Therefore, from these points of view, the "nascent state" may be defined more comprehensively as *an unstable condition of a substance which manifests an adaptability and a tendency to lose electrons or to gain electrons and thereby revert to a more stable condition. If the substance (ion, atom, or compound) lose negative electrons it acts as a reducing agent. If it combines with negative electrons it acts as an oxidizing agent.* As a matter of fact practically all actions classed as "nascent" are of an oxidation or a reduction type.

CINCINNATI, OHIO.

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

THE MOLECULAR REARRANGEMENT OF TRIARYLMETHYLHYDROXYLAMINES AND THE "BECKMANN" REARRANGEMENT OF KETOXIMES.[1]

BY JULIUS STIEGLITZ AND PAUL NICHOLAS LEECH.[2]

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Acid halogen amides[3] RCONH(Hal), hydroxamic acids RCONHOH, dihydroxamic acids[4] RCO.NH.OCOR, and acid azides[5] $RCON_3$ undergo readily, under the influence of appropriate reagents, molecular rearrangements as the result of which derivatives of the amines RNH_2 are formed. According to the theory of one of us[6] all of these rearrangements may be interpreted as resulting from the primary formation and subsequent rearrangement of a *univalent* nitrogen derivative, acyl imide, RCO.N<. The reagents used for effecting the rearrangement are in each instance those one would expect to use on the basis of this theory to facilitate the formation of the univalent nitrogen derivative and bring about the re-

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[1] See a preliminary report (abstract) by Stieglitz, Reddick and Leech, *VIII Internat. Congr. Appl. Chem.*, **25**, 443 (1912), and by Stieglitz and Leech, *Ber.*, **46**, 2147 (1913).

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

[3] A. W. Hofmann, *Ber.*, 14, 2725 (1882); **15**, 408 (1883); Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 373 (1887); **8**, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893), etc.

[4] Lossen, *Ann.*, **161**, 359 (1872), etc.; Thiele and Pickard, *Ibid.*, **309**, 189 (1899); and especially L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

[5] Curtius, *Ber.*, **27**, 778 (1895); *J. prakt. Chem.*, **50**, 289 (1894), etc.

[6] Stieglitz, *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); Stieglitz and Earle, *Ibid.*, **30**, 399, 412 (1903); Stieglitz and Slossen, *Ber.*, **34**, 1613 (1901); Slossen, *Am. Chem. J.*, **29**, 289 (1903); Hilpert, *Ibid.*, **40**, 155 (1908); Stieglitz and Peterson, *Ber.*, **43**, 782 (1910); Peterson, *Am. Chem. J.*, **46**, 325 (1911); Stieglitz and Leech, *loc. cit.*; Stieglitz and Vosburgh, *Ber.*, **46**, 2151 (1913); Schroeter, *Ber.*, **42**, 2340 (1909); **44**, 1207 (1911); Stoermer, *Ibid.*, **42**, 3133; Wieland, *Ibid.*, **42**, 4207 (1909); Montague, *Ibid.*, **43**, 2014 (1910); L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

arrangement. Thus, in Hofmann's rearrangement of acid halogen amides, bases are used and the reaction is interpreted as following the course:[1]

$$\mathrm{RCONHBr + NaOH \longrightarrow RCONNaBr + HOH \longrightarrow}$$
$$\mathrm{RCO.N< + NaBr + HOH \longrightarrow CO : NR + NaBr + H_2O} \quad (1)$$

and

$$\mathrm{CO : NR + 2NaOH \longrightarrow RNH_2 + Na_2CO_3 + H_2O} \quad (2)$$

Isocyanates CO : NR have indeed been the first isolated[2] products of this rearrangement. For dihydroxamic acids, bases are also used to effect the rearrangement, the salts formed decomposing in a way analogous to that indicated for the halogen amides, and again, isocyanates have been observed as the first product of the rearrangement.[3] For hydroxamic acids, RCO.NHOH, dehydrating agents or dry distillation are employed, and with acid azides $\mathrm{RCO.N_3}$ gentle heat alone is sufficient to cause an evolution of nitrogen, leading to the formation of isocyanates[4] and their derivatives (*e. g.*, of urethanes when azides are warmed with alcohols). Where the formation of univalent nitrogen is interfered with, as in the case of alkyl derivatives RCO.NR'(Hal)[5] and RCO.NR'OH,[6] no corresponding rearrangement has heretofore been brought about by the reagents and under the conditions effective with the nonalkylated compounds.

When the above theory was developed it was recognized that certain important questions remained to be solved in connection with it.[7] A number of these have already been answered[8] by the investigations carried on continuously in this laboratory. One of the most important of the problems still under investigation[9] from several sides is that of the theory of the rearrangement of ketoximes, a rearrangement discovered and first investigated by Beckmann.[10] The work reported on in this paper is intended to throw some further light on this problem.

[1] Stieglitz, *loc. cit.*

[2] Hofmann, *Ber.*, **15**, 412 (1882). Dry salts of the acid halogen amides decompose, when warmed, forming isocyanates (unpublished work of Stieglitz and O. Eckstein, 1905).

[3] L. W. Jones, *loc. cit.*

[4] Schroeter, *Ber.*, **42**, 2336 (1911).

[5] Stieglitz and Slossen, *loc. cit.*

[6] Stieglitz and O. Higbee, *Am. Chem. J.*, **29**, 52 (1903).

[7] *Am. Chem. J.*, **18**, 751 (1896); **29**, 49 (1903); see also L. W. Jones, *loc. cit.*, pp. 23, 28.

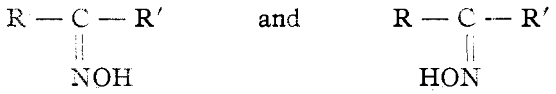
[8] Stereoisomeric chloroimido esters were prepared and investigated to determine the relation of stereoisomerism to the rearrangement of acid halogen amides (Stieglitz and Earle, Hilpert, *loc. cit.*) and stereoisomeric chloroimidoketones were prepared to investigate the same relations in connection with ketoximes (Stieglitz and Peterson, *loc. cit.*).

[9] Stieglitz and Peterson, *loc. cit.*; Stieglitz and Watkins, Reddick, Leech, Vosburgh, Senior (unpublished work).

[10] *Ber.*, **19**, 988 (1886); **20**, 1507, 2508 (1887), etc.

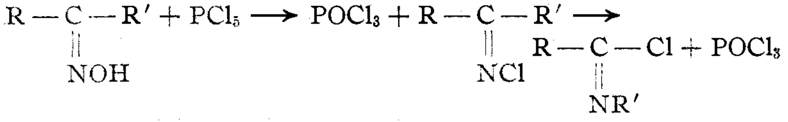
The Rearrangement of Ketoximes.

Ketoximes suffer the "Beckmann" rearrangement when they are treated with any one of a variety of reagents, such as phosphorus pentachloride, concentrated sulfuric acid, acetic anhydride, etc. These reagents have in common the property that they are dehydrating agents. A further, very important fact observed is that *stereoisomeric* oximes



$$R-\underset{\underset{\text{NOH}}{\|}}{C}-R' \quad \text{and} \quad R-\underset{\underset{\text{HON}}{\|}}{C}-R'$$

give, according to Beckmann,[1] primarily derivatives of such amines as would result from a *direct exchange* of the OH group and the radical R or R′ *immediately opposite* to the OH group in the configuration of the stereoisomer. Beckmann assumed,[2] as regards the mechanism of this interesting reaction, that such a direct exchange takes place, without the formation of any intermediate products. He compared the exchange with the well-known exchange of *ions* between molecules, the atoms being considered as held in the molecules by electrical forces.[3] Actual ionization of ketoximes, in the direction indicated, has never been detected and Beckmann did not postulate any measurable ionization. Beckmann's theory is further characterized by ascribing the rearrangement to a "catalytic" action of the rearranging agents. But, according to modern theory, catalyzers act in a specific and definite way upon the catalyzed substances, either physically (*e. g.*, as solvents, with attendant changes in condition, dissociation, etc.) or chemically, forming "intermediate products." The very intimate relation between the *chemical* nature of the rearranging compounds and of the reagents used, as indicated above, shows clearly that the action of the reagents is essentially *chemical* and that we must look for intermediate products, resulting from the action of the reagents, for the explanation of the rearrangement. A number of chemists have in fact assumed that intermediate products are first formed, which then undergo the actual molecular rearrangements. Thus, Hantzsch[4] assumes that the ketoximes form with phosphorus pentachloride chloroimides, which then rearrange by a direct exchange of chlorine and the radicals R or R′:



(3)

$$R-\underset{\underset{\text{NOH}}{\|}}{C}-R' + PCl_5 \longrightarrow POCl_3 + R-\underset{\underset{\text{NCl}}{\|}}{C}-R' \longrightarrow R-\underset{\underset{\text{NR}'}{\|}}{C}-Cl + POCl_3 \quad (3)$$

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[1] *Ann.*, **252**, 44 (1889); **274**, 1 (1892); **296**, 279 (1897), etc.

[2] *Ber.*, **27**, 300 (1894). He originally (*Ber.*, **19**, 988 (1886)) made the same assumption as Hantzsch did later (see further on in the text).

[3] No discussion of the specific charges on the various atoms was entered into. Later on in this paper an attempt is made to shed light on this all-important detail on the basis of the experimental results obtained by us.

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

To test this view Stieglitz and Peterson[1] prepared from imidoketones and hypochlorous acid, chloroimido ketones of the structure indicated. They succeeded also in obtaining stereoisomeric chloroimidoketones, corresponding to the stereoisomeric oximes. But these were found, in every instance, to be stable and not to rearrange up to temperatures of 100° to 120°, the highest temperatures used, because the "Beckmann" rearrangements occur far below these temperatures. In fact, every effort to rearrange these chloroimido ketones under any conditions has, thus far, been futile.[2] The conclusion was drawn that chloroimido ketones could not be the intermediate products undergoing the "Beckmann" rearrangement.

It is necessary now to discuss another possibility in this connection, that has recently suggested itself as the result of the important work of W. A. Noyes[3] on the possible existence of *electromeric* nitrogen chlorides NCl_3. It is possible that the chloroimides obtained by Stieglitz and Peterson are *electromers* of the chloroimides supposed to be intermediate products in the rearrangement of ketoximes by phosphorus pentachloride. The chloroimido ketones prepared by us, according to their method of preparation and especially according to their behavior, were recognized by us[4] as derivatives of *positive chlorine*[5] $RR'C^{++} : N^{---}Cl^{+}$.[6] They are prepared from imido ketones by the action of hypochlorous acid

$$RR'C^{++} : {}^{--}N^{-} - {}^{+}H + HO^{-} - {}^{+}Cl \longrightarrow RR'C^{++} : {}^{--}N^{-} - Cl^{+} + H_2O. \quad (4)$$

They yield again, by hydrolysis, hypochlorous acid (a proof that the chlorine has not changed its charge[7]) and they are strong oxidizing agents (*e. g.*, $RR'C : N^{-}Cl^{+} + 2\,{}^{+}HI^{-} \longrightarrow RR'C : N^{-}H^{+} + I^{+}.I^{-} + {}^{+}HCl^{-}$, a second proof that the chlorine has not changed its charge). Now, oximes are not infrequently obtained by the action of *nitrous acid* on organic

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[1] *Loc. cit.*

[2] Stieglitz and Peterson, *loc. cit.*; unpublished work by Stieglitz and P. H. Watkins; Vosburgh, see a later article in THIS JOURNAL. These results do not exclude the possibility that in the future some means may be found to effect their rearrangement and new methods are being tried by us from time to time (cf. *Ber.*, **46**, 2151 (1913) and Vosburgh, *loc. cit.*).

