The Rearrangements of Allylic Hydroperoxides Derived from (+)-Valencene

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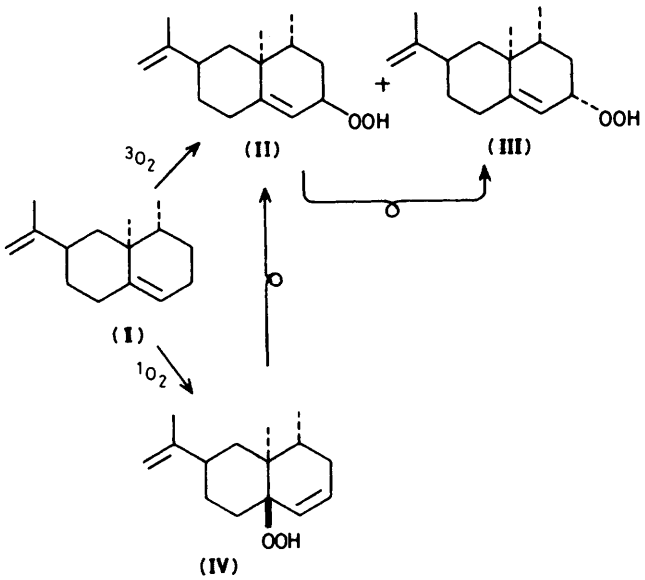
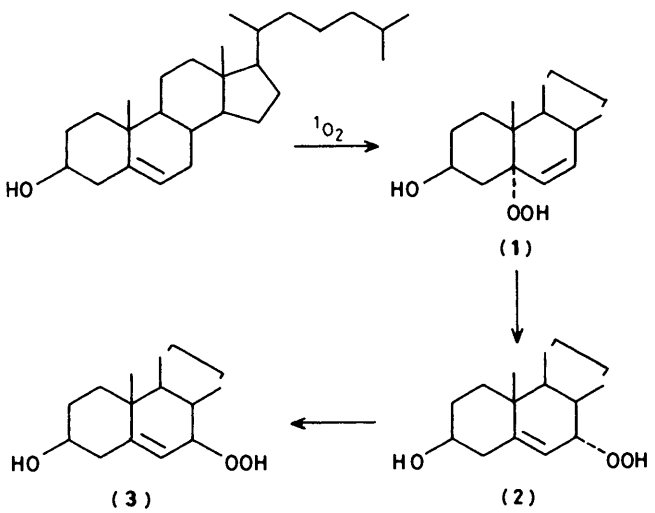
(+)-Valencene (**I**) reacts with triplet oxygen to give 84% of the secondary β-hydroperoxide (**II**) and 15% of the α-hydroperoxide (**III**); reaction with singlet oxygen gives principally (*ca.* 80%) the tertiary β-hydroperoxide (**IV**). This undergoes a Schenck rearrangement to give suprafacially the β-



hydroperoxide (**II**) by a non-dissociative mechanism which does not involve exchange of oxygen in an atmosphere of $^{18}O_2$. The hydroperoxide (**II**) then undergoes a slower Smith epimerization to the α-hydroperoxide (**III**) by a dissociative mechanism which involves substantial (>55%) exchange.

In 1958, Schenck showed that 5α-hydroperoxy-3β-hydroxycholest-6-ene (**1**) which is formed from cholesterol and singlet oxygen, rearranges in a non-polar solvent to give the 7α-hydroperoxycholest-5-ene (**2**).[1] Fifteen years later, Smith showed that (**2**) then underwent a slower epimerization to the 7β-hydroperoxide (**3**) (reaction 1).[2] These reactions are important because allyl hydroperoxides are also formed when alkenes react with triplet oxygen (autoxidation) but only a few further examples of these rearrangements have been clearly identified. In general it appears that the products from singlet oxygenation rearrange, in principle reversibly, to the products of triplet oxygenation.[3]

