

sodium bicarbonate solution, washed, dried, and distilled to yield 2.07 g. of product, b.p. 79–80.5° (0.6 mm.); infrared bands at 1780, 1175, and 970 (last two bands of equal intensity); homogeneous on g.l.c.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 69.61; H, 9.18.

**Lactone of *cis*-2-Hydroxy-*trans*- $\alpha$ -methylcyclohexaneacetic Acid.** (10).—Attempted epimerization of 9 with potassium carbonate in refluxing xylene was unsuccessful. However, it was found that equilibration was complete when 1.0 g. of 9 was refluxed with 10 ml. of tetralin and 0.1 g. of potassium carbonate for 12 hr. Further heating caused no change in the infrared spectrum or gas-liquid chromatogram of the product except for an increase in the proportion of  $\alpha$ -tetralone (*vide infra*). The solvent was removed by distillation; the residue was taken up in ether, washed, dried, and distilled to give 0.5 g. of product, b.p. 75–76° (0.6 mm.); g.l.c. analysis of the distillate indicated the presence of  $\alpha$ -tetralone and 9 and 10 in a ratio of 2:3.

The distillate was chromatographed over 20 g. of alumina. Benzene-pentane (2:3) eluted 0.04 g. of  $\alpha$ -tetralone, identified by comparison with an authentic sample (g.l.c. and infrared spectrum). This was followed, with some overlap, by 10, 0.094 g.,

eluted with benzene-pentane (1–1), and then by 9, 0.092 g., eluted with benzene-pentane (4:1). The remainder of the product could not be removed from the column, possibly because of cleavage to the hydroxy acids. Distillation of 10 furnished material, b.p. 78° (0.6 mm.); infrared bands at 1780, 1185, and 1025  $cm^{-1}$  (last band weaker than band at 1185  $cm^{-1}$ ); this was homogeneous on g.l.c. analysis.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15; Found: C, 70.18; H, 9.15.

**Lactone of *trans*-2-Hydroxy- $\alpha$ -methylcyclohexaneacetic Acid** (11).—This lactone was prepared by refluxing 28.8 g. of cyclohexene oxide and 54 g. of diethyl methylmalonate in 250 ml. of sodium ethoxide solution (from 7.25 g. of sodium) for 6 hr. The usual work-up and hydrolysis by the literature method<sup>6</sup> gave 16.2 g. of a lactone, b.p. 80–83° (0.4 mm.), lit.<sup>6</sup> 125–128° (10 mm.); infrared bands at 1790, 1180, and 1020  $cm^{-1}$  (last band more intense than band at 1180  $cm^{-1}$ ). This material appeared to be homogeneous when subjected to g.l.c. analysis using a number of different columns, but the n.m.r. spectrum indicated the presence of about 10% of 12.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.00; H, 9.28.

## The Rearrangement of Limonene and Carvomenthene Epoxides

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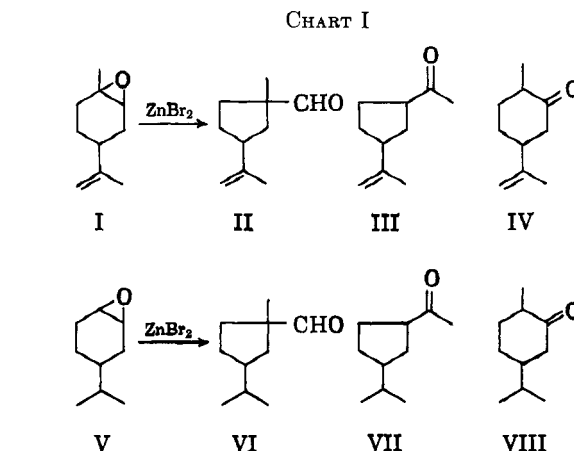
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The monocyclic terpene oxides, limonene oxide, and carvomenthene oxide have been reported previously to yield a variety of six-membered ring products by reaction with alumina or Lewis acid catalysts. It has been found that limonene oxide in the presence of zinc bromide rearranges with ring contraction to 1-methyl-3-isopropenylcyclopentyl-1-carboxaldehyde and methyl (3-isopropenylcyclopentyl) ketone and isomerizes to dihydrocarvone. Similarly, carvomenthene oxide rearranges to 1-methyl-3-isopropylcyclopentyl-1-carboxaldehyde and methyl (3-isopropylcyclopentyl) ketone and isomerizes to carvomenthone. Structural elucidation of the rearranged products was achieved by chemical synthesis and supported by nuclear magnetic resonance. Several alcohol and acetate derivatives of rearranged products were prepared.

