with chloroform. The combined chloroform fractions were dried over anhydrous sodium sulfate and then evaporated to dryness. The oil obtained was crystallized from an acetone–water mixture producing 0.50 g. (33%) of white cubic crystals, m.p. 67–68°.

Anal. Calcd. for $C_{16}H_{16}ClNO_4$: C, 59.72; H, 5.01; N, 4.35. Found: C, 59.66; H, 5.17; N, 4.29.

Diethyl (4-Amino-3-quinolyl)malonate (VII).—A mixture of 2.10 g. of III and 200 mg. of 10% palladium on charcoal in 250 ml. of chloroform was reduced with 40 p.s.i. of hydrogen. To the reduced mixture 10 ml. of phosphorus trichloride was added, and the mixture was refluxed 3 hr., cooled, and evaporated to dryness. The residue was dissolved in ethanol, and the solution was filtered to remove the catalyst. A yellow solid separated from the filtrate on standing. When recrystallized from ethanol, yellow needles (0.45 g. 25%), which charred when heated to 300°, were formed.

Anal. Calcd. for $C_{16}H_{18}N_2O_4$: C, 63.56; H, 5.00; N, 9.27. Found: C, 63.83; H, 5.96; N, 9.36.

4-Methyl-4-carbethoxy-5-oxopyrrolino[2,3-*c*]quinoline 1-Oxide (VIII).—A mixture of 0.90 g. of IV and 200 mg. of 10% palladium on charcoal in 100 ml. of absolute ethanol was reduced with 40 p.s.i. of hydrogen. The reduced mixture was filtered and the solution deposited 0.35 g. (50%) of a yellow solid on standing. When crystallized from ethanol, yellow needles were formed, m.p. 214°.

Anal. Calcd. for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.93, N, 9.78. Found: C, 62.78; H, 5.18; N, 9.97.

4-Methyl-4-carbethoxy-5-oxopyrrolino[2,3-*c*]quinoline (IX).—A solution comprising 0.40 g. of VIII, 5. ml. of phosphorus trichloride, and 50 ml. of chloroform was refluxed for 30 min. The solvent was evaporated, leaving an oil which was diluted with water and made basic with 10% sodium hydroxide. The white precipitate (0.20 g. 53%) which formed was removed by filtration and crystallized from an acetone–water mixture, m.p. 229–230°.

Anal. Calcd. for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36. Found: C, 66.47; H, 5.37; N, 10.52.

Small Charged Rings. V. Expansion of the Aziridinium Ring by Reaction with Ketones[1–4]

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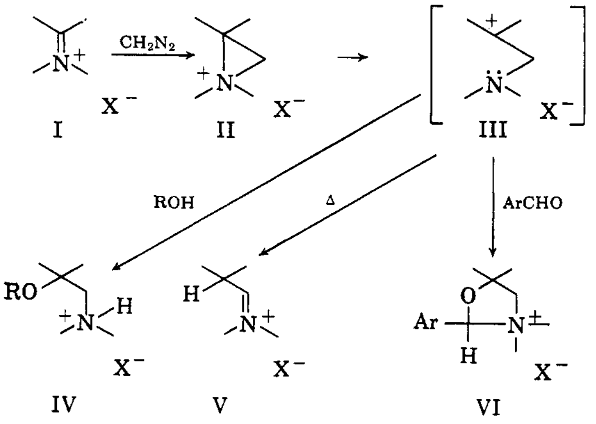
An aziridinium salt (VII) has been shown to react with cyclic, acyclic, and aryl ketones to give oxazolidinium salts (IX and XII–XVII). The structures of the products were established by analogy to the products of aziridinium salts and aromatic aldehydes[1,3,4] and by nuclear magnetic resonance spectroscopy including comparison with model compounds. The further generality of the cyclic addition with inclusion of the ketone carbonyl group was established by varying the aziridinium compound as well as the ketone (XVIII–XXII). The over-all result of the reaction may be represented as ③$^+$ + 2 → ⑤$^+$, descriptive of a broad type in which a charged, three-membered cycle is increased in size to a charged, five-membered cycle.

