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1-(Aziridine) Carbonyl Chlorides and 1-(Aziridine) Carbonyl Quaternary Ammonium Chlorides. Rearrangement to 2-(Chloroalkyl) Isocyanates.

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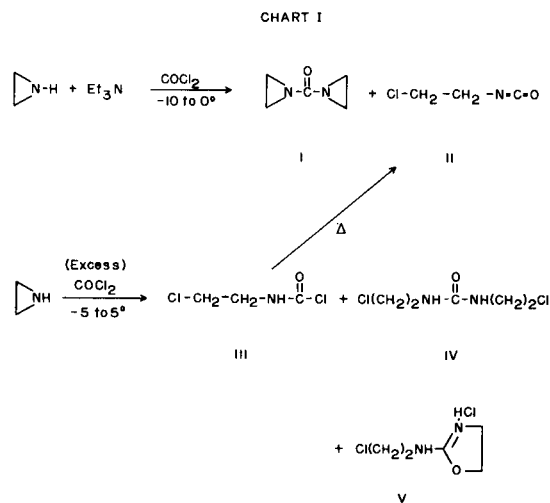
Aziridine reacted with phosgene in the presence of an acid acceptor or with 1,1'-carbonylbis(pyridinium) chloride to produce 1-(aziridine)carbonyl chloride (XII) or 1-(aziridine)carbonyl pyridinium chloride (XIII), respectively, as transient intermediates. Attempts to trap and observe (XII) and (XIII) at -10° were unsuccessful. These elusive materials underwent facile rearrangements to 2-chloroethyl isocyanate under these conditions. Aziridine reacted with 1,1'-carbonylbis(triethylammonium)chloride (VII) at -20° to give 1-(aziridine) carbonyl triethylammonium chloride (X) as a transient intermediate which proceeded to 2-chloroethyl isocyanate. At -10° this reaction produced *N,N*-diethyl-1-aziridinecarboxamide. Aziridine reacted with a large excess of phosgene in the absence of an acid acceptor to give *N*-2-(chloroethyl) carbamoyl chloride (III), 1,1'-bis(2-chloroethyl) urea (IV) and 2-(β -chloroethylamino)-2-oxazoline hydrochloride (V). Possible mechanisms for these reactions are discussed.

Recently it was shown that contrary to an earlier report (1), 1-(aziridine) thiocarbonyl chloride is a rather thermolabile material which can be trapped only at reduced temperatures of -10° to 0° . At temperatures above 0° , this material undergoes a facile isomerization to 2-chloroethyl isothiocyanate (2). This work describes an extension of these reactions to the phosgene-aziridine system and our attempts to observe 1-(aziridine) carbonyl chloride or its quaternary ammonium derivatives.

In an attempt to trap 1-(aziridine) carbonyl chloride, as previously described for the sulfur analog, a carbon tetrachloride solution containing equimolar amounts of aziridine and triethylamine was added to an equivalent amount of phosgene in carbon tetrachloride at -10 to -5° . Triethylamine hydrochloride was removed at -10° followed by n.m.r. analysis of the cold filtrate at a probe temperature of -15° . 1-(Aziridine) carbonyl chloride could not be detected; however, substantial amounts of 1,1'-carbonylbis-aziridine (I) and 2-(chloroethyl) isocyanate (II) were observed accompanied by a small amount of *N,N*-diethylcarbamoyl chloride (3). Distillation of this crude reaction mixture at reduced pressure gave only low yields of impure 2-chloroethyl isocyanate and sizeable amounts of unidentified polymer.

In contrast to the aziridine-thiophosgene system (2), the reaction of an equimolar amount of aziridine with phosgene in the absence of an acid acceptor did not give 2-chloroethyl isocyanate, but instead produced a predominance of 1,1'-bis(2-chloroethyl) urea (IV), as reported by Bestian, (4) and a lesser amount of 2-chloroethylcarbamoyl chloride (III). Increasing the phosgene-aziridine ratio to 5:1 increased the amount of (III) and was accompanied by substantial amounts of the urea (IV) and the oxazoline salt (V);

however, little isocyanate was found in the crude reaction mixture. Attempts to distill this reaction mixture did produce 2-chloroethyl isocyanate which was shown to result from pyrolysis of (III).

