

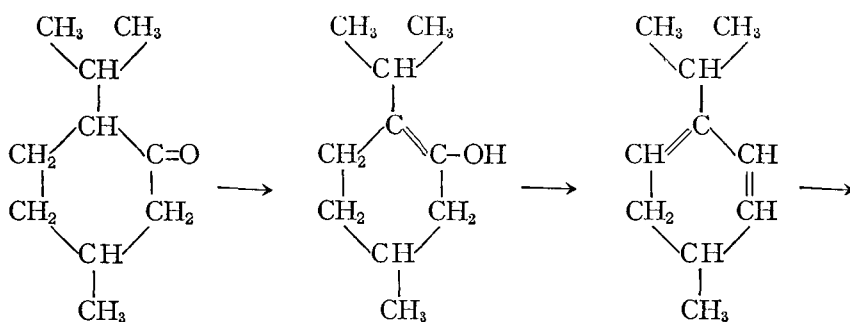
**Studies on Catalytic Action, XXII.**  
**Catalytic Action of Reduced Copper on**  
**Unsaturated Hydrocarbons.**

By

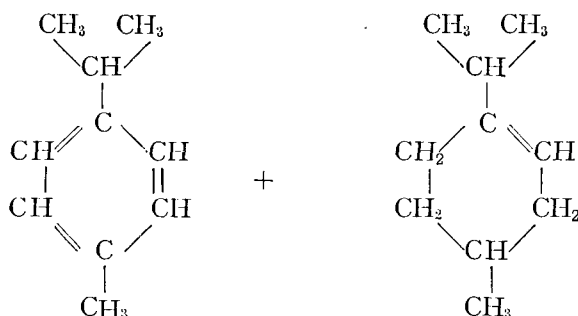
**Shigeru Komatsu and Masao Kurata.**

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In the course of the catalytic action of reduced copper on menthone at 300°, the writers noticed the occurrence of thymol, cymene and menthene in the reaction product, and the formation of these hydrocarbons from menthone was explained as follows<sup>1</sup>:



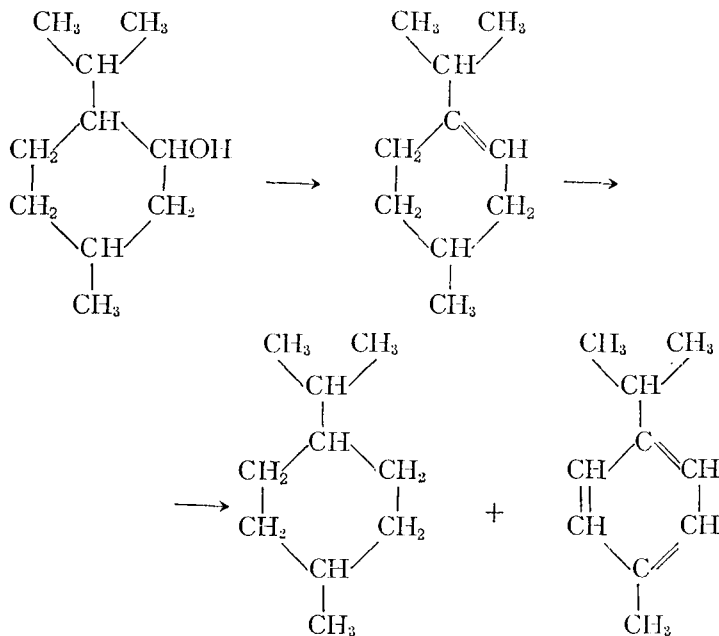
<sup>1</sup> These Memoirs: A. 9, 23 (1925).



The menthadien formed as an intermediate reaction product, by the dehydration of menthenol resulting from the keto-enolic transformation of menthone, was converted by catalytic oxidation and reduction taking place simultaneously, into menthene and cymene.

Admitting that the assumption for the formation of these hydrocarbons was correct, the index of refraction of the fraction of hydrocarbons being  $n_D^{25} = 1.4599$  indicated that the fraction composed of cymene and menthene in a mole ratio of 43:57.

The formation of cymene and menthane from menthol by the contact action of reduced copper and reduced nickel heated at  $200^\circ$ ,<sup>2</sup> will also be expressed analogously by the following interpretation :



<sup>2</sup> Ibid., A, 8, 35, 65 (1925).

The other cases which would provide examples of the non-reversible catalysis of unsaturated hydrocarbons have been previously mentioned by one of the present writers (S. K.) and his co-workers<sup>1</sup> in the occurrence of naphthalene and dihydro- and tetrahydronaphthalenes in the course of the catalytic reduction of the  $\alpha$ - and  $\beta$ -naphthyl ethers in the presence of reduced nickel heated at 200°, and of benzene and its hydrogenated compounds in the reaction products from cyclohexanol or cyclohexyl amine by the contact action of reduced copper.