During our investigation of the chemical composition of Florida orange oil (Valencia), limonene oxide (I), a constituent of this oil, was found to undergo acid-catalyzed rearrangement. This reaction of I was observed to occur during both its gas chromatographic analysis on acid-washed support and in the presence of Lewis acid catalysts. Thus, reaction of limonene oxide (I) with zinc bromide in refluxing benzene yielded three products, an aldehyde (II, 30%), a ketone (III, 10%), and dihydrocarvone (IV, 59%). An analogous reaction with carvomenthene oxide (V) yielded an aldehyde (VI), a ketone (VII), and carvomenthone (VIII) in similar proportions (Chart I). That the reaction does proceed in a similar manner is shown by the catalytic hydrogenation of II, III, and IV to VI, VII, and VIII, respectively.

The formation of dihydrocarvone and carvomenthone from limonene oxide and carvomenthene oxide, respectively, has been the subject of previous investigations<sup>3,4</sup>; however, there has been no report of materials having a cyclopentane structure, although in this case, they constitute 40% of the reaction mixture.

The isomerization or rearrangement of epoxides to



carbonyl compounds is a general reaction.<sup>5–9</sup> The structures of the rearranged products depend on a variety of factors, *i.e.*, the direction of oxide ring opening, the relative migratory aptitudes of the different substituent groups,<sup>10</sup> and the steric requirements

(5) S. M. Naqvi, J. P. Horwitz, and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957).

(6) E. A. Braude, A. A. Webb, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

(7) B. A. Arbuzov, *Ber.*, **68**, 1430 (1935).

(8) L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961).

(9) R. Dulou, Y. Chretien-Bessiere, and J. P. Montheard, *Compt. rend.*, **254**, 3374 (1962).

(10) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, R. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 1.

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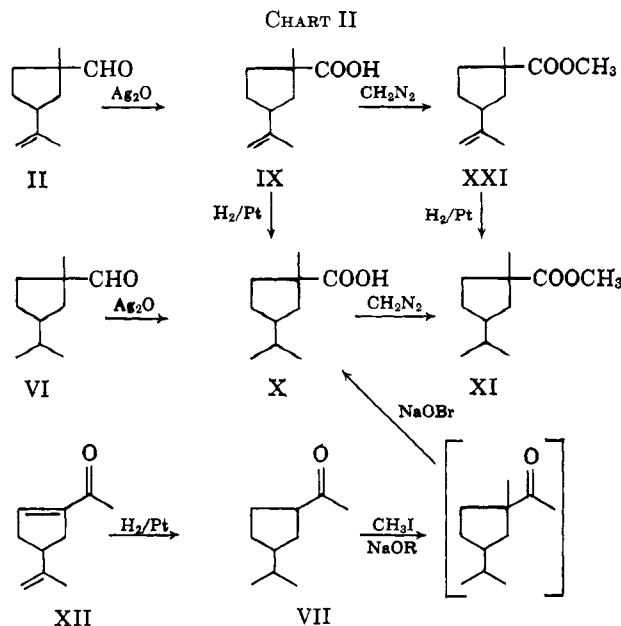
(2) One of the laboratories of the Southern Utilization Research and Development Division, Agriculture Research Service, U. S. Department of Agriculture. References to specific products of commercial manufacture are for illustration only and do not constitute endorsement by the U. S. Department of Agriculture.

(3) E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955).

