

# PHOTOCHEMICAL TRANSFORMATIONS OF SOME 4'-AMINO-2-STYRYLPYRIDINES AND THEIR SALTS

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Dedicated to Professor R. B. Sandin on the Occasion of his Sixty-Eighth Birthday

#### ABSTRACT

The photochemical behavior of 4'-amino-, 4'-dimethylamino-, 4'-diethylamino-, and 4'-di-*n*-propylamino-substituted *trans*-2-styrylpyridine were studied. Ultraviolet irradiation of aqueous solutions of the bishydrochlorides and methiodide-hydrochlorides for moderate periods of time produced mixtures of the corresponding *cis* and *trans* isomers. Long irradiation times produced the corresponding dimers in all cases except that of *trans*-4'-di-*n*-propylamino-2-styrylpyridine. The *cis* isomers of the free bases and methiodides were isolated from the *cis*-*trans* mixtures. The *trans*-methiodides are not photochemically labile. The spectra of each pair of isomers were determined in water and in 50% methanol-water, with the exception of the 4'-di-*n*-propylamino derivative, which is not sufficiently water soluble. In addition, the spectra of the corresponding methiodides, hydrochlorides, bishydrochlorides, and methiodide-hydrochlorides were determined. The basic strengths of the nitrogens in the *cis*-*trans* isomer pairs of the free bases and methiodides have been determined spectroscopically in water and in 50% methanol-water.

#### INTRODUCTION

Earlier papers (1, 2) discussed the photoisomerization and photodimerization of some substituted styrylpyridines. When dimethylamino groups were placed in the 4'-position (4-position in the phenyl group), dimerization of *trans*-2-styrylpyridine methiodide (Ia) in the solid state did not take place.



This effect appearing in the solid state was attributed to improper spacing of the double bonds in the crystal lattice. The corresponding bismethosulfate (XII) did, however, photodimerize in the solid state.



Furthermore, dimerization and photoisomerization of *trans*-4'-dimethylamino-2-styrylpyridine methiodide (Ia) and *trans*-5-ethyl-4'-dimethylamino-2-styrylpyridine (XI) failed to occur in aqueous solution. On the other hand, the 4'-methyl- and 4'-methoxyl-substituted *trans*-2-styrylpyridine methiodides gave *cis*-*trans* mixtures and dimers when irradiated in water solution. The photochemical behaviors of the hydrochlorides of the

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monobasic styrylpyridines were analogous to those of the monoquaternary salts (2). Tables I and II summarize the symbols which represent the various derivatives studied in the present work.

# DISCUSSION

The fact that Ia, IIa, and IIIa do not photoisomerize in solution suggests that extreme structures in which the ethylenic double bonds do not exist as such contribute greatly to the ground state of the molecules. One such example would be:



The lack of double-bond character at the ethylenic bond could be responsible for the failure of Ia, IIa, and IIIa to undergo photochemical change.

In the present work the spectra and photochemical behavior of 4'-dimethylamino-2styrylpyridine (I), 4'-diethylamino-2-styrylpyridine (II), 4'-(di-n-propyl)-2-styrylpyridine (III), 4'-amino-2-styrylpyridine (IV), and their salts were studied. A second purpose was to study the base strengths of the *cis* and *trans* isomers prepared during the work. Base strengths were determined by the method of Hammett (3), as modified for difunctional compounds by Rosenblatt (4). The use of the Rosenblatt scheme was necessary, since during determinations of base strength the monohydrochlorides Ib to IXb never exist in their pure form. The wavelengths of  $\lambda_{max}$  and molecular extinction coefficients of these monohydrochlorides were obtained from the ultraviolet absorption curves measured at various values of pH and by calculation. Both the spectra and the base strength values were determined in water and in 50:50 methanol-water, since III is not water soluble. Table I summarizes the ultraviolet absorption data of the trans forms of the free bases and salts of I, II, III, and IV. The free bases (I-IV) show wavelengths of  $\lambda_{\text{max}}$  in the range of 337–380 m $\mu$ , whereas the *trans*-methiodides (Ia–IVa) and trans-monohydrochlorides (Ib-IVb) show corresponding absorptions in the range of  $385-470 \text{ m}\mu$ . Under the same conditions, the *trans*-bishydrochlorides (Ic-IVc) and the trans-methiodide-hydrochlorides (Id-IVd) show wavelengths of  $\lambda_{max}$  in the range of  $324-328 \text{ m}\mu$ . Thus, it appears that the ethylenic linkage in the *trans* free bases (I-IV), the trans-bishydrochlorides (Ic-IVc), and the trans-methiodide-hydrochlorides (Id-IVd) possesses greater double-bond character than in the trans-methiodides (Ia-IVa) and monohydrochlorides (Ib-IVb). As a result, photochemical change takes place when compounds I-IV, Ic-IVc, and Id-IVd are irradiated. The unsubstituted salt, trans-2-styrylpyridine methiodide (Va), absorbs at a wavelength of  $\lambda_{max}$  of 340 m $\mu$ . In all the other cases we have examined, including 4'-CH3-, 4'-OCH3-, 4'-chloro-, and 4'-nitro-substituted trans-2-styrylpyridine methiodides, a bathochromic shift of the wavelength of  $\lambda_{max}$  occurred upon introduction of a substituent into the 4'-position of trans-2-styryl-

pyridine methiodide (Va). The charged group  $--HN(CH_3)_2Cl^-$  caused the reverse effect, a hypsochromic shift due to the high electrophilicity of the positive group. A similar difference was noted by Phillips (5) between the spectra of the bismethiodide of *trans*-4'dimethylamino-2-styrylpyridine (I), I, and Ia.

