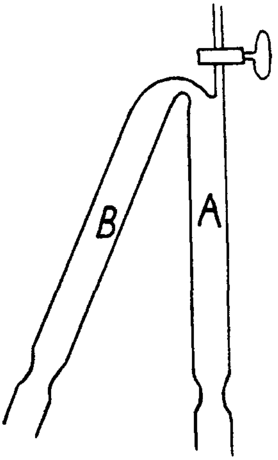
was then poured over into B. A was washed free of cupric nitrate by distilling some ammonia over from B, and then pouring it back again. This was repeated until no color was obtained in A. The solution was then allowed to stand in contact with the copper foil until the color of deep blue gave way to a practically colorless solution.

The solution was then transferred to A, and B washed by repeated distillations of the ammonia from A to B, and then pouring back into A. The ammonia was then allowed to gradually distil off through the stopcock. As the solution concentrated, the cuprous nitrate crystallized out. A was then sealed off, evacuated, and weighed. The salt was then dissolved in dilute nitric acid, washed out, and the copper determined electrolytically. The tube was dried, evacuated and weighed.



The weight of the crystallized salt was 0.5786 gram; weight of copper 0.2292 gram, giving 39.61 per cent. copper, in fair agreement with the formula $CuNO_3.2NH_3$ which requires +39.86 per cent. The increased weight of salt obtained corresponds (weighings of cupric nitrate and copper foil approximate) to the loss of weight in the copper foil.

The salts obtained were not entirely pure. A few blue crystals separated out with the colorless cuprous nitrate, showing the presence of a little cupric nitrate. This could not be separated owing to their similar solubility. Possibly this could be avoided by using more elaborate apparatus, but it seemed as if there was a point of equilibrium reached when the cupric nitrate was nearly reduced. The salt is not stable in the air, oxidizing very rapidly.

A recent analysis of another sample by Mr. G. H. Bohart, of this laboratory, in which the nitrogen was also determined, gave practically the same result for the copper content, and also agreed very closely with the theoretical nitrogen content for the above formula.

The preparation of the above salt was suggested by Prof. E. C. Franklin.

W. H. Sloan.

[Contribution from the Chemical Laboratory of the Massachusetts Institute of Tech.]

THE CONDENSATION OF SOME PRIMARY AROMATIC AMINES WITH CHLORAL-ANILINE.

By Stroud Jordan.

Received June 10, 1910.

It has been known for a long time that when one molecule of an amine, as aniline, is brought in contact with one molecule of an aldehyde, as chloral, an addition product will be formed, but if the amine is increased to two molecules while the aldehyde is kept constant at one molecule a condensation product will be formed and a molecule of water will be eliminated.[1] Further than this, no definite relationship has been established between these two reactions, so that the purpose of this paper will be to point out some of the relations existing between these two reactions and their products.

It has been shown in the following work that it is possible to form a condensation product by the action of one molecule of a free amine with one molecule of an addition product, without the presence of free chloral. It has also been shown that it is possible to form a condensation product in which two unlike amines will be joined to the same chloral residue, by the action of one molecule of a free amine with the addition product of chloral and an unlike amine. By these two experiments it has been shown that the addition product *can* be an intermediate step in the formation of the condensation product and that it will change over into the condensation product upon the addition of an excess of a free amine.

The products which will be studied in the following work are:

First, the condensation of aniline with chloral-aniline, and

Second, the condensation of 1,3,4-nitrotoluidine with chloral-aniline. In this second product it will be noticed that it was very difficult to prepare a pure sample of the condensation product, on account of the ease with which it decomposed in nearly every solvent. This decomposition product was proved to be 5-chlorine-3-nitro-4-toluidine and this work will be taken up later, in this laboratory, as a probable method of chlorination for the aromatic amines. This work will also be followed up later to determine the rate of reaction and also as a study of intermediate reactions.

Experimental.

