

# Catalytic Action of Reduced Copper on Oximes. (On Beckmann's Rearrangement, XV.)

By

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In the previous article<sup>1</sup> 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 aldoximes 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.

## 1. FURFURALDOXIME.

20 gm. of the oxime, M. p. 89°, prepared according to the directions suggested by H. Goldschidt and E. Zanoli<sup>2</sup> were passed with hydrogen on reduced copper heated to 200°, and 2.8 gm. of solid and 4.5 gm. of liquid reaction products were obtained.

### A. Pyromusic Acid Amide.

The solid reaction product described above, 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 gm. It shows a blue colour, when treated with bromine water and caustic soda solution, as mentioned by Saunders,<sup>3</sup> which, on standing,

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<sup>1</sup> These Memoirs, A, 9,33 (1925).

<sup>2</sup> Ber. D. Chem. Ges., 25, 2573 (1892).

<sup>3</sup> Am. Chem. J., 15, 135 (1893).

changed to violet and then to red.

On analysis, it gave the following results:

0.1121	0.2225	CO <sub>2</sub>	and	0.0528	gm. H <sub>2</sub> O.
0.1276	14.6	c. c. N <sub>2</sub>	at	23.5°	and 750.2 m. m.
		C.		H.	N.
Found	54.13		5.27		12.81
Calc. for C <sub>5</sub> H <sub>5</sub> O <sub>2</sub> N	54.04		5.54		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 by Saunders, and this was found to melt at about 125° with decomposition, and gave the following analytical results:

0.2416	0.4183	AgBr.
		Br.
Found	73.68	
Calc. for C <sub>5</sub> H <sub>5</sub> O <sub>2</sub> NBr <sub>4</sub>	74.21	

### **B. The Acidic and the Basic Substances.**

The liquid reaction product (4.5 gm.) 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, where as 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 a 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.<sup>1</sup>**

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

<sup>1</sup> Tiemann: Ber. D. Chem. Ges. **17**, 128 (1884)

**A. Benzamide.**

It was isolated, in white crystals, M. p.  $126^{\circ}$ , from the solid reaction product, by treating it with absolute ether and then dilute alcohol. The yield was 1.2 gm. It was analysed with the following results:

0.1188 gm. subst. gave 0.2991 gm.  $\text{CO}_2$  and 0.0638  $\text{H}_2\text{O}$ .

0.1312 gm. subst. gave 0.15016 gm.  $\text{N}_2$  (by Kjeldahl's Method).

	C.	H.	N.
Found.	68.62	6.009	11.43
Cal. for $\text{C}_7\text{H}_7\text{ON}$ .	69.39	5.82	11.57

**B. The Acidic and the Basic Substances.**

The liquid reaction product and the ethereal washing of the solid reaction product 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 gm., was identified to be benzoic acid from its melting point ( $121^{\circ}$ ) and other chemical properties, after the salt was converted into a free acid and purified.

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 gm., and was confirmed as 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<sup>1</sup>, from 20 gm. of cinnamylaldehyde, B. p.  $125^{\circ}$ – $138^{\circ}$ , 12 m. m., and 15 gm. of hydroxylamine hydrochloride, and purified by crystallisation from benzene. It melted at  $126^{\circ}$ , and its yield was 16 gm.

16 gm. of the oxime were passed with pure hydrogen on finely divided copper heated at  $200^{\circ}$ , and obtained a tar-like substance and 6.8 gm. 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,

<sup>1</sup> J. Chem. Soc., 121, 2103 (1922).

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 the hydrochloric acid solution by extracting it with ether as usual.

The yield was 1.1 gm. On standing it for a few days some crystals were separated from the oily matter, and this was confirmed as composed of cinnamic acid from the melting point of  $132^{\circ}$ – $133^{\circ}$ , and the reaction. The oily residue separated from cinnamic acid was supposed from 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 gm.).

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 gm. of di-benzyl ketoxime<sup>1</sup> which melted at  $119^{\circ}$ – $120^{\circ}$  were passed with hydrogen over reduced copper at  $200^{\circ}$ , and 1.9 gm. pasty substance and 1.1 gm. of the liquid one were obtained. The former was treated with absolute ether and then recrystallised from hot water, and colourless crystals which melted at  $155^{\circ}$  were obtained.

The yield was 0.2 gm.

0.0919 gm. of the subst. 0.00958 gm.  $N_2$  (by Kjeldahl's method).

	Found	Calc. for $C_9H_9NO$
N	10.42	10.37

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

The acidic substance separated from the reaction product mentioned above, by means of ammonia in the form of an ammonium salt, decomposed into free acid by means of hydrochloric acid, and was identified as phenyl acetic acid from its melting point  $76^{\circ}$ – $77^{\circ}$ .

