

# Studies on Camphor Series, IV.

By

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## I. THE ELIMINATION OF HYDROGEN CHLORIDE FROM PINENE HYDROCHLORIDE AND BORNYL CHLORIDE.

In finding a suitable catalyst for the preparation of camphene from the corresponding terpene monochloride, the catalytic action of the chlorides of iron, copper, antimony, aluminium, barium, magnesium and phosphorus on pinene hydrochloride and bornyl chloride was investigated<sup>1</sup>.

Pinene was obtained from the turpentine oil (pharm. Jap.) by repeated fractional distillations on metallic sodium, the fraction B. p. 156–161°  $[\alpha]_D^{25} = -2.19^\circ$  was transformed into pinene hydrochloride by passing dry hydrochloric acid gas, and cooling with ice<sup>2</sup>.

It melts at 125°, showed  $[\alpha]_D^{25} = -4.72^\circ$  in alcohol solution.

Bornyl chloride was prepared from dextro-borneol M. p. 127°,  $[\alpha]_D^{25} = +17.21^\circ$  in alcohol solution (d-borneol 71.73% isoborneol

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<sup>1</sup> Refer W. F. Faragher and F. H. Garner: J. A. C. S., **43**, 1715 (1921); P. Sabatier and Mailhe: C. R., **138**, 407 (1904); **141**, 238 (1905); P. Sabatier and Sanderens: Ibid., **146**, 1211 (1908); J. Nef: Lieb. Ann., **318**, 1 (1901); O. Wallach: Lieb. Ann., **259**, 6 (1887); O. Aschan: Ber. D. Chem. Ges., **40**, 2750 (1907); Lieb. Ann., **387**, 27 (1912); **410**, 222 (1915); J. Kondakow: J. prak. Chem., **54**, 452 (1896).

<sup>2</sup> B. T. Brooks: The Non-benzenoid Hydrocarbons, 439 (1922).

28.27%), and phosphorus pentachloride, which melts at 148°, and showed  $[\alpha]_D^{25} = +12.93^\circ$  in alcohol solution.

In the experiment, 1 gram. of the sample was mixed with 2 gram. of the catalyst in a sealed tube and heated at a temperature of 100° and 200° by means of a water bath or an air bath. After heating for a certain time, the reaction product was subjected to steam distillation, and the amount of unsaturated hydrocarbon which resulted as a dechlorinated product, and was distilled with steam, was calculated from the iodine number estimated as usual. The results are shown in the following table:

Pinene hydrochloride  
100°  
yield (in %)

Times (in Minutes)	FeCl <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub>	BaCl <sub>2</sub>	MgCl <sub>2</sub>	SbCl <sub>3</sub>	PCl <sub>3</sub>
10	60	20	23	—	32	60	—
20	70	17	31	—	32	62	—
30	55	17	33	14	—	64	35
60	43	17	44	19	35	56	90
90	40	18	29	16	35	48	80
120	65	17	44	19	—	60	79
150	25	15	33	—	—	—	—
180	20	—	27	—	—	—	—
210	25	—	26	—	—	—	—

Pinene hydrochloride  
200°  
yield (in %)

Times (in Minutes)	FeCl <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub>	BaCl <sub>2</sub>	MgCl <sub>2</sub>	SbCl <sub>3</sub>	PCl <sub>3</sub>
15	25	56	39	0	31	15	—
30	28	44	56	0	—	18	—
60	18	29	50	0	25	11	—
90	18	15	32	0	21	11	—

Bornyl chloride and  $\text{FeCl}_3$   
yield (in %)

Times (in Minutes)	100°	200°
10	2	0
20	3	0
30	4	1
60	3	0.5
90	5	0
120	3	0
150	3	0
180	6	0
210	6	0
240	2	0

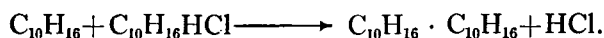
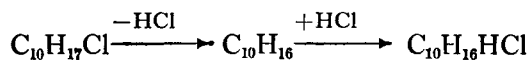
As seen in the foregoing table, ferric chloride is the most active catalyst up to 100°, while a higher temperature, such as 200°, alumina and aluminium chloride serve more effectively than other catalysts.

