was no longer present. The bulk of the reaction mixture was added dropwise with stirring to 100 ml. of anhydrous ether. The colorless solid was washed with ether: 0.62 g. (95%), identical with earlier preparations of 3-benzyl-2-methyl-1,3-diazaspiro-[4.5]dec-1-ene perchlorate.

G.—A glass rod was dipped into 72% aqueous perchloric acid, shaken free of adhering drops of acid and then dripped into a suspension of 0.100 g. (0.27 mmole) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate in 10 ml. of water. The mixture was warmed on a steam bath until solution was complete (*ca.* 3 min., maximum temperature of mixture 78°), cooled, and extracted with four 5-ml. portions of ether. Evaporation of the aqueous solution gave 0.070 g. (92%) of solid product identical with other samples of 3-ethyl-2-methyl-1,3-diazaspiro[4.5]-dec-1-ene perchlorate. The ether extract was dried (Na_2SO_4), and concentration gave a few drops of an oil which on vapor phase chromatography (silicone rubber column, 175°) gave a single peak identical in retention time with that of benzyl alcohol under the same conditions.

1-Benzyl-3-ethyl-2-methyl-3-aza-1-azoniaspiro[4.5]dec-1-ene Perchlorate (IV).—To a stirred suspension of 0.73 g. (2.6 mmoles) of 3-ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate in 10 ml. of water were added 2.8 ml. of 1 *N* sodium hydroxide solution and 10 ml. of ether. The mixture was stirred for 15 min. and separated; the aqueous phase was further extracted with four 5-ml. portions of ether. The combined ether solution was dried ($MgSO_4$) and treated with 0.321 ml. (462 mg.; 2.7 mmoles) of benzyl bromide. The sirupy residue (0.58 g.) resulting from evaporation of the solvent could not be made to crystallize: ν_{max}^{liq} 1610 and 1555 cm.$^{-1}$. A solution of the sirup in 17 ml. of methanol was treated with 344 mg. (1.66 mmoles) of silver perchlorate in 10 ml. of methanol. Filtration afforded 301 mg. (96%) of silver bromide. The methanol solution was concentrated and treated with ether. The sticky solid was recrystallized from ethyl acetate: 0.51 g. (83%); m.p. 120–121°; ν_{max}^{KBr} 1615 and 1560 cm.$^{-1}$; n.m.r. τ-values ($CDCl_3$, TMS) 2.66 (5H, aromatic protons), 5.31 (s, 2H, benzyl CH_2), 6.16 (s, 2H, imidazolinium CH_2), 6.34 (*q*, J = 7 c.p.s., 2H, CH_2CH_3), 7.77 (s 3H, 2-CH_3), 7.9–8.9 (unresolved m, 10H, cyclohexane protons), and 8.67 p.p.m. (t, 3H, CH_2CH_3).

Anal. Calcd. for $C_{18}H_{27}ClN_2O_4$: C, 58.29; H, 7.34; N, 7.55. Found: C, 58.05; H, 7.27; N, 7.52.

Small Charged Rings. VII. Interconversion of Substituted β-Chloroethylamines and Aziridinium Salts[1–3]

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Stable aziridinium perchlorates have been synthesized from β-chloroethylamines by treatment with silver perchlorate. 1,1-Diethylaziridinium perchlorate (III), 1,1,2,2-tetramethylaziridinium perchlorate (VIII), and 3-azoniaspiro[2.5]octane perchlorate (XI) have been prepared as examples. Their structures were established by direct comparison of spectra and properties to the possible dimeric isomers, or by comparison with authentic material as in the case of VIII. The "reverse" reaction of stable aziridinium salts XVI and XIX with chloride ion has been shown to give β-chloroethylamines XIII and XX more highly substituted at the chlorine-bearing carbon. In addition, evidence is presented that treatment of iminium chlorides XXIII and XXIV with diazomethane proceeds in a manner similar to that proposed for the addition of diazomethane to iminium perchlorates. The proposed intermediate aziridinium chlorides react further to give β-chloroethylamines XVII and XX, identical with those obtained from the treatment of stable aziridinium salts with chloride ion. The structures of the β-chloroethylamines XVII and XX were established by n.m.r. spectra.

Quaternary aziridinium salts, particularly the perchlorates and fluoborates, are very conveniently prepared by the reaction of diazoalkanes with iminium salts.[4–6] Other examples of aziridinium salt formation which have appeared in the literature have been limited to special cases where physical properties, *e.g.*, solubility, have facilitated isolation or where steric factors have played a role.[7–11] In the past, reliance has been placed upon bulky anions, such as picrylsulfonate,[12–15] to provide low solubility and thereby permit the trapping of aziridinium intermediates. Since kinetic studies have clearly shown the accumulation of aziridinium ions from β-chloroethylamines prior to dimerization, hydrolysis, and displacement,[16–19] we decided to try to trap these cations with perchlorate anion, the choice being directed by our previous favorable experience with the isolation of stable aziridinium perchlorates.[1,4–6]

In a previous paper we described the conversions of two special β-bromoethylamines, 13-bromomethyl-1-azatricyclo[4.3.2.0.^{1,13}O^{5,13}]tetradecane and N-(1-bromocyclohexylmethyl)pyrrolidine, to the respective aziridinium perchlorates, 1-azoniatetracyclo[7.3.2.-0.^{1,13}0^{5,13}]tetradecane perchlorate and 5-azoniadispiro-[4.0.5.1]dodecane perchlorate.[20] We have now examined the reaction in more detail and with simpler β-chloroethylamines.

