Preparation of Indenyllithium–Ethylenediamine. From Lithium Metal.—The apparatus was the same as that used above.

Lithium metal powder (0.37 g.-atom) was placed in the reactor and was followed by toluene (370 ml.). Ethylenediamine (0.37 mole) was added dropwise over a period of 20 min. with stirring. The temperature rose to reflux[13] during the addition and was maintained at reflux by heating for 30 min.

Indene (0.37 mole) was added over a 15-min. period. After an additional 15 min. the flask was cooled to room temperature. The resultant oil was crystallized by the addition of a seed crystal. The product was isolated as above in 95% recovered yield.

The same general procedure can be used with other hydrocarbons and diamines.

Preparation of Lithium Phenylacetylide Using Catalytic Quantities of 1,4-Diaminobutane.—The apparatus was the same as that used above.

Lithium metal powder (0.370 g.-atom), toluene (370 ml.), phenylacetylene (0.370 mole), and 1,4-diaminobutane (0.037 mole) were combined and heated at reflux for 4 hr. The resultant slurry was cooled to room temperature, filtered, washed with pentane, and dried under argon. The product was recovered in 88% yield.

Preparation of Sodium Phenylacetylide Using Catalytic Quantities of Ethylenediamine.—The apparatus was the same as above, except a 500-ml. flask was used.

Sodium metal (0.200 g.-atom) was dispersed in toluene (200 ml.). The slurry temperature was adjusted to 35° and ethylenediamine (0.020 mole) was added. Phenylacetylene (0.200 mole) was added over a 15-min. period (cooling to maintain 35°). The system was maintained at 35° for 5 hr. The product was recovered in 95% yield.

Analytical Procedures.—The analytical procedure was similar to that previously described.[1] Unreacted free metal was determined by measuring the hydrogen evolved from a hydrolyzed sample. Total lithium was determined spectrophotometrically. Diamines were determined as the difference between total basicity and total lithium.

Vapor phase chromatographic analyses were run isothermally on a silicone 200 column against known standards.

(13) In some cases initial reaction was sluggish. Warming aided initiation.

Small Charged Rings. VI. Expansion of the Aziridinium Ring by Reaction with Nitriles. A New Type of Benzylating Agent[1-3]

NELSON J. LEONARD AND LEONARD E. BRADY

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

Received September 14, 1964

The general (③$^+$ + ^{2} → ⑤$^+$) ring-expansion reaction of aziridinium salts has been extended to include reaction with nitriles, leading to formation of imidazolinium salts. Some N-alkyl-N-benzylimidazolinium salts have been found to undergo facile removal of the benzyl group and can serve as benzylating agents toward a variety of nucleophiles under acidic conditions.

We have extended the scope of the general[1,4] ③$^+$ + ^{2} → ⑤$^+$ ring-enlargement reaction of aziridinium salts to include synthesis of imidazolinium salts by interaction with nitriles[5] as weak nucleophiles. Postulated[1,4] for this general reaction is, as a first stage, the development of the more stable carbonium ion resulting from cleavage of the aziridinium ring, a β-3°-amino-3°-carbonium ion. At least two mechanistic pathways are available for the second stage of the reaction, which results in the formation of the five-membered ring (eq. 1). One possibility involves the intermediacy of a resonance-stabilized carbonium–oxonium ion in the case of aldehydes[4] and ketones[1] and a carbonium–nitrilium ion in the case of nitriles,[6] the subject of the present investigation. Attack of the nitrogen unshared pair of electrons on the carbonium ion center would complete the cyclization. The other major possibility is for an effective "1,3-polar cycloaddition" of the nucleophile to occur directly, with no semiattached intermediate detectable. Possible analogy may be found in the reaction of nitriles with azide anion[7] and with "1,3-dipolar" units such as hydrazoic acid,[8] alkyl azides,[9] diazoalkanes,[10] ketocarbenes,[11] azomethine imines,[12] nitrile imines,[13] nitrile oxides,[14] and nitrile ylides.[15]