[3] THIS JOURNAL, **35**, 767 (1913); see also Nelson and Falk, *Ibid.*, **32**, 1637 (1910); and **33**, 1140 (1911).

[4] *Ber.*, **43**, 782 (1910); cf. Seliwanow, *Ber.*, **25**, 3617 (1892); Lengfeld and Stieglitz, *loc. cit.*; L. W. Jones, *loc. cit.*

[5] Cf. W. A. Noyes, THIS JOURNAL, **23**, 460 (1901); Stieglitz, *Ibid.*, **23**, 796 (1910); Walden, *Z. physik. Chem.*, **43**, 385 (1903).

[6] Only the significant charges are indicated in all of the electronic structures used.

[7] Seliwanow, Lengfeld and Stieglitz, L. W. Jones, *loc. cit.*; Stieglitz, THIS JOURNAL, **23**, 796 (1901). Since this was written, Nelson, Beans and Falk (THIS JOURNAL, **35**, 1810 (1913)) have emphasized the value of this method of determining the nature of the charge on an atom.

compounds: such is the case, for instance, for oximido mesoxalic esters and quinone oxime, which may be obtained from malonic esters and phenol, respectively, by the action of nitrous acid, as well as from the ketones by the action of hydroxylamine. Oximes[1] could, consequently have besides the probable electronic structure $\mathrm{RR'C^{++} : {}^{--}N^{-} — {}^{+}O^{-} — {}^{+}H}$ also the structure of a nitrous acid derivative $\mathrm{RR'C^{--} : {}^{++}N^{+}{}^{-}O^{-}{}^{+}H}$. A compound of the latter structure could form with phosphorus pentachloride a chloride corresponding to nitrosyl chloride $\mathrm{O^{--} = {}^{++}N^{+} — {}^{-}Cl}$. The products $\mathrm{RR'C^{--} : {}^{++}N^{+} — Cl^{-}}$ would be *electromers* of the chloroimido ketones, prepared by Stieglitz and Peterson, and could *possibly* suffer a rearrangement into $\mathrm{RC^{+++}({}^{-}Cl) : {}^{--}N^{-}R'^{+}}$ or $\mathrm{R'C^{+++}({}^{-}Cl) : {}^{--}N^{-}R^{+}}$, involving, it is true, a complex and *unlikely* shifting of charges! But such an assumption that these electromers of the non-rearranging chloroimides of Stieglitz and Peterson might undergo the "Beckmann" rearrangement of ketoximes is altogether in conflict with the facts and highly improbable, although it must be taken into account. As is shown by the rearrangement of acid halogen amides $\mathrm{R.CO.NH(Hal^{+})}$, it is just the *positive* halogen derivatives which are known to rearrange readily, and most likely the ultimate reason for the disturbance of the valences (electrons), which results in the rearrangement, is the tremendous tendency of positive chlorine and positive bromine to capture electrons in order to form their stable negative ions $\mathrm{Cl^{-}}$ and $\mathrm{Br^{-}}$ (see below, page 280). Consequently, of the series of electromeric chloroimido ketones, the chloroimides of Stieglitz and Peterson *should be the rearranging ones* and they do *not rearrange.*

Hence this possibility of electromeric chloroimido ketones, of the nature indicated, does not help out the theory of Hantzsch regarding the "Beckmann" rearrangement. In fact, a direct exchange of chlorine and a radical R or R′ under these circumstances not only offers no advantages over the assumption made by Beckmann of a direct exchange of OH against the radicals, but has the very great disadvantage, as we have just seen, of being obliged to assume a far more thorough-going and complicated shifting of electrons than is necessary in the Beckmann theory. This can only be avoided by assigning to the intermediate product, the chloroimide, an electron structure which belongs to the product obtained by Stieglitz and Peterson, and, as stated, this does not suffer rearrangement.

Further on it will be shown how our present work has led us to consider a *third* electromer of the chloroimido ketone, the assumption of the formation of which as an intermediate product in the rearrangement of ketoximes by phosphorus pentachloride might solve all the problems involved in this reaction.

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[1] Cf. Nelson and Falk, *loc. cit.*

In the application of Stieglitz's theory of the formation of a rearranging univalent nitrogen derivative as an intermediate product to the rearrangement of ketoximes under the influence of phosphorus pentachloride, it was assumed[1] that there is a preliminary addition of hydrogen chloride (always present in the ethereal solutions used) to the oximes and that a subsequent loss of water leads to the formation of the rearranging univalent nitrogen derivative. For benzophenone oxime we have:

$$R_2C:NOH \xrightarrow{+HCl} R_2CCl(NHOH) \xrightarrow{-HOH} R_2CCl.N: \longrightarrow RCCl(:NR) \quad (5)$$

Benzochloroanilide is the first isolated product of the action. The addition of hydrogen chloride to the double bond between the carbon and nitrogen would tend to destroy *stereoisomeric differences* due to the double bond, and therefore a more extended and closer investigation of the relation between stereoisomerism and rearrangement, as observed by Beckmann (see above), was pointed out as being necessary before the theory of univalent nitrogen could be finally accepted as applying to the rearrangement of ketoximes.[2] The stereoisomeric chloroimido ketones, prepared by us as a first step to investigate these relations, would not rearrange at all, as has been explained above, and did not throw the light expected on this phase of the problem. In the meantime important work by Schroeter,[3] on the rearrangement of stereoisomeric ketoximes, showed that different products are obtained from stereoisomers according to the nature of the reagents used and the conditions of the experiment, confirming the suspicion originally entertained[2] that closer investigation might remove the apparent contradiction between the behavior of stereoisomers and our theory. Schroeter indeed considers that all of his experimental work agrees with this theory.

In spite of this and further important work by other investigators confirming the theory (besides Schroeter, Wieland,[1] Stoermer,[1] and L. W. Jones[1] have recently found valuable confirmatory evidence), we have considered it necessary to continue our investigations into the nature of these typical rearrangements, particularly as a way has shown itself which promises to reduce these problems to their simplest possible terms, by the systematic investigation of rearrangements of triphenylmethylhydroxylamine and related compounds.[4] Our newest results have

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[1] *Loc. cit.*

[2] See Stieglitz, *Am. Chem. J.*, 18, 754 (footnote) (1896). Montagne (*Ber.*, 43, 2014 (1910)) has criticized the theory because of the same facts outlined in the text. From the outset, as the above footnote shows (cf. L. W. Jones, *Am. Chem. J.*, 48, 28 (1912)) this complication was recognized, only it was considered that the relation of stereoisomerism to the rearrangement was not so firmly established that it should be allowed to discourage a more critical investigation of these relations on the basis of the univalent nitrogen theory of rearrangement.

[3] *Ber.*, 43, 2014 (1910); see also Schroeter, 42, 2336 (1909); 44, 1207 (1911).

[4] Parallel with the work reported by us are investigations by Miss Isabelle Vosburgh on triphenylmethylhalogenamines $(C_6H_5)_3CNH(Hal)$ and $(C_6H_5)_3CN(Hal)_2$ and re-

indeed brought to light facts which indicate the necessity of a broader theoretical basis (see below) than has hitherto been deemed necessary.

The Rearrangement of Triphenylmethylhydroxylamine.

Triphenylmethylhydroxylamine $(C_6H_5)_3C.NHOH$ has the same kind of structure as was assumed for the hydrogen chloride addition product $(C_6H_5)_2CCl(NHOH)$ in the rearrangement of benzophenone oxime (see equation 5, above)—its examination therefore eliminated the need of any assumption on one phase of the problem. Furthermore, it and its analogs are in every way the simplest products yet investigated in regard to these rearrangements—they are saturated in regard to the carbon valences (oximes and chloroimides are not) and they do not contain, outside of the hydroxylamine or analogous group,[1] any reactive group (acid halogen amides and similar compounds have reactive C : O groups) or reactive hydrogen (as in tautomeric forms[2] of acid chloroamides, etc.). Finally, the nature of the charges on the various radicals can be more convincingly determined than in the case of acid derivatives.

Four problems of special interest have been included in the scope of the present investigation of these compounds and their derivatives. The first problem consisted in determining whether any rearrangement at all could be effected and what reagents would be effective. The second problem was the investigation of possible rearrangements of derivatives like $(C_6H_5)_3C.N(CH_3)OH$ which could not readily form any univalent nitrogen derivative. In the third place, the behavior of benzoyltriphenylmethylhydroxylamine was studied, one of the hydrogen atoms of the hydroxylamine group being replaced by the benzoyl radical, in place of by a methyl group as in the case just discussed. Finally, as a fourth problem, the relation of the positive and negative character of radicals (C_6H_4X), etc., in the rearrangement of compounds $(C_6H_4X)(C_6H_4Y)(C_6H_4Z)C.NHOH$, etc., to the question as to *which* radical or radicals *migrate* from the carbon to the nitrogen in a rearrangement was investigated as a necessary basis for distinguishing such influences from stereoisomeric effects in the study of the rearrangement of stereoisomeric oximes $(C_6H_4X)(C_6H_4Y)C : NOH$.

In regard to the first problem, we have found[3] that triphenylmethyl-

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lated compounds, and by Mr. James K. Senior on triphenylmethylhydrazines and hydrazones of ketones, etc. It is interesting that closely related as are hydrazine and hydroxylamine derivatives, no rearrangement, of this type, of the hydrazines seems as yet to have been accomplished, whereas, hydroxylamines rearrange easily (the benzidine rearrangements, etc., are of a different type).

[1] NH(Hal), etc.

[2] See Stieglitz and Vosburgh, *loc. cit.*

[3] The first observation was made by Stieglitz and Guy Reddick in 1909–1910. Mr. Reddick's illness compelled him to abandon his work and it was continued by Mr. Leech.

