

Catalytic Action of Reduced Copper on laevo-Menthone Oxime. (On Beckmann's Rearrangement, XI)

By

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One of the present authors and S. Yamaguchi¹ have reported that when dextro-camphor oxime passed with pure hydrogen on reduced copper heated at 200°, it yielded α -campholenamide, α -campholenic acid and α -camphlenitrile, and that these compounds were assumed to be derived from camphorisoxime, a hypothetical substance, by the catalytic action of the reduced copper, which resulted from the Beckmann rearrangement of the camphor oxime. The isolation of the isoxime from the reaction product did not succeed, due to its unstable nature *vis-a-vis* chemical reagents or heat, being spontaneously transformed into the compounds mentioned above.

The menthone oxime, however, is interesting on account of the fact that it undergoes the Beckmann rearrangement by being treated with conc. sulphuric acid to give stable menthonisoxime² which corresponds to camphorisoxime in constitution and other respects, and the isoxime by dehydration yields menthonitrile³. The present experiment, therefore, was undertaken with the expectation of isolation menthonisoxime, and thereby to bring strong support for the present authors'

¹ These Memoirs, **6**, 245 (1923)

² Lieb. Ann., **277**, 156 (1893); **278**, 304 (1894); **329**, 105 (1903).

³ Lieb. Ann., **278**, 309 (1894).

opinion that the rearrangement of the oxime would be effected by the catalytic action of the reduced copper.

laevo-Menthone was prepared from 90 grm. menthol, following Beckmann's directions¹, and 78 grm. of the pure ketone B. p. 205—206°, $d_4^{25}=0.8903$, $[\alpha]_D^{25}=-28.3^\circ$, were obtained. It was transformed into its ketone oxime as usual, which showed $[\alpha]_D^{25}=-44.0^\circ$ in an alcohol solution, and the yield was 91% of the theory.

40 grm. of the oxime were passed in an interval of 16 hours, with pure hydrogen on reduced copper heated at 200°, which was prepared from 9 grm. of copper oxide, and repeating the operation five times, 167 grm. of the reaction product of a light reddish-coloured liquid were obtained. In the course of the reaction, a deposit of white crystals was noticed at the end of the reaction tube, and also the evolution of ammonia gas, the former melting at 103—106° and greatly resembling decylenic amide² in property.

The product separated from the bluish water layer which formed during the reaction, was treated with aqueous ammonia, dilute hydrochloric acid and water successively to separate the acidic, basic, and neutral substances from each other, and the each portion was subjected to the following treatment :

I. ACIDIC SUBSTANCE

Decylenic Acid.²

A substance was, on acidifying the ammonia extract with dilute sulphuric acid, separated out from the solution, which on being extracted with ether, dried with anhydrous sodium sulphate, and dry ammonia gas passed in, gave an insoluble ammonium salt.

It yields silver salt with silver nitrate, and was assumed to be decylenic acid, but was not further examined, owing to lack of material.

¹ Lieb. Ann., **250**, 325 (1889).

² Ibid., **296**, 126 (1897).

II. BASIC SUBSTANCES.

1. *laevo*-Menthyl Amine.¹

The acidic extract, on alkalifying with caustic solution, yields oily basic substances which separated from the solution, suspended in water and passed in carbon dioxide gas, separate into two parts; one is soluble in the carbonic acid solution and the other is insoluble.

The free bases isolated from the carbonic acid solution, boiled at 203—218°, amounting to 1.1 gm., and yielded the acetates and the oxalates with the following melting point :

	M. p. of the salts of the bases	M. p. of salts of the	
		mixture of the bases and 1-menthyl amine	mixture of the bases and menthonyl amine
Acetate	151—152°	127°	—
Oxalate	158°	163—164°	142—143°

The melting point determination of the salts indicate that the sample was a mixture of two or more bases.

The hydrochlorides of bases, therefore, were treated with absolute ether to separate 1-menthyl amine salt from the other substance, the insoluble salt (m. p. above 260°) with platinum chloride gave yellow crystals of the double salt which melt at 203—204°, and gave on analysis the following results :

Pt=25.50, theory requires Pt=25.80 for $(C_{10}H_{12}NHCl)_2PtCl_4 \cdot 2H_2O$.

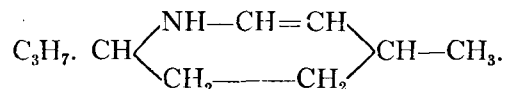
Its properties and analytical results agree well with those of 1-menthyl amine platinum chloride prepared from menthone oxime by reduction.

The other hydrochloride which was soluble in the ether solution, melted at 190—220°, being quite different in its properties from menthonyl amine salt, was regarded as consisting of d-menthyl amine salt and an other salt. Further examination of this part, however, was not carried out.

¹ A. Mailhe and M. Murat : Bull. soc. chim., (4), 9, 464 (1911).

