(malonic acid melts at 136°). Two recrystallizations of the benzene-soluble material gave a very small amount of solid, m.p. 93–95°, mixed m.p. with a sample of glutaric acid, m.p. 94–96°.

C, from the above ozonolysis, gave 1.35 g. of white solid, m.p. 179–185°. After recrystallization from water it melted at 186–189°, mixed m.p. with a sample of succinic acid 187–189°.

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β-2-Pyrrole-ethylamine

BY WERNER HERZ

RECEIVED SEPTEMBER 5, 1952

In view of the appearance of two recent articles in which the synthesis of β-2-pyrrole-ethylamine from ethyl 2-pyrroleacetate is described,[1,2] we wish to report work carried out in this Laboratory which led to this amine and related substances *via* a different and very convenient route.

As outlined below we have utilized our earlier discovery that Mannich bases derived from pyrrole readily serve as alkylating agents.[3] 2-Dimethylaminomethylpyrrole methiodide, available from pyrrole in 80–85% yield,[4] was treated with sodium cyanide in aqueous solution and the resulting nitrile, obtained in 52% yield, was reduced to the amine using lithium aluminum hydride. This sequence of reactions obviates the difficulties caused during the last step by the relative insolubility of the amide in ether and appears to be generally applicable, as exemplified by the preparation of β-2-(N-methylpyrrole)-ethylamine.

The physiological properties of these amines are now being investigated and will be reported elsewhere.

Acknowledgment.—This work was supported in part by a grant from the United States Public Health Service. We wish to thank Dr. H. J. Barrett of the Electrochemicals Division, du Pont de Nemours and Company, Inc., for the generous gift of chemicals.

Experimental[5]

2-Pyrroleacetonitrile.—2-Dimethylaminomethylpyrrole was prepared in 87% yield by the Mannich reaction[4] and was converted to the methiodide by dropwise addition to excess methyl iodide with stirring and cooling to avoid the formation of by-products.[6] The freshly prepared methiodide, wt. 34 g. (91%), which quickly turns dark on standing, was heated on the steam-bath for 1.5 hours with 17 g. of sodium cyanide and 200 ml. of water. The dark mixture was cooled and thoroughly extracted with ether. Fractionation of the dried ether extracts yielded 7.1 g. (52%) of product, b.p. 110–115° (2 mm.). The analytical sample boiled at 102–103° (1.1 mm.), n^{23}D 1.5230.

Anal. Calcd. for $C_6H_6N_2$: C, 67.92; H, 5.70. Found: C, 67.70; H, 5.82.

β-2-Pyrrole-ethylamine.—A solution of 36 g. of the nitrile in 400 ml. of anhydrous ether was added dropwise with stirring to 17 g. of lithium aluminum hydride in one liter of ether. The mixture was worked up as recommended by Amundsen and Nelson.[7] On distillation there was obtained 24.5 g. (66%) of a rather viscous basic substance, b.p. 90–98° (2 mm.). The analytical sample boiled at 91–92° (1.7 mm.).

Anal. Calcd. for $C_6H_{10}N_2$: C, 65.40; H, 9.16. Found: C, 65.28; H, 9.01.

The orange picrate, m.p. 154.5–155° (dec.), lit.[1] 156°, was prepared by mixing alcoholic solutions of the amine and picric acid and heating. Crystals separated only after dilution with water and prolonged chilling.

β-2-(N-Methylpyrrole)-ethylamine.—The yield of 2-N-methylpyrroleacetonitrile[3b] was improved considerably by carrying out the reaction on a steam-bath. From 201 g. of 2-dimethylaminomethyl-N-methylpyrrole methiodide there was obtained 36 g. (42%) of the nitrile and 11.6 g. (12%) of crude 2-N-methylpyrroleacetamide. Lithium aluminum hydride reduction of the nitrile in the manner described above yielded on fractional distillation 19.7 g. (53%) of a basic substance which decomposed slowly at room temperature and readily absorbed carbon dioxide from the air; b.p. 70–75° (1.5 mm.). The analytical sample boiled at 70–71° (1.5 mm.), n^{24}D 1.5248.