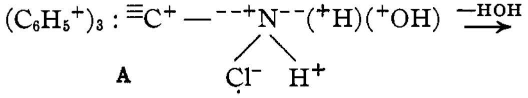
hydroxylamine and chlorotriphenylmethylhydroxylamine are in fact readily (practically quantitatively) rearranged by phosphorus pentachloride under exactly the same conditions that are used in the rearrangement of benzophenone oximes. We have, apparently,

$$(C_6H_5)_3C.NHOH \xrightarrow{-HOH} (C_6H_5)_3C.N \longrightarrow (C_6H_5)_2C : NC_6H_5. \qquad (6)$$

The product, phenylimido benzophenone, was identified by a comparison with a synthetic preparation, by analysis and by the products of its hydrolysis, aniline and benzophenone. Occasionally[1] a slight *decomposition* of triphenylmethylhydroxylamine by phosphorus pentachloride, or by the hydrogen chloride formed in the main action was observed:

$$(C_6H_5)_3C.NHOH + HCl \longrightarrow (C_6H_5)_3CCl + NH_2OH \qquad (7)^2$$

With other reagents employed to rearrange oximes, such as acetic anhydride and Beckmann's reagent, this kind of *decomposition* was found to become the chief action and no rearrangement products were observed. On the other hand, when solid triphenylmethylhydroxylamine *hydrochloride* was treated with phosphorus pentoxide, the rearrangement expressed in equation 6 was again easily accomplished. We believe this is the first time that this dehydrating agent *par excellence* has been used to effect this type of rearrangement. The result raises an interesting question, which must be considered here particularly because of its relations to the behavior of N-methyl-triphenylmethylhydroxylamine (see below) and to the problem of the influence of stereoisomerism on the rearrangement of *ketoximes*: does the phosphorus pentoxide act on the *free base* of decomposed triphenylmethylhydroxylamine hydrochloride, forming triphenylmethylimide $(C_6H_5)_3C.N$ as a rearranging intermediate product, or can it affect the hydrochloride itself as follows:[3]



$$(C_6H_5^+)_3 : \equiv C^+ \text{---} {}^+\underset{Cl^- \quad H^+}{N}{}^{--}({}^+H)({}^+OH) \xrightarrow{-HOH}$$

A

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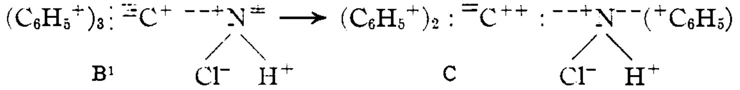
[1] Work with Reddick.

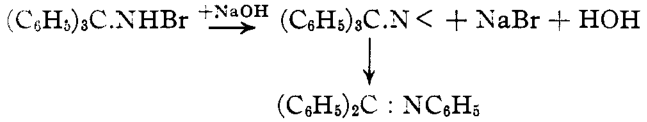
[2] The action was recognized by the formation of some triphenylcarbinol and its ethyl ether by the treatment of the reaction product with alcohol and water. Possibly a derivative such as $(C_6H_5)_3C.NHOPCl_4$ is first formed (see Werner, *Ber.*, **25**, 40 (1892)).

[3] Only the significant charges are indicated. Triphenylmethyl chloride and its derivatives are considered to have *positive phenyl* groups attached to the methyl carbon atom, as is indicated in equation 8. One of the most convincing pieces of evidence in favor of this assumption is the following: if triphenyl carbinol had the electronic structure $(C_6H_5^-)_3{}^{+++}C^{+-}O^-H^+$, it would be a *pronounced acid,* the positive charges on the methyl carbon atom repelling the positive hydrogen and causing it to ionize (cf. W. A. Noyes, THIS JOURNAL, 34, 663 (1912)). Triphenyl carbinol is no pronounced acid, but shows a tendency to exchange its OH group rather easily for other negative radicals (Cl^-, etc.)—which is to be expected from $(C_6H_5^+)_3\equiv C^{+-}O^-H^+$.



$$\underset{\text{B}[1]}{(C_6H_5^+)_3}\,\vdots\,{}^{\overline{=}}C^+ \text{--}{}^+\underset{\mathrm{Cl^-}\ \ \mathrm{H^+}}{N}{}^{\pm} \longrightarrow \underset{\text{C}}{(C_6H_5^+)_2 : {}^{=}C^{++}} : \text{--}{}^+\underset{\mathrm{Cl^-}\ \ \mathrm{H^+}}{N}{}^{--}({}^+C_6H_5) \quad (8)?$$

We note that the OH group in the compound **A** is considered to be positive, as it most probably is in hydroxylamine, and surely is for one of the two hydroxyl groups in hydrogen peroxide,[2] and as chlorine and bromine are in the corresponding triphenylmethylhalogen amines and in all their other halogen amine derivatives. In the formation of water, containing the stable *negative* hydroxyl, the oxime hydroxyl deprives the nitrogen atom of two electrons,[3] leaving the product **B**. The rearrangement of **B** takes place as follows: first the migration of two electrons from the carbon atom to the nitrogenatom gives the latter a normal, stable charge, such as it has in ammonium salts: the resulting positive charge on the carbon can not hold one of the positive phenyl groups, which, following the electrical field of force from the negatively charged nitrogen, moves to the latter, thus consummating the rearrangement:[4] the remaining negative charge on the nitrogen holds the new positive charge on the carbon atom, a double bond resulting. In other words, the compound B would be a *hydrochloride* of *triphenylmethylimide* $(C_6H_5)_3C.N^{\pm}$ or $(C_6H_5)_3C.N$ and if it *could exist* even for a very short time,[5] it *might well have the latter's property of causing a rearrangement in the manner indicated.* The compound **B** would also be an *electromer* of triphenylmethylchloroamine $(C_6H_5)_3C.NH(Cl^+)$. This substance itself has not been prepared,[6] but the corresponding bromoamine $(C_6H_5)_3C.NH(Br^+)$ has been prepared by Miss Vosburgh and one of us.[7] By the action of soda lime it is rearranged:



$$\begin{array}{ll} (C_6H_5)_3C.NHBr \xrightarrow{+NaOH} & (C_6H_5)_3C.N< + NaBr + HOH \qquad (9) \\ & \qquad\qquad \downarrow \\ & \qquad (C_6H_5)_2C : NC_6H_5 \end{array}$$

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[1] We may also assign to B the structure $(C_6H_5^+)_3\overline{=}C^{+-}\underset{\wedge}{N}{}^{-+}(H^+Cl^-)$.

[2] Many analogies between hydrogen peroxide, hydroxylamine and hydrazine ($H_2N^- — {}^+NH_2$, Stieglitz and Curme, *Ber.*, **46**, 911 (1913)) agree with this assumption; cf. Angeli, *Chem. Zentr.*, **1910**, II, 861.

[3] Stieglitz, *loc. cit.*; L. W. Jones, *loc. cit.*

[4] Similar series of changes, applied to univalent nitrogen intermediate products, represent the "electronic" expression of the molecular rearrangements of halogen amides, azides, oximes, etc., from the point of view of the theory of the univalent nitrogen intermediate product.

[5] See Stieglitz and Curme, *loc. cit.* and THIS JOURNAL, **35**, 1143 (1913), for evidence of the temporary existence of nitrogen radicals of low nitrogen valence; see also Wieland, *loc. cit.*

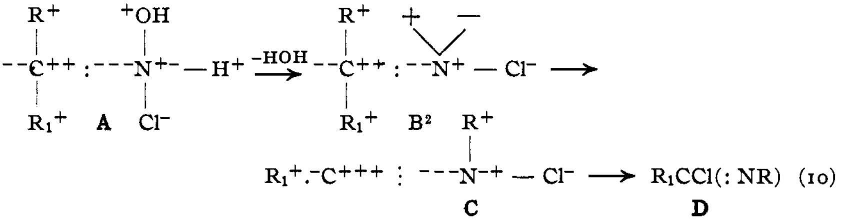
[6] The dichloroamine, $(C_6H_5)_3C.NCl_2$ is formed in attempts to prepare the chloroamine.

[7] *Ber.*, **46**, 2151 (1913).

but it does not rearrange without the loss of hydrogen bromide—in other words, it has different properties from the hypothetical substance **B**. The same difference would undoubtedly exist between **B** and the electromeric substance $(C_6H_5)_3C.NH(Cl^+)$. The problem of the possibility even of the momentary existence of such an electromeric substance as **B**, with different properties from those of the more stable chloroamine, is a problem of the future: the probability of such relations would be tremendously increased, if Noyes should confirm his preliminary indications of electromeric nitrogen trichlorides, but, even if final confirmation of such indications should not be forthcoming, considerations of this character are in themselves justified and must be dealt with, if progress is to be made in the study of the mysteries of structure and of rearrangements in organic chemistry.[1]

A New Interpretation of the Rearrangement of Ketoximes.

Should the momentary existence and the properties of the compound **B** in the rearrangement of triphenylmethylhydroxylamine hydrochloride by phosphorus pentoxide prove to be valid and reasonable assumptions, then the "Beckmann" rearrangement of benzophenone oxime and similar *oximes* might be formulated as follows in a perfectly analogous fashion:



$$\underset{R_1^+}{\overset{R^+}{{}^{-}{}^{-}C^{++}}}:{}^{-}{}^{-}{}^{-}\underset{Cl^-}{\overset{{}^+OH}{N^{+-}}}-H^+ \xrightarrow{-HOH} \underset{R_1^+}{\overset{R^+}{{}^{-}{}^{-}C^{++}}}:{}^{-}{}^{-}\overset{+\ \ -}{\overset{\vee}{N^+}}-Cl^- \longrightarrow$$

A **B**[2]

$$R_1^+.{}^-C^{+++} \vdots {}^{-}{}^{-}{}^{-}\overset{R^+}{N^{-+}}-Cl^- \longrightarrow R_1CCl(:NR) \quad (10)$$

C **D**

We note that it is assumed, as usual, that the hydroxide group in the oxime is positive, that its great tendency to change into the exceedingly

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[1] The electrolysis of salts of organic acids yields results fundamentally similar to those of the Hofmann-Lossen-Curtius-Beckmann rearrangements, a parallel which the one of us has had in mind for years and which seems of sufficient interest to present at this point because it connects the electronic explanation of the rearrangements with similar effects of an electric current, *i. e.*, of a current of electrons. As far as we know the relation has never, as yet, been pointed out, although Nef discusses the rearrangement and the electrolytic decompositions from the point of view of methylene reactions. Characteristic both for the rearrangements we are discussing and for the results of electrolysis, for instance of sodium acetate, is that carbon radicals are separated from a carbon atom which is directly linked to atoms of abnormal valence (univalent nitrogen, univalent oxygen; bivalent nitrogen may possibly have the same effect (see below)). We have $RCO.N: \longrightarrow CO:NR$ and $H_3C.CO.O^- + \oplus \longrightarrow H_3C.CO.O-$, and $2H_3C.CO.O- \longrightarrow 2CO:O + H_3C.CH_3$ or $2H_3C.CO.O- \longrightarrow H_3C.CO.OCH_3 + CO:O$: The interpretation of these equations from the electronic point of view as involving essentially migrations of electrons from carbon atoms to the univalent oxygen is obvious.

[2] The nitrogen may also be considered to be $:{}^{-}{}^{-}\overset{\vee}{N}{}^{+}Cl^{-}$.

stable ordinary negative hydroxide group, as found in water, acids and bases, leads to the formation of water under the influence of dehydrating agents, the nitrogen atom losing thereby two electrons to the oxygen atom. The product **B** is an ammonium salt with two of the nitrogen valences unsaturated in the same way as they are unsaturated in univalent nitrogen derivatives and the salt **B** is obviously of the same type as the product **B** in equation 8. It is these unsaturated valences, again, which are considered to be the direct cause of the rearrangement, two electrons passing from the carbon atom to the nitrogen, to give this a normal and stable charge such as it has in ammonium salts. With the change of electronic forces, the positive radical R, *nearest*[1] *to the field of force,* is lost by the now positive carbon and carried to the now negative nitrogen. Such a series of actions would account for the nature and action of the reagents used to accomplish the rearrangement (acid dehydrating agents) and it gives a rational picture of the electrical forces in play in the rearrangement of the valences of the molecule. Such a course would *also* account for the *influence* of *stereoisomerism* on the rearrangement,[2] if such an influence should finally be established as beyond doubt—the radical (R in the above illustration) nearest to the electrical fields of force produced by the migration of electrons from carbon to nitrogen passing under the influence of this force to the nitrogen.