The values of the red shifts produced in the *trans*-methiodides (Ia-IVa) when the

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		In water		In 50% methanol–water	
		$\lambda_{\max} (m\mu)$	é	$\lambda_{\max}$ (m $\mu$ )	e
$     \begin{bmatrix}       I a \\       I b \\       I c \\       I d     \end{bmatrix}   $	trans-4'-Dimethylamino-2-styrylpyridine Methiodide Monohydrochloride Bishydrochloride Methiodide-hydrochloride	$     348 \\     437 \\     425 \\     324 \\     326     $	$\begin{array}{r} 26\ 200\\ 26\ 400\\ 17\ 900^*\\ 31\ 600\\ 27\ 400 \end{array}$	359 453 442 325 327	$\begin{array}{r} 27\ 700\\ 33\ 200\\ 32\ 200^*\\ 31\ 600\\ 28\ 200 \end{array}$
11 11a 11b 11c 11d	trans-4'-Diethylamino-2-styrylpyridine Methiodide Monohydrochloride Bishydrochloride Methiodide-hydrochloride	$368 \\ 456 \\ 446 \\ 326 \\ 325$	$\begin{array}{c} 22\ 800\\ 33\ 300\\ 17\ 900^*\\ 32\ 500\\ 28\ 100 \end{array}$	$376 \\ 469 \\ 455 \\ 327 \\ 328$	$\begin{array}{c} 32 \ 400 \\ 39 \ 400 \\ 28 \ 200^* \\ 32 \ 600 \\ 28 \ 400 \end{array}$
III IIIa IIIb IIIc IIId	trans-(4'-Di-n-propylamino)-2-styrylpyridine Methiodide Monohydrochloride Bishydrochloride Methiodide-hydrochloride	459 327	$37\ 100$ 29 100	$380 \\ 470 \\ 458 \\ 326 \\ 328$	$\begin{array}{c} 34\ 400\\ 41\ 700\\ 37\ 000^*\\ 32\ 000\\ 29\ 200 \end{array}$
IV IVa IVb IVc IVd	<i>trans</i> -4'-Amino-2-styrylpyridine Methiodide Monohydrochloride Bishydrochloride Methiodide-hydrochloride	337 392 385 328 327	$\begin{array}{c} 30 \ 100 \\ 25 \ 300 \\ 32 \ 100^* \\ 30 \ 700 \\ 25 \ 600 \end{array}$	339 398 328	29 500 27 800* 30 400
V Va Vb	<i>trans-</i> 2-Styrylpyridine Methiodide Hydrochloride	$309 \\ 340 \\ 334$	$\begin{array}{c} 26 \ 300 \\ 28 \ 000 \\ 27 \ 900 \end{array}$	310	26 300

	TABLE I	
Absorption spectra	of trans-4'-amino-substituted	2-styrylpyridines

\*Calculated. The monohydrochlorides do not exist as such in dilute acid solution, since they are in equilibrium with free base and bishydrochloride. Their complete ultraviolet absorption curves cannot be determined but the values of  $\lambda_{max}$  and their corresponding molecular extinction coefficients can be determined by calculation.

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alkyl group of the amino group was changed from hydrogen to methyl, ethyl, and propyl are  $45 \text{ m}\mu$ ,  $64 \text{ m}\mu$ , and  $67 \text{ m}\mu$ . Thus, there seems to be very little steric interference of the dialkylamino groups with the phenyl ring, and coplanarity of the dialkylamino groups and the phenyl ring is possible. The molecular extinction coefficients increase in the same order. On the basis of absorption spectra, the methyl group appears to be less effective in promoting the release of electrons into the conjugated system via the amino nitrogen than does ethyl or propyl.

Furthermore, there is little or no solvent shift when the spectra of Ic-IVc and Id-IVd are determined in water or in 50% methanol-water. The localized electron pairs of the amino groups of I-IV, Ia-IVa, and Ib-IVb do participate in solvent interactions, as evidenced by the shifts of wavelengths of  $\lambda_{max}$ . These species, Ia-IVa and Ib-IVb, undergo photochemical change only after extremely long irradiation times. Since the species I-IV,



**REACTION SCHEME 1.** 

28.

Ic-IVc, and Id-IVd do undergo rapid photoisomerization, the *cis* isomers were prepared by solution irradiation according to the sequence shown in Reaction Scheme 1. The scheme involving bishydrochlorides, Ic-IVc, was analogous.

Difficulty was at first encountered during the isolation of the *cis* isomers. Since the *cis* isomers are readily thermally isomerized to their *trans* forms, all operations were carried out at room temperature or below. At the same time, it was necessary to carry out manipulations under dark conditions to avoid photoequilibration of the products. Table II summarizes the absorption spectra data of the *cis* isomers. In general, the changes

TABLE	Π	

A	bsorption	spectra of	cis-4	'-amino-su	bstituted	2-styry	lpyridines
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		In water		In 50% methanol-wate	
		$\lambda_{max}$ (m $\mu$ )	e	$\lambda_{\max}$ (m $\mu$ )	e
VI VIa VIb VIc VId	<i>cis-4</i> '-Dimethylamino-2-styrylpyridine Methiodide Hydrochloride Bishydrochloride Methiodide–hydrochloride	$323 \\ 403 \\ 410 \\ 310 \\ 308$	$\begin{array}{c} 10\ 900\\ 8\ 400\\ 8\ 000^*\\ 9\ 920\\ 11\ 000 \end{array}$	$323 \\ 403 \\ 428 \\ 308$	12 800 8 400 7 950* 9 380
VII	cis-4'-Diethylamino-2-styrylpyridine	328	10 900	353 333	$11\ 440$ 11\ 380
VIIa VIIb VIIc VIId	Methiodide Hydrochloride Bishydrochloride Methiodide–hydrochloride	434 435 307 309	$\begin{array}{c} 10\ 000\\ 3\ 600^*\\ 9\ 920\\ 6\ 800 \end{array}$	$\frac{446}{308}$	$9\ 000^{*}\ 10\ 400$
VIII	cis-(4'-Di-n-propylamino)-2-styrylpyridine			356 335	12970 12600
VIIIa	Methiodide	440	$11\ 150$	440	12 000 8 800
VIIId	Bishydrochloride Methiodide-hydrochloride	$\begin{array}{c} 309\\ 310 \end{array}$	$\frac{11\ 000}{10\ 720}$	309	8 800 10 880
IX IXa	<i>cis-</i> 4'-Amino-2-styrylpyridine Methiodide	$\begin{array}{c} 313\\ 374 \end{array}$	$12\ 800\ 9\ 020$	319	$12\ 800$
IXb IXc IXd	Hydrochloride Bishydrochloride Methiodide-hydrochloride	378 317 313	$10\ 320*\ 12\ 680\ 11\ 000$	388 318	$12 200^{*} \\ 12 500$
X Xa	cis-2-Styrylpyridine Methiodide	$288 \\ 325 \\ 217$	$9\ 500\ 14\ 600\ 10\ 680$	288	10 200
л0	пудгоспотие	517	12 080	318	9700

\*Calculated. The monohydrochlorides do not exist as such in dilute acid solution, since they are in equilibrium with free base and bishydrochloride. Their complete ultraviolet absorption curves cannot be determined but the values of  $\lambda_{max}$  and their corresponding molecular extinction coefficients can be determined by calculation.

of wavelengths of  $\lambda_{max}$  of the *cis* isomers with substitution on the nitrogens and acidity conditions follow those of the *trans* forms. However, the *cis* forms consistently show wavelengths of  $\lambda_{max}$  at shorter wavelengths than do the *trans* isomers.

