A. Mailhe's[1] reduction of the amides to amines by passing the vapors of the former along with hydrogen over finely divided nickel and copper may be explained by assuming that the amides decompose into the cyanide and water and that the cyanides were then reduced to the amines. On passing acetamide over finely divided nickel at 180° to 200° without hydrogen it was found that a slight decomposition into cyanide and water had taken place.

Summary.

The acid amides may be completely decomposed into the cyanides and water by passing their vapors along with air over various contact material at a temperature of about 425°.

SYRACUSE, N. Y.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES. VI. THE UTILIZATION OF HYPOCHLORITE COLOR REACTIONS IN ESTABLISHING THE MECHANISM OF THE ACTION OF DIMETHYLSULFATE ON ANILINE.

BY NORMAN A. SHEPARD.

Received August 19, 1916.

The method of alkylating amines recently proposed by Werner,[2] by means of which monomethylated amines can be obtained by alkylation with dimethylsulfate in benzene solution, gave promise of important practical applications. According to this investigator a primary amine like aniline and this ester interact in molecular proportions, under such conditions, giving practically a quantitative yield of the methylsulfuric acid salt of the monomethylated derivative. The transformation was expressed by him in the following manner:

$$C_6H_5NH_2 + (CH_3)_2SO_4 = C_6H_5.NH_2CH_3.CH_3SO_4 \qquad (1)$$

Having occasion to apply this method for the production of methyl β-phenylethylamine, $C_6H_5CH_2CH_2NHCH_3$, the writer was surprised to find that the crystalline addition product formed by interaction of dimethylsulfate and β-phenylethylamine did not give the desired alkyl derivative when decomposed with alkali. On the contrary, the greater portion of the original amine was recovered unaltered. In order to determine the cause of the failure to obtain alkylation in this case, attention was naturally turned to a study of Werner's reaction. This work has now been completed and the purpose of this paper is to record new data that have been obtained, which are not in accord with his interpretation.

Previous to the work of Werner, Ullmann[3] had investigated the be-

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[1] *Chem. Ztg.*, **31**, 1146 (1907).

[2] *J. Chem. Soc.*, **105**, 2762 (1914).

[3] *Ann.*, **327**, 104 (1903).

havior of dimethylsulfate toward aniline. According to him, *two* molecular proportions of the base react with *one* of the ester in ether solution, forming one molecule of the methylsulfuric acid salt of aniline and leaving one molecule of monomethylaniline in solution as expressed in the following equation:

$$(CH_3)_2SO_4 + 2RNH_2 = RNH_2.CH_3HSO_4 + RNHCH_3 \qquad (2)$$

The writer has now obtained data which indicate clearly that the interpretation of Ullmann is the correct one. Using equimolecular proportions of aniline and ester and following the directions of Werner exactly, not only did the crystalline addition product prove to be the methylsulfuric acid salt of the *un*alkylated base, but the yields produced in no case approached the theoretical value based on his equation. In fact, these yields were only approximately one-half what should have been produced according to Equation 1. While 9.3 g. of aniline should yield theoretically 21.9 g. of addition product, in six separate experiments, taking special precautions to keep the temperature low and exclude moisture, the yields actually obtained were 13.7, 9.9, 11.2, 10.25, 12.5 and 11.1 g., respectively. On the other hand, these yields approach very closely the calculated value according to Ullmann's interpretation, 10.25 g., in fact, being exactly the theoretical quantity based on Equation 2. That the addition product was the methylsulfuric acid salt of aniline and not methylaniline, was shown by decomposing it with strong alkali. The base, which separated as an oil, was identified as unaltered aniline by its color reaction with hypochlorite solution, by conversion into its hydrochloride, and further by transformation into *sym.* diphenylthiourea when treated with phenylisothiocyanate. Thus the yields and chemical nature of the crystalline addition product confirm the conclusions of Ullmann.