(4) A. Kergomard and M. Th. Geneix, *Bull. soc. chim. France*, 390 (1958).

of the molecule itself with respect to a heterogeneous catalyst. The latter is exhibited by the apparent discrepancy in the aldehyde products from bicyclic terpene oxides<sup>7-9</sup> when compared to those from cyclohexane oxides.<sup>5,6</sup> For example, in the case of  $\alpha$ -pinene oxide,<sup>7</sup> the rearrangement is a ring contraction by migration of a carbon atom attached to the carbon  $\alpha$  to the tertiary carbon of the oxirane ring followed by closure of a double bond with fission of a cyclopentane ring. In cyclohexene oxide<sup>5</sup> the rearrangement is a ring contraction by migration of a carbon atom  $\beta$  to the tertiary carbon atom of the oxirane ring and  $\alpha$  to the secondary carbon atom followed by or during the fission of the cyclohexane ring and thence formation of the carbonyl. Thus a study was undertaken to investigate the structure of the rearrangement products of limonene and carvomenthene oxide.

Compound II gave a positive silver mirror test with Tollens reagent. Catalytic hydrogenation of II with platinum-on-charcoal catalyst at room temperature yielded aldehyde VI with rapid absorption of 1 mole of hydrogen per mole of compound. The infrared spectrum of II clearly showed the presence of a terminal double bond exhibiting sharp absorption peaks at 885 and 1625  $\text{cm}^{-1}$ . The nuclear magnetic resonance spectrum<sup>11</sup> of II exhibited one singlet methyl peak at 70 c.p.s., one allylic singlet methyl at 103 c.p.s., two vinyl protons unsplit (equivalent) at 380 c.p.s., and one aldehydic proton unsplit at 564 c.p.s. It can be seen quite clearly that there are no hydrogens  $\alpha$  to the aldehydic group; there is one tertiary methyl and one terminal double bond.



Oxidation of aldehydes II and VI with silver oxide yielded the corresponding acids IX and X, respectively. Hydrogenation of IX gave acid X which was identified as 1-methyl-3-isopropylcyclopentyl-1-carboxylic acid by its synthesis from methyl (3-isopropenylcyclopent-1-ene) ketone (XII) as shown in Chart II. Compound XII was prepared from limonene-1,2-diol<sup>12</sup> and re-

duced to methyl (3-isopropylcyclopentyl) ketone. A comparison of the infrared spectrum of this material with that of unknown ketone VII showed them to be identical. Ketone III was shown to be methyl (3-isopropenylcyclopentyl) ketone since on hydrogenation it yielded VII as indicated by the loss of the terminal methylene absorption in the infrared spectrum and absorption of 1 mole of hydrogen per mole of compound. Alkylation of VII with methyl iodide and sodium *t*-butoxide followed by hypobromite oxidation yielded acid X. A comparison of the gas chromatographic retention times and infrared spectra of the methyl ester XI derived from XII and aldehyde VI showed them to be identical. Thus aldehyde II must be 1-methyl-3-isopropenylcyclopentyl-1-carboxaldehyde and aldehyde VI, its saturated counterpart, 1-methyl-3-isopropylcyclopentyl-1-carboxaldehyde.

Recently cyclopentyl alcohol derivatives have been of particular interest as perfumery and aromatic chemicals. According to Eschinazi<sup>13</sup> 1,3-isopropylcyclopentyl-1-ethanol possesses a rose linalool type fragrance. In order to investigate aromatic and olfactory properties, aldehydes II and VI were converted to their corresponding alcohol and acetate derivatives. Further evaluation of these materials is indicated, however; all possess a mild pleasant odor not unlike linalool.

## Experimental

**Limonene Oxide.**—Limonene oxide was redistilled giving a colorless liquid, b.p. 70–71 (6 mm.),  $n_D^{20}$  1.4694 (1.4697, F.M.C. Corp.). Gas chromatography of this material shows it to be a mixture of *cis* and *trans* epoxides.

**Carvomenthene Oxide.**—The procedure of Newhall<sup>14</sup> was followed, and the product boiling over the range 63–64° (4 mm.) was collected.