Each pair of cis isomers of the free bases (VI–IX) required a different method of separation because of the changes in physical properties resulting from the variation of substituents on the amino nitrogen. The methods used were cold extraction, column chromatography, and fractional crystallization. The *cis*-methiodide salts (VI*a*–IX*a*) were even more sensitive to heat and light than VI–IX and thus their melting points were of no use in characterization. Further irradiation of the methiodide–hydrochloride photoequilibrium mixtures did not produce dimers. However, when the irradiations of the bishydrochloride photoequilibrium mixtures were continued, the dimers of Ic, IIc, and IVc were produced and were subsequently treated with base to give the dimers of I, II, and IV. Long irradiation of IIIc gave several unidentified products but no dimers.

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The base strengths of the various 4'-amino substituents are influenced by the conjugated 2-styrylpyridyl group. At the same time, the base strengths of the pyridine nitrogens are interdependent with those of the 4'-amino nitrogen through the conjugated system. Both nitrogens can therefore alter their base strength by the interaction of their lone-pair electrons in the  $\pi$ -system. In all cases examined, the 4'-amino nitrogens possessed lower basic strengths than aniline, indicating donation of the electron pairs from the 4'-amino group into the  $\pi$ -system of the 2-styrylpyridyl group. Table III demonstrates that,

TABLE	111
Base strengths of 4'-amino-	substituted 2-styrylpyr-
idine methi	odides

	In water			
R	trans, $pK_{a_2}$	cis, pKa2		
$\begin{array}{c} & \\ \mathrm{NH}_{2} \\ \mathrm{N}(\mathrm{CH}_{3})_{2} \\ \mathrm{N}(\mathrm{C}_{2}\mathrm{H}_{5})_{2} \\ \mathrm{N}(n\text{-}\mathrm{C}_{3}\mathrm{H}_{7})_{2} \end{array}$	$2.83 \\ 3.10 \\ 4.48 \\ 4.67$	3.20 3.44 4.83 4.42		

when the lone pair of the pyridine nitrogen is tied up by quaternization to form the methiodide, the difference between the base strength values of the 4'-amino nitrogen of the *cis* isomers and *trans* isomers of 4'-dimethylamino- (Ia and VIa), 4'-diethylamino- (IIa and VIIIa), 4'-amino- (IVa and IXa), and 4'-di-*n*-propylamino- (IIIa and VIIIa) 2-styrylpyridines is a constant value of  $0.35 \pm 0.02$  pH unit. The basic strengths of the amino groups are in the same relative order as reported (6) in the aniline-dialkyl-aniline series:

# $N(C_2H_5)_2 > N(C_3H_7)_2 > N(CH_3)_2 > NH_2.$

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Furthermore, in the methiodide series, the 4'-amino nitrogens of the *cis* isomers (VIa, VIIa, VIIIa, and IXa) have higher base strengths than those of the corresponding *trans* isomers (Ia, IIa, IIIa, and IVa), indicating reduced interaction between the pyridinium and phenyl rings via the double bond. Jaffé and Orchin (7) attributed the reduced interaction between the two phenyl rings of *cis*-stilbene to steric interference and resulting noncoplanarity of the rings. The same effect can operate in the case of the *cis*- and *trans*-methiodides (Va–IXa and Ia–IVa) to cause changes in the basicity of the amino nitrogens. This effect was noted earlier in the differences of absorption spectra between the *cis* isomers (Va–IXa) and the *trans* isomers (Ia–IVa).

The base strength value of the pyridine nitrogen in *trans*-2-styrylpyridine (V),  $pK_{a}$  5.23, is slightly larger than that of pyridine,  $pK_{a}$  5.15. This indicates that the unpaired electrons of the pyridine nitrogen in V are not donated to the styryl system and that, in fact, a shift in the reverse direction occurs. The  $pK_{a}$  value for the nitrogen in *cis*-2-styrylpyridine is 5.20. Table IV summarizes the base strength figures determined for the *cis* and *trans* free bases (I-IX).

The contribution of the electron pair from the pyridine nitrogen via the conjugated system can reduce the value of  $pK_a$  of the amino nitrogen. The value of  $pK_a$  of the 4'-amino group in *trans*-4'-amino-2-styrylpyridine (IV) is 2.92, compared to 4.58 for aniline. The  $pK_a$  value of the pyridine nitrogen in IV is 5.72, compared to 5.23 for V and 5.15 for pyridine. Replacement of the amino-group hydrogens by alkyl groups which donate electron character increases the base strength of the 4'-amino and pyridine

	Base sti	rengths* o	of 4'-amm	io-substitu	ted 2-styry	pyridines	6	
	In water				In 50% methanol-water			
	trans		cis		trans		cis	
R	$pK_{a_1}$	$pK_{a_2}$	$pK_{a_1}$	$pK_{a_2}$	$pK_{n_1}$	$pK_{n_2}$	$pK_{a_1}$	$pK_{n_2}$
$\begin{array}{c} H \\ NH_2 \\ N(CH_3)_2 \\ N(C_2H_5)_2 \\ N(n-C_3H_7)_2 \end{array}$	5.23 5.72 6.40 6.11	$2.92 \\ 3.54 \\ 4.55 $	5.20 5.78 5.52 6.18	$2.99 \\ 3.70 \\ 4.50$	$\begin{array}{r} 4.25 \\ 5.11 \\ 5.28 \\ 5.59 \\ 5.52 \end{array}$	$2.40 \\ 2.25 \\ 3.31 \\ 2.94$	$\begin{array}{r} 4.10 \\ 4.84 \\ 4.96 \\ 5.55 \\ 5.31 \end{array}$	2.50 2.64 3.42 3.06

	TABLE IV	
Base strengths*	of 4'-amino-substituted	2-styrylpyridine

 $pK_{a_1}$  corresponds to the pyridine nitrogen and  $pK_{a_2}$  to the 4'-amino nitrogen.

nitrogens by a factor similar to that seen for the base strengths in the aniline-dialkylaniline series (6). Methyl groups are generally accepted to be superior in their electrondonating ability to ethyl or propyl groups because of hyperconjugation effects (8).

