0.0754 g. of the mixed hydrochlorides required 21.68 cc. of 0.1 *N* KBrO₃; and 0.2128 g. required 12.85 cc. 0.1 *N* AgNO₃. Found: aniline hydrochloride, 38.0; chloroaniline hydrochloride, 28.8; and bromoaniline hydrochloride, 33.2.

0.0318 g. of the mixed hydrochlorides required 9.24 cc. of 0.1 *N* KBrO₃, and 0.1276 g. of the same mixture required 7.85 cc. of 0.1 *N* AgNO₃. Found: aniline hydrochloride, 36.2; chloroaniline hydrochloride, 38.9; and bromoaniline hydrochloride, 24.9.

I wish to express my indebtedness to Professor Stieglitz, not only for the constant interest that he has shown in this investigation and the many helpful suggestions, but also for the encouragement and his kindness toward me personally.

CHICAGO, ILL.

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

THE MOLECULAR REARRANGEMENT OF TRIPHENYLMETHYLHALOGENAMINES.¹

BY ISABELLA VOSBURGH.²

Received August 1, 1916.

The characteristic Hofmann rearrangement³ of acid halogen amides, RCONH(Hal), to derivatives of amines RNH₂ forms the basis of the well-known general method of preparation of amines.⁴ The rearrangement⁵ is analogous in many important respects to the "Beckmann" rearrangement of oximes.⁶ When it was found in this laboratory by Stieglitz and Reddick⁷ that triphenylmethylhydroxylamine undergoes a rearrangement quite as smoothly as any oxime, Professor Stieglitz proposed to me that I undertake under his direction a parallel investigation on the possibility of effecting rearrangements of the triphenylmethylhalogenamines, Ar₃CNH(Hal). The investigation of these particularly simple halogen amine derivatives promised to shed light on a number of questions connected with the rearrangements: of those taken up in this in-

¹ See a preliminary report (abstract) by Stieglitz and Vosburgh, *8th Intern. Congr. Appl. Chem.*, **25**, 445 (1912); *Ber.*, **46**, 2151 (1913).

² The work reported on in this paper formed the basis of a dissertation submitted to the University of Chicago in part fulfillment of the requirements for the Ph.D. degree. Before Miss Vosburgh could come up for her final examinations, she was the victim of a fatal automobile accident, Dec. 4, 1914, near Mt. Holyoke, Mass. The present posthumous report, except for editing, is in the form in which it was written by Miss Vosburgh.—J. STIEGLITZ.

³ A. W. Hofmann, *Ber.*, **14**, 2725 (1882); **15**, 408 (1883), etc.

⁴ Hofmann, *loc. cit.*; Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893); Elizabeth Jeffreys, *Ber.*, **30**, 898 (1897); *Am. Chem. J.*, **22**, 14 (1899).

⁵ The analogy was pointed out by Hoogewerff and van Dorp, *loc. cit.*; and by Stieglitz, *Am. Chem. J.*, **18**, 751 (1896).

⁶ Beckmann, *Ber.*, **19**, 988 (1886), etc.

⁷ See Stieglitz, Reddick and Leech, *8th Intern. Congr. Appl. Chem.*, **25**, 444 (1912).

vestigation, we have, first, that it promised to lend itself to a further study of the extent to which Stieglitz's theory¹ of the related "Hofmann-Beckmann-Lossen²-Curtius³ rearrangements would hold in the new group of rearrangements, if such should indeed be found to occur. In the second place, it would contribute to a knowledge of the nature of the metal salts that are the active components in the Hofmann rearrangement of acid halogen amides, in which the question of the nature of the salts involved is complicated by the formation of tautomeric salts.

The results obtained have brought definite information concerning both of the questions outlined. The Stieglitz theory⁴ of these rearrangements ascribes the rearrangements to the intermediate formation of univalent nitrogen derivatives (*e. g.*, RCO.N from RCO.NH(Hal)) which are considered to be the real rearranging substances.⁵ The alkyl or aryl group R is subsequently torn from the carbon atom by virtue of the powerful unsaturated affinities of the univalent nitrogen atom. We have, for instance, $\text{RCO.N} \longrightarrow \text{CO} : \text{NR}$.

The reagents selected to effect the rearrangement of the various classes of compounds are just those which one would anticipate would be necessary to facilitate the formation of the univalent nitrogen derivative from the original material.

In agreement with these considerations we have found that triphenylmethylhalogenamines readily undergo the same kind of rearrangement under the influence of *bases*.

It is of interest to note how, once again, the relation of the reagent to the compound that is to be rearranged is shown and to compare this action with the rearrangement of triphenylmethylhydroxylamine under the influence of phosphorus pentachloride,⁶

It has been found, further, that triarylmethyldichloroamines, like the acid azides $\text{RCO.N(N}_2\text{)}$, require simply heat to undergo the rearrange-

¹ *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1901).

² *Ann.*, **161**, 359 (1872), etc.; L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

³ *Ber.*, **27**, 778 (1895); *J. prakt. Chem.*, **50**, 289 (1894), etc.

