

tively. However, treatment with an alkylating agent such as trimethyl phosphate provides only about 30% of 1,4-dimethyloctaphenyltetrasilane in the first case, while yields in excess of 80% of 1,5-dimethyldecaphenylpentasilane can be obtained in the latter case. This can be accounted for by the fact that octaphenylcyclotetrasilane is more susceptible to cleavage by silyllithium compounds than is decaphenylcyclopentasilane.²⁵ The greatly enhanced reactivity of octaphenylcyclotetrasilane over that of decaphenylcyclopentasilane can be accounted for by the relative ease of formation of a pentacovalent intermediate.²⁶

The infrared spectra of octaphenylcyclotetrasilane, decaphenylcyclopentasilane, Compound C, and 1,5-di-*n*-butyldecaphenylpentasilane were obtained (Fig. 2). The first three which are phenylated cyclosilanes have

(25) A. W. P. Jarvie and H. Gilman, *J. Org. Chem.*, **26**, 1999 (1961).

(26) H. Gilman and G. L. Schwabke, in F. G. A. Stone and R. West, Ed., "Advances in Organometallic Chemistry," Academic Press, Inc., New York, N. Y., 1964.

almost identical spectra in the 5000–700 cm^{-1} range. However, in the 700–200 cm^{-1} region significant differences in the spectra are evident. The three cyclosilanes have absorptions centered at 333 cm^{-1} . In 1,5-di-*n*-butyldecaphenylpentasilane absorption at this point is lacking; however, a new strong absorption band appears at 294 cm^{-1} . Absorption in this region has been attributed, in the case of hexaphenyldisilane, to axial deformation of the two silicon atoms.²⁷ Whether absorptions for these more complex molecules can be attributed to the same linkage cannot, of course, be certain.

Acknowledgment.—This research was supported in part by the United States Air Force under Contract AF 33(616)-6463 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

(27) L. A. Harrah, M. T. Ryan, and C. Tamborski, *Spectrochim. Acta*, **18**, 21 (1962).

[CONTRIBUTION FROM THE THOMPSON CHEMICAL LABORATORY, WILLIAMS COLLEGE, WILLIAMSTOWN, MASS.]

Rearrangement of Aromatic N-Oxides. II. Rates and Mechanism for the Reaction of Acridine N-Oxide with Acetic Anhydride^{1a}

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The kinetics of the rearrangement of acridine N-oxide with excess acetic anhydride to form acridone have been studied over the temperature range 0–25° by spectrophotometric and conductometric methods. Four possible reaction courses were considered: intramolecular, intermolecular, ion pair, and free radical. All runs, which were followed to at least 60% completion, exhibited pseudo-first-order kinetics; the value of *k* was constant over a fivefold change in concentration. A free radical chain mechanism was excluded by the absence of gaseous decomposition products commensurate with such a process. The intramolecular rearrangement of a free cation was excluded by the kinetic data. Additional runs with added sodium perchlorate and tetra-*n*-butylammonium acetate permitted a choice to be made between pathways involving free ions and ion pairs. The stoichiometry of the rate enhancement observed with added perchlorate ion was consistent with an external ion pair as the significant intermediate. This interpretation was supported by the values of the activation parameters.

Recently there has been interest in the mechanisms by which picoline N-oxides can undergo rearrangements with acid anhydrides.^{2–5} In a previous report from this laboratory results of a kinetic study of the rearrangement of pyridine N-oxide with acetic anhydride were presented.⁶ It was shown that under the conditions studied a free radical chain process was not operative. Since the reaction was pseudo-first order in excess acetic anhydride, the rate-determining step did not involve an intramolecular rearrangement of the free cation (N-acetoxypyridinium ion) to product (2-acetoxypyridine, isolated as 2-pyridone). No distinction was possible between intermolecular and ion pair pathways.

In the present study rates and products have been determined for the rearrangement of acridine N-oxide

with acetic anhydride. This represents the first systematic study of such a rearrangement in which both α -positions of the aromatic N-oxide are blocked. It is arresting that in no study of the rearrangement of pyridine N-oxide with acetic anhydride has 4-pyridone ever been detected as product. The only report of the reaction of acridine N-oxide with acetic anhydride stated that acridone was obtained when the reactants were heated.⁷ It was anticipated, therefore, that the latter reaction may proceed by a different mechanism. Accordingly, a kinetic study of this system was undertaken.