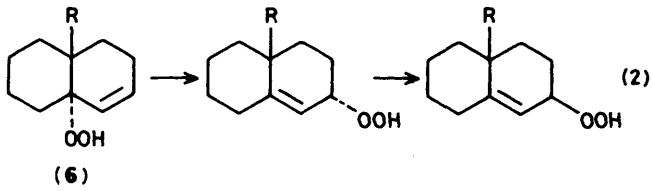


Both types of rearrangement proceed through the corresponding allylperoxyl radicals. We found that when reaction (**1**) ⟶ (**2**) was carried out under an atmosphere of $^{18}O_2$, no ^{18}O was incorporated into (**2**), but the reaction (**2**) ⟶ (**3**) involves extensive exchange of oxygen with the atmosphere. We proposed that the first reaction was non-dissociative, and perhaps involved a pericyclic process with the transition state (**4**), but that the epimerization involved a dissociative mechanism with kinetically free allyl radicals and triplet dioxygen (**5**).[4] Similarly Porter showed that the allylic isomerization of the hydroperoxides derived from oleic acid did not incorporate oxygen from the atmosphere into the product, and he concluded similarly that the mechanism was non-dissociative, and perhaps pericyclic.[5]

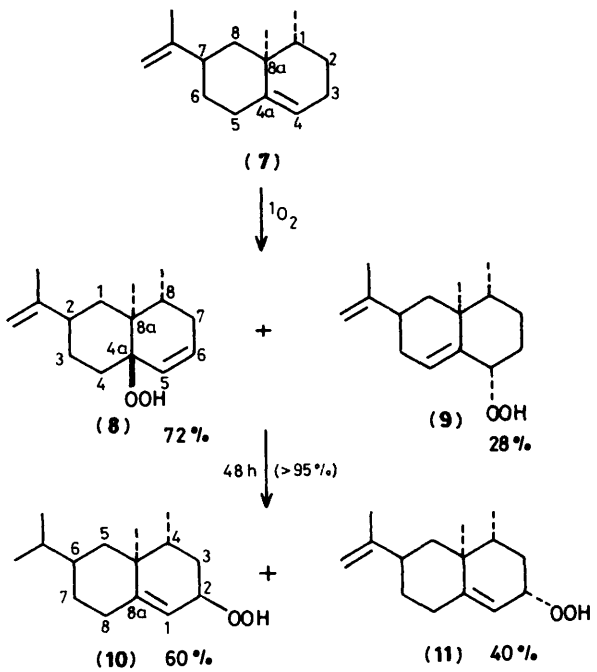
(4)

(5)

We have also examined the analogous rearrangements in the simpler context of the hydroperoxides (**6**; R = Me or Et) derived from methyl- or ethyl-octalin [reaction (2)].[6] Again, it appeared that the allylic shift took place wholly suprafacially, and then was followed by a subsequent slower epimerization.



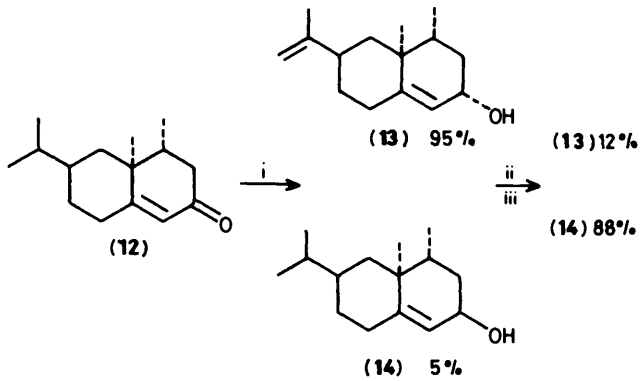
We were therefore interested in a report that the tertiary β-hydroperoxide (**8**) which is the major product of the dye-sensitized oxygenation of (+)-valencene (**7**) rearranged spontaneously at room temperature to a mixture of the secondary hydroperoxides (**10**) and (**11**) containing, by g.l.c. analysis, a substantial amount of the α-epimer (**11**) (Scheme 1).[7] Details of these reactions are published in two patents.[8] It appeared that this might present an example of the allylic arrangement which was not suprafacially specific and this would have important implications as to the mechanism of the rearrangement. We have therefore re-examined the reaction of (+)-valencene with triplet oxygen and with singlet oxygen, and the rearrangement of the hydroperoxide (**8**).



Scheme 1.

