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# CHARACTERIZATION OF THE HYDROPEROXIDES DERIVED FROM SINGLET OXYGEN OXIDATION OF (+)-LIMONENE

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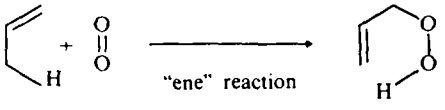
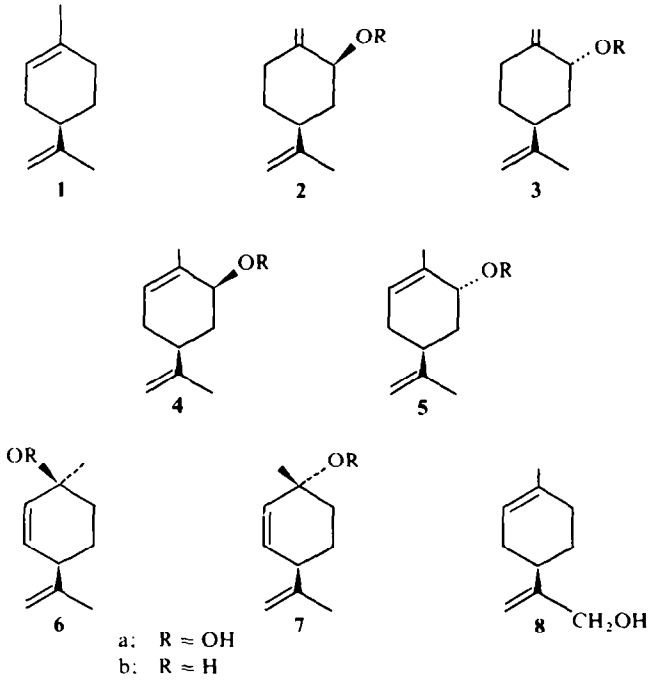
**Abstract**—Six hydroperoxides (**2a–7a**) have been identified as the primary reaction products of the singlet oxygen oxidation of (+)-limonene. The products were isolated by semi-preparative hplc and characterized by NMR, IR, glc pyrolysis, and reduction to known alcohols.

(+)-Limonene (**1**) has been employed in several of the pioneering studies concerning the reaction of singlet oxygen ($^1O_2$) with olefins.[1–5] It has also been used to test for the presence of $^1O_2$.[4] The postulated primary reaction products of limonene $^1O_2$ oxidation, hydroperoxides **2a–7a**, are formed by the well known "ene" reaction,[5] the 1,3-addition of $^1O_2$ at the endocyclic, most highly substituted double bond. They have never been separated and characterized; rather, their structures have been inferred from the reduction products (**2b–7b**).




A previous report of a partial resolution of limonene hydroperoxides performed by tlc[6] appeared to hold little promise for their complete separation and subsequent characterization. Recent studies have demonstrated the power of high performance liquid chromatography (hplc) in the separation of lipid[7,8] and cholesterol[9] hydroperoxides. By modifying the hplc procedures developed for the separation of terpene alcohols,[10] we have resolved the limonene $^1O_2$ hydroperoxides on a semipreparative scale and have characterized them fully.

Limonene hydroperoxides were prepared in methanol by $^1O_2$ oxidation, using a modification of published procedures.[1,11] The composition of the reaction mixture was determined by glc after reduction with aqueous sodium bisulfite to alcohols **2b–7b** and **8**. The weight percent of each alcohol and unreacted limonene, corrected for glc detector response, is given in Table 1 along with the area percent of each alcohol. The area percents agree very well with previously reported data[1,2,11] for alcohols **2b–7b**. (Absolute weight percents are reported here for the first time.) The alcohols **2b–7b** were identified by IR and MS comparison either to spectra of authentic samples or known spectra.




