[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

THE BECKMANN REARRANGEMENT OF KETOXIMES WITH BORON FLUORIDE. DEVELOPMENT OF THE THEORY AND OF A NEW METHOD

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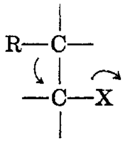
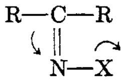
There is considerable evidence (1) that, like the acid-catalyzed rearrangement of an alcohol or a derivative (I), the Beckmann rearrangement of a ketoxime or a derivative (II) involves the removal (ionization) of hydroxyl or other group X with its bonding pair of electrons and the 1,2-shift of R with its bonding pair.



$$\begin{array}{c} | \\ R\text{—}C\text{—} \\ | \\ \text{—}C\text{—}X \\ | \end{array}$$

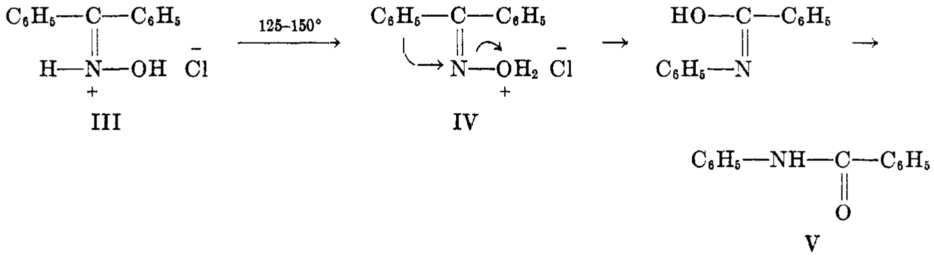
I



$$\begin{array}{c} R\text{—}C\text{—}R \\ \| \\ N\text{—}X \end{array}$$

II

However, in contrast to the rearrangement of an alcohol, the Beckmann rearrangement of a ketoxime is not at first facilitated by an acid. This is because the proton of the acid coordinates preferentially with the nitrogen of the oxime to form the relatively stable immonium ion, such as the cation of III, rather than with the hydroxyl oxygen to give the reactive oxonium ion such as the cation of IV. The positive charge on the former ion hinders the ionization of hydroxyl as required for the rearrangement. Thus, benzophenone oxime is first converted by hydrogen chloride to the relatively stable immonium chloride III. This salt, in either the solid state or in aqueous solution, exhibits appreciable Beckmann rearrangement to form benzanilide only at 125–150° (2, 3). Under these rather drastic conditions, the immonium ion of III is presumably converted to the oxonium ion of IV which undergoes the rearrangement as suggested by Bennett (4). Even then, the main rearrangement appears to involve the intermediate formation of the imidol derivative of the ketoxime. Thus Chapman (3) has presented evidence that, under certain conditions, such an intermediate is generated through the conversion of initially formed benzanilide to its imido chloride which reacts with the oxime.



$$\begin{array}{c} C_6H_5\text{—}C\text{—}C_6H_5 \\ \| \\ H\text{—}\overset{+}{N}\text{—}OH\ \ \overset{-}{Cl} \end{array} \xrightarrow{125\text{–}150^\circ} \begin{array}{c} C_6H_5\text{—}C\text{—}C_6H_5 \\ \| \\ N\text{—}\overset{+}{O}H_2\ \ \overset{-}{Cl} \end{array} \rightarrow \begin{array}{c} HO\text{—}C\text{—}C_6H_5 \\ \| \\ C_6H_5\text{—}N \end{array} \rightarrow \begin{array}{c} C_6H_5\text{—}NH\text{—}C\text{—}C_6H_5 \\ \| \\ O \end{array}$$

III IV V

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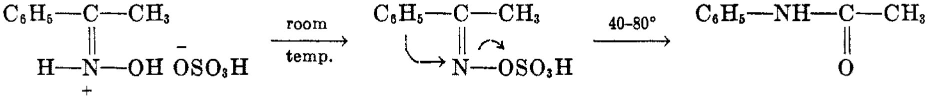
[1] Allied Chemical and Dye Corporation Fellow, 1954–1955.

