

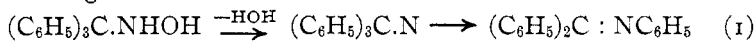
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THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYL-HYDROXYLAMINES.

By BERT ALLEN STAIGNER.¹

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That the hydroxylamine derivatives of triphenylmethane undergo a rearrangement entirely analogous to the Lossen rearrangement of hydroxamic acids and the Beckmann rearrangement of oximes and under exactly similar conditions, was shown by the work of Stieglitz, Reddick and Leech.² The rearrangement is effected by the action of phosphorus pentachloride on the hydroxylamine derivative or by the action of phosphorus pentoxide on the hydrochloride of the base.³ The product of the rearrangement is a phenylimidobenzophenone. According to the theory of Stieglitz⁴ the action is formulated as follows:



When a substituting group replaces hydrogen in one or more of the phenyl groups, as in $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$, the rearrangement leads to the formation of two substituted phenylimidobenzophenones, part of the substance yielding the phenylimide of the substituted benzophenone, for instance $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} : \text{NC}_6\text{H}_5$, part forming a substituted phenylimido derivative of benzophenone itself, namely, $(\text{C}_6\text{H}_5)_2\text{C} : \text{NC}_6\text{H}_4\text{X}$.

A study of the proportions in which the groups migrate in a series of such derivatives promises to shed light on a number of interesting questions. In the first place, exactly the same rearrangements have been observed by Stieglitz and Vosburgh⁵ in the study of triarylmethylhalogenamines, and, recently, by Stieglitz and Senior⁶ in the case of the triarylmethyl azides. In all three series the assumption of the formation of intermediate univalent nitrogen derivatives as the actually rearranging substances gives us, according to Stieglitz, the best explanation of the rearrangements. Then, corresponding compounds in the three series, such as $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NHOH}$, $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.NH}(\text{Hal})$, $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}(\text{N}_2)$ could well yield the identical rearranging compound $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C.N}$. The conditions for the rearrangement in each of these series vary as to the temperature and other environment factors,

¹ The material presented here forms part of a dissertation in fulfillment of the requirements for the Ph.D. degree (1914).

² *8th Intern. Congr. Appl. Chem.*, **25**, 443 (1912); *Ber.*, **46**, 2147 (1913); *THIS JOURNAL*, **36**, 272 (1914).

³ Stieglitz and Leech, *THIS JOURNAL*, *loc. cit.*

⁴ See the references to the literature, *THIS JOURNAL*, **36**, 272 (1914).

⁵ *8th Intern. Congr. Appl. Chem.*, **25**, 444 (1912) and dissertation work of Isabella Vosburgh, University of Chicago, completed in 1913.

⁶ Dissertation work of James K. Senior, University of Chicago, completed in 1914.

but the rearrangement of the univalent nitrogen derivative, being intramolecular, might very well be largely independent of environment. The determinations of the proportions in which the various radicals C_6H_5 , XC_6H_4 , migrate in the rearrangement of corresponding compounds in each of the three series would give us, therefore, the necessary data for quantitative comparisons of the reactions in the three series.

In the second place, such quantitative determinations would show what differences, if any, are shown in the migration of aryl groups XC_6H_4 with various negative or positive substitution groups in them ($X = H, Cl, Br, NO_2, CH_3$, etc.), thus giving a definite answer to the question whether certain groups are more easily lost by carbon and drawn to nitrogen than others. In previous studies of this problem, conclusions have been based, either on the behavior of the groups in question in related but different substances (*e. g.*, $C_6H_5CONHBr$ and $NO_2C_6H_4CONHBr^1$) or on the behavior of ketoximes, in which stereoisomerism is supposed to play the major role in determining the migration of a given radical. For the triphenylmethane derivatives this complication is eliminated and we have, furthermore, all the groups in question in exactly the same rearranging molecule, *e. g.*, $(C_6H_5)(XC_6H_4)(YC_6H_4)C.N$ and, therefore, under strictly comparable conditions. The problem is thus reduced to its simplest terms.²

Stieglitz and Leech having examined only *p*-chlorophenyldiphenylmethylhydroxylamine in regard to the proportion in which the phenyl and the chlorophenyl groups migrate to the nitrogen, I took up, at the suggestion and under the direction of Professor Stieglitz, the further investigation of this problem at this point. For this purpose the rearrangement of *p*-bromophenyl-diphenylmethylhydroxylamine, of di-*p*-chlorophenyl-phenylmethylhydroxylamine and finally of *p*-chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine was studied by me.

