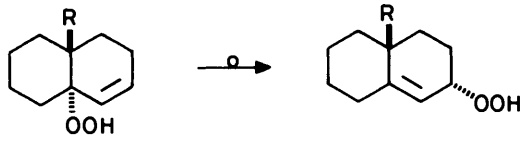
Stereoselectivity in the Formation and Allylic Rearrangement of 8a-Methyl- and 8a-Ethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalenyl Hydroperoxides

David V. Avila, Alwyn G. Davies,* and Ian G. E. Davison
Chemistry Department, University College London, 20 Gordon Street, London, WC1H 0AJ

4a-Methyl- and 4a-ethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene have been subjected to singlet oxygen oxygenation, and the various hydroperoxides which are formed have been characterised. Evidence is presented that the 8aβ-alkyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-4aα-yl hydroperoxides (**I**; R = Me or Et) rearrange suprafacially and irreversibly in chloroform at 25 °C to give only the 4aβ-alkyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2α-yl hydroperoxides (**II**). Under the same conditions, the corresponding 8aβ-alkyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-4aβ-yl hydroperoxides rearrange much more slowly.



(I) (II)

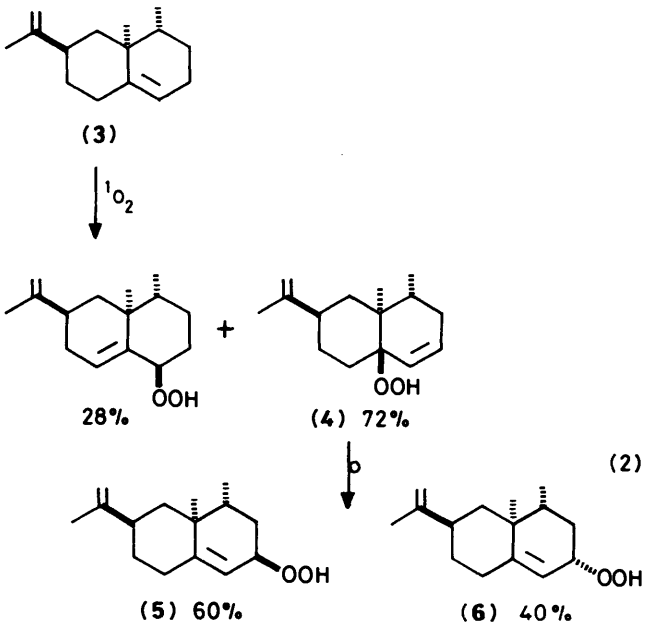
In 1958,[1] Schenck showed that 5α-hydroperoxycholest-6-en-3β-ol (**1**; R = OH, R′ = C_8H_{17}) rearranged in chloroform to give 7α-hydroperoxycholest-5-en-3β-ol (**2**).[2]

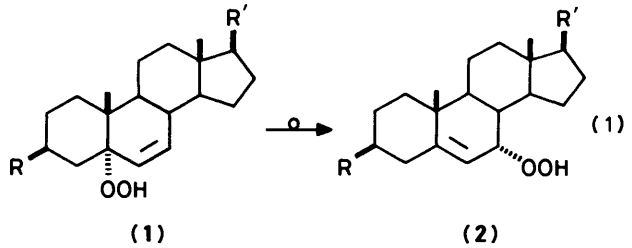
In general this allylic rearrangement is reversible,[3] and it is presumably ubiquitous in allyl hydroperoxides such as those which are formed in the autoxidation of unsaturated lipids. However, autoxidation gives an equilibrium mixture of the isomeric hydroperoxides, and observation of the rearrangement has depended on the difference in the isomeric composition of the allylic hydroperoxides which are obtained when alkenes react with singlet or triplet oxygen.

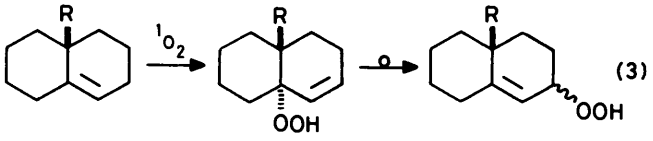
Only some ten examples of the rearrangement have as yet been demonstrated.[1,4–7] Five of these relate to derivatives of cholest-6-ene (**1**; R, R′: HO, C_8H_{17};[1] HO, COMe;[1] $MeCO_2$, O;[1] $MeCO_2$, C_8H_{17};[1] H, C_8H_{17}), and in each the reaction appears to occur suprafacially, giving only the 7α-hydroperoxide (**2**).

