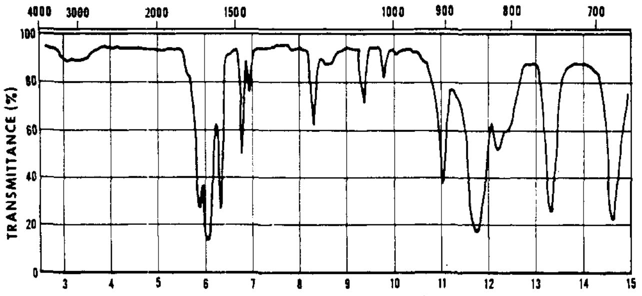


Figure 1.—Infrared spectrum of N-phenyl-S-chloroisothiocarbamoyl chloride (liquid phase between NaCl plates).

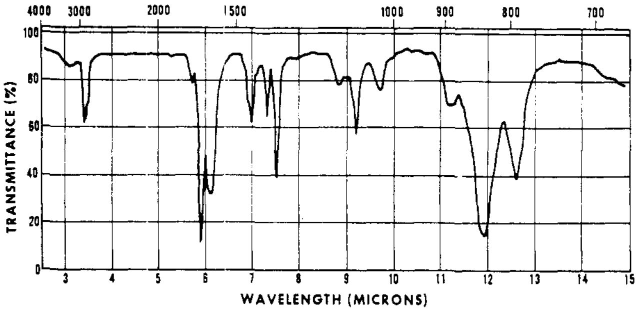
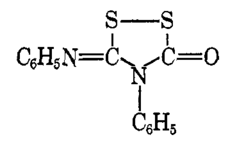


Figure 2.—Infrared spectrum of N-ethyl-S-chloroisothiocarbamoyl chloride (liquid phase between NaCl plates).

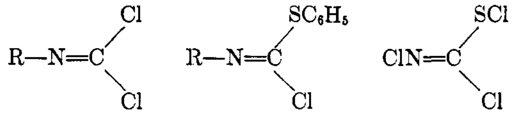
azolidin-3-one (XVII), described by Bradsher and coworkers.[13]



XVII

Consistent with the S-chloroisothiocarbamoyl chloride structure I are (1) the gradual disappearance and final extinction of the -NCS absorption above 2000 cm^{-1} after 1 mole of chlorine/-NCS group is added; (2) the formation of isocyanide dichlorides and SCl_2 upon further chlorination of the carbamoyl chlorides; (3) the reaction of compounds of structure I with olefins to form 2-chloroethyl thio ethers in high yields[14] (4) the infrared absorption spectrum; and (5) elemental analysis and molecular weight determination.

The infrared absorption spectra of N-phenyl- and N-ethyl-S-chloroisothiocarbamoyl chloride are presented in Figures 1 and 2. Characteristic infrared absorptions of the S-chloroisothiocarbamoyl chlorides are two neighboring bands at about 1650 and 1700 cm^{-1}, and a broad band in the vicinity of 840 cm^{-1}. The sharp absorption at about 1650 cm^{-1} can only be associated with the -N=C< stretching vibration, for it is known that the C=N linkage in compounds having a similar structure, such as the isocyanide dichlorides[15] (XVIII) and S-phenylisothiocarbamoyl chloride (XIX), gives rise to an absorption at or about 1650 cm^{-1}. Thiocyanogen trichloride[16] (XX) shows a strong absorption at 1600 cm^{-1}.

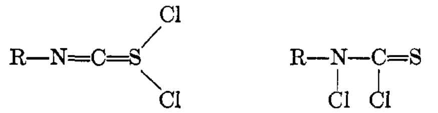


XVIII XIX XX

The broad band at about 840 cm^{-1} appears to be associated with the carbon–chlorine linkage of the S-chloroisothiocarbamoyl chlorides. This absorption, which is shifted to even higher frequencies (870 cm^{-1}) in isocyanide dichlorides, disappears if the chlorine atoms are substituted by other groups, such as the aziridinyl moiety in N,N′-bis(1,2-alkylene)guanidines.[15]

The origin of the strong band at approximately 1700 cm^{-1} is not clear. The possibility that it represents a second C=N absorption due to *cis–trans* isomerism as has been suggested for thiocyanogen trichloride[16] cannot be ruled out. However, it is also possible that this band originates from a Fermi resonance interaction[17] of the band at about 1650 cm^{-1} with the overtone of the strong absorption at about 840 cm^{-1}.

Other structures which were first considered to represent the compounds of this paper are XXI and XXII.