Experimental⁸

Materials.—Acridine N-oxide was prepared by the method of Acheson, *et al.*⁹ The crude product (42% yield, m.p. 164–165°) was chromatographed in dichloromethane on alumina, and the recovered yellow crystals were dehydrated over phosphorus pentoxide under vacuum in an Abderhalden apparatus warmed by refluxing acetone. The final yield was 22%, m.p. 168.0–169.0° (lit.⁹ m.p. 169°). The bright yellow crystalline product was stored in the dark under nitrogen. Acridone (Eastman

(1) (a) This work was supported by a grant from the National Science Foundation; (b) based on the Honors Thesis of M.-K. Ahn, 1963.

(2) (a) S. Oae, T. Kitao, and Y. Kitaoka, *J. Am. Chem. Soc.*, **84**, 3359 (1962); (b) *ibid.*, **84**, 3362 (1962).

(3) (a) V. J. Traynelis and R. F. Martello, *ibid.*, **80**, 6590 (1958); (b) *ibid.*, **82**, 2744 (1960); (c) V. J. Traynelis, A. I. Gallagher, and R. F. Martello, *J. Org. Chem.*, **26**, 4365 (1961).

(4) (a) V. Boekelheide and D. L. Harrington, *Chem. Ind. (London)*, 1423 (1955); (b) V. Boekelheide and W. J. Linn, *J. Am. Chem. Soc.*, **76**, 1286 (1954).

(5) J. A. Berson and T. Cohen, *ibid.*, **77**, 1281 (1955).

(6) J. H. Markgraf, H. B. Brown, Jr., S. C. Mohr, and R. G. Peterson, *ibid.*, **85**, 958 (1963); considered as paper I in this series.

(7) A. Kliegel and A. Fehrlé, *Ber.*, **47**, 1629 (1914).

(8) Melting points and boiling points are uncorrected. Infrared spectra were obtained as mineral oil mulls with a Perkin-Elmer Infracord spectrophotometer, Model 137.

(9) R. M. Acheson, B. Adcock, G. M. Glover, and L. E. Sutton, *J. Chem. Soc.*, 3367 (1960).

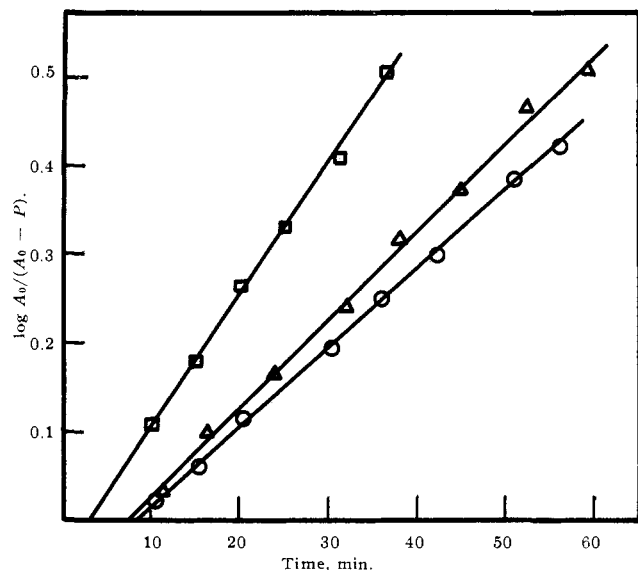


Fig. 1.—Pseudo-first-order rates of rearrangement of acridine N-oxide (0.01 *M*) in acetic anhydride at 16° as affected by added substances: ○, none; △, Bu₄NOAc (0.01 *M*); □, NaClO₄ (0.01 *M*); data from Tables I and III.

Kodak, practical grade) was recrystallized twice from isoamyl alcohol¹⁰; m.p. 357–358° (lit.¹⁰ m.p. 354°).

Acetic anhydride (J. T. Baker, analyzed reagent, assay 99.9%) was refluxed for 2 hr. over magnesium turnings and distilled through a 15 in. column. A middle fraction was collected, b.p. 138.2° (745 mm.), and stored in the dark under nitrogen.

Tetra-*n*-butylammonium acetate was described previously.⁶ Anhydrous sodium perchlorate and 72% aqueous perchloric acid (maximum total impurities 0.003%) were used as received from the G. Frederick Smith Chemical Co.