When 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (I), $C_{16}H_{24}ClNO_4$, was heated with excess acetonitrile a new substance, $C_{18}H_{27}ClN_2O_4$, was formed. Evidence that aziridinium ring expansion had taken place as expected[1,4] to give 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate (II) was seen in the infrared spectrum, where C=N stretching absorption appeared at 1715 cm.$^{-1}$. The high frequency was consistent with a neighboring positive charge. The structure assignment was also substantiated by the n.m.r. spectrum, in which signals were found for the imidazolinium methylene as an AB system of doublets at τ 6.13 and 6.55 and for the 2-

(1) Paper V: N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *J. Org. Chem.*, **29**, 3383 (1964).

(2) This investigation was supported by a research grant (USPHS-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.

(4) N. J. Leonard, E. F. Kiefer, and L. E. Brady, *J. Org. Chem.*, **28**, 2850 (1963).

(5) We wish to acknowledge the initial observation by Dr. Bertold Müller in this laboratory of the alteration in structure of an aziridinium salt on refluxing in acetonitrile.

(6) Analogy is found in the Ritter reaction: J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, **70**, 4045 (1948); J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948).

(7) R. M. Herbst and K. R. Wilson, *J. Org. Chem.*, **22**, 1142 (1957); W. G. Finnegan, R. A. Henry, and R. Lofquist, *J. Am. Chem. Soc.*, **80**, 3908 (1958); R. Huisgen, J. Sauer, H. J. Sturm, and J. H. Markgraf, *Ber.*, **93**, 2106 (1960).

(8) J. S. Mihina and R. M. Herbst, *J. Org. Chem.*, **15**, 1082 (1950).

(9) W. R. Carpenter, *ibid.*, **27**, 2085 (1962); L. Möbius and H. Wagenhofer, unpublished results, Munich, 1962, cited by R. Huisgen, *Angew. Chem., Intern. Ed. Engl.*, **2**, 565 (1963).

(10) A. Peratoner and E. Azzarello, *Gazz. chim. ital.*, **38**, 76 (1908); A. Tamburello and A. Milazzo, *ibid.*, **38**, 195 (1908); E. Oliveri-Mandala, *ibid.*, **40**, 120 (1910); C. Pederson, *Acta Chem. Scand.*, **13**, 888 (1959).

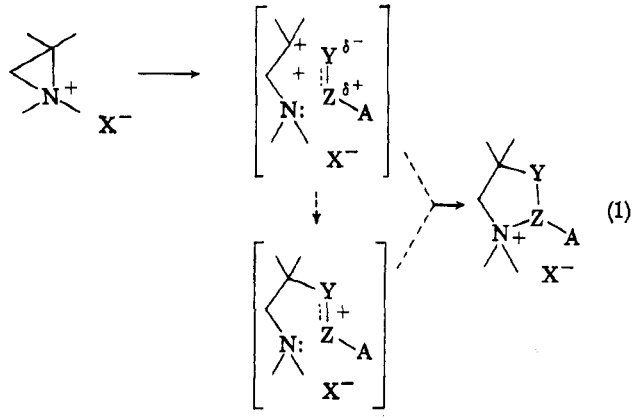
(11) R. Huisgen, H. König, G. Binsch, and H. J. Sturm, *Angew. Chem.*, **73**, 368 (1961); F. Weyland, H. Dworschak, K. Koch, and S. Konstas, *ibid.*, **73**, 409 (1961).

(12) R. Grashey, H. Leitermann, R. Schmidt, and K. Adelsberger, *ibid.*; **74**, 491 (1962); *Angew. Chem., Intern. Ed. Engl.*, **1**, 406 (1961); R. Huisgen, *ibid.*, **2**, 565 (1963).

(13) R. Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, **24**, 892 (1959); R. Huisgen, R. Grashey, M. Seidel, G. Wallbillich, H. Knupfer, and R. Schmidt, *Ann.*, **653**, 105 (1962).

