

**Kinetics of Hydrogen-Deuterium Exchange.** Reaction mixtures were analyzed by nmr using published methods.<sup>5</sup> A mesitylene vapor bath was employed to maintain constant temperature,  $164.6 \pm 0.5^\circ$ . Tetramethylammonium chloride and/or the 3,5 positions of substrate were used as nmr reference (area) standards. The nmr signal position of methyl groups containing one or two deuterium atoms is slightly upfield relative to the original singlet.<sup>32</sup> This gave rise to shoulders on the original peak as the exchange proceeded.

Pseudo-first-order rate constants,  $k\psi$ , were obtained from plots by visually fitting the best straight line through the points. Reactions generally were followed by taking nine points over three half-lives. Only in cases where the total concentration of substrate exceeded 0.5 M and hydrogen exchange did not go to completion, an "infinity" method was employed.<sup>5c</sup> Note that  $k\psi$  reflects reactivity for a single hydrogen atom, *i.e.*, results are "statistically" corrected for the number of hydrogen atoms undergoing reaction.

Constants  $k_B$  and  $k_{OD}K_w/K_a$  were evaluated in several ways. (1) Serial dilution plots, Figure 1, have slopes  $k_B[B]/([BD^+] + [B])$  and intercepts  $k_{OD}K_w[B]/K_a([BD^+] + [B])$ . Four values of  $k\psi$

were used to determine each line. Concentrations are corrected for thermal expansion using a density factor of 0.905. This method gives the least reliable values of  $k_{OD}K_w/K_a$ . (2) Plots of  $k\psi([BD^+] + [B])/[B]$  vs.  $[BD^+]$  have slopes  $k_B$  and intercepts  $k_{OD}K_w/K_a$ ; see Figure 3. All the data obtained for a substrate were employed in constructing the plot. (3) For kinetic runs involving reaction mixtures not containing deuterium chloride,  $k = k_{OD}K_w/K_a$ . (4) This method was employed only for 2,6-dimethylaminopyridine. A plot of  $k\psi$  vs.  $[B]/([BD^+] + [B])$  has slope  $k_{OD}K_w/K_a$  and zero intercept.

**Control Runs to Determine the Stability of the Alkylpyridine.** To ensure that the disappearance of nmr signal was due to the incorporation of deuterium and not to the decomposition of substrate, control runs were carried out using proteo water and hydrochloric acid and substrate approximately half converted to its conjugate acid. In all cases no decomposition was observed, as evidence by comparison with tetramethylammonium chloride internal standard. Compounds were heated at  $164.6^\circ$  for periods corresponding to the number of half-lives for H-D exchange indicated: 2-methylpyridine (45), 2,6-dimethylpyridine (134), and 2,6-dimethyl-4-aminopyridine (94).

**Acknowledgment.** This work was generously supported by the National Science Foundation (GP-9488).

(32) H. Batiz-Hernandez and R. A. Bernheim, *Progr. Nucl. Magn. Resonance Spectrosc.*, **3**, 63 (1967).

## Small Charged Rings. XV.<sup>1</sup> Kinetics and Stereochemistry of the Ring Expansion Reaction of 2-Arylaziridinium Salts with Benzaldehyde<sup>2</sup>

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**Abstract:** The preparation and isolation of 2-aryl-substituted aziridinium (ethyleniminium) salts are described for the first time. Ethyleniminium ions of this type have previously been implicated as intermediates in adrenaline blockade. Using a series of 2-aryl-1,1-dimethylaziridinium fluoroborates with benzaldehyde, the stereochemistry of the ring expansion reaction of aziridinium salts with aldehydes,  $\textcircled{3}^+ + 2 \rightarrow \textcircled{5}^+$ , has been determined. This representative of a family of aziridinium ring expansion reactions was shown to be highly stereoselective, since only *cis*-5-aryl-3,3-dimethyl-2-phenyloxazolidinium fluoroborates were produced. The kinetics of the reaction, determined by following the nmr spectra, showed the reaction to be first order in aziridinium salt, zero order in benzaldehyde, and dependent on the substituents on the aryl ring. A Hammett correlation with  $\sigma^+$ ,  $\rho^+ = -1.25$  was observed. The stereochemical and kinetic findings preclude several mechanisms including concerted cycloaddition and favor the intermediacy of aminocarbonium ions.

In earlier reports<sup>4</sup> of ring expansion reactions of aziridinium salts with aldehydes,<sup>5</sup> ketones,<sup>6,7</sup> nitriles,<sup>7,8</sup> and nitrones<sup>7,9</sup> we have drawn conclusions concerning the

mechanism(s) of these reactions based on product studies alone. Although these  $\textcircled{3}^+ + 2 \rightarrow \textcircled{5}^+$  and  $\textcircled{3}^+ + 3 \rightarrow \textcircled{6}^+$  reactions<sup>4</sup> reveal apparent similarity, in that the heteroatom of the reacting species (aldehyde, ketone, nitrile, nitron) generally combines with the more substituted carbon of the substituted aziridinium ring to produce what have been termed normal ring expansion products, in some cases abnormal ring expansion products have been observed.<sup>7</sup> We have now undertaken a detailed study of the ring expansion reaction of some 2-aryl-1,1-dimethylaziridinium fluoroborates with benzaldehyde to clarify certain features of the mechanism.

Major possible pathways are outlined in Scheme I. The first mechanism shown involves formation of an aminocarbonium ion, **2**, which would be stabilized by the aromatic ring (a). Attack of benzaldehyde would produce a second aminocarbonium ion, **3**, from which the five-membered ring compound, 5-aryl-3,3-dimethyl-

(1) For the preceding article in this series, see N. J. Leonard and J. A. Klainer, *J. Heterocycl. Chem.*, **8**, 215 (1971).

(2) We are pleased to acknowledge the support of the National Science Foundation by Research Grant GP-8407X.

(3) National Aeronautics and Space Administration Trainee, 1966-1969; Lubrizol Foundation Fellow, 1969-1970.

(4) For reference and a summary of work in this field, see (a) N. J. Leonard, *Rec. Chem. Progr.*, **26**, 211 (1965); (b) D. R. Crist and N. J. Leonard, *Angew. Chem.*, **81**, 953 (1969); D. R. Crist and N. J. Leonard, *Angew. Chem., Int. Ed. Engl.*, **8**, 962 (1969). We wish to thank Dr. DeLanson R. Crist, Georgetown University, for helpful criticism.

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

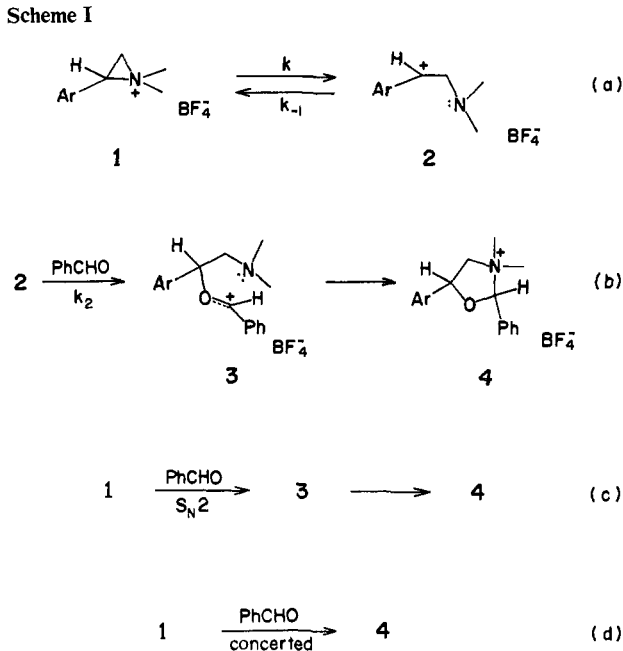
(6) N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *ibid.*, **29**, 3383 (1964).

(7) N. J. Leonard, D. B. Dixon, and T. R. Keenan, *ibid.*, **35**, 3488 (1970).

(8) N. J. Leonard and L. E. Brady, *ibid.*, **30**, 817 (1965).

(9) N. J. Leonard, D. A. Durand, and F. Uchimaru, *ibid.*, **32**, 3607 (1967).

Scheme I

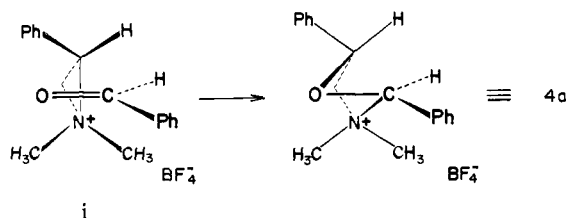


2-phenyloxazolidinium fluoroborate (4), would be formed (b). Pathway c involves nucleophilic attack by benzaldehyde on the aziridinium salt, 1, to give 3 in one step. A concerted<sup>10</sup> process (d) would give 4 directly.<sup>12</sup> These possibilities could be restricted by the accumulation of fresh experimental data.

