

Researches on Camphor, Borneol and Their Allied Substances.

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(1) **Catalytic Reduction and Oxidation of Camphor, Borneol and Their allied Substances.** According to the researches by Aloy and Brustier⁽¹⁾ camphor is obtained quantitatively by passing borneol over copper heated to 300°C, and Neave⁽²⁾ under the reaction condition akin to that of Aloy and others, obtained *d*-camphor from *d*-borneol but camphene from isoborneol. Later, Masumoto⁽³⁾ observed that catalytic oxidations of borneol into camphor by reduced copper differ according to the manufacturing process of the latter.

A sample of copper (1) was obtained by reducing copper oxide which was gained from copper nitrate and sodium hydroxide. When this copper was used as a catalyser, the yield of camphor from borneol was at its best at 200°C amounting to 80%, while at 300°C the yield decreased to its half. On the other hand when copper (2) obtained by reducing copper oxide which was gained by using ammonium hydroxide instead of sodium hydroxide was used as a catalyser, the yield of camphor hardly reached 10% even under the best condition. Copper (3) was made according to Sabatier's process by reducing copper oxide which was gained by heating copper nitrate. When this catalyser was used, the results were generally satisfactory, the yield of camphor amounting to 75%. Ikeda⁽⁴⁾ reports that when isoborneol was passed over reduced copper prepared by Sabatier's process, only dehydration occurred, and at 130°–140°C, 90% of the isoborneol was changed to camphene.

Isoborneol, inspite of its being a secondary alcohol, is promoted to dehydrate under the catalytic reaction of metals, and thus behaves unlike borneol. In order to investigate more closely the behaviour of the two isomers, the writer, just as Masumoto did, used the three kinds of copper and examined its catalytic reaction upon borneol at 400°C. The result showed that copper (1) yielded camphor quantitatively, copper (2) yielded camphor and camphene in the proportion of 80:20, and copper (3) of 87:13. It seems, therefore, that copper (1) promotes only oxidation of borneol, while coppers (2) and (3), not only oxidation but to some extent dehydration. On the other hand, isoborneol under the catalytic reaction of copper (1) at 150°C and also at 300°C yielded camphor as a reaction product in each case, and with copper (2) at 150°C all of the isoborneol was changed to camphene, and at 300°C camphor and camphene were formed in the proportion of 24:76. In short, copper (1) acts against isoborneol as to promote oxidation independent of the reaction tempera-

(1) *Bull. Soc. Chim.*, [4] **9** (1911), 733.

(2) *J. Chem. Soc.*, **101**, 513.

(3) *Memoirs Coll. Sci. Kyoto Imp. Univ. A.* **9** (1925), 219.

(4) *Bull. Institute Phys. Chem. Research*, **4** (1925), 343.

ture, while copper (2) promotes dehydration at low temperatures, but oxidation as the temperature is raised. Therefore, for the purpose of synthesising camphor from borneol and isoborneol copper (1) seems to be the most appropriate catalyser.

The fact that nickel as a catalyser plays an analogous role as copper does has often been pointed out, and according to two patents⁽⁵⁾ regarding the action of reduced nickel toward borneol and isoborneol, reduced nickel is almost or completely defective of the power to promote oxidation, but when small quantity of either caustic soda, sodium nitrate or sodium sulphate is added, the oxidation is very strongly promoted. The writer examined the catalytic action of reduced nickel toward borneol and isoborneol and found that though oxidation is promoted, there is some difference in the reaction conditions compared with those in the case of reduced copper.

With respect to the catalytic reduction from camphor to borneol and isoborneol, Komatsu and Masumoto⁽⁶⁾ obtained isocamphane besides small quantity of borneol by reducing camphor in the stream of hydrogen at 180°C under the catalytic reaction of reduced nickel,⁽⁷⁾ and Ipatiev,⁽⁸⁾ using nickel oxide as a catalyser, tried the reduction in an atmosphere of hydrogen under the pressure of 129 atms. and at 200°C, and obtained borneol and isocamphane. Further, Kubota and Hayashi⁽⁹⁾ reported that using reduced copper as a catalyser, camphor was reduced under high pressure of hydrogen and at high temperatures to borneol and isoborneol in the range of proportion from 29:71% to 21:79%. Vavon⁽¹⁰⁾ inferred that by the reduction of camphor isoborneol is formed at first and then this undergoes a rearrangement to form borneol.