The interpretation, as is evident, is an extension of the original theory of the one of us, assuming, as it does, the rearranging power of an intermediate hydrochloride of a univalent nitrogen derivative, acting in place of the ordinary free univalent nitrogen compound. The new view would by no means exclude the old, which has had such wide confirmation in the behavior of chloroamides, azides, hydroxamic acids, etc. *In the case of the ketoximes* the older view of an addition of hydrogen chloride to the double bond between the carbon and nitrogen (see p. 277) would account, as a *parallel action,* for results such as Schroeter obtained,[3] where *stereoisomeric influences were largely destroyed.* Further, the rearranging product B would be a third electromer of the chloroimido ketones of Stieglitz and Peterson (see p. 276), and would represent a logically active form of the chloride which Hantzsch assumed as the intermediate product in the rearrangement of ketoximes. This fundamental difference between the latter's theory and the one now developed should be carefully noted: Hantzsch assumes a direct exchange of R and Cl in the rearrangement, the new view assigns the rearranging power to *free valences* of the nitrogen atom, comparable with the free valences of univalent nitrogen.

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[1] The stereochemical nature of the isomerism of oximes is assumed.

[2] Schroeter, *Ber.*, 44, 1208 (1911) has made suggestions along another line to account for such an influence.

[3] *Loc. cit.*

The Rearrangement of N-Methyltriphenylmethylhydroxylamine.

The considerations just outlined become of prime importance in connection with the results of our work on the second problem investigated in this research, the problem of the rearrangement of N-methyltriphenylmethylhydroxylamine, $(C_6H_5)_3C.N(CH_3)OH$. When the non-methylated derivative is acted upon by phosphorus pentachloride in ether solution, the compound is rearranged in twenty to thirty minutes and practically quantitatively at the temperature of boiling ether. Under the same conditions and acted upon for the same time, its methyl derivative is hardly affected, most of it being recovered as the hydrochloride. If the action is continued for two or three hours, most of the substance (over 75%) is decomposed into triphenylmethylchloride[1] and methylhydroxylamine (see equation 7):

$$(C_6H_5)_3C.N(CH_3)OH + 2HCl \longrightarrow (C_6H_5)_3CCl + H_2N(CH_3)OH.Cl \quad (11)$$

But in the reaction products the presence of a small amount of a derivative of *methylaniline* could also be recognized. By hydrolysis of the reaction product by hydrochloric acid, a solution was obtained in which methylaniline was identified, not only by its characteristic reaction with hypochlorite, described in a recent paper,[2] and by its reaction with nitrous acid, but also by the preparation of acetomethylanilide. From a gram of substance, only enough acetomethylanilide was obtained for a few melting-point determinations of the recrystallized substance, but the identification was supported by the fact that the melting point of the product was not depressed when some of the substance was mixed with an equal amount of pure synthetic acetomethylanilide. Saponification of the substance thus identified gave a solution still showing the hypochlorite test for methylaniline. Other trials of the effect of phosphorus pentachloride on methyltriphenylmethylhydroxylamine led to the same result—in every case the main action was that of decomposition and only enough methylaniline was formed to be identified by the above tests, not enough to be isolated. With other agents of rearrangement, decomposition without the formation of any methylaniline resulted.

A supply of methylhydroxylamine, necessary for the preparation of N-methyl-triphenylmethylhydroxylamine on a large scale, has been ordered and the investigation of the action of phosphorus pentachloride on it will be continued, to verify the result obtained[3] and to find the conditions, if possible, for the formation of the methylaniline derivative as a main product, or in sufficient quantity for the isolation of methylaniline. From the work thus far done the following conclusions are worthy of special

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[1] Identified after hydrolysis to triphenylcarbinol.

[2] Leech, THIS JOURNAL, 35, 1072 (1913).

[3] The exceedingly poor yield makes repetition of the experiment on a much larger scale desirable.

considerations: (1) The formation of a methylaniline derivative, as just described, seems to represent the first instance on record of the rearrangement of an alkylderivative N(alkyl)X of a hydroxylamine or halogen amine ($X = OH$, Cl or Br), corresponding to the rearrangement of the nonalkylated derivatives (—NHX). Although the formation of only very small quantities of a methylaniline derivative is indicated, this discovery—when verified by us[1]—must be taken into consideration in any theory of the Hofmann-Beckmann-Lossen-Curtius rearrangements that have been discussed in this paper. The observation clearly shows the necessity of further exhaustive investigations of analogous substances. (2) The contrast of the speed and smoothness with which triphenylmethylhydroxylamine rearranges under the influence of phosphorus pentachloride with the difficulty encountered in the case of its methyl derivative, emphasizes the great hindering influence of the methyl group. In this respect the result agrees with the observations made on benzoylphenylhydroxylamine[2] $C_6H_5CO.N(C_6H)_5OH$, acylchloroalkylamines,[3] RCO.NCl(Alkyl) and recently by Miss Vosburgh[4] on triphenylmethylchloromethylamine, $(C_6H_5)_3C.NCl(CH_3)$: in all these cases the prevention of the rearrangement by this interference seems to be complete.

We may consider, on the basis of the facts summarized in (2), that the *easiest path* to the rearrangement of the molecule into a more stable one, representing a more stable distribution of electrons, is over the univalent nitrogen derivatives $RCO.N<$, $R_3C.N<$, etc. But it seems now that there must[5] be a *second* path since the formation of a methylaniline derivative indicated in the work just discussed probably[6] cannot go over a simple alkylimide derivative. Of the various possibilities that present themselves, only the most important will be mentioned now.

(1) We may consider again a direct exchange of radicals, such as Beckmann assumed, to wit:

$$(C_6H_5)_3C.N(CH_3)OH \longrightarrow (C_6H_5)_2C(OH).N(C_6H_5)(CH_3) \longrightarrow (C_6H_5)_2CO + C_6H_5NHCH_3 \quad (12)$$

Such a view would still be subject to the objections formerly made against it—it leaves out of account such facts as the role of the rearranging reagents in this action and in *the whole list of analogous rearrangements*, the difficulty of rearranging alkyl derivatives, as compared with nonalkylated compounds, and the rearrangement of azides, in which an exchange seems impossible. But even if such an assumption should finally have to be

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[1] See footnote 3, p. 283.

[2] Stieglitz and Higbee, *loc. cit.*

[3] Stieglitz and Slossen, *Ibid.*

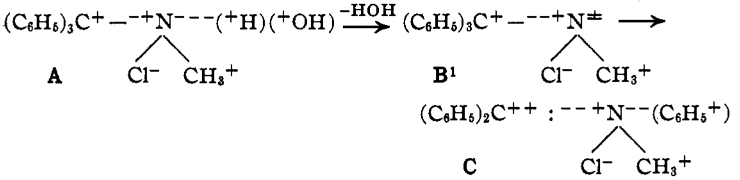
[4] *Loc. cit.*

[5] In the discussions on pp. 276 and 281 it was only considered that there might be such a second, closely related path.

[6] See (3) below. in the text.

accepted—which is not likely—it would not preclude the formation of rearranging univalent nitrogen derivatives, where such can be readily formed. Frequently analogous results are obtained by quite different paths (for instance in the formation of hydrochlorides of metal bases and in the formation of alkyl halides from alcohols by the action of halogen acids, a reaction which has all the earmarks of not being a simple ionic reaction).

(2) The rearrangement of methyltriphenylmethylhydroxylamine may follow the course indicated for triphenylmethylhydroxylamine hydrochloride (Equation 8):

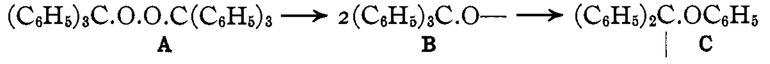


$$\underset{\mathbf{A}}{(C_6H_5)_3C^+ -{}^{-+}\underset{Cl^- \;\; CH_3^+}{N}{}^{---}(^+H)(^+OH)} \xrightarrow{-HOH} \underset{\mathbf{B}^1}{(C_6H_5)_3C^+ -{}^{--+}\underset{Cl^- \;\; CH_3^+}{N}{}^{\pm}} \longrightarrow \underset{\mathbf{C}}{(C_6H_5)_2C^{++} : {}^{--+}\underset{Cl^- \;\; CH_3^+}{N}{}^{--}(C_6H_5^+)} \quad (13)$$

This represents the action as a rearrangement of a methyl chloride derivative **B** of triphenylmethylimide $(C_6H_5)_3C.N$. **B** would be an *electromer* of $(C_6H_5)_3C^+ - {}^-N^{--}(^+Cl)(^+CH_3)$, which has been prepared by Stieglitz and Vosburgh[2] and found *not* to rearrange. This view takes into account the action of the rearranging agent. It has been discussed in some detail above, and further experiments on its plausibility will be made.

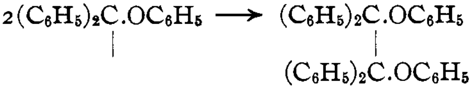
(3) Phosphorus pentachloride might cause methyltriphenylmethylhydroxylamine to lose alcohol and form methyl chloride, which could subsequently methylate the aniline derivative formed by a primary rearrangement (Equation 6). In this event some of the phenylimidobenzophenone (Equation 6) should remain nonmethylated and aniline should be observed side by side with methylaniline. The hypochlorite tests gave no indication of its presence, but this possibility will also be further investigated.

(4) Wieland[3] has made the very interesting observation that triphenylmethylperoxide is decomposed by heat in the following way:



$$\underset{\mathbf{A}}{(C_6H_5)_3C.O.O.C(C_6H_5)_3} \longrightarrow \underset{\mathbf{B}}{2(C_6H_5)_3C.O-} \longrightarrow \underset{\mathbf{C}}{\underset{|}{(C_6H_5)_2C}.OC_6H_5} \quad (14)$$

and



$$2\underset{|}{(C_6H_5)_2C}.OC_6H_5 \longrightarrow \begin{array}{c}(C_6H_5)_2C.OC_6H_5\\ |\\ (C_6H_5)_2C.OC_6H_5\end{array} \quad (15)$$

This rearrangement, which we shall call the "Wieland rearrangement," is, in its essential features, practically an exact parallel of the rearrangements of the nitrogen derivatives under discussion: we have univalent

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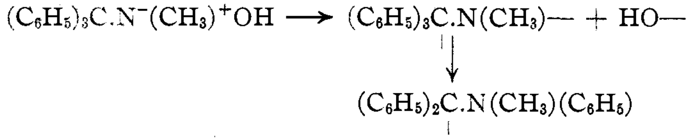
[1] See footnote [1], p. 280.

[2] The work will be published later.