The Condensation of Aniline with Chloral-aniline.—For this preparation eight grams of the freshly prepared addition product were dissolved in one hundred cc. of 95 per cent. alcohol and to this were added three grams of pure aniline after which the whole mass was heated up to boiling and then allowed to stand for six hours. This gave a light yellow solution which crystallized out, on evaporation over a water bath. This crude compound consists of yellowish crystal masses which melted at 98–100°, but after two crystallizations from alcohol and petroleum ether it gave pure, white needles, melting at 107–8°. This compound was proved to be the condensation product, by making its hydrochloride and hydrobromide, by the melting point of the aceto derivative, by its crystalline form and melting point and by the detection of free aniline and chloral, when the condensation product was decomposed.

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[1] *Ann.*, 302, 340–80 (1898). THIS JOURNAL, 31, 937 (1909).

From the above reactions it may be concluded that the condensation of aniline and chloral may be made by the interaction of one molecule of aniline with one molecule of chloral-aniline, thus dividing the condensation reaction into two steps: $C_6H_5NH_2 + CCl_3CHO = C_6H_5NH—CCl_3CHOH$, and $C_6H_5NH—CCl_3CHOH + C_6H_5NH_2 = (C_6H_5NH)_2CCl_3CH + H_2O$.

The Condensation of 1,3,4-Nitrotoluidine with Chloral-aniline.—For this preparation one and one-half grams of aniline and two and one-half grams of chloral were brought together in an open vessel, without the presence of a solvent. The temperature was never allowed to exceed 40° so that no water would be driven out from the reaction, thus guarding against the formation of any condensation product. This reaction gave the addition product of aniline and chloral, described by A. Eibner.[1] To this addition product were added two and six-tenths grams of 1,3,4-nitrotoluidine, which had been previously dissolved in one hundred cc. of benzene, after which the whole mass was heated at a slow boiling temperature for two and one-half hours, under a reflux condenser. This solution was then filtered off from any byproduct that might be present and the clear benzene solution was allowed to crystallize out, which gave a yield of six and two-tenths grams of a crude product melting at 90–6°, being approximately a 95 per cent. yield of the theoretical amount of condensation product which should have been formed by this reaction. The crude product, obtained in this manner, was purified by crystallization from benzene at room temperature, raising the melting point to 98–9°. This compound crystallized from benzene in light, yellowish-brown, crystal masses which crawled up the sides of the beaker. It was easily soluble in alcohol, acetic acid, acetone, benzene, ether and toluene, but not so soluble in gasoline, petroleum ether and ligroin.

Three analyses of this compound, for chlorine, gave: 28.44, 27.45 and 28.07 per cent. Cl; calculated for $C_{15}H_{14}N_3O_2Cl_3$, 2840 per cent.

This condensation product was apparently unaffected when treated with water, either hot or cold, for only a slight amount of decomposition was ever noticed, but when it was treated with concentrated hydrochloric acid a mixture of aniline hydrochloride, nitrotoluidine hydrochloride and free chloral was obtained. These compounds were recognized by making the hydrochloric acid solution alkaline with sodium hydroxide and distilling with steam. The aniline came over in the first distillate, mixed with a little nitrotoluidine, while the nitrotoluidine remained behind in the distilling flask, mixed with a little aniline. These two compounds were proved to be present by their behavior with acids, melting points and other derivatives. The toluidine gave a melting

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[1] *Ann.*, 302, 340–80 (1898).

point of 78° and formed a hydrochloride which decomposed at 230–4°, while the aniline gave the characteristic phenyl isocyanide odor and an acid derivative with hydrochloric acid, which was proved to be the hydrochloride of aniline.

When bromine was added to a glacial acetic acid solution of the condensation product it reacted very vigorously, forming a white, crystalline precipitate and liberating chloral. This bromine derivative was proved to be a mixture of the aniline and nitrotoluidine hydrobromides and some of the higher bromine derivatives, by making it alkaline with sodium hydroxide and distilling with steam. Free aniline was the first to come over with the steam and was recognized by making its hydrochloride and acetyl derivative. The nitrotoluidine remained behind in the distillation flask and was recognized by its melting point and the decomposition point of its hydrochloride. The separation of these two amines was not complete, for there was always a trace of the nitrotoluidine in the aniline distillate and the residue, left in the distillation flask, was mixed with some of the higher bromine derivatives and some free aniline.