Anal. Calcd. for $C_7H_{12}N_2$: N, 22.55. Found: N, 22.39.

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[1] K. Eiter, *Monatsh.*, **83**, 252 (1952).

[2] W. Kutscher and O. Klamerth, *Z. physiol. Chem.*, **289**, 229 (1952).

[3] (a) W. Herz, K. Dittmer and S. J. Cristol, THIS JOURNAL, **70**, 504 (1948); (b) W. Herz and J. L. Rogers, *ibid.*, **73**, 4923 (1951).

[4] W. Herz, K. Dittmer and S. J. Cristol, *ibid.*, **69**, 1698 (1947).

[5] Melting points are uncorrected. Analyses by Clark Microanalytical Laboratory, Urbana, Illinois.

[6] C. Schöpf and J. Thesing, *Angew. Chem.*, **63**, 377 (1951); J. Thesing and F. Schülde, *Ber.*, **85**, 324 (1952).

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Metachromasy of Rhodamine 6G Produced by Polyvinyl Sulfate

BY M. KOIZUMI AND N. MATAGA

RECEIVED SEPTEMBER 12, 1952

In the course of the study of metachromasy, we have found that the system Rhodamine 6G and K-polyvinyl sulfate (PVSK) (of which sulfonation degree is 61%) shows a very interesting type of concentration effect which differs from the result reported recently by Levine and Schubert.[1]

The main features of our experimental results can be summarized as follows. (a) The absorption spectrum of the aqueous Rhodamine 6G solution has a peak at 526 mμ accompanied by a small shoulder at 500 mμ in the range of lower concentration, but the shoulder at 500 mμ grows gradually as the concentration increases, the peak at 526 mμ declining at the same time. These results are the same as those reported by other investigators and the peaks at 526 mμ and at 500 mμ can be attributed, respectively, to the monomer (M-band) and the dimer (D-band)[2] (*cf.* Fig. 1).

(b) When PVSK is added step by step to the aqueous Rhodamine 6G solution of a definite concentration, the D-band grows quite rapidly, at first, accompanied with the reduction of M-band, but when the quantity of the added PVSK reaches a certain critical value, the M-band begins to grow again (*cf.* Fig. 2), though the turning point is not so sharp and varies with the dye concentration. Such behaviors are always observed at any concentration of dye between 5×10^{-6} mole/liter and 5×10^{-5} mole/liter. It is to be added that although position of the M-band does not change at

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[2] W. L. Levshin, *Acta Physicochim. U.R.S.S.*, **1**, 684 (1935).

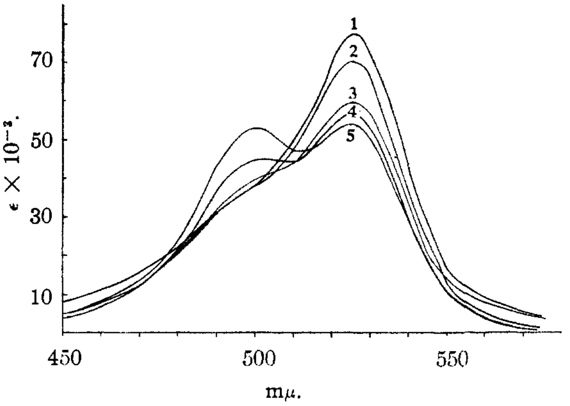

Fig. 1.—The absorption spectra of the pure aqueous Rhodamine 6G solution: dye concentration in mole/liter: 1, 5 × 10^{-6}; 2, 20 × 10^{-6}; 3, 50 × 10^{-6}; 4, 100 × 10^{-6}; 5, 200 × 10^{-6}.

all, there may exist a slight shift of D-band toward the shorter wave length. We can say little about the magnitude of this shift, but it must be very small if it really exists, since the peak of D-band, even in pure aqueous solution, should move toward shorter wave lengths to some extent when the concentration becomes much higher than that in Fig. 1.

