

previously described for such reactions<sup>6</sup> to give 8.2 g. of pale, yellow needles, recrystallized from 95% alcohol, m. p. 166–167°.

*Anal.* Calcd. for  $C_{24}H_{30}N_2O_3$ : C, 73.07; H, 7.67. Found: C, 72.85; H, 7.78.

**Reaction of Phenylmagnesium Bromide with  $\alpha,\beta$ -Dimorpholinobenzyl-*p*-methylacetophenone.**—The Grignard reagent was prepared from 1.85 g. (4 equiv.) of magnesium and 12 g. (4.1 equiv.) of bromobenzene in 40 ml. of dry ether. To this solution was added in one minute 7.5 g. of the diamino ketone dissolved in 60 ml. of dry benzene. After refluxing for two hours the solution remained clear. The reaction mixture was decomposed as before and the benzene–ether solution washed with water, dried over anhydrous sodium sulfate and evaporated to leave a brown oil that would not crystallize from benzene–petroleum ether solutions.

The oily product was dissolved in warm 85% alcohol. From this solution was eventually obtained a high melting compound which gave, after four recrystallizations from benzene and petroleum ether mixtures, a slightly soluble, colorless, crystalline product (V), m. p. 217–220°; yield 1.1 g., 12%.

*Anal.* Calcd. for  $C_{30}H_{36}N_2O_3$ : C, 76.24; H, 7.68. Found: C, 75.96; H, 7.71.

Concentration and strong cooling of the 85% alcohol filtrates from (V) gave 0.8 g. (17% yield) of benzhydrylmorpholine (VI), m. p. 75–77°. Treatment of the residual oil from the evaporation of the filtrates of (VI) with hydroxylamine in alcohol–potassium hydroxide solutions<sup>7</sup> gave 0.60 g. (14% yield) of a flaky, colorless, oxime (VIII), m. p. 149–153°, identical with  $\omega$ -morpholino-*p*-methylacetophenone oxime.

The filtrate from (VIII) was evaporated and the residual oil dissolved in dry ether. Gaseous hydrogen chloride was added to this solution to precipitate all of

the remaining basic products. The ether solution was washed with water, dried over anhydrous calcium sulfate and evaporated to leave 0.51 g. of a brown oil. This oil was crystallized from 85% alcohol to give only traces of biphenyl. No trace of phenyl *p*-tolyl ketone nor diphenyl *p*-tolyl carbinol was obtained.

**$\omega$ -Morpholino-*p*-methylacetophenone Oxime (VIII).**—From 4.0 g. of  $\omega$ -morpholino-*p*-methylacetophenone hydrochloride<sup>15</sup> was obtained 3.6 g. of colorless, flaky crystals, m. p. 150–154°, using the method previously described for  $\omega$ -morpholinoacetophenone oxime.<sup>7</sup> The product was recrystallized from 85% alcohol.

*Anal.* Calcd. for  $C_{13}H_{18}N_2O_2$ : C, 66.64; H, 7.74. Found: C, 66.81; H, 7.88.

### Summary

1.  $\alpha,\beta$ -Dimorpholinobenzylacetone reacts readily with Grignard reagents to give the expected  $\alpha,\beta$ -diamino carbinols in fair yields.

2.  $\alpha,\beta$ -Dimorpholinobenzylacetophenones contain a hindered carbonyl group. Addition to the carbonyl group is slowed, so that the expected  $\alpha$ - $\beta$ -diamino carbinol is accompanied by considerable amounts of lower molecular weight products resulting from cleavage by the Grignard reagent of the bond between the *alpha* and *beta* carbon atoms. An explanation of this type of cleavage is presented and compared with a similar cleavage of open chain 1,3-diketones.

(15) German Patent 667,356, Nov. 9, 1938; *C. A.*, **33**, 2287<sup>1</sup> (1939).