A molecular weight determination was next made, using glacial acetic acid as a solvent, but there was always an error, due to the fact that the condensation product was unstable and would break down into 5-chlorine-3-nitro-4-toluidine. While this decomposition was very slight, it was sufficient to keep the molecular weight low and the best result that was obtained, by the freezing point method, was 348.+. The theoretical molecular weight for this compound should be 374.+. This molecular weight will show, however, which of the three following possibilities this compound really is:

Substance.	M.P.	M.W.	Per cent. Cl.	Color.	Form.
The condensation of aniline and chloral	107–8°	315·35	33·72	White	Needles
The condensation of nitrotoluidine and chloral	108–9°	433·35	24·52	Golden yellow	Needles
	Found.	Found.	Found.	Found.	
The condensation of aniline, chloral and nitrotoluidine	98–9°	348	28.44	Yellowish	Masses
		Theoret.	Theoret.		
		374·35	28.40		

In considering the two possibilities with which the mixed-type condensation has been compared it has been assumed that when the nitrotoluidine is added to the addition product of aniline and chloral either a mixed-type condensation has been formed or a reaction has taken place causing the addition product to change over into a simple condensation product with the liberation of half of the chloral and one molecule of a free amine, either aniline or nitrotoluidine. No mention has been made of the possibility of a mixture which would contain the condensations of aniline and chloral and nitrotoluidine and chloral because the crude products, and also the purified products, which have been obtained by this work, have always shown very constant melting points and the behavior towards acids has always been the same.

From the foregoing work it has, therefore, been concluded that the mixed-type condensation product has been prepared in which one molecule of aniline and one molecule of nitrotoluidine are condensed with one molecule of chloral, according to the following reactions: $CCl_3CHO + C_6H_5NH_2 = CCl_3CHOH.NHC_6H_5$, and $CCl_3CHOH.NHC_6H_5 + C_7H_5N_2O_2 = C_{15}H_{14}N_3O_2Cl_3 + H_2O$.

The subsequent decomposition of this condensation product, giving 5-chlorine-3-nitro-4-toluidine, would probably take place in the following two steps, for the reason that nitrotoluidine and chloral will form an addition product which breaks down into the same chloral derivative, without the presence of either free or combined aniline: $C_{15}H_{14}N_3O_2Cl_3 \longrightarrow CCl_3CHOH.NHC_6H_3NO_2CH_3 + C_6H_5NH_2$, and $CCl_3CHOH.NHC_6H_3NO_2CH_3 + HCl \longrightarrow C_7H_8N_2O_2Cl$ + aldehyde derivative.

BOSTON, MASS.

THE DETERMINATION OF TOTAL SULPHUR IN ORGANIC MATTER.

BY HERMAN SCHREIBER.

Received June 7, 1910.

Introduction.

A great many methods have been proposed for the determination of total sulphur in organic matter, but probably only two of these are either easy to manipulate or accurate, namely, the Barlow-Tollen,[1] or absolute method, and the Osborne,[2] or peroxide method. When the latter is applied to solid material, however, it leaves much to be desired in the way of ease of manipulation and speed, and has absolutely no claim to exactness of detail. It is true that the water used for moistening the sample is measured and the sodium carbonate is weighed, but the amount of sodium peroxide added varies with the material analyzed and with the rate at which the reagent is added. The amount of acid which must be added after fusion is also an unknown factor; it varies in each case which necessitates making the solution alkaline again, and then acid. These, however, are not all of the difficulties encountered. The fusions have a tendency to burn and blow out of the crucible, and this happens most frequently when the determinations must be rapidly made, for the

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[1] THIS JOURNAL, **26**, 341 (1904).

[2] U. S. Dept. Agr., **Bureau of Chemistry** *Bull.* **107**, revised, p. 23.