Heterocyclic Compounds Derived From Aliphatic Amines

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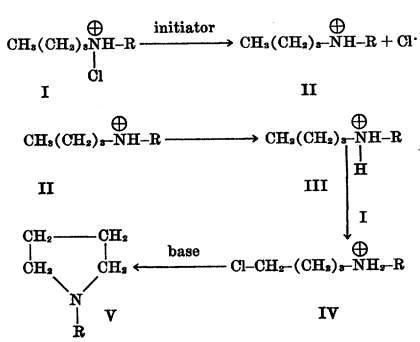
Abstract

The photolytic rearrangement of N-chloroamines derived from secondary fatty amines, such as N-methyloctadecylamine, has been investigated. The intermediate δ- or ε-chloroamines, or both, were not isolated from the reaction medium but were converted directly to their corresponding N-methyl-2-alkylpyrrolidine or piperidine analogs, or both, by treatment with alkali. The synthetic utility of this reaction has been extended to include the two functionally substituted secondary amines, N,N-dimethylazelaylamine and methyl 11-methylaminoundecanoate. The yields of isolated pure products are in the range of 50–80%.

Introduction

The synthetic applications of the Hofmann-Loeffler N-chloroamine rearrangement have been the subject of a number of studies (1). Through the efforts of Wawzonek and Thelen (2) the mechanism of this free-radical chain process has been shown to proceed through the intermediacy of nitrogen cation radicals $R_2\overset{+}{N}H$ (amminium radicals, II). The amminium radical (II) intramolecularly abstracts a sterically favored hydrogen atom to give an alkyl radical (III) which, in a chain propagation sequence, abstracts a chlorine atom from another N-chloroammonium ion to form an alkyl chloride (IV) and a new amminium radical (II). The alkyl chloride is later cyclized under the influence of alkali to afford the cyclic tertiary amine (V).

In more recent studies by Neale et al. (3,4), the influence of acid strength, solvent and chloroamine structure has been studied in the photochemical rearrangement of N-chloroamines. Their work, concerned mainly with rates of chloroamine rearrangement, has more fully defined the various reaction parameters of this reaction.



The purpose of this paper is to report the preparation of heterocyclic nitrogen compounds derived from readily accessible fatty materials. Towards this goal the photolytic rearrangement of N-chloro-N-methylalkylamines, derived from fatty amines, has been investigated under conditions of the Hofmann-Loeffler reaction.

Experiment Procedures

Compounds

N-Methylstearamide. Stearic acid (85 g, 0.30 mole) was converted to its acid chloride by reaction with oxalyl chloride (40 g, 0.315 mole) employing the procedure of Bosshard et al. (5). The acid chloride (91 g, 0.30 mole) was then added dropwise to an ice-cold aqueous solution of methylamine (40%, 200 ml). The precipitated crude methylamide was filtered and washed with water and dried. The pure amide was obtained by recrystallization from benzene, mp = 91–91.5 C (lit. mp 91.2 C) (6), yield 90%.

N-Methylpalmitamide. Prepared from palmitic acid as described above for N-methylstearamide. The pure amide was obtained by recrystallization from benzene, mp 85–85.5 C (lit. mp 85.5 C) (6).

N-Methyloleamide. Prepared from oleic acid by the method described for N-methylstearamide. The pure amide was obtained by recrystallization from hexane at −15 C in 90% yield, mp 34–35 C (lit. mp 34.5–35 C) (7).

N,N′-Dimethylazelaamide. Prepared from the diacid chloride of azelaic acid and methylamine in 75% yield. The amide was recrystallized from chloroform, mp 133–134 C.

N-Methyloctadecylamine (VIb). Into a 3-liter flask equipped with a mechanical stirrer, condenser, thermometer and nitrogen inlet tube was placed lithium aluminum hydride (19 g, 0.50 mole) in tetrahydrofuran (400 ml). To the stirred mixture, cooled to 10 C, was added a slurry of N-methylstearamide (74 g, 0.25 mole) in tetrahydrofuran (1600 ml) in small portions over a period of 2 hr. The reaction mixture was refluxed for 18 hr, cooled in an ice bath, and 100 ml of 20% aqueous sodium hydroxide solution was added dropwise with vigorous stirring over a period of 3 hr. The mixture was filtered and the homogeneous filtrate dried over anhydrous sodium sulfate. Removal of solvents on a rotary evaporator gave 68 g of the crude amine. It was recrystallized from petroleum ether (bp 30–60 C) at −20 C to give the pure amine in 80% yield, mp 42–43 C (lit. mp 41–42 C) (8).

