

Catalytic Reduction of Dextro-Camphor. I.

By

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It is a well known fact that ketones by a catalytic reduction by the method of Professor Paul Sabatier, the $>CO$ group in the molecule is reduced to the $>CHOH$ group. In this manner aliphatic ketone can be transformed into secondary alcohol; aromatic ketone, on the other hand, tends to yield hydrocarbon.¹ Such different results in the reduction of aliphatic and aromatic compounds may be explained by assuming that aromatic alcohol formed during the process of reduction of the ketones is less stable toward heat than aliphatic alcohol and consequently the dehydration of the former taking place with the formation of hydrocarbon and water. Extending this assumption, we can naturally imagine a simultaneous formation of alcohol and hydrocarbon from a ketone of the polymethylene series by catalytic reduction below 180° . And such expectation was realized by the experiments of A. Skita and H. Ritter on cyclohexanone²; and N. Zelinsky on methylcyclopentanone.³ It is therefore, anticipated that camphor by the catalytic reduction can be transformed into camphane and borneol.

W. Ipatiew has stated that when dextro-camphor was reduced with hydrogen in presence of nickel oxide under 100 atmospheric pressure and $320-350^{\circ}$, dextro-borneol was obtained⁴ and also that

¹ P. Sabatier: *La Catalyse en Chimie Organique*, 1920, p. 145.

² *Ber. d. Chem. Gesell.*, **44**, 668 (1911).

³ *Ibid.*, **44**, 2781 (1911).

A. Skita: *Über Katalytische Reduktionen Organischer Verbindungen*, 1912, S. 68.

isocamphane was formed by subjecting camphor, borneol, isobornel and camphene respectively to the action of hydrogen in presence of nickel oxide and alumina at 200–240° and high pressure.¹

Referring to the literature² we have learned that the results of Ipatiew's work are on the whole very similar to those obtained by Professor Sabatier's process.

The present investigation was undertaken by the authors to ascertain whether borneol, camphane or isocamphane could be obtained from camphor by catalytic hydrogenation.

Dextro-camphor (Pharm. Jap.), purified by sublimation, melted at 176° and showing $[\alpha]_D = +39^{\circ}10'$ in alcohol solution, was passed with hydrogen generated with zinc and sulphuric acid and purified by washing with concentrated sulphuric acid and concentrated sodium hydroxide solution successively and by passing on heated copper and then dried with caustic potash, on reduced nickel heated 175–185° which was prepared according to the direction of Professor Sabatier.³ Thus 73 gr. of the product were obtained from 105 gr. dextro-camphor. It is a white crystalline substance, and is easily sublimable at ordinary temperature. To purify, 40 gr. of the product were subjected to fractional distillation for 5 times under atmospheric pressure and the following results were obtained:

Ist. distillation under 752 m.m. pressure.

Fraction: 165–168°, 168–177°, above 177°

Yield: 17 gr. 20 gr. 1.5 gr.

IVth. distillation under 757 m.m. pressure.

Fraction: 164–166°, 166–168°, 168–170°, 170–175°, above 175°,

Yield: 18.5 gr. 13.7 gr. 5 gr. 5 gr. 3 gr.

Vth. distillation under 757 m.m. pressure.

Fraction: 164–165°, 165–168°, 168–170°, 170–175°, above 175°,

Yield: 27.5 gr. 9 gr. 1.5 gr. 2 gr. —gr.

The melting point and optical rotatory power of each fraction were determined, and the results are shown in the following table with the results of their analysis:

¹ Ber. d. Chem. Gesell., 45, 3208 (1912).

² P. Sabatier: *La Catalyse en Chimie Organique*, 1920; A. Skita: *Über Katalytische Reduktionen Organischer Verbindungen*, 1912; G. Woker: *Die Katalyse*, 1915; G. G. Henderson: *Catalysis in Industrial Chemistry*, 1919.

³ Loc.cit.

Fraction: 164-165°, 165-168°, 168-170°, 170-175°, 175°-

M. p. 65° 63° 76° 82° 170°

Fraction, 164-165°:

0.206 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -9'$ in 10 c.m. tube; whence $[\alpha]_D = -7^\circ.17'$.

