THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYL-AZIDES.[1]

BY JAMES KUHN SENIOR.[2]

Molecular rearrangements have been observed by Stieglitz and his collaborators in the triphenylmethane series when triphenylmethyl hydroxylamines[3] $Ar_3C.NHOH$ are subjected to the action of phosphorus pentachloride, and when triphenylmethylhalogenamines[4] $Ar_3C.NH(Hal)$ are treated with alkaline reagents. These rearrangements are entirely analogous,[5] 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 triphenyl-methane series were anticipated and explored as the result[6] 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[7] derivatives, $RCO.N$, $R_3C.N$, etc., made it appear certain that triphenyl-methylazides $(C_6H_5)_3C.N_3$ 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[8] alone would be required

$$(C_6H_5)_3C.N(N_2) \xrightarrow{\text{Heat}} (C_6H_5)_3C.N + N_2 \longrightarrow (C_6H_5)_2C:NC_6H_5 + N_2. \quad (1)$$
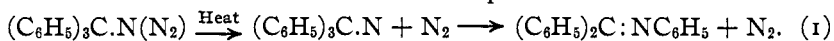
With the object of determining these relations, I undertook, at the

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

[2] The work presented in this paper forms, in part, the basis of a dissertation presented to the University of Chicago in partial fulfilment of the requirements for the Ph.D. degree.

[3] Stieglitz, Reddick and Leech, *Eighth Intern. Congr. Appl. Chem.*, **25**, 44 (1912); Stieglitz and Leech, *Ber.*, **46**, 2147 (1913); and THIS JOURNAL, **36**, 272 (1914).

[4] Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913); Vosburgh, THIS JOURNAL, **38**, 2081 (1916).

[5] The literature references are given by Stieglitz and Leech, THIS JOURNAL, **36**, 272 (1914), and Stieglitz and Stagner, *Ibid.*, **38**, 2046 (1916).
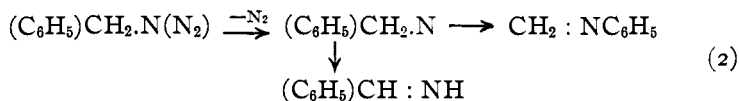
[6] Cf. *Ber.*, **46**, 2147 (1913).

[7] 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); THIS JOURNAL, **36**, 276, 280, 288; and Jones, *Loc. cit.*, and *Am. Chem. J.*, **48**, 1 (1912).

[8] 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:

$$(C_6H_5)CH_2.N(N_2) \xrightarrow{-N_2} (C_6H_5)CH_2.N \longrightarrow CH_2 : NC_6H_5$$
$$\downarrow \qquad\qquad\qquad (2)$$
$$(C_6H_5)CH : NH$$

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[4] 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.
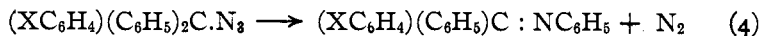
$$(C_6H_5)_2C : NC_6H_5 + HOH + HCl \longrightarrow (C_6H_5)_2CO + C_6H_5NH_3Cl. \quad (3)$$
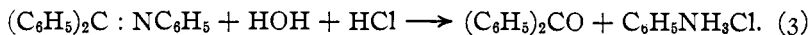
As a further main object of the present investigation, it was proposed to examine substitution derivatives of this azide, such as $(XC_6H_4)(C_6H_5)_2C.N_3$ and $(XC_6H_4)(YC_6H_4)(C_6H_5)C.N_3$. In the rearrangement of the intermediate univalent nitrogen derivatives, in some of the molecules the phenyl 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
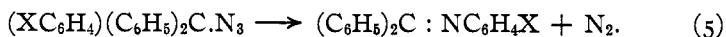
[1] Beckmann, *Ber.*, **19,** 988 (1886); **27,** 300 (1894); Hoogewerff and van Dorp, *Rec. trav. chim.*, **8,** 173 (1889); Hantzsch, *Ber.*, **24,** 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng., Kyoto*, **1,** 254 (1908); **2,** 368 (1909–1910); **6,** 1 (1913); *Ibid.*, **1,** 25 (1914); cf. Stieglitz 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

[1] THIS JOURNAL, **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 triphenylmethyl-hydrazine 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.

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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.

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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 triphenyl-methylazide 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 to 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

[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 0.1278 g. subs. gave 0.1258 and 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

$$(C_6H_5)_3CN_3 \xrightarrow{\text{Heat}} (C_6H_5)_2C = NC_6H_5 + N_2. \qquad (6)$$
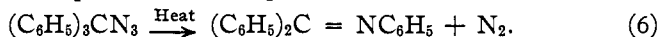
The phenylimido-benzophenone produced is then hydrolyzed by the dilute acid:

$$(C_6H_5)_2C = NC_6H_5 + H_2O + HCl \longrightarrow (C_6H_5)_2C = O + C_6H_5NH_3Cl \quad (7)$$
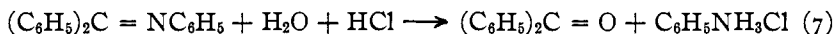
Attempts to isolate the intermediate phenylimido-benzophenone were given up on account of the large proportion of tarry products present.

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$_2$HCl: HCl, 10.57.   Found: 11.75.

A small amount of symmetrical bis-p-chlorophenyl-diphenylmethyl-hydrazine 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:
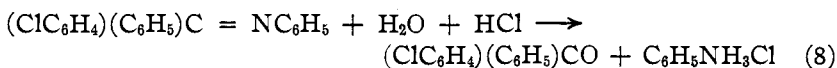
(1) One portion was dissolved in water, made alkaline with sodium hydroxide and extracted with ether. The ether extract was dried over anhydrous potassium carbonate. To it was then added a solution of anhydrous oxalic acid in absolute ether. The white crystalline precipitate which immediately formed 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.
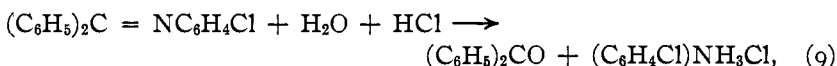
(3) A third portion of the dry hydrochlorides described under (B) was treated like the portion (2), except that the precipitation process was carried out a third time. All three yields of precipitate in this case were combined, and from the mixture, analysis Sample IV was taken.

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

$$(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{C} = \text{NC}_6\text{H}_5 + \text{H}_2\text{O} + \text{HCl} \longrightarrow$$
$$(\text{ClC}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{CO} + \text{C}_6\text{H}_5\text{NH}_3\text{Cl} \quad (8)$$

and chlorophenylimido-benzophenone

$$(\text{C}_6\text{H}_5)_2\text{C} = \text{NC}_6\text{H}_4\text{Cl} + \text{H}_2\text{O} + \text{HCl} \longrightarrow$$
$$(\text{C}_6\text{H}_5)_2\text{CO} + (\text{C}_6\text{H}_4\text{Cl})\text{NH}_3\text{Cl}, \quad (9)$$

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.	0.1N KBrO₃ 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).

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.

CHICAGO, ILL.

[1] THIS JOURNAL, **35,** 1143 (1913).