


## An Isomer of Cymene from Camphor.

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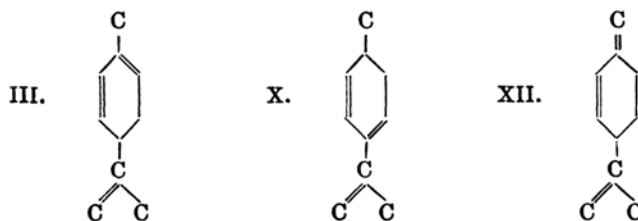
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Cymene in 50–60% yields has been obtained from camphor by treatment with phosphorus pentoxide.<sup>(1)</sup> We have found that prolonged heating with 85% phosphoric acid,<sup>(2)</sup> gives as the large fraction, an isomer of cymene, but little or no cymene.

The theoretical isomers of cymene are  and those with double bonds indicated by the following numbers:

- |                 |                     |                    |
|-----------------|---------------------|--------------------|
| I. 1, 3, 8(9)   | V. 2, 5, 1(7)       | IX. 3, 5, 1(7)     |
| II. 1, 4, 8(9)  | VI. 2, 5, 4(8)      | X. 3, 5, 8(9)      |
| III. 1, 5, 8(9) | VII. 2, 5, 8(9)     | XI. 5, 1(7), 4(8)  |
| IV. 1, 5, 4(8)  | VIII. 3, 1(7), 8(9) | XII. 5, 1(7), 8(9) |

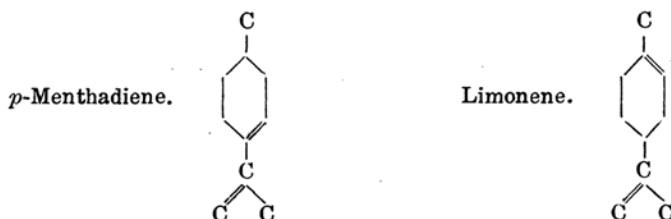
and of these only III, X, and XII contain asymmetrical carbon atoms. Since our large fraction boiled at 180–182°, possessed the formula  $C_{10}H_{14}$  and a specific rotation of 6.82°, it must be one of these three:



Since it agrees more closely in boiling point with *p*-menthadiene (b.p. 184°) than with limonene (b.p. 176.5°), formula X or 1-methyl-4-isopropenyl-cyclohexadiene-(2,4) is indicated.

(1) Fittica, *Ann.*, **172** (1874), 307.

(2) Dehn and Jackson, *J. Am. Chem. Soc.*, **55** (1933), 4284. These authors showed that phosphoric acid (85%) yields hydrocarbons from certain oxygenated terpenes etc.



Formula XII is surely excluded for the reason that methylene groups attached directly to the ring are unstable in the presence of acids. Formula III is probably excluded on the basis of Horiuchi's<sup>(3)</sup> isomer (b.p. 183–186°) formed by the dehydration of citral. Though he reports no optical activity, he assigns to his isomer formula II or III. Wallach<sup>(4)</sup> also reports an isomer of cymene (b.p. 183°) derived from limonene tri-bromide, but assigns to it no structural formula.

### Experimental.

A mixture of 340 g. of camphor and 290 g. of 85% phosphoric acid in a flask was heated under a reflux air condenser in an oil bath heated at 200° for about 7 hours after all the camphor had liquefied. The mixture was then distilled with steam. The distillate was extracted with ether and the ether was evaporated. Some of the unchanged camphor that came over with the steam was separated from the oil by freezing out in a salt-ice mixture and filtering. A trace of camphor that remained was transformed into cymene by repeated distilling over phosphorus pentoxide. The yield of oil was 75 g. or about 25% of the theoretical. The oil was then fractionated eleven times giving the following fractions: below 176°, 3 c.c.; 176–178°, 2; 178–180°, 13; 180–182°, 20; 182–184°, 2; 184–186°, 6; 186–188°, 2; 188–190°, 3; 190–192°, 8; 192–194°, 2; 194–196°, 2; 196–198°, 2; 198–200°, 3; above 200°, 10.

Evidently longer refluxing would have yielded more oil because both camphor and phosphoric acid were contained in the mixture.

Fraction boiling at 180–182° was analysed (Found: C, 89.27; H, 10.77. Calc. for  $C_{10}H_{14}$ : C, 89.48; H, 10.52%). Its odour was different from that of cymene. At 22° its refractive index was  $n_D = 1.4874$ ; its specific rotation was  $[\alpha]_D = 6.94^\circ$ ; its specific gravity was 0.875.

That cymene was not first formed by the dehydration of camphor was proved by an experiment in which cymene itself was refluxed for 5 hours with 85% phosphoric acid; it was recovered unchanged at its lower boiling point.

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(3) Horiuchi, *Mem. Coll. Sci., Kyoto Imp. Univ.*, A, **11** (1928), 171.

(4) Wallach, *Ann.*, **264** (1891), 27. This isomer at 20° has a refractive index of  $n_D = 1.49693$  and a specific gravity of 0.863. No optical activity was reported.