

Inasmuch as microscopic and X-ray examinations of the alumina catalyst showed that the laboratory-prepared alumina was more crystalline than the commercial alumina tested, it may be that the greater catalytic activity of the former is connected with its higher degree of crystallinity.

The ferric chloride-Filtrol catalyst was tested at 200° (expt. 28) and at 300° (expt. 29). Hydrogen chloride was evolved initially at both temperatures but no toluene was produced. The iron in the used catalysts was at least 95% in the ferrous state. Reduction of ferric chloride catalyst in the Friedel-Crafts reaction has been previously observed.<sup>6</sup> The ferrous chloride-activated carbon catalyst was tested at 300° (expt. 30) and at 400° (expt. 31). Toluene was not produced at either temperature. Hydrogen chloride was absent in the exit gas from the 300° experiment, but it was present in the 400° experiment.

The "solid" phosphoric acid catalyst showed no activity at approximately ten seconds contact time at 300, 350, 400 and 450°. Aluminum chloride adsorbed on activated carbon was active as would be expected, but three consecutive eight-hour periods (expts. 36-A, 36-B, 36-C) at 150° showed that the activity dropped off rapidly. The higher temperatures used with the other catalysts could not be employed with the aluminum chloride-activated carbon catalyst because of the sublimation of aluminum chloride.

(6) Ipatieff and Corson, *THIS JOURNAL*, **59**, 1417 (1937).

**By-products of Methyl Chloride.**—The exit gas from expt. 2-A (after removal of hydrogen chloride) showed the following composition: 85% of paraffin (index 1.2), 4% of hydrogen, 11% of olefin (ethylene being less than 10% of the total olefin). The gas production accounted for 5% of the methyl chloride fed to the reactor, the remaining 95% of the methyl chloride being accounted for as methylated benzenes.

**Methylation of Naphthalene with Methyl Chloride.**—The monomethylated portion of the methylated naphthalene product showed constants (b. p. 240–246° (760 mm.); f. p., 4° (cooling curve);  $n_D^{20}$  1.6135) which corresponded to a mixture of approximately 15% of the  $\alpha$ -isomer and 85% of the  $\beta$ -isomer.<sup>7</sup>

**Acknowledgment.**—The authors express their thanks to Mrs. M. M. Goettman for assistance in the experimental work.

### Summary

Benzene, toluene and naphthalene were methylated in vapor phase over solid catalysts. The methylating agents were methyl chloride and methyl bromide (methyl iodide was not effective), and the catalysts were alumina, alumina-silica, and aluminum chloride-activated carbon. Barium chloride-pumice, ferric chloride-Filtrol, ferrous chloride-activated carbon, and "solid" phosphoric acid did not catalyze the reaction.

(7) Coulson, *J. Soc. Chem. Ind.*, **60**, 123 (1941).

PITTSBURGH, PENNSYLVANIA RECEIVED MARCH 15, 1945

CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION

## Absorption Spectra. II. Some Aldehyde Condensation Products of Methyl Pyridines

BY ELKAN R. BLOUT AND VIRGINIA W. EAGER

Although there has been great interest in the light absorbing properties of compounds, only recently have there been any concerted attempts to correlate the structure of molecules with their light absorption.<sup>1</sup> A previous paper from this Laboratory has discussed the relation between the electronic nature and the absorption spectra of certain aldazines.<sup>2</sup> The ultraviolet absorption spectra of some substituted pyridines are discussed herein.

It is evident that the simplest aromatic hydrocarbon, benzene, and its nitrogen analog, pyridine, show many gross similarities. For example, they have approximately the same resonance

energy<sup>3</sup>; they both absorb at approximately the same wave length (maximum at 255  $m\mu$ ); and both compounds show anionoid and cationoid reactions.<sup>4</sup> We propose to illustrate some differences between the electronic natures of carbon and nitrogen by a comparison of the absorption spectra of some pyridine derivatives and their hydrocarbon analogs.

