

Studies on Camphor Series, XI.  
Synthesis of Camphor, II.  
Preparation of Liquid and Solid Camphenes  
from Pinene Hydrochloride by the Catalytic  
Dehydrochlorination of Copper Oxides.

By

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It was noticed by Prof. S. Komatsu, C. Fujio and T. Yukitomo,<sup>1</sup> that camphene, by the action of finely divided copper oxide on pinene hydrochloride, was obtained with a yield of nearly 90 %.

Repeating the same experiment, it was observed that the activity of the dehydrochlorination of copper oxides, though they are prepared equally from copper nitrate solution and ammonia water, varies with the conditions under which they are prepared, and therefore, in this experiment, the preparation of camphene from pinene hydrochloride by using the following eight varieties of copper oxides as catalyst was studied.

Copper oxides.

CuO (I) Copper hydroxide gel was prepared according to the method suggested by Bemmelen<sup>2</sup> from a cupric nitrate and a potassium hydroxide solution, which was washed with water three times, filtered, dried on a tone-plate, and ignited on a sand-bath heated to 250°-300°. The density of the oxide was 5.8135.

CuO (II) This was prepared from crystalline copper hydroxide

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<sup>1</sup> Unpublished paper.

<sup>2</sup> Zs. anorg. Chem., **5**, 466(1894).

following Böttger's directions.<sup>1</sup> The greyish basic copper nitrate, prepared from cupric nitrate and 20% ammonia water, was boiled with a 6% sodium hydroxide solution. The brown-coloured hydroxide thus formed, was centrifuged, washed with water five times, and ignited at 250°–300°. Its density was 4.9504.

CuO (III) A blue-coloured, amorphous copper hydroxide<sup>2</sup> which was obtained by diluting an ammoniacal copper nitrate solution with water, was filtered, washed and ignited at 250°–300°; its density was 4.2832.

CuO (IV) A basic copper nitrate of grey colour, which was obtained by the action of 20% ammonia water on a boiling solution of copper nitrate, was ignited at 250°–300°. Its density was 5.4193.

CuO (V) A black cupric oxide was prepared from a copper nitrate solution and 20% ammonia water, following the directions suggested by Mellor.<sup>3</sup> Its density was 5.2543.

CuO (VI) This was prepared in a similar manner to CuO (IV), but in this case an excess of ammonia water was employed. The density of the oxide was 5.3630.

CuO (VII) This was prepared from copper nitrate by ignition at 250°–300°. It coloured brownish black, and its density was 5.7683.

CuO (VIII) A hot aqueous solution of copper nitrate is treated with an excess of a sodium hydroxide solution, the precipitate thus formed, was washed, filtered and ignited at 250°. The density of the oxide was 6.3814.

#### Experiment.

Pinene hydrochloride which melts at 127° and shows  $[a]_D = +35.67$  in an alcohol solution, was passed with a constant velocity over 8 gr. of the copper oxide mentioned above, heated at 220°.

As reaction proceeded, the colour of the catalyst changed from black or brown to yellow or yellowish grey, and water was noticed to form by the reaction, but no hydrogen chloride gas was evolved.

The reaction product was composed of oily and water layers which were weighed separately, and the latter was washed twice with a sodium carbonate solution, dried over anhydrous sodium carbonate, and then subjected to fractional distillation.

The physical and chemical properties of each fraction was studied, and the results are shown in the following tables. In the table, the fraction boiling at 150°–165° is assigned for camphene.

1 *Zs. anorg. Chem.*, **5**, 474 (1894).

2 *Bonsdorff: Ibid.*, **41**, 132 (1904).

3 *Comprehensive treatise on inorg. chem.*, vol. III, p. 132.

Table I.