The facile synthesis of stable aziridinium salts (II, generalized formula, X = ClO_4 or BF_4)[5,6] from ternary iminium salts (I)[7] and diazomethane has fostered a continuing study of the chemistry of small charged rings, and some reactions involving the opening of the aziridinium ring accompanied by ring expansion have been previously described.[1,3,4,8] Solvolysis (→ IV)[5,6,8] and thermal rearrangement (→ V)[3,9] of substituted aziridinium perchlorates and fluoborates (II) appear to proceed with development of a carbonium ion, the more stable (III) of two possibilities resulting from aziridinium ring opening. The same intermediate would account for the ring expansion brought about by heating II in the presence of a weak nucleophile such as an aldehyde carbonyl (→ VI).[1] The analogous reaction of aziridinium salts with ketones has now been found to proceed smoothly to give oxazolidinium salts.[10]



The model aziridinium salt, 1,1,2,2-tetramethylaziridinium perchlorate (VII), prepared from N-isopropylidenedimethylaminium perchlorate[7] (or N, N-dimethylisopropylideneiminium perchlorate) and diazomethane, was used because of its simplicity, ready availability, and the ease with which its ketone reaction products could be identified by n.m.r. spectroscopy. The aziridinium salt VII was characterized by correct analysis for $C_6H_{14}ClNO_4$, solvolysis with alcohols,[8] infrared spectrum (absence of absorption maxima corresponding to $C{=}N^+$ or $N^+{-}H$), and n.m.r. spectrum. The n.m.r. spectrum in methylene chloride, with tetramethylsilane as the internal standard (τ 10.0),[11] exhibited signals, all singlets, at τ 8.28

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(1) For the preceding article in this series, see N. J. Leonard, E. F. Kiefer, and L. E. Brady, *J. Org. Chem.*, **28**, 2850 (1963).

(2) This investigation was supported by a research grant (USPHS-RG 5829, 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 in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, Abstracts, p. 30M, and at the XIXth International Congress of Pure and Applied Chemistry, London, England, July, 1963, Abstracts, A5-6, p. 207.

(4) N. J. Leonard, E. F. Kiefer, L. E. Brady, and J. V. Paukstelis, *Angew. Chem.*, **75**, 1031 (1963).

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

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

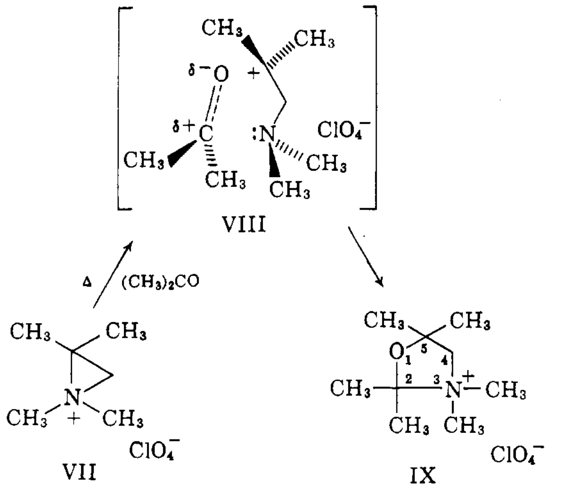
(7) N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).

(8) N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *ibid.*, **28**, 1499 (1963).

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

(10) In point of fact, the first reaction of a ketone with an aziridinium salt was not guided by analogy[1] but was recognized independently by one of us (J. V. P.) in attempting to carry out quite another reaction of an aziridinium salt using acetone as the solvent.

(11) 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).