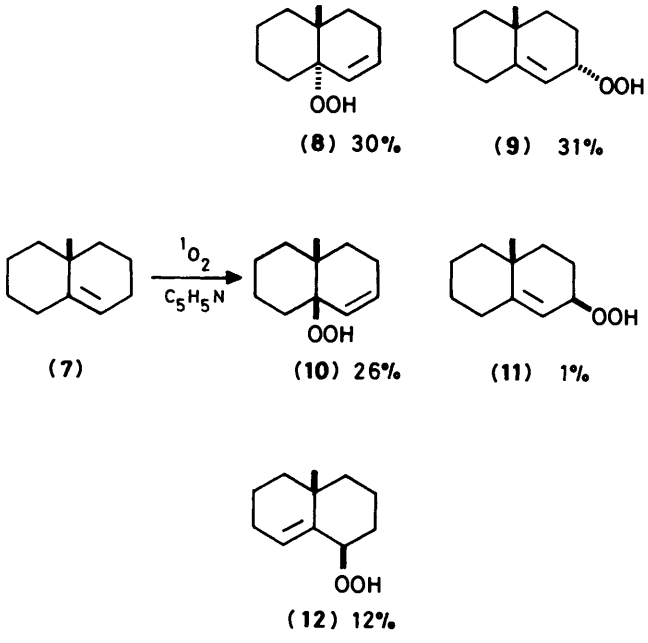
We are interested in the mechanism of this rearrangement,[8] and noted the unpublished observation by Schulte-Elte, Francheboud, and Ohloff[7] that the hydroperoxide (**4**) obtained from (+)-valencene (**3**) rearranged to give a mixture of the products (**5**) and (**6**).

This apparent antarafacial component to the reaction has important mechanistic implications. We have therefore examined the stereochemistry of the rearrangement of the simpler octahydronaphthalenyl hydroperoxides derived from the singlet oxygen oxygenation of 4a-methyl-[9] and 4a-ethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene [equation (3), R = Me or Et].

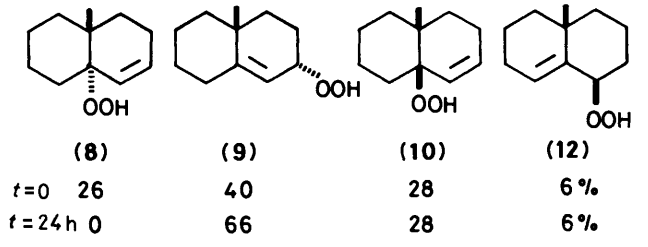








Scheme 1.



Scheme 2.

Results

Photo-oxygenation of 4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**7**) in pyridine gave a mixture of the five hydroperoxides (**8**)—(**12**) which were partially separated by chromatography and were identified (see below) by ^{1}H n.m.r. spectroscopy. Yields are given in Scheme 1. The β-configuration assigned to (**12**) is justified in the Discussion section.

The 4aβ-methyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2-yl hydroperoxides (**9**) and (**11**) cannot be products of the reaction of singlet oxygen which always involves allylic shift of the double bond,[10] and these compounds must arise from the allylic rearrangement of the initial 8aβ-methyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-4a-yl hydroperoxides (**8**) and (**10**) (or, less likely, from the incursion of some reaction by triplet oxygen).

The allylic rearrangement of the hydroperoxides (**8**) and (**10**) was followed by monitoring the ^{1}H n.m.r. spectra of a mixture of the hydroperoxides (**8**), (**9**), (**10**), and (**12**) in $CDCl_3$ (Figure 1).

The percentage composition of the mixture at zero time and after 24 h is shown in Scheme 2. The 4aα-hydroperoxide (**8**) rearranged cleanly into the 2α-hydroperoxide (**9**), whereas over this period the 4aβ-hydroperoxide (**10**) showed no reaction. If the rearrangement of the 1β-hydroperoxide (**12**) occurred suprafacially, the reaction would involve only enantiomeric inversion and would not have been detected.

