

Catalytic Action of Reduced Copper on Acetophenone Oxime. (On Beckmann's Rearrangement, XII)

By

Shozo Yamaguchi.

(Received Dec. 12, 1923).

120 gm. of acetophenone oxime were passed with pure hydrogen over reduced copper heated at 200°, and 70 gm. oily substance with 1.5 gm. of some pasty stuff were obtained. In the progress of the reaction, the generation of ammonia gas was perceived, which indicates that hydrolysis of the oxime had occurred.

A. ACIDIC SUBSTANCE.

1. Benzoic Acid.

In order to isolate the acidic substance from the oily reaction product, it was treated with ammonia, and then wash with water until the washings indicated neutral reaction to the test paper. The washings combined with alkaline solution, were acidified with dilute sulphuric acid, whereby the acidic substance separated which was then extracted with ether, dried with anhydrous sodium sulphate, and then the solvent distilled off.

The crystalline substance, thus obtained, amounting to 3.8 gm., was purified by recrystallisation from a hot aqueous solution. It consisted of white scaly crystals soluble in organic solvents and hot water, but scarcely in cold water, and melted at 121–122°, and yielded a silver salt from the ammonium salt solution and silver nitrate. The physical and chemical properties so far as the author studied agree with those of benzoic acid.

The insoluble part in an alkaline solution was dissolved in ether, and then treated with conc. hydrochloric acid to separate the neutral substance from the basic substance. A white crystalline material appeared between the etherial and acidic solutions, which when separated from solutions by filtration, was confirmed to be the hydrochloride of *α-α*-di-phenyl ethyl amine.

B. BASIC SUBSTANCES.

2. *α*-Phenyl Ethyl Amine.¹

The acidic solution after being washed again with ether to remove neutral substances completely, was alkalinized with caustic soda solution, the bases extracted with ether, and passed in vigorously wet carbon-dioxide gas, and then the aqueous solution was separated from the etherial solution. The operation for extracting basic substance with carbonic acid solution was repeated several times.

The carbonic acid-extracts were alkalinized with caustic soda, and the free basic substance extracted with ether. On evaporating off the solvent, after it was dried with anhydrous sodium sulphate, there remained an oily substance which amounted to 4 gm. and boiled at 183–186°, 760 mm.

It gave on analysis the following results :

0.1152 grm. substance gave 0.3360 grm. CO₂ and 0.0391 grm. H₂O

0.1037 grm. substance gave 10.9 cc. of N₂ at 20°, 753.5 mm.

	C	H	N
Found	79.55	9.04	11.94
Calc. for C ₉ H ₉ NH ₂	79.95	8.39	11.66

On standing in the air, it yielded a white amorphous carbonate which was easily soluble in alcohol and water, but scarcely in ether, and melted at 95–98° Its hydrochloride melted at 148–150°.

3. *α-α*- Di-phenyl Ethyl Amine².

¹ Ber. D. Chem. Ges., 19, 1929. (1886); 23, 2783 (1890).

² J. pract. Chem. (2) 77, 5. (1908).

The ethereal solution separated from the carbonate of α -phenyl ethyl amine, dried with anhydrous sodium sulphate, passed in dry hydrochloric acid gas, and white crystals separated, filtered and recrystallised from hot alcohol. The yield was 1.2 gm. It was soluble in hot alcohol and water. It did not melt below 250°.

On analysis, it gave the following results :

0.1626 gm. substance gave 8.6 cc. N₂ at 21°, 755.2 mm.

0.1848 gm. substance gave 0.1010 gm. of AgCl

0.1254 gm. substance gave 0.3356 gm. CO₂ and 0.0303 gm. H₂O.

	C	H	N	Cl
Found	72.99	8.06	6.00	13.52
Calc. for (C ₈ H ₉) ₂ NHCl	73.39	7.70	5.35	13.55

C. NEUTRAL SUBSTANCES.

The ethereal solution supposed to contain neutral substances only, was evaporated to a syrup which was subjected to steam distillation and then extracted with ether. On evaporating the ether, there remained neutral substances amounting to 38 gm.

It was confirmed to consist largely of acetophenone and benzonitrile by subjecting it to the following treatments :

1. Reduction.

10 gm. of the sample were reduced with 18 gm. of metallic sodium in 100 c.c. boiling amylalcohol, and the solution acidified with hydrochloric acid and then subjected to steam distillation. From the distillate 6 gm. of oily substance were obtained, which was confirmed to be a mixture of methyl phenyl carbinol and the pinakone, which resulted from acetophenone by reduction. The nonvolatile substance remaining in the distilling flask was again distilled with steam, after being alkalined with caustic soda, and a basic oily substance was isolated from distillate, which boiled at 182–185°. The yield was 0.5 gm. It seems, in its properties, to be a mixture of benzylamine and α -phenyl ethyl amine.

All of these compounds except the benzoic acid and a neutral substance which by hydrolysis yields benzoic acid, were already reported by A. Mailhe¹ to be obtained by the catalytic reduction of acetophenone oxime in presence of reduced copper or nickel, but in his research he never seems to have touched upon the formation of benzoic acid or benzonitrile. A. Angeli and L. Alessndri² have reported that acetophenone oxime is apt when stored to decomposed spontaneously into acetophenone, nitrogen, and ammonia, and this decomposition is facilitated in presence of copper oxide.

A. Kötze and Wunstorff³, however, studying the thermal decomposition of acetophenone oxime, have concluded, that the oxime suffers the nitrile decomposition under the influence of heat but not the Beckmann change, yielding benzonitrile and benzoic acid. Recently, E. Beckmann and E. Bark⁴ have reported that benzophenone oxime does not undergo the rearrangement by heating at about 200° in presence of metallic oxides such as calcium oxide, ferric oxide, mercuric oxide and alumina.

As a matter of fact, the acetophenone oxime by the action of the reduced copper and hydrogen at 200°, yielded the amines, benzoic acid and benzonitrile.

The author, therefore, ventures to express the opinion that the catalytic action of the reduced copper facilitates, on the one hand, the hydrogenation, and on the other, the formation of benzoic acid and benzonitrile, no matter what hypothesis for the explanation of the benzoic acid or nitrile-formation from the oxime may be proposed.

Sept. 1923. Laboratory of Organic-and Bio-Chemistry.

¹ C. R. **140**, 1691; **141**, 113 (1905).

² J. Chem. Soc., **104**, 913 (1913).

³ J. prak. Chem., (2). **88**, 519 (1913).

⁴ Ibid., (2). **105**, 108 (1923).