[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, LEHIGH UNIVERSITY]

Equilibrium Constants for Pyridinium Iodide Charge-Transfer Complex Formation[1]

BY EDWARD M. KOSOWER[2] AND JOHN C. BURBACH[3]

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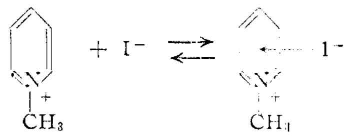
The previous formulation of the "new species" found in aqueous solutions of 1-methylpyridinium iodides as charge-transfer complexes is further confirmed by a study of the equilibrium constants for complex formation. While the K for association of 1-methylpyridinium and iodide ions is 2.3 ± 0.3 l. mole^{-1}, the three additional methyl groups present in 1,2,4,6-tetramethylpyridinium ion only reduce the K for complexing with iodide ion to 1.83 ± 0.3 l. mole^{-1}. From comparison with the data for complexing and addition to benzene derivatives (π- and σ-complexes), it is clear that the present case fits the pattern expected for "loose" bonding, or charge-transfer complex formation. In ethanol, there is considerable association to ion-pairs and 1,2,4,6-tetramethylpyridinium iodide forms complex in accordance with Beer's law over certain concentration ranges. A comparison of "absorption" curves for the complex in ethanol and water indicates that the absorption band is shifted to longer wave lengths in solvents of lower solvating ability, as had been suggested previously.

The unusual ultraviolet absorption properties of 1-methylpyridinium iodide solutions in water[4] have been attributed to the presence of a charge-transfer complex.[5] The present paper confirms the interpretation of the "new species"[4] as a complex and reports several other interesting results.

Equilibrium Constant Determinations.—Keefer and Andrews[6] and Ross[7] have given an equation from which the equilibrium constant for complex formation can be derived from a study of the variation in ultraviolet absorption with concentration. The equation for the equilibrium of interest here (1) is given in eq. 2.



(1)

$$X/D = Z/K\epsilon + 1/\epsilon \qquad (2)$$

where $X = c_0^2/(2c_0 - z)$, $Z = 1/(2c_0 - z)$, c_0 is the initial concentration of the pyridinium iodide, z is the concentration of the complex, ϵ the absorption coefficient for complex, K the equilibrium constant for complex formation and D the optical density due to complex.

Preliminary calculations revealed that equilibrium (1) was sensitive to the ionic strength of the medium. It was therefore necessary to make measurements of D at different ionic strengths, followed by extrapolation to a particular ionic strength. Lithium perchlorate was used as the inert salt and $\mu^{1/2} = 0.1$ ($\mu = 0.01$) was chosen as the "standard" ionic strength.

Three of the pyridinium iodides used previously[5] were examined in this work: 1-methylpyridinium iodide (MPI), 1,2,6-trimethylpyridinium iodide (TMPI) and 1,2,4,6-tetramethylpyridinium iodide (TeMPI).

Experimental

The iodides and 1-methylpyridinium perchlorate have been reported.[5] 1,2,6-Trimethylpyridinium perchlorate, m.p. 192.5–193.5° (recryst. from a mixture of isopropyl alcohol and methyl alcohol) and 1,2,4,6-tetramethylpyridinium perchlorate, m.p. 204.5–205.5° (reported 206–207°[8]) (recryst. from isopropyl alcohol), were prepared from the corresponding iodides and silver perchlorate.[5]

Lithium perchlorate (G. F. Smith Co.) was washed with ether and air-dried; m.p. 94.5–96.0°.

A solution containing approximately 0.005 M lithium thiosulfate and 0.05 M lithium chloride was prepared by grinding sodium thiosulfate pentahydrate with lithium chloride, leaching the pasty mass with absolute ethanol and diluting to the desired concentration with absolute ethanol.