In the present work, the superior release of electron character by the methyl group is evident when the relative base strengths of the 4'-amino groups in the methiodide series or the free bases are compared in water and in 50% methanol-water solution (Table IV). Quaternization causes the pyridine nitrogen to become very electron attracting. Since the methyl groups donate electron character, there is a greater decrease in the base strength of the 4-dimethylamino group in the methiodide salt (Ia), compared to the free base (I), than occurs in the other pairs of 4'-amino-substituted derivatives (IIa and II, IIIa and III). A similar situation exists when the base strengths of the free bases (I, II, III, and IV) are compared in water and in 50% methanol-water. The base strengths of all free amino groups are dependent on the number of hydrated (-N  $\stackrel{+}{\rightarrow}$ HOH) bonds associated with the nitrogen (9). In aqueous solution, the pyridine nitrogen is preferentially ionized and stabilized by solvation. Such solvation causes the nitrogen to act as an electron-withdrawing group similar to that of the quaternary methiodide group. The fact that the 4'-dimethylamino group is the superior electron-releasing group explains the fact that the pyridine nitrogen in I has the highest base strength ( $pK_{a}$ 6.40) of any amino group in the present series of compounds. In 50% methanol-water the solvation effects are much reduced, causing all the nitrogen atoms to have lower base strengths than in water.

As already pointed out, solvation effects are seen in the absorption spectra. By changing the system from 50% methanol-water to water, more hydrogen bonding can occur. Accordingly, the wavelengths of  $\lambda_{max}$  of the free bases (I–IV) and of the monohydrochlorides (Ib–IVb) shift to shorter wavelengths. The greatest shift occurs with I and Ib. The shift of both is equal and corresponds to an energy increase of approximately 2.6 kcal/mole. This value represents the energy necessary to break the hydrogen bond so that a nonbonding electron of the amino group or molecule can be raised to the first excited state. Therefore, hydrogen bonding cannot be maintained in the excited state (10).

In 50% methanol-water solution, the absence of large solvation effects changes the order of magnitude of the effect of the groups that contribute the most electron character to the conjugated system. The absence of strong solvation effects involving the pyridine nitrogen of the *trans* free bases (I) lowers its electron-attracting power, and electron character is not drawn to the conjugated system as readily from the 4'-amino group.

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Therefore, the base strength of the pyridine nitrogens of I–IV becomes directly proportional to the base strength or electronegativity of the 4'-amino groups.

The base strength of the nitrogens becomes weaker in all cases when the solvent is changed from water to 50% methanol-water. The largest change occurs in I, the smallest in IV.

## CONCLUSIONS

The trans-methiodides, Ia-IVa, are not photochemically isomerized in solution to the cis isomers (Va-IXa) because of the lack of double-bond character at the ethylenic bond. The corresponding bishydrochlorides (Ic-IVc) and methiodide-hydrochlorides (Id-IVd) absorb light at wavelengths shorter than those of Ia-IVa or even the corresponding free bases I-IV and can be photoisomerized and photodimerized. The photochemical susceptibility is due to the tying-up of the lone-pair electrons on the positively charged nitrogens, thereby imparting sufficient double-bond character to the ethylenic bonds. The molecules under these conditions become more stilbene-like. Under highly acid conditions, existence of the bishydrochloride (Ic-IVc) and methiodide-hydrochloride (Id-IVd) species would promote  $\pi \to \pi^*$  transitions at the ethylenic bonds. The excited molecule can then rotate about the ethylenic bond. The excitation of the monohydrochlorides (Ib-IVb) and the methiodides (Ia-IVa) would not involve promotion of an electron at the same site in the molecule, making rotation about the ethylenic bond impossible. Currently, we are undertaking measurements of basic strengths, in their excited states, of the nitrogens in these compounds to provide a truer picture of the role of the lone-pair electrons in the excited state. The solvent shifts (between water and 50% methanol-water) of wavelengths of  $\lambda_{max}$  indicate that electrons are available on the amino groups for hydrogen bonding. Comparison of the double-salts series (Ic-IXc, Id-IXd (no solvent shift) with the free bases (I-IX) and the monosalts (Ia-IXa, Ib-IXb, which do show a solvent shift, illustrates this fact.

Interaction of the lone-pair electrons of the two nitrogens via the conjugated system in both isomers is indicated by the fact that the free bases of both *cis* and *trans* isomers (I-IX) absorb at longer wavelengths than do the double salts (I*c*-IX*c*, I*d*-IX*d*). This effect is also illustrated by the interdependent changes of value of base strength of the two nitrogens in the free bases (I-IX). However, release of electron character to the conjugated system by the amino group is more striking in the case of the methiodide salts (I*a*-IX*a*). The values of  $pK_a$  of the amino nitrogen of the methiodide *cis* isomers (VI*a*-IX*a*) are all greater than those of the *trans* isomers (I*a*-IV*a*) by 0.35 ± 0.02 pH unit.

#### EXPERIMENTAL

#### Determination of the Basic Strength of cis- and trans-4'-Amino-substituted 2-Styrylpyridines

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A  $5 \times 10^{-4} M$  stock solution in dilute hydrochloric acid of each compound was prepared. Such stock solutions were diluted further, to  $2.5 \times 10^{-5} M$  for the *trans* compounds or to  $5 \times 10^{-5} M$  for the *cis* compounds in a solution of the desired pH made by the addition of hydrochloric acid or sodium hydroxide solutions. The total ion concentrations were kept low and did not exceed  $5 \times 10^{-3} M$ , except for the measurements made in strong acids. The pH measurements were made by using a Beckman pH meter equipped with a calomel reference cell and a glass electrcde. The absorption spectra were measured at several pH values ranging between 1 and 10. All measurements involving the *cis* compounds were obtained in red safelight illumination because of the sensitivity of the co-derivatives to yellow light.

