

(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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### $\beta$ -2-Pyrrole-ethylamine

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In view of the appearance of two recent articles in which the synthesis of  $\beta$ -2-pyrrole-ethylamine from ethyl 2-pyrroleacetate is described,<sup>1,2</sup> 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.<sup>3</sup> 2-Dimethylaminomethylpyrrole methiodide, available from pyrrole in 80–85% yield,<sup>4</sup> 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  $\beta$ -2-(N-methylpyrrole)-ethylamine.

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

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#### Experimental<sup>5</sup>

**2-Pyrroleacetonitrile.**—2-Dimethylaminomethylpyrrole was prepared in 87% yield by the Mannich reaction<sup>4</sup> and was converted to the methiodide by dropwise addition to excess methyl iodide with stirring and cooling to avoid the formation of by-products.<sup>6</sup> 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.),  $n_D^{20}$  1.5230.

*Anal.* Calcd. for  $C_6H_8N_2$ : C, 67.92; H, 5.70. Found: C, 67.70; H, 5.82.

**$\beta$ -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.<sup>7</sup> 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.<sup>1</sup> 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.

**$\beta$ -2-(N-Methylpyrrole)-ethylamine.**—The yield of 2-N-methylpyrroleacetonitrile<sup>8</sup> 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.),  $n_D^{20}$  1.5248.

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

(7) L. H. Amundsen and L. S. Nelson, *THIS JOURNAL*, **73**, 242 (1951).

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### Metachromasy of Rhodamine 6G Produced by Polyvinyl Sulfate

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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.<sup>1</sup>

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 m $\mu$  accompanied by a small shoulder at 500 m $\mu$  in the range of lower concentration, but the shoulder at 500 m $\mu$  grows gradually as the concentration increases, the peak at 526 m $\mu$  declining at the same time. These results are the same as those reported by other investigators and the peaks at 526 m $\mu$  and at 500 m $\mu$  can be attributed, respectively, to the monomer (M-band) and the dimer (D-band)<sup>2</sup> (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  $5 \times 10^{-6}$  mole/liter and  $5 \times 10^{-5}$  mole/liter. It is to be added that although position of the M-band does not change at

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

(2) W. Kutscher and O. Klammer, *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 Micro-analytical Laboratory, Urbana, Illinois.

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

(1) A. Levine and M. Schubert, *THIS JOURNAL*, **74**, 91 (1952).

(2) W. L. Levshin, *Acta Physicochim. U.R.S.S.*, **1**, 684 (1955).