To check the possibility of the slower rearrangement of the

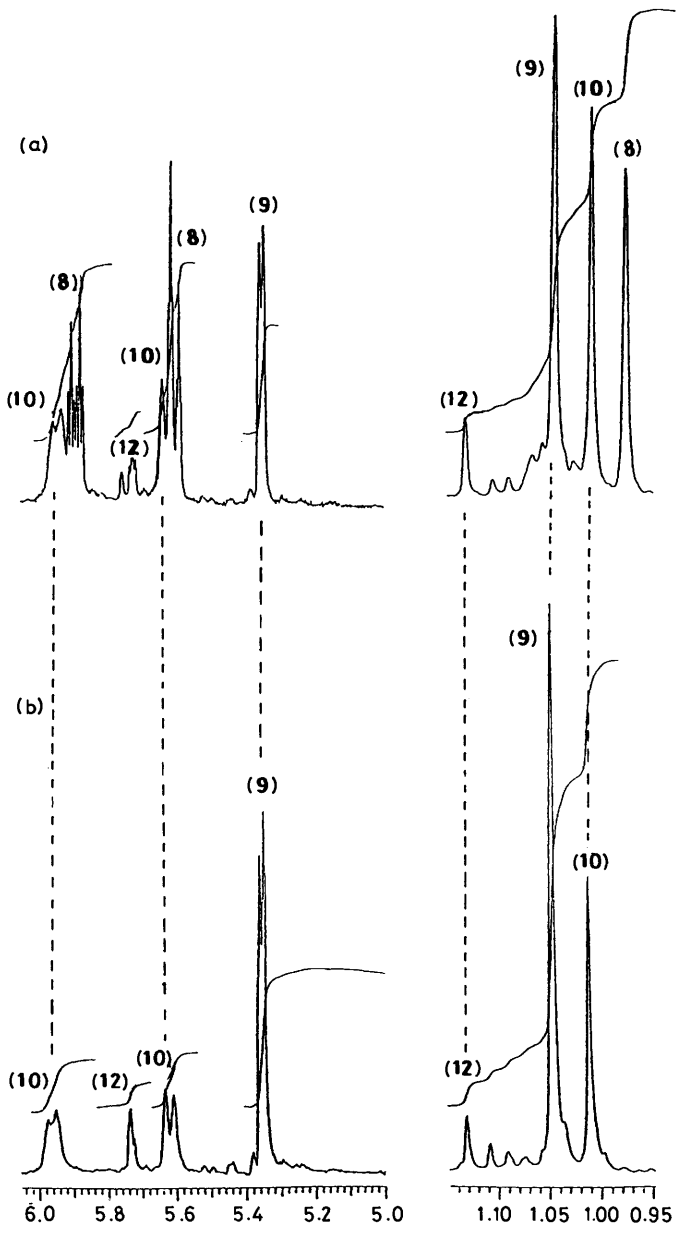


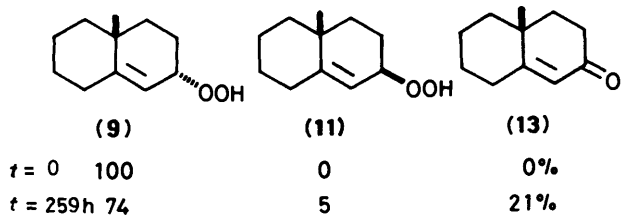
Figure 1. ^{1}H N.m.r. spectra (400 MHz) of the methyl and the olefinic signals, illustrating the rearrangement (**8**) ⟶ (**9**) of Scheme 1; (a) t = 0; (b) t = 24 h

2α-hydroperoxide (**9**), and of the 4aβ-hydroperoxide (**10**), these compounds were separated by preparative h.p.l.c. from the products of an oxidation which had been allowed to stand for 24 h. Solutions of pure (**9**) and of a mixture of (**10**) with the 1β-hydroperoxide (**12**) in $CDCl_3$ were then kept at room temperature for 259 h; the hydroperoxides were reduced to alcohols by triphenylphosphine and the compositions were determined by 400 MHz n.m.r. The results are shown in Schemes 3 and 4.