The interesting result was obtained that whereas bromophenyl-diphenylmethylhydroxylamine, $(BrC_6H_4)(C_6H_5)_2CNHOH$, exactly as the corresponding chloro derivative studied by Leech, rearranges so that, roughly, in two-thirds of the rearranging molecules a phenyl group and in the remaining third the bromophenyl group migrates, the ratio is reversed when one subjects dichlorophenyl-phenylmethylhydroxylamine, $(ClC_6H_4)_2(C_6H_5)CNHOH$, to the rearrangement. In this case for two-thirds of the rearranging molecules it is the chlorophenyl group that migrates and in the remaining third the phenyl group. Furthermore,

¹ Hoogewerff and van Dorp, *Rec. trav. chim.*, 6, 373 (1887), etc.

² A further question which is being studied is that of the effect of the positions of the substituting groups (ortho, meta and para) on the migration. It is expected to produce experimental evidence concerning the nature of the charges on the carbon atoms holding the aryl groups to the methyl carbon atoms and thus to secure evidence on certain of Fry's assumptions concerning the charges in the benzene derivatives.—J. S.

in the case of chlorophenyl-bromophenyl-phenylmethylhydroxylamine, $(\text{ClC}_6\text{H}_4)(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CNHOH}$, roughly one-third of the rearranging molecules show a migration of the chlorophenyl group, the bromophenyl group and the phenyl group, respectively. This result certainly would indicate that there is no marked effect of the halogens on the tendency of the aryl group to migrate to the nitrogen.¹

Experimental Part.

p - Bromophenyldiphenylmethylhydroxylamine, $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNHOH}$.—This was prepared according to Gomberg² from benzophenone-dichloride and bromobenzene by the Friedel and Craft reaction. The chloride was treated with hydroxylamine by a modification of the methods of Mothwurf³ and of Stieglitz and Leech.⁴ Many futile preliminary attempts by these methods showed that it is necessary to have the hydroxylamine solution very concentrated, for otherwise the principal reaction takes place between the triarylmethylchloride and the alcohol, forming the ether $(\text{C}_6\text{H}_5)_2(\text{BrC}_6\text{H}_4)\text{COCH}_3$. Even with this precaution some of the ether was always formed.

A saturated solution of 3.2 g. of hydroxylamine hydrochloride in warm methyl alcohol was added to a solution of sodium methylate (1 g. of sodium dissolved in the least quantity of methyl alcohol). It is desirable not to have any excess of the sodium methylate present and this was carefully determined by evaporation of a drop of the solution on a crucible lid and gentle ignition of any residue. If any alkaline substance remained, more hydroxylamine hydrochloride was added to the methylate solution until the test gave a negative result. The sodium chloride formed in the reaction was removed by filtration and the filtrate evaporated at 20 mm. pressure and 40° to a volume of 10 cc. This treatment gave a very concentrated hydroxylamine solution and but little of the hydroxylamine escaped.⁵ The approximate strength of the solution was determined by titration of 0.5 cc. of it with 0.1 *N* hydrochloric acid, methyl orange being used as the indicator.⁶

Three grams of *p*-bromophenyl-diphenylmethyl chloride, dissolved in 30 cc. of anhydrous benzene, were added to the 10 cc. of the alcohol solution of hydroxylamine. After the mixture had stood a few hours the small quantity of hydroxylamine hydrochloride which had separated was removed by filtration and the filtrate evaporated at 20 mm. pressure

¹ The discussion of minor differences in the migration of these radicals and the comparison of the results obtained with corresponding hydroxylamines, chloroamines and azides will be presented in another paper by Professor Stieglitz.

² *Ber.*, **37**, 1633 (1904).

³ *Ibid.*, **37**, 3152 (1904).

⁴ *THIS JOURNAL*, **36**, 3152 (1913).

⁵ See Lobry de Bruyn, *Rec. trav. chim.*, **10**, 100 (1891).