1 2 3 4 5 6 7 8

a: R = OH
b: R = H

Alcohol **8**, previously unreported from the $^1O_2$ oxidation of limonene, was found present in 0.3% weight percent. It was identified by comparison of the IR to a published spectrum,[12] and the MS to a MS of authentic material.[13] Alcohol **8** is present in nature as a minor constituent in a variety of essential oils[13] and in tangerine essence.[14] The unisolated precursor hydroperoxide of compound **8** should result from attack of $^1O_2$ on the exocyclic, least substituted double bond of limonene, unlike all the previously found products.

The crude photolysate was purified on a silica gel (Activity III) column to yield the hydroperoxides. Previously reported IR absorptions of free OOH in some representative hydroperoxides occurred over the range of 3512- 3555 $cm^{-1}$, while absorptions of the free OH in corresponding alcohols were observed at 3613-3632 $cm^{-1}$.[15] An IR of the above purified hydroperoxide fraction shows a strong free hydroperoxide absorption at 3550 $cm^{-1}$, a trace of alcohol at 3610 $cm^{-1}$ and no carbonyl. The alcohol and hydroperoxide bands are sharp and well resolved.

The six individual hydroperoxides (**2a**-**7a**) were isolated by semipreparative hplc, and they were best separated using both a 10 $\mu$m and a 5 $\mu$m silica gel column in tandem. They were first separated with ethyl acetate: toluene (0.5:99.5, v/v) into five fractions, with peak identifications as shown in Fig. 1a. The unisolated hydroperoxide precursor to alcohol **8**, which would be present in *ca* 0.5%, co-eluted with compound **6a**. The fraction containing **3a** and **5a** was then resolved by rechromatography employing 100% methylene chloride. (A chromatogram of the six hydroperoxides using 100% methylene chloride is shown in Fig. 1b.) Each compound could be prepared in greater than 95% purity. In order to calculate the area percents for the individual hydroperoxides shown in Table 1, a third run using ethyl acetate:hexane (4:96, v/v) was also necessary. The hplc area percents of the hydroperoxides correspond very well with the glc area percents of the reduction products, alcohols **2b**-**7b**. This supports the previously postulated, direct qualitative and quantitative correspondence of a particular alcohol to its hydroperoxide precursor.

The structures of the purified hydroperoxides were confirmed mainly by IR and 60 MHz NMR analysis. In addition, some stereochemical assignments were secured by reduction of selected hplc fractions and glc pyrolysis. The IR spectrum of each individual hydroperoxide in carbon tetrachloride exhibits a strong free OOH band at 3550 $cm^{-1}$. Additionally, two terminal double bonds are confirmed for both **2a** and **3a**, by adsorptions at 3085, 1648, and a doublet at *ca* 890 and 905 $cm^{-1}$. Both a terminal double bond at *ca* 3080, 1645 and 890 and an endocyclic double bond at *ca* 3030 and 1680 $cm^{-1}$ are observed for **4a**-**7a**.

The NMR spectrum of hydroperoxide **2a** shows a narrow 3-proton multiplet at

$$\delta\ 1.73 (C{=}C(\text{-}CH_3),$$

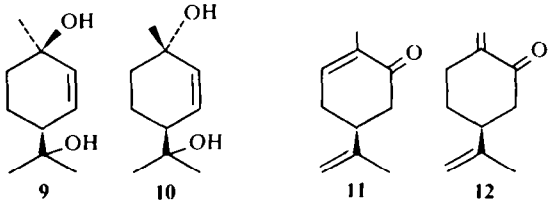
a broad 1-proton triplet with additional splitting at 4.46 (J = 10 Hz, H C-OO-), a narrow 2-proton multiplet at 4.73 (isopropenyl $C = C\begin{smallmatrix}H\\H\end{smallmatrix}$), two one-proton multiplets at 4.78 and 4.90 (exocyclic $C = C\begin{smallmatrix}H\\H\end{smallmatrix}$), and a narrow 1-proton multiplet at 7.90 (OOH). As would be expected, the NMR of *trans*-isomer **3a** exhibits very similar resonances with two exceptions: (1) the 1-proton triplet at 4.46 (H-C-OO-) has a J = 3 Hz, and (2) the 2-proton exocyclic vinylic resonance at 4.98 shows a narrow multiplet indicating almost equivalent protons. These results confirm the stereochemical assignments for **2a** and **3a**, since inspection of models shows that for *cis*-isomer **2a**, the proton $\alpha$ to OOH is axial and split by an axial vicinal proton (180° dihedral angle), giving a large coupling (J = 10 Hz); for *trans*-isomer **3a**, the equatorial proton $\alpha$ to OOH has a gauche butane type interaction with both vicinal protons yielding a much smaller coupling (J = 3 Hz). The models further indicate a severe interaction between one of the exocyclic vinylic protons and the OOH function in *cis*-**2a**, thus, the 1-proton multiplets at 4.78 and 4.90. No such interaction is present in *trans*-**3a**.

