

Studies on Catalytic Action, II. Catalytic Preparation of para-Cymene and Its Formation in Sulphite Terpentine.

By

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Klason¹ first noticed that the ethereal oil collected during the manufacture of pulp from spruce by the sulphite process, consists mainly of para-cymene and not of terpenes. Sulphite terpentine from the pulp mills of U. S. A. was studied by Herty and Graham,² A.W. Schorger³ and M. Philips⁴ with a view to the utilization of para-cymene in it. O. Aschan⁵ and J. Alftan⁶ have, also, studied the terpentine in Finland.

The sulphite terpentine, we studied, was obtained from the pulp mill at Ochiai, Karafuto, where sulphite pulp was manufactured from Yezo-matsu and Todo-matsu. The crude oil which amounted to 140 gm., was dark brown in colour, $d_4^{15} = 0.965$. It was subjected to steam distillation and a light-yellow oil was obtained, which, after drying with anhydrous sodium sulphate, was distilled:

First fraction, B. p., 174–270°. 70 gm.

Second fraction, B. p., above 270°. 35 gm.

Two fractions were fractionated on metallic sodium, and the fraction boiling at 173–175° was collected. The yield was 50% of the crude oil.

¹ Ber. D. Chem. Ges., **33**, 2343 (1900).

² J. Ind. & Eng. Chem., **6**, 803 (1914).

³ Ibid., **10**, 258 (1918).

⁴ J. Amer. Chem. Soc., **44**, 1775 (1922).

⁵ Zellstoff Chem. Abhand., **1**, 73 (1920).

⁶ Ber. D. Chem. Ges., **53**, 78 (1920).

The physical constants and the elementary composition of the purified substance were determined with the following results :

It gave C=89.33; H=10.34; ($C_{10}H_{14}$, requires C=89.48; H=10.52), $d_4^{25} = 0.85381$; $n_D^{25} = 1.4821$; M.R.=44.80.

For identification with para-cymene, it was oxydized with potassium permanganate into tere-phthalic acid¹ and para-hydroxyisopropyl benzoic acid² and the latter melts at 156° and gave on analysis C=66.23; H=6.64; ($C_{10}H_{12}O_3$ requires C=66.64; H=6.72).

On the other hand, the substance was sulphonated with conc. sulphuric acid following Claus' directions,³ and sodium salts of mono- and di-sulphonic acids were separated by aid of their solubility in alcohol solution, and di-sulphonic acid salt was analysed; Ba = 31.32 ($C_{10}H_{12}O_6S_2Ba$ requires Ba = 31.95).

Terpenes of the formula $C_{10}H_{16}$ by dehydrogenation, were ultimately converted into para-cymene; consequently the transformation was sometimes made use of in the determination of the constitution of the compounds.⁴

Kekule⁵ has studied the conversion of terpene into cymene by oxydation with phosphorous sulphide. L. Ruzika, J. Meyer and M. Mingazzini⁶ have obtained para-cymene from limonene and terpinene by catalytic oxydation with sulphur, following Vesterberg's directions,⁷ and the same process was applied by W. Friedmann⁸ to naphthene hydrocarbons.

The authors have succeeded in the catalytic preparation of para-cymene, the main constituent of sulphite terpentine, from pinene and menthene respectively.

136 gm. pinene obtained from commercial terpentine oil, were heated with 70 gm. sulphur in a flask at 200° for 23 hours, the reaction product was distilled under reduced pressure and 71.5 gm. of the product was obtained. It was distilled under ordinary pressure

1 R. Fittig, A. Kobrich & T. Jilke: *Lieb. Ann.*, **145**, 144 (1868).

2 O. Wallach: *Ibid.*, **264**, 10 (1891).

3 *Ber. D. Chem. Ges.*, **14**, 2140 (1881).

4 V. Meyer & P. Jacobson: *Lehrbuch d. Org. Chem.*, II, 110 (1902).

5 *Ber. D. Chem. Ges.*, **2**, 121 (1869).

6 *Hel. Chim. Acta*, **5**, 356 (1922).

7 *Ber. D. Chem. Ges.*, **36**, 4200 (1903).

8 *J. Chem. Soc.*, **112**, 13 (1917).

after treating with 10% caustic soda solution, dried with calcium chloride, and a fraction boiling at 170–275° was collected. The yield was 55 gm. (52% of the theoretical).