⁶ Lobry de Bruyn, *loc. cit.*

and 50°. A yellow, gummy residue, consisting chiefly of the bromophenyl-diphenylmethylhydroxylamine, was left. This base was extracted with dry ether and the extract treated with an excess of dry hydrogen chloride. The salt, $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2\text{OHCl}$, separated at once as a white solid. The salt becomes slightly soluble in ether after a large excess of the acid is introduced. It was collected on a filter, washed several times with ether, and once quickly with cold dilute (about 3 molar) hydrochloric acid to remove hydroxylamine hydrochloride.¹

From 3 g. of bromophenyl-diphenylmethylchloride, 1.8 g. of the purified salt was obtained. This was analyzed by titration of the hydrochloric acid with silver nitrate solution by the Volhard method.

Subst. 0.1711, 0.1730; cc. 0.1 *N* AgNO₃, 4.34, 4.37.

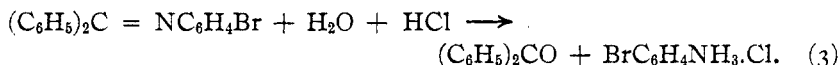
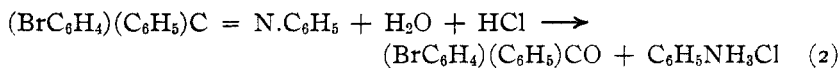
Calc. for $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNH}_2\text{OHCl}$: HCl, 9.33. Found: 9.25, 9.19.

The salt reduces Fehling's solution when boiled, but not in the cold, melts at 144-5° with decomposition, is soluble in alcohol, but not in ligroin and but slightly soluble in ether.

Rearrangement of *p*-Bromophenyl-diphenylmethylhydroxylamine.—The free base, $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{CNHOH}$, was obtained from the hydrochloride just described by treatment of the latter with 20% sodium hydroxide solution and extraction of the base with ether. The ether solution was dried with potassium carbonate and the solvent evaporated in a current of dry air. The base thus obtained was a pale yellow viscous liquid or gum. Some of it (1.35 g.) was dissolved in 30 cc. of anhydrous ether and powdered phosphorus pentachloride (2.5 g.) was added to it. When the mixture was allowed to stand at room temperature for a few hours a trace of a yellow deposit collected on the phosphorus chloride. The mixture was then heated on an electric bath for two hours and a greater amount of the yellow deposit collected. The molecular rearrangement was expected to yield the two phenylimidobenzophenones, *p*-bromophenylimidobenzophenone, $(\text{C}_6\text{H}_5)_2\text{C} : \text{NHC}_6\text{H}_4\text{Br}$ and phenylimidobromobenzophenone, $(\text{BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} : \text{NH.C}_6\text{H}_5$. To insure that these bases should be present in the form of their salts, some ether (2 cc.) saturated with hydrogen chloride was added to the reaction product. The supernatant liquid was then decanted through a filter from the main residue and the residue was washed with ether containing some hydrogen chloride. Since partial hydrolysis of some of the imidoketones by traces of moisture would form anilines and since aniline hydrochlorides are somewhat soluble in ether containing an excess of hydrogen chloride, it was always possible that some of the aniline, if any were present here, might be dissolved by this treatment. For the recovery of any such substance, the ether filtrate was evaporated almost to dryness, a small amount of

¹ The presence of this salt was indicated by the hydrogen chloride content of the product when it was not purified in this way.

water added to the residue, and this warmed to decompose the phosphorus oxychloride. This aqueous solution and the trace of solid on the filter were then added to the main residue. This was then warmed with alcohol (10 cc.) and dilute hydrochloric acid (5 cc.) for an hour on a steam bath to completely hydrolyze the imidoketones.



The alcohol was removed by evaporation of the solution almost to dryness, followed by a second evaporation after some acidulated water had been added to the residue. Now, water (15 cc.) was added to the product and the solution twice extracted with 15 cc. of ether to remove the ketones. These ketones were identified as described further on. The aqueous solution contained the aniline and bromoaniline hydrochlorides. It was made alkaline, saturated with sodium chloride and the free anilines extracted with two portions of 25 cc. each of ether. The extract was filtered into a weighed beaker and 2 to 3 cc. of ether saturated with hydrogen chloride were added to this filtrate to convert the anilines into hydrochlorides. Because of the partial solubility of these salts in such an acid-ether solution, the ether and the water held in solution by it were evaporated in a current of dry air and the salts remaining were dried *in vacuo*. The dried salts were washed once with 10–15 cc. of absolute ether, dried again, and weighed. The *p*-bromophenyl-diphenylmethylhydroxylamine (1.35 g.) used in the rearrangement yielded 0.2075 g. of aniline hydrochloride and bromoaniline hydrochloride.