The NMR spectrum of *trans*-hydroperoxide **5a** shows a narrow 6-proton multiplet at

$$\delta\ 1.76 (2 \times C{=}C(\text{-}CH_3),$$

a broad 1-proton multiplet at 4.23 (H-C-OO-), a narrow 2-proton multiplet at 4.71 ($C{=}C\begin{smallmatrix}H\\H\end{smallmatrix}$), a broad 1-proton multiplet at 5.68 ($\begin{smallmatrix}H\\ \\ \end{smallmatrix}\!>\!C{=}C\!<$), and a broad 1-proton multiplet at 7.66 (OOH). The *cis*-isomer (**4a**) exhibits a very similar pattern; therefore, the stereochemistry for this pair (**4a**, **5a**) was determined by reduction and glc pyrolysis.

The *trans*-hydroperoxide (**6a**) exhibited a 3-proton singlet at $\delta$ 1.26 ($CH_3$ C-OO-), a narrow 3-proton multiplet at 1.70 ($CH_3$-C=C-), a broad 1-proton multiplet at 2.56 ( $\overset{H}{\diagup\!\!=\!\!\diagdown}$ ), a narrow 2-proton multiplet at 4.72 ($C{=}C\begin{smallmatrix}H\\H\end{smallmatrix}$), a 2-proton AB quartet at 5.46 and 5.75 (J = 11 Hz) with additional splitting ($\begin{smallmatrix}H\\ \\ \end{smallmatrix}\!>\!C{=}C\!<\!\begin{smallmatrix}H\\ \\ \end{smallmatrix}$), and a narrow 1-proton multiplet at 6.98 which exchanges with $D_2O$ (OOH). The NMR of *cis*-isomer **7a** shows similar features except for the vinylic protons. The endocyclic vinylic protons ($\begin{smallmatrix}H\\ \\ \end{smallmatrix}\!>\!C{=}C\!<\!\begin{smallmatrix}H\\ \\ \end{smallmatrix}$) exhibit a broad 2-proton singlet at 5.70. This is consistent with the stereochemistry assigned to **6a** and **7a**, since the NMR of diols **9** and **10** shows a quartet for the vinylic protons of *trans*-isomer **9** and a singlet for those of *cis*-isomer **10**.[16]




**9** **10** **11** **12**

Table 1. Composition of selected reaction mixtures

| Compound number | REDUCTION PRODUCTS Weight %† - alcohols and unreacted limonene | Area %* alcohols | HYDROPEROXIDES Area %* HPLC | Area %* GLC pyrolysis |
|---|---|---|---|---|
| 1 | 21 | | | |
| 2 | 14 | 21.1 | 19.8 | 9.9 |
| 3 | 12 | 18.1 | 20.0 | 10.9 |
| 4 | 3 | 4.5 | 5.7 | 1.2 |
| 5 | 6 | 9.1 | 10.7 | 4.1 |
| 6 | 25 | 37.7 | 34.9 | 31.5 |
| 7 | 6 | 9.1 | 8.9 | 9.0 |
| 8 | 0.3 | 0.5 | | |
| 11 | | | | 13.6 |
| 12 | | | | 19.8 |

† Employing Tetradecane as internal standard and correcting for response.