N-Methylhexadecylamine (VIIb). Prepared in 82% yield by the lithium aluminum hydride reduction of N-methylpalmitamide as described above. The amine was recrystallized from petroleum ether (bp 30–60 C) at −20 C, mp 35–36 C (lit. mp 32 C) (9).

N-Methyloleylamine (VIIIb). Prepared in 75% yield by the lithium aluminum hydride reduction of N-methyloleamide by the above procedure. The amine was purified by distillation through a spinning band column, bp 118–119 C at 0.05 mm Hg (lit. bp 150–155 C at 0.4 mm Hg) (8).

N,N′-Dimethyl-1,9-nonanediamine (IXb). Prepared in 30% yield by the lithium aluminum hydride reduction of N,N′-dimethylazelaamide. The pure amine was obtained by distillation through a spinning band column, bp 64–65 C at 0.10 mm Hg.

Analysis calculated for $C_{11}H_{26}N_2$: C, 70.90; H, 14.06; N, 15.03. Found: C, 70.78; H, 13.84; N, 14.93.

11-Methylaminoundecanoic Acid. Prepared in 60% yield from 11-bromoundecanoic acid and methylamine by the method of Champetier et al. (10). The pure amino acid was obtained by recrystallization from water, mp 136–137 C, (lit. mp 136–137 C) (10).

Methyl-11-methylaminoundecanoate (Xb). Prepared from 11-methylaminoundecanoic acid (22 g, 0.10 mole) by reaction with boron trifluoride etherate (20% in methanol, 100 ml) with refluxing for 1 hr. The cooled solution was poured into 500 ml of 10% sodium carbonate solution and extracted with ether (3 × 100 ml). The combined organic layers were washed with water (2 × 100 ml), dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude oily product was distilled on a spinning band column, bp 96–98 C at 0.2 mm Hg. Yield, 80%.

Analysis calculated for $C_{12}H_{27}NO_2$: C, 66.31; H, 12.52; N, 6.44. Found: C, 66.27; H, 12.54; N, 6.30.

Rearrangement of N-chloro-N-methylamines. A typical procedure is given. N-Methyl-2-tetradecylpyrrolidine (XIIa). To a solution of N-methyloctadecylamine (28.2 g, 0.10 mole) in ether (300 ml) was added in one portion N-chlorosuccinimide (14.7 g, 0.11 mole). The mixture was stirred at ambient temperature for 1.5 hr. The solids were separated by filtration, and the ether layer was washed with water (2 × 100 ml) and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residual yellow oil (27.2 g) was used without further purification. Its active chlorine content was found to be 86% of theoretical by iodometric analysis (3).

The N-chloroamine was added in one portion to a cold acetic acid solution, 1.5 M in sulfuric acid and 1.5 M in water (400 ml) (3). The reaction temperature rose to 25 C, and a white precipitate formed. The heterogeneous mixture was purged with nitrogen gas (20 ml/minute) and kept under a nitrogen sweep. The mixture was stirred and was irradiated with a Hanovia Model 30600 medium pressure mercury arc lamp until complete disappearance of active chlorine (3.5 hr) as determined by iodometric analysis. The reaction mixture, homogeneous at this point, was poured on to 500 g of ice, diluted with 200 ml of water, and made basic with 50% sodium hydroxide solution. The temperature rose spontaneously to 60 C and was maintained there with heating for 1.5 hr to ensure cyclization of the alkylchloroamines. The mixture was cooled to room temperature and extracted with ether (3 × 200 ml). The combined organic layers were washed with water (2 × 100 ml), dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to leave a brown oil (24 g). This oil was taken up in benzene (100 ml) and the occluded water was removed azeotropically. Evaporation of the benzene gave a clear brown oil (21 g). This oil was distilled on a spinning band column to give 15.6 g of a clear oil, bp 113–114.5 C at 0.12 mm Hg (56% yield). Methiodide salt mp 194–195 C.

