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(21) We have run this reaction only with sublimed magnesium. Hence we cannot say whether the improved yield is due to the magnesium or to the scrupulous care used in obtaining pure starting materials and solvent.

(22) See L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, **85**, 1549 (1963), for many references.

(23) Obtained from Engelhardt.

(24) A column, 8 ft × 0.25 in., packed with 30% silicone gum rubber, SE-30, on fire brick in a Varian Aerograph A90-P3 apparatus, was used.

(25) Methyltricaprylammonium chloride obtained from the General Mills Co., Kankakee, Ill.

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Selenium Dioxide Oxidation of d-Limonene. A Reinvestigation[1]

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In several studies[3-6] of the selenium dioxide oxidation of limonene (1), the tertiary alcohol 3 has been reported to be formed in yields varying from only a trace to almost 40%.[3] Although some authors[3,6,7] have worried about why the less electron-rich disubstituted double bond was preferentially attacked by selenium dioxide, it is not so surprising in view of the fact that oxymercuration[8] and especially the ene reaction with formaldehyde[9] both preferentially attack the disubstituted olefinic linkage in limonene (1).

The great enigma in connection with the d-limonene oxidation, however, was the reports[3,6] that the product alcohol 3 was optically active. In the body of their paper Trachtenberg and Carver[3] made no mention of the fact that 3 was optically active, but, in the Experimental Section they report for alcohol 3 [α]D +13.6° (neat, isolated by preparative glc). It should be noted that this formation of optically active alcohol 3 is inconsistent with their proposed mechanism.[7] Wilson and Shaw[6] reported [α]²⁹D −43.0° (c 1.24, isolated by preparative glc) for alcohol 3 and noted that the formation of this optically active product was inconsistent with all of the proposed mechanisms for the selenium dioxide oxidation of olefins.[10,11] Sakuda[4] reported [α]D +1.40° for 3 but said that this small rotation could be ascribed to impurities in the product. Thomas and Bucher[5] reported [α]D 0° for their distilled alcohol 3.

The mechanism which we have proposed[11] for the selenium dioxide oxidation of olefins (Scheme I) would involve an initial ene reaction between selenious acid and d-limonene followed by dehydration to produce the allylseleninic acid 2. A [2, 3] sigmatropic rearrangement followed by solvolysis would then give the product $\Delta^{1,8(9)}$-p-menthadien-4-ol (3). According to this mechanistic sequence, the reac-
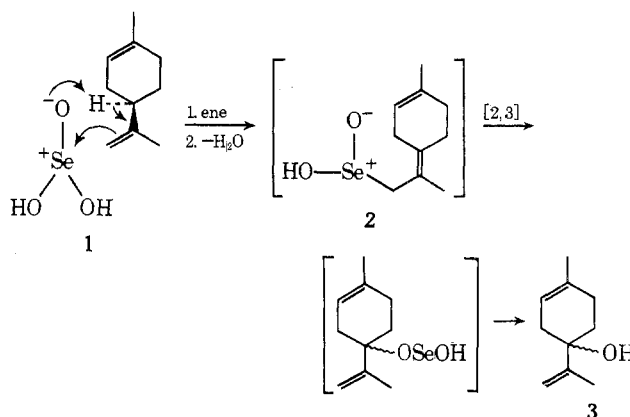
Scheme I

Table I
Experimental Conditions for the SeO₂–H₂O₂ Oxidation of d-Limonene

Expt	SeO₂, mmol	H₂O₂, mol	d-Limonene, mol	Reaction time
a	32	0.66	0.6	4 hr
b	32	0.66	0.3	4 hr
c	16	0.66	0.6	4 hr
d	32	0.66	0.6	20 min

tion proceeds through the symmetric allylseleninic acid 2; thus, the allylic alcohol 3 would be produced as the racemate. Therefore, Wilson's and Shaw's[6] claim of optically active alcohol 3 was incompatible with our proposed mechanism.[11]

