[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
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RESEARCHES ON THIAZOLES. XIV. THE SYNTHESIS OF 2-ORTHO- AND META-AMINOPHENYL-6-METHYL-BENZOTHIAZOLES; NEW ISOMERS OF DEHYDROTHIO-PARA-TOLUIDINE, AND OF INCIDENTAL COMPOUNDS[1]

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In recent papers by Bogert and Allen,[3,4] there have been described isomers of the well-known dye intermediate dehydrothio-*p*-toluidine carrying the methyl group in Positions 5 or 7, and the amino groups in various positions on the 2-phenyl nucleus. The present contribution supplements this by reporting additional isomers in which the methyl, but not the amino, group is located as in dehydrothio-*p*-toluidine itself.

These new isomers were synthesized in the same way as outlined in previous papers from these Laboratories dealing with other isomers, namely, by condensing the zinc salt of the appropriate aminothiocresol with *o*- or *m*-nitrobenzoyl chloride to the 2-nitrophenyl-6-methylbenzothiazole and then reducing the latter to the amine.

These amines should yield dyes corresponding to Chloramine Yellow (Colour Index No. 814), when their sodium sulfonates are oxidized by alkaline hypochlorite solution. This reaction followed a normal course with the *m*-aminophenyl derivative, giving a product of similar properties to Chloramine Yellow, which dyed cotton a much paler shade and was manifestly inferior to it. In the case of the *o*-aminophenyl derivative on the other hand, the reaction pursued an abnormal course and no Chloramine Yellow dye was obtained.

Experimental Part

2-(*m*-Nitrophenyl)-6-methylbenzothiazole.—An intimate mixture of 3 g. of zinc 2-amino-5-methylphenyl mercaptide with 3.7 g. of *m*-nitrobenzoyl chloride was heated at 100° for an hour while the viscous melt was well stirred. The pulverized cold fusion cake was warmed for an hour with *N* sodium hydroxide solution and the undissolved material then removed, washed, dried and crystallized from glacial acetic acid. Small yellow needles were obtained, m. p. 166° (corr.), readily soluble in chloroform, moderately soluble in boiling alcohol and practically insoluble in ether, acetone or benzene; yield, 1.4 g. or 58%.

Anal. Calcd. for $C_{14}H_{10}O_2N_2S$: C, 62.22; H, 3.70. Found: C, 62.09; H, 4.02.

2-(*m*-Aminophenyl)-6-methylbenzothiazole.—A mixture of 1.5 g. of the above nitro derivacive, 5 cc. of concd. hyrochloric acid, 95 cc. of water and 10 g. of granulated

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[1] Presented in abstract before the Division of Dye Chemistry at the Baltimore Meeting of the American Chemical Society, April 8, 1925.

[2] DuPont Fellow at Columbia University for the academic year 1923–24.

[3] Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926).

[4] Bogert and Allen, THIS JOURNAL, **49**, 1315 (1927).

tin was boiled for two hours, although a clear solution resulted after one hour's boiling. The acid solution was made strongly alkaline with 4 *N* sodium hydroxide solution and kept warm for an hour. The insoluble material, when removed and crystallized from alcohol, formed colorless needles, m. p. 181° (corr.), easily soluble, without appreciable fluorescence, in alcohol, acetone, ether, chloroform or benzene; yield, 0.85 g. or 64%.

Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 70.00; H, 5.00. Found: C, 70.29; H, 5.14.

Sulfonation of 2-(*m*-Aminophenyl)-6-methylbenzothiazole.—A solution of 0.75 g. of the thiazole in 5 cc. of concd. sulfuric acid was cooled to 25° and 5 cc. of fuming (50% free SO_3) sulfuric acid added gradually while the temperature of the solution was maintained below 50°. After the solution had been kept at 40–50° for eight hours, it was entirely soluble in dilute ammonium hydroxide solution and the sulfonation was adjudged complete. It was poured upon cracked ice, the yellow flocculent precipitate collected, dissolved in warm dil. caustic alkali, the alkaline solution reprecipitated with sulfuric acid and the precipitate dried in the oven. The product was a dark brown solid; yield, 0.7 g.

A Yellow Dye Analogous to Chloramine Yellow.—A solution of 0.5 g. of the above sulfo acid in 100 cc. of water and 0.1 g. of sodium hydroxide, when oxidized at 10–15° by an aqueous solution of sodium hypochlorite, turned violet at first, then wine-red and cloudy. After it had stood for twenty-four hours, dil. sulfuric acid was added and the precipitate removed and dried. It formed a brown powder which gave a deep carmine-red color with concd. sulfuric acid, similar to that produced from Chloramine Yellow itself.