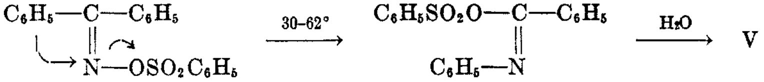
Similarly a ketoxime is first converted by sulfuric acid to the corresponding immonium hydrogen sulfate such as VI. But in contrast to the immonium chloride, salt VI is readily converted to the O-sulfonic ester VII which undergoes the Beckmann rearrangement at relatively low temperatures. This has been demonstrated by Pearson and Ball (5) who showed that salt VI is converted to ester VII at room temperatures, and that VII undergoes the rearrangement at its melting point (80°) or even at 40–45° in ethylene chloride solution.



$$C_6H_5-C(=\overset{+}{N}H-OH)-CH_3\ \ \overset{-}{O}SO_3H \xrightarrow[\text{temp.}]{\text{room}} C_6H_5-C(=N-OSO_3H)-CH_3 \xrightarrow{40\text{–}80^\circ} C_6H_5-NH-C(=O)-CH_3$$

VI VII

Although ester VII is also an acid, acid catalysis is evidently not required for sulfonic esters to rearrange readily. Thus Kuhara (6) has shown that the neutral benzenesulfonic ester of benzophenone oxime (VIII) rearranges at its melting point (62°) or even at room temperature in chloroform solution in the absence of an acid catalyst. Similarly neutral picryl ethers of ketoximes have been found to rearrange in chloroform solution at 50° (7).

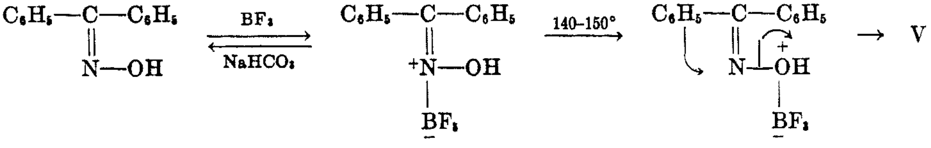


$$C_6H_5-C(=N-OSO_2C_6H_5)-C_6H_5 \xrightarrow{30\text{–}62^\circ} C_6H_5SO_2O-C(=N-C_6H_5)-C_6H_5 \xrightarrow{H_2O} \text{V}$$

VIII

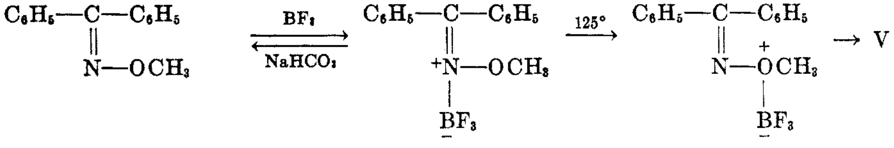
In general, the reagents that effect the Beckmann rearrangement of ketoximes at relatively low temperatures, including phosphorus pentachloride in refluxing ether, presumably convert the oximes to ester-like intermediates (8) which have a greater tendency to ionize and, consequently, to rearrange. Certainly the reactive intermediate with phosphorus pentachloride is not a chlorimido ketone since such compounds have been shown not to rearrange under similar conditions (9). Apparently benzophenone chlorimine has been rearranged only with antimony pentachloride with which it forms a complex that rearranges at 40–45° in carbon tetrachloride (10).

In the present investigation it was found that, similar to hydrogen chloride, boron fluoride first converts benzophenone oxime to the relatively stable coordination complex IX which was precipitated almost quantitatively on saturating a ligroin solution of the oxime with the reagent at room temperatures. Thus, this salt-like complex was recovered after heating a suspension of it in toluene at 90° for 30 minutes, and the oxime was regenerated on treating the recovered complex with sodium bicarbonate solution. Even the small amount of the complex that had dissolved in the toluene was recovered apparently unchanged. However, on heating to 140–150°, the complex melted and underwent a vigorous exothermic reaction to form benzanilide (83 %). It was also observed to rearrange at this temperature in Dowtherm solution. Under these conditions, the immonium type complex IX is presumably converted to the oxonium type complex X which undergoes the Beckmann rearrangement. The rearrangement was realized at a somewhat lower temperature (115–120°) in acetic acid solution, but these conditions might have produced the oxime acetate which rearranges more readily than the oxime (see below). It should be mentioned that boron fluoride has previously been reported to convert acetophenone oxime to the corresponding coordination complex (11), and to effect Beckmann rearrangements (12), although the details have not been available. The similar Lewis acid, aluminum chloride, has been shown to initiate the rearrangement of benzophenone oxime at 110° (13).



