

Citation:

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$$3(k-n) = \Sigma v_1 - \Sigma t_1 \dots \dots \dots (9)$$

The equation of reality (2), can thus be written in the following form: ¹

$$\Sigma t_1 - \Sigma v_1 = 3(\Sigma' t_1 - \Sigma' v_1) \dots \dots \dots (10)$$

If farthermore $\Sigma'' t_1$ indicates a summation over the *imaginary points*, $\Sigma'' v_1$ over the *imaginary tangents*, then $\Sigma t_1 = \Sigma' t_1 + \Sigma'' t_1$, etc. so that (10) becomes

$$\Sigma'' t_1 - \Sigma'' v_1 = 2(\Sigma' t_1 - \Sigma' v_1) \dots \dots \dots (11)$$

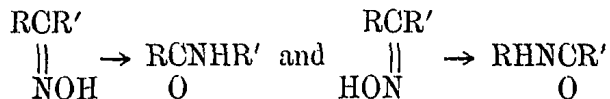
The equations (2), (9) and (10) are of course but different forms for the same relation of reality.

Sneek, March 1904.

Chemistry. — Professor LOBRY DE BRUYN presents communication N° 7 on intramolecular rearrangements: C. A. LOBRY DE BRUYN and C. H. SLUITER. "*The BECKMANN-rearrangement; transformation of acetophenoxime into acetanilide and its velocity.*"

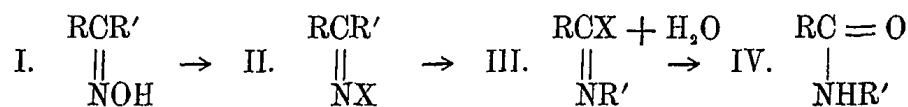
(Communicated in the meeting of February 27, 1904).

Among the many intramolecular rearrangements known in organic chemistry, the one associated with the name of BECKMANN belongs to one of the most important series on account of the extent of its region and its scientific significance. As is well known, it consists in the transformation of the oximes, under the influence of a certain number of reagents, into the isomeric acid amides, for instance: $R_2CNOH \rightarrow RCONHR$. Its extent is obvious if we remember that all ketones and aldehydes are capable of yielding oximes and that a large number of these, particularly of the ketoximes, can undergo the rearrangement. Its scientific importance is chiefly due to the fact that its application to the stereoisomeric ketoximes has been the means of determining the configuration of those stereoisomers, in this manner:

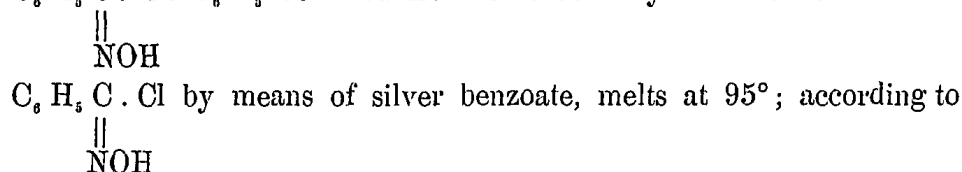


The rearrangement generally takes place under the influence of different reagents such as sulphuric acid, hydrochloric acid, phosphorus pentachloride and -oxide, acylchlorides, acetic acid with its anhydride and HCl, zincchloride, alkalis. As these substances are always applied in relatively large quantities, it is thought most probable, that the actual rearrangement nearly always relates to inter-

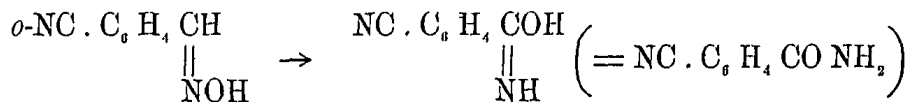
mediate products, additive compounds or derivatives of the oximes, which occasionally have been separated ¹⁾. These intermediate products then contain a negative group (or the group OK) attached to the nitrogen which changes place with the C-combined alkyl- or aryl-group. On subsequent treatment with water the amide is generated. We then have;



That hydroxyl itself can assume the function of the group X which changes place with R' is shown by the interesting observations of WERNER and BUSS ²⁾, WERNER and SKIBA ³⁾, POSNER ⁴⁾ and AUWERS and CZERNY ⁵⁾, who have noticed some cases of the BECKMANN-rearrangement in the absence of any reagent. Dibenzhydroximic acid $\text{C}_6\text{H}_5\text{COCO}\text{C}_6\text{H}_5$ obtained from chlorobenzhydroximic acid



WERNER and BUSS it changes after some days spontaneously into its isomer $\text{C}_6\text{H}_5\text{CO}\cdot\text{NHO}\text{CO}\text{C}_6\text{H}_5$ m.p. 161° ; on heating this takes place more rapidly. POSNER observed that *o*-cyanobenzaldoxime changes into its isomer when simply heated above its melting point; it first melts at 175° , then solidifies and finally melts again at 203° . Here we consequently have the direct conversion:



Finally, AUWERS and CZERNY have found that *o*-oxy-*m*-methylbenzophenonoxime: $\text{HO}\cdot\text{H}_3\text{CC}_6\text{H}_4\text{C}\cdot\text{C}_6\text{H}_5$ partly undergoes the

$$\begin{array}{c} || \\ \text{NOH} \end{array}$$

BECKMANN-rearrangement when submitted to distillation.