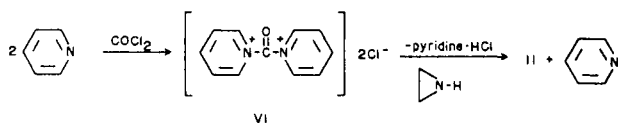


Because of the seemingly elusive nature of 1-(aziridine) carbonyl chloride, it was hoped that this species might be trapped as the triethylammonium or pyridinium salt by reacting an equimolar amount of aziridine with the 1:2 phosgene-triethylamine or 1:2 phosgene-pyridine complexes, respectively.

The 1:2 phosgene-pyridine complex has been well characterized and is stable at room temperature (5). The nature of 1:2 phosgene-trialkylamine complexes is not as well established. Lasstowski (6) reports that trialkylamines form 1:2 phosgene-amine complexes which undergo pyrolysis with loss of alkyl chloride to yield tetra-substituted ureas at elevated

temperatures (*i. e.* 200°). Relatively little is known, however, about the stability and reactivity of these dications at lower temperatures. In view of the fact that the 1:1 phosgene-trialkylamine complexes undergo loss of alkyl chloride to yield *N,N*-dialkylcarbamoyl chlorides even at -10° (7), it was deemed essential to establish the existence and stability of the 1:2 phosgene-triethylamine complexes at our reaction temperatures. The 1:2 and 1:1 phosgene-triethylamine complexes were prepared at -20° in liquid sulfur dioxide and compared by n.m.r. spectroscopy with triethylamine hydrochloride and triethylamine. (See Table I). The existence of the dication was established by comparing the relative chemical shifts for the ethyl groups. The order of the chemical shifts is consistent with the dication assignment; however, the amount of deshielding from the monocation is surprisingly small. Products obtained from the reaction of aziridine with the presumed dication at -20° to -10° provide further evidence for the existence of the 1:2 phosgene-triethylamine complex under our reaction conditions.

Aziridine was allowed to react with an equimolar amount of the 1:2 phosgene-pyridine complex (VI) which had been prepared according to the method of Scholtissek (5). At temperatures of -10 to 0°, aziridine displaced a stoichiometric amount of pyridine from the complex to produce pyridine hydrochloride and approximately equimolar amounts of free pyridine and 2-chloroethyl isocyanate. Attempts to distill these crude reaction mixtures, after removing the amine salt, generally led to considerable loss of isocyanate due to trimerization and polymerization (8a, b); however, treatment with dry hydrogen chloride followed by removal of pyridine hydrochloride and distillation gave 7-12% yields of 2-chloroethyl isocyanate. The identity of the monomeric product was established by comparison of n.m.r. and infrared spectra with an authentic sample which had been prepared according to the method of Siefken (9).

