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On the Reaction of Limonene with Chloranil[1,2]

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In 1942, one of the present authors[3] examined the reaction of *d*-limonene with chloranil and proved the formation of dipentene and *p*-cymene, together with a large amount of polymerized substances. A further study of this reaction will be reported here.

Experimental

Materials. The *d*-limonene (**1**) was found to be 98.2% pure by gas-liquid chromatography (GLC), it had the following properties; bp 177°C/765 mmHg, d_4^{30} 0.8393, n_D^{30} 1.4678, $[\alpha]_D^{15}+99.75°$. The chloranil (**2**) was a commercial product of an extra pure grade; mp 288°C.

Reaction I. A mixture of 5.0 g (0.037 mol) of **1** and 1.1 g (0.005 mol) of **2** was heated at 170°C for 1 hr. The reaction mixture turned brown, and the generation of a small amount of hydrogen chloride was observed. The reaction product was then distilled with steam, and the distilled oil was extracted with ether and subsequently dried over anhydrous sodium sulfate. When the solvent was removed, 4.1 g of oil were obtained.

Reactions II_1, II_2, and II_3. Mixtures of 5.0 g of **1** and 2.2 g (0.009 mol) of **2** were heated at 130°C for 1 hr and 6 hr, and another at 170°C for 1 hr. After the same treatment, 4.4 g, 3.8 g, and 2.7 g respectively of oils were obtained.

Reactions III_1 and III_2. Mixtures of 5.0 g of **1** and 4.5 g (0.018 mol) of **2** were heated at 150°C and 170°C for 1 hr; 2.3 g and 1.4 g of oils respectively were thus obtained.

Reaction IV. A mixture of 5.0 g of **1** and 9.0 g (0.037 mol) of **2** was heated at 170°C for 2 hr, 1.6 g of oil were thus obtained.

Examination of the Reaction Products. The GLC was carried out by using Yanagimoto GC-3D Model equipment equipped with a thermal conductivity detector; the contents of the components were calculated from the peak areas of the gas-chromatograms. The components were isolated by preparative GLC with PEG 6000 column, and were identified by a comparison of their IR spectra with those of authentic samples.

d-*Limonene (1) and Dipentene (6).* Component **1** was isolated from the reaction product of I, and was identified as limonene. However, the specific rotation of this limonene was $[\alpha]_D^{20}+27.56°$, indicating that it contained about 70% of dipentene; this compound also afforded tetrabromide, mp 124°C.

*8-*p*-Menthene (3), 1-*p*-Menthene (4), α-Terpinene (5), γ-Terpinene (7), *p*-Cymene (8), Terpinolene (9), 1-Methyl-4-isopropenylbenzene (10).* Each component was isolated from the reaction products of II_3—IV and was identified by a comparison of the IR spectrum[4] and retention time of GLC with those of authentic sample.

Reactions V, VI, VII, and VIII. Mixture of 5.0 g (0.037 mol) of *p*-cymene (**8**) (98.7% purity by GLC; bp 176°C/760 mmHg, d_4^{30} 0.8546, n_D^{30} 1.4867), and 1.1 g (0.005 mol), 2.2 g (0.009 mol), 4.5 g (0.019 mol), and 9.0 g (0.037 mol) of chloranil (**2**) were each heated at 170°C for 1 hr. By this treatment, 4.0 g, 3.6 g, 3.3 g, and 1.9 g of oils respectively were obtained. The reaction products consisted of **10** and large amounts of unreacted **8**. These results are shown in Fig. 1 and in Tables 1 and 2.

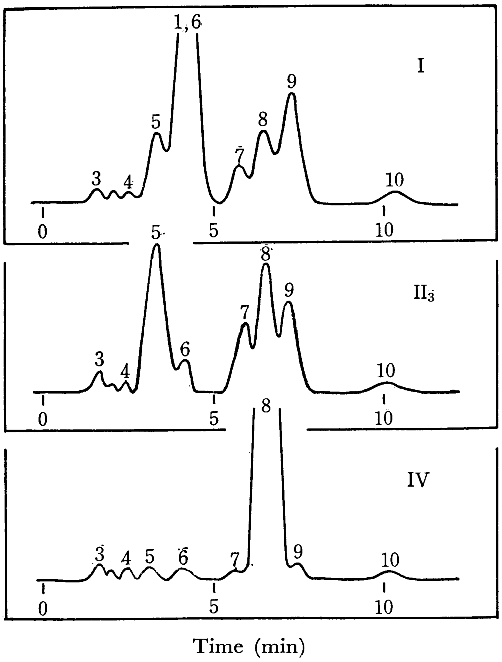

Fig. 1. Gas chromatograms of the volatile products of the reactions I, II_3 and IV.
Condition: PEG 6000 (30%), 2m×5mmφ, 165°C, 40 ml/min H_2.

Nonvolatile Products. The nonvolatile residues of the steam distillation of the products of the reactions IV and VIII were each extracted with ether; after the separation of the chloranol (mp 233°C) formed, 1.6 g and 1.5 g portions of viscous oils were obtained respectively. These components were examined by GLC. In the case of the reaction VIII, the main component amounted to 76% of the oil. The IR spectrum of this compound showed bands at 1515(s), 1495(m), 1455(s), 1385(m), 1375(m), 1365(m), 1190(m), 1020(m), 815(s),

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[1] Biogenetical Studies of Essential Oils. XXI.