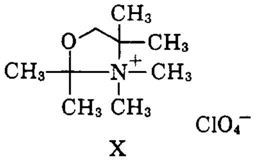


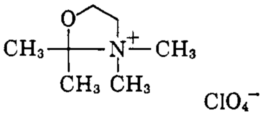
VIII

VII

IX

$[C(CH_3)_2]$, 6.98 ($-CH_2-N^+$), and 6.84 $[^+N(CH_3)_2]$. The position of the signal for the methylene protons indicated their attachment to the carbon ($-N^+$) of a three-membered ring.[5,6,8,9,11] When compound VII, $C_6H_{14}ClNO_4$, was heated at reflux in excess acetone, a new compound, $C_9H_{20}ClNO_5$, m.p. 188–189°, was obtained which had incorporated the elements of acetone. No absorption attributable to N^+—H or C=O was detected in the infrared, and the product was assigned structure IX, 2,2,3,3,5,5-hexamethyloxazolidinium perchlorate, by analogy with the products (VI) of the reaction of aziridinium salts with aromatic aldehydes.[1,3,4] The alternative structure X could be ruled out by spectral data alone. The n.m.r. spectrum in methylene chloride had signals (all singlets) at τ 8.47, 8.28, 6.75, and 6.10, with relative areas in the ratio of 3:3:3:1. The signal at τ 6.10 was assigned to the only methylene group in the molecule, placed next to $-\overset{+}{N}-$ since in the oxazolidinium salts derived from aldehydes the N^+-methylene signal occurred within the relatively narrow range, 6.08–6.23. The signals at τ 6.75, 8.28, and 8.47 were assigned to the N^+-methyl, C-2-methyl, and C-5-methyl protons, respectively. Reaction of VII with acetone-d_6 permitted the identification of the signal for the C-2-methyl protons, since the signal at τ 8.28 was absent in the hexadeuterated product while the rest of the spectrum was identical with that of IX.

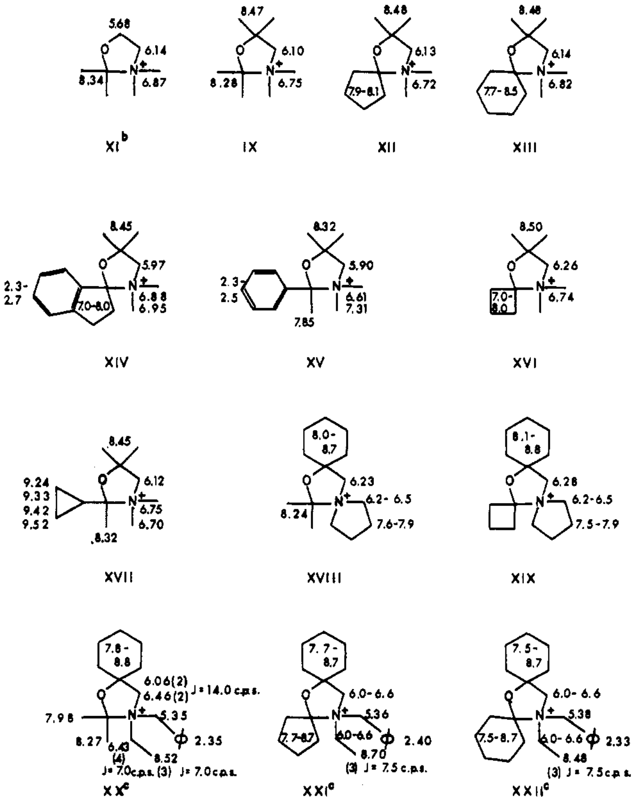

X


XI

A further check of the spectral assignments was made by the synthesis of an oxazolidinium salt in which an O-methylene group was present. N-Methylethanolamine was condensed with acetone to give 2,2,3-trimethyloxazolidine.[12a] Methylation with methyl iodide followed by treatment with perchloric acid yielded 2,2,3,3-tetramethyloxazolidinium perchlorate (XI). The n.m.r. spectra of compounds XI and IX were examined in deuterium oxide as 35% w./v. solutions with an internal standard, $(CH_3)_3SiCH_2CH_2CH_2SO_2OH$, under which conditions the compounds were sufficiently stable for the determination. The τ-values for IX obtained thereby were similar to those cited above: 8.48, 8.31, 6.83, and 6.14. The signals for compound XI appeared at τ 8.34, 6.87, 6.14, and 5.68, with those at 6.14 and 5.68 forming an easily recognizable A_2B_2 pattern. The signal for the methylene protons next to oxygen in XI were at much lower field than any of the previously observed methylene-proton resonances in oxazolidinium salts of known structure VI and those here described.[12b]

TABLE I

STRUCTURES AND N.M.R. SPECTRAL VALUES OF THE OXAZOLIDINIUM PERCHLORATES[a]



[a] Determined in CH_2Cl_2 unless otherwise stated. [b] In D_2O. [c] In CF_3COOH.