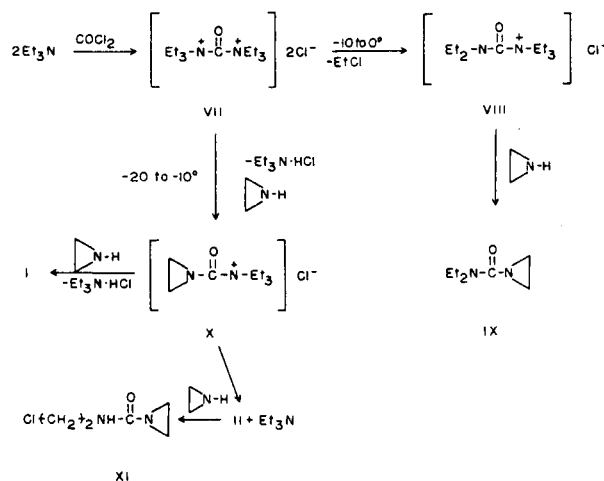


In a similar manner, 2-methylaziridine was allowed to react with 1,1'-carbonylbis (pyridinium chloride) at 10 to 0°. After removal of pyridine hydrochloride, the crude reaction mixture was analyzed by n.m.r. spectroscopy and found to consist of a mixture of 2-chloropropyl isocyanate, (XVII) and 1-chloromethyl ethyl isocyanate (XVIII) accompanied by an equivalent amount of pyridine. The isomeric isocyanates (XVII) and (XVIII) were present in a ratio of 1:1.9, respectively. Yields of monomeric isocyanate were around 5-10%. The identities of the monomeric isocyanates were established by spectral comparison with authentic samples obtained by independent synthesis (10).

The reaction of two moles of aziridine with a mole of the 1:2 phosgene-triethylamine complex at -10 to 0° gave unexpectedly a 58% yield of *N,N*-diethyl-1-aziridinecarboxamide (IX) and a small amount of (I) rather than 2-chloroethyl isocyanate. A structure proof for (IX) was garnered by the independent synthesis of this material according to Bestian (4).

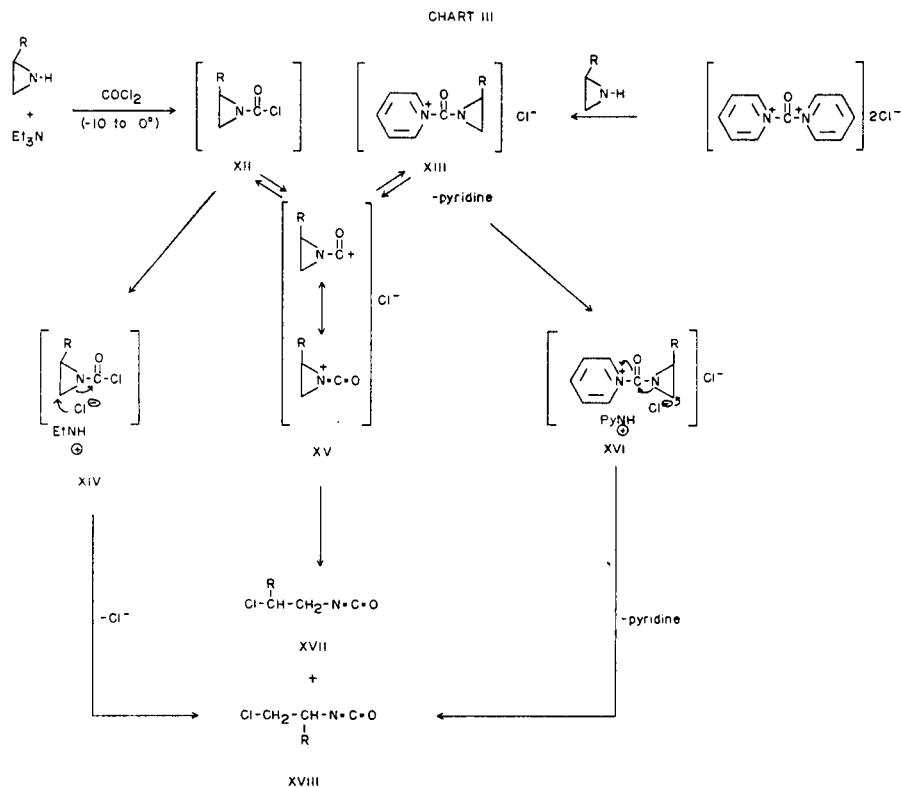
When this same reaction was carried out at -20 to -10°, n.m.r. analysis of the crude reaction mixture, after removal of triethylamine hydrochloride, revealed a mixture of (I), (XI) and triethylamine. The mole per cent of (I) and (XI) was 42% and 58%, respectively, according to n.m.r. analysis. Reacting one equivalent of aziridine with the 1:2 phosgene-triethylamine complex at -20 to -10° yielded small amounts of (I) and *N,N*-diethylcarbamoyl chloride as well as substantial amounts of 2-chloroethyl isocyanate and triethylamine, according to n.m.r. analysis of the crude reaction mixture. A 6% yield of 2-chloroethyl isocyanate and a 9% yield of *N,N*-diethylcarbamoyl chloride were isolated from this reaction.