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

Fraction	$85^{\circ}$ – $120^{\circ}$	$120^{\circ}$ – $130^{\circ}$	residue
Yield	0.8 gm.	1.2 gm.	trace

<sup>1</sup> Ber. D. Chem. Ges., 21, 1316 (1888).

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

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

### V. BENZOPHENONE OXIME.

14. gram. of the oxime were passed on reduced copper at  $200^\circ$  in an atmosphere of hydrogen, and 6.8 gram. of a liquid, and 0.3 gram. of pasty, substance were obtained.

From these reaction products a 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  $202^\circ - 205^\circ$ . The yield was 0.2 gram. It was soluble in hot benzene and chloroform. On analysis, it gave the following results:

0.1233 gram. subst. gave 0.4206 gram.  $CO_2$  and 0.0765  $H_2O$ .

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

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

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

The latter substance amounting to 4 gram., boiled at  $135^\circ - 140^\circ$ , 10 m. m., melted at  $27^\circ$ . On analysis, it gave the following results:

0.1583 gram. subst. gave 0.5367 gram.  $CO_2$  and 0.0930 gram.  $H_2O$ .

	C.	H.
Found	92.47	6.57
Calc. for $C_{13}H_{12}$	92.81	7.19

It was, thus, confirmed to be diphenyl methane.

In another experiment, 20 gram. of benzophenone oxime were passed with pure hydrogen over reduced copper heated at  $200^\circ$ , and 10 gram. of

a liquid reaction product, were obtained in a receiver cooled below  $0^{\circ}$  with a freezing mixture, and the product immediately treated with absolute ether. To the ethereal solution dry hydrochloric acid gas, after drying with anhydrous sodium sulphate, was passed, whereas hydrochloride was separated, filtered, and washed well with absolute ether. The hydrochloride, thus obtained, amounting to 0.5 gm., was supposed to be a mixture of the hydrochloride of amine, ketimine and ammonia, and the hydrochloride of diphenyl ketimine was separated from the other constituents and purified by the method of Hantzsch and Kraft<sup>1</sup>. The yield was 0.1 gm.

The physical and chemical properties of the hydrochloride agreed well with those of the ketimine hydrochloride described already by Mignonac<sup>2</sup> and Lachmann<sup>3</sup>.

Lastly, 1.0 gm. of benzophenone, 1.0 gm. tetraphenyl ethane and 1.3 gm. diphenyl methane were actually isolated from the residue separated from the diphenyl ketimine by means of hydrochloric acid.

## VI. ACETONOXIME.

20 gm. of the oxime and hydrogen were passed on reduced copper at  $200^{\circ}$  at 15 gm. of a liquid reaction product were obtained in a receiver cooled with a freezing mixture.

The reaction product was subjected to distillation on a water bath and the distillate boiling to  $84^{\circ}$  was collected. The distillate amounting to 12 gm. was treated with ether in an acidic solution to separate a basic from a neutral substance. The ether solution evaporated off the solvent, and acetone was separated by means of sodium bisulphide. The yield was 3 gm.

The acid solution separated from the ether solution, was evaporated to 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 gm., was analysed after being transformed into the double salt of platinum.

0.1778 gm, Subst. gave 0.0655 gm. Pt. on ignition.

	Pt.
Found	36.84
Calc. for $(C_3H_5NH_2 \cdot HCl)_2PtCl_4$	36.96

From the analytical result and the carbylamine test, the basic substance

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

2 C. R., **170**, 936 (1920).

3 J. Am. Chem. Soc., **49**, 1477 (1924).

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 a disagreeable odour and of unknown chemical nature, was isolated from the residue in a distillation flask.

### SUMMARYS AND DISCUSSION.

Since the first report of these researches was published by the writer and Professor Komatsu<sup>1</sup>, the present writer has described some experimental results on the same subject, which are now summarised with the present experiment in the following table:

Oxime used	Reaction product in Mol %				
	RCONH <sub>2</sub>	RCN	RCOOH	Base	$\frac{R}{R'} > C=O$
1. $C_6H_5-C(H)=NOH$	51.9	27.5	20.6	—	—
2. $\begin{array}{c} HC-CH \\    \quad    \\ HC \quad C-C-H \\ \quad \quad \quad    \\ \quad \quad \quad NOH \\ \quad \quad \quad O \end{array}$	44.6	—	trace	trace	55.4
3. $C_6H_5CH=CH-C(H)=NOH$	—	+	—	trace	+
4. $C_6H_5-C(NH_2)=NOH$	58.3	29.3	12.4	—	—
5. $C_6H_5-CH_2-C(CH_2-C_6H_5)=NOH$	11.2	12.9	11.1	—	64.8
6. $\begin{array}{c} CH_2-CH-CH_2 \\   \quad   \quad   \\ CH_3-C-CH_3 \\   \quad   \\ CH_2-C-C=NOH \\   \quad   \\ CH_3 \end{array}$	+	+	+	trace	+
7. $C_6H_5-C(CH_3)=NOH$	—	+	+	+	+
8. $CH_3-C(CH_3)=NOH$	—	—	—	+	+
9. $C_6H_5-C(C_6H_5)=NOH$	—	—	—	trace	+
	Diphenyl- ketimine 3.3	Tetraphenyl ethane 17.8	Diphenyl methane 46.1	Ketone 32.8	

<sup>1</sup> These Memoirs, 6, 245 (1923).