Analysis calculated for $C_{19}H_{39}N$: C, 81.06; H, 13.96; N, 4.98. Found: C, 81.04; H, 13.70; N, 4.92.

N-Methyl-2-dodecylpyrrolidine (XIIb). Reaction of N-methylhexadecylamine (25.5 g, 0.10 mole) with N-chlorosuccinimide (14.8 g, 0.11 mole) in ether (300 ml) gave N-chloro-N-methylhexadecylamine (purity 90% by iodometry). The crude N-chloroamine was added in one portion to 400 ml of the acid solution. Photolysis, as described above, was complete in 3.0 hr. Cyclization and isolation of the reaction product was carried out as described in the previous example. The product was distilled on a spinning band column to give 16.5 g of a clear oil bp 87–88 C at 0.05 mm Hg (65% yield), methiodide salt mp 177–178 C.

Analysis calculated for $C_{17}H_{35}N$: C, 80.56; H, 13.92; N, 5.53. Found: C, 80.52; H, 13.99; N, 5.37.

Methyl 7-(2-N-methylpyrrolidinyl)heptanoate (XIIc). To a solution of methyl 11-methylaminoundecanoate (11.45 g, 0.050 mole) in ether (100 ml) was added N-chlorosuccinimide (7.40 g, 0.055 mole) in one portion. The N-chloroamine (purity 90%) was isolated in the usual manner and added to 100 ml of the standard acid solution. This solution was then irradiated for 2 hr for complete disappearance of active chlorine. The reaction mixture was poured on to ice and was made basic with 50% aqueous sodium hydroxide. The solution was evaporated in vacuo and the residual solids dried in a vacuum oven. The solids were then added to 200 ml of 20% sulfuric acid in methanol, and the solution was refluxed for 3.5 hr. This mixture was then poured into 800 ml of 20% sodium carbonate solution and the resulting solution extracted with ether (3 × 100 ml). The combined ether layers were washed with water (2 × 50 ml), dried, and the solvents removed in vacuo to give a yellow oil. This oil was distilled to give 8.3 g of clear oil, bp 81–82 C at 0.1 mm Hg (72% yield), methiodide salt mp 57–58 C.

Analysis calculated for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.60; H, 10.99; N, 6.36.

Bis-(2-N-methylpyrrolidinyl)methane (XVI). To a solution of N,N′-dimethylnonanediamine (9.3 g, 0.050 mole) in ether (100 ml) was added N-chlorosuccinimide (14.8 g, 0.110 mole) in one portion. The crude chloroamine was isolated by the usual techniques and was analyzed to be 95% dichloro derivative. It was then added in one portion to 100 ml of the acid solution. Irradiation for 4 hr caused the complete loss of active halogen content. Cyclization and isolation of the reaction products was carried out as previously described. The crude oil (9.6 g) was distilled to give 7.4 g of clear oil, bp = 72–81 C at 0.50 mm Hg (80% yield). This material was found to be a mixture of three components in the ratio of 5:60:35 by gas liquid chromatographic (GLC) analysis on a 4 ft × ¼ in. column of 10% XE-60 on Diataport at 100 C, helium flow of 60 ml/min. The major component was isolated by preparative GLC and identified as *bis*-(2-N-methylpyrrolidinyl)methane by IR and mass spectra analysis. (See Discussion.)

Analysis calculated for $C_{11}H_{22}N_2$: C, 72.47; H, 12.16; N, 15.37. Found: C, 72.25; H, 12.04; N, 15.33.

The second major component was also isolated by preparative GLC and identified as N-methyl-5-(2-N-methylpyrrolidinyl)pentylamine (XVII) by its IR and mass spectra. (See Discussion.)

