mirable work of the Bureau of Standards has been completed by the determination of the actual amount of inclusion in their deposits; to emphasize the fact that in view of the newly discovered effect of invisible traces of platinum black, we overrated the significance and certainty of some of our recent conclusions, reasonable although they seemed at the time; and to state that further experiments are in progress.

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MOLECULAR REARRANGEMENTS OF β-TRIPHENYLMETHYL-β-METHYL HYDROXYLAMINES AND THE THEORY OF MOLECULAR REARRANGEMENTS.[1]

BY JULIUS STIEGLITZ AND BERT ALLEN STAGNER.[2]

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The earliest observations of molecular rearrangements of hydroxylamine derivatives were those of Lossen[3] in the case of hydroxamic acids, RCO.NHOH, and of dihydroxamic acids, $RCO.NHOCOR_1$.[4] In explanation of these and similar rearrangements, the one of us proposed the theory[5] that they take place through the intermediate formation of univalent nitrogen derivatives under the influence of the reagent used to effect the rearrangement. Thus, a hydroxamic acid could form such a univalent nitrogen derivative by the loss of water in the presence of dehydrating agents.

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

Dihydroxamic acids would yield the same products with the loss of a molecule of acid under the influence of bases or heat.

$$RCO.NH.OCOR_1 \xrightarrow{-R_1COOH} RCO.N \longrightarrow CO : NR. \qquad (2)$$

The free or latent valences of the unsaturated nitrogen atom were considered to have the power to take the radical R from the carbon atom. Of the many facts brought out in support of this theory by the one of us and by a number of independent investigators,[6] only the most important need be summarized here: (1) The ready application of the theory

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[1] A brief preliminary report appeared in *Proc. Nat. Acad. Sciences*, 1, 205 (1915). For literature references to previous papers, see Stieglitz and Leech, THIS JOURNAL, 36, 272 (1914).

[2] The material presented here is used by Stagner in his dissertation in part fulfilment of the requirements for the Ph.D. degree of the University of Chicago.

[3] *Ann.*, 161, 359 (1872).

[4] This is tautomeric with $RC(OH) : NO.COR_1$.

[5] See the literature references given by Stieglitz and Leech, *loc. cit.*

[6] Schroeter, *Ber.*, 42, 2340 (1909); 44, 1207 (1911); Stoermer, *Ibid.*, 42, 3133; Wieland, *Ibid.*, 42, 4207; L. W. Jones, *Am. Chem. J.*, 48, 1 (1912); 50, 440 (1913).

without any further assumptions, to Hofmann's rearrangement of acyl halogenamides, to the Curtius rearrangement of acyl azides, to the rearrangement of triphenylmethyl hydroxylamines, halogen amines and azides, as investigated by the one of us and his collaborators. (2) The *non-occurrence* of rearrangements of compounds $RCO.N(CH_3)OH$,[1] $RCO.N(CH_3)Cl$, $RC(:NCl)OCH_3$,[2] which appear to have everything in common with the rearranging substances except the possibility of readily forming univalent nitrogen derivatives. (3) The close relation the reagents used to effect each rearrangement bear to the facilitating of a dissociation leading to univalent nitrogen derivatives (see Equations 1 and 2).

No other theory of the rearrangements, that has been proposed, could give as complete an explanation of any one of these sets of facts, we believe, not to speak of all three of them.

In recent years the initial force leading to the rearrangements has been more sharply defined, on the basis of the electron theory of valence, *as residing in the instability of the charges on the radicals held by the nitrogen* in the various classes of rearranging compounds and to the great tendency of these radicals to go over into their common stable forms.[3] This tendency has been compared with the electrolytic solution tension of elements.[4] Thus, in the hydroxylamine derivatives $RCO.NH^{-}\ {}^{+}OH$,[5] we have to deal with the tendency of the positive OH radical to go over into its common negative form; in the chloroamines, $RCO.NH^{-}\ {}^{+}Cl$,[6] we have positive chlorine with its enormous tendency to form its stable negative atom or ion. In satisfying these tendencies by the absorption of electrons from neighboring atoms, these radicals (${}^{+}OH$, ${}^{+}Cl$, ${}^{+}Br$, and also[7] ${}^{+}N^{=}$, etc.) disturb the valence electrons of the neighboring atoms in the compounds under discussion and rearrangement is inevitable. Whatever view of the mechanism of the rearrangements may finally obtain, this, it

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[1] This question is being re-investigated by Miss Quaesita Drake, as a result of the work described in this paper.

[2] Destruction distillation effects a rearrangement and the loss of methylchloride (Stieglitz, Earle and W. J. Hale, unpublished work).

[3] The electron interpretation of the rearrangements was presented independently and practically simultaneously (see THIS JOURNAL, **36**, 287 (1914)) by L. W. Jones (*Am. Chem. J.*, **50**, 448, published at the end of January, 1914) and by one of us (February number of THIS JOURNAL (1914)). The interpretations differ in some important respects, but they agree as to the fundamental relations. Preliminary suggestions were made by Stieglitz, *Ber.*, **43**, 782 (1910); *Am. Chem. J.*, **46**, 327 (1911); *Ber.*, **46**, 2149 (1913), and by Jones, *Am. Chem. J.*, 48, 1 (1912). The same idea, expressed in the older terms then current, was clearly recognized in the earlier papers on the rearrangement of acyl halogen amides (Hoogewerff and van Dorp, *Rec. trav. chim.*, **8**, 173 (1889); Lengfeld and Stieglitz, *Am. Chem. J.*, **15**, 215, 504 (1893)).

[4] Stieglitz. THIS JOURNAL, **36**, 276, 280 (1914).

[5] *Ibid.*

[6] *Ibid.*, and *Ber.*, **43**, 782 (1910); **46**, 2149 (1913).

[7] In hydrazine derivatives, including probably the azides, we have the unstable **radical** ${}^{+}N^{=}$ (Stieglitz and Curme, *Ber.*, **46**, 911 (1913)).

seems to us, is the most vital consideration[1] and should form the common ground on which all theories of the rearrangements must meet.

The one arrangement for which, from the outset, any further special assumptions had to be made in the univalent nitrogen theory has been the Beckmann rearrangement of oximes. For this rearrangement, under the influence of acid dehydrating agents, the one of us assumed, provisionally,[2] that the rearrangement is preceded by the absorption of acid and the subsequent loss of water (or its equivalent) as indicated in the equation

$$R_2C:NOH \xrightarrow{+HX} R_2CX.NHOH \xrightarrow{-HOH} R_2CX.N \longrightarrow RCX(:NR). \quad (3)$$

This interpretation seemed to be borne out by the proof that triarylmethylhydroxylamines, $R_3C.NHOH$, of exactly the same structure as the assumed intermediate product, $R_2CX.NHOH$, rearrange in exactly the same way and under the same conditions.[3] But the assumption met difficulties[4] in explaining the observed differences in the migration of the radicals R and R′ of stereoisomeric oximes RR′C : NOH. In this one case the conception of a direct exchange of radicals, *e. g.*:

$$\begin{array}{c} R\!-\!C\!-\!R' \\ \| \\ N\!-\!OH \end{array} \longrightarrow \begin{array}{c} R\!-\!C\!-\!OH \\ \| \\ N\!-\!R' \end{array} \quad (4)$$

as postulated by Beckmann,[5] seemed to agree with the facts rather better than the univalent nitrogen theory. In view of this fact, attempts have been included in all the investigations planned by the one of us, to effect this type of rearrangement with compounds *which could not be expected to form a univalent nitrogen derivative* without an easily recognized destructive change in the product. Compounds of the type RCO.N(Alkyl)-OH, RCO.N(Alkyl)Cl, had been used for this purpose. All efforts to rearrange such compounds had given negative results, but the attempts were repeated with every new class of compounds investigated. A first clue to such a rearrangement was finally discovered last year, when the one of us, together with Leech,[6] examined the effect of phosphorus pentachloride on β-triphenylmethyl-β-methylhydroxylamine, $(C_6H_5)_3C.NCH_3.OH$. The product of the action seemed to give methylaniline on hydrolysis and this could only be formed as the result of a rearrangement.

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[1] See also L. W. Jones, *loc. cit.*

[2] *Am. Chem. J.*, **18**, 754 (1896) (footnote), and THIS JOURNAL, **36**, 277 (1914), footnote 2.

[3] Stieglitz and Leech, *Ber.*, **46**, 2147 (1913).

[4] Stieglitz, *Am. Chem. J.*, **18**, 754 (1896); Montague, *Ber.*, **43**, 2014 (1910); L. W. Jones, *Am. Chem. J.*, **48**, 28 (1912).