* (Area of peak of interest/Total area of peaks of interest) x 100.

Lier[17] and Teng[18] observed that the attempted separation of cholesterol hydroperoxides by glc led to a complex but reproducible mixture of alcohols and carbonyls. An analytical glc determination on our limonene hydroperoxide mixture also yielded, by pyrolysis, alcohols **2b**–**7b** and ketones **11** and **12** in addition to several unidentified products, with no remaining hydroperoxides. Table 1 shows the expected correspondence between the area percents of the alcohols and their hydroperoxide precursors. The glc results for the major pyrolysis products of the individually purified hydroperoxides are given in Table 2. Each of the secondary hydroperoxides (**2a**–**5a**) yields a ketone and the specific alcohol in high yield (Table 2), confirming the assigned stereochemistry. The pyrolysis[19] of **2a** can be pictured as involving homolytic cleavage to yield ·OH followed by both a $\beta$-scission of the resulting alkoxy radical to yield ketone **12**, and a transformation of the alkoxy radical by a multistep chain mechanism to alcohol **2b**. For each tertiary hydroperoxide (**6a**–**7a**), the related alcohol predominates in the complex mixture of pyrolysis products.

Table 2. GLC pyrolysis of individual limonene hydroperoxides

| Starting compound | Product (Area %)† |
|---|---|
| 2a | 2b (15) + 12 (69) |
| 3a | 3b (20) + 12 (56) |
| 4a | 4b (8) + 11 (68) |
| 5a | 5b (17) + 11 (73) |
| 6a | 6b (55) |
| 7a | 7b (54) |

† (Area of peak of interest/Total area of all peaks) x 100.

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The proposed structure of ketone **12** is compatible with its MS which exhibits a molecular ion at $m/z$ 150, and also a peak at 108 which is similar in intensity to that in the MS of carvone for loss of ketene. The structure was confirmed by LAH reduction of **12** to alcohol **2b**. Ketone **12** was prepared by glc pyrolysis of a mixture of **2a** and **3a**; the yield was dependent upon concentration, sample size, and instrument conditions. If samples of greater than *ca* 1 $\mu$l in size and 5000 ppm in concentration were used, the yield of ketone was drastically lowered relative to alcohols **2b** and **3b**. In spite of these difficulties a few $\mu$g of **12** were collected.

To further confirm the stereochemistry of hydroperoxides **4a** and **5a**, the individual peaks from the methylene chloride hplc separation (Fig. 1b) were reduced with aqueous sodium bisulfite. The first peak, which contained hydroperoxides **2a**, **3a** and **4a**, yielded only alcohols **2b**, **3b** and **4b**. The second one, which contained only hydroperoxide **5a**, gave alcohol **5b** exclusively. The third and fourth peaks yielded alcohols **6b** and **7b**, respectively, as expected.

## EXPERIMENTAL

Analyses by glc were performed on a PE-900 or Varian-3700 equipped with an on-column injector, an FID detector, and a 12 ft, $\frac{1}{8}$ in. i.d. glass column packed with 5% Triton X-305 on Chromosorb W.H.P. 80–100 mesh. The oven temp was generally programmed from 70° to 170° at 5°/min with 5 min initial hold. The injector and detector were maintained at 150° and 250°, respectively. A flow rate of 35 ml/min of helium was employed. Compounds isolated by glc were collected in glass capillaries from an F & M 810 equipped with a TC detector and a $\frac{1}{4}$ in. glass column packed and used as above.

The hplc system was a Waters Model ALC/GPC 201 which included a M-6000 pumping system, a M-U6K universal injector, and a M-R 401 differential refractometer. The columns were Whatman Partisil-PXS consisting of 25 cm × 4.5 mm I.D. stainless steel tubing packed with 10 or 5 $\mu$m microparticulate silica. The columns were used in tandem. A description of the hplc conditions adopted in this work is being reported elsewhere in greater detail. IR spectra were determined using a PE-281; NMR, a Varian T-60; and GC MS, a HP-5993 or Hitachi-RMU-6L.

