

On the Beckmann Rearrangement. III.

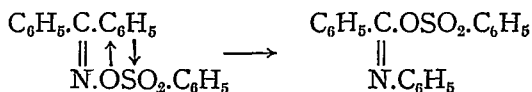
By

Mitsuru Kuhara and Teppei Okada.

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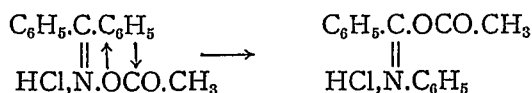
An explanation for the mechanism of the Beckmann rearrangement has been brought forward by one of us and Todo in their recent article¹, based upon the assumptions that the primary cause of rearrangement consists in the dissociation of an acid residue from nitrogen in the oxime ester formed in reaction, and as its consequence an interchange of positions between a hydrocarbon radical linked to carbon and an acid residue attached to nitrogen may be effected, and that such a mobility of the acid residue may stand in a close connection with the strength of its negative character, since in the case of the acetyl oximes rearrangement is hardly brought about by heat alone when an acid such as hydrochloric acid is not present, while in the case of the benzenesulphonyl oximes rearrangement is spontaneously effected.

Now the presence of the acid residue must be a necessary condition of the Beckmann rearrangement; it is then assumed that the oximes would at first yield their esters, say by acid chlorides, and subsequently an acid residue and a hydrocarbon radical may exchange their positions, the dissociation primarily taking place in the case of the oxime esters containing the residue of strong acid without the aid of any reagent, sometimes by mere elevation of temperature, while in the case of the esters containing the residue of weak acid the tendency to dissociate may be accelerated by the aid of hydrochloric acid forming their hydrochlorides, or by its joint action with heat; as has been already pointed out²:



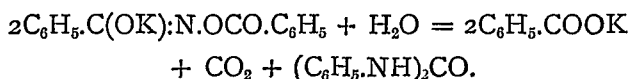
¹ Mem. Coll. Sci. Engin., Kyoto, 2, 387 (1909-1910).

² *Ibid.*, 2, 394 (1909-1910).

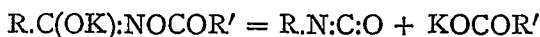


Admitting the presence of the acid residue in the oxime as a necessary condition of rearrangement, the several facts relating to the decomposition of dihydroxamic acids may be regarded as giving a support to the authors' view.

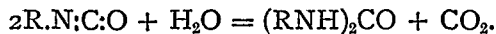
Lossen and Rotermund¹ have shown that the neutral potassium salt of dibenzhydroxamic acid in its aqueous solution gives benzoic acid, carbon dioxide and diphenylurea on standing by itself or by heating:



Thiele and Pickard² have also pointed out that in the rearrangement of potassium salts of dihydroxamic acids the splitting up of a salt into an isocyanate and a potassium salt of the acid related to the acid residue linked to the nitrogen of the oxime group must be brought about at first:



and then the formation of a symmetrical disubstituted urea would take place by the interaction of the isocyanate formed and water:



The free dihydroxamic acids also yield the analogous products of decomposition by heating at high temperature or by dry distillation.³

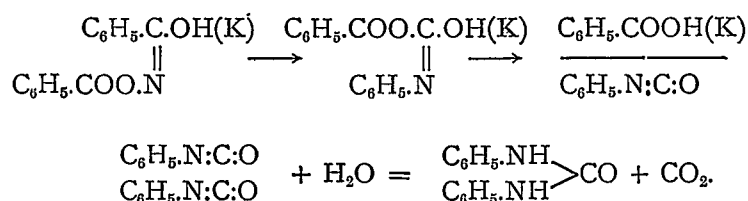
The authors have now to assert that in those cases of decomposition of dihydroxamic acids and their salts through the Beckmann rearrangement which is, we believe, wholly dependent upon the presence of acid residue, the interchange of positions between an acid residue and a hydrocarbon radical must occur, being preceded by the dissoci-

¹ Lieb. Ann., 161, 359 (1872); 175, 257 (1875).

² *Ibid.*, 309, 189 (1899).

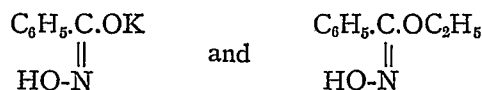
³ *Ibid.*, 175, 311, 312 (1875); 309, 189 (1899); Ber. D. chem. Ges., 27, 1256 (1894).

ation of the former as the primary cause of rearrangement, and resulting in the formation of an acyl derivative of a substituted iminocarbonic acid as an intermediate product which would break up into an isocyanate and an acid or salt, and finally in the production of a disubstituted urea by the action of water upon the isocyanate; then, taking as an example the decomposition of dibenzhydroxamic acid and its potassium salt, the course of reaction should be represented as follows¹:



Thus, in the rearrangement of several other dihydroxamic acids and their potassium salts² which behave similarly as dibenzhydroxamic acid and its potassium salt, giving the analogous decomposition products under an analogous condition, the mechanism of reaction should be analogous.