[5] *Ber.*, **19**, 988 (1886); **27**, 300 (1894). Other prominent adherents of this view, in one form or another, have been Hoogewerff and van Dorp, *Rec. trav. chim.*, **8**, 173 (1889); Hantzsch, *Ber.*, **24**, 3516 (1891); Kuhara, *Mem. Coll. Sci. Eng. Kyoto*, **1**, 254 (1903–1908); **2**, 367 (1909–1910); **6**, 1 (1913); *Mem. Coll. Sci. Kyoto*, **1**, 25 (1914).

[6] THIS JOURNAL, *loc. cit.*

The yield of methylaniline was so small, however, that the evidence of its formation was limited to the characteristic chloride of lime color test, discovered by Leech,[1] and of the melting-point tests of the acetyl derivative. It was not beyond the range of possibility that the substance resulted from an alkylation of aniline rather than as a primary product of rearrangement. Under the circumstances, an exhaustive investigation of the reaction was undertaken by us. The results of this work and the conclusions drawn from it are presented in this paper.

It should be said at once that the observations of Stieglitz and Leech have been confirmed in every respect and conclusive evidence brought that methylaniline is formed in quantity by the hydrolysis of the product of the rearrangement of β-triphenylmethyl-β-methylhydroxylamine.[2] The methylaniline was identified by the analysis of its chloroplatinate, by the examination of its hydrochloride, as well as, again, by its characteristic reaction with chloride of lime. It was not considered necessary to repeat the identification as acetylmethylaniline.

Furthermore, *benzophenone* has been isolated and identified by us as the compound formed, with methylaniline, in the hydrolysis of the product of rearrangement.

The demonstrated rearrangnement of β-triphenylmethyl-β-methylhydroxylamine must be considered to open up the whole problem of the theory of the molecular rearrangements outlined above: *the formation of a simple univalent nitrogen derivative*, $R_3C.N$, *is impossible* in this case. Of the various theories which suggested themselves[3] when the first indication of this rearrangement was obtained, an important one is excluded by the identification of benzophenone just mentioned: the possibility of a primary dissociation of triphenylmethymethylhydroxylamine into a *bivalent* nitrogen derivative,[4] corresponding to the dissociation of the related triphenylmethylperoxide into a univalent oxygen derivative, with a subsequent rearrangement, as discovered by Wieland,[5] is excluded[6] by the formation of benzophenone. A rearrangement proceeding along these lines should yield tetraphenylbenzpinacone by hydrolysis of the product.[7] Not the slightest indication of the presence of the pinacone was observed, although a careful search for it was made. The pinacone is known to be decomposed by heat into benzophenone and benzhydrol,

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[1] This Journal, 35, 1042 (1913).

[2] The behavior of acyl-β-hydroxylamines, $RCON(CH_3)OH$ and similar compounds is being re-investigated by Miss Quaesita Drake as a result of this work.

[3] Stieglitz and Leech, *loc. cit.*, p. 284.

[4] *Loc. cit.*, p. 286.

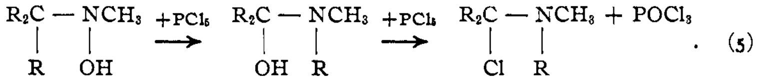
[5] *Ber.*, 44, 2550 (1911).

[6] A modification of this theory is discussed further on.

[7] This is readily apparent from a consideration of the product given in Equation 17, This Journal, 36, 286 (1914).

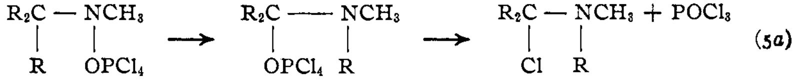
but no such decomposition takes place under the conditions obtaining in the reaction studied by us: this was confirmed by parallel experiments carried out with a preparation of the pinacone.

This leaves only two important theories that we need take into account:[1] first, the theory of Beckmann that the rearrangements involve simply direct exchanges of radicals (see Equation 4), the reagents used acting "catalytically." For the rearrangement of β-triphenyl-β-methylhydroxylamine we would have



$$\underset{\underset{R}{|}}{R_2C} - \underset{\underset{OH}{|}}{NCH_3} \xrightarrow{+PCl_5} \underset{\underset{OH}{|}}{R_2C} - \underset{\underset{R}{|}}{NCH_3} \xrightarrow{+PCl_5} \underset{\underset{Cl}{|}}{R_2C} - \underset{\underset{R}{|}}{NCH_3} + POCl_3 \quad . \quad (5)$$

A variation of this view, which finds its chief modern support in the important work of Kuhara,[2] is that in the rearrangement of hydroxylamine derivatives under the influence of acetyl chloride, acetic anhydride, sulfuric acid, etc., it is not the OH radical that migrates but an acyl derivative of it, RCO.O—. This view is practically identical with Beckmann's first interpretation[3] of the reaction that bears his name. From this point of view, as understood now, phosphorus pentachloride presumably reacts first on a hydroxylamine derivative like triphenylmethyl-methylhydroxylamine to form the product $R_3C.N(CH_3)OPCl_4$,[4] which then rearranges according to



$$\underset{\underset{R}{|}}{R_2C} - \underset{\underset{OPCl_4}{|}}{NCH_3} \longrightarrow \underset{\underset{OPCl_4}{|}}{R_2C} —— \underset{\underset{R}{|}}{NCH_3} \longrightarrow \underset{\underset{Cl}{|}}{R_2C} - \underset{\underset{R}{|}}{NCH_3} + POCl_3 \quad (5a)$$

In the second place, we have the theory of the intermediate formation of univalent (or other unsaturated) nitrogen derivatives in these and re-

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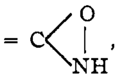
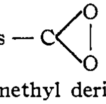
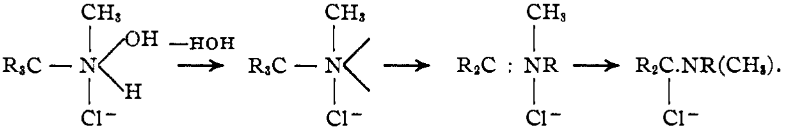
[1] All other theories that have been proposed are quite untenable in view of the facts now known; the formation of ring derivatives in which the nitrogen is connected with the migrating alkyl or aryl radical (Nef, *Ann.*, **298**, 308 (1897); **318**, 39, 227 (1901)), is incompatible with the position the nitrogen invariably takes in the migrating alkyl or aryl (cf. Stieglitz, *Am. Chem. J.*, **29**, 58 (1903)). The formation of unstable triatomic rings,  $= C\langle\begin{matrix} O \\ | \\ NH \end{matrix}$, proposed by v. Baeyer as a result of his observations of rearrangements of peroxides  $— C\langle\begin{matrix} O \\ | \\ O \end{matrix}$ (*Ber.*, **32**, 3627 (1900)) is quite impossible in view of the fact that triphenylmethyl derivatives, such as $(C_6H_5)_3C.NHCl$ behave exactly as do the acyl derivatives; they cannot possibly form the rings demanded by Baeyer's theory. (See below, p. 2060, and see also, Stieglitz, *Am. Chem. J.*, **29**, 49 (1903), and Wieland, *Ber.*, **42**, 4207 (1909)).

[2] *Loc. cit.* See also Sluiter, *Rec. trav. chim.*, **24**, 372 (1905).

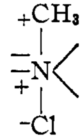
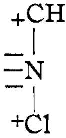
[3] *Ber.*, **19**, 988 (1886).

[4] Werner, *Ber.*, **25**, 40 (1892); Stieglitz and Leech, THIS JOURNAL, **36**, 279 (1914). The assumption of this intermediate product would be in far better agreement with the facts than the assumption of the intermediate formation of N-Cl derivatives, as made by Beckmann and others.

lated rearrangements. The observation that phosphorus pentoxide effects the rearrangement of triphenylmethyl hydroxylamine *hydrochloride*[1] suggested to the one of us the possibility that *salts* of hydroxylamines, by being deprived of water or its equivalent, could form *salts* of univalent nitrogen compounds, which could rearrange in exactly the same way as the univalent nitrogen compounds $R_3C.N$. We would have[2]


(6)

These two theories,[3] it seems to us, are worthy of critical consideration on the basis of the new facts discovered,[4] and we shall indicate here, as briefly as possible, the facts, as at present known, which appear to favor the one theory or the other. We shall then attempt to show the common ground, on which both theories rest.