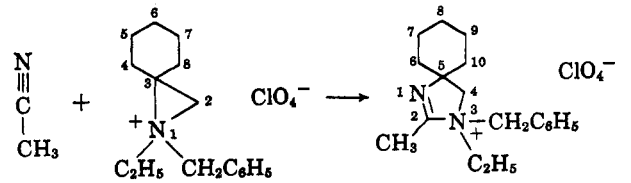
(14) G. Leandri and M. Pallotti, *Ann. chim.* (Rome), **47**, 376 (1957); R. Huisgen, W. Mack, and E. Anneser, *Tetrahedron Letters*, 587 (1961).

(15) R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem., Intern. Ed. Engl.*, **1**, 50 (1962); *Angew. Chem.*, **74**, 31 (1962).



(1)

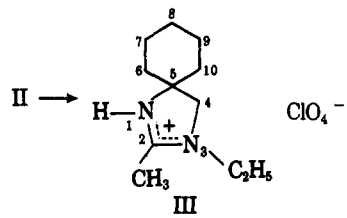
methyl group as a three-proton singlet at 7.42 p.p.m. An alternate structure, namely, 1-benzyl-1-ethyl-2-methyl-3-aza-1-azoniaspiro[4.5]dec-2-ene perchlorate, might result from the less likely route in which acetonitrile would attack the 2-position of I in an SN2 man-



I II

ner followed by cyclization. In such a formulation, n.m.r. signals for the imidazolinium protons, which would then be β to $-N^+<$ and α to $N{=}C<$, would be expected from consideration of models available in this laboratory to appear *below* 6.0 p.p.m.

A new type of combined functionality ($-N{=}\overset{|}{C}\ N^+<$) is contained in II as formulated. Catalytic debenzylation of the α-imino-4°-ammonium salt using palladium on carbon catalyst furnished chemical evidence for the structure proposed. Toluene was detected and 3-ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (III),

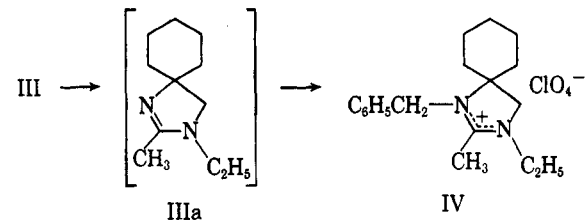


III

$C_{11}H_{21}ClN_2O_4$, was isolated. The structure III was supported by the n.m.r. spectrum with τ-values for the signals of one (N-H) proton at τ 1.47 (singlet) and a two-proton singlet for the imidazolinium methylene at 6.32 p.p.m. The infrared spectrum of III had absorption maxima at 3285 (N-H), 1620, and 1575 cm.$^{-1}$. The last two bands are believed due to symmetric and antisymmetric compound vibrations of the N-C-N structure analogous with similar bands in the spectra of carboxylate anion[16a] and amidinium salts.[16b] That these bands were not due to Fermi resonance or combination band phenomena involving the N-H deformation frequencies was shown by a deuterium-exchange experiment giving material the infrared spectrum of which showed marked diminution of the bands at ν_{max}^{KBr} 3285 and 1575 cm.$^{-1}$ and simultaneous appearance of new bands at ν_{max}^{KBr} 2450 and 1555 cm.$^{-1}$. The direction and magnitude of the shift from 1575 to 1555 cm.$^{-1}$ are appropriate for the simple mass difference between N-H and N-D at the end of a vibrating system.

Additional information concerning these absorption bands is obtained by conversion of III by treatment with sodium hydroxide to its ether-soluble, distillable free base. The base, which can be reconverted to III by addition of perchloric acid, has no infrared absorption assignable to N-H vibrations but has a single absorption band at 1620 cm.$^{-1}$.

Further evidence against the participation of N-H vibrations in these maxima was secured by synthesis of an equivalent structure without N-H. Conversion of III to the free base, 3-ethyl-2-methyl-1,3-diazaspiro-[4.5]dec-1-ene (IIIa), alkylation with benzyl bromide, and treatment with silver perchlorate gave pure 1-benzyl-3-ethyl-2-methyl-3-aza-1-azoniaspiro[4.5]dec-1-ene perchlorate (IV), isomeric with II but shown different by melting point, mixture melting point, and comparison of infrared and n.m.r. spectra; no N-H absorption was detectable, ν_{max}^{KBr} 1615 and 1560 cm.$^{-1}$. The n.m.r. spectrum was consistent with the structure IV (see Experimental).