I.	0.1532 gr. substance gave	0.4802 gr. CO ₂ and	0.1795 gr. H ₂ O.
II.	0.1585 „	0.4978 „	0.1848 „
III.	0.1548 „	0.4840 „	0.1816 „
IV.	0.1551 „	0.4873 „	0.1827 „
V.	0.1524 „	0.4774 „	0.1790 „

	Calc. for	Found.				
	C ₁₀ H ₁₈ .	I.	II.	III.	IV.	V
Carbon	86.87	85.48	85.65	85.27	85.68	85.43
Hydrogen	13.13	13.11	13.05	13.13	13.18	13.14

Fraction, 165-168°:

0.2106 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -2'$ in 10 c.m. tube; whence $[\alpha]_D = -1^\circ.35'$.

I.	0.1590 gr. substance gave	0.4994 gr. CO ₂ and	0.1800 gr. H ₂ O.
II.	0.1534 „	0.4814 „	0.1787 „
III.	0.1556 „	0.4907 „	0.1920 „
IV.	0.1556 „	0.4886 „	0.1898 „

	Calc. for	Found.			
	C ₁₀ H ₁₈ .	I.	II.	III.	IV.
Carbon	86.87	85.65	85.58	86.00	85.63
Hydrogen	13.13	12.67	13.04	13.81	13.65

Fraction, 168-170°:

0.2 gr. substance, dissolved in alcohol, made up to 10. c.c., gave $\alpha = 0$ in 10 c.m. tube.

I.	0.1274 gr. substance gave	0.3944 gr. CO ₂ and	0.1471 gr. H ₂ O.
II.	0.1278 „	0.4009 „	0.1494 „
III.	0.1408 „	0.4400 „	0.1615 „

	Calc. for		Found.		
	C ₁₀ H ₁₈ .	C ₁₀ H ₁₈ O.	I.	II.	III.
Carbon	86.87	77.83	84.42	85.55	85.22
Hydrogen	13.13	11.77	12.92	13.08	12.84

Fraction, 170-175°:

0.1559 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = +8'$ in 10 c.m. tube; whence $[\alpha]_D = +8^\circ.33'$.

- I. 0.1596 gr. substance gave 0.4964 gr. CO₂ and 0.1819 gr. H₂O.
 II. 0.1868 ,, 0.5773 ,, 0.2106 ,,

	Calc. for		Found.	
	C ₁₀ H ₁₈ .	C ₁₀ H ₁₈ O.	I.	II.
Carbon	86.87	77.83	84.82	84.28
Hydrogen	13.13	11.77	12.85	12.57

Fraction, above 175° :

0.2 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = +26'$, in 10 c.m. tube; whence $[\alpha]_D = +21^\circ.40'$.

- I. 0.1571 gr. substance gave 0.4528 gr. CO₂ and 0.1585 gr. H₂O.
 II. 0.1291 ,, 0.3729 ,, 0.1288 ,,

	Calc. for		Found.	
	C ₁₀ H ₁₈ .	C ₁₀ H ₁₈ O.	I.	II.
Carbon	86.87	77.83	78.60	78.98
Hydrogen	13.13	11.77	11.29	11.17

As seen in the foregoing table, the first fraction consists of a hydrocarbon C₁₀H₁₈ requires C. 86.87%; H. 13.13% and the main portion of the last fraction is a mixture of *d*-borneol and unchanged *d*-camphor which requires C. 77.83%; H. 11.77% and C. 78.85%; H. 10.60% respectively, and other fractions contain both the hydrocarbon and the alcohol in different proportions.

The hydrocarbon of the first fraction, a white crystalline substance, has a pleasant odour different from that of camphor or borneol, and is easily soluble in organic solvents but insoluble in water. From its chemical and physical properties so far as we studied, it seems to be identical with isocamphane obtained by P. Lipp¹ from camphene by catalytic hydrogenation with nickel at 180°. For confirmation, the substance was subjected to oxidation with nitric acid following Lipp's direction and carboxylic acid of apocamphoric acid was obtained which separated from the hydrocarbon unchanged and an oily product which formed simultaneously during the oxidation of the substance, was analysed of its silver salt:

0.1769 gr. substance gave 0.1203gr.CO₂, 0.0361gr.H₂O and 0.1069 gr. Ag.