I. The following facts at present seem to us to weigh in favor of Beckmann's theory of a direct exchange of radicals (see Equations 4, 5 and 5*a*): 1. We have the fact, now established by us, that triphenylmethyl-β-methylhydroxylamine is rearranged in the same way and under the same conditions as triphenylmethylhydroxylamine itself. For the rearrangement to proceed by way of the hydrochloride of a univalent nitrogen derivative (Equation 6), it would be necessary to assume the temporary existence of a compound, which we will call Compound A, R_3C^+  and which would be an *electromer* of a compound B, triphenylmethylchloromethylamine, R_3C^+ 

$$R_3C^{+}\ {}^{-}_{-}\overset{+CH_3}{\underset{+Cl}{N}}$$

; the latter compound has been prepared in this laboratory by the late Isabella Vosburgh[5] and found *not* to undergo rearrangement. Now, the possibility of the existence of electromers was recognized by J. J. Thomson[6] as a consequence of the ap-

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[1] Stieglitz and Leech, *loc. cit.*

[2] The electronic interpretation is given in detail, p. 285, *loc. cit.*

[3] Our theory will be taken in its broadest sense, as including the intermediate formation of univalent or bivalent nitrogen and univalent oxygen derivatives, etc.

[4] These will include the more recent and especially important observations of Kuhara, *loc. cit.*

[5] THIS JOURNAL, 38, 2081 (1916).

[6] Cf. "Corpuscular Theory of Matter," 1907, p. 131.

plication of the electron theory to chemical valence and structure, and a number of other writers[1] have applied his ideas to specific cases and found definite *indications* of the existence of electromers in equilibrium. As to the separate existence of electromers, W. A. Noyes,[2] in an important investigation of electromerism in the case of nitrogen chlorides, has found experimental indications, but no final proof, of such a relation. Convincing evidence of the separate existence of electromers has been uncovered by L. W. Jones[3] in a brilliant critical review of the chemistry of hydroxylamine derivatives. For the critical consideration of the consequences which would follow from the postulated relation between the electromers A and B and especially of the question whether they necessarily must be convertible into each other, it will be best to discuss in a few words the fundamental relations that must exist between electronic isomers.

Theoretically considered,[4] when one electromer is changed into another, a transfer of electrons between atoms contained in the same molecule occurs —that is, we have a case of intramolecular oxidation and reduction of atoms. This, if reversible, should be subject to the same laws that hold for reversible intermolecular oxidations and reductions, notably to the law of equilibrium. As is well known, such a condition of equilibrium may be almost, although not quite, one-sided (as in $2Fe^{++} + Cl_2 \rightleftarrows 2Fe^{+++} + 2Cl^-$) or it may involve a reaction that is to a distinct extent reversible (as in $2Fe^{++} + I_2 \rightleftarrows 2Fe^{+++} + 2I^-$).[5] Similarly, we must expect cases of electromerism, in which one electromer would be extraordinarily stable and the other capable of existence only in traces; in other instances, we should have electromers, for which "the oxidation-reduction constants"[6] of the differently charged elements make possible the existence, in some quantity, of the two electromers side by side. In view of the tremendous mobility of electrons, the equilibria should establish themselves, as a rule, with enormous speed whenever the atoms, whose charges cause the electromerism, are directly linked with each other. When atoms, which cause electromerism, are not directly linked together, tolerably permanent separate existence of electromers seems to be possible, as is shown by the fact that the only electromers whose separate existence has been convincingly

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[1] Fry, THIS JOURNAL (Proc.), 30, 34 (1908); *Z. physik. Chem.*, 76, 387 (1911); THIS JOURNAL, 36, 248 (1914), etc.; Falk and Nelson, *School of Mines Quarterly*, 30, 179 (1909); THIS JOURNAL, 32, 1637 (1910), etc.; L. W. Jones, *loc. cit.*; W. A. Noyes, THIS JOURNAL, 35, 767 (1913), and others.

[2] *Loc. cit.*

[3] THIS JOURNAL, 36, 1268 (1914).

[4] Cf. also the authors referred to above.

[5] Cf. Stieglitz, "Qualitative Analysis," Vol. 1, pp. 272–276.

[6] Constants comparable with electrolytic solution tension constants are referred to.

established are the hydroxylamines[1] of the general type, $R_3N\pm{}^{-OR}_{+OH}$ and $R_3N\pm{}^{-OH}_{+OR}$, which belong to the second class. Indeed, their separate existence and comparative stability is apparently due to the very fact that the different distribution of charges, which causes the electromerism, relates to two radicals OH and OR (more exactly, to their oxygen atoms), *which are not directly linked together.* Further, the following vital fact which has hitherto been too readily ignored, must be taken into account with the first class of electromers, whose differently charged atoms are directly linked and which must be considered to be reversibly convertible into each other. We will represent this type briefly as $X^+ \,{}^-Y$, $X^- \,{}^+Y$. The reversible reaction $X^+ \,{}^-Y \rightleftarrows X^- \,{}^+Y$ involves the transfer of *two* electrons and, if we use the ordinary conceptions of electronic valence (the older or original Thomson conceptions), this should lead through the migration, first, of a single electron, to an intermediate stage, where neither X nor Y would be charged with excess of positive or negative electricity; in other words, the usual valence force between the two atoms would be lacking and, consequently, *dissociation into X and Y should take place.* The only alternative to this conclusion, which has apparently been entirely overlooked in the assumptions of electromeric relations before this, is that in the intermediate product X Y, *nonpolar valences,* of the type suggested by Bray and Branch,[2] G. N. Lewis,[3] Thomson,[4] and A. L. Parsons,[5] unite X and Y.[6] Indeed, the evident absence of such dissociation in indicated cases of electromerism would, if electromerism and nondissociation were proved beyond a doubt, be excellent chemical evidence in favor of the existence of some form of nonpolar valences. The well-known specific and generally one-sided actions of absorption, metathesis, etc., which are obviously *directed* by the nature of the specific *polar* charges on atoms both in inorganic and organic compounds, would find their explanation in the fact that *the chemically active molecules are those whose reacting atoms have polar charges.*[7]

On the basis of these general considerations concerning the relations

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[1] Jones, *loc. cit.*

[2] THIS JOURNAL, **35**, 1440 (1913).

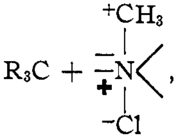
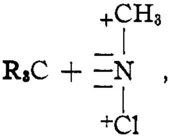
[3] *Ibid.*, **35**, 1448 (1913); **38**, 762 (1916).

[4] *Phil. Mag.*, **27**, 784 (1914).

[5] Cf. "A Magneton Theory of the Structure of the Atom," Vol. **65**, No. 11, Smithsonian Collections. On p. 30, such an intermediate phase is considered.

[6] Cf. Falk and Nelson, THIS JOURNAL, **36**, 209 (1914); W. A. Noyes, *Ibid.*, p. 214; R. F. Brunel, *Ibid.*, **37**, 709 (1915); Stieglitz, *Proc. Nat. Acad. Sci.*, **1**, 196 (1915).

[7] Cf. Bray and Branch, Lewis, Thomson, Parsons, *loc. cit.*

of electromers, Compound A,  $R_3C + \underset{\begin{array}{c}\mathbf{+}\\|\\-Cl\end{array}}{\overset{\begin{array}{c}+CH_3\\|\\-\end{array}}{N}}\langle$, which, according to the univalent nitrogen theory would be the rearranging univalent nitrogen salt in the rearrangement of triphenylmethyl-β-methylhydroxylamine, $(C_6H_5)_3C.N(CH_3)OH$, by phosphorus pentachloride, and Compound B,  $R_3C + \underset{\begin{array}{c}-\\|\\+Cl\end{array}}{\overset{\begin{array}{c}+CH_3\\|\\-\end{array}}{N}}$, which Miss Vosburgh found to be nonrearranging, would, as far as composition is concerned, seem to be electromers of the first (XY) class. If this is their relation, one should expect them to be convertible into each other: then, either B should undergo the molecular rearrangement as a result of going over first into A, or A should be transformed, in part at least, into the stable electromer B—or both actions should take place. No indications of any such results have been observed.[1] It still remains possible—or, indeed, probable—that the *fifth* (positive[2]) valence of nitrogen which enables ammonium radicals to combine with anions and form salts, and which also holds the chlorine in compound A in the *salt* form, is of a different character, in regard to its position in the atom or some other relation, from the remaining four valences, and not capable of going over electromerically into one of these other (negative) valences. In that event, the two electromers would really belong to the second group of electromeric substances, of which the hydroxylamine derivatives, discovered by Jones and discussed above, are the best known representatives, and they would not necessarily be convertible into each other. The hydroxylamine electromers are themselves ammonium compounds, in which the valence in question is concerned.