XXI XXII

Structure XXI, however, cannot explain the relative stability of compounds of structure I in view of the known instability of tetravalent sulfur chlorides, such as SCl_4,[18] $RSCl_3$,[19] and R_2SCl_2.[20] It is also inconsistent with the infrared spectra obtained, since the cumulated double bond system -N=C=S of XXI would be expected to cause an absorption above 2000 cm^{-1}. Structure XXII was abandoned because it is inconsistent with the strong C=N absorption observed at about 1650 cm^{-1}. Moreover, the conversion of the S-chloroisothiocarbamoyl chlorides to isocyanide dichlorides, as well as their addition to olefinic double bonds cannot be explained on the basis of structure XXII.

Experimental Section

Melting points and boiling points are not corrected. Infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer 137 B. All operations should be performed under exclusion of moisture.

N,N′-(2,4-Tolylene)bis(S-chloroisothiocarbamoyl Chloride) (V).—An amount of 42.6 g (0.6 mole) of chlorine was passed into a gently stirred solution of 61.8 g (0.3 mole) of 2,4-tolylene diisothiocyanate in 75 ml of chloroform at a rate of 7.0 to 7.5 g/hr and at a temperature of 15–18°. After the reaction mixture was allowed to stand overnight at 0°, a crystalline precipitate was separated by filtration on a Büchner funnel. Recrystallization of the filter cake from 500 ml of warm *n*-hexane (45–50°) afforded, upon cooling to 0°, 67.5 g of pure V. An additional amount of 16.5 g of pure V was obtained by cooling the hexane filtrate to −20°.

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[13] C. K. Bradsher, F. C. Brown, E. F. Sinclair, and S. T. Webster, *J. Am. Chem. Soc.*, **80**, 414 (1958).

[14] To be published elsewhere.

[15] G. Ottmann and H. Hooks, unpublished results.

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N,N′-(5-Chloro-2,4-tolylene)bis(S-chloroisothiocarbamoyl Chloride) (VII). A.—A solution of 17.4 g (0.05 mole) of V in 70 ml of chloroform was treated with 3.6 g of chlorine in a manner described for the preparation of compound V. After standing for 24 hr at 0° the yellow precipitate was separated and recrystallized from 50 ml of warm *n*-heptane (~60°) yielding 15.2 g of VII in form of shiny yellow needles.

B.—A solution of 45 g (0.218 mole) of IV in 90 ml of chloroform was treated with 46.5 g (0.65 mole) of chlorine under conditions described for the preparation of compound V. After the reaction mixture was stored for 18 hr at −20°, the precipitate was separated by filtration and recrystallized from 150 ml of *n*-heptane, affording 45.6 g of pure VII in form of yellow plates. An additional amount of 23.0 g was obtained by concentrating the mother liquor to one-third of its original volume and cooling to 0°.

N,N′-(1,4-Phenylene)bis(S-chloroisothiocarbamoyl Chloride) (XV).—A solution of 36.0 g (0.187 mole) of 1,4-phenylene diisothiocyanate in 325 ml of chloroform was treated with 26.6 g (0.374 mole) of chlorine under conditions described for the preparation of V. The solvent was removed *in vacuo* at a temperature not exceeding 20°. The remaining crystalline solid amounted to 61.2 g (yield 97.8%). It was recrystallized from *n*-hexane to provide 43.0 g of XV in form of yellow needle-like crystals.

N-Phenyl-S-chloroisothiocarbamoyl Chloride (X).—An amount of 35.5 g (0.5 mole) of chlorine was passed into a solution of 67.6 g (0.5 mole) of phenyl isothiocyanate in 67 ml of $CHCl_3$ as described for V. After the addition of chlorine was completed, the yellow reaction solution was diluted by 400 ml of dry pentane, filtered from a small amount of a fluffy precipitate, and freed from solvents by distillation *in vacuo* at 0 to −10°. The remaining yellow oil was dissolved in 350 ml of dry pentane; the solution was filtered from a yellow precipitate and concentrated *in vacuo* at 0 to −10°, yielding 98 g of X in form of a clear yellow liquid.

N-(4-Chlorophenyl)-S-chloroisothiocarbamoyl Chloride (XII).—The reaction between 102.0 g (0.6 mole) of 4-chlorophenyl isothiocyanate and 43.0 g (0.6 mole) of chlorine in 125 ml of chloroform afforded 140 g of a crude reaction product in form of a yellow oil. It was dissolved in 300 ml of dry *n*-pentane at room temperature; the solution was treated with charcoal, filtered, and stored at −20°. From this solution, 130.6 g of pure N-(4-chlorophenyl)-S-chloroisothiocarbamoyl chloride precipitated in form of yellow needles and was separated by filtration.

