mixture was heated on an oil bath at 135–140° for 1 hr during which time it was stirred with a glass rod. After cooling, ice water was carefully added to remove excess phosphorus pentoxide. The aqueous mixture was extracted with ether, the solution was dried over sodium sulfate, and the solvent was evaporated. The yield was 0.20 g (91%), mp 177–183°. The product was dissolved in methanol, decolorized with charcoal, concentrated, and allowed to crystallize. Colorless crystals formed weighing 0.16 g and melted at 183–187°. Recrystallizations from ethyl acetate–petroleum ether and methanol failed to raise the melting point. A mixture melting point with **1a** showed no depression and the infrared spectra of the two were identical.

Reactions of Aziridines. I. A Mechanism of Piperazine Formation from Aziridines[1]

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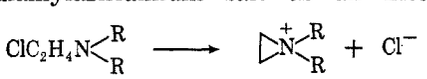
The reaction of certain 1-alkylaziridines with alkyl, alkenyl, or benzyl halides as well as with dialkylchloroethylamines has been found to give nearly quantitative yields of the corresponding 1,1,4-trialkylpiperazinium halides. The replacement of the alkyl halides with alkyl *p*-toluenesulfonates resulted in the formation of only poly(1-alkylaziridines). It was concluded that the presence of halide ions was necessary for the formation of piperazines from aziridines. It was also demonstrated that not only halide ions, but a solvent such as acetone was required. The use of water as a solvent resulted in polymer formation. Thus, the necessary presence of halide ions in a solvent of moderate polarity strongly suggests that an SN2 reaction of the halide ion with an intermediate is the product-determining step in the formation of piperazines from aziridines. A mechanism is postulated.

The conversion of aziridines into piperazines has received little attention. Fruton[2] has briefly mentioned the subject in his review of aziridine chemistry, but the reference given for the conversion of 1-methylaziridine into 1,4-dimethylpiperazine appears to be misquoted. Clapp[3] has reported the isolation of piperazine as a by-product from the aminoethylation of phenol with aziridine. More recently, Heine[4] and co-workers reported the conversion of 1-phenylaziridine into 1,4-diphenylpiperazine in 65% yield. No mechanism was postulated.

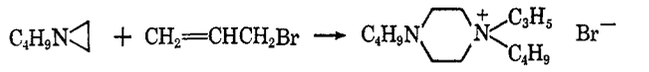
Bartlett[5–7] reported the isolation of 1,1,4,4-tetrasubstituted piperazinium halides from β-chloroethylamines and not aziridines. However, kinetic studies of these reactions by Bartlett strongly support the concept that the chloroethylamine first cyclized to form the 1,1-dialkylaziridinium salt as an intermediate



which underwent further reactions to form the corresponding piperazinium salt. While the aforementioned references demonstrate that aziridines can be considered as precursors of piperazines, a systematic study of this reaction has not been reported.

The reaction of acids or alkylating agents with excess aziridines is generally conceded to produce polyaziridines.[8] However, the data herein presented demonstrate that by the proper choice of conditions one can produce high yields of either a polymer or a piperazine from the same reagents.

The treatment of allyl bromide with a 9-mole excess of 1-*n*-butylaziridine in dry acetone gave a 96% yield of 1,4-di-*n*-butyl-1-allylpiperazinium bromide (reaction 13, Table III) and the excess aziridine was recovered



unchanged. This is the first reported preparation of a 1,1,4-trisubstituted piperazine salt from an aziridine. The structure of this was established by comparison of the infrared spectrum with that of an authentic sample prepared from piperazine, *n*-butyl bromide, and allyl bromide. The mixture melting point showed no depression while the elemental analysis and molecular weights agreed with the proposed structure. Similarly, the reaction of 1-ethylaziridine with ethyl bromide (reaction 3) gave a 99% yield of 1,1,4-triethylpiperazinium bromide whose structure was established in a like manner.

In order to study the role of the alkylating agent in determining the course of this reaction, methyl iodide (reaction 2), methyl *p*-toluenesulfonate (reaction 10), ethyl bromide (reaction 3), and ethyl *p*-toluenesulfonate (reaction 12) were allowed to react with a 9-mole excess of 1-ethylaziridine in acetone at 25°. The reactions of methyl iodide and ethyl bromide resulted in the formation of the corresponding 1,1,4-trialkylpiperazinium halide in 91 and 99% yields, respectively, while the use of methyl and ethyl *p*-toluenesulfonates resulted in the formation of poly(1-ethylaziridine) in 97 and 99% yields, respectively. Infrared analysis indicated that these polymers contained less than 3.0% piperazine rings. These data clearly demonstrate that those alkylating agents which produce halide ions on reacting with aziridines result in piperazine formation, while those producing *p*-toluenesulfonate anions result in polymer as the only product. Thus an anion which is both a good nucleophile and leaving group, such as halide, is necessary for piperazine formation under these conditions. Reaction 10 was therefore repeated (reaction 11) with the addition of 1 mole of sodium iodide per mole of methyl *p*-toluenesulfonate. The

(1) Presented at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1965, Abstract K 93.