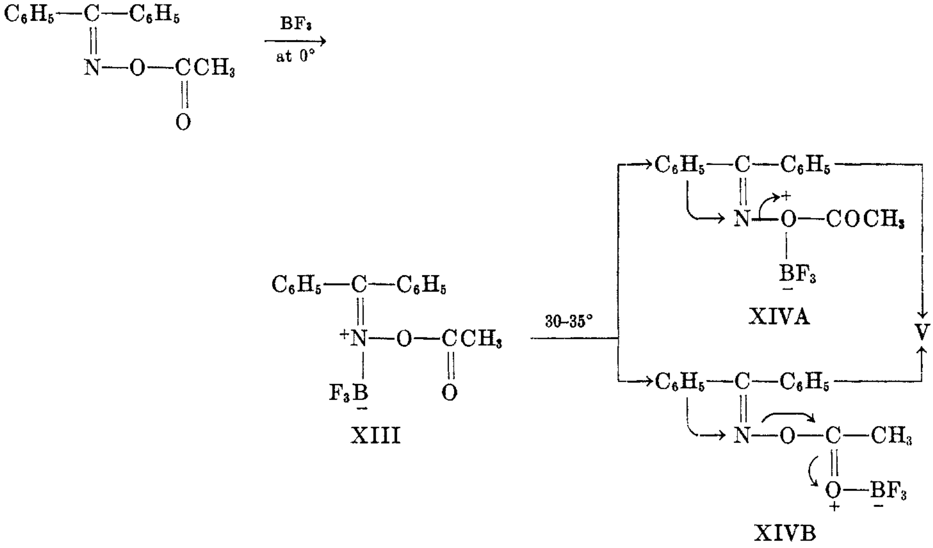
IX X

Similarly boron fluoride first converts the O-methyl ether of benzophenone oxime to the relatively stable coordination complex XI which was obtained at room temperatures as a low-melting solid or liquid. Thus the complex was recovered as a liquid after it had been heated under toluene at 90° for 20 minutes, and the O-methyl ether was regenerated on treating the recovered complex with sodium bicarbonate solution. Indeed, the liquid complex did not rearrange until heated to 125° at which temperature a vigorous exothermic reaction occurred, producing benzanilide (53%). Benzanilide (52%) was similarly obtained on saturating an acetic acid solution of the O-methyl ether with boron fluoride (temperature rising to 115°–120°). Under these conditions the immonium type complex XI is presumably converted to the oxonium type complex XII which undergoes the rearrangement. The benzanilide apparently resulted from the cleavage of the imido ether (14) which Theilacker and co-workers (15) have shown to be formed in the Beckmann rearrangement of the O-methyl ether with antimony pentachloride and hydrogen chloride at 110°.