The authors repeated Lossen and Rotermond's³ experiment, by distilling an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, and also observed the production of aniline which must be due to the formation of diphenylurea, caused by the Beckmann rearrangement owing to the presence of the benzoic acid residue. We could, however, not find even a trace of aniline from the potassium salt of benzhydroxamic acid and from ethylsynbenzhydroximic acid⁴:



by distilling an aqueous solution of the former, and by heating the latter above its melting point for several hours and then distilling the product with aqueous alkali. This makes it evident that the Beckmann rearrangement would not take place in the salt and ester of benzhydrox-

¹ Such a scheme of reaction is seen in Meyer and Jacobson's *Lehrbuch d. org. Chemie*, 1st ed., II, 560, but nothing is said about the essence which may lead to rearrangement.

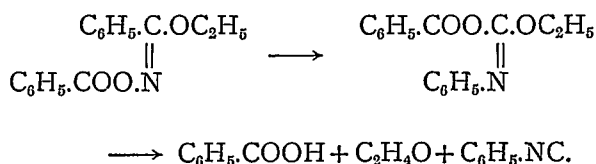
² *Lieb. Ann.*, 175, 311, 312 (1875); 309, 189 (1899); *Amer. Chem. J.*, 48, 1 (1912).

³ *Ibid.*, 161, 359 (1872); 175, 257 (1875).

⁴ *Ber. D. chem. Ges.*, 25, 37 (1892).

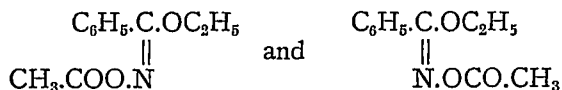
amic acid, for the necessary acid residue is lacking in each. Also, the facts already observed by Hantzsch¹ appear to give a further support to the authors' view. He has shown that by gently warming the potassium carbonate solution of acetylbenzhydroxamic acid, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OK})\text{:N}\cdot\text{OCO}\cdot\text{CH}_3$, diphenylurea abundantly separates out, while with the potassium carbonate solution of free benzhydroxamic acid, $\text{C}_6\text{H}_5\text{C}(\text{OK})\text{:N}\cdot\text{OH}$, no such a decomposition takes place even by boiling. The authors, now, dare to explain by ascribing such a difference of the behaviours of two compounds to the presence and absence of the acetic acid residue in acetylbenzhydroxamic and benzhydroxamic acids respectively.

It is already known that ethyl dibenzhydroxamate of the syn form (i.e., ethylsynbenzhydroximic acid benzoyl ester)² is decomposed into benzonitrile, benzoic acid and acetaldehyde by heating above its melting point; and the reaction has been pointed out as follows³:



So, we declare that in the case of ethylsynbenzhydroximic acid benzoyl ester, the Beckmann rearrangement should take place, for it may be regarded as the ethylbenzhydroximic acid derivative containing the benzoic acid residue linked to nitrogen in the syn form.

In order to get a further confirmation for the authors' view, two isomeric acetyl esters of ethylbenzhydroximic acid⁴:



were heated above their melting points for some hours, and the product from each ester was subjected to steam distillation in alkaline solution, as in the experiment of ethylbenzhydroximic acid. By such

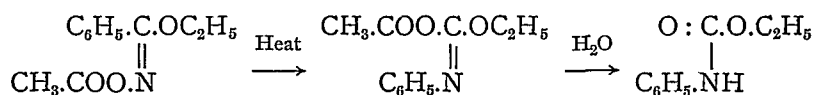
¹ Ber. D. chem. Ges., **27**, 1257 (1894).

² Lieb. Ann., **205**, 279 (1880); Ber. D. chem. Ges., **25**, 44 (1892).

³ Meyer and Jacobson's Lehrbuch d. org. Chemie, 1st ed., II, 561.

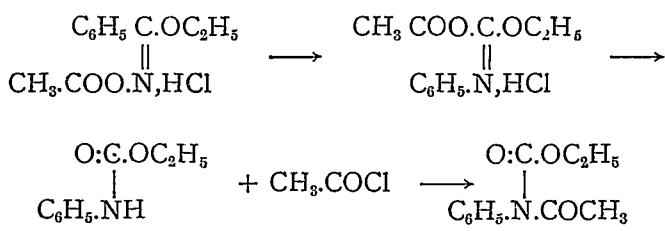
⁴ Ber. D. chem. Ges., **25**, 40-41 (1892).

a treatment a small quantity of aniline was found to be formed from the syn acetyl ester, but not a trace from the anti ester; so the production of aniline may be due to the decomposition of urethane somewhat formed from the syn ester as the result of the Beckmann rearrangement by heat, the reaction being assumed to be:



Such a course of reaction as we assume, and that for the production of phenylurethane from ethylsynbenzhydroxamic acid by phosphorus pentachloride and water, which has been pointed out by Werner¹, should be no doubt same in essence.