Two other quantitative rearrangements of the base were made by this method. In the first a yield of 0.2145 g. of aniline salts was obtained from 1.08 g. of the base and in the second the yield of the salts was 0.2865 g. when 1.17 g. of the base was used. Theoretically 1 g. of the base could yield either 0.36 g. of aniline hydrochloride or 0.58 g. bromoaniline hydrochloride.

These mixtures of aniline and bromoaniline hydrochlorides were analyzed to ascertain the molar ratios of the aniline and bromoaniline. The bromination method of Curme¹ was used.

Subst. 0.0589, 0.0569, 0.0659; cc. 0.1 *N* KBrO₃, 21.65, 21.31, 24.63. Found: aniline hydrochloride, 74.73, 76.81, 76.58; bromoaniline hydrochloride, 25.27, 23.19, 23.42.

Identification of Aniline and Bromoaniline.—The method of separating aniline and chloroaniline used by Stieglitz and Leech² proved satisfactory for separating and identifying the aniline and bromoaniline of this re-

¹ THIS JOURNAL, 35, 1162 (1913).

² *Loc. cit.*

arrangement. The hydrochlorides were converted into the oxalates and the greater solubility of the aniline oxalate in hot water permitted its separation from the bromoaniline oxalate. The former, in water solution and made alkaline, gave the violet color with bleaching powder solution; and the latter, freed from the acid, gave crystals from ether solution, which melted at 62°. These when mixed with pure *p*-bromoaniline,¹ melted at 62–63°.

Identification of Benzophenone and Bromobenzophenone.—The ether containing the ketones in solution was evaporated. The residue was quickly washed with a small amount of ligroin and then about seven-eighths of the residue was dissolved in warm ligroin (b. p. 70–80°). The small quantity of residue remaining melted at 81° (pure *p*-bromobenzophenone melts at 82.5°). The ligroin solution was evaporated to dryness and two-thirds of the residue dissolved. This treatment was repeated until about one-eighth of the original residue was in solution. A few crystals obtained from this solution melted at 46–47° and when they were mixed with pure benzophenone they melted at 47–48° (pure benzophenone melts at 48.5°).

Rearrangement of *p*-Bromophenyl-diphenylmethylhydroxylamine Hydrochloride by Means of Phosphorus Pentoxide.—Bromophenyl-diphenylmethylhydroxylamine hydrochloride (0.8 g.) and phosphorus pentoxide (0.9 g.) were placed together in a test tube and gradually warmed in a metal bath. At 107° a rapid reaction took place and the mixture expanded to about three times its original volume into a brown gummy mass. The mass was kept at this temperature for 20 minutes and then cooled.² The subsequent treatment was similar to that described above for the product of the rearrangement of the free base. Approximately 0.1 g. of the hydrochlorides of aniline and bromoaniline was obtained. The aniline gave the characteristic test with bleaching powder solution. No further attempts at effecting rearrangements by means of phosphorus oxide were made as the pentachloride seemed to give more satisfactory yields.

Di-*p*-chlorophenyl-phenylmethylhydroxylamine, (ClC₆H₄)₂(C₆H₅)CNHOH.—This was made by Gomberg's method³ from dichlorobenzophenone by the Grignard reaction. The reagent was used according to the proportions given by Houben,⁴ *i. e.*, 2.36 g. of special magnesium, 17.5 g. of bromobenzene, and 120 cc. of ether. After a few hours, when the reaction between the magnesium and the bromobenzene was com-

¹ Kahlbaum's pure bromoaniline, melting at 63–64°.

² The reaction seems to take place slowly even when the mixture is heated only slightly, as shown by the fact that the yellow tint of the mixture grew deeper in color when it was pressed hard against the sides of the test tube with a glass rod.

³ *Ber.*, 39, 3279 (1906).