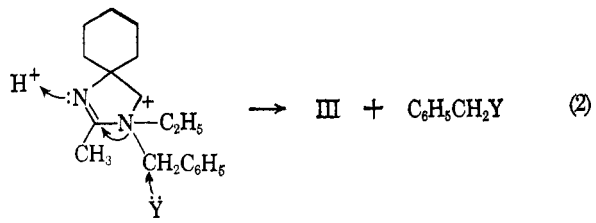
IIIa IV

Re-examination of the crystallization mother liquor from purification of the product II from the reaction of I with acetonitrile disclosed the presence of a second product which was easily identified as III by direct comparison with the compound obtained by catalytic hydrogenolysis. The implied ease of debenzylation of II was investigated and this reaction was found to proceed with remarkable facility. Since recrystallization of II had been from hot ethyl acetate solution, a sample of II was heated under reflux for 72 hr. in ethyl acetate. At the end of this period chilling gave 68% of III; dilution of the filtrate with ether gave additional material whose infrared spectrum showed it to be a mixture of debenzylation product with unreacted II. Concentration of the liquor gave a few drops of liquid shown, by comparison of infrared spectra and of retention times in vapor phase chromatography, to be identical with a known sample of benzyl acetate.

Suspicion that debenzylation of II in ethyl acetate might be due to the presence of small amounts of acetic acid was strengthened by the finding that II could be debenzylated quantitatively to III by dissolving it in glacial acetic acid and reprecipitating immediately with ether.

We have suggested[3] a mechanism for this reaction involving attack by a proton at N-1 as nucleophilic displacement of N-3 from the benzyl group takes place (eq. 2). This view of the course of debenzylation with

(16) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 174. (b) E. Lieber, D. R. Levering, and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951); T. Goto, K. Nakanishi, and M. Ohashi, *Bull. Chem. Soc. Japan*, **30**, 723 (1957).



loss of the benzyl group leading to formation of the more stable delocalized structure III is consistent with the mechanism proposed for other dealkylations in which delocalization energy supplies the driving force for reaction, *e.g.*, nucleophilic displacement of certain esters or the dealkylation of barbituric acid derivatives (breaking of a C–C bond).[17] The tendency of imidazoline itself to undergo 1,3-dialkylation rather than monoalkylation[18] supplies another instance of reaction favored by development of a delocalized system with structural features almost identical with those of III.[19]

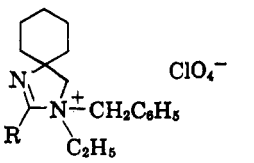
Pilot synthetic application of our proposed mechanism was made by heating II in a phenol melt. Work-up by dilution with ether gave III in high yield. A similar debenzylation with *p*-cresol gave virtually quantitative conversion of II. In each of these procedures the ether solution was base and acid washed, and vapor phase chromatography showed the presence of two peaks whose retention times matched those of the expected aryl benzyl ether and (in each case) dibenzyl ether. The appearance of the latter compound was unexpected but could be rationalized by postulating partial hydrolysis of II producing III and benzyl alcohol, followed by alcoholysis of more II to give dibenzyl ether. This hypothetical sequence was supported by experiments designed to demonstrate the feasibility of each step. Compound II was heated in benzyl alcohol, and the mixture worked up by dilution with ether yielded debenzylated product and starting material. In another experiment, a suspension of II in very dilute aqueous perchloric acid was warmed only until solution was complete and then cooled and extracted with ether. Evaporation of the aqueous solution gave pure III in high yield, and vapor phase chromatography of the concentrated ether solution revealed the presence of a single solute whose retention time matched that of benzyl alcohol.

