CATALYTIC ACTION OF REDUCED COPPER ON OXIMES (ON BECKMANN'S REARRANGEMENT, XV.)

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In the previous article⁽¹⁾ on this subject, the writer has stated that benzaldoximes when passed on reduced copper heated at 200° in an atmosphere of hydrogen were transformed into benzamide, benzonitrile and benzoic acid. The same experiment was extended to some aldoxime and ketoximes to draw some general conclusion from the experimental results, which might have an intimate connection with the explanation for the mechanism of Beckmann's rearrangement.

I. Furfuraldoxime.

20 gr. of the oxime, m.p. 89°, prepared according to the directions suggested by H. Goldschidt and E. Zanoli⁽²⁾, were passed with hydrogen on reduced copper heated to 200°, and 2.8 gr. of solid and 4.5 gr. of liquid reaction products were obtained.

(A) Pyromusic Acid Amide.

The solid reaction product described above, was washed well with absolute ether, and then the amide, insoluble in ether, was recrystallised from hot alcohol in white beautiful crystals which melted at 141°–142°. The yield was 1.2 gr. It shows a blue colour, when treated with bromine water and caustic soda solution, as was mentioned by Saunders,⁽³⁾ which on standing, changed to violet and then to red.

On analysis, it gave the following results :

0.1121 gr. subst. gave 0.2225 gr. CO_2 and 0.0528 gr. H_2O
0.1276 gr. subst. gave 14.6 c.c. N_2 at 23.5° and 750.2 mm.

Found :	C=54.13	H=5.27	N=12.81
Calc. for $C_5H_5O_2N$:	C=54.04	H=5.54	N=12.60

The compound seems, so far as studied, to be identical with pyromusic acid amide. For the confirmation, it was converted into the bromoderivative following the direction given by Saunders, and this substance melted at about 125° with decomposition, and gave the following analytical results :

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Uni., A,* 9 (1925) 33.

(2) *Ber. D. Chem. Ges.,* 25 (1892) 2573.

(3) *Am. Chem. J.,* 15 (1893) 135.

0.2416 gr. subst. gave 0.4183 gr. AgBr.
Found : Br=73.68
Calc. for $C_5H_5O_2NBr_4$: Br=74.21

(B) The Acidic and the Basic Substances.

The liquid reaction product (4.5 gr.) was combined together with the ether washing of the solid reaction product, and dry ammonia gas was passed into the mixed solution to isolate the acidic substance, when a small quantity of the ammonium salt of an acid was separated, but further study of its chemical nature was not possible owing to the modicum of the sample. The ethereal solution separated by filtration from the ammonium salt, was evaporated to dryness to get rid off the solvent, and the residue was treated with a mixture of ether and hydrochloric acid solution to separate the neutral substance from the basic one. To the acid solution a platinum chloride solution was added and a platinum double salt was obtained.

(C) The Neutral Substance.

From the neutral ethereal solution separated from the acidic solution, furfural was isolated in the usual way, and confirmed to be so from its boiling point and the colour reaction.

II. Benzamidoxime⁽¹⁾.

4.5 gr. of the oxime, m.p. 76°–77°, were passed on reduced copper heated to 200° in an atmosphere of hydrogen, and 1.9 gr. of solid and 1.3 gr. of liquid reaction products were obtained.

(A) Benzamide.

It was isolated, in white crystals, m.p. 126°, from the solid reaction product, by treating it with absolute ether and then dilute alcohol. The yield was 1.2 gr. It was analysed and the following results were obtained :

0.1188 gr. subst. gave 0.2991 gr. CO_2 and 0.0638 gr. H_2O.
0.1312 gr. subst. gave 0.15016 gr. N_2 (by Kjeldahl's Method).

Found :	C=68.62	H=6.009	N=11.43
Cal. for C_7H_7ON :	C=69.39	H=5.82	N=11.57

(B) The Acidic and the Basic Substances.

