

state, *i. e.*, that the colored modification is the simplest *quinocarbonium base*.

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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

## A COLOR REACTION OF HYPOCHLORITES WITH METHYLANILINE AND ETHYLANILINE.

BY PAUL NICHOLAS LEECH.

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*Methylaniline*.—In connection with an investigation on the molecular rearrangement of derivatives of triphenylmethylhydroxylamine pursued with, and under the guidance of, Professor Stieglitz, mono-methylaniline and aniline were possible products, which had to be taken into consideration and tested for. According to Hofmann,<sup>1</sup> upon the addition of bleaching powder solution, pure methylaniline gives no color reaction and a careful search of the literature failed to show any observation contrary to this statement. However, in preliminary trials on methods for detecting aniline and methylaniline, side by side, the action of chloride of lime solution on an aqueous solution of methylaniline was tried, and it was noticed that if the water solution of methylaniline was made alkaline (not strongly) and a small amount of one-half saturated bleaching powder solution was added, after a number of seconds, a navy blue color would appear, gaining in intensity, and then fading, finally leaving a pale yellow solution (and a white precipitate, probably calcium carbonate). To verify this observation, the following method of preparing *pure* methylaniline was employed:

(1) Kahlbaum's "Special" mono-methylaniline was dried over fused potassium hydroxide, and twice fractionated by distillation, with the aid of a Glinsky distilling tube. The methylaniline obtained, almost colorless, was treated in the usual manner with nitrous acid, and converted into nitrosomethylaniline. This was reduced with tin and hydrochloric acid, the regenerated free base was liberated by means of alkali, and distilled over with steam, etc. The methylaniline thus obtained was dried and twice fractionated. The treatment assured the absence of aniline and dimethylaniline.

(2) Kahlbaum's "Special" mono-methylaniline was dried over fused potassium hydroxide, twice fractionated as before, and the methylaniline obtained was subjected to the same method of purification as was used by Hofmann.<sup>2</sup> That is, it was converted into methylacetanilide, which was thrice recrystallized from water, giving the melting point 103°, and

<sup>1</sup> *Ber.*, 7, 526 (1874).

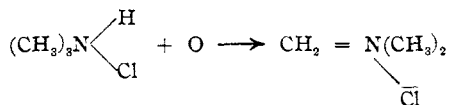
<sup>2</sup> *Ibid.*, 7, 523 (1874).

then saponified by digestion with aqueous hydrochloric acid. The methylaniline was distilled as described under (1).

The methylaniline, purified by the nitrous acid treatment, was used to make a 1/100 M aqueous solution, with which tests were made. The intensity of blue color and time of appearance varies with concentration. For 1 cc. of 1/100 M solution, made alkaline with three drops to 1/2 cc. of 6 N sodium hydroxide solution and treated with 1/2 cc. to 2 cc. of one-half saturated calcium oxychloride solution, the color begins to appear in about twelve seconds, and reaches the maximum intensity of color, a distinct navy blue, in about thirty-five seconds; after about one minute the color begins to fade slowly, leaving a yellow solution and a white precipitate (CaCO<sub>3</sub>). With larger amounts the intensity of the tint is a little greater, and the time of retaining the color, of longer duration. As small an amount as 1 mg. in 8 cc. can very readily be identified. However, a large excess of alkali, and especially an excess of bleaching powder solution, is to be avoided. The test is indeed very satisfactory and delicate.

The methylaniline purified according to Hofmann's method (see 2) gave the same characteristic test.

A possible explanation of the reaction may be as follows: According to Willstätter and Glauer,<sup>1</sup> and Hantzsch and Graf,<sup>2</sup> trimethylamine is converted by hypochlorous acid into dimethylchloramine. As has recently been shown by Meisenheimer,<sup>3</sup> the cause of this action is that hypochlorous acid oxidizes a methyl group of the trimethylamine to a formal group



This product, by hydrolysis, produces formaldehyde and dimethylamine, which with more hypochlorous acid forms the chloramine. It is quite possible, in the action of hypochlorites on methylaniline, that at some stage of the action the methyl group is oxidized away in the same manner, thus making possible condensations to the blue dye substance observed (a member possibly of the "indo" series of the dyes). This interpretation is given with all reserve as no investigation has been made of the nature of the blue substance.

The presence of alkali seems to retard the action, and very likely it is owing to our employing a decidedly alkaline solution that led to the observation of this interesting color change as an intermediate action in the formation of a non-characteristic yellow solution. The advantage of

<sup>1</sup> *Ber.*, 33, 1636 (1900).

<sup>2</sup> *Ibid.*, 30, 2134 (1897).

<sup>3</sup> *Ibid.*, 46, 1148 (1913).

not having a large amount of calcium oxychloride is obvious. The navy blue tint cannot be mistaken for the purple tint of aniline.

*Ethylaniline.*—Monoethylaniline, according to Hofmann,<sup>1</sup> also gives no color reaction with bleaching powder solution. Kahlbaum's ethylaniline was purified by two fractionations, with the aid of a Glinsky apparatus and made up to a 1/100 M solution. It gave an analogous color reaction to that of methylaniline, except that the blue color goes through green and dark brownish hues, before finally leaving a yellow solution. Also the time of appearing and the period of retaining color is two to three times longer than with methylaniline. It is especially to be noted that an excess of the reagents should be avoided. The tests were also found to be very delicate in showing small quantities of the base. An interpretation, similar to that given above for the production of a dye in the case of methylaniline, would also be possible here. It is quite likely that all monoalkylanilines will be found to show a similar behavior; no further representatives have been examined by me.

### THE PREPARATION OF BENZOYLCHLOROAMIDE.

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Benzoylchloroamide<sup>2</sup> is generally prepared by treating a cold aqueous solution of benzamide with acetic acid and then adding a concentrated solution of bleaching powder and finally extracting with ether. On evaporation of the ethereal solution and crystallization of the residue from water, the substance is obtained in fine needles. The addition of bleaching powder solution and extraction with ether have to be repeated to completely transform all the benzamide present in solution into benzoylchloroamide. Since benzamide is only sparingly soluble in water, the quantity turned out at each operation even with a large amount of water is necessarily small. Moreover, it necessitates the employment of a good quantity of ether, the free use of which is troublesome and expensive. Besides, the method is very clumsy and inconvenient.

Linebarger<sup>3</sup> showed that benzoylbromamide, which is prepared by the action of bromine and caustic potash on benzamide, when treated with concentrated hydrochloric acid is transformed into benzoylchloroamide. But as is evident, this is not a very satisfactory method of preparing the compound.

Having had to prepare large quantities of the compound, we found both the above methods unsuited for our purpose. This led to a search for a better method of preparing the compound and it is found that chlorine is

<sup>1</sup> *Ann.*, **77**, 130 (1851).

<sup>2</sup> *Bender, Ber.*, **15**, 410 (1882).

<sup>3</sup> *Am. Chem. J.*, **16**, 218 (1894).