(2) J. S. Fruton, "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p 69.

(3) L. B. Clapp, *J. Am. Chem. Soc.*, **73**, 2584 (1951).

(4) H. W. Heine, W. G. Kenyon, and E. M. Johnson, *ibid.*, **83**, 2570 (1961).

(5) P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, **69**, 2971 (1947).

(6) P. D. Bartlett, J. W. Davis, S. D. Davis, and C. G. Swain, *ibid.*, **69**, 2977 (1947).

(7) P. D. Bartlett, S. D. Ross, and C. G. Swain, *ibid.*, **71**, 1415 (1949).

(8) G. D. Jones in "The Chemistry of Cationic Polymerizations," P. H. Plesch, Ed., The Macmillian Co., New York, N. Y., 1963, Chapter 14; P. E. Fanta in "The Chemistry of Heterocyclic Compounds," Part I, A. Weissberger, Ed., John Wiley and Sons, Inc., New York, N. Y., 1964, Chapter 2.

corresponding 1,4-diethyl-1-methylpiperazinium iodide was isolated in a 96% yield. Sodium *p*-toluenesulfonate, the other product, quantitatively precipitated during the course of the reaction.

Although bromides and iodides react rapidly to produce high yields of piperazines, allyl chloride reacted slowly and produced only a 54% yield of 1,4-diethyl-1-allylpiperazinium chloride (reaction 6) with the balance of the allyl groups being found attached to polymer. A similar reaction between allyl chloride and 1-phenethylaziridine (reaction 16) produced an 85% yield of the corresponding piperazine plus an undetermined quantity of polymer. The addition of 0.033 mole of sodium iodide per mole of allyl chloride (reaction 17) eliminated the polymer formation and raised the yield of piperazine to 97% thereby lending further support to the role of the anion in determining the product distribution.

The effect of solvent polarity was evaluated by treating ethyl bromide with a 9-mole excess of 1-ethylaziridine at 25° in various ratios of water and acetone (Table I).

TABLE I

EFFECT OF SOLVENT ON PRODUCT DISTRIBUTION

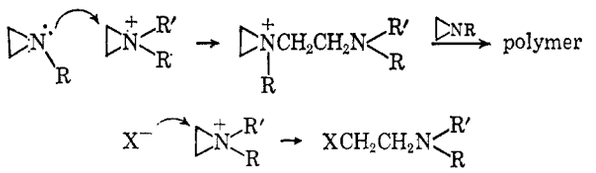
Solvent	Yield of quaternized piperazine,[a] %	Yield of poly(1-ethylaziridine),[b] %
Acetone	99	<1
10 vol. % water/acetone	80	19
50 vol. % water/acetone	<1	99
2-Propanol	81	20[c]

[a] Isolated yield of quaternized piperazine based on number moles of ethyl bromide charged to the reaction. Ethyl bromide conversions exceeded 99.8% as determined by gas–liquid partition chromatography. [b] As determined by infrared, these polymers contained less than 0.2% (analytical limit) quaternized piperazines. [c] The polymer can be separated from the piperazine by washing with ether.

It was found that a solvent such as acetone favors the formation of piperazines while those of high polarity and solvating power such as water tend to favor polymer formation.