[2] Presented at the 12th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics of the Chemical Society of Japan, Hamamatsu, October, 1968.

[3] Y. Fujita and S. Ōhashi, *Nippon Kwagaku Kwaishi*, **63**, 1443 (1942).

[4] B. M. Mitzner, E. T. Theimer, and S. K. Freeman, *Appl. Spectrosc.*, **19**, 169 (1965); M. J. Murray and W. S. Gallaway, *J. Amer. Chem. Soc.*, **70**, 3867 (1948).

Table 1. Compositions of the volatile products of reactions I—IV

The compounds identified	Compositions (%)						
	I	II$_1$	II$_2$	II$_3$	III$_1$	III$_2$	IV
8-*p*-Menthene (**3**)	0.1			3.9	2.8	8.6	0.9
(unidentified)	0.3			1.7	1.2	1.4	0.2
1-*p*-Menthene (**4**)	0.2			2.5	1.5	4.9	0.7
α-Terpinene (**5**)	8.4			23.7	21.1	2.5	0.1
d-Limonene (**1**) and Dipentene (**6**)	54.2	93.3	90.4	1.3	1.8	0.1	0.1
γ-Terpinene (**7**)	3.7			13.2	15.8	1.3	0.1
p-Cymene (**8**)	8.3	1.0	1.4	33.2	34.8	75.6	94.6
Terpinolene (**9**)	20.4	1.7	2.0	16.8	16.9	2.2	2.5
1-Methyl-4-isopropenylbenzene (**10**)	4.1	3.1	5.7	3.5	3.9	3.2	2.5

Table 2. Compositions of the volatile products of reactions V—VIII

The compounds identified	Compositions (%)			
	V	VI	VII	VIII
p-Cymene (**8**)	91.7	94.2	95.2	89.9
1-Methyl-4-isopropenylbenzene (**10**)	7.9	5.5	4.3	9.5
(unidentified compounds)	0.4	0.3	0.5	0.6

and 725(m) cm^{-1}; it was identified as 1,3,3,6-tetramethyl-1-*p*-tolylindan (**11**) by comparison with the IR spectrum of authentic one,[5] though the minor components have not yet been determined. The gas chromatograms of these products are shown in Fig. 2.

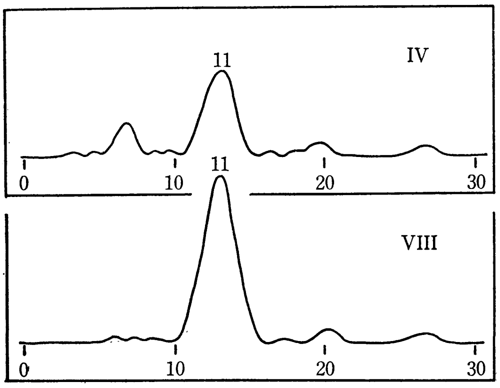

Fig. 2. Gas chromatograms of the nonvolatilve products of the reactions IV and VIII.
Condition: PEG 6000 (30%), 1m×5mmϕ, 175°C, 200 ml/min H$_2$.

Results and Discussion

When *d*-limonene (**1**) is heated at 150—170°C with chloranil (**2**), there occur several reactions, such as racemization, isomerization, dehydrogenation, disproportionation, and dimerization. Moreover, the formation of 8-*p*-menthene (**3**), 1-*p*-menthene (**4**), α-terpinene (**5**), dipentene (**6**), γ-terpinene (**7**), *p*-cymene (**8**), terpinolene (**9**), 1-methyl-4-isopropenylbenzene (**10**), and 1,3,3,6-tetramethyl-1-*p*-tolylindan (**11**) has been confirmed. These reactions may be concluded to be as is shown in Fig. 3.

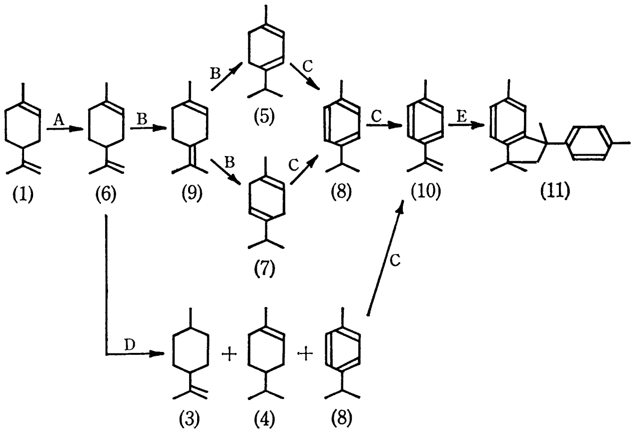

Fig. 3. The schematic mode of formation of the reaction products of *d*-limonene (1) with chloranil (2).
A: Racemization, B: Isomerization, C: Dehydrogenation, D: Disproportionation, E: Dimerization

The monoterpene compounds obtained in these reactions frequently occur in natural essential oils and can be considered in some cases to be formed by similar complex reactions of quinonoid compounds *in vivo*.

In a previous paper,[6] the present authors examined the reaction of citral with chloranil in a benzene solution under refluxing and proved the formation of **6**, **8**, and **10**.

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[5] V. N. Ipatieff, H. Pines, and R. C. Olberg, *J. Amer. Chem. Soc.*, **70**, 2123 (1948).

[6] S. Fujita, Y. Kimura, R. Suemitsu, and Y. Fujita, *Nippon Kagaku Zasshi*, **92**, 175 (1971).