The Allylic Rearrangement of Hydroperoxides: the Allylperoxyl Radical

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The free-radical rearrangement of pinocarveyl hydroperoxide (1) or myrtenyl hydroperoxide (2) in hexane produces an equilibrium mixture of both hydroperoxides. The absence of carbon skeletal rearrangement suggests that the intermediate radical involved in hydroperoxide isomerization has its unpaired electron localized elsewhere than the α-carbon atom. The failure of oxygen to react with pinocarveyl, myrtenyl, and acyclic hydroperoxides (8) and (9) during the allylic rearrangement supports this suggestion. The kinetics of the rearrangement of 1-isopropyl-2-methylallyl hydroperoxide (8) is compatible with a mechanism in which the intermediate is a common allylperoxyl radical produced directly from either allylic isomer.

α,β-Unsaturated hydroperoxides rearrange by a free-radical mechanism in dilute, non-polar solutions and produce an equilibrium mixture of allylic isomers.[1] In earlier work, an inverse dependence of isomerization rate on hydroperoxide concentration was noted and the chain mechanism outlined in equations (1)—(4) was proposed.[2] Several features distinguish

Initiation:

$$\underset{D}{(ROOH)_2} \overset{K}{\rightleftharpoons} \underset{M}{2\,ROOH} \xrightarrow{k_1} RO^{\cdot} + {}^{\cdot}OH \qquad (1)$$

$$ROOH + RO^{\cdot}({}^{\cdot}OH) \longrightarrow ROO^{\cdot} + ROH\ (H_2O) \qquad (2)$$

Propagation:

$$\underset{a}{{}^{\cdot}OO{-}C{-}C{=}C} \rightleftharpoons \underset{CR}{C{-}\dot{C}{-}C} \rightleftharpoons \underset{b}{C{=}C{-}C{-}OO^{\cdot}} \qquad (3)$$

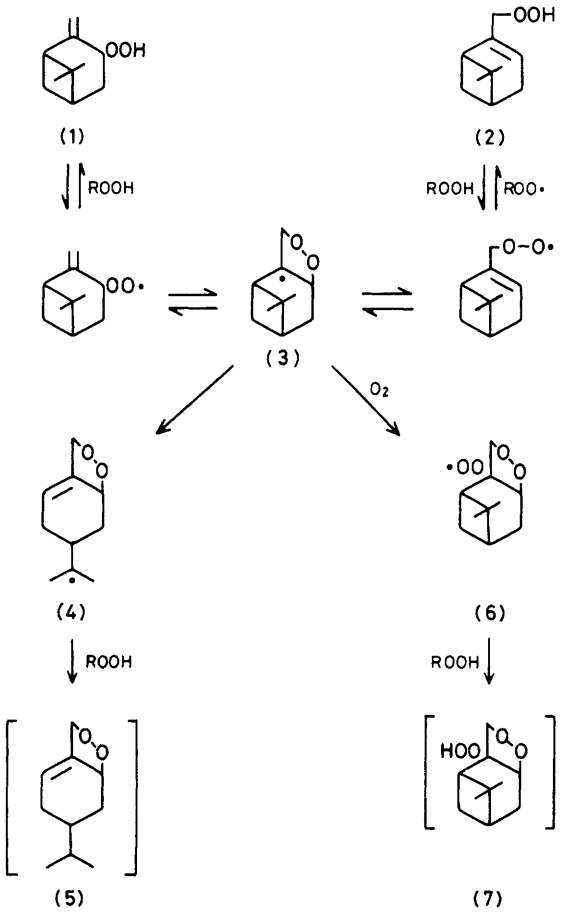
$$C{=}C{-}C{-}OO^{\cdot} + \underset{M_1}{HOO{-}C{-}C{=}C} \rightleftharpoons C{=}C{-}COOH + \underset{M_2}{{}^{\cdot}OO{-}C{-}C{=}C} \qquad (4)$$

this mechanism. First, it was suggested that an allylic peroxyl radical is formed by hydrogen atom abstraction from hydroperoxide monomer but not from the strongly hydrogen-bonded dimer whose formation is favoured in neat hydroperoxide and concentrated solutions. This assumption explained the observed inverse dependence of isomerization rate on concentration. Secondly, it was suggested that the isomerization of allylic peroxyl radicals proceeds through a cyclic carbon-centred radical intermediate (CR) as shown in equation (3). In the present work, an attempt was made to demonstrate the existence of the cyclic carbon radical CR during the isomerization. Two types of experiments were carried out: (i) isomerization of hydroperoxides for which the expected intermediate would undergo a rearrangement of its carbon skeleton; and (ii) attempted trapping of the proposed carbon-centred radical with molecular oxygen. In either case, the intermediate should be present at a low steady-state concentration in dilute solution both during the approach to and at equilibrium. Side reactions of the intermediate, such as the proposed skeletal rearrangement or reaction with oxygen, if they do not terminate the chain but produce different products, should be detectable regardless of their rate. Despite this experimental advantage, no evidence for either reaction was obtained in any of the experiments to be described. These results suggest that if a common intermediate radical is involved, it does not have its unpaired electron localized on carbon. The previously proposed mechanism was modified and the kinetics of the isomerization were studied in greater detail.