Generality of the aziridinium ring-expansion reaction with nitriles was tested by heating 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (I) in boiling propionitrile to form 3-benzyl-2,3-diethyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate (V) in fair yield. The infrared and n.m.r. spectra of this product were very similar to those of II except that the imidazolinium methylene protons were equivalent in V.

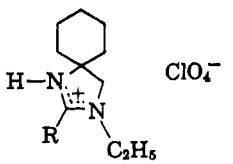
That V underwent debenzylation readily was shown by warming a sample in glacial acetic acid to effect solution followed by immediate dilution with ether to give 2,3-diethyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (VI) in excellent yield. The infrared spectrum of VI contained absorption bands at ν_{max}^{KBr} 3300 (N–H), 1615, and 1580 cm.$^{-1}$ as anticipated by analogy with III. The n.m.r. spectrum of VI was virtually the same as that of III showing as the principle difference the (C-ethyl) methylene quartet.

Aziridinium ring expansion of I with phenylacetonitrile yielded the already N-debenzylated product, 2-benzyl-3-ethyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (VII), in good yield. Finally, when I was heated with benzonitrile, the product isolated in modest yield was 3-ethyl-2-phenyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (VIII). These two products were characterized by elemental analysis and infrared and n.m.r. spectra.

The chemical conversions forming the subject matter of this paper have enabled us to extend the scope of synthetic utilization of aziridinium salts in the ③$^+$ + 2 → ⑤$^+$ reaction and have introduced a new type of benzylating agent. While the specific compounds used for benzylation in this paper may not have general utility because of their complexity, it may be that the principle demonstrated may lead to development of alkylation procedures using reagents of structure analogous to the new α-imino-4°-ammonium salts.



V, R = C_2H_5



VI, R = C_2H_5
VII, R = $C_6H_5CH_2$
VIII, R = C_6H_5

Experimental[20]

1-Benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (I) was prepared[21] by a modification of the general synthesis[22,23] of such salts. A solution of N-benzyl-N-ethylcyclohexylideneiminium perchlorate in methylene chloride was treated with a slight excess of ethereal diazomethane at 0°. Dilution with ether and cooling to −70° caused separation of the pure aziridinium salt in greater than 90% yield: m.p. 115° (122.5° upon rapidh eating); no infrared absorption assignable to N–H, C=O, or C=N$^+$; n.m.r. τ-values (DMSO-d_6, TMS) 2.38 (5H), 5.60 (s, 2H), 6.6–7.1 (unresolved multiplet, 2H), 6.92 (s, 2H, aziridinium ring protons), 8.2–9.0 (unresolved, 10H), and 8.66 p.p.m. (t, J = 7 c.p.s., 3H).

Anal. Calcd. for $C_{16}H_{24}ClNO_4$: C, 58.26; H, 7.33; N, 4.25. Found: C, 58.25; H, 7.24; N,4.09.

Reaction of I with Acetonitrile.—A solution of 3.00 g. (9.1 mmoles) of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate in 25 ml. of acetonitrile was heated under gentle reflux for 2 hr. The solvent was removed in a rotary evaporator and the residual sirup was crystallized by making a solution in boiling ethyl acetate turbid by addition of ether. In this way was obtained 1.92 g. (57%) of **3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate** (II): m.p. *ca.* 150° (varies widely with rate of heating); ν_{max}^{KBr} 1715 cm.$^{-1}$; n.m.r. τ-values ($CDCl_3$, TMS) 2.53 (5H, aromatic protons), an AB system of doublets (J = 13.5 c.p.s.) at 5.02 (1H) and 5.26 (1H, benzyl CH_2), 6.02 (q, J = 6.8 cps, 2H, CH_2CH_3), an AB system of doublets (J = 13.5 c.p.s.) at 6.13 (1H) and 6.55 (1H, imidazolin-

(17) E. W. Maynert and E. Washburn, *J. Am. Chem. Soc.*, **75**, 700 (1953).

(18) K. Hofmann, "Imidazole and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, p. 224; E. S. Schipper and A. R. Day, "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p. 238.

(19) Further exemplified by the synthesis of IV in this paper.