Results

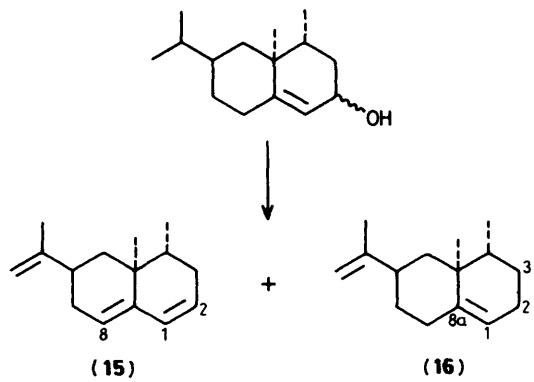
Nootkatone (**12**) was reduced with lithium aluminium hydride to give a mixture of the epimeric secondary alcohols (**13**) and (**14**), with one isomer predominant (95:5; 400 MHz ^{1}H n.m.r.). These mixed alcohols were then epimerized by the Mitsunobu reaction,[9] to give a mixture rich in the other isomer (12:88). These two mixtures were examined by ^{1}H n.m.r. spectroscopy, and the nuclear Overhauser effect (n.O.e.) between the hydrogen atoms at C-1 and C-3 established the structures of the components to be as shown in Scheme 2. Although the



Scheme 2. *Reagents:* i, $LiAlH_4$; ii, Ph_3P, $PhCO_2H$, $(EtO_2C)_2N_2$; iii, KOH.

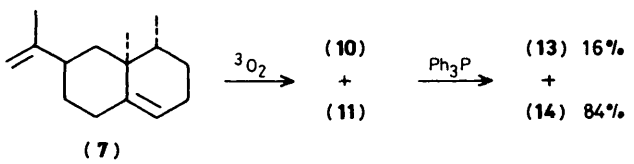
two isomers could readily be distinguished by ^{1}H n.m.r. spectroscopy (see Figure) and h.p.l.c., g.l.c. analysis on a Carbowax column at 200 °C (the conditions used in ref. 8), or on a silicone oil column at 200 °C, showed similar chromatograms whatever the epimeric composition of the starting material (see the Figure). The two components were collected from a Carbowax column on a preparative scale. ^{1}H N.m.r. spectroscopy showed that both fractions contained three alkenic protons apart from those of the $=CH_2$ group, and identified the major component as the known nootkatene (**15**) (Scheme 3). The minor component decomposed before it could be investigated further, but we believe that it may be the alternative diene (**16**).

Apparently rapid elimination occurs in the injector and/or on the column, caused perhaps by metallic or polar materials inducing ionization of the C–OH bond. All subsequent analyses were therefore carried out by ^{1}H n.m.r. spectroscopy.



Scheme 3.

Valence was subjected to oxidation with triplet oxygen using di-t-butyl hyponitrite as the initiator. The hydroperoxides (**10**) and (**11**) which were formed were reduced with triphenylphosphine and, using the information derived in Scheme 2, the alcohols were identified as consisting of 16% of the α-epimer (**13**) and 84% of the β-epimer (**14**) (Scheme 4).



Scheme 4.

