in the determination must be carefully avoided or compensated, as the final result will be altered by the square of any such error. The determination may be made by volumetric, gravimetric, optical, or any other method. The above formula has an advantage over the similar one used by Wiley[1] in his well-known "double dilution" method in that only one sample of the original material is required. WARREN RUFUS SMITH.

LEWIS INSTITUTE, CHICAGO,
May 25, 1909.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.]

CONDENSATION OF CHLORAL WITH PRIMARY AROMATIC AMINES. III.[2]

BY ALVIN S. WHEELER AND STROUD JORDAN.

Received May 31, 1909.

The other papers upon this subject were published in THIS JOURNAL in 1902[3] and 1908.[4] A review of earlier work was given in the second paper and therefore will not be repeated here. Chloral does not combine with all primary aromatic amines. We have been unable to condense it with those containing more than two negative substituents in the nucleus such as trichloraniline. Eibner[5] noticed this fact, but we gave the reaction a more thorough study. The condensation products with aniline and the toluidines are less stable than those containing one or two negative atoms or groups substituted in the benzene ring. The action of chloral upon the former takes place rapidly with the liberation of considerable heat while with the latter it is necessary to apply heat in order to bring the reaction to completion. Addition products of one molecule of chloral and one molecule of the amine are quite generally possible but we describe here only two which made their appearance in our attempts to prepare the condensation products. These are addition products of chloral with 2-nitro-4-toluidine and 3-chlor-4-toluidine. Such compounds are usually best prepared in ether solution at a low temperature.

The condensation products are resolved into their constituents by heating with strong mineral acids. A special study was made of the action of bromine upon them when dissolved in cold glacial acetic acid. No bromine derivative was obtained in any case, but cleavage al-

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[1] THIS JOURNAL, **18**, 430.

[2] This paper forms part of a thesis presented to the Faculty of the University of North Carolina in May, 1909, by Stroud Jordan, candidate for the degree of Doctor of Philosophy.

[3] Wheeler and Weller, THIS JOURNAL, **24**, 1063.

[4] Wheeler, *Ibid.*, **30**, 136.

[5] Eibner, *Ann.*, **302**, 370.

ways occurred with the reformation of chloral, which was isolated as chloroform, and secondly, either the hydrobromide of the original amine or a brominated amine. This may or may not depend on the amount of bromine used. In the case of the aniline condensation product, one molecule of bromine yields aniline hydrobromide while two molecules yield *p*-bromaniline hydrobromide. Bromine always enters in the para position, if this is unoccupied, otherwise in the ortho position. With the *p*-nitraniline compound bromine enters both ortho positions. We hoped to find that the bromination of these condensation products would yield better results in preparing brominated amines than the direct bromination of the amine, but we were disappointed. Some odd results were observed in one series of brominations of trichlorethylidinediphenamine. It seemed as if nitrogen bromides were first formed, rapidly isomerizing to the substituted amine. Another series, however, gave no such indications. This is probably what actually occurs as suggested by Chattaway and Orton.[1] It is a very plausible way to explain the mechanism of substitution and we hope to look into this reaction again.

The new compounds which are described in this paper include the condensation products of chloral with *m*-bromaniline, *p*-aminobenzoic acid, *m*-aminobenzoic acid, 5-brom-2-aminobenzoic acid, 2-nitro-4-toluidine, 4-nitro-2-toluidine, 3-nitro-4-toluidine, 3-chlor-4-toluidine, 4-brom-2-nitraniline, 4-brom-3-nitraniline, *p*-iodaniline, 4-brom-1-naphthylamine, *p*-aminoacetophenone, and also the addition products with 2-nitro-4-toluidine and 3-chlor-4-toluidine.

One of us having failed to condense chloral with naphthylamine,[2] we tried a bromnaphthylamine and obtained a compound which we feel certain is a condensation product of the usual type, but we were unable to get complete proof. We got a satisfactory analysis for the formula proposed but could not determine the toluene of crystallization because the compound began to decompose before all of this could be expelled.

Experimental.