Results

Pinocarveyl [pin-2(10)-en-3-yl] hydroperoxide (1) and myrtenyl (pin-2-en-10-yl) hydroperoxide (2) were prepared by the photosensitized oxidation of α-pinene (pin-2-ene) and β-pinene [pin-2(10)-ene][3] respectively. The rearrangement of either isomer to a mixture of isomers was observed in hexane solution at 40 °C. If the intermediate (3) is involved in the isomerization, radical ring opening similar to that usually observed during the addition of various radicals to α or β-pinene[4] may occur. Since opening of the 4-membered ring produces a radical (4) able to continue chain propagation, the formation of a new product (*e.g.* 5) should accompany the isomerization. A gradual increase in its concentration could occur in the equilibrium mixture as long as any hydroperoxide remains. In fact, no such by-product or derivative was detected by g.c. analysis of dilute hexane solutions after a long period at 40 °C.

The isomerization rates were followed closely as shown in Figures 1 and 2 by periodic g.c. analysis after treatment of the mixture with triphenylphosphine. From the changes in the relative amounts of alcohols present with time, shown in Figure 3, the equilibrium concentrations may be determined. Myrtenyl hydroperoxide (2) isomerizes in dilute hexane and produces an equilibrium mixture containing *ca.* 78% of myrtenyl and 22% of pinocarveyl hydroperoxides. Isomerization of pinocarveyl hydroperoxide (1) under identical conditions yielded somewhat less reproducible data, with the equilibrium mixture containing closer to 70% of the more stable myrtenyl hydroperoxide. Although many trace impurities are detected by g.c. in the neat starting hydroperoxides,[5] no perceptible change in their concentration occurs, and no new product peaks appear, even after long reaction times, other than those derived directly from the hydroperoxides. An eventual decrease in titratable hydroperoxide results from the formation of an insoluble oil which coats the walls of the reaction vessel and from the expected hydroperoxide decomposition to the corresponding alcohols and carbonyl compounds: myrtenol, myrtenal, pinocarveol, and pinocarvone. The slow formation of oils during experiments with the pinene hydroperoxides is typical of the reactions of α-pinene[6] and its derivatives. The nature of the oil was briefly examined. The oils obtained by removal of solvent from the rearrangement reaction mixture or from the reduced α-



Scheme.

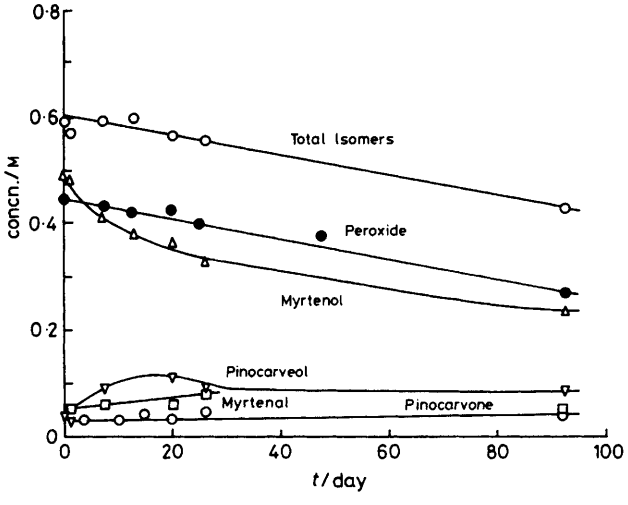


Figure 1. Isomerization of myrtenyl hydroperoxide (2) in hexane at 40 °C showing peroxide concentration determined by iodometric titration and concentrations of products after reduction

pinene photo-oxygenation product, and directly produced during the isomerization of pinocarveyl hydroperoxide, all yielded solids on treatment with methanol which appeared to be normal polymerization products. The characteristic i.r. absorption bands associated with the pinocarveyl double bond at 3 060, 1 640, and 880 cm^{-1} were absent from all three

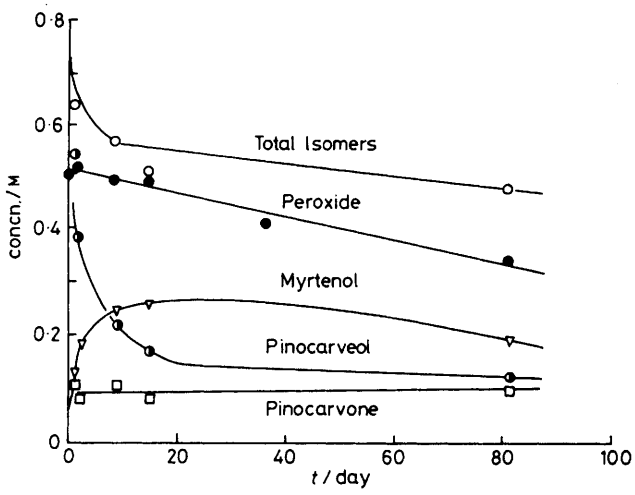


Figure 2. Isomerization of pinocarveyl hydroperoxide (1) in hexane at 40 °C showing peroxide concentrations determined by iodometric titration and concentrations of products after reduction

