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The Molecular Rearrangement of Triarylmethylazides

The Molecular Rearrangement of *sym.-bis*-Triarylmethylhydrazines

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The Molecular Rearrangement of Triarylmethylazides.[1]

Molecular rearrangements have been observed by Stieglitz and his collaborators in the triphenylmethane series when triphenylmethyl hydroxylamines[2] $Ar_3C.NHOH$ are subjected to the action of phosphorus pentachloride, and when triphenylmethylhalogenamines[3] $Ar_3C.NH(Hal)$ are treated with alkaline reagents. These rearrangements are entirely analogous,[4] respectively, to the Lossen-Beckmann rearrangements of acyl hydroxylamines and ketoximes and the Hofmann rearrangement of acyl halogenamines RCO.NH(Hal)—in fact the rearrangements in the triphenylmethane series were anticipated and explored as the result[5] of the investigations of Stieglitz on the nature of the Lossen-Beckmann-Hofmann rearrangements. There is a third group of acyl derivatives, the azides $RCO.N_3$, which, as Curtius found, undergo exactly the same kind of rearrangement as do the acyl hydroxylamines and halogenamines. This parallelism, together with Stieglitz's theory that the rearrangement in all of these cases is due to the primary formation of univalent nitrogen[6] derivatives, RCO.N, $R_3C.N$, etc., made it appear certain that triphenylmethylazides $(C_6H_5)_3C.N_3$ would be found, on investigation, to undergo a rearrangement analogous to that of triphenylmethyl hydroxylamines and halogenamines. Further, it was anticipated that for the rearrangement of the azides heat[7] alone would be required

$$(C_6H_5)_3C.N(N_2) \xrightarrow{\text{Heat}} (C_6H_5)_3C.N + N_2 \longrightarrow (C_6H_5)_2C{:}NC_6H_5 + N_2. \quad (1)$$

With the object of determining these relations, I undertook, at the

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[1] A brief preliminary report by Stieglitz and Senior appeared in the *Proc. Nat. Acad. of Sciences*, **1**, 207 (1915).

[2] Stieglitz, Reddick and Leech, *Eighth Intern. Congr. Appl. Chem.*, **25**, 44 (1912); Stieglitz and Leech, *Ber.*, **46**, 2147 (1913); and *J. Am. Chem. Soc.*, **36**, 272 (1914).

[3] Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913); Vosburgh, *J. Am. Chem. Soc.*, **38**, 2081 (1916).

[4] The literature references are given by Stieglitz and Leech, *J. Am. Chem. Soc.*, **36**, 272 (1914), and Stieglitz and Stagner, *Ibid.*, **38**, 2046 (1916).

[5] Cf. *Ber.*, **46**, 2147 (1913).

[6] For the electronic formulation of the theory, see Stieglitz and Leech, *Loc. cit.*, and L. W. Jones, *Am. Chem. J.*, **50**, 440 (1913) (published in 1914); for preliminary suggestions, see Stieglitz, *Ber.*, **43**, 782 (1910); *J. Am. Chem. Soc.*, **36**, 276, 280, 288; and Jones, *Loc. cit.*, and *Am. Chem. J.*, **48**, 1 (1912).

[7] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903).

suggestion of Professor Stieglitz, the investigation of triphenylmethyl azide. This seemed particularly desirable because, for the azides, the alternative theory of a direct exchange[1] of radicals in these rearrangements seems quite inapplicable. Cumulative evidence that in every instance the azides behave exactly as do the hydroxylamines and the halogenamines was anticipated.

A rearrangement somewhat analogous to the one I proposed to investigate had already been observed by Curtius[2] in the case of benzyl azide, and Curtius also interprets the formation of the main products of the rearrangement by assuming the formation of a univalent nitrogen derivative:

$$\begin{tikzcd}(C_6H_5)CH_2.N(N_2) \arrow[r, "-N_2"] & (C_6H_5)CH_2.N \arrow[r] \arrow[d] & CH_2 : NC_6H_5 \\ & (C_6H_5)CH : NH & \end{tikzcd} \qquad (2)$$

The reagent used was not heat alone, but a strong acid and heat, and the reactions were complicated by subsequent changes of the main products.

On the other hand, triphenylmethylazide itself had been prepared by Wieland[3] in 1909 and found to be remarkably stable for an azide, differing markedly in this respect from the well-known acyl azides. Nevertheless, it was noted that Wieland had observed that triphenylmethylazide turns yellow with decomposition at its melting point. This is the color of phenylimido-benzophenone, the product of rearrangement anticipated by us. Experiment showed, without difficulty, that triphenylmethylazide does indeed form this product in good quantity when it is heated, the rearrangement proceeding as indicated in Equation 1. The phenylimido-benzophenone was identified by its products of hydrolysis, aniline and benzophenone formed under the influence of acids.

$$(C_6H_5)_2C : NC_6H_5 + HOH + HCl \longrightarrow (C_6H_5)_2CO + C_6H_5NH_3Cl. \quad (3)$$

As a further main object of the present investigation, it was proposed to examine substitution derivatives of this azide, such as $(XC_6H_4)(C_6H_5)_2C.N_3$ and $(XC_6H_4)(YC_6H_4)(C_6H_5)C.N_3$. In the rearrangement of the intermediate univalent nitrogen derivatives, in some of the molecules the phenyl radical would presumably migrate from the carbon to the nitrogen, in other molecules the derived radical (XC_6H_4) or (YC_6H_4), would be the migrating group. For a mono substitution product we should have the simultaneous rearrangements

[1] 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 (1908); 2, 368 (1909–1910); 6, 1 (1913); *Mem. Coll. Sci., Kyoto,* 1, 25 (1914); cf. Stieglitz and Stagner, *Loc. cit.*

[2] *J. prakt. Chem.*, 63, 428 (1901); *Ber.*, 35, 3229 (1902).

