[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE BECKMANN REARRANGEMENT. II

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The formation of benzophenone oxime according to the equation

$$(C_6H_5)_2CO + NH_2OH + HCl \rightleftharpoons (C_6H_5)_2C = NOH + H_2O \tag{1}$$

is a reversible process. An increase of hydrochloric acid concentration shifts equilibrium sharply to the left; in alkaline media the reaction proceeds quantitatively to the right. A second state of equilibrium according to the equation

$$(C_6H_5)_2C{=}NOH + HCl \rightleftharpoons (C_6H_5)_2C{=}NH_2OH)^+Cl^- \tag{2}$$

arises from the weakly basic nature of benzophenone oxime.[1] The salt is largely hydrolyzed by water. In anhydrous solvents, salt formation is quantitative.

It has been shown in the previous paper[2] that free benzophenone oxime does not undergo the Beckmann rearrangement. It is the *salt* of the oxime which is characterized by this reaction. If, therefore, as was suggested at the time, the rearrangement is not preceded by a forcible dehydration, a system containing the components of Equation 1 should yield benzanilide regardless of the presence of water. This proved to be the case, under certain special conditions.

It has now been found that the rearrangement of benzophenone oxime takes place readily enough in the presence of larger amounts of water, if due regard be had to the considerations outlined above. The condition necessary for the formation of oxime salt in the presence of water, namely, high concentration of acid, is also the condition which brings about hydrolysis of the oxime into benzophenone and hydroxylamine. It is thus not possible to have more than traces of oxime salt present at any given moment. But all of the reactions concerned, including the Beckmann rearrangement itself, are very rapid, and as the rearrangement is not reversible, benzanilide will accumulate in the system if sufficient time is allowed. At temperatures between 100° and 150°, a period of one to two days is ample to give very definite evidence of such a reaction. As benzanilide itself is also hydrolyzed under the experimental conditions, the final products are aniline and benzoic acid. Details will be found in the experimental section. It will also be shown there that the presence of an excess

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[1] Derick and Bornmann [THIS JOURNAL, **35**, 1269 (1913)] give $K = 2 \times 10^{-11}$.

[2] Lachman, *ibid.*, **46**, 1477 (1924). A brief summary of literature references given there need not be repeated. A correction, however, must be made. The rearrangement of pure oxime hydrochloride, without added catalyst, was first noted by Kuhara, *Mem. Coll. Sci. Imp. Kyoto Univ.*, **3**, 1 (1917). In the previous paper, credit was erroneously given to Lehmann.

of hydroxylamine increases the speed of the rearrangement, as must be expected from the equilibrium conditions shown in Equation 1.

The reaction products, aniline and benzoic acid, are always accompanied by notable amounts of phenol. This appeared to be direct evidence of the actual interchange of phenyl and hydroxyl radicals which Beckmann's version of the reaction mechanism assumes.[3]

The fact is, however, that phenol is formed by a side reaction. Hydroxylamine formed by hydrolysis (Equation 1) is decomposed to some extent with the formation of nitrous acid, and this acts upon aniline to yield phenol. The correctness of this explanation was shown when a mixture of hydroxylamine, hydrochloric acid and benzanilide was heated to 150°; a measurable amount of phenol was isolated.

Discussion

The facts considered here are not in harmony with the Stieglitz version of the mechanism of the Beckmann rearrangement, at least, not with its present form. Stieglitz assumes a forcible removal of water from oxime salt; this leaves an unsaturated nitrogen atom, which in turn compels rearrangement in order to saturate itself.

The chief function of dehydrating agents is rather to increase the concentration of oxime salt, thus increasing the rate of rearrangement. The ordinary rearranging agents have a second function. Kuhara and his pupils[4] have found that replacement of acetic anhydride in Beckmann's mixture by more negative acyl chlorides, such as chloro-acetyl or benzenesulfonyl chloride, results in an increase in the reaction rate and in a lowering of the reaction temperature. It has long been known that the use of antimony trichloride and still more, of antimony pentachloride, has a similar effect.