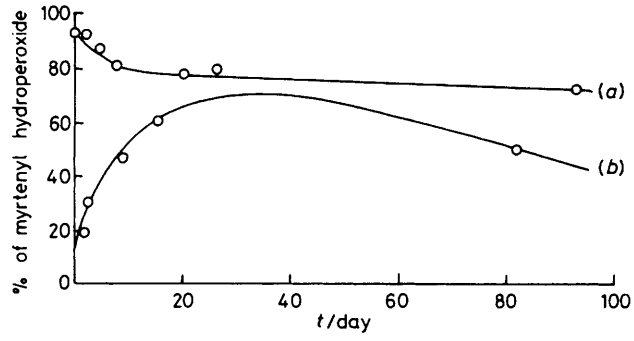


Figure 3. Composition of isomeric hydroperoxide during isomerization of (a) myrtenyl and (b) pinocarveyl hydroperoxides in hexane at 40 °C. The molar concentrations are shown in Figures 1 and 2

samples, while major bands were present for hydroxy and conjugated carbonyl groups (1 670 cm^{-1}), as well as a moderate band for a saturated carbonyl group (1 720 cm^{-1}). The i.r. spectra suggest that polymerization occurs partially with ring opening, leading to a conjugated carbonyl structure, both with neat hydroperoxide (which does not isomerize) and with hydroperoxide in hexane solution.

Attempts to demonstrate the existence of the proposed cyclic intermediate by trapping it with molecular oxygen produced no detectable trapping products. Oxygen might be expected to react during the isomerization to produce the peroxy intermediate (6), leading to the new product (7) without causing significant chain termination. This product, if formed, could accumulate after equilibrium is reached. Its reduction would give alcohols or epoxides of predictable structures which would be readily detectable by gas chromatography, as would be its thermal decomposition products. Isomerization of pinocarveyl hydroperoxide was conducted in dilute hexane under 500 lb in^{-2} of oxygen. Analysis of the reaction mixture showed it to be identical with a control sample left for an equal time under nitrogen.

To confirm the behaviour of oxygen towards rearranging hydroperoxides, a more representative allylic hydroperoxide, 1-isopropyl-2-methylallyl hydroperoxide (8), was prepared and studied. Photosensitized oxidation of 2,4-dimethylpent-2-ene produced almost exclusively the single hydroperoxide (8)

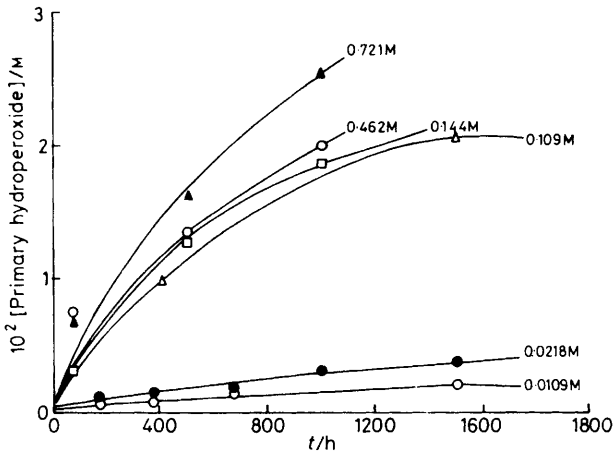


Figure 4. Effect of hydroperoxide concentration on isomerization of the hydroperoxide (8) in hexane at 40 °C

which was found to be easily isolated and purified by simple distillation. Isomerization of (8) in dilute hexane solution under high oxygen pressure produced the hydroperoxide (9) and no products additional to those formed in a similar isomerization in the absence of oxygen.

$$Me_2CHCHCMe{=}CH_2 \rightleftharpoons Me_2CHMeCH{=}CMeCH_2OOH$$
$$\quad\;\; OOH$$
(8), 80% (9), 20%

Attempts to prepare several other hydroperoxides with suitable substituents to favour rearrangement or to stabilize the intermediate radical were not pursued because of difficulties involved in their purification. The attempted oxidation of the unseparated oxygenation products from 2,2,4,6,6-pentamethylhept-3-ene again demonstrated, however, that the isomerization intermediate does not react with O_2. The n.m.r. spectrum of the mixed hydroperoxides used in this experiment indicated that the major component, which accounted for two thirds of the total hydroperoxide, was 4,4-dimethyl-2-methylene-1-t-butylpentyl hydroperoxide, $Me_3CCH(OOH)$-$C(=CH_2)CH_2CMe_3$. A dilute solution of these undistilled hydroperoxides was kept at 40 °C for 11 weeks under 500 lb in^{-2} of oxygen. No change in composition was indicated by g.c., showing that the starting hydroperoxides were present in close to an equilibrium mixture. The chromatogram was identical with that obtained with a control sample of the same solution kept under nitrogen.