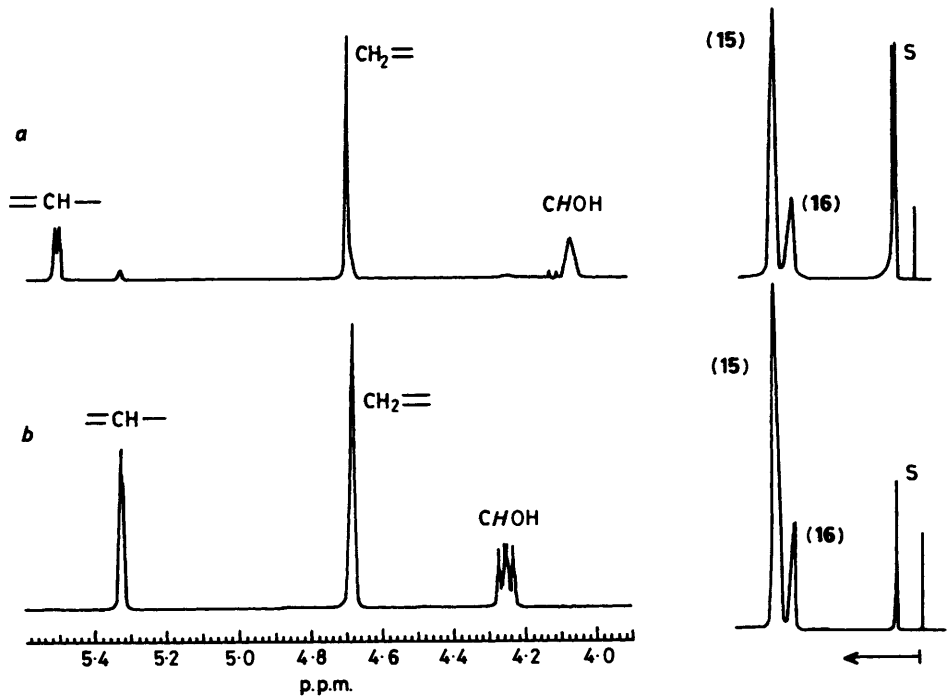


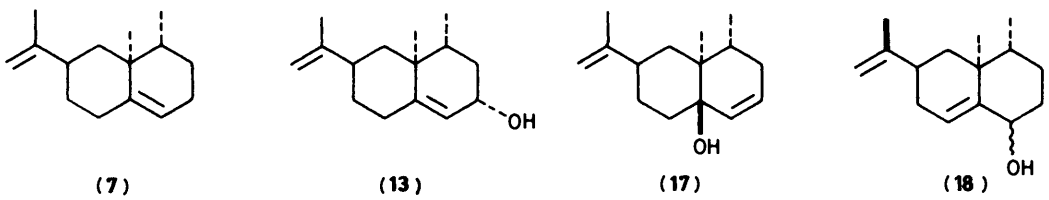
Figure. Partial ^{1}H n.m.r. spectrum (400 MHz), and gas liquid chromatogram (silicone oil, 200 °C) of (*a*) 88% β-alcohol (**14**) + 12% α-alcohol (**13**) and (*b*) 95% α-alcohol (**13**) and 5% β-alcohol (**14**). In the g.l.c., the peak S is due to solvent (ethyl acetate), and the other peaks are ascribed to the dienes (**15**) and (**16**) as shown.

Valencene was then subjected to dye-sensitized singlet oxygenation. After the reaction was complete, aliquots were periodically removed, reduced with triphenylphosphine, and analysed by ^{1}H n.m.r. spectroscopy. The percentage composition at zero time and after 123 h for a typical experiment is shown in Scheme 5. A sample of valencene was similarly oxidized with $^1O_2$, and the mixed hydroperoxides which were formed were then allowed to rearrange in chloroform at room temperature under an atmosphere enriched in $^{18}O_2$, using di-t-butyl hyponitrite as a radical initiator. Aliquots were removed at zero time and after 90 h, reduced with triphenylphosphine, and analysed by n.m.r. spectroscopy. The alcohols which were formed were separated by preparative h.p.l.c., and analysed for ^{18}O by mass spectrometry. The approximate concentrations of the hydroperoxides (**8**), (**10**), and (**11**) in the mixture and the ^{18}O contents which these results imply, are shown in Scheme 6.

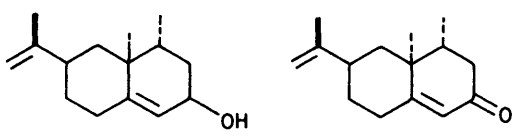
Discussion

Ohloff was able to isolate the epimeric alcohols (**13**) and (**14**) from preparative g.l.c.,[8] but we have found this technique to give misleading results when it was used for analysis, and we have used instead n.m.r. spectroscopy for estimating the alcohols.

In the reduction of nootkatone (**12**) with lithium aluminium



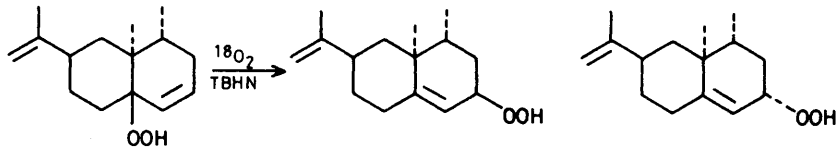
	(7)	(13)	(17)	(18)
0 h	24.7	0	37.1	10.2 %
123 h	21.0	*ca.* 1.5	15.0	10.0 %



unidentified material

	(14)	(12)	
0 h	16.8	0.0	12.2 %
123 h	39.5	2.5	10.8 %

Scheme 5.