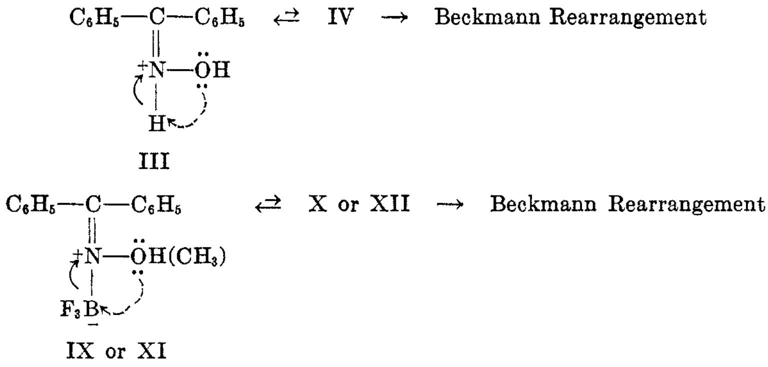


XI XII

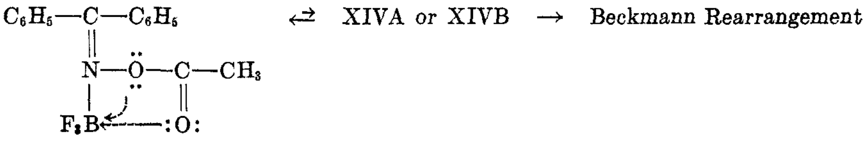
Also, boron fluoride first converts the acetate of benzophenone oxime to the immonium type complex XIII. However, this complex is much less stable than those from the oxime and the O-methyl ether. Thus, complex XIII separated as a liquid on saturating a toluene solution of the oxime acetate at 0° or at −70°, whereas rearrangement occurred when the saturation was carried out in the usual manner under which conditions the temperature rose slightly (30–35°). The rearrangement is assumed to involve the intermediate formation of the oxonium type complex XIVA or XIVB. The liquid complex obtained at 0° or lower was shown to be unrearranged by the recovery of benzophenone oxime on treatment with cold methanol followed by water. These results are in line with the well known fact that an oxime acetate undergoes the Beckmann rearrangement more readily than the oxime (16). Actually Beckmann (17) early observed that the rearrangement of the oxime is readily effected with a mixture of acetic anhydride, acetic acid, and hydrogen chloride, with which the oxime acetate is presumably formed as an intermediate.



Mechanism of conversion of immonium complexes to oxonium complexes. The transfer of the proton or of boron fluoride from nitrogen to oxygen in passing from the immonium type complexes III, IX, and XI to oxonium type complexes IV, X, and XII might occur either intermolecularly or intramolecularly. We suggest that it involves the intramolecular three-atom ring displacement mechanism indicated below, at least in the absence of a solvent having considerable proton- or boron fluoride-accepting capacity. This mechanism is considered to be in agreement with the relatively high temperature requirement for the rearrangement, since, although the oxonium type complex should readily undergo the rearrangement, the equilibrium between this complex and the immonium complex should be far on the side of the latter.

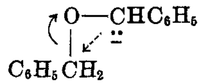


The fact that the immonium type complex of the oxime acetate (XIII) readily undergoes the rearrangement is not surprising since this complex may be converted to oxonium type complexes not only through the three-atom ring mechanism to form XIVA, but also through a five-atom ring mechanism involving the carbonyl oxygen to give XIVB. Moreover, these oxonium complexes from the oxime acetate should have a greater tendency to rearrange than that from the oxime or the O-methyl ether since they should have the greater capacity for ionization.

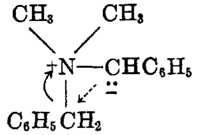


XIII

It should be pointed out that the 1,2-shift of the proton or of boron fluoride without its bonding pair of electrons on passing from the immonium complexes III, IX, or XI to the oxonium complexes IV, X, and XII respectively, is similar to the 1,2-shift of an alkyl group without its bonding pair of electrons within the carbanions of a benzyl ether (XV) or of a quaternary ammonium ion (XVI) which likewise have been regarded as an intramolecular displacement (18).



XV



XVI

Boron fluoride-acetic acid method for Beckmann rearrangements. Although ketoximes are first converted by boron fluoride to relatively stable N-coordination complexes, the Beckmann rearrangement can, nevertheless, be realized in excellent yield with these complexes especially in acetic acid solution at 115–120°. Thus, the boron fluoride complex of benzophenone oxime (IX) was rearranged in this solvent to form benzanilide in 96% yield. Recently (19) the boron fluoride complex of acetomesitylene oxime was similarly rearranged in 86% yield.