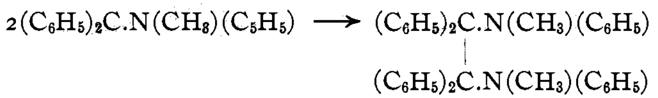
[3] *Ber.*, **44**, 2550 (1911).

oxygen active (in **B**), in place of univalent nitrogen.[2] This suggests for the rearrangement of triphenylmethylhydroxylamine the following as a possible course:



$$(C_6H_5)_3C.N^-(CH_3)^+OH \longrightarrow \begin{array}{c}(C_6H_5)_3C.N(CH_3)— + HO— \\ \Big\downarrow \\ (C_6H_5)_2C.N(CH_3)(C_6H_5)\end{array} \qquad (16)$$

and



$$2(C_6H_5)_2C.N(CH_8)(C_5H_5) \longrightarrow \begin{array}{c}(C_6H_5)_2C.N(CH_3)(C_6H_5) \\ | \\ (C_6H_5)_2C.N(CH_3)(C_6H_5)\end{array} \qquad (17)$$

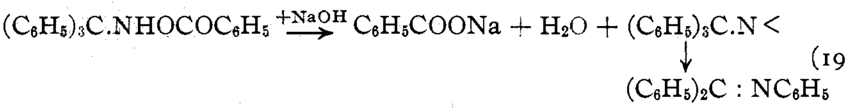
and

$$4HO— \longrightarrow 2HOH + O_2 \qquad (18)$$

Bivalent nitrogen in $(C_6H_5)_3C.N(CH_3)—$ would, in this case, be the cause of the rearrangement. The electron interpretation of this action would follow the same lines as laid down above. Mr. Stagner, who is continuing this work, will pay particular attention to this interesting possibility.[2]

The Rearrangement of Triphenylmethylbenzoylhydroxylamine.

The third problem raised in this investigation was on the behavior of benzoyltriphenylmethylhydroxylamine in reference to any rearrangement. Such a benzoyl derivative of triphenylmethylhydroxylamine was prepared (see the experimental part) and the product presumably has one of the following structures: $(C_6H_5)_3C.NHO.COC_6H_5$ or $(C_6H_5)_3C.N(COC_6H_5)OH$. The absence of any acid properties and of a ferric chloride reaction[3] rather favors the first structure given, the absence of hydrochloride formation favors the second structure and we consider the structure as undetermined. Which structure is correct is of less importance than the fact that the compound is found to undergo a rearrangement quite readily when it is heated with soda lime. We note at once the successful adaptation of the *reagent* to the compound to facilitate the primary loss of *benzoic acid* (sodium benzoate) in order to form the univalent nitrogen compound for the rearrangement. We may write:



$$(C_6H_5)_3C.NHOCOC_6H_5 \xrightarrow{+NaOH} C_6H_5COONa + H_2O + \begin{array}{c}(C_6H_5)_3C.N< \\ \downarrow \\ (C_6H_5)_2C : NC_6H_5\end{array} \qquad (19)$$

The Influence of Substitutions in the Aryl Groups.

The last question examined deals with the influence of substituting groups in determining which aryl radicals shall migrate from carbon to nitrogen in the rearrangement of triarylmethylhydroxylamines. It is a

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[1] See footnote 1, p. 281.

[2] Mr. Senior is investigating the behavior of the corresponding hydrazine derivatives.

[3] See experimental part.

very large problem and only a beginning has been made in it by the study of the action of phosphoric pentachloride on *p*-chlorotriphenylmethylhydroxylamine $(ClC_6H_4)(C_6H_5)_2C.NHOH$. The rearrangement occurs quite as readily as in the case of triphenylmethylhydroxylamine. Part of the substance forms phenylimidochlorobenzophenone

$$(ClC_6H_4)(C_6H_5)_2C.NHOH \xrightarrow{-HOH} (ClC_6H_4)(C_6H_5)_2C.N< \longrightarrow (ClC_6H_4)(C_6H_5)C : NC_6H_5 \qquad (20)$$

and another part forms *p*-chlorophenylimidobenzophenone:

$$(ClC_6H_4)(C_6H_5)_2C.N< \longrightarrow (C_6H_5)_2C : NC_6H_4Cl \qquad (21)$$

The quantitative examination of the reaction product showed, curiously enough, that roughly *two-thirds* of the substance rearranges according to the first action (equation 20), and one-third according to the second action: this represents a ratio which is also the ratio (2 : 1) of the number of phenyl to chlorophenyl radicals in chlorotriphenylmethylhydroxylamine, and such a result should follow if there were no particular effect at all of the halogen in the aryl radical on its likelihood to migrate to the nitrogen. A much larger experimental material will be needed before any final conclusions can be drawn as to such influences. It should, however, be further noted that Miss Vosburgh has obtained just *the same result* in examining the rearrangement of chlorotriphenylmethyldichloroamine $(ClC_6H_4)(C_6H_5)_2C.NCl_2$ by soda lime. It is evident that both the hydroxylamine derivative and the chloroamine

$$(ClC_6H_4)(C_6H_5)_2C.NCl_2 \xrightarrow{2NaOH} (ClC_6H_4)(C_6H_5)_2C.N< + NaCl + NaOCl + H_2O \qquad (22)$$

would form, according to our theory, exactly the same intermediate product $(ClC_6H_4)(C_6H_5)_2C.N<$. *Under the same conditions*, it should form identical products in the same proportions. In the present instance the temperature and other possibly vital conditions were quite different, and therefore too much emphasis must not be placed on the interesting result that identical products in the same proportions were actually obtained. The work, however, opens up a line of quantitative investigation which may lead to a means of applying quantitative tests of the validity of the theory.

Further studies along the lines indicated are in progress and it is hoped, in particular, that more light may be shed on the important questions of electromeric relations, which are so closely interwoven with the problem of the mechanism of these rearrangements.

NOTE.—In an important article in the December number of the *American Chemical Journal*, received today, Professor L. W. Jones develops more fully his views on the Beckmann and allied rearrangements and also contributes an interpretation of the rearrangements from the electron point of view. In two or three important details the views of the writer and of his colleague and friend are somewhat at variance. In the first place, the writer considers the oxygen in hydroxylamine and in oximes to have a positive charge and to be held by a negative charge on the nitrogen (although less stable electromers are not excluded)—Dr. Jones has assumed the oxygen to be negative and the nitrogen positive. The similar behavior of hydroxylamines and halogen amines, of hydroxylamine and hydrogen peroxide, still more the fundamental similarity existing between hydroxylamines and ammonia and between their salts, and, above all, the fact that, as far as the writer is aware, no hydroxylamine derivative has been found to exchange hydroxyl for halogen by treatment with halogen acids or phosphorus halides are the facts on which the writer's views are based. (According to a later private communication from Dr. J. he has now reached the same conclusion on this question and has discovered further evidence supporting it.) In the next place, the writer considers that his original theory of "the potency of the free valences of univalent nitrogen" is in complete accord with the electronic expressions of this theory given by the writer and by Dr. Jones. In such univalent nitrogen derivatives, *e. g.*, RCO.N, it is not necessary to consider that the two free valences consist of a positive and a negative charge, though there will be a great, but not necessarily exclusive tendency toward the formation of such charges. In other words we would still distinguish between two closely related substances, easily convertible into each other, $\text{RCO.N}<$ and $\text{RCO.N}\pm$. The distinction is an important one (cf. Stieglitz and Curme, THIS JOURNAL, **35**, 1146 (1913)). In the first substance only one of the three nitrogen valences is satisfied, the other two are present in the form of latent or potential valences, much as free metals like sodium or calcium have only latent or potential valences: exactly as we ascribe the tremendous activity of sodium to its tendency to throw off electrons and form sodium ion, so the activity of univalent nitrogen in effecting these rearrangements may well be due to the potency of the free or, in modern terms, latent valences of univalent nitrogen, *i. e.*, to its great tendency to absorb, for each nitrogen atom, two electrons and go from $\text{RCO.}^{-}\text{N}<$ into $\text{RCO.}^{-}\text{N}^{=}$. On the other hand, we may also have, through the absorption of two electrons for each nitrogen atom, the transformation $\text{RCO.}^{-}\text{N}\pm$ into $\text{RCO.}^{-}\text{N}^{=}$, corresponding to the transformation of Cl^{+} into Cl^{-} by the absorption of electrons. We would leave the way open to either interpretation of the absorption of electrons, as more in accordance with the facts. This broader view of "the potency of the free valences of univalent nitrogen" is particularly emphasized because it enables the writer to include under the same theory not only all the rearrangements previously discussed by himself and so ably presented by Jones, but also the rearrangement of peroxides (the Wieland and other rearrangements) through the potency of univalent *oxygen* derivatives, the rearrangement of hydroxylamine derivatives RR'NOH possibly through *bivalent nitrogen* derivatives and the decomposition, by electrolysis, of organic acids. Finally, the writer believes that the explanation of the migration of a freed positive radical (see the text) to a negative atom under the influence of an electrical field of force gives an adequate explanation of the mechanism of the migration or "wandering," for which Professor Jones concludes that no satisfactory mechanism has, as yet, been offered. In regard, however, to the most fundamental questions of these rearrangements, considered from the electronic point of view, postulating a shifting of electrons from carbon to nitrogen, and a migration of a positive radical, Professor Jones and the writer are happily in entire agreement and the writer is glad to express here his great satisfaction thereat.—J. STIEGLITZ, *Jan. 10, 1914.*

Experimental Part.[1]

β-Triphenylmethylhydroxylamine $(C_6H_5)_3CNHOH$.[2]—The work on this

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[1] The experimental part of this investigation was carried out by Dr. Leech and I wish to use this opportunity to acknowledge my grateful appreciation of his conscientious and skilful assistance.—J. Stieglitz.

[2] *Report of the VIII Internat. Congr. Appl. Chem.*, **25**, 443 (1912).

compound was first undertaken by Stieglitz and Reddick[1] but not completed, therefore it was repeated. Triphenylmethylchloride was prepared according to Gomberg[2] and melted at 112–113°. For the preparation of β-triphenylmethylhydroxylamine, a modification of Mothwurf's[3] method was employed: A solution of sodium methylate was prepared by the addition of 7.3 grams of sodium to 100 cc. of acetone-free methyl alcohol. To this was added 19.5 grams of hydroxylamine hydrochloride, dissolved in methyl alcohol, and the precipitated sodium chloride was filtered off by suction. The hydroxylamine solution was evaporated, under reduced pressure, to 40–50 cc., and 10 grams of triphenylchloromethane, in about 25–30 cc. of benzene, were added. The methyl alcohol remaining was distilled over at ordinary pressure, but the benzene[4] was entirely removed by distillation under reduced pressure at about 70°. The dry residue was extracted with absolute ether, the solution filtered and the triphenylmethylhydroxylamine hydrochloride precipitated by dry hydrogen chloride gas. The salt was filtered, washed well with ether, and shaken in a separatory funnel with a layer of ether and dilute sodium hydroxide solution. The ether extract was drawn off, dried with fused calcium chloride, and the ether evaporated, leaving crystals of triphenylmethylhydroxylamine, melting at 130–135°. The yield was 73–75% of the theoretical.