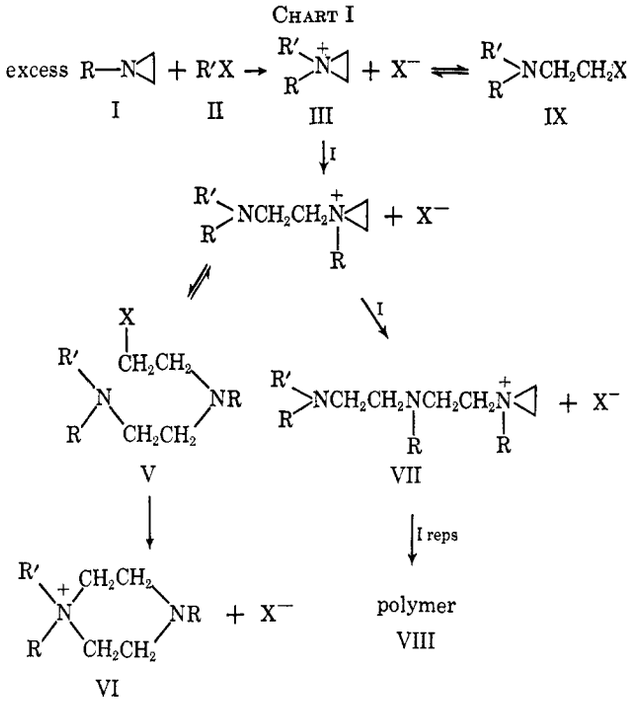
Based on the foregoing data, one can write a plausible reaction sequence (Chart I) that is consistent with the data.

It is well known that basic aziridines are not reactive toward nucleophilic reagents unless the basic aziridine nitrogen has been neutralized by protonation, quaternization, or formation of a Lewis acid adduct. It is also well established that the mechanism for ring opening of a 1-alkylaziridine, catalyzed by alkyl halide, involves SN2 attack of a nucleophilic reagent on the ring carbon of the quaternized aziridine specie (*e.g.*, by basic aziridine nitrogen as nucleophile leading to polymer or by halide ion leading to 2-haloethyldialkylamine).[8]



Thus the logical initial reaction is that of 1-alkylaziridines I with the alkylating agent II to produce a

CHART I



reps = repeating reaction

1,1-dialkylaziridinium salt III which is supported by the work of Bottini[9] and Helmkamp.[10] Subsequently III undergoes an SN2 reaction with I to produce IV, a "dimer" of I. The dimer is also a 1,1-dialkyl-substituted aziridinium salt and should undergo reaction at the ring carbons by the same mechanism that III underwent reaction with I. If, at this point X^- is a relatively strong nucleophile such as halide, IV reacts with X^- to produce V which undergoes ring closure to form VI, the piperazinium salt. This occurs despite the large excess of I. However, if X^- is a weak nucleophile such as the *p*-toluenesulfonate anion, it cannot compete with I for intermediate IV, and the predominant reaction becomes the formation of the "trimer" VII and ultimately polymer VIII.

The observed effect of solvent polarity on the product distribution is in agreement with the foregoing reaction scheme. A solvent such as acetone generally favors a reaction involving charge destruction, such as indicated for the reaction of IV with halide ion X^-.[11] Thus acetone favors piperazine formation. A solvent of high polarity tends to favor charge stabilization or charge transfer, such as one would encounter in the polymerization steps IV → VII → VIII. Therefore, polymer or quaternized piperazine can be prepared in high yields from the same reactants by the proper choice of solvent.

As previously stated, the cyclization of haloethylamines to form aziridinium salts has been well documented.[12] It would therefore be expected that the cyclization of IX to form III should be an alternate route to both VI and VIII. This route was established when it was demonstrated that 1,1-dimethyl-4-phenethylpiperazinium chloride could be isolated as the

(9) A. T. Bottini and R. L. VanEtten, *J. Org. Chem.*, **30**, 575 (1965).

(10) G. K. Helmkamp, R. D. Clark, and J. R. Koskinen, *ibid.*, **30**, 666 (1965).

(11) For a discussion of solvent effects on nucleophilic substitution reactions, see C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 345–357.

(12) N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **30**, 821 (1965).

TABLE II

EFFECT OF 1-ALKYL SUBSTITUENTS ON PRODUCT DISTRIBUTION

1 substituent	Yield[a] of quaternized piperazine, %	Yield of polyaziridine, %	$K_B \times 10^7$ [b]
Ethyl	99	..	8.1
Butyl	96	..	8.0
Phenethyl	90	10[c]	2.29
2-Hydroxyethyl	<1[d]	99[e]	1.32
Cyanoethyl	<0.2[d]	99[e]	0.028

[a] Yield based on initial number of moles of allyl bromide. [b] Determined at 25° by perchloric acid titrations according to the method of C. E. O'Rourke, L. B. Clapp, and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 2159 (1956). [c] Estimated as balance of allyl bromide. [d] Represents analytical limit of infrared method used for analysis. [e] Yield based on initial number of moles of aziridine.

ethylamine. Besides the usual elemental and infrared analysis, the structure of X was established by nmr which confirmed the six methyl protons on a quaternized nitrogen.