LINCOLN, NEBRASKA

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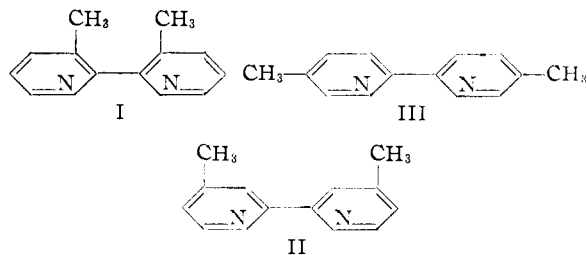
[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

## Effect of the Symmetrical Situation of Methyl Groups on the Property of Dimethyl-2,2'-bipyridyl to Complex the Ferrous Ion

BY F. WM. CAGLE, JR., AND G. FREDERICK SMITH

The complex 2,2'-bipyridyl ferrous ion  $Fe(C_{10}H_8N_2)_3^{++}$  has long been known.<sup>1</sup> Salts of this ion and their solutions are intensely red, and this color together with the observation that the solutions conform closely to Beer's law have made 2,2'-bipyridyl a very desirable reagent for colorimetric iron determinations.<sup>2</sup> For an extended discussion and bibliography of the analytical uses of 2,2'-bipyridyl, the reader is referred to two monographs containing this material.<sup>3,4</sup>

The purpose of this investigation was to compare and contrast, in so far as possible, the ferrous complexes of three symmetrically substituted dimethyl 2,2'-bipyridyls. These were 3,3'-dimethyl-2,2'-bipyridyl (I), 4,4'-dimethyl-2,2'-bipy-



ridyl (II) and 5,5'-dimethyl-2,2'-bipyridyl (III).<sup>5</sup> Previous work on 6,6'-dimethyl-2,2'-bipyridyl has shown that this compound does not form a ferrous iron complex<sup>6</sup> so it may be eliminated from this investigation. An analogous condition is met with 2,2'-biquinoyl.<sup>7</sup> In fact, the substitution of only one of the 6 positions on 2,2'-bipyridyl suffices to much weaken the ability to

(1) F. Blau, *Ber.*, **21**, 1077 (1888); *Monatsh.*, **10**, 375 (1889).

(2) J. T. Woods and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **13**, 551 (1941).

(3) G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," The G. Frederick Smith Chemical Co., Columbus, Ohio, 1944.

(4) "Organic Reagents for Metals," Hopkin and Williams Ltd., London, 1944, ed. 4, p. 66–69.

(5) These compounds were furnished by Professor Francis H. Case of Temple University, *THIS JOURNAL*, **68**, 2574 (1946).

(6) F. Feigl, *Ind. Eng. Chem., Anal. Ed.*, **8**, 406 (1936).

(7) A. P. Smirnov, *Helv. Chim. Acta*, **4**, 802 (1921).

complex the ferrous iron.<sup>8</sup> This shielding effect of a single group in the 6 positions is evident in the failure of 2-(2'-pyridyl)-quinoline to complex the ferrous ion.<sup>7</sup>

A preliminary investigation of the three dimethylbipyridyls shown above revealed that all gave the characteristic red color with a ferrous solution. The color in the cases of compounds II and III was stable over a considerable range of pH (3-8) while in the case of compound I the range is much narrower, pH (4-6). The complex stability depends on the concentration of the complex and time and nature of storage.

### Experimental

Solutions of known strengths of the ferrous complexes of compounds I, II and III were prepared by weighing the pure bases and adding them to a weighed amount of water in a glass-stoppered Pyrex flask. The calculated amount of analyzed  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added. The flask was then closed and shaken mechanically for eight hours. The complexes made from bases II and III gave clear red solutions while that from I soon decomposed. In order to remedy this the complex of base I was prepared in a buffer solution which was 0.5 N in acetic acid and 0.5 N in sodium acetate. This solution was stable.

These stock solutions were added from a weight buret into weighed quantities of water. In this fashion solutions were made up over the range of approximately 0.00003 to 0.0002 mole/1000 g. of solution. These dilute solutions were relatively stable in the cases of bases II and III but quite unstable in the case of base I.

Absorption spectra of the solutions containing complexes of bases II and III were obtained on a General Electric (Hardy) recording spectrophotometer.<sup>9</sup>

Dilute solutions of the ferrous complex of base I were not sufficiently stable to be transported to the instrument so these solutions, made up in a buffer, were examined for the wave length of maximum absorption and the per cent. transmittancy at that wave length with a Beckman spectrophotometer.<sup>10</sup>

Table I gives data on wave length of maximum absorption and the molecular extinction coefficient ( $K$ ) at that wave length for the ferrous complexes of each of the bases. The corresponding values for 2,2'-bipyridyl are added from the work of Moss and Mellon for the purpose of comparison.<sup>11</sup>

TABLE I

COLOR CONSTANTS OF SUBSTITUTED BIPYRIDYLS		
Base	$m\mu$	$K^{12}$
I	526	1770
II	529	8470
III	510	8300
2,2'-Bipyridyl	522	8650

### Theoretical

For the purpose of comparison, figures showing

(8) F. H. Burstall, *J. Chem. Soc.*, 1664 (1938).

