Studies on the Camphor Series, X : Synthesis of Camphor, I : Catalytic Action of Reduced Copper on Borneols

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Studies on the Camphor Series, X.
Synthesis of Camphor, I.
Catalytic Action of Reduced Copper on Borneols.[1]

By

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According to Prof. P. Sabatier,[2] reduced copper is regarded as the sole catalyst suitable for oxidizing alcohols into aldehydes or ketones without any side-reaction.

When, however, cyclohexanol was passed on reduced copper heated at 200° and 300° respectively, as observed by Prof. S. Komatsu and the present author,[3] phenol, cyclohexene, cyclohexyl ether were obtained with cyclohexanone, and the ether and the hydrocrabon were regarded as resulting from the dehydration of the alcohol, that is to say, reduced copper promotes not only the dehydrogenation of alcohol but also the dehydration.

Recently, Prof. Komatsu and M. Kurata[4] have observed that when menthol was passed over various forms of reduced copper heated at 200° and 300° respectively, it was transformed into menthone, menthene, thymol and p-cymene and that the relative amount of these compounds present in the reaction products varies with the reaction temperature, and also with the method of preparation of the catalyst. The catalytic activities of dehydration and dehydrogenation of reduced copper, therefore, seem to depend upon the mode of preparation of the oxide from its salts, the reducing temperature of the oxide with hydrogen, and also the conditions under which the catalyst is employed—the reduction temperature, and the velocity of passing of the substance over the catalyst.

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[1] This paper was read before the annual meeting of the Chemical Society of Japan on April 4, 1925.

[2] La catalyse en chimie organique, 251–256 (1920).

[3] These Memoirs, A, **9**, 17 (1925).

[4] Ibid., 23 (1925).

The catalytic oxidation of borneol in the presence of reduced copper was already studied by many chemists,[1] and Neave[2] has observed that borneol by passing over reduced copper heated at 300°, yields quantitatively camphor, while isoborneol under the same condition gives camphene, but the method of preparation of the catalyst used in these experiments were not entirely stated.

The present investigation was undertaken to study the catalytic behavior of various forms of reduced copper, and to find, if possible, the most suitable conditions and the most suitable form of the catalyst for the preparation of camphor from borneol. The sample used in the experiment was bought from Fujisawa & Co. in Osaka, which was prepared from d-camphor by reduction with sodium in alcohol solution, M. p. 205°–205°·5 and shows $[\alpha]_D = +19°\cdot88$ in 2% alcoholic solution. Consequently it consists of 75·5% d-borneol and 24·5% of l-isoborneol, calculated from the specific rotation of the solution.[3] Copper oxide is prepared (1) by adding the excess of hot dilute sodium hydroxide solution to hot copper nitrate solution (denoted by Cu I.), (2) by the interaction with ammonia water and hot copper nitrate solution (denoted by Cu II.), (3) by ignition of copper nitrate (denoted by Cu III.), and (4) by adding an excess of hot dilute sodium hydroxide solution to a hot solution of copper sulphate (denoted by Cu IV.). In each experiment, 10 gr. of copper oxide are placed in the reaction tube of 1 m. length and reduced at 180° with a slow current of pure hydrogen as usual, and then the vapour of a mixture of borneols is passed with various velocities on the catalyst heated at a required temperature. 2 gr. of the reaction product were treated with 2 gr. of hydroxylamine hydrochloride, 3·6 gr. of sodium bicarbonate, 20 c.c. of alcohol to separate the camphor from the borneol and the camphene by converting it into the oxime[4] which was then extracted with dilute sulphuric acid (sp. g. 1·17) and the free oxime was filtered, dried and weighed. The yield of camphor is calculated from the amounts of the oxime. The residue separated from camphor was treated with bromine to detect the formation of camphene or bornylene. The results of the experiments are shown in the following Table I.

From the above experimental results the following conclusions are drawn.

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[1] E. Schering Co.: D.R.P. 166722, 271147; Aloy and Brustier: Bull. Soc. Chim., (4) **9**, 733 (1911); Goldsmith: E. P. 17573 (1906).

[2] J. Chem. Soc., **101**, 513 (1912).

[3] E. Beckmann: J. prak. Chem., (2) **55**, 34 (1897).

[4] Ibid., 17 (1897).

Table I.