Not all 1-alkylaziridines will form piperazinium salts in high yields even under the most favorable conditions. A series of aziridines was allowed to react with allyl bromide in acetone at 25° (Table II). It was noted that those aziridines having increasingly stronger electron-withdrawing groups on the 1 position, as evidenced by their base strength, tend to form polymers at the expense of piperazines.

The replacement of the allyl bromide of Table II with dimethylchloroethylamine gave the same general

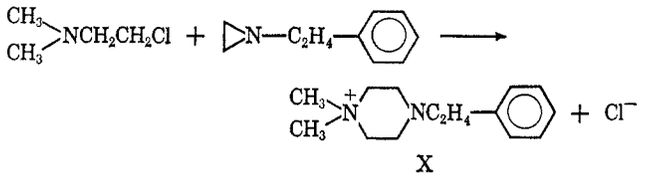
TABLE III

REACTION OF 1-ALKYLAZIRIDINE WITH ALKYLATING AGENTS

Reaction	1-Alkylaziridine	Alkylating agent	Acetone solvent, ml	Quat piperazines: Yield,[a] %	Mp, °C	Nitrogen, % Calcd	Nitrogen, % Found	Halide, % Calcd	Halide, % Found	Wt of polymer recovd
1	Methyl	Ethyl bromide	200	99	155–157	12.55	12.77	35.85	35.62	...
2	Ethyl	Methyl iodide	900	91	143–145	9.86	10.14	44.70	44.50	...
3		Ethyl bromide[b]	36	99	204–205	11.15	11.21	31.85	31.90	...
4		Ethyl iodide	450	98	146–148	9.41	9.66	...	...	...
5		*n*-Dodecyl bromide	500	92	194–196	7.17	7.39	...	...	...
6		Allyl chloride	36 (40°)	54	122–123	12.82	12.94	...	...	3.8
7		Allyl bromine	200	94	152–154	10.64	10.69[c]	...	...	...
8		Chloroacetone	36	75	177–179	11.94	12.12	15.14	15.00	8.2
9		*p*-Xylylene dibromide[d]	700	98	197–200	10.72	10.62	...	...	...
10		Methyl *p*-toluenesulfonate	450	<0.2	...	...	...	...	...	20.6
11		Methyl *p*-toluenesulfonate (4.5 g of NaI)	450	96 (of corresponding piperazinium iodide, sodium *p*-toluenesulfonate precipitated from reaction mixture)						
12		Ethyl *p*-toluenesulfonate	450	<0.2	...	...	...	...	...	22.1
13	*n*-Butyl	Allyl bromide	900	96	134–135.5	8.78	8.80[e]	25.05	25.22	...
14		Methyl *p*-toluenesulfonate	500	<0.2	...	...	...	...	...	13.3
15	*n*-Decyl	Ethyl bromide	200	90	217–219	5.90	6.00	...	...	...
16	Phenethyl	Allyl chloride	200 (40°)	85	161–165	7.55	8.00	...	...	...[i]
17		Allyl chloride (0.015 g of NaI)	200 (40°)	97	163–165	7.55	7.53	...	...	...
18		Allyl bromide	900	90	161–163	6.75	7.08[f]	...	...	3.1
19	2-Hydroxyethyl	Ethyl bromide	200	<1.0	...	...	...	...	...	16.1
20		Allyl bromide	200	<1.0	...	...	...	...	...	29.2
21	Cyanoethyl	Allyl bromide	200	<0.1	...	...	...	...	...	26.8
22		Methyl *p*-toluenesulfonate	200	<0.1	...	...	...	...	...	25.0
23	Ethyl	Dimethylchloroethylamine	300	99[g]	234–237	15.68	15.58	19.89	19.77	...
24		Diethylchloroethylamine	300	99[h]	200–202	13.56	13.39	...	...	...
25	Phenethyl	Dimethylchloroethylamine	300	99[i]	254–256	11.00	11.00	13.95	14.00	...
25	2-Hydroxyethyl	Dimethylchloroethylamine	300	...	...	...	...	...	...	39.6
27	Cyanoethyl	Dimethylchloroethylamine	(2.7 g of 1,1,4,4-tetramethylpiperazinium dichloride only product isolated)							