Trichlorethylidenedi-m-bromphenamine, $CCl_3CH(NHC_6H_4Br)_2$, is readily prepared by treating 20 g. of *m*-bromaniline dissolved in 50 cc. of benzene with 9.0 g. chloral. The reaction takes place at once with the liberation of heat. In order to remove a small amount of a by-product which melted at 215–20° it was found best to distil off the benzene and extract the residue with benzene, in which the condensation product is readily soluble. The benzene extract was evaporated to a sirupy consistency, cooled and scratched. The sirup was quickly converted into a mass of colorless crystals melting at 98–104°. On recrystallizing twice from carbon tetrachloride the melting point was raised to 115–6°. The microscope showed the crystalline form to be rhombic bi-pyramids. Calculated for $C_{14}H_{11}N_2Br_2Cl_3$: Br + Cl, 56.24. Found: Br + Cl, 56.38, 55.88. The compound is not affected by boiling water but hydrochloric acid resolves it into its constituents.

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[1] Chattaway and Orton, *J. Chem. Soc.*, **75**, 1046 (1899).

[2] Wheeler and Daniels, *J. Elisha Mitchell Sci. Soc.*, **22**, 90 (1906).

Action of Bromine.—The action of bromine upon this condensation product was studied quantitatively in order to make a comparison with the action of bromine upon *m*-bromaniline, which was worked out by Wheeler and Valentine.[1] For this purpose 29.7 g. of the pure condensation product were dissolved in the least possible amount of glacial acetic acid at room temperature. To this solution were added 20 g. of bromine dissolved in glacial acetic acid so as to make a 10 per cent. solution. A dense mass of colorless scales was immediately obtained. This precipitate weighed 20 g. The addition of much water to the filtrate gave a precipitate of tetrabromaniline, weighing 2.6 grams. On treating the main precipitate with water, 8.0 g. of 3,4-dibromaniline were dissolved out, present as the hydrobromide, leaving undissolved 5.0 g. of a mixture of 3,4,6-tribromaniline and 2,3,4-tribromaniline. The results do not differ essentially from the bromination of *m*-bromaniline.

Trichlorethylidenedi-p-aminobenzoic acid, $CCl_3CH(NHC_6H_4COOH)_2$, was prepared by suspending 10.0 g. of *p*-aminobenzoic acid in 100 cc. of benzene, adding 5.5 g. of chloral and boiling 3 hours under a reflux condenser. Solution did not take place. The crude product darkened at 186° and turned black at 220°. Recrystallization from glacial acetic acid gave the pure condensation product, melting at 215–20° with much decomposition. It consists of colorless masses of ill-defined crystals. It is easily soluble in methyl or ethyl alcohol, difficultly soluble in glacial acetic acid and insoluble in benzene, toluene, carbon tetrachloride and carbon disulphide. The yield was 88 per cent. of the theoretical. Calculated for $C_{16}H_{13}O_4N_2Cl_3$: Cl, 26.57. Found: Cl, 26.33.

It is stable in boiling water but is broken down by concentrated hydrochloric acid into chloral and *p*-aminobenzoic acid. To study the action of bromine 11.0 g. of the condensation product were suspended in 100 cc. benzene, to which were added 8.7 g. of bromine. Action was allowed to take place in the cold. An abundant precipitate of the hydrobromide of 3,5-dibrom-4-aminobenzoic acid formed. Treatment with water gave the free base, melting at 292–3°, decomposing to a black mass. Further identification was obtained by diazotizing the product in absolute alcohol, which yielded 3,5-dibrombenzoic acid.

Trichlorethylidenedi-m-aminobenzoic acid, $CCl_3CH(NHC_6H_4COOH)_2$, was prepared by dissolving 10.0 g. of *m*-aminobenzoic acid, melting at 174°, in 100 cc. of benzene, adding 5.5 g. of chloral and boiling one and one-half hours on the steam-bath. The benzene was driven off and the residue extracted several times with benzene. The extracts were mixed and the condensation product was allowed to crystallize out slowly. It consisted of a colorless mass of ill-defined crystals, which melted at 240° with decomposition. It is soluble in the alcohols, benzene and glacial acetic acid, insoluble in ligroin and chloroform and difficultly soluble in ether. Calculated for $C_{16}H_{13}O_4N_2Cl_3$: Cl, 26.37. Found: Cl, 26.50, 25.93.

