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## The Oxidation of Limonene with Selenium Dioxide

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The oxidations of limonene with selenium dioxide have been reported;<sup>1-4</sup> in them it was found that the two methyl groups of C-7<sup>3</sup>) and C-10<sup>3</sup>) and the methylene group of C-6<sup>1,2</sup>) were oxidized. In a previous paper<sup>5</sup>) dealing with the selenium dioxide oxidation of *cis*-carvyl acetate, which contained both a methine and methyl group allylic to the double bond, it was found that the methine group is oxidized mainly.<sup>6</sup>) Because limonene has the same carbon skeleton as *cis*-carveol, it was expected that the methine group of C-4, in addition to the methyl and methylene groups, is oxidized with selenium dioxide. Therefore, in this paper *d*-limonene was taken as the sample and was oxidized with selenium dioxide. The oxidation was carried out in an alcoholic solution at reflux with a half-molar amount of selenium dioxide. The reaction products were analysed by gas chromatography using a polyethylene glycol 6000 column at 160°C. All the identities were confirmed by a comparison

of the IR and NMR spectra. The *dl*-limonen-4-ol(1,8-*p*-menthadien-4-ol) was obtained as a major product (11% based on the sample taken), while *d*-*trans*-carveol, *cis*-carveol, perillyl alcohol, limonen-10-ol(1,8-*p*-menthadien-10-ol), and carvone were obtained as minor products (total, 6.5%).

In a study of the mechanism by which olefins are oxidized with selenium dioxide, Schaefer and

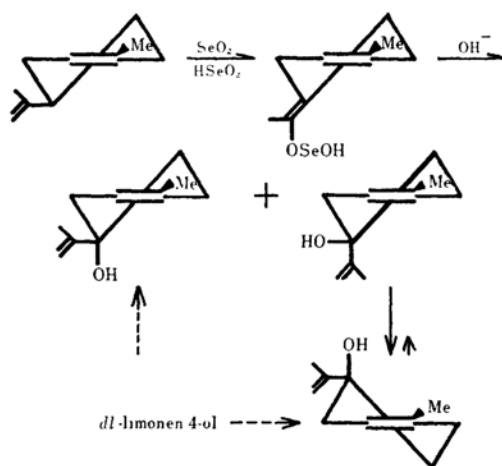


Fig. 1. Oxidation of methine group of limonene.

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4) W. Zacharewicz, *Chem. Abstr.*, **45**, 5661 (1951).

5) Y. Sakuda, *This Bulletin*, **42**, 475 (1969).

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Wiberg<sup>7)</sup> have shown that selenium dioxide or its conjugate acid acts as an electrophile and attacks a double bond, thus forming an allylic selenium ester that then decomposes to products through solvolysis reaction. When Schaefer's mechanism is applied when the methine group allylic to the double bond at C-8 of limonene is oxidized, the reaction process is as is shown in Fig. 1. This view of the mechanism of the oxidation appears to accord well with that by which *dl*-limonen-4-ol is produced. Furthermore, considering the fact that the isolated carveol consists mainly of *d-trans*-carveol, which possesses an axial hydroxyl group and which retains its optical activity, it was assumed that the displacement of the allylic selenium ester by a solvent molecule occurs through the  $S_N2'$  process.<sup>7)</sup>

### Experimental

**Oxidation.** To 136 g (1 mol) of *d*-limonene (bp 61°C/13 mmHg,  $d_4^{25}$  0.8422,  $n_D^{25}$  1.4720,  $[\alpha]_D +122.6$ ) in 150 cc of ethanol, which was being stirred at room temperature, there was added, drop by drop over a period of 30 min, 55 g (1/2 mol) of selenium dioxide dissolved in a mixture of 10 cc of water and 250 cc of ethanol. The mixture was heated to reflux for 1 hr and then left to stand at room temperature overnight. The reaction mixture was filtered, giving 4.7 g of selenium. The filtrate was concentrated using a rotary evaporator, and the residue was steam-distilled. The distillate was extracted twice with ether. The combined ether solution was washed with water, dried over anhydrous sodium sulfate, and distilled to remove the solvent. The residue was distilled at reduced pressure, giving three fractions: (1) bp 62–94°C/13 mmHg, 29.2 g; (2) bp 94–96°C/12 mmHg, 13.5 g; (3) 96–108°C/12 mmHg, 16.0 g. Fraction 1 consisted mainly of unchanged *d*-limonene.

