Studies on Camphor Series, III. Catalytic Action of Reduced Copper on dextro-Camphoroxime.

By

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When camphoroxime was reduced with hydrogen in the presence of reduced nickel, it yielded bornylamine.[1] The authors, therefore, expected from the analogy between the catalytic action of copper and of nickel on acetophenonoxime,[2] that camphoroxime by the catalytic action of reduced copper and hydrogen, would be transformed into bornylamine. Contrary to our anticipation, the main reaction was actually a molecular rearrangement, with reduction as a side reaction.

35 grm. dextro-camphoroxime were passed with pure hydrogen over reduced copper heated to 200°, which had been prepared from copper oxide by reduction at 180° with hydrogen, following Prof. P. Sabatier's direction. In the progress of the reaction, there was observed the formation of a solid substance accompanied by a liquid one in the receiver. At the beginning of the reaction, however, a liquid substance only was formed. On the apparatus being opened after the reaction had ended, the odour of ammonia was perceptible, indicating that the decomposition of the oxime into camphor and hydroxylamine had taken place.

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[1] Aloy and Brustier, Bull. soc. chim., (4), **9**, 734 (1911).
Mailhe, C.R., **140**, 1691; **141**, 113 (1905).

[3] La Catalyse en Chimie Organique, 1920, 18.

17 grm. of a yellowish green oily substance were obtained, which was treated with dilute hydrochloric acid and then subjected to distillation after drying with anhydrous sodium sulphate. 8 grm. of the distillate, thus obtained, were fractionated five times under 753–756 mm.

Fraction	yield	density	Carbon	Hydrogen	Nitrogen
Below 85°	0·2 grm.	——	——	——	——
140–185°	0·3 ,,	——	——	——	——
185–210°	0·6 ,,	——	78·81	10·92	——
210–220°	0·6 ,,	liquid.	78·96	10·92	4·81
	0·9 ,,	solid.	78·12	10·80	2·01
220–230°	1·5 ,,	0·9276	78·52	10·48	5·30
230–240°	0·5 ,,	0·9463	75·33	10·64	5·24
240–250°	0·5 ,,	1·0052	73·14	9·99	3·53
250–263°	1·5 ,,		71·87	10·08	1·85

As seen in the foregoing table, the third and fourth fractions seem to contain camphor and some nitrogenous substance which is the main constituent of the fifth and sixth fractions, the last fraction being composed of a carboxylic acid.

In another experiment, 60 grm. of dextro-camphoroxime were passed with hydrogen over reduced copper heated to 200°, and 35 grm. of reaction product were obtained which was separated mechanically into liquid and solid substances. The yield was 20 grm. of the former and 10 grm. of the latter.

The solid substance was treated with dilute hydrochloric acid, and then recrystallized from the hot aqueous solution. The white scaly crystals separated from the solution, were found to melt at 126°. They were soluble in organic solvents and hot water and the yield was 2 grm. It gave, on analysis;

$C=71{\cdot}77$; $71{\cdot}95$; $H=10{\cdot}79$; $10{\cdot}67$; $N=8{\cdot}35$ (by Kjeldahl's method) ($C_{10}H_{17}ON$, requires $C=71{\cdot}81$; $H=10{\cdot}23$; $N=8{\cdot}38$) $[\alpha]_D^{17}=-4^\circ{\cdot}6'$ (in 96% alcohol solution).

When the substance was treated with zinc and conc. hydrochloric acid, it yielded a primary amine, and when hydrolysed with alcoholic potash was transformed into a carboxylic acid which gave a silver salt from its ammonium salt solution with silver nitrate.

The results of analysis quite agree with those of α-campholenamide obtained from α-campholenitrile by hydrolysis,[1] from *d*-camphoroxime by treating with mineral acids or acetyl chloride,[2] and by heating the ammonium salt of α-campholenic acid.[3]

With the object of further confirming the identity of our substance with α-campholenamide, it was hydrolysed with alcoholic potash into α-campholenic acid which was separated from the reaction products by steam distillation, and extracted with ether. The etherial solution was dried with anhydrous sodium sulphate, the solvent expelled by distillation, and the residue was then fractionated under 764·7mm.