	(8)	(10)	(11)
0 h	45±3%	12±1%	1±1 %[a]
90 h	0%	53±3%	5±1 %[b]
		(0% ^{18}O)	(54% ^{18}O)

Scheme 6. [a] By ^1H n.m.r. [b] Isolated by h.p.l.c.

hydride (Scheme 2) to give mainly the α-alcohol (**13**), the reagent approaches at the β-face which is less hindered by the two α-methyl substituents. Similarly the formation of a preponderance of the β-hydroperoxide (**10**) in the autoxidation of valencene (Scheme 4) is compatible with approach of $^3O_2$ at the less hindered β-face of the intermediate allylic radical. The radical chain conditions of the autoxidation would however be ideal for catalysing both the Schenck and the Smith rearrangements, and the composition of the products when the reaction is complete need not necessarily reflect the regio- and stereo-selectivity of the reaction of $^3O_2$ with the radical.

In the reaction of valencene with singlet oxygen, only (**18**) (Scheme 5) results (after reduction) from attack of $^1O_2$ at the secondary alkenic carbon atom. The hydroperoxides corresponding to the nootkatone (**12**) and to the alcohols (**13**), (**14**) and (**17**) are all the direct or indirect (after rearrangement) result of attack at the tertiary alkenic position. At this stage the yield of the α-hydroperoxide (**11**) corresponding to the α-alcohol (**13**) is negligible.

When the hydroperoxide derived from singlet oxygenation is allowed to stand, the principal reaction which occurs (Scheme 5) is the rearrangement of the tertiary β-hydroperoxide (**8**) to give very largely, and probably completely, the secondary β-hydroperoxide (**10**) (Scheme 6), and this suprafacial rearrangement, like that of the corresponding cholesteryl hydroperoxide (**1**) on the β-face, proceeds without exchange of oxygen with an $^{18}O_1$ atmosphere.

The small amount of α-hydroperoxide (**11**) which can be detected at this stage probably results from the subsequent epimerization of (**10**), and as in the corresponding reaction of the cholesteryl hydroperoxide (**2**) it involves exchange of oxygen with the atmosphere, which would be compatible with a dissociative mechanism involving the allylic radical and triplet oxygen as intermediates. As the rearrangement is slow, even in the presence of an initiator the ultimate composition of epimers which would be reached is not known, but it would be expected to be the same (β 84%, α 16%) as is obtained in the autoxidation of valencene, which involves the same intermediate allylic radical and triplet oxygen.

The precise degree of incorporation of $^{18}O_2$ during epimerization (**10**) ⟶ (**11**) is not known because of a number of complicating factors. First some of the isotopically normal α- hydroperoxide (**11**) is formed during the singlet oxygenation, before the $^{18}O_2$ atmosphere is introduced; this would reduce the concentration of ^{18}O in the final hydroperoxide (**11**). Second, some residual valencene was present during the rearrangement (**10**) ⟶ (**11**), and the presence of an oxygen atmosphere and of an initiator might lead to the formation of hydroperoxide by autoxidation. If this did occur it would give ^{18}O-labelled hydroperoxide, but it cannot be significant here because it would give principally the β-hydroperoxide (**10**) (Scheme 4), and this was found to be isotopically normal in the rearrangement product (Scheme 6). Third, because of operational difficulties the isotopic composition of the oxygen which was used is not known accurately.

The limits which can be put on the amount of exchange are between 55 and 100%; in the case of the rearrangement of the cholesteryl hydroperoxide (**2**), in different experiments between 72 and 83% ^{18}O was incorporated into the product (**3**).

Conclusions

We conclude that there is nothing anomalous about the valencene system. We have established conditions for the reaction and for the analysis of products, under which we find that the tertiary β-hydroperoxide (**8**) rearranges suprafacially to the secondary β-hydroperoxide (**10**). The secondary α-hydroperoxide is apparently formed in a subsequent slower process.