Spectral Studies.—Solutions of pyridinium iodides in dilute aqueous sodium thiosulfate (*ca.* 5×10^{-4} M) containing various quantities of lithium perchlorate were prepared. Their ultraviolet absorptions (as D) were measured with a Warren Spectracord. A sample plot of D *versus* $\mu^{1/2}$ for MPI at 3100 Å. is given in Fig. 1.

Solutions of MPI and TeMPI in ethanol containing lithium thiosulfate were also studied. The data for TeMPI are presented in Fig. 2 in the form of a D *versus* c_0 plot.

The corrections for the ultraviolet absorption due to the pyridinium ions themselves were obtained by examining solutions of the appropriate perchlorate salt solutions. At

TABLE I

SUMMARY OF CALCULATIONS FOR AQUEOUS SOLUTIONS OF PYRIDINIUM IODIDES ($\mu = 0.01$)

	$K\epsilon$	K	ϵ
(a) 1-Methyl—3080 Å.			
1st approx.	871	2.50	348
1st iteration	931	2.60	312
2nd iteration	865	2.51	345
(b) 1-Methyl—3100 Å.			
1st approx.	736	1.58	466
1st iteration	742	1.92	385
2nd iteration	766	2.39	320
(c) 1-Methyl—3150 Å.			
1st approx.	515	1.29	400
1st iteration	513	1.02	500
2nd iteration	540	1.40	385
3rd iteration	566	2.04	278
(d) 1,2,6-Trimethyl—3040 Å.			
1st approx.	590	1.60	370
1st iteration	572	1.03	556
2nd iteration	585	1.60	364
3rd iteration	590	1.59	371
(e) 1,2,4,6-Tetramethyl—3000 Å.			
1st approx.	437	1.09	400
1st iteration	487	1.90	256
2nd iteration	488	2.05	238
3rd iteration	483	1.83	263

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[1] Pyridinium Rings. IV. The previous article in this series was E. M. Kosower, THIS JOURNAL, **78**, 3497 (1956).

[2] Department of Chemistry, University of Wisconsin, Madison 6, Wisconsin.

[3] Taken in part from a thesis submitted by J. C. B. in partial fulfillment of the requirements for the M.S. degree.

[4] E. M. Kosower, THIS JOURNAL, **77**, 3883 (1955).

[5] E. M. Kosower and P. E. Klinedinst, Jr., *ibid.*, **78**, 3493 (1956).

[6] R. M. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952).

[7] S. D. Ross, *et al.*, *ibid.*, **76**, 69 (1954), and subsequent papers.

[8] A. Baeyer and J. Piccard, *Ann.*, **384**, 208 (1911).

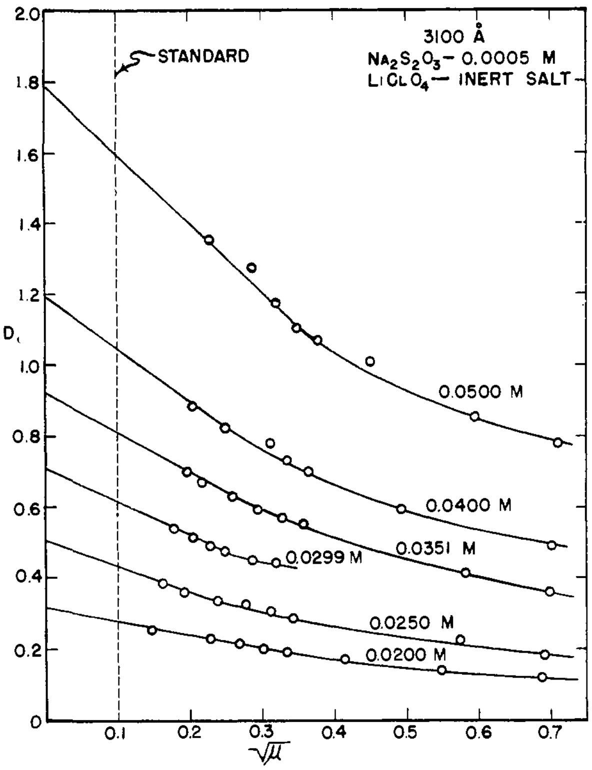

Fig. 1.—*D versus* $\mu^{1/2}$ for MPI in water at 3100 Å.