	Found	Calc. for C ₁₀ H ₁₁ O ₆ Ag ₃
Carbon	18.55	21.78

¹ Ann. d. Chem., 382, 279 (1911).

Hydrogen	2.28	2.02
Silver	59.86	58.78

30 gr. of laevo-borneol of melting point 207° and of $[\alpha]_D = -39^{\circ}31'$ in alcohol solution were passed with hydrogen on the reduced nickel heated at 180° , and 24 gr. of white crystalline substance were obtained.

17 gr. of the product were also subjected to fractional distillation on metallic sodium under the pressure of 758 m.m..

Ist. distillation:

Fraction: $160-170^{\circ}$, $175-206^{\circ}$

Yield: 11.5 gr. 5 gr.

IInd. distillation:

Fraction: $164-165^{\circ}$, $165-168^{\circ}$, $168-170^{\circ}$, above 170°

Yield: 6 gr. 2.5 gr. 0.5 gr. 2 gr.

M. p. $63-63.5^{\circ}$ 61° 69° 110°

Fraction, $164-165^{\circ}$:

0.2 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -9'$ in 10 c.m. tube; whence $[\alpha]_D = -7^{\circ}.30'$.

I. 0.1895 gr. substance gave 0.5973 gr. CO_2 and 0.2213 gr. H_2O .

II. 0.1382 ,, 0.4335 ,, 0.1597 ,,

	Calc. for $\text{C}_{10}\text{H}_{18}$.	Found.	
		I.	II.
Carbon	86.87	85.96	85.54
Hydrogen	13.13	13.07	12.93

Fraction, $165-168^{\circ}$:

0.1621 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = 0$ in 10 c.m. tube.

I. 0.1415 gr. substance gave 0.4439 gr. CO_2 and 0.1647 gr. H_2O .

II. 0.1435 ,, 0.4491 ,, 0.1629 ,,

	Calc. for $\text{C}_{10}\text{H}_{18}$.	Found.	
		I.	II.
Carbon	86.87	85.55	85.35
Hydrogen	13.13	13.02	12.70

Fraction, $168-170^{\circ}$:

0.1933 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = 0$ in 10 c.m. tube.

0.1359 gr. substance gave 0.4221 gr. CO_2 and 0.1542 gr. H_2O .

	Calc. for $\text{C}_{10}\text{H}_{18}$.	Found.
Carbon	86.87	84.71
Hydrogen	13.13	12.70

Fraction, above 170° :

0.2043 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -12'$ in 10 c.m. tube ; whence $[\alpha]_D = -9^\circ.47'$.

I. 0.1701 gr. substance gave 0.5198 gr. CO₂ and 0.1872 gr. H₂O.

II. 0.1503 ,, 0.4582 ,, 0.1647 ,,

	Calc. for		Found.	
	C ₁₀ H ₁₈ .	C ₁₀ H ₁₈ O.	I.	II.
Carbon	86.87	77.83	83.34	83.14
Hydrogen	13.13	11.77	12.32	12.26

As seen in the above table, laevo-isocamphane is the main reaction product from laevo-borneol by passing it with hydrogen on the heated nickel.

It is quite noteworthy that laevo-isocamphane is also obtained from dextro-borneol by the same treatment as in the cases of laevo-borneol and dextro-camphor.

25 gr. dextro-borneol, prepared from dextro-camphor by reduction with metallic sodium in its alcohol solution, melted at 199° and showing $[\alpha]_D = +28^\circ.23'$ in alcohol solution, yielded 19 gr. of white crystalline substance by passing the dextro-borneol with hydrogen on reduced nickel heated at 180°. The product was purified by fractional distillation on metallic sodium and 3.2 gr. laevo-isocamphane of b. p.: 164–165° under 753 m.m., m.p.: 65–66° were obtained.

Ist. distillation under 753 m.m. pressure.

Fraction: 164–174°, above 174°

Yield: 14 gr. 3 gr.