⁴ *Ibid.*, 36, 3087 (1903).

plete, 9 g. of the solid di-*p*-chlorobenzophenone were added. This ketone is only moderately soluble in ether but it dissolved at once in the Grignard reagent. The solution must be kept free from moisture. It was warmed for three hours on a water bath and the magnesium compound was then decomposed with water. The excess of bromobenzene used in making the Grignard reagent and the benzene formed from it later were removed by steam distillation and the light colored insoluble gum remaining in the water was washed free from magnesium hydroxide with dilute hydrochloric acid. The gum was dissolved in ligroin and dried with fused calcium chloride. The solution was filtered and the solvent evaporated spontaneously in a desiccator over paraffin shavings. In three hours crystals of the carbinol began to form and 8.6 g. of the carbinol had separated out overnight. The carbinol melted at 85° without recrystallization. Gomberg did not succeed in obtaining this carbinol crystallized until he had taken it through a long troublesome method of purification. The preparation was twice repeated and the crystallization similarly obtained. The carbinol was converted into the chloride, $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$, in the usual manner by dry hydrogen chloride passed into a carbon disulfide solution of the carbinol. The chloride thus formed was a gum at first and assayed 94% of the calculated amount of chlorine when it was hydrolyzed in alcohol solution with excess of alkali. This gum was used for the preparation of the hydroxylamine, but about 5 g. of it were left in a desiccator over solid potassium hydroxide and in a month's time crystals had formed on the sides of the beaker. These were pushed down into the gum and in several days the whole had become solid. This impure solid melted at 43–50°.

Subst. 0.4333 g.; cc. 0.1 *N* KOH 11.58. Calc. for $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$: Cl, 10.21. Found: 9.50.

Gomberg was not successful in getting this gum to solidify. The solidification is slow and time did not permit further efforts at the purification of the product. The chloride, as a gum, was allowed to act on a strong solution of hydroxylamine, in the way described above for bromophenyl-diphenylmethylchloride. The free base remaining after the alcohol and benzene were removed, was extracted with ether and hydrogen chloride added to the ether extract. The hydrochloride, $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{-CNH}_2\text{OHCl}$, separated at once as a white solid. The salt was removed by filtration and washed well with ether and once quickly washed with cold dilute hydrochloric acid. It is slightly soluble in ether, soluble in alcohol, but insoluble in ligroin and benzene. It reduces boiling Fehling's solution, and melts at 129–30° into a pale yellow liquid which soon reddens when left at that temperature.

Subst. 0.2287, 0.2869; cc. 0.1 *N* AgNO₃, 5.85, 7.29.
Calc. for $(\text{ClC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{OHCl}$: HCl, 9.58. Found: 9.32, 9.26.

Rearrangement of Di-*p*-chlorophenyl-phenylmethylhydroxylamine.—

The free base was obtained from the hydrochloride described above by treatment of the salt with 20% alkali solution and extraction with ether. The ether solution was dried over potassium carbonate and the ether evaporated. The base was left as a pale yellow, syrupy liquid or gum which is soluble in ether, alcohol, ligroin, and benzene. The substance (1.47 g.) was dissolved in ether (30–40 cc.) and phosphorus pentachloride (2.5 g.) was added to the solution. The subsequent treatment was similar to that of the bromophenyl-diphenylmethylhydroxylamine as given above.

A yield of 0.4229 g. of mixed aniline hydrochlorides was obtained from 1.47 g. of the base. A second rearrangement of 1.21 g. of the base gave 0.354 g. of the aniline salts.

A complete rearrangement would yield at most 0.37 g. of aniline hydrochloride, or 0.47 g. of chloroaniline hydrochloride per gram of substance.

A quantitative analysis of the aniline salts obtained from each of the rearrangements was made by the bromination method for their molar ratios.

Subst. 0.0794, 0.0767; cc. 0.1 *N* KBrO₃, 25.13, 23.93.

Found: aniline hydrochloride, 38.41, 36.30; chloroaniline hydrochloride, 61.56, 63.70.

Identification of the Anilines.—A qualitative separation of the two anilines was made by the method of Stieglitz and Leech.¹ When separated, the aniline gave the violet color test with bleaching powder and the chloroaniline gave crystals which melted at 68–69°, and when they were mixed with pure chloroaniline they melted at 68–69° (pure chloroaniline melts at 69°).