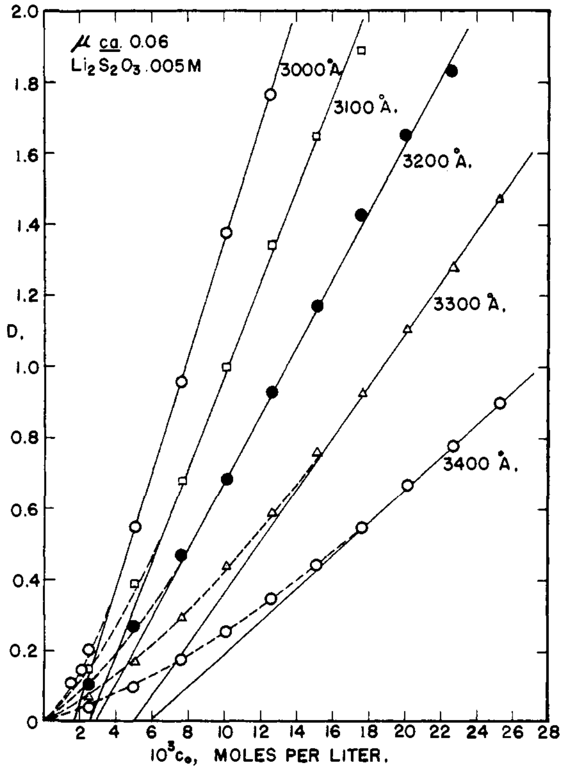

Fig. 2.—*D versus* c_0 for TeMPI in EtOH.

the wave lengths used for calculations, these corrections were negligible.

Control measurements showed that (a) no significant change in thiosulfate absorption occurred over a period of 3 days (all measurements were actually carried out on the same day that the pyridinium salt solutions were prepared), (b) no significant interaction between 1-methylpyridinium ions (as perchlorate) and thiosulfate was apparent at the concentration levels used in this work and (c) only a small shift in absorption maximum or absorption intensity was observed upon changing from water to ethanol (TeMPI λ_{max} 2690 Å. (log ϵ 3.82) for water; λ_{max} 2695 Å. (log ϵ 3.81) for ethanol).

Calculations.—A first approximation was derived using equation 2, with $z = 0$, and the resulting K used to calculate a value of z. Iteration was repeated until K was approximately constant. A typical iteration is shown in Fig. 3. The results of the calculations for aqueous solutions are summarized in Table I.

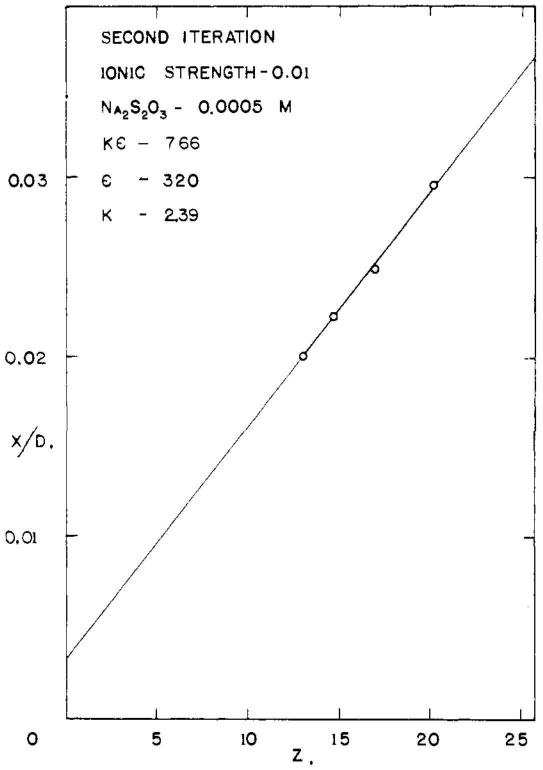

Fig. 3.—Second iteration of MPI in water at 3100 Å.