In operations conducted at 0–5°, treatment of the commercially available β-diethylaminoethyl chloride hydrochloride (I) in aqueous solution with 1 equiv. of

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(1) For the preceding articles in this series, see N. J. Leonard and L. E. Brady, *J. Org. Chem.*, **30**, 817 (1965); N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *ibid.*, **29**, 3383 (1964).

(2) This investigation was supported by a research grant (USPHS-RG5829, currently GM 05829-06) from the National Institutes of Health, U. S. Public Health Service, to whom we are pleased to acknowledge our thanks.

(3) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstracts, p. 157.

(4) N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, **84**, 4806 (1962).

(5) N. J. Leonard and K. Jann, *ibid.*, **82**, 6418 (1960).

(6) Abstracts, 17th National Organic Chemistry Symposium of the American Chemical Society, Bloomington, Ind., June 1961, pp. 1-10.

(7) P. E. Fanta, L. J. Pandya, W. R. Groskopf, and H.-J. Su, *J. Org. Chem.*, **28**, 413 (1963).

(8) P. E. Fanta, R. Golden, and H.-J. Su, *J. Chem. Eng. Data*, **9**, 246 (1964).

(9) W. A. Skinner, A. P. Martinez, H. F. Cram, L. Goodman, and B. R. Baker, *J. Org. Chem.*, **26**, 148 (1961).

(10) G. F. Hennion and P. E. Butler, *ibid.*, **27**, 2088 (1962).

(11) R. D. Clark and G. K. Helmkamp, *ibid.*, **29**, 1316 (1964).

(12) C. Golumbic, J. S. Fruton, and M. Bergmann, *ibid.*, **11**, 518 (1946).

(13) N. B. Chapman and J. W. James, *J. Chem. Soc.*, 2103 (1954).

(14) J. D. P. Graham, *Brit. J. Pharmacol.*, **12**, 489 (1957).

(15) J. F. Allen and N. B. Chapman, *J. Chem. Soc.*, 1482 (1960).

(16) P. D. Bartlett, S. D. Ross, and C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2971 (1947).

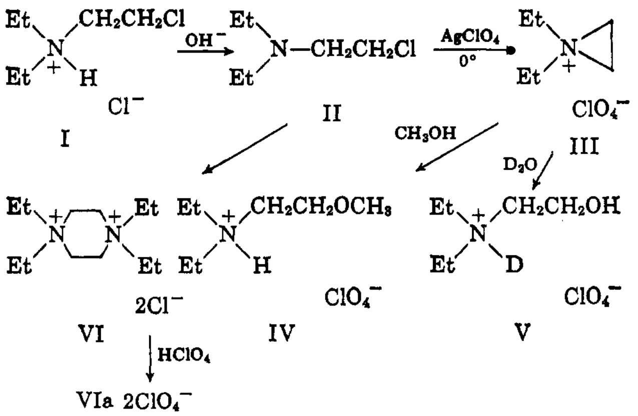
(17) P. D. Bartlett, J. W. Davis, S. D. Ross, and C. G. Swain, *ibid.*, **69**, 2977 (1947).

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

(19) B. Cohen, E. R. Van Artsdalen, and J. Harris, *ibid.*, **74**, 1875 (1952).

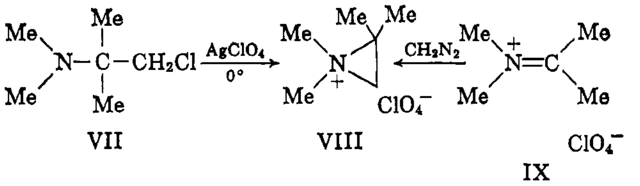
(20) N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963).

base followed by extraction with benzene resulted, on removal of the benzene, in the isolation of β-diethylaminoethyl chloride. The n.m.r. spectrum of the free base indicated the ethyl groups plus an A_2B_2 pattern, consistent with the open formulation II. Treatment of β-diethylaminoethyl chloride in anhydrous acetone at 0° with silver perchlorate and isolation of the resulting salt gave 1,1-diethylaziridinium perchlorate (III) in 94% yield. The aziridinium salt was identified by the absence of $^+$N–H absorption in the infrared and the presence in the n.m.r. spectrum of a singlet (methylene chloride solution) at τ 6.92, indicative of two equivalent methylene groups next to positively charged nitrogen in a three-membered ring.[4,5,20,21] The n.m.r. spectrum had additional signals at τ 6.72 (quartet, J = 7.5 c.p.s.) and 8.64 (triplet, J = 7.5 c.p.s.), corresponding to the $^+N\text{-}CH_2CH_3$ groups. The structure of the aziridinium salt III was confirmed chemically by reactions with methanol and deuterium oxide.[20] The methanolysis was effected by refluxing in methyl alcohol for 35 min., and the crude reaction product after removal of the solvent *in vacuo* was examined by n.m.r. The spectrum showed signals (deuteriochloroform) at τ 6.24 (part of an A_2B_2 pattern, area 2 protons, $-CH_2O$) and 6.58 (singlet, area 3 protons, $O\text{-}CH_3$), indicating ring opening had occurred (IV). The hydrolysis reaction with deuterium oxide (→ V) was carried out in 1 *M* solution in an n.m.r. sample tube which was placed in a bath maintained at 100.0 ± 0.2° for various lengths of time before measurement. The half-life of the first-order or pseudo-first-order reaction under these conditions was approximately 1150 sec.