[3] *Ber.*, 42, 3020 (1909). Wieland did not look for any molecular rearrangement.

$$(XC_6H_4)(C_6H_5)_2C.N_3 \longrightarrow (XC_6H_4)(C_6H_5)C : NC_6H_5 + N_2 \qquad (4)$$

and

$$(XC_6H_4)(C_6H_5)_2C.N_3 \longrightarrow (C_6H_5)_2C : NC_6H_4X + N_2. \qquad (5)$$

A determination of the ratio in which the groups migrate in a given case seemed of particular importance for the purpose of comparing such a ratio with the results obtained from similar studies of the rearrangement of the corresponding compounds in the triphenylmethyl hydroxylamine and halogenamine series. All these series should give, according to Stieglitz's theory, the same intermediate product $(XC_6H_4)(C_6H_5)_2C.N$ and might well show the same ratio of migrating radicals in spite of the difference in environment (temperature, reagents, etc.), since the rearrangement of the univalent nitrogen derivative is an intramolecular reaction. The time at my disposal has permitted the exhaustive investigation of only one instance of this kind, namely the rearrangement of *p*-chlorophenyldiphenylmethylazide. I found that in 68.1% of the rearranging molecules the phenyl radical migrates to the nitrogen, in 31.9% the chlorophenyl group is the migrating one. For the corresponding *p*-chlorophenyldiphenylmethylhydroxylamine, Leech[1] obtained the ratio 70.8/29.2. These results compare very favorably with mine. A broader basis of comparison between the series will ultimately be necessary, if coincidences are to be excluded.

It is evident that, thus far, the triarylmethylazides behave qualitatively and quantitatively like the corresponding triarylmethylhydroxylamines—a result, which is decidedly in favor of the Stieglitz theory of these molecular rearrangements, and against the Beckmann theory of a direct exchange of the migrating groups.

Experimental Part.

Triphenylmethylhydrazine Hydrochloride, $(C_6H_5)_3CNH.NH_2,HCl$ **and Symmetrical *Bis*-Triphenylmethylhydrazine,** $(C_6H_5)_3CNH.NHC(C_6H_5)_3$.—Some attempts to prepare the first of these substances by the method described by Wieland[2] were unsuccessful. The source of this unexpected failure was not sought, instead the following alternative procedure which gave satisfactory results was developed. Triphenylmethylchloride was prepared according to the method of Gomberg.[3] Hydrazine hydrate (8 g.) and triphenylmethylchloride (21 g., 95% pure) were boiled in the presence of 60 cc. of absolute ether in a flask fitted with a reflux condenser. After a few hours, a precipitate appeared, and in ten hours the reaction was complete. The contents of the flask were then filtered and the precipitate, chiefly *bis*-triphenylmethylhydrazine, washed with ether and with water. The ethereal filtrate was shaken twice with water to remove

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[1] *J. Am. Chem. Soc.*, 36, 272 (1914).

[2] *Ber.*, 42, 3021, 3025 (1909).

[3] *Ibid.*, 33, 3147 (1900).

traces of hydrazine hydrochloride, and the ether layer then dried over calcium chloride. To the dried ethereal solution a strong solution of dry hydrogen chloride in anhydrous ether was added. The triphenylmethylhydrazine hydrochloride was precipitated as a gummy mass, which, on being scratched, quickly turned granular. The flask was cooled in ice for half an hour and the precipitate then collected in a filter and dried. The yield was 11.5 g. of substance, melting at 108–113°.

The compound was analyzed by titration according to the Volhard method.

0.2469 g. subs. required 7.89 cc. of 0.1 *N* $AgNO_3$.
Calc. for $C_{19}H_{18}N_2HCl$: HCl, 11.74. Found: 11.65.

Analyses of many samples prepared by this method always showed that the substance was nearly pure. It was, therefore, used without further refinement. Attempts to purify it by recrystallization from absolute alcohol and ether, according to the method of Wieland, failed in every case. The substance was always rapidly "alcoholyzed" by the solvent.

The precipitate formed in the flask when the hydrazine hydrate and triphenylmethylchloride were boiled together was symmetrical *bis*-triphenylmethylhydrazine. After it had been washed with ether and water on the filter, it was removed and boiled with alcohol, collected again on a filter and dried. The yield was 4 g. of material melting at 205°. The substance was further purified by the method of Wieland.[1] When pure, it melted at 210°.

Triphenylmethylazide, $(C_6H_5)_3CN_3$.—This compound was prepared from triphenylmethylhydrazine hydrochloride according to the method of Wieland.[2] The crude reaction product melting at 57° was used for the rearrangements. A small portion, recrystallized from alcohol, melted at 61°.

Rearrangement of Triphenylmethylazide.—Two portions of triphenylmethylazide of 0.5 g. each were heated in sealed tubes at 225° for one hour. The tarry product of the reaction was examined for the expected rearrangement product, phenylimido-benzophenone, as follows: it was extracted with about 20 cc. of benzene and the extract evaporated to dryness in a flask on the steam bath. No attempt was made first to isolate the pure phenylimido-benzophenone from the residue thus obtained; instead, it was hydrolyzed and identified by its decomposition products, aniline and benzophenone. For this purpose this residue was dissolved in alcohol, a little hydrochloric acid was added to the solution, and the mixture boiled for half an hour in a flask fitted with a reflux condenser. Excess of sodium hydroxide was then added to the solution, and the liquid distilled with steam to isolate the aniline and benzophenone

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[1] *Loc. cit.*

[2] *Ber.*, 42, 3027 (1909).

formed. The milky distillate gave a strong purple color with hypochlorite. It was acidified, the solution washed with ether to remove benzophenone, and the aqueous solution evaporated. It yielded 0.276 g. of substance, equivalent to 60% of the aniline hydrochloride, which could, theoretically, be obtained from the rearrangement of the amount of azide used. From the hydrochloride, the chloroplatinate of aniline was obtained and analyzed.

(1) 0.3772 and (II) 0.1278 g. subs. gave (I) 0.1258 and (II) 0.0413 g. Pt.
Calc. for $C_{12}H_{16}N_2PtCl_6$: Pt, 32.75%. Found: (I) 33.35; (II) 32.32.

The ether extract of the acidified steam distillate on evaporation to dryness gave an oily residue. When this was seeded with a tiny crystal of benzophenone it quickly crystallized. The solid, after recrystallization from alcohol and water, melted at 47–47.5°. A mixture of this substance with benzophenone (melting point 47–47.5°) also melted at 47–47.5°.