⁴ The theory is given in detail in *Am. Chem. J.*, **29**, 49 (1901), and only one or two of its most salient features need be considered here.

⁵ The theoretical possibility of a direct exchange of R for the halogen atom in certain cases is not excluded by the theory, which emphasizes simply that the path over the univalent nitrogen derivatives seems to be the easiest and the ordinary one and possibly in the majority of cases the only path. See Stieglitz and Leech, *Ber.*, **46**, 2147 (1913) and Stieglitz and Leech, *THIS JOURNAL*, **36**, 272 (1914).

⁶ Stieglitz, Reddick and Leech, *loc. cit.*

ment, chlorine being given off and the rearrangement taking place with explosive violence at 120–130°.

Again, we have found that alkylated triarylchloroamines, *e. g.*, $R_3CN(CH_3)Cl$, in which the formation of univalent nitrogen would be very greatly obstructed, or altogether prevented, do not undergo the rearrangement¹ when treated exactly in the same way as the halogen amines, $R_3CNH(Hal)$ or as the dihalogen amines, $R_3CNC l_2$.

All of these results, therefore, show that the above theory of the rearrangements is borne out by the behavior of triarylmethylhalogenamines, as thus far observed.

Closely related to these questions is the following: all attempts to effect a rearrangement of chloroimidobenzophenone, $(C_6H_5)_2C : NCl$, by the action of heat, or of alkalies, under various conditions have proved unsuccessful,² although this is the very compound which one should expect to be readily rearranged, if the rearrangements involve simply direct exchanges of radicals, as is assumed by Beckmann and some other prominent chemists:³

This is in interesting contrast to the ready rearrangement of the closely related triphenylmethylbromoamine, $(C_6H_5)_3CNHBr$, the essential difference between the two compounds being that the latter by the loss of hydrogen bromide can give a univalent nitrogen derivative, the former cannot; the chloroimide corresponds in that respect essentially to $(C_6H_5)_3CN(CH_3)Cl$, which also does not rearrange, as has been stated above. Now, the behavior of triphenylmethyldichloroamine, $(C_6H_5)_3CNC l_2$, in rearranging under the influence of heat suggested⁴ that the action of chlorine on the chloroimide might lead to the formation of an intermediate addition product which would correspond in structure to triphenylmethyldichloroamine and which might lose chlorine from the nitrogen and then rearrange.

¹ Stieglitz and Leech (*THIS JOURNAL*, 36, 272 (1914)) have recently made the important observation that the analogous $(C_6H_5)_3CN(CH_3)OH$ is rearranged to a methyl-aniline derivative.

² Unpublished work of Stieglitz and Parke H. Watkins.

³ Beckmann, *Ber.*, 19, 988 (1886); 27, 300 (1894); Hoogewerff and van Dorp, *Rec. trav. chim.*, 8, 173 (1889); Hantzsch, *Ber.*, 24, 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng. Kyoto*, 1, 254 (1903–1908); 2, 387 (1909–1910); 6, 1 (1913).

⁴ Stieglitz and Leech, *Ber.*, 46, 2147 (1913).

Under the conditions tried by us, namely, the action of chlorine at 120° to 150° , no rearrangement of this nature was, however, observed. Possibly at that high temperature no measurable absorption of chlorine by the $-\text{C} : \text{N}-$ group takes place.

Concerning the second question raised in connection with this investigation (see above), the relations, briefly are as follows: the rearrangement of acid halogen amides is effected by bases, (alkalies,¹ calcium oxide,¹ silver carbonate,¹ alkali alcoholates,² etc.) and there is no doubt that the active substances leading presumably primarily to the formation of acyl-imides, RCO.N , as just now discussed, are the metal salts of the acid halogen amides. Now, these salts may have either of two structures—they may be nitrogen salts, RCO.NMe(Hal) or oxygen salts, RC(OMe)N-Hal . The first structure was assumed for them by their discoverer, Hofmann,³ by Hoogewerff and van Dorp,³ Lengfeld and Stieglitz³ and others of the early workers in this field. The second structure was suggested for them by Hantzsch⁴ as the result of his study of acid chloro-amides as tautomeric compounds, and by Stieglitz, in some later work, on the basis of the formation of oxygen ethers by the methylation of the acylchloroamides with diazomethane.⁵ As a result of the investigations of Ley,⁶ Hantzsch,⁷ Baly, Marsden and Stewart,⁸ and Acree⁹ on tautomeric salts, it seems now reasonably certain that we have both salts present together in solution in a condition of equilibrium. It is, therefore, uncertain which form of salt, nitrogen salt,¹⁰ or oxygen salt, is directly involved in the rearrangement. In our present investigation the rearrangement of triarylmethylhalogenamines is also effected by bases and there is again no question as to the action being due to the formation of salts, which favor the subsequent reactions that lead to the rearrangements more than do the hydrogen derivatives. In the present instance, these salts can only have the structure $\text{R}_3\text{CNMe(Hal)}$, that is, they must be nitrogen salts. This result makes it quite probable that the active components in the rearrangement of the salts of acid halogen amides is also the nitrogen salt, RCO.NMe(Hal) , in spite of the fact that it is most likely present in considerably smaller proportions than the oxygen salt, the equilibrium favoring the oxygen salt, according to the work of Hantzsch.