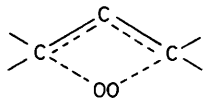
Kinetics.—Since the hydroperoxide (8) was available in high purity and isomerized without the complicating factor of polymer formation encountered with the pinene hydroperoxides, the kinetics of its isomerization in hexane at 40 °C were examined over a much wider range of concentrations (0.01—0.72M) than previously reported for 1,1-dimethylbut-2-enyl hydroperoxide.[2] The low dependency of rate on initial hydroperoxide concentration above 0.1M was confirmed. The rates at zero time were determined from the plot of the concentration of the rearranged product against time shown in Figure 4. For initial hydroperoxide concentrations > 0.1M the reaction order approached zero (about 0.1) as demonstrated in the Table.

Appropriate treatment of the data [7] indicates that the rate of approach to equilibrium is second order at a given total hydroperoxide concentration. The final mixture contains 20% of the rearranged product 2,4-dimethylpent-2-enyl hydroperoxide. The reaction order has not been determined for the rearrangement of 1,1-dimethylbut-2-enyl hydroperoxide because of the difficulties in analysing data when equal concentrations of isomers are produced at equilibrium. Both the second-order rate constants determined in this way or the experimental fractional life-times demonstrate the fractional dependency of rate on initial concentration.

Analysis of solutions more dilute than 0.1M at early reaction stages was difficult. While the low concentration of rearranged hydroperoxide limited the accuracy of the kinetic analysis, the isomerization does appear to be a nearly first-order process in the most dilute solutions.

Discussion

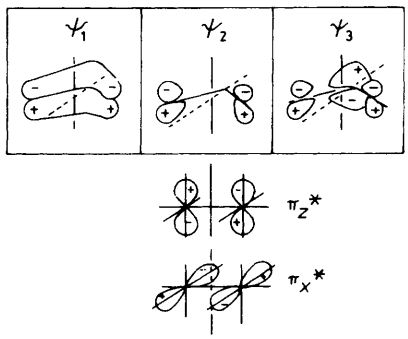
The experimental results suggest that if an intermediate radical is involved in the allylic rearrangement of hydroperoxides, it does not possess a cyclic structure with an unpaired electron localized on the α-carbon atom [*e.g.*, CR in reaction (3)]. The simplest representation of an intermediate with the observed reactivity would be a resonance hybrid of the two allylperoxy forms [a and b in reaction (3)]. A better representation would be structure (A), in which 4 electrons are



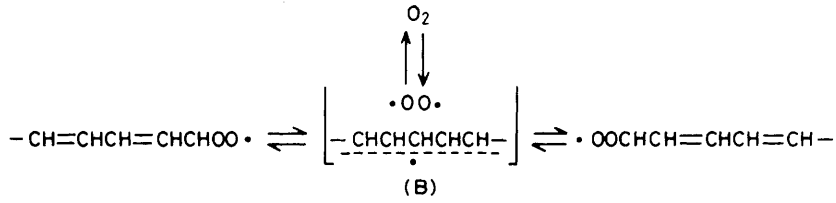
(A)

involved in the bonding shown by the dotted lines * and one electron is in a π* orbital of oxygen. Such a radical could conceivably form almost directly by hydrogen abstraction from monomeric hydroperoxide having internal hydrogen bonding to the double bond. Formation from hydroperoxide dimer, in which hydrogen bonding is to external oxygen, would involve considerable skeletal movement and require the prior existence of discreet, isomeric allylperoxyl radicals. It is suggested that structure (A) represents well the allylperoxyl radical formed during autoxidation of olefins directly

* An orbital picture of the allyl oxygen system analogous to that proposed for π-allyl transition metal complexes by Coates may be made: [8]



This presentation shows (above) the π-allyl molecular orbitals ψ_1, ψ_2, and ψ_3 and (below) the π* orbitals of O_2. Allowing an electron pair to occupy the orbital formed by interaction by the ψ_2 non-bonding allyl and the π_z* oxygen orbital gives weak allyl–oxygen bonding. The remaining pair occupies the allyl bonding ψ_1 orbital while the odd electron occupies the π_x* orbital of O_2.



from allyl radical and molecular oxygen, and which has conventionally been considered as a single stable allylic isomer with a fixed double bond (R–C=C–COO·).* The absence of a strong carbon–oxygen σ-bond is also suggested by the exchange of molecular oxygen with ^{18}O-enriched hydroperoxide during the similar isomerization of methyl linoleate hydroperoxides reported by Chan.[9] A single intermediate (B) which exchanges its oxygen with molecular oxygen was proposed for the 1,5-rearrangement: a direct analogy cannot be drawn, however, since diene isomers with hydroperoxide α to a *cis*-double bond, capable of allowing the cyclic configuration required for bonding analogous to that currently proposed, were not detected.