## Results

Five aziridinium fluoroborates, 6a–e, were prepared by a modification of an earlier route in which only intermediacy of the aziridinium ion was detected.<sup>1</sup> The aralkyldiminium fluoroborates, 5, prepared from the corresponding aldehydes and dimethylamine fluoroborate, were routinely isolated in a drybox to avoid hydrolysis. The nmr spectra were similar to those reported<sup>1</sup> for the corresponding 5a, e, f perchlorates. The  $^+NCH_3$  singlets appeared as resolved resonances in the region  $\tau$  5.8–6.2 and exhibited long-range coupling,<sup>13</sup>  $J = 0.8$ –1.3 Hz, with the iminium proton, which appeared as a broadened singlet in the range  $\tau$  1.1–1.6 in trifluoroacetic acid solution. The improved solubility of the fluoroborate salts over the perchlorate salts permitted choice of a solvent of relatively low polarity for the treatment of 5 with di-

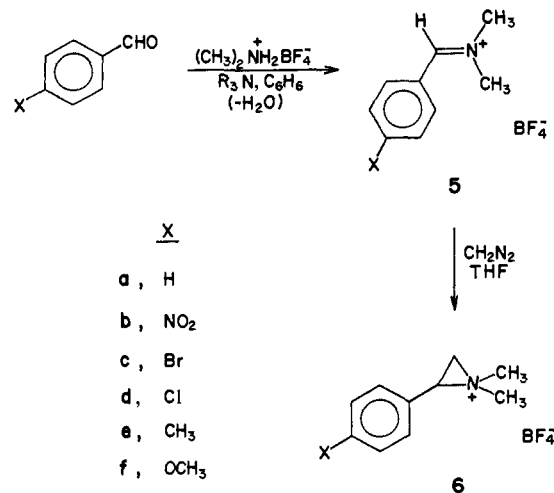
(10) A one-step thermal [ $\sigma_{2s} + \pi_{2s}$ ] or [ $\sigma_{2s} + \pi_{2s}$ ] process is theoretically allowed.<sup>11</sup> The geometry for the latter case is difficult to visualize but the former possibility can be pictured as i, where trans addition to the carbonyl double bond would give the product, 4 (cis geometry shown).



(11) For a recent review, see (a) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797 (1969); (b) R. B. Woodward, and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

(12) A one-step process  $2 \rightarrow 4$  can also be envisaged.

(13) (a) For a review of long-range coupling, see S. Sternhell, *Rev. Pure Appl. Chem.*, 14, 15 (1964); (b) also M. Barfield and B. Chakrabarti, *Chem. Rev.*, 69, 757 (1969).



azomethane. When a slight excess of (standardized) ethereal diazomethane was added slowly to a cold, stirred suspension of the iminium fluoroborate in anhydrous tetrahydrofuran, immediate evolution of nitrogen was observed and the starting material gradually dissolved. The aziridinium salt could then be precipitated with ether and recrystallized. (The 1,1-dimethyl-2-*p*-methoxyphenylaziridinium fluoroborate, 6f, could not be isolated by this procedure, but decomposed even at 0°, a feature that had been observed<sup>1</sup> for the corresponding perchlorate.) The nmr spectra of the aziridinium salts exhibited characteristic aryl resonances, and the benzylic proton appeared as a triplet,  $J = 8$  Hz, in the range  $\tau$  5.1–5.5. The methylene protons appeared as the AB portion of an ABX system<sup>14</sup> at  $\tau$  6.0–6.6. The chemical shifts of the nonequivalent methyl groups differed by approximately 0.7 ppm ( $\tau$  6.5–6.7 and 7.1–7.5, both singlets) owing to the anisotropy of the aromatic ring.<sup>15</sup> The resonance at higher field was assigned to the methyl cis to the aryl group. Additional confirmation of structure came from correct elemental analyses<sup>16</sup> and from the actual reaction with benzaldehyde. The crystalline aziridinium salts decompose slowly at room temperature but can be stored for several months at  $-20^\circ$  in a desiccator. This general procedure permitted the first isolation of aryl-substituted aziridinium salts (type 1).

A pilot reaction of 6a in benzaldehyde solution at ambient temperature was followed by nmr. The peaks for the starting material were gradually replaced by six resonances:<sup>17</sup> a singlet at  $\tau$  3.6, a triplet at  $\tau$  4.0,  $J = 7$  Hz, a doublet of doublets at  $\tau$  5.2,  $J = 7, 12$  Hz, a doublet of doublets at  $\tau$  6.0,  $J = 7, 12$  Hz, a singlet at  $\tau$  6.4, and a singlet at  $\tau$  7.1 with relative areas 1:1:1:1:3:3, respectively. The transformation proceeded cleanly with no buildup of intermediates or resonances attributable to other products within the limits of nmr detectability. Qualitative experiments indicated that the product and the rate of reaction were

(14) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, New York, N. Y., 1961, p 71 ff.

(15) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp 18, 125–129.

(16) The *p*-bromo-substituted aziridinium salt, 6c, could not be purified by repeated recrystallization, but the crude material could be used directly in subsequent experiments (see Experimental Section). Elemental composition was established for both 5c and 4c.

(17) The aromatic region was masked by solvent (benzaldehyde).

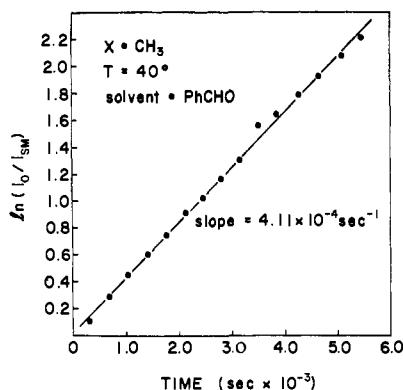
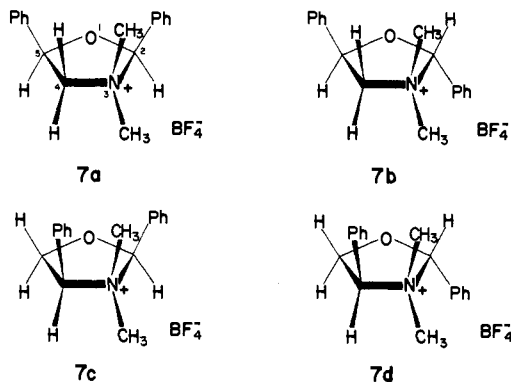


Figure 1. Typical kinetic plot for the reaction of 1,1-dimethyl-2-*p*-methylphenylaziridinium fluoroborate (**6e**) in benzaldehyde solution (value used in Table I).

unaffected by degassing the solution, small amounts of silver fluoroborate, or 1 equiv of added anhydrous fluoroboric acid.

The product from the pilot reaction was obtained in 95% yield as pure needles which had an elemental composition appropriate for a 1:1 adduct (**6a** + benzaldehyde). The nmr spectrum of the isolated material had a ten-proton multiplet in the aromatic region as well as the first-order spectrum described above which was shifted slightly in the solvent system used (see Experimental Section). Anisotropic shielding<sup>15</sup> by the aromatic rings was again largely responsible for the differentiation of the methylene protons as well as the N<sup>+</sup>-methyl groups, the higher field resonance of each being attributable to the group *cis* to an adjacent benzene ring.<sup>15,18,19</sup> The spectrum corresponded well for only one (**7a**) of the four possible *cis*-*trans* or positional isomers of a 3,3-dimethyldiphenyloxazolidinium fluoroborate (**7a-d**).<sup>20</sup> That **7a** was the correct



structure was established by observation of nuclear Overhauser effects (NOE).<sup>21-24</sup> When the lower field

(18) J. B. Hyne, *J. Amer. Chem. Soc.*, **81**, 6058 (1959).

(19) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

(20) Although for convenience only one optical isomer is shown, in each case we would like *dl*-racemates to be understood.  
(21) For theoretical discussion of this effect, see (a) R. A. Hoffmann and S. Forsén, *Progr. Nucl. Magn. Res. Spectrosc.*, **1**, 15 (1966); (b) R. Kaiser, *J. Chem. Phys.*, **39**, 2435 (1963); (c) R. Freeman and W. A. Anderson, *ibid.*, **37**, 2053 (1962).

(22) For recent reviews covering the application of this effect in organic chemistry, see (a) T. N. Huckerby, *Annu. Rep. Nmr Spectrosc.*, **3**, 1 (1970); (b) B. D. Nageswara Rao, *Advan. Magn. Resonance*, **4**, 271 (1970).