The course of the reaction, however, varied somewhat from that described by Ullmann. It will be seen, when using equimolecular proportions of ester and base, that, after the first stage of the reaction is complete, one-half of the dimethylsulfate should still remain unaltered. This complicates the reaction considerably, for the monomethylaniline does not remain free in the benzene solution under such conditions, but separates in the form of an oil as the salt of methylsulfuric acid as expressed in Equation 3, and the tertiary base simultaneously formed, can then also

$$2CH_3NHC_6H_5 + (CH_3)_2SO_4 = C_6H_5NHCH_3.CH_3SO_4H + C_6H_5N(CH_3)_2. \qquad (3)$$

further react with the excess of ester, giving a methylsulfuric acid salt, as has been shown by Claesson and Lundvall.[1] These various stages in the reaction can actually be demonstrated by keeping the temperature of the reaction mixture at 0°. The progress of the alkylation can then be readily observed and followed by means of the hypochlorite

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[1] *Ber.*, 13, 1703 (1880).

color reactions. If the oily addition product, formed in the second stage of the reaction, begins to separate before the crystalline product is removed, it clings very tenaciously to the latter and it is for this reason that the yields of the latter recorded above lack greater uniformity. This oil was never entirely homogenous. It consisted chiefly of the methylsulfuric acid salt of methylaniline but always contained some aniline and dimethylaniline also in combination as methylsulfuric acid salts. The product of the reaction was thus *not* exclusively a salt of monomethylaniline as claimed by Werner, but a mixture consisting of the salts chiefly of unaltered material with some mono- and di-alkylated base, but with these latter forms not in sufficient quantity to make the application of equimolecular proportions of base and ester in cold benzene solution of any practical value for alkylating purposes.

Further proof for Ullmann's interpretation of this reaction is found in the fact that the yield of crystalline addition product is largely increased on using two molecular proportions of aniline. Werner states, to the contrary, that under these conditions the excess of aniline was recovered unaltered in the mother liquors. The writer finds that the yield is largely increased with these proportions, giving 88% of the theoretical quantity of crystalline addition product based on Equation 2.

Werner based his entire proof, that the crystalline product was a derivative of methylaniline, on a hypochlorite color reaction for this base. In view of the fact that Beilstein's Handbuch[1] states that this base gives no coloration with bleaching powder solution, as is also stated of both methyl- and dimethylaniline in the latest edition of Richter's *Organische Chemie* (1913), it seemed of distinct value to make a comparative study of all the hypochlorite color reactions of these three bases. It was found that, under certain conditions, each of these bases gives a well-defined and characteristic color reaction with bleaching powder solution and the results of this work are recorded in Tables I and II, illustrating the behavior in different concentrations. The deep reddish purple coloration produced by aniline in neutral or alkaline solution with bleaching powder solution, discovered by Runge,[2] confirmed by Hofmann,[3] and carefully studied by Nietzki,[4] is a very satisfactory color test for this base. The writer has found, however, that in the presence of large amounts of methylaniline (25% or more), the test is unreliable, giving only an indefinite brown precipitate with no purple coloration. The first observation, as far as the writer is aware, of a hypochlorite color reaction for methyl- and dimethylaniline, is recorded by Willm and Girard.[5] These investigators

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[1] Vol. II, p. 325.

[2] *Pogg. Ann.*, **31**, 66 (1834).

[3] *Ann.*, **47**, 54 (1843).

[4] *Ber.*, **27**, 3263 (1894).

[5] *Bull. soc. chim.*, **28**, 49 (1877).

state that the former gives a dark blue-violet and the latter a yellow color with bleaching powder solution, but no mention of the conditions, such as concentration or acidity, under which these colors were obtained, was made. Three years previous to this, Hofmann[1] made the observation that methylaniline gives no coloration with hypochlorite solution, which is absolutely correct, *provided the solution is neutral.* In *alkaline* solution Leech[2] has recently shown that this base gives a fine transient navy blue, easily distinguishable from the aniline coloration. The writer has found this test to be very satisfactory indeed and more sensitive to traces of methylaniline than the method of testing in *acid* solution employed by Werner (cf. Table II). This latter method consists in adding bleaching powder solution and then a few drops of dilute sulfuric acid to an aqueous solution of the base, when a deep indigo-blue color develops if methylaniline is present. This test is very brilliant and quite satisfactory, provided the reagents are added in the order given above, *i. e.*, bleaching powder solution *first* and *then* the acid. It has now been found on the other hand that if the order of adding the reagents is reversed and the bleaching powder solution is added to an acid solution of the base, aniline also will give a deep navy blue color, very easily confused with that produced by methylaniline. In fact only on very careful observation can the two colors be distinguished, but when compared side by side it was found that the blue produced by aniline is less brilliant, almost always murky and distinctly more fugitive than that produced by methylaniline. On short standing (about one hour), it changes to a murky brown suspension, while the test with methylaniline will remain clear and retain its intensity without appreciable fading for twenty-four hours. Even after forty-eight hours the color is still quite brilliant. It is advisable in this test to use a moderate excess of bleaching powder solution, but an excess of sulfuric acid should be avoided.