(20) All melting points were determined in open capillary tubes and are uncorrected. We are indebted to Mr. Josef Nemeth and his staff for microanalyses and to Mr. Dick H. Johnson and his co-workers for infrared and n.m.r. spectra using a Perkin-Elmer Model 521 grating spectrophotometer and a Varian Associates Model A-60 spectrometer.

(21) The supply of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate used in this investigation was prepared by Mr. P. C. Kelley in this laboratory. See forthcoming article by N. J. Leonard, P. C. Kelley, J. E. Mulvaney, B. Müller, and A. G. Cook, *J. Org. Chem.*

(22) N. J. Leonard and K. Jann, *J. Am. Chem. Soc.*, **82**, 6418 (1960).

(23) N. J. Leonard and K. Jann, *ibid.*, **84**, 4806 (1962).

ium CH_2), 7.42 (s, 3H, 2-CH_3), 8.0–9.5 (unresolved m, 10H, cyclohexane protons), and 8.67 p.p.m. (*t*, J = 6.8 c.p.s., 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, 58.20; H, 7.31; N, 7.59.

From the recrystallization mother liquors by evaporation and recrystallization from ethanol–ether was isolated 0.50 g. (20%) of **3-ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (III)**: colorless platelets; m.p. 164.5–165.5°; ν_{max}^{KBr} 3285, 1620, and 1575 cm.$^{-1}$; n.m.r. τ-values ($CDCl_3$, TMS) 1.47 (s, 1H, N–H), 6.32 (s, 2H, imidazolinium CH_2), 6.43 (q, J = 7.5 c.p.s., 2H, CH_2-CH_2), 7.67 (s, 3H, 2-CH_3), 7.9–8.8 (unresolved m, 10H, cyclohexane protons), and 8.72 p.p.m. (t, J = 7.5 c.p.s., 3H, CH_2CH_3).

Anal. Calcd. for $C_{11}H_{21}ClN_2O_4$: C, 47.04; H, 7.53; N, 9.98. Found: C, 47.32; H, 7.55; N, 9.81.

3-Ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene-1-*d* Perchlorate.—A small sample of 3-ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (III) was dissolved in 99.5% deuterium oxide and then the solvent was removed on a rotary evaporator. This operation was repeated twice more, giving finally a solid whose infrared absorption spectrum showed marked diminution of the bands at ν_{max}^{KBr} 3285 and 1575 cm.$^{-1}$ and appearance of new bands at ν_{max}^{KBr} 2450 and 1555 cm.$^{-1}$; determination of the infrared absorption spectrum in Nujol mull showed even less absorption at 3280 and 1575 cm.$^{-1}$, indicating reversal of exchange in the KBr pellet; ν_{max}^{Nujol} 3280, 2440, 1615, 1575, and 1540 cm.$^{-1}$.

Reaction of I with Propionitrile.—A mixture of 2.00 g. (6.07 mmoles) of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate with propionitrile (25 ml.) was heated under reflux for a total of 2.5 hr., cooled, and added dropwise to 150 ml. of anhydrous ether with stirring. The crude **3-benzyl-2,3-diethyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate (V)** (1.00 g., 43%; m.p. 158–163°) was recrystallized from ethanol to give colorless prisms: m.p. 170.5–171°; ν_{max}^{KBr} 1710 cm.$^{-1}$; n.m.r. τ-values (DMSO-d_6, TMS) 2.47 (5H, aromatic protons), an AB system of doublets (J = 14 c.p.s.) at 5.03 (1H) and 5.20 (1H, benzyl CH_2), 6.20 (q, J = 7 c.p.s., 2H), 6.41 (q, J = 5.5 c.p.s., 2H), 6.56 (s, 2H, imidazolinium CH_2), 8.3–9.0 (unresolved m, 10H, cyclohexane protons), and 8.71 p.p.m. (t, apparent J = 7 c.p.s., 6H).

Anal. Calcd. for $C_{19}H_{39}ClN_2O_4$: C, 59.28; H, 7.59; N, 7.28. Found: C, 59.12; H, 7.38; N, 7.10.