The solvent system used in quenching aliquots of the reaction solution and in subsequent dilutions for absorbance measurements was prepared by mixing 4 ml. of 72% aqueous perchloric acid with methanol (J. T. Baker, analyzed reagent) and diluting with methanol to a volume of 1 l.

Apparatus.—The constant-temperature water bath with double cooling coils was regulated to less than $\pm 0.01^\circ$ over the range 0–25°. The thermometer was marked in tenths of a degree; its accuracy was certified by the Bureau of Standards.

Rate Measurement.—An accurately weighed sample (about 0.05 to 0.25 g.) of acridine N-oxide was placed in a nitrogen-swept flask. A 25-ml. sample of acetic anhydride, previously thermostated at the temperature at which the rate studies were to be conducted, was added to the flask. The time was noted, the weight of the anhydride was determined, and the reaction flask was placed in the water bath. At definite intervals 2-ml. aliquots of known weight were withdrawn from the magnetically stirred solution with pipets which had been previously thermostated within a water-tight rubber sleeve in the constant-temperature bath. Each aliquot was quenched by delivery into a volumetric flask containing acidified methanol. Appropriate dilutions were made and the absorbances of these solutions were determined with a Beckman Model DU spectrophotometer. It was necessary to store these solutions in the dark prior to the absorbance measurements to avoid a photochemical reaction of acridine N-oxide with methanol.¹¹

It was found that solutions of acridine N-oxide and acridone in acidified methanol exhibited absorption maxima at 359 and 381 $m\mu$, respectively. Acidified methanol was chosen as solvent to induce a hypsochromic shift for acridine N-oxide⁹ and thus reduce any overlap of the reactant and product peaks. For both compounds standard solutions were prepared by weight, and Beer's law curves were determined for absorbance *vs.* mole fraction of the compound over a tenfold change in concen-

tration. Excellent linearity was demonstrated for both compounds; the origin was the intercept in all cases. The absorbivities were obtained by the method of least squares. The mole fraction of acridine N-oxide in each aliquot of the reaction solution was then calculated from the usual equation employing absorbivities and absorbances. It was established that acetic anhydride, sodium perchlorate, and tetra-*n*-butylammonium acetate affected neither the wave length nor the absorbance of either compound.

Calculations of the rate constants were made graphically by a plot of *t vs.* $\log n_{\text{ANO}}(\text{calcd.})/n_{\text{ANO}}(\text{obsd.})$ and the slopes were obtained by the method of least squares. Good pseudo-first-order plots were observed for all runs, which were followed to 60–70% reaction: eight or nine points were usually plotted in each run. The intercept was not the origin because *t*₀ was taken as the time at which acetic anhydride was added and several minutes was usually required to obtain complete solution. Results of a typical kinetic run are given in Table I.

TABLE I
REACTION OF ACRIDINE N-OXIDE WITH ACETIC ANHYDRIDE
Initial concentration: 0.0100 *M* acridine N-oxide in acetic anhydride; temp. 16.00 \pm 0.01°

Time, sec.	Absorbance at—		$n_{\text{ANO}}(\text{calcd.})^a \times 10^2$	$n_{\text{ANO}}(\text{obsd.})^b \times 10^2$
	359 $m\mu$	381 $m\mu$		
644	0.223	0.075	7.663	1.043
928	.214	.083	7.804	1.146
1230	.198	.090	7.818	1.300
1541	.192	.098	8.049	1.438
1845	.181	.100	7.997	1.564
2182	.166	.105	7.868	1.788
2520	.158	.110	7.917	1.994
3050	.144	.115	7.991	2.422
3370	.138	.119	7.916	2.664

^a Initial mole fraction of acridine N-oxide. ^b Mole fraction of acridine N-oxide at time *t*.

For kinetic runs with added salts it had been previously determined that sodium perchlorate and tetra-*n*-butylammonium acetate were adequate.⁶ The procedure was identical with that described above.

Product Isolation.—A solution of acridine N-oxide (1.00 g., 0.00512 mole) in excess acetic anhydride (10 ml.) was refluxed 4 hr. Greenish yellow crystals, which had separated from the solution, were collected, washed with anhydrous ether, and dried to give 0.858 g. (85.8%) of acridone, m.p. 358°. Infrared spectra of the product and authentic acridone were identical; a mixture m.p. was undepressed.

