

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  $230^\circ$  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 benzochloroanilide 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.

CHICAGO, ILL.

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

## THE MOLECULAR REARRANGEMENT OF SOME TRIARYLMETHYLCHLOROAMINES.<sup>1</sup>

BY AGNES FAY MORGAN.

Received August 1, 1916.

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.<sup>2</sup> Triphenylmethylhydroxylamines rearrange under the influence of phosphorus pentachloride,<sup>3</sup> triphenylmethylchloroamines rearrange under the influence of alkaline reagents,<sup>4</sup> and, according to recent work, triphenylmethyl azides also undergo rearrangement under the influence of heat.<sup>5</sup> 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

<sup>1</sup> 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.

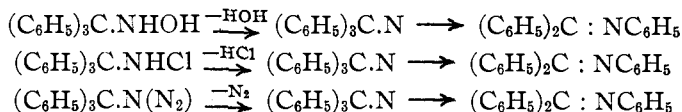
<sup>2</sup> See the literature references in an article by Stieglitz and Leech, *THIS JOURNAL*, 36, 272 (1914).

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

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 Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913), and unpublished work of Isabella Vosburgh, 1913.

<sup>5</sup> Unpublished work by J. K. Senior, 1913-1914.

of a univalent nitrogen derivative. In the first series, this product is formed by the loss of water through the action of phosphorus pentachloride, in the second one through the loss of halogen acid by the action of the alkali used, and in the final series through the loss of nitrogen under the influence of heat. We have, thus:



When substituted triphenylmethane derivatives, such as  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHCl}$ , are employed, mixtures are obtained, containing some  $(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_4\text{X}$  and some  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_5$ . It seemed an interesting question to determine in each of the series the ratios in which these products are formed, since such determinations might throw light on the mechanism of the rearrangements, especially on the question whether the same intermediate product  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$ , yielding the same proportions of the above two derivatives, may be considered to be the real rearranging substance in all three cases. For this purpose it was necessary to follow, quantitatively, the rearrangement in a number of cases in which X is varied. For the chloroamines, Miss Vosburgh examined the monochlorine derivative. In continuation of her work, I have, at the suggestion and under the direction of Professor Stieglitz, studied the behavior of two further derivatives of this series, dichlorophenylphenylmethylchloroamine and chlorophenylbromophenylphenylmethylchloroamine. Mr. Stagner has determined the ratios of the products formed for the corresponding hydroxylamine derivatives.<sup>1</sup>

#### Experimental Part.

**Di-*p*-chlorophenyl-phenylmethylaminehydrochloride**,  $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{Cl}$ .—For the preparation of di-*p*-chlorophenyl-phenylmethylchloroamine it was necessary to obtain the amine itself from the corresponding triaryl methylchloride. For this purpose di-*p*-chlorobenzophenone was first prepared through the condensation of carbon tetrachloride and chlorobenzene with the aid of aluminium chloride at ordinary temperature, the reaction described by Norris and Twiege<sup>2</sup> being followed. The mixture of dichlorobenzophenones was recrystallized from hot dilute alcohol, and then from warm ligroin (40 to 60°). Di-*p*-chlorobenzophenone was obtained as a glistening flaky crystalline substance which melted at 144°. The ortho-ortho and ortho-para forms of the dichlorobenzophenone are very much more soluble in alcohol and in ligroin than the para-para compound, and the separation is thus made almost quantitatively.

<sup>1</sup> The results obtained in the different groups of triphenylmethyl derivatives will be compared with one another by Professor Stieglitz.

<sup>2</sup> *Am. Chem. J.*, 30, 392 (1903).