The observed kinetic behaviour of the hydroperoxide (8) is consistent with the mechanism previously proposed and simplified by the present work. By retaining the initiation step (1) and replacing step (2) with (5), the isomerization may be treated as a chain reaction which proceeds with a single propagation step (6), and which involves the radical intermediate (A) and the isomeric hydroperoxides M_1 and M_2 (M = total monomeric hydroperoxide).

$$M + RO^{\cdot}\ (^{\cdot}OH) \longrightarrow (A) \qquad (5)$$

$$(A) + M_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M_2 + (A) \qquad (6)$$

Termination:

$$2(A) \xrightarrow{k_t} \qquad (7)$$

Assuming steady-state conditions, second-order termination, and making the simplifying assumption that K and k_t do not change significantly with the isomer involved, the isomerization rate is given by equation (8). At zero time

$$dM_2/dt = [k_1M/k_t]^{\ddagger}\,[k_1M - (k_1 + k_2)M_2] \qquad (8)$$

starting with pure M_1, this equation simplifies and may be expressed in terms of total hydroperoxide H, (M + 2D), and the association constant K [equation (9)]. As shown in the

$$dM_2/dt = k_1k_t^{\ddagger}M^{3/2} = (k_1k_1^{\ddagger}/8K^{3/2}k_t^{\ddagger})(\sqrt{1 + 8HK} - 1)^{3/2} \qquad (9)$$

Table, an acceptable fit to equation (9) may be made using the experimental data by arbitrarily assigning a high value to K(100), commensurate with the expectation that hydroperoxides are highly associated.[2,10]

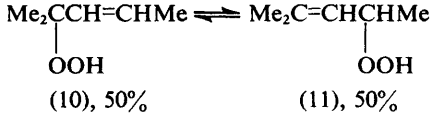
Similarly, rate expressions were derived by assuming initiation by decomposition of either associated or total hydroperoxide or by unlikely first-order termination. The experimental data could not be fitted to any of these forms of the rate equation.

Table. Effect of concentration on isomerization of 2,4,4-trimethylpent-1-ene -3-hydroperoxide in hexane at 40 °C

H [a]/M	r [b] × 10^5 / mol l^{-1} h^{-1}	A [c] for K = 100	C [c]	$t_{0.2}$ [d]/ h	$t_{0.5}$ [d]/ h	$t_{0.5}$ [e]/ h	n [f]
0.0109	0.32	3.06	1.0	135	480	500	0.5
0.0218	0.56	5.97	0.9	160	780	700	1.3
0.109	2.48	24.3	1.0	130	460	461	0.1
0.144	4.47	30.6	1.5	150	590	625	0.5
0.462	9.28	78.0	1.2	850	—	3 440	0.3
0.721	10.30	110	0.9	1 200	—	4 700	

[a] Initial hydroperoxide concentration. [b] Rate determined from first analysis (72 h). [c] A in the expression $r = CA$ where $C = k_1k_t^{\ddagger}/8K^{3/2}k_t^{\ddagger}$ and $A = (\sqrt{1 + 8HK} - 1)^{3/2}$ as in equation (9), A calculated with K = 100. [d] Fractional time to attain equilibrium (at 20% rearranged isomer) from curves in Figure 3. [e] From plot of second-order approach to equilibrium: ref. 7, p. 304. [f] $r = KM_1^n$, where n is calculated from the preceding column ($t_{\frac{1}{2}}$) by the Noyes equation (ref. 7, p. 61).

The mild conditions under which allylic hydroperoxides can be isomerized to an equilibrium composition allows the determination of relative stabilities of isomeric pairs which is not usually accomplished readily. The equilibrium mixture from the hydroperoxide (8) contains 20% primary and 80% secondary isomer, while the equilibrium mixture from the hydroperoxide [2] (10) contains equal concentrations of tertiary and secondary (11) isomers. That 78% of the primary pino-



carveyl hydroperoxide (1) and 22% of the secondary myrtenyl hydroperoxide (2) is observed at equilibrium shows that steric effects strongly influence the relative stabilities of hydroperoxides. Using the group values developed by Benson for calculating thermochemical data in the gas phase,[11] the standard Gibbs free-energy change for isomerization of the pinene hydroperoxides shows the equilibrium values expected without corrections for steric or ring effects to be 15% of the primary and 85% of the secondary isomer, which is the opposite of that observed. This may simply reflect the greater reported stability of the α-pinene over the β-pinene skeleton,[12] but their relative stabilities are not convincingly determined experimentally because thermal or catalysed isomerization gives a variety of ring-opened products.[13] Alternatively, the steric effect introduced by the hydroperoxide group itself may be considered, but no real information is available concerning the stability of 3-substituents of pinene derivatives.

* A referee has suggested that an allyl radical and an oxygen molecule in a solvent cage be considered as an alternative to (A). This is considered unlikely for at least two reasons: formation of an allylic hydroperoxide by hydrogen abstraction would require the simultaneous formation of two new bonds, and dimerization of the allyl radicals would become competitive with isomerization over the very long reaction times employed.