9(10)-Chloro-10(9)-hydroxy-N-methyloleylamine (XIX). To a solution of N-methyloleylamine (28.1 g, 0.10 mole) in ether (200 ml) was added N-chlorosuccinimide (14.8 g, 0.11 mole). The crude N-chloroamine (27.3 g) was isolated in the usual manner. Its purity by iodometry was found to be 96%. Addition of this N-chloroamine to an acetic acid solution, 1.5 M in sulfuric acid and 1.5 M in water (400 ml), caused the formation of a royal blue solution. Irradiation for 1.5 hr caused complete loss of active halogen content. The solution was poured on to ice, made basic with 50% sodium hydroxide solution, and heated to 70 C for 1.0 hr. Ex-

traction with ether (3 × 200 ml) and removal of solvent gave 26 g of a yellow oil. Trituration of this oil with petroleum ether (bp 30–60 C) (200 ml) deposited a crystalline solid, 12.4 g, mp 74–76 C (37% yield). Two recrystallizations from acetone gave the analytical sample, mp 80–81 C.

Analysis calculated for $C_{19}H_{40}ClNO$: C, 68.32; H, 12.07; N, 4.19; Cl, 10.61. Found: C, 68.13; H, 11.79; N, 4.28; Cl, 10.52.

Results

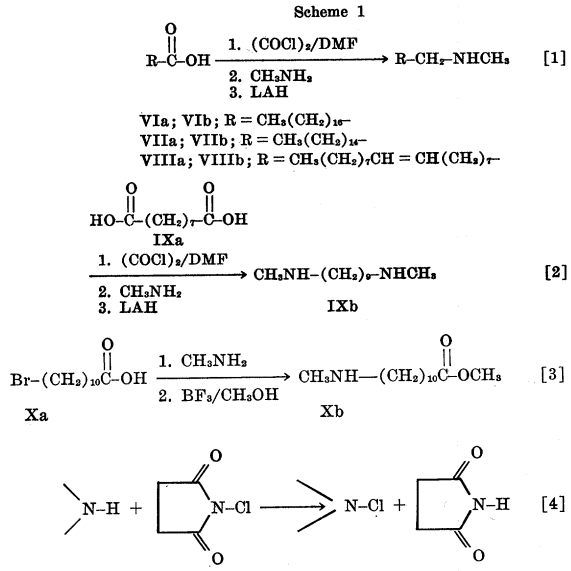
The N-chloro- derivatives of amines VIb to Xb were synthesized from the corresponding carboxylic acids by the procedure outlined in Scheme 1.

Four of the free acids (VIa–IXa) were converted to their acid chlorides by reaction with oxalyl chloride in the presence of a catalytic quantity of dimethylformamide (4). Reaction of the acid chlorides with aqueous methylamine gave the N-methylamides in essentially quantitative yields. Reduction of the amides to the corresponding amines was effected with lithium aluminum hydride in tetrahydrofuran. This procedure gave good yields of the expected amines except that the reduction of N,N′-dimethylazelaamide gave only a 30% yield.

Methyl 11-methylaminoundecanoate (Xb) was prepared by reaction of 11-bromoundecanoic acid with an excess of aqueous methylamine (10) followed by methylation of the free acid.

Reaction of the free amines with N-chlorosuccinimide in ether (Scheme 1, Equation 1) gave the N-chloroamines which were 90–95% pure by iodometric titration. Absence of significant amounts of N-chlorosucinimide in the N-chloroamines was demonstrated by infrared spectroscopy. These materials were used without further purification.

Scheme 1



Previous studies by Neale (3) have demonstrated that an acetic acid solution 1.5 M in sulfuric acid and 1.5 M in water is an excellent acid medium for the photolytic rearrangement of N-chloroamines. Accordingly, this medium was employed exclusively for the photolytic rearrangements in the present investigation.

Addition of the crude N-chloro- derivative of N-methyloctadecylamine (VIb) or N-methylhexadecylamine (VIIb) to the acid medium resulted in the immediate formation of a precipitate. The mixture was irradiated until complete disappearance of active chlorine occurred as judged by iodometric titration. Alternatively, the reaction could be judged complete when the reaction mixture achieved homogeneity. The N-chloroamine of methyl 11-methylaminoundecanoate (Xb) and the N,N′-dichloro- derivative of N,N′-dimethylazelaamine (IXb) did not give a precipitate in acid medium, but irradiation resulted in the complete loss of their active chlorine content.