Rearrangement of β-Triphenylmethylhydroxylamine with Phosphorus Pentachloride.—Triphenylmethylhydroxylamine (4 grams) was dissolved in absolute ether (about 40 cc.), and phosphorus pentachloride (4 grams) was added to the solution. The mixture was kept, under a reflux, at the boiling temperature of ether for twenty to thirty minutes. A yellow precipitate formed, which was filtered off and washed well with absolute ether. After the precipitate was dried and allowed to stand *in vacuo* over night, it melted at 187–189°, indicating it to be phenylimidobenzophenone hydrochloride, $(C_6H_5)_2C : NC_6H_5.HCl$. The yield was 4.1 grams or 96% of the theoretical. Upon hydrolysis of a small portion of this precipitate, the hypochlorite test for aniline was affirmative. Benzophenone was also identified by its melting point (47–50°) taken with the product itself and for a mixture (47–50°) of the product with pure benzophenone (melting point 48–52°). Further, for the liberation and identification of the free base, phenylimidobenzophenone, 3.3 grams of the hydrochloride was shaken in a separatory funnel with a concentrated solution of potassium carbonate and a layer of ether. The ether extract was

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[1] Peterson, P. P., *Am. Chem. J.*, **46**, 327 (1911).

[2] *Ber.*, **33**, 3147 (1900).

[3] *Ibid.*, **37**, 3152 (1904).

[4] In the first experiments, the benzene was driven off at the temperature of boiling water, under ordinary pressure. An exceedingly severe explosion occurred once, and hence the modification to reduced pressure.

dried over calcium chloride for one-half hour, and the ether allowed to evaporate spontaneously in a current of dry air in a bell jar desiccator. The residue was purified by treatment with ligroin. The yield was 2.2 grams and the melting point was 113°, agreeing with the melting point of phenylimidobenzophenone.

0.2911 gram substance gave 14.2 cc. N (over 33% KOH) at 21.5° and 747.5 mm. Calculated for $C_{19}H_{15}N$: 5.45% N. Found: 5.49% N.

Upon distillation of the original ether filtrate (after the treatment with phosphorus pentachloride) only a very small residuum remained after the phosphorus oxychloride had passed over.[1] These results completely identify the product of the action of phosphorus pentachloride on triphenylmethylhydroxylamine as phenylimidobenzophenone, formed by a molecular rearrangement according to:

$$(C_6H_5)_2C.NHOH + PCl_5 \longrightarrow (C_6H_5)_2C : NC_6H_5HCl + POCl_3 + HCl.$$

The hydrolysis of this product to aniline and benzophenone is expressed in the equation:

$$(C_6H_5)_2C : NC_6H_5HCl + HOH \longrightarrow (C_6H_5)_2C{=}O + C_6H_5NH_3Cl.$$

When triphenylmethylhydroxylamine is dissolved in phosphorus oxychloride and phosphorus pentachloride is added to the solution, the triphenylmethylhydroxylamine undergoes decomposition. Half a gram of the hydroxylamine derivative was dissolved in 5 cc. of phosphorus oxychloride and 0.5 gram of phosphorus pentachloride was added to the solution. After standing three days the mixture was poured on ice and the precipitate filtered off. The product gave the melting point of 155°, and after a portion of it was mixed with triphenylcarbinol (melting point of carbinol 159–161°) it melted at 157–159°. The yield was 98% of the theoretical. The filtrate reduced Fehling's solution, showing the presence of hydroxylamine.

Action of Beckmann's Mixture (Glacial Acteic Acid, Acetic Anhydride and Hydrogen Chloride), of Glacial Acetic Acid, and of Acetic Anhydride on Triphenylmethylhydroxylamine.—All attempts to effect a rearrangement of triphenylmethylhydroxylamine by means of the above agents failed, as the hydroxylamine derivative was decomposed. The reaction mixtures were poured on ice and in all cases triphenylcarbinol was found quantitatively, and the presence of hydroxylamine detected in the filtrate

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[1] In the older work with Mr. Reddick small quantities of triphenylcarbinol were occasionally identified when this residue was purified by treatment with aqueous alcohol. This result, indicating a slight decomposition of triphenylmethylhydroxylamine into triphenylmethylchloride, is parallel to the main action, the rearrangement into phenylimidobenzophenone. It is a product of some interest since we have found (see below) that in the treatment of the methylated derivative, $(C_6H_5)_3CN(CH_3)OH$, with phosphorus pentachloride, almost all the substance is decomposed in this way, forming triphenylmethylchloride, and only very small quantities are rearranged.

by reduction of Fehling's solution. Half a gram of triphenylmethylhydroxylamine was treated with 6 cc. of Beckmann's mixture (4 parts glacial acetic acid, 1 part acetic anhydride, saturated with dry hydrogen chloride) and allowed to stand three weeks. At the expiration of that time, quite a little triphenylmethylchloride had crystallized out of the solution and it was identified by its melting point, which remained unchanged when pure triphenylchlormethane was mixed with the product. The remaining triphenylmethylchloride, converted into triphenylcarbinol, was recovered in theoretical quantity. Hydroxylamine was detected as above.

Action of Phosphorus Pentoxide on β-Triphenylmethylhydroxylamine-hydrochloride $(C_6H_5)_3CNH_2(OH)Cl$.—Triphenylmethylhydroxylamine hydrochloride was prepared from a solution of the free base in absolute ether by precipitation with dry hydrogen chloride. The salt was washed with absolute ether and dried *in vacuo*. The hydrochloride softens some at 143–147°, with change of form, and melts at 158–160°. It is soluble in alcohol, insoluble in cold water, ligroin or ether. Half a gram of the hydrochloride was intimately mixed with the same weight of phosphorus pentoxide in a test tube, and heated until a reaction took place.[1] The reaction mixture was then treated with a few drops of alcohol and some dilute hydrochloride acid water in order to hydrolyze any phenylimidobenzophenone formed. A little of this solution, made slightly alkaline with sodium hydroxide, gave upon the addition of bleaching powder solution, the purple color test for aniline, proving that a rearrangement to phenylimidobenzophenone had taken place. The remainder of the solution was shaken with ether, which removed the benzophenone and some acid. The aqueous solution was drawn off, the ether extract shaken with sodium hydroxide solution to remove the acid, the ether was separated and allowed to evaporate, leaving a residue which melted at 46–47°, the melting point of benzophenone. A melting point of a mixture of the product with synthetic benzophenone completed its identification as benzophenone, a product of the hydrolysis of phenylimidobenzophenone.

Triphenylmethylbenzoylhydroxylamine $(C_6H_5)_3C.N(COC_6H_5)OH$ or $(C_6H_5)_3C.NH(OCOC_6H_5)$.—Triphenylmethylhydroxylamine was dissolved in about forty times its weight of absolute ether and treated with benzoyl chloride, in the proportion of one molecule of the latter to two molecules of the former. The mixture stood from four to six days. A white precipitate formed, which was collected on a filter and found to consist chiefly of triphenylmethylhydroxylamine hydrochloride, with some benzoylated triphenylmethylhydroxylamine. The benzoyl derivative can be recovered by extraction of the precipitate with a very small amount of chloroform, and treatment of the extract with low boiling ligroin to pre-

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[1] The reaction proceeds rapidly at 75°.

cipitate the product fractionally. The original ether filtrate from the hydrochloride was allowed to evaporate in a current of dry air in a desiccator; the residue was washed with low boiling ligroin to remove benzoyl chloride, dissolved in a small amount of chloroform, and subsequently subjected to fractional precipitation with ligroin. After repeated fractionations a substance was obtained giving a constant melting point of 155°. The yield of pure substance was small.

0.2762 gram substance gave 9.7 cc. N (over 33% KOH) at 18.8° and 736.5 mm.; 0.4963 gram substance gave 16.9 cc. N (over 33% KOH) at 23.3° and 752.6 mm.; Calculated for $C_{26}H_{21}NO_2$: N, 3.70%. Found: N, 3.94%, 3.83%.

Benzoyltriphenylmethylhydroxylamine is soluble in ether, chloroform and benzene. There are two possible structures for this benzoylated triphenylmethylhydroxylamine: the benzoyl group may have entered into the β-position of the hydroxylamine radical, forming $(C_6H_5)_3C.N(COC_6H_5)OH$, or it may have entered the hydroxyl group (in the α-position), forming $(C_6H_5)_3CNH(OCOC_6H_5)$. The method of preparation corresponds to the one by means of which Beckmann[1] obtained β,β-benzoylbenzylhydroxylamine $(C_6H_5CO)(C_7H_7)N(OH)$ from β-benzylhydroxylamine and benzoyl chloride in an ether solution, and this makes the corresponding structure for our product probable. The latter did not, however, show the ferric chloride test (red coloration, characteristic of Beckmann's product) nor did it show any indications of acid (salt forming) properties at all. A hydrochloride of this compound could not be prepared by the usual method. This also agrees with Beckmann's failure to obtain a hydrochloride of β-benzoyl-β-benzylhydroxylamine. Attempts to obtain an isomeric α-benzoyl-β-triphenylmethylhydroxylamine, by the long and indirect process used by Beckmann[2] in preparing α-benzoyl-β-benzylhydroxylamine, were unsuccessful (see below). The exact position of the benzoyl group in our product therefore remains uncertain, though it most probably occupies the β-position.

Rearrangement of Triphenylmethylbenzoylhydroxylamine by Soda Lime.—Triphenylmethylbenzoylhydroxylamine (0.55 gram) was intimately mixed with pulverized soda lime (1 gram) and the mixture was heated in a test tube immersed in a metal bath, at 160–165°. At this temperature the rearrangement was found to proceed more favorably than at lower temperatures. The mixture became yellow, the color of phenylimidobenzophenone. The rearrangement product was extracted with a number of portions of benzene and the combined benzene extracts were evaporated in a current of dry air. A gummy residue was washed repeatedly with ligroin (b. p. 30–50°). A few yellow crystals were removed and identified as phenyliminobenzophenone by their melting point 108–110°. A mixture of the

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[1] *Ber.*, 26, 2283 (1893).

[2] *Loc. cit.*

product with analyzed phenyliminobenzophenone (m. p. 113°) melted at 110–112°. The remainder of the phenylimidobenzophenone was then hydrolyzed by solution in 6–8 drops of alcohol and 2–3 cc. of dilute hydrochloric acid, and evaporation of the solution on a steam bath. Before the solution had become quite dry, cold water was added and a precipitate was removed by filtration. The precipitate was identified as benzophenone (0.21 gram). The filtrate was concentrated and chloroplatinic acid was added to it to precipitate aniline chloroplatinate which was identified by analysis.

0.2338 gram substance gave 0.0763 gram Pt. Calculated for $C_{12}H_{16}N_2PtCl_6$: 32.78% Pt. Found: 32.63% Pt.

Some doubt existing as to the exact structure of the benzoyl derivative of triphenylmethylhydroxylamine (see above), whose rearrangement has just been described, it was decided to attempt to prepare an isomeric benzoyl derivative by the method used by Beckmann for the preparation of α-benzoyl-β-benzylhydroxylamine.[1] The method, it will be recalled, is indirect, depending on the action of benzoyl chloride on the condensation product of benzyl hydroxylamine with benzaldehyde. The action of benzaldehyde on triphenylmethylhydroxylamine was, therefore, studied next.