The non-reversible catalysis of the unsaturated hydrocarbons was already noticed by H. Wieland on the study of dihydronaphthalene which by shaking with platinum black dissolved in benzene, yields naphthalene and tetrahydronaphthalene.<sup>2</sup>

The conversion of the incompletely hydrogenated aromatic hydrocarbons, such as cyclohexene, menthene and limonene, into aromatic hydrocarbons and a saturated cyclic compound was noticed by N. Zelinsky and his co-workers, in which finely divided platinum, palladium, iridium and nickel were noticed to serve as possible catalysts in this reaction.<sup>3</sup>

In order to verify whether cymene and menthane or naphthalene and tetrahydronaphthalene were formed by non-reversible catalysis or some other reaction from menthene or dihydronaphthalene which were regarded as being formed as an intermediate reaction product from menthol or tetrahydronaphthol by dehydration respectively, the present investigation was undertaken with menthene, limonene and  $\beta$ -phellandrene as a starting material.

The reduced copper used in the reaction was prepared by reduction with hydrogen at 200° from copper oxide formed by the action of a dilute caustic soda solution on copper sulphate.

### Menthene.

Menthene was prepared from l-menthol by passing on thoria heated at 400°, and purified as usual, and the physical constants of the hydrocarbon were mentioned in the table.

54 gm. of pure menthene were passed on reduced copper prepared from 10 gm. oxide which was heated at 290–300°, at a rate of 4.5 gm. per hour; hydrogen gas was noticed to evolve only at the beginning of the reaction and amounted to 450 c.c. (at 0°, 760 mm.) The

1 These Memoirs: A, 7, 135 (1924); A, 8, 135 (1925); A, 9, 15 (1925)

2 Ber. D. Chem. Ges., 45, 486 (1912).

3 Ibid., 56, 1723 (1923); 57, 1066, 1070, 2055 (1924); 53, 864 (1925); 60, 1096 (1927); and also refer: Büeseken: Rec. trav. chim., 37, 255 (1918).

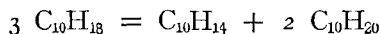
reaction product which shows the physical constants shown in the table, was confirmed to consist of cymene and menthane with unchanged menthene.

Menthene in the reaction product was confirmed by converting into nitrosochloride showing M.p.  $127^{\circ}$ ,  $[\alpha]_D = +17.28^{\circ}$ .

Cymene. The occurrence of this compound in the reaction product was confirmed by transforming into p-oxy-isopropyl benzoic acid M. p.  $156^{\circ}$ - $157^{\circ}$ . However, the yield of the acid from the reaction product by oxidation was very small owing to the presence of menthene in it, which prevents the oxidation of cymene, as we learnt from the behaviour of the oxidizing agent in the mixture of cymene and menthene.

In the isolation of menthane from the reaction product, 30 gm. of the sample were treated with a 10 % fuming sulphuric acid solution at  $5^{\circ}$  to free menthene and cymene from menthane by converting them into soluble forms in sulphuric acid, and the residual oil amounting to 5.1 gm., was treated again with fuming sulphuric acid. 3 gm. of oily substance which had escaped from the reaction from the sulphuric acid, were distilled on metallic sodium, the fraction (B. p.  $165^{\circ}$ - $168^{\circ}$ ) amounted to 2.5 gm., which shows  $n_D^{25} = 1.4332$ ;  $d_4^{25} = 0.7889$ ; M.R. = 46.14; and was optically inactive. It decolorizes neither bromine nor potassium permanganate and the properties agree with those of menthane.

The non-reversible catalysis of menthene in the presence of reduced copper heated at  $300^{\circ}$ , by the study of the chemical and the physical properties of the reaction products, was observed actually to happen, resulting in the formation of cymene and menthane,



### **d-Limonene.**

Pure d-limonene from Theodor Schuchardt, of the properties shown in the table, by passing on reduced copper heated at  $280^{\circ}$ - $300^{\circ}$ . was converted completely into cymene.

