ON THE CATALYTIC ACTION OF JAPANESE ACID EARTH. II. THE ACTION ON OXIMES.

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Mailhe and Godon[1] have noticed that aldoximes and ketoximes were transformed into nitriles by the catalytic action of alumina at high temperature. The action of Japanese acid earth on oximes, therefore, was studied by the present writer from the view point of contact action, and the following interesting results were obtained.

1. Acetophenone oxime. 20 grams of acetophenone oxime (m.p. 58–59°) mixed with 10 grams of Japanese acid earth in a flask, were heated gradually on an oil-bath. When the temperature of the bath reached 180°, a violent reaction suddenly took place as we sometimes meet in case of Beckmann's rearrangement of oximes, and whereas some volatile liquid distilled out through the side tube of the flask, a solid reaction product remained in it. Both the liquid and solid reaction products were treated separately with ether and then hot water; the ethereal solution was treated with ammonia and dilute hydrochloric scid successively to get off the acidic and basic substances from a neutral substance which is formed simultaneously by the reaction. Acetic and benzoic acids from the acidic fraction, and ammonia and aniline from the basic one were isolated and confirmed to be so by their chemical properties. Benzonitrile was isolated from the neutral reaction product, which was confirmed, by saponification with alcoholic potash, by transforming into benzoic acid (m.p. 121°) and ammonia. Acetophenone was also noticed to occur with the nitrile in the neutral reaction product in isolating in a pure state. From the hot aqueous solution, acetanilide (m.p. 115°, N=10.32%) was obtained in a pure state. The yield of the reaction products is shown in Table 1.

2. Benzophenone oxime. When benzophenone oxime (m.p. 139°) was treated in the same manner as the acetophenone oxime, the rearrangement

(1) Mailhe and Godon, *Bull. Soc. Chim.*, (4), **23** (1918), 18.

was noticed to take place at 145° and benzanilide (m.p. 160°), benzonitrile, benzoic acid and other substances of unknown chemical nature were actually obtained from the reaction product, and the quantity of these substances is shown in Table 1.

3. **Menthone oxime.** Menthone oxime (m.p. 53–55°), when treated with the catalyst at 200°, was transformed into decylenic acid, methonitrile, menthone and a hydrocarbon, and the yield of these substances is shown in Table 1.

TABLE 1.

Oximes	Sample used gr.	Acid gr.	Base gr.	Acid amide gr.	Nitrile gr.	Neutral subst. gr.	NH_3
Acetophenone oxime	20.0	0.69	0.81	1.33	0.55	4.20	+
Benzophenone oxime	12.5	0.12	0.63	2.04	0.04	4.81	+
Menthone oxime	12.9	0.46	0.60	—	0.55	5.81	+

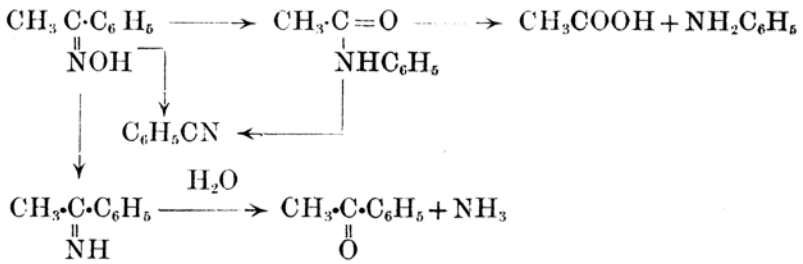
As a matter of fact, acids, nitriles, acid amides and bases were formed from oximes by contact action of Japanese acid earth, and the nitriles were naturally regarded as forming directly from the oximes as in the case of the catalytic action of alumina and also indirectly from acid amides or isoximes which resulted from the oximes by the Beckmann rearrangement. In the present case, the writer was inclined to believe that the Beckmann rearrangement was one of the principal reactions of oximes caused by the contact action of Japanese acid earth at about 150–200°, since acetanilide and benzanilide were actually isolated with a large yield from the reaction products of acetophenone and benzophenone oximes respectively, and aniline which occurs in the reaction product in both cases, was explained to be formed by hydrolysis of the anilides. In order to confirm the above assumption for the transformation of anilides into aniline, acid and nitrile, by the contact action of the earth, 10 grams of acetanilide and of benzanilide were passed respectively on the catalyst heated at 300°, aniline, acids and nitrile were confirmed to occur in the reaction products as will be seen in the following table.

TABLE 2.

Acid amides	Acid amide unchanged gr.	Nitrile	Base (aniline) gr.	Acid gr.	NH_3
Acetanilide	0.55	a little	1.87	0.014	+
Benzanilide	0.55	a little	0.37	0.012	+

When, however, 20 grams of benzonitrile (b. p. 183—184°; density = 1,0068) were passed on the same catalyst heated at 250°, no appreciable reaction was noticed to take place.

Thus, the transformation of ketoximes by the contact action of Japanese acid earth, into their isomeric acid amides, nitriles, acids, amines and ketones was represented with an example of acetophenone oxime, by the following scheme:



The formation of acetophenone from its oxime was explained by the direct hydrolysis of the oxime on the one side, and on the other by assuming the formation of methyl phenyl-ketimine as an intermediate, as indicated by Lachman.[1]

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(1) Lachman, *J. Am. Chem. Soc.*, **46** (1924), 1477.