

## NOTES

**A Note on the Use of Aniline in the Preparation of Amino Acids.—**

A standard method of isolating certain amino acids is to precipitate them from the alcoholic solutions of their hydrochlorides with pyridine. Cox, *J. Biol. Chem.*, **78**, 475 (1928), used aniline in preparing *d*-arginine monohydrochloride. A consideration of the basic ionization constants of glycine, alanine and aniline indicated that aniline should precipitate these amino acids from their hydrochlorides. Experiment justified this prediction. Glycine can be prepared by the method of Clarke and Taylor, "Organic Syntheses," **4**, 31 (1925), using aniline instead of pyridine. Alanine has been prepared by mixing acetaldehyde (1 mole), aqueous ammonium chloride (2 moles), and sodium cyanide (1 mole), and hydrolyzing by concentrated hydrochloric acid. This solution is then evaporated under reduced pressure to a thick paste, treated with absolute methanol (10 moles), filtered to remove solid chlorides and treated with aniline (1.3 moles). The yield of recrystallized alanine is 50% of the theoretical amount.

$\alpha$ -Amino-*isobutyric* and  $\alpha$ -amino-*n*-valeric acids can be easily prepared in a similar manner.

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DENTAL SCHOOL  
NORTHWESTERN UNIVERSITY  
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H. C. BENEDICT

**$\beta,\beta$ -Dinaphthyl Sulfide as a By-product in the Preparation of  $\beta$ -Naphthoic Nitrile. Reduction of the Sulfone with Sodium Cyanide.—** Colver and Noyes,<sup>1</sup> while working on the synthesis of anthracene from naphthalene, found that the hydrolysis of the crude nitrile of  $\beta$ -naphthoic acid by boiling with a 30% solution of sodium hydroxide "left an unsaponifiable residue which is a reddish colored liquid at the temperature of the hot water-bath, but solidifies to a dirty red solid upon cooling. It is heavier than water, easily soluble in benzene but much more difficultly soluble in alcohol and ether." Other properties of the substance were not ascertained and no further investigation was made by them as to its identity.

Several years ago, during the course of an investigation on the preparation of certain ketones derived from  $\beta$ -naphthoic acid, a considerable amount of this unsaponifiable residue was accumulated and an investigation was undertaken to identify the material. It was distilled with steam, first in a concentrated alkaline solution and then in a concentrated acid solution; the non-volatile residue was separated from the water, dried and then distilled under reduced pressure. The distillate was a

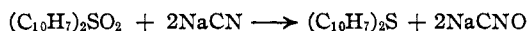
<sup>1</sup> Colver and Noyes, *THIS JOURNAL*, **43**, 901 (1921).

greenish-yellow liquid which on cooling became a light yellow solid. On standing exposed to the air the surface of the material turned red; crystallization from benzene removed the impurity responsible for the red color; a second recrystallization from benzene and washing with petroleum ether gave colorless, glistening, crystalline flakes, m. p. 151°; further recrystallizations from benzene and from ethyl alcohol did not change the melting point.

*Anal.* Calcd. for C<sub>20</sub>H<sub>14</sub>S: C, 83.86; H, 4.93; S, 11.2. Found: C, 84.06; H, 4.88; S, 11.7.

The melting point and the analysis indicated that the compound at hand was  $\beta,\beta$ -dinaphthyl sulfide.<sup>2</sup> Further evidence as to its identity was obtained by the melting point remaining unchanged on mixing with a sample of pure dinaphthyl sulfide prepared by heating the lead salt of  $\beta$ -thionaphthol; when oxidized in acetic acid solution with potassium dichromate and sulfuric acid,  $\beta,\beta$ -dinaphthyl sulfone, m. p. 177°, was obtained.<sup>3</sup>

These results show that the unsaponifiable portion of crude  $\beta$ -naphthoic nitrile, prepared by the fusion of sodium  $\beta$ -naphthalene sulfonate and sodium cyanide, consists mostly of  $\beta,\beta$ -dinaphthyl sulfide; this sulfide is probably formed by the reduction of  $\beta,\beta$ -dinaphthyl sulfone



This sulfone is formed in small quantities when naphthalene is sulfonated at 180°,<sup>4</sup> and is present as an impurity in the sodium naphthalene sulfonate which was used as the starting product for the synthesis of the nitrile.

CONTRIBUTION FROM THE  
CHEMICAL LABORATORY OF THE  
CASE SCHOOL OF APPLIED SCIENCE  
CLEVELAND, OHIO

N. A. LANGE,  
H. S. HAUPT

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**A New Series of Sulfonephthaleins.**—In a recent article under the above title Harden and Drake, *THIS JOURNAL*, **51**, 562–566 (1929), a number of new compounds suitable for use as indicators for determining hydrogen-ion concentration were announced. Dr. I. M. Kolthoff, of the University of Minnesota, has kindly directed our attention to the fact that one of these compounds, tetrabromophenoltetrabromosulfonephthalein, has distinct advantages over brom phenol blue as an indicator. The new indicator shows a color change from yellow to blue, just as do brom cresol green and brom thymol blue, but without the interfering dichromatism.

<sup>2</sup> Kraft and Schönherr, *Ber.*, **22**, 825 (1899).

<sup>3</sup> Kraft, *ibid.*, **23**, 2366 (1890).

<sup>4</sup> Stenhouse and Groves, *ibid.*, **9**, 682 (1876).