Errors.—The major sources of deviation were threefold. The absorption blank tended to drift slightly over periods of several hours, introducing possible errors of a few per cent. To minimize this difficulty, an effort was made to use optical densities above 0.20. The solutions were not thermostated, and although room temperature did not vary too widely, it is probable that K and possibly even ϵ are sensitive to temperature.[9] The greatest trouble was the inaccuracy of ϵ, as estimated in the iterations. The severe limitation imposed by the narrow concentration limits which could be used (see Fig. 1) coupled with the lack of temperature control forces us to accept ±15% variation in the values for the equilibrium constants.

Results

The values for the equilibrium constants are listed in Table II. It is also clear from the data

TABLE II

EQUILIBRIUM CONSTANTS FOR ASSOCIATION OF PYRIDINIUM IODIDES

Pyridinium ion	K, l. mole^{-1} [a]
1-Methyl-	2.3 ± 0.3
1,2,6-Trimethyl-	1.6 ± .3
1,2,4,6-Tetramethyl-	1.8 ± .3

[a] At $\mu^{1/2} = 0.1$.

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(9) F. A. Posey and H. Taube, THIS JOURNAL, **78**, 15 (1956).

that K decreases with increasing ionic strength. The rate of decrease is not linear; a change in slope occurs at about $\mu = 0.06$, and although no calculations have been carried out for high ionic strengths, the behavior of the optical density with $\mu^{1/2}$ indicates that the lower slope at higher ionic strengths is relatively constant (Fig. 1). Activity coefficients for 1–1 electrolytes often vary in this manner.

TABLE III

VARIATION OF K WITH $\mu^{1/2}$[a]

$\mu^{1/2}$	K
0.0	3.14
.1	2.63
.2	1.96
.3	1.84

[a] 1-Methylpyridinium iodide at 3100 Å. The average ϵ, 292, from first approximations ($z = 0$) was used to obtain K. It would not be expected that the K in this table would be exactly the same as that in Table II at $\mu^{1/2} = 0.1$.

As might have been expected, the behavior of the pyridinium salts becomes complicated when the solvent is changed to ethanol (DC 25). The extent of complexing rises, the charge-transfer absorption band shifts to longer wave lengths[10] and, in certain concentration ranges, complex absorption is proportional to the initial concentration, c_0, thus establishing that the salt is largely associated into ion-pairs. Although a quantitative comparison is not possible without additional information on the alcohol systems, it is sufficient to remark that absorption due to the complexing of 1-methylpyridinium and iodide ions is barely observable in water at a c_0 of 6.37×10^{-3} M,[4] although a similar concentration in ethanol has a very high D for complex absorption.

In Fig. 2, it may be seen that D for TeMPI is fairly linear with c_0 over certain concentration ranges. The situation is made somewhat obscure by the fact that the solvent already has an ionic strength of 0.06. D/c_0 *versus* c_0 plots are very roughly linear (with zero slope) at the higher concentrations and fall off badly as the concentration of pyridinium salt decreases but appear to be approximately linear at the lowest concentrations, presumably with slopes equal to $K\epsilon$. The latter situation corresponds to that existing in water. A much more complete investigation will be necessary to establish the precise behavior in alcoholic solvents.