Identification of Chlorobenzophenone and Dichlorobenzophenone.—

The ether was evaporated from the *p*-chlorobenzophenone and di-*p*-chlorobenzophenone solution, leaving a large bulk of flaky crystals. Preliminary tests with a mixture of known mono- and di-chlorobenzophenones showed that the latter is the less soluble in ligroin and that the two could be separated by virtue of this difference. The ketones obtained from the rearrangement were dissolved in a small quantity of warm ligroin. When a few crystals had separated from the solution, as it cooled, they were collected in a filter. They melted at 139° and when they were mixed with pure *p*-dichlorobenzophenone they melted at 141–142° (pure *p*-dichlorobenzophenone melts at 143°). The filtrate still containing the greater portion of the ketones, was evaporated to dryness and three-quarters of the residue again dissolved in ligroin. This process was repeated until the last extraction contained about one-eighth of the original ketone residue. About one-half of this was crystallized from the solution and the melting point of these crystals determined. They melted at 79–

¹ *Loc. cit.*, p. 296.

80°, and when they were mixed with pure *p*-chlorobenzophenone¹ they melted at 78–80°.

Di - *p* - bromophenyl - phenylmethylhydroxylamine Hydrochloride, $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{C.NH}_2\text{OH.Cl}$. — Di-*p*-bromophenyl-phenylmethylchloride was prepared by Gomberg's method.² The corresponding carbinol, $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{COH}$, which was first obtained, melted at 113.5° when recrystallized from ligroin. It melted at the same temperature when twice recrystallized. Gomberg gives the melting point as 110°. The chloride, $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CCl}$, was dissolved in benzene and added to a solution of hydroxylamine in alcohol. The molecular proportions of substances, and the method of procedure used in the previous preparations were repeated here. The alcohol and benzene were removed by distillation under diminished pressure and without the temperature rising above 60°. A gummy residue remained and consisted principally of the free base dibromophenyl-phenylmethylhydroxylamine. This base was extracted with ether and hydrogen chloride introduced into the solution. A small quantity of white precipitate separated out at first but it redissolved as the solution became more strongly acid. The acid and ether were now evaporated and a mobile liquid was left. Low boiling ligroin (b. p. 40–60°) was added to it and the mixture stirred. The liquid, which was but little soluble in the ligroin, began to solidify immediately. The di-*p*-bromophenyl-phenylmethylhydroxylamine hydrochloride thus formed is as soluble in methyl and ethyl alcohol and ether as is the dibromophenyl-phenylmethylchloride itself, but it is not soluble in ligroin, while the latter is. The salt was washed well with ligroin (b. p. 70–80°) and once with cold dilute hydrochloric acid. It reduces boiling Fehling's solution and softens at about 75°.

Subst. 0.2850, 0.3113; cc. 0.1 *N* AgNO₃, 5.73, 6.31.

Calc. for $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNH}_2\text{OHCl}$: HCl, 7.73. Found: 7.34, 7.40.

Rearrangement of Di-*p*-bromophenyl-phenylmethylhydroxylamine. — The free base, $(\text{BrC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{CNHOH}$, was prepared from the hydrochloride in the usual way. It was obtained as a yellow viscous liquid. Some of the base (1.6 g.) was dissolved in 30 cc. of ether and 3 g. of phosphorus pentachloride added to the solution. The mixture was warmed at the boiling point of the ether for two hours. The imido-benzophenones appeared in that time as indicated by the yellow color of the mixture. The mixture was then subjected to hydrolysis and to the isolation of the ketones and the aniline hydrochlorides. The yield of the mixed aniline and bromoaniline hydrochlorides from the base (1.6 g.) was 0.4785 g. A second rearrangement of 1.11 g. base gave 0.3104 g. of mixed aniline salts. Theoretically one gram of base could give 0.30 g. aniline hydro-

¹ Kahlbaum's *p*-chlorobenzophenone melted at 77–78°.

² *Ber.*, 39, 3280 (1906).

chloride or 0.48 g. of bromoaniline hydrochloride. Each quantity of the mixed aniline hydrochloride was analyzed for the molar ratios of the anilines by the bromination method.

Subst. 0.0513, 0.0439; cc. 0.1 *N* KBrO₃, 12.80, 11.04.

