TABLE I

No.	Guanylurea sulfate, mg.	Urea added, mg.	HCl, ml. cor.	Urea found, mg.
1	100	0	−0.03	..
2	0	30.0	10.68	29.8
3	100	30.0	10.62	29.7
4	100	30.0	10.36	28.9
5	100	30.0	10.39	29.0

chloric acid required for an end-point when guanylurea sulfate and urease were incubated together. Similar results were obtained when the incubation time for the mixture was increased to thirty minutes. In experiment 3 the urease was added to a mixture of guanylurea sulfate and urea. To determine whether the action of urease on urea would be influenced by previous treatment with guanylurea sulfate, the urease was added to the guanylurea sulfate in Expts. 4 and 5 and kept in contact with it at room temperature for five and for fifteen minutes, respectively, before the urea was added.

Results.—The experiments indicate that urease does not catalyze the hydrolysis of guanylurea sulfate. A solution of urease which has first been treated with guanylurea sulfate gives somewhat low values in the determination of urea; this effect is, however, very slight.

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PHILADELPHIA 40, PA. RECEIVED APRIL 25, 1946

Picrolonates of Bufotenine, Bufotenidine and Dehydrobufotenine

BY VENANCIO DEULOFEU AND BLANCA BERINZAGHI

Following our work[1] on the basic constituents of the venom of some South American toads, we have prepared the picrolonates of the indolic bases present in toad venom.

The picrolonates of bufotenidine and dehydrobufotenine can be prepared and purified more easily than bufotenine picrolonate. Dehydrobufotenine can be isolated more readily as the picrolonate than as its picrate, from the final residual mother liquors of the toad venom when the bases are extracted according to our procedure.[1] Dehydrobufotenine picrolonate, however, has too high a melting point to be of ready use in identification.

Bufotenine Picrolonate.—Amorphous bufotenine from *B. arenarum* was dissolved in ethanol and treated with an small excess of picrolonic acid. By heating the acid dissolves and when the solution was cooled crystals were obtained melting not sharply at 110°. By recrystallizing from ethanol, small, yellow prisms, melting 120–121° were obtained.

Anal. Calcd. for $C_{12}H_{16}ON_2 \cdot C_{10}H_8O_5N_4$: N, 17.94. Found: N, 18.34.

Bufotenidine Picrolonate.—Bufotenidine iodide was obtained from amorphous bufotenine and methyl iodide according to Wieland, Konz and Mittasch,[2] and melted at 210°. The iodide was dissolved in a little amount of water and treated with a slight excess of picrolonic acid. This was dissolved by heating, and on cooling yellow prisms melting 253–255° were obtained. Recrystallized from 50% ethanol, the fine yellow needles melted 255°.

Anal. Calcd. for $C_{13}H_{18}ON_2 \cdot C_{10}H_8O_5N_4$: N, 17.42. Found: N, 17.14.

Dehydrobufotenine picrolonate was obtained by treating a water solution of dehydrobufotenine hydrochloride with an excess of picrolonic acid, heating to dissolution and cooling. The picrolonate precipitates and after crystallization from ethanol (50%) yellow prisms melting above 300° and darkening from 275° (quick heating) were obtained.

Anal. Calcd. for $C_{12}H_{14}ON_2 \cdot C_{10}H_8O_5N_4$: N, 18.02. Found: N, 17.99.

A similar picrolonate was obtained from the solution of crude bases of *B. arenarum* after separation of bufotenine.

FACULTAD DE CIENCIAS EXACTAS F. Y. N.
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BUENOS AIRES, ARGENTINA RECEIVED MARCH 20, 1946

(1) V. Deulofeu and R. Duprat, *J. Biol. Chem.*, **153**, 459 (1944).
(2) H. Wieland, W. Konz and H. Mittasch, *Ann.*, **513**, 1 (1934).

The Use of Liquid Phase Oxidation for the Preparation of Nuclearly Substituted Styrenes. II. *p*-Vinylphenyl Acetate

BY WILLIAM S. EMERSON, JOSEF W. HEYD, VICTOR E. LUCAS, WILLIAM B. COOK, GRAFTON R. OWENS AND ROBERT W. SHORTRIDGE

In a previous paper[1] we have shown that methyl *p*-ethylbenzoate is smoothly oxidized to methyl *p*-acetylbenzoate by air in the presence of chromium oxide and calcium carbonate. While the oxidation of *p*-ethylphenyl acetate to *p*-acetylphenyl acetate is a great deal more difficult, we have accomplished it successfully (24% conversion and 79% yield) by means of oxygen in the presence of a chromium oxide–cobalt hydrate–calcium carbonate catalyst. Any free phenol in the reaction mixture inhibits the oxidation altogether, so that its presence must be rigorously avoided.

The *p*-acetylphenyl acetate was smoothly hydrogenated in the presence of copper chromite to *p*-(α-hydroxyethyl)-phenyl acetate. Distillation of the latter compound from potassium bisulfate yielded 48% of *p*-vinylphenyl acetate based on this carbinol.

The authors are grateful to Dr. G. F. Deebel and Messrs. C. E. Wheelock, E. L. Ringwald and R. P. Haase for the preparation of considerable quantities of *p*-ethylphenol.

Experimental

***p*-Ethylphenol** was prepared essentially according to the method of Hartman.[2] One hundred fifty-two grams (58%) was obtained from the fusion of 450 g. of sodium *p*-ethylbenzenesulfonate with 300 g. of potassium hydroxide and 750 g. of sodium hydroxide. It boiled at 95–101° (10 mm.) (218.5–219.5°).[3]

***p*-Ethylphenyl Acetate.**—*p*-Ethylphenyl acetate was prepared by refluxing for six hours 713 g. of *p*-ethylphenol with 1 liter of acetic anhydride containing 100 g. of sodium acetate. The reaction mixture was diluted with water and benzene, the layers separated and the benzene layer dis-

(1) Emerson, Heyd, Lucas, Chapin, Owens and Shortridge, THIS JOURNAL, **68**, 674 (1946).
(2) Hartman, "Org. Syntheses," Coll. Vol. I, p. 175.
(3) Béhal and Choay, *Bull. soc. chim.*, [3] **11**, 209 (1894).

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).

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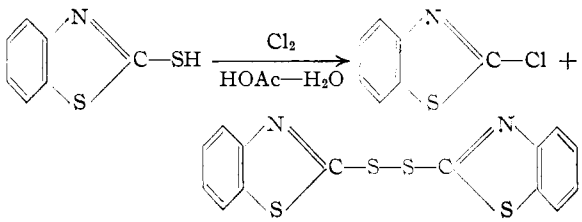
The Action of Chlorine on 2-Mercaptobenzothiazole in Aqueous Acetic Acid

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).

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Crystalline Racemic Calcium Pantothenate

BY JARED H. FORD

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