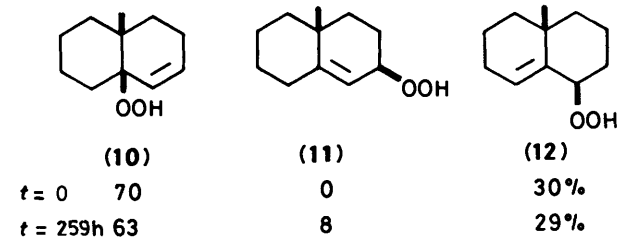
It will be seen that (**9**) epimerises to the 2β-hydroperoxide (**11**), and (**10**) undergoes a suprafacial rearrangement to the same hydroperoxide (**11**), but these reactions are much slower than the suprafacial rearrangement, on the α-face, of (**8**) to (**9**).

The structure of the 2α-hydroperoxide (**9**) was established as shown in Scheme 5.

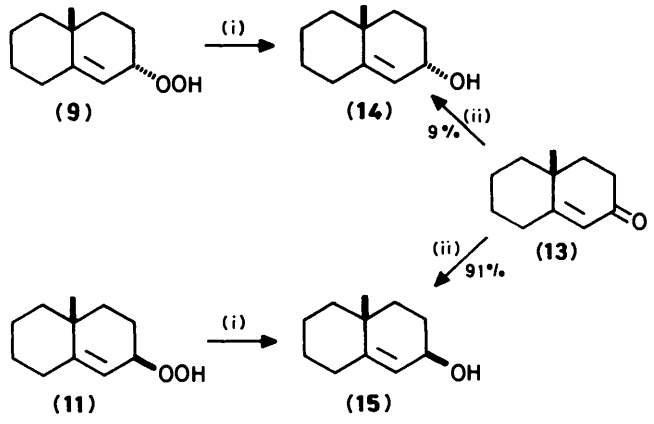
Reduction of the 4a-methyl-4,4a,5,6,7,8-hexahydro-3*H*-naphthalene-2-one (**13**) with lithium aluminium hydride gave as



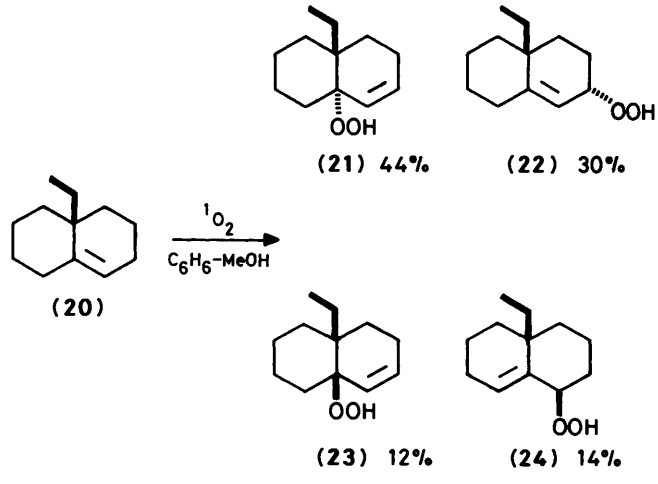
Scheme 3.



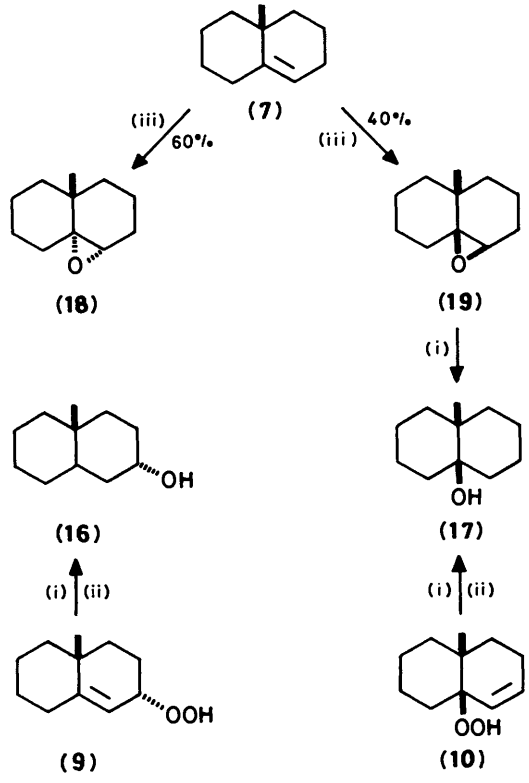
Scheme 4.



