

# On Beckmann's Rearrangement, X.

By

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A few words concerning the continuation of this research in the author's laboratory seem called for here. In 1907, Professor M. Kuhara communicated the first paper on this subject to the *Memoirs of Science and Engineering of the University*. Subsequently, until 1918, nine papers were issued in co-operation with fellow-investigators, but the problem has not yet been satisfactorily solved.

In 1919, the Chair of Organic Chemistry was kindly bestowed on the author, one of Prof. Kuhara's old students, and the research on the subject came to be undertaken here again, since it would have grieved the author greatly to give up the greatest work of his life which was being carried on right up to the very day of his death. Besides, it is also the sincere desire of the author's colleagues to follow in the steps of their grand father in chemistry. The hypothesis, however, on which further work in this field is based may not be in every respect the same as the teacher's.

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<sup>1</sup> M. Kuhara & T. Kainosho : On Beckmann's Rearrangement I, *Memoirs of Coll. Science & Eng.*, **1**, 254 (1907); M. Kuhara & Y. Toda : II, *Ibid.*, **II**, 387 (1910); M. Kuhara & T. Okada : III, *These Memoirs*, **1**, 1 (1914); M. Kuhara & K. Suitsu : VI, *Ibid.*, **1**, 25 (1914); M. Kuhara, K. Matsu-miya & N. Matsunami : V, *Ibid.*, **1**, 105 (1914); M. Kuhara & H. Wata-nabe : VI, *Ibid.*, **1**, 349 (1916); M. Kuhara & F. Ishikawa : VII, *Ibid.*, 355 (1916); M. Kuhara, N. Agatsuma & K. Araki : VIII, *Ibid.*, **3**, 1 (1917); M. Kuhara & K. Kashima : IX, *Ibid.*, **4**, 69 (1920).

The intramolecular conversion of an oxime into its isomeric acid amide, the so-called Beckmann rearrangement, can usually be effected by the mineral and organic acids, acid anhydrides and acid chlorides. Their employment as reagents, however, is likely to bring about misapprehension that the *raison d'être* of the rearrangement, as the author had conjectured, was due to the effect of the dehydration of the oxime, on account of these numerous reagents which are commonly used as the dehydrating agent in organic chemistry. Such unwarranted assumption of the cause of the change will be proved to be erroneous by mentioning here a few interesting examples of the Beckmann change noticed by O. Baudisch<sup>1</sup> in the transformation of acetone oxime into methyl acetamide by the action of the ultraviolet ray, and also by the author's co-operators on the catalytic action of reduced copper on various oximes<sup>2</sup>.

The reaction for the nitrile formation from oxime by action of these reagents, which actually taking place by the removal of water from the oxime, was sometimes confused with the Beckmann reaction. The mechanism for the formation of benzonitrile from anti-benzaldoxime will be a different from that for the acetonitrile formation from diacetyl monoximine benzoyl ester<sup>3</sup>.

The nitrile formation, in general, from the oxime should be explained in two different manners: one is the direct formation and the other is the indirect. The formation of *o*-cyano diphenyl carboxylic acid from  $\alpha$ -nitroso- $\beta$ -naphthol<sup>4</sup>, benzonitrile from the oximes of benzoyl formic acids<sup>4</sup>, camphonitrile from camphor oxime<sup>5</sup> and menthonitrile from menthone oxime<sup>6</sup> should be classified as belonging to the indirect formation. In the latter case which was formerly named 'Beckmannsche

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<sup>1</sup> Ber. D. Chem. Ges., **44**, 1009 (1911); A. Werner: Lehr. d. Stereochem., 278 (1904).

<sup>2</sup> These Memoirs, **6**, 245 (1923); **7**, 151 (1923).

<sup>3</sup> O. Diels and M. Stern: Ber. D. Chem. Ges., **40**, 1630 (1907).

<sup>4</sup> A. Werner and A. Piguet: *Ibid.*, **37**, 4310 (1904).

<sup>5</sup> These Memoirs, **6**, 245 (1923).

<sup>6</sup> *Ibid.*, **7**, 151 (1923).

Umlagerung zweiter Art<sup>1</sup> by A. Werner, two entirely different reactions occur successively: the rearrangement of oxime into acid amide or isoxime (in cyclic compound) and the dehydration of the acid amide by the action of the same reagent used for bringing the rearrangement, which immediately followed the molecular conversion. The examples which afford supply the supposition for the author's interpretation for the indirect nitrile formation, can easily be cited here from literature, and they are: the reaction between phosphorus pentachloride and pivalophenone oxime<sup>2</sup> or benzoyl piperidine<sup>3</sup> and that between phosphorus pentoxide and menthone oxime<sup>4</sup>.

The conversion of cinnamyl aldoxime into isoquinoline has been misunderstood by chemists as an abnormal manifestation of the Beckmann change<sup>5</sup> which was also considered by the author to be very nearly true in explaining that the cinnamyl formamide yielded by the Beckmann change from the oxime, suffers dehydration as a result of forming isoquinoline as final product. V. Meyer and P. Jacobson<sup>6</sup> have distinguished the nitrile decomposition from the Beckmann change in the case of the menthone oxime. They made no distinction between the nitrile decomposition and 'Beckmannsche Umlagerung zweiter Art.' The differences between these reactions, however, are principally due to differences in the mechanism of these reactions as already stated above.

The Beckmann reaction is the hitherto employed unique method for determining the configuration of an oxime from its products of transformation since adopted by Hantsch to distinguish the isomeric oximes<sup>7</sup>. There were, however, very curious examples of the Beckmann change

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<sup>1</sup> A. Werner and A. Piguet: *Loc. cit.*; O. Diels: *Lieb. Ann.*, **432**, 1 (1923).

<sup>2</sup> G. Schroeter: *Ber. D. Chem. Ges.*, **44**, 1204 (1911).

<sup>3</sup> J. v. Braun: *Ibid.*, **37**, 2915 (1904).

<sup>4</sup> O. Wallach and F. E. Tuttle: *Lieb. Ann.*, **277**, 157 (1893).

<sup>5</sup> J. B. Cohen: *Org. chem. for advan. stud.*, 1907, 213.

<sup>6</sup> *Lehr. d. Org. Chem.*, II, **1**, 897 (1902); also refer A. Kötze and Wunsdorf: *J. prac. Chem.*, **88**, 519 (1913); O. Wallach: *Lieb. Ann.*, **329**, 105 (1903).

<sup>7</sup> *Ber. D. Chem. Ges.*, **24**, 22 (1891).

observed by E. Beckmann and Köster<sup>1</sup>, and other chemists<sup>2</sup>, which resulted in the same ultimate reaction products though they started in the reaction with isomeric oximes.

Consequently the author was inclined to side with the opinion of S. Schroeter<sup>3</sup> and others that the reaction is not a reliable method for distinguishing stereoisomerides of oximes unless the great care is taken in the conversion of oximes by the action of heat and light, and also by some treatments into one another.

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<sup>1</sup> Lieb. Ann., **274**, 15 (1893).

<sup>2</sup> S. Schroeter : Ber. D. Chem. Ges., **44**, 1204 (1911) ; A. Werner & A. Piguet : Loc. cit ; J. Meisenheimer : Ber. D. Chem. Ges., **54**, 3206 (1921) ; S. Yamaguchi : Unpublished work.

<sup>3</sup> Loc. cit, and also refer to Annual reports of the progress of chemistry XIX, 95 (1923).