From such data a plot of absorption of the different  $\lambda_{max}$  vs. pH was drawn. For a monobase, the  $pK_a$  can be determined by finding the point on such a curve halfway between the free base value and the value for 100% salt. However, when a dibase of which the  $\Delta pK_a$  is less than 4 is considered, this method does not give a true  $pK_a$  value. The incorrect  $pK_a$  value results from the fact that the molecule will never

exist as a 100% monosalt. Therefore, the absorption spectra of the monosalts remain unknown. By extrapolation of the straight-line portions of absorbance vs. pH curves, a better approximation of the  $pK_a$  value is found. For a more accurate determination, the  $pK_a$ 's of the compounds were also calculated using the method described by Rosenblatt (4). The absorption of all three species (free dibase, monosalt, and disalt) and the two equilibrium constants can be calculated by setting up five simultaneous equations using measurements at five different pH values. The general form of the equations is as follows:

$$a_n \epsilon_n \left(\frac{1}{K_2}\right) + \frac{\epsilon_n}{a_n} \left(K_1\right) - a_n \frac{(\epsilon_\alpha)}{K_2} - \frac{1}{a_n} \left(\epsilon_\gamma K_1\right) - \epsilon_\beta = -\epsilon_n,$$

where  $a_n$  = hydrogen activity,  $\epsilon_n$  = extinction coefficient at the measured pH,  $K_2$  = second equilibrium constant,  $K_1$  = first equilibrium constant (Note:  $K_1$  and  $K_2$  are interchanged from Rosenblatt's equation since his applied to dibasic acids rather than to bases),  $\epsilon_{\alpha}$  = extinction coefficient of double salt,  $\epsilon_{\gamma}$  = extinction coefficient of free base, and  $\epsilon_{\beta}$  = extinction coefficient of monosalt.

Since points were found at which addition of more acid did not change the absorption spectra of the double salt or the addition of base did not change the absorption spectra of the free base, the extinction coefficients were thereby determined. These constants can then be placed in the equation, which can be simplified to the following:

$$a_n(\epsilon_n - \epsilon_\alpha) \frac{1}{K_2} + \frac{(\epsilon_n - \epsilon_\gamma)}{a_n} K_1 - \epsilon_\beta = -\epsilon_n.$$

Since the total concentration and the same cell path length were used for all measurements, these two values will cancel out.  $\epsilon = A/Cl$ , where A = absorption,  $\epsilon =$  excitation coefficient, C = concentration, and l = cell thickness. Thus, the absorption value can be used rather than the extinction coefficient. The equation then becomes

$$a_n(A_n - A_\alpha) \frac{1}{K_2} + \frac{(A_n - A_\gamma)}{a_n} K_1 - A_\beta = -A_n,$$

where  $a_n$  = hydrogen activity,  $A_n$  = absorption of solution at  $a_n$ ,  $A_{\alpha}$  = absorption of double salt,  $A_{\gamma}$  = absorption of free base, and  $A_{\beta}$  = absorption of monosalt.

For the present calculation,  $[H^+]$  was used rather than  $a_n$ , but the error introduced is small, since the calculations were carried out using values obtained for solutions where the ion concentrations would be about  $10^{-3} M$ . Thus, the activity coefficients would be very close to unity. The fact that the ultraviolet absorption curves all passed through isosbestic points at these ion concentrations is further evidence of the insignificant effect of ion concentration. Therefore, the equation was further modified to

$$[\mathrm{H}^+](A_n - A_{\alpha})\frac{1}{K_2} + \frac{(A_n - A_{\gamma})}{[\mathrm{H}^+]}K_1 - A_{\beta} = -A_n.$$

The values were calculated at the three wavelengths corresponding to the absorption maxima of each form and using three different pH values for each calculation.

# trans-4'-Dimethylamino-2-styrylpyridine (I)

This was prepared as described previously (11).

# trans-4'-Diethylamino-2-styrylpyridine (II)

A mixture of 56 g (0.6 mole) of 2-picoline, 106 g (0.6 mole) of 4-diethylaminobenzaldehyde, and 2 g of anhydrous  $ZnCl_2$  was placed in an autoclave and heated at 200 °C for 16 h. The cooled reaction mixture was poured into ether and stirred at room temperature for a short time. The solid was collected by filtration and crystallized from ethanol to yield 74 g (50.3%) of a yellow solid (II), m.p. 319-141°. Anal. Calcd. for  $C_{1T}H_{20}N_2$ : C, 81.0; H, 8.0; N, 11.1. Found: C, 81.4; H, 7.9; N, 10.8.

#### trans-4'-Di-n-propylamino-2-styrylpyridine (III)

A mixture of 56 g (0.6 mole) of 2-picoline, 82 g (0.4 mole) of 4-dipropylaminobenzaldehyde, and 2 g of anhydrous ZnCl<sub>2</sub> was placed in an autoclave and heated at 200 °C for 16 h. The reaction mixture was then distilled using a pot temperature of  $142-167^{\circ}/8 \mu$  to give 70.5 g (63%) of a red oil (III) which could not be crystallized.

Anal. Calcd. for C19H24N2: C, 81.4; H, 8.6; N, 10.0 Found: C, 81.1; H, 8.6; N, 10.1.

#### trans-2-(4'-Aminostyryl)pyridine (IV)

The following procedure is an adaptation of that used for the preparation of 4-(4'-aminostyryl) pyridine (12).

A solution of 22.6 g (0.1 mole) of 2-(4'-nitrostyryl)pyridine in 200 ml of hot 5% hydrochloric acid was added over a 10-min period to a stirred solution of 60 g of stannous chloride in 100 ml of concentrated

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hydrochloric acid while the solution was heated on a steam bath. The heating and stirring were continued and hydrogen chloride was passed through the reaction mixture for 1 h. The mixture was cooled and 20% sodium hydroxide solution was added until the mixture was strongly basic. The solid was collected, washed with water, dried, and extracted with acetone in a Soxhlet extractor. The extract was cooled to room temperature and filtered, and the filtrate was diluted with water and chilled to yield 16 g of crude product which was recrystallized from toluene to give IV, 15.1 g (77%), m.p. 137-138° (lit. (13) m.p. 138-139°). Anal. Calcd. for C13H12N2: C, 79.6; H, 6.1; N, 14.3. Found: C, 79.8; H, 6.3; N, 14.1.

trans-4'-Dimethylamino-2-styrylpyridine Methiodide (Ia)

This was prepared as previously described (11).

#### trans-4'-Diethylamino-2-styrylpyridinium Methiodide (IIa)

A mixture of 23.5 g (0.1 mole) of 2-picoline methiodide, 35.4 g (0.2 mole) of 4-diethylaminobenzaldehyde, 150 ml of methanol, and 5 ml of piperidine was refluxed on a steam bath for 1 h. The reaction mixture was chilled and the product isolated by filtration. The solid was crystallized from acetonitrile to yield IIa, 33 g (84.5%), m.p. 242-245° (lit. (5) m.p. 246-247°).

Anal. Calcd. for C18H23IN2: C, 54.8; H, 5.9; I, 32.2; N, 7.1. Found: C, 54.7; H, 5.7; I, 32.4; N, 7.0.