**The Identification of Reaction Products.** *dl*-Limonen-4-ol. Fraction 2 was analysed by gas chromatography and was found to consist 90% of limonen-4-ol and 10% of unknown hydrocarbons; it was purified by redistillation. Bp 104–106°C/27 mmHg,  $d_4^{25}$  0.9475,  $n_D^{25}$  1.4877,  $[\alpha]_D +1.40$ ; phenylurethane, mp 130–131°C.<sup>8)</sup> Gas chromatography of this oil indicated the presence of small amounts of unknown hydrocarbons in addition to limonen-4-ol. Accordingly, the small optical rotation value is due to unknown contaminating hydrocarbons. IR spectrum: 3400  $\text{cm}^{-1}$  (OH); 3100, 1645, 900  $\text{cm}^{-1}$  ( $\text{CH}_2=\dot{\text{C}}-$ ). NMR spectrum: 1.75 ppm, 3H s, 4.71, 1H, q, 4.90, 1H, s ( $\text{CH}_3-\dot{\text{C}}=\text{CH}_2$ );

1.65, 3H s, 5.21, 1H unresolved ( $\text{CH}_3-\dot{\text{C}}=\text{CH}-$ ). The IR and NMR spectra of this alcohol coincided with those of limonen-4-ol, which was isolated from Japanese pepper by Sakai.<sup>9)</sup> This alcohol was hydrogenated with Raney Ni in ethanol to give two known *p*-menthan-4-ols.<sup>8)</sup>

**Carvone.** A gas chromatogram of Fraction 3 showed eleven peaks, which corresponded to limonen-4-ol (17%), carvone (3%), *trans*-carveol (33%), *cis*-carveol (10%), limonen-10-ol (16%), perillyl alcohol (16%), and five unknown minor components (5%). Chromatography of Fraction 3 on silica gel, with elution with ethyl acetate-petroleum ether (1:3), gave four fractions. The first fraction consisted a mixture of unknown hydrocarbons. The second fraction was rechromatographed on a silica-gel column and eluted with ethyl acetate-petroleum ether (1:20) giving carvone; 2,4-dinitrophenylhydrazones, mp 188–189°C.

***d-trans*-Carveol.** The third fraction consisted mainly of *trans*-carveol. The 3,5-dinitrobenzoate was prepared from this fraction and was recrystallized three times from ethanol-ethyl acetate (2:1), giving pale yellow needles; mp 108–110°C,  $[\alpha]_D +174.1$  ( $c$  1.6,  $\text{CHCl}_3$ ); reported<sup>10)</sup> mp 111.5°C,  $[\alpha]_D +232.0$  ( $c$  2.0,  $\text{CHCl}_3$ ) for *d-trans*-carvyl 3,5-dinitrobenzoate. The liquid alcohol obtained by the saponification of this 3,5-dinitrobenzoate gave a single peak upon gas chromatography; it was identified as *trans*-carveol by a direct comparison of the IR spectrum. Calculating from the specific rotation value of the 3,5-dinitrobenzoate, *trans*-carveol retained 75% of its optical activity.

***cis*-Carveol.** The fourth fraction consisted of a mixture of *trans*- and *cis*-carveol, limonen-10-ol, and perillyl alcohol. Chromatography of the fourth fraction on silica gel, with elution with ethyl acetate-petroleum ether (1:3), gave fractions which were analysed by gas chromatography. The fractions rich in *cis*-carveol, limonen-10-ol, and perillyl alcohol were combined. The crude *cis*-carveol thus obtained was purified by rechromatography on alumina; it was identified as *cis*-carveol by a direct comparison of the IR spectrum. The crude limonen-10-ol and perillyl alcohol obtained were purified too by rechromatography on silica gel.

**Limonen-10-ol.** IR spectrum: 3300  $\text{cm}^{-1}$  (OH); 3100, 1645, 900  $\text{cm}^{-1}$  ( $\text{CH}_2=\dot{\text{C}}-$ ). NMR spectrum: 1.65 ppm 3H s, 5.37, 1H unresolved ( $\text{CH}_3-\dot{\text{C}}=\text{CH}-$ ); 4.02, 2H s ( $-\text{CH}_2\text{OH}$ ); 4.84 1H s, 5.00 1H d ( $\text{CH}_2=\dot{\text{C}}-$ ). The oxidation product of this alcohol with chromic acid gave a semicarbazone, mp 209°C.<sup>2)</sup>

**Perillyl Alcohol.** IR spectrum: 3300  $\text{cm}^{-1}$  (OH); 3080, 1643, 890  $\text{cm}^{-1}$  ( $\text{CH}_2=\dot{\text{C}}-$ ). NMR spectrum: 1.73 ppm 3H t, 4.77, 2H d ( $\text{CH}_3-\dot{\text{C}}=\text{CH}_2$ ); 3.93, 2H s ( $-\text{CH}_2\text{OH}$ ); 5.72, 1H unresolved ( $-\dot{\text{C}}=\text{CH}-$ ).

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