¹ Hofmann, *loc. cit.*

² Lengfeld and Stieglitz, *loc. cit.*

³ *Loc. cit.*

⁴ *Ber.*, **35**, 228 (1902).

⁵ Stieglitz and Ransom, *Ber.*, **31**, 1055 (1898); *Am. Chem. J.*, **23**, 1 (1900).

⁶ *Ber.*, **32**, 1357 (1899); **38**, 973 (1905), etc.

⁷ Ley and Hantzsch, *Ber.*, **39**, 3149 (1906).

⁸ *J. Chem. Soc.*, **89**, 966 (1906).

⁹ *Am. Chem. J.*, **37**, 71 (1906), etc.

¹⁰ Schroede, *Ber.*, **42**, 2336 (1909) favored this view.

Experimental Part.

Triphenylmethylbromoamine, $(\text{C}_6\text{H}_5)_3\text{CNHBr}$.—The first halogen derivative of a triarylmethylamine prepared was triphenylmethylbromoamine. Hemilian and Silberstein¹ had previously studied the effect of halogens upon triphenylmethylamines and had concluded that compounds containing from two to seven atoms of the halogen resulted. They gave the formula $(\text{C}_6\text{H}_5)_3\text{CNH}_2\text{Br}_2$ to the bromine derivative. For the present investigation triphenylmethylchloride, obtained by the Friedel and Crafts² method, was converted into the amine hydrochloride by the Elbs method, with the modification that ammonia was passed repeatedly into the benzene solution of the chloride in order to obtain a satisfactory yield. The free base was obtained from the hydrochloride by precipitation by ammonium hydroxide in aqueous solution, and was brominated by treatment with bromine and aqueous sodium hydroxide,

The preparation is not an easy one and the observation of the following details will be found useful: Bromine (1.39 g.), weighed in a small bulb with capillary, was added to the dry amine (2.1 g.). The mixture, placed in an ice and salt preparation, was treated with a few drops of chloroform and a 10% solution of sodium hydroxide (3.25 cc.). The mixture was shaken for fifteen minutes, then more chloroform was added to it, and the two layers separated by means of a separatory funnel. The chloroform solution was dried a few minutes with calcium chloride and the chloroform then immediately evaporated in a blast of air. A yellow gum remained, part of which dissolved on the addition of ligroin (b. p. 70–80°). The evaporation of the ligroin in the cold gave a yellowish substance, which is likely to remain semi-solid. In one case, however, a few large crystals were obtained, and, thereafter, inoculation made the preparation of a crystalline product comparatively simple. By repeated recrystallizations from ligroin, a compound melting at 63° was obtained. The triphenylmethylbromoamine thus prepared, was analyzed by titration of the iodine liberated according to the equation

Subst., 0.0746; cc. 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$, 4.39.

Calc. for $\text{C}_{18}\text{H}_{15}\text{NBr}$: Br, 23.64%. Found: 23.57.

The structure of triphenylmethylbromoamine was confirmed as follows:³ Treatment of the bromoamine with dry hydrogen chloride gas in ether solution precipitated triphenylmethylamine hydrochloride. This was identified by its melting point (244°), and by its conversion into the

¹ *Ber.*, 17, 748 (1884).

² *Ibid.*, 33, 3147 (1900).

³ See Stieglitz and Earle, *Am. Chem. J.*, 30, 399, 412 (1903); Hilpert, *Ibid.*, 40, 155 (1908); Peterson, *Ibid.*, 46, 325 (1911).

free base, which melted at 102° , when heated by itself or mixed with synthetic triphenylmethylamine, we have:

The Rearrangement of Triphenylmethylbromoamine.—*1. By Treatment with Soda-lime.* Preliminary experiments showed that when the bromoamine is heated with soda-lime over a flame, a sudden action occurs with the evolution of brown fumes and the formation of a bright yellow substance. From this mass the yellow substance phenylimidobenzophenone may be extracted and identified by hydrolysis, the aniline formed being readily recognized by the chloride of lime test. Occasionally, however, this method gave negative results, probably because the mixture of bromoamine and soda-lime had not been heated sufficiently high.

The following method gives uniformly good results: Half a gram of the bromoamine is mixed with a gram of finely powdered soda-lime and the mixture is heated in a hard glass test tube by immersion in a metal-bath kept at 110 – 120° . As soon as the intense yellow product is formed, a small part of the mixture is tested by being boiled with an excess of hydrochloric acid, the resulting solution being neutralized and tested with calcium hypochlorite. If a strong aniline reaction is shown, the remainder of the mass is extracted with benzene. The evaporation of the solvent leaves crude phenylimido-benzophenone, melting at 89° . Recrystallized from absolute alcohol, it formed yellow crystals which softened a little at 106° but melted at 110° . A synthetic preparation,¹ obtained from aniline and benzophenonedichloride, gave a melting point of 111 – 112° . A mixture of this preparation with the product obtained by the rearrangement of the bromoamine melted at 111° . Their identity is thus established.