#### trans-4'-Di-n-propylamino-2-styrylpyridine Methiodide (IIIa)

A mixture of 11.8 g (0.05 mole) of 2-picoline methiodide, 11.3 g (0.055 mole) of 4-dipropylaminobenzaldehyde, 50 ml of methanol, and 2.5 ml of piperidine was refluxed on the steam bath for 1 h. The reaction mixture was chilled, and the product isolated by filtration and then crystallized from ethanol to yield IIIa, 3.9 g (66%), m.p. 209-211°.

Anal. Calcd. for C20H27IN2: C, 57.0; H, 6.5; I, 30.1; N, 6.6. Found: C, 56.8; H, 6.2; I, 30.4; N, 6.4.

# 4'-Amino-2-styrylpyridine Methiodide (IVa)

A mixture of 7.4 g (0.02 mole) of 4'-nitro-2-styrylpyridine methiodide, 14 g of stannous chloride, and 50 ml of concentrated hydrochloric acid was heated on the steam bath, with stirring, for 1 h. The mixture was cooled and the solid collected. The solid was added to 250 ml of water and 10 ml of concentrated hydrochloric acid. Hydrogen sulfide was passed through the mixture, with heating, until no further tin sulfide was precipitated. The hot mixture was filtered and the filtrate was neutralized with solid sodium bicarbonate to yield 4.1 g (61%) of IVa, m.p. 260°. Anal. Calcd. for C<sub>14</sub>H<sub>15</sub>IN<sub>2</sub>: C, 49.7; H, 4.4; N, 8.3. Found: C, 49.5; H, 4.3; N, 8.2.

#### Purification of cis Isomers

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The irradiation mixtures containing primarily the cis isomer were subjected to column chromatography or fractional crystallization. The various fractions from elution of the column or from crystallization were analyzed by determination of their ultraviolet absorption spectra. The fractions which contained material exhibiting the shortest wavelength of  $\lambda_{max}$  were selected as the pure *cis* fractions. We have found that the accuracy of infrared spectroscopy for determining the present cis-trans ratios is less than that of ultraviolet absorption spectroscopy methods. Further evidence of the purity of the cis isomers is found when their ultraviolet absorption spectra are determined at several values of pH (14). When such a series of ultraviolet absorption spectra are plotted, a precise isosbestic point is obtained only if the free base and the conjugate acid of a single species are present. The presence of trans isomer in cis isomer would cause the junction of the series of curves to scatter and give a number of scattered isosbestic points. The cis isomers isolated and purified as reported below gave precise isosbestic points when subjected to the above method.

#### cis-4'-Dimethylamino-2-styrylpyridine (VI)

A solution of 5 g (0.0223 mole) of trans-4'-dimethylamino-2-styrylpyridine (I) in 21 of 1 N hydrochloric acid was placed in an irradiation flask equipped with a nitrogen inlet tube at the bottom. A 450-W mediumpressure Hanovia mercury arc lamp equipped with a Pyrex glass water jacket was then immersed in the solution. The solution was stirred by a Teflon-covered stirring bar, driven magnetically through the bottom of the flask. Nitrogen was bubbled through the solution while the irradiation was conducted for 25 min, with stirring. The irradiated solution was made alkaline with potassium carbonate and was extracted with three 250-ml portions of chloroform. The chloroform solutions were dried over anhydrous potassium carbonate. The dried chloroform extracts from five such irradiations were combined and the chloroform evaporated at room temperature and reduced pressure, using a rotary evaporator and an ice-chilled collection flask. The residue was triturated with 400 ml of cold petroleum ether (b.p. 66-75°) for 30 min, after which time the solids were removed by filtration. The solid weighed 5.0 g, and consisted principally of I. The petroleum ether extract was evaporated at room temperature and reduced pressure to give 19.5 g cis-4'-dimethylamino-2-styrylpyridine (VI):  $\lambda_{max}$  (MeOH) 348 m $\mu$ ,  $\epsilon$  9 100;  $\lambda_{max}$  (1 N hydrochloric acid) 308 mµ, ε 7 920.

This material was further purified by column chromatography by means of an activated alumina column with ethyl acetate as the solvent and eluent. The ultraviolet absorption spectra of each fraction were determined and the fractions containing material having  $\lambda_{max}$  of 347 m $\mu$  were combined. The ethyl acetate

was evaporated at room temperature and reduced pressure to give VI, a pale yellow liquid,  $\lambda_{max}$  (MeOH) 347 mµ,  $\epsilon$  10 300.

Anal. Calcd. for C15H16N2: C, 80.3; H, 7.2; N, 12.5. Found: C, 80.5; H, 7.3; N, 12.4.

cis-4'-Diethylamino-2-styrylpyridine (VII)

The procedure used was the same as that used for VI. Five runs using 5.72 g of II yield 22.4 g (78%) of VII,  $\lambda_{max}$  359 m $\mu$ ,  $\epsilon$  13 100. A 5-g sample was further purified by column chromatography, as described for VI, to give 2.6 g of VII, a yellow oil,  $\lambda_{max}$  (MeOH) 359 m $\mu$ ,  $\epsilon$  13 500.

Anal. Calcd. for C17H20N2: C, 80.9; H, 8.0; N, 11.1. Found: C, 80.9; H, 8.3; N, 11.4.

# cis-4'-Di-n-propylamino-2-styrylpyridine (VIII)

Three 5-g portions of III were irradiated and combined as described for VI. The residue from the combined chloroform extract was dissolved in 400 ml of ethyl acetate. The solution was then passed through an activated alumina column, as described for VI. Eluate samples of approximately 20 ml were taken and the one containing a sample of VIII, which showed the shortest wavelength of  $\lambda_{max}$ , was selected. Its characteristics were  $\lambda_{max}$  (ethyl acetate) 355 m $\mu$ ;  $\lambda_{max}$  (CH<sub>3</sub>OH) 359 m $\mu$ ,  $\epsilon$  14 400, and 330 m $\mu$ ,  $\epsilon$  12 000. Anal. Calcd. for C<sub>19</sub>H<sub>24</sub>N<sub>2</sub>: C, 81.5; H, 8.5; N, 9.7. Found: C, 81.2; H, 8.4; N, 9.7.