(9) For a concise description of this useful instrument see M. G. Mellon, "Colorimetry for Chemists," *The G. Frederick Smith Chemical Co.*, Columbus, Ohio, 1945, pp. 70-75.

(10) For a discussion of this instrument see M. G. Mellon, *ibid.*, pp. 68-70.

(11) M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **14**, 862 (1942).

(12) Note that in the work of Moss and Mellon, as well as in most work, the units of  $K$  are liters moles<sup>-1</sup> cm.<sup>-1</sup> while in our work the value is expressed as kilograms moles<sup>-1</sup> cm.<sup>-1</sup>. For dilute aqueous solutions whose density is about 1 g./milliliter the difference between these two values is within the limit of optical measurement and thus the values are interchangeable.

graphs of the per cent. transmittancy vs. wave length in  $m\mu$  for various solutions of the ferrous complex of bases II and III are included. Figure 1 is for the ferrous complex of base II and data from the figure together with concentrations of the solutions are given in Table II. Similarly for base III, Fig. 2 and Table III are given. The ferrous complexes of bases II and III obey Beer's law over the range considered.

TABLE II  
THE FERROUS COMPLEX OF BASE II

Solution	Moles/1000 g. of solution	$T(529 m\mu)$	$K$
1	0.0000375	0.514	7740
2	.0000788	.219	8380
3	.0001006	.143	8560
4	.0001465	.0540	8650
5	.0002027	.0155	9000

$K$  (average) is 8470 kg. moles<sup>-1</sup> cm.<sup>-1</sup>

TABLE III  
THE FERROUS COMPLEX OF BASE III

Solution	Moles/1000 g. of solution	$T(510 m\mu)$	$K$
1	0.0000448	0.444	7890
2	.0000879	.188	8300
3	.0001185	.102	8360
4	.0001325	.0770	8400
5	.0001879	.0250	8540

$K$  (average) is 8300 kg. moles<sup>-1</sup> cm.<sup>-1</sup>

One thing to be especially noted is the much less intense color of the ferrous complex of base I.

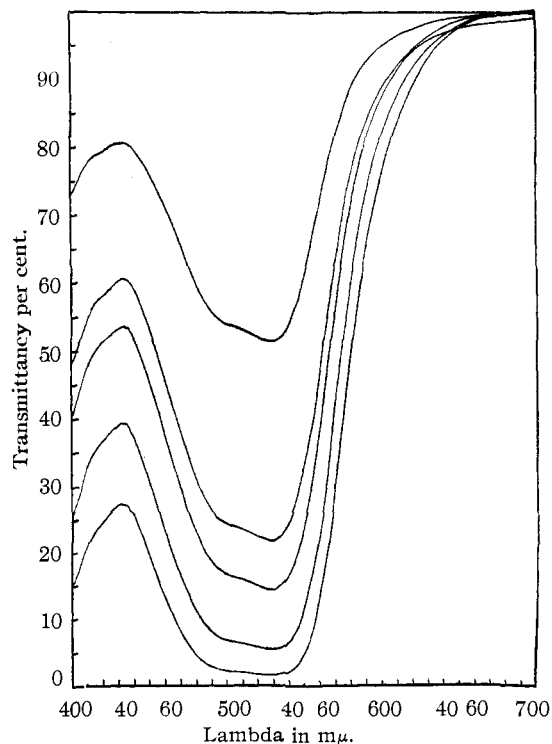


Fig. 1.

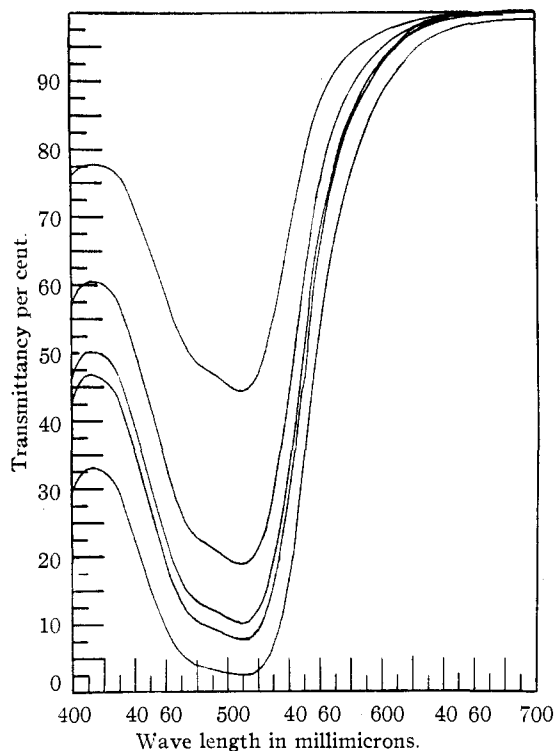


Fig. 2.