The alkylchloroamines derived from the photochemical rearrangement of compounds XIa and XIb (Scheme 2) were chemically cyclized by treatment with alkali to the corresponding pyrrolidine (XII) or piperidine (XIII) analogs, or both, in yields of 56% and 65%, respectively, based on amine. Cyclization of the alkylchloroamines from XIc was accompanied by hydrolysis of the ester function located in the side chain. Re-esterification gave the cyclic amines XIIc and XIIIc in 70% yield. Alkali treatment of the rearrangement products derived from the N,N′-dichloroamine XIV (Scheme 3) gave a mixture of cyclic amines in 80% yield. The identity of these materials is given in the Discussion section.

Photolysis of N-chloro-N-methyloleylamine (XVIII, Scheme 4) and subsequent alkali treatment did not lead to any isolable cyclic amines. Addition of the chloroamine to the acid reaction medium resulted in the immediate formation of a deep blue solution. Analysis of the latter for active chlorine content indicated that half of the chlorine was lost on solution. The remainder of the active chlorine disappeared upon irradiation. The crude reaction mixture after treatment with base caused the deposition of a crystalline material acyclic in nature.

Discussion

Previous work has demonstrated that rearrangement and alkali treatment of low molecular weight secondary N-chloroamines give rise to cyclic tertiary amines. These products have been found to be predominantly five-membered heterocycles (pyrrolidines) contaminated with minor amounts of six-membered heterocycles (piperidines) (3,11,12). Since the Hofmann-Loeffler reaction has not been applied previously to N-chloro-N-methyl fatty amines it was necessary to establish the identity of the products obtained and to determine the ratio of these products.

Establishment of the structures assigned to the reaction products obtained from the N-chloroamines XIa to XIc is based on the following chemical and physical considerations. Elemental analysis and molecular weight by mass spectrometry are consistent with the assigned structures as cyclic tertiary amines. The products gave quaternary ammonium iodide salts on reaction with methyl iodide, substantiating that they are tertiary amines. Proof of the structures as N-methyl cyclic tertiary amines is based on infrared spectroscopy, the Hofmann degradation sequence and mass spectrometry.

Evidence for the cyclic nature of the reaction products was obtained by a comparison of their infrared spectra with those of the starting amines. The major difference noted in these spectra was the overall increase in intensity of the carbon-hydrogen stretching vibration of the N-methyl group (13) (2780 cm^{-1}, Fig. 1) in the reaction products as compared to their open chain counterparts. This increase in intensity in going from open chain amine to pyrrolidine has also been observed with the model compound N-methylpyrrolidine and its acyclic analog N-methyldiethylamine.

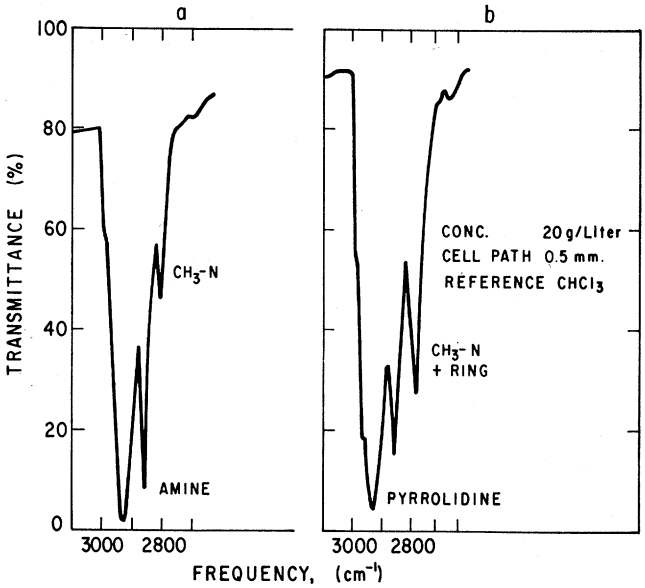
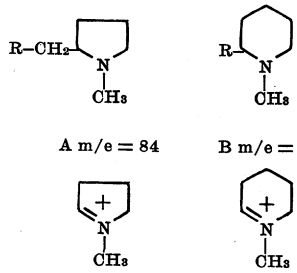


FIG. 1. Infrared spectrum of cyclic amines. (a) N-methyloctadecylamine (VIb); (b) 2-tetradecyl 1-N-methylpyrrolidine (XIIa).