The behavior with water and with hydrochloric acid is the same as that of the para acid. On treating 5.5 g. of the condensation product dissolved in 100 cc. of glacial acetic acid with 4.3 g. of bromine there was obtained 7.0 g. of a bromine derivative melting at 279–82° and decomposing to a dark purple liquid. Boiling water set free hydrobromic acid and extraction by ether of this solution yielded a substance melting at 215–6°. The product is therefore 5-brom-3-aminobenzoic acid. It was further identified by the preparation of its sulphate and hydrochloride.

Trichlorethylidenedi-5-brom-2-aminobenzoic acid, $CCl_3CH(NHC_6H_4COOHBr)_2$.—The 5-brom-2-aminobenzoic acid used in this preparation was made by the convenient method of Wheeler and Oates,[2] who treated anthranilic acid in glacial acetic solu-

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[1] Wheeler and Valentine, *Am. Chem. J.*, **22**, 266.

[2] Wheeler and Oates, THIS JOURNAL, **41**, 568 (1909).

tion directly with bromine. Five g. of the brom acid, melting at 210°, were dissolved in 100 cc. of toluene and, after adding 1.8 g. of chloral, boiled one and one-half hours. On cooling an abundant crystallization took place. The product crystallized out of benzene in clusters of needles, melting at 174–5°. Calculated for $C_{16}H_{11}O_4N_2Br_2Cl_3$: Br, 28.52; Cl, 18.95. Found: (1) Br, 28.01; Cl, 18.62; (2) 28.63, 18.96.

The condensation product is soluble in alcohol, benzene, toluene and glacial acetic acid. It is readily decomposed by water into chloral and 5-brom-2-aminobenzoic acid, likewise by hydrochloric acid. On treatment with an excess of bromine in glacial acetic acid solution the same decomposition takes place, the main product being the hydrobromide of 5-brom-2-aminobenzoic acid.

Trichlorethylidenedi-2-nitro-4-tolamine, $CCl_3CH(NHC_6H_3NO_2CH_3)_2$, was prepared by dissolving 5.0 g. of 2-nitro-4-toluidine, melting at 77.5°, in 100 cc. of toluene, adding 2.6 g. of chloral and boiling one and one-half hours. The solution was cooled down and enough gasolene added to precipitate the product. It came down as an oil but solidified after standing on a warm water-bath for a half hour. The substance was purified by two crystallizations from a mixture of toluene and gasolene. It consists of a bright yellow crystalline powder, melting to a clear liquid at 108–9°. It is soluble in alcohol, benzene, toluene, glacial acetic acid, insoluble in gasolene and only slightly soluble in ether. Calculated for $C_{16}H_{15}O_4N_4Cl_3$: Cl, 24.52. Found: Cl, 24.77, 25.02.

The condensation product is stable in boiling water but is resolved by boiling concentrated hydrochloric acid into its constituents. The hydrochloride of 2-nitro-4-toluidine melted at 230–40°, decomposing to a black liquid. It consisted of long silvery white needles. Bromine gave the same reaction, no bromine entering the ring.

Addition Product of 2-Nitro-4-toluidine and Chloral. Chloral-2-nitro-4-toluidine, $C_9H_9O_3N_2Cl_3$, was prepared by dissolving 2.5 g. of 2-nitro-4-toluidine (1 mol.) in benzene, adding 2.5 g. of chloral (1 mol.) and boiling for an hour. On concentrating and cooling the solution a fine crop of beautiful yellow needles separated. On recrystallization from a mixture of benzene and gasolene the compound was obtained pure, melting at 187–8°. It is easily soluble in alcohol, benzene, or glacial acetic acid, but insoluble in gasolene or xylene. Calculated for $C_9H_9O_3N_2Cl_3$: Cl, 35.54. Found: Cl, 35.91, 35.98.

Trichlorethylidenedi-4-nitro-2-tolamine, $CCl_3CH(NHC_6H_3NO_2CH_3)_2$, was prepared by dissolving 2.5 g. of 4-nitro-2-toluidine melting at 109°, in 50 cc. benzene, adding 1.5 g. of chloral and boiling one and a half hours. The solvent was boiled off and the residue extracted with fresh benzene. A small amount of by-product remained insoluble, decomposing to a black liquid at 215–30°. The solution yielded a crude product amounting to 85 per cent. of the theoretical. It was practically pure but was recrystallized from glacial acetic acid for analysis. It consists of long golden-yellow needles, melting to a clear liquid at 142–3°. It is easily soluble in carbon tetrachloride and benzene, less soluble in alcohol and glacial acetic acid. Calculated for $C_{16}H_{15}O_4N_4Cl_3$: Cl, 24.52. Found: Cl, 24.26.