The generality of the reaction has been established by combination of 1,1,2,2-tetramethylaziridinium perchlorate (VII) with a series of cyclic, acyclic, and aromatic ketones (Tables I and II). The conditions employed were excess ketone at about 65° for 12–24 hr. Each new oxazolidinium salt was characterized by analytical and spectral data and by structural analogy to IX. The yields of the oxazolidinium perchlorates (XII–XVII) as initially obtained were high throughout the series, but loss was encountered in the isolation of the

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[12] (a) E. Bergmann, E. Zimkin, and S. Pinchas, *Rec. trav. chim.*, **71**, 237 (1952). (b) Whereas the N^+-CH_2 signal was assigned initially by analogy, confirmation of the chemical shift for the O-CH_2 was obtained from the model compound, 2,2,3,4,4-pentamethyloxazolidine iodide (Xa), prepared by treatment of 2,2,4,4-tetramethyloxazolidine with methyl iodide. The τ-values observed in deuterium oxide with $(CH_3)_3SiCH_2CH_2CH_2SO_2OH$ as an internal standard are shown.

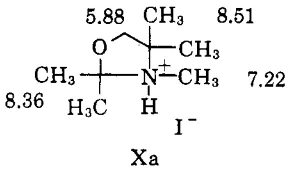
Xa

TABLE II[a]

Structure	Perchlorate	Yield, %	M.p., °C.	Formula	C, %		H, %		N, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
XI	2,2,3,3-Tetramethyloxazolidinium		230–231	$C_7H_{16}ClNO_5$	36.61	36.66	7.02	6.91	6.10	5.86
IX	2,2,3,3,5,5-Hexamethyloxazolidinium	55	188–189	$C_9H_{24}ClNO_5$	41.95	41.93	7.82	7.86	5.43	5.39
XII	2,2,4,4-Tetramethyl-1-oxa-4-azoniaspiro[4.4]nonane	60	163.5–164.5	$C_{11}H_{22}ClNO_5$	46.55	46.27	7.82	7.79	4.94	5.12
XIII	2,2,4,4-Tetramethyl-1-oxa-4-azoniaspiro[4.5]decane	52	175.5–176.0	$C_{12}H_{24}ClNO_5$	48.39	48.31	8.13	8.16	4.70	4.54
XIV	3′,3′,5′,5′-Tetramethylspiro[indan-1,2′-oxazolidinium]	60	142.5–143.0	$C_{15}H_{22}ClNO_5$	54.29	54.02	6.98	6.84	4.22	4.02
XV	2,3,3,5,5-Pentamethyl-2-phenyloxazolidinium	27	150–151	$C_{14}H_{22}ClNO_5$	52.57	52.34	6.93	6.98	4.38	4.54
XVI	6,6,8,8-Tetramethyl-5-oxa-8-azoniaspiro[3.4]octane	73	165–166	$C_{10}H_{20}ClNO_5$	44.53	44.52	7.47	7.44	5.19	5.31
XVII	2-Cyclopropyl-2,3,3,5,5-pentamethyloxazolidinium	47	164.5–165.5	$C_{11}H_{22}ClNO_5$	46.55	46.71	7.82	7.90	4.94	4.70
XVIII	14,14-Dimethyl-13-oxa-5-azoniadispiro[4.1.5.2]tetradecane	81	183.5–184.0	$C_{14}H_{26}ClNO_5$	51.92	51.80	8.09	8.17	4.33	4.24
XIX	Cyclohexanespiro-5′-oxazolidine-3′-spiro-1″-pyrrolidinium-2′-spirocyclobutane	52	163–164	$C_{15}H_{26}ClNO_5$	53.65	53.69	7.80	7.86	4.17	4.32
XX	3-Benzyl-2,2-dimethyl-3-ethyl-1-oxa-3-azoniaspiro[4.5]decane	40	123.5–124.0	$C_{19}H_{30}ClNO_5$	58.82	58.83	7.79	7.87	3.61	3.77
XXI	14-Benzyl-14-ethyl-6-oxa-14-azoniadispiro[4.1.5.2]tetradecane	32	136–137	$C_{21}H_{34}ClNO_5$	60.94	61.08	7.79	7.86	3.38	3.43
XXII	14-Benzyl-14-ethyl-7-oxa-14-azoniadispiro[5.1.5.2]pentadecane	44	154–155	$C_{22}H_{34}ClNO_5$	61.73	61.30	8.01	8.28	3.27	3.02