On the whole, however, interpretations of the rearrangement that can do without assumptions concerning electromeric substances, must, for the present, be considered the more conservative. For this reason, the proved rearrangement of triphenylmethyl-β-methylhydroxylamine should at the present moment be judged as weighty, although not conclusive, evidence in favor of Beckmann's view, that these rearrangements take place by a direct exchange of radicals.

2. The relation of stereoisomeric ketoximes to the products of their rearrangement (see Equation 4) still remains as indicated in the earliest report by one of us on his own theory,[3] an important, although not conclusive, fact, weighing in favor of Beckmann's view. It *may* find its ex-

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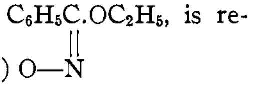
[1] Further work is suggested by these considerations.

[2] This valence is indicated by heavy type as **+** in the above formula for A.

[3] Stieglitz, *Am. Chem. J.*, 18, 754 (1896); THIS JOURNAL, 36, 277 (1914).

planation in the theory of a univalent nitrogen *salt* derivative, undergoing rearrangement, as discussed in detail in a previous paper by the one of us.[1] But such an interpretation is open to the same objections as raised by us in the previous paragraph against the salt theory, and, consequently, at present the relation of stereoisomerism to the rearrangement still remains important evidence in favor of a rearrangement by direct exchange of radicals.

3. A number of observations made by Kuhara[2] in a series of admirable investigations seem, at the first glance, to weigh heavily in the scales in favor of Beckmann's views. Among these facts we have as a most notable one, that syn-acetylethylbenzhydroximic ester,  $\begin{array}{r} C_6H_5C.OC_2H_5 \\ \| \\ \text{(acyl) O—N} \end{array}$, is rearranged when it is heated for some time above its melting point.[3] The anti-derivative is not rearranged.[4] Kuhara formulates the rearrangement of the syn-derivative essentially in the way Beckmann would (Equation 4), but he also emphasizes the effect of the strength of the acid of the acyl radical attached to the oxygen of the oxime group on the ease with which the rearrangement takes place—a most important contribution to the subject. Further, it is characteristic, as Kuhara found, that the rearrangement of syn-acetylethylbenzhydroximic ester, as well as that of the analogous acetyl derivative of benzophenone oxime, $(C_6H_5)_2C$:NO(Acyl), is *accelerated* by the presence of hydrogen chloride as a "catalytic agent," the velocities of rearrangement being found proportional to the concentration of acid present. Since acids act as "catalyzers" most commonly by salt formation, it is altogether likely that the rearranging substances, in the experiments with solutions, are the *salts*[5] of the acyl esters, rather than the esters themselves.[6] It is not at all impossible that, similarly, salts formed by the presence of traces of free acid should also be the active components even in the rearrangement by fusion. As a matter of fact, Kuhara found it impossible to rearrange the acetyl ester of benzophenoneoxime "by itself, even by the rise of temperature." It is always necessary to use hydrogen chloride as a catalytic agent. He ascribes this to the "weak negative character[7] of the acetic acid residue." In support of this view, he brings the important observation that the

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[1] Stieglitz and Leech, *loc. cit.*, p. 281.

[2] *Loc. cit.*

[3] *J. Chem. Soc.*, 106, 538 (1914).

[4] Cf. Werner, *Ber.*, **25**, 33 (1892); **26**, 1652 (1893); **29**, 1153 (1896).

[5] The question of the ionization of these salts is not considered here.

[6] Kuhara proposed this view for the rearrangement of acetylbenzophenoneoxime by hydrogen chloride [*Mem. Coll. Sci. Kyoto*, 1, 25 (1914)].

[7] *Loc. cit.* As a matter of fact, in these hydroxylamine derivatives we really have the unstable positive radical $CH_3CO.O^+$ (see below).

benzenesulfonyl ester of benzophenone oxime, "owing to the presence of the strong negative acid residue," undergoes the rearrangement apparently spontaneously, without the need of a catalyzing acid, slowly in the cold, very rapidly when it is heated above its melting point of 62°. This whole evidence is open to quite another interpretation: it would seem as if the acetyl derivatives might not rearrange spontaneously on account of the fact that any traces of acetic acid, formed by the action of moisture on the ester, might be too weak to form a *salt* in sufficient quantity with the oxime ester, and in the absence of the salts, there would be no rearrangement; but any traces of benzene sulfonic acid, so liberated, could act autocatalytically, since the acid would be strong enough to form a salt with the ester. It would be important to determine whether the spontaneous rearrangement of the sulfonyl ester would not be *accelerated* by the presence of hydrogen chloride.[1] Beyond suggesting that the hydrochloric acid helps out the weak acetic acid residue in its tendency to exchange positions with the phenyl radical, Kuhara does not explain how the formation of the hydrochlorides of the acetyl derivatives should facilitate the rearrangement. Two explanations suggest themselves: one, obviously, is that *the apparent necessity for the formation of a rearranging salt* would be in excellent agreement with the view that a *salt* of a *univalent nitrogen derivative* is the *real rearranging component in these reactions*[2] and that the rearrangement does not proceed until salt formation gives the molecule its only opportunity to form any univalent nitrogen derivative. Kuhara's view that the "weak negative character of the acetic acid residue" is responsible for the nonrearrangement of acetyl benzophenoneoxime without the aid of hydrochloric acid seems to be contradicted by the peculiar fact that all attempts to rearrange chloroimidobenzophenone, $(C_6H_5)_2C : NCl$, have failed to indicate the least trace of a rearrangement;[3] the hydride corresponding to the radical Cl is hydrogen chloride itself,[4] an acid fully as strong as, or stronger than, benzene-

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[1] Since this was written, Mr. Sidney Cadwell has investigated this question for me and found that added acid (hydrogen chloride, benzene sulfonic acid) does decidedly *accelerate* the rearrangement of the benzene sulfonic acid ester of benzophenone oxime, but he has also found that there is a slow, spontaneous rearrangement of the ester itself even at 0° and even in the presence of a weak base like pyridine (cf. Kuhara). This result will be published later in detail.—J. S.

[2] The equation representing the rearrangement from this point of view is given by Stieglitz and Leech, *loc. cit.*, p. 281.

[3] Heat, bases, chlorine, phosphorus pentachloride have been tried. Kuhara's work suggests a further trial with *acids* and this will be undertaken. (Since this was written, Henry R. Curme has studied the action of concentrated sulfuric acid on the chloroimide: no trace of a rearrangement product could be found, under exactly the same conditions of work as led to a rearrangement of benzophenoneoxime.)

[4] Kuhara takes no account of the positive charges on the radicals $CH_3CO.^{-}O^{+}$ and $C_6H_5SO_2{}^{-}O^{+}$ in the oxime esters (Stieglitz and Leech, *loc. cit.*) and contrasts the

sulfonic acid. Acid decomposes the chloroimide and hence salts, when formed, decompose in another way than by rearrangement, and it is certainly significant that just in this case we cannot secure a rearrangement of the free chloroimide itself. It seems possible, therefore, that Kuhara's interesting results, from which we can recognize the importance of salt formation with acids for the rearrangements of oximes and their esters, may really signify that the easiest path for these rearrangements is over univalent nitrogen compounds, *including their salts*, and that a direct exchange of radicals is a much more difficult process.

We wish to point out, however, that the major role played by salt formation in the rearrangement of the oxime esters may consist not simply in making possible or facilitating the formation of a univalent nitrogen compound, but may well be a further instance of what seems to be a broad and fundamental principle, namely that *acids* are found to *facilitate changes and migrations of unstable positive atoms or radicals,*[1] *which in their migration or change go over into their stable negative forms.* Besides the cases just discussed, we find this principle applying to the various forms of rearrangement of hydrazines with the unstable atom $^{+}N^{=}$,[2] such as $C_6H_5HN^{-}\ ^{+}NHC_6H_5$ (*e. g.*, the rearrangement into benzidine with the stable atoms $^{-}N^{=}$), applying to the rearrangement of phenylhydroxylamine,[3] $C_6H_5HN^{-}\ ^{+}OH$, with the unstable atom $^{+}O^{-}$, into amino phenols[4] $HO^{-}\ ^{+}C_6H_4.NH_2$, with the stable atom $^{-}O^{-}$, of acylhalogenanilides[5] $RCO.N(Cl^{+})C_6H_5$, with the unstable atom Cl^{+}, to acylchloroanilides $RCO.NHC_6H_4Cl^{-}$, with the stable atom Cl^{-}, which are all accomplished or accelerated with the aid of acids: *all involve the change*

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strength of the hydrides of the radicals, namely, acetic and benzenesulfonic acids. This is why HCl and not HOCl is used in the text for purposes of comparison. As a matter of fact, the real acids, of which the compounds may be said to be derivatives for the purposes of comparison, are the per-acids $CH_3CO.^{-}O^{+-}OH$, $C_6H_5SO_2{}^{-}O^{+-}OH$, and hypochlorous acid $Cl^{+-}OH$.