The insoluble bases in carbonic acid solution.

2. γ -Methyl- α' -isopropyl cyclohexene-imine,



The basic substances were fractionated into two portions ;

1. B. p. 235—300°, yield 3.4 gm. pale yellow oil.

2. B. p. 300—320°, 3.6 yellow oil.

The first fraction was subjected to steam distillation, and the oily substance distilled with steam, extracted with ether, transformed into the hydrochloride and then into a double salt of chloroplatinate, which shrinks at 187° and melts at 206° with decomposition after purification and was analysed with the following results :

C=32.75 ; H=4.92 ; Pt=26.48, theory requires

C=33.52 ; H=5.63 ; Pt=27.25 for $\text{C}_{20}\text{H}_{40}\text{N}_2\text{PtCl}_6$.

It resembles piperidine of its odour, and seems to be an unsaturated base by its chemical properties, and was considered as formed by the catalytic dehydration of reduced copper on γ -methyl- α' -isopropyl cyclohexanolimine¹ which resulted from menthonisoxime by reduction.

3. Dimenthyl amine.²

The second fraction, B. p. 300-320°, was treated with hydrochloric acid to convert the amine which was regarded as forming the main part of the fraction into the hydrochloride, the salt was transformed into the double salt of platinum chloride which melts at 196° with decomposition.

For confirmation, it was analysed with the following results :

C=46.11 ; H=7.83 ; Pt=19.85 (theory requires C=48.17,

H=8.09 ; Pt=19.58 for $(\text{C}_{20}\text{H}_{40}\text{NCl})_2 \text{PtCl}_4$).

III. NEUTRAL SUBSTANCES.

¹ O. Wallach : Lieb. Ann., 324, 301 (1902).

² Bull. soc. chim., (4), 9, 464 (1911).

This portion was subjected to steam distillation to separate the volatile part from the nonvolatile, and the former was subjected to fractional distillation :

	Fraction	Yield	Nitrogen	
1.	205—210°	111.4 gm.	—	colourless
2.	210—250°	7.8	+	light yellow
3.	above 250°	$\frac{2}{121.2}$	+	brownish yellow

1. Menthone.

The first fraction was confirmed to be a mixture of isomenthone and 1-menthone by the determination of the physical constants of the purified sample, B. p. 205—206°, by distillation : $d_4^{25}=0.8912$; $[\alpha]_D^{25}=-4.0^\circ$.

2. Menthonitrile.

The second fraction was reduced with metallic sodium and alcohol, and the reaction product was separated into two parts, one was neutral and the other basic, and the former amounting to 6.6 gm. was confirmed to be menthol by its properties, and the latter amounting to 0.34 gm. was also identified to be 1-menthonyl amine¹ by transformation into the oxalate.

M. p. 162°; N=5.83 (by Duma's method), theory requires N=5.51 for $C_{10}H_{21}NC_2H_4O_4 \cdot \frac{1}{2}H_2O$.

The isolation of the amine from the neutral reaction product by reduction, supports the theory of the existence of menthonitrile in it. The detection and the isolation of menthonisoxime of the reaction products were attempted but ended in negative results.

Of 84 gm. reaction product from 100 gm. 1-menthone oxime, 60 gm. menthone, 2 gm. dimethylamine, 1 gm. 1-menthyl amine with some d-menthyl amine, 0.2 menthonitrile, a small quantity of decylenic acid and its amide, and γ -methyl- α' -isopropyl cyclohexene-imine were isolated and confirmed.

Of these substances, 1-menthone, 1-menthyl amine and dimethyl

² Lieb. Ann., **278**, 314 (1891).

amine were reported as having been obtained by A. Milhe and M. Murat¹ from 1-menthone oxime by catalytic reduction with hydrogen and nickel.

It may, therefore, be concluded that the catalytic action of reduced copper on menthone oxime resembles in some respect, that of the reduced nickel, and on the other hand, the formation of menthonitrile and decylenic acid resembles that of concentrated sulphuric acid and phosphor pentoxide.

Menthonitrile and decylenic acid were supposed to be derived by catalytic dehydration and hydration of decylenic amide respectively, this last mentioned amide being regarded as an intermediate compound in the transformation of menthonisoxime into the nitrile and the acid.

Although the authors could not succeed in the isolation of menthonisoxime, its momentary formation, in the course of the reaction, will be admitted by the isolation of the compound supposed to be γ -methyl- α' -isopropyl cyclohexene-imine, and accordingly we can no more deny that 1-menthone oxime suffers the Beckmann rearrangement, by the catalytic action of reduced copper.

The catalytic action of reduced copper on the oxime, which has been described above, is not only a new example of the Beckmann change but is of interest for the sake of the fact that it accelerates both reactions, hydration and dehydration of the acid amide, and the latter reactions will be discussed fully in another paper.

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¹ Loc. cit.