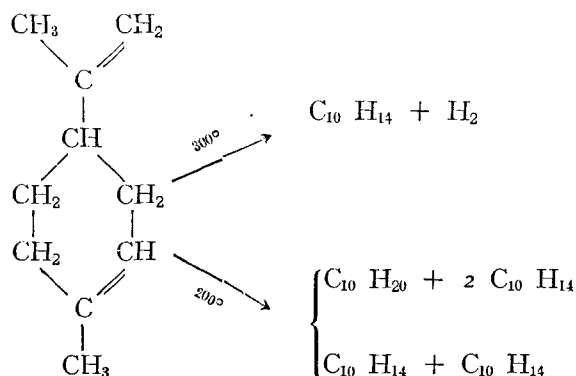
When, however, 4.5 gm. of limonene were passed on the catalyst heated at  $200^{\circ}$  during an interval of one hour, no hydrogen was evolved, and 4.2 gm. of the reaction product of the physical properties shown in the table were obtained, which was subjected to fractional distillation:

Fraction	Yield	$n_D^{25}$
1. B.p., 169°-172°	0.8 gm.	1.4670
2. " 172°-175°	2.6 "	1.4679
3. " 175°-177°	0.5 "	1.4692
	3.9 "	

The first fraction was treated with conc. sulphuric acid and the remaining oil showed  $n_D^{25} = 1.4605$  which indicates the occurrence of cymene and menthane in it. The latter substance was isolated from the mixture by treating it with fuming sulphuric acid and the resulting oil shows B.p. 165°-168°,  $n_D^{25} = 1.4331$ . The occurrence of dipentene in the second fraction B.p. 172°-175°, was proved by converting it into dipentene tetrabromide M.p. 124°.

The second fraction was also found to consist of limonene and carvomenthene by isolating the nitrosochlorides which possessed the same melting-points as limonene nitrosochloride M. p. 100°-103°, and also carvomenthene nitrosochloride M.p. 94°-95°. The formation of carvomenthene from limonene was reported by G. Vavon<sup>1</sup> by subjecting it to partial reduction in the presence of platinum black.

The behaviour of d-limonene towards the reduced copper will be represented in the following scheme :



**d-β- Phellandrene.**

d-β-Phellandrene from Theodor Schuchardt, purified by distillation

<sup>1</sup> C. R., 152, 1677 (1911).

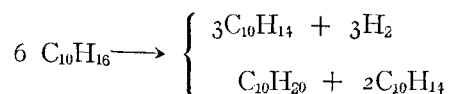
under reduced pressure, indicating the physical constants shown in the table, was passed in a glass tube heated at 300°, and 2.6 gm. of the product were obtained from 3 gm., of the sample, and the product shows the constants of pure phellandren :

$$[\alpha]_D = +6.72 \text{ (in } \frac{1}{2} \text{ dm. tube)}; d_4^{25} = 0.8401; \text{ B.p. } 170^\circ\text{--}175^\circ.$$

When 5.3 gm. of phellandrene were passed on the reduced copper heated at 300°, during a period of 2 hours, 5.2 gm. of the reaction product having the physical properties shown in the table, were obtained. In the course of the reaction, hydrogen gas was evolved continuously, and the total volume was estimated to be 411 c.c. under normal conditions (0°, 760 mm.) which are equivalent, by assuming that the conversion of phellandren by catalytic oxidation into cymene has happened, to the quantity of hydrogen generated from 2.47 gm. of phellandrene :



The reaction product indicates, faintly as we had anticipated, its unsaturated character toward potassium permanganate, and also absorbs hydrogen in presence of palladium black. The occurrence of cymene and menthane in the reaction product was confirmed as usual by isolating these compounds, and the percentage of cymene in the product was calculated to be 82.5 % by assuming that the reactions shown in the following schemes take place simultaneously.



This value agree quite well with the calculated value, 82 % of cymene, by means of the index of refraction of the reaction products.

So far as the writers have investigated, monocyclic terpenes such as menthene, d-limonene and  $\beta$ -phellandrene, were converted, as we had expected, by non-reversible catalysis of reduced copper into cymene and menthane, and the reduced copper shows the behavior toward these unsaturated hydrocarbons similar to nickel and palladium, though the velocity of the reaction depends largely upon the constitution of the hydrocarbons.

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Table

	B. p	$\alpha_D^{(I=1dm.)}$	$d_{4}^{25}$	$n_D^{25}$	$n_{\alpha}^{25}$	$n_{\beta}-n_{\alpha}$	$n_{\gamma}-n_{\alpha}$			
Menthene	Sample	+ 30.42°	0.8066	1.44956	1.44492	0.01123	0.01667			
	Reaction product at 300°	+ 21.95°	0.8060	1.45137	1.44852	0.00956	0.01533			
Limonene	Sample	+ 103.72°	0.8389	1.47082	1.46786	0.01094	—			
	Reaction product at	200°	172-175°	—	0.12°	0.8498	1.48750	1.48379	0.01383	—
		300°	169-178°	+ 62.00°	0.8333	1.46817	1.46525	0.01088	—	
$\beta$ -Phellandren	Sample	65-67° *	+ 16.42°	0.8448	1.47674	1.47335	0.01200	0.01961		
	Reaction product at 300°	166-174°	+ 0.38°	0.8377	1.47650	1.47325	0.01337	0.02073		

\* at 12mm.