*Singlet oxygen oxidation of limonene.* The photolysis apparatus consisted of a cylindrical, one-necked flask equipped with a very efficient magnetic stirrer and a water cooled condenser. $O_2$ was introduced into the bottom of the vessel with a $\frac{1}{16}$ in. teflon tube at a rate of 6.7 ml/min. A 200 W clear tungsten light was employed with the bulb positioned about 5 in. from the flask and slightly above it so that it could be aimed into the mixture at a 45° angle. The lamp was shaded with Al foil and foil was placed under the vessel. The apparatus was placed in a hood and a combination of air and condenser cooling maintained the reaction at about 25°.

(+)-Limonene (98.5% from distilled, cold pressed orange oil) was further purified by percolation through a column of basic alumina (Activity I) to yield material of 99.8% purity by glc. Rose bengal (0.26 g, $2.5 \times 10^{-4}$ mole) was dissolved in MeOH (200 ml; dried over molecular sieves), and limonene (13.6 g, 0.1 mole) was added with the aid of MeOH (60 ml). The mixture was periodically sampled, extracted, and analyzed by glc using a tetradecane internal standard. When only 20% of the original limonene remained (48 hr), the mixture was concentrated to 50 ml. The concentrate was taken up in ether (175 ml), washed with water ($1 \times 50$, $1 \times 30$ ml) and sat NaCl aq ($1 \times 30$ ml), and concentrated to yield crude hydroperoxide (17.1 g) containing a small amount of solvent. Chromatography on $SiO_2$ (Activity III) consisted of elution, first, of limonene with hexane, followed by elution of the pure hydroperoxide mixture with $CH_2Cl_2$.

*Reduction of hydroperoxide mixture.* In a separate reaction, the above described hydroperoxide:methanol mixture was concentrated to 50 ml. $Na_2SO_3$ (25 g, 0.2 mole) in water (150 ml) was added dropwise to the above mixture, with ice cooling and stirring. After one-half of the $Na_2SO_3$ had been added, a thick ppt formed and stirring was then facilitated by removal of the ice bath. The mixture was stirred overnight at r.t., heated 2.5 hr at 70°, cooled, water (50 ml) added to dissolve the ppt, and extracted with ether ($3 \times 100$ ml). The combined ethereal soln was washed with water (40 ml) and sat $NaHCO_3$ aq (40 ml), dried over $Na_2SO_4$, and concentrated to yield 12.2 g (65.5% absolute yield of alcohols from limonene by glc, using an internal standard and correcting for unreacted limonene). The weight % of each component is given in Table 1.

*Preparative hplc separation of hydroperoxides.* The hydroperoxides were separated into 5 fractions using EtOAc:toluene (0.5:99.5, v/v) with *ca* 10 μl injections. Toluene was removed by rotary evaporation at 28°, full aspirator vacuum, to a volume of 0.5 ml in order to avoid decomposition of the hydroperoxides. Rechromatography (twice) of the sample of interest with $CH_2Cl_2$ resulted in removal of interfering toluene.

*Reduction of hydroperoxide fractions.* Fractions (2–4 mg) were collected for each peak using the $CH_2Cl_2$, hplc separation (Fig. 1b). The fractions were concentrated at 25°, aspirator vacuum, to 0.25 ml with no change by glc. MeOH (0.5 ml) was added to each fraction and most of the remaining $CH_2Cl_2$ removed as above. Each fraction was transferred, with the aid of MeOH (1 ml), to a flask and $Na_2SO_3$ (1.5 ml of $1.19 \times 10^{-3}$ M) soln added. The mixture was periodically shaken 4 hr at r.t., heated 25 hr at 75°, cooled, extracted with $CH_2Cl_2$ ($2 \times 3$ ml), washed with water (2 ml) and concentrated.