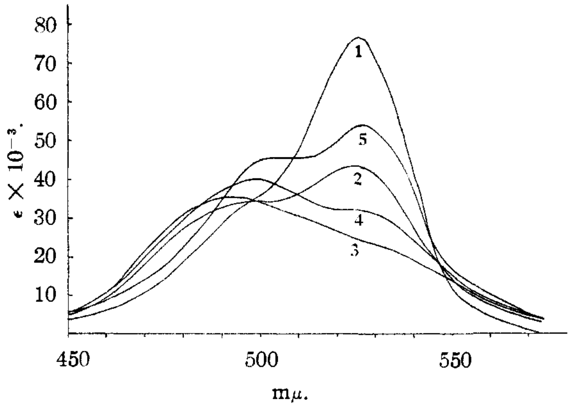

Fig. 2.—Examples of spectral change produced by the addition of PVSK: dye concentration 10^{-5} mole/liter; 1, without PVSK; 2, 1 (× 7.56 × 10^{-6} g./cc.); 3, 10 (× 7.56 × 10^{-6} g./cc.); 4, 125 (× 7.56 × 10^{-6} g./cc.); 5, 1000 (× 7.56 × 10^{-6} g./cc.).

On the basis that the above spectral change is attributable to the shift of monomer–dimer equilibrium caused by the adsorption of dye ions on PVSK molecules and also with some simple assumptions as to the adsorption, we have been able to explain almost quantitatively the variation of the height of M-band, covering from 5 × 10^{-6} mole/liter to 5 × 10^{-5} mole/liter in the dye concentration and from 0 to 7.56 × 10^{-3} g./cc. in the quantity of added PVSK.

In this treatment, we have assumed, as a first approximation, that the spectral behaviors of monomer and dimer are not influenced by the adsorption, neglecting the possible shift of D-band, and have calculated the concentration of monomer and dimer in the whole system from the height of the M-peak. The treatment, except the assumption about the adsorption, is quite analogous to that performed by Levschin[2] and Rabinowitch[3] in explaining the spectral behaviors of the pure aqueous solution in terms of monomer–dimer equilibrium.

Qualitatively speaking our interpretation can be stated as follows; when a small amount of PVSK is added to the aqueous Rhodamine 6G solution, the concentration of dye ions adsorbed on the surface of PVSK becomes large and the fraction of dimer in the whole system is increased, while a too large quantity of PVSK makes the surface concentration of dye ions on PVSK diluted, producing the phenomenon of recovery.

Thus, it becomes clear that metachromasy in this system is caused mainly by the shift of monomer–dimer equilibrium produced by the adsorption of dye ions on PVSK. We may consider that the metachromasy of this system is of one ideal type in which only the state of aggregation of dye ions is influenced by the adsorption, while we may imagine another ideal type in which only the electronic state of the dye ion is influenced by the adsorption on the metachromatic substance without any change of the aggregation of the former. Many cases would perhaps be the superposed ones of the above two types.

Analogous phenomena of recovery were also found in the case of Trypaflavin, Thionin, Toluidine blue and Pyronine.

No marked new band appears in the case of Trypaflavin and the behavior is comprehended as the same type with Rhodamine 6G at least qualitatively.

Toluidine blue, Thionine and Pyronine resemble the system studied by Levine in the point that a new metachromatic band appears, which declines at higher concentration of PVSK with the simultaneous rise of M- and D-band.

The phenomena of recovery in these cases can also be comprehended with the properly interpreted adsorption model.

It must, however, be added that the picture of adsorption is a mere model; the real state of affairs would be of such a nature that at low concentration of PVSK a dye ion attaches to a functional group of PVSK one-to-one, while at higher concentration of PVSK, many functional groups surround one dye ion (this corresponds to the decrease of surface concentration in the adsorption model) competing with each other for the dye ion. In the latter circumstance, the interaction between the dye ion and the metachromatic molecule will become more or less weakened, and this state might also be expressed with the word "leveling out of the medium" which is nothing but Levine's idea.

The full data and the details of discussion will be published in Journal of the Institute of Polytechnics, Osaka City University.

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