Found: aniline hydrochloride, 30.25, 31.05; bromoaniline hydrochloride, 69.76, 68.95.

Identification of Aniline and Bromoaniline.—The aniline and bromoaniline were separated exactly as were the bases from the rearranged *p*-bromophenyl-diphenylmethylhydroxylamine. The aniline oxalate, after separation from the bromoaniline salt, was made alkaline and tested with bleaching powder solution. The violet color confirmed the identity of the aniline. The less soluble bromoaniline oxalate was freed from the oxalic acid and crystallized from ether. The crystals melted at 62–63°, and, when they were mixed with pure bromoaniline, they melted at 63–64° (pure bromoaniline melts at 64°).

Identification of Bromobenzophenone and Dibromobenzophenone.—The ether solution of the ketones was evaporated to dryness in a current of air. Of the *p*-bromobenzophenone and *p*-dibromobenzophenone, the latter is the less soluble in ligroin (b. p. 70–80°) and by fractional crystallization from that solvent some of it was isolated. It melted at 167° and when it was mixed with synthetic dibromobenzophenone it melted at 167–168° (pure dibromobenzophenone melts at 172–173°). The ligroin solution containing the more soluble portion of the ketones was evaporated to dryness and the process for separating monochlorobenzophenone from dichlorobenzophenone was followed. The crystals thus isolated melted at 78–80° (pure *p*-bromobenzophenone melts at 82.5°).

***p*-Chlorophenyl-*p*-bromophenyl-phenylcarbinol**, (ClC₆H₄)(BrC₆H₄)-(C₆H₅)COH.—This carbinol and the corresponding chloride required for the next experiment are not described in the literature and probably have not been made. For the preparation of the carbinol, *p*-chlorobenzophenone was first obtained from benzoylchloride and chlorobenzene with the aid of the Friedel and Crafts reaction.¹ The chlorobenzophenone was converted into the dichloride by treatment with phosphorus pentachloride by the method used by Kekulé and Franchement in converting benzophenone into benzophenone dichloride.² The dichloride was fractionally distilled.³ Then, one molar proportion of the *p*-chlorobenzophenone dichloride and two to three of bromobenzene were placed on a steam bath in a round bottom flask with a reflux condenser attached, and to this solution 1.4 molar proportions of aluminum chloride were gradually added in portions of 5 to 10 g. After

¹ Gomberg, *B. r.*, **39**, 3278 (1906).

² Mackenzie, *J. Chem. Soc.*, **69**, 987 (1896).

³ Overton, *Ber.*, **26**, 28 (1893); Peterson, *Am. Chem. J.*, **46**, 332 (1911).

all of the aluminum chloride had been added the mixture was heated two hours longer. It was then cooled and poured on ice and water to decompose the aluminum compound. The excess of bromobenzene was removed by steam distillation and the residue, a dark gum insoluble in water, was well washed with dilute hydrochloric acid to remove the aluminum hydroxide. The gummy residue was extracted with carbon disulfide, the carbon disulfide solution filtered, the filtrate dried over fused calcium chloride, and the solvent evaporated. The dark colored gum remaining was dissolved in warm ligroin (b. p. 70–80°) and the solution left in a cold place overnight. The carbinol separated out in light colored crystals. Recrystallization was twice repeated and the carbinol then melted at 91–93°.

0.2161 g. of the carbinol gave 0.4850 g. CO₂ and 0.0760 g. H₂O.

Calc. for C₁₉H₁₄OClBr: C, 61.03%; H, 3.77%. Found: C, 61.22%; H, 3.93%.

***p*-Chlorophenyl-*p*-bromophenyl-phenylmethylchloride**, (ClC₆H₄)-(BrC₆H₄)(C₆H₅)CCl.—The carbinol was converted into the chloride, (ClC₆H₄)(BrC₆H₄)(C₆H₅)CCl, by a stream of hydrogen chloride passed into a carbon disulfide solution of the carbinol. After the acid was added, the disulfide solution was dried over fused calcium chloride and filtered and the excess of acid and the carbon disulfide evaporated *in vacuo*. The chloride was left as a very viscous liquid. When it was hydrolyzed with excess of 0.1 *N* KOH and the excess of alkali was titrated with 0.1 *N* HCl, it showed 93% of the calculated amount of chlorine. Attempts to crystallize the chloride were, at first, unsuccessful and for this reason the liquid chloride was used in making the hydroxylamine preparation. Later, however, the chloride crystallized from low boiling ligroin. The solid was twice recrystallized from higher boiling ligroin by inoculation of the solution with the crystals first obtained. It now melted at 69–72°.