Comparative dyeing tests (2%) on cotton showed that the shades obtained were paler than those yielded by Chloramine Yellow, but that in other respects it resembled the latter closely.

2-(*o*-Nitrophenyl)-6-methylbenzothiazole.—When a mixture of dry *o*-nitrobenzoyl chloride and the zinc mercaptide was warmed, a reaction ensued with explosive violence and carbonization. When the chloride (2 cc.) and mercaptide (2 g.) were dissolved in glacial acetic acid (5 cc.), no reaction was perceived in the cold, so the solution was heated at 100° for thirty minutes, then poured into water and the precipitate collected and warmed for an hour with *N* sodium hydroxide solution, which changed it to a viscous tar from which no crystalline product could be obtained. It was therefore distilled under diminished pressure and a product secured which congealed to a yellow gum; yield, 0.9 g. or 57%. As this product looked like unpromising material for analysis, it was reduced (1 g.) directly to:

2-(*o*-Aminophenyl)-6-methyl-benzothiazole, by boiling it for three hours with concd. hydrochloric acid (10 cc.), water (90 cc.) and granulated tin (10 g.). The double salt formed remained insoluble in the acid solution and was removed and digested with warm caustic soda. The crude, insoluble amine was crystallized from alcohol and then appeared in rosets of colorless needles, m. p. 137° (corr.); yield, 0.7 g. or 62%. The compound dissolved freely in alcohol, acetone, chloroform, carbon tetrachloride, ether, carbon disulfide or benzene. The solution in alcohol or acetone exhibited a fine blue fluorescence.

Anal. Calcd. for $C_{14}H_{12}N_2S$: C, 70.00; H, 5.00. Found: C, 69.90; H, 5.12.

The Acetyl Derivative, from the amine and acetic anhydride, crystallized from alcohol in colorless needles, m. p. 150° (corr.), easily soluble in alcohol, ether or benzene; yield, 77%.

Anal. Calcd. for $C_{16}H_{14}ON_2S$: C, 68.08; H, 4.96. Found: C, 67.64; H, 4.87.

The sulfonation of the *o*-aminophenyltoluthiazole (1 g.) was attempted with fuming sulfuric acid, by the process outlined for the *m*-isomer. The sulfonation solution when poured upon ice gave a dark green, gelatinous precipitate which dried out in the oven to a hard, black solid; yield, 0.8 g. The color of an aqueous solution of the sodium salt was deep blue, which changed to dark green when acidified. Hypochlorite oxidation of this supposititious sodium sulfonate failed to yield any dye.

Summary

1. By the action of *o*- and *m*-nitrobenzoyl chlorides upon the zinc salt of 2-amino-5-methylphenyl mercaptan, the corresponding 2-nitrophenylbenzothiazoles have been prepared.

2. Reduction of these nitro derivatives gave amines isomeric with dehydrothio-*p*-toluidine.

3. From the *m*-aminophenyl derivative, by hypochlorite oxidation of its sodium sulfonate, a direct cotton dye was prepared, presumably isomeric with Chloramine Yellow (Colour Index No. 814), but giving paler yellow shades. From the isomeric *o*-aminophenyl derivative, no similar dye could be obtained.

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[Contribution from the Physical and Chemical Laboratories of the Ohio State University]

ULTRAVIOLET ABSORPTION SPECTRA OF CYCLOHEXENE, ETHYL ETHER, METHYL-NORMAL-AMYL ETHER AND ETHYLENE CHLOROHYDRIN. A CORRECTION TO OUR PREVIOUS ARTICLE[1] UNDER THIS TITLE AND REPLY TO DR. DE LASZLO[2]

By Alpheus W. Smith, Cecil E. Boord, Clyde S. Adams and Charles S. Pease

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The results contained in our previous paper have been challenged by Dr. de Laszlo with the contention that the absorption was in every case due to benzene. It is concluded "that benzene may have been present as an impurity either in the material or apparatus in amounts sufficient to explain the results as reported by these authors."

After a careful re-examination of ethylene chlorohydrin, methyl-*n*-amyl ether and ethyl ether in the light of these contentions we are compelled to admit that the results shown in our paper are due to benzene. It will be of general interest to know wherein this error arose.

As to cleanliness let it be said that it has been our unvarying practice to wash the absorption cells with chromic acid mixture after each run and that blank exposures through these same cells showed no absorption.

One comes then to the second alternative, namely, that the compounds examined contained benzene as a common impurity. A careful re-exami-

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[1] Smith, Boord, Adams and Pease, This Journal, 49, 1335 (1927).

[2] De Laszlo, *ibid.*, 49, 2106 (1927).