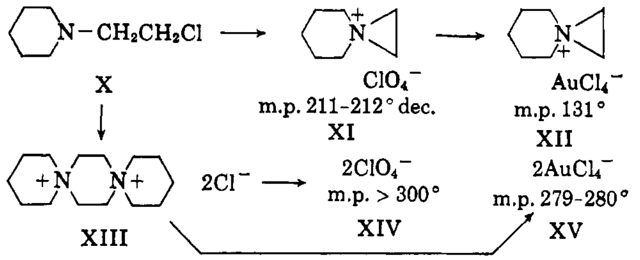


It had been shown previously[18] that β-diethylaminoethyl chloride dimerizes readily in 2:1 acetone–water to give 1,1,4,4-tetraethylpiperazinium dichloride (VI). The conversion II → VI was effected on a preparative scale and the product,[22,23] m.p. >310°, was isolated and converted to the diperchlorate salt VIa, different from III, by treatment with perchloric acid. The n.m.r. spectrum of VI in deuterium oxide (the diperchlorate was not soluble in organic solvents or water) showed a singlet at τ 6.08, a quartet at 6.34, and a triplet at 8.63 of relative area 2:2:3. The n.m.r. uniquely defined the structure VIa. The position of the signal for the ring protons provides valuable information since the difference between this figure (τ 6.08) and the one observed (6.92) for the ring protons in the 1,1-diethylaziridinium salt III—in a range typical of other aziridinium salts[4,5,20]—is sufficient to be diagnostic of structure where a decision is to be made between a piperazinium and an aziridinium salt.

In a conversion similar to I → III, 1-chloro-2-dimethylamino-2-methylpropane (VII), obtained from 2-dimethylamino-2-methyl-1-propanol and thionyl chloride,[18] was treated with silver perchlorate in acetone to give 1,1,2,2-tetramethylaziridinium perchlorate (VIII),[1] m.p. 149–149.5° in 98% yield. Since this aziridinium salt had been prepared previously by addition of diazomethane[1] to N,N-dimethylisopropylideniminium perchlorate (IX),[24] a positive comparison of the product from the two sources was possible by mixture melting point and identity of the infrared and n.m.r. spectra.



It may be recalled that the first postulate of the formation of an aziridinium salt was that of Marckwald and Frobenius[25] for the compound resulting from the treatment of N-β-chloroethylpiperidine (X) with base. While the interpretation of Bestian,[26] that the conditions under which the reaction and isolation were conducted favored the piperazinium dichloride structure XIII, has been widely accepted, we felt that a direct comparison of "monomeric" and "dimeric" structures would be instructive. N-β-Chloroethylpiperidine hydrochloride was treated with 1 equiv. of base, giving X, which, when treated with silver perchlorate in acetone at room temperature for 3 hr., gave the resulting perchlorate salt, $C_7H_{14}ClNO_4$, m.p. 211–212° dec. The infrared spectrum had no signals corresponding to $^+$N–H. The n.m.r. spectrum in methylene chloride had a sharp singlet at τ 6.93 indicating the presence of the aziridinium ring. Also present in the n.m.r. spectrum were signals at τ 6.70 and 8.19, both multiplets, for four and six protons. The perchlorate salt XI, 3-azoniaspiro[2.5]octane perchlorate, was converted to the tetrachloroaurate salt XII by treatment with hydrogen tetrachloroaurate. The yellow crystalline solid had a melting point of 131 to 135° depending on the rate of heating. The presence of the three-membered ring was confirmed by n.m.r. in acetonitrile, in which the spectrum was essentially the same as that of the perchlorate. The Marckwald–Frobenius salt had a re-



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[21] G. V. D. Tiers, "Tables of τ-Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[22] K. H. Slotta and R. Behnisch, *Ann.*, **497**, 170 (1932).

[23] A. C. Cope and M. Berg, *J. Am. Chem. Soc.*, **74**, 611 (1952).

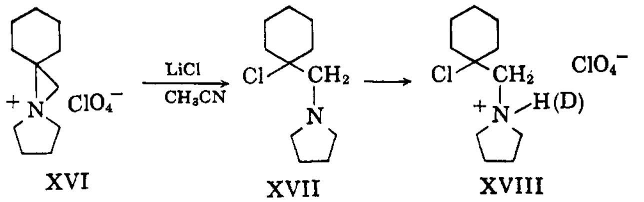
[24] N. J. Leonard and J. V. Paukstelis, *ibid.*, **28**, 3021 (1963).

[25] W. Marckwald and O. Frobenius, *Ber.*, **34**, 3544 (1901).

[26] H. Bestian, "Methoden der Organischen Chemie," Houben-Weyl, Georg Thieme Verlag, Stuttgart, Germany, 1958, Vol. XI/2, p. 234.