Subst. 0.2229; cc. 0.1 *N* KOH, 5.44. Calc. for (C₁₉H₁₃ClBr)Cl: 9.05% Cl (hydrolyzable). Found: 8.67%.

***p*-Chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine Hydrochloride**, (ClC₆H₄)(BrC₆H₄)(C₆H₅)CNH₂OHCl.—The chlorophenyl-bromophenyl-phenylmethylchloride (7 g.) was dissolved in benzene (200 g.) and condensed with a saturated alcoholic solution of hydroxylamine. The solvents were removed by evaporation. The gummy residue remaining was extracted with ether and the ether solution made strongly acid with hydrogen chloride. The hydrogen chloride salt of the hydroxylamine derivation does not precipitate out from the ether solution. After the ether and excess acid were evaporated the triarylmethylhydroxylamine hydrochloride remained as a syrupy liquid; it was treated with low boiling ligroin and the mixture stirred with a glass rod. The salt began to solidify immediately. It is insoluble in ligroin and was purified by being washed well with that solvent. It cannot be washed with dilute

hydrochloric acid as it forms a soft, sticky mass as soon as brought into contact with the water. It is soluble in alcohol, ether, and chloroform. It reduces boiling Fehling's solution and softens at 45° , but has no true melting point.

Subst. 0.4155; cc. 0.1 *N* AgNO₃, 9.41. Calc. for (C₁₉H₁₅NOCIBr)HCl: Cl, 8.58%. Found: 8.27.

A yield of 5 g. of this salt was obtained from the chloride (7 g.) used.

Rearrangement of *p*-Chlorophenyl-*p*-bromophenyl-phenylmethylhydroxylamine.—The free base of the salt just described was obtained as a yellow syrupy substance, which under low pressure began to expand as a kind of foam and to spread throughout the beaker as a viscous gum. This behavior is characteristic of all these bases.

Some of the base (2.37 g.) was dissolved in 30–40 cc. of ether and phosphorus pentachloride (4 g.) added to the solution. In twelve hours a slight change in color to yellow indicated a slow formation of the imido ketones at room temperature. The mixture was then heated for two hours at the temperature of boiling ether to complete the rearrangement. The mixture was next subjected to hydrolysis of the imido ketones,¹ and the isolation of the benzophenones and the anilines carried out in the manner described for the previous rearrangements.

The yield of the mixed aniline, chloroaniline and bromoaniline hydrochlorides from the 2.37 g. of base was 0.626 g. In a second rearrangement of 1 g. of base 0.1595 g. of the aniline salts was obtained. A complete rearrangement would give 0.33 g. of aniline hydrochloride, or 0.42 g. of chloroaniline hydrochloride or 0.54 g. of bromoaniline hydrochloride per gram of substance.

A trace of the aniline mixture was made alkaline and treated with bleaching powder solution. A violet color was produced, proving the presence of the unsubstituted aniline. Another part of the aniline mixture was freed from hydrogen chloride and precipitated from ether solution with oxalic acid. The precipitate showed the presence of halogen when heated in a bunsen flame with copper oxide and also when fused with sodium and tested with silver nitrate solution.

The mixed aniline hydrochlorides obtained from each of the rearrangements were analyzed volumetrically for the determination of the molar ratios of the three salts: the hydrochlorides of aniline, chloroaniline and bromoaniline. The bromination and the Volhard methods were used jointly to give sufficient data for the calculations.²

¹ Three imido ketones were present, (ClC₆H₄)(BrC₆H₄)C = N(C₆H₅), (ClC₆H₄)(C₆H₅)C = NC₆H₄Br, and (BrC₆H₄)(C₆H₅)C = NC₆H₄Cl.

² The reliability of this method of analysis was determined with a known mixture of the three hydrochlorides. For the Volhard method a larger quantity of the mixed salts was used than for the bromination method, as the data show. The method is reliable only to within 5%.

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

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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).