These results identify the products of hydrolysis of the chief end product of the action of heat on triphenylmethylazide as aniline and benzophenone. These are the products of hydrolysis of phenylimido-benzophenone. Triphenylmethylazide undergoes rearrangement therefore under the influence of heat, as expressed in the equation

$$(C_6H_5)_3CN_3 \xrightarrow{\text{Heat}} (C_6H_5)_2C = NC_6H_5 + N_2. \qquad (6)$$

The phenylimido-benzophenone produced is then hydrolyzed by the dilute acid:

$$(C_6H_5)_2C = NC_6H_5 + H_2O + HCl \longrightarrow (C_6H_5)_2C = O + C_6H_5NH_3Cl \quad (7)$$

Attempts to isolate the intermediate phenylimido-benzophenone were given up on account of the large proportion of tarry products present.

p**-Chlorophenyl-diphenylmethylhydrazine Hydrochloride,** $(C_6H_4Cl)(C_6H_5)_2C.NH.NH_2.HCl$.—Dichlorodiphenylmethane, $(C_6H_5)_2C.Cl_2$, was prepared according to Mackenzie,[1] and from it *p*-chlorophenyl-diphenylmethylchloride was obtained by the method of Gomberg.[2] The substance used in the preparations to be described melted at 86°. It was analyzed by hydrolysis with standard alkali.

Calc. for $C_{19}H_{14}Cl_2$: hydrolyzable Cl, 11.33%. Found: 11.27.

In the preparation of *p*-chlorophenyl-diphenylmethylhydrazine hydrochloride and symmetrical *bis*-*p*-chlorophenyl-diphenylmethylhydrazine, the proportions of *p*-chlorophenyl-diphenylmethylchloride and hydrazine hydrate used must be varied according to which of these two products is desired. The method used to obtain the mono derivative is given here.[3] *p*-Chlorophenyl-diphenylmethylchloride (5.75 g.) and hydrazine hydrate (4 g.) were boiled with a small amount of absolute ether in a flask fitted

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[1] *J. Chem. Soc.*, 69, 987 (1896).

[2] *Ber.*, 37, 1633 (1904).

[3] The preparation of the *bis*-derivative is described in the following paper.

with a reflux condenser. The hydrazine hydrate did not dissolve in the ether, and the two layers of liquid persisted till the end of the reaction. After a few hours a precipitate appeared, and at the end of eight hours the reaction was finished. The flask was stoppered and allowed to stand overnight. The reaction mixture was then poured through a filter moistened with absolute ether on a Hirsch funnel. The filtrate consisted of two layers. The upper layer was an ethereal solution of *p*-chlorophenyl-diphenylmethylhydrazine and the lower was a mixture of hydrazine hydrate and hydrazine hydrochloride. The ethereal layer was dried over calcium chloride and then an excess of dry hydrogen chloride in absolute ether was added to the solution. After a few minutes, a heavy precipitate of *p*-chlorophenyl-diphenylmethylhydrazine hydrochloride appeared. The flask was cooled in ice for about 15 minutes and the solid then collected on a filter and dried on a clay plate. It melted at 122°. The yield was 4 g.

The compound is not very stable. It is slowly decomposed by the moisture of the air, and all attempts to purify it by recrystallization failed. Consequently the crude substance was used to prepare the azide. It was analyzed by titration by the Volhard method.

0.1524 g. subs. required 4.91 cc. of 0.1 *N* $AgNO_3$.
Calc. for $C_{19}H_{17}ClN_2HCl$: HCl, 10.57. Found: 11.75.

A small amount of symmetrical *bis*-*p*-chlorophenyl-diphenylmethylhydrazine was always formed during the boiling of the *p*-chlorophenyl-diphenylmethylchloride with hydrazine hydrate. It crystallized out of the reaction mixture and was removed by the filtration on the Hirsch funnel. It was washed with alcohol and water to remove adhering traces of hydrazine, etc., and then dried. The yields were always small. The compound melted at 201°.

***p*-Chlorophenyl-diphenylmethylazide,** $(C_6H_4Cl)(C_6H_5)_2CN_3$.—For the preparation of this azide 4.8 g. of the corresponding hydrazine hydrochloride were dissolved in 60 cc. of absolute alcohol, and to this solution were added 30 cc. of hydrochloric acid, containing 7 g. of hydrogen chloride per 100 cc. of the acid. The flask was immersed in ice and 20 cc. of sodium nitrite solution, containing 1.6 g. of sodium nitrite, were run slowly into the solution while the flask was constantly shaken. The original solution in alcohol and acid was clear, but as the sodium nitrite was run in, the solution became cloudy and, on standing a few hours in the cold, the milky emulsion settled out at the bottom of the vessel as a yellowish gum. After the aqueous liquid had been decanted, the gum was dissolved in ether and the solution dried over calcium chloride. When the ether was boiled off, the yield of gum was 3.75 g.

All attempts to crystallize the material were unsuccessful. A variety of solvents and extreme cold were tried without avail. No analyses were therefore attempted, and the crude substance was used directly for rearrangement.

Rearrangement of *p*-Chlorophenyl-diphenylmethylazide.—A solution of 3.75 g. of *p*-chlorophenyl-diphenylmethylazide in ether was placed in a hard glass test-tube, the ether was boiled out, and the tube containing the gum heated in a metal bath. At about 185° a fairly active evolution of gas began. The temperature was slowly raised until 215° was reached at the end of about ten minutes. The tube was then cooled, and the tarry mass examined for the products of rearrangement, phenylimido-chlorobenzophenone and chlorophenylimido-benzophenone, by the isolation of the products of hydrolysis of these two imides. The mass was extracted with ether, the ether extract transferred to a flask and the ether boiled off on the steam bath. About 30 cc. of alcohol and a little hydrochloric acid were added to the residue and the mixture boiled for half an hour with a reflux condenser. The liquid was then made alkaline with sodium hydroxide and distilled with steam. The distillate was a milky liquid containing oily drops which crystallized in standing. With hypochlorite it gave a strong purple color. It was acidified with hydrochloric acid, to convert the anilines into their salts, the ketones were removed by extraction with ether, and the ether extract (*A*) separated from the aqueous solution (*B*). The rearrangement was found to be far from quantitative[1] and on account of the small yields some difficulty was experienced in identifying the products.

(*A*) **Identification of Benzophenone and *p*-Chlorobenzophenone.**—The ether extracts (*A*) of the acidified steam distillates of several reactions like the one described above were combined. The ether was dried over calcium chloride and evaporated in an open dish. A crystalline residue was left. About three-fourths of this residue was dissolved by alcohol. The remainder, when dried on a clay plate, melted at 71–72°. When this substance was mixed with *p*-chlorobenzophenone (melting point 74.5–75.5°), the mixture melted at 72.5–73.5°. These results established the identity of this fraction of the unknown substance with *p*-chlorobenzophenone.