Discussion

Brown and Brady[11] have divided the "complexes" of aromatic rings into two general groups: π- and σ-complexes. The former are characterized by an insensitivity of the equilibrium constant for complex formation to the substitution on the aromatic ring; their failure to respond to substitutive influences is best interpreted as meaning that only a weak or "loose" bond is formed between the aromatic ring and the complexing agent. Thus, the K for interaction of HCl with isodurene (1,2,3,5-tetramethylbenzene) is only 1.82 times that for toluene.[11]

The other type, the σ-complex, is extraordinarily sensitive to the degree of methyl-substitution, a situation probably due to the formation of a covalent bond between an atom of the aromatic ring and the complexing agent. With HF–BF$_3$, the equilibrium constant for isodurene is 560,000 times as great as that for toluene.[12]

Although the aromatic ring serves as an electron donor in the above complexes, it would be expected that analogous but opposite behavior would be observed for the aromatic ring as an electron acceptor. In other words, a lack of dependence of K upon methyl-substitution would be evidence for π-complex formation, while strong dependence would indicate σ-complex formation. In the case of pyridinium compounds, a σ-complex would be an addition product, a 1,2- or 1,4-dihydropyridine, and while methyl substitution should not have as great an effect as with benzene rings, an easily observable reduction in K would be expected on electronic as well as steric[5] grounds.

The equilibrium constants found in the present study for the association of 1-methylpyridinium ions and iodide ions (Table II) demonstrate clearly that additional methyl-substitution has virtually no effect upon K. The previous conclusion that the new species present in aqueous solutions of 1-methylpyridinium iodides was a charge-transfer complex[13] is thus substantiated.[5]

π-Complexes have been further classified into two categories, "general," where the complexing group is located more or less symmetrically with respect to the aromatic ring[17] and exemplified by the benzene–iodine complex, and "localized," bearing the complex group on one side of the aromatic ring. The latter type, involving the association of one π-bond of the ring with the complexing molecule, is represented by the benzene–silver ion complex.[14] Although the experimental distinction between these two sub-classes is not as clear-cut as between σ- and π-complexes, nevertheless, the "localized" π-complexes may be distinguished by their greater sensitivity to the steric requirements of complex formation. One may estimate that the equilibrium constant for argentation of tetramethylbenzenes should be about 3–4 times greater than that for toluene.[18] In actuality, in the case of in-

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(10) A clear example of this behavior is shown by 3-carbomethoxy-1-methylpyridinium iodide (λ_{max} for the charge-transfer band changes from *ca.* 2720 Å. in water to 3150 Å. in ethanol to 3700 Å. in chloroform.) However, the results obtained with 1-methylpyridinium iodides were actually the first clear indications of the solvent sensitivity of the charge-transfer band. An article dealing with this phase of charge-transfer complex behavior will be submitted at an early date. Unpublished results by F. R. Ells and J. C. Burbach.

(11) H. C. Brown and J. D. Brady, THIS JOURNAL, **74**, 3570 (1952).

(12) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

(13) The term charge-transfer complex, as used here and in previous papers of this series, refers to a loose, or π-complex. Spectral characteristics due to "charge-transfer"[14,15] are not the same as those observed for σ-complexes ("inner complexes").[16]

(14) R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952).

(15) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

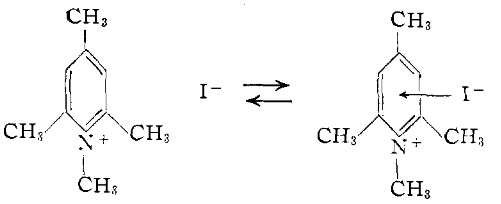
(16) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

(17) Complete symmetry, at least in the case of benzene–halogen complexes, seems excluded on the basis of an infrared active absorption band due to the X$_2$ bond; R. S. Mulliken, *J. Chem. Phys.*, **23**, 397 (1956). See, however, E. E. Ferguson, *J. Chem. Phys.*, **25**, 577 (1956), and R. L. Scott, *Ann. Rev., Phys. Chem.*, **7**, 57 (1956).