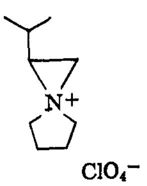
ported melting point of 273–274°.[25] The dimer, 6,9-diazoniadispiro[5.2.5.2]hexadecane dichloride (XIII), was prepared by allowing X to stand in 2:1 acetone–water[18] and then converting it to the bistetrachloroaurate salt XV, for which a melting point of 279–280° was observed. The structure of the dimer was established by n.m.r. signals at τ 6.03 (a sharp singlet), 6.30 (multiplet identical with low-field multiplet of XI), and 8.18 (multiplet identical with high-field multiplet of XI). It has thus been shown by our synthesis of the bistetrachloroaurate salt and comparison of the melting points that the Marckwald–Frobenius compound was indeed of the "dimeric" type. It has also been shown that our salt XI, prepared from N-β-chloroethylpiperidine and silver perchlorate, is of the aziridinium type originally postulated in 1901.

The reaction of 5-azoniadispiro[4.0.5.1]dodecane perchlorate (XVI)[4,5] with lithium chloride in acetonitrile was carried out at room temperature with continuous extraction of the product formed with pentane. The pentane was removed *in vacuo* and the product was examined by n.m.r. The product had a signal at τ 7.20 (singlet, 2H) consistent with the structure N-(1-chlorocyclohexylmethyl)pyrrolidine. The perchlorate salt, $C_{11}H_{21}Cl_2NO_4$, m.p. 170–171°, $\nu_{\max}^{\mathrm{Nujol}}$ 3100 cm.$^{-1}$ for $^+$N–H (ClO_4^-), exhibited a doublet at τ 6.37 (2H) in the n.m.r. spectrum in deuteriochloroform, with a coupling constant, J = 5.5 ± 0.2 c.p.s., indicative of splitting of the *exo*-methylene protons by the proton on nitrogen in the conjugate acid XVIII. When the $^+$N–H was exchanged by deuterium a singlet at τ 6.37 replaced the original doublet, confirming the structure assignment of XVII, N-(1-chlorocyclohexylmethyl)-pyrrolidine, for the base.

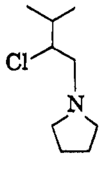


XVI XVII XVIII

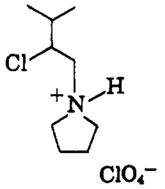
Treatment of another representative aziridinium salt, 1-isopropyl-3-azoniaspiro[2.4]heptane perchlorate (XIX), with lithium chloride in acetonitrile gave a β-chloroethylamine in 92% yield, to which the structure N-(2-chloro-3-methylbutyl)pyrrolidine (XX) was tentatively assigned. The n.m.r. spectrum (deuteriochloroform) had signals at τ 6.05 (two overlapping triplets, 1 proton, CHCl[21]), 7.27 (doublet, J = 6.9 ± 0.2 c.p.s., 2 protons), 7.45 (multiplet, 4 protons), 7.85 (multiplet, 1 proton), 8.25 (multiplet, 4 protons), and 8.97 and 9.03 (two doublets, J = 6.8 ± 0.2 c.p.s., 3 protons each) The doublet at 7.27 was shown by double resonance to be coupled to the multiplet at 6.05. The multiplet at 6.05 was shown to be coupled to the multiplet at *ca.* 7.85. The multiplet at *ca.* 7.85 was shown to be coupled to the two doublets at τ 8.97 and 9.03. The compound consistent with the observed chemical shifts and coupling pattern was XX. The isomeric structure XXII was not; *e.g.*, it would have required 2 protons for the lowest field signal (CH_2Cl). The perchlorate salt, $C_9H_{19}Cl_2NO_4$, was prepared: $\nu_{\max}^{\mathrm{Nujol}}$ 3120 cm.$^{-1}$ ($^+$N–H ClO_4^-), m.p. 191–192°. The n.m.r. spectrum showed a broad multiplet at τ 5.5–7.0 of area 7 protons.



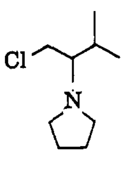
XIX



XX

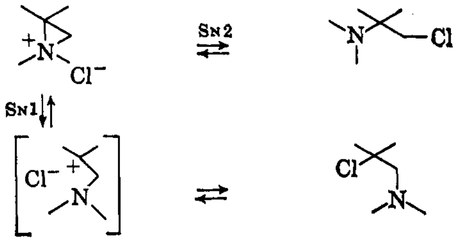


XXI

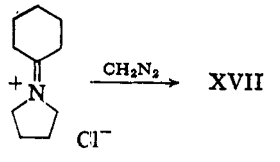


XXII

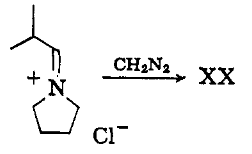
The products formed from the aziridinium perchlorates with chloride ion and bromide ion are anomalous if one considers these anions as good nucleophiles, since the products are not those obtained by a direct S_N2 displacement on the methylene of the aziridinium ring. The process can be visualized as arising by an ionization and collapse of the ion pair to give product, as shown below. If displacement by chloride ion or bromide ion were to occur, the step would be reversible and the more stable product would result, *i.e.*, that with the halogen at the carbon corresponding to the more highly substituted carbonium ion, so long as this steric situation were not unfavorable.[20]