As we had previously discovered in the case of the reaction between aniline and monochloroacetic acid<sup>1</sup>, the reaction in a closed vessel is more complicated than that in an open vessel; unsaturated hydrocarbon formed by the dechlorination, remaining in the reaction tube with hydrochloric acid, unchanged chloro compound and the catalyst, is apt to recombine on one hand with hydrochloric acid, forming camphene hydrochloride which will be soon transformed into stable isobornyl chloride<sup>2</sup>, and on the other hand, to react with the chloro compound remaining unchanged or formed by isomeric change by virtue of the catalyst as in the case of Friedel-Crafts' reaction, generating a condensed hydrocarbon of higher molecules<sup>3</sup>, as will be shown in the following schemes:

<sup>1</sup> S. Komatsu and R. Nodzu: *These Memairo*, **6**, 73 (1922).

<sup>2</sup> H. Meermein and K. van Emster: *Ber. D. Chem. Ges.*, **53**, 1815 (1920).

<sup>3</sup> K. Bartelt: *Terpene u. Campherarten*, 110 (1908); J. Kachler: *Ber. D. Chem. Ges.*, **2**, 510 (1869); J. Kondakow: *J. prak. Chem.*, **54**, 452 (1896); K. G. Falk: *Chem. Reaction*, 95 (1920).



Thus, the catalyst serves to separate the hydrogen chloride from the pinene hydrochloride or bornyl chloride forming in the way camphene which is added to the unchanged pinene hydrochloride or bornyl chloride by the influence of the same catalyst to form a compound such as dibornylene.

Moreover, the catalyst will play a role as polymerising agent of the unsaturated hydrocarbon to condense to higher molecule content.

Accordingly, it was anticipated that when the reaction proceeded, the yield of volatile unsaturated hydrocarbon would be gradually diminished with time. Such a hypothesis harmonizes with the experimental results as seen in the table. For confirmation of the hypothesis, we tried to isolate the compound which was considered to be formed from camphene and camphene hydrochloride or bornyl chloride and actually we succeeded in getting a hydrocarbon of the molecular formula  $\text{C}_{20}\text{H}_{32}$  from the reaction product.

25 gm. pinene hydrochloride and 25 gm. ferric chloride were heated in a sealed tube at  $100^\circ$  for one hour, the reaction product was subjected to steam distillation and the non-volatile substance remaining in the flask was a dark brown mass which was extracted with ether. On distilling off the solvent, there remained a brown viscous oil which distilled out from  $320^\circ$  to  $340^\circ$ ; the yield was 1.2 gm. After repeated fractional distillations on metallic sodium, the fraction boils at  $208\text{--}210^\circ$  10 mm., was analysed :

C=88.93 ; 89.13 ; H=11.23 ; 11.44.  $n_D^{20} = 1.5304$  ;  $d_4^{20} = 0.9649$ .

The analytical figures agree with C=88.88 ; H=11.12 for  $\text{C}_{20}\text{H}_{32}$ .

When bornyl chloride was used instead of the pinene hydrochloride, the product had the same appearance as that obtained from pinene hydrochloride, boiled at 189°, 12 mm., and gave on analysis the following results:

C=89.40; H=10.34.  $d_4^{25^\circ}=0.9633$ ;  $n_D^{25^\circ}=1.5285$ .

Moreover, the molecular weight determination of the first sample in benzene solution showed M. W.=283 which agrees the required value for  $C_{20}H_{32}$ .

On reduction with hydrogen, 0.1499 gm. of the substance absorb 12.3 c.c. hydrogen in presence of colloidal palladium, which indicate it contains one ethylene bond in the molecule as we expected.

## II. SOLID AND LIQUID MODIFICATIONS OF CAMPHENE.

In the previous article, one of the authors (S. Komatsu) and R. Nakai<sup>1</sup> have reported that there exist two modifications of camphene, one, liquid at ordinary temperature B. p. 158–162°,  $d_4^{25^\circ}=0.8613$ ;  $d_D^{15^\circ}=1.4689$  and the other, a solid M. p. of 50°.

According to Brühl<sup>2</sup>, camphene is prepared from pinene hydrochloride, melting at 51–52°, B. p. 158.5–159.5°,  $n_D^{25^\circ}=1.4551$  and the same substance derived from bornyl chloride, melting at 53.5–54°,  $d_4^{58^\circ}=0.83808$ ;  $n_D^{58^\circ}=1.54314$ .