(23) For a quantitative application of NOE and a useful discussion of technique, see R. E. Schirmer, J. H. Noggle, J. P. Davis, and P. A. Hart, *J. Amer. Chem. Soc.*, **92**, 3266 (1970), and references therein.

(24) (a) N. Abe, R. Onoda, K. Shirahata, T. Kato, M. C. Woods, and

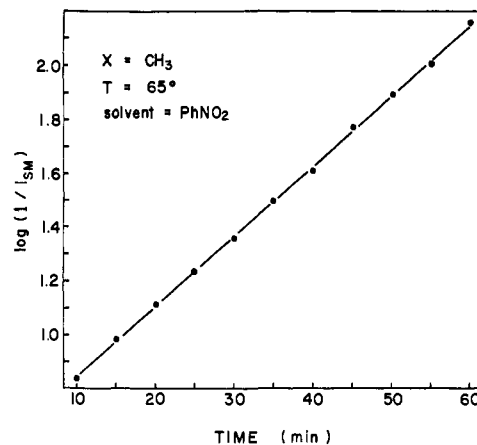
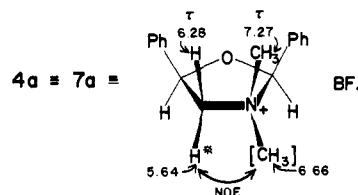


Figure 2. Reaction of equimolar quantities of **6e** and benzaldehyde in nitrobenzene solution (arbitrary units for the ordinate axis).

methyl signal ( $\tau$  6.66) was irradiated at low power levels (see Experimental Section) a 15% enhancement



of the integrated intensity of the lower field methylene proton ( $\tau$  5.64) was observed. The magnitude of this effect is appropriate for an adjacent *cis* proton and methyl pair located on a five-membered ring.<sup>24</sup> The nmr spectra of all of the 1:1 adducts, **4a-e**, show only minor differences, with the exception of the aromatic region, and a similar experiment on the *p*-nitro derivative, **4b**, revealed a 16% nuclear Overhauser effect. It is apparent that all of the 1:1 adducts possess the *cis* configuration of the two aryl groups.

The kinetics of the ring expansion reaction in degassed benzaldehyde solution could be conveniently determined by nmr by observing the disappearance of the higher field methyl signal of **6** and the appearance of the higher field methyl signal of the corresponding product, **4**. The sum of the integrated intensities of these peaks remained constant throughout the reaction relative to an internal reference signal (hexamethyldisiloxane), and the rate of disappearance of **6** was equal to the rate of appearance of **4** (see Experimental Section). The product was stable to the reaction conditions as was evidenced by an unchanged nmr spectrum after more than 20 half-lives. Plots of  $\ln(I_0/I_{sm})$  vs. time, where  $I_0$  = the initial total integral of the higher field methyl region, in arbitrary units, and  $I_{sm}$  = the integrated intensity of the starting material methyl signal, gave good straight lines extending over more than 2.5 half-lives, indicating a rate-determining step which is pseudo first order in aziridinium salt, **6** (see Figure 1). That the rate-determining step was zero order in benzaldehyde was established by a straight line plot of  $\log(I_1/I_{sm})$  vs.  $t$  extending over more than three half-lives which was obtained when an equimolar mixture of **6e** and benzaldehyde was allowed to react in nitrobenzene solution at 65° (Figure 2). The reaction in nitroben-

Y. Kitahara, *Tetrahedron Lett.*, 1993 (1968); (b) G. R. Newkome and N. S. Bhacca, *Chem. Commun.*, 385 (1969).

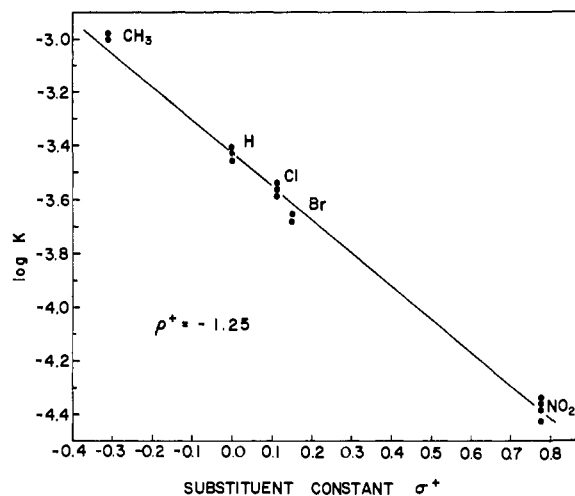


Figure 3. Plot of  $\log k$  against  $\sigma^+$  for the reaction of 2-aryl-1,1-dimethylaziridinium salts (6a-f) with benzaldehyde at 50.0°.

zene was not of synthetic utility, however, because approximately 25% of the starting material was diverted to other products,<sup>1</sup> 4e accounting for 75% of the product mixture. We therefore returned to benzaldehyde solvent for the rest of the kinetic measurements.

Rates of reaction were determined using a conventional, unweighted linear squares treatment<sup>25</sup> of the experimental data which was accomplished using an IBM 360 computer. Activation parameters were similarly determined from an Arrhenius plot of  $\ln(k)$  vs.  $1/T$  for the reaction of 6e at three temperatures in the usual manner<sup>26</sup> and are summarized in Table I.

Table I. Rate of Reaction of 6e with Benzaldehyde

$T, ^\circ\text{C}$	$k \times 10^4, \text{sec}^{-1}$	$E_a, ^b$ kcal/mol	$\Delta H^\ddagger, ^b$ kcal/mol	$\Delta G^\ddagger, ^c$ kcal/mol	$\Delta S^\ddagger, ^d$ cal/mol deg
30.0	1.25, 1.46	19.9	19.3	23.1	-12.8
40.0	3.98, 4.11, 3.94				
50.0	10.14, 10.39				
65	8.61 <sup>e</sup>				

<sup>a</sup>  $\pm 0.1^\circ$ . <sup>b</sup>  $\pm 0.6$ , determined from the scatter of the points,  $r = -0.998$ , %  $s = 2.74$ ; see ref 25 and W. F. Dixon and F. J. Massey, Jr., "Introduction to Statistical Analysis," McGraw-Hill, New York, N. Y., 1957, pp 193, 194, 199, 200. <sup>c</sup>  $\pm 0.5$  (calcd for 25°). <sup>d</sup>  $\pm 2.0$ . <sup>e</sup> Reaction in nitrobenzene solution.

The rate constants for reaction of all of the aziridinium salts, 6a-e, with benzaldehyde at 50.0° are summarized in Table II. These data were used in a Hammett plot<sup>27</sup> of  $\log k$  vs. the electrophilic substituent constant  $\sigma^+$ .<sup>28,29</sup> The plot, Figure 3, gave a reasonably

(25) W. C. Hamilton, "Statistics in Physical Science; Estimation, Hypothesis Testing, and Least Squares," Ronald Press, New York, N. Y., 1964.

(26) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., p 178 ff.

(27) For reviews, see (a) P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968; (b) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 171 ff; (c) E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 45; (d) C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964); (e) S. Ehrenson, *ibid.*, **2**, 195 (1964); (f) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (g) H. H. Jaffé, *ibid.*, **53**, 191 (1953).

(28) (a) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); (b) Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem.*

Table II. Rate Constants for the Reaction of Aziridinium Salts with Benzaldehyde at 50.0°

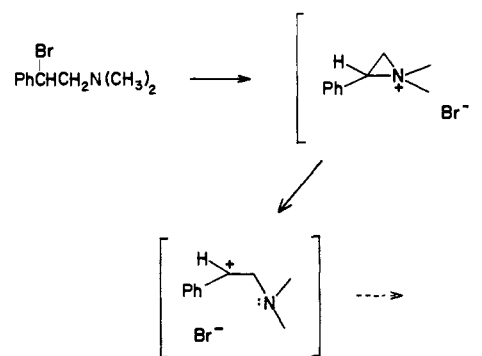
Compd no.	X	$k \times 10^4, \text{sec}^{-1}$	$\sigma^+$
6a	H	3.96	0.000
		3.62	
		3.70	
6b	NO <sub>2</sub>	0.433	0.778
		0.437	
		0.377	
		0.435	
6c <sup>a</sup>	Br	2.23	0.150
		1.97	
6d	Cl	2.77	0.114
		2.94	
		2.60	
6e	CH <sub>3</sub>	10.14	-0.311
		10.39	

<sup>a</sup> A small impurity<sup>16</sup> appears not to have affected the rate appreciably.

good regression line ( $x = -0.997$ ) from which the slope,  $\rho^+ = -1.25$ , was calculated.