[a] Per cent yield of recovered product based on moles of alkylating agent. [b] Reaction of 71.0 g (1.0 mole) of 1-ethylaziridine with 0.109 g (0.001 mole) of ethyl bromide in 100 ml of acetone at 25° produced 0.226 g (90% yield) of 1,1,4-triethylpiperazinium bromide. [c] Molecular weight: calcd, 263; found, 277 (by boiling point in methyl ethyl ketone). Per cent unsaturation as C_2: calcd, 9.12; found, 9.21. [d] 0.015 mole instead of 0.03 mole as indicated in the Experimental Section. [e] Molecular weight: calcd, 319; found, 333. Per cent unsaturation: calcd, 7.48; found, 7.52. [f] Per cent unsaturation: calcd, 5.78; found, 6.18. [g] At approximately 40% conversion of the chloroethylamine. [h] At approximately 100% conversion of the chloroethylamine. [i] At approximately 51% conversion of the chloroethylamine. [j] Polymer weight not determined, estimate less than 10 g.

only product from the reaction of dimethylchloroethylamine with a 9-mole excess of 1-phenethylaziridine in acetone (reaction 25). In a similar manner, 1,1-



X

dimethyl-4-ethylpiperazinium chloride (reaction 23) and 1,1,4-triethylpiperazinium chloride (reaction 24) were prepared from the corresponding dialkylchloro-

order of results with the exception that 1-cyanoethylaziridine did not enter into the reaction at all. The only product isolated from this particular reaction was 1,1,4,4-tetramethylpiperazinium dichloride, the self-condensation product of the chloramine.

The data thus far discussed have been taken on reactions involving aziridine to alkylating agent ratios of 10. This particular ratio was chosen because it afforded rapid conversions of the alkylating agents into products and because it was thought that an excess of aziridine favored polymer formation. One run was carried out at a ratio of 1000 (footnote *b*, Table III) and a 90% yield of the corresponding piperazinium salt

was isolated. Hence, nearly quantitative yields of piperazines became even more significant in view of this excess.

Experimental Section[13]

1,4-Di-*n*-butylpiperazine.—To a mixture of 64 g (1.0 mole) of piperazine in 500 ml of dry dimethylformamide was added dropwise with stirring 287.7 g (2.1 moles) of *n*-butyl bromide. The temperature was allowed to increase slowly to 100° during the addition and was held there with the aid of a water bath. After standing overnight at room temperature, the volatiles were removed on a rotary evaporator. The resulting gum was mixed with 500 ml of 20% aqueous sodium hydroxide and the water-insoluble oil was separated, dried over sodium sulfate, and distilled, bp 114° (10 mm), $n^{20}D$ 1.4539.

Anal. Calcd for $C_{12}H_{26}N_2$: N, 14.14. Found: N, 14.11.

1,4-Di-*n*-butyl-1-allylpiperazinium Bromide.—In 500 ml of dry acetone were mixed 19.8 g (0.1 mole) of 1,4-di-*n*-butylpiperazine and 14.5 g (0.12 mole) of allyl bromide. After standing for 72 hr at 25° a small quantity of a white precipitate was observed. The precipitate was removed by filtration and was found to be crude 1,4-di-*n*-butyl-1,4-diallylpiperazinium dibromide, mp 182–185°.

Anal. Calcd for N: 6.37. Found: 6.51.

The remaining liquid was evaporated leaving a gum which was converted into a white powder by washing with anhydrous ether. This product was shown into be 1,4-di-*n*-butyl-1-allylpiperazinium bromide, mp 134–136°.

Anal. Calcd for $C_{15}H_{31}BrN_2$: N, 8.73; mol wt, 319. Found: N, 8.55; mol wt, 319 (ebulliometrically in methyl ethyl ketone).

The infrared spectrum of this compound had the following characteristic piperazine bands[14] (KBr): 1348, 1145, 1108, 1030, and 935 cm^{-1}. A new band characteristic of the monoquaternized piperazines was found at 1212 cm^{-1}.

1,4-Diethyl-1-methylpiperazinium *p*-Toluenesulfonate.—In 50 ml of dry acetone were mixed 7.1 g (0.05 mole) of 1,4-diethylpiperazine and 1.9 g (0.01 mole) of methyl *p*-toluenesulfonate. After standing for 48 hr at 25°, the volatiles were removed at 70° and the resulting solid was recrystallized from acetone, mp 105–106°. The infrared spectrum was consistent with that of the expected product.

Anal. Calcd for $C_{16}H_{28}N_2O_3S$: N, 8.54. Found: N, 8.66.