Kuhara has further found that the benzene sulfonic ester of benzophenone oxime, $(C_6H_5)_2C{=}N{-}O{-}SO_2C_6H_5$, rearranges spontaneously at room temperature without any added catalyst.

$$(C_6H_5)_2C = N{-}O{-}SO_2C_6H_5 \longrightarrow C_6H_5C({=}NC_6H_5)(OSO_2C_6H_5) \qquad (3)$$

It is difficult to reconcile this reaction with Stieglitz's mechanism of rearrangement.[5]

The failure of free benzophenone oxime to rearrange, as contrasted with the ready reaction of its salts, may perhaps be interpreted, in analogy with Kuhara's views, as a matter of loosening the ties that bind a radical to

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[3] Details will be found under Ref. 2.

[4] Many papers in *Mem. Coll. Sci. Imp. Kyoto Univ.*, **1907** to **1921**. This important work is being continued by Komatsu in the same publication.

[5] Compare also the work of Werner and Piguet [*Ber.*, **37**, 4295 (1904)] and of Werner and Detschoff [*Ber.*, **38**, 69 (1905)] who found that rearrangement takes place readily when certain oximes were treated with benzene sulfone chloride in pyridine solution and in dil. aqueous alkali.

the nitrogen atom. In the oxime salts, a part of the valence forces of the nitrogen has been satisfied by the addition of hydrogen ion (Equation 2), and the remaining forces have been correspondingly weakened, at least sufficiently to permit hydroxyl to migrate.

In a discussion of Kuhara's work, Stieglitz and Stagner[6] call attention to the difference between benzophenone oxime benzenesulfonate, which rearranges spontaneously, and diphenylmethane-imide chloride, $(C_6H_5)_2C=NCl$, which has not yet been found to rearrange under any conditions. They point out that the latter substance may be regarded as the hydrochloric acid ester of the oxime, that is, as analogous to Kuhara's compound with respect to the "negativity" of the group attached to nitrogen. There is, however, a marked difference in one of the factors involved. Though perhaps equally negative, the chlorine radical may become attached to the nitrogen atom by direct substitution of hydrogen; the benzene sulfonyl radical can be introduced only by way of double decomposition of the oxime salts of the alkalies. The negativity of the radicals, then, differs from their affinity for nitrogen, and is no measure of the strength of the bonds involved. Kuhara's interpretation, that the weakness of the bond determines the ease of rearrangement, agrees best with the facts just discussed, and seems also to account best for the difference in behavior of benzophenone oxime and its salts.

Experimental Section

The completeness and the speed with which the equilibrium in Equation 1 is shifted to the right in alkaline media, are apparent from the method of preparing benzophenone oxime, given in the previous paper. The following, improved method of preparation also indicates the same result.

Preparation of Benzophenone Oxime.—A mixture of 50 g. of benzophenone, 30 g. of hydroxylamine hydrochloride, 100 cc. of alcohol, 200 cc. of water and 55 g. sodium hydroxide is heated to gentle boiling under a reflux condenser. The liquid becomes homogeneous in five minutes. It is then cooled, and poured into a liter of water containing 150 cc. of concd. hydrochloric acid. After the product is washed with water and dried, it is practically pure; yield, 53 g., or 98%. It may be recrystallized from dil. alcohol. Benzophenone oxime must be preserved perfectly dry, in an atmosphere free from oxygen.

Rapidity of Reversal of Oxime Formation.—Six g. of oxime was heated, in a sealed tube, with 5 cc. of alcohol and 5 cc. of 10 *N* hydrochloric acid. The temperature was 125°, and the total time of exposure to heat, including warming up, was 30 minutes. The mixture became homogeneous after a few minutes, but shortly afterward separated into two layers. As it cooled, crystals of hydroxylamine hydrochloride separated. Water was added, and the mixture treated as described below in detail. Benzophenone was the only product obtained, weighing 5.6 g. (calcd., 5.6 g.).

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[6] Stieglitz and Stagner, This Journal, **38**, 2056 (1916).

