Studies on Camphor Oils, IV.
On the Reaction of Japanese Acid Clay to Terpinhydrate and Terpineol.

By

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(Received July 9, 1924)

In my previous investigation[1] I confirmed that the simple terpinic hydrocarbons and the terpinic oxides such as cineol are easily transformed into p-cymene and p-menthane by the action of Japanese acid clay. The present work was undertaken in order to extend the study to the tertiary terpinic alcohol such as terpineol.

200 grams of terpineol (b. p. 103—107° (12—14 m.m.), $d_{20°}$ 0·9356 and $n_D^{21°}$ 1·4822) were treated with Japanese acid clay in a manner analogous to that described in the previous report.

Japanese	Oil formed		
acid clay	Yield	$d_{15°}$	$n_D^{14.5°}$
grs. 50	grs. 144·3	0·8599	1·4832
100	130·6	0·8556	1·4811
200	117·4	0·8391	1·4751
300	114·0	0·8315	1·4722

In order to know what substances are thus produced 200 grams of the oil ($d_{22°}$ 0·8348, $n_D^{22°}$ 1·4739) obtained by treating 400 grams of terpineol with 600 grams of Japanese acid clay, were fractionated by dis-

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[1] These Memoirs, 7, 350 (1924).

tilling it under atmospheric pressure, and the following fractions were collected :

Fraction	Yield	n_D^{42}
	grs.	
up to 100°	0·7	1·3879
100—110°	0·5	1·4071
110—120°	0·4	1·4160
120—130°	1·2	1·4241
130—140°	1·9	1·4350
140—150°	4·3	1·4394
150—160°	51	1·4472
160—170°	13·6	1·4551
170—180°	84·5	1·4670
180—190°	35·8	1·4730
190—200°	16·1	1·4782
200—210°	3·7	1·4811
210—220°	2·1	1·4846
220—230°	1·9	1·4880
230—240°	1·7	1·4920
240—250°	2·2	1·4963
250—260°	2·3	1·5107
260—270°	1·2	1·5109
270—280°	1·9	1·5119
280—290°	1·7	1·5133
290—300°	2·5	1·5170
300—310°	3·9	1·5190
above 310°	10·1	1·5259

80 grams of the fraction boiling at 170—180° (d$(\frac{25}{4})$˙ 0·8251) were then treated with a dilute potassium permanganate solution and conc. sulphuric acid in the cold, and nitrated. A nitro-compound which changes into o—nitro–p–oxyisopropyl benzoic acid on oxidation was obtained. The part remaining unacted upon (d$(\frac{22·5}{4})$˙ 0·8181, n_D^{23}˙ 1·4489) was fractionated by distilling it on metallic sodium.

1st. distillation (20 grams)

Fraction	Yield	$n_D^{23°}$
	grs.	
up to 167°	2·5	1·4339
167—171°	5·1·	1·4362
171—175°	4·2	1·4381
175—130°	4·3	1·4400
above 180°	3·2	1·4720

5th. distillation

Fraction	Yield	$n_D^{23°}$
	grs.	
148—160°	0·3	1·4320
160—165°	0·6	1·4329
165—168°	1·5	1·4350
168—170°	4·4	1·4371
170—175°	2·8	1·4380
175—180°	1·6	1·4402
above 180°	1·9	1·4678

The physical properties and chemical composition of the fractions boiling at 165—168° and at 168—170° were determined as follows :

Fraction	Substance	CO_2	H_2O	C%	H%
	grs.	grs.	grs.		
165—168°	0·1208	0·3770	0·1545	85·11	14·29
168—170°	0·1347	0·4218	0·1746	85·39	14·48
Calc. for $C_{10}H_{20}$				85·62	14·38

Fraction	$d(\frac{21}{4})°$	$n_D^{23°}$	M.R.
165—168°	0·7850	1·4350	46·53
168—170°	0·7952	1·4371	46·15

M.R. Calc. for $C_{10}H_{20}$, 46·18

From its chemical and physical properties so far studied, the 4th. fraction boiling at 168—170° seems to be p–menthane and is identical

with the compound obtained by treating d–limonene and cineol[1] with Japanese acid clay. For confirmation, the substance was dehydrogenated by treating it with sulphur and then oxidized with an alkaline potassium permanganate solution, when p–oxy–isopropyl benzoic acid, melting at 156° was produced.

300 grams of terpinhydrate, melting at 116—117°, were next taken and treated with 600 grams of Japanese acid clay, and about 178 grams of new oil were obtained.

180 c.c. of the oil (d_{25}. 0·8409, n_D^{25} 1·4742) were distilled under atmospheric pressure.