[1] The result of the migration is always a stronger and more stable base and the effect of the acid is, therefore, in agreement with the energy relations that must be involved. Probably potential relations of the unstable positive forms of the elements, akin (*mutatis mutandis*) to solution tensions, are favorable to their transformation in *acid* media into the stable negative forms of the elements. Investigations from this point of view are greatly to be desired.

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

[3] Stieglitz and Leech, *loc. cit.*

[4] Bamberger, *Ber.*, **33**, 3600 (1900); **34**, 1 (1901).

[5] Stieglitz and Slosson, *Ber.*, **28**, 3265 (1895); Armstrong, *J. Chem. Soc.*, **77**, 1047 (1900); Acree and Johnson, *Am. Chem. J.*, **38**, 265 (1907), who brought evidence indicating that the salts are the rearranging components. These chemists did not discriminate between positive and negative halogens in these compounds. See also Orton, *J. Chem. Soc.*, **95**, 1456 (1909).

of unstable positive, to stable negative, atoms.[1] *Underlying all of these rearrangements* is the tendency of these unstable atoms *to absorb electrons:* and they thus disturb, *eo ipso*, the valence relations in a molecule and the rearrangements are necessary sequels.[2]

II. We will turn now to the consideration of the most important facts which appear to favor the view that unsaturated (primarily univalent, possibly also bivalent[3]) nitrogen derivatives are intermediate products in the rearrangements of the various classes of compounds which suffer this typical rearrangement, such as the hydroxylamines, the halogenamines, the azides.

1. By losing nitrogen, the azides, $RCO.N_3$, $R_3C.N_3$, rearrange and give exactly the same products as do the other classes of compounds discussed. Recently, in this laboratory, Senior[2] found that $(ClC_6H_4)(C_6H_5)_2C.N_3$, even gives the same proportion of aniline and chloroaniline in the rearrangement as does $(ClC_6H_4)(C_6H_5)_2C.NHOH$. A "direct exchange" of nitrogen with the radical R, (C_6H_5) or (ClC_6H_4) seems out of the question.

2. When univalent nitrogen derivatives can be formed readily, we have smooth reactions, proceeding at low temperatures, in marked contrast with those cases where univalent nitrogen cannot be obtained readily and, at best, only indirectly: (*a*) Dry salts of acylchloroamides rearrange explosively when warmed gently,[4] and in solution the salts rearrange rapidly at low temperatures.

$$RCO.N\begin{matrix}Me\\Cl\end{matrix} \xrightarrow{-MeCl} RCO.N \longrightarrow CO : NR. \qquad (7)$$

In contrast with this behavior we find that alkyl derivatives, $RCO.NCl(CH_3)$, do not rearrange[5] and none of the choloroimidoesters, $RC(: NCl)OCH_3$, which have been obtained in syn and antistereoisomeric forms corresponding to those of the hydroxamic esters, is rearranged, until destructive distillation is resorted to, in which the methyl group is lost.[6] According to the univalent nitrogen theory of the one of us, these results are to be expected, but they cannot be explained without further specific assumptions on the basis of the Beckmann theory of direct exchanges, since there is no apparent reason why there should not be an equally ready direct exchange of the radical R and the (positive) chlorine atom in these cases and in the non-alkylated compounds. (*b*) The dry

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[1] Miss De Sale is investigating the question to what extent acids accelerate the rearrangement of azides. The rearrangement of peroxides by acids will also be studied from this point of view.

[2] *Proc. Nat. Acad. Sci.*, **1**, 207 (1915).

[3] Stieglitz and Leech, *loc. cit.*

[4] Unpublished work with O. Eckstein.

[5] Slosson, *Am. Chem. J.*, **29**, 289 (1903).

[6] Unpublished work with Earle and W. J. Hale.

metals salts of dihydroxamic acids[1] also rearrange spontaneously and explosively at room temperatures, forming isocyanates (see Equation 2). The corresponding esters, $RC(OC_2H_5) : NO.COCH_3$, rearrange very slowly, if at all, and then only at elevated temperatures. Their salts with acids rearrange much faster and may even be present in all of their rearrangements (see I, 3 above) and these salts may produce univalent nitrogen derivatives. (*c*) Triphenylmethyldichloroamine, $(C_6H_5)_3C.NCl_2$, is readily rearranged by heat[2] with loss of chlorine; triphenylmethylbromoamine, $(C_6H_5)_3C.NHBr$, is likewise readily rearranged when heated with alkali with a loss of hydrogen bromide; but triphenylmethylchloromethylamine, $(C_6H_5)_3C.NClCH_3$, is not rearranged by heat, by alkali, or, even by destructive distillation.[3] Chloroimidobenzophenone, $(C_6H_5)_2C : NCl$, has resisted every effort to effect its rearrangement and the same is true of the stereoisomeric chloroimides,[4] $(C_6H_5)(XC_6H_4)C : NCl$. If the theory of direct exchange were correct, these substances, above all others, should show a spontaneous exchange of the aryl and halogen radicals. It is true, however, that it is still possible that the favorable medium has not yet been discovered for effecting the rearrangement of these compounds.

3. As has often been pointed out by the one of us, the reagents used to effect the different varieties of rearrangement are the very ones which we would select in attempting to obtain univalent nitrogen derivatives as intermediate products: Bases for the acyl halogenamides, RCO.NH(Hal), for dibenzhydroxamic acids, RCO.NH(OCOR), for triphenylmethylhalogen amines, $R_3C.NH(Hal)$, for benzoyltriphenylmethylhydroxylamine,[5] $R_3C.NH(OCOC_6H_5)$; acid dehydrating agents for oximes, R_2C :-NOH, for hydroxylamines, $(C_6H_5)_3C.NHOH$ and $(C_6H_5)_3C.N(CH_3)OH$, phosphorus pentoxide for the hydrochloride, $(C_6H_5)_3C.NHOH.HCl$; heat for acylazides, $RCO.N.N_2$ (with loss of nitrogen), for triphenylmethylazides,[6] $R_3C.N.N_2$, for triphenylmethyldichloroamine, $(C_6H_5)_3C.$-NCl_2 (chlorine being lost). To these cases may now be added the apparent necessity of using a catalyzing acid for the rearrangement of the acetyl ester of benzophenone oxime[7] (see I, 3 above), the very agent required to make a univalent nitrogen derivative possible.

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

[2] Isabella Vosburgh, THIS JOURNAL, 38, 2081 (1916).

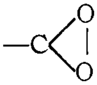
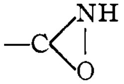
[3] Stieglitz and Vosburgh, *Ber.*, 46, 2151 (1913).

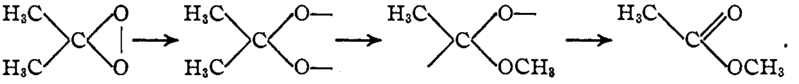
[4] Peterson, *Am. Chem. J.*, 46, 325 (1911).

[5] In the article by Stieglitz and Leech doubt was expressed about the position of the benzoyl group on account of the inability of the benzoate to form a salt (*loc. cit.*, p. 292). Difficulty in salt formation has now been found to be common in the triphenylmethyl derivatives we are studying. The absence of the ferric chloride test for an OH group makes the above structure probable.

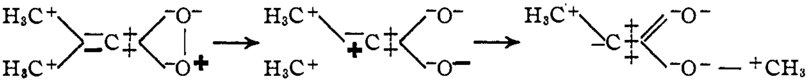
[6] J. K. Senior and Stieglitz, *Proc. Nat. Acad. Sci.*, 1, 207 (1915).