cis-2-*Methylene*-5-(1-*methylethenyl*)-*cyclohexyl hydroperoxide* (**2a**). IR ($CCl_4$), $\nu_{max}$ 3550 (free OOH), 3085 and 1648 ($C{=}C\begin{smallmatrix}H\\H\end{smallmatrix}$), 1440 and 1455 (d), 1320 and 1340 (d), 1010, 892 and 905 ($C{=}C\begin{smallmatrix}H\\H\end{smallmatrix}$) $cm^{-1}$. NMR ($CCl_4$), δ 1.73 (3 H, n, m), 4.46 (1 H, br, t with additional splitting, J = 10 Hz), 4.73 (2 H, n, m), 4.78 (1 H, br, m), 4.90 (1 H, br, m) 7.90 (1 H, m, m).

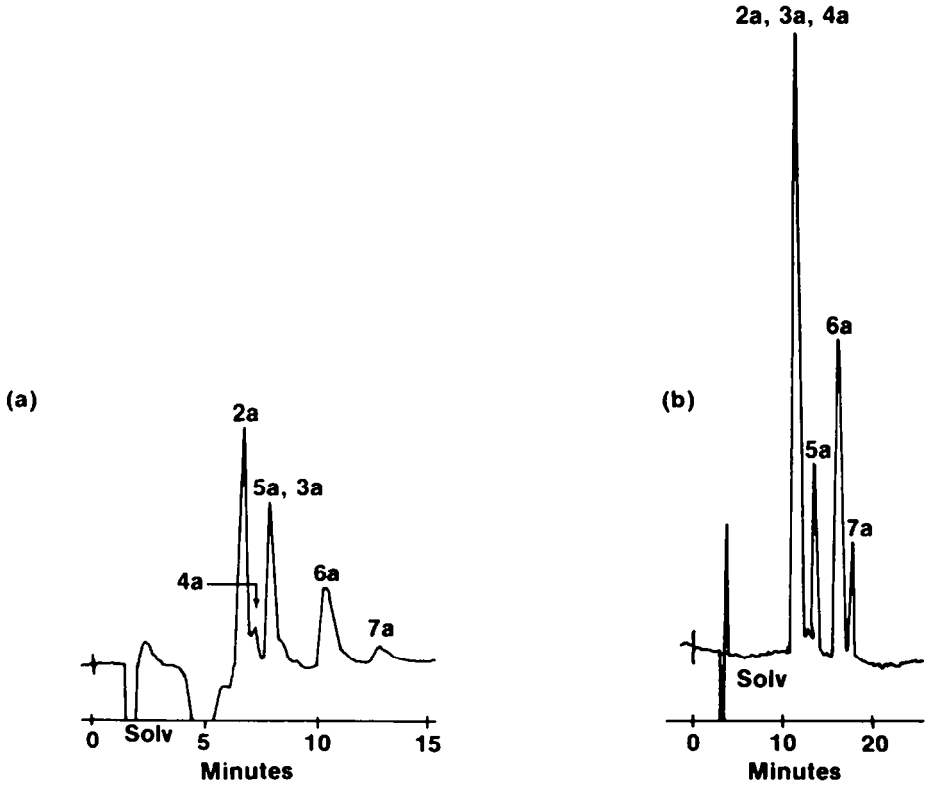


Fig. 1. Hydroperoxide separations on Partisil 10 + 5. (a) 0.5% ethyl acetate: 99.5% toluene (10 μl), (b) 100% methylene chloride (5 μl).

*trans-2-Methylene-5-(1-methylethenyl)-cyclohexyl hydroperoxide* (**3a**). IR ($CCl_4$), $\nu_{max}$ 3450 (free -OOH), 3440 (H bonded OOH), 3088 and 1648 (C=C<sup>H</sup>), 1440 and 1452 (d), 1300 and 1360 (d), 1075, 965, 885 and 905 (C=C<sup>H</sup>). NMR ($CCl_4$), $\delta$ 1.73 (3 H, n, m), 4.46 (1 H, t with additional splitting, J = 3 Hz), 4.73 (2 H, n, m), 4.98 (2 H, n, m), 7.45 (1 H, br, m).