## Discussion

Chapman and Triggles have reported the rate of solvolysis of 2-bromo-*N,N*-dimethylphenethylamine in 1:1 acetone-water.<sup>30</sup> Their results were explained by the postulation of rapid formation of an aziridinium ion identical with 1 (except for counterion) which then reacted *via* rate-determining formation of the aminocarbenium ion 2. This mechanism was supported by the observation of good first-order rate coefficients for disappearance of the aziridinium ion over 80-90% reaction despite the formation of several products, none of



which was formed by cleavage of the methylene-nitrogen bond. We are now able to determine rate constants directly on the 2-aryl-substituted aziridinium ions.

The first-order kinetics observed for the reaction of 6e with an equimolar quantity of benzaldehyde in nitrobenzene solution (*i.e.*, zero order in benzaldehyde) rules out the possibility that pathways c or d (Scheme I) participate significantly in the ring expansion reaction. The steps included in (b) of Scheme I are also eliminated from consideration as possible rate-determining processes. Apparently the aminocarbenium ion, 2, is not efficiently trapped by benzaldehyde in nitrobenzene solution and some other products are observed in addition.

*Soc.*, **80**, 4972 (1958); (c) H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

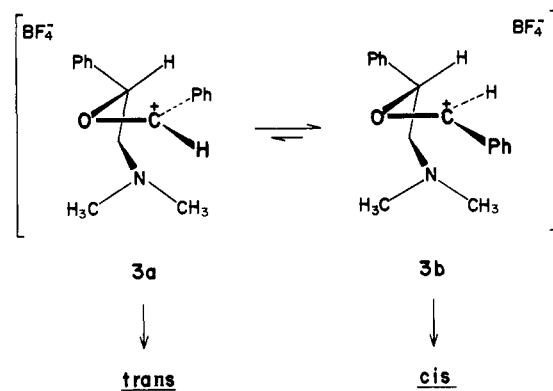
(29) The values of  $\sigma^+$  were taken from the compilation by J. S. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, pp 87, 90.

(30) N. B. Chapman and D. J. Triggles, *J. Chem. Soc.*, 1385 (1963).

tion to the major product, **4**. Side reactions are effectively eliminated in benzaldehyde solution, as would be expected for the trapping of **2** with benzaldehyde.

The Hammett correlation with  $\sigma^+$  and a negative  $\rho^+$  value agrees with the hypothesis that the transition state for the rate-determining step places additional positive charge on the benzyl carbon atom which can be stabilized by delocalization into the benzene ring as well as by the inductive effect of substituents. There are several factors which help to explain the somewhat small magnitude of  $\rho^+$  ( $-1.25$ ) relative to typical ionic processes ( $-3.3$  to  $-4.3$ ).<sup>28c,31</sup> The conjugation-extending property of three-membered rings<sup>32</sup> may place a significant portion of the positive charge into the aromatic ring in the ground state of these molecules. The proportional increase of positive charge introduced into the aromatic nucleus in going to the transition state should be less, in this case, than would be expected assuming the normal insulating effect of a saturated carbon atom. Increased strain effects in the aziridinium ring, which would be partially relieved in the transition state, might also serve to place the transition state closer to starting material in this case relative to typical ionic processes. The result would be to reduce the sensitivity of the reaction toward aromatic substituents and to decrease the magnitude of  $\rho$ .

The detection of only one product of the two possible *cis*-*trans* isomers of **4** indicates that there is considerable selectivity in the transition state leading to products. This highly stereoselective<sup>33</sup> step can best be explained by considering the conformations of the aminocarbenium ion, **3**, which are appropriate for ring closure to form product. The conformation represented by **3b** requires the least nonbonded interactions between substituents on the carbonium center and the asymmetric center.<sup>20</sup> The transition states leading to ring closure should have different energy. The one sterically more favored would produce the *cis* product when the C-N bond is formed.<sup>34</sup> In most stereoselective



processes a small proportion of the less favored isomer is also formed. We feel that this may be the case in this instance, but that a more sensitive method of detection would be required to reveal a small percentage of the *trans* isomer, corresponding to **7b** in the product mixtures.

In conclusion, the mechanism which best explains the available data for the  $\text{3}^+ + 2 \rightarrow \text{5}^+$  ring expansion reaction of 2-arylaziridinium salts with benzaldehyde is that shown in eq a and b. The rate of reaction is determined by  $k$ , the rate constant for the conversion of the aziridinium ion **1** to the  $\beta$ -aminocarbenium ion **2**. Attack by the benzaldehyde carbonyl oxygen on **2** would then produce a second aminocarbenium ion, **3**, the preferred conformation of which (**3b**) would ring-close preferentially to give the high degree of stereoselectivity observed for the oxazolidinium product.

### Experimental Section<sup>37</sup>

**Dimethylamine Fluoroborate.** A solution of 25.4 g (0.57 mol) of dimethylamine in 500 ml of absolute ethanol was stirred and cooled in an ice bath while 48–50% aqueous fluoroboric acid was added at a rate sufficient to maintain the temperature of the solution at 10–20°. The addition was discontinued when the pH reached 3 (pHdriion paper) (70 ml of fluoroboric acid), and dimethylamine was added slowly until the solution was slightly basic to pHdriion paper. The solvent was removed on a rotary evaporator, and the syrupy residue was dissolved in 400 ml of absolute ethanol and concentrated to give a semisolid, which was dissolved in 300 ml of absolute ethanol and layered with 700 ml of ether. The mixture was refrigerated ( $-20^\circ$ ) overnight, and the colorless crystals which formed were filtered and washed with ether to give 75 g (99%) of a hygroscopic solid: nmr ( $\text{CF}_3\text{COOH}$ )  $\tau$  2.0–5.0 (br m, 2,  $^+\text{NH}_2$ ), 7.02 (t, 6,  $J = 6.0$  Hz,  $\text{CH}_3\text{N}^+\text{H}_2$ ). An analytical sample was obtained by crystallization from ethanol-ether, mp 64–69°.

*Anal.* Calcd for  $\text{C}_2\text{H}_8\text{BF}_4\text{N}$ : C, 18.08; H, 6.07; N, 10.54. Found: C, 18.16; H, 6.18; N, 10.29.

***N,N*-Dimethylbenzylidiminium Fluoroborate (5a).** A mixture of 10.0 g (76 mmol) of dimethylamine fluoroborate, 20.0 ml (21.0 g, 198 mmol) of benzaldehyde, 5 drops of diisopropylethylamine, and 130 ml of benzene was heated at reflux under nitrogen with continuous removal of water with a Dean-Stark trap. After 2 days 1.4 ml (theory 1.36 ml) of water was collected, the benzene was

“Conformational Analysis,” Interscience, New York, N. Y., 1965, pp 200–203.

(36) W. G. Dauben and K. S. Pitzer in “Steric Effects in Organic Chemistry,” M. S. Newman, Ed., Wiley, London, 1956, p 36.

(37) Melting points are corrected. Nuclear magnetic resonance spectra were obtained on a Varian Associates T-60, A-60A, A-56/60, or HA-100 spectrometer using tetramethylsilane as an internal reference, unless otherwise noted. Kinetic runs were followed with an A-60A or HA-100 spectrometer equipped with a variable-temperature probe. We thank Mr. Robert L. Thrift for his assistance with the nuclear Overhauser experiments. Microanalyses were performed by Mr. Josef Nemeth and his associates. In nuclear magnetic resonance data, s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, v = very, and br = broad. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer.

(31) (a) E. Berliner and M. Q. Malter, *J. Org. Chem.*, **33**, 2595 (1968); (b) E. D. Bergmann, J. E. Dubois, and A. F. Hegarty, *Chem. Commun.*, 1616 (1968); (c) S. Nishida, *J. Org. Chem.*, **32**, 2692, 2697 (1967); (d) J. E. Dubois and W. V. Wright, *Tetrahedron Lett.*, 3101 (1967); (e) J.-P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 52 (1966); (f) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964); (g) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); (h) K. B. Wiberg, “Physical Organic Chemistry,” Wiley, New York, N. Y., 1965, p 404. (i) NOTE ADDED IN PROOF. We recognize that while the reactions in benzaldehyde and in nitrobenzene may not be ideally analogous, they do provide a reasonable means of comparison. We also recognize that in neat benzaldehyde this surrounding weak nucleophile may solvate the developing carbonium ion with appreciable inversion at C-1. We are grateful to Professor C. C. Price, University of Pennsylvania, for his suggestion that our Hammett plot can be accommodated by an  $\text{S}_{\text{N}}2$  process, but with increased cationic character on carbon in the transition state, and that this process would be favored by weakly nucleophilic entering (C=O) and leaving ( $(\text{CH}_3)_2\text{N}$ ) groups.

(32) H. H. Jaffé and M. Orchin, “Theory and Applications of Ultraviolet Spectroscopy,” Wiley, New York, N. Y., 1962, p 254.