It can now readily be seen how Werner drew wrong conclusions from his color test. A water solution of the crystalline addition product, $C_6H_5NH_2.CH_3SO_4H$, is strongly acid to litmus paper and therefore on adding bleaching powder solution all conditions are favorable for producing the navy blue color from aniline. The writer has found that the water solution of his addition product gives an excellent deep navy blue when tested as Werner directed. If, however, the methylsulfuric acid is first neutralized before testing, this navy blue color is not obtained and the familiar reddish purple of aniline appears. As Werner made no attempt apparently to liberate the free base and identify it other than through this color reaction, he failed to realize that this navy blue was not peculiar

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[1] *Ber.*, **7**, 526 (1874).

[2] THIS JOURNAL, **35**, 1042 (1913).

to methylaniline alone and therefore gave an erroneous interpretation to his reaction.

To identify dimethylaniline, Werner employed the deep orange-yellow color reaction, first mentioned by Willm and Girard,[1] but he does not state the conditions necessary for the successful production of this coloration. The writer finds that this test is very satisfactory and reliable, provided it is carried out in a slightly *acid* medium, for this base gives no coloration in neutral or alkaline solution. Strong acid solutions, however, should be avoided, for the test may be entirely negative under such conditions; the yellow color is quickly destroyed by alkalies or a large excess of calcium hypochlorite solution.

TABLE I.—COMPARATIVE COLOR TESTS FOR ANILINE, METHYL- AND DIMETHYLANILINE.
Concentration of base: 1 drop of base in 5 cc. H_2O for each test.
Concentration of $CaOCl_2$ solution: one-half saturated.

	Reagents		
Base.	0.5 cc. $CaOCl_2$.	0.5 cc. $CaOCl_2$ followed by 3 drops dil. H_2SO_4.	3 drops dil. H_2SO_4 followed by 0.5 cc. $CaOCl_2$.
$C_6H_5NH_2$	Deep reddish purple *characteristic* Changed to brown by excess $CaOCl_2$	Dark murky bluish green	Deep reddish purple, changing to deep indigo-blue
$C_6H_5NHCH_3$	Yellowish to brownish murky solution	Very intense indigo-blue (x) *characteristic*	Indigo-blue developing more slowly than x
$C_6H_5N(CH_3)_2$	Colorless murky solution	Deep orange-yellow *characteristic*	Deep orange-yellow *characteristic*

TABLE II.—COMPARATIVE COLOR TESTS FOR ANILINE, METHYL- AND DIMETHYLANILINE.
Concentration of base: 1.0 cc. $^1/_{100}$ mole solution of base for each test.
Concentration of $CaOCl_2$: one-half saturated.

	Reagents.		
Base.	1 drop $CaOCl_2$.	1 drop $CaOCl_2$ followed by 1 drop dil. H_2SO_4.	3 drops 6 N NaOH followed by 0.5 cc. $CaOCl_2$.
$C_6H_5NH_2$	Deep reddish purple *characteristic*	Insignificant pink or brown	White precipitate and deep purple solution
$C_6H_5NHCH_3$	Insignificant yellow with slight turbidity	Insignificant pale blue	White precipitate with distinct navy blue color developing slowly and then slowly fading to yellow *characteristic*
$C_6H_5N(CH_3)_2$	Colorless	Deep orange *characteristic*	White precipitate

Experimental Part.