Attempts to isolate pure benzophenone from the alcoholic solution were unsuccessful. Efforts were made to use the fact that benzophenone is much more soluble than *p*-chlorobenzophenone in cold ligroin (boiling point 30–50°). The alcoholic solution was evaporated to dryness, extracted with ligroin, and the extract evaporated to dryness. The crystalline residue was again extracted with ligroin and the ligroin evaporated. The process was repeated once more. On evaporation, the final ligroin solution left behind the roset-shaped aggregates characteristic of *p*-chloro-

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[1] Attempts to improve the yield by the use of acids and other reagents will be made in this laboratory.

benzophenone, and a few drops of oily liquid. When these drops were seeded with a tiny crystal of benzophenone, they crystallized. This action, often observed in this laboratory to be characteristic of benzophenone, was taken as an indication that the oily droplets consisted of benzophenone, but there was not enough pure material to confirm the conclusion.

(*B*) **Identification of Aniline and *p*-Chloroaniline.**—After the steam distillates of several reactions like the one described above had been acidified and extracted with ether, the aqueous solutions (*B*) were combined, made alkaline with excess sodium hydroxide and again extracted with ether. The ether extract was acidified with a little aqueous hydrochloric acid and evaporated to dryness. A white crystalline residue of hydrochlorides of aniline bases was left. This was divided into several portions and treated as follows:

(1) One portion was dissolved in water, made alkaline with sodium hydroxide and extracted with ether. The ether extract was dried over anhydrous potassium carbonate. To it was then added a solution of anhydrous oxalic acid in absolute ether. The white crystalline precipitate which immediately formed was filtered out, dried, and dissolved in a small amount of hot water containing a little oxalic acid. When the liquid was cooled, a precipitate appeared. This oxalate was brought on a filter and dried. The mother liquor gave with hypochlorite a strong purple color, showing definitely the presence of aniline in the original mixture. The oxalate just described was dissolved in a very little water, and to the solution a few drops of ammonia were added. An oil immediately separated, which, on standing a few minutes, solidified. The solid was brought on a filter and dried on a clay plate. It melted at 67.5°. When this substance was mixed with *p*-chloroaniline (melting point 70.5°) the mixture melted at 69.5°. These results showed that this fraction of the unknown substance was *p*-chloroaniline. When burned on a clean copper wire, it gave a green flame, confirming the presence of halogen (chlorine).

(2) Another portion of the dry hydrochlorides described under (*B*) was dissolved in absolute alcohol and, after filtration of the solution, the hydrochlorides were reprecipitated by the addition of absolute ether containing a small amount of dry hydrogen chloride. The precipitate was collected and dried on a clay plate. From it were taken Samples I and II for the analyses given below under C. The alcohol-ether mother-liquor was evaporated to dryness, the residue taken up with absolute alcohol and the hydrochlorides again precipitated by means of absolute ethereal hydrochloric acid. This second precipitate was collected and dried as before. From it, analysis Sample III was taken.

(3) A third portion of the dry hydrochlorides described under (*B*) was treated like the portion (2), except that the precipitation process was carried out a third time. All three yields of precipitate in this case were combined, and from the mixture, analysis Sample IV was taken.

The qualitative results thus far obtained have shown that products of the action of heat on *p*-chlorophenyl-diphenylmethylazide yield on hydrolysis chlorobenzophenone and benzophenone besides aniline and chloroaniline. These are the products to be expected from the hydrolysis of phenylimido-chlorobenzophenone

$$(ClC_6H_4)(C_6H_5)C = NC_6H_5 + H_2O + HCl \longrightarrow (ClC_6H_4)(C_6H_5)CO + C_6H_5NH_3Cl \quad (8)$$

and chlorophenylimido-benzophenone

$$(C_6H_5)_2C = NC_6H_4Cl + H_2O + HCl \longrightarrow (C_6H_5)_2CO + (C_6H_4Cl)NH_3Cl, \quad (9)$$

the two imido ketones which are the anticipated products of the rearrangement of the azide (see Equations 3 and 4).

(*C*) **The Determination of the Ratio of the Rearrangement Products.**—A determination of the ratio in which the two imidoketones are formed was a matter of considerable theoretical interest (see the theoretical part of this paper). For this reason the molecular proportions of the hydrochlorides of the two bases were next determined, the samples enumerated under (*B*) being analyzed volumetrically by the bromination method of Curme.[1]

	Mixed hydrochloride.	0.1*N* $KBrO_3$ required.	Molecular % aniline.	Molecular % *p*-chloroaniline.
(I)	0.0384 g.	14.75 cc.	69.2	30.8
(II)	0.0415	15.68	66.5	33.5
(III)	0.0221	8.14	62.4	37.6
(IV)	0.0418	16.15	74.1	25.9
		Average,	68.1	31.9

The proportions in which the pair of rearrangement products of *p*-chlorophenyl-diphenylmethylazide are formed are very close to those found by Leech for *p*-chlorophenyl-diphenylmethylhydroxylamine (70.8/29.2).

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[1] *J. Am. Chem. Soc.*, 35, 1143 (1913).

The Molecular Rearrangement of *sym.-bis*-Triarylmethylhydrazines.[1]

The fundamental analogy between hydroxylamine and hydrazine is a well-established fact,[2] equally evident from the reactions of the substances and from the parallelism existing between their organic derivatives, a parallelism which extends even to the formation of stereoisomeric oximes and hydrazones.[3] It seems to have escaped comment, however, that in one important respect there exists a gap between the chemistry of hydroxylamine derivatives and that of the corresponding derivatives of hydrazine. Hydroxamic acids[4] RCO.NHOH, dihydroxamic acids[5] RCO.NHO.COR, ketoximes[6] $R_2C : NOH$, and triphenylmethylhydroxylamines[7] $R_3C.NHOH$, under the influence of appropriate reagents, readily undergo molecular rearrangements in which a radical R migrates from the carbon atom originally holding it to the neighboring nitrogen atom. Similar rearrangements[8] of hydrazine derivatives have never been observed or even attempted, as far as we can find. It is worthy of note, too, that even derivatives of hydrogen peroxide, the third member[9] of the hydrazine-hydroxylamine family,[10] undergo rearrangements analogous to those of the hydroxylamine derivatives; this fact has been observed, for instance,

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[1] A brief statement appeared in *Proc. Nat. Acad. Sciences,* 1, 207 (1915) and this article was published as a preliminary report by J. Stieglitz and J. K. Senior in *J. Am. Chem. Soc.* 38, 2727 (1916).