By combination and evaporation *in vacuo* of the eluates containing VIII of wavelength  $\lambda_{max}$  355–360 m $\mu$ (ethyl acetate), there was obtained 4.0 g of VIII showing  $\lambda_{max}$  (CH<sub>3</sub>OH) 362 m $\mu$ ,  $\epsilon$  14 400; 330 m $\mu$ ,  $\epsilon$  11 000, which corresponded to 95% cis isomer (VIII). The remaining elates, which were the first to traverse the column, were combined to give 0.5 g of essentially trans isomer (III),  $\lambda_{max}$  (ethyl acetate) 362–372 m $\mu$ .

#### cis-4'-Aminostyrylpyridine (IX)

Three 5-g portions of IV were irradiated and the product was extracted as described for the preparation of VI. The residue from the combined, dried, and evaporated chloroform extracts was triturated with 400 ml of cold cyclohexane. The volume of the cyclohexane solution was reduced at room temperature in vacuo to 40 ml and chilled to 1 °C. The yellow crystals (IX) which separated and were collected weighed 0.06 g, m.p. 80–83°,  $\lambda_{max}$  (CH<sub>3</sub>OH) 330 m $\mu$ ,  $\epsilon$  12 350. The residue from the cyclohexane trituration was triturated with 250 ml of cold diethyl ether. The undissolved material which was collected and dried weighed 5.2 g, m.p. 113-135°, and consisted principally of trans isomer (IV). The diethyl ether solution was cooled at 1 °C to give 0.2 g of a dimer - trans isomer mixture which melted at 169-188°. On longer storage, two crops of essentially cis isomer (IX) separated: m.p. 78-82°, 0.7 g,  $\lambda_{max}$  (CH<sub>3</sub>OH) 332 m<sub>H</sub>,  $\epsilon$  7 140; and m.p. 79-81°, 0.1 g,  $\lambda_{max}$  (CH<sub>3</sub>OH) 342 m $\mu$ ,  $\epsilon$  12 100. The diethyl ether solution was then evaporated to dryness and the residue dissolved in 90 ml of 50:50 benzene-heptane. After the solution had cooled to 1 °C, the oil which separated crystallized to give 4 g of IX melting at 73-80°,  $\lambda_{max}$  (CH<sub>3</sub>OH)  $337 \text{ m}\mu$ ,  $\epsilon 13500$ . On evaporation, the mother liquors yielded 1.5 g of IX, m.p. 71-85°,  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH) 330 m $\mu$ ,  $\epsilon$  11 750. The 4-g sample of IX was dissolved in 50 ml of diethyl ether. When the solution was cooled to 1 °C, 1.9 g of IX, m.p. 80–100°,  $\lambda_{max}$  (CH<sub>3</sub>OH) 337 m $\mu$ ,  $\epsilon$  13 500, was collected. The diethyl ether was evaporated, leaving 2.0 g of IX, m.p. 70–75°,  $\lambda_{max}$  (CH<sub>3</sub>OH) 333 m $\mu$ ,  $\epsilon$  12 200.

Anal. Calcd. for C13H12N2: C, 79.6; H, 6.1; N, 14.2. Found: C, 79.2; H, 6.2; N, 13.9.

The yield of combined fractions containing greater than 97% cis isomer (XI) was 4.1 g.

#### cis-4'-Dimethylamino-2-styrylpyridine Methiodide (VIa)

A solution of 10 g (0.0274 mole) of trans-4'-dimethyl-amino-2-styrylpyridine methiodide in 21 of 0.5 N hydrochloric acid was placed in a Pyrex glass irradiation flask. The solution was irradiated during 2 h in the same manner as already described for the preparation of cis-4'-dimethylamino-2-styrylpyridine (VI). The solution was concentrated to 500 ml at room temperature and reduced pressure and made alkaline with sodium bicarbonate. The resulting solution was warmed gently to dissolve all material and then cooled to room temperature. The first crop of crystals collected was principally trans isomer (Ia), weighing 4.0 g, m.p. 253-264°,  $\lambda_{max}$  (H<sub>2</sub>O) 437 m $\mu$ ,  $\epsilon$  25 100. The second crop consisted of red prism-like crystals weighing 2.6 g and was cis-4'-dimethylamino-2-styrylpyridine methiodide (VIa),  $\lambda_{max}$  (H<sub>2</sub>O) 404 mµ,  $\epsilon$  8 400. The sample of VIa melted at 268-270°, since, when it was heated, it reverted to the trans isomer (Ia). This was confirmed by ultraviolet absorption data.

Anal. Caled. for C16H19IN2: C, 52.4; H, 5.2; I, 34.7; N, 7.7. Found: C, 52.1; H, 5.2; I, 34.9; N, 7.5.

The remaining material in the mother liquors was the trans isomer (Ia).

#### cis-4'-Diethylamino-2-styrylpyridine Methiodide (VIIa)

A solution of 10.0 g of trans-4'-diethylamino-2-styrylpyridine methiodide (IIa) in 21 of 1 N hydrochloric acid was irradiated for 1 h. The irradiation conditions and product isolation were carried out as described for VIa. However, the first material which crystallized from aqueous solution consisted of 75% inorganic salts. The expected product (VIIIa) did not crystallize from water. Therefore, the inorganic salts and mother liquors were extracted with chloroform. The chloroform extract was concentrated at room temperature and reduced pressure until the solid began to crystallize. The crops of crystals collected were the trans isomer (IIa). The solubility of the cis isomer was so high in chloroform that it was necessary to add diethyl ether to cause crystallization. In this manner, a yield of 4.8 g of cis-4'-diethylamino-2-styrylpyridine methiodide, m.p. 238–241°,  $\lambda_{max}$  (H<sub>2</sub>O) 437 m<sub>µ</sub>,  $\epsilon$  10 100, was obtained. Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>IN<sub>2</sub>: C, 54.9; H, 5.8; I, 32.2; N, 7.1. Found: C, 54.5; H, 5.4; I, 31.9; N, 6.9.

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cis-4'-Di-n-propylamino-2-styrylpyridinium Methiodide (VIIIa)

A single 5-g sample of IIIa was irradiated as described for VIIa. The aqueous solution was made basic with sodium bicarbonate and concentrated at reduced pressure and room temperature to 600 ml. The aqueous solution was extracted with 60 ml of chloroform (extract A). The aqueous solution was then extracted with three 60-ml portions of chloroform, which were then combined and evaporated to 80 ml (extract B). To both extracts there was added 100 ml of diethyl ether. When both solutions were cooled to 1 °C, *trans* isomer (IIIa) separated from them: A, 1.3 g, B, 0.6 g. On addition of 80 ml of diethyl ether to solution B, an additional 0.3 g of IIIa was obtained. Both solution A and solution B were then evaporated to dryness at room temperature and reduced pressure. The residues were held *in vacuo* for several hours at 0.3 mm pressure. Sample A weighed 1.0 g,  $\lambda_{max}$  (H<sub>2</sub>O) 440 m $\mu$ ,  $\epsilon$  11 100.