The behavior with water, concentrated hydrochloric acid and bromine is identical in each case with that of the 2-nitro compound.

Trichlorchlorethylidenedi-3-nitro-4-tolamine, $CCl_3CH(NHC_6H_3NO_2CH_3)_2$, was prepared by dissolving 2.5 g. of 3-nitro-4-toluidine in 100 cc. of toluene, adding 1.5 g. of chloral and boiling for 3 hours. A brownish yellow mass of needles settled out on cooling, which melted at 162–3°. Recrystallization from toluene raised the melting point to 165–6°. It is soluble in alcohol, benzene, toluene and glacial acetic acid. Calculated for $C_{16}H_{15}O_4N_4Cl_3$: Cl, 24.52. Found: Cl, 24.77.

This condensation product is less stable than the two previous nitro compounds, for it is decomposed by boiling water. It is resolved into its constituents by hydrochloric acid and by bromine.

Trichlorethylidenedi-3-chlor-4-tolamine, $CCl_3CH(NHC_6H_3ClCH_3)_2$, was prepared by dissolving 5.0 g. of 3-chlor-4-toluidine in 100 cc. of benzene, adding 3.5 g. of chloral and boiling one and a quarter hours. On cooling there crystallized out long silvery-white needles, melting at 182°. The filtrate from these crystals was evaporated to a sirup which, on standing and scratching, was converted into a mass of fine, short, white needles melting at 108–10°. The first crop proved to be the addition product and the second crop the condensation product.

The second crop of crystals was purified by treatment with cold alcohol, in which the addition product was insoluble. The pure substance melts sharply at 110°. It is easily soluble in alcohol, benzene, toluene, ether and glacial acetic acid. Calculated for $C_{16}H_{15}N_2Cl_5$: Cl, 42.98. Found: Cl, 43.10.

Concentrated hydrochloric acid gave the hydrochloride of 3-chlor-4-toluidine, decomposing to a black liquid at 230–5°. Treatment of the condensation product with bromine in cold glacial acetic solution gave a bromine derivative, melting at 78–80°, which was proved not to be a hydrobromide. No such bromine derivative of 3-chlor-4-toluidine was found described in the literature.

The Addition Product. Chloral-3-chlor-4-toluidine, $CCl_3CHOH.NHC_6H_3ClCH_3$.—The first crop of crystals was well washed with cold alcohol to remove any of the condensation product that might be present. The melting point was raised to 182–3°. It is only slightly soluble in alcohol, easily soluble in ether, benzene, and glacial acetic acid. Calculated for $C_9H_9ONCl_4$: Cl, 49.10. Found: Cl, 49.42.

Trichlorethylidenedi-4-brom-2-nitrophenamine, $CCl_3CH(NHC_6H_3BrNO_2)_2$, was prepared by dissolving 5.0 g. of 4-brom-2-nitraniline, melting at 110°, in 100 cc. of toluene, adding 6.5 g. of chloral (which is a large excess) and boiling for six hours. On cooling, a crop of long, lemon-yellow needles crystallized out, melting at 232–3°, with decomposition. These crystals undoubtedly consisted of the addition product. The filtrate was evaporated to a sirup, which soon became a mass of smaller lemon-yellow needles. These melted at 190–1° and were pure, for recrystallization from toluene did not raise the melting point. The compound is soluble in alcohol, glacial acetic acid, benzene and toluene, fairly soluble in dilute alcohol, ether and carbon tetrachloride. Calculated for $C_{14}H_9O_4N_4Br_2Cl_3$: Cl, 18.71; Br, 28.41. Found: Cl, 18.60; Br, 28.13.

The condensation product is stable in boiling water but is resolved by hydrochloric acid into its constituents. Bromine yields a yellow crystalline compound, melting at 130–1° when recrystallized from glacial acetic acid. It was not identified.