(33) (a) E. L. Eliel, “Stereochemistry of Carbon Compounds,” McGraw-Hill, New York, N. Y., 1962, pp 68–74; (b) K. Mislow, “Introduction to Stereochemistry,” W. A. Benjamin, New York, N. Y., 1966, pp 128, 129.

(34) A single major product can be less satisfactorily explained by postulation of a fast equilibrium  $7a \rightleftharpoons 7b$ . A conservative limit for the sensitivity of nmr detection is ca. 10%, which would require ca. 1.3 kcal/mol  $\Delta G^\circ_{25}$  for an equilibrium of the isomers. Although the *cis* product would be preferred, as in *cis*- and *trans*-1,3-dimethylcyclopentane ( $\Delta G^\circ = 0.53$  kcal/mol),<sup>35,36</sup> the slight additional steric requirement of the benzene rings would be offset by the presence of heteroatoms in the ring.<sup>35</sup>

(35) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison,

removed by distillation, and a fresh 130-ml portion of benzene was added and removed by distillation. The yellow oily residue was triturated with two 170-ml portions of dry ether, and the oil was then stirred vigorously with a fresh 170-ml portion of dry ether. The solid which formed was ground under ether and filtered in a drybag to give 16.3 g (98%) of tan crystals. A saturated solution of a small portion of the product in tetrahydrofuran at 25° gave colorless hygroscopic crystals when cooled to -78°: mp 49–52°;  $\nu_{\text{max}}^{\text{Nujol}}$  1660  $\text{cm}^{-1}$  (C=N<sup>+</sup>); nmr (CD<sub>2</sub>Cl<sub>2</sub>)  $\tau$  0.99 (br s, 1, <sup>+</sup>N=CH), 2.05–2.60 (m, 5, Ar), 6.13 (d, 3, *J* = 1.0 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.27 (d, 3, *J* = 1.2 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>); nmr (CF<sub>3</sub>COOH)  $\tau$  1.09 (m, 1, <sup>+</sup>N=CH), 2.0–2.7 (m, 5, Ar), 6.01 (d, 3, *J* = 1.0 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.08 (d, 3, *J* = 1.2 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>) (identical with the spectrum of 5a perchlorate<sup>1</sup>).

***N,N*-Dimethyl-*p*-methoxybenzylideneiminium Fluoroborate (5f).** **General Method of *N,N*-Dimethylbenzylideneiminium Fluoroborate Formation.** A mixture of 10.0 ml (11.2 g, 82 mmol) of *p*-anisaldehyde, 5.0 g (38 mmol) of dimethylamine fluoroborate, and 6 drops of diisopropylethylamine in 150 ml of benzene was stirred and heated at reflux under nitrogen with continuous removal of water in a Dean-Stark trap. After 60 hr, 1.1 ml (theory 0.68 ml) of water was collected and 50 ml of benzene was removed by distillation. Benzene (50 ml) and 5 drops of diisopropylethylamine were added and heating was continued for a total of 4.5 days. Most of the benzene was then removed by distillation. The oil which remained slowly crystallized on cooling. Ether (100 ml) was then added in a drybox, and the light yellow solid was filtered and washed with ether to give 9.1 g (96%) of the crude product, mp 98–102°. One recrystallization from methylene chloride-ether gave pure material; mp 108–110°; nmr (CF<sub>3</sub>COOH)  $\tau$  1.24 (br s, 1, <sup>+</sup>N=CH), 1.92 (d, 2, *J* = 9.0 Hz, Ar), 2.55 (d, 2, *J* = 9.0 Hz, Ar), 5.92 (s, 3, OCH<sub>3</sub>), 6.04–6.05 (br s, 6, <sup>+</sup>NCH<sub>3</sub>). *Anal.* Calcd for C<sub>10</sub>H<sub>14</sub>BF<sub>4</sub>N: C, 47.85; H, 5.62; N, 5.58. Found: C, 47.74; H, 5.33; N, 5.69.

***N,N*-Dimethyl-*p*-methylbenzylideneiminium fluoroborate (5e)** was prepared in 93% crude yield from 10.0 ml (10.2 g, 85 mmol) of *p*-tolualdehyde and 5.0 g (38 mmol) of dimethylamine fluoroborate, mp 95–103°. One recrystallization from methylene chloride-ether gave the pure product; mp 114–116.5°; nmr (CF<sub>3</sub>COOH)  $\tau$  1.12 (br s, 1, <sup>+</sup>N=CH), 2.08 (d, 2, *J* = 9.0 Hz, Ar), 2.31 (d, 2, *J* = 9.0 Hz, Ar), 5.98 (d, 3, *J* = 1.0 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.03 (d, 3, *J* = 1.2 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>), 7.40 (s, 3, ArCH<sub>3</sub>). *Anal.* Calcd for C<sub>10</sub>H<sub>14</sub>BF<sub>4</sub>N: C, 51.10; H, 6.00; N, 5.96. Found: C, 50.91; H, 6.02; N, 6.17.

***N,N*-Dimethyl-*p*-chlorobenzylideneiminium fluoroborate (5d)** was prepared in 86% yield from 12.0 g (85 mmol) of *p*-chlorobenzaldehyde and 5.0 g (38 mmol) of dimethylamine fluoroborate: mp 104–105°; nmr (CF<sub>3</sub>CO<sub>2</sub>H)  $\tau$  1.16 (m, 1, <sup>+</sup>N=CH), 2.18 (dd, 4, *J*<sub>AB</sub> = 9 Hz, Ar), 6.03 (d, 3, *J* = 0.9 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.11 (d, 3, *J* = 1.1 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>). An analytical sample was recrystallized from methylene chloride-ether. *Anal.* Calcd for C<sub>9</sub>H<sub>11</sub>BClF<sub>4</sub>N: C, 42.32; H, 4.34; N, 5.48; Cl, 13.88. Found: C, 42.36; H, 4.42; N, 5.74; Cl, 13.67.

***N,N*-Dimethyl-*p*-bromobenzylideneiminium fluoroborate (5c)** was obtained from 15 g (81 mmol) of *p*-bromobenzaldehyde and 5.0 g (38 mmol) of dimethylamine fluoroborate in 86% yield after two recrystallizations from methylene chloride-ether: mp 57–59°; nmr (CF<sub>3</sub>CO<sub>2</sub>H)  $\tau$  1.1 (br s, 1, <sup>+</sup>N=CH), 2.0–2.4 (m, 4, Ar), 6.01 (d, 3, *J* = 1.0 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.10 (d, 3, *J* = 1.2 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>). *Anal.* Calcd for C<sub>9</sub>H<sub>11</sub>BBrF<sub>4</sub>N: C, 36.04; H, 3.70; N, 4.67; Br, 26.64. Found: C, 35.87; H, 3.80; N, 4.79; Br, 26.88.

***N,N*-Dimethyl-*p*-nitrobenzylideneiminium fluoroborate (5b)** was obtained from 8.6 g (57 mmol) of *p*-nitrobenzaldehyde and 5.0 g (38 mmol) of dimethylamine fluoroborate in 43% yield after two recrystallizations from acetonitrile-ether in a drybox. Two additional recrystallizations from acetonitrile-ether gave an analytical sample: mp 122–125°; nmr (CF<sub>3</sub>CO<sub>2</sub>H)  $\tau$  0.80 (s, 1, <sup>+</sup>N=CH), 1.70 (dd, 4, *J*<sub>AB</sub> = 9 Hz, Ar), 5.84 (d, 3, *J* = 0.9 Hz, *trans*-<sup>+</sup>NCH<sub>3</sub>), 6.02 (d, 3, *J* = 1.3 Hz, *cis*-<sup>+</sup>NCH<sub>3</sub>). *Anal.* Calcd for C<sub>9</sub>H<sub>11</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 40.64; H, 4.17; N, 10.53. Found: C, 40.73; H, 4.10; N, 10.69.

**Assignment of Nmr Signals of Iminium Salts.** With the exception of 5f, all of the iminium salts prepared exhibit nmr spectra characterized by resolved *N*-methyl signals, each of which is split into a doublet by spin-spin coupling with the iminium proton. The methyl doublet at higher field has a larger coupling constant than does the lower field methyl signal. The configuration of each methyl group relative to the iminium proton (and the aromatic ring) was assigned on the basis of a nuclear Overhauser experiment. A 40-mg (0.17 mmol) sample of *N,N*-dimethyl-*p*-methylbenzyl-

ideniminium fluoroborate, 5e, was dissolved in 0.65 ml of deuterio-methylene chloride which contained 10 drops of tetramethylsilane. The solution was filtered into a specially prepared high quality nmr tube (see Kinetics Section) and degassed on a high-vacuum line using the freeze (liquid N<sub>2</sub>)-pump-thaw cycle. The tube was then sealed under vacuum. A nuclear Overhauser experiment was performed by irradiating each of the <sup>+</sup>*N*-methyl signals at low power levels and observing the effect on the iminium proton. The iminium proton signal sharpened when either signal was irradiated (long-range coupling) but the integrated intensity increased by 11% when the methyl signal at lower field ( $\tau$  5.98) was irradiated over its value when the high field ( $\tau$  6.03) signal was irradiated. Thus the methyl group which resonates at lower field is *cis* to the iminium proton and *trans* to the aromatic ring. These findings were extrapolated to the interpretation of the spectra of the other iminium salts, 5a–d, because of their pronounced similarity.