[7] Kuhara, *loc. cit.*

4. The same theory of the rearrangement applies *without any new assumptions* to the *rearrangement* of *peroxides*—a dissociation into univalent oxygen derivatives preceding the rearrangement, in place of a dissociation into an unsaturated nitrogen derivative.[1] Baeyer[2] was the first to recognize the inherent analogy in the rearrangements of peroxides and of the hydroxylamine derivatives. But he was misled by the analogy into the wrong view, that in both cases rings,  and  must be formed, whose instability was supposed to cause the rearrangements. That such is not the case is most decisively shown by the fact that triphenylmethylhydroxylamines,[3] $(C_6H_5)_3C.NHOH$, triphenylmethylchloroamines,[4] $(C_6H_5)_3C.NHCl$, and triphenylmethylperoxide,[5] $(C_6H_5)_3CO.OC(C_6H_5)_3$, rearrange in a perfectly normal manner: in all of these compounds, such rings are absolutely impossible. The assumption of a primary dissociation of peroxides into univalent oxygen derivatives gives us a complete explanation of their rearrangements. The rearrangement of triphenylmethylperoxide has already been explained in this way by Wieland.[6] The rearrangement of one of the v. Baeyer peroxides, for instance of acetone peroxide, would follow the analogous course


(9)

The fundamental similarity between this series of actions and the one we are discussing is still more clear from the point of view of the electron theory of valence. The whole rearrangement follows from the tendency of an oxygen atom with a positive charge in the peroxide to acquire two electrons and become wholly negative, as it is in all stable oxygen compounds. The securing of these electrons from the carbonyl carbon atom[7] leads to the molecular rearrangement


(10)

The charges in heavy type are the ones that change.

5. The same theory applies without any new assumptions to the rear-

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[1] Stieglitz and Leech, *loc. cit.*

[2] *Ber.*, 32, 3627 (1899).

[3] Stieglitz and Leech, *Ber.*, 46, 2147 (1913).

[4] Stieglitz and Vosburgh, *Ibid.*, 46, 2151 (1913).

[5] Wieland, *Ibid.*, 44, 2550 (1911); Stieglitz and Leech, THIS JOURNAL, 36, 285 (1914).

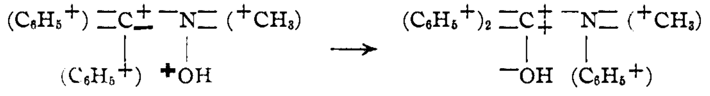
[6] *Loc. cit.*

[7] An electron may also pass first from the negative to the positive oxygen, severing the bond between them, and the univalent oxygen atoms may then receive an electron each from the carbon atom in question. The question of a possible accelerating effect of acids on this rearrangement is an interesting one and will be investigated.

rangements produced by the action of an electric current on the salts of organic acids. The fundamental analogy of the resulting changes to the rearrangements of the nitrogen derivatives under discussion has already been pointed out by the one of us.[1]

III. If one considers the evidence in I and II, one must be impressed by the fact that certain facts are more simply interpreted on the basis of Beckmann's theory of a direct exchange of radicals, that still other facts are quite incompatible at present with Beckmann's views and in striking agreement with the intermediate product theory of the one of us. Common to both views and *the most important fact in any theory of the rearrangements, is that the latter originate from the presence of unstable positive atoms, Cl^+, $^-O^+$, $\equiv N^+$, in the molecules of the compounds in question, and these atoms, by satisfying their tendencies to absorb electrons and form the common, stable, negatively charged atoms, disturb the valences which hold all atoms in the structure of the molecules and start the rearrangement into stable molecules.*[2] From this point of view, it must be evident that *both* forms of rearrangement might well be possible, one by a direct exchange, the other by way of a dissociation into unsaturated radicles. The question of the mechanism of the rearrangements resolves itself then largely into a question of the path followed by the migrating electrons. For these reasons it seems desirable to analyze, as briefly as possible, the electronic interpretations of the rearrangements from the different points of view: they bring out their relations more precisely than do the structural considerations alone and they point the direction for further experimentation.

A. The electronic interpretation of Beckmann's assumption of a direct exchange of radicles has never been presented, we believe. In illustration of it, we have for the rearrangement of β-triphenylmethyl-β-methyl hydroxylamine,[3]



$$\underset{(C_6H_5^+)}{(C_6H_5^+)\,\underline{=}C\overset{+}{\mathbf{-}}}\ \underset{\mathbf{+}OH}{{}^-N\underline{=}}\ (^+CH_3) \longrightarrow \underset{^-OH}{(C_6H_5^+)_2\,\underline{=}C\overset{+}{\underset{+}{-}}}\ \underset{(C_6H_5^+)}{{}^-N\underline{=}}\ (^+CH_3) \qquad (11)$$

The shifting charges are indicated by heavy type.

Characteristic of this theory, evidently, is that the unstable positive radical ^+OH secures its electrons *directly* from the carbon atom of the triphenylmethane nucleus, an exchange of radicals (the new negative ^-OH and the positive phenyl radical) occurring practically simultaneously with this shifting of electrons. This mode of expression brings out in the most striking fashion some of the most important objections to Beck-

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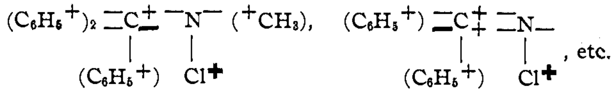
[1] Stieglitz and Leech, *loc. cit.*, p. 281.

[2] Stieglitz, *Proc. Nat. Acad. Sci.*, 1, 207 (1915). See also L. W. Jones, *loc. cit.* and Stieglitz and Leech, *Ibid.*

[3] In place of ^+OH we may put its acyl derivatives, $RCO.O^+$

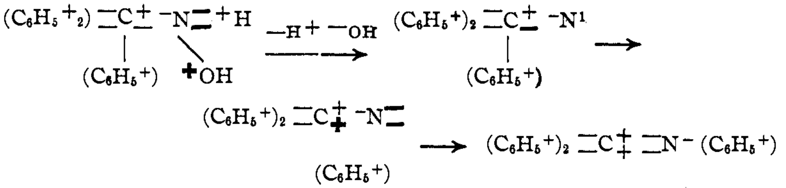
mann's theory: it fails utterly to explain why we have no rearrangements of compounds strictly analogous to the above, such as



$$\underset{(C_6H_5{}^+)}{(C_6H_5{}^+)_2\equiv C^{\pm}}\;\underset{Cl^+}{{}^-N^-}\;(^+CH_3),\quad \underset{(C_6H_5{}^+)}{(C_6H_5{}^+)\equiv C^{\ddagger}}\;\underset{Cl^+}{\equiv N-}\;,\ \text{etc.}$$

In these nonrearranging compounds the tendency for the exchange of electrons should be even greater than in the preceding rearranging compound, if we judge by comparing the activity of (positive) chlorine in chloroamines and hypochlorites with that of (positive) oxygen in such a substance as hydrogen peroxide.

B. According to the univalent nitrogen theory of the rearrangements, we should have, for instance, for triphenylmethylhydroxylamine:



$$\underset{(C_6H_5{}^+)}{(C_6H_5{}^+{}_2)\equiv C^{\pm}}\;\underset{{}^+OH}{{}^-N\equiv{}^+H}\xrightarrow{-H^+\ -OH}\underset{(C_6H_5{}^+)}{(C_6H_5{}^+)_2\equiv C^{\pm}}\;{}^-N^1\longrightarrow \underset{(C_6H_5{}^+)}{(C_6H_5{}^+)_2\equiv C^{\ddagger}}\;{}^-N\equiv\longrightarrow(C_6H_5{}^+)_2\equiv C^{\ddagger}\equiv N^-(C_6H_5{}^+)\qquad(12)$$

The characteristic feature of this theory is that the unstable positive element secures its electrons from the nitrogen to which it is attached, by capturing two of its valence electrons. One of these two available electrons attached to the nitrogen in the original molecule is the one holding the positive radical itself (here ^+OH), the other is taken from the nitrogen only if it holds hydrogen, a metal (either may be ionized or nonionized) or some other easily displaced atom, *but it is not available when it holds an alkyl group or its equivalent.*[2]

In turn, the unsaturated nitrogen, comparable with an element like fluorine,[3] secures from the carbon atom, to which it is attached, two electrons again, the rearrangement following as a result. This view explains the very facts which the Beckmann theory fails utterly to explain: thus, in $(C_6H_5{}^+)_3\equiv C^+\ {}^-N\equiv\ (Cl^+)(^+CH_3)$, the nitrogen has only one readily

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[1] It was originally considered (Stieglitz and Leech, *loc. cit.* and Jones, *Ibid.*) that in the univalent nitrogen derivative the nitrogen might have the structure $^-N^{\pm}$ in place of ^-N. The latter was given the preference by the one of us. Below, under C, additional reasons for distinguishing sharply between the two closely related forms will be brought.