2,3-Diethyl-1,3-diazaspiro[4.5]dec-1-ene Perchlorate (VI).—A suspension of 0.10 g. (0.26 mmoles) of 3-benzyl-2,3-diethyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate (V) in 2 ml. of glacial acetic acid was warmed on a steam bath to effect solution (4 min.). Dilution with ether caused separation of 0.069 g. (90%) of prisms: m.p. 165–166°; ν_{max}^{KBr} 3300, 1615, and 1580 cm.$^{-1}$; n.m.r. τ-values (TFA, TMS) 6.73 (s, 2H, imidazolinium CH_2), 6.92 (q, J = 7.5 c.p.s., 2H, N-CH_2CH_3), 7.85 (q, J = 7.5 c.p.s., 2H, C-CH_2CH_3), 8.5–9.3 (unresolved, 10H, cyclohexane protons), and 9.16 p.p.m. (t, J = 7.5 c.p.s., 6H, CH_3).

Anal. Calcd. for $C_{12}H_{23}ClN_2O_4$: C, 48.88; H, 7.87; N, 9.51. Found: C, 48.78; H, 7.86; N, 9.37.

Reaction of I with Phenylacetonitrile.—Phenylacetonitrile (10 ml.) and 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate (2.00 g., 6.07 mmoles) were heated at 80–82° for 3 hr. in a stoppered flask immersed in an oil bath. The mixture was cooled and added with stirring to 100 ml. of anhydrous ether. The oil which separated was washed with ether and crystallized from ethyl acetate–ether or ethanol–ether to give 1.73 g. (80%) of **2-benzyl-3-ethyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (VII)**: m.p. 157.5–158°; ν_{max}^{KBr} 3260, 1620, and 1580 cm.$^{-1}$; n.m.r. τ-values (TFA, TMS) 2.62 (5H, aromatic protons), 6.03 (s, 2H, benzyl CH_2), 6.21 (s, 2H, imidazolinium CH_2), 6.43 (q, J = 7 c.p.s., 2H, CH_2CH_2), 8.0–8.7 (unresolved m, 10H, cyclohexane protons), and 8.82 p.p.m. (t, J = 7 c.p.s., 3H, CH_2CH_3).

Anal. Calcd. for $C_{17}H_{25}ClN_2O_4$: C, 57.22; H, 7.06; N, 7.85. Found: C, 57.13; H, 7.02; N, 7.69.

Reaction of I with Benzonitrile.—A solution of 1.65 g. (5.0 mmoles) of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate in 10 ml. of benzonitrile was heated at 64° for 17 hr., then poured with stirring into 150 ml. of anhydrous ether. The ether was decanted and the residual paste was recrystallized from ethyl acetate–isopropyl alcohol to give **3-ethyl-2-phenyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate (VIII)**: 0.43 g. (25%); colorless prisms; m.p. 224–225°; ν_{max}^{KBr} 3270, 1600, and 1565 cm.$^{-1}$; n.m.r. τ-values (TFA, TMS) 2.33 (5H, aromatic protons), 6.01 (s, 2H, imidazolinium CH_2), 6.36 (q, J = 7.5 c.p.s., 2H, CH_2CH_3), 7.9–8.9 (unresolved m, 10H, cyclohexane protons), and 8.64 p.p.m. (t, J = 7.5 c.p.s., 3H, CH_2CH_3).

3-Ethyl-2-methyl-1,3-diazaspiro[4,5]dec-1-ene perchlorate (III) was prepared from 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro-[4.5]dec-1-ene perchlorate by (A) hydrogenolysis, (B) long refluxing in ethyl acetate solution, and by treatment with (C) glacial acetic acid, (D) phenol, (E) *p*-cresol, (F) benzyl alcohol containing a trace of perchloric acid, and (G) extremely dilute aqueous perchloric acid.