Anal. Calcd. for C20H27N2: C, 57.0; H, 6.4; N, 6.6. Found: C, 56.7; H, 6.6; N, 6.4.

Sample B weighed 1.5 g,  $\lambda_{max}$  448 m $\mu$ ,  $\epsilon$  8 320.

# cis-4'-Amino-2-styrylpyridine Methiodide (IXa)

A solution of 2.5 g of IVa in 1 l of 1 N hydrochloric acid was irradiated for 1 h as described earlier for VIa. The irradiated solution was made alkaline with sodium bicarbonate and evaporated to dryness at room temperature and reduced pressure.

The residue was triturated at room temperature with three portions of acetone: 150 ml, 400 ml, and 250 ml. The acetone solutions were successively concentrated and cooled to yield fractions of crystalline materials consisting of *cis*- and *trans*-isomer mixtures. The fractions containing IX*a*, which exhibited  $\lambda_{max}$  (H<sub>2</sub>O) 374 m $\mu$ ,  $\epsilon$  9 000, and which totaled 1.4 g, were selected to be essentially pure IX*a*.

Anal. Calcd. for C14H15IN2: C. 49.7; H. 4.4; I. 37.6; N. 8.3. Found: C. 49.6; H. 4.4; I. 37.3; N. 8.0.

# Dimerization of trans-4'-Dimethylamino-2-styrylpyridine (I)

A solution of 5 g of I in 1 l of 1 N hydrochloric acid was irradiated for 27 h in the manner described for the preparation of VI. The irradiation solution was made basic with potassium carbonate and extracted with two 200-ml portions of benzene and one 200-ml portion of diethyl ether. The combined extracts were dried over anhydrous potassium carbonate and evaporated at room temperature and reduced pressure. The residue was stirred with 40 ml of cold diethyl ether for 20 min. The crude dimer which was isolated by filtration weighed 1.7 g, m.p. 246-253°. Recrystallization from 50 ml of benzene gave 1.2 g of dimer, m.p. 255-257°. An earlier sample (see ref. 2) melted at 248-250°. The ultraviolet spectra of the two samples of dimer I were identical. The combined mother liquors were evaporated to give 3.3 g of a mixture of I and VI.

#### Dimerization of 4'-Diethylamino-2-styrylpyridine (II)

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A solution of 5.0 g of 11 in 1 l of 1 N hydrochloric acid was irradiated during 30 h as described for VII. The solution was made basic with potassium carbonate and extracted with four 125-ml portions of chloroform. The extracts were combined and dried over anhydrous potassium carbonate. The chloroform solution was evaporated at room temperature and reduced pressure and the residue was triturated with 200 ml of cold low-boiling petroleum ether. The material not soluble in the petroleum ether was separated by filtration (1.5 g) and recrystallized from 40 ml of a 50:50 mixture of diethyl ether and methanol. Thus, 0.9 g of dimer. m.p. 184-185°,  $\lambda_{max} = 268 \text{ m}\mu$  (methanol),  $\epsilon = 40.400$ , was obtained.

of dimer, m.p. 184–185°, λ<sub>max</sub> 268 mμ (methanol), ε 40 400, was obtained. Anal. Calcd. for C<sub>34</sub>H<sub>49</sub>N<sub>4</sub>: C, 80.9; H, 8.0; N, 11.1; mol. wt., 504. Found: C, 80.6; H, 8.1; N, 11.5; mol. wt., 510.

The petroleum ether mother liquor was evaporated at room temperature and reduced pressure, leaving 3.3 g of a mixture of II and VIII,  $\lambda_{max}$  (MeOH) 363 m $\mu$ ,  $\epsilon$  8 000.

# Dimerization of 4'-Amino-2-styrylpyridine (IV)

A solution of 5.0 g of IV in 21 of 1 N hydrochloric acid was irradiated during 43 h in the manner described for VI. The solution was made basic and the solids were separated by filtration. The crude product was dried *in vacuo* and melted at 160–187°; yield, 4.3 g. The solid was recrystallized from a 100 ml 50:50 benzene-chloroform solution. The first crop of crystals, which melted at 207–209° and weighed 2.5 g,  $\lambda_{max}$  (MeOH) 243 m $\mu$ ,  $\epsilon$  23 200, was recrystallized from benzene to give 2.2 g of dimer IV, m.p. 213–214°,  $\lambda_{max}$  (methanol) 243 m $\mu$ ,  $\epsilon$  24 800.

Anal. Calcd.: C, 79.6; H, 6.1; N, 14.3; mol. wt., 392. Found: C, 80.1; H, 6.4; N, 13.8; mol. wt., 428.

The mother liquors were evaporated and 1.8 g of a mixture of *cis*- and *trans*-4'-amino-2-styrylpyridine was obtained,  $\lambda_{max}$  342 m $\mu_i \in 7$  160.

#### Attempted Photoisomerization of Ia-IVa

For irradiation purposes a 1-cm quartz spectrophotometer cell was filled with a  $2.5 \times 10^{-5} M$  aqueous solution of the *trans* isomer of the compound to be studied. The absorption spectrum of the starting solution was first determined. The cell was then irradiated sequentially using the light sources tabulated below. After each irradiation (A and D) the ultraviolet absorption spectra were determined.

A. The sample cell was placed at a distance of 10 cm from a 500-W Hanovia water-cooled mediumpressure mercury arc lamp. A Kodak Wratten 18A filter was interposed between the sample cell and the light source. (The 18A filter transmits light of wavelengths  $310-390 \text{ m}\mu$ .)

B. The sample cell was placed at a distance of 10 cm from the source used in A. The 18A filter was not used.

C. The sample cell was placed at a distance of 10 cm from the source used in A. A Kodak Wratten 2A filter was interposed between the sample cell and the source. (The 2A filter transmits all wavelengths of light longer than 410 mµ.)

D. The sample cell was placed at a distance of 10 cm from a 100-W (80 W at 253°) Hanovia mercury resonance lamp.

Prolonged irradiation of solutions of Ia-IVa with any of the above sources failed to produce significant changes in their ultraviolet absorption spectra. Thus, Ia-IVa were considered to be photochemically stable in dilute aqueous solution.

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