The di-*p*-chlorobenzophenone thus obtained was next converted into di-*p*-chlorophenylphenyl carbinol by the method of Gomberg and Cone<sup>1</sup> by means of the Grignard reaction. The resulting yellow gum crystallized at once from cold ligroin (40 to 60°). On recrystallization several times from ligroin a product melting at 87° was obtained.<sup>2</sup>

From the carbinol the *p,p'*-dichlorophenylphenylmethylchloride was prepared in carbon disulfide solution by saturation with anhydrous hydrogen chloride. The chloride made in this way remained as a yellowish semisolid gum when the carbon disulfide was removed.<sup>3</sup> It was, however, quite pure, as shown by the hydrolysis of a weighed portion in alcohol with an excess of 0.1 *N* alkali and titration of the excess with 0.1 *N* hydrochloric acid.

Subst. 0.5035 g.; cc. of 0.1 *N* KOH, 14.39. Calc. for (C<sub>13</sub>H<sub>13</sub>Cl<sub>2</sub>)Cl: 10.20% hydrolyzable Cl. Found: 10.13%.

The chloride was converted into the amine by means of ammonia. The chloride (2 g.) was dissolved in hot benzene, and dry ammonia gas from a liquid ammonia tank passed into the solution, for at least half an hour. After the first twenty minutes a small quantity of absolute ethyl alcohol was added through the reflux condenser, to aid in the precipitation of ammonium chloride. The precipitated salt was at once filtered off and the clear benzene solution of the dichlorophenylphenylmethylamine evaporated on an electric plate. The gum remaining was dissolved in absolute ether and the solution saturated with dry hydrogen chloride. Most of the amine hydrochloride was at once precipitated, and the rest recovered by evaporation of the solution to dryness, the residue being washed with a little absolute ether. By this method 75% of the theoretical yield of the hydrochloride was obtained. The substance was purified by solution in chloroform and fractional precipitation with low-boiling ligroin. The purest product melted at 201°. For the analysis a weighed portion of the hydrochloride was dissolved in alcohol, an excess of 0.01 *N* NaOH was added, and the excess titrated with 0.01 *N* HCl, phenolphthalein being used as the indicator.<sup>4</sup>

Subst. 0.0381 g.; cc. of 0.01 *N* NaOH, 10.18. Calc. for (C<sub>13</sub>H<sub>13</sub>Cl<sub>2</sub>N)HCl: HCl, 10.00%. Found: 9.74%.

***p*-Dichlorophenyl-phenylmethylchloroamine, (ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>)CNHCl.**—The dichlorophenyl-phenylmethylchloroamine was prepared from the amine hydrochloride by treatment with sodium hypochlorite. The

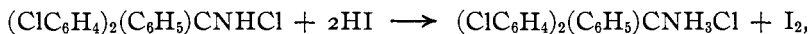
<sup>1</sup> *Ber.*, **39**, 3280 (1906); cf. Stagner, *THIS JOURNAL*, **38**, 2069 (1916).

<sup>2</sup> Gomberg and Cone found the same melting point for the purest dichlorophenylphenyl carbinol made by them.

<sup>3</sup> Stagner, *loc. cit.*, obtained the chloride in crystallized form by allowing the gum to stand a month.

<sup>4</sup> For this analysis special carbondioxide-free reagents and special apparatus were used, prepared by S. D. Wilson for measurements of velocities of saponification.

hypochlorite solution was prepared by Graebe's method by passing chlorine (from 5 g. of potassium permanganate and 40 cc. of concentrated hydrochloric acid) into an ice-cold solution of sodium carbonate (8 g.). The dichlorophenylphenylmethylamine hydrochloride (1 g.), dissolved in 2 or 3 cc. of chloroform, and potassium carbonate (2 g.) were added to the hypochlorite solution, and the mixture stirred with a Schultze stirrer at  $-2^{\circ}$  for ten minutes. The chloroform solution of the chloroamine was then separated from the aqueous mixture by means of a separating funnel, and dried with a little granular calcium chloride. The solvent was then removed in a blast of dry air, and the gum remaining extracted with low-boiling ligroin. Most of the ligroin was driven off by air also and the last traces removed by prolonged drying in a vacuum desiccator. The chloroamine formed at first a thick, viscous yellow gum which dried to a hard, varnish-like substance that could be pulverized. The solid melted at  $55^{\circ}$ . A weighed portion of the substance was dissolved in a little alcohol, small quantities of acetic acid and of a 5% solution of potassium iodide were added, and the iodine, released according to the equation



was titrated with 0.1 *N* thiosulfate solution. No starch was used, the yellow color of the iodine giving a perfectly satisfactory end point.