The authors, therefore, intended to get two modifications of camphene from one and the same substance, and compare their physical properties, and whereby to ascertain the nature of the modifications.

50 gm. of pinene hydrochloride were heated with 10 gm. anhydrous ferric chloride in a flask with reflux condenser at 210–215° for 1½ hours, and the reaction product was subjected to distillation. The product collected between 150–164°, was washed with water and

<sup>1</sup> These Memoirs: **6**, 70 (1922).

<sup>2</sup> Ber. D. Chem. Ges., **25**, 147, 160 (1892).

distilled on metallic sodium after drying with sodium sulphate as usual. The yield of fraction B. p. 150–165°, was 25 gm., 160 gm. of the hydrocarbon, thus obtained, were fractionated under ordinary pressure into 10 portions, and each portion was analysed and its properties determined.

Fractions	Yield	$n_D^{25^\circ}$	$d_4^{25^\circ}$	C	H
145–150°	8.5	1.4550	0.84834	87.53	12.37
150–152	14.0	1.4574	0.85224	86.69	12.07
152–154	36.5	1.4597	0.85560	87.41	11.98
154–156	15.5	1.4621	0.85838	87.62	12.08
156–157	18.0	1.4629	0.85868	87.33	11.83
157–158	18.0	1.4639	0.85974	87.64	11.94
158–159	5.0	1.4642	0.85886	87.64	12.13
159–162	12.0	1.4651	0.85838	87.06	12.04
162–164	5.0	1.4667	0.85828	87.17	12.02
above 164	4.5	1.4696	0.85806	—	—

Cal. for  $C_{10}H_{16}$  88.12 11.88

Cal. for  $C_{10}H_{18}$  86.95 13.05

When pinene hydrochloride was dechlorinated with the same catalyst at a lower temperature 125–135°, it yielded as a result a solid hydrocarbon with the same composition as liquid camphene.

The reaction product obtained by the interaction of 25 gm. pinene hydrochloride and 10 gm. ferric chloride at 125–135° for 1½ hours, which was distilled and collected, the fraction boiling to 195°. The boiling point of the product by heating with metallic sodium was found to be depressed from 170–195° to 150–165°. From 140 gm. of the reaction product, 25 gm. of the liquid substance and 115 gm. of the solid were separated.

The solid substance was fractionated into 7 portions and each fraction distillation 13 times, was analysed.

Fractions	Yield	M.p.	C	H
to 152°	3.5			
152—154	10.5	42—37	87.37	12.15
154—155	12.0	49—50	87.37	11.97
155—156	14.5	56—57	87.28	11.98
156—157	12.5	60—61	87.87	12.01
157—158	12.0	65—67	87.42	11.78
158—159	2.0	—	—	—
above 159	3.5	—	—	—

Calc. for C<sub>10</sub>H<sub>16</sub> 88.12 11.88

Calc. for C<sub>10</sub>H<sub>18</sub> 86.95 13.05

Fractions	n <sub>D</sub> <sup>58°</sup> (Liquid)	n <sub>D</sub> <sup>58°</sup> (Solid)
152—154°	1.4432	1.4415
154—155	1.4443	1.4657
155—156		1.4662
156—157	1.4478	1.4665
157—158	1.4478	1.4678
158—159	1.4485	1.4687

Fractions	d <sub>4</sub> <sup>25°</sup> (Liquid)	d <sub>4</sub> <sup>25°</sup> (Solid)	n <sub>D</sub> <sup>70°</sup> (Liquid)	n <sub>D</sub> <sup>70°</sup> (Solid)	M. p.
152—154°	0.82260	0.82318	1.4367	1.4351	42—47
154—155	0.82556	0.82498	1.4376	1.4361	49—50
155—156		0.82615		1.4370	56—57
156—157	0.82585	0.82674	1.4385	1.4380	60—61
157—158	0.82615	0.82733	1.4400	1.4394	65—67

The physical constants of some fractions of the liquid modification were measured at 25°, 58° and 70°, and the results were compared with those of the corresponding fractions of the solid.

Further researches are required to attain the desired conclusion about the true nature of these modifications, and these researches will be undertaken in our laboratory.

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