Fraction	248–255°	255–258°	258–263°
Colour	colourless	pale yellow	yellow
n_D^{25}	1·4605	1·4614	1·4600

The second fraction boiled at 143° under 15 mm., $d_4^{25}=0{\cdot}9963$, $[\alpha]_D^{16}=+17^\circ{\cdot}40'$, and gave on analysis, C=71·25; H=9.62 ($C_{10}H_{16}O_2$, requires C=71·39; H=9·59).

It gave an insoluble silver salt from its ammonium salt solution with silver nitrate. The physical properties and analytical results of the fraction agreed with those of α-campholenic acid prepared by other investigators from α-campholenitrile, α-campholenamide[4] and bromcamphor.[5]

The liquid reaction product was subjected to steam distillation and the oily distillate in the flask was extracted with ether, and the extract, after the solvent had been distilled off, was fractionated four times under 753 mm.

Fraction	**yield**	**Carbon**	**Hydrogen**	**Nitrogen**
Below 200°	trace	——	——	——
200–210°	0·5 grm.	——	——	——
210–220°	3·5 „	78·02	10·93	——
		78·22	10·68	2·00
220–225°	2·0 „			

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[1] E. Nageli, Ber. D. Chem. Ges., **17**, 805 (1885); F. Tiemann, Ibid, **29**, 3006 (1896); A. Behal, C.R., **120**, 1167 (1895).

[2] F. Tiemann, Ber. D. Chem. Ges., **28**, 1083 (1895).

[3] H. Goldschmidt and R. Zurrer, Ibid, **17**, 2071; J. Kachler and F. V. Spitzer, Ibid, **17**, 2400 (1884).

[4] F. Tiemann, Ber. D. Chem. Ges., **28**, 2167 (1895).

[5] Kachler and Spitz, Ibid., **17**, 2400 (1884); Monatsh. Chem., **3**, 216 (1882).

Fraction	**yield**	**Carbon**	**Hydrogen**	**Nitrogen**
225–230°	2·7 „	80·95	11·14	——
230–240°	1·5 „	78·02	10·67	4·17
		78·15	10·56	——
240–250°	1·5 „	75·60	10·40	——
		75·64	10·59	——
250–260°	1·5 „	74·34	10·19	——
		74·19	10·38	——

The fraction B.p. 210–220°, was a mixture of solid and liquid substances which were separated from each other by filtration. The solid substances was confirmed to be dextro-camphor by its analysis and by the determination of melting point, 118°, and of the optical rotatory power of its oxime, $[\alpha]^{20}_{\mathrm{D}}=-40^{\circ}{\cdot}9'$.

The two fractions B.p. 210–220° (liquid part) and B.p. 230–240° combined together, and were digested with barium hydroxide in a flask with reflux condenser for three hours to get campholenitrile free from campholenic acid and its acid amide. Some crystals were observed to be deposited on the wall of the condenser, which melted at 90–110°, and were too small in quantity to allow of their chemical nature being confirmed. The alkaline solution was subjected to steam distillation, and the oily distillate in the receiver was extracted with ether, and dried with anhydrous sodium sulphate. The residue remaining after distilling off the solvent was all distilled off between 220–230°. The alkaline solution remaining in the distillation flask, was acidified with sulphuric acid and again subjected to steam distillation, and an oily distillate then obtained was found to consist of *α*-campholenic acid.

The oily substance B.p. 220–230°, regarded to consist of *α*-campholenitrile, combined with the fractions boiling at 220–225°; and 225–230°, and the mixture was fractionated under 8 mm.

Fraction.	B.p.	98–118°	2·5 grm.
	B.p.	118–120°	2·5 grm.

The fraction B.p. 98–118°, assumed to be a mixture of *d*-camphor and *α*-campholenitrile, was digested with alcoholic potash to convert the latter substance into *α*-campholenic acid which, after separating from camphor by steam distillation, was transformed into ammonium salt. The ammonium salt was converted into silver salt which gave C=43·03; H=5·80; Ag=39·47 ($C_{10}H_{15}O_2Ag$ requires C=43·65; H=5·50; Ag=39·22).

The fraction B.p. 118–120° under 8 mm., $d_4^{25}=0{\cdot}91966$, $n_D^{25}=1{\cdot}4592$; $[\alpha]_D^{15}=+23^\circ{\cdot}0$ (in 95% alcohol); gave on analysis $C=80{\cdot}65$; $H=10{\cdot}32$; $N=9{\cdot}6$ (by Duma's method). ($C_{10}H_{15}N$ requires $C=80.47$; $H=10{\cdot}13$; $N=9{\cdot}39$).