Catalyst.	$d_4^{11}$	Wt. increased of CuO.	H <sub>2</sub> O formed.	Pinene-HCl used.	Velocity. gr./h.	Reaction product.	Yield of camphene.
CuO (I)	5.8135	3.5 gr.	1.5 gr.	20.6 gr.	27.4	16.0 gr.	63.4 %
CuO (II)	4.9504	3.5 "	2.0 "	20.9 "	20.9	18.0 "	74.6 "
CuO (III)	4.2832	1.9 "	1.5 "	20.8 "	28.0	17.5 "	72.5 "
CuO (IV)	5.4193	2.0 "	1.1 "	23.8 "	31.7	20.0 "	56.5 "
CuO (V)	5.2543	1.6 "	2.0 "	21.1 "	28.0	18.5 "	62.5 "
CuO (VI)	5.3630	2.4 "	2.0 "	20.4 "	20.4	18.0 "	71.5 "
CuO (VII)	5.7683	0.3 "	0.0 "	20.3 "	22.0	19.5 "	14.4 "
CuO (VIII)	6.3814	3.2 "	2.1 "	21.4 "	21.4	18.0 "	74.7 "

Table II.

(a) CuO (I).

Fraction.	Yield.	$n_D^{25}$	$d_4^{25}$	Remarks.	
				Cl.	Unsaturation
-150°	0.6 gr.	1.4610	/	-	+
150°-155°	5.1 "	1.4625	0.86370	trace	+
155°-160°	3.9 "	1.4645	0.86730	+	+
160°-165°	0.7 "	1.4699	0.88095	+	+
165°-166°	0.4 "	1.4746	/	+	trace
166°-	0.1 "	/	/	+	-

(b) CuO (II).

Fraction.	Yield.	$n_D^{25}$	$d_4^{25}$	Remarks.	
				Cl.	Unsaturation
-140°	1.5 gr.	1.3475	/	+	-
140°-150°	0.3 "	1.4605	/	+	+
150°-155°	2.1 "	1.4615	0.86012	-	+
155°-160°	7.0 "	1.4639	0.86248	-	+
160°-165°	2.9 "	1.4673	0.86731	trace	+
165°-170°	0.9 "	1.4721	/	+	+
170°-173°	0.5 "	1.4775	/	+	+
173°-	0.9 "	/	/	+	-

## (c) CuO (III).

Fraction.	Yield.	$n_D^{25}$	$d_D^{25}$	Remarks.	
				Cl.	Unsaturation.
140°-150°	0.9 gr.	1.4600	0.86348	+	+
150°-155°	3.6 "	1.4629	0.86418	+	+
155°-160°	5.4 "	1.4647	0.86488	+	+
160°-165°	2.0 "	1.4726	0.88148	+	+
165°-	2.0 "	/	/	+	-

## (d) CuO (IV).

Fraction.	Yield.	$n_D^{25}$		M. Pt.	Remarks	
		liq.	solid.		Cl.	Unsaturation.
150°-155°	2.8 gr.	/	1.4864	43°-44°	+	+
155°-160°	6.7 "	/	1.4882	44°-45°	+	+
160°-165°	1.1 "	1.4679	1.4880	47°-48°	+	+
165°-170°	1.4 "	1.4710	1.4897	58°-59°	+	-
170°-190°	1.9 "	1.4747	1.4891	/	+	-
190°-	2.3 "	/	/	/	+	/

## (e) CuO (V).

Fraction.	Yield.	$n_D^{25}$		M. Pt.	Remarks.	
		liq.	solid		Cl.	Unsaturation.
130°-150°	0.5 gr.	/	1.4873	44°-45°	-	+
150°-155°	1.6 "	/	1.4887	43°-44°	-	+
155°-160°	6.7 "	/	1.4873	44°-45°	-	+
160°-165°	1.6 "	1.4679	1.4896	46°-47°	+	+
165°-175°	0.3 "	1.4713	1.4905	59°-61°	+	+
175°-190°	1.1 "	1.4751	1.4899	89°-90°	+	-
190°	3.3 "	/	/	/	+	/

(f) CuO (VI).

Fraction.	Yield.	$n_D^{25}$		M. Pt.	Remarks.	
		liq.	solid.		Cl.	Unsaturation.
145°-150°	0.6 gr.	1.4626	1.4849	39°-40°	-	+
150°-155°	5.0 "	1.4639	1.4863	42°-43°	-	+
155°-160°	5.0 "	1.4655	1.4873	43°-44°	trace	+
160°-165°	0.9 "	1.4627	/	/	+	+
165°-175°	0.3 "	1.4727	/	/	+	+
175°-185°	0.5 "	1.4769	/	/	+	+
185°-	0.5 "	/	/	/	+	/

(g) CuO (VII).