Subst. 0.2032 g.; 0.0649; cc. of 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_3$ , 11.02, 3.39. Calc. for  $(\text{C}_{13}\text{H}_{13}\text{Cl})\text{-NHCl}$ : active Cl, 9.78%. Found: 9.61, 9.26.

It was evident from the analysis that the monochloroamine was formed in this case. With chlorophenyldiphenylmethylamine, Miss Vosburgh<sup>1</sup> found that the formation of the dichloroamine was favored, and the monochloroamine could not be obtained by her.

**Rearrangement of *p,p'*-Dichlorophenyl-phenylmethylchloroamine.**—In order to effect the rearrangement of the chloroamine, soda lime (2 g.) was heated with the chloroamine (1 g.) for five minutes in a metal bath at 160 to 180°. As the chloroamine was obtained chiefly as a sticky solid gum, the mixture with soda lime was best prepared by allowing the ligroin solution of the gum to evaporate to dryness, after it had been mixed with soda lime in an Erlenmeyer flask. The mixture when heated turned yellow, the color of the phenylimidobenzophenones. The mass was extracted with several portions of benzene and the benzene solution filtered and evaporated to dryness. The resulting gum, consisting of a mixture of phenylimido-*p*-dichlorobenzophenone and *p*-chlorophenylimido-*p*-chlorobenzophenone, was hydrolyzed at once by solution in a little alcohol, and by being heated with a small amount of dilute hydrochloric acid for fifteen minutes. After evaporation of the alcohol, the ketones were extracted with ether and the aqueous solution examined for the hydrochlorides of aniline and *p*-chloroaniline.

<sup>1</sup> Isabella Vosburgh, *THIS JOURNAL*, 38, 2081 (1916).

**Identification of *p*-Chlorobenzophenone and *p,p'*-Dichlorobenzophenone.**—The ether extract of the hydrolyzed mixture described above was spontaneously evaporated, and the resulting flaky crystals recrystallized from alcohol. Enough alcohol was added to dissolve about three-fourths of the entire mass, the residue was collected and dissolved in a small amount of hot alcohol. The few crystals precipitated on cooling, were collected on a Hirsch filter and dried *in vacuo*. The melting point of this substance was 141°. *p,p'*-Dichlorobenzophenone melts at 144°, and a mixture of the product obtained with some synthetic substance melted at 141°, which proved the identity of the isolated ketone. The alcoholic filtrate was allowed to evaporate spontaneously, the residue taken up with a few drops of alcohol, the solution decanted through a cotton filter, the filtrate evaporated almost to dryness, and the remaining few drops of solution decanted from a small crystalline residue. When dried, this melted at 77 to 78°; *p'*-chlorobenzophenone, according to different authors, melts at 74 to 78°, and a mixture of some synthetic substance (m. p. 74°) with the product isolated as described, melted at 74°.

**Identification of Aniline and *p*-Chloroaniline.**—The aqueous solution recovered from the hydrolysis of the rearranged product was placed in a separatory funnel, strong sodium hydroxide solution and solid sodium chloride added to it, and the liberated aniline and *p*-chloroaniline extracted with two portions of ether. An ether solution of hydrogen chloride was used to form aniline hydrochloride and *p*-chloroaniline hydrochloride. As the hydrochlorides are somewhat soluble in ether containing hydrogen chloride, most of the ether was driven off on the electric oven, and the hydrochlorides finally dried over solid potassium hydroxide *in vacuo*. Part of the dry salts was dissolved in water and on the addition of a few drops of concentrated ammonium hydroxide, *p*-chloroaniline separated out in white crystals. The difference in solubility in water of aniline and *p*-chloroaniline was great enough to secure an almost perfect separation. The *p*-chloroaniline thus obtained melted at 69.5° and mixed with pure synthetic *p*-chloroaniline (m. p. 70.5°) melted at 70.5°. The filtrate gave a strongly positive test for aniline when tested with bleaching powder solution in the usual way.