In this connection, our attention was directed to a report by Opitz and Griesinger[27] on the reaction of iminium chlorides with diazomethane to yield β-chloroethylamines. We have previously reported the reaction of an iminium bromide, $\Delta^{1(6)}$-tetrahydrojulolidinium bromide with diazomethane to yield a β-bromoethylamine, specifically 13-bromomethyl-1-azatricyclo-[7.3.1.0^{5,13}]tridecane.[20] Opitz and Griesinger[27] reported that the β-chloroethylamines formed in general were those *less* substituted at the chlorine-bearing carbon. In our hands the reaction of iminium chlorides XXIII and XXIV with diazomethane yielded products XVII and XX, respectively, identical with the ring-opened products from the corresponding stable aziridinium perchlorates XVI and XIX and lithium chloride. These chlorides XVII and XX were examined by n.m.r. in an impure state to minimize decomposition or change in structure. Distillation gave the identical material but in poor recovery. The observation that identical products are formed from both methods, an aziridinium salt with chloride and an iminium chloride with diazomethane, strongly implies that a single aziridinium intermediate is involved. Optiz and Griesinger did not consider the possibility of such an intermediate



XXIII



XXIV

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(27) G. Opitz and A. Griesinger, *Ann.*, **665**, 101 (1963).

and consequently favored the wrong (isomeric) structures.

Experimental[28]

Aziridinium Perchlorates Made by Addition of Diazomethane to Iminium Perchlorates.—1,1,2,2-Tetramethylaziridinium perchlorate (VIII)[1] and 5-azoniadispiro[4.0.5.1]dodecane perchlorate (XVI)[4,5] were made as previously described. 1-Isopropyl-3-azoniaspiro[2.4]heptane perchlorate (XIX)[29] was made as follows. A solution of 5.0 g. (22.2 mmoles) of N-isobutylidenepyrrolidinium perchlorate[24] (XXIV, ClO_4^-) in 200 ml. of methylene chloride maintained at 0° was treated with an ether solution of diazomethane until in excess. The solvent was removed *in vacuo* and the remaining oil was treated with ether. The crystalline solid formed, 4.8 g. (91%), m.p. 58–59°, had no maxima corresponding to $^+N–H$ or $C{=}N^+$. The n.m.r. spectrum (CH_2Cl_2) had signals at τ 6.2–7.1 (area 7 protons, 4 pyrrolidine ring protons and 3 aziridinium ring protons), 7.76 (multiplet, 4 protons), 8.75 (doublet, J = 6.5 c.p.s., 3 protons), and 8.87 (doublet, J = 6.5 c.p.s., 3 protons).

β-Haloamine Hydrochlorides. 1-Chloro-2-dimethylamino-2-methylpropane Hydrochloride.[18]—A solution of 117 g. (1.0 mole) of 2-dimethylamino-2-methyl-1-propanol in 75 ml. of chloroform was added to 166 g. (1.4 mole) of thionyl chloride in 75 ml. of chloroform at 0°. The reaction was violent at the beginning of the addition but gradually subsided. After addition was complete, the solution was heated at reflux for 4 hr. The solvent was removed *in vacuo*, yielding 150.9 g. (88%) of 1-chloro-2-dimethylamino-2-methylpropane hydrochloride, m.p. 239–240°. The hydrochloride was used without further purification. Its n.m.r. signals (D_2O) were τ 6.28 (singlet, 2 protons, $–CH_2Cl$), 6.85 (singlet, 6 protons, $^+N–CH_3$), and 8.52 (singlet, 4 protons, $C–CH_3$).

N-β-Chloroethylpiperidine (X) Hydrochloride.—The reaction was carried out in the same manner. N-β-Hydroxyethylpiperidine (46.5 g., 0.36 mole) was converted to N-β-chloroethylpiperidine hydrochloride in 96% yield.

Aziridinium Perchlorates Made from β-Chloroethylamines and Silver Perchlorate. 1,1-Diethylaziridinium Perchlorate (III).—A mixture of 17.1 g. (0.10 mole) of β-diethylaminoethyl chloride hydrochloride in 100 ml. of water and 150 ml. of benzene at 0–5° was treated with 100 ml. of 0.100 *N* sodium hydroxide and the mixture was stirred for 5 min. The benzene was separated and a fresh 100-ml. portion was added, stirred, and separated. The aqueous solution was extracted once more, and the benzene extracts were combined and concentrated *in vacuo* below room temperature. The n.m.r. spectrum of the benzene solution had signals (relative to benzene, τ 2.73) at τ 6.60 (part of A_2B_2 with $J = \sim 7.5$ c.p.s., 2 protons, $CH_2C\mathbf{H}_2Cl$), 7.35 (part of A_2B_2 with $J = \sim 7.5$, 2 protons, $NC\mathbf{H}_2–CH_2Cl)_2$, 7.63 (quartet, $J = 7.3 \pm 0.2$, 4 protons, $N–C\mathbf{H}_2–$), and 9.07 (triplet, $J = 7.3 \pm 0.2$, area 6 protons).