Gas Collection.—A gas collection run was carried out with a reaction cell and gas buret system described elsewhere.¹² A magnetically-stirred solution of acridine N-oxide (0.0494 g., 0.000253 mole) and acetic anhydride (0.0253 *M*) was maintained in a constant-temperature bath at 25° for 105 min. The net volume of gas evolved was 0.0 ml.

Conductance Measurements.¹³—The same procedures and calculations as reported previously were followed.⁶ The results are given in Table IV.

A kinetic run was carried out in the following way. The resistance of a magnetically-stirred solution (150 ml., 0.0588 *M*) of acridine N-oxide in acetic anhydride was measured with a Wheatstone bridge at 2-min. intervals over 1.3 hr.; an infinity point was obtained after 17 hr. The reaction cell was a water-jacketed flask fitted with the electrode unit and the certified thermometer; the reaction solution was maintained at 16.2 \pm 0.1°. A plot of the corrected conductances (*G*) by the standard first-order treatment, $\log(G_0 - G_\infty)/(G - G_\infty)$ *vs.* *t*, was linear; calculation of the rate constant was made graphically. The reaction was followed to 80% completion.

Results

The rates of rearrangement of acridine N-oxide in acetic anhydride were measured at 25, 16, and 0°. The extent of the reaction was determined spectrophotometrically by following the decrease in absorption at

(12) R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

(13) We are indebted to Dr. Raymond C. Petersen of the Sprague Electric Co. for these determinations.

(10) C. F. H. Allen and G. H. W. McKee in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., p. 17.

(11) There appears to be no report of this reaction in the literature. Definite changes in the ultraviolet spectrum of acridine N-oxide were effected when a methanolic solution was exposed to daylight. Such changes occurred in the absence of both acetic anhydride and perchloric acid. The nature of this reaction is under current investigation.

359 m μ due to acridine N-oxide. A correction was made for the absorption of the product, acridone, at 359 m μ . The rate studies are summarized in Table II and are illustrated in Fig. 1. In all cases a good pseudo-first-order plot was obtained. The constancy of the rate over a fivefold change in concentration of acridine N-oxide verified the observed order. There was satisfactory agreement between the values of k at 16° derived independently from spectrophotometric and conductometric data.

TABLE II
RATES OF REARRANGEMENT OF ACRIDINE N-OXIDE IN ACETIC ANHYDRIDE

$A_0,^a M$	Temp., °C.	$k \times 10^4, \text{sec.}^{-1}$
0.0498	25.00	6.55
.0097	25.00	6.42
.0285	16.04	3.57
.0100	16.00	3.45
.0059	16.2	3.94 ^b
.0099	0.10	0.91

^a Initial concentration of acridine N-oxide. ^b Calculated from conductance data.

The changes in rate caused by added salts were studied. The results are given in Table III and Fig. 1. No change in the order of the reaction was observed.

TABLE III
RATES OF REARRANGEMENT OF ACRIDINE N-OXIDE IN ACETIC ANHYDRIDE AT 16.00°

$A_0,^a M$	—Added substances—		$k \times 10^4, \text{sec.}^{-1}$	Relative rate
	Identity	M		
0.0100	None		3.45	1.00
.0101	NaClO ₄	0.0009	3.97	1.15
.0097		.0046	4.75	1.38
.0094		.0093	5.69	1.65
.0096		.0147	5.62	1.63
.0105		.0199	5.65	1.64
.0105	But ₄ NOAc	.0090	3.86	1.12
.0106		.0206	3.85	1.12

^a Initial concentration of acridine N-oxide.

A rearrangement was carried out at 25° for approximately five half-lives in a system designed to measure gas evolution. The total absence of evolved gases was consistent with the absence of a free radical chain process.¹⁴ In the case of the picoline N-oxides, gaseous products from free radical intermediates were identified by Traynelis and Martello.^{3a,b} They demonstrated, however, that the free radical species were not the precursors of the principal products. The results with acridine N-oxide, which were analogous to those previously obtained with pyridine N-oxide,⁶ were not unexpected since there is evidence that free radical species may only be generated at elevated temperatures.¹⁴

The product study confirmed the earlier report⁷ that acridone was produced in the reaction medium. The fact that the presumed initial product, 9-acetoxyacridine, was converted directly to acridone was consistent with the reported inability to acetylate acridone in acetic anhydride.¹⁵

The resistances (R) of a series of solutes in acetic anhydride were measured, and the specific conductances (κ) were calculated. The data are presented in Table IV.