CHART II



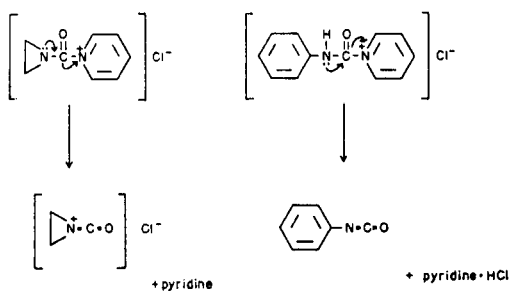
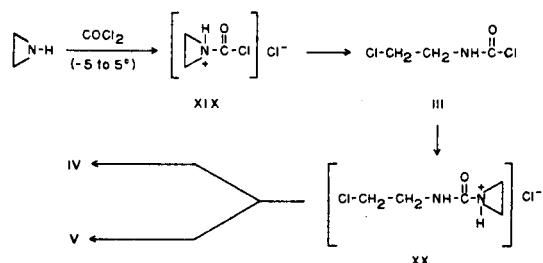
DISCUSSION

In view of the precedence for the isomerization of 1-(aziridine) thiocarbonyl chlorides to 2-chloroethyl isothiocyanates the formation of 2-chloroethyl isocyanate from the reaction of aziridine and triethylamine or pyridine with phosgene may be best rationalized in terms of a transient intermediate such as 1-(aziridine) carbonyl chloride (XII) or a 1-(aziridine) quaternary ammonium chloride (X) or (XIII). At this time it is an open question whether the isomerization of these intermediates is primarily a result of internal ion return by means of ionization to a carbamoyl cation (XV) or whether it is the result of an S_N2' type reaction (11), whereby amine hydrochloride provides the chloride ion source as illustrated by (XIV) and (XVI).



Ionization to the carbamoyl cation is not inconceivable since the driving force could be provided by involvement of the free pair of electrons of the aziridine nitrogen. This driving force undoubtedly accounts for the facile formation of phenyl isocyanate when a mole of aniline is reacted with the pyridine-phosgene dication (5). Precedence for such a unimolecular dissociation via an N,N -dialkylcarbamoyl

phosgene is used, (III) is isolated as one of the major products, accompanied by substantial amounts of (IV) and (V) (13) whereas, the reaction of stoichio-



cation has been established in analogous systems by the work of Hall (12). It should be noted, however, that in the case of the 2-methylaziridine derivatives a predominance of product resulting from cleavage at the unsubstituted ring carbon suggests the prevalence of an $\text{S}_{\text{N}}2$ process under the conditions described.

Reaction of aziridine with phosgene in the absence of an acid acceptor undoubtedly involves the cationic intermediates (XIX) and (XX). These kinds of intermediates have been proposed previously by Bestian (4) for analogous systems. When an excess of

metric amounts of aziridine and phosgene yields only the urea (IV). This presents an interesting contrast to the analogous aziridine-thiophosgene reaction (2), wherein, equimolar amounts of aziridine and thiophosgene produce 45-50% yields of 2-chloroalkyl isothiocyanates. In this latter case aziridine functions as an acid acceptor to yield 2-chloroalkyl amine salts as an accompanying product rather than reacting sequentially to produce 1,1'-bis(2-chloroethyl)thiourea.