The writer using reduced nickel as a catalyser submitted camphor to the catalytic reduction with hydrogen at high temperature and high pressure and found that at about 180°C the proportions of borneol and isoborneol formed were 51:49, 50:50, 47:53 when the pressure of hydrogen were 23, 49, 85 atms. respectively; and when the reaction temperatures were 140–160°C, and 170–190°C the proportions of formation of both of the isomers were 51:49 and 47:53 respectively (cf. Fig. 1–5). When the temperature of reaction is raised above 200°C, hydrogen is absorbed more than 1 mole, and it seems that the alcohol formed at first is subsequently dehydrated and reduced successively, and as a matter of fact isocamphane and a small quantity of water were formed as reaction products (cf. Fig. 6–7). This fact can be explained by deciding experimentally the temperatures of dehydration of borneol and isoborneol; the writer's experiment shows that borneol is dehydrated at 220–260°C and isoborneol

(5) Schering, D.R.P., 219043 (1908); cf. D.R.P. 219044 (1908).

„ D.R.P., 211147 (1908); cf. D.R.P. 271157 (1909).

(6) *Mem. Coll. Sci. Kyoto Imp. Univ.*, **5** (1922), 225.

(7) O. Aschan, "Naphth. Therp. Campherarten" p. 152, 1929; D.R.P. 213154 (1907); *Chem. Zentr.*, **1909**, II, 1025.

(8) *J. Russ. Phys. Chem. Soc.*, **38** (1906); *Chem. Zentr.*, **1906**, II, 87; *Ber.*, **45** (1912), 3212.

(9) *Bull. Chem. Soc. Japan*, **1** (1926), 69.

(10) G. Vavon and P. Peignier, *Bull. soc. chim.*, **39** (1926), 924; *Compt. rend.*, **181** (1925) 183; *P. Lipp, Ber.*, **68** (1935), 1029.

at 160–190°C. From this it is to be seen that the dehydration temperature of isoborneol being in close vicinity of the temperature adequate to the reduction of camphor, the reduction is usually accompanied by the dehydration (cf. Fig. 8–10).

In order to investigate how the yield of catalytic reduction is influenced by the introduction of solvents, cyclohexane as a non-polar substance on the one hand, and absolute alcohol, acetic acid and pyridine as polar substances on the other hand, were used, and the proportions of borneol and isoborneol formed were 23:77, 12:88, 37:63, 36:64 respectively (cf. Fig. 11–15). In the above case, the introduction of solvents increased remarkably the yield of isoborneol, but any relation between this increase and the polarity of solvents is barely recognisable. The addition of absolute alcohol raised the yield of isoborneol, and yield of some 90% was gained.

When camphor (I) is reduced with metallic sodium and ethyl alcohol, borneol is formed mainly, and when camphor is catalytically reduced with metallic catalyser and hydrogen in alcoholic solution the main product is isoborneol. Epi-camphor (II), when reduced with metallic sodium and alcohol gives epi-borneol only, and when catalytically reduced with platinum black and hydrogen in acetic acid solution it gives epi-isoborneol.⁽¹¹⁾ Nor-camphor (III) gives nor-isoborneol when reduced either with metallic sodium and alcohol or with palladium chloride, platinum colloid and hydrogen in alcoholic solution.⁽¹²⁾ This may be due to the fact that the molecular construction of nor-camphor differ from those of camphor and epi-camphor, and a mobile hydrogen is linked with the α -carbon adjacent to C=O group. Then as the chemical constitution of dimethylcamphor, (IV) differs from that of nor-camphor, having in the α -position CH_3 substituted for the mobile hydrogen, under the expectation that dimethylcamphor unlike nor-camphor may form a derivative of borneol as the reduction product, the writer synthesised, according to Haller's process,⁽³⁾ α , α' -dimethylcamphor from camphor and then reduced it with metallic sodium and alcohol. Thus two kinds of alcoholic compounds A and B were gained in the proportion 88:12, as shown in the following table.