**Reaction of Limonene Oxide with Zinc Bromide in Benzene.**—To a refluxing solution of 1 g. of zinc bromide (freshly fused) in 100 ml. of dry benzene was slowly added a solution containing 39 g. (0.26 mole) of freshly distilled limonene oxide in 100 ml. of dry benzene. External heating was discontinued during this addition due to the exothermicity of the reaction. After addition was completed, the mixture was refluxed for 2 hr. and 200 ml. of water was added. The benzene solution was washed with water to remove zinc salts. Separation of the organic layer followed by removal of the solvent at reduced pressure yielded a pleasant smelling, colorless liquid. Distillation of this material at reduced pressure using a Nester–Faust spinning-band column yielded two fractions. Fraction A (12 g., 30%, b.p. 75–76° at 10 mm.) was an aldehyde whose infrared spectrum indicated a terminal olefin absorption. Gas-liquid chromatographic analysis has shown this to be pure 1-methyl-3-isopropenylcyclopentyl-1-carboxaldehyde (B); semicarbazone, m.p. 106°–107°. Fraction B (23 g., 57%, b.p. 84–90 at 10 mm.) contained only two ketonic materials which were separated by gas-liquid chromatography.<sup>15</sup> The material represented by the first peak was shown to be methyl (3-isopropenylcyclopentyl) ketone (III, 10%) by reduction to methyl (3-isopropylcyclopentyl) ketone (VII). The second peak was shown to be dihydrocarvone (IV, 47%) by comparative infrared spectroscopy with an authentic sample and its semicarbazone, m.p. 189–190°, lit.<sup>16</sup> m.p. 189–191°. No other volatile materials were present, and a pot residue of 5 g. remained.

**Reaction of Carvomenthene Oxide with Zinc Bromide.**—In a similar manner 45 g. (0.29 mole) of carvomenthene oxide reacted with 20 g. of zinc bromide in dry benzene to yield 39 g. (83%) of

(13) H. E. Eschinazi, *Chem. Eng. News*, **37**(39), 52 (1959).

(14) W. F. Newhall, *J. Org. Chem.*, **24**, 1673 (1959).

(11) Proton n.m.r. spectra were obtained in carbon tetrachloride solution at 60 Mc. (spinning) on a Varian A-60 spectrometer. Chemical shifts (c.p.s.) are relative to tetramethylsilane.

(12) J. Wolinsky and W. Barker, *J. Am. Chem. Soc.*, **82**, 636 (1960).

(15) Analytical gas chromatographic column data: length, 25 ft.  $\times$   $\frac{3}{8}$  in.; packing, Carbowax 30 M 30% on Chromosorb P; temp., 175°; carrier gas, helium at 150 ml./min.

(16) E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 408.

TABLE I  
 ANALYTICAL AND PHYSICAL DATA OF COMPOUNDS

Compound	B. p. (mm.), °C.	$n_D^{20}$	Formula	Calcd., %		Found, %		Infrared absorption, $\nu_{\max}^{\text{NaCl}}$
				C	H	C	H	
II	75-76 (10)	1.4623	C <sub>10</sub> H <sub>16</sub> O	78.68	10.67	78.20	10.87	2900 (vs), 2650 (s), 1700 (vs), 1625 (s), 885 (s)
VI	68-69 (7)	1.4440	C <sub>10</sub> H <sub>18</sub> O	77.85	11.77	78.07	11.92	2900 (vs), 2625 (s), 1700 (vs), 1360 (s, doublet), 935 (w), 875 (w)
VII	59-60 (1)	1.4499	C <sub>10</sub> H <sub>18</sub> O	77.85	11.77	77.82	11.98	2875 (vs), 1690 (vs), 1320 (s), 1160 (s)
XXI	70-71 (2)	1.4610	C <sub>11</sub> H <sub>18</sub> O <sub>2</sub>	72.47	9.96	72.27	99.90	2900 (s), 1700 (vs), 1150 (vs), 885 (s)
XI	60-61 (1)	1.4456	C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>	71.64	10.95	71.21	10.69	2900 (s), 1710 (vs), 1155 (vs)
XXIV	75-76 (1)	1.4745	C <sub>10</sub> H <sub>18</sub> O	76.85	12.91	76.48	12.79	3300 (s), 2900 (vs), 1640 (w), 1025 (s, split), 885 (s)
XXVI	76-77 (1)	1.4551	C <sub>10</sub> H <sub>20</sub> O	77.85	11.77	77.49	11.81	3300 (s), 2900 (vs), 1030 (vs, broad)
XXV	95-96 (4)	1.4584	C <sub>12</sub> H <sub>20</sub> O <sub>2</sub>	73.41	10.28	73.12	10.21	2900 (vs), 1710 (vs), 1220 (vs), 1030 (s), 885 (s)
XXVII	91-92 (2)	1.4419	C <sub>12</sub> H <sub>22</sub> O <sub>2</sub>	72.59	11.18	72.71	11.17	2900 (vs), 1710 (vs), 1220 (vs), 1030 (s)