IIInd. distillation:

Fraction: 164–165°, 165–166°, 166–168°, 168–174°, 174°–

Yield: 3.2 gr. 4.4 gr. 3.8 gr. 1.5 gr. 1 gr.

M. p.: 65–66° 65° 71° 86° —

Fraction, 164–165° :

0.1984 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -5'$ in 10 c.m. tube ; whence $[\alpha]_D = -4^\circ.12'$.

0.1602 gr. substance gave 0.5040 gr. CO₂ and 0.1893 gr. H₂O.

	Calc. for C ₁₀ H ₁₈ .	Found.
Carbon	86.87	85.80
Hydrogen	13.13	13.22

Fraction, 165–166° :

0.2297 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = -4'$ in 10 c.m. tube ; whence $[\alpha]_D = -2^\circ.54'$.

0.1803 gr. substance gave 0.5667 gr. CO₂ and 0.212 gr. H₂O.

	Calc. for C ₁₀ H ₁₈ .	Found.
Carbon	86.87	85.71
Hydrogen	13.13	13.16

Fraction, 166–168° :

0.2057 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = +3'$ in 10 c.m. tube ; whence $[\alpha]_D = +2^\circ.26'$.

0.1449 gr. substance gave 0.4560 gr. CO₂ and 0.1724 gr. H₂O.

	Calc. for C ₁₀ H ₁₈ .	Found.
Carbon	86.87	85.82
Hydrogen	13.13	13.31

Fraction, 168–174° :

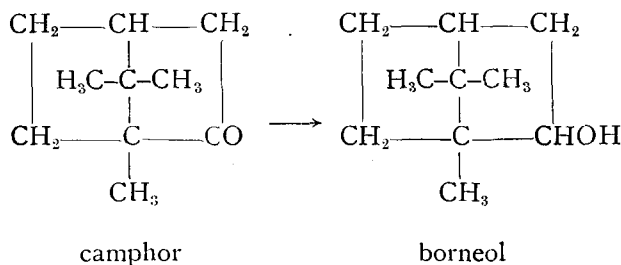
0.2095 gr. substance, dissolved in alcohol, made up to 10 c.c., gave $\alpha = +7'$ in 10 c.m. tube ; whence $[\alpha]_D = +6^\circ.34'$.

0.1693 gr. substance gave 0.5273 gr. CO₂ and 0.1994 gr. H₂O.

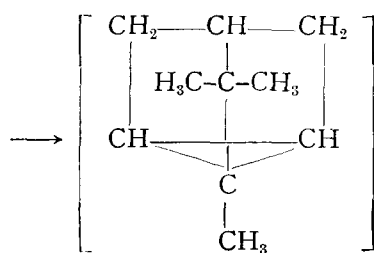
	Calc. for C ₁₀ H ₁₈ .	Found.
Carbon	86.83	84.94
Hydrogen	13.13	13.18

From these experimental results it would appear that the main portion of dextro-camphor by the catalytic hydrogenation in presence of reduced nickel heated at 180° can transform into laevo-isocamphane but not into camphane.

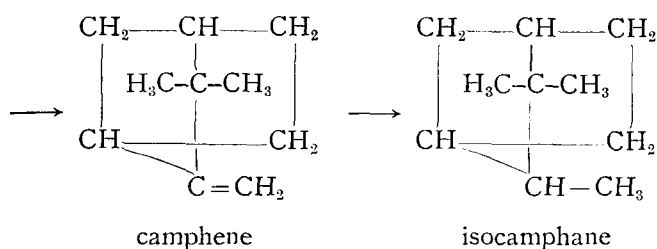
The formation of laevo-isocamphane from dextro-camphor, dextro- and laevo-borneol respectively and also that of isocamphane from camphene observed by Lipp¹ naturally lead us to propose the mechanism of the transformation of camphor into isocamphane by the catalytic hydrogenation, as will be indicated by the following scheme :



¹ Lec. cit.



intermediate product



We do not dare, however, to introduce any assumption in which an explanation is made for such an extraordinary case in stereochemistry and further work to prove laevo-isocamphane is derived from dextro- and laevo-borneol, will be attempted.