No. of Expt.	Catalyst	Reac. Temp.	Time	Borneol	Velocity	Reaction Product	M. P.	$[\alpha]_D$	Oxime	Camphor	Yield	Unchanged borneol	M. P.
(9)	Cu I.	200°	90 m.	13·9 gr.	9·2 gr./h.	13 gr.	179 – 180°	+40°	1·8 gr.	1·6 gr.	80 %	0·3 gr.	183—184°
(10)	„	300°	20 „	19 „	57 „	18 „	189—190°	+36°·31	1·0 „	0·9 „	45 „	1·1 „	173—175°
(11)	„	200°	25 „	18·5 „	44 „	18 „	180—181°	+41°·13	1·8 „	1·6 „	80 „		
(12)	„	220°	35 „	18 „	31 „	17·9 „	176 – 177°	+40°·00	1·4 „	1·3 „	65 „	0·6 „	118 – 119°
(13)	Cu II.	220°	25 „	19 „	46 „	18·5 „	197 – 198°	+33°·1	0·3 „	0·2 „	10 „	1·6 „	180 – 181°
(14)	Cu III.	220°	25 „	18·5 „	44 „	17·5 „	178—179°	+40°·00	1·7 „	1·5 „	75 „	0·3 „	178—180°
(15)	Cu IV.	220°	30 „	17·5 „	35 „	16 „	177 – 178°	+37°·00	1·4 „	1·3 „	65 „	0·4 „	180°

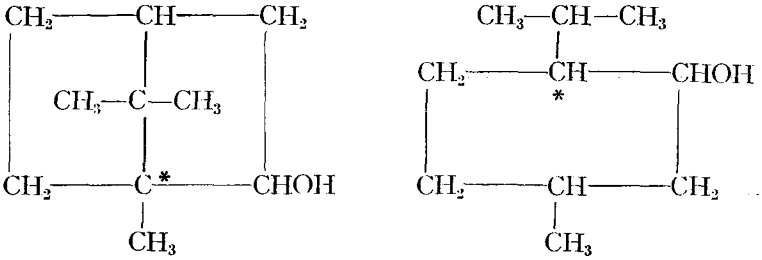
Table II.

No. of Expt.	Catalyst	Acetone	Camphor	Time	Velocity	Temp.	H	Product	M. P.	$[\alpha]_D$	Borneol	
											Phenyl Urethane	Acid Phthalate
(1)	Cu I.	–	25 gr.	4 h.	6 gr. h.	150—180°	16—20 cc./m.	24 gr.	167°	+46°·04	(—)	(—)
(2)	„	–	10 „	1·5 „	6 „	200°	„	9 „	173—174°		(—)	
(3)	„	–	15 „	1·5 „	10 „	250°	„	14 „	169—170°			
(4	„	–	12 „	1·5 „	8 „	300°	„	11·8 „	158—160°			
(5)	„	17 gr.	– „	4 „	4 „	220°	„	13 „	—			
(6)	„	70 cc.	15 „	3 „	5 „	250°	„	14 „	170—171°			
(7)	„	50 „	10 „	10 „	1 „	220°	„	10 „	165°			
(8)	5 gr. Cu I. + 5 gr. Ni.	–	13 „	5 „	3 „	180°	„	12·3 „	173 – 174°			

1 The oxidation of borneols (d-borneol and l-isoborneol) into camphor by the catalytic action of reduced copper is more effective in yield and simpler in manipulation than oxidation by chemicals.

2 d-Borneol and l-isoborneol in the catalytic action of reduced copper, are equally oxidized to camphor without any side-reaction such as the formation of camphene or bornylene as described by Neave. When menthol is passed over the same catalyst under the same condition as in the experiment (10) of Table I., as Prof. Komatsu and Kurata[1] have observed, it is converted mostly into menthone with a small yield of menthene. Such difference between borneol and menthol, in the formation of hydrocarbon due to the dehydration of alcohols, would be explained by the difference of the nature of the carbon atom (C* in Fig. 1.) neighbouring the CHOH- group in the molecule of borneol or menthol; in the former a quaternary carbon atom combined with the CHOH- group, while in the latter, a tertiary carbon atom instead of the quaternary one occupies the analogous position of the molecule, or as consequence of the difference in stability of the polymethylene ring—cyclohexane and cyclopentane—towards the dehydrating catalyst as in the case of the catalytic action of platinum black heated at 300—305°, on indene-octahydride as observed previously by N. D. Zelinsky and P. Borisson.[2]

3 In the catalytic oxidation of d-menthol in the presence of reduced copper, menthone, thus formed, suffers racemisation, as observed by Prof. Komatsu and Kurata,[3]



Borneol Menthol

Fig. I.

while camphor resulting from borneols by the same treatment as menthone, suffers no racemisation as will be seen from the specific rotatory power of the reaction products shown in Table I. This phenomenon may also be probably explained by the difference in chemical structure of menthone

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[1] Loc. cit.