[2] Similarly, in $(H^+)_2\ {}^=S$, the $^=S$ is very easily deprived by oxidizing agents of both its electrons, but in $(CH_3{}^+){}^-S^{-+}H$ it is deprived only of the electron holding the hydrogen atom. This is most likely due to the fact that the *ions,* HS^-, $S^=$ CH_3S^-, *with exposed electrons,* are the components, which are most easily deprived of these electrons (cf. Stieglitz, "Qualitative Analysis," Vol. I, Chapters XIV and XV). Possibly, too, the union with CH_3 is of the nonpolar type.

[3] Stieglitz and Leech, *loc. cit.*

available[1] electron, not the two necessary for the formation of a univalent nitrogen derivative and no rearrangement occurs. On the other hand, the present view does not explain, without further assumptions (see p. 2051) the reärrangement of β-triphenylmethyl-β-methyl hydroxylamine.

Now, the *force* with which electrons would be drawn by the unstable positive atom from another atom in the same molecule must depend on at least two factors, namely a tension factor measuring the intensity of the selective tendency with which each element holds or seeks to absorb electrons—comparable with the solution tension of the free elements—and secondly, on the distance separating the atoms between which a transfer of electrons may occur. As to the tension factors in all of these rearrangements, the final products prove beyond question that these factors must favor the gain of electrons by the unstable positive element at the expense of the *carbon* atom holding the nitrogen. In other words, the carbon must lose two electrons, as far as tension is concerned, more readily than the nitrogen; otherwise the univalent nitrogen derivative would be tolerably stable. Consequently, unless the direct migration of electrons from the carbon to the unstable positive element is obstructed by virtue of the important factor of distance and intervening atoms, as far as the tension factor is concerned, *the direct migration would be the natural path for the transfer of electrons.* Instances of such direct migration under favorable conditions might therefore not be unexpected (see A).

But, further, the important factor of distance unquestionably must favor the absorption of electrons first from the nitrogen by the unstable positive element, which is in direct union with it; the nitrogen can then recover its electrons from the carbon with which it is in direct union. This probably is the reason why *the path of least resistance* to the rearrangements[2] seems to be over the univalent nitrogen products and why certain compounds, which have the necessary instability of charges, do not rearrange, when the path over the univalent nitrogen is blocked. This mechanism has the advantage therefore of having *both* factors, which control the movement of electrons, leading to the final readjustment.

It seems especially important, from these considerations, to subject the nonrearranging compounds to a still more searching experimental investigation, in order to determine whether the path toward a rearrangement really is altogether blocked.

C. There is a third electronic interpretation[3] of the rearrangements, which contains in it elements of both of the preceding interpretations; we may have a dissociation, preceding the exchange of radicals.

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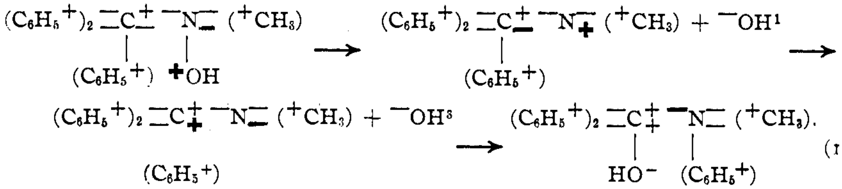
[1] The union with CH_3 may even be of the nonpolar type, if such valences should be found to exist.

[2] Stieglitz and Vosburgh, *Ber.*, 46, 2149 (1913).

[3] Cf. Stieglitz and Leech, *loc. cit.*, and L. W. Jones, *Ibid.*



$$\underset{(C_6H_5^+)}{(C_6H_5^+)_2 \equiv C^{\pm}} - \underset{^{+}OH}{{}^{-}N^{=}_{-}} (^+CH_3) \longrightarrow \underset{(C_6H_5^+)}{(C_6H_5^+)_2 \equiv C^{\pm}_{-}} - {}^{-}N^{-}_{+} (^+CH_3) + {}^{-}OH^{1} \longrightarrow \underset{(C_6H_5^+)}{(C_6H_5^+)_2 \equiv C^{+}_{+}} - {}^{-}N^{=}_{-} (^+CH_3) + {}^{-}OH^{3} \longrightarrow \underset{HO^-}{(C_6H_5^+)_2 \equiv C^{+}_{+}} - \underset{(C_6H_5^+)}{{}^{-}N^{=}} (^+CH_3). \qquad (13)$$

This interpretation would labor under the same difficulties as the theory of Beckmann (see A) in accounting for the nonoccurrence of rearrangements of certain halogen derivatives (see A) and would have the added difficulty that the factor of proximity would be no obstruction to a similar rearrangement in this case. It should be borne in mind for those rearrangements which seem to take place without the intermediate formation of a univalent nitrogen derivative.[2]

Our conclusions may be summarized as follows:

1. Unless conclusive evidence is brought that *salts* leading to the intermediate formation of salts of univalent nitrogen derivatives, are involved in their rearrangement, the rearrangement of β-triphenylmethyl-β-methylhydroxylamine, established in this paper, the relation of stereoisomerism of oximes to their rearrangement products, established by Beckmann, Werner and Kuhara, and also the spontaneous rearrangement of the sulfonic ester of benzophenone-oxime, observed by Kuhara, would be inconsistent with the theory of the intermediate formation of univalent nitrogen derivatives in the rearrangement of hydroxylamines and at present these facts agree better with Beckmann's theory of a direct exchange of radicals or with a modification of this theory (see C, above). Intermediate salt formation, if established, would harmonize these facts with the univalent nitrogen theory.

2. Other facts, such as the rearrangements of azides and especially also the nonrearrangement of chloroimidobenzophenones, of chloroimidoesters, and of β-triphenylmethyl-β-methylchloroamine, are inconsistent, without further specific assumptions, with Beckmann's theory of a direct exchange of radicals, but are in striking agreement with Stieglitz's theory of the intermediate formation of unsaturated nitrogen derivatives in the rearrangements of chloroamines, hydroxylamines, and azides.

3. Unless further experimentation should modify these facts or their bearing, one should consider that both types of rearrangement may take place.

4. Common to both theories and *the most important feature* in their modern forms is that the rearrangements originate from the tendency of unstable positive atoms, Cl^+, $^-O^+$, $\equiv N^+$, etc., to go over into their

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[1] Or some equivalent ion, such as Cl^-, $C_6H_5SO_3^-$, etc.

[2] Other variations of this fundamental idea are possible.

stable negative forms, Cl^-, $^-O^-$, $N^=$, by a capture of electrons from other atoms in the same molecule a change which is effected in the rearrangements in question. It is quite consistent with this fundamental relation that the rearrangement should go over one or the other path, the one over the unsaturated nitrogen derivatives forming probably the path of least resistance.

5. The same fundamental cause, the charge on unstable atoms, with consequent shifting of electrons, underlies the rearrangement of peroxides, of hydrazines, of acylhalogenanilides, of aryl hydroxylamines, and similar compounds.

Experimental Part.[1]

The Rearrangement of Triphenylmethyl - β - methylhydroxylamine, $(C_6H_5)_3C.N(CH_3)OH$.—The method of Stieglitz and Leech[2] for preparing triphenylmethylmethylhydroxylamine hydrochloride was followed, but it was found better to purify this salt by washing it thoroughly with ligroin (b. p. 70–80°) than to crystallize it from a chloroform-ether solution. By the latter process there is always some dissociation into triphenylmethylchloride and methylhydroxylamine hydrochloride. The free base may also be extracted with ligroin instead of ether, as the base is quite soluble in it, and then the hydrochloride precipitated from the solution by the introduction of the dry acid gas.

The purity of the salt was determined by its melting point and by the analysis for the content of hydrogen chloride. The free base was prepared from it by treatment with alkali solution and extraction of the base with ether. The ether solution was dried with fused calcium chloride and the solvent evaporated. The base remaining was a very mobile, almost colorless liquid, which, without further purification, solidified, at once, when stirred with a glass rod. The solid melted at 106° and when it was once recrystallized from ligroin, it melted at 111°. Leech found 113° as the constant melting point, after prolonged recrystallization. The yield is good—5.5 g. were obtained from 9 g. of triphenylmethylchloride.

To rearrange the base, 3 g. of it were dissolved in 30–40 cc. of ether and 5 g. of phosphorus pentachloride added to the solution. The mixture stood at room temperature for 24 hours, during which time a slightly yellow coloration appeared. The coloration increased when the mixture was heated on an electric bath for four hours. After the heating, a strong ether solution (3 cc.) of hydrogen chloride was added to the mixture to insure the presence of an excess of the acid. The supernatant liquid was decanted through a filter and the residue washed well with ether.