Fraction	Yield	n_D^{24}
	c.c.	
up to 100°	0·9	1·3930
100—110°	0·7	1·3958
110—120°	1·9	1·4179
120—130°	1·7	1·4311
130—140°	1·6	14381
140—150°	2·5	1·4426
150—160°	5·0	1·4483
160—170°	14·1	1·4550
170—180°	68·7	1·4635
180—190°	30·3	1·4699
190—200°	10·1	1·4743
200—210°	5·9	1·4790
210—220°	1·4	1·4812
220—230°	1·4	1·4850
230—240°	1·5	1.4897
240—250°	1·7	1·4952
250—260°	1·9	1·5016
260—270°	1·6	1·5075
270—280°	2·0	1·5130
280—290°	2·1	1·5178
290—300°	2·7	1·5210
300—310°	3·6	1·5224
310—320°	6·9	1·5236
above 320°	8·8	1·5367

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[1] *Loc. cit.*

60 c.c. of the fraction boiling at 170—180° were treated with a dilute potassium permanganate solution and conc. sulphuric acid, and then nitrated.

10 grams of the part remaining unacted upon $(d(\frac{24}{4})°\ 0\cdot8107,$ $n_D^{24.5°}\ 1\cdot4465)$ were distilled on metallic sodium.

1st. distillation

Fraction	Yield	$n_D^{24°}$
	grs.	
up to 165°	1·3	1·4342
165—170°	3·8	1·4370
170—175°	2·5	1·4387
175—180°	1·0	1·4407
above 180°	0·7	—

5th. distillation

Fraction	Yield	$n_D^{24°}$
	grs.	
up to 160°	0·1	1·4330
610—165°	0·2	1·4354
165—168°	1·2	1·4363
168—170°	2·4	1·4372
170—175°	1·1	1·4385
175—180°	5·7	1·4397
above 180°	0·6	—

The fraction boiling at 168—170° $(d(\frac{24}{4})°\ 0\cdot7948,$ M.R. 46·16) was analysed with the following results :

0·1008 gr. substance gave 0·3171 gr. CO_2 and 0·1271 gr. H_2O.

	Found	Calc($C_{10}H_{20}$)
Carbon	85·78%	85·62%
Hydrogen	14·09	14·38

The nitrated compound, after having been purified by super-heated steamdistillation, was oxidized with an alkaline potassium permanganate solution, and yellowish small needles, melting at 167—168°, were obtained. It was identified as o–nitro–p–oxyisopropyl benzoic acid.

The fact that both terpineol and terpinhydrate change into p-cymene and p–menthane by the action of Japanese acid clay, and that the same products are also produced from monoterpenes[1] such as limonene under similar treatment may well be explained if we assume that terpinyhdrate and terpineol undergo dehydration before decomposition as is seen in the following scheme :

[1] *Loc. cit*

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\begin{bmatrix}
\text{CH}_3 \\
\text{C(OH)} \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{CH} \\
\text{C(OH)} \\
\text{CH}_3 \quad \text{CH}_3
\end{bmatrix} + \text{H}_2\text{O}
\quad \xrightarrow{\text{dehydration}} \quad
\begin{matrix}
\text{CH}_3 \\
\text{C} \\
\text{HC} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{CH} \\
\text{C(OH)} \\
\text{CH}_3 \quad \text{CH}_3
\end{matrix}
\quad \xrightarrow{\text{dehydration}} \quad
\begin{matrix}
\text{CH}_3 \\
\text{C} \\
\text{HC} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{CH} \\
\text{C} \\
\text{CH}_2 \quad \text{CH}_3
\end{matrix}
\quad \xrightarrow{\text{polymerisation}} \quad
\begin{bmatrix}
\text{CH}_3 \\
\text{C} \\
\text{HC} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{CH} \\
\text{C} \\
\text{CH}_2 \quad \text{CH}_3
\end{bmatrix}_2
\quad \xrightarrow{\text{decomposition}} \quad
\begin{matrix}
\text{CH}_3 \\
\text{C} \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{H}_2\text{C} \quad \text{CH}_2 \\
\text{CH} \\
\text{CH} \\
\text{CH}_3 \quad \text{CH}_3
\end{matrix}
\quad + \quad
\begin{matrix}
\text{CH}_3 \\
\text{C} \\
\text{HC} \quad \text{CH} \\
\text{HC} \quad \text{CH} \\
\text{C} \\
\text{C} \\
\text{CH}_2 \quad \text{CH}_3
\end{matrix}
$$

Terpinhydrate   Terpineol   Monoterpenes   Diterpenes   p–Menthane   p–Tolyl-propylene

decomposition ↓ ↓ decomposition

$$
\begin{matrix}
\text{CH}_3 \\
\text{C} \\
\text{HC} \quad \text{CH} \\
\text{HC} \quad \text{CH} \\
\text{C} \\
\text{CH} \\
\text{CH}_3 \quad \text{CH}_3
\end{matrix}
$$

p–Cymene