Fraction.	Yield.	M. Pt	Remarks.	
			Cl.	Unsaturation.
130°-160°	1.3 gr.	52°-52°.5	+	+
160°-170°	1.0 "	54°	+	+
170°-180°	1.0 "	55°	+	-
180°-190°	1.5 "	/	+	-
190°-195°	1.5 "	/	+	-
195°-	8.5 "	/	+	-

(h) CuO (VIII).

Fraction.	Yield.	$n_D^{25}$	$d_4^{25}$	Remarks.	
				Cl.	Unsaturation.
-13°	2.7 gr.	1.3483	/	+	-
130°-154°	1.3 "	1.4602	0.85800	+	+
154°-160°	8.3 "	1.4633	0.86054	trace	+
160°-165°	3.0 "	1.4680	0.86582	+	+
165°-169°	1.4 "	1.4737	0.90628	+	+
169°-	0.9 "	/	/	+	/

As will be seen in the above tables, the catalytic activity of copper oxide on pinene hydrochloride, measured with the yield of camphene, is the same with CuO (II), (IV), (VI) and (VIII), and these catalysts could

be classified into two groups according to the physical state of the reaction product, camphene; one group denoted by A, to which CuO (I), (II), (VIII) and (III) belonged, by the catalytic action of the oxides of this group a liquid camphene resulted from pinene hydrochloride. The other oxides were included into the other group, denoted by B, the action of these catalysts, solid camphene with a small quantity of liquid modification was usually obtained.

The copper oxides of the B group are, on the whole, prepared by ignition of copper nitrate or basic copper nitrate, while those of the A group are prepared from copper hydroxide, precipitated with a sodium hydroxide solution, hence a trace of some sodium compound such as sodium nitrate would be expected to remain as an impurity in the catalysts of the A group by adsorption, which might exert some influence, in the forming of liquid camphene, on the catalytic action of the copper oxide. The same experiment was repeated by using CuO (IV) as catalyst, to which 1% sodium nitrate was added, but, contrary to my expectation, solid camphene was obtained with a yield of 63.4% as will be seen in Table III.

Table III.

Fraction.	Yield.	Cl.	Unsaturation
150°-155°	2.1 gr.	—	+
155°-160°	6.4 "	trace	+
160°-165°	1.8 "	+	+
165°-175°	1.0 "	+	+
175°-195°	2.0 "	+	—
195°-	2.2 "	+	/

When, however, dry hydrogen chloride gas alone passed for one hour over 5 gr. of copper oxides heated to 220°, it was noticed that in the case of the copper oxides of group A, the colour of the oxides changed from brown to yellowish grey, the weight of the catalyst increased, and water was formed; while no visible changes were produced in the case of those of B group, although both groups are capable of decomposing pinene hydrochloride into camphene under the same conditions. From these facts, it was anticipated some intimate relation might exist between the chemical reactivity of copper oxides with hydrogen chloride gas, and the physical states of camphene formed by the catalytic action

of the oxides on pinene hydrochloride.

Table IV.

Catalyst.	Weight increased.	Colour change.	
A {	CuO (I)	3.5 gr.	+
	CuO (II)	2.7 "	+
	CuO (III)	1.6 "	+
	CuO (VIII)	3.7 "	+
B {	CuO (V)	1.0 "	-
	CuO (VI)	0.4 "	-
	CuO (VII)	0.3 "	-

It has been already mentioned by Komatsu and C. Fujio<sup>1</sup> that solid and liquid camphene could be obtained separately from pinene hydrochloride by using same catalyst such as ferric chloride at different temperatures.

As a matter of fact, as will be seen in the present research, any modification of camphene may result from pinene hydrochloride by choosing a suitable copper oxide as catalyst, though the interpretation for the formation of these two modifications, at present, is lacking.

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<sup>1</sup> Mem. Coll. Sci. Kyoto Imp. Univ., 7, 389(1924).