The Action of Dimethylsulfate on Aniline at Room Temperature.—To 9.3 g. of aniline (freshly distilled) in 75 cc. of benzene (distilled over

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[1] *Loc. cit.*

sodium), 12.6 g. of dimethylsulfate (1 mol) in 25 cc. of benzene were added cooling at first to prevent any rise in temperature. Every precaution was taken to have all the reagents absolutely dry and the ester was washed with sodium bicarbonate to remove any methylhydrogen sulfate, carefully dried and then twice distilled *in vacuo* before use. The crystalline addition product began to separate almost immediately and, after standing for 24 hours at room temperature, was filtered by suction. A thick, yellow oil adhered to the crystals, which was partially removed by thorough pressing out and washing with benzene. After drying over concentrated sulfuric acid, the last traces of this oily material were pressed out on a porous plate. The weight was then 9.9 g. The yield of this crystalline addition product will vary considerably; in three duplicate experiments 9.3 g. of aniline yielded 13.7, 11.2, and 10.25 g., respectively. In every case, even after long drying, the products were oily and did not melt sharply. The water solution was acid but did not give a precipitate with barium chloride. When this addition product was decomposed in aqueous solution with strong potassium hydroxide, a yellowish brown oil separated, which was extracted with ether and dried over caustic potash. Dry hydrochloric acid was then passed into this ether solution, when aniline hydrochloride separated as crystals melting at 198°.

The benzene mother liquor from the crystalline product contained a yellow oil, insoluble in benzene, which became dark green on standing. The benzene was decanted from this oil and allowed to stand, when more oil gradually deposited. An aqueous solution of this oil was acid to litmus, gave no test for sulfates with barium chloride, but gave a strong color reaction for methylaniline. When decomposed with sodium hydroxide, 1.4 g. of mixed bases were liberated. Treatment of this mixture with phenylisothiocyanate gave 0.5 g. of *sym.* diphenylthiourea (corresponding to 0.2 g. of aniline) and 0.7 g. of methyldiphenylthiourea (corresponding to 0.3 g. of methylaniline). These urea derivatives were separated by crystallization from alcohol, when the former separated in plates, melting at 150–1°. The alcohol mother liquor did not deposit crystals and it was only after removing the alcohol, triturating with petroleum ether and cooling to —16°, that the methyldiphenylthiourea would deposit in a crystalline state. This was then recrystallized from alcohol when it separated in stout prisms, melting at 85–7°. No lowering of the melting point was observed, when both these urea derivatives were mixed with the corresponding pure substance. Extraction of the residues from the mother liquors of the thiourea derivatives, with dilute hydrochloric acid and neutralization of the resulting solution with potassium hydroxide, gave 0.6 g. of a light brown oil. The solution of this oil in 3.0 g. of 20% hydrochloric acid, cooled to —5° and then treated with 0.35 g. of sodium nitrite dissolved in the least possible quantity of water. deposited 0.5 g.

of a deep orange-yellow powder, which decomposed with explosive violence at 165–7°. Though decomposing somewhat low, it agreed in all its properties with *p*-nitroso-dimethylaniline hydrochloride (m. p. 177°), which was prepared for comparison.

The original benzene solution was now allowed to evaporate spontaneously. About 2.0 g. of oil remained, which was soluble in water. Bleaching powder solution showed this to be a mixture of dimethylaniline with some methylaniline, both in the form of salts. An aqueous solution is acid, but gives no precipitate with barium chloride.

The Action of Dimethylsulfate on Aniline at 0°.—The above reaction was repeated, using the same proportions, but allowing the reaction to proceed at continued low temperature in a refrigerator. After standing for 15 hours, the crystalline addition product was pure white but, at the end of 18 hours, a very light yellow color was beginning to appear. Upon filtering at once, 12.5 g. of addition product (after drying over sulfuric acid) were obtained. It was only very slightly oily and no oil had as yet separated in the benzene mother liquor. In a duplicate experiment, also carried out at 0°, the salt was filtered after 3.5 hours. The deposition of addition product was not yet complete, under these conditions, but there was no oil and the product was pure white. On standing 16 hours longer, still at 0°, the remainder of the product, separating in crystalline leaves and free from any oil, deposited, bringing the total yield up to 11.1 g. It melted sharply at 158–60°, gave no test for sulfate and on prolonged exposure to the air did not appear particularly hygroscopic. The aqueous solution was strongly acid and gave a strong color reaction for aniline with calcium hypochlorite after neutralization with alkali. Liberation of the free base with alkali and treatment with phenylisothiocyanate gave *sym.* diphenylthiourea in 66% yield (after complete purification).