As to the stereochemical configuration of the two alcohols formed, just like in the case of borneol and isoborneol, the less easily dehydrated was defined as dimethylborneol and the easily dehydrated as dimethylisoborneol. Now, dimethylcamphor was heated in hydrogen under 60 atms. at 220–230°C in the presence of reduced nickel and it was found that this reduction was much more difficult than that of camphor, the yield of alcohol being only 19% even after about 27 hours. The proportion of dimethylborneol and dimethylisoborneol formed being 85:15, it was almost the same as when the reduction was done with metallic sodium and alcohol (cf. Fig. 16). When the catalytic reduction was done by adding absolute

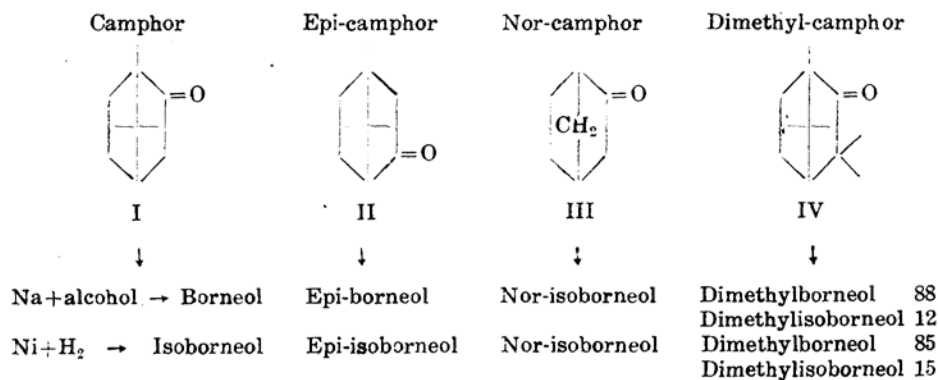
(11) M. Lipp geb. Bredt Savelsbery, E. Bund. Ber., **68** (1935), 249; cf. Bredt and Perkin, *J. prakt. Chem.*, [2] **89** (1914), 254.

(12) Komppa and Beckmann, *Ann.*, **512** (1934), 174; Alder and Stein, *Ann.*, **514** (1934), 220.

(13) *Compt. rend.*, **148** (1909), 1645.

Substance	A	B
B. p.	90.5~93/5 mm	82~83/3 mm
M. p.	57°C	47~49°C
[α] _D	+50.72° (in alcohol) at 26° +53.76° (in toluene) at 26°	+36.47° (in alcohol) at 15° +42.71° (in toluene) at 15°
Phenylurethane	112–113°C	116–117°C
<i>p</i> -Nitrobenzoate	Needle crystal of silky luster and of faintly greenish white colour. 115–115.8°C	Nearly colourless and lustrous needle crystal. 114.5–115°C
Phthalic acid monoester	Fine, white needle crystal 177–178°C	Lustrous, fine scaly crystal 173–174°C
Magnesium phthalate	Lustrous white scaly crystal 175–176.2°C	Crystalline white powder 180–182°C
Reacting with ZnCl ₂ or with phthalic anhydride	Not dehydrated	Dehydrated

alcohol or a little acetic acid, the proportions of both of the isomers produced were 66:34 and 86:14 respectively, and the use of absolute alcohol as a solvent increased the yield of iso-compound as in the case of camphor (cf. Fig. 17). When the reduction temperature was raised to 260°–280°C, more than 1 mole hydrogen was absorbed dehydration occurred, and hydrocarbon was formed (cf. Fig. 18).



(2) **Isomeric Change between Borneol and Isoborneol.** Applying the aforesaid method of separation⁽¹⁴⁾ of borneol and isoborneol to the crude isoborneol (90%), gained by the catalytic reduction of camphor in alcoholic solution, isoborneol which may be considered pure was obtained, and its properties were compared with those of its isomer, borneol.

(14) *J. Chem. Soc. Japan*, **53** (1932), 807.

