

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

PREPARATION AND PROPERTIES OF ORTHO-TOLUIDINE¹

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As a dye intermediate *o*-toluidine has its purity specifications. Methods of analyzing this intermediate for its content of *p*-toluidine are numerous. Most of them make use of the colors formed upon the addition of an oxidizing agent such as ferric chloride, potassium dichromate, calcium hypochlorite, and many others. Rosenstiehl² pointed out some of these color reactions. He observed, for example, that an aqueous solution of *o*-toluidine hydrochloride formed an insoluble greenish-black precipitate when treated with a cold saturated potassium dichromate solution. Under similar conditions, *p*-toluidine formed a maroon precipitate partly soluble in dilute acid.

Schoen³ employed these observations as the basis of his method of analyzing *o*-toluidine colorimetrically for the *para* isomer. With mixtures whose *para* content was below 8%, he recommended that a dil. hydrochloric acid solution of the toluidines be treated with potassium dichromate and allowed to stand for an hour during occasional shaking. He stated that "under these circumstances *o*-toluidine gives a black lake, while mixtures of *o*- and *p*-toluidine give a light brown precipitate and a red solution. This is observed in the filtered solution, and the color is more or less intense according to the amount of *p*-toluidine in the mixture."

When Schoen's method was applied to several samples of C. P. *o*-toluidine obtained from different sources, each sample appeared to contain some *p*-toluidine. This was not entirely a surprise, but upon adding definite amounts of *p*-toluidine to these samples the calculated increased percentage of *para* present seldom agreed with the analytical results. The method was put through the usual course of modifications, such as changing the relative concentrations, temperature, etc., with mediocre success. Schoen's statement, "the (red) color is more or less intense according to the amount of *p*-toluidine in the mixture," was found not to be true, unless one interpreted his statement broadly and put undue emphasis upon his expression "more or less."

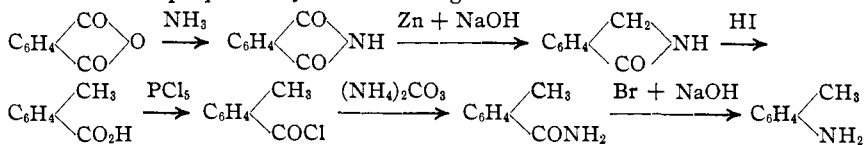
These results created a strong suspicion that *o*-toluidine itself was partly responsible for the red color which Schoen attributed entirely to the *para* isomer. To prove this there was required some *o*-toluidine prepared

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² Rosenstiehl, *Ann. chim. phys.*, [4] 26, 246 (1872); *Bull. soc. chim.*, 10, 201 (1868).

³ Schoen, *Chem.-Zig.*, 12, 494 (1888).

in such a manner as to preclude the possibility of any of the *para* compound being present. Phthalic anhydride was selected as the starting material because of its complete freedom from all isomers. From it *o*-toluidine was prepared by the following series of reactions.



Phthalic anhydride was converted into phthalimide by bubbling ammonia through the melted anhydride until absorption ceased.

Phthalide was prepared from phthalimide by the method given by Reissert,⁴ and the resultant phthalide converted into *o*-toluic acid by hydriodic acid according to the procedure of Hessert.⁵

***o*-Toluy Chloride from *o*-Toluic Acid.**—Fifty g. of *o*-toluic acid was melted in a 250cc. distilling flask and the temperature raised to 120°. A total of 55 g. of phosphorus pentachloride was added and, since the reaction was very vigorous, the chloride was added a little at a time. Upon distillation, the fraction above 205° was collected and converted into *o*-toluamide without further purification. The yields obtained averaged about 75%.

***o*-Toluamide from *o*-Toluy Chloride.**—One hundred g. of pulverized ammonium carbonate was placed in a beaker and to it was added, during vigorous stirring, 45 g. of well cooled *o*-toluy chloride. When the reaction started the mixture became quite warm. For good yields the temperature should be kept low. The reaction was complete in a few minutes and then the ammonium salts were extracted with cold water. *o*-Toluyamide is not appreciably soluble in cold water but dissolves in boiling water from which it may be recrystallized. The recrystallized product melted at 140° instead of 138° as given by Weith;⁶ yield, 50%.

***o*-Toluidine from *o*-Toluamide.**—The transformation of *o*-toluamide into *o*-toluidine by the Hofmann reaction was the most difficult procedure of all. A method was finally evolved which produced a 50% yield.

A solution of 75.3 g. of sodium hydroxide in 189 g. of water was cooled by an ice-bath, and 30 cc. of bromine was added slowly. This solution was kept cool until used. Ninety g. of recrystallized *o*-toluamide was rubbed with water to a thick cream and cooled by an ice-bath. To this was added, in very small portions, the cold sodium hypobromite solution described above. After each addition of the hypobromite the mixture was stirred vigorously for several minutes, the temperature being kept below 5° at all times.

⁴ Reissert, *Ber.*, 46, 1484 (1913).