In confirmation of the structure of the rearrangement product, 0.32 g. of it was warmed with alcohol and dilute hydrochloric acid for half an hour, water was then added to the mixture and the precipitate which formed was collected and identified as benzophenone by its melting point, 46 – 48° , which was not changed by the addition of synthetic benzophenone to the product. The filtrate from the benzophenone yielded aniline hydrochloride, which was converted into the chloroplatinate for analysis.

Subst., 0.1247, Pt 0.0404. Calc. for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{PtCl}_6$: Pt, 32.78%. Found: 32.41.

The formation of phenylimidobenzophenone by the action of soda-lime on triphenylmethylbromoamine has thus been established beyond question

2. By Treatment with Calcium Oxide.—Some of the bromoamine (0.8 g.) was mixed with pulverized calcium oxide (0.8 g.) and the mixture gently heated in a hard glass test tube. The benzene extract was dried and evaporated *in vacuo*. Some of the yellow-brown substance obtained was

¹ Pauly, *Ann.*, 187, 198 (1877).

treated without further purification with hot dilute acid. The neutralized solution was tested with some calcium hypochlorite solution for aniline and the characteristic color reaction for aniline was shown intensely.

3. *By Treatment with Sodium Methylate.*¹—Owing to the reducing power of sodium alcoholates and the sensitiveness of bromoamines to reducing agents, the rearrangement of triphenylmethylbromoamine by this reagent was expected to be accompanied by a partial reduction of the compound to triphenylmethylamine. Such a reduction does take place to a certain extent, but no difficulty was encountered in showing that a large part of the substance is rearranged when it is treated with a methyl alcohol solution of sodium methylate.

Two grams of bromoamine were added to a hot solution of sodium methylate, prepared from 1 g. sodium and 40 g. of methyl alcohol. The bromoamine melted, forming an oil which soon went into solution. In fifteen minutes a little of the solution gave the test for aniline, when treated as described above. The whole solution was then cooled and diluted with twice its volume of water. A yellow oil was formed which, on standing overnight, gave yellow crystals of phenylimidobenzophenone and a little of a white powder (benzophenone). The solids were treated with hot dilute acid and a small amount of recovered triphenylmethylamine hydrochloride was removed by filtration. Alkali was added to the solution and the aniline was distilled over with steam. Benzoyl chloride was added to the distillate and a white substance resulted, which on recrystallization gave 0.7 g. of benzanilide, melting at 158–160°. A mixture of the substance with synthetic benzanilide gave the same melting point.

The rearrangement also takes place if the bromoamine is added to a cold sodium methylate solution, but it is necessary to heat the mixture on the water bath for one-half hour instead of fifteen minutes, and the yield of benzanilide is not as good.

Benzotriphenylmethanamide, $C_6H_5CO.NHC(C_6H_5)_3$.—In order to become familiar with the properties of the benzoyl derivative of triphenylmethylamine itself, which might have been met with in the preceding experiment, it seemed best to prepare the compound. For this purpose, the amine (3 g.) was dissolved in 30 cc. of absolute ether and treated with a gram of benzoyl chloride. The mixture was shaken and allowed to stand for forty-eight hours. Since the odor of benzoyl chloride was still perceptible, the mixture was heated in a water bath with reflux for fifteen minutes. The ether was then filtered off and the precipitate dried. Two substances could be discerned: the hydrochloride of the amine and the benzoylated amine. Hot water removed the hydrochloride. Yellow crystals remained, a further portion of which was obtained by evaporation

¹ Cf. Lengfeld and Stieglitz, *loc. cit.*

of the ether solution. Recrystallization of the product from alcohol gave white crystals melting at 160–162°.

Subst., 0.2619, cc. moist N, 23°, 752.7 mm.: 8.99. Calc. for $C_{26}H_{21}NO$: N, 3.86%. Found: 3.84.

Triphenylmethyldichloroamine, $(C_6H_5)_3CNCl_2$.—Hemilian and Silberstein¹ found that the passing of dry chlorine into a benzene solution of triphenylmethylamine gave ammonium chloride and triphenylmethylcarbinol. I obtained quite different results when the amine was treated with hypochlorous acid in an attempt to prepare the chloroamine corresponding to the bromoamine just described. It was found that a dichloroamine could readily be isolated. This compound apparently is more stable than the monochloroamine. Some monochloroamine is probably formed but it could not be isolated and identified despite many efforts to do so (see below). Berg² observed similar relations for chloroamines and dichloroamines of amines of the aliphatic series.