[2] See, for instance, Angeli, *Chem. Zentr.*, 1910, II, 861; Stieglitz and Curme, *Ber.*, 46, 911 (1913).

[3] Hantzsch and Kraft, *Ber.*, 24, 3516 (1891).

[4] Lossen, *Ann.*, 161, 359 (1872), etc.

[5] Lossen, *Ibid.*; L. W. Jones, *Am. Chem. J.*, 48, 1 (1912).

[6] Beckmann, *Ber.*, 19, 988 (1886); 27, 300 (1894), etc.

[7] Stieglitz, Reddick and Leech, *Eighth Intern. Congr. Appl. Chem.*, 25, 443 (1912); Stieglitz and Leech, *Ber.*, 46, 2147 (1913); *J. Am. Chem. Soc.*, 36, 272 (1914); Stieglitz and Stagner, *Ibid.*, 38, 2046 (1916); Stagner, *Ibid.*, 38, 2069 (1916), and Vosburgh, *Ibid.*, 38, 2081 (1916).

[8] The benzidine and related rearrangements are of a different type, although arising no doubt from the same source of instability in the molecules involved (see Stieglitz and Stagner, *J. Am. Chem. Soc.*, 38, 2051 (1916).

[9] Cf. Angeli, *Loc. cit.*; Stieglitz and Curme, *Loc. cit.*; Stieglitz and Leech, *Loc. cit.*

[10] The list might well be extended to include hypochlorous, hypobromous and hypoiodous acids and their derivatives. The members have as a common characteristic an atom with an unstable positive charge and a tendency to convert this atom into the common, stable negative variety.

in the cases of ketone peroxides[1] and triphenylmethyl peroxide.[2] The fundamental analogy between hydrazines, hydroxylamines and peroxides suggested the desirability of investigating hydrazine derivatives from this point of view, and of attempting to close the gap which at present exists between these groups in this one respect. The theory of one of us as to the mechanism and cause of the molecular rearrangements of this type made it appear altogether likely that similar rearrangements might be brought about without great difficulty in hydrazine derivatives. As is known, according to this theory,[3] the rearrangement of a triarylmethylhydroxylamine, for instance, is considered to be due to the formation of a univalent nitrogen derivative by the loss of water, or its equivalent, under the influence of a dehydrating agent like phosphorus pentachloride.

$$R_3C.NHOH \xrightarrow{-HOH} R_3C.N \longrightarrow R_2C:NR. \qquad (1)$$

To effect the rearrangement of the corresponding hydrazines, it seemed only necessary to use a suitable reagent to induce the loss of ammonia.

$$R_3C.NH.NH_3 \xrightarrow{-NH_3} R_3C.N \longrightarrow R_2C:NR. \qquad (2)$$

From the point of view of the electronic theory of valence, we consider[4] that the primary force leading to the rearrangement of hydroxylamine derivatives[5] resides in the *unstable positive charge* on the oxygen atom.[6] There must be a great tendency of the positive hydroxyl group to go over into its common, stable negative form, as it does, if water or its equivalent is taken from the hydroxylamine derivative by dehydrating agents. We have

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[1] Baeyer, *Ber.*, 32, 3627 (1900). The relation of the peroxide rearrangement to the rearrangements of hydroxylamine derivatives was first recognized by Baeyer, but both were given a wrong interpretation (see Stieglitz, *Am. Chem. J.*, 29, 49 (1903); and Stieglitz and Stagner, *Loc. cit.*). Especially the results in this laboratory on the rearrangements of triphenylmethane derivatives make Baeyer's assumptions quite untenable. The peroxides have now been included in our studies of the theory from the point of view of the one of us.

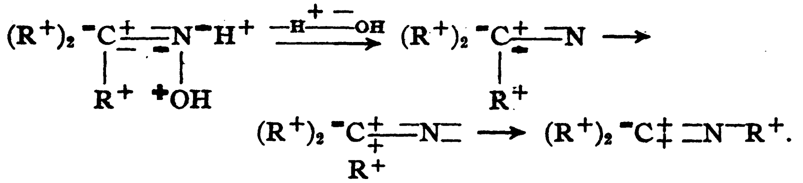
[2] Wieland, *Ber.*, 44, 2550 (1911).

[3] The literature references are given by Stieglitz and Leech, *Loc. cit.*, and Stieglitz and Stagner, *Loc. cit.*

[4] The electronic version of the univalent nitrogen theory of one of us for this and analogous rearrangements is found in detail in *J. Am. Chem. Soc.*, 36, 272 (1914). While the article was in press an article by L. W. Jones appeared (*Am. Chem. J.*, 50, 440 (1913)), giving an interpretation of this theory, differing from the Stieglitz views in some important details, but agreeing with them in the fundamental considerations. See footnote, *J. Am. Chem. Soc.*, *Loc. cit.*, p. 287.

[5] Stieglitz and Leech, *Loc. cit.*

[6] For the rearrangement of the closely related chloroamines similar relations hold, as expressed by Stieglitz and Leech, *Ber.*, 46, 2147 (1913).



$$(R^+)_2{}^-\underset{\underset{R^+}{|}}{C}\stackrel{+\,-}{\underset{-\;-}{—}}\underset{\underset{{}^+OH}{|}}{N}{}^-H^+ \xrightarrow{\overset{+\;-}{-H—OH}} (R^+)_2{}^-\underset{\underset{R^+}{|}}{C}\stackrel{+\,-}{\underset{-}{—}}N \longrightarrow$$

$$(R^+)_2{}^-\underset{R^+}{C}\stackrel{+\,-}{\underset{+}{—}}N\overset{-}{\underset{-}{}} \longrightarrow (R^+)_2{}^-C\ddagger\stackrel{-}{\underset{-}{=}}N^-R^+. \quad (3)$$

The shifting of electrons is indicated by heavy type for the charges which are about to undergo change.

In hydrazines, $H_2N \stackrel{+\,-}{—} NH_2$, there is likewise an unstable positive group,[1] which should have a decided tendency to go over into the stable negative radical $N\equiv$ as it exists in ammonia $N\equiv(H^+)_3$. If this tendency showed itself in the loss of ammonia by certain hydrazine derivatives, it might lead to a series of reactions similar to those just described and ending in the postulated molecular rearrangement.

From this point of view the reagents that suggest themselves for effecting such rearrangements are strong acids and zinc chloride. To our disappointment, not a single rearrangement of this character was observed in studying the effect of concentrated sulfuric acid on a great variety of hydrazine derivatives.[2] Simple hydrolysis or sulfonation was the only reaction detected. The heating of dry hydrochlorides of hydrazine derivatives was no more effective in producing rearrangements.