Chemical proof for the pyrrolidine and piperidine ring structures was obtained by means of the Hofmann degradation sequence (Scheme 5) for products XIIa and XIIIa obtained from N-methyloctadecylamine. The purified mixture of cyclic amines was converted to the methiodide salt by reaction with methyl iodide in methyl acetate. Conversion to the quaternary ammonium hydroxide followed by olefin formation via ring scission was effected with potassium hydroxide in refluxing ethylene glycol. The crude mixture of olefins was ozonized (14) and the resulting mixture of aldehydes was analyzed by quantitative GLC against a standard aldehyde mixture.

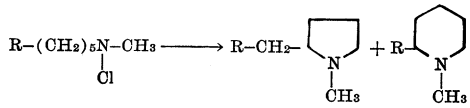
As seen from Scheme 5 the two aldehydes obtainable from the substituted pyrrolidine are C_{14} and C_{15} homologs; whereas, from the substituted piperidine C_{13} and C_{14} aldehydes are expected. Although the C_{14} aldehyde is common to both ring structures, the C_{15} aldehyde can be obtained only from the pyrrolidine ring, and the C_{13} aldehyde only from the piperidine ring. Accordingly, the presence of both the C_{15} and C_{13} aldehydes establishes the presence of both ring systems in the reaction mixture. The experimental ratio of these aldehydes was 15:2 indicating the reaction mixture to be composed of 88% pyrrolidine and 12% piperidine.

TABLE I
Mass Spectrum Analysis of Cyclic Amines



R	%A	%B
$CH_3(CH_2)_{12}$-	94	6
$CH_3(CH_2)_{10}$-	92.5	7.5
$CH_3O_2C(CH_2)_5$	92.5	7.5

TABLE II
GLC Analysis of Cyclic Amines



R	Pyrrolidine, %	Piperidine, %
$CH_3(CH_2)_{12}$-	93.5	6.5
$CH_3(CH_2)_{10}$-	91	9
$CH_3O_2C(CH_2)_5$-	93	7

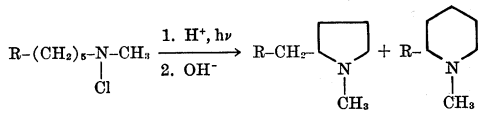
Further proof of structure for the principal reaction products was obtained by an examination of the mass spectra of compounds XII and XIII (see Table I). The parent ion in all cases gave the correct theoretical molecular weight of two mass units less than the starting acyclic amines. The base peak ion in all the spectra was at m/e of 84 corresponding to the N-methylpyrrolidinium ion (Table I, A). In all spectra a peak at m/e of 98 was also observed. This peak corresponds to the N-methylpiperidinium ion (Table I, B). The ratio of these peaks is a measure of the relative amounts of pyrrolidine and piperidine derivatives. Verification that the ion at m/e of 98, obtained in the pyrrolidine and piperidine reaction mixtures is indeed from the N-methylpiperidinium ion was obtained by isolation of the pure pyrrolidines XIIa and XIIb. In the isomerically pure pyrrolidine samples the intensity of the ion at m/e of 98 was less than 0.5% of the ion at m/e of 84.

The final determination of the pyrrolidine to piperidine ratio was obtained by quantitative GLC analysis. The purified mixture of cyclic amines was analyzed on an ethylene glycol succinate column. Results are summarized in Table II, and are the average of several determinations. Comparisons of these results with those obtained from the mass spectral data are in agreement within 1%. The conclusion made from the above data is as follows. The rearrangement and cyclization of N-chloro-N-methyl fatty amines under conditions of the Hofmann-Loeffler reaction does indeed give cyclic tertiary amines. These amines have been identified as 2-substituted N-methylpyrrolidines and 2-substituted N-methylpiperidines. The relative distribution of these two heterocyclic ring systems was determined to be in the range of 15:1 to 9:1 with the pyrrolidine ring structure predominating.