When the oximes of different ketones or aldehydes, passed on reduced copper heated at about  $200^{\circ}$ , in an atmosphere of hydrogen, as will be seen in the above table, yield acid amide ( $R\text{CONH}_2$ ), nitrile ( $\text{RCN}$ ), acid ( $\text{RCOOH}$ ), bases ( $\text{R}_2\text{C}=\text{NH}$ ,  $\text{R}_2\text{CHNH}_2$ ,  $(\text{R}_2\text{CH}_2)_2\text{NH}$ ,  $\text{NH}_3$ ) ketone or aldehyde and hydrocarbons ( $\text{R}_2\text{CH}_2$ ) and  $(\text{R}_2\text{CH})_2$ , the yield of these compounds seems to depend more or less on the structure of the oximes; all oximes except of benzaldoximes and benzhydroxamic acid by hydrolysis yield principally the ketones or aldehydes from which the oximes were derived, the oxime of cinnamyl aldehyde, of acetone, of acetophenone and of benzophenone yields an acid-amide of the type  $\text{RCONH}_2$  as a main reaction product.

The oxime, thus, will be classified into three groups according to the chemical nature of the principal reaction products by the contact action of reduced copper at  $200^{\circ}$ .

#### 1st. Group.

The oxime of this group yields aldehyde or ketone and some basic compounds as the main reaction products, and the benzophenone and acetone oximes belong to this group. The carbonyl compound resulting by hydrolysis of the oxime, will be transformed by the further catalytic action of reduced copper in an atmosphere of hydrogen into hydrocarbons, as actually observed in the case of benzophenone oxime.

#### 2nd. Group.

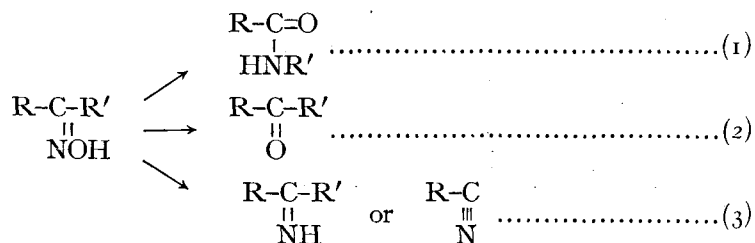
Benzaldoxime and benzhydroxamic acid each yields an acid amide which by the contact action of reduced copper is transformed into nitrile and acid.

#### 3rd. Group.

The oxime of this group stands between the two groups of oximes above-mentioned, in its behavior toward reduced copper heated at  $200^{\circ}$ , yielding the compounds, the acid amide and carbonyl compounds with some basic ones, their relative amount in the reaction product depending more or less upon the chemical or electronical nature of the hydrocarbon radicals linked to the carbon atom of the methane nucleus of the oxime, and furfuraldoxime, cinnamylaldoxime, dibenzylketoxime camphoroxime and acetophenone oxime belong to this group.

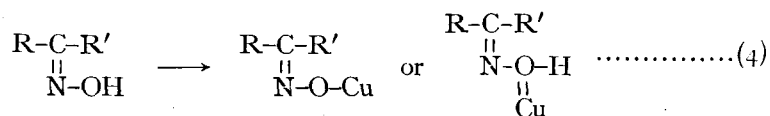
As a matter of fact, aldoximes and ketoximes, or their salts, probably suffer the chemical reactions from heat, being transformed directly into (1) isomeric acid amides — Beckmann's rearrangement (2) into carbonyl compounds — aldehyde or ketone by hydrolysis (3) into imine or nitrile by dehydration and the latter substance will also result from an acid amide:





Such direct transformations of the oximes or their salts by heat would take place independently or simultaneously according to the chemical nature of the oximes. In presence of reduced copper, the velocity of these reactions will also evidently be modified, some reactions being accelerated and others retarded, and as a consequence, the oxime from the view point of the nature of chemical reactions, were classified into the three groups mentioned above.