	M.p.	$[\alpha]_D$	$[\alpha]_D^{15}$		
Borneol	204–204.5°C (in a sealed tube)	+38.10°C = 3.57 (in alcohol, at 11°)	+38.44°C = 3.92 (in toluene)		
Isoborneol	212–213°C (in a sealed tube)	–34.42°C = 3.35 (in alcohol, at 7°)	–19.59°C = 5.17 (in toluene)		
Acetate					
	Combustion heat	B.p.	d_4^{20}	n_D^{20}	$[\alpha]_D$
Borneol	Kcal/mol 1489.3	98/11 mm	0.9864	1.4655	+42.75° at 11°
Isoborneol	1472.5	76–77/3 mm	0.9867	1.4623	–51.98° at 18°
Magnesium phthalate			Methoxy value after etherification with HCl—methyl alcohol		
	M.p.	$[\alpha]_D^{15}$			
Borneol	103–104°C	+31.9°C = 1.99 (in alcohol)	0.42		
Isoborneol	95–97°C	–29.46°C = 4.0 (in alcohol)	12.5		

Borneol and isoborneol being stereoisomers of *cis*- and *trans*-form,⁽¹⁵⁾ a transformation from one into the other may be possible as we expect from heats of combustion of the two isomers. And hitherto the transformation of isoborneol into borneol was accomplished by adding alkaline metal to the solution of isoborneol in alcohol, in xylene or in ligroin and then it was heated under pressure;⁽¹⁶⁾ otherwise the solution in cyclohexane was heated to about 200°C in the presence of nickel catalyser with hydrogen under 30 atmos.⁽¹⁷⁾ When isoborneol was heated for about 4 hours in the presence of reduced nickel under 50 atm. hydrogen at 130–150°C and 140–165°C, 16% and 51% of the sample was changed to borneol in each case; conversely it was seen that only 1% of borneol was transformed to isoborneol, when heated for about 20 hours in the presence of reduced nickel under 70 atm. hydrogen at 170–190°C (cf. Fig. 19). Further, when each of the solutions of borneol and isoborneol in absolute alcohol was heated for 20 hours in the presence of reduced nickel under 70 atms. hydrogen at 150–160°C and 130–140°C respectively, 10% of borneol was transformed to isoborneol and 11% of isoborneol to borneol (cf. Fig. 20–21).

(3) **Dehydration of Borneol and Its allied Substances.** Formerly dehydrating agents used for the dehydration of borneol and isoborneol

(15) Vavon and Peignier, *Bull. soc. chim.*, [4] **39** (1926), 666, 924; Hüchel, *Ann.*, **477** (1930), 157.

(16) Wagner and Brickner; *Chem. Zentr.*, **1909**, II, 25; Schmitz & Co., D.R.P., 212, 908; *Chem. Zentr.*, **1909**, II, 1392.

(17) H. Sandkühl, Rhein. Kampf. Fabr. Düsseldorf–Oberkassel. D.R.P., 408666, *Chem. Zentr.*, **1925**, I, 1809.

were zinc chloride, phosphorus pentoxide, potassium bisulphate, sulphuric acid, oxalic acid, glacial acetic acid, phthalic anhydride and active carbon; and although isoborneol forms easily camphene, the dehydration of borneol is very difficult, and therefore the reaction has been utilized to distinguish these two isomers. But, if an adequate reagent is found, the dehydration of borneol may be executed. Therefore, for the dehydration of borneol and isoborneol the writer used $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, which Sendrens⁽¹⁸⁾ recommended as a good dehydrating agent for alcohol. When 0.07 mol of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ was added to 1 mol of isoborneol and the mixture was heated at 140–145°C for 10 hours, dehydration occurred easily and 56% camphene and 18% ether compound of high boiling point were obtained; borneol, under the same condition, gave 63% camphene and 12% ether.

No.	Substances	Method of preparation	M.p. °C	B.p. °C	d_4	n_D	$[\alpha]_D$
1	Di- <i>d</i> -bornyl-ether ⁽¹⁹⁾	Dehydration with ZnCl_2	43–44	317/753 mm	—	45°C 1.4810	18°C +65.6°
2	Di- <i>l</i> -bornyl-ether ⁽²⁰⁾	Dehydration with conc. H_2SO_4	liquid	312–314	18°C 0.9600	24°C 1.4940	—88.56°
3	Di- <i>d, l</i> -isobornylether ⁽²¹⁾	Action of conc. H_2SO_4 to camphene	90–91	322	—	—	—
4	Di- <i>d</i> -bornyl-ether	Dehydration with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	liquid	134–137/2 mm	20°C 0.9564	20°C 1.4927	27°C +41.68°
5	Di- <i>d, l</i> -isobornylether	„	„	134–145/2 mm	20°C 0.9672	20°C 1.5010	—

In addition, when dry alumina is acted on borneol at 350°C dehydration occurs and a good yield of racemic camphene is obtained.