A solution of 5.02 g. (37 mmoles) of β-diethylaminoethyl chloride (II) in 50 ml. of anhydrous acetone at 0–5° was treated with 10.4 g. (50 mmoles) of silver perchlorate in 50 ml. of dry acetone. A precipitate formed immediately. The solution was decanted and the acetone was removed *in vacuo*. The remaining oil was dissolved in methylene chloride and filtered to remove insoluble silver chloride and silver perchlorate; the methylene chloride was removed *in vacuo*. On addition of ether the oil solidified. Recrystallization from 2-propanol yielded 7.0 g. (94%) of colorless crystals, m.p. ~192° dec. (*violently!*). The n.m.r. spectrum (methylene chloride) had signals at τ 6.72 (quartet, $J = 7.5 \pm 0.2$ c.p.s., 4 protons), 6.92 (singlet, 4 protons, aziridinium $^+NCH_2–$), and 8.64 (triplet, $J = 7.5 \pm 0.2$, 6 protons). The n.m.r. spectrum [deuterium oxide with $(CH_3)_3SiCH_2CH_2CH_2SO_3H$ as internal standard] had signals at τ 6.77, 6.97, and 8.69 of the same areas and multiplicity as described above.

Anal. Calcd. for $C_6H_{14}ClNO_4$: C, 36.09; H, 7.07; N, 7.01. Found: C, 36.48; N, 6.82; Cl, 6.78.

Methanolysis of 1,1-Diethylaziridinium Perchlorate (III).—A solution of 1.0 g. (5.0 mmoles) of VII in 10 ml. of methanol was refluxed for 35 min., and the solvent was evaporated to dryness. The remaining solid was used for the spectral measurements of N,N-diethyl-β-methoxyethylamine perchlorate (IV) without further purification. The n.m.r. spectrum ($CDCl_3$) had signals at τ 6.24 (part of A_2B_2, 2 protons, $–CH_2–O–$), 6.58 (singlet, 3 protons, $–OCH_3$, 6.4–7.0 (complex multiplet, 6 protons, $^+N–CH_2$), 8.63 (triplet, J = 7.0 c.p.s., area 6 protons, $^+N–CH_2CH_3$). Treatment with D_2O simplified the spectrum but did not allow the individual assignments.

Hydrolysis of 1,1-Diethylaziridinium Perchlorate (III). A Semiquantitative Study.—A sample (~100 mg.) was dissolved in 0.5 ml. of 99.5% D_2O, placed in an n.m.r. sample tube, and sealed with a plastic cap. The n.m.r. sample tube was placed in a bath maintained at 100.0 ± 0.2° for various lengths of time, withdrawn, and cooled for measurement. The spectrum of the starting material consisted of a quartet at τ 6.77, a singlet at 6.97, and a triplet at 8.69. In the product, the 2 protons α to oxygen occur at τ ~6.0. It was therefore possible to integrate the area from 5.5 to 7.5 and determine the ratio of $(CH_2–O)$ to the total integral in this area. The total integral remains constant, since 8 protons are found in the starting material and product. The integrations were performed at least five times and averaged. A plot of log $a/(a-x)$ *vs.* time gave a straight line corresponding to a half-life at 1 *M* concentration of 1150 sec. for the reaction.

1,1,4,4-Tetraethylpiperazinium Dichloride (VI).[18]—A sample of β-diethylaminoethyl chloride was allowed to stand in 2:1 acetone–water for 4 days at 25°. The solvent was removed and the solid remaining was recrystallized from ethanol, m.p. >310°. The infrared spectrum had no maxima corresponding to $^+N–H$ or O–H. The n.m.r. spectrum [deuterium oxide with $(CH_3)_3SiCH_2CH_2CH_2SO_3H$ as internal standard] had signals at τ 6.08 (singlet, $N–CH_2$), 6.34 (quartet, $J = 7.5 \pm 0.2$ c.p.s.), and 8.63 (triplet, $J = 7.5 \pm 0.2$), in a ratio of 2:2:3. These data established the dimer structure VI.

Anal. Calcd. for $C_{12}H_{28}Cl_2N_2$: C, 53.13; H, 10.39; N, 10.33. Found: C, 53.37; H, 10.68; N, 10.29.

1,1,2,2-Tetramethylaziridinium Perchlorate (VIII).[1]—The procedure for the preparation was identical with the one used in the preparation of 1,1-diethylaziridinium perchlorate (III). Starting with 7.0 g. (0.052 mole) of 2-dimethylamino-2-methyl-1-chloropropane (VII) hydrochloride[18] resulted in isolation of 11.4 g. (98%) of 1,1,2,2-tetramethylaziridinium perchlorate (VIII), m.p. 149–149.5°. The n.m.r. spectrum (methylene chloride) had signals at τ 6.84, 6.98, and 8.28, all singlets of relative area 3:1:3. The infrared and n.m.r. spectra of the aziridinium salt obtained from the β-chloroethylamine were identical with the spectra of the aziridinium salt made by reaction of N,N-dimethylisopropylideneiminium perchlorate (IX)[24] and diazomethane.

3-Azoniaspiro[2.5]octane Perchlorate (XI).—To a solution of 9.2 g. (0.050 mole) of N-β-chloroethylpiperidine hydrochloride in 25 ml. of water and 100 ml. of benzene was added 25 ml. of 2.0 *N* potassium hydroxide. After stirring for 5 min. the benzene was separated. The aqueous layer was extracted two more times with 100-ml. portions of benzene. The benzene extracts were combined and concentrated *in vacuo* below room temperature. The n.m.r. spectrum (relative to benzene τ 2.73) had signals at τ 6.61 (part of A_2B_2, 2 protons, $NCH_2C\mathbf{H}_2Cl$), 7.48 (part of A_2B_2, 2 protons), 7.73 (multiplet, 4 protons), and 8.60 (multiplet, 6 protons).