4-Styrylpyridine has a single absorption maximum at 307  $m\mu$ , and the shape of its spectrum is almost identical with that of stilbene where the maximum is at 294  $m\mu$ <sup>5</sup> (Fig. 1). The fact that

(1) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Bury, *THIS JOURNAL*, **57**, 2115 (1935); Pauling, *Proc. Nat. Acad. Sci.*, **25**, 577 (1939); Mulliken, *J. Chem. Phys.*, **7**, 121, 364, 570 (1939); Pauling, "Organic Chemistry," H. Gilman, Editor, 2nd ed., Vol. II, pp. 1944 ff. (1943).

(2) Blout and Gofstein, *THIS JOURNAL*, **67**, 13 (1945).

(3) Pauling in "Nature of the Chemical Bond" gives 39 kcal./mole for benzene and 43 kcal./mole for pyridine.

(4) Bowen, *Chem. Soc. Lond., Ann. Rep.*, **40**, 25 (1943), states that the replacement of carbon by nitrogen in aromatic organic compounds does not greatly alter the energy value of the  $\pi$  orbitals and hence there is little change in the absorption spectra.

(5) Arends, *Ber.*, **64**, 1936 (1931). A reexamination of the spectrum of stilbene gives results in good agreement with these data (Table I).

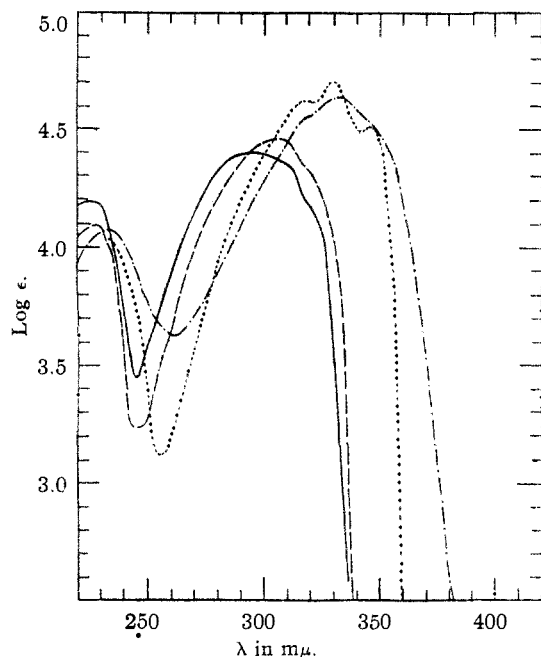
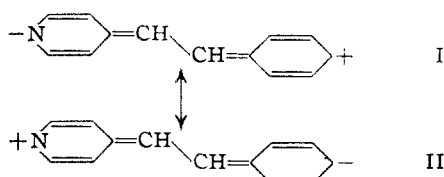
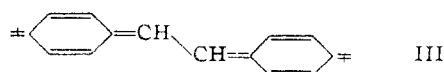


Fig. 1.—Stilbene, ———; 4-styrylpyridine, - - - -; 4-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine, - · - · -; 1,4-diphenylbutadiene-1,3, · · · · ·.

the maximum for the nitrogen containing compound lies 13  $m\mu$  toward the visible may be attributed to the electronegative nature of nitrogen as compared with the corresponding carbon in stilbene; hence there is a greater contribution of charge separation forms such as I and II where I is recognized as the larger contributor.



Transitions to similar forms III are responsible for the spectrum of stilbene.<sup>6</sup>



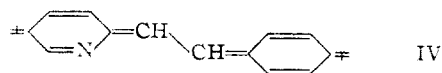
Absorption at longer wave lengths may also result from an increase in the length of the conjugated absorbing system as well as from increasing the charge separation; for example, 1,4-diphenylbutadiene-1,3 has its principal maximum at 328  $m\mu$ ,<sup>7</sup> a shift of 34  $m\mu$  toward the visible as compared with stilbene. Comparison of its spec-

(6) Jones, *THIS JOURNAL*, **65**, 1820 (1943).