By dehydrating borneol $[\alpha]_D + 18.62^\circ$ and isoborneol $[\alpha]_D - 15.72^\circ$ with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, there were obtained solid camphenes $[\alpha]_D + 3.3^\circ$ and $[\alpha]_D + 4.35^\circ$ respectively; and by dehydrating isoborneols $[\alpha]_D - 15.72^\circ$ and $[\alpha]_D - 34.42$ with phthalic anhydride, solid camphenes $[\alpha]_D + 25.25$ and $+49.33$ were obtained respectively. The rotatory powers of camphenes thus formed were seen to be influenced both by the time and temperature of reaction. And, in order to find out the cause of this change in the rotatory power of camphene, active camphene was directly treated with alumina, phthalic anhydride, hydrochloric acid, $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, 50% H_2SO_4 and acetic acid, and in each case the rotatory power decreased gradually and it was recognised that the velocity of racemisation was affected not only by the time and temperature of reaction but also by the kind, concentration, and quantity of the acid itself. When bornyl acetate was set to reaction of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ for 10 hours at 140–145°C, both isomerisation and dehydration occurred and 0.5 mol % isobornyl acetate and 3 mol % camphene were obtained; again when treated under the same conditions, 75 mol % isobornyl acetate

(18) Sendrens, *Compt. rend.*, **154** (1912), 1168; *ibid.*, **177** (1923), 1183.

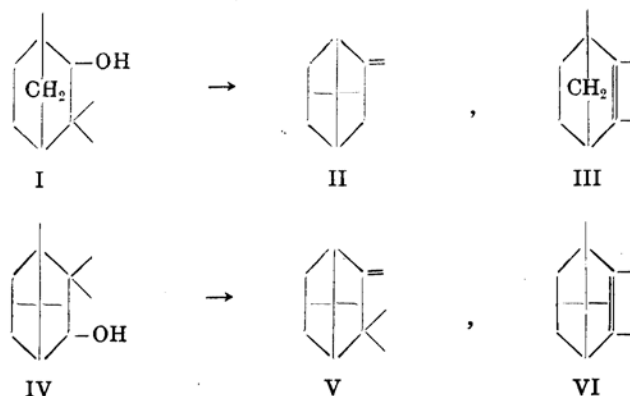
(19) Tetsusaku Ikeda, *J. Chem. Soc. Japan*, **48** (1927), 491.

(20) Gulbew, *Chem. Zentr.*, **1913**, I, 24.

(21) Bouchardat and Lafont, *Bull. soc. chim.*, [3] **11**, 902.

changed into camphene. Camphene in acetic acid solution changed as much as 50 mol % into isoboryl acetate, when treated under the same conditions.

Some time ago, Toivonen and Tikkanen⁽²²⁾ obtained a mixture of α -fenchene (II) and methylsantane (III) by dehydrating fenchyl alcohol (I) with aluminium phosphate. Hence, it is suspected that the hydrocarbons obtained by dehydrating dimethylborneol (IV), which has a chemical constitution similar to that of fenchyl alcohol, may be camphene form (V) and bornylene form (VI), as will be shown below:



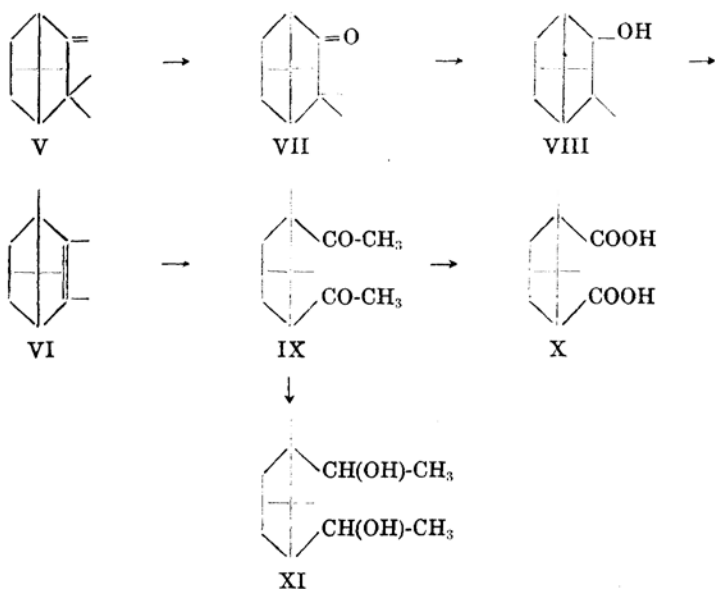
When dimethylborneol was heated with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ at $140\sim 145^\circ\text{C}$ for over 10 hours, a mixture of hydrocarbons (B.p. $48\sim 82^\circ/5\text{ mm.}$) was obtained, the yield being 71%. When dehydrated with phosphorus pentoxide, a single hydrocarbon (VI) (b.p. $192\sim 193^\circ\text{C}$, $d_4^{25} 0.8754$, $n_D^{25} 1.4765$, $[\alpha]_D^{19} -5.76^\circ$) was obtained; and when dehydrated with phthalic anhydride, a product to be suspected as a mixture of hydrocarbons was obtained, but as the sample was too scanty, further study could not be executed. The hydrocarbons obtained by dehydrating with $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ were most probably a mixture of two hydrocarbons; but as it was impossible to separate it into its components even after eight fractional distillations, the writer tried anew to separate it in the form of oxidised compound, by submitting its chloroform solution to ozone oxidation. As its result, two compounds were obtained:

Subs.	B.p.	d_4^{25}	n_D^{25}	$[\alpha]_D$	Remarks
A	72-73/6 mm	0.9473	1.4712	$+27.06^\circ$ at 9°C	Colourless
B	120-123/6 mm	1.0087	1.4746	-6.87°	Yellowish green, viscous, easily decomposes during distillation.

Substance A, as it forms semicarbazone (M.p. $243.6\sim 243.9^\circ\text{C}$), and gives a product to be considered as alcohol VIII (B.p. $82\sim 86^\circ/5\text{ mm.}$, d_4^{25}

(22) *Chem. Zentr.*, 1931, II, 2150.

0.9581, n_D^{25} 1.4831, $[\alpha]_D +1.5$) when reduced with metallic sodium and alcohol, might be a monoketone (further confirmation was desirable, but as the sample run short we postponed it to the future.) Substance B was inferred to be a diketone (IX), as it is changed to camphoric acid (X) by the oxidation with nitric acid of sp. gr. 1.29 or by decomposition during distillation, and also as it gives three kinds of what may be considered as glycol isomers (XI) when reduced with metallic sodium and alcohol. The reactions are shown by the following scheme:



In addition, when the mixture of hydrocarbons was oxidised with ozone in a solution of benzene, the following substance of the physical constants, to be considered as a dextro-rotatory diketone, was obtained.

B.p. 112-114°/4 mm	d_4^{25} 1.0166	n_D^{25} 1.4749	$[\alpha]_D +38.91^\circ$
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The content of the A- and B-compounds in the product of ozone oxidation was determined to be in the proportion of 43:57. Borneol and isoborneol, when dehydrated, give chiefly camphene alone; while dimethylborneol, a substitution product of methyl radical in place of α -hydrogen, forms hydrocarbons of both camphene and bornylene forms after dehydration.

(4) **Hydration of Camphene.** Camphene, by the hydration with a mixture of 50% H_2SO_4 and glacial acetic acid, gives in addition to isoborneol about 10% of borneol. Camphene $[\alpha]_D +72.69^\circ$, obtained by the process of A. Reychler,⁽²³⁾ was hydrated with 50% sulphuric acid and glacial acetic acid for 1/3 hour, and there was formed isoborneol $[\alpha]_D -10.56^\circ$. During this reaction, as the time of reaction was prolonged, the

(23) A. Reychler, *Ber.*, **29** (1896), 696.

rotatory power decreased gradually; and after the elapse of 110 hours the isoborneol obtained was quite inactive.

