ON THE CATALYTIC ACTION OF JAPANESE ACID CLAY UPON CINEOL. (STUDIES ON CAMPHOR OILS, VIII.)

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In the previous investigation,⁽¹⁾ K. Ono supposed the formation of monoterpene such as dipentene as the intermediate product of the reaction of Japanese acid clay upon cineol, but he could not isolate it. Afterwards K. ONO⁽²⁾ confirmed that the Japanese acid clay is a catalyst for dehydration of varionos terpene alcohols in the liquid system.

On the other hand, Wallach and Brass⁽³⁾ have shown that cineol changes into dipentene in the presence of zinc chloride. These facts naturally lead us to suppose that the dehydration of cineol would take place in the presence of Japanese acid clay. This view was found to be correct from the following experiment.

500 Gr. of cineol ($d_4^{20}=0.9245$; $n_D^{20.5}=1.4590$; $[\alpha]_D=\pm 0$) were treated with 150 gr. of Japanese acid clay (dried at 100°) in a manner analogous to that described in the previous communication. After 2 hours (temperature of oil bath is 180°), the violent reaction took place and 102 gr. of oily product ($d_4^{22}=0.8670$; $n_D^{23}=1.4720$) and 5.24 gr. of water were obtained.

(I) After removing unchanged cineol with 50% solution of resorcine, the product was subjected to steam distillation. 60 Gr. of the oily distillate after having been dried with anhyd. sodium sulphate was distilled under 760 mm.

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(1) *The Memoirs Coll. Sci. Kyoto Imp. Univ.*, A, 7 (1924), 360.

(2) This Journal, 1 (1926), 248: 2 (1927), 16.

(3) *Ann.*, 225 (1888), 268.

Fraction.	Yield.	d.	n_D
173—175°	8.4 gr.	0.8642 $\left(\frac{17.5}{4}\right)$	1.4718
175—177°	31.4	0.8488 $\left(\frac{20}{4}\right)$	1.4720
177—180°	13.2	0.8649 $\left(\frac{17.5}{4}\right)$	1.4740
above 180°	5.7	———	———

The fraction boiling at 175–177’ was analyzed with the following result.

0.1012 Gr. subst. gave 0.3263 gr. CO_2 and 0.1092 gr. H_2O. (Found, C=87.73, H=12.07. $C_{10}H_{16}$ requires C=88.15, H=11.85 %). Molecular refraction 44.91. $C_{10}H_{16}F_2$ requires 45.24.

The compound seems, so far as studied, to be identical with dipentene. For comfirmation, it was converted into tetrabromoderivative, it melted at 124.5–125° and was proved to be identical with dipentene-tetrabromide by a direct comparison with a pure specimen.

(II) The part remaining in the reaction flask was extracted with ether. On distilling off ether, the residue⁽¹⁾ was subjected to steam distillation. 70 Gr. of the oily distillate ($d_4^{21}=0.8415$; $n_D^{20}=1.4746$) were twice redistilled on metallic sodium under 767 mm.

Fraction.	Yield	$d_{\frac{18.5}{4}}$	n_D^{18}
170—173°	3.3 gr.	0.8327	1.4700
173—175°	41.0	0.8376	1.4732
175—177°	11.3	0.8434	1.4780
above 177°	3.7	——	——

From its chemical behaviour the fraction boiling at 173–175° was found to consist of p-cymene. In order to remove some terpenic compounds, the p-cymene fraction was treated with a diluted permanganate solution in cold, and then transformed into barium salt of p-cymene-disulphonic acid following the direction given by M. Phillips.⁽²⁾

0.3163 Gr. subst. gave 0.1699 gr. $BaSO_4$. (Found, Ba=31.66. $C_{10}H_{12}(SO_3)_2Ba$ requires Ba=31.99 %).

The residue by the steam distillation was a yellow viscous oil with a fluorescence and confirmed to be composed mostly of dipinene⁽³⁾ by distilling it.

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(1) The residue did not contain any cineol.

(2) *J. Am. Chem. Soc.*, **46** (1924), 689.

(3) C.S. Venable, *J. Am. Chem. Soc.*, **45** (1923), 733.

From these experimental results it appears evident that the main portion of cineol changes into dipentene, p-cymene and dipinene by the action of Japanese acid clay. The formation of p-cymene may be assumed to be formed by the decomposition of dipinene.

$$(C_{10}H_{16})_2 \rightarrow C_{10}H_{16} + C_{10}H_{18}$$

dipinene p-cymene Δp-menthene (?)

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