The reaction of aziridine with the 1:2 phosgene-triethylamine complex at -10 to 0° provides a new route to N,N -diethyl-1-aziridinecarboxamides. The transformation appears to involve a facile loss of ethyl chloride even at -10° to produce the monocation (VIII) which then reacts directly with aziridine to produce (IX). This conjecture is supported by the fact that only a very small amount of (I) is formed

even when two equivalents of aziridine are used; whereas, reducing the temperature leads to nearly equimolar amounts of (I) and the isocyanate derived product (XI). The comparatively large amounts of (II) and (XI) produced at -20 to -10° indicate that temperature reduction dramatically effects the stability of the triethylammonium dication (VII); however, unsuccessful attempts to observe (X) under these conditions suggest that the lifetime of 1-(aziridinyl) carbonyl triethylammonium chloride (X) is not increased to any extent by such a minor reduction in temperature.

In conclusion, it appears that the stability of 1-(aziridine) carbonyl chlorides and 1-(aziridine) carbonyl quaternary ammonium chlorides differ considerably from 1-(aziridine) thiocarbonyl chloride. However, isomerization of these derivatives to 2-chloroalkyl isocyanates does parallel the formation of 2-chloroalkyl isothiocyanates which are obtained by isomerization of the sulfur analogues.

TABLE I

N. M. R. Chemical Shifts of Triethylamine Derivatives in SO_2 at -20° (p. p. m. relative to TMS)

	(δ , CH_3^-)	(δ , $-\text{CH}_2^-$)
$(\text{CH}_3-\text{CH}_2)_3\text{N}:\text{SO}_2$	-1.16 (t)	-2.77 (q)
$[(\text{CH}_3-\text{CH}_2)_3\text{N}^+\text{H}]\text{Cl}^-$	-1.36 (t)	-3.25 (m)
$[(\text{CH}_3-\text{CH}_2)_3\text{N}^+\text{C}(=\text{O})\text{Cl}]\text{Cl}^-$	-1.46 (t)	-3.92 (q)
$[(\text{CH}_3-\text{CH}_2)_3\text{N}^+\text{C}(=\text{O})\text{N}^+(\text{CH}_2-\text{CH}_3)_3]2\text{Cl}^-$	-1.46 (t)	-3.94 (q)

EXPERIMENTAL

Nuclear magnetic resonance (n. m. r.) spectra were obtained with a Varian A-60 spectrometer. Chemical shifts are reported as δ (p. p. m.) relative to tetramethyl silane. Infrared spectra were scanned on a Perkin Elmer 337 spectrometer.

2-(Chloroethyl) Isocyanate (II).

A. Reaction of Aziridine with an Equimolar Amount of Phosgene in the Presence of an Acid Acceptor.

A solution of aziridine (21.5 g., 0.5 mole) and triethylamine (50.5 g., 0.5 mole) in 300 ml. of carbon tetrachloride was added dropwise to a stirred solution of phosgene (49 g., 0.5 mole) in 700 ml. of carbon tetrachloride at a temperature of -10 to -5° . This addition was made over a period of 2 hours. The reaction mixture was vacuum filtered into a pre-cooled flask (-10°) to remove triethylamine hydrochloride. The filtrate was analyzed immediately by n. m. r. at a probe temperature of -15° . No absorption bands that could be assigned to 1-(aziridine) carbonyl chloride were observed. A predominance of 1,1'-carbonyl bisaziridine accompanied by modest amounts of 2-(chloroethyl) isocyanate and trace amounts of *N,N*-diethylcarbamoyl chloride were identified in the crude reaction mixture by n. m. r. and infrared spectroscopy. The aziridine compound displayed a singlet

$\overset{\text{O}}{\parallel}$
-2.18 p. p. m. (CCl_4), ($>\text{N}-\text{C}-\text{N}<$) 1700 cm^{-1} (s), (aziridine, C-H stretching) 3025 cm^{-1} (w) and 3090 cm^{-1} (w) which was consistent with an authentic sample prepared according to the method of Bestian (4). 2-(Chloroethyl) isocyanate was identified by a slightly split singlet at -3.60 p. p. m. (CCl_4) and the characteristic intense band for ($-\text{N}=\text{C}=\text{O}$) at 2280 cm^{-1} . The solvent was removed under vacuum at room temperature leaving a colorless oil with strong lachrymatory properties, weight, 22.7 g. When an attempt was made to distill this crude

product through a short path column (6 in Vigreux) only a small amount of distillate came over at $35-40^\circ/1\text{ mm.}$, weight, 6.9 g. This material was identified as impure 2-(chloroethyl) isocyanate. Most of the product polymerized in the distillation pot when the temperature reached $75^\circ/1\text{ mm.}$ The polymerization was accompanied by a strong exotherm.