N-(2,5-Dichlorophenyl)-S-chloroisothiocarbamoyl Chloride (XIII).—The chlorination of 102.0 g (0.5 mole) of 2,5-dichlorophenyl isothiocyanate by 35.5 g (0.5 mole) of chlorine in 125 ml of chloroform at 15–20° gave 132 g of a straw-yellow oil which was dissolved in 700 ml of dry *n*-pentane. The solution was treated with charcoal at room temperature, filtered, and cooled to −50°. The precipitate thus obtained was separated by decanting the solvent from the crystalline product, which then was once more recrystallized from *n*-pentane, yielding 98.0 g of pure XIII in the form of yellow plates.

Like XIII were prepared N-(4-methoxyphenyl)-S-chloroisothiocarbamoyl chloride (XVI) (26.0 g), from 39.0 g (0.236 mole) of 4-methoxyphenyl isothiocyanate and 16.8 g (0.237 mole) of chlorine, and N-(4-nitrophenyl)-S-chloroisothiocarbamoyl chloride (XIV) (38.0 g), from 39.0 g (0.216 mole) of 4-nitrophenyl isothiocyanate and 15.4 g (0.217 mole) of chlorine.

N-Cyclohexyl-S-chloroisothiocarbamoyl Chloride (General Procedure for the Preparation of N-Alkyl-S-chloroisothiocarbamoyl Chlorides.—A 500-ml three-neck flask equipped with gas-inlet tube, stirrer, thermometer, and condenser with drying tube was charged with 101.0 g (0.716 mole) of cyclohexyl isothiocyanate and 125 ml of dry pentane. A total amount of 51.0 g (0.72 mole) of chlorine was passed into the solution at a rate of 7.0 to 7.5 g/hr while the temperature of the reaction mixture was controlled at −15 to −10°. After complete addition the clear, yellow reaction solution was freed from solvent *in vacuo* at 0 to −10°. The residue consisted of 149.0 g of pure N-cyclohexyl-S-chloroisothiocarbamoyl chloride in form of a clear yellow liquid.

Conversion of N-Phenyl-S-chloroisothiocarbamoyl Chloride (X) to Phenyl Isocyanide Dichloride (XI).—An amount of 17.8 g (0.25 mole) of chlorine was passed at a rate of 7.0–7.5 g/hr into a solution of 51.0 g (0.25 mole) of X in 60 ml of carbon tetrachloride at 0°. After complete addition, the reaction solution was warmed to room temperature over a period of 1.5 hr and then distilled *in vacuo*, affording 35.0 g (82.0% yield) of phenyl isocyanide dichloride, bp 83° (10 mm), $n^{28}\text{D}$ 1.5675. The purity of the product was 99.1% (by vapor phase chromatography).

Thermal Decomposition of X.—An amount of 50.0 g of N-phenyl-S-chloroisothiocarbamoyl chloride was heated at 150° for 3 hr under a nitrogen blanket. In the early part of the heating period the evolution of chlorine and SCl_2 was observed. The reaction product, a dark liquid, amounted to 33.5 g and was composed to 2.25% of an unidentified low-boiling product, 71.8% of phenyl isocyanide dichloride, 24.1% of phenyl isothiocyanate, and 1.9% of an unidentified high-boiling material (by vpc).

The heat treatment of N-butyl-S-chloroisothiocarbamoyl chloride afforded only little of a mixture of butyl isothiocyanate and butyl isocyanide dichloride but a substantial amount of heavy tar.

Reaction of X with Water in Dioxane.—A mixture of 25 ml of dioxane and 25 ml of water was added dropwise with stirring to a solution of 52 g of X in 100 ml of dioxane immersed in an ice–water bath. The addition was done at such a rate that the temperature of the reaction mixture did not exceed 25°. After complete addition, the reaction mixture containing a solid precipitate was poured into 2000 ml of water and filtered. The filter cake was dried and recrystallized from 1000 ml of *n*-heptane, yielding 24.1 g of XVII, mp 120–121°, lit.[13] mp 116–118°.

Anal. Calcd for $C_{14}H_{10}N_2OS_2$: C, 58.75; H, 3.52; N, 9.78; S, 22.35. Found: C, 59.10, H, 3.56; N, 9.53; S, 22.46.

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