The liquid reaction product and the ethereal washing of the solid reaction product were combined together, and an acidic, basic and a neutral substances were isolated from the mixed solution by treating with dry ammonia gas, and then with hydrochloric acid successively. The acidic substance which separated in the form of an ammonium salt, amounting to 0.4 gr., was identified to be benzoic acid from its melting point (121°) and from other chemical properties, after the salt was converted into a free acid and purified.

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(1) Tiemann, *Ber. D. Chem. Ges.*, 17 (1884) 128.

The basic substance was found to consist of a modicum of the reaction product.

(C) The Neutral Substance.

The neutral reaction product obtained in a liquid state, amounted to 0.6 gr., and was confirmed to be composed mostly of benzonitrile by subjecting it to reduction with metallic sodium and alcohol, and a trace of a basic substance was detected in the product.

III. Cinnamylaldoxime.

The oxime used in this experiment was prepared, according to the direction given by O. Brady and C. Thomas⁽¹⁾, from 20 gr. of cinnamylaldehyde, b.p. 125°–138°, 12 mm., and 15 gr. of hydroxylamine hydrochloride, and purified by crystallisation from benzene. It melted at 126°, and its yield was 16 gr.

16 gr. of the oxime were passed with pure hydrogen on finely divided copper heated at 200°, and obtained a tar-like substance and 6.8 gr. of a liquid reaction product. In order to isolate the acidic substance from the reaction product, dry ammonia gas was passed into its ethereal solution, but no precipitate appeared. It was then treated with hydrochloric acid to separate the basic substance from the neutral one.

The neutral substance was isolated in an oily form from the hydrochloric acid solution by extracting it with ether as usual. The yield was 1.1 gr. On standing it for a few days some crystals were separated from the oily matter, and it was confirmed that this was composed of cinnamic acid from its melting point of 132°–133°, and from its reaction. The oily residue separated from cinnamic acid was supposed, from the analogy of other cases, to be a mixture of cinnamyl aldehyde and the nitrile, but their presence could not be confirmed owing to the small amount of these substances (0.1 gr.)

Lastly, a resinous matter which remained with the copper in a reaction tube, was regarded as being formed by polymerisation of the reaction products mentioned above, though the chemical test for its confirmation was lacking.

IV. Di-benzyl Ketoxime.

8 gr. of di-benzyl ketoxime⁽²⁾ which melted at 119°-120° were passed with hydrogen over reduced copper at 200°, and 1.9 gr. of pasty substance and 1.1 gr. of liquid were obtained. The former was treated with absolute ether and then recrystallised from hot water, and colourless crystals which

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(1) *J. Chem. Soc.*, **121** (1922) 2103.

(2) *Ber. D. Chem. Ges.*, **21** (1888) 1316.

melted at 155° were obtained. The yield was 0.2 gr.

0.0919 gr. subst. gave 0.00958 gr. N_2 (by Kjeldahl's method).

Found: N=10.42, Calc. for C_8H_9NO: N=10.37.

The chemical properties and the analytical results agree well with those of phenylacetamide. The oily reaction product and the ether washing of the solid one were combined together, and acidic and neutral substances were isolated as usual.

The acidic substance was separated from the reaction product mentioned above, by means of ammonia in the form of an ammonium salt, then decomposed into free acid by means of hydrochloric acid, and was identified as phenylacetic acid from its melting point 76°–77°.

The neutral substance amounting to 2.6 gr. was subjected to distillation under 757 mm. and the following fractions were obtained:

Fraction	85°–120°	120°–130°	residue.
Yield	0.8 gr.	1.2 gr.	trace.

The second fraction was composed of liquid and solid substances, and the latter was separated by filtration, the liquid was supposed to be a mixture of 92% di-benzyl ketone and 8% benzyl nitrile by the nitrogen determination.

0.1205 gr. of the mixture gave 0.00154 gr. N_2 by Kjeldahl's method, whence it contains 0.00116 gr. of the nitrile. The existence of the ketone was confirmed by oximiration with hydroxylamine.

V. Benzophenone oxime.

14 gr. of the oxime were passed on reduced copper at 200° in an atmosphere of hydrogen, and 6.8 gr. of a liquid, and 0.3 gr. of a pasty substance were obtained.