a colorless material, b.p. 75-90° (10 mm.). Gas chromatographic analysis<sup>15</sup> of this material showed it to consist of three components. The mixture was distilled to give 10 g. (26%) of 1-methyl-3-isopropylcyclopentyl-1-carboxaldehyde (VI), b.p. 68-69° (7 mm.); semicarbazone, m.p. 140-141°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>21</sub>N<sub>3</sub>O: C, 62.51; H, 10.02; N, 19.89. Found: C, 62.56; H, 10.01; N, 19.92.

Methyl (3-isopropylcyclopentyl) ketone (VII), 4 g. (11%), was also produced, b.p. 72-73° (7 mm.), lit.<sup>17</sup> b.p. 56-57° (3 mm.); semicarbazone, m.p. 156-157°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>21</sub>N<sub>3</sub>O: C, 62.51; H, 10.02; N, 19.89. Found: C, 62.61; H, 9.90; N, 19.78.

Another product was 24 g. (63%) of carvomenthone (VIII); semicarbazone, m.p. 193-194°, lit.<sup>18</sup> m.p. 194-195°. Compounds VII and VIII were confirmed by comparison of their infrared spectra with authentic materials.

**Methyl (3-Isopropenylcyclopent-1-ene) Ketone (XII).**—The procedure of Wolinsky and Barker<sup>12</sup> was followed in part. It was found desirable to reflux the liquid, obtained by treating 3-isopropenyl-6-oxoheptanal with base, at atmospheric pressure. The subsequent elimination of water increased the yield of XII to 53% from limonene oxide, b.p. 64-65° (1 mm.), lit.<sup>12</sup> b.p. 67-68° (1.5 mm.).

**Methyl (3-Isopropylcyclopentyl) Ketone (VII).**—Fifty-three grams (0.35 mole) of methyl (3-isopropenylcyclopent-1-ene) ketone (XII) was dissolved in 150 ml. of ethyl acetate and hydrogenated (Parr-type hydrogenation apparatus) over 0.1 g. of platinum-black catalyst. The progress of the reaction was followed by infrared spectral analysis, the reduction being complete when the carbonyl band shifted from 1640 to 1690 cm.<sup>-1</sup>. Distillation of the reduced material yielded a clear oil, b.p. 59-60° (1 mm.), lit.<sup>18</sup> b.p. 56-57° (3 mm.),  $n_D^{20}$  1.4471.

**Methyl (3-Isopropenylcyclopentyl) Ketone (III).**—A 600- $\mu$ l. sample of the reaction mixture obtained by the zinc bromide-catalyzed rearrangement of limonene oxide was separated by preparative gas-liquid chromatography.<sup>15</sup> There were obtained three materials in three separate peaks, the first containing 1-methyl-3-isopropenylcyclopentyl-1-carboxaldehyde, the third containing dihydrocarvone, and the second peak collected to yield 50  $\mu$ l. of compound III. A small amount of platinum black was added to the collection vial and the material (III) was hydrogenated in a microhydrogenation apparatus to yield a saturated ketone with absorption of 1 mole of hydrogen per mole of material. A comparison of this saturated ketone with VII by comparison of infrared spectra showed them to be identical. Since the original ketone III showed terminal methylene absorption in its infrared spectrum, III is shown to be 1-methyl (3-isopropenylcyclopentyl) ketone.