We have repeated all of the four d-limonene oxidations reported by Wilson and Shaw.[6] The reaction conditions are summarized in Table I and are described more fully in ref 6. The procedure of Thomas and Bucher[5] was used to synthesize an authentic sample of alcohol 3. Glc of the above four reaction product mixtures indicated that each reaction did yield some of the alcohol 3, along with at least 27 other products. Experiment a was examined in order to determine the optical activity of the product alcohol 3, formed in 0.2% yield (by glc). Isolation of alcohol 3 by distillation followed by preparative glc resulted in a material which showed optical activity; [α]²⁹D +11.9° (c 1.27). Although this material appeared to be homogeneous when examined by glc on OV-17, it showed several impurities on DEGS, which could possibly have been responsible for the observed rotation. The alcohol 3 was then isolated again, this time using a more elaborate purification sequence.

After a rapid distillation, the alcohol 3 was isolated by preparative tlc followed by preparative glc on an OV-17 column. This alcohol was then further purified by another preparative glc on a DEGS column. This very pure alcohol 3 was optically inactive; [α]²⁹D 0.000° (c 1.27). That alcohol 3 had survived this sequence follows from the observations that the ir of the purified material was identical with that of authentic alcohol 3 and the melting point of the purified material's phenylurethane was not depressed by admixture of the phenylurethane of authentic alcohol 3.[12]

We submit, therefore, that the selenium dioxide oxidation of d-limonene (1) results in racemic $\Delta^{1,8(9)}$-p-menthadien-4-ol (3), as predicted by our mechanism[11] and as shown in Scheme I. The reports[3,6] which describe formation of optically active alcohol 3 are apparently in error. The optical activity which they observed in alcohol 3 was likely due to optically active impurities, for, if the alcohol 3 is rigorously purified, it is found to be optically inactive.

Experimental Section

Gas–liquid chromatography was performed on Hewlett-Packard Models 402 (flame ionization), 700 (flame ionization), and 700 (thermal conductivity) gas chromatographs with the following columns: column a, 0.25 in. × 48 ft stainless steel containing 10% OV-17 on Chromosorb W; column b, 0.125 in. × 6 ft glass containing 3% OV-17 on 100–120 mesh Chromosorb Q; column c, 0.25 in. × 6 ft stainless steel containing 5% DEGS on 100–120 mesh Chromosorb W; column d, 0.125 in. × 4 ft glass containing 3.8% UCW-98 on 100–120 mesh Chromosorb W; column e, 0.125 in. × 6 ft stainless steel containing 10% Carbowax 20M on 80–100 mesh Chromosorb W.

d-Limonene (1) was obtained from Eastman Kodak and was purified by passing it through an alumina column followed by distillation: bp 91–92° (45 mm); $[\alpha]^{29}D$ +112.5° (*c* 1.24) [lit.[6] $[\alpha]^{29}D$ +116.5° (*c* 1.24)]. Glc showed the material to be >99% pure.

$\Delta^{1,8(9)}$-*p*-Menthadien-4-ol (3). The procedure of Thomas and Bucher[5] was used to prepare an authentic sample of alcohol 3. After distillation, bp 40–41° (0.18 mm), preparative glc on column a afforded the alcohol 3: $n^{20}D$ 1.4969; ir (neat) 3400 (OH), 3015 (>C=C(H)), 3095, 1640, 1440 and 895 cm^{-1} (>C=CH$_2$); nmr (CDCl$_3$) δ 5.36 (*w*/2 = 10 Hz, 1, vinyl H), 5.05 (m, *w*/2 = 4 Hz, 1, vinyl H), 4.86 (m, *w*/2 = 4 Hz, 1, vinyl H), 2.13 (m, 4, C=CCH$_2$), 2.01 (s, 1, OH, removed by D$_2$O wash), 1.85 (s, 3, C=CCH$_3$), 1.8–1.7 (2, CH$_2$), and 1.71 ppm (s, 3, C=CCH$_3$); mass spectrum (70 eV) *m/e* (rel intensity) 152 (16) (M$^+$), 137 (11), 134 (47), 124 (9), 123 (17), 119 (63), 109 (16), 105 (17), 97 (18), 94 (4), 93 (20), 92 (15), 91 (44), 84 (92), 83 (12), 79 (17), 77 (20), 69 (100), 68 (18), 67 (18), 65 (13), 55 (17), 53 (16), 51 (11), 43 (30), 41 (51), 39 (34); phenylurethane mp 124–125.5° [lit.$^{4-6,13}$ bp 50° (0.01 Torr); $n^{20}D$ 1.4967; ir 3370, 3100, 1640, and 900 cm^{-1}; nmr δ 5.3 (m, 1), 5.05 (s, 1), 4.85 (s, 1), 2.5–1.8 (m, 6), 1.9 (s, 3), and 1.7 ppm (s, 3); mass spectrum, *m/e* (rel intensity) 69 (100), 84 (86), 41 (55), 43 (30), 39 (25), fragments at *m/e* 53, 55, 67, 68, 77, 79, 83, 91, 93, 94, 97, 109, 119, 123, 124, 137 (10–20), and 152 (13) (M$^+$); phenylurethane mp 126–127°^{3} or 130–121°^{4}].