Although these experiments were preliminary ones, they were sufficiently extensive and thorough to make us pause and consider the theoretical relations in greater detail. In the case of the hydroxylamine derivatives which undergo rearrangement, there can be no question as to the distribution of the original charges—the hydroxyl in hydroxylamine $H_2N \stackrel{-\,+}{—} OH$ is originally positive and ultimately forms water (or its equivalent) with a negative hydroxyl group.[3] For the substituted hydrazines, however, we have as yet no trustworthy basis for determining the exact electronic structure.[4] A single illustration will make the point clear: triphenylmethylhydrazine may have either of two electronic structures:

(A) $(C_6H_5)_3C.HN \stackrel{-\,+}{—} NH_2$ or (B) $(C_6H_5)_3C.HN \stackrel{+\,-}{—} NH_2$

Either one, according to the mechanism of the possible loss of ammonia, might account for the failure of acids to induce the loss of ammonia and subsequent rearrangement. In B, for instance, the NH_2 group is already negative and in its most stable electronic structure, and so the funda-

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[1] Stieglitz and Curme, *Ber.*, 46, 911 (1913).

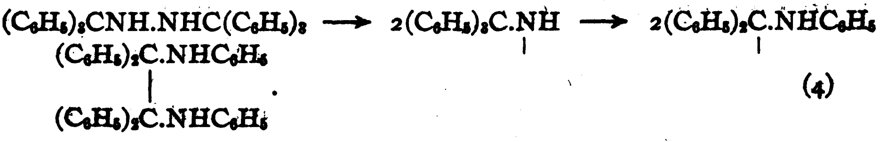
[2] Some of these experiments and their results will be described later by Mr. Senior.

[3] See the evidence given by Stieglitz, *J. Am. Chem. Soc.*, 36, 288 (1914), and by Jones, *Ibid.*, 36, 1268 (1914).

[4] In the salts the wholly negative nitrogen atom is probably the one that is combined with the acid, but this does not help us toward a solution of the problem before us.

mental force leading to its elimination from the molecule as ammonia with the subsequent rearrangement of the organic radical might well be altogether lacking.[1] These considerations made it appear desirable to attempt the rearrangement of a *symmetrical molecule*, *bis*-triphenylmethylhydrazine, about whose electronic structure there can be no doubt: $(C_6H_5)_3C.HN \overset{+\quad -}{\text{——}} NH.C(C_6H_5)_3$. A loss of triphenylmethylamine *from either side* would yield a univalent nitrogen derivative $(C_6H_5)_3C.N$ and rearrangement should inevitably follow. Whether this argument is ultimately found to be right or wrong, it certainly is of peculiar interest that in this instance we were at last successful in effecting a rearrangement. Zinc chloride was the agent used. The occurrence of a rearrangement was proved by the isolation and identification of aniline as a product of the action: aniline could be formed only by migration of a phenyl radical from carbon to nitrogen—the typical migration of this class of molecular rearrangements. As far as we can discover, this is the first time any hydrazine derivative has been observed to rearrange in this fashion. *sym.-bis-p*-Chlorophenyl-diphenylmethylhydrazine, $(ClC_6H_4)(C_6H_5)_2C.NH.NHC(C_6H_5)_2(C_6H_4Cl)$, has been found by us to suffer the same rearrangement, producing aniline and, probably, *p*-chloroaniline as well. This agrees with the results obtained in the molecular rearrangements of *p*-chlorophenyl-diphenylmethylhydroxylamine $(ClC_6H_4)(C_6H_5)_2C.NHOH$ and the corresponding chloroamine $(ClC_6H_4)(C_6H_5)_2C.NHCl$.

As to the mechanism of the rearrangement of the hydrazine we can state nothing positive, since the action is not a smooth one and the products, other than aniline and triphenylmethane, a product of a parallel reaction, have not, as yet, been identified. It is altogether likely, however, that the rearrangement is the result either of a primary dissociation into a univalent nitrogen derivative, along the lines indicated above, or of a dissociation into bivalent nitrogen radicals, according to



$$(C_6H_5)_3CNH.NHC(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C.\underset{|}{N}H \longrightarrow 2(C_6H_5)_2\underset{|}{C}.NHC_6H_5$$

$$\begin{array}{l}(C_6H_5)_2C.NHC_6H_5\\ \qquad\quad |\\ (C_6H_5)_2C.NHC_6H_5\end{array} \qquad (4)$$

The latter reaction would correspond to the molecular rearrangement of triphenylmethylperoxide under the influence of heat, as observed and interpreted by Wieland.[2] It may be remarked in this connection that, in the case of the rearrangement of β-triphenylmethyl-β-methylhydroxylamine, where the same alternative was presented, exhaustive examina-

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[1] A decomposition $(C_6H_5)_3C.NH - NH_2 \longrightarrow (C_6H_5)_3C.NH_2 + (NH)$ would not lead to a rearrangement. This would hold either for A or B.

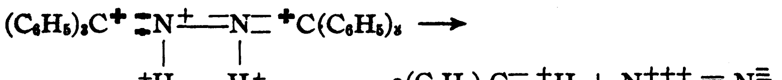
[2] *Loc. cit.*

tion of the secondary products finally decided against this type of rearrangement for the hydroxylamine compound in question.[1]

The formation of triphenylmethane is probably the result of a parallel decomposition of the symmetrical hydrazide, as expressed in the equation

$$(C_6H_5)_3C.NH.NH.C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3CH + N_2. \qquad (5)$$

The reaction is of some interest from the electronic point of view. We have:[2]



$$(C_6H_5)_3C^{+}\,{=}\underset{\substack{|\\ {}^{+}H}}{N}\overset{\pm}{-\!\!=}\underset{\substack{|\\ H^{+}}}{N}{=}\;{}^{+}C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C^{-}\;{}^{+}H + N^{+++} \equiv N^{\equiv} \qquad (6)$$[3]

According to this equation, the instability of the radical $\equiv N^{+}$ leads to a breakdown of the molecule, in which the extraordinarily stable nitrogen is formed by a transfer of electrons to (*i. e.*, reduction of) the methyl carbon atoms.[4]

Experimental Part.[5]

sym.-bis-**Triphenylmethylhydrazine,** $(C_6H_5)_3CNH.NHC(C_6H_5)_3$. — The compound was prepared according to the method described by one of us,[6] and purified by the method of Wieland.[7] The substance used for rearrangement melted at 210°.