**Proportion of Aniline to *p*-Chloroaniline.**—From two grams of the rearranged substance 0.6 g. of the mixed aniline hydrochloride and *p*-chloroaniline hydrochloride was obtained as described above. A weighed portion was analyzed by the bromination method of Curme<sup>1</sup> for the determination of the proportion of aniline and chloroaniline present.

The calculation is made with the aid of the simultaneous equations  $0.1295x + 0.164y = a$  and  $60x + 40y = b$ , when  $x$  and  $y$  represent, respectively, the millimols of aniline hydrochloride and *p*-chloroaniline hydrochloride present,  $a$  the weight of the mixture of salts used, and  $b$  the number of cubic centimeters of 0.1 *N*  $\text{KBrO}_3$  used.

<sup>1</sup> THIS JOURNAL, 35, 1143 (1913).

Subst. 0.0382, 0.0556, 0.242; cc. of 0.1 *N* KBrO<sub>3</sub>, 11.54, 16.88, 7.41. Found, in molar %: C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>Cl, 31.4, 32.1, 33.2; ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>Cl, 68.6, 67.9, 66.8.

***p*-Chlorophenyl-*p*-bromophenyl-phenylmethylamine Hydrochloride**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)NH<sub>2</sub>Cl.—For the preparation of this compound a start was made from *p*-chlorobenzophenone, obtained from chlorobenzene and benzoyl chloride with the aid of aluminium chloride: the ketone first obtained was semisolid and was distilled at 220° at 35 mm. pressure, and recrystallized from hot alcohol. The ketone then melted at 74°. The yield was 80% of the theoretical amount. This *p*-chlorobenzophenone was converted into the ketone dichloride,<sup>1</sup> which was purified by distillation under reduced pressure, as directed by Overton.<sup>2</sup> The fraction of the oil used distilled at 190° at 10–12 mm. pressure and gave, by hydrolysis, 26.02% HCl (theory 26.12%). The yield of purified dichloride was 90% of the theoretical.

The dichloride was converted into *p*-chlorophenyl-*p*-bromophenyl-phenylcarbinol in the way described by Stagner.<sup>3</sup> The carbinol was found to be more difficult to crystallize than the corresponding dichloroderivative and recourse was had to the method described by Gomberg and Cone<sup>3</sup> for the crystallization of the latter compound. Anhydrous ferric chloride in ethyl acetate solution in molecular proportions was added to an ethyl acetate solution of the carbinol. The resulting ferric salt crystallized out in glistening greenish scales which yielded a yellowish oil on hydrolysis. This oil was easily converted into crystals by solution in warm ligroin (70 to 80°); after purification by recrystallization the compound melted at 92°. The chloride was obtained from this carbinol by saturation of a dry carbon disulfide solution of the latter with hydrogen chloride. Without further purification, this *p*-chlorophenyl-*p*-bromophenyl-phenylmethyl chloride was treated with ammonia in benzene solution as described for the dichloro compound and from the product the amine hydrochloride was precipitated from its solution in ether. The hydrochloride was purified by precipitation by ligroin out of chloroform solution, and was found to melt at 196°.

Subst. 0.1019; cc. of 0.01 *N* NaOH, 25.42. Calc. for (C<sub>19</sub>H<sub>16</sub>ClBrN)HCl: HCl, 8.91%. Found: 9.10%.

***p*-Bromophenyl-*p*-chlorophenyl-phenylmethylchloroamine**, (ClC<sub>6</sub>H<sub>4</sub>)(BrC<sub>6</sub>H<sub>4</sub>)(C<sub>6</sub>H<sub>5</sub>)CNHCl.—The amine hydrochloride, dissolved in chloroform, was stirred with an ice-cold solution of sodium hypochlorite and potassium carbonate exactly as described above for the dichloro substance. The chloroamine, purified by extraction with ligroin, remained in a semi-solid condition. It was dissolved in alcohol and analyzed iodometrically.

