ethyl ketone gave a yellow product, m.p. 264–266°; analysis (calcd. for $C_{15}H_{14}O_6$: C, 62.06; H, 4.86. Found: C, 62.10; H, 5.00) indicated that this material of unknown structure had the same composition as the usual product.

Ozonolysis of VI.—A solution of 0.30 g. of VI in 150 ml. of chloroform was treated with a stream of ozone for 30 minutes. The solution was stirred vigorously with 75 ml. of 5% sodium hydroxide solution containing 24 ml. of perhydrol (30%) for 15 minutes, and after separation of the chloroform the organic solution was washed with 5% sodium hydroxide solution, with dilute acetic acid, with 5% sodium bicarbonate solution, and with water. After drying and evaporation of the chloroform there was obtained 0.1 g. of veratraldehyde, identified through the 2,4-dinitrophenylhydrazone (m.p. 260–262°, undepressed on mixture with an authentic sample).

Reduction of VI.—When VI was subjected to catalytic reduction in acetic acid at 70° with a 5% palladium–carbon catalyst, sufficient hydrogen to reduce the olefinic linkage was absorbed. It was not possible to isolate crystalline material after the reduction; cyclization studies on the reduced material were inconclusive, and, while a reaction apparently occurred with 2,4-dinitrophenylhydrazine, the product could not be purified.

Hydrolysis and Cyclization of VI.—A suspension of 2.0 g. of VI in 30 ml. of 5% sodium hydroxide solution was heated (95–100°) for 20 minutes; the resulting clear solution was diluted and acidified strongly with concd. hydrochloric acid. After standing at room temperature for one hour, a small amount of gum was removed, and after further dilution to a total volume of 100 ml. the solution was allowed to stand for five days. The crystalline product was separated and recrystallized from aqueous ethanol to yield nearly colorless plates, m.p. 248–247° (with shrinking and discoloration), of material whose analysis and ultraviolet spectrum (Fig. 3) indicated that cyclization had occurred; the product was evidently **1-methyl-6,7-dimethoxy-3-naphthoic acid.**

Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73; neut. equiv., 246.3. Found: C, 68.71; H, 5.87; neut. equiv., 246.

Acylation Experiments.—In attempts to define the scope of the acylation reaction leading to VI, reactions were carried out with the corresponding diester (obtained by complete esterification of I) rather than the diacid or anhydride, with benzylsuccinic anhydride, and with benzoic anhydride in place of acetic anhydride in the usual acylation. No products corresponding to VI could be found.

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Beckmann Rearrangements. Aldoximes

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The Beckmann rearrangement has been extended to aldoximes through use of polyphosphoric acid as a reagent for the rearrangement. For the first time this permits a direct study of the configuration of an aldoxime through examination of the products of rearrangement. The present assignment of *syn* and *anti* structures to the two known benzaldoximes has been confirmed.

A few limited observations may be found in the older literature[1-3] on reactions involving the conversion of an aldoxime to an amide *via* a Beckmann rearrangement. In general, however, the usual conditions of Beckmann rearrangements result in partial or complete dehydration of aldoximes to give the corresponding nitriles, and as a result special or indirect methods have been employed where rearrangement is desired. N-Alkyl ethers[4,5] and acetyl derivatives[6] have been used in such studies.

We have recently found that polyphosphoric acid is an excellent agent for effecting Beckmann rearrangements of ketoximes,[7] and the study has now been extended to aldoximes. As an example of an aliphatic aldoxime, we investigated the rearrangement of *n*-heptaldoxime. Under the conditions described in the experimental section, a 92% yield of *n*-heptamide was obtained. This result is comparable to the yields obtained with ketoximes,[7] and it indicates that the Beckmann rearrangement is indeed a general reaction of both ketoximes and aldoximes.

Since the Beckmann rearrangement is stereospecific, the structure of the starting oxime may be determined from the structure of the product, provided that the configuration of the oxime is not affected during the reaction, or that both oximes can be isolated and are found to give different products. In the case of ketoximes, it is sometimes possible to isolate two stereochemically different oximes whose structure can be determined in this way. Some oximes, such as acetophenone oxime, are known to exist in only one form, and in these cases only one rearrangement product has been observed. Other ketoximes, including methyl *n*-propyl ketoxime, are apparently homogeneous, but give two amides on rearrangement, indicating that both forms of the oxime are present during rearrangement.

The assignment of configuration to aldoximes has of necessity been based upon indirect evidence. Hantzsch[8] first recognized the possibility of isomerism of aldoximes, and it has since become standard practice to treat the acetyl[6] or benzoyl[9] derivatives of aldoximes with alkali in order to determine the structure. The acylated *anti*-oxime yields a nitrile, while the *syn* compound does not react or regenerates the original oxime. The rearrangement of an aldoxime with polyphosphoric acid provides a means of studying aldoxime structures in a direct way, and we have therefore examined the best-known case of aldoxime isomerism, that of benzaldoxime,[10] with this method. When the *syn*-oxime (liquid) was treated with poly-

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(9) G. Vermilion and C. R. Hauser, THIS JOURNAL, **62**, 2939 (1940) C. R. Hauser and G. Vermilion, *ibid.*, **63**, 1224 (1941).
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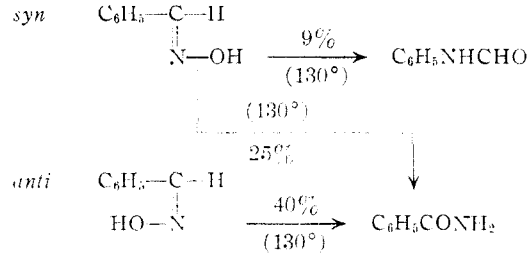
phosphoric acid at 90°, an 8% yield of formanilide and a 10% yield of benzamide resulted; 13% of the oxime was recovered unchanged. At 130° the



yields of formanilide and benzamide were 9 and 25%, respectively, and at this temperature no oxime was recovered. It is apparent that both forms of the oxime are present during rearrangement in this case.