Rearrangement of *sym.-bis*-Triphenylmethylhydrazine.—One gram of the substance was triturated with 6 g. of anhydrous zinc chloride in a warm mortar. The mixture turned bright yellow. It was transferred to a hard glass test-tube and heated in a metal bath at 300° for ten minutes. After the tube had been cooled, the dark-colored melt was dissolved out with ether and water. Sufficient sodium hydroxide was added to get all the zinc into alkaline solution and the liquid was then shaken twice

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[1] Stieglitz and Stagner, *J. Am. Chem. Soc.*, 38, 2046 (1916).

[2] The electronic structure given to free nitrogen is simply illustrative. The formula used agrees with the formation of nitrogen from ammonia and nitrous acid, but the reversed action, the saponification of nitrogen (nitrous acid nitril) does not seem to have been accomplished as yet. Free energy calculations, made at the suggestion of Professor G. N. Lewis, indicate, as anticipated, that the hydrolysis would involve the absorption of a great deal of energy. The combination of nitrogen, as a substituted amine, has also not yet been accomplished, although preliminary experiments to combine it with hydrogen chloride were made by one of us some years ago. An investigation of these problems and of the electronic structure of nitrogen is being undertaken.—J. S.

[3] The electronic changes are indicated by heavy type.

[4] The decomposition of the hydrazide in this direction is being further investigated by Mr. R. L. Brown.

[5] I am glad to take this opportunity to thank my young collaborator for his painstaking experimental work and tenacious energy in an investigation that at first brought only disappointing results.—J. S.

[6] See the preceding article.

[7] *Ber.*, 42, 3022 (1909).

in a separatory funnel with ether. The ether layers were combined, transferred to a flask, and the ether boiled off on the steam bath. A tarry residue remained behind. With the object of having any aniline derivative present hydrolyzed, this residue was dissolved in alcohol and some hydrochloric acid added to the solution, which was then boiled for half an hour under a reflux condenser. Excess of sodium hydroxide was next added, and the mixture steam distilled. The cloudy distillate was collected in two portions. The first portion gave a strong purple color with hypochlorite, thus showing the presence of aniline. When the droppings ceased to give this test, the receiver was changed. Throughout the distillation a white solid (later identified as triphenylmethane) was deposited in the condenser. When this substance ceased to come over, distillation was stopped. The first portion of the distillate was acidified with hydrochloric acid and extracted with ether, the acid solution (A) being preserved for further investigation. The second portion of the distillate was also extracted with ether, and the water layer discarded. The two ether extracts were combined and to them was added the ethereal solution of the solid which collected in the condenser.

The acid solution (A) of the first distillate, on evaporation, yielded a small amount of white crystalline residue. From the qualitative tests, the substance was presumed to be aniline hydrochloride. For the quantitative study, the process described had to be repeated several times to obtain sufficient material for analysis. When this material was treated with chloroplatinic acid, the precipitate was found to be pure aniline chloroplatinate.

0.1375 g. subs. gave 0.0451 g. Pt. Calc. for $C_{12}H_{16}N_2PtCl_6$: Pt, 32.75. Found: 32.80.

The combined ether extracts of the distillate were dried over calcium chloride and the ether then evaporated. There was left a gummy residue which, on being scratched, quickly crystallized. The crystals, when dried on a clay plate, melted at 79–81°. When the yields of several experiments such as the one described above had been collected, the substance was crystallized from alcohol. After two recrystallizations, the compound apparently had a constant melting point of 81.5–82°.

0.1496 and 0.1620 g. subs. gave 0.0834 and 0.0903 g. H_2O and 0.5062 and 0.5476 g. CO
Calc. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 92.28 and 92.19; H, 6.24 and 6.24.

Qualitative and quantitative (combustion) tests showed the absence of nitrogen, and a qualitative test for halogen also proved negative. The melting points of mixtures showed that the material was neither triphenylcarbinol nor triphenylmethylether, which might have been formed by hydrolysis or alcoholysis of the hydrazine or of one of its decomposition products. A mixture of equal quantities of triphenylmethane (m. p. 89–90°) and the substance, melted at 85–89°, and a mixture of four parts of the substance with one part of triphenylmethane showed no depression of the melting point of the substance. The compound gave the (spectroscopic) *p*-rosaniline test for triphenylmethane. The substance seems therefore to be somewhat impure triphenylmethane.[1]

In an effort to obtain a smoother rearrangement and reaction, attempts were made to rearrange *sym.-bis*-triarylmethylhydrazine by heat (in a sealed tube) and also by the action of dry hydrogen chloride at 300°. In both cases the substance was decomposed, but no trace of aniline could be found in the hydrolyzed reaction products. The reactions were not further investigated.[2]

sym.-bis-p-**Chlorophenyl-diphenylmethylhydrazine,** $(C_6H_4Cl)(C_6H_5)_2CNH.NHC(C_6H_5)_2(C_6H_4Cl)$.—Dichlorodiphenylmethane, $(C_6H_5)_2CCl_2$, was prepared according to Mackenzie,[3] and from it *p*-chlorophenyl-diphenylmethylchloride by the method of Gomberg.[4] The action of this chloride on hydrazine gives fair yields either of the mono-substituted hydrazine or of the *bis*-derivative, according to the conditions used. The preparation of the mono-derivative is described in the preceding article. For the preparation of the bis-derivative, *p*-chlorophenyl-diphenylmethylchloride (5.75 g.) and hydrazine hydrate (2 g.) were boiled for seven hours in the presence of a small amount of absolute ether in a flask fitted with a reflux condenser. A considerable amount of precipitate was formed. The mixture was filtered on a Hirsch funnel, the filter being wet with ether, and the precipitate washed with ether, water and alcohol to remove adhering impurities. When dried on a clay plate, it melted at 201°. Attempts were made to recrystallize this material by the same method as that used in the case of *sym-bis*-triphenylmethylhydrazine. The substance was dissolved in hot benzene. On addition of warm alcohol it crystallized out. There was no apparent decomposition, but that some change had occurred was shown by the fact that the melting point of the substance was much lower than that of the original substance. Several repetitions of the process yielded a product melting at 171°. This substance was analyzed.

0.2903 g. subs. gave 0.1377 g. Ag Cl (Carius' method).

(I) 0.3610 g. subs. gave 5.12 cc. of N_2 at 28.0° and 729.9 mm.; (II) 0.3727 g. gave 5.31 cc. at 28.8° and 729.1 mm.