B. Reaction of Aziridine with 1,1'-Carbonylbis(pyridinium) Chloride at -10 to 0° .

A solution of pyridine (40 g., 0.50 mole) in 150 ml. of carbon tetrachloride was added dropwise to a stirred solution of phosgene (24.5 g., 0.25 mole) in 350 ml. of carbon tetrachloride while maintaining the temperature at -10 to 0° . The addition took approximately 2 hours. To this stirred reaction mixture at -10 to 0° , a solution of aziridine (11 g., 0.25 mole) was added in dropwise manner over a period of 2.5 hours. After addition was complete, the reaction mixture was stirred for 0.5 hour in the cold. Pyridine hydrochloride was filtered off in a dry box and dried, weight, 33.5 g. The filtrate was placed back in a reaction flask (under anhydrous conditions) and a solution of hydrogen chloride (16 g.) in 200 ml. of diethyl ether was added over a period of 2.5 hours while maintaining the temperature at 0 to 5° . Pyridine hydrochloride was filtered off in a dry box and found to weigh 20 g. Solvent was removed from the filtrate by vacuum distillation at $25-44^\circ/180-200\text{ mm.}$ Further distillation gave 3.1 g. (12%) of 2-(chloroethyl) isocyanate. Infrared and n. m. r. spectra of this material were identical to an authentic sample prepared according to the method of Siefken (9).

Attempts to isolate 2-(chloroethyl) isocyanate from the crude reaction mixture without first removing pyridine with hydrogen chloride gave only trace amounts of the isocyanate and a predominance of pot residue upon distillation.

N-(2-Chloroethyl) Carbamoyl Chloride (III).

Reaction of Aziridine with an Excess of Phosgene in the Absence of an Acid Acceptor (1:5 Molar Ratio).

A solution of aziridine (86 g., 2.0 moles) in 350 ml. of dry toluene was added dropwise to a stirred solution of phosgene (990 g., 10.0 moles) in 2500 ml. of toluene, while maintaining the temperature at -5 to 5° . Addition was carried out over a period of 3.5 hours. Excess phosgene was removed from the system by bubbling nitrogen through the reaction mixture overnight. A substantial amount of light yellow crystals precipitated from the solution during this time. The solid was filtered and dried, weight, 164 g., m. p. $105-115^\circ$. Spectral analysis indicated that this solid was a mixture of 1,1'-bis(2-chloroethyl) urea and 2-(β -chloroethylamino)-2-oxazoline hydrochloride, yield, 44% (13). Comparison was made with authentic samples of the urea and oxazoline salt obtained according to the method of Bestian (4) and McKay, *et al.* (14), respectively. Toluene was removed from the filtrate by use of vacuum (1-2 mm.) at room temperature. A dark brown liquid residue was obtained which weighed 124 g. An infrared spectrum of this material indicated this product was predominantly 2-(chloroethyl) carbamoyl chloride, yield, 50%; N-H (3420 cm^{-1})

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and $-\text{N}-\text{C}-\text{Cl}$ (1760 cm^{-1}). An attempt was made to distill a portion of this product at $<100^\circ/1\text{ mm.}$ No well-defined boiling point could be obtained, whereas hydrogen chloride was liberated freely. A liquid possessing strong lachrymatory properties was collected in the dry ice trap. This material was mostly 2-(chloroethyl) isocyanate as determined by infrared analysis, $-\text{N}=\text{C}=\text{O}$ (2280 cm^{-1}).

Pyrolysis of *N*-(2-Chloroethyl) Carbamoyl Chloride.