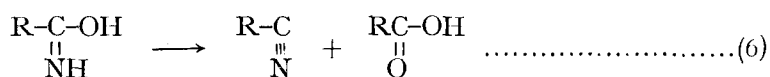
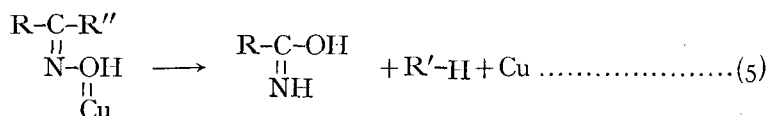
With regard to the catalytic action of reduced copper on the behavior of the oxime toward heat, the writer has now attempted to explain its mechanism with the following interpretations: an oxime when passed in a vapour state over finely divided copper, would be condensed in a thin layer on the surface of the catalyst, and temporarily form a compound - a salt or an oxonium compound, though its combination is in a labile state.



Moreover, in the present case, an hypothetical substance of the composition  $\text{CuH}_2$  should occur in the reaction system, since hydrogen is spread uniformly in the reaction system. The dissociation of these compounds will take place, in the course of evaporation, on the surface of the metal, and where the chemical transformations mentioned above take place. During the evaporation of the oxonium compound on a surface of the catalyst, the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms, and moreover, when the metal combined with the oxime behaves to lose the strength of the former affinity by acting as a donor of electrons, as sodium does in the molecular rearrangement of the oxime observed by S. Komatsu and T. Hiraidzumi<sup>1</sup>, the molecular rearrangement of the oxime into its isomeric acid amide will

<sup>1</sup> These Memoirs, A, 8, 273 (1925).

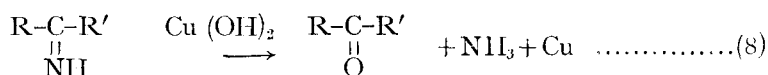
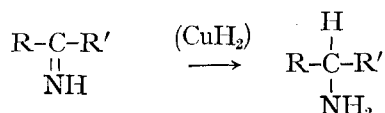
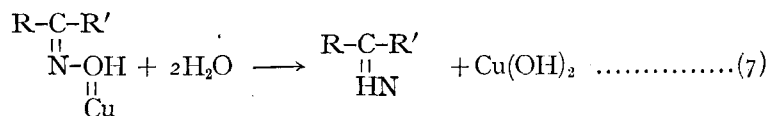
take place with a prominent yield, but in the meantime, the hydrocarbon radical detached by the influence of the catalyst, is left in a free state without entering into combination with the nitrogen atom, and the simple acid amide of the formula  $RCONH_2$  as a consequence is the result, and this by further action of the catalyst is soon transformed partly into nitrile and acid, which may be represented by the following scheme:

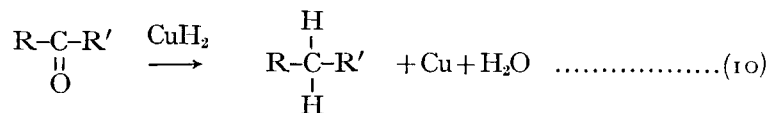
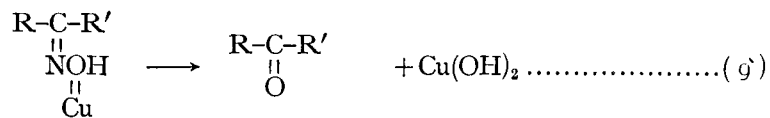


The transformation of the second group of oximes into acid amide, nitrile and acid by the contact action of the catalyst, will be represented by the schemes (1) and (6).

When, however, the linkings between the hydrocarbon radicals or the hydrogen and the carbon atom of the methane nucleus of the oxime are quite strong, and the metal exerts no appreciable influence on these affinities, the hydrolysis will result in the formation of an aldehyde or a ketone, one part of which by the catalytic action of reduced copper in an atmosphere of hydrogen will be reduced into hydrocarbon, as noticed in the case of the benzophenone oxime. The hypothesis would be applied to the explanation of the reactions of the first group of oximes.

The formation of imine or nitrile will occur when the dissociation of the combination between the hydroxyl group and the nitrogen atom, by heat or by the catalytic influence of reduced copper, takes place very easily, and the conversion of the imine into base or ketone by catalytic reduction or hydrolysis in presence of the catalyst will take place in turn:





The behavior of the oximes of the first group, by the contact action of reduced copper will be represented in schemes (7) (8) and (10)

As was mentioned in the XIV the article on the Beckmann rearrangement by S. Komatsu and T. Hiraizumi, the chemical reactions of the oximes will depend more or less upon the chemical and electronical nature of the hydrocarbon radicals, or in other words, the mobility of the radicals from the carbon atom of the methane nucleus depending mostly upon their electronical character, and also upon the catalytic influence of the catalyst presented in the reaction system, and all of the reactions shown in the schemes (1) (7) (8) and (10) would take the place of some oximes belonging to the 3rd group, possessing the chemical characters of both groups, in some degree. The conception of these ideas with respect to the conversion of the oxime into the acid amide, the carbonyl compound, and bases was thus fully illustrated by the experimental results mentioned in the above table.

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