Quantitative studies of similar mixtures were vitiated by the rapid formation of ethyl chloride and were therefore discontinued. In all cases where the time of heating was prolonged sufficiently for the Beckmann rearrangement to be manifested, a considerable amount of ethyl benzotae was noted. Thus, 2 g. of oxime in 10 cc. of ordinary alcoholic *N* hydrochloric acid, heated to 150° for 18 hours, gave 0.3 g. of ethyl benzoate. This was isolated by diluting the reaction mixture with sodium bicarbonate solution and distilling with steam. The distillate was extracted with ether. The crude ethyl benzoate was hydrolyzed with alkali and yielded 0.2 g. of benzoic acid.

General Method of Treating Reaction Mixtures.—The results obtained with various mixtures of oxime, hydrochloric acid and hydroxylamine hydrochloride are given below in tabular form. The reaction product in each case was dissolved in a little warm water and a slight excess of sodium bicarbonate solution was added. After cooling, the mixture was filtered and the insoluble portion, containing benzophenone, benzophenone oxime, and benzanilide, was dried in a vacuum and weighed. This material was then extracted with cold, low-boiling ligroin, which removes only benzophenone. The insoluble portion was dried and weighed again, the loss giving the amount of benzophenone (plus traces of phenol in many instances; see below). It was then extracted with cold 2% sodium hydroxide solution, which dissolves benzophenone oxime; the residue, after it was again dried, consisted of benzanilide (plus traces of tarry material). The alkaline solution of oxime was occasionally acidified and the oxime recovered as such.

The aqueous sodium bicarbonate extract was acidified with hydrochloric acid and extracted with ether. The ether, when evaporated, gave

TABLE I

REARRANGEMENT OF BENZOPHENONE OXIME IN THE PRESENCE OF WATER

In each case, 1.8 g. of benzophenone (=0.01 mole) was taken. Hydroxylamine hydrochloride varied from 0.01 mole (=0.7 g.) to 0.03 mole, as indicated. Volume and composition of added liquids are given in Cols. 2 and 3, respectively. × indicates "not weighed."

$(NH_4O)Cl$ G.	Vol. Cc.	Composition	Time Hrs.	Benzoic acid G.	Tribromoaniline G.	Benzophenone G.	Rearrangement %
0.7	5	H_2O	21[a]	0.02	×	1.7	2
2.1	5	H_2O	21[a]	.06	×	1.6	5
0.7	10	H_2O	48[a]	.11	×	1.5	9
.7	5	0.5 *N* HCl	22[b]	.05	×	1.7	4
.7	5	*N* HCl	22[b]	.10	×	1.4	8
.7	5	6 *N* HCl	24[a]	.10	0.21	×	8
2.1	5	6 *N* HCl	24[a]	.30	0.78	1.2	24
0.7	5	12 *N* HCl	24[b]	.57	1.41	×	47
2.1	5	12 *N* HCl	28[b]	1.15	2.90	×	94
0.7	no liquid	....	22[a]	0.75	1.88	×	70

[a] Temperature, 150°. [b] Temperature, 148°.

a residue of benzoic acid, practically pure (the melting point varied from 120° to 122°). The hydrochloric acid solution was freed from ether by a current of warm air and treated with bromine water. A voluminous precipitate of aniline tribromide (*m. p.* 119°, after recrystallization from dil. alcohol) was filtered off, dried in a vacuum and weighed.

Owing to the ready establishment of equilibrium between benzophenone and hydroxylamine salt, it was found most convenient to operate with these materials rather than with the oxime itself. In a few cases, oxime was the actual starting material; but for the sake of uniformity in reporting the data, these instances have been recalculated to a similar basis.

Is Benzoic Acid Produced from Benzophenone?—In a number of instances the amount of benzoic acid produced was taken as the measure of progress of the Beckmann rearrangement, as it is the easiest of the products to isolate and measure with reasonable accuracy. This involved the assumption that benzoic acid was not formed from benzophenone by hydrolysis with acids. To assure absence of disturbance from this source, a mixture of 2 g. of benzophenone was heated with 10 cc. of 6 *N* hydrochloric acid to 150° for 48 hours. No benzoic acid could be detected by the above method and the weight of recovered benzophenone was 1.95 g.