We have:

Hypochlorous acid was prepared according to Graebe's³ method: the chlorine obtained from 13 cc. of concentrated hydrochloric acid and potassium permanganate (2 g.) was passed into an ice-cold solution of anhydrous sodium carbonate (3 g.) in 40 cc. of water. To this cold hypochlorous acid solution was added a solution of triphenylmethylamine (1 g.) in 5 cc. of alcohol and 10 cc. of water. This mixture was shaken for ten minutes in the freezing bath. Chloroform was then added to dissolve the white cheesy substance which had separated out, the chloroform solution was drawn off and the solvent evaporated in a blast of air. The addition of a little ligroin to the residue, and the continued scratching of the substance in the cold gave a white substance melting at 128°. This was analyzed iodometrically.

Subst., 0.0397 g. Cl, 0.00825. Calc. for $C_{19}H_{15}NHCl$: Cl, 12.09%; $C_{19}H_{15}NCl_2$: Cl, 21.64%. Found: 20.79.

Various attempts were made to prepare the monochloroamine by the mixing of theoretical amounts of the dichloroamine and the free base. Analysis and melting point determinations lead to the conclusion that if the monoderivative is formed at all, it is unstable, reverting to the amine and the dichloroamine.

Rearrangements of Triphenylmethyldichloroamine.—*I. By Heat.* Triphenylmethyldichloroamine (0.2 g.) was heated in a hard glass test tube to 132° in a metal bath. There was a slight explosion, and the odors of chlorine and hydrogen chloride and a penetrating odor, similar to that

¹ *Ber.*, 17, 750 (1884).

² *Ann. chim. phys.*, [7] 3, 289 (1894).

³ *Ber.*, 35, 2754 (1902).

of isonitriles,¹ were detected. The contents of the tube were dissolved in alcohol, water and acid added and the solution heated on a water bath with reflux for one hour. A small amount of a dark brown oil separated. The solution was poured off from it, and the oil extracted with ether. On evaporation of the solvent the characteristic crystals of benzophenone were obtained, melting at 46° , alone, and when the crystals were mixed with synthetic benzophenone.

The acid solution was made alkaline, and again extracted with ether. Anhydrous oxalic acid was added to the dried extract and the oxalates of aniline and chloroaniline were precipitated. The mixture of oxalates was treated with cold water, the chloroaniline oxalate remaining undissolved. The oxalate solution when treated with alkali and chloride of lime solution gave a splendid aniline test. From the insoluble oxalate, treatment with alkali and ether gave *p*-chloroaniline melting, alone, at 67° , and at 69° when mixed with synthetic *p*-chloroaniline (m. p. 69°). With chloride of lime solution it produced a yellow color analogous to that obtained with *p*-chloroaniline. The formation of *p*-chloroaniline was evidently due to the chlorination of the phenyl group previous to, after, or during, its passage from the carbon to the nitrogen atom. The amount formed was very small.

2. *By Treatment with Soda-lime.*—The dichloride (0.2 g.) was intimately mixed with dry soda-lime (3 g.) and the mixture heated in a metal bath. At 132° a white smoke was given off, in which the odor of chlorine could be discerned. The benzene extraction of the residue was brown and on evaporation gave yellow-brown crystals. Recrystallization from hot absolute alcohol gave yellow crystals of phenylimidobenzophenone, melting at 109° alone, or at 110° , when mixed with the synthetic product. The soda-lime prevented any appreciable chlorination of a phenyl group, and no chloroaniline was obtained.

Triphenylmethylchloromethylamine, $(\text{C}_6\text{H}_5)_3\text{CNCl}(\text{CH}_3)$.—Triphenylmethylchloromethylamine was the next object of investigation with the view of determining whether the introduction of an alkyl radical into the amine group would prevent the rearrangement of a chloro- or bromoamine by interfering with the formation of a univalent nitrogen derivative.

Considerable difficulty was experienced in preparing methyltriphenylmethylamine from which the chloroamine has to be made. It was first made according to the method of Hemilian and Silberstein² by passing dry methylamine gas into a hot benzene solution of triphenylmethylchloride or bromide. The methylamine salt was removed by filtration and

¹ It will be recalled that a similar odor of isonitrile is observed when phenylhydroxylamine is heated. (Bamberger, *Ber.*, 32, 62; 33, 3605.) In both of these cases the odor may be due to a free univalent nitrogen derivative $\text{C}_6\text{H}_5\text{N:}$ and $(\text{C}_6\text{H}_5)_3\text{CN}$.

² *Ber.*, 17, 745 (1884).

the filtrate evaporated to dryness. Recrystallization of the residue from alcohol gave a small yield of the amine and some ethoxytriphenylmethane $(C_6H_5)_3COC_2H_5$. With other solvents the yield was better but at no time was it very good. It was decided to try the preparation with sodium methylate and methylamine hydrochloride, following the method used successfully by Mothmer¹ and by Stieglitz and Leech² in the preparation of triphenylmethylhydroxylamine. Methylamine hydrochloride (2.9 g.) was added to a concentrated solution of sodium methylate obtained from sodium (1 g.) and methyl alcohol (9 g.). After the precipitation of sodium chloride, triphenylmethylchloride (4.6 g.) dissolved in benzene was added and the mixture shaken for one-half hour. The precipitated methylamine hydrochloride was recovered by filtration and the filtrate taken to dryness in a vacuum desiccator. This must be done slowly and with only a slight reduction of pressure, as the solution shows a great tendency to spatter. The residue was treated with dry ether and dry hydrogen chloride gas. A fine powder, triphenylmethylmethylamine-hydrochloride, $(C_6H_5)_3CN(CH_3)H_2Cl$ (m. p. 216°), was obtained. It was converted into the free base with potassium hydroxide solution and the base extracted with ether. Evaporation of the solvent gave a substance which on recrystallization from ligroin melted at 73° .³