Selenium Dioxide Oxidation of *d*-Limonene (1). We have repeated all of the four oxidations reported by Wilson and Shaw;[6] see Table I and ref 6. A description of experimental procedure a follows. A solution of selenium dioxide (3.6 g, 32.4 mmol) in 75 g of 30% hydrogen peroxide solution (0.66 mol) was added to a solution of 81 g (0.6 mol) of purified *d*-limonene (1) in 100 ml of THF. The solution was briefly heated whereupon a vigorous exotherm commenced. During the exothermic reaction, the stirred flask was intermittently cooled with an ice bath as necessary to keep the solution from boiling out through the condenser. After the exotherm subsided, the solution was heated at reflux for 4 hr whereupon the mixture became red. The two-phase system was cooled, brine was added, and the lower phase was removed. Glc, column b, indicated that the upper layer contained the desired alcohol 3. The upper layer was distilled at reduced pressure. A large forerun contained mostly pure limonene, bp 30–50° (0.65 mm). A fraction, bp 50–58° (0.65 mm), contained the desired alcohol 3 along with several other products. Glc, column b, indicated that the overall yield of the alcohol 3 was 0.2%. A glc purified sample, using column a, coinjected with the alcohol 3 prepared earlier and showed optical activity: $[\alpha]^{29}D$ +11.9° (*c* 1.23). Although this glc purified sample appeared

to be homogeneous on column b, it was seen to be impure when examined on column c. Since these impurities could have been responsible for the observed rotation, the alcohol 3 was carried through a more extensive purification procedure.

The bp 50–58° (0.65 mm) fraction was subjected to preparative tlc on silica gel. The alcohol 3 was removed from the plate (R_f 0.4, 10% ethyl acetate in hexane). The resultant alcohol 3 was then subjected to preparative glc on column a, followed by another preparative glc on column c to give alcohol 3 which appeared to be homogeneous on glc columns b, c, d, and e. This very pure alcohol 3 was optically inactive; $[\alpha]^{29}D$ 0.000 (*c* 1.27).

Since there was a possibility that the extensive purification had somehow altered the alcohol 3, an ir spectrum of this very pure material was taken and shown to be identical with the spectrum of the authentic alcohol 3 prepared earlier. The phenylurethane of this extensively purified alcohol 3 had mp 126–127°, which was not depressed upon mixing with the phenylurethane of the authentic alcohol 3 (mmp 125–127°).[12]

References and Notes

(1) Taken from the Ph.D. Thesis of H.P.J., Massachusetts Institute of Technology, May,1974.
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(12) We consider it unlikely that alcohol 3 could have racemized during the purification procedure. Samples of alcohol 3 were usually injected into the glc columns as neat liquids. The glc peaks corresponding to impurities were gradually eliminated during the purification sequences and there were never any hints of decomposition of alcohol 3. No compounds corresponding to dehydration of alcohol 3 were seen in the glc trace of purified product.
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