Moreover, each of two isomeric acetyl esters was heated in a sealed tube, dissolved in chloroform saturated with hydrochloric acid, at the temperature of 100–102° for twelve hours. The product from the syn acetyl ester was observed to contain phenylurethane and acetyl phenylurethane, but that from the anti ester not at all. The authors, then, admit it as correct that in the case of the syn acetyl ester the Beckmann rearrangement is accelerated by the aid of hydrochloric acid, just as has been shown in the rearrangement of the acetyl ester of diphenylketoxime², thus being represented as follows:



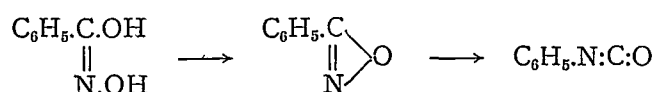
Lossen³ has announced that benzhydroxamic acid and its barium salt decompose into aniline and carbon dioxide by dry distillation. According to his statement, rearrangement actually takes place in

¹ Ber. D. chem. Ges., 25, 39 (1892).

² Mem. Coll. Sci. Engin., Kyoto, 2, 394 (1909-1910).

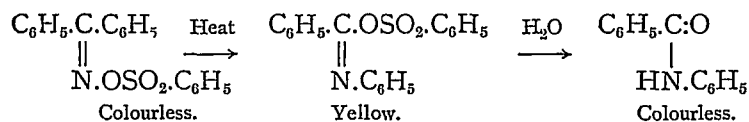
³ Lieb. Ann., 175, 320, 323 (1875).

benzhydroxamic acid and its salt, although they do not contain the negative acid residue; in this case, therefore, the decomposition can not be accounted for as the result of the Beckmann rearrangement of the usual type, as we assume, so it may be founded upon some other scheme of reaction. The authors then put forward an explanation by applying Hantzsch's view¹ on the rearrangement of benzhydroxamic acid, that is to say, that benzhydroxamic acid forms an anhydride which intramolecularly undergoes rearrangement:



Now, it has become evident that rearrangement does not take place in an aqueous solution of the salt of benzhydroxamic acid, as has already been stated, because the formation of an anhydride is not possible on account of the presence of water. Nevertheless, in an aqueous solution of the salt of hydroxamic acid acyl ester (dihydroxamic acid), in fact rearrangement takes place, as is indicated by the production of disubstituted urea as has been stated, although the formation of hydroxamic acid or its salt is possible by hydrolysis, but their rearrangement should not take place as their dehydration can not be effected in presence of water; in such a case, therefore, the migration of a negative acid residue must be brought about as the primary cause of rearrangement.

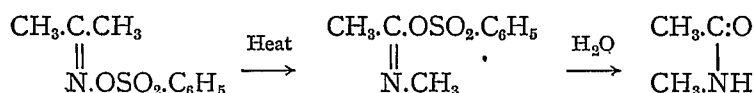
Recently an interesting observation was made by one of us (M.K.), Nakaseko and Matsunami in our laboratory with regard to the rearrangement of benzenesulphonyl ester of diphenylketoxime, viz., that the ester prepared from the sodium salt of diphenylketoxime by the action of benzenesulphonyl chloride at a low temperature, which is a colourless crystalline substance, changes to a yellow coloured compound gradually on standing by itself, but instantaneously with explosive violence accompanied by a hissing sound by heating; the yellow compound being unstable, changes readily to benzanilide by treating with water. The course of reaction shall be represented by the following scheme:



¹ Ber. D. chem. Ges., 27, 1255 (1894).

in which the formula of the intermediate product points out the presence of a characteristic chromophoric group, $>\text{C}:\text{N}.\text{C}_6\text{H}_5$.¹

Also, Hermann Weg² has shown that benzenesulphonyl ester of acetoxime, $(\text{CH}_3)_2\text{C}:\text{N}.\text{OSO}_2.\text{C}_6\text{H}_5$, decomposes explosively with a hissing noise by heating, but nothing is said about the production of a substituted acid amide. Yura, however, found as the result of an experiment suggested by one of us (M.K.) that the principal decomposition product consists of a methylamine-producing compound which may be regarded as methylacetamide, as it yields methylamine by treating with alkali; thus the reaction shall be represented as follows:



He further experimented with the benzoyl and acetyl esters of acetoxime, and observed, likewise, the production of methylamine from the decomposition product, although not so much as in the case of benzenesulphonyl ester.