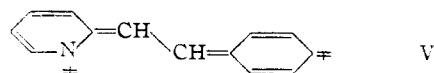
(7) Friedmann and Heyningen, *J. prakt. Chem.*, **146**, 165 (1938), report a single broad peak,  $\log E = 4.57-4.59$  at 314-330  $m\mu$ . This is not in agreement with our determination. It should be noted we have observed a principal maximum and two subsidiary maxima in the spectrum of 1,4-diphenylbutadiene-1,3 in good agreement with the determination of Kuhn, *Z. physik. Chem.*, **B29**, 384 (1935), who reports two maxima at 328 and 345  $m\mu$ .

trum with that of the corresponding pyridine derivative, 4-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine, (maximum at 332  $m\mu$ ) again shows the shift of the maximum toward longer wave lengths in the nitrogen containing compound.

The isomeric 2-styrylpyridine derivative shows a principal absorption maximum at approximately the same wave length (310  $m\mu$ ) as the 4-substituted compound (Fig. 2). The main absorption band is associated with electronic transitions to excited states represented by dipolar forms such as IV in which there is maximum charge separation.



In addition to the main band there is a subsidiary band at shorter wave lengths indicated by an inflection point at 275-285  $m\mu$ . Since this subsidiary maximum lies at shorter wave lengths, it is attributed to charge separation forms such as V which are appreciably less important in the case of stilbene and have no effect on its spectrum.



An analogous situation occurs with the isomeric 2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine where the spectrum shows a main peak at 333  $m\mu$  and a point of inflection at 285-295  $m\mu$  (Fig. 2). 6-Methyl-2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine shows an absorption spectrum similar to that of 2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine, as would be expected.

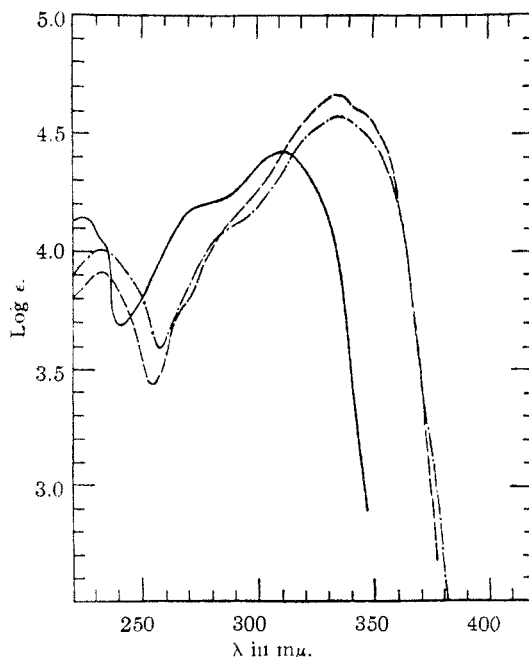


Fig. 2.—2-( $\delta$ -Phenylbutadiene- $\alpha,\gamma$ )-pyridine, - - - -; 2-styrylpyridine, ———; 6-methyl-2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine, - · - · -.

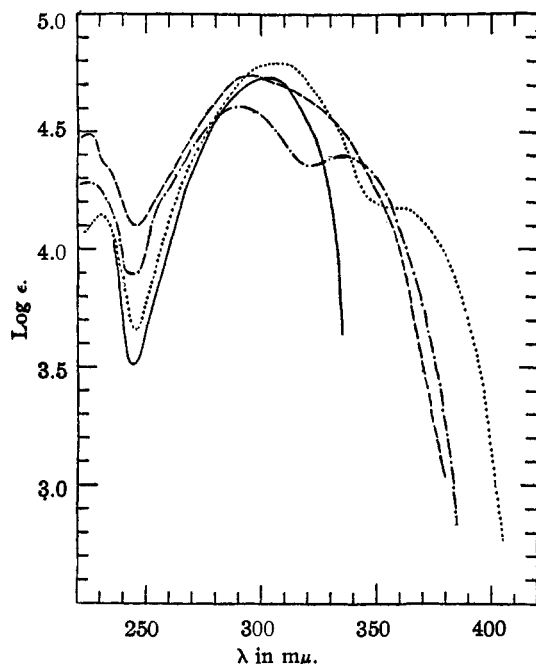


Fig. 3.—1,3-Distyrylbenzene, ———; 2,4-distyrylpyridine, — — —; 2,6-distyrylpyridine, — · — · —; 2,4,6-tristyrylpyridine, - - - - -.