(14) See, for instance, footnote 32 of ref. 6.

(15) C. Graebe and K. Lagodzinski, *Ann.*, **276**, 35 (1893).

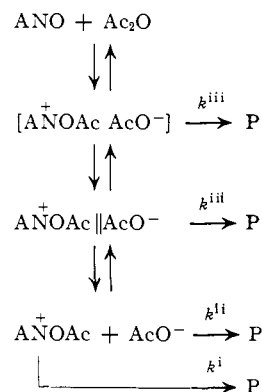
TABLE IV
CONDUCTANCES OF SOLUTES IN ACETIC ANHYDRIDE

Solute	M	$R,$ ohms	$\kappa,$ ohm ⁻¹ cm. ⁻¹
None		45,000	3.41×10^{-7}
Acridine N-oxide	0.0100	2,630	5.83×10^{-6}
Bu ₄ NOAc	.0098	51	3.01×10^{-4}
NaClO ₄	.0100	34	4.46×10^{-4}

From the kinetic data of Table II the thermodynamic activation parameters were calculated¹⁶ from the theory of absolute reaction rate. The enthalpy of activation, ΔH^\ddagger , obtained from the least-squares slope of the line from a plot of $\log k/T$ vs. $1/T$ was 12.2 ± 0.1 kcal./mole. The entropy of activation, ΔS^\ddagger , was -32.2 ± 0.5 e.u.¹⁷

Discussion

As in the cases of previously studied aromatic N-oxides, there are four mechanisms which must be considered: (i) an intramolecular rearrangement of the free cation, (ii) an intermolecular reaction between the dissociated ions, (iii) an ion pair process, and (iv) a free radical chain reaction. Within the ion pair process, of course, there is the possibility of intramolecular, intermolecular, and radical pair pathways. The absence of any gas evolution commensurate with a free radical chain process excludes mechanism iv. The path of the reaction is perhaps best discussed in terms of the following equilibria, where ANO represents acridine N-oxide, P represents product (acridone), and the rate constant superscript indicates the type of pathway outlined above. The existence of dissociated ions is



consistent with the conductance data, which indicated some free ions were present immediately after the acridine N-oxide was dissolved in acetic anhydride. The formation of an N-acetoxy cation has been generally accepted as the initial step in such rearrangements.^{3c,18} In the present case a subsequent, rate-determining intramolecular step converting free cation ANOAc⁺ to product P would involve

$$(A_0 - P)^{1/2} = A_0^{1/2} - (kt/2)$$

as the rate expression. The observed pseudo-first-

(16) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 195.

(17) Calculated for 25° from the expression $\Delta S^\ddagger = 2.303R \log (k/T) - \log (k'/h) + \Delta H^\ddagger/2.303RT$ where k is the pseudo-first-order rate constant at temperature T (°K.), k' is the Boltzmann constant, h is the Planck constant, and R is the gas constant.

(18) Professor C. W. Muth has kindly informed us of his studies with quinaldine N-oxide in acetic anhydride from which the N-acetoxyquinaldinium ion is isolable as the perchlorate salt.

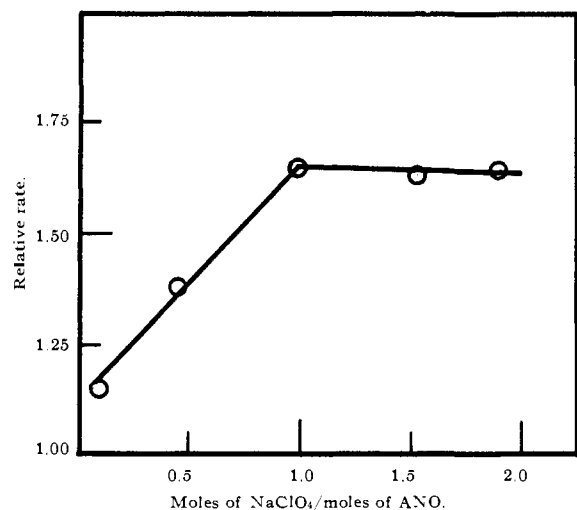


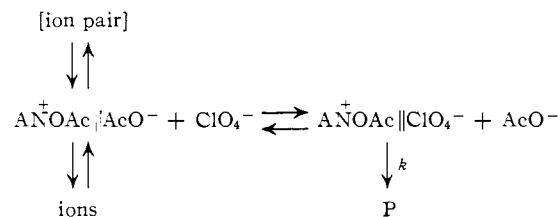
Fig. 2.—Relative rates of rearrangement of acridine N-oxide (0.01 M) in acetic anhydride at 16° as affected by added NaClO₄.

order behavior and the effect of added acetate ion permit the exclusion of mechanism i.