Experimental

Photo-oxygenations were conducted in a magnetically stirred reaction vessel fitted with a thermometer, gas sparger, condenser, and water-cooled Pyrex immersion well containing a 200 W mercury lamp (Hanovia 654A36). I.r. spectra were determined with a Beckman IR 7 spectrophotometer. N.m.r. spectra were measured by the Sadtler Research Laboratories, Philadelphia, Pennsylvania, on a Varian A-60A, 60 MHz spectrometer in carbon tetrachloride solution. Chemical shifts are reported in p.p.m. downfield from internal tetramethylsilane.

A Varian Aerograph 1 840 gas chromatograph with flame ionization detectors was used for analytical and preparative chromatography. The following retention times in minutes are reported for a $\frac{1}{8}$ in × 5 ft column packed with 3% SE30 on 100/80 Varaport (or 10% Carbowax 20M on 60/80 Chromosorb W) used under the following conditions: injector temperature, 250 °C; column programmed after 2 min at 15 °C/min to 215 °C; He flow rate, 25 ml/min: SE30, pinocarveol (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptan-3-ol), 6.4; pinocarvone (6,6-dimethyl-2-methylenebicyclo[3.1.1]-heptan-3-one), 6.6; myrtenal (6,6-dimethylbicyclo[3.1.1]-hept-2-ene-2-carbaldehyde), 7.0; myrtenol (6,6-dimethylbicyclo[3.1.1]hept-2-en-2-ylmethyl alcohol), 7.2; Carbowax 20M, pinocarvone, 8.2; pinocarveol + myrtenal, 8.9; myrtenol, 9.9; 2,4-dimethylpent-2-en-1-ol, 4.4. Hydroperoxide concentrations were determined by gently boiling the sample (1—5 ml) in isopropyl alcohol (5 ml) containing saturated aqueous potassium iodide (1 ml) and acetic acid (2 ml) and titrating the liberated iodine with potassium thiosulphate (0.1M).

Materials.—Hexane was Phillips pure grade. Other solvents were Matheson Coleman & Bell spectroquality or chromatoquality grade. (+)-α-Pinene (2,6,6-trimethylbicyclo[3.1.1]-hept-2-ene) and (−)-β-pinene (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane) were obtained from Aldrich Chemical Co.

Pinocarveyl Hydroperoxide (6,6-*Dimethyl*-2-*methylenebicyclo*[3.1.1]*heptan*-3-*yl Hydroperoxide*) (1).—The photo-oxygenation of both α- and β-pinene to pinocarveyl hydroperoxide and myrtenyl hydroperoxide was described by Schenck,[3] and the products were characterized by a variety of derivatives. Irradiation at 28 °C of a stirred solution of (+)-α-pinene (81.7 g, 0.6 mol) and Methylene Blue (0.6 g) in methanol (1.2 l) in the presence of oxygen for 31 h gave a pale green solution of the peroxide (1) (0.027M). After removal of the methanol *in vacuo*, a 5.13 g portion of the oxidation residue (total 72 g) was transferred to a 10 ml flask fitted with a short-path distillation head. The hydroperoxide (1) was collected at 70 °C and 0.4 mmHg. The final temperature of the flask was 95 °C and 2.5 g of residue remained. The i.r. spectrum of the distillate showed bands at 3 400 (OH); 3 090 and 900 cm^{-1} (vinyl H); 1 640 cm^{-1} (unsaturation); and a very weak carbonyl band at 1 700 cm^{-1}. The n.m.r. spectrum was similar to that of β-pinene except that the two vinyl hydrogen resonances appeared as doublets at δ 4.92 and 5.12 instead of a multiplet at δ 4.58 and the methyl groups resonated at δ 0.68 and 1.28. The peroxy proton gave a very broad signal at δ *ca.* 7.4.

Pinocarveol.—This alcohol was prepared by reduction of the oxidation mixture used to prepare pinocarveyl hydroperoxide with sodium sulphite at 70 °C after removal of part of the methanol as described by Schenk.[3] The alcohol was purified by gas chromatography using a $\frac{3}{8}$ in × 20 ft column containing Carbowax 20M; its i.r. spectrum was identical to that of pinocarveyl hydroperoxide.

Myrtenyl Hydroperoxide (2,6,6-*Trimethylbicyclo*[3.1.1]*hept*-2-*en*-10-*yl Hydroperoxide*) (2).—Photo-oxidation at 21 °C of β-pinene (81.7 g, 0.6 mol) and Methylene Blue (0.5 g) in methanol (1.2 l) gave an oxidation product which titration showed was 0.225M in peroxide (calc. 45.4 g) after 64 h. Removal of the solvent at 40 °C and 20 mmHg gave 69 g of crude hydroperoxide containing 3.23 mequiv./g of peroxide (59% of myrtenyl hydroperoxide). Distillation of 20 g of the crude hydroperoxide through a short-path head yielded 12 g of hydroperoxide. The centre fraction collected at 78 °C and 0.2 mmHg was the purest (4.52 mequiv./g peroxide, 76%) and the final fraction was least pure (2.99 mequiv./g peroxide) with 5.26 g of residue remaining.