These observations from WERNER and his pupils, of POSNER and of AUWERS and CZERNY are of fundamental importance for the under-

¹⁾ BECKMANN for instance (Ber. 19, 988) obtained $\text{C}_6\text{H}_5\text{CCl}:\text{NC}_6\text{H}_5$ from $(\text{C}_6\text{H}_5)_2\text{C}:\text{NOH}$ and PCl_5 . It is very probable that $(\text{C}_6\text{H}_5)_2\text{C}:\text{NCl}$ is formed first as an intermediate product.

²⁾ Ber. 27, 2198 (1894).

³⁾ Ber. 32, 1654 (1899).

⁴⁾ Ber. 30, 1693 (1897).

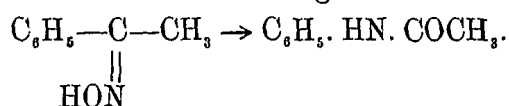
⁵⁾ Ber. 31, 2692 (1898).

standing of the mechanism of the BECKMANN-rearrangement. They prove that this important transformation is most decidedly a real intramolecular rearrangement, which may occur in some cases with the oxime, but in the majority of cases with derivatives in which, instead of the OH-group, another negative group or a halogen has been attached to the nitrogen. In that case the change from II into III represents the actual rearrangement.

AUWERS and CZERNY have already pointed out that the above rearrangement caused by distillation deserves the closest attention. They are of opinion that this observation leads to the view that the BECKMANN-rearrangement is a catalytical process which is in accord with BECKMANN's own ideas. But is it permissible to speak of a catalytic process when the catalyzer is wanting? And do not AUWERS and CZERNY withdraw their own statement when they say that "es sich vielmehr handelt um die directe Ueberföhrung eines weniger stabilen System in ein stabileres?"

The BECKMANN-rearrangement has not, up to the present, been subjected to a dynamical investigation. Such a study is not rendered less desirable or less important by the fact that, as a rule, the rearrangement of the intermediate product and not that of the oximes themselves will be investigated.

The oxime which has been studied in the first place is acetophenonoxime of which only one form is known and which quantitatively passes into acetanilide. Its configuration is therefore:



The rearrangement, which BECKMANN found to take place under the influence of concentrated sulphuric acid was studied in the first place. Before starting it was necessary to work out an analytical method allowing the quantitative determination of the resulting anilid in the presence of the unchanged oxime. After several preliminary experiments it was found that the anilide formed on adding water was completely hydrolyzed by boiling for a few hours and that the acetic acid could then be distilled off and titrated; the excess of oxime did not interfere. We have in consequence determined the velocity with which the anilide was formed. In carrying out the experiments 2.5 grams of the oxime were dissolved in 50 or 100 cc. of sulphuric acid, previously heated to the temperature at which the experiment was made (60° or 65°) and at definite periods a certain quantity was pipetted off from the bottle (which was placed in a thermostat) and analysed.

The reaction proved to be one of the first order, the velocity constant did not change with the concentration; so it is a monomolecular one. At 65°, for instance $k = 0.0019$ for a solution of 2.5 grams of the oxime in 50 as well as in 100 cc. of 93.6% sulphuric acid (time in minutes; transformation of $\frac{1}{2}$ of the oxime after 160 minutes).

The transformation velocity increases with the concentration of the acid as shown from the following table:

Temp. 60°. Concentration H_2SO_4 .	Velocity- constant.	Time of $\frac{1}{2}$ transformation.
93.6	0,0011	275 min.
94.6	13	232
97.2	38	75
98.7	70	43

At 65°, a 86.5% sulphuric acid gave a constant of 0.0006 (time of $\frac{1}{2}$ transformation = 501 minutes). When using 99.2% acid at 60°, practically all the oxime had been converted after 15 minutes.

The influence of the temperature is apparent from the following figures:

at 60°, 93.6% H_2SO_4 , $k = 0.0011$; 94.6% H_2SO_4 , $k = 0.0013$
 65°, „ „ „ $= 0.0019$ „ „ „ $= 0.0021$

The temperature-coefficient for 10° is therefore about 3.

A solution of SO_3 in chloroform did not appear to cause any transformation of the oxime.

The results of this research therefore confirm the view that in the BECKMANN-transformation we are dealing with a real intramolecular rearrangement. Even if the application of sulphuric acid should cause the formation of an intermediate compound (which has not yet been positively proved, but which is very probable¹⁾) our experiments show that this formation (or the conversion I into II) takes place with immeasurably great velocity. The very perceptible development of heat which occurs on mixing the oxime with the concentrated sulphuric acids also points to this fact.