Scheme 5. *Reagents:* (i) Ph_3P; (ii) $LiAlH_4$



Scheme 7.



Scheme 6. *Reagents:* (i) $LiAlH_4$; (ii) H_2/Pt; (iii) *m*-$ClC_6H_4CO_3H$

a major product the alcohol (**15**), and as a minor product the alcohol (**14**) which was identical with the product obtained by reducing the hydroperoxide (**9**) with triphenylphosphine. As reduction of (**13**) will occur most readily from the less hindered α-face,[11] the minor product alcohol (**14**) must have the α-configuration, and the hydroperoxide (**9**) has the same configuration, as shown in Scheme 5.

The 4aα-hydroperoxide (**8**) was differentiated from the 4aβ-hydroperoxide (**10**), by reducing a mixture of (**9**) and (**10**), to give a similar mixture of the saturated 2α- and 4aβ-alcohols (**16**) and (**17**), respectively. The structure of these alcohols is known because they can be formed by reduction of the epoxides (**18**) and (**19**) which can be prepared in known stereoselectivity from 4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalene[9] (Scheme 6).

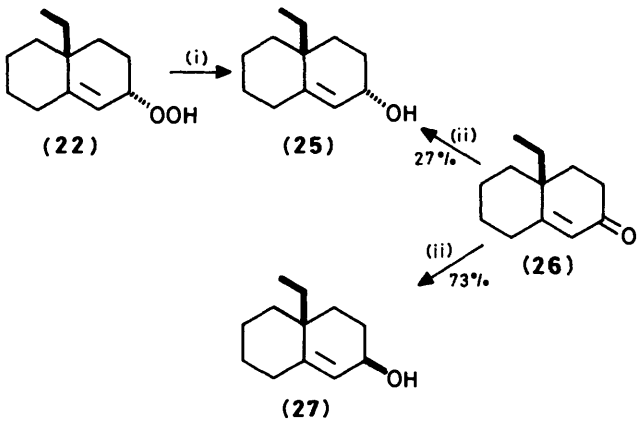
4a-Ethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**20**) was similarly subjected to photosensitised oxidation in benzene–methanol solution (Scheme 7).

By chromatography, the 4aα-hydroperoxide (**21**) and its rearrangement product (**22**), and a mixture of the β-hydroperoxides (**23**) and (**24**) was separated and the components characterised by ^1H n.m.r. spectroscopy.

The progress of the allylic rearrangement of the 4aα-hydroperoxide (**21**) in $CDCl_3$ solution was followed by ^1H n.m.r. spectroscopy as shown in Figure 2. In 45 h the reaction was half complete, and after 72 h the mixture consisted of 20% of (**21**) and 80% of the 4aβ-ethyl-2,3,4,4a,5,6,7,8-octahydronaphthalen-2α-yl hydroperoxide (**22**); during this period, no change was observed in the signals of the small amount of the 4aβ-hydroperoxide (**23**) which was present.

The assignment of the structure of (**21**) is discussed below. The structure of (**22**) was determined in the same way as that of the 4a-methyl analogue (**9**) (Scheme 8).

Reduction of the hydroperoxide (**22**) gave the corresponding alcohol (**25**), which was obtained as a minor product, along with its epimer (**27**), when 4a-ethyl-4,4a,5,6,7,8-hexahydro-3*H*-naph-