Jones³ has recently mentioned in his article that the potassium salt of the benzoyl ester of phenylacethydroxamic acid, $\text{C}_6\text{H}_5.\text{CH}_2\text{C}(\text{OK}):\text{N}.\text{OCO}.\text{C}_6\text{H}_5$, died upon a porous support, suddenly decomposes in the course of a few minutes, accompanied by a hissing sound and a dense cloud of benzyliisocyanate, and also that in a similar manner, certain other salts of hydroxamic acids, when heated to a temperature considerably above room temperature, decompose explosively. Thiele and Pickard⁴ already noticed that acetyl and benzoyl esters of hydroxamic acid yield potassium salts which exploded by heating. So, the authors believe that such a decomposition is due to the spontaneous rearrangement analogous to that of the ketoxime esters as above stated.

Now, such an explosion with a hissing sound, which occurs suddenly in the decomposition of the different compounds of the oxime type may be regarded as a particular phenomenon accompanying the spontaneous Beckmann rearrangement, viz., the self-migration of an acid residue and a hydrocarbon radical.

¹ Mem. Coll. Sci. Engin., Kyoto. 2, 356 (1909-1910).

² Ber. D. chem. Ges., 24, 3537 (1891).

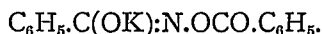
³ Amer. Chem. J., 48, 8 (1912).

⁴ Liebig Ann. 309, 190 (1899).

The investigation relating to the rearrangement of benzenesulphonyl and other acyl esters of different ketoximes is now in progress; the details of the result will be communicated in a near future.

EXPERIMENTAL.

1. *Potassium Dibenzhydroxamate*,



Five grams of dibenzhydroxamic acid prepared according to the method by Lossen¹, was suspended in water, and a solution of potassium hydroxide was carefully added until it dissolves, and then the solution was subjected to distillation by passing a current of steam. Adding a drop of a solution of bleaching powder to a small portion of the distillate, there was observed the characteristic colour-reaction of aniline. The principal portion of the distillate was extracted with ether, and the liquid substance left on evaporation of ether was confirmed to be aniline by changing it to the double salt of its hydrochloride with platinum chloride.

The similar experiment was conducted by using an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, prepared as usual, by treating the acid with alcoholic potash. The result was found to be same as above described.

2. *Potassium Benzhydroxamate*, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OK})\text{:N}\cdot\text{OH}$.

The experiment exactly similar to that above stated was performed with the potassium salt of benzhydroxamic acid from the acid prepared according to the statement given by Lossen², but not a trace of aniline was found to be formed, not giving the characteristic delicate colour-reaction of aniline.

3. *Ethylbenzhydroxamic acids*, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OC}_2\text{H}_5)\text{:N}\cdot\text{OH}$.

Each of both geometrical isomers of ethylbenzhydroxamic acid (the syn ester melts at 53° and the anti at 67°)³ was heated at the tem-

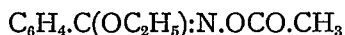
¹ Lieb. Ann., **161**, 347 (1872).

² *Ibid.*

³ Ber. D. chem. Ges., **17**, 1587 (1884); **25**, 37-39 (1892); Lieb. Ann., **205**, 279 (1880.)

perature of 70–80° for twelve hours over a water bath. The product from each was subjected to steam distillation in an alkaline solution, but the distillate gave no colour-reaction of aniline at all. Hence, it is concluded that the Beckmann rearrangement would not take place in the potassium salt and both esters of benzhydroxamic acid.

4. *Ethylbenzhydroximic Acetates,*



Syn and anti acetates of ethylbenzhydroximic acid prepared according to Werner's description¹ melt at 38–39° and 57° respectively.

Three grams of the syn acetate were heated at the temperature of 67–70° for twelve hours, and the product was subjected to steam distillation in an alkaline solution. The production of a small quantity of aniline was confirmed in the distillate by the colour-reaction with a bleaching powder solution.

5. *Action of Hydrochloric Acid upon Ethylbenzhydroximic Acetates.*

Three grams of ethylsynbenzhydroximic acetate dissolved in 30 c.c. of chloroform saturated with hydrochloric acid were heated in a sealed tube at 100–102° for twelve hours. When the tube was opened, the escapement of ethyl chloride was noticed; the contents of the tube were poured into a glass vessel where chloroform and hydrochloric acid were driven out by evaporation, a reddish brown liquid being left as a residue. From this liquid, phenylurethane and acetyl benzhydroxamic acid were isolated. In order to conduct the separation of those compounds, the reaction products were first treated with ether and then with benzene, as phenylurethane and acetyl phenylurethane are soluble in ether while acetyl benzhydroxamic acid not in ether but in benzene and water. Each of those substances was identified by its melting point and other characteristic behaviours.

¹ Ber. D. chem. Ges., 25, 40–41 (1892).