**1,1-Dimethyl-2-phenylaziridinium Fluoroborate (6a).** A suspension of 300 mg (1.4 mmol) of freshly prepared *N,N*-dimethylbenzylideneiminium fluoroborate (5a) in 300 ml of tetrahydrofuran, which was stirred and cooled in an ice bath, was treated with diazomethane which was entrained in a stream of dry nitrogen. The addition was interrupted when all of the iminium salt had dissolved and the solution was slightly yellow (0.75 hr). Dry nitrogen was bubbled through the solution to remove excess diazomethane, and the light yellow solution was concentrated on a rotary evaporator below 25° with protection from moisture to ca. 20 ml. The mixture, which contained some water-insoluble polymeric material, was diluted with 225 ml of tetrahydrofuran and filtered, and a layer of diethyl ether (150 ml) was added by pouring the diluent down the sides of the flask. The mixture was refrigerated (-20°) overnight, and the pure colorless plates which formed (89 mg, 29%) were filtered and washed with ether: mp 55–57°; nmr (CD<sub>2</sub>Cl<sub>2</sub>)  $\tau$  2.48 (s, 5, Ar), 5.48 (t, 1, *J* = 8.0 Hz, CHN<sup>+</sup>), 6.48 (d, 2, *J* = 8.0 Hz, CH<sub>2</sub>N<sup>+</sup>), 6.68 (s, 3, *trans*-<sup>+</sup>NCH<sub>3</sub>), 7.39 (s, 3, *cis*-<sup>+</sup>NCH<sub>3</sub>). *Anal.* Calcd for C<sub>10</sub>H<sub>14</sub>BF<sub>4</sub>N: C, 51.10; H, 6.00; N, 5.96. Found: C, 51.13; H, 6.13; N, 6.17.

**1,1-Dimethyl-2-*p*-methylphenylaziridinium Fluoroborate (6e).** **General Method for the Preparation of 2-Arylaziridinium Salts.** A 6.60-g (27.6 mmol) sample of *N,N*-dimethyl-*p*-methylbenzylideneiminium fluoroborate (5e) was suspended in 200 ml of dry tetrahydrofuran and stirred at 0° under nitrogen while 44.5 ml (30.4 mmol) of 0.69 *M* ethereal diazomethane<sup>38</sup> was slowly added from a pipet. After the addition was complete (ca. 30 min) the mixture was stirred for 30 min and then 200 ml of dry ether was added to the stirred mixture. After the oily precipitate settled the solvent was decanted, and the residue was dissolved in methylene chloride (in a drybox) and precipitated with ether. Crystallization was effected by dissolving the oil in 100 ml of methylene chloride, layering the solution with 200 ml of dry ether, and placing the mixture in a freezer (-20°) for 4 days. This method gave 4.31 g (62%) of pure colorless prisms: mp 72–73°; nmr (CD<sub>2</sub>Cl<sub>2</sub>)  $\tau$  2.68 (dd, 4, *J*<sub>AB</sub> = 9 Hz, Ar), 5.57 (t, 1, *J* = 8 Hz, CHN<sup>+</sup>), 6.55 (d, 2, *J* = 8 Hz, CH<sub>2</sub>N<sup>+</sup>), 6.73 (s, 3, *trans*-NCH<sub>3</sub>), 7.43 (s, 3, *cis*-N<sup>+</sup>CH<sub>3</sub>), 7.64 (s, 3, CH<sub>3</sub>Ar). *Anal.* Calcd for C<sub>11</sub>H<sub>16</sub>BF<sub>4</sub>N: C, 53.05; H, 6.48; N, 5.62. Found: C, 52.83; H, 6.53; N, 5.66.

**1,1-Dimethyl-2-*p*-chlorophenylaziridinium fluoroborate (6d)** was prepared by the general method in 72% yield from 4.3 g (17 mmol) of *N,N*-dimethyl-*p*-chlorobenzylideneiminium fluoroborate (5d) and 19 mmol of ethereal diazomethane. The product was purified by triturating the initially precipitated (solid) product with dry ethyl acetate in a drybox: mp 84.5–85.5°; nmr (acetone-*d*<sub>6</sub>)  $\tau$  2.34 (dd, 4, *J*<sub>AB</sub> = 8 Hz, Ar), 5.23 (br t, 1, *J*<sub>AX} = *J*<sub>BX} = 8 Hz, CHN<sup>+</sup>), 6.24 (AB portion of ABX pattern, 2, *J*<sub>AX} = *J*<sub>BX} = 8 Hz, *J*<sub>AB} = 5 Hz, CH<sub>2</sub>N<sup>+</sup>), 6.55 (s, 3, *trans*-<sup>+</sup>NCH<sub>3</sub>), 7.20 (s, 3, *cis*-<sup>+</sup>NCH<sub>3</sub>). *Anal.* Calcd for C<sub>10</sub>H<sub>13</sub>BClF<sub>4</sub>N: C, 44.57; H, 4.86; N, 5.20; Cl, 13.16. Found: C, 44.68; H, 4.82; N, 5.47; Cl, 12.96.</sub></sub></sub></sub></sub>

**1,1-Dimethyl-2-*p*-bromophenylaziridinium fluoroborate (6c)** was prepared by the general method in 74% crude yield from 5.9 g (19.8 mmol) of *N,N*-dimethyl-*p*-bromobenzylideneiminium fluoroborate (5c) and 22 mmol of ethereal diazomethane. Product purity could not be significantly improved by repeated recrystal-

(38) Ethereal diazomethane was prepared from *N*-nitrosomethylurea, distilled, and dried over sodium hydroxide pellets according to the method of Arndt.<sup>39</sup>

(39) F. Arndt, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 165.

lization from methylene chloride-ether or ethylene chloride-ether: mp 45–60°; nmr (acetone- $d_6$ )  $\tau$  2.30 (s, 4, Ar), 5.30 (t, 1,  $J = 8$  Hz, CHN<sup>+</sup>), 6.30 (AB portion of ABX pattern, 2,  $J_{AX} = J_{BX} = 8$  Hz,  $J_{AB} = 5$  Hz, CH<sub>2</sub>N<sup>+</sup>), 6.57 (s, 3, *trans*-NCH<sub>3</sub>), 6.72 (m, 2.5, impurity), 7.20 (s, 3, *cis*-NCH<sub>3</sub>), 8.2–8.6 (m, 1.8, impurity).

**1,1-Dimethyl-2-*p*-nitrophenylaziridinium Fluoroborate (6b).** A stirred solution of 5.06 g (19 mmol) of *N,N*-dimethyl-*p*-nitrobenzylideneiminium fluoroborate (5b) in 100 ml of acetonitrile was cooled in an ice-salt bath while 40 ml (*ca.* 23 mmol) of a solution of diazomethane in methylene chloride was slowly added. Nitrogen evolution was spontaneous and the initially yellow solution turned orange. The mixture was then stirred in the ice bath under nitrogen for 45 min. Then 300 ml of ether was carefully added down the sides of the flask and the mixture was refrigerated at –20°. The oil which initially precipitated slowly crystallized on standing at –20° for 6 months. Filtration of the solid product gave 2.68 g of yellow prisms. The mother liquors deposited a second crop of 1.0 g on treatment with ether, total yield 3.68 g (69%). Two recrystallizations from acetone-ether gave an analytical sample: mp 114–116°; nmr (acetone- $d_6$ )  $\tau$  1.75 (dd, 4,  $J_{AB} = 8$  Hz, Ar), 5.02 (t, 1,  $J = 8$  Hz, CHN<sup>+</sup>), 6.10 (AB portion of ABX system, 2,  $J_{AX} = J_{BX} = 8$  Hz,  $J_{AB} = 4$  Hz, CH<sub>2</sub>N<sup>+</sup>), 6.42 (s, 3, *trans*-NCH<sub>3</sub>), 7.03 (s, 3, *cis*-NCH<sub>3</sub>).

*Anal.* Calcd for C<sub>10</sub>H<sub>13</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>2</sub>: C, 42.89; H, 4.68; N, 10.00. Found: C, 43.01; H, 4.89; N, 9.86.