Scheme 8. *Reagents:* (i) Ph_3P; (ii) $LiAlH_4$

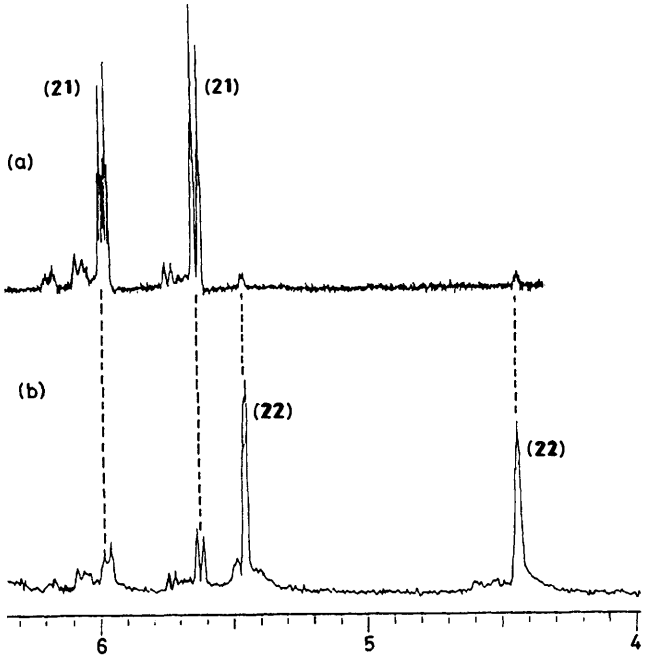


Figure 2. ^1H N.m.r. spectra (400 MHz) of the olefinic signals, illustrating the rearrangement (**21**) ⟶ (**22**); (a) $t = 0$; (b) $t = 72$ h

thalen-2-one (**26**) was reduced with lithium aluminium hydride (Figure 3). The hydroperoxide (**22**) therefore has the α-configuration.

The hydroperoxides (**21**) [containing a small amount of (**23**)] and (**22**) were photolysed in chloroform solution at 232 K in an e.s.r. cavity, when the spectra of the corresponding alkylperoxyl radicals (**28**) were observed [equation (4) and Figure 4].

$$\text{ROOH} \xrightarrow{h\nu} \text{RO}^{\cdot} + {}^{\cdot}\text{OH} \xrightarrow{\text{ROOH}} \underset{(28)}{\text{ROO}^{\cdot}} \qquad (4)$$

The spectrum of the radical derived from the tertiary hydroperoxide (**21**) appeared as a singlet, ΔH_{pp} 1.5 G, g 2.0149, but that from (**22**) showed a doublet, a(1 H) 5.1 G, ΔH_{pp} 1.6 G, g 2.0147. This is in accord with the tertiary structure of (**21**), and the secondary structure of (**22**).

Discussion

We have shown (Scheme 1) that the reaction of singlet oxygen with 4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**7**) gives

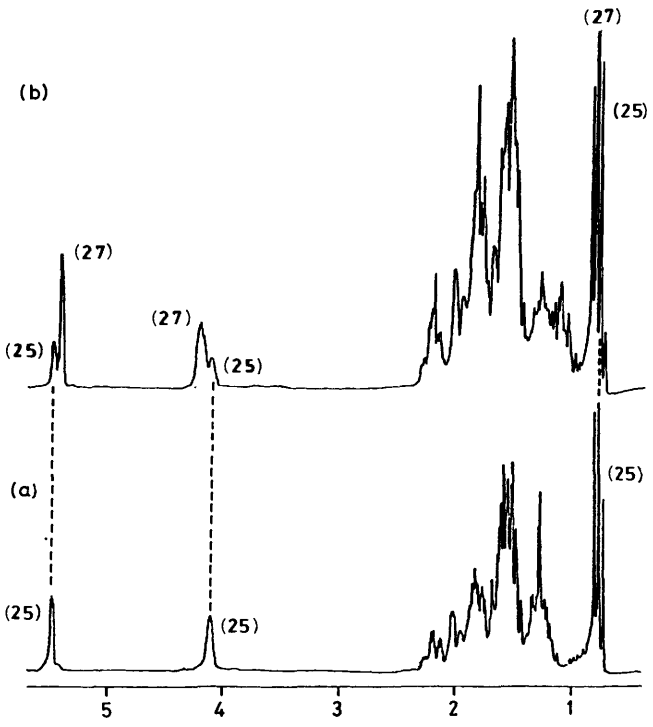
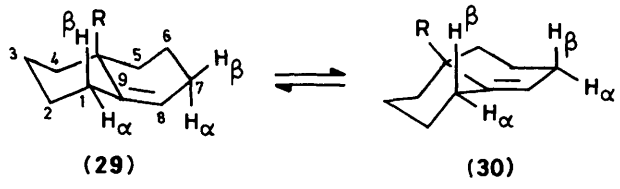