It is well known that increasing the number of benzene rings in a molecule does not shift the position of the maximum unless the additional unsaturated groupings are conjugated with the initial absorbing system. For example, *m*-terphenyl absorbs at the same wave length as diphenyl, whereas *p*-terphenyl absorbs at longer wave lengths.<sup>8</sup> We have examined the spectrum of 1,3-distyrylbenzene (Fig. 3) and have observed that the maximum lies at approximately the same wave length as that of stilbene, but the intensity of the absorption has doubled (Table I). Thus it may be said that the absorbing system in stilbene and *m*-distyrylbenzene is the same and may be represented by forms such as III. The corresponding 2,4-distyrylpyridine shows a maximum at 295  $m\mu$  with broadening of the band head toward longer wave lengths. The 2,6-distyrylpyridine shows two maxima; a principal band at 290  $m\mu$  and a secondary band at 335  $m\mu$ . We believe that the principal maximum located at  $295 \pm 5 m\mu$  in the three foregoing spectra is due to forms in which the charge separation is of the same type as that of stilbene. The subsidiary maximum noted in 2,6-distyrylpyridine is associated with forms in which there is an excess of electrons on the nitrogen atom and a deficiency of electrons or a positive charge spread over the whole remaining portion of the molecule. Thus one obtains in effect a fairly long absorbing system terminated by benzene rings. The broadening of the spectrum of 2,4-distyrylpyridine is attributable to the same effect, but owing to the fact that the absorbing

(8) Gillam and Hey, *J. Chem. Soc.*, 1170 (1939).

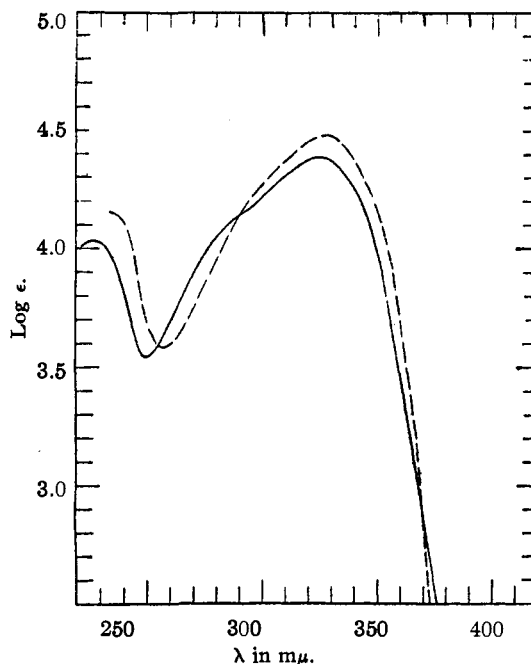


Fig. 4.—2-(*p*-Methoxystyryl)-pyridine, ———; 4-(*p*-methoxystyryl)-pyridine, - - - - -.

system is shorter by one ethylenic group and hence absorbs at shorter wave lengths, no actual band separation may be observed. The 2,4,6-tristyrylpyridine exhibits an analogous spectrum to the 2,6 compound, as one would expect, with the

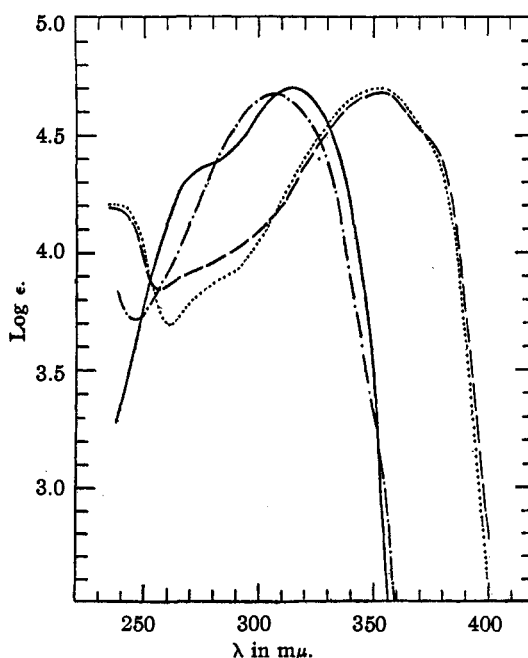
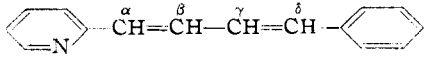
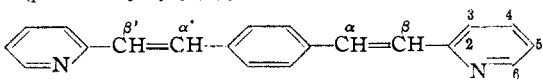