In general, the coordination complex need not first be prepared. Thus, four typical ketoximes were rearranged in this investigation by either saturating an acetic acid solution of the oxime with gaseous boron fluoride (Procedure A) or by heating a mixture of the oxime and boron fluoride–acetic acid complex at 115–120° for ten minutes (Procedure B). In the former procedure the heat of the reaction usually increases the temperature of the solution to 115–120°. The boron fluoride–acetic acid complex employed in Procedure B was either obtained commercially[2] or was prepared by saturating the acetic acid with gaseous boron fluoride. At least the commercial complex[2] consists of two molecules of acetic acid to one of boron fluoride. Procedure B has also been shown to be effective

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[2] Available from the General Chemical Division, Allied Chemical and Dye Corporation.

TABLE I

BECKMANN REARRANGEMENT OF KETOXIMES WITH BORON FLUORIDE IN ACETIC ACID TO FORM AMIDES

Oxime of	Amide	Procedure A		Procedure B		Lit M.P., °C.
		Yield, %	M.P., °C.	Yield, %	M.P., °C.	
Benzophenone...	Benzanilide	98	161–162	99 (95)[a]	162–163	162–163
Acetophenone...	Acetanilide	96	112–113	87[b]	113–114	113–114
Cyclohexanone..	ε-Caprolactam			98	64–66	65–68
Phenylacetone...	N-Benzylacetamide	35	49–51	40	53–55	60–61

[a] Yield obtained with catalytic amount of reagent (see experimental). [b] A second crop (6%; m.p. 107–109°) was obtained from the mother liquor.

for the rearrangement of benzophenone oxime with only 20 mole-per cent of boron fluoride. The results are summarized in Table I.

It can be seen from Table I that the yields of the amides from the oximes of benzophenone, acetophenone, and cyclohexanone were almost quantitative. Even the yield of benzanilide with only a catalytic amount of boron fluoride was 95%. Apparently these yields have previously been equaled only with polyphosphoric acid (20) which likewise appears to require a relatively high temperature (115–125°). The yield with the more common reagents, phosphorus pentachloride and sulfuric acid, have been somewhat lower; for example, that with cyclohexanone oxime with sulfuric acid has been 59–65% (21).

It can further be seen from Table I that the yield of Beckmann rearrangement product from the oxime of phenylacetone was 35–40% which is somewhat better than that (29%) obtained with polyphosphoric acid (22). This ketoxime is known to exhibit the Neber reaction under certain Beckmann rearrangement conditions (23).

Sometimes better results are achieved by employing a higher-boiling solvent than acetic acid. Thus, the rearrangement of the boron fluoride complex of mesityl phenyl ketoxime was realized recently (19) in 94% yield in butyric acid at 154°, whereas a lower yield of pure product was obtained in acetic acid at 115–120°. However, unsatisfactory results were obtained with fluorenone oxime and boron fluoride in acetic acid at 115–120° or in 2-ethylhexoic acid at 180°. Recently (22) this oxime was rearranged in excellent yield with polyphosphoric acid at 175–180°.

EXPERIMENTAL[3]

Boron fluoride complex of benzophenone oxime (IX). A. *Formation and stability.* A stirred solution of 9.85 g. (0.05 mole) of benzophenone oxime in 100 ml. of purified ligroin was saturated at room temperature with gaseous boron fluoride. This reagent was introduced through a tube leading to within about 1 cm. of the surface of the liquid until copious white fumes were evolved as described for the acylation of ketones (24). The precipitated coordination complex IX was collected on a funnel and sucked dry to give a white powder; yield, 13.2 g. (98%), m.p. 149–150° dec.

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[3] Melting points are uncorrected.

The complex was similarly obtained in 76% yield on saturating a thiophene-free benzene solution of benzophenone oxime with boron fluoride. More (3%) of the complex was recovered from the benzene filtrate.

The melting or decomposition point of the complex was not changed by dissolving it in refluxing benzene (in which it was only sparingly soluble) and cooling the solution to room temperature, or by dissolving it in ethylene chloride at room temperature and cooling the solution to −70°. The complex was stable on standing in air for several days but, like benzophenone oxime itself (25), the complex decomposed within two weeks.