Figure 3. ^1H N.m.r. spectra (200 MHz) showing the reduction of (a) (**22**) ⟶ (**25**), and (b) (**26**) ⟶ (**25**) + (**27**)

initially 61% of the 4aα-hydroperoxide (**8**) and 27% of the 4aβ-hydroperoxide (**10**), though the 4aα-hydroperoxide undergoes substantial rearrangement to the 2α-hydroperoxide (**9**) before isolation.

This selectivity for the attack of the singlet oxygen at the α-face can be understood in terms of the steric requirements of the cyclic transition state which the reaction involves.



(**29**) (**30**)

The two conformations (**29**) and (**30**) (R = Me) of (**7**) are close in energy. In both, the α-face is open to attack by $^1O_2$, but in (**29**) the β-face is sterically shielded by the methyl group R, and an excess of the 4aα-hydroperoxide is formed.[10] Only this 4aα-hydroperoxide, and not the 4aβ-isomer, readily undergoes subsequent rearrangement. We ascribe the β-configuration to the hydroperoxide (**12**), because in either the conformation (**29**) or (**30**) only the β-face can present an axial hydrogen at C-1 to accommodate the cyclic mechanism by which the singlet oxygen reacts.[12]

In the reaction of 4a-ethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**20**), the facial stereoselectivity is more pronounced, and the hydroperoxide which undergoes subsequent rearrangement is formed in an initial yield of 74%. By analogy with the results obtained with the methyloctahydronaphthalene (**7**), we assume that this rearrangeable hydroperoxide is the 4aα-hydroperoxide (**2**); this assignment is supported by the fact that the larger ethyl group would be expected in (**29**) and (**30**) (R = Et) to direct the attack of the singlet oxygen more to the α-face.

With respect to the allylic rearrangement of the hydroper-

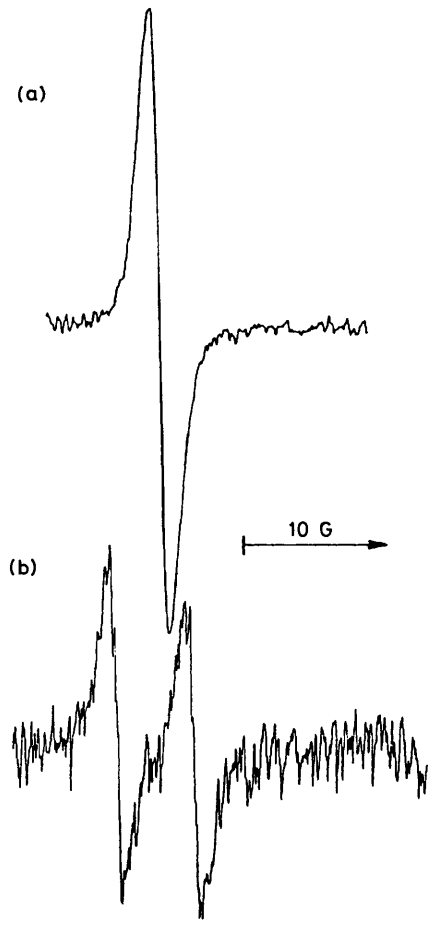


Figure 4. E.s.r. spectra ($CHCl_3$; 232 K) of the alkylperoxyl radicals derived from (a) (**21**), and (b) (**22**)

oxides, two observations stand out. First, we have established that the rearrangement of the 8aβ-methyl-4aα-hydroperoxide (**8**) occurs suprafacially to give the 2α-hydroperoxide (**9**), and, in all probability, the rearrangement of the corresponding 8aβ-ethyl-4aα-hydroperoxide, (**21**) ⟶ (**22**), is similarly suprafacial.

Second, as noted above, under similar conditions, the corresponding 4aβ-hydroperoxides (**10**) and (**23**) undergo negligible rearrangement.

These results are relevant to the mechanism of the rearrangement, and will be discussed in a forthcoming publication.