This is very probably due to the crowding of the methyl groups in the base and the resulting non-coplanarity of the pyridine rings. It seems reasonable to assume that the stabilities of the complexes are dependent on resonance between

the rings and that with this lost the complex becomes more and more difficult to form and also less and less stable. This is in agreement with observations at this laboratory that 3,3'-dicarboxy-2,2'-bipyridyl gives no complex with ferrous iron.<sup>13</sup>

We intend to inspect the ultraviolet absorption of the bases themselves as a further check on the postulates above.<sup>14</sup>

**Acknowledgment.**—We wish to thank Professor J. O. Kraehenbuehl of the Electrical Engineering Department of the University of Illinois for the curves with the General Electric recording spectrophotometer and Miss Ruth M. Johnston for special measurement of unstable solutions on the Beckman spectrophotometer.

### Summary

1. The ferrous complexes of 3,3'-dimethyl-2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl and 5,5'-dimethyl-2,2'-bipyridyl have been prepared and their absorption spectra have been studied.

2. An explanation is offered for the much smaller molecular extinction coefficient of 3,3'-dimethyl-2,2'-bipyridyl ferrous complex compared with the other two and that of the 2,2'-bipyridyl complex.

3. The ferrous complexes of 4,4'-dimethyl-2,2'-bipyridyl and 5,5'-dimethyl-2,2'-bipyridyl conform to Beer's law over the range 0.00003 to 0.0002 mole/1000 g. of solution.

(13) F. P. Richter, Ph. D. Thesis, University of Illinois (1941).

(14) For some recent work in this direction see: W. H. Rodebush, and I. Feldman, *THIS JOURNAL*, **68**, 896 (1946).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Measurement of Potentials at the Interface between Vitreous Silica and Solutions of Thorium Chloride and Lanthanum Chloride

BY LLOYD A. WOOD<sup>1</sup> AND LAWRENCE B. ROBINSON<sup>2</sup>

Earlier papers<sup>3</sup> have described the improved apparatus for the measurement of streaming potentials and have reported the measurement of the zeta-potential of vitreous silica in contact with pure water, and with potassium chloride and barium chloride solutions. Herein are reported measurements with thorium chloride and lanthanum chloride solutions.

### Experimental

Thorium chloride was prepared by the method described by Jones and Frizzell,<sup>4</sup> yielding a white

(1) Present address: Department of Chemistry, Cornell University, Ithaca, New York.

(2) Present address: Department of Physics, Howard University, Washington, D. C.

(3) (a) Grinnell Jones and L. A. Wood, *J. Chem. Phys.*, **13**, 106 (1945); (b) L. A. Wood, *ibid.*, **13**, 429 (1945); (c) *THIS JOURNAL*, **68**, 437, (1946); (d) L. A. Wood and L. B. Robinson, *J. Chem. Phys.*, **14**, 251 (1946).

(4) Grinnell Jones and L. D. Frizzell, *ibid.*, **8**, 986 (1940).

hygroscopic solid of high purity. Professor Grinnell Jones kindly supplied a sample of lanthanum chloride which he had carefully purified.<sup>5</sup> The apparatus for producing and measuring the streaming potentials has been previously described,<sup>3a</sup> and consisted essentially of two Pyrex reservoirs connected by means of a vitreous silica capillary. The connections were made with ground joints sealed with paraffin wax which had been washed repeatedly, while melted, with boiling conductivity water. The solutions were forced through the capillary by nitrogen pressure, the gas having been passed in succession through tubes of soda lime and moist glass wool to remove carbon dioxide and dust. Silver-silver chloride electrodes were located at either end of the capillary to make possible the measurement of the stream-

(5) Grinnell Jones and C. F. Bickford, *THIS JOURNAL*, **56**, 602 (1934).