[a] It has come to our attention that compounds Va–i and IX in ref. 1 were incorrectly named by giving numbering priority to the hetero atoms rather than to the spiro atoms as required by the I.U.P.A.C. 1957 Rules for Nomenclature of Organic Chemistry [*J. Am. Chem. Soc.*, **82**, 5572 (1960)]; for example, compound Va in ref. 1 is properly named 14-phenyl-13-oxa-5-azoniadispiro[4.1.5.2]tetradecane perchlorate.

products in analytically pure form. No rearrangements of the ketone moieties were encountered. The main side reaction observed in the cases where the crude products were examined by n.m.r. spectra was thermal rearrangement,[3,9] leading to an iminium salt of type V, specifically N-isobutylidenedimethylaminium perchlorate (or N,N-dimethyliosbutylideneiminium perchlorate). The presence of trace quantities of water in the ketone gave an additional product derived from hydrolysis of the aziridinium salt (→ type IV).[5,6,8] The ratio of oxazolidinium salt to iminium salt formed during the reaction of VII wih acetone varied with temperature. At 55° the ratio was 3.0:1 and at 80°, 1.8:1.

Further generality was achieved by variation of the aziridinium compound. Reaction of 5-azoniadispiro[4.0.5.1]dodecane perchlorate[4,5] with acetone gave 14,14-dimethyl-13-oxa-5-azoniadispiro[4.1.5.2]tetradecane perchlorate (XVIII). The reaction of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate[13] with acetone gave 3-benzyl-2,2-dimethyl-3-ethyl-1-oxa-3-azoniaspiro[4.5]decane perchlorate (XX). The properties of these and other products from the reaction of 5-azoniadispiro[4.0.5.1]dodecane perchlorate and 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate with ketones are given in Tables I and II.

It was expected that in some of the oxazolidinium salts the $-\overset{|}{\underset{|}{N}}{}^{+}$-methyl resonances would be nonequivalent. The differences observed between the signals for the protons of the two N$^+$-methyl groups for 3′,3′,5′,5′-tetramethylspiro[indan-1,2′-oxazolidinium] perchlorate (XIV) and 2-cyclopropyl-2,3,3,5,5-pentamethyloxazolidinium perchlorate (XVII) were 5 and 3 c.p.s., respectively. A much larger chemical shift difference, 42 c.p.s., was observed for 2,3,3,5,5-pentamethyl-2-phenyl oxazolidinium perchlorate (XV). The large diamagnetic shift of the N$^+$-methyl protons *cis* to the phenyl ring can be accounted for by the anisotropy of the aromatic nucleus.[14]

The over-all results of the reaction of aziridinium salts with aldehydes and ketones may be represented as ③$^+$ + 2 → ⑤$^+$, descriptive of a broad type in which a charged, three-membered cycle is increased in size to a charged, five-membered cycle. Since the ring-expansion reaction occurs under conditions which may also lead to thermal rearrangement and to solvolysis, and since the products of all three reactions may be explained satisfactorily by the development of a carbonium ion (III → IV, V, and VI), a further description of the general reaction includes as a first stage (*e.g.*, VII → VIII) the opening of the aziridinium ring, with the generation of the electrophilic center, and as a second stage (*e.g.*, VIII → IX) the "1,3-polar cycloaddition" of the nucleophile.[15] In sequels to this paper we shall describe the reaction of aziridinium salts with other weak nucleophiles, such as nitriles, as part of our study of general methods and mechanisms of ring-size conversions.

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(13) N. J. Leonard, B. Müller, and P. C. Kelley, unpublished results.