For the conversion of the amine into the chloroamine, the hydrochloride (2 g.) was dissolved in 10 cc. of 50% alcohol and the solution poured into a hypochlorous acid solution made from 4 g. of chlorine and 6 g. of anhydrous sodium carbonate, to which had been added 2 g. of potassium carbonate. The cheesy substance formed was dissolved in chloroform, the solution was separated and brought to dryness in a desiccator. The residue was slightly yellow, but was not recrystallized. It melted at $102-104^\circ$.

Subst., 0.2777, Cl 0.03136. Calc. for $C_{20}H_{18}NCl$: Cl, 11.52%. Found: 11.30.

When hydrogen chloride gas was passed into an ether solution of the chloroamine, chlorine was given off and triphenylmethylmethylamine-hydrochloride was precipitated quantitatively. This proves the structure of the compound to be $(C_6H_5)_3CNCl(CH_3)$.

Attempts to Rearrange Methyltriphenylmethylchloroamine.—1. *By Heat.* Some of the chloroamine (0.4 g.) was placed in a hard glass test tube and heated in a metal bath. The substance melted at 102° ; the temperature was raised to $130-135^\circ$ and maintained there for four minutes. On cooling, the slightly colored gum hardened; it was dissolved in ligroin and the original white substance melting at $102-104^\circ$ was obtained in practically a quantitative yield. There were no signs of chemical action.

¹ *Ber.*, 37, 3152 (1904).

² *THIS JOURNAL*, 36, 272 (1914).

³ Hemilian and Silberstein, *loc. cit.*, give the melting point as 73° .

2. *By Treatment with Soda-lime.*—Some of the methyltriphenylmethylchloroamine (0.6 g.) was mixed with powdered soda-lime (0.6 g.). The mixture was placed in a hard glass test tube and heated at 140° for five minutes. The only visible sign of reaction was the darkening of the soda-lime. When cool, water was added to the mixture, a part of the extract was made neutral and tested with calcium hypochlorite solution. No trace either of the purple test for aniline or of the blue color due to methylaniline¹ was observed. Nor was there any color reaction when the rest of the aqueous extract was boiled with acid, the solution made neutral and then tested as above.

The residue left by the water was boiled with dilute hydrochloric acid; a brown substance resulted which was contaminated with calcium oxide and melted at 184–190°. It was purified by treatment with potassium hydroxide solution, and extraction with ether. Hydrogen chloride gas was run into the ether extract, and a substance resulted, which melted at 216° when heated by itself or when mixed with methyltriphenylmethylamine hydrochloride. This shows that the chloroamine was converted back into the amine either by the action of the soda-lime

or by the subsequent action of hydrochloric acid,

No product of a rearrangement could, therefore, be detected.

3. *With Calcium Oxide.*—The methylchloroamine (0.5 g.) was mixed with powdered calcium oxide (0.6 g.) and treated as with soda-lime, save that the temperature was maintained at 130–140° for forty-five minutes. The tests with chloride of lime solution were made as previously and failed to show the slightest trace either of aniline or methylaniline. From the residue, methyltriphenylmethylamine was recovered as before. Therefore, no traces of any molecular rearrangement could be observed.

4. *By Destructive Distillation.*—Some of the methylchloroamine (0.6 g.) was placed in a small retort and heated in a metal bath. The end of the tube extended into acidulated water. At 180° the melted substance began to fume, and as the temperature was raised to 250° a gas was given off which smelled like hydrogen chloride. A part of the water solution was made neutral and tested with hypochlorite solution, but no indications of the presence even of traces of aniline or methylaniline were observed. The rest of the solution was evaporated, and no residue remained, which proved that the distillate contained no hydrochloride of aniline, methylaniline or methylamine.

The residue in the retort was heated with acid and part of it tested in slightly alkaline solution with chloride of lime solution. There were

¹ P. N. Leech, *THIS JOURNAL*, 35, 1042 (1913).

no color reactions. The remainder of the acid solution was treated with alkali and extracted with ether. The ether solution was saturated with hydrogen chloride gas, but there was no precipitate. It is evident that the compound was destroyed by heat, but there were no evidences of a molecular rearrangement leading to the formation of an aniline or methylaniline derivative.

***p*-Chlorophenyldiphenylmethylamine**, $(p\text{-ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2$.—The behavior of chlorophenyldiphenylmethylchloroamine was next investigated as a first step toward studying the influence of substitution groups in the phenyl groups in determining which of the aryl groups would pass from the carbon to the nitrogen in this rearrangement.

