tilled to obtain the product. The yield was 880 g. (92%), b. p. 120–121° (20 mm.), $n^{25}D$ 1.4977. Pure *p*-ethylphenyl acetate boiled at 113–114° (16 mm.), (226–227°),[4] $n^{25}D$ 1.4970, d^{25}_{25} 1.030.

Anal.[5] Calcd. for $C_{10}H_{12}O_2$: C, 73.3; H, 7.33. Found: C, 73.6; H, 7.60.

***p*-Acetylphenyl Acetate.**—Oxygen was blown through an alundum disperser into 317 g. of *p*-ethylphenyl acetate containing 5% of a 1:1:8 mixture of chromium oxide, cobalt hydrate and calcium carbonate held at 140–145° for fifteen hours. Water was removed by means of a Dean and Stark trap. Upon cooling, the catalyst was removed by filtration and washed with benzene. The combined filtrate and washings were refluxed for two hours with 100 cc. of acetic anhydride containing 10 g. of sodium acetate. This mixture was washed thoroughly with water and then distilled to give 222 g. (70% recovery) of *p*-ethylphenyl acetate, b. p. 109–124° (13 mm.), $n^{25}D$ 1.4961, and 81 g. (24% conversion, 79% yield) of *p*-acetylphenyl acetate, b. p. 157–162° (13 mm.) [160° (22 mm.)].[6]

***p*-(α-Hydroxyethyl)-phenyl Acetate.**—One hundred and nine grams of *p*-acetylphenyl acetate was hydrogenated (2000 lb. initial pressure) in the presence of 11 g. of copper chromite, at 130°. The hydrogenation was stopped as soon as one mole of hydrogen had been taken up. The hydrogenated product boiled at 138–142° (3 mm.), $n^{25}D$ 1.5160; yield was 86 g., 78%. An analytical sample boiled at 89–93° (0.07 mm.), $n^{25}D$ 1.5178, d^{25}_{25} 1.134.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.7; H, 6.67. Found: C, 66.2; H, 6.87.

A sample of this compound was acetylated. The main fraction of the product distilled at 94.5–98.0° (0.09 mm.), (b. p. 145–6° (7 mm.), m. p. 51°),[7] $n^{25}D$ 1.4980, d^{25}_{25} 1.128.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.9; H, 6.31. Found: C, 65.4; H, 6.48.

***p*-Vinylphenyl Acetate.**[8]—Eighty-six grams of *p*-(α-hydroxyethyl)-phenyl acetate, 0.9 g. of potassium bisulfate, and 0.9 g. of hydroquinone were placed in a 500-ml. flask equipped with a Vigreux column and heated by an oil-bath. Hydroquinone was placed in the receiver. The product was distilled as formed at an oil-bath temperature of 175–200° and a pressure of 60-13 mm. This product was twice distilled in the presence of hydroquinone to yield 37 g. (45%) of *p*-vinylphenyl acetate; b. p. 100–105° (4 mm.), (b. p. 83–86° (1 mm.)),[7] $n^{25}D$ 1.5356, ($n^{25}D$ 1.5368),[7] d^{25}_{25} 1.065, (d^{25}_4 1.0586).[7]

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.18. Found: C, 73.8; H, 6.41.

(4) Clemmensen, *Ber.*, **47**, 53 (1914).

(5) All of the analyses are microanalyses performed by the Arlington Laboratories, Fairfax, Virginia.

(6) Verley, *Bull. soc. chim.*, [3] **19**, 140 (1898).

(7) Alderman and Hanford, U. S. Patent 2,276,138; *C. A.*, **36**, 4732 (1942).

(8) Essentially the method of Brooks, THIS JOURNAL, **66**, 1295 (1944).

CENTRAL RESEARCH DEPARTMENT
MONSANTO CHEMICAL COMPANY
DAYTON, OHIO

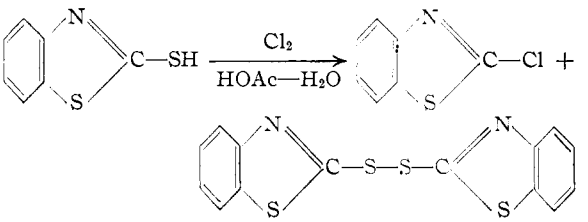
RECEIVED APRIL 5, 1946

The Action of Chlorine on 2-Mercaptobenzothiazole in Aqueous Acetic Acid

BY STEPHEN P. FINDLAY AND GREGG DOUGHERTY

The action of aqueous chlorine on sulfides and disulfides to produce sulfonyl chlorides and thence sulfonic acids is a familiar preparative method.[1,2,3] Under these conditions one mole of 2-mercaptobenzothiazole reacts with half a mole of chlorine to give the corresponding disulfide.[4] However, if the chlorination is conducted in aqueous acetic acid and an excess of the halogen is used, the sulfhydryl group is to a considerable extent replaced by chlorine. Besides 2-chlorobenzothiazole minor quantities of bisbenzothiazolyl 2,2′-disulfide, bisbenzothiazolyl 2,2′-monosulfide, water soluble dyes, and tarry products are formed.

The chlorination of the thiazole in aqueous acetic acid is an exothermic reaction and the best yields of 2-chlorobenzothiazole were obtained when the admission of chlorine to the reaction mixture was so slow that the temperature did not rise above 45°.



Experimental

2-Mercaptobenzothiazole was obtained by treating the commercial product (Captax) with sodium carbonate solution, filtering off the insoluble material, acidifying the filtrate, and separating the precipitated mercaptan. This material after one recrystallization from glacial acetic acid melted at 174–176°.[5]

Procedure.—In a typical run gaseous chlorine was passed slowly for twenty-four hours through a mixture of 50 g. of 2-mercaptobenzothiazole in 200 ml. of glacial acetic acid and 50 ml. of water. The dark-brown product was poured into 350 ml. of water and, after stirring, the heavier phase was separated and steam distilled. The distillate was saturated with salt and extracted with ether. On standing long, pale yellow filaments of the monosulfide separated from the lighter phase and, after two recrystallizations from benzine (b. p. 70°), gave 0.07 g. of pure product, m. p. 99°. Admixture of this with an authentic sample of dibenzothiazolyl 2,2′-monosulfide, prepared by heating in absolute alcohol equimolecular quantities of **2-chlorobenzothiazole** and the potassium salt of 2-mercaptobenzothiazole in the presence of a trace of potassium iodide, did not depress the melting point. Removal of the ether from the extract gave 24 g. (yield 47%) of **2-chlorobenzothiazole,** b. p. 116–122° (3 mm.) and 248° (760 mm.), which, according to Hofmann's directions,[6] yielded a 6-nitro derivative, m. p. 190°. During the steam distillation about 7% of this was hydrolyzed to the hydroxy derivative.

A tarry residue after the steam distillation when recrystallized twice from benzene gave 3.1 g. (6.2%) of **dibenzothiazolyl 2,2′-disulfide,** m. p. 178°.

(1) Lee and Dougherty, *J. Org. Chem.*, **5**, 81–85 (1940).

(2) Schiller and Otto, *Ber.*, **9**, 1638 (1876).

(3) Douglass and Johnson, THIS JOURNAL, **60**, 1486 1489 (1938).

(4) U. S. Patent 2,265,347.

(5) All melting points are uncorrected.

(6) Hofmann, *Ber.*, **13**, 10 (1880).

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

RECEIVED APRIL 15, 1946

Crystalline Racemic Calcium Pantothenate

BY JARED H. FORD

The preparation of macrocrystalline calcium (+)-pantothenate has been reported by Levy,