Triphenylmethylhydroxylamine and Benzaldehyde, $(C_6H_5)_3C.\underbrace{N.CH}_{O}C_6H_5$.—A small excess of triphenylmethylhydroxylamine (1.1 equivalent), was mixed with benzaldehyde in an Erlenmeyer flask, connected with a short reflux condenser. A small amount of absolute ether was added to the mixture, which was warmed for fifteen minutes at the temperature of boiling ether; the temperature was then slowly elevated, the ether being allowed to escape gradually, and a temperature of 120–140° was maintained for two hours. The resulting gum was successively triturated with small portions of low-boiling ligroin and the extracts collected until the sticky characteristic of the residue had been entirely removed and a nearly white powder produced. This powder consisted mostly of triphenylcarbinol. A sticky substance remained after the evaporation of the ligroin *in vacuo*. The solid was crushed on a clay plate, removed to a Hirsch funnel and washed a few times, without suction, with small amounts of cold absolute alcohol. The residue was then dissolved in a small amount of hot absolute alcohol and this solution separated from any insoluble portion by filtration. When the solution was allowed to cool slowly it deposited white crystals which were found to be the condensation product of benzaldehyde and triphenylmethylhydroxylamine. After a number of recrystallizations the condensation product melted at 114°.

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[1] *Loc. cit.*

0.4929 gram substance gave 17.8 cc. N (over 33% KOH) at 23.5° and 745.4 mm.; 0.1723 gram substance gave 0.5445 gram CO_2, 0.0975 gram H_2O. 0.1912 gram substance[1] gave 0.6028 gram CO_2, 0.1000 gram H_2O. Calculated for $C_{26}H_{21}NO$: 85.92% C; 5.78% H; 3.86% N. Found: 86.22, 86.00% C; 6.29%, 5.86% H; 4.02% N.

Triphenylmethylbenzaldoxime is soluble in ether, chloroform, benzene and hot alcohol, and not very soluble in ligroin. When it is dissolved in absolute ether and the solution is saturated with dry hydrogen chloride gas, the hydrochloride is precipitated quantitatively.

With the view of obtaining α-benzoyl-β-triphenylmethylhydroxylamine, benzaldehyde-triphenylmethylhydroxylamine was dissolved in absolute ether and treated with an equivalent quantity of benzoyl chloride. The mixture was allowed to stand for twenty-four hours and subsequently treated, as described by Beckmann in the preparation of α-benzoyl-β-benzyl-hydroxylamine. After repeated attempts, all of which yielded negative results, the project was abandoned.

Parachlorophenyldiphenylmethylhydroxylamine, $(ClC_6H_4)(C_6H_5)_2CNH(OH)$.—Parachlorophenyldiphenylmethylchloride was prepared by Gomberg's[2] method from benzophenonedichloride and chlorobenzene with the aid of the Friedel and Craft's reaction. The chloride was generally recrystallized four or five times from hot ligroin (b. p. 70–80°) and melted at 88–88.5°. Gomberg gives 87° as its melting point. The chloride was condensed with hydroxylamine by a modification of Mothwurf's method as follows: Hydroxylaminehydrochloride (2.8 grams) was dissolved in the least amount of methyl alcohol possible and to it was added a solution of sodium methylate (0.91 gram sodium in 14 cc. alcohol). The precipitated sodium chloride was removed by rapid filtration, and the hydroxylamine solution treated with five grams of *p*-chlorophenyldiphenylmethylchloride in 50 cc. of benzene. The mixture stood for a number of hours, during which time a precipitate of hydroxylamine hydrochloride formed, but this was not removed. After the methyl alcohol had been evaporated, the benzene was removed by distillation under reduced pressures, at a temperature of 65–70°, until a "gummy dry" residue remained. This was extracted with dry ether, the hydroxylamine hydrochloride removed by filtration. An ether solution of pure anhydrous oxalic acid was added to the filtrate until no further precipitation occurred. The oxalate was collected on a filter, washed with ether by suction, and shaken in a separatory funnel with a solution of potassium hydroxide and an ether layer. The ether extract of the free base was dried with potassium carbonate; upon evaporation of the ether a gum resulted. This gum was transferred to a beaker by means of a little alcohol and

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[1] This was some of the unchanged substance recovered after treatment with benzoyl chloride (see next section); it was identified by its melting point, which was unchanged when the melting point of a mixture with a previously analyzed sample was taken.

[2] *Ber.*, 37, 1634 (1904).

placed in a desiccator *in vacuo*. Care must be taken to add alcohol, or else the substance will form a taffy-like foam, spreading over the entire vessel. After some time, generally twelve to eighteen hours, the gum changed to a solid. The yield of crude material was about 65–70% of the theoretical.

The pulverized substance was treated with the smallest amount of ligroin (b. p. 70–80°) necessary to dissolve it, and the solution allowed to stand over night. In this manner a good part of the substance precipitated out and most of the gummy matter remained in solution. The precipitate was collected on a filter and washed with low-boiling ligroin; after this operation the product was dissolved in a small amount of benzene, four to six volumes of low-boiling ligroin were added to the solution, and the beaker, with contents, immersed in ice water for fifteen minutes. The precipitate of quite impure chlorophenyldiphenylmethylhydroxylamine, thus formed, was brought on a filter and the filtrate allowed to evaporate spontaneously in the air until the volume was about one-third the original one, crystals being deposited in this process. The remaining solution was then decanted into another vessel and the crystals, adhering to the sides of the beaker, were washed with ligroin (b. p. 30–50°). They were then dissolved in the least amount of hot ligroin[1] (b. p. 70–80°). After the solution had stood twelve hours the crop of new crystals was removed. One or two more recrystallizations completed the purification of the compound. The melting point is 117°. The yield was 25–30° of the theoretical.

0.1796 gram substance gave 0.4874 gram CO_2 and 0.0845 gram H_2O. Calculated for $C_{19}H_{16}NOCl$: C, 73.62%; H, 5.20%. Found: C, 74.01%; H, 5.27%.

Parachlorophenyldiphenylmethylhydroxylamine is soluble in ether, benzene, chloroform and hot high-boiling ligroin. If it is dissolved in absolute ether and dry hydrogen chloride gas is passed into the solution, the hydrochloride is thrown down. This salt is soluble in alcohol, insoluble in ether, ligroin and cold water; it is decomposed by warm water, probably into chlorophenyldiphenylcarbinol and hydroxylamine.

Rearrangement of Parachlorophenyldiphenylmethylhydroxylamine by Phosphorus Pentachloride.—In a round bottom flask, 0.5 gram of the hydroxylamine derivative was dissolved in 30 cc. of absolute ether, 0.5 gram of phosphorus pentachloride was added to the solution, and the flask was connected with a reflux condenser. The entrance of moisture was guarded against. The mixture was heated on an electric oven for two hours, during which time a yellow precipitate had collected in the flask. The precipitate was collected, washed well with ether and dried *in vacuo*. Upon evaporation of the filtrate, and subsequent distillation of the phosphorus oxychloride produced in the action, only one drop of residue remained. The yellow precipitate consisted of a mixture of *p*-chloro-

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[1] One part alcohol and three parts ligroin also serves as a good crystallizing solvent.

phenyldimidobenzophenone and phenylimido-*p*-chlorobenzophenone (see below). The salts were immediately hydrolyzed by solution in a few drops of alcohol and treatment with a small amount of very dilute hydrochloric acid, the mixture being heated about fifteen minutes to assure complete hydrolysis of the imido compounds. The ketones were extracted in the usual manner with ether, and the aqueous solution (see A) was examined for aniline and parachloraniline.

A. Identification of Aniline and Parachloroaniline.—The aqueous acid solution was placed in a small separatory funnel, strong caustic soda solution was added, and the free bases were extracted with ether. The ether extract was dried well with potassium carbonate and an ether solution of anhydrous oxalic acid[1] added to precipitate the oxalates of the two anilines. The precipitate was collected, washed well with absolute ether, transferred to a test tube and dissolved in the least amount of almost boiling water. Upon cooling the solution to about 40°, a precipitate again formed (*p*-chloroaniline oxalate), which was collected. The filtrate from it was made alkaline and gave with bleaching powder solution the characteristic test, proving the presence of aniline. The precipitate, consisting mostly of chloroaniline oxalate, and a small amount of aniline oxalate, was treated in a small dropping funnel, with alkali, and the mixture shaken with ether. After the ether solution had been dried it was allowed to evaporate spontaneously, and the residue placed in a vacuum desiccator. In a few hours crystals of *p*-chloroaniline appeared. These were washed quickly with ligroin, to remove any aniline present, dried, and melted at 65°. A melting point (68–69°) of a mixture of the product with pure parachloroaniline (70°) was identified the substance as *p*-chloroaniline.

B. Identification of Benzophenone and Chlorobenzophenone.—The ether solution containing the ketones, was spontaneously evaporated and the residue washed quickly with ligroin. Enough alcohol[2] was added to the residue just to dissolve about three-quarters to seven-eighths of it; the residue was collected and melted at 73–75°. *p*-Chlorobenzophenone melts at 77–78° and a mixture of the product with some synthetic substance melted at 75–77°, proving the identity of the product. The alcoholic filtrate was allowed to evaporate spontaneously to a very small volume, the solution filtered through a cotton plug, and the filtrate evaporated to dryness. The residue was then treated with ten to fifteen drops of alcohol, the solution decanted through a cotton filter, the filtrate evaporated

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[1] The oxalic acid salts were prepared because of the greater relative solubility in water of the aniline salt than that of α-chloroaniline. The accuracy of the method of separation based on this difference was, of course, first tested and proved by preliminary experiments with known materials.

[2] Benzophenone is very soluble in alcohol, while *p*-chlorobenzophenone is less soluble.

almost to dryness, the remaining few drops of liquid once decanted from a small solid residue, which when dried, melted at 48–50°. Benzophenone melts at 48–52°.

A quantitative study of the rearrangement of *p*-chlorophenyldiphenylmethylhydroxylamine with phosphorus pentachloride was next made, in order to determine the proportions in which the rearrangement yields an aniline and a *p*-chloroaniline derivative. The hydroxylamine (0.85 gram) was dissolved in 30 cc. of absolute ether, and heated on the electric bath, as described above, with a gram of phosphorus pentachloride. After two hours the yellow precipitate was collected, washed well, with absolute ether, and then hydrolyzed in the usual manner. The ketones were removed by extraction with ether. The aqueous solution was then saturated with sodium chloride, placed in a small separatory funnel, made alkaline with strong sodium hydroxide solution and the two anilines twice extracted. The collected ether extracts were poured through a cotton filter and the solution dried with potassium carbonate. It was filtered into a beaker and the hydrochlorides of the anilines were precipitated by a freshly made ether solution of dry hydrogen chloride.[1] The salts were brought on a filter, well washed and dried; they weighed 0.212 gram.

A weighed portion of the chlorides was analyzed volumetrically for aniline and chloroaniline by the bromination method.[2]

0.0712 gram of the mixed hydrochlorides required 27.8 cc. of $N/10$ $KBrO_3$. Found: aniline hydrochloride, 66.9%; chloroaniline hydrochloride, 33.1%.

In order to run analyses of other hydrochloride samples, two more rearrangements were made as above. The results of the bromination determinations were as follows:

0.0674 gram of the mixed hydrochlorides required 25.8 cc. of $N/10$ $KBrO_3$. Found: aniline hydrochloride 63.4%; chloroaniline hydrochloride, 36.6%; 0.0625 gram of the mixed hydrochlorides required 24.45 cc. of $N/10$ $KBrO_3$. Found: aniline hydrochloride, 67.3%; chloroaniline hydrochloride, 32.7%.