GLC analysis of the purified reaction product, obtained from the rearrangement and alkali cyclization of the *bis*-dichloroamine of N,N′-diazelaamine, indicated it to be a mixture of 3 components in the ratio of 5:65:30 (Scheme 3). The components were isolated by GLC and their structures assigned on the basis of the following data. The major component, *bis*-(2-N-methylpyrrolidinyl)methane (XVI), gave the correct elemental analysis and molecular weight (182 by mass spectrometry) for the empirical formula $C_{11}H_{22}N_2$. In the mass spectrum of XVI the base peak corresponded to m/e of 84 for the N-methylpyrrolidinium ion as expected. The infrared spectrum of XVI, as previously noted, displayed the characteristic absorption at 2790 cm^{-1} the intensity of which was greater than the carbon-hydrogen stretching frequency at 2980 cm^{-1}.

The second major component, N-methyl-5-(2-N-methylpyrrolidinyl)pentylamine (XVII), was also identified by its infrared and mass spectra. Its molecular weight (184 by mass spectrometry) was two mass units larger than compound XVI. The base

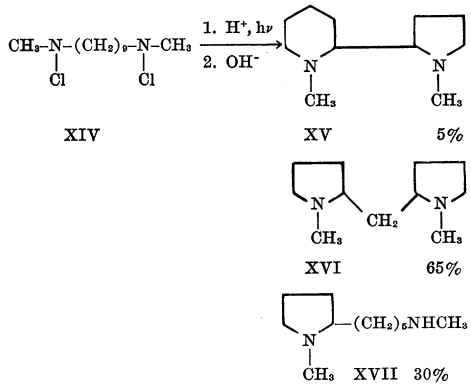
Scheme 2



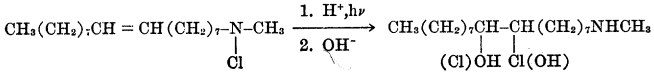
XI XII XIII

XIa ; XIIa ; XIIIa. R = $CH_3(CH_2)_{12}^-$
XIb ; XIIb ; XIIIb. R = $CH_3(CH_2)_{10}^-$
XIc ; XIIc ; XIIIc. R = $CH_3O_2C(CH_2)_5^-$

Scheme 3

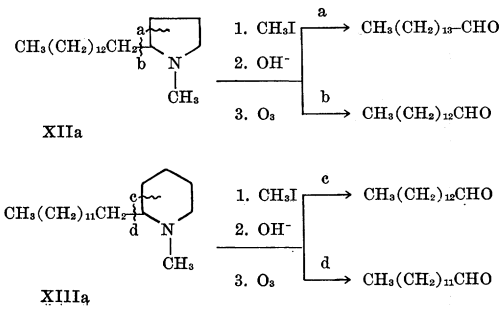


Scheme 4



XVIII XIX

Scheme 5



peak in its mass spectrum also corresponded to the N-methylpyrrolidinium ion. Identification as the monocyclic product was made on the basis of its infrared spectrum, which showed an N–H absorption at 3250 cm^{-1} and a strong absorption at 2790 cm^{-1} indicative for a pyrrolidine ring structure.

Compound XV, 2-(2-N-methylpyrrolidinyl)N-methylpiperidine, gave a molecular weight by mass spectrometry of 182 indicating it to be isomeric with compound XVI. It is assigned its structure on the basis of its mass spectrum which, aside from the base peak at m/e of 84 corresponding to the N-methylpyrrolidinium ion, gave a strong ion peak at m/e of 98 (70% base peak), corresponding to the N-methylpiperidinium ion.

The acyclic reaction product obtained from the photolysis of N-methyl-N-chlorooleylamine (Scheme 4) was identified on the basis of its elemental analysis and infrared spectrum. Analysis of this material gave an empirical formula of $C_{19}H_{40}ClNO$. Its infrared spectrum showed absorption for both O–H and N–H stretching frequencies at 3450 and 3250 cm^{-1}, respectively. From the above data this product was assigned the structure of 9(10)chloro-10(9)hydroxy-N-methyloctadecylamine (XIX).

The formation of chlorohydrin XIX as the major reaction product from the photolysis of N-chloro-N-methyloleylamine is accountable on the basis of the following reaction pathway. The initial step requires the electrophilic addition of chlorine to the internal double bond of N-methyloleylamine followed by termination with acetic acid to give a β-chloroacetate derivative. Basic hydrolysis of the ester gives the chlorohydrin. The use of N-chloroamines as a source of electrophilic chlorine has been observed previously by Neale (16) in his studies on the addition of amminium radicals to olefinic compounds.

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