Fig. 5.—*m*-( $\beta, \beta'$ -Di-2-pyridyl)-divinylbenzene, ———; *m*-( $\beta, \beta'$ -di-4-pyridyl)-divinylbenzene, — · — · —; *p*-( $\beta, \beta'$ -di-2-pyridyl)-divinylbenzene, — — —; *p*-( $\beta, \beta'$ -di-4-pyridyl)-divinylbenzene, - - - - -.

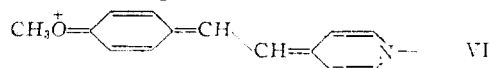
TABLE I

Compound	M. p., °C., reported	M. p., °C., (cor.) observed	Crystn. solvent	$\lambda_{\max}$ . in $m\mu$	Log $\epsilon$
2-Styrylpyridine	90-91 <sup>a</sup>	88-88.5	Alc.-water	~275-285 310	4.44
4-Styrylpyridine	127 <sup>b</sup>	130	Ligroin	307	4.47
2,4-Distyrylpyridine	174 <sup>c</sup>	175	Ligroin	295 290	4.75 4.61
2,6-Distyrylpyridine	167.5 <sup>d</sup>	167.5	Ligroin	335	4.41
2,4,6-Tristyrylpyridine	187-188 <sup>e</sup>	189-189.5	1:1 alcohol: chloroform	305 ~350-360	4.79
					
2-( $\delta$ -Phenylbutadiene- $\alpha,\gamma$ )-pyridine	123-124 <sup>f</sup>	121.5-122	Ligroin	~285-295 333	4.67
4-( $\delta$ -Phenylbutadiene- $\alpha,\gamma$ )-pyridine	137-138 <sup>g</sup>	159.5	Ligroin	332	4.65
6-Methyl,2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine	103-104 <sup>g</sup>	108	Ligroin	~285-295 335	4.59
Stilbene	124 <sup>h</sup>	123.5-124		295	4.42
1,3-Distyrylbenzene	<sup>i</sup>	169.5-170	Heptane	298 316	4.73 4.64
1,4-Diphenylbutadiene-1,3	152.5-153.5 <sup>k</sup>	152-152.5	Bz-alc.	328 345	4.72 4.53
2-( <i>p</i> -Methoxystyryl)-pyridine	76 <sup>l</sup>	75-75.5	Pet. ether	~280 325	4.39
4-( <i>p</i> -Methoxystyryl)-pyridine	<sup>m</sup>	135	Ligroin	328	4.48
					
<i>p</i> -( $\beta,\beta'$ -Di-2-pyridyl)-divinylbenzene	<sup>n</sup>	231.5-232	Alc.-chloroform	354	4.68
( <i>p</i> - $\beta,\beta'$ -Di-4-pyridyl)-divinylbenzene	<sup>o</sup>	265-266	Xylene	353	4.70
<i>m</i> -( $\beta,\beta'$ -Di-2-pyridyl)-divinylbenzene	<sup>p</sup>	121-122	Ligroin	~270-280 314	4.70
<i>m</i> -( $\beta,\beta'$ -Di-4-pyridyl)-divinylbenzene	<sup>q</sup>	211-212	Benzene	308	4.67