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, 1959, p. 18.

(15) In the second stage, the reaction does not conform to the definition given by R. Huisgen [*Angew. Chem., Intern. Ed. Engl.*, **2**, 565 (1963)] for 1,3-dipolar cycloaddition, to which it bears resemblance. Both the initial compound and the possible polar intermediate in our sequence bear a full formal positive charge, unlike the 1,3-dipoles which Professor Huisgen has considered.

Experimental[16]

1,1,2,2-Tetramethylaziridinium Perchlorate (VII).—A solution of 13.0 g. (0.070 mole) of N-isopropylidenedimethylaminium perchlorate[7] in 250–300 ml. of anhydrous acetonitrile maintained at 0° was treated with excess diazomethane in 200 ml. of ether. During the addition nitrogen was evolved very rapidly, and the diazomethane solution was decolorized. When the acetonitrile–ether solution remained colored, the addition was stopped. The solution was stirred at 0° for 15 min., a few drops of acetic acid were added to remove excess diazomethane, and then ether was added to perceptible turbidity. After standing for 2 days at −20° the solution was filtered, yielding 13.0 g. (93%) of a colorless solid, m.p. 149.0–149.5°. No infrared maxima corresponding to N^+—H and $C{=}N^+$ were found. N.m.r. signals occurred (CH_2Cl_2, TMS as internal standard) at τ 6.84 (six protons), 6.98 (two protons), and 8.28 (six protons).

Anal. Calcd. for $C_6H_{14}ClNO_4$: C, 36.09; H, 7.07; N, 7.01; Cl, 17.76. Found: C, 36.03; H, 7.08; N, 6.94; Cl, 17.55.

2,2,3,3,5,5-Hexamethyloxazolidinium Perchlorate (XX).—A solution of 2.00 g. (9.28 mmoles) of 1,1,2,2-tetramethylaziridinium perchlorate (VII) in 10 ml. of dry acetone was heated under reflux for 12 hr. and allowed to cool. The acetone was removed *in vacuo* and the solid remaining was recrystallized from 2-propanol giving 1.37 g. (55%) of material, m.p. 188–189° (see Tables I and II).

The reaction with other ketones was carried out usually at about 65° for 12–24 hr. The reaction mixture was worked up by removing the ketone *in vacuo* or by pouring the reaction mixture into ether, followed by recrystallization of the resulting solid from 2-propanol or 2-propanol–ethyl acetate. The oxazolidinium salts were usually soluble in water. However, treatment of the crude reaction mixture with a small quantity of water hydrolyzed any iminium salt present and on extraction with methylene chloride separated the amine perchlorate from the reaction mixture. The removal of one salt from the mixture in some cases facilitated further purification.

2,2,3-Trimethyloxazolidine.[12a]—A solution of 78.0 g. (1.04 moles) of N-methylethanolamine in 200 ml. of anhydrous acetone containing 100 g. of Linde Molecular Sieves 4A was allowed to stand at 25° for 18 hr. The solution was decanted from the sieves and the liquid was distilled through a 1-ft. saddle column, giving 78.0 g. (73%) of 2,2,3-trimethyloxazolidine, b.p. 120–121°, n^{25}_{D} 1.4250 (lit. b.p. 123°, n^{30}_{D} 1.4214).[12a] The n.m.r. spectrum in carbon tetrachloride with tetramethylsilane as internal standard had signals at τ 6.27, 7.13, 7.74, and 8.89 of area ratio 2:2:3:6, respectively. The signals at τ 6.27 and 7.13 formed an A_2B_2 pattern with the two equal AB coupling constants J = 6.5–7.0 c.p.s.[17]

2,2,3,3-Tetramethyloxazolidinium Iodide.—A solution of 10.3 g. (0.10 mole) of 2,2,3-trimethyloxazolidine in 100 ml. of ether was treated with 20.0 g. (0.14 mole) of methyl iodide. The mixture was allowed to stand at room temperature for 24 hr., and the colorless solid was collected giving 22.1 g. (85%) of 2,2,3,3-tetramethyloxazolidinium iodide, m.p. 224–226°. The infrared spectrum did not possess any maximum corresponding to N^+–H.