Crude *N*-(2-(chloroethyl) carbamoyl chloride, 80 g., in 250 ml. of *o*-dichlorobenzene was refluxed under anhydrous conditions for 8 hours. Distillation of this reaction mixture gave 12 g. of nearly pure 2-chloroethyl isocyanate, b. p. $44-48^\circ/25\text{ mm.}$

1:1 Phosgene-Triethylamine Complex.

Triethylamine (1 g., 0.01 mole) was added dropwise to a solution of phosgene (1.0 g., 0.01 mole) in 20 ml. of liquid sulfur dioxide (-30°) under anhydrous conditions. A sample of the light yellow homogeneous solution was scanned at a probe temperature of -20° providing the data shown in Table I.

1:2 Phosgene-Triethylamine Complex.

Using the same method as above 2 g. (0.02 mole) of triethylamine was added to a solution of phosgene (1 g., 0.01 mole) in 20 ml. of liquid sulfur dioxide.

N,N-Diethyl-1-aziridinecarboxamide (IX).

Reaction of Aziridine with 1,1'-Carbonylbis(triethylammonium) Chloride.

A. At -10 to 0°.

A solution of triethylamine, (101.0 g., 1.0 mole), in 150 ml. of carbon tetrachloride was added dropwise to a stirred solution of phosgene, (49.0 g., 0.5 mole) in 700 ml. of carbon tetrachloride while maintaining the reaction temperature at -10 to 0°. The addition was made over a period of 3 hours during which time a slightly yellow precipitate was formed. To this stirred solution at -10 to 0°, was added a solution of aziridine, (43.0 g., 1.0 mole) in 150 ml. of carbon tetrachloride over a period of 2 hours. After addition was completed, the reaction mixture was stirred at -10 to 0° for 2 hours followed by removal of triethylamine hydrochloride. Solvent was removed under vacuum at room temperature leaving a light yellow oil, weight, 40.7 g. N.m.r. analysis of this crude product indicated it was nearly all *N,N*-diethyl-1-aziridinecarboxamide accompanied by trace amounts of 1,1'-carbonyl bisaziridine. The crude product was distilled giving a small amount of forerun, b.p. 25-42°/2 mm., weight, 1.2 g. which was mostly 1,1'-carbonyl bisaziridine. The n.m.r. spectrum consisted of a singlet at -2.18 p.p.m. (CCl₄) and infrared showed a carbonyl absorption at 1700 cm⁻¹. The major fraction boiled at 42-44°/2 mm., weight, 28.2 g. and gave n.m.r. and infrared spectra which were identical to those obtained for an authentic sample which had been prepared according to the method of Bestian (4). The n.m.r. spectrum consisted of a multiplet at -1.38 p.p.m. to -0.92 p.p.m., a singlet at -1.97 p.p.m. and another multiplet at -3.78 to -3.00 p.p.m. in a ratio of 2:2:3. Infrared displayed a carbonyl band at 1670 cm⁻¹ (neat film).

B. At -20°.

A solution of triethylamine, (50.5 g., 0.5 mole) in 75 ml. of carbon tetrachloride was added dropwise to a stirred solution of phosgene (24.5 g., 0.25 mole) in 350 ml. of carbon tetrachloride at -20°. To this reaction mixture was added a solution of aziridine (22 g., 0.5 mole) in 75 ml. of carbon tetrachloride. The reaction mixture was allowed to stir for 18 hours at -20°. The amine salt was filtered off under anhydrous conditions in a nitrogen filled dry box. Solvent was removed from the filtrate under reduced pressure (180 mm.) to give an oily residue. N.m.r. and infrared analysis of this residue revealed the presence of triethylamine, *N*-(2-chloroethyl)-1-aziridinecarboxamide and 1,1'-carbonyl bisaziridine. According to n.m.r. analysis, the latter two components were present in a ratio of 58:42 mole %, respectively. Attempted distillation led to polymerization in the distillation flask.

2-(Chloroethyl)-1-aziridinecarboxamide (XI).