<sup>r</sup> denotes inflection point. <sup>a</sup> Baurath, *Ber.*, **20**, 2719 (1887). <sup>b</sup> Friedlander, *ibid.*, **38**, 159 (1905). <sup>c</sup> Schuster, *ibid.*, **25**, 2398 (1892). <sup>d</sup> Clemo and Gourlay, *J. Chem. Soc.*, 478 (1938). <sup>e</sup> Koenigs and Bentheim, *Ber.*, **38**, 3908 (1905). <sup>f</sup> Späth, Kubiczek and Dubensky, *ibid.*, **74**, 873 (1941). <sup>g</sup> Proske, *ibid.*, **42**, 1450 (1909). <sup>h</sup> Michaelis, *ibid.*, **8**, 1314 (1875). <sup>i</sup> Calcd. for C<sub>22</sub>H<sub>18</sub>: C, 93.58; H, 6.43. Found: C, 93.57; H, 6.43. <sup>k</sup> "Organic Syntheses", Vol. XVI, p. 28. <sup>l</sup> Koelsch, *THIS JOURNAL*, **66**, 2126 (1944). <sup>m</sup> Calcd. for C<sub>11</sub>H<sub>13</sub>NO: C, 79.66; H, 6.18. Found: C, 80.02; H, 6.09. <sup>n</sup> Calcd. for the four isomeric condensation products—C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>: C, 84.47; H, 5.67. Found: C, 84.83; H, 5.84. <sup>o</sup> Found: C, 84.63; H, 5.68. <sup>p</sup> Found: C, 84.11; H, 5.66. <sup>q</sup> Found: C, 84.79; H, 5.90. All elementary analyses by Dr. Carl Tiedcke.

principal maximum at 305  $m\mu$  and a subsidiary maximum at 350-360  $m\mu$  (Fig. 3).

Further illustration of the effect of increased charge separation upon the position of the absorption maximum is offered by the spectra of the isomeric *p*-methoxystyrylpyridines. These compounds show maximum absorption at 327  $\pm$  2  $m\mu$  (Fig. 4). The shift of the maximum toward longer wave lengths compared with the unsubstituted styrylpyridines may be attributed to both an increase in the length of the absorbing system and the easier charge separation due to the electron-donating properties of the oxygen containing group and the electron accepting properties of the nitrogen atom. Forms such as VI



illustrate the probable contributing states of 4-(*p*-methoxystyryl)-pyridine. The 2-*p*-methoxy com-

pound shows an inflection point characteristic of the styrylpyridines substituted in the 2-position.

The pyridine condensation products prepared from iso- and terephthalaldehydes show spectral characteristics consistent with the generalizations already developed. For example, the di-condensation product from isophthalaldehyde and 4-picoline shows a single maximum (308  $m\mu$ , Fig. 5) in the same region as *m*-distyrylbenzene (298  $m\mu$ , Fig. 1) and 2,4-distyrylpyridine (295  $m\mu$ , Fig. 3). Similarly, the di-condensation product from isophthalaldehyde and 2-picoline shows a single maximum at approximately the same wave length (314  $m\mu$ ) and in addition an inflection point at 270-280  $m\mu$  analogous to that obtained with 2-styrylpyridine (*cf.* Figs. 1 and 5). Terephthalaldehyde readily condensed with 4-picoline to give the expected divinyl compound which showed an absorption maximum at 353  $m\mu$  (Fig. 5). The position of the maximum is at slightly longer wave

lengths than that obtained from the corresponding benzenoid compound, *p*-distyrylbenzene.<sup>9</sup> The isomeric condensation product with 2-picoline shows a single maximum at 354  $m\mu$  and a slight change of slope in the expected region of secondary absorption, *ca.* 280  $m\mu$ . It should further be noted that the intensity of the absorption of the di-condensation products is approximately double that of the mono-aldehyde pyridine condensates.

**Acknowledgment.**—The authors wish to express their appreciation to Miss Esther Polson and Mr. W. A. Davis for the determination of the absorption spectra reported in this paper.

### Experimental

**General Method.**—The pyridine condensation products were prepared in the usual manner<sup>10</sup> by refluxing for approximately fifteen hours with acetic anhydride using 1 to 3 times the molar proportion of aldehyde. The dark colored reaction mixtures were dissolved in chloroform extracted with dilute hydrochloric acid, and the acid layer neutralized under cooling with concentrated ammonium hydroxide. The free bases were separated either by decanting the aqueous layer or by extracting it with ether. The 2,6- and 2,4,6-styrylpyridines separated as their hydrochloride salts. The free bases were isolated by treating the salts with alcoholic sodium hydroxide in alcohol-benzene suspension. They were recrystallized from the solvents indicated in Table I.