Myrtenol.—To a cooled solution (150 ml) of the untreated methanolic reaction product from the photo-oxygenation of β-pinene (containing 0.0343 mol of hydroperoxide) was slowly added powdered sodium borohydride (2.6 g, 0.0684 mol). The mixture was left overnight, water (50 ml) was then added, and the solution concentrated by removing most of the methanol through a Vigreaux column. The product was extracted from the aqueous residue with ether and distilled at 68—75 °C and 0.3 mmHg. Its i.r. spectrum was identical with that of myrtenyl hydroperoxide.

2,4-*Dimethylpent*-2-*ene.*—This olefin was prepared by dehydration of commercial 2,4-dimethylpentan-2-ol. Equal weights of the alcohol and potassium pyrosulphate were heated under reflux for several hours. The product was obtained by distillation, and dried and refractionated to yield the olefin, b.p. 84 °C, 99.6% pure by g.c.

1-*Isopropyl*-2-*methylallyl Hydroperoxide* (8).—Photo-oxygenation of 2,4-dimethylpent-2-ene (58.9 g, 0.6 mol) in methanol (1.2 l) containing Methylene Blue (0.6 g) for 9.4 h at 27 °C yielded a solution shown to be 0.281M in hydroperoxide by iodometric titration. The methanol was removed from 1 060 ml of the oxidation product by distillation through a 6 in Vigreaux column at 8 mmHg. The residue (41.6 g) was transferred to a still equipped with a short-path distillation head. Distillation at 1 mmHg yielded the hydroperoxide (8) (27 g). The centre fraction (17 g), collected at 25—26 °C, was 86% pure by titration: i.r. (liq.) 3 400 (OH); 3 090 and 892 (−C=CH_2); 1 650 and 1 010 cm^{-1} (−CHO−); n.m.r. (CCl_4) δ 4.98 (q, 2 H, *J* 1.5 Hz), 3.88 (d, 1 H, *J* 8 Hz), 1.71 (d, 3 H, *J* 1 Hz), 1.07 (d, 3 H, *J* 6 Hz), and 0.88 (d, 3 H, *J* 6 Hz). Chromatography of the distilled hydroperoxide produced a chromatogram with a single large peak with the retention time of the derived ketone, owing to decomposition of the hydroperoxide in the injector. The largest impurity detected (retention time 9 min) amounted to *ca.* 1% by area.

2,4-*Dimethylpent*-1-*en*-3-*ol.*—This alcohol was prepared by treating the solution (100 ml) from the photo-oxygenation of 2,4-dimethylpent-2-ene (0.028 mol) with sodium borohydride (1.0 g, 0.025 mol). The mixture was left overnight and heated with water (10 ml), and the methanol removed through a Vigreaux column. The residue was extracted with ether and the alcohol obtained in > 90% purity by simple distillation, b.p. 142 °C; its i.r. spectrum was identical with that of the hydroperoxide (8).

4,4-*Dimethyl*-2-*methylene*-1-*t*-*butylpentyl Hydroperoxide.*—Photo-oxygenation at 31 °C of 2,2,4,6,6-pentamethylhept-3-ene (84.15 g, 0.5 mol) in methanol (1.2 l) containing Methylene Blue (0.6 g) gave a solution 0.251M in hydroperoxide after 54 h. Removal of solvent at 15 mmHg left 75 g of 70% pure hydroperoxide residue. Direct gas chromatography produced

major peaks with retention times of 7.8 and 8 min. After reduction of a portion of the methanolic oxidation product or of the concentrated hydroperoxide a peak was obtained with a retention time of 6.7 min followed by an incompletely separated peak with one half the area, probably due to isomeric alcohols. Distillation of 6 g of the hydroperoxide gave 4.9 ml of distillate at 54—55 °C and 0.1 mmHg. When the viscous distillate was left for some time, a white solid formed. Removal of the solid, m.p. 42 °C, left an oil which titration showed contained 91% of pentamethylheptene hydroperoxide. Direct gas chromatography of the solid gave major peaks with retention times of 2 and 6.3 min, the 7.8 and 6.7 min peaks being absent in the solid. All four peaks were shown by the oil indicating incomplete separation of the solid. The i.r. spectrum of the oil had strong absorptions at 3 450, 2 950, 1 475, and 1 360 cm^{-1}, with olefinic bands at 1 640, 3 090, 970, and 890 cm^{-1}. Its n.m.r. spectrum showed impurities to be present but all the major peaks for the expected α-olefinic product were present with approximately correct integrals: δ 0.9, 1.0, and 1.15 (18 H); 1.95 (d, 1.5 H, CH_2); 4.15 (s, 1.8 H, HCOO); 5.15 and 5.28 (m, 2 H, $C{=}CH_2$); impurities: δ 1.75 (m, 1 H, $CH_3C{=}C$), 4.9 (m, 0.2 H), and 5.45 (m, 0.2 H).