When *anti*-benzaldoxime (solid, m.p. 126°) was subjected to rearrangement with polyphosphoric acid at 90°, a 5% yield of benzonitrile resulted, with a 30% recovery of oxime. At 130°, a 40% yield of benzamide was obtained. No formanilide was found. Although these yields are not high, it may be concluded that the *syn* and *anti* configurations are indeed correctly assigned, but that direct rearrangement of the *syn* compound is accompanied by partial isomerization to the *anti* form, with subsequent formation of both possible amides.

The hydrochloride of the *anti*-oxime may be obtained by treatment of the *syn*-oxime with hydrogen chloride. The *anti*-oxime, a solid, is obtained from this salt, and is reported to be unstable with respect to the *syn*-oxime, a liquid. The conversion has been described as occurring on heating or on contact with acids. Our experiments indicate that the *anti*-oxime is not isomerized by heating in polyphosphoric acid, but that these conditions do result in partial isomerization of the *syn* form. This is the reverse of what might be expected from the nature of the reaction conditions, if the assumption that the *syn* form is the most stable form is accepted.

Although Beckmann rearrangements have been demonstrated to occur through the influence of heat alone on certain acyl derivatives of oximes,[11] it is likely that acid catalysis is a part of the usual Beckmann procedure. Polyphosphoric acid is not a strong acid, but by using the oxime hydrochloride rather than the free oxime, it is possible to provide more effective conditions of acid catalysis. Since the stable hydrochloride of benzaldoxime is that derived from the *anti* form, this salt should yield benzamide on rearrangement. When the *anti*-oxime hydrochloride was treated with polyphosphoric acid at 130° for five minutes, an 80% yield of benzamide was obtained. The configuration of the oxime in the *anti* form was evidently retained in the salt. This modification of the usual rearrangement may be useful where stable salts can be prepared.

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(11) M. Kuhara, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **1**, 105 (1914).

Experimental

Rearrangement of *n*-Heptaldoxime.—A 2.00-g. sample of *n*-heptaldoxime was heated in polyphosphoric acid at 130°, according to the previously published Procedure A.[7] The yield was 1.83 g. (92%) of crude *n*-heptamide, m.p. 78–81°. Recrystallization from pentane–benzene gave colorless rods, m.p. 91–92°. The identity of the crude product and the purified material was established by comparison of the infrared absorption spectra with that of an authentic sample. A mixed melting point determination with an authentic sample showed no depression.

Rearrangement of *syn*-Benzaldoxime.—The rearrangement of 20.0 g. of *syn*-benzaldoxime (liquid form) was carried out in polyphosphoric acid at 90° according to Procedure B.[7] The result was 7.4 g. of light yellow oil which was separated into its components by chromatography on alumina. The chief fractions, with the solvents employed, were as follows: (a) 1.55 g. (8%) of formanilide, m.p. 40–43°, with 3:1 pentane–benzene; (b) 2.66 g. (13%) of recovered oxime (identified by infrared spectra), with 1:1 benzene–ethyl acetate; and (c) 1.94 g. (10%) of benzamide, m.p. 126–128°, with 9:1 ethyl acetate–ethanol. The products were identified by mixed melting points and by comparison of the infrared spectra with those of authentic samples.

A similar rearrangement was carried out, on a smaller scale (14.3 g. of oxime), at 130°, according to Procedure B.[7] Two products were isolated by chromatography on alumina of the crude product (5.2 g.): 1.25 g. (9%) of formanilide and 3.51 g. (25%) of benzamide, identified as before.

Rearrangement of *anti*-Benzaldoxime.—The rearrangement was carried out as described for the *syn*-oxime, and the products were separated in pure form by chromatography on alumina. With a temperature of 90°, the yield of benzamide was 5%, with 30% of recovered oxime. At 130°, no oxime was recovered, and a 41% yield of benzamide was obtained. Identifications were made as before.

Rearrangement of *anti*-Benzaldoxime Hydrochloride.—A mixture of 2.0 g. of *anti*-benzaldoxime hydrochloride and 50 g. of polyphosphoric acid was heated to 130° and maintained at 130–135° for five minutes. Hydrogen chloride was evolved. The mixture was treated with cold water, and the clear aqueous solution was neutralized with potassium hydroxide at a temperature below 10°. The aqueous solution was extracted with ether, and the ether solution was dried and evaporated with the aid of an air jet. A yield of 1.2 g. (80%) of colorless benzamide, m.p. 118–122°, was obtained. The crude and a purified sample were identified by infrared spectra.

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