Reaction of N-Substituted Aziridines with Alkylating Agents.—Into a small-mouth bottle was weighed 0.30 mole of the aziridine and the indicated volume of dry solvent was added. This mixture was placed in a thermostated 25° bath. Subsequently 0.03 mole of the alkylating agent was added with shaking. After 96 hr the bottles were removed from the bath, their contents were transferred to a rotary evaporator, and all volatiles were removed leaving either a powder or gummy residue. The residue was triturated with anhydrous diethyl ether resulting in the deposition of a white powder which was separated by filtration and dried. The piperazinium salts were subsequently recrystallized from acetone, vacuum dried, and analyzed.

In some cases the gummy residue did not solidify, but dissolved in the ether, thereby indicating polymer. Polymers which were not ether soluble were those containing functional groups such as those from 1-(2-hydroxyethyl)aziridine and 1-cyanoethylaziridine. It is also worth noting that those piperazines prepared from dihalides usually precipitated from the reaction mixture. This general procedure was used for all runs listed in Table III.

The poly(1-ethylaziridine) polymers prepared in reactions 10 and 12 were found to contain less than 3.0% piperazine rings ($C_4H_8N_2$) which was the analytical limit of the infrared method employed. This limit was established by preparing blends of 1,4-diethyl-1-methylpiperazinium *p*-toluenesulfonate and poly(1-ethylaziridine) and evaluating their infrared spectra.

Reaction of N-Alkylaziridines with Dimethylchloroethylamine and Diethylchloroethylamine.—The chloroethylamine was prepared by treating 0.031 mole of the corresponding hydrochloride with an excess of cold 20% aqueous sodium hydroxide and extracting with diethyl ether. The ether solution was dried over anhydrous sodium sulfate and this solution (20–30 wt % amine) was introduced into the bottle containing the aziridine–solvent mixture. The remainder of the procedure was the same as the preceding one.

The nmr spectrum of a D_2O solution of 1,1-dimethyl-4-phenethylpiperazinium chloride had signals (relative to sodium 1-trimethylsilylpropane-3-sulfonate) at δ 2.81 (4 H, singlet, NCH_2CH_2O methylenes), at 2.90 (4 H, multiplet, NCH_2 ring methylenes), at 3.18 (6 H, singlet, $^+NCH_3$), at 3.43 (4 H, multiplet, $^+NCH_2$ ring methylenes), and at 7.35 (5 H, singlet, phenyl ring).

Acknowledgment.—The author gratefully acknowledges the able assistance of C. L. Sechrest and R. M. Cook. Infrared spectra were obtained and interpreted by H. L. Spell and nmr data were furnished by R. P. Vander Wal.

(13) All melting points are uncorrected. Nmr spectra were obtained with a Varian Associates Model A-60 spectrophotometer equipped with a variable-temperature probe. The chemical shifts were measured using sodium 1-trimethylsilylpropane-3-sulfonate as an internal standard. Infrared spectra were obtained on a Beckman IR-9. Glpc data were taken on an F & M 810 chromatograph.

(14) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **18**, 305 (1962).

Pseudo-Halogens. VIII.[1] New Synthesis of Aziridines and Oxazolidones

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Aziridines or 2-oxazolidones are readily prepared from unsaturated compounds by direct conversion into β-chlorocarbamates followed by reaction with base or by pyrolysis, respectively. Yields are good and are comparable with those from the corresponding iodocarbamates. β-Chlorocarbamates prepared from 1-olefins have chlorine on C-2 and nitrogen on C-1; the oxazolidones obtained, therefore, are the 5-alkyl isomers. Proof of structure of the 2-oxazolidones has been obtained by independent synthesis of one pair of 4- and 5-alkyl isomers.

Aziridines can be prepared by numerous synthetic pathways of which two of the most widely used are the Gabriel and Wenker methods, both of which require a suitably substituted β-amino alcohol.[3] Limitations of these two reactions have been adequately discussed and will not be repeated.

A voluminous literature also exists on the preparation of 2-oxazolidones.[4] The most important synthetic routes involve various ring-closing techniques on β-amino alcohols and β-halamines or their derivatives.

β-Amino alcohols and β-halamines are not always readily accessible in good yield and/or of known stereochemistry and often they are obtained by multistep sequences. Our interest in aziridines and 2-

(1) Pseudo-halogens. VII: T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

(2) Work to be submitted in partial fulfillment of the requirements for the Ph.D. degree.

(3) P. E. Fanta in "Heterocyclic Compounds with Three and Four-Membered Rings," Part I, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 524–575, and references listed therein.

(4) M. E. Dyen and D. Swern, *Chem. Rev.*, in press. For a brief review of the literature to 1953, see J. W. Cornforth, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, pp 396–402.