(18) From the data of N. Ogimachi, L. J. Andrews and R. M. Keefer, THIS JOURNAL, **78**, 2210 (1956). Since it is clear from the trend of the constants that methyl groups have a steric effect which hinders complex formation, a K per free position was estimated by assuming that a methyl group blocked 2/3 of a bond on either side, or a total of 4/3

terest for the present work, that of 1,2,3,5-tetramethylbenzene, the argentation constant is only about 0.75 of that for toluene,[16] a discrepancy which indicates that the substituent methyl groups exclude complexing sterically while helping it electronically. The very small difference in complexing constants for 1-methylpyridinium iodide and 1,2,-4,6-tetramethylpyridinium iodide make it likely that localized complex formation is not occurring since, on the above basis, a greater difference in K should result. "General" complexing is indicated, although it is not certain whether the iodide ion is located over the center of the ring, or over the nitrogen, as suggested by Mulliken.[19]

The fact that "new species" absorption in ethanol solution obeys the Beer law in certain concentration ranges is best interpreted as evidence that the salt concerned, 1,2,4,6-tetramethylpyridinium iodide, exists largely as ion-pairs. The equilibrium is shown in (3). The comparatively low dielectric constant of ethanol would favor ion-pair association. Without doubt, the ion-pair must be of the "solvent-separated" type,[20,21] as a true ion-pair must necessarily be converted to charge-transfer complex.



(3)

Perhaps the most interesting change occurring in ethanol is the distinct shift of absorption to longer wave lengths (Fig. 4).[10] The related explanation previously put forward to explain the change in color of solutions of pyridinium cyclopentadienylide[5] is thus further verified. If an excited state has materially less charge-separation than the ground state, then it will be less affected in changing from a solvent of one dielectric constant and solvating ability to another solvent of greatly different dielectric constant and solvating ability. A ground state with considerable charge separation would be destabilized in ethanol relative to water, and this destabilization would be far less serious for the excited state. Thus, the transition energy would be lowered and absorption shifted to longer wave lengths.

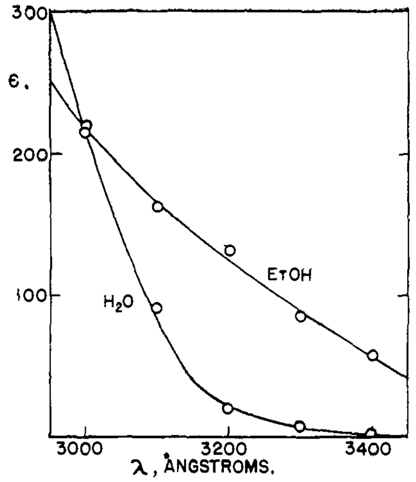
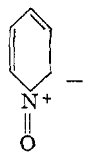


Fig. 4.—"Absorption" curves for the charge-transfer complex from 1,2,4,6-tetramethylpyridinium iodide in water and ethanol. The curve for ethanol was derived from the linear portion of the curves in Fig. 2, by assuming that ε at 3000 Å. was 220. The curve for water was derived from the $K\epsilon$ curve (ref. 5) by dividing by the value of K.

The case of pyridine-1-oxide, like that of pyridinium cyclopentadienylide, fits these considerations, even though pyridine-1-oxide is also not actually a charge-transfer complex. Ito[22,23] has analyzed the ultraviolet spectrum of pyridine-1-oxide, classifying a weak transition in the region of 3100 Å. as n-π^*, and the stronger absorption near 2900 Å. as $\pi - \pi^*$. The latter category, however, does not seem to completely describe the effect of solvent upon the position of the maximum, which changes from 2840 Å. in hexane to 2640 Å. in ethanol to 2535 Å. in water, unless the contribution of forms I and II to the excited state is emphasized. Ito and Hata[22] attribute the shift to perturbation of the π-electron configuration by hydrogen-bonding with solvent, but if the transition were simply $\pi - \pi^*$, the excited state would be perturbed to about the same extent as the ground state, and the position of the maximum should not change. One can conclude that the promoted electron arises "largely" from the region of the O⁻ group and is somewhat "neutralized" by entering an upper orbital on the pyridinium ring. The behavior of pyridine-1-oxide with respect to solvent change is parallel to that of the pyridinium iodide charge-transfer complexes.