No distinction between the intermolecular (ii) and ion pair (iii) pathways is possible on the basis of the observed kinetics alone, since both routes should exhibit a pseudo-first-order relationship. An ion pair must be considered, however, both because of the kinetic implications and the recent study of the rearrangements of isoquinoline N-oxide and pyridine N-oxide with tosyl chloride, where it was shown by oxygen-18 techniques that internal ion pairs were involved.¹⁹ The inclusion of both internal and external (solvent-separated) ion pairs in the above series of equilibria is based on the experiments with added salts. These data permit a distinction between mechanisms ii and iii and implicate a solvent-separated ion pair as the key intermediate. These conclusions follow from the rate enhancement caused by added sodium perchlorate. It is known that perchlorate ion is an effective trap for solvent-separated ion pairs, and it thus prevents internal return.²⁰ When the increase in rate is correlated with the molar ratio of sodium perchlorate to acridine N-oxide (Table III and Fig. 2), the rate is observed to increase linearly until an equimolar ratio is reached. Beyond this point additional salt is without further effect. From such stoichiometry it is inferred that the external ion pair is intercepted in the following manner. The increase in rate is thus due to elimination of return from $\text{ANOAc}^+||\text{ClO}_4^-$. The increase in rate observed with added acetate ion can be attributed to a mass action effect, which increases the concentration of the external ion pair. Both runs with added tetra-*n*-butylammonium acetate

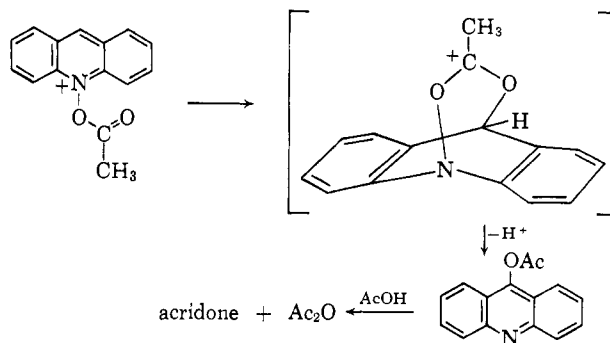
(19) S. Oae, T. Kitao, and Y. Kitaoka, *Tetrahedron*, **19**, 827 (1963).

(20) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *Chem. Ind. (London)*, 644 (1954).



gave a 12% increase in the rate. Since the concentration of dissociated ions is small relative to that of the added acetate ion (*cf.* conductance data), it follows that doubling the Bu₄NOAc concentration only increases slightly the concentration of $\text{ANOAc}^+||\text{AcO}^-$.

Conversion of ANOAc to product *via* the perchlorate external ion pair can only occur by an intramolecular pathway, such as that depicted. Whether the formation of the carbon-oxygen bond at C-9 is a concerted



process, as shown, or a radical pair process²¹ remains moot and can only be resolved by oxygen-18 techniques. A concerted attack is not unreasonable, however, because a radical pair intermediate would require an unfavorable acridyl ion radical. Furthermore, the π -electron deficiency at C-9 renders that position susceptible to nucleophilic attack.²¹

The concerted intramolecular mechanism is entirely consistent with the thermodynamic activation parameters. The rather low value of 12.2 kcal./mole for ΔH^\ddagger indicates the facile bond formation at C-9, and the ΔS^\ddagger value of -32.2 e.u. strongly supports the formation of the proposed bicyclic species.

A comparison of the rates and activation parameters for acridine N-oxide and pyridine N-oxide shows significant differences. For the latter compound ΔH^\ddagger and ΔS^\ddagger are 29.2 kcal./mole and -5.5 e.u., respectively.⁶ These data correspond to a rate constant at 25° of about 1.6×10^{-10} sec.⁻¹ giving $k_{\text{ANO}}/k_{\text{PNO}} = 4 \times 10^6$. Such striking differences suggest the possibility that the two reactions proceed through completely different mechanisms. Studies currently in progress with mixed anhydrides may permit comment on such aspects.

(21) C. Valdemoro, *Compt. rend.*, **263**, 277 (1961).