The parallel with the cholesterol system[4] extends to the mechanism. The first reaction does not incorporate ^{18}O from the atmosphere into the hydroperoxide group, and follows a non-dissociative (pericyclic?) mechanism. The epimerization does involve exchange with $^{18}O_2$, and probably follows a dissociative mechanism.

Experimental

^1H N.m.r. spectra were recorded in $CDCl_3$ at 400 MHz using a Varian VXR-400 spectrometer, and F.t.i.r. spectra on a Perkin-Elmer PE 983 instrument.

Commercial valencene [1α,8aα-dimethyl-7β-(1-methylethenyl)-1,2,3,5,6,7,8,8a-octahydronaphthalene (**7**); de Monchy p.l.c.] was purified by preparative g.l.c. on a 50 × 1 cm o.d. column of Carbowax (20% w/w) on 60–80 mesh Chromosorb W. The pure product (typically 0.45 g from 0.72 g) showed δ_H 0.87 (3 H, d, *J* 6.35 Hz, 1-Me), 0.95 (3 H, s, 8a-Me), 1.71 (3 H, s, MeC=), 4.68 (2 H, br s, CH_2=), and 5.33 (1 H, m, =CH–).

Reduction of Nootkatone.—(+)-Nootkatone [4α,4aα-dimethyl-6β-(1-methylethenyl)-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one, (**12**), Bush Boake Allen] showed δ_H 0.96 (3 H, d, *J* 6.83 Hz, 4-Me), 1.12 (3 H, s, 4a-Me), 1.74 (3 H, br s, MeC=), 4.73 (1 H, br s CH_2=C), 4.75 (1 H, br s, CH_2=C), and 5.77 (1 H, d, *J* 1.62 Hz, 4-H).

Nootkatone (3.20 g, 14.7 mmol) in ether (5 cm^3) was added over 30 min to a stirred suspension of lithium aluminium hydride (1.04 g, 27.4 mmol) in ether (10 cm^3). After 4 h, water (5 cm^3) and 10% NaOH solution (4 cm^3) were added. After a further 4 h of stirring, the granulated salts were filtered off to give a mixture of the crude alcohols (3.03 g) which was chromatographed on silica gel using ethyl acetate–pentane (3:8) as the eluant to yield the mixed alcohols (**13**) and (**14**) (2.55 g) in the ratio 95:5 (by ^1H n.m.r.).

Epimerization of Alcohols.—The isomeric ratio of the above alcohols was then reversed using the Mitsunobu reaction. Diethyl azodicarboxylate (0.237 g, 1.37 mmol) in tetrahydrofuran (THF) (5 cm^3) was added dropwise to a solution of the mixed 4α,4aα-dimethyl-6β-(1-methylethenyl)-2,3,4,4a,5,6,7,8-

octahydronaphthalene-2α- and -2β-ols (**13**) and (**14**) (0.301 g, 1.37 mmol), triphenylphosphine (0.358 g, 1.37 mmol) and benzoic acid (0.167 g, 1.37 mmol) in THF (5 cm^3). Next day, the solvent was removed to give a mixture of the benzoates of inverted configuration; δ_H 0.92 (3 H, d *J* 6.62, 4-Me), 0.95 (3 H, s, 4a-Me), 1.73 (3 H, s, MeC=), 4.71 (2 H, br s, CH_2=C), 5.38 [1 H, m, C(H)O], 5.59 (1 H, d, *J* 5.05 Hz, =CH–), 7.40–7.54 (3 H, m, Ph), and 8.04–8.07 (2 H, m, Ph).

A mixture of the benzoates in hot methanol (10 cm^3) and of KOH (2 mol dm^{-3}; 1.7 cm^3) was stirred overnight at 40 °C. Hydrolysis with dilute hydrochloric acid followed by chromatography on silica gave the mixed alcohols (**13**) and (**14**) in the ratio 12:88.

^{1}H N.m.r. for (**13**): $\delta_H(CDCl_3)$ 0.89 (3 H, d, *J* 6.88 Hz, 4-Me), 0.99 (3 H, s, 4a-Me), 1.71 (3 H, s, MeC=), 4.25 (1 H, m, C*H*OH), 4.68 (2 H, br s, CH_2=C), and 5.33 (1 H, d, *J* 1.65 Hz, =CH–); $\delta_H(CCl_4)$ 0.89 (3 H, d J 6.91 Hz, 4-Me), 0.99 (3 H, s, 4a-Me), 1.68 (3 H, s, MeC=), 4.09 (1 H, m, =CH–), 4.62 (2 H, br s, CH_2=C), and 5.22 (1 H, d, *J* 1.56 Hz, C*H*OH); *m/z* (e.i.; 70 eV) 220 (M^+).