A.—A stirred suspension of 1.00 g. of 5% palladium on carbon catalyst in 20 ml. of absolute ethanol was saturated with hydrogen at 1 atm. pressure and to this mixture was added a solution of 0.927 g. (2.50 mmoles) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate in 120 ml. of absolute ethanol. The mixture consumed 1 equiv. of hydrogen when stirred at 1 atm. of hydrogen pressure for 20 min. at room temperature; during the next hour no further hydrogen was used. The mixture was filtered and the catalyst was washed with ethanol. The filtrate was diluted with 15 ml. of water and boiled gently; toluene could be detected (ultraviolet) in the first few milliliters of distillate. The reaction solution was evaporated to dryness in a rotary evaporator and the solid residue was recrystallized from ethanol–ether to yield 0.557 g. (79%) of **3-ethyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate**, identical with that isolated as one of the products of reaction of 1-benzyl-1-ethyl-1-azoniaspiro[2.5]octane perchlorate with acetonitrile (see above).

B.—A solution of 0.50 g. (1.35 mmoles) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate in 50 ml. of reagent grade ethyl acetate from a freshly opened bottle was heated under reflux for 72 hr. protected by a drying tube (Drierite). Chilling and filtration gave 0.258 g. (68%) of pure **3-benzyl-2-methyl-1,3-diazaspiro[4.5]dec-1-ene perchlorate**. Dilution of the filtrate with ether caused separation of material whose infrared spectrum indicated that it consisted of the debenzylation product admixed with starting material. Concentration of the liquor gave an oil identified as benzyl acetate by comparison of infrared spectrum and retention time upon vapor phase chromatography (diisodecyl phthalate on Chromosorb P, 175°) with those of an authentic sample.

C.—A mixture of 0.10 g. (0.27 mmole) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate with 5 ml. of glacial acetic acid was warmed on a steam bath until solution was complete (approximately 15–20 sec.) then the solution was treated immediately with 50 ml. of ether. The precipitated solid was 0.75 g. (99%) of pure 3-ethyl-2-methyl-1,3-diazaspiro[4.5]-dec-1-ene perchlorate identical with that prepared above.

D.—A melt consisting of 1.0 g. of phenol and 0.200 g. (0.54 mmole) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]-dec-1-ene perchlorate was heated for 2 hr. at 60°, then dropped into 20 ml. of ether. The solid was recrystallized from ethanol–ether to give 0.135 g. (89%) of product identical with that prepared above. The ether solution was washed with 5% sodium hydroxide solution, with 6 *N* hydrochloric acid, and with water, and then dried over magnesium sulfate. Vapor phase chromatography of the residual oil from concentration of the dried ether solution (silicone rubber, 175°) showed the presence of two components whose retention times on this column were the same as those of benzyl phenyl ether and dibenzyl ether.

E.—A mixture of 0.10 g. (0.27 mmole) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate and 1.0 ml. of *p*-cresol was heated at 60° for 2 hr., cooled, and introduced with stirring into 50 ml. of anhydrous ether. The crystalline precipitate was 0.735 g. (97%) of debenzylated material identical with that from other preparations. The ether solution was washed with 5% sodium hydroxide, with 6 *N* hydrochloric acid, and with water. After drying ($MgSO_4$), the ether solution was concentrated; vapor phase chromatography on a silicone rubber column at 175° revealed the presence in the residual oil of two components whose retention times matched those of dibenzyl ether and benzyl *p*-cresyl ether.

F.—A solution of 0.86 g. (0.23 mmole) of 3-benzyl-3-ethyl-2-methyl-1-aza-3-azoniaspiro[4.5]dec-1-ene perchlorate in 10 ml. of benzyl alcohol was heated at 60° for 3 hr. After standing at room temperature overnight, a small sample of the mixture was removed and diluted with ether. The infrared spectrum of the solid thus obtained showed bands typical of the starting material as well as those of the product. A glass stirring rod was dipped into 1:1 ethanolic perchloric acid, shaken off, and then used to stir the remaining reaction mixture briefly. The mixture was then heated at 60° for 2 hr. The infrared spectrum of another small sample worked up as before indicated that starting material

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]

NELSON J. LEONARD AND JOSEPH V. PAUKSTELIS

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois

Received September 14, 1964

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}0^{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

(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).