From these reaction products trace of both acidic and basic substances could be isolated, but further confirmation of them was lacking owing to the small yield of the materials.

The neutral substance composed the larger part of the reaction products, and from this a crystalline substance was isolated through an alcohol solution, which melted at 202°–205°. The yield was 0.2 grm. It was soluble in hot benzene and chloroform. On analysis, it gave the following results:

0.1233 gr. subst. gave 0.4206 gr. CO_2 and 0.0765 gr. H_2O.

Found:	C=93.03	H=6.94
Calc. for. $C_{26}H_{22}$:	C=93.36	H=6.65

It was, thus, supposed to be a substance identical with tetraphenylethane.

To the alcoholic solution separated from the hydrocarbon, 4 gr. of hydroxylamine hydrochloride and 6 gr. of caustic soda were added to separate some benzophenone, and the mixture was left to stand for 4 hours, and then the solvent was distilled off from the reaction products. 2.2 gr. of benzophenone oxime and a hydrocarbon were obtained.

The latter substance amounting to 4 gr., boiled at 135°–140°, 10 mm., melted at 27°. On analysis, it gave the following results:

0.1583 gr. subst. gave 0.5367 gr. CO_2 and 0.0930 gr. H_2O.
Found: $C=92.47$ $H=6.57$
Calc. for. $C_{13}H_{12}$: $C=92.81$ $H=7.19$

It was, thus, confirmed to be diphenyl methane.

In another experiment, 20 gr. of benzophenone oxime were passed with pure hydrogen over reduced copper heated at 200°, and 10 gr. of a liquid reaction product was obtained in a receiver cooled below 0° with a freezing mixture, and the product was immediately treated with absolute ether. To the ethereal solution dry hydrochloric acid gas, after drying with anhydrous sodium salphate, was passed, whereas hydrochloride was separated, filtered, and washed well with absolute ether. The hydrochloride, thus obtained, amounting to 0.5 gr. was supposed to be a mixture of the hydrochlorides of amine, ketimine and ammonia, and the hydrochloride of diphenylketimine was separated from the other constituents and purified by the method of Hantzsch and Kraft⁽¹⁾. The yield was 0.1 gr.

The physical and chemical properties of the hydrochloride agreed well with those of the ketimine hydrochloride described already by Mignonac⁽²⁾ and Lachmann⁽³⁾.

Lastly, 1.0 gr. of benzophenone, 1.0 gr. of tetraphenylethane and 1.3 gr. of diphenyl methane were actually isolated from the residue separated from the diphenylketimine by means of hydrochloric acid.

VI. Acetonoxime.

20 gr. of the oxime and hydrogen were passed on reduced copper at 200° and 15 gr. of a liquid reaction product was obtained in a receiver cooled with a freezing mixture.

The reaction product was subjected to distillation on a water bath and the distillate boiling below 84° was collected. The distillate amounting to 12 gr. was treated with ether in an acidic solution to separate a basic from a neutral sabstance. From the ether solution, the solvent was evaporated off, and acetone was separated by means of sodium bisulphite. The yield was 3 gr.

The acid solution separated from the ether solution, was evaporated to

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(1) *Ber. D. Chem. Ges.*, 24 (1891) 3516.

(2) *Comp. rend.*, 170 (1920) 936.

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

dryness, and by treating it with chloroform an amine hydrochloride was separated from ammonium chloride by the difference of their solubilities in the solvent.

The amine hydrochloride, amounting to 1.5 gr., was analysed after being transformed into the double salt of platinum.

0.1778 gr. subst. gave 0.0655 gr. Pt. on ignition.

Found: Pt=36.84

Calc. for. $(C_3H_8NH_2 \cdot HCl)_2\,Pt\,Cl_4$: Pt=36.96

From the analytical result and the carbylamine test, the basic substance was confirmed to be isopropyl amine. The occurrence of a secondary amine in the reaction product was confirmed by further reactions.

A small amount of the oxime which escaped from the reaction together with some substance of disagreeable odour and of unknown chemical nature, was isolated from the residue in a distillation flask.

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