^{1}H N.m.r. for (**14**): $\delta_H(CDCl_3)$ 0.88 (3 H, d, *J* 5.78, 4-Me), 0.89 (3 H, s, 4a-Me), 1.70 (3 H, s, MeC=), 4.05 (1 H, m, C*H*OH), 4.68 (2 H, br s, CH_2=C), and 5.49 (1 H, d, *J* 1.51 Hz, –CH=); *m/z* (e.i.; 70 eV) 220 (M^+).

Gas Liquid Chromatography.—G.l.c. analysis was carried out using a Perkin Elmer F11 chromatograph fitted with a 4 m × 3 mm stainless steel column packed with 10% silicone oil MS200/200 or 10% Carbowax 20 M on Chromosorb W AW DMCS, and an inlet pressure of nitrogen of 10 psi.

The alcohol (**13**) on the silicone column at 200 °C gave peaks with retention times 592 and 667 s with relative areas 1:1.78, whereas (**14**) gave peaks with retention times 592 and 668 s with relative areas 1:2.46. On the Carbowax column at 200 °C, (**13**) gave peaks at 185 and 202 s, relative areas 1:3.85, and (**14**) gave peaks at 185 and 201 s, relative areas 1:2.95.

Preparative g.l.c. was carried out as described above for valencene, and two fractions were collected at 44 min and 54.2 min (relative areas 1:2.93).

The major fraction was identified as nootkatene (**15**), δ_H 0.88 (3 H, d, 4-Me, *J* 6.73 Hz), 0.91 (3 H, s, 4a-Me), 1.75 (3 H, s, CH_3C=), 4.74 (2 H, s, C=CH_2), 5.42 (1 H, m, 8-H), 5.58 (1 H, m, 1-H), and 5.96 (1 H, m, 2-H); *m/z* 202 (Calc. for $C_{15}H_{22}$, 202). [Lit.,[10] δ_H 0.89 (3 H, d), 0.92 (3 H, s), 1.75 (3 H, s), 4.735 (2 H, s), 5.4 (1 H, m), 5.56 (1 H, m), and 5.97 (1 H, d)].

The minor fraction was tentatively identified as the diene (**16**); δ_H 0.83 (3 H, s, 4a-Me), 1.02 (3 H, d, 4-Me, *J* 7.44 Hz), 1.75 (3 H, s, MeC=), 4.72 (2 H, s, C=CH_2), 5.36 (1 H, d, HC=, *J* 9.32 Hz), 5.59 (1 H, d, HC=, *J* 4.54 Hz), and 5.78 (1 H, m, HC=).

The epimerization during g.l.c. of cholest-5-ene-3β,7α-and 3β,7β-diol with concomitant elimination has been reported.[11]

Nuclear Overhauser Effect.—Irradiation of the methyl doublets in the alcohols at δ 0.88 and 0.89 showed that the proton geminal to the methyl group at C-4 showed a multiplet at δ 1.42–1.52.

N.O.e. experiments were conducted on 7.5 mmol dm^{-3} solutions of the β-alcohol [88% (**14**) and 12% (**13**)] and of the α-alcohol [95% (**13**) and 5% (**14**)] in $CDCl_3$ at 30 °C and 25 °C, respectively. Both solutions were freeze–thawed three times before being sealed. An n.O.e. effect was observed in the α-alcohol (**13**) between the C*H*OH proton at δ 4.25 and the C*H*Me proton at δ 1.42—1.52, but not in the β-alcohol (**14**).

Autoxidation of Valencene.—The reaction was carried out in the apparatus illustrated in ref. 4 for singlet oxygen reactions.