⁵ Hessert, *Ber.*, 11, 238 (1878).

⁶ Weith, *Ber.*, 6, 420 (1873).

A solution of sodium hydroxide was prepared from 300 g. of sodium hydroxide and 790 cc. of water. This solution was heated to 75° and to it was added the mixture containing the hypobromite. This addition must be done quickly and in such a manner as to produce as rapid mixing as possible. The resultant mixture was shaken for several minutes and then boiled under a reflux condenser for five minutes. An oily layer of *o*-toluidine appeared on the top of the liquid and was removed by steam distillation.

Purification of the *o*-Toluidine.—The *o*-toluidine was removed from the aqueous distillate by saturating the latter with sodium chloride and extracting with ether. The ether extract was dried overnight with solid potassium hydroxide, filtered, and distilled at 20 mm. pressure. The fraction boiling between 94° and 95° was collected and redistilled at atmospheric pressure (749 mm.) in an atmosphere of carbon dioxide to prevent oxidation. At this pressure, it boiled between 198° and 199°.

The entire amount (32 g.) was dissolved in dil. hydrochloric acid from which solution it was crystallized as the hydrochloride. Several crops of crystals were removed but only the first two were used. These were dissolved in 250 cc. of water and an excess of dil. sodium hydroxide solution was added. The toluidine was extracted with ether and the extract dried with solid potassium hydroxide. After evaporation of the ether, the *o*-toluidine was distilled in an atmosphere of carbon dioxide. Only the middle fraction was saved. It distilled between 200.5° and 200.7° at 754.6 mm. pressure. The thermometer used had a short stem and narrow range. It had been standardized by Thüringisches Staatsprüfamt für Glasgerate.

Properties of *o*-Toluidine.—When this *o*-toluidine was treated with potassium dichromate according to the method of Schoen, a green-black precipitate formed. The filtrate from this mixture was bluish-red, practically identical with that given by the *para* isomer. The experiment was conducted at 20°. Repeating it at 5° decreased the amount of precipitate and the intensity of the red color, but by no means eliminated the latter. A solution of 1% *p*-toluidine in pure *o*-toluidine developed a much stronger red color than pure *o*-toluidine alone, which indicates that *p*-toluidine is more easily oxidized.

This proved that Schoen's and probably other colorimetric methods for the determination of *p*-toluidine can yield only approximate results, the error becoming larger with increased purity of sample.

o-Toluidine distilled at 200.6° (754.6 mm.); d_{20}^{20} , 1.0053; n_D^{20} , 1.5688.

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Summary

Schoen's colorimetric method of analyzing *o*-toluidine for its content of the *para* isomer has been shown to be faulty. This was proved by synthesizing *o*-toluidine from phthalic anhydride, thereby avoiding the possibility of any of the *para* isomer being present. However, upon oxidation with potassium dichromate, *o*-toluidine developed a red color indistinguishable from that attributed by Schoen to the *para* isomer only.

The boiling point, density and index of refraction of *para*-free *o*-toluidine were measured.

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THE ADDITION OF METHYL HYPOBROMITE AND METHYL HYPOCHLORITE TO CERTAIN ETHYLENE DERIVATIVES

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In a previous paper¹ it was shown that solutions of cinnamic acid and benzalacetophenone in 85% aqueous methyl alcohol at 0° react with bromine with the resulting addition of methyl hypobromite to the unsaturated compounds. In all probability the reaction proceeds as follows: $\text{Br}_2 + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OBr} + \text{HBr}$; $>\text{C}=\text{C}< + \text{CH}_3\text{OBr} \longrightarrow >\text{C}(\text{OCH}_3)\text{CBr}<$. As would be expected the addition of bromine takes place simultaneously. Only one other method of adding methyl hypobromite seems to be on record. By the action of bromotrinitromethane with ethylene derivatives in the presence of the appropriate alcohol, E. Schmidt² has added methyl hypobromite and certain other alkyl hypobromites to a number of unsaturated compounds.

The present investigation was undertaken with a view to finding the conditions most suitable for the addition of methyl hypobromite by the reaction of bromine and methyl alcohol with ethylene derivatives and to study the reaction with chlorine. If the reaction proceeds as indicated in the above scheme one would not expect the presence of water to be necessary for the addition of methyl hypobromite. In the preliminary paper, on the basis of tests with solutions of cinnamic acid at 0°, it was stated that in 90% or stronger alcohol the reaction is too slow to be practicable. A more extensive investigation of this point, however, has shown that while the reaction is not feasible with solutions of cinnamic acid in absolute methyl alcohol at 0°, the addition of methyl hypobromite in general takes

¹ Conant and Jackson, *THIS JOURNAL*, **46**, 1727 (1924).

² Schmidt, Bartholomé and Lübke, *Ber.*, **55**, 2099 (1922). Schmidt, Schumacher and Asmus, *Ber.*, **56**, 1239 (1923). Schmidt and Bartholomé, *Ber.*, **57**, 2039 (1924).