Production of Phenol from Benzanilide.—Two g. of benzanilide was heated with 2 g. of hydroxylamine hydrochloride and 10 cc. of *N* hydrochloric acid to 150° for 22 hours. The reaction mixture was strongly acidified with hydrochloric acid and distilled with steam. The distillate was treated with bromine water and gave 0.4 g. of tribromophenol.

Rearrangement at Lower Temperatures.—In the work reported in the earlier paper, as well as in that of Kuhara and of Lehmann, it was found that pure benzophenone oxime hydrochloride rearranged at about 125°. All of the data of Table I were obtained at 150°. It seemed worth while to try a lower limit.

A mixture of 3.6 g. benzophenone (0.02 mole) and 2.8 g. hydroxylamine hydrochloride (0.04 mole) was heated in a sealed tube with 1 cc. of water and 1 cc. of acetic acid; temperature, 95°; time, 48 hours. Benzoic acid weighing 0.04 g. was obtained, equivalent to 1.7% rearrangement.

Summary

1. The Beckmann rearrangement of benzophenone oxime salts takes place in the presence of water; but the rate is slow, as oxime salts are hydrolyzed and therefore exist only in low concentration in the presence of water.

2. Kuhara's modification of Beckmann's theory, that the rearrangement of oximes and oxime esters depends chiefly on a weakening of the bond between nitrogen and hydroxyl (or acyl), seems to account best for the behavior of oximes and their derivatives.

3. An extension of Kuhara's views offers a reasonable explanation of

the difference between free benzophenone oxime, which does not rearrange, and its salts, which rearrange readily.

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[CONTRIBUTION FROM THE CARBOHYDRATE LABORATORY, BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

RELATIONS BETWEEN ROTATORY POWER AND STRUCTURE IN THE SUGAR GROUP. VI.[1] THE ROTATORY POWERS OF THE ALPHA AND BETA FORMS OF METHYL d-XYLOSIDE AND OF METHYL l-ARABINOSIDE

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The rotatory powers of the alpha and beta forms of methyl *d*-glucoside and of methyl *d*-galactoside are known with precision from the careful reinvestigation of these substances by E. Bourquelot.[3] The present investigation was undertaken with the purpose of determining accurately the rotations of the alpha and beta forms of methyl *d*-xyloside and of methyl *l*-arabinoside as a supplement to Bourquelot's data so that the rotations of these four isomeric pairs of methyl glycosides of the four aldoses may be used for a more exact quantitative study of the relation between rotatory power and structure than has been possible in the past.[4] The principal problem in the obtaining of accurate data respecting such compounds is the purification of the substances themselves and particularly the thorough separation of isomeric forms by crystallization from suitable solvents.

The two forms of methyl xyloside and one of the forms of methyl arabinoside were discovered by Emil Fischer.[5] The present results agree with his values of the rotations of the methyl xylosides within about 0.5%. He did not record the rotation of the arabinoside. The second form of methyl arabinoside was discovered by Purdie and Rose[6] who measured not only its rotation but the rotation of the first form as well. The present results closely confirm their value of the rotation of the first, or Fischer's arabinoside, but give a greatly different value from theirs in the case of the second arabinoside ($[\alpha]_D^{20} = +17.3$ in place of $+73$). The difference is probably due to the presence of some of the first arabinoside in their compound, which is readily accounted for by the great difficulty of separating the two isomers, especially when only small quantities of material

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[1] Part V was published in THIS JOURNAL, **46**, 2591 (1924).

[2] This work was done in 1917 in the Carbohydrate Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.

[3] Bourquelot, *Ann. chim.*, **7**, 219 (1917).

[4] Hudson, THIS JOURNAL, **31**, 66 (1909).

[5] Fischer, *Ber.*, **28**, 1145 (1895).

[6] Purdie and Rose, *J. Chem. Soc.*, **89**, 1204 (1906).