The product, thus obtained, on distilling with metallic sodium, was all distilled out between 165–175°. It was purified by repeated distillation with metallic sodium.

The purified substance $d_4^{25} = 0.8542$; $n_D^{25} = 1.4743$; M.R. = 44.41, was analysed; it gave C = 88.37; H = 11.34; ($C_{10}H_{14}$ requires C = 89.45; H = 10.55.).

It was oxydised with potassium permanganate into para-hydroxy-isopropyl benzoic acid¹ which melted at 156–156.5° and gave C = 66.44; H = 6.33; ($C_6H_4C(OH)(CH_3)_2COOH$ requires C = 66.64; H = 6.72).

In the same manner, menthene prepared from menthol by catalytic dehydration with thoria was transformed into para-cymene.

140 gm. menthol were passed on thoria heated at about 400°, and yield 125 gm. light greenish yellow liquid substance, $d_4^{25} = 0.817$, which distilled between 155–210°. It was purified by repeated distillation with metallic sodium, and the following fractions were obtained:

The fraction boils at 145–164° under 752 mm., with 10% of the yield.

Other fraction boils at 164–167° under 752 mm., with 40% of the yield.

The second fraction was confirmed by analysis to consist of menthene,² $d_4^{25} = 0.8096$; $n_D^{25} = 1.4469$; M.R. = 45.60; which gave C = 86.10; H = 12.92; ($C_{10}H_{18}$ requires C = 86.87; H = 13.13).

Menthene, thus obtained, was heated with sulphur at 200° for 24 hours, and the reaction product was subjected to distillation on metallic sodium to purify. The cymene fraction boiling at 170–173.5°, $d_4^{25} = 0.8389$, $n_D^{25} = 1.4740$; M.R. = 44.94; gave on analysis C = 87.68; H = 10.92, ($C_{10}H_{14}$ requires C = 89.45; H = 10.55).

The conversion of menthol and borneol by simply heating with sulphur at about 200° into cymene, was tried but with no result.

Terpenes of the formula $C_{10}H_{16}$, on the contrary, can easily be transformed into cymene by catalytic oxydation with sulphur.

Aromatic hydrocarbons and their oxygen derivatives such as para-cymene and safrol are widely distributed, being generally associated

¹ O. Wallach: *Loc. cit.*

² P. Walter: *C. R.*, **6**, 473 (1838); *Lieb. Ann.*, **32**, 288 (1839).

with the essential oils in plants. The origin and the mechanism of the formation of the aromatic compounds in the flora were interesting problems.

As to the formation of para-cymene in sulphite terpentine, Klason¹ has already put forward the following opinion :

„Alles Terpentinöl soll ja auch nach den vorhandenen Angaben etwas Cymol enthalten, und im Holze sind die aetherische Oele lange Zeit dem Einfluss der Luft ausgesetzt worden. Wie man nun diesen Uebergang im Lichte der Engler'schen Theorie der Autoxydation erklären soll, mögen künftige Untersuchungen darthun. Entweder wurden von der zunächst entstandenen superoxydartigen Verbindung zwei Wasserstoffatome direct weg oxydirt oder es entsteht intermediär ein Alcohol, welcher durch Wasserabspaltung in Cymol übergeführt wird.“ Much more probably the formation of cymene in wood may be attributed to the autoxydation of etherial oils, as Klason stated. Whether the sulphite terpentine was formed in a digester during the manufacture of pulp, by the same mechanism is very doubtful.

Our hypothesis, however, for the formation of the sulphite terpentine, is quite different from Klason's, and is grounded on the experiments described above; the terpene existing in the wood would probably be transformed during the manufacture of pulp by the sulphite process, into para-cymene by catalytic oxydation with sulphur which is liberated in a free state in the digester.

The evidences in favor of our view of the formation of sulphite terpentine, are easy to quote here from literature.

Shinozaki² has isolated from the essential oils obtained by steam distillation of Yezo-matsu and Todo-matsu pinene and phellandrene, which were proved by our experiments to transform into para-cymene.

We cannot pass over without mention here the most important fact that free sulphur actually exists in the acid-liquor used for pulp manufacture, cited in Klason's article.³

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¹ Loc. cit.

² Kogyo-Kwagaku Zasshi, 15, 730 (1912).

³ Üregelmässige Gang v. Sulphitstoff-Kochung u. desen Ursache, 1910, p. 63.