(9) Hertel and Siegel, *Z. physik. Chem.*, **B52**, 174 (1942). give  $\log E = 4.76$  at 340  $m\mu$  for *p*-distyrylbenzene.

(10) Shaw and Wagstaff, *J. Chem. Soc.*, 26 (1933).

The picoline-phthalaldehyde condensation products formed in small yields (*ca.* 5%) except in the case of 2-picoline-terephthalaldehyde, which gave 73% yield.

Eastman Kodak Co. stilbene was used without further purification.

*m*-Distyrylbenzene was prepared by adding an ethereal solution of 1.5 g. of isophthalaldehyde to benzylmagnesium bromide in proportion of 1:2 moles. The dark red addition complex which formed at once was hydrolyzed with cold 20% sulfuric acid. The resulting carbinol was dehydrated by refluxing with excess acetyl chloride and slowly heating the product to 275° to remove the elements of acetic acid from the molecule. *m*-Distyrylbenzene crystallized from hexane as white plates, melting point 169.5–170°, yield 0.30 g.

1,4-Diphenylbutadiene-1,3 was prepared by the method of Corson (ref. *k*, Table I).

The absorption spectra measurements were made on a Beckman quartz spectrophotometer model DU using a 1-cm. quartz cell and a hydrogen tube as an ultraviolet source. Absolute ethyl alcohol was used as a solvent throughout. All the samples were  $1 \times 10^{-5}$  *M* except 2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine and 4-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ )-pyridine (both  $1.485 \times 10^{-5}$  *M*); 6-methyl, 2-( $\delta$ -phenylbutadiene- $\alpha,\gamma$ -pyridine) ( $1.185 \times 10^{-5}$  *M*); and *p*-( $\beta,\beta'$ -di-2-pyridyl)-divinylbenzene ( $3 \times 10^{-5}$  *M*).

### Summary

Examination of the spectra of several substituted pyridines has shown them to be different from their hydrocarbon analogs. These differences have been correlated with the electronic nature of the compounds.

CAMBRIDGE 39, MASS.

RECEIVED APRIL 23, 1945

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 991]

## The Kinetics of the *cis-trans* Isomerization of Diiodoethylene and of its Exchange with Iodine

BY RICHARD M. NOYES, ROSCOE G. DICKINSON,<sup>1</sup> AND VERNER SCHOMAKER

The iodine catalysis of *cis-trans* isomerization has been investigated by several workers, the thermal<sup>1a</sup> and photochemical<sup>2</sup> isomerization of the cinnamic acids and the thermal isomerization of the dichloroethylenes<sup>3</sup> being among the reactions studied in solution. The rates of isomerization observed were proportional to the square root of the concentration of iodine in thermal experiments, and to the square root of the intensity of illumination in photochemical experiments in which the concentration of iodine did not vary, indicating, as the authors pointed out, that the isomerizations are induced by iodine atoms.

For isomerization reactions of this type Berthoud and Urech<sup>2</sup> suggested a mechanism in-

volving addition of the catalytic halogen atom to one of the carbon atoms of the double bond to produce an intermediate, represented by the authors as



in which the carbon-carbon double bond has been converted into a single bond about which internal rotation can occur. Isomerization then results if at the time of dissociation of the halogen atom from the complex the groups attached to the two carbon atoms have undergone a relative rotation of 180°. If both X and Y are iodine atoms, then the formation of a complex like (1) may result in exchange with the added iodine atom either concurrently with the isomerization or separately. The relative probabilities of the three possible processes—exchange, isomerization, and isomerization with exchange—should depend upon the actual properties of the reaction intermediate

(1) This manuscript in essentially its present form was completed before the death of Dr. Dickinson on July 13, 1945. The junior authors have assumed responsibility for some minor changes made during his last illness.

(1a) Roscoe G. Dickinson and H. Lotzkar, *THIS JOURNAL*, **59**, 472–475 (1937).

(2) A. Berthoud and C. Urech, *J. chim. phys.*, **27**, 291–306 (1930).

(3) Reuben E. Wood and Roscoe G. Dickinson, *THIS JOURNAL*, **81**, 3259–3262 (1939).