For the preparation of *p*-chlorophenyldiphenylmethylamine, which is not described in the literature, the corresponding chloride was first prepared according to the method of Gomberg¹ from benzophenonedichloride, chlorobenzene, and aluminium chloride. It was recrystallized from ligroin and melted at 86–89°.

Some of the substance (5.0 g.) was dissolved in hot benzene and dry ammonia gas was run into the solution. The addition of a little absolute alcohol aided the precipitation of ammonium chloride. After the treatment with ammonia gas had been continued for at least one-half hour, the solution was filtered and heated slightly to remove excess of ammonia gas; then dry hydrogen chloride gas was run into it. Part of the amine hydrochloride was precipitated, and the rest was obtained by evaporation of the benzene solution. A better yield resulted when the benzene solution saturated with ammonia gas was filtered to remove the ammonium chloride, the filtrate taken to dryness, the residue extracted with ether and the solution saturated with hydrogen chloride gas. The *p*-chlorophenyldiphenylmethylamine hydrochloride was precipitated, in part, and recovered in part by evaporation of the ether solution.

Some of the hydrochloride was treated with alkali to liberate the base; the ether extract of the latter gave a gum, which all attempts failed to convert into a crystallized solid. An analysis was, therefore, made of the hydrochloride, which was purified by conversion into the free base, the oxalate, the free base again and finally the hydrochloride. The latter melted at 185–186°. It was used for the preparation of the chloroplatinate; the latter was found to contain one molecule of water of crystallization and to melt at 155°.

Subst., 0.1587 g., heated three times, for five minutes each to 100–120° gave a constant weight of 0.1555 g. Calc. for 1 molecule H_2O : H_2O , 1.77%. Found: 2.01. (Anhydrous) 0.1528: Pt, 0.0296. Calc. for $\text{C}_{18}\text{H}_{14}\text{N}_2\text{Cl}_2\text{Pt}$: Pt, 19.57%. Found:

19.37.

***p*-Chlorophenyl-diphenylmethylidichloroamine**, $(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNCl}_2$.—One gram of the amine hydrochloride was added to a mixture of two

¹ *Ber.*, 39, 3278 (1906).

grams of potassium carbonate and of hypochlorous acid, prepared from 8 g. of anhydrous sodium carbonate dissolved in 150 cc. of water and treated with 5 g. of chlorine. The solution became milky as the hydrochloride dissolved. After the mixture had been shaken ten minutes in the freezing bath, chloroform was added to it to dissolve the semisolid mass. The evaporation of the chloroform left a gum, part of which dissolved in ligroin (b. p. 40–60°). The extract was placed in a stoppered tube and left in the icebox for three days. A white crystalline substance melting at 110–112° resulted. This was used for seeding subsequent preparations, and also for analysis.

Subst. 0.1321, active¹ chlorine 0.02578. Calc. for $C_{19}H_{14}Cl.NHCl$: Cl, 10.84%; $C_{19}H_{14}Cl.NCl_2$: Cl, 19.56%. Found: Cl, 19.51.

Rearrangement of *p*-Chlorophenyl-diphenylmethyldichloroamine.—

1. *By Heat.* A little of the substance was heated to 150°, at which temperature there was a sudden evolution of yellow smoke. When the resulting product was tested in the usual way, after it had been heated with acid, the characteristic aniline test was observed. No further test was made of this product.

2. *By Soda-lime.*—The main experiments were performed with soda-lime in order to prevent the formation of any chloroaniline by chlorination. The reaction was carried out in the same way as described for triphenylmethyldichloroamine. The mixture was heated to 150°, the benzene extract saturated with hydrogen chloride and taken to dryness. It was then heated with alcohol and dilute hydrochloric acid for ten minutes, and shaken with ether to remove the benzophenone and chlorobenzophenone formed by the hydrolysis of the imido ketones. Potassium hydroxide solution was added to the water solution and the alkaline mixture extracted with ether. Anhydrous oxalic acid was added to the dried ether solution and the oxalates of aniline and chloroaniline obtained as a white precipitate. This was dissolved in the least amount of hot water and the solution then cooled to 40°. The precipitate of *p*-chloroaniline oxalate, which formed, was decomposed by alkali and chloroaniline extracted with ether. *p*-Chloroaniline resulted, melting at 67° alone and at 69° when mixed with the pure product (m. p. 69°). It gave a yellow-red-brown color with hypochlorite in the same way as pure *p*-chloroaniline does.

The dissolved aniline oxalate gave the characteristic aniline color reaction with hypochlorite.

Determination of the Proportion of Aniline and Chloroaniline Formed.²

—Two experiments were performed to determine the proportion of phenyl-

¹ Only two of the three chlorine atoms are determined, they being active toward the iodide which was used in the analysis.