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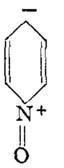

II

Some old observations of Hantzsch[24] are explicable on the same basis. The salt, 1-ethylpyridinium iodide, is colorless in water solution (DC 80), yellowish when concentrated in methanol (DC 33), yellow when concentrated in ethanol (DC 25), yellow in acetonitrile (DC 39), acetone (DC 31) and pyridine (DE 12.5), and intense yellow in tetrachloroethane (DC 8.2) and chloroform (DC 5.5). The depth of color follows dielectric constant. Qualitatively, judging from the shifts observed for 1-methylpyridinium iodide from water to ethanol,

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bond. Thus K_{fp} for benzene is 1.10/6 or 0.183, K_{fp} for toluene is 1.19/(14/3) or 0.255, and so on. Other K_{fp} values obtained in this way are 0.390 (1,2-dimethylbenzene), 0.405 (1,3-dimethylbenzene), 0.342 (1,4-dimethylbenzene), 0.40 (1,3,5-trimethylbenzene), 0.557 (1,2,4-trimethylbenzene), 0.66 (1,2,4,5-tetramethylbenzene), 0.66 (1,2,3,5-tetramethylbenzene) and 1.00 (1,2,3,4-tetramethylbenzene). These values are more or less parallel to the HCl-complexing constants obtained by Brown and Brady.[11] It can be seen that the K_{fp} for tetramethylbenzenes is *ca.* 3–4 times as large as the K_{fp} for toluene.

(19) R. S. Mulliken, private communication.

(20) S. Winstein, *et al.*, (a) THIS JOURNAL, **76**, 2597 (1954); (b) **78**, 328 (1956); (c) *Chemistry and Industry*, 664 (1954).

(21) H. Sadek and R. M. Fuoss, THIS JOURNAL, **76**, 5905 (1954).

(22) M. Ito and N. Hata, *Bull. Chem. soc. Japan*, **28**, 260 (1955).

(23) M. Ito and W. Mizushima, *J. Chem. Phys.*, **23**, 495 (1955).

(24) A. Hantzsch, *Ber.*, **52**, 1544 (1919).

and for 3-carbomethoxy-1-methylpyridinium iodide from water to ethanol to chloroform.[10] these colors are due to a shift of the charge-transfer band toward longer wave lengths. A more complete study of this interesting and valuable phenomenon will appear in a future publication.[10]

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BETHLEHEM, PA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF TEMPLE UNIVERSITY]

The Preparation of Some Substituted 2,6-Bis-(2-pyridyl)-pyridines

BY FRANCIS H. CASE AND THOMAS J. KASPER

RECEIVED MAY 24, 1956

The following substituted 4-phenylpyridines have been synthesized by a modified Tschitschibabin reaction: 2,6-bis-(4-methyl-2-pyridyl), 2,6-bis-(4-ethyl-2-pyridyl), 2,6-bis-(4-phenyl-2-pyridyl), 2,6-bis-(6-phenyl-2-pyridyl) and 2,6-bis-(2-quinolyl). The preparation of 4,4'-diethyl- and diphenyl-2,2'-bipyridines is also described.

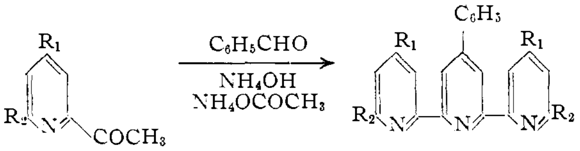
The extreme sensitiveness of the color given by the ferrous complex of 2,6-bis-(2-pyridyl)-pyridine (molecular extinction coefficient 12,500) and of 2,6-bis-(2-pyridyl)-4-phenylpyridine[1] (I), (*E* 22,000) have been pointed out by Wilkins and Smith.[2] It seemed to us, on the basis of experience in the 1,10-phenanthroline series, that the introduction of further alkyl or phenyl substituents, particularly in the 4-positions to nitrogen, should further enhance the sensitivity of the molecule. This has already been confirmed by the above authors in the case of 2,6-bis-(4-methyl-2-pyridyl)-4-phenylpyridine (II) (*E* 26,300) prepared by us.