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[1] I take pleasure in giving expression to my grateful appreciation of the painstaking and skilful work of Mr. Stagner, who carried out the experimental work under my direction.—J. S.

[2] *Loc. cit.*

Water (20 cc.), containing hydrochloric acid, was now added to the residue and any trace of residue on the filter was washed into the flask with the larger residue. Some of this residue was insoluble in the dilute acid. The mixture was warmed an hour on the water bath. The insoluble residue melted but did not dissolve. The mixture was cooled and ether added to it. This dissolved the residue which was not soluble in the aqueous solution. The ether solution was separated and the water solution extracted twice again with ether. The ether extracts, containing benzophenone, was examined as described later on. The aqueous solution remaining was made alkaline, saturated with sodium chloride, and the free methyl aniline twice extracted with ether. The base was next twice extracted from the ether solution with 20 cc. of very dilute hydrochloric acid (0.5 *N*). The acid solution was filtered into a weighed beaker and the solution evaporated nearly to dryness on a steam bath and the last traces of moisture removed *in vacuo*. The residue (methylaniline hydrochloride) weighed 0.535 g.

A second rearrangement was similarly made in which a gram of the free base gave 0.151 g. of methylaniline hydrochloride. The theoretical yield is 0.496 g. methylaniline hydrochloride per gram of triarylmethylmethylhydroxylamine.

Identification of Methylaniline.—The following tests proved the salt to be methylaniline hydrochloride:

1. A small quantity of the residue was dissolved in water and the solution made alkaline. Bleaching powder solution was added and gave the characteristic deep blue color, discovered by Leech as a test for methylaniline.[1]

2. A small quantity of the residue, when twice crystallized from dry chloroform by the addition of ether, melted at 119–122°. When these crystals were mixed with synthetic methylaniline hydrochloride they melted at the same temperature, 119–122°. Methylaniline hydrochloride, obtained from a redistilled Kahlbaum preparation, melted at 119–121°.

3. 0.1392 g. of the residue, which had been twice recrystallized from chloroform and ether, required 9.76 cc. of 0.1 *N* $AgNO_3$, when analyzed by the Volhard method. Theoretical quantity for $C_7H_{10}NCl$, 9.70 cc.

4. A quantitative analysis of the chloroplatinate was made. The older literature[2] states that methylaniline chloroplatinate is unstable and darkens quickly, with decomposition. But this is erroneous. The chloroplatinate prepared from synthetic methylaniline hydrochloride forms a nice looking yellow precipitate which does not darken at all and which contains the theoretical quantity of platinum. After this fact

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[1] THIS JOURNAL, 35, 1042 (1913).

[2] Graham-Otto-Kolbe, III*a*, 178 (1878).

had been determined, the methylaniline salt obtained from the rearrangement products was analyzed. About 0.22 g. of the hydrochloride, that had been once crystallized from chloroform and ether, was dissolved in 10–15 drops absolute alcohol. This solution was added to 0.4 g. of chloroplatinic acid dissolved in 15–20 drops of alcohol. The yellow precipitate of methylaniline chloroplatinate formed at once. The precipitate was transferred to a filter, washed first with 10–20 drops of alcohol, and then slowly with 30 cc. of a half and half mixture of absolute ether and alcohol. The solid was brought to constant weight *in vacuo* in an hour or two.

Subst. 0.3493 g. gave 0.1097 g. Pt.
Calc. for $C_{14}H_{20}N_2PtCl_6$: Pt, 31.27%. Found: Pt, 31.40%.

Identification of Benzophenone.—The ether solution of the benzophenone, which was extracted from the acid solution of the hydrolyzed products of the rearrangement, was freed from the ether by evaporation in a current of air. A red tinted very mobile liquid remained which weighed 0.611 g. This substance remained liquid for several days. Finally, when it was touched by a minute trace of pure benzophenone clinging to the rounded end of a melting point tube, it solidified at once. Some of it was twice crystallized from ligroin and melted at 46–47° and when it was mixed with pure benzophenone, it melted at 46.5–48°. Pure benzophenone melted at 47–48.5°.

Triphenylcarbinol.—The triphenylmethylmethylhydroxylamine did not rearrange quantitatively. This was shown by the fact that approximately 1.5 g. of triphenylcarbinol was obtained in addition to the aniline and benzophenone already described. A part of the base appeared to dissociate into triphenylmethylchloride and hydroxylamine, as observed by Stieglitz and Leech. The ether solution which had been decanted from the insoluble rearranged products was freed from ether by evaporation and the gummy residue remaining was hydrolyzed with alkali solution. The carbinol thereby produced was crystallized from ligroin and identified by its melting point.

Rearrangement of β,*p*-bromophenyldiphenylmethyl-β-methylhydroxylamine, $(BrC_6H_4)(C_6H_5)_2C.NCH_3OH$.—*p*-Bromotriphenylmethylchloride was condensed with methyl hydroxylamine. The concentrations of solutions were the same as those used in the preparation of triphenylmethylmethylhydroxylamine. The solvents were evaporated and the gummy residue was extracted with ligroin,[1] (b. p. 70–80°). From this solution the hydrochloride of the base was precipitated by dry hydrogen chloride.

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[1] Attempts were made to precipitate the hydrochloride from an ether solution but the salt is very soluble in ether and solidification cannot be obtained if ether is present. A few drops of ether added to the salt purified from ligroin softens it into a gum—probably due to the base being very weak and the salt being decomposed by the oxonium valences of the ether.

The salt separates out very white. It is quite insoluble in the ligroin but is soluble in chloroform, alcohol, and ether. It reduces boiling Fehling's solution, softens at 70°, but has no true melting point. The yield of the salt is good; 8 g. of it was obtained from 12 g. bromotriphenylmethylchloride. From its behavior it seems to be an unstable salt, easily losing its acid.

For analysis, it was placed in a flat crystallization dish and stirred in an atmosphere of dry hydrogen chloride and then placed in a desiccator over potassium hydroxide and left in an ice chest for five days. Analysis for the content of the hydrochloric acid was then made by titration with 0.1 *N* KOH. The salt was dissolved in 25 cc. of absolute alcohol and ten drops of phenolphthalein indicator used. It required 0.06 cc. of alkali to correct for CO_2 in the alcohol.

Subst. 0.2437, 0.1950; cc. 0.1 *N* KOH, 6.12, 4.88.

Calc. for $(BrC_6H_4)(C_6H_5)_2CNCH_3OH.HCl$: HCl, 9.01. Found: 9.16, 9.12.

The salt was next left *in vacuo* at room temperature over sticks of potassium hydroxide for three days. It then showed 92% of the calculated amount of hydrogen chloride. The salt evidently is not stable and dissociates slowly at room temperature into the free base and free hydrogen chloride.

Rearrangement of *p*-Bromophenyldiphenylmethyl-β-methylhydroxylamine.—The base, $(BrC_6H_4)(C_6H_5)CNCH_3OH$, was obtained from its hydrochloride by treatment of the latter with alkali solution and extraction with ether. The ether solution was freed from moisture by means of fused calcium chloride. The solvent was then evaporated, leaving a liquid substance. Some of this liquid (2.25 g.) was dissolved in 30–40 cc. of ether and phosphorus pentachloride (4 g.) was added to the solution. The mixture was heated on an electric bath for four hours. After the heating, 3 cc. of ether containing hydrogen chloride was added, and the supernatant liquid poured from the insoluble yellow colored compounds. The insoluble substance was washed twice with 15 cc. of ether. The residue was hydrolyzed and the ketones (benzophenone and bromobenzophenone) and the aniline salts (the hydrochlorides of methylaniline and methyl bromoaniline) were isolated exactly as they were in the case of the rearrangement of triphenylmethylmethylhydroxylamine.

The base (2.25 g.) yielded 0.172 g. of mixed aniline hydrochlorides and 0.301 g. of the two ketones, benzophenone and bromobenzophenone. A second rearrangement of 1.6 g. of base gave 0.111 g. of the mixed aniline salts.

A trace of the hydrochlorides, when made alkaline and treated with bleaching powder solution, gave a navy blue color, the test for methyl aniline (methylbromoaniline does not give this color test). Another small quantity of the aniline salts was freed from the hydrochloric acid and precipitated from ether solution by means of oxalic acid. This oxalate showed the presence of halogen when tested with copper oxide in Bunsen flame.

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