² The method of analysis used was worked out by Stieglitz and Leech, *loc. cit.*, for the study of the rearrangement of the corresponding chlorophenyl-diphenylmethylhydroxylamine.

imidochlorobenzophenone and chlorophenylimidobenzophenone formed by the migration of the (C_6H_5) and (ClC_6H_4) radicals, respectively, from carbon to nitrogen in the molecular rearrangement of the chloroamine as induced by soda-lime. The reaction and subsequent treatment were carried out as described above, save that the two anilines were precipitated as hydrochlorides instead of as oxalates, the precautions given by Leech being observed. From 0.5 g. of the dichloroamine, 0.1 g. of mixed dry hydrochlorides was obtained. The proportion of aniline and chloroaniline was found by Curme's bromination method.¹

Subst., 0.0689, 0.0528; cc. 0.1 N $KBrO_3$ 27.30, 20.97. Found: Aniline, 74.2, 76.6 molar per cent., chloroaniline 25.8, 25.4.

An Attempt to Effect the Rearrangement of Benzophenonechloroimide, $(C_6H_5)_2C : NCl$.²—It was hoped that chlorine might be absorbed by benzophenonechloroimide to form a substance, $(C_6H_5)_3CCl.NCl_2$, similar in structure to $(C_6H_5)_3CNCl_2$, which might rearrange at a high temperature, and produce benzchloroanilide, $C_6H_5CCl : NC_6H_5$, by a series of reactions discussed in the theoretical part of the paper. The chloroimide was prepared in the way described by P. P. Peterson³ and melted at 37° .

Five attempts were made to rearrange this product but all were unsuccessful. For the sake of future workers in this field, the experiments will be described briefly to indicate the path followed. After each attempt the substance was tested in the following ways: (a) It was boiled with acid, the solution was made neutral and hypochlorite solution was added. A color reaction would have indicated the presence of aniline or chloroaniline.

(b) The substance was heated with soda-lime and then boiled with acid. The mixture was made neutral and tested with hypochlorite solution as above. The treatment with soda-lime was applied because benzochloroanilide on hydrolysis would give benzanilide which does not show the aniline test until it has been decomposed by soda-lime.

1. Dry chlorine gas was passed for one-half hour over the chloroimide (0.5 g.) maintained at a temperature of 130 – 140° in a metal bath. When cooled, the product was the unchanged compound melting at 37° . It gave no test for the anilines.

2. The second and third experiments were similar and were as follows: The chloroimide (0.5g.) was placed in a small tube and dry chlorine gas was run into the tube for fifteen minutes. The substance became yellow, and melted slightly. The tube was sealed, and heated for two hours in a furnace at 150° . When cool, some of the substance was removed and treated as described above. It gave no test for the anilines.

¹ THIS JOURNAL, 35, 1143 (1913).

² See p. 2083.

³ Stieglitz and Peterson, *Ber.*, 43, 782 (1910); Peterson, *Am. Chem. J.*, 46, 325 (1911).

3. Chloroimide (0.5 g.) was dissolved in ether and phosphorus pentachloride (0.5 g.) was added to the mixture. This was heated with reflux for two hours. The precipitate was filtered off, and proved to be the imido-hydrochloride, $(C_6H_5)_2C = NH_2Cl$. When tested, no color reactions were observed.

4. The fifth attempt to effect the rearrangement of benzophenone-chloroimide was similar to the second and third attempts, except that the closed tube was heated to 230° for two hours. The substance was colored owing to decomposition, but no trace of aniline or chloroaniline could be observed.

Although this work was negative in regard to the formation of benzo-chloroanilide by rearrangement, the results are of interest, in that they emphasize the remarkable difference in behavior of $(C_6H_5)_3CNHCl$ and $(C_6H_5)_2C : NCl$ and that they bring additional evidence against the theory by some chemists that $R_2C = NCl$ is an intermediate product in the rearrangement of $R_2C = NOH$ to $R.CCl(:NR)$ by means of phosphorus pentachloride.

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

THE MOLECULAR REARRANGEMENT OF SOME TRIARYLMETHYLCHLOROAMINES.¹

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Three series of triphenylmethane derivatives have been found, in this laboratory, to undergo molecular rearrangements akin to each other and quite analogous to the Lossen-Curtius-Hofmann-Beckmann rearrangements of acid and ketone derivatives.² Triphenylmethylhydroxylamines rearrange under the influence of phosphorus pentachloride,³ triphenylmethylchloroamines rearrange under the influence of alkaline reagents,⁴ and, according to recent work, triphenylmethyl azides also undergo rearrangement under the influence of heat.⁵ In all three series the same products of rearrangement are obtained, a result which we may most easily interpret on the basis of Stieglitz's theory of the intermediate formation

¹ The work presented in this paper is used in a dissertation presented to the University of Chicago in part fulfillment of the requirements for the Ph.D. degree.

² See the literature references in an article by Stieglitz and Leech, *THIS JOURNAL*, 36, 272 (1914).

³ Stieglitz, Reddick and Leech, *8th Intern. Congr. Appl. Chem.*, 25, 443 (1912); Stieglitz and Leech, *Ber.*, 46, 2147 (1913); *THIS JOURNAL*, *loc. cit.*

⁴ Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913), and unpublished work of Isabella Vosburgh, 1913.

⁵ Unpublished work by J. K. Senior, 1913-1914.