Addendum. Of late years, STIEGLITZ and his coworkers (Amer. Chem. J. 1896—1903) have been engaged in the study of the BECKMANN-rearrangement. In my opinion STIEGLITZ's ideas cannot be accepted in their entirety. Recently this chemist has given a summary of his conclusions in a separate article "on the BECKMANN-rearrange-

¹⁾ If to an ethereal solution of the oxime is added a solution of sulphuric acid in ether, a precipitate is obtained the nature of which will be investigated.

ment" (Amer. Chem. J. 7, 29.49 (1903)). He then arrives at the following views.

The analogy of the HOFMANN-transformation of the amides into amines with the BECKMANN-rearrangement (an analogy first pointed out by HOOGWERFF and VAN DORP (Rec. 6.373, 8.173 etc.)) and the fact that the acid azides of CURTIUS are converted with elimination of nitrogen into the same isocyanates which occur as intermediate products in the HOFMANN-transformation, induces STIEGLITZ to attempt to explain these reactions from a same point of view. He believes that in the three above transformations there must be formed intermediate molecule-residues containing univalent nitrogen; with the azides for instance $\text{CH}_3\text{CO.N.N}_2 \rightarrow \text{CH}_3\text{CO.N} + \text{N}_2$; with the bromoamides for instance, $\text{CH}_3\text{CONHBr} \rightarrow \text{CH}_3\text{CO.N} + \text{HBr}$. These molecule-residues are then supposed to be converted straight into the isocyanate: $\text{CH}_3\text{—CO.N} \rightarrow \text{CONCH}_3$. In order to arrive, in the transformation of oximes into amides, at such molecules with univalent N-atoms, STIEGLITZ assumes that first of all HCl is attached to the oxime owing for instance to the action of PCl_5 . $\text{R}_2\text{C}=\text{NOH} + \text{HCl} \rightarrow \text{R}_2\text{CCl—NHOH}$; this additive compound under the influence of PCl_5 then loses one mol. of water and gives $\text{R}_2\text{CCl—N}$ which molecule-residue is then supposed to be converted into RCCl=NR , which on treatment with water yields the amide.

Now, first of all it is difficult to see where the HCl, which gets attached to the oxime, is to come from; it is of course known that some oximes yield with PCl_5 compounds such as $\text{R}_2\text{C ClN}$ with formation of HCl, but this is not the formation which STIEGLITZ had in mind. We also fail to see how sulphuric acid, acting as dehydrating reagent will, in the rearrangement, cause a mol. of water to be first attached and then to be again eliminated; neither do we understand how the transformation under the influence of, say, P_2O_5 or Zn Cl_2 can be reconciled with the ideas of STIEGLITZ. Finally, STIEGLITZ himself admits of his own theory that "it does not agree so well with the more obscure relations of the theory of stereoisomerism of ketoximes and their influence on the rearrangement of these isomers. It is hoped that future work will remove this difficulty". (Am. Ch. J. 7, 29, 67). The difficulty is this, that STIEGLITZ theory utterly ignores a fact of fundamental importance, namely the formation of two different amides from the stereoisomeric ketoximes; these according to STIEGLITZ ought to lead to the same intermediate product from which the same amide only could be formed. And finally the transformations of an oxime into the isomeric amide without any reagent whatever, as observed by WERNER and his

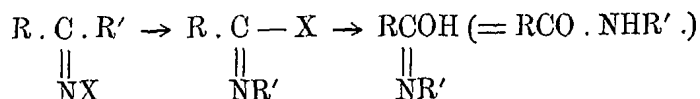
coworkers, by POSSNER and by AUWERS and CZERNY are directly opposed to his representations.

In his last theoretical paper, STIEGLITZ attributes the transformation of some more hydroxylamino-derivates to the intermediary formation of molecule-residues with univalent nitrogen; he includes all these under the name of "BECKMANN-arrangement".

I think, I have shown that this classification is not permissible. If it were so, the HOFMANN-transformation might claim priority over the "BECKMANN-arrangement", which is of more recent date.

In order to avoid confusion I think it absolutely necessary to let each of the said transformations retain its own name and to treat them as separate reactions. In the CURTIUS-transformation $\text{CH}_3\text{CON} \cdot \text{N}_2 \rightarrow \text{CONCH}_3 + \text{N}_2$, the assumption of the intermediary occurrence of a molecule residue $\text{CH}_3\text{CO} \cdot \text{N}$ is permissible; in the HOFMANN-reaction $\text{CH}_3\text{CONHBr} \rightarrow \text{CONCH}_3 + \text{HBr}$ such is possible but not necessary, $\text{Br} \cdot \text{C} - \text{OK}$

$\begin{array}{c} \parallel \\ \text{NCH}_3 \end{array}$ may also have been formed as an intermediate product (HANTZSCH); finally we may admit in the BECKMANN rearrangement.



a same mechanism as in the HOFMANN-transformation, but according to my opinion, not the presence of a molecule residue with univalent nitrogen.

The physico-chemical investigation of the BECKMANN-rearrangement is being continued.

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Amsterdam, February 1904.

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¹⁾ X = Cl, Br, OH or SO₃H [respectively H₂SO₄], OCOCH₃.