A solution of aziridine (4.3 g., 0.1 mole) in 50 ml. of diethyl ether was added dropwise to a stirred solution of 2-chloroethyl isocyanate in 75 ml. of diethyl ether at such a rate that reflux was maintained. The colorless, homogeneous reaction mixture was refluxed for 30 minutes. Solvent was removed with vacuum at room temperature, leaving a semi-viscous liquid residue, weight, 13.2 g. (89%). The crude product solidified upon storing overnight in a refrigerator. Recrystallization from diethyl ether gave a white solid, m.p. 34-36°. This material was very hygroscopic so all operations were carried out in a dry box.

Anal. Calcd. for C₃H₅ClN₂O: C, 40.41; H, 6.10; N, 18.86. Found: C, 40.50; H, 5.82; N, 18.70.

2-(Chloropropyl)isocyanate (XVII) and 1-Chloromethyl ethyl isocyanate (XVIII).

Reaction of 2-Methylaziridine with 1,1'-Carbonylbis(pyridinium) Chloride at -10 to 0°.

A solution of pyridine (237 g., 3.0 moles) in 900 ml. of carbon tetrachloride was added dropwise to a stirred solution of phosgene (147 g., 1.5 mole) in 2100 ml. of carbon tetrachloride while maintaining the temperature at -10 to 0°. After the addition, the reaction mixture was stirred at this temperature for 0.5 hours. A solution of 2-methylaziridine (85.5 g., 1.5 mole) in 450 ml. of carbon tetrachloride, was added dropwise to the stirred reaction mixture while keeping the temperature at -10° to 0°. After addition the reaction mixture was stirred for 2 hours in the cold. Pyridine hydrochloride was filtered off giving a light yellow colored filtrate. Immediate n.m.r. analysis of this cold filtrate revealed the presence of pyridine,

2-chloropropyl isocyanate, 1-chloromethyl ethyl isocyanate and isomeric isocyanate dimers or trimers. Integration showed that pyridine was present in approximately stoichiometric amount compared to the isocyanate, dimer and/or trimer. The relative amounts of the isomeric isocyanate monomers could not be assessed since overlapping dimer and/or trimer peaks interfered. The spectrum consisted of a multiplet at -4.52 to -3.35 p.p.m. and three overlapping but distinguishable doublets at -1.53 p.p.m., *J* = 6.3 c.p.s., -1.35 p.p.m., *J* = 6.3 c.p.s. and -1.31 p.p.m., *J* = 6.5 c.p.s. (CCl₄). Integration of the multiplet and the three doublets showed that they were present in a ratio of 1:1. The solvent was removed from the crude reaction mixture under vacuum at room temperature leaving an amber colored oil which turned dark upon standing. Infrared analysis at this point revealed intense bands at 2270 cm⁻¹ (-N=C=O), 2235 cm⁻¹, (tentatively assigned to the dimer), 1740 cm⁻¹ (trimer). No -NH absorption was observed. The oil was distilled giving a small amount of pyridine and one broad cut, b.p. 25-47°/5 mm. Near the end of the distillation, a strong exotherm was observed in the distillation pot at which time the contents were transformed from a dark mobile oil into a black viscous resin. The colorless distillate was found by n.m.r. and infrared analysis to contain a small amount of pyridine and a mixture of 2-chloropropyl isocyanate and 1-chloromethyl ethyl isocyanate. The former isocyanate exhibited in carbon tetrachloride a doublet at -1.35 p.p.m. and the latter showed a methyl doublet at -1.53 p.p.m. in a ratio of 1.19:1.00. The assignments were made after comparison with authentic samples prepared by an independent synthesis (10). Redistillation of this sample gave a pyridine-free mixture of isocyanates with a boiling point of 76-78°/96 mm., weight, 19.2 g. (11%).

Anal. Calcd. for C₄H₈ClNO: C, 40.18; H, 5.06; N, 11.72. Found: C, 40.10; H, 5.25; N, 11.65.

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