Trichlorethylidenedi-4-brom-3-nitrophenamine, $CCl_3CH(NHC_6H_3BrNO_2)_2$, was prepared by dissolving 5.0 g. of 4-brom-3-nitraniline, melting at 129–30°, in 100 cc. of benzene, adding 1.55 g. of chloral and boiling for two hours. The solution was cooled and a small insoluble by-product was filtered off. The filtrate was evaporated to a sirup. On adding a little alcohol and stirring this became a mass of yellow needles, melting at 147–8°. Calculated for $C_{14}H_9O_4N_4Br_2Cl_3$: Cl, 18.71; Br, 28.41. Found: Cl, 18.55; Br, 28.04.

Its behavior with water and hydrochloric acid is similar to that of the previous compound. A cold glacial acetic acid solution, treated with an excess of bromine, gave a precipitate of yellow needles which melted at 88°. Purification raised the melting point to 101° showing it to be 2-4-6-tribrom-3-nitraniline.

Trichlorethylidenedi-4-iodophenamine, $CCl_3CH(NHC_6H_4I)_2$, was prepared by mixing 1.5 g. of *p*-iodaniline with 35 cc. of benzene and 0.6 g. of chloral and boiling for an hour. A small amount of a by-product remained insoluble. This was filtered off and the filtrate was evaporated to a sirup. On adding a little alcohol this became a mass of steel-gray branching needles, which melted at 123°. Calculated for $C_{14}H_{11}N_2Cl_3I_2$: Cl, 18.70; I, 44.74. Found: Cl, 18.49; I, 44.71.

It is soluble in alcohol, benzene, glacial acetic acid, less soluble in dilute alcohol and gasolene. Hydrochloric acid resolves it into its constituents and so does bromine. Bromine also yields a brominated iodaniline, melting at 83–9°.

Trichlorethylidenedi-4-brom-1-naphthylamine, $CCl_3CH(NHC_{10}H_6Br)_2.C_6H_5CH_3$, was prepared by heating a mixture of 2.5 g. of 4-brom-1-naphthylamine with sufficient chloral to dissolve it, for two hours on the steam bath with frequent stirring. It was then boiled a few minutes with 100 cc. of toluene. Addition of gasolene completed the precipitation of a purple amorphous substance. On being heated in a melting point tube this substance sublimed at 135–50°, leaving behind a charred mass. The product was soluble in alcohol, toluene and glacial acetic acid but insoluble in gasolene. Calculated for $C_{29}H_{23}N_2Cl_3Br_2$: Cl, 15.99; Br, 24.06. Found: Cl, 15.90; Br, 23.20.

This formula includes one molecule of toluene of crystallization. Its presence is indicated not only by the analysis but also by the change which the reaction product undergoes when treated with toluene. It increases in bulk and changes somewhat in color. We were unsuccessful in our attempts to determine the toluene of crystallization. The theoretical loss in weight for one molecule of toluene is 13.84 per cent. Heated at 100°, the substance began to decompose after a loss in weight of 7.83 per cent. The substance also decomposes on prolonged heating at 80°.

Trichlorethylidenedi-p-aminoacetophenone, $CCl_3CH(NHC_6H_4COCH_3)_2$, was prepared by triturating 2.0 g. of *p*-aminoacetophenone with 1.0 g. of chloral. The mixture was then boiled with 50 cc. of toluene. Solution took place and a yellowish white flocculent by-product in small amount settled out. This was filtered off and the filtrate was concentrated one-half. On cooling, a mass of colorless crystals came down. Recrystallized from dilute alcohol, these appeared under the microscope as thin rectangular plates, usually with the four corners uniformly rounded off. The pure substance melted at 162° to a red liquid. It is soluble in alcohol, benzene, and hot dilute alcohol. The last is the best crystallizing medium. Calculated for $C_{18}H_{17}O_2N_2Cl_3$: Cl, 26.63. Found: Cl, 26.36.

This condensation product reacts with hydrochloric acid in the usual way. The reaction with bromine was complicated. Some *p*-aminoacetophenone was isolated from the mixture of products.

Action of Chloral upon Trichloraniline.—Eibner states that trichloraniline (2,4,6) does not react with chloral. He heated them together for two hours in an open vessel. We tried three other experiments, heating (1) in toluene, (2) in xylene and (3) in a sealed tube, but found that in each case the trichloraniline was unaffected.