The flask was filled with oxygen to a pressure of 0.9 atm, then a solution of valencene (**7**) (0.395 g, 1.94 mmol) and di-t-butyl hyponitrite (0.010 g, 0.06 mmol) in $CHCl_3$ (6 cm^3) was injected through the septum. The mixture was stirred for 90 h at room temperature, then reduced with triphenylphosphine (0.101 g, 0.38 mmol). Analysis by h.p.l.c. using 1:9 ethyl acetate–light petroleum (b.p. 60–70 °C) as eluant showed that the alcohols (**13**; retention time 517 s), and (**14**; retention time 409 s) were present in the ratio of 5.4:1. No alcohols could be detected when the initial valencene was treated with triphenylphosphine.

Photo-oxidation of Valencene.—(i) A solution of valencene (0.376 g, 1.84 mmol) and Rose Bengal in a 1:1 mixture of methanol and benzene (8 cm^3) was irradiated under the conditions described previously for cholesterol.[4] After 3.3 h, when the uptake of oxygen had essentially stopped, the irradiation was discontinued, and an aliquot (0.5 cm^3) was removed and reduced with triphenylphosphine, and analysed by ^{1}H n.m.r. spectroscopy. The results at 0 h and 123 h are shown in Scheme 5.

(ii) Valencene (0.278 g, 1.36 mmol) was photo-oxygenated under the same conditions. After 1.5 h the reaction was stopped and the solvent was removed under reduced pressure. The residue was reduced with triphenylphosphine and alcohol (**15**) (0.072 g) was isolated by chromatography using pentane–ether (10:1.5) as the eluant, and purified by h.p.l.c. to yield pure (**15**) (0.044 g), δ_H 0.83 (3 H, s, 8a-Me), 0.84 (3 H, d, *J* 6.21 Hz, 1-Me), 1.75 (3 H, s, MeC=), 4.70 (1 H, s, CH_2=C), 4.74 (1 H, s, CH_2=C), 5.61 (1 H, m, =C–), and 5.71 (1 H, m, –CH=).

Experiments with $^{18}O_2$.—Valencene (0.730 g, 3.58 mmol) was photo-oxygenated in the presence of Rose Bengal as above. After 2.25 h, the reaction was stopped and the residue (0.807 g) was dissolved in chloroform (6 cm^3) containing di-t-butyl hyponitrite (0.010 g, 0.06 mmol). An aliquot (0.335 cm^3) was reduced with triphenylphosphine and analysed by n.m.r. spectroscopy.

The rest of the solution was transferred by syringe to the same flask which was used for the autoxidation and which was charged with $^{18}O_2$ gas. The solution was stirred for 90 h then reduced with triphenylphosphine (0.896 g, 3.42 mmol). H.p.l.c. of the product using ethyl acetate initially to remove triphenylphosphine oxide and then ethyl acetate–light petroleum (1:9) to separate the alcohols, yielded three fractions.

The first (0.058 g) contained 22.5% of nootkatone and 77.5% of an alcohol which is probably (**18**); δ_H 0.88 (3 H, d, *J* 6.71 Hz, 1-Me), 1.15 (3 H, s, 8a-Me), 1.73 (3 H, s, MeC=), 4.21 (1 H, t, *J* 2.80 Hz, C*H*OH), 4.71 (2 H, br s, CH_2=C), 5.62 (1 H, dd, *J* 5.20 and 2.22 Hz, =CH–); *m/z* (e.i.; 70 eV) 220 (M^+) [Lit.,[8] (**18**β), δ_H 0.84 (3 H, s), 0.85 (3 H, d, *J* 5 Hz), 1.68 (3 H, s), 3.9 (1 H, m), 4.2 (2 H, m), and 5.4 (1 H, m); (**18**α) 0.85 (3 H, d, *J* 5 Hz), 1.12 (3 H, s), 1.68 (3 H, s), 3.84 (1 H, m), 4.64 (2 H, m), and 5.5 (1 H, m)].

The second fraction (0.169 g) contained the β-alcohol (**14**), and the third fraction (0.015 g) the α-alcohol (**13**). Analysis of these alcohols by m.s. showed 0% ^{18}O in (**13**) and 54% ^{18}O in (**14**). The gaseous phase had been analysed *ca.* 8 weeks before the reaction was carried out, and was re-analysed immediately after the reaction, and showed 96 and 27% ^{18}O, respectively.

Acknowledgements

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