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"BECKMANN" REARRANGEMENT OF
KETOXIMES. A COLOR REACTION OF
HYPOCHLORITES WITH METHYLANILINE
AND ETHYLANILINE; A DISSERTATION**

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The Molecular Rearrangement of Triarylmethylhydroxylamines and the "Beckmann" Rearrangement of Ketoximes¹

Acid halogen amides² $RCONH(Hal)$, hydroxamic acids $RCONHOH$, dihydroxamic acids³ $RCO.NH.OCOR$, and acid azides⁴ $RCON_3$ 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 us¹ 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-

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). The work presented in this paper was published as a joint article by Julius Stieglitz and Paul N. Leech in the *Journal of the American Chemical Society*, February, 1914.

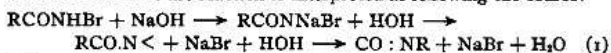
² A. W. Hofmann, *Ber.*, 14, 2725 (1881); 15, 408 (1881); Hoogewerff and van Dorp, *Rec. trav. chim.*, 6, 373 (1887); 8, 173 (1889), etc.; Lengfeld and Stieglitz, *Am. Chem. J.*, 15, 215, 504 (1893), etc.

³ Lossen, *Ann.*, 167, 359 (1872), etc.; Thiele and Pickard, *Ibid.*, 309, 189 (1899); and especially L. W. Jones, *Am. Chem. J.*, 48, 1 (1912).

⁴ Curtius, *Ber.*, 27, 778 (1895); *J. prakt. Chem.*, 50, 289 (1894), etc.

⁵ 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



and



Isocyanates CO:N have indeed been the first isolated² 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 RCO.N₃, gentle heat alone is sufficient to cause an evolution of nitrogen, leading to the formation of isocyanates⁴ 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 answered⁸ by the investigations carried on continuously in this laboratory. One of the most important of the problems still under investigation⁹ 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); 20, 49 (1903); see also L. W. Jones, *loc. cit.*, pp. 23, 28.

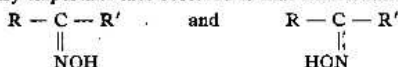
⁸ Stereoisomeric chloroimido esters were prepared and investigated to determine the relation of stereoisomerism to the rearrangement of acid halogen amides (Stieglitz and Earle, Hilpert, *loc. cit.*) and stereoisomeric chloroimidoketones were prepared to investigate the same relations in connection with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

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

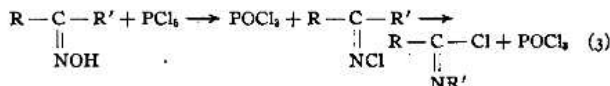
¹⁰ *Ber.*, 19, 988 (1886); 20, 1507, 2508 (1887), etc.

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



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, Hantzsch⁴ assumes that the ketoximes form with phosphorus pentachloride chloroimides, which then rearrange by a direct exchange of chlorine and the radicals R or R':



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

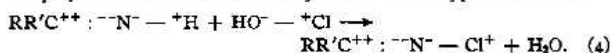
² *Ber.*, 27, 300 (1894). He originally (*Ber.*, 19, 988 (1886)) made the same assumption as Hantzsch did later (see further on in the text).

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 Peterson¹ 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. Noyes³ on the possible existence of *electromeric* nitrogen chlorides NCl. 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 us⁴ as derivatives of *positive chlorine*⁵ $RR'C^{++}:N^{-}Cl^{+}$.⁶ They are prepared from imido ketones by the action of hypochlorous acid



They yield again, by hydrolysis, hypochlorous acid (a proof that the chlorine has not changed its charge⁷) 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

¹ *Loc. cit.*

² Stieglitz and Peterson, *loc. cit.*; unpublished work by Stieglitz and P. H. Watkins; Vosburgh, see a later article in the *Journal of the American Chemical Society*. 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 *J. Am. Chem. Soc.*, 35, 767 (1913); see also Nelson and Falk, *Ibid.*, 32, 1637 (1910); and 33, 1140 (1911).

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

⁵ Cf. W. A. Noyes, *J. Am. Chem. Soc.*, 23, 460 (1901); Stieglitz, *Ibid.*, 23, 796 (1901); Walden, *Z. physik. Chem.*, 43, 385 (1903).

⁶ Only the significant charges are indicated in all of the electronic structures used.
⁷ Sellwanow, Lengfeld and Stieglitz, L. W. Jones, *loc. cit.*; Stieglitz, *J. Am. Chem. Soc.*, 23, 796 (1901). Since this was written, Nelson, Beans and Falk (*J. Am. Chem. Soc.*, 35, 1810 (1913)) have emphasized the value of this method of determining the nature of the charge on an atom.

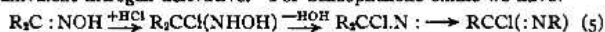
compounds: such is the case, for instance, for oximido mesoxalic esters and quinone oxime, which may be obtained from malonic esters and phenol, respectively, by the action of nitrous acid, as well as from the ketones by the action of hydroxylamine. Oximes¹ could, consequently have besides the probable electronic structure $RR'C^{++}:^{-}N^{-}-^{+}O^{-}-^{+}H$ also the structure of a nitrous acid derivative $RR'C^{-}:^{++}N^{+}-O^{-}-^{+}H$. A compound of the latter structure could form with phosphorus pentachloride a chloride corresponding to nitrosyl chloride. $O^{-}-^{++}N^{+}-Cl$. The products $RR'C^{-}:^{++}N^{+}-Cl^{-}$ would be *electromers* of the chloroimido ketones, prepared by Stieglitz and Peterson, and could *possibly* suffer a rearrangement into $RC^{+++}(Cl):^{-}N^{-}R'^{+}$ or $R'C^{+++}(Cl):^{-}N^{-}R^{+}$, 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 $R.CO.NH(Hal^{+})$, 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 Cl^{-} and 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.

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 assumed¹ 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:



Benzochloroanilidè 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 entertained³ 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. Jones¹ 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

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 (C₆H₅)₃CNH(Hal) and (C₆H₅)₂CN(Hal), 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 $(C_6H_5)_3CCl(NHOH)$ 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 forms² 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 $(C_6H_5)_3C.N(CIL_2)OH$ 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 found³ that triphenylmethylated 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.