<sup>1</sup> Cf. Mackenzie, *J. Chem. Soc.*, 69, 987 (1896).

<sup>2</sup> *Ber.*, 26, 28 (1893).

<sup>3</sup> *Loc. cit.*

Subst. 0.1722, 0.0950; cc. of 0.1 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, 7.80, 4.62. Calc. for (C<sub>19</sub>H<sub>13</sub>ClBr)-NHCl: active Cl, 8.71%. Found: 8.03, 8.62.

**Rearrangement of *p*-Bromophenyl-*p*-chlorophenyl-phenylmethylchloroamine.**—This substance was heated with soda-lime in a metal bath at 200 to 210° for five minutes in order to effect its rearrangement. The extraction with benzene was carried out as explained before and the hydrolysis of the resulting mixture of arylimidobenzophenones yielded a mixture of ketones (*p*-chlorobenzophenone, *p*-bromobenzophenone, and *p*-bromo-*p*-chlorobenzophenone) and an aqueous solution of the hydrochlorides of *p*-chloroaniline, *p*-bromoaniline, and aniline. This mixture of the aniline hydrochlorides was made alkaline and extracted with ether, and the hydrochlorides reprecipitated with a freshly made solution of hydrogen chloride in absolute ether. The resulting crystalline mass was further purified by precipitation by ether from absolute alcohol solution and the product and then carefully dried *in vacuo*.

The proportions of aniline, *p*-chloroaniline, and *p*-bromoaniline in the hydrolyzed product of the above rearrangement were found by determinations of the hydrochloric content of, and the bromine absorbed by, a definite weight of the mixed hydrochlorides.

We have then the three simultaneous equations,  $0.1295x + 0.164y + 0.2084z = a$ ;  $60x + 40y + 40z = b$ ; and  $x + y + z = c$ . In these equations,  $x$ ,  $y$  and  $z$  represent, respectively, the millimols of aniline hydrochloride, chloroaniline hydrochloride and bromoaniline hydrochloride present in a given weight  $a$  of the mixed salts,  $b$  is the number of cc. of 0.1 *N* KBrO<sub>3</sub> used to brominate the salts, and  $c$  represents the number of cc. of *N* NaOH (1/100 of the volume of 0.01 *N* solution actually used) required to neutralize the same weight of the mixed hydrochlorides. In carrying out the determinations, the titration with alkali is made first, phenolphthalein being the indicator, and the same solution is used for the bromination process. In view of the determinations representing an indirect method for three unknown components, the molecular weights of two of which are not very far apart, the method gives only approximate results.

Subst. 0.0315, 0.0262 and 0.0573 g.; cc. of 0.1 *N* KBrO<sub>3</sub>, 9.11, 7.47, 15.23; cc. of 0.01 *N* NaOH, 19.35, 15.94, 33.14.

	Molar percentages.			Average.
Aniline hydrochloride:.....	35.3	34.4	29.8	33
Chloroaniline hydrochloride.....	40.0	38.10	27.0	35
Bromoaniline hydrochloride.....	24.7	27.5	43.2	32

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

## DIETHYLAMINO-*m*-HYDROXYBENZOYL TETRACHLOROBENZOIC ACID AND TRICHLORODIETHYLAMINOXANTHONE-CARBOXYLIC ACID AND SOME OF THEIR DERIVATIVES.

By W. R. ORNDORFF AND C. C. ROSE.

Received August 3, 1916.

### Historical.

Diethylamino-*m*-hydroxybenzoylbenzoic acid is first mentioned by Graebe, Kohn and Huguenin.<sup>1</sup> They obtained it by fusing tetraethylrhod-

<sup>1</sup> *Archives des sciences physiques et naturelles de Genève*, 2, 91 (1893).