[2] Ber. D. Chem. Ges., **57**, 2060 (1924).

[3] Loc. cit.

and camphor; in the former, there exists an asymmetric carbon atom neighbouring the carbonyl group, with which the isopropyl radical (R) and, the hydrogen atom are combined; while in the latter these atomic groups are lacking, and as a consequence, the racemisation of menthone should be attributed to the keto-enolic change $-RCH-CO- \rightleftarrows -RC=C(OH)-$ of the groups of a special nature in the molecule, which was brought about as already mentioned in the fifth paper of the same article, by the contact action of reduced copper used in the reaction.

4 When copper oxide prepared from copper nitrate and sodium hydroxide solution, was reduced with hydrogen at 200° and heated at 200–220,° it yielded a suitable catalyst for oxidizing borneols into camphor.

The reverse reaction of catalytic oxidation of alcohols—the reduction of ketones into secondary alcohols, was usually regarded as taking place by the catalytic action of reduced copper as in the case of reduced nickel,[1] though the activity of the reaction is much more predominant with the latter catalyst.

Prof. Komatsu and the present author[2] have observed, by passing d-camphor with hydrogen over reduced nickel heated at 180°, that the reduction proceeded further to form l-isocamphane instead of borneols as the main reaction product. From this result, the reduction of camphor to borneol in presence of reduced copper seems to take place to some extent.

Moreover, it was noticed by Armstrong and Hilditch[3] that acetaldehyde by reduction with hydrogen in the presence of reduced copper heated at 200–210° yields 88% ethyl alcohol. From these facts, one can naturally surmise that if the condition of reaction be properly attained, the catalytic hydrogenation of camphor with hydrogen in presence of reduced copper could be performed.

The author, therefore, has tried the following experiment expecting that borneol might be obtained from camphor by reducing with hydrogen, employing reduced copper instead of reduced nickel as catalyst. d-Camphor, which shows M. p. 174–176°, $[\alpha]_D = +40°.7$ in 2% alcoholic solution, is passed with pure hydrogen over reduced copper obtained from 10 gr. of its oxides above-mentioned. 2 gr. of the reaction product were treated

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[1] La catalyse en chi-mie organique, (1920) 6, 194, 251, 254.

[2] These Memoirs, **5**, 225 (1922).

[3] Proc, Roy. Soc., A, **97**, 259 (1920).

with phenyl isocyanate to transform borneol supposed to be formed by reduction, into its phenyl urethane and the excess of phenyl isocyanate and unchanged camphor in the reaction vessel was extracted with petroleum ether[1], (in Expt. 1. and 2.). In other experiments, to convert borneol only into its acid phthalate, the reaction product was treated with phthalic anhydride according to the direction of Haller.[2]

In experiments 1, 2, 3, and 4, reaction temperature, velocity of passing of camphor over reduced copper, are varied; in experiments 6, and 7, camphor was passed with acetone, having in mind that the reduction of camphor might be performed by induced action of the reducible substance which presents side by side with camphor in one reaction system; and in experiment 8, the mixture of equal quantities of reduced copper and reduced nickel (nickel oxide, prepared by ignition of its nitrate, and reduced with hydrogen at 280–300°) was used as catalyst, but in all cases no borneol was obtained.

In conclusion, the author wishes to express his hearty thanks to Prof. S. Komatsu for his kind guidance and valuable suggestions throughout this work and also to the Association for the Commemoration of the Tercentenary Anniversary of the Tosho-shrine for a research grant.

April, 1925. Laboratory of Organic- and Bio-Chemistry.

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[1] H. Meyer: Analyse und Konstitutionsermittlung Org. Verb., III Aufl., s. 566 (1916).

[2] C. R., **108**, 1308 (1889).