2,2,3,3-Tetramethyloxazolidinium Perchlorate (XI).—A solution of 3.0 g. (0.012 mole) of 2,2,3,3-tetramethyloxazolidinium iodide in 10 ml. of water was treated with 1 part of 70% aqueous perchloric acid with 1 part of ethanol and warmed for a few minutes on a steam bath. To the solution was added 50 ml. of ethanol and 50 ml. of ether. The resulting precipitate was collected and dried *in vacuo* yielding 2.45 g. (91%) of the perchlorate, m.p. 230–231°. The n.m.r. spectrum in deuterium oxide as 35% w./v. solution with $(CH_3)_3SiCH_2CH_2CH_2SO_3H$ as internal standard had signals at τ 5.68, 6.14, 6.87, and 8.34. The signals at τ 5.68 and 6.14 formed an easily recognizable A_2B_2 pattern.

Anal. Calcd. for $C_7H_{16}ClNO_5$: C, 36.61; H, 7.02; N, 6.10. Found: C, 36.66; H, 6.91; N, 5.86.

Examination of the Reaction of VII and Acetone by N.m.r.—A sample of VII (*ca.* 100 mg.) was dissolved in 0.4 ml. of acetone, placed in an n.m.r. sample tube, and sealed. The sample was heated at the appropriate temperature (55 and 80°) for various lengths of time. When the relative areas of the various signals remained constant (12 and 3 hr. at 55 and 80°, respectively) the reaction was stopped. The aziridinium salt (VII) had signals at τ 6.83, 6.90, and 8.24. The oxazolidinium salt IX had signals at τ 6.07, 6.74, 8.24, and 8.48. The iminium salt V had signals at τ 1.62, 6.18, 6.28, ~7.07, and 8.68. The areas of the various signals were intergrated five times, and the ratio of the oxazolidinium salt to iminium salt was calculated. The ratios at 55 and 80° were 3.0 ± 0.1 to 1 and 1.8 ± 0.1 to 1, respectively.

Thermal Rearrangement of 1,1,2,2-Tetramethylaziridinium Perchlorate (VII).—A sample (0.50 g., 2.5 mmoles) of 1,1,2,2-tetramethylaziridinium perchlorate was heated at about 120° for 45 min. The sample very slowly melted and formed a clear oil which crystallized on cooling. Rapid recrystallization from ethanol yielded 0.39 g. (78%) of material, m.p. 139–140°, ν_{max}^{Nujol} 1698 cm.$^{-1}$. The n.m.r. spectrum in methylene chloride had signals at τ 1.76 (doublet, 1H, J = 9.0 c.p.s. with further splitting into a septuplet, J = 1.4 c.p.s., $HC{=}N^+$), 6.24 (doublet, 3H, J = 0.9 c.p.s.), 6.40 [doublet, 3*H*, J = 1.5 c.p.s., $N^+(CH_3)_2$], *ca.* 7.07 [multiplet, 1H, $(CH_3)_2CH$], and 8.70 [doublet, 6H, J = 6.7 c.p.s., $(CH_3)_2CH$]. In acetone the signals appeared at τ 1.62, 6.18, 6.28, 7.07, and 8.68 and had the same multiplicity and relative area. The n.m.r. and infrared spectra were identical with the spectra of N-isobutylidenedimethylaminium perchlorate[18] prepared from isobutyraldehyde and dimethylamine perchlorate.[7]

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(16) All melting points are corrected; boiling points are uncorrected. We are indebted to Mr. Josef Nemeth, Mrs. Mary Rose Kung, Mrs. Mary-Ann Weatherford, Mr. G. D. Callahan, and Mrs. Ancilla S. Bay for the microanalyses and to Mr. Dick H. Johnson and Miss Gail Gregory for some of the n.m.r. spectra, obtained with a Varian Associates Model A-60 n.m.r. spectrometer. We also wish to thank Mr. Johnson for the infrared spectra obtained with a Perkin-Elmer Model 21 or Model 521 spectrophotometer.

(17) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 144.

(18) N. J. Leonard and W. Musliner, unpublished results.