Isomerization of Pinocarveyl Hydroperoxide (1).—The crude pinocarveyl hydroperoxide (1) (18 g) was diluted to 1.0 l with hexane containing toluene (0.5 g) as an internal standard and the mixture was cooled in an ice-bath for 15 min. The clear solution which was removed from the oil which had formed was 0.0502M in hydroperoxide. Gas chromatographic analysis of a sample of the solution after reduction showed that it was equally as pure as the reduced solution prepared from the distilled hydroperoxide, pinocarveol comprising *ca.* 90% of the detectable peak areas. The solution was placed in a constant-temperature bath at 40 °C and samples were removed periodically, titrated for peroxide, and analysed by gas chromatography after reduction. Since pinocarveol–pinocarvone and myrtenone–myrtenol were incompletely separated on SE30 packing and pinocarveol–myrtenone gave a single peak on Carbowax packing, analysis on two columns was necessary. Reduction was accomplished by adding triphenylphosphine (0.1 g) to each sample (2 ml) and leaving the solution for several hours at room temperature. Reduction by shaking each sample with an equal volume of sodium sulphite (3.0M) for 24 h gave incomplete reduction. Figure 2 shows the formation of products with time. The reason for the apparent decrease in myrtenol at 81 days is unknown. At extreme reaction times (>81 days) a definite increase in the percentage of pinocarveol was detected.

After 135 days, the entire solution was taken from the bath and the hexane removed *in vacuo*. The residue (21 g) in methanol (200 ml) was reduced with sodium borohydride (4.2 g, 0.11 mol). Water was added and most of the methanol removed by distillation; the product was extracted with ether, and the mixed alcohols distilled at 43—75 °C and 0.3 mmHg. The reduced isomerization product was isolated by preparative chromatography using a ⅜ in × 20 ft Carbowax 20M column. It was identified as myrtenol by its i.r. spectrum.

Isomerization of Myrtenyl Hydroperoxide (2).—In the manner described in the preceding section, a solution of myrtenyl hydroperoxide (0.0444M; 1 l) in hexane was prepared from the crude hydroperoxide (16.23 g). The isomerization was followed at 40 °C for 147 days, and the products were reduced with sodium borohydride and isolated by preparative chromatography.

Kinetic Procedure.—A solution of distilled 1-isopropyl-2-methylallyl hydroperoxide (0.544M) in hexane containing 1% benzene (as an internal standard) was diluted with hexane to prepare 0.0109, 0.0218, and 0.109M solutions. More concentrated solutions were prepared directly from the same distillate. Samples were removed periodically and a 1 ml portion was shaken overnight with 1 ml of 1.5M-sodium sulphite. The hexane layer was analysed (Carbowax 20M-column) and the peak areas of the isomeric alcohols and benzene were determined. A similar reduction with triphenylphosphine was found to give the same ratio of isomeric alcohols.

Attempted Oxidation of Hydroperoxides.—Dilute solutions of hydroperoxides were prepared and 200 ml portions placed in a thermostatted 500 ml stainless steel pressure vessel (14.5 × 2 in o.d.); the vessel was pressurised to 500 lb in^{-2} with C.P. oxygen. The vessel was placed on its side to provide the maximum gas–liquid interface since agitation was impractical over the reaction times investigated. A pressure drop of 20 lb in^{-2} occurred in the first hour in every case although no variation of the vessel jacket temperature was observed. A control sample of each solution was kept under nitrogen at atmospheric pressure. Portions of each solution were reduced at the termination of the reaction with sodium sulphite or triphenylphosphine and both reduced and untreated samples examined by gas chromatography. The column temperature was maintained at 220 °C during 20 min for the Carbowax 20M column and at 300 °C for the SE30 column.

A 0.0157M solution prepared in hexane from distilled pinocarveyl hydroperoxide was kept at 40 °C under oxygen for 21 days in the pressure vessel. The clear solution removed from the pressure vessel was found to be 0.0150M in hydroperoxide by titration. The control solution was 0.0162M and cloudy, and contained a slight amount of a solid. Gas chromatography showed *ca.* 20 trace impurities in addition to the expected alcohols and ketones. Of these, only a single minor peak (< *ca.* 0.1%) due to a high boiling impurity was present exclusively in the oxidized solution.

A 0.14M solution of 2,4-dimethylpent-1-enyl hydroperoxide kept at 40 °C for 5 days under oxygen showed a hydroperoxide concentration of 0.128M by titration, and gave a chromatogram with numerous minor peaks (detectable to < 0.1%), identical with that from a 0.132M control sample. Both solutions after treatment with sodium sulphite also gave identical chromatograms. Similar results were obtained with a 0.0870M solution of the hydroperoxide in benzene.

A 0.0675M solution of 2,2,4,6,6-pentamethylhept-3-enyl hydroperoxide in hexane, prepared from undistilled hydroperoxide, kept at 40 °C under 500 lb in^{-2} of oxygen, showed no detectable change by gas chromatography after 6 days. The hydroperoxide concentration was 0.0697M. A portion was recharged into the pressure vessel. After a total time of 11 weeks, titration indicated an increase in hydroperoxide concentration to 0.0745M. Although this represents the first definite increase in peroxide on oxidation of a hydroperoxide, no detectable differences were observed between the chromatograms of the oxidation and control solutions.

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