The solution of N-β-chloroethylpiperidine (X) in 25 ml. of acetone was treated with 11.4 g. (0.055 mole) of silver perchlorate in 25 ml. of acetone. A precipitate started to form immediately. The reaction was complete in 3–4 hr. at room temperature as judged by lack of formation of additional silver chloride. The silver chloride was removed by filtration and the acetone was removed *in vacuo*. The remaining oil was dissolved in methylene chloride, filtered, concentrated *in vacuo*, and treated with ether. The colorless solid which separated was recrystallized from 2-propanol, yielding 7.8 g. (73%) of material, m.p. 211–213° dec. The n.m.r. spectrum (methylene chloride) had signals at τ 6.70 (multiplet, 4 protons), 6.93 (singlet, 4 protons), and 8.19 (multiplet, 6 protons). In deuterium oxide the signals appeared at τ 6.78, 7.00, and 8.22, and had the same relative areas and multiplicity.

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(28) All melting points are corrected. All boiling points are uncorrected. N.m.r. spectra were obtained with a Varian Associates Model A-60 spectrometer equipped with a variable temperature probe. The chemical shifts were measured using tetramethylsilane as an internal standard for all spectra in nonaqueous solvents and $(CH_3)_3SiCH_2CH_2CH_2SO_2OH$ for spectra in deuterium oxide. Double resonance experiments were performed with a Varian Associates Model V-4300B spectrometer equipped with a superstabilizer. Infrared spectra were obtained by using Perkin-Elmer spectrometers: Models 21, 521, 137, and 237. The author wishes to thank Mr. Josef Nemeth and his associates for the microanalyses, Mr. Dick Johnson and his associates for the n.m.r. and infrared spectra, and Mr. Oliver W. Norton for the double resonance experiments.

(29) First made by Dr. J. Mulvaney in this laboratory.

Anal. Calcd. for $C_7H_{14}ClNO_4$: C, 39.72; H, 6.67; N, 6.62. Found: C, 39.42; H, 6.56; N, 6.45.

A tetrachloroaurate salt (XII) was prepared by addition of hydrogen tetrachloroaurate to the perchlorate in water as a yellow crystalline solid, m.p. 131–135° (sharp melting but dependent on the rate of heating). The aziridinium structure for the tetrachloroaurate was confirmed by examination of the n.m.r. spectrum in acetonitrile. The aziridinium salt supposedly of this structure originally reported by Marckwald and Frobenius[25] had m.p. 273–274°.

6,9-Diazoniadispiro[5.2.5.2]hexadecane Dichloride (XIII).[25]—A solution of 1.84 g. (10.0 mmoles) of N-β-chloroethylpiperidine hydrochloride in 5 ml. of water was treated with 5 ml. of 2.0 *N* potassium hydroxide and extracted with ether. The ether was removed *in vacuo*, 10 ml. of 2:1 acetone–water was added, and the solution was heated on a steam bath for 1 hr. The solvent was removed leaving a yellow solid which on recrystallization from 95% ethanol gave colorless crystals, m.p. >300°. The **bistetrachloroaurate salt XV** was prepared by treatment of the dichloride with hydrogen tetrachloroaurate in water, giving a yellow solid, m.p. 279–280°, on recrystallization from acetonitrile. The **diperchlorate salt XIV**, prepared by treatment of the dichloride with perchloric acid in water, separated immediately, m.p. >300°. The **dichloride** had no maxima corresponding to O–H or $^+$N–H in the infrared. The n.m.r. spectrum [deuterium oxide with $(CH_3)_3SiCH_2CH_2CH_2SO_3H$ as internal standard] had signals at τ 6.03 (singlet, 2 protons, $^+NCH_2$–), 6.30 (multiplet, 2 protons), and 8.18 (multiplet, 3 protons).

Anal. Calcd. for $C_{14}H_{28}Cl_2N_2$: C, 56.93; H, 9.56; N, 9.48. Found: C, 56.85; H, 9.44; N, 9.24.

N-(1-Chlorocyclohexylmethyl)pyrrolidine (XVII). A.—A solution of 3.0 g. (11 mmoles) of 5-azoniadispiro[4.0.5.1]dodecane perchlorate (XVI) in 50 ml. of dry acetonitrile was treated with 1.0 g. (23.6 mmole) of solid lithium chloride.[20] The heterogeneous mixture was continuously extracted with pentane for 12 hr. The pentane extracts were evaporated *in vacuo* leaving an oil, n^{27}D 1.4961. An n.m.r. spectrum of the crude product ($CDCl_3$) had signals at τ 7.20 (singlet, 2 protons), 7.28 (multiplet, 4 protons), and 8.27 (multiplet, 14 protons). Addition of perchloric acid (1 part ethanol to 1 part 70% aqueous perchloric acid) to an ethereal solution of the free base afforded the perchlorate, 3.1 g. (100%), m.p. 170–171°, $\nu_{\text{Max}}^{\text{Nujol}}$ 3100 cm.$^{-1}$ ($^+$N–H). The n.m.r. spectrum ($CDCl_3$) had signals at τ 5.8–7.0 (broad unresolved multiplet, 4 protons), 6.37 (doublet, J = 5.5 ± 0.2 c.p.s., 2 protons), 7.80 (multiplet, 4 protons), and 8.37 (multiplet, 10 protons). Five drops of deuterium oxide were added and the sample was shaken for 1 min.; examination of the spectrum now showed a singlet at τ 6.37 while the rest of the spectrum was essentially unchanged. These results are consistent only with a structure with an exocyclic $^+N–CH_2$, thus establishing the structures of the β-chloroethylamine as N-(1-chlorocyclohexylmethyl)-pyrrolidine (XVII) and the perchlorate as XVIII.