The complex was largely recovered unchanged after heating 2 g. of it as a suspension in toluene on an oil-bath at 90° for 30 minutes. Some of the complex had dissolved in the toluene and was recovered on evaporation of the solvent. Total recovery was 1.9 g. (95%), m.p. 149–150° dec. Treatment of the recovered complex with sodium bicarbonate solution yielded benzophenone oxime, m.p. 142–143°.

B. *Beckmann rearrangement.* A sample (2 g.) of complex IX was placed in a small flask which was immersed in an oil-bath at 150°. A vigorous exothermic reaction occurred immediately, the temperature rising to 210°. After cooling, the dark residue was triturated with ether. The red ethereal solution was decanted from the tarry residue and refluxed with Norit. Removal of the solvent left a solid which was recrystallized from 95% ethanol to give (two crops) 1.24 g. (83%) of benzanilide m.p. 162–163°. This melting point was not depressed on admixture with an authentic sample of benzanilide.

Similar results were obtained when a flask containing complex IX was immersed in a bath at 140° and kept at this temperature for 20 minutes, and when boron fluoride was passed over melted benzophenone oxime at 150°.

When a suspension of 1.1 g. of complex IX in 50 ml. of freshly distilled Dowtherm was heated slowly to 90–100° the solid dissolved, and when the solution was heated to 150°, a dark oil separated. The Dowtherm was decanted, and the semi-solid residue taken up in ether. After refluxing with Norit, the solvent was removed to give, after recrystallization from 95% ethanol, 0.5 g. (61%) of benzanilide, m.p. 161–162°.

When a solution of 8.6 g. of complex IX in 50 ml. of glacial acetic acid was refluxed for 10 minutes and the resulting deep red solution was refluxed with Norit and filtered, there was obtained on adding water to the clear filtrate and recrystallizing the precipitate, 6.3 g. (96%) of benzanilide, m.p. 162–163°. This yield is equal to that obtained as described below in which benzophenone oxime is rearranged without first preparing complex IX.

Benzophenone oxime O-methyl ether. This compound was prepared by a modification of the method of Vermillion and Hauser (26) for anisaldoxime O-methyl ether. To a stirred suspension of 30 g. (0.15 mole) of benzophenone oxime in 89 g. (0.64 mole) of methyl iodide was added in 10-g. portions at 30-minute intervals 90 g. (0.4 mole) of silver oxide. The mixture then was refluxed for 3 hours, and then was filtered. The residue then was refluxed with three 100-ml. portions of chloroform (20 minutes each time) and filtered. The combined filtrates were dried over Drierite and the solvents were removed under reduced pressure. The residue slowly solidified. After recrystallization from the minimum of acetone, an equal volume of methanol, and enough water to produce a cloudiness, there was obtained 22.6 g. (71%) of benzophenone oxime O-methyl ether melting at 60–61°; reported m.p. 60° (27) and 60–61° (28).

Boron fluoride complex of benzophenone oxime O-methyl ether (XI). A. *Formation and stability.* This complex was obtained essentially as described for complex IX, employing 2 g. of benzophenone oxime O-methyl ether in 100 ml. of ligroin. The yield of white solid was 1.3 g. (50%), m.p. 45–65°.

When benzene was used instead of ligroin, the complex was obtained as a benzene-insoluble liquid (lower layer).

On warming with 10% sodium bicarbonate solution, the complex (XI) was reconverted in 94% yield to benzophenone oxime O-methyl ether, m.p. 60–61°.

When 0.5 g. of the solid complex (XI) was suspended in toluene and the mixture was heated to 90°, the solid melted to a partially insoluble oil (lower layer). After being kept at this temperature for 20 minutes, the oil was separated, and warmed with sodium bicarbonate solution to give 0.3 g. (79%) of benzophenone oxime O-methyl ether, m.p. 59–60° (identity confirmed by mixture melting point method).

B. *Beckmann rearrangement.* A sample (3 g.) of benzophenone oxime O-methyl ether was converted to its boron fluoride coordination complex (XI), and the complex (a liquid) was heated slowly to 125°, at which temperature a vigorous reaction took place. There was isolated, on treatment of the reaction mixture with water, 1.5 g. (over-all yield, 53%) of benzanilide, m.p. 162–163°.

