## *p*-Nitrobenzoates of Some Thiophenols

By the use of *p*-nitrobenzoyl chloride the authors have formed *p*-nitrobenzoate esters of some of the simple thiophenols by an easily executed procedure which is described below. These derivatives successfully differentiate among the various thiophenols studied. The procedure for the preparation of these esters has been adapted to the needs of a standard course in qualitative organic analysis.

The physical properties, yield and analysis of the *p*-nitrobenzoate esters of the thiophenols studied are summarized in Table I.

Table I

*p*-Nitrobenzoates of Some Thiophenols

| Thiol | Mol. form. of ester | Yield, % | M. p., °C. | Analyses, % Calcd. | Analyses, % Found |
|---|---|---|---|---|---|
| Thiophenol | $C_{13}H_9O_3SN$ | 71 | 157–158 | S, 12.37 | 12.35 12.52 |
| *o*-Thiocresol | $C_{14}H_{11}O_3SN$ | 78 | 90–91 | S, 11.73 | 11.73 11.64 |
| *m*-Thiocresol | $C_{14}H_{11}O_3SN$ | 71 | 95–96 | S, 11.73 | 11.74 11.48 |
| *p*-Thiocresol | $C_{14}H_{11}O_3SN$ | 88 | 114–115 | S, 11.73 | 11.99 11.59 |
| 1-Thionaphthol | $C_{17}H_{11}O_3SN$ | .. | 121–123 | C, 66.1[a] | 65.92 |
| | | | | H, 3.56 | 3.66 |
| 2-Thionaphthol | $C_{17}H_{11}O_3SN$ | 73 | 183–184 | S, 10.61 | 10.24 10.29 |

[a] This carbon and hydrogen analysis was carried out by James Rigas, 470 Eastern Parkway, Brooklyn 25, New York.

**Experimental.**—The thiophenols used with the exception of the 1-thionaphthol were of the reagent grade, as furnished by Eastman Kodak Company. The *p*-nitrobenzoyl chloride used was prepared in our laboratory by the action of phosphorus pentachloride on *p*-nitrobenzoic acid using the method described in "Organic Syntheses."[1]

A modification of the method described by Shriner and Fuson[2] was employed in the preparation of these *p*-nitrobenzoate esters. The thiophenol (0.06 mole) was dissolved in 10 ml. of pyridine. To this solution was added with stirring 12.3 g. (0.066 mole) of *p*-nitrobenzoyl chloride and the mixture was gently heated until solution was complete. The resulting solution was then poured into 100 ml. of cold water. After stirring, the water was removed from the precipitate by decantation and the precipitate was washed with 50 ml. of a 5% solution of sodium bicarbonate. It was then washed with small quantities of water and alcohol. The residue was dissolved in a minimum amount of hot chloroform and alcohol was then added to this hot solution until a precipitate just began to form. On slow cooling the *p*-nitrobenzoate esters crystallize as well defined pale yellow crystalline solids. These were analyzed for their sulfur content by the sodium peroxide fusion method described by Shriner.[3]

In forming derivatives for the qualitative determination of a thiophenol, the procedure and quantities specified by Shriner and Fuson[2] for the preparation of the *p*-nitrobenzoates of alcohols are very satisfactory.

**The *p*-Nitrobenzoate of 1-Thionaphthol.**—The 1-thionaphthol was obtained from a sample of a rubber peptizing agent R. P. A. 4, kindly furnished us by Mr. M. A. Youker of the Jackson Laboratories of E. I. du Pont de Nemours and Company. The fraction distilling at 20 mm. pressure, boiling at 160–161° and which amounted to about 30% of the original sample was taken as the desired material. When the *p*-nitrobenzoate of this supposed 1-thionaphthol was prepared, a product was obtained in a yield of 73% of the theory and which melted at 118–151°.

*Anal.* Calcd. for $C_{17}H_{11}O_3SN$: S, 10.61. Found: S, 10.58, 10.49.

By careful fractionaton of this material from a chloroform–alcohol solvent, two portions of material were obtained. Both fractions were recrystallized three times. The less soluble portion melted at 179–181° and gave no depression of the melting point with an authentic sample of the *p*-nitrobenzoate of 2-thionaphthol. The more soluble portion, a pale yellow solid melting at 121–123°, is apparently the *p*-nitrobenzoate ester of 1-thionaphthol.

*Anal.* Calcd. for $C_{17}H_{11}O_3SN$: C, 66.1; H, 3.56. Found: C, 65.92; H, 3.66.

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[1] Gilman and Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 394.

[2] Shriner and Fuson, "The Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 164.

[3] Shriner, "Quantitative Analysis of Organic Compounds," Edward Bros., Ann Arbor, Mich., 1938, p. 23.

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## 3-(4-Amino-3,5-dibromobenzoxy)-1-di-*n*-butylaminopropane Picrolonate

Five grams of 3-(4-aminobenzoxy)-1-di-*n*-butylaminopropane (butacaine) was dissolved in a mixture of 200 cc. of water and 30 cc. of concd. hydrochloric acid, and the solution was treated with portions of bromine water until a slight excess of the reagent was present. After an hour, free bromine was removed with bisulfite, and the mixture was basified with ammonia. A quantitative yield of oily 3-(4-amino-3,5-dibromobenzoxy)-1-di-*n*-butylaminopropane base[1] was obtained from the chloroform extract of the mixture.

A solution of 1.50 g. of picrolonic acid in 60 cc. of 95% ethanol was added to 2.56 g. of the bromination product in 20 cc. of the same solvent. The picrolonate which precipitated amounted to 3.78 g. (94%); m. p. 158–160° (cor., dec.), unchanged after recrystallization from 95% ethanol (40 cc. per g., 87% recovery).

*Anal.* Calcd. for $C_{18}H_{28}Br_2N_2O_2tC_{10}H_8N_4O_5$: N, 11.54. Found: N,[2] 11.26, 11.24.

The substance crystallized as yellow elongated rods and occasional tablets exhibiting the following microscopic-crystallographic properties[3]: *refractive indices*, $\alpha = 1.472$ ($\pm 0.002$), $\beta = 1.74$, $\gamma = 1.78$ (both $\pm 0.01$); *optic axial angle*, $2V = 35$–$45°$; *dispersion*, $r < v$, strong; *sign of double refraction*, negative; *extinction*, inclined.

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[1] Moore and Volwiler, This Journal, **62**, 2799 (1940), have prepared the hydrobromide. Preparation of the hydrochloride has been reported by Wells, *J. Assoc. Official Agric. Chem.*, **25**, 537 (1942).

[2] Semi-micro Kjeldahl determinations by Charles Graichen, Cosmetic Division, Food and Drug Admin.

[3] Examination by Wm. V. Eisenberg, Division of Microbiology, Food and Drug Admin.