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

THE MOLECULAR REARRANGEMENT OF *sym.-bis*-TRIARYLMETHYLHYDRAZINES.[1] PRELIMINARY REPORT.

BY JULIUS STIEGLITZ AND JAMES KUHN SENIOR.[2]

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The fundamental analogy between hydroxylamine and hydrazine is a well-established fact,[3] 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.[4] 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[5] RCO.NHOH, dihydroxamic acids RCO.NHO.COR, ketoximes[7] $R_2C : NOH$, and triphenylmethylhydroxylamines[8] $R_3C.NHOH$, 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[9] 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[10] of the hydrazine-hydroxylamine family,[11] undergo rearrangements analogous to those of the hydroxylamine derivatives; this fact has been observed, for instance,

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[1] A brief statement was published in *Proc. Nat. Acad. Sciences*, 1, 207 (1915).

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

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

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

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

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

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

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

[9] 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, THIS JOURNAL, 38, 2051 (1916).

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

[11] 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.

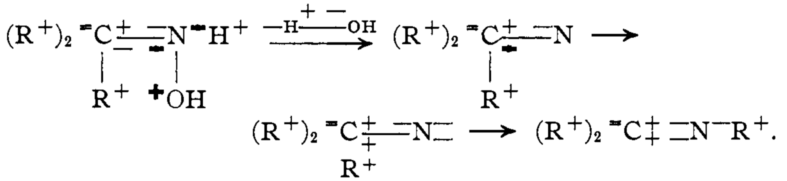
[2] Wieland, *Ber.*, 44, 2550 (1911).

[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 THIS JOURNAL, **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, THIS JOURNAL, *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).



$$\underset{\substack{|\\R^+}}{(R^+)_2{}^{-}C}\overset{+}{\underset{-}{—}}\underset{\substack{|\\\mathbf{+}OH}}{\overset{-}{\underset{\mathbf{-}}{—}}N}{}^{\mathbf{-}}H^+ \xrightarrow{-\overset{+}{H}\text{——}\overset{-}{OH}} \underset{\substack{|\\R^+}}{(R^+)_2{}^{-}C}\overset{+}{\underset{\mathbf{-}}{—}}\overset{-}{—}N \longrightarrow$$

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

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

In hydrazines, $H_2N\overset{+\;\;-}{—}NH_2$, 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 $H_2N\overset{-\;\;+}{—}OH$ 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) $(C_6H_5)_3C.HN\overset{-\;\;+}{—}NH_2$ or (B) $(C_6H_5)_3C.HN\overset{+\;\;-}{—}NH_2$

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).

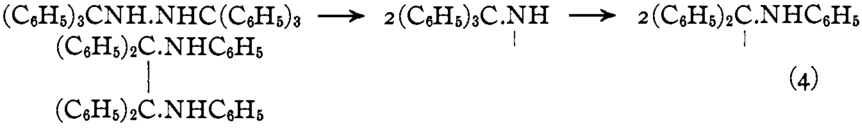
[2] Some of these experiments and their results will be described later by Mr. Senior.

[3] See the evidence given by Stieglitz, THIS JOURNAL, 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: $(C_6H_5)_3C.HN \overset{+\ \ -}{\text{——}} NH.C(C_6H_5)_3$. 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 a 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



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

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

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.

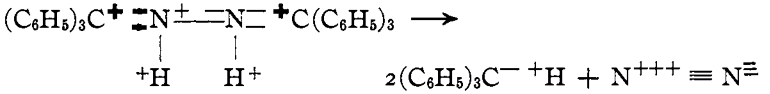
[2] *Loc. cit.*

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]



$$(C_6H_5)_3C^{\boldsymbol{+}}\,\boldsymbol{\sqsupset}\underset{{}^{+}H}{\underset{|}{N}}\overset{\pm}{-}\!\!=\underset{H^{+}}{\underset{|}{N}}\sqsubset\,{}^{\boldsymbol{+}}C(C_6H_5)_3 \longrightarrow 2(C_6H_5)_3C^{-}\,{}^{+}H + N^{+++}\equiv N^{\overset{+}{=}}$$

(6)[3]

According to this equation, the instability of the radical $\sqsupset N^{+}$ 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, THIS JOURNAL, **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°.

(I) 0.1496 and 0.1620 g. subs. gave 0.0834 and 0.0903 g. H_2O and 0.5062 and 0.5476 g. CO_2
Calc. for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: (I) 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,** $(C_6H_4Cl)(C_6H_5)_2$-$CNH.NHC(C_6H_5)_2(C_6H_4Cl)$.—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, *Am. Chem. J.*, **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.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

HALOGENATION. XIII. METHODS OF ESTIMATION OF SEMICARBAZIDE, SEMIOXAMAZIDE AND OXALYLHYDRAZIDE BY THEIR INTERACTIONS WITH HALOGENS AND HALOGEN OXYACIDS.

BY RASIK LAL DATTA AND JOGENDRA KUMAR CHOUDHURY.

Received February 28, 1916.

In a previous paper[1] one of us has given reactions for the volumetric estimation of semicarbazide, using potassium chlorate, bromate and iodate in the presence of strong hydrochloric acid as oxidizing agents. Since hydrochloric acid decomposes chlorate, bromate and iodate with the evolution of halogens, the reactions described are evidently due to free halogens only. Hence a systematic study of the reactions of semicarbazide with the potassium salt of halogen oxyacids with dilute sulfuric acid was undertaken. Furthermore, it was found that substances which are similar in constitution, as those containing a hydrazine group—$NHNH_2$, also undergo decomposition when subjected to the action of the halogens and halogen oxyacids with the liberation of a constant volume of nitrogen.

When semicarbazide is treated with potassium bromate, iodate or periodate in conjunction with sulfuric acid, a quantity of nitrogen which is always three-fourths of the theoretical is liberated. Bromine water also gives the same amount of nitrogen. Chlorine, which cannot be obtained in suitable concentration, is not suitable for such reactions. Potassium chlorate and sulfuric acid do not cause evolution of nitrogen since semicarbazide hydrochloride is stable in the presence of chloric acid and is not decomposed by it. Hypobromite solutions decompose semicarbazide with quantitative evolution of nitrogen. These reactions could be used for the volumetric estimation of the compound, since a constant quantity of nitrogen is always evolved under different conditions of dilution. Semioxamazide is also decomposed by the halogen oxyacids with the liberation of three-fourths of its nitrogen. With bromine, as also with hypobromite, quantitative liberation of nitrogen is the result. Oxalylhydrazide is decomposed by potassium bromate, iodate or periodate in conjunction with sulfuric acid as also by bromine water and hypobromite with the evolution of nitrogen, carbon diozide and carbon monoxide. The evolu-

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[1] Datta, THIS JOURNAL, 36, 1014 (1914).