Calc. for $C_7H_{11}O_4NS(C_6H_5NH_2.CH_3SO_4H)$: N, 6.83. Found: N, 6.67, 6.68.

Titration with 0.1061 N KOH, using phenolphthalein as the indicator:

I. 0.1803 g. required 8.35 cc. II. 0.4039 g. required 18.75 cc. KOH.

Calc. for $C_7H_{11}O_4NS$: CH_3SO_4H, 54.63. Found: CH_3SO_4H, 55.06, 55.19.

The benzene mother liquor, containing *no* oil, was allowed to stand at 0.° The yellow oil soon began to separate. The benzene was decanted after 29 hours' standing at 0° and then let stand at room temperature for 2 days. A second crop of oil had then separated. The benzene solution, which, previous to the second deposition of oil, had given color tests for both mono- and di- methylaniline, now gave *no* test for the former, but a strong test for the latter. The combined oily layers weighed about 6.0 g., but contained a considerable quantity of benzene. This yellow oil turned green on standing as before and an aqueous solution was acid to litmus but gave no test for sulfuric acid. It gave a strong test for methylaniline, but was not homogeneous, for, on conversion into thiourea with phenylisothiocyanate as in the previous experiment, 1.6 g. of free bases gave about 0.3 g. of *sym.*-diphenylthiourea (corresponding to 0.12 g. of aniline), 1.5 g. of methyldiphenylthiourea (corresponding to 0.7 g. of methylaniline), and 0.2 g. of dimethylaniline was extracted from the residues by hydrochloric acid. The last product was identified by the deep yellow coloration produced by bleaching powder in acid solution.

The benzene mother liquor from the yellow oil left a residue of 2.7 g. on spontaneous evaporation, which consisted of a light yellow syrup containing a few drops of a non-miscible brownish oil, which did not dissolve when treated with water. This was extracted with ether (weight = 0.10 g.); it was not dimethylaniline as shown by color tests, but, on boiling with caustic soda, the white precipitate with barium chloride in acid solution indicated that it was unaltered dimethylsulfate. The water soluble portion of the above residue gave no precipitate with barium chloride until saponified with boiling alkali; the test for sulfate was then strong. Sodium hydroxide liberated 0.15 g. of oil which was identified, by its color reactions and also by conversion into *p*-nitrosodimethylaniline hydrochloride, as dimethylaniline.

The Action of One Molecular Proportion of Dimethylsulfate on Two Molecular Proportions of Aniline at 0°.—Three and five-tenths grams of of dimethylsulfate in 7 cc. of benzene were added to 5.2 g. of aniline (2 molecular proportions), in 21 cc. of benzene and the mixture allowed to stand for 16 hours in a refrigerator. The product, which was not oily, weighed 5.0 g. after standing for one week over concentrated sulfuric acid. This yield corresponds to 88% of the theoretical quantity, calculated from Ullmann's equation. The benzene mother liquor was a light brown color and contained no oil. This was allowed to stand for 8 hours at 0°; no oil deposited. A water extract of a portion of the now deep brown benzene solution gave a strong color test for methylaniline. After standing for several days at room temperature, only a trace of oil separated.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

ACTION OF OXALYL CHLORIDE ON PRIMARY, SECONDARY AND TERTIARY ALCOHOLS.

BY ROGER ADAMS AND L. F. WEEKS:

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Staudinger,[1] who was the first to find a convenient method for the preparation of pure oxalyl chloride, studied several of its reactions. He found that it reacted normally with ethyl alcohol to give ethyl oxalate,

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[1] *Ber.*, **41**, 3558 (1908); 46, 1426 (1913); *Chem. Zentr.*, **1910**, I, 307.