***cis*-3,3-Dimethyl-2,5-diphenyloxazolidinium Fluoroborate (4a).** A 50-mg (0.21 mmol) sample of 1,1-dimethyl-2-phenylaziridinium fluoroborate (6a) was dissolved in 0.50 ml of freshly distilled benzaldehyde, and the solution was degassed and sealed in an nmr tube. The sample was kept at 23–25° and the nmr spectrum was recorded at intervals. After 3 days the solution was diluted with 7 ml of absolute ethanol, and three crops of tan needles were precipitated by adding first ethyl acetate and then ether, yield 69 mg (95%), mp 143–145°. The rate of reaction and the product were unaffected by degassing or by excess added anhydrous fluoroboric acid or traces of silver fluoroborate. A half-life of 10 hr was determined by comparison of peak height and integrated intensities of the (resolved) methyl signals of the starting material and product: nmr (CD<sub>2</sub>Cl<sub>2</sub>-CF<sub>3</sub>CO<sub>2</sub>H)  $\tau$  2.3–2.5 (m, 10, Ar), 4.04 (s, 1, ArCHN<sup>+</sup>), 4.29 (t, 1,  $J_{cis} = 7.5$  Hz,  $J_{trans} = 6.5$  Hz, ArCHCH<sub>2</sub>N<sup>+</sup>), 5.64 (dd, 1,  $J_{gem} = 12.0$  Hz,  $J_{cis} = 7.5$  Hz, 4-H *cis* to 5-H), 6.28 (dd, 1,  $J_{gem} = 12.0$  Hz,  $J_{trans} = 6.5$  Hz, 4-H *trans* to 5-H), 6.67 (s, 3, CH<sub>3</sub> *trans* to 2-Ph), 7.27 (s, 3, CH<sub>3</sub> *cis* to 2-Ph).

*Anal.* Calcd for C<sub>17</sub>H<sub>20</sub>BF<sub>4</sub>NO: C, 59.85; H, 5.91; N, 4.11. Found: C, 59.80; H, 6.17; N, 4.11.

***cis*-3,3-Dimethyl-5-*p*-nitrophenyl-2-phenyloxazolidinium Fluoroborate (4b).** A 100-mg (0.36 mmol) sample of 1,1-dimethyl-2-*p*-nitrophenylaziridinium fluoroborate (6b) was dissolved in 0.75 ml of benzaldehyde, and the solution was treated with 1 drop of TMS, placed in an nmr tube, stoppered with a plastic cap, and kept at 23–25°. The nmr spectrum was recorded at intervals, and a half-life of 90 hr was determined in the usual manner. After 3 weeks yellow prisms were deposited in small amounts. The mixture was diluted with 7 ml of absolute ethanol and then treated with 50 ml of ether. The solid which separated (140 mg) was recrystallized from ethanol-ether to give two crops of small yellow prisms: 102 mg (74%); mp 191–192.5°; nmr (DMSO- $d_6$ )  $\tau$  1.79 (dd, 4,  $J_{AB} = 8.0$  Hz, *p*-O<sub>2</sub>NPh), 2.06–2.44 (m, 5, Ph), 3.63 (s, 1, PhCHN<sup>+</sup>), 4.06 (t, 1,  $J = 8$  Hz, *p*-O<sub>2</sub>NPhCH<sub>2</sub>N<sup>+</sup>), 5.42 (dd, 1,  $J_{gem} = 12$  Hz,  $J_{AX} = 8$  Hz, 4-H *cis* to 5-H), 6.07 (dd, 1,  $J_{gem} = 12$  Hz,  $J_{AX} = 8$  Hz, 4-H *trans* to 5-H), 6.57 (s, 3, CH<sub>3</sub> *trans* to Ph), 7.25 (s, 3, CH<sub>3</sub> *cis* to Ph).

*Anal.* Calcd for C<sub>17</sub>H<sub>19</sub>BF<sub>4</sub>N<sub>2</sub>O<sub>3</sub>: C, 52.88; H, 4.96; N, 7.25. Found: C, 52.61; H, 4.93; N, 7.31.

**Determination of Structure of Oxazolidinium Salts 4a and 4b Using the Nuclear Overhauser Effect.** A 0.5-ml sample of a *ca.* 0.25 *M* solution of 4a in deuteriomethylene chloride-trifluoroacetic acid which contained 7 drops of tetramethylsilane was filtered into a specially prepared (see Kinetics Section) high quality nmr tube and degassed on a high vacuum line using the freeze (liquid N<sub>2</sub>)-pump-thaw cycle. The tube was then sealed under vacuum. A nuclear Overhauser experiment was performed by irradiating the N<sup>+</sup>-methyl signals at  $\tau$  6.67 and 7.27 at low power levels. The only NOE observable for the sample was observed when the +NCH<sub>3</sub> signal at lower field ( $\tau$  6.67) was irradiated and the lower field methylene proton ( $\tau$  5.64) was observed to increase in relative area by 15%. A similar experiment was run with a *ca.* 0.25 *M* solution of 4b in DMSO- $d_6$ -acetone- $d_6$  prepared in the same way. An effect (NOE) of 16% was observed when the lower field +NCH<sub>3</sub> signal ( $\tau$  6.57)

was irradiated and the lower field methylene proton ( $\tau$  5.42) was observed.

**Kinetics of the Reaction of 1,1-Dimethyl-2-arylaziridinium Fluoroborates with Benzaldehyde.** Benzaldehyde (Mallinckrodt reagent grade) was distilled at atmospheric pressure under a nitrogen atmosphere prior to use, and a 1% stock hexamethyldisiloxane solution (for internal reference and integral standard) was prepared and stored in a brown bottle in a drybox under a nitrogen atmosphere. The aziridinium salts were purified by recrystallization until the samples had correct elemental analyses and had no extraneous peaks in the nmr spectra of concentrated solutions.<sup>19</sup>

Standard nmr tubes were specially prepared by joining a 5-cm length of similar diameter Pyrex tubing to the open end of the tube. The tubes were washed with water, rinsed with acetone, and dried by inverting them over a long Teflon syringe needle through which a rapid stream of dry nitrogen was passed. Solutions were prepared by weighing out 0.97 mmol of the aziridinium salt and dissolving in 2.0 ml of the stock benzaldehyde solution at room temperature in a drybox. The solution was then rapidly filtered through a glass frit into four modified nmr tubes which were capped with tight-fitting plastic caps and placed in a Dry Ice bath. The tubes were then attached to a high vacuum line using an Ace Glass "O"-ring screw seal which was attached by a piece of rubber tubing to a stopcock of the vacuum line. Degassing was accomplished either by the usual freeze-pump-thaw cycle or by simply evacuating the tubes at room temperature while gently shaking the tube to avoid bumping during the initial effervescence. After the degassing process the tubes were cooled in a Dry Ice bath and sealed off using a hand torch.

For samples with half-lives less than 40 min, the tube was removed from the cold bath and placed in a thermostatted water bath at the desired temperature ( $\pm 0.05^\circ$ ) for 20 sec and then placed in the nmr probe which had been previously equilibrated at the desired temperature ( $\pm 0.1^\circ$ ). The temperature of the nmr probe was measured using a standardized copper constantan thermocouple which was positioned inside an nmr tube. The spectrum of the region of the higher field +NCH<sub>3</sub> signal ( $\tau$  7.1–7.3) was taken with multiple integrations using the electronic integrator of the Varian A-60-A or HA 100 nmr instrument.

The ratio of starting material to product +NCH<sub>3</sub> signals was measured as a function at time, and the total integral of the region was occasionally compared with the standard (hexamethyldisiloxane) signal. No significant change in this ratio was observed throughout each kinetic run. The total integral to standard integral ratio was found to remain unchanged even after 15–20 half-lives. For samples having half-lives greater than 40 min, several runs were carried out concurrently by alternately placing each tube in the thermostatted bath or in the nmr probe at the same temperature. Special tuning of the nmr instrument when samples were changed was generally found to be unnecessary and the integrated area of the total high field +NCH<sub>3</sub> region and its ratio to the standard signal remained constant throughout each run.

A plot of  $\ln(I_0/I_{sm})$  vs. time ( $I_0$  = the total integral,  $I_{sm}$  = the integral of the starting material +NCH<sub>3</sub>) gave good straight lines ( $r = 0.995$ ) over more than 2 half-lives, establishing pseudo-first-order kinetics. The rates of reaction were determined from the slope of the least-squares regression line<sup>10</sup> for a plot of  $\ln(I_0/I_{sm})$  vs.  $t$  taken over at least 2 half-lives; data are summarized in Tables I and II.