Boron fluoride complex of benzophenone oxime acetate (XIII). A. *Formation and stability.* A solution of 3 g. of the benzophenone oxime acetate, m.p. 72–73° (29), in 100 ml. of toluene was cooled to 0° and then was saturated with boron fluoride. The toluene was decanted from the liquid complex (XIII) that had separated, and the complex was stirred with methanol at 0°. Addition of water precipitated 1.8 g. of benzophenone oxime (m.p. 141–142°). More (0.4 g.) benzophenone oxime, m.p. 140–142°, was obtained by concentration of the filtrate. Total yield; 95%. Admixture with an authentic sample of benzophenone oxime gave no depression in the melting point of either crop.

The complex (XIII) was similarly prepared at −70° and decomposed at 0° to give benzophenone oxime in 91% yield.

B. *Beckmann rearrangement.* When a solution of 3 g. of benzophenone oxime acetate in 100 ml. of toluene was saturated with boron fluoride without external cooling, the temperature rose from 25° to 31°, and benzanilide, m.p. 161–162°, was obtained on decanting the toluene, and treating the residual oil with methanol followed by water. The yield (two crops) was 90%.

Boron fluoride-acetic acid method for Beckmann rearrangements (*Table I*). *Procedure A.* A solution of 2–3 g. of the oxime in 20 ml. of glacial acetic acid contained in a 125-ml. Erlenmeyer flask was saturated with boron fluoride (passed over surface of the solution until copious white fumes were evolved). The temperature rose spontaneously to 115–120°, color sometimes being produced. After cooling to room temperature, the reaction mixture was made basic with 100 ml. of 6 *N* sodium hydroxide (added cautiously), and the solid was taken up with several portions of a mixture of equal amounts of ether and ethyl acetate. The solvents were removed (after refluxing with Norit if colored), and the residue was recrystallized from an appropriate solvent.

Procedure B. A mixture of 2–3 g. of the oxime and 20 g. of commercial boron fluoride-diacetic acid complex[2] in a 125-ml. flask was heated on an oil-bath at 115–120° for 10 minutes, cooled, and worked up as described in Procedure A.

On working up the reaction mixture from phenylacetone oxime (3 g.) removal of the ether and ethyl acetate left an oil which partially solidified on standing. Distillation *in vacuo* gave 0.6 g. of yellow oil, b.p. 90–95° at 14 mm., and 1.7 g. of a fraction b.p. 169–171° at 14 mm., which solidified (m.p. 46–49°). Recrystallization of the latter fraction from ether and petroleum ether gave 1.2 g. (40%) of benzylacetamide (white needles) m.p. 53–55°.

The rearrangement of benzophenone oxime was also carried out with a catalytic amount of the reagent in the following manner. A solution of 10 g. (0.05 mole) of the oxime in 30 ml. of glacial acetic acid and 3.0 g. (0.02 mole; 20 mole-per cent) of boron fluoride-acetic acid complex was refluxed for 1 hour giving a red solution. After cooling, the solution was made basic with alkali and the amide isolated as described in Procedure A.

SUMMARY

1. Boron fluoride was found to convert benzophenone oxime and its O-methyl ether to relatively stable N-coordination complexes which underwent the Beckmann rearrangement only at 125–150° or at 115–120° in acetic acid solution. The acetate of benzophenone oxime similarly first formed the N-coordination complex but it rearranged at 30–35°.

2. Although higher temperatures are required, the yields of Beckmann rearrangement products from certain ketoximes with boron fluoride in acetic acid were higher than those reported with the usual reagents, sulfuric acid and phosphorus pentachloride. In general, the yields were comparable to those obtained recently with polyphosphoric acid.

3. Whereas the reagents that effect the Beckmann rearrangement of ketoximes at relatively low temperatures probably involve the intermediate formation of more reactive ester-like compounds, boron fluoride (and hydrogen chloride) presumably effect the rearrangement through the intermediate formation of the O-coordination (oxonium) complex. An intramolecular mechanism for the conversion of the N-coordination complex to the O-coordination complex is suggested.

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