Anal. Calcd. for $C_{11}H_{21}Cl_2NO_4$: C, 43.72; H, 7.01; N, 4.64. Found: C, 43.68; H, 6.94; N, 4.57.

B.—A solution of 1.62 g. (10.6 mmoles) of 1-N-pyrrolidylcyclohexene in 50 ml. of ether was treated at 0° with anhydrous hydrogen chloride until acid. The resulting precipitate was washed five times with 50-ml. portions of ether to remove excess hydrogen chloride. The remaining solid XXIII was dissolved in 100 ml. of anhydrous methylene chloride and cooled to 0°; diazomethane was added until in excess. The solution was allowed to stand for 15–30 min. at 0°. The solvent was removed *in vacuo* and the crude material was examined by n.m.r. The n.m.r. spectrum in methylene chloride was identical with that of N-(1-chlorocyclohexylmethyl)pyrrolidine previously obtained. On distillation, 0.912 g. (43%) of material, b.p. 67–68° (0.10 mm.), n^{24}D 1.4968 (reported[27] b.p. 65–66° at 0.01 mm., n^{20}D 1.4980) was obtained. During the distillation a large portion of the material decomposed. The perchlorate prepared from the distillate was identical with the perchlorate previously prepared.

N-(2-Chloro-3-methylbutyl)pyrrolidine (XX). A.—A solution of 2.0 g. (8.02 mmoles) of 1-isopropyl-3-azoniaspiro[2.4]heptane perchlorate (XIX) in 100 ml. of dry acetonitrile was treated with 1.0 g. (22.6 mmoles) of solid lithium chloride. The heterogeneous mixture was continuously extracted with pentane for 22 hr. The pentane extracts were concentrated *in vacuo* leaving an oil, 1.29 g. (92%). The n.m.r. spectrum ($CDCl_3$) had signals at τ 6.05 (two overlapping triplets with central peak split, 1 proton, –CHCl), 7.27 (doublet, J = 6.9 ± 0.2 c.p.s., 2 protons), 7.45 (multiplet, 4 protons), 7.85 (multiplet, 1 proton, established by doublet resonance), 8.25 (multiplet, 4 protons), 8.97 (doublet, J = 6.8 ± 0.2 c.p.s., 3 protons), and 9.03 (doublet, J = 6.8 ± 0.2 c.p.s., 3 protons). Double resonance confirmed that groups at τ 8.97 and 9.03 were doublets coupled to a single proton at 7.85 ± 0.10. The doublet at τ 7.27 was shown to be coupled to the single proton at 6.05. Distillation yielded 0.683 g. (49%), n^{27}D 1.4644. After distillation of the β-chloroethylamine the n.m.r. spectrum was unchanged.

A solution of 0.316 g. (1.8 mmoles) of the free amine in 20 ml. of ether was treated with 70% aqueous perchloric acid, 1:1 in ethanol. The colorless solid, 0.450 g. (91%), $\nu_{\text{max}}^{\text{Nujol}}$ 3120 cm.$^{-1}$, had m.p. 190–191.5°. Recrystallization of N-(2-chloro-3-methylbutyl)pyrrolidine perchlorate (XXI) from ethyl acetate raised this to 191–192°. The n.m.r. spectrum ($CDCl_3$) had signals at τ 5.5–7.0 (complex multiplet, 7 protons), 7.80 (multiplet, 4 protons), 7.8–8.5 (complex multiplet, 1 proton), 8.93 (doublet, J = 6.6 ± 0.2, 3 protons), and 8.99 (doublet, J = 6.6 ± 0.2, 3 protons). After the addition of deuterium oxide and shaking, the n.m.r. signals at τ 5.5–7.0 became simpler since the protons on the carbons α to the nitrogen were no longer coupled to $^+$N–H.

Anal. Calcd. for $C_9H_{19}Cl_2NO_4$: C, 39.29; H, 6.96; N, 5.09. Found: C, 39.16; H, 6.89; N, 4.97.

B.—A solution of 4.0 g. (33.9 mmoles) of 2-methyl-1-N-pyrrolidyl-1-propene prepared from pyrrolidine and isobutyraldehyde in 100 ml. of ether at 0° was treated with an ethereal solution of hydrogen chloride until in excess. The solid thus formed (XXIV) was washed with ether five times, and 100 ml. of dry methylene chloride was added. To the solution was added diazomethane until in excess. Methylene chloride was added as needed to keep the iminium salt in solution. The solvent was removed *in vacuo*. The n.m.r. of the crude product was identical with material previously obtained and identified as N-(2-chloro-3-methylbutyl)-pyrrolidine (XX). Distillation yielded 2.813 g. (50%) of material, b.p. 96–98° (14 mm.), n^{28}D 1.4643 (reported[26] b.p. 80–82° at 10 mm., n^{20}D 1.4698). The yields after distillation were always very low because considerable decomposition occurred on heating. Dehydrohalogenated products could also be detected after distillation.