It yielded, on hydrolysis with alcoholic potash, *α*-campholenic acid and ammonia. There can, therefore, be no doubt that the above fraction consists of pure *α*-campholenitrile which was obtained by E. Nageli and A. Behal from camphoroxime by the action of acetyl chloride,[1] also from the oxime by treating with sulphuric acid or hydrochloric acid.[2]

It was anticipated that the fractions B.p. 240–250°, 250–260°, of the liquid reaction product would contain *α*-campholenic acid, and in order to isolate the substance, it was dissolved in absolute ether and dry ammonia gas was passed over it, and the ammonium salt precipitated out from the solution separated, washed with ether, dried and dissolved in water. For the sake of comparison, the ammonium salt, converted into silver salt with silver nitrate, was analysed.

The fraction B.p. 230–240°, obtained from the liquid reaction product and also the fraction with the same boiling point isolated from the mixed fractions B.p. 210–220°, and 230–240° after treatment wth barium hydroxide, were both confirmed to be a mixture of campholenic acid and campholenitrile, by transforming into silver campholenate after separating the latter substance from the former by means of ammonia.

The acid washing of the solid reaction products above mentioned, on alkalining with caustic soda solution yielded bornylamine, which was separated by steam distillation, extracted with ether, and then converted into the hydrochloride.

For confirmation, the specific rotatory power of the hydrochloride in aqueous solution was determined with the following result:

$$[\alpha]_D=-36^\circ{\cdot}9'$$

It gave the platinum double salt with platinum chloride.

Of the reaction products from *d*-camphoroxime, reduced copper and hydrogen at 200°, we have actually isolated the following substances.

d-*α*-campholenamide (laevo rotatory), *α*-campholenic acid, *d*-camphor, *α*-campholenitrile, and a trace of bornylamine.

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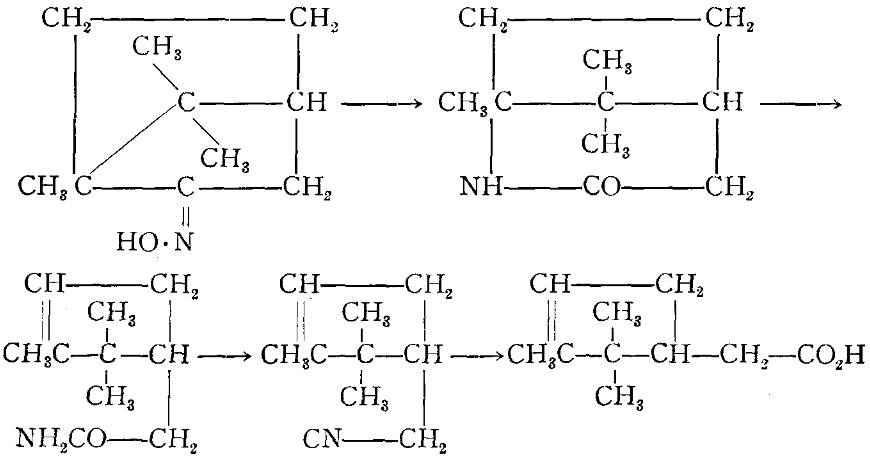
[1] Loc. cit.

[2] Loc. cit.

These compounds, except bornylamine and camphor, resulted from the molecular rearrangement of *d*-camphoroxime, which is effected by numerous reagents, such as acetyl chloride, sulphuric and hydrochloric acids.

The formation of these compounds, therefore, from comphoroxime by the catalytic action of reduced copper, should be explained by the same mechanism which applied in the reaction between camphoroxime and acetyl chloride, namely Beckmann's molecular rearrangement of the oxime (the reaction being probably analogous to that which occurs between nitrosocamphor and acetic acid); it occurs with rapture of the cyclopentamethylene ring, whereby the oxime converts into isoxime. The decomposition of the isoxime into campholenamide occurring soon after the rearrangement, is represented in the following fashions:



We are, now, forced to conclude that a large part of the oxime is is configurated in syn-form as indicated in the above formula, since it yields the acid amide by the rearrangement.

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[1] A. Nageli, Ber. D. Chem. Ges., **26**, 68 (1893); O. Manasse, Ibid., **26**, 242 (1893).