No greater degree of accuracy than 5% was aimed at in these results.

β,β-Triphenylmethylmethylhydroxylamine, $[(C_6H_5)_3C.N(CH_3)OH]$.—This compound was prepared by the action of triphenylmethylchloride on methylhydroxylamine hydrochloride. The β-methylhydroxylaminehydrochloride was prepared by a series of preparations, all of which are described in the literature.[3]

β-Methylhydroxylaminehydrochloride (2.5 equivalents) was dissolved in ten times its weight of methyl alcohol (acetone free) and a solution of

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[1] Experiments showed that hydrogen chloride precipitates aniline and chloroaniline quantitatively as hydrochloride from a dry ether solution.

[2] See Curme, THIS JOURNAL, **35**, 1143 (1913).

[3] Beckmann, *Ber.*, **20**, 1509, 2766 (1887); **22**, 432 (1889); **23**, 1685 (1890); Dittrick, *Ber.*, **23**, 3548 (1890). We found it better to use methyl bromide rather than the iodide.

sodium methylate, prepared from an equivalent weight of sodium dissolved in another equal volume of methyl alcohol, was poured into the hydroxylamine solution, which operation, after the flask had been shaken, was quickly followed by the addition of triphenylmethylchloride (one equivalent), dissolved in 30-40 times its weight of dry benzene. The reaction mixture generally stood over night, though more or less time can be allowed. The precipitates of sodium chloride and methylhydroxylamine hydrochloride were not removed from the liquid, but the contents evaporated, under reduced pressures, to a gummy dryness and the residue extracted with dry ether and the extract filtered. To the filtrate, with vigorous stirring, a saturated ether solution of dry hydrogen chloride was added, the precipitate was collected and washed well with ether.[1] The hydrochloride was then dissolved in the least amount of chloroform, and again precipitated with absolute ether, to which a few drops of ethereal hydrogen chloride was added. This process was once more repeated. The purified hydrochloride was shaken with an ether layer and a fairly strong solution of potassium hydroxide, the ether extract, after separation, dried with calcium chloride, and the ether evaporated. It left a gum. This gum was transferred, with the aid of a little alcohol, to a beaker, which, with contents, was placed in a bell jar[2] *in vacuo*. After standing some time, and with frequent rubbing, solidification took place. The solid was washed with ligroin (b. p. 30–50°), dissolved in hot ligroin (b. p. 70–80°). After this solution had cooled an equal volume of low-boiling ligroin was added to it. The solution was allowed to evaporate very slowly, spontaneously, small crystals forming upon the walls of the vessel. These were removed and the recrystallization repeated, until a constant melting point of 113° was obtained for the compound.

0.1695 gram substance gave 0.5156 gram CO_2 and 0.1001 gram H_2O. Calculated for $C_{20}H_{19}NO$: C, 82.99%; H, 6.63%. Found: C, 82.95%; H, 6.64%.

β-Triphenylmethyl-β-methylhydroxylamine is soluble in alcohol, benzene, chloroform, ether and hot ligroin. When it is heated with aqueous hydrochloride acid, it is hydrolyzed, forming triphenylcarbinol and methylhydroxylamine hydrochloride.

The Action of Phosphorus Pentachloride on β,β-Triphenylmethylmethylhydroxylamine.—One gram of the hydroxylamine was placed in a round bottom flask with 10–12 cc. of absolute ether and one gram of pure phosphorus pentachloride was added to the solution. The flask, frequently rotated, was heated for four hours, the boiling ether being refluxed by a condenser, care having been taken that no moisture could enter. A

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[1] Oxalic acid, in ether solution, will not cause a precipitate.

[2] If paraffin shavings are present in the jar, the solidification seems to take place sooner.

yellowish white precipitate[1] resulted, which was brought on a filter and washed well. (For the examination of the filtrate "F" see later.) The precipitate was treated with 6 cc. of acidulated cold water in which it all dissolved. A drop or so of the solution reduced a correspondingly small amount of Fehling's solution, indicating the presence of methylhydroxylamine. The aqueous solution was placed in a separatory funnel, saturated with sodium chloride, made alkaline with strong sodium hydroxide solution and shaken with absolute ether. The alkaline solution was drawn off (it gave forth the odor of methylhydroxylamine), the ether extract poured through a cotton filter separatory funnel, and shaken with a solution of one cc. of N/HCl in five cc. of water. The aqueous extract was drawn off, and delivered through a cotton filter into a weighed beaker. The ether was again treated as above and the second aqueous extract combined with the previous one. The hydrochloric acid solution was evaporated in a desiccator to dryness, leaving a residue weighing 0.0672 gram. The residue was partly crystalline, partly oily. Upon evaporation of the ether, no residue remained.

A small portion of the solid residue was dissolved in water and made slightly alkaline with sodium hydroxide. Part of this solution was tested with a half-saturated solution of bleaching powder and gave no test for aniline, but with a very small amount of calcium oxychloride solution it gave the very delicate and characteristic test,[2] a navy blue fading into yellow, for monomethyl or monoethyl aniline. Another portion of the solution, neutralized, gave a small amount of yellow oil (nitro-nitrosomethylaniline), with nitrogen trioxide, and when the mixture was heated it did not smell of nitrophenol, again assuring the absence of aniline. In order to determine positively whether methyl- or ethyl-aniline was present, it was decided to convert the base into its acetyl derivative. The remaining portion of the solid in the beaker was dissolved in $^1/_2$ cc. of water, the beaker rinsed with $1^1/_2$ cc. of strong potassium hydroxide solution into a weighing bottle, and to the strong alkaline mixture, a large excess of acetylchloride was added in small portions, with vigorous shaking of the bottle. After standing some time, the solution was shaken with ether in a separatory funnel, the ether drawn off, and evaporated, and the residue crystallized out of ligroin. Crystals melting at 95.5° were obtained. Some synthetic methyl-acetanilide[3] melted at 101–102°; a mixture of the compound melting at 95.5° and some pure methyl-acetanilide melted at 99.5–100°, thus indicating the identity of the two.

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[1] If the mixture is heated for only a short time, twenty to thirty minutes, which is amply sufficient for the rearrangement of phenylmethylhydroxylamine, one recovers quite a large proportion of the hydrochloride.

[2] Leech, This Journal, **35**, 1042 (1913).

[3] Hofmann, *Ber.*, **7**, 523 (1874); Leech, *loc. cit.*

Only a few milligrams of the methylacetanilide[1] were obtained. After saponification of the methylacetanilide with boiling hydrochloric acid, the solution was made alkaline; the addition of calcium hypochlorite again gave the methylaniline test.

The original ether filtrate, "F" obtained in the treatment of triphenylmethylmethylhydroxylamine with phosphorus pentachloride, was placed in a separatory funnel and shaken with an alkaline solution. After separation of the ether, and on evaporation of the latter, a residue remained, which was identified as triphenylcarbinol by its melting point and its behavior when the melting point of a mixture of the product and pure carbinol was taken. Its weight was 0.68 gram, or 75% of the theoretical for a complete decomposition of triphenylmethylmethylhydroxylamine by phosphorus pentachloride, into triphenylmethylchloride.

The Action of Phosphorus Oxychloride and Phosphorus Pentachloride on β-Triphenylmethyl-β-methylhydroxylamine.—Half a gram of the hydroxylamine derivative was dissolved in 6 cc. of phosphorus oxychloride, to which was added half a gram of phosphorus pentachloride; the mixture was allowed to stand three or four days. The solution was then poured on crushed ice and the precipitate filtered off and dried. It was identified as triphenylcarbinol. The yield was quantitative. The filtrate reduced Fehling's solution and after being made alkaline, it gave the characteristic odor of methylhydroxylamine.

The Action of Beckmann's Mixture on β,β-Triphenylmethylmethylhydroxylamine.—Half a gram of the hydroxylamine derivative was dissolved in 6 cc. of Beckmann's mixture, and allowed to stand a week. As in the previous case, the mixture was poured on ice, the precipitate filtered off and identified as triphenylcarbinol. The yield was quantitative. The filtrate reduced Fehling's solution, and upon treatment with alkali it gave methylhydroxylamine which was detected by its odor.

The Action of Phosphorus Pentoxide on β,β-Triphenylmethylmethylhydroxylamine Hydrochloride.—Pure triphenylmethylmethylhydroxylamine was dissolved in absolute ether, a solution of hydrogen chloride in ether was added to it, and the precipitate that formed was collected. β,β-Triphenylmethylmethylhydroxylaminehydrochloride melts at 102°, and is soluble in alcohol and chloroform; insoluble in ether, ligroin, and cold water.

Half a gram of the hydrochloride salt was intimately mixed, in a test tube, with half a gram of phosphorus pentoxide, the mixture heated a few minutes in the free flame until no further action was apparent. The contents were treated with a few drops of alcohol, hydrolyzed with acidulated water, transferred to a separatory funnel and shaken with ether.

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[1] This method of acetylation, if care is taken, produces yields of 90–95% of the theoretical, as was ascertained with pure methylaniline.

The ether extract was separated, evaporated, and the residue upon purification identified as triphenylcarbinol. The acid aqueous solution was placed in a separatory funnel, made alkaline, and shaken with ether. The aqueous extract was drawn off and soon smelled of methylhydroxylamine. The ether extract was shaken with a solution of one cc. of N/HCl in 5 cc. water, the acid extract was drawn off, and after having been made slightly alkaline, the addition of bleaching powder solution gave no test for methylaniline or aniline.

CHICAGO, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

OCTOIODOPARAQUINHYDRONE.[1]

BY C. LORING JACKSON AND E. K. BOLTON.

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The work described in this paper grew out of the suggestion of the late Professor H. A. Torrey that one of us (Bolton) should take up the study of iodoanil, begun by him and Dr. Hunter.[2] After the too early death of Professor Torrey the research was continued by us, and among other derivatives of iodoanil, the description of which will appear soon in another paper, we tried to make the corresponding octoiodoquinhydrone. For this purpose we exposed a benzene solution of iodoanil to the action of sulfurous acid at ordinary temperatures and, after four weeks, were rewarded by the appearance of glistening black crystals of considerable size. These differed in color from crystals of iodoanil (prepared from benzene for the sake of comparison), as the latter were brown, but both formed flattened prisms or long plates terminated by two planes at an obtuse angle, and, although slight differences appeared, they seemed to us more in habit than real crystalline form. It was therefore necessary to bring convincing proofs that these black crystals were not iodoanil but a new substance, and we think, these will be found in the following observations: Treatment of the black crystals with benzene and alcohol, toluene, or glacial acetic acid yielded in each case a yellow solution, from which, in addition to the brown crystals of iodoanil, a quantity of a white substance soluble in sodium hydroxide was obtained, which can hardly be anything but tetraiodohydroquinone. An aqueous solution of sodium hydroxide disintegrated the crystals, leaving a brown powder (iodoanil), and dissolving a white substance (tetraiodohydroquinone). Parallel experiments with iodoanil showed that the alkaline solution was without action under the same conditions, and that the organic solvents yielded only brown crystals with no white admixture whatever. The crystals

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Elmer Keiser Bolton.

[2] THIS JOURNAL, 34, 702 (1912).