Camphene $[\alpha]_D + 8.28^\circ$ when treated separately with 50% sulphuric acid and glacial acetic acid, gave camphene of $[\alpha]_D + 5.20^\circ$ in the former case and of $[\alpha]_D + 6.22^\circ$ in the latter; while isoborneol $[\alpha]_D \pm 0^\circ$ was formed when treated with the mixture of the two acids. Further, isobornyl acetate $[\alpha]_D - 47.81^\circ$ was treated with 50% sulphuric acid, glacial acetic acid, and their mixture. When each of the acids was used separately, no appreciable change in the rotatory power of the ester was seen although the reaction was continued for 3 hours; however, when the acid mixture was used, even after the reaction of only $1/3$ hour, there was seen appreciable change in the rotatory power of the ester, and the longer the time of reaction, the more remarkable was the change.

Conclusion.

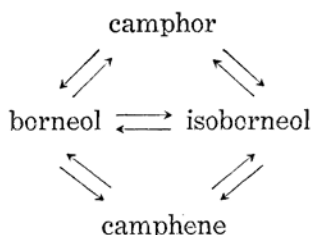
Camphor, when reduced, forms borneol and isoborneol, and both of them change into camphor when oxidised. Camphor and epicamphor form mainly borneol and alcohol of borneol type respectively when reduced with metallic sodium and alcohol, and mainly isomeric alcohol corresponding to it when reduced with metallic catalyser and hydrogen, while nor-camphor in these cases gives constantly alcohol of isoborneol type as a main product. On the other hand, dimethylcamphor always forms alcohol of borneol type as a reduction product due to the asymmetric synthesis.⁽²⁴⁾

Vavon⁽²⁵⁾ has inferred that by the reduction of camphor, isoborneol is formed, which is soon transformed into borneol. This inference of Vavon that isoborneol is transformed into borneol was confirmed by the writer's experiment, and it was also recognized, conversely, that borneol may be transformed into isoborneol. This fact that isoborneol is as well transformed to borneol as it is formed from borneol, is also explained by the result of determination of the heats of combustion of both of these compounds. However, from these values of heat of combustion, it will be considered that borneol 1489.3 Kcal is at first formed which changes into isoborneol 1472.5 Kcal. The proportion of diastereoisomers of alcohol thus formed by the reduction of camphor depends on the mobility of hydrogen in α -position caused by the process and condition of the reduction. It was observed that the velocity of the isomeric change was greatly influenced in the presence of alcohol. The intramolecular change between borneol and isoborneol was also seen, when their acetates were treated with sulphuric acid. Although borneol which was considered very difficult to convert into camphene, the transformation was easily effected by using dehydrating agent such as alumina or $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$. Bornyl acetate forms camphene as well as isobornyl acetate by the action of $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, and it is an interesting phenomenon that dimethylborneol, when dehydrated, forms hydrocarbons of not only the camphene form but also the bornylene form.

(24) J. H. Van't Hoff, *Die Lagerung d. Atome in Raum*, 1894, 30.

(25) Vavon and Peignier, *Bull. soc. chim.*, [4] 39 (1926), 666, 924.

When camphene is treated with 50% H_2SO_4 and glacial acetic acid, borneol as well as isoborneol is formed. Therefore, it is supposed⁽²⁶⁾ that there is the following chemical relation between camphor, borneol, isoborneol, and camphene.



The fact that in the course of the dehydration of borneol and isoborneol inactive camphene was formed, was explained by some investigators⁽²⁷⁾ that when borneol and isoborneol are changed to camphene, an isomer, named camphene hydrate, is formed which converts itself to the racemic compound. That, during the change from camphene to isoborneol by hydration, camphene hydrate is formed as an intermediate product is quite acceptable, but with regard to the racemisation of camphene hydrate, it is rather inconceivable from the standpoint of stereochemistry and only a future investigation will explain it. (*To be continued*).

(26) cf. Meerwein and Van Ernster, *Ber.*, **53** (1920), 1815; *ibid.*, **55** (1922), 2500.

(27) J. Bredt, *J. prakt. Chem.*, **131** (1931), 137; J. Houben and E. Pfankuch, *Ann.*, **489** (1931), 193.