Action of Bromine on Other Condensation Products.

Trichlorethylidenediphenamine, $CCl_3CH(NHC_6H_5)_2$, was dissolved in cold glacial acetic acid and treated with 1 molecule of bromine. This gave aniline hydrobromide, decomposing about 282° after recrystallizing. Calculated for C_6H_8NBr: Br, 45.97. Found: Br, 45.85. Treatment with 2 molecules gave a precipitate of shining scales which decomposed at 228–30°. Calculated for $C_6H_6NBr.HBr$: Br, 63.24. Found: Br, 63.40. Decomposition with alkali gave *p*-bromaniline, melting at 63° and boiling with acetic anhydride, gave *p*-bromacetanilide, melting at 160–3°.

Trichlorethylidenedi-p-nitrophenamine, treated with a slight excess of bromine under the same conditions as above, gave an excellent yield of 2,6-dibrom-4-nitraniline, melting at 202°. Calculated for $C_6H_5O_2N_2Br_2$: Br, 54.05. Found: Br, 53.95.

Trichlorethylidenedi-p-tolamine gave with one molecule of bromine the hydrobromide of *p*-toluidine while two molecules gave a mixture of the hydrobromide of *p*-toluidine, hydrobromide of 3-brom-4-toluidine and the hydrobromide of 3,5-dibrom-4-toluidine.

Trichlorethylidenedi-o-tolamine gave chiefly the hydrobromide of 5-brom-2-toluidine, melting with decomposition at about 280°.

CHAPEL HILL, N. C.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 168.]

RESEARCHES ON QUINAZOLINES (TWENTY-SECOND PAPER). ON 2-METHYL-3-AMINO-4-QUINAZOLONE AND CERTAIN OF ITS DERIVATIVES.[1]

BY MARSTON TAYLOR BOGERT AND ROSS A. GORTNER.

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The N-amino quinazolones present an interesting case of unsymmetrical secondary hydrazine structure. The first one described in the literature seems to be the 6-nitro-3-amino-4-quinazolone which Kratz[2] obtained by the action of glacial formic acid upon 5-nitro-2-aminobenzhydrazide. From a foot-note at the close of Kratz's article, it appears that Finger endeavored to prepare the simple 3-amino-4-quinazolone from *o*-aminobenzhydrazide, but Finger himself does not mention it in his paper on *o*-aminobenzhydrazide,[3] and it was not until 1904 that this unsubstituted N-amino-4-quinazolone was prepared by Thode[4] from the *o*-aminobenzhydrazide and glacial formic acid. From the phenylhydrazide, Thode obtained the 3-anilino-4-quinazolone. In 1902, Anschütz, Schmidt and Greiffenberg[5] produced the 2-methyl-3-anilino-4-quinazolone by condensing acetanthranil with phenylhydrazine. From the corresponding nitro acetanthranils and hydrazine hydrate, Bogert and his co-workers prepared the 5-nitro-,[6] 6-nitro-[7] and the 7-nitro-2-methyl-3-amino-4-quinazolone,[8] and various derivatives thereof.

Very closely related to these N-amino-4-quinazolones are the 3-amino benzoylene urea of Kunckell,[9] Spiegelberg[10] and Lederer,[11] and the 1-methyl-3-amino benzoylene urea of Spiegelberg.[12]

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[1] Read at the meeting of the New York Section, March 5, 1909.

[2] *J. prakt. Chem.*, **53** [2], 224 (1896).

[3] *Ibid.*, **48**, 92 (1893).

[4] *Ibid.*, **69**, 100 (1904).

[5] *Ber.*, **35**, 3483 (1902).

[6] Bogert and Seil, THIS JOURNAL, **28**, 884 (1906).

[7] Bogert and Cook, *Ibid.*, **28**, 1449 (1906).

[8] Bogert and Klaber, *Ibid.*, **30**, 807 (1908).

[9] *Ber.*, **38**, 1212 (1905).

[10] *Inaug. Dissert.*, Rostock, 1905.

[11] *Inaug. Dissert.*, Rostock, 190 .

[12] *Loc. cit.*