The synthesis of II was effected in the following manner: 2-bromo-4-methylpyridine[3] was converted to the nitrile by the method of Craig[4] and this in turn to the acetyl derivative by a methyl Grignard. The 4-methyl-2-acetyl pyridine was then converted to II by reaction with benzaldehyde, ammonium acetate and ammonium hydroxide (method of Frank and Seven[5]). The synthesis of 2,6-bis-(4-ethyl-2-pyridyl)-4-phenylpyridine (III) was accomplished in a similar manner, starting from the hitherto unknown 2-amino-4-ethylpyridine.

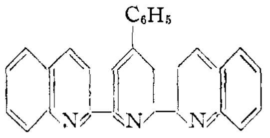
In the case of 2,6-bis-(4-phenyl-2-pyridyl)-4-phenylpyridine (IV), and 2,6-bis-(6-phenyl-2-pyridyl)-4-phenylpyridine (V), 4-phenylpyridine[6] and 2-phenylpyridine,[7] respectively, were converted to their 2-cyano derivatives through the 2-amino and 2-bromo compounds. In these cases conversion to the 2-acetyl derivatives by a methyl Grignard was found unsuccessful. The cyano compounds were therefore converted to the carbethoxy derivatives which were condensed with ethyl acetate to form the substituted ethyl acetoacetate derivatives. Hydrolysis then yielded the acetyl derivatives[8] which were condensed with benzaldehyde and ammonia as before.

For the preparation of 2,6-bis-(2-quinolyl)-4-phenylpyridine (VI), 2-acetylquinoline[9] was used in the above reaction. Compound VI has been found lacking in chelating properties.[2]

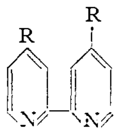
From 2-bromo-4-ethyl-and 2-bromo-4-phenylpyridine an Ullmann reaction yielded the corresponding 4,4'-diethyl-(VII) and 4,4'-diphenyl-(VIII)-2,2'-bipyridines. These will also be tested for metal-chelating properties.



I, R_1 = H; R_2 = H
II, R_1 = CH_3; R_2 = H
III, R_1 = C_2H_5; R_2 = H
IV, R_1 = C_6H_5; R_2 = H
V, R_1 = H; R_2 = C_6H_5



VI



VII, R = C_2H_5
VIII, R = C_6H_5

Experimental

Preparation of 2-Aminopyridines.—A mixture of one molar proportion of 2- or 4-substituted pyridine, 1.18 moles of sodamide and 2.2 moles of dimethylaniline was heated at 150–160° (130–140° in the case of 4-ethylpyridine) for 6 hr. The reaction mixture, after cooling, was poured into water, and the dimethylaniline layer separated and dried over anhydrous potassium carbonate. After removal of solvent *in vacuo* the residue was distilled *in vacuo* (except in the case of the 4-phenyl-2-aminopyridine, which solidified at once). The distillates then solidified and were purified by crystallization.

Preparation of 2-Bromopyridines.—(The method of Craig[4] was used).—To a solution of 0.3 mole of substituted 2-aminopyridine in 175 ml. of 48% hydrobromic acid was added 42 ml. of bromine. A solution of 52 g. of sodium nitrite in 74 ml. of water was then added gradually, keeping the temperature below 5° until near the end of the reaction, when it rose spontaneously to 12°. A solution of 112 g. of sodium hydroxide in 285 ml. of water was then added keeping the temperature below 20°. The reaction mixture was extracted with ether, the ether removed and the resulting oil distilled *in vacuo*. Except in the case of 2-bromo-4-

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[1] R. L. Frank and E. F. Riener, THIS JOURNAL, **72**, 4183 (1950).
[2] D. H. Wilkins and G. F. Smith, *Anal. Chim. Acta*, **9**, 338 (1953).
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