Calc. for $C_{38}H_{30}N_2Cl_2$: Cl, 12.12; N, 4.79. Found: Cl, 11.73; N, (I) 1.54, (II) 1.54.

On account of the obvious decomposition encountered in the attempt to recrystallize it, the crude substance melting at 201° was next analyzed.

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[1] To confirm this conclusion and especially to secure sufficient material for a molecular-weight determination, the preparation will be repeated as soon as occasion offers. (Since this was written, Mr. R. L. Brown has obtained the product as pure triphenylmethane, melting at 92°.—J. S.)

[2] They are now being investigated by Mr. R. L. Brown.

[3] *J. Chem. Soc.*, **69**, 987 (1896).

[4] *Ber.*, **37**, 1633 (1904).

0.3600 g. subs. gave 21.21 cc. of N_2 at 22.4° and 740.1 mm.
Calc. for $C_{38}H_{30}N_2Cl_2$: N, 4.79. Found: 6.63.

The high nitrogen content of this crude substance melting at 201° was supposed to be due to an impurity of hydrazine. The substance was assumed for the present to be *sym.-bis-p*-chlorophenyl-diphenylmethylhydrazine and was used in a preliminary way as material for rearrangements. This compound and its decomposition product, melting at 171°, will be investigated further in this laboratory.

Rearrangement of *sym.-bis-p*-Chlorophenyl-diphenylmethylhydrazine.—The rearrangement was carried out with the aid of zinc chloride in exactly the same way as described above for the corresponding chlorine-free compound. A considerable portion of the original melt was found to be insoluble in both ether and water. Steam distillation, after the hydrolysis of the product (see above), yielded a slightly cloudy distillate which gave a purple color with hypochlorite. No substance solidified in the condenser as in the case of the triphenylmethyl compound. The distillate was acidified with hydrochloric acid and shaken with ether. After the ether layer had been dried over calcium chloride, it was evaporated to dryness. The gummy residue left behind was so trifling in amount that it was not further investigated. The acidified water layer was evaporated to dryness. A small white crystalline residue was left behind. This was presumably a mixture of the hydrochlorides of aniline and *p*-chloroaniline.

When the yields of several reactions like the one described above had been collected and combined, the substance was dissolved in water, and a little sodium hydroxide added to the solution. The solution was shaken twice with ether, and the ether layer separated and dried over anhydrous potassium carbonate. To it was added an absolute ethereal solution of anhydrous oxalic acid. The precipitate formed was filtered out and dried on a clay plate. A small portion of it, when heated on a clean copper wire, gave a green flame, indicating that probably some *p*-chloroaniline was present. The main part of the precipitate was dissolved in a small amount of hot water containing a little oxalic acid. When the solution was cooled, a crystalline precipitate separated out. This was filtered off and dried. The mother liquor gave a strong purple color with hypochlorite, thus confirming the presence of aniline. The precipitate was dissolved in a little water and a few drops of ammonia added. The solution became cloudy, but the expected separation of solid *p*-chloroaniline did not occur. The solution was shaken with ether and the ether layer separated and evaporated to dryness. When the small gummy residue was scratched with a tiny crystal of *p*-chloroaniline, it crystallized. This indicated that the gum was probably impure *p*-chloroaniline, but the amount of material was too small to permit of further identification.

Attempts to Rearrange Unsymmetrical Hydrazines and Hydrazones.

A number of attempts were made to rearrange unsymmetrical hydrazines and hydrazones. These attempts were in all cases unsuccessful. A short account of them is appended.

Triphenylmethylhydrazine Hydrochloride, $(C_6H_5)_3C—NH—NH_2HCl$.—The preparation of this compound has already been described.[1] Some of the substance (0.5 g.) was triturated with anhydrous zinc chloride (3 g.) and the mixture heated in a test tube to 300°. No trace of aniline could be detected in the hydrolyzed reaction product.

Benzophenonehydrazone, $(C_6H_5)_2C=NNH_2$.—The substance was prepared according to Curtius.[2] The sample used melted at 96.5°. A small portion was heated for half an hour at 100° with an excess of concentrated sulfuric acid. No aniline or aniline sulfonate could be detected in the reaction product.

Benzophenonehydrazone Hydrochloride, $(C_6H_5)_2CNNH_2HCl$.—The substance was prepared according to Curtius.[3] The sample used melted at 182.5°. One gram of substance was heated to 275° for ten minutes in a stream of dry hydrogen chloride. No aniline could be detected in the reaction product.

Benzophenonephenylhydrazone, $(C_6H_5)_2C = NNH(C_6H_5)$.—The substance was prepared according to Pickel.[4] The sample used melted at 136.5°. Some of the substance (2 g.) was heated for one hour at 100° with 20 cc. of concentrated sulfuric acid. No trace of aniline could be found in the reaction product. When the substance was treated at room temperature with dry hydrochloric acid gas, it was observed to turn red and absorb two molecules of hydrochloric acid which were given off again when the addition product was heated in the air. No formation of aniline could be detected.

One phenyl hydrazine derivative, after treatment with zinc chloride, gave a test for aniline. But as this might have been formed from the original substance by some process other than intramolecular rearrangement, its presence was not considered significant.

α-Triphenylmethyl-β-phenylhydrazine, $(C_6H_5)_3C—NHNH(C_6H_5)$.—The substance was prepared according to the method of Gomberg.[5] The sample used melted at 130°. Some of the compound (0.5 g.) was triturated with 3 grams of anhydrous zinc chloride and the mixture heated at 300°. The steam distillate of the hydrolyzed reaction product gave a purple color with hypochlorite. It is not known whether the aniline, the presence

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[1] See the preceding article.

[2] Curtius and Rauterberg, *J. prakt. Chem.*, [2] 44, 194 (1891).

[3] Curtius and Rauterberg, *Loc. cit.*

[4] Pickel, *Ann.*, 232, 228 (1886).

[5] Gomberg and Berger, *Ber.*, 36, 1089 (1903).

of which is thus indicated, is formed by intramolecular rearrangement or by some other method. Lack of time prevented further investigation of the subject for the present. Further and more exhaustive work along all the lines opened by the experiments tried in this preliminary investigation will be carried out in the Kent Chemical Laboratory.

In conclusion I wish to express my gratitude to Professor Stieglitz under whose direction this work was done, and to whom I am much indebted for the kind assistance and advice which enabled me to carry it out.