*cis-2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-yl hydroperoxide* (**4a**). IR ($CCl_4$), $\nu_{max}$ 3550 (free OOH), 3080 (C=C<sup>H</sup>), 3040 and 1672 (H>C=C<), 1645 (C=C<sup>H</sup>), 1435 and 1450 (d), 1375, 1320, 1015, 890 (C=C<sup>H</sup>). NMR ($CCl_4$), $\delta$ 1.76 (6 H, n, m), 4.73 (2 H, n, m), 5.56 (1 H, br, m).

*trans-2-Methyl-5-(1-methylethenyl)-2-cyclohexen-1-yl hydroperoxide* (**5a**). IR ($CCl_4$), $\nu_{max}$ 3550 (free OOH), 3080 (C=C<sup>H</sup>), 3030 and 1680 (H>C=C<), 1645 (C=C<sup>H</sup>), 1445 and 1455 (d), 1300 and 1320 (d), 890 (C=C<sup>H</sup>). NMR ($CCl_4$), $\delta$ 1.76 (6 H, n, m), 4.23 (1 H, br, m), 4.71 (2 H, n, m), 5.68 (1 H, br, m), 7.66 (1 H, br, m).

*trans-1-Methyl-4-(1-methylethenyl)-2-cyclohexen-1-yl hydroperoxide* (**6a**). IR ($CCl_4$), $\nu_{max}$ 3555 (free OOH), 3440 (H bonded OOH), 3080 (C=C<sup>H</sup>), 3030 and 1680 (H>C=C<H), 1645 (C=C<H), 1445, 1370, 1320, 1145, 1105, 890 (C=C<sup>H</sup>). NMR ($CCl_4$), $\delta$ 1.26 (3 H, s), 1.70 (3 H, n, m), 2.56 (1 H, br, m), 4.72 (2 H, n, m), 5.46 and 5.75 (2 H, quartet with additional splitting, J = 11 Hz), 6.98 (1 H, n, m) exchanges $D_2O$.

*cis-1-Methyl-4-(1-methylethenyl)-2-cyclohexen-1-yl hydroperoxide* (**7a**) IR ($CCl_4$), $\nu_{max}$ 3550 (free -OOH), 3420 (H bonded, OOH), 3075 (C=C<sup>H</sup>), 3022 (H>C=C<H), 1642 (C=C<sup>H</sup>), 1450, 1365, 1320, 1205, 1135 (d), 1100 (d), 895 (C=C<sup>H</sup>), 840. NMR ($CCl_4$), $\delta$ 1.26 (3 H, s), 1.73 (3 H, n, m), 2.71 (1 H, br, m), 4.68 (1 H, n, m), 4.75 (1 H, n, m), 5.70 (2 H, br, s), 7.05 (1 H, m).

*4-Methyl-β-methylene-3-cyclohexene-1-ethanol* (**8**). The minor product from reduction of the hydroperoxide mixture was isolated by preparative glc and shown to be **8**: IR ($CCl_4$), $\nu_{max}$ 3610 (free -OH), 3070 (C=C<sup>H</sup>), 1660 (H>C=C<), 1640 (C=C<sup>H</sup>), 1430 and 1445 (d), 1370, 1100, 1065, 1035, 1010, 890 (C=C<sup>H</sup>). MS: *m/z* (relative abundance) 152 (7.3), 134 (33), 119 (66), 106 (85), 93 (55), 91 (71), 79 (85), 77 (48), 68 (84), 67 (100), 55 (69), 53 (57), 41 (76), 39 (80).

*2-Methylene-5-(1-methylethenyl)-cyclohexanone* (**12**). MS: *m/z* (relative abundance) 150 (62), 135 (40), 122 (26), 108 (85), 107 (81), 93 (50), 81 (61), 79 (100), 67 (49), 53 (62), 41 (50).

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