**1-Methyl-3-isopropenylcyclopentyl-1-carboxylic Acid (IX).**—1-Methyl-3-isopropenylcyclopentyl-1-carboxaldehyde (II) (21.5 g., 0.14 mole) was dissolved in a solution of 4 g. (0.24 mole) of silver nitrate in 150 ml. of alcohol, and 100 ml. of water. To this was added, with stirring, a solution of 20 g. (0.50 mole) of

sodium hydroxide in 250 ml. of water. The silver precipitate was filtered off and the water removed under reduced pressure. The residue was extracted with ether, acidified, and again extracted with ether. Evaporation of the solvent followed by distillation of the residue at reduced pressure yielded 12 g. of IX, b.p. 94-95° (0.1 mm.),  $n_D^{20}$  1.4745. The material was shown to be pure by gas chromatographic analysis of its methyl ester (XXI) prepared from diazomethane (Table I). The hydrogenation of 2 g. (0.01 mole) of XXI over platinum-black catalyst yielded ester XI with absorption of 1 mole of hydrogen per mole of ester. This material was identical with XI prepared from acid X (obtained by oxidation of aldehyde VI) and with XI prepared from acid X (obtained from ketone XII), as shown by their identical infrared spectra.

**1-Methyl-3-isopropylcyclopentyl-1-carboxylic Acid (X).**—In a manner similar to the above, 8 g. (0.05 mole) of VI, obtained from the rearrangement of carvomenthone oxide, was oxidized to the corresponding acid to give 5.5 g. boiling at 83-84° (0.07 mm.),  $n_D^{20}$  1.4557. The methyl ester (XI) of this acid prepared from diazomethane was shown to be pure by gas chromatography (see Table I).

**Hydrogenation of 1-Methyl-3-isopropenylcyclopentyl-1-carboxylic Acid.**—Hydrogenation of 5 g. (0.03 mole) of 1-methyl-3-isopropenylcyclopentyl-1-carboxylic acid (IX) in 25 ml. of ethyl acetate with 0.2 g. of platinum black quantitatively yielded acid X, b.p. 83-84° (0.06 mm.),  $n_D^{20}$  1.4551. Infrared spectra comparison of the methyl ester of this material with the methyl ester of the above acid, prepared with diazomethane, showed them to be identical.

**1-Methyl-3-isopropenylcyclopentyl-1-carbinol (XXIV).**—Sixteen grams (0.11 mole) of II in 50 ml. of anhydrous ether was added to a slurry of 2.7 g. (0.06 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether at a rate so as to maintain reflux. The mixture was hydrolyzed with water and extracted with three 50-ml. portions of ether. The ether was removed to yield a clear, pleasant smelling oil. Distillation of this material (b.p. 75-76° at 1 mm.) yielded 10 g. (60%) of XXIV (see Table I). Acetylation of 1.7 g. of this alcohol with acetyl chloride in pyridine-benzene solution yielded 1.2 g. of the corresponding acetate (XXV) boiling at 96-97° (4 mm.) (see Table I).

**1-Methyl-3-isopropylcyclopentyl-1-carbinol (XXVI).**—One gram of 1-methyl-3-isopropenylcyclopentyl-1-carbinol (XXIV) was dissolved in 10 ml. of *n*-pentane and 0.05 g. of platinum black was added. The mixture was placed in a Parr hydrogenation apparatus and, after hydrogen absorption ceased, the catalyst was removed by filtration. The solvent was removed at reduced pressure and the residue distilled to give 0.9 g. (90%) of 1-methyl-3-isopropylcyclopentyl-1-carbinol, b.p. 77° (1 mm.). The corresponding acetate XXVII was prepared as above and listed in Table I. The latter compounds were shown to be pure by gas-liquid chromatographic analysis.<sup>15</sup>

**Acknowledgment.**—We wish to thank Dr. Werner Herz, Florida State University, Tallahassee, Florida, for carrying out the n.m.r. analysis. We are grateful to F.M.C. Corporation for their generous sample of limonene oxide.

(17) H. E. Eschinazi, U. S. Patent 2,946,823 (1960).

(18) E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 394.