A solution of 120 mg (0.48 mmol) of 1,1-dimethyl-2-(*p*-methylphenyl)aziridinium fluoroborate (6e) and 49  $\mu$ l (51 mg, 0.48 mmol) of benzaldehyde in 1.0 ml of nitrobenzene was prepared in a similar fashion and placed in the nmr probe at 65°. The rate of disappearance of starting material was followed in the usual manner. After *ca.* 5 half-lives the high-field +NCH<sub>3</sub> region had decreased in total intensity by *ca.* 25%. The spectrum of the oxazolidinium salt (4e) was clearly discernible as well as some signals attributable to other products. A plot of the data obtained is shown in Figure 2; the rate of reaction was  $8.61 \times 10^{-4} \text{ sec}^{-1}$ .

**Isolation of Oxazolidinium Fluoroborates from Kinetic Runs.** The tubes from the kinetic run were cooled in a Dry Ice bath and opened, and each was rinsed with 5–7 ml of solvent (methylene

(40) We are indebted to Dr. J. H. Craig, University of Illinois, for supplying a computer program for the computation of the least squares slope of the line. An IBM 360 computer was used for these computations. We also thank John A. Secrist III, University of Illinois, and Dr. DeLanson R. Crist, Georgetown University, for their criticism and assistance.

chloride or ethanol). The resulting solution was layered with 75 ml of ether and refrigerated ( $-20^{\circ}$ ) overnight. The crystalline, nonhygroscopic product was then filtered and washed with ether. One recrystallization from ethanol-ether gave analytically pure material. The compounds isolated in this manner were as follows. *cis*-3,3-Dimethyl-5-*p*-methylphenyl-2-phenyloxazolidinium fluoro-borate (4e) was in 78% yield: mp 146.5–147.5°; nmr ( $\text{CD}_2\text{Cl}_2$ )  $\tau$  2.3–2.6 (m, 5, Ph), 2.75 (dd, 4,  $J = 8$  Hz, *p*- $\text{CH}_3\text{Ph}$ ), 3.99 (s, 1, PhCHO), 4.36 (t, 1,  $J = 8$  Hz, *p*- $\text{CH}_3\text{PhCHCH}_2\text{N}^+$ ), 5.62 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{cis}} = 8$  Hz, 4-H trans to 5-*p*- $\text{CH}_3\text{Ph}$ ), 6.35 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{trans}} = 8$  Hz, 4-H cis to 5-*p*- $\text{CH}_3\text{Ph}$ ), 6.74 (s, 3,  $^+\text{NCH}_3$  trans to 2-Ph), 7.42 (s, 3,  $^+\text{NCH}_3$  cis to 2-Ph), 7.72 (s, 3, *p*- $\text{CH}_3\text{Ph}$ ).

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{22}\text{BF}_4\text{NO}$ : C, 60.87; H, 6.24; N, 3.94. Found: C, 60.71; H, 6.26; N, 3.80.

*cis*-5-*p*-Chlorophenyl-3,3-dimethyl-2-phenyloxazolidinium fluoro-borate (4d) was in 74% yield: mp 145.5–146.5; nmr ( $\text{CD}_2\text{Cl}_2$ )

$\tau$  2.2–2.44 (m, 5, Ph), 2.51 (s, 4, *p*-ClPh), 3.85 (s, 1, PhCHO), 4.18 (t, 3,  $J = 8$  Hz, *p*-ClPh $\text{CHCH}_2\text{N}^+$ ), 5.42 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{cis}} = 8$  Hz, 4-H trans to 5-*p*-ClPh), 6.22 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{trans}} = 8$  Hz, 4-H cis to 5-*p*-ClPh), 6.60 (s, 3,  $^+\text{NCH}_3$  trans to 2-Ph), 7.39 (s, 3,  $^+\text{NCH}_3$  cis to 2-Ph).

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{19}\text{BClF}_4\text{NO}$ : C, 54.36; H, 5.10; N, 3.73; Cl, 9.44. Found: C, 54.60; H, 5.00; N, 3.81; Cl, 9.26.

*cis*-5-*p*-Bromophenyl-3,3-dimethyl-2-phenyloxazolidinium fluoro-borate (4c) was in 70% yield (based on pure starting material): mp 152–153°; nmr ( $\text{CD}_2\text{Cl}_2\text{-CF}_3\text{CO}_2\text{H}$ )  $\tau$  2.1–2.5 (m, 5, Ph), 2.30 and 2.55 (dd, 4,  $J = 9$  Hz, *p*-BrPh), 3.96 (s, 1, PhCHO), 4.24 (t, 1,  $J = 8$  Hz, *p*-BrPh $\text{CHCH}_2\text{N}^+$ ), 5.53 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{cis}} = 8$  Hz, 4-H trans to 5-*p*-BrPh), 6.25 (dd, 1,  $J_{\text{gem}} = 12$  Hz,  $J_{\text{trans}} = 8$  Hz, 4-H cis to 5-*p*-BrPh), 6.62 (s, 3,  $^+\text{NCH}_3$  trans to 2-Ph), 7.25 (s, 3,  $^+\text{NCH}_3$  cis to 2-Ph).

*Anal.* Calcd for  $\text{C}_{17}\text{H}_{19}\text{BBrF}_4\text{NO}$ : C, 48.61; H, 4.56; N, 3.33; Br, 19.02. Found: C, 48.66; H, 4.57; N, 3.34; Br, 19.18.

## Cation–Anion Combination Reactions. IV. Reactions of Aryldiazonium Ions with Hydroxide and Cyanide Ions in Aqueous Solution<sup>1,2</sup>

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**Abstract:** The rates and equilibria of the reactions of a series of substituted benzenediazonium ions with hydroxide and cyanide ions in aqueous solution at  $23^{\circ}$  have been studied. The rate constant for the reaction of *p*-nitrobenzenediazonium ion with water was also determined. The following Hammett equations were found to correlate the reactions of the substituted benzenediazonium ions: (1)  $\log K_{\text{CN}} = 3.53\sigma + 1.82$ ; (2)  $\log k_{\text{CN}} = 2.31\sigma + 2.32$ ; (3)  $\log K_{\text{O}^-} = 6.58\sigma + 4.76$ ; and (4)  $\log k_{\text{OH}^-} = 2.61\sigma + 3.72$ ; where  $K_{\text{CN}}$  and  $k_{\text{CN}}$  are the equilibrium and rate constants for formation of the *syn*-diazocyanides, and  $K_{\text{O}^-}$  and  $k_{\text{OH}^-}$  are the corresponding quantities for formation of the *syn*-diazotates. The  $\rho$  value for the diazocyanide reaction is significantly smaller than expected and forces us to change our previous conclusion concerning the identity of the rate-determining step in the reactions of aryldiazonium ions with azide ion. It now appears that this latter reaction involves a rapid formation of the diazoazide, followed by slow decomposition to the aryl azide and aryl pentazole. The most striking facet of the present work comes from a comparison of the relative rates of reactions of *p*-nitrobenzenediazonium and of previously studied reactions of triarylmethyl cations with the three nucleophiles, water, hydroxide ion, and cyanide ion. The entirely different cations react with any given nucleophile at rates differing by at least  $10^4$ , but show amazingly similar selectivities for the three nucleophiles.

The present series of papers is concerned with delineating the factors affecting the reactivities of various nucleophiles in simple cation–anion combination reactions. Our curiosity was initially aroused by the fact that Malachite Green cations (specifically: bis(*p*-dimethylaminophenyl)phenylmethyl, bis(*p*-dimethylaminophenyl), *p*-nitrophenylmethyl, and tris(*p*-dimethylaminophenyl)methyl cations, which we refer to as Malachite Green, *p*-nitro Malachite Green, and Crystal Violet, respectively), in their reactions with nucleophiles to form the covalent combination products, showed the unusual rate order with azide ion reacting faster than methoxide ion, and hydroxide or methoxide ions reacting faster than cyanide ion.<sup>3</sup>

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(2) Previous paper in this series: C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 2429 (1971).

(3) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2067 (1967).

The two previous papers in this series have reported the results of the studies of the reactions of a series of aryldiazonium ions with azide ion in aqueous solution,<sup>2</sup> and of the complex reactions of *p*-nitrobenzenediazonium ion with hydroxide ion in aqueous solution.<sup>4</sup> In the present paper, we report the results of our studies of the rates and equilibria of the reactions of a series of aryldiazonium ions with hydroxide and cyanide ions in aqueous solution.

The products of these reactions and measurements of the equilibrium constants have been reported by other investigators. Aryldiazonium ions react with cyanide ion to form the *syn*-diazocyanides,<sup>5</sup> and with hydroxide ion to form the *syn*-diazotates.<sup>6</sup> The rate constants for these reactions have not been measured previously,

(4) C. D. Ritchie and D. J. Wright, *ibid.*, **93**, 2425 (1971).

(5) E. S. Lewis and H. Suhr, *Chem. Ber.*, **92**, 3043 (1959), and earlier references cited there.

(6) E. S. Lewis and H. Suhr, *ibid.*, **91**, 2350 (1958), and earlier ref cited there.