Experimental

^{1}H N.m.r. spectra were recorded in $CDCl_3$ with a Varian XL 200 or VXR 400 spectrometer, and e.s.r. spectra with a Varian E109 instrument fitted with a 500 W high-pressure mercury arc focussed on the cavity.

4a-*Methyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalene* (**7**). Condensation of 2-methylcyclohexanone and methyl vinyl ketone gave 4a-methyl-4,4a,5,6,7,8-hexahydro-3*H*-naphthalen-2-one (**13**);[13] δ 1.25 (3 H, s, Me), 1.00—2.55, and 5.72 (1 H, br s, =CH–). This was reduced with lithium aluminium hydride[9] to give a mixture of the 2α-alcohol (**14**) and the 2β-alcohol (**15**) in the ratio of 1:10 (n.m.r.) in agreement with previously work by g.l.c.[11] (**14**): δ 1.03 (3 H, s, Me), 1.15—2.25, and 4.08 [1 H, m, ^3J 9.0 Hz, C*H*(OH)], and 5.43 (1 H, d, *J* 4.4 Hz, =CH–). (**15**): δ 1.11 (3 H, s, Me), 1.15—2.25, and 4.19 [1 H, m, ^3J 16.0 Hz, CH(OH)], and 5.29 (1 H, d, *J* 1.6 Hz, =CH–). The alcohols were converted into the corresponding acetates[9] and reduced with lithium in ethylamine to give compound (**7**)[9] (31%); δ 1.06 (3 H, s, Me), 0.80—2.20, and 5.29 (1 H, br s, =CH–).

Photo-oxygenation of 4aβ-*Methyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalene* (**7**).—A solution of (**7**) (0.85 g, 5.7 mmol) and Rose Bengal (0.01 g, 0.01 mmol) in pyridine (5 cm^3) in a water-cooled flask (17 °C) was irradiated with a 400 W sodium lamp at a distance of 5 cm. The flask was provided with magnetic stirring, and was connected to a burette containing oxygen maintained at a pressure of 1 Atm.

After 1.5 h, the uptake of oxygen ceased. The pyridine was removed under reduced pressure. The crude mixture of hydroperoxides was immediately chromatographed on alumina using as an eluant pentane containing an increasing proportion of ether. Early fractions yielded a mixture of the hydroperoxides (**8**), (**9**), and (**10**), then a mixture of (**9**), (**11**), and (**12**) and finally pure (**9**). Overall, 0.534 g of hydroperoxide was obtained with the composition (**8**) 30.3, (**9**) 30.4, (**10**) 25.9, (**11**) 1.1, and (**12**) 12.2%, with the following characteristics.

8aβ-*Methyl*-1,2,3,4,4a,7,8,8a-*octahydronaphthalen*-4aα-*yl hydroperoxide* (**8**). δ 0.97 (3 H, s, Me), 1.20—2.20, and 5.60 (1 H, d of t, *J* 10.0 and 2.4, Hz 6-H), and 5.90 (1 H, d of t, *J* 10.0 and 3.2 Hz, 5-H).

8aβ-*Methyl*-1,2,3,4,4a,7,8,8a-*octahydronaphthalen*-4aβ-*yl hydroperoxide* (**10**). δ 1.01 (3 H, s, Me), 1.20—2.20, and 5.62 (1 H, m, *J* 17.0 Hz, 6-H), and 5.96 (1 H, m, *J* 19.6 Hz, 5-H).

4aβ-*Methyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalen*-1β-*yl hydroperoxide* (**12**). δ 1.13 (3 H, s, Me), 1.20—2.20, and 4.31 [1 H, m, C*H*(OOH), *J* 8.2 Hz], and 5.66 (1 H, m, *J* 9.1 Hz, 8-H).

4aβ-*Methyl*-2,3,4,4a,5,6,7,8-*octahydronaphthalen*-2α-*yl hydroperoxide* (**9**). (Found: C, 72.4; H, 9.94. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95%), δ 1.04 (3 H, s, CH_3), 1.20—2.20, and 4.38 [1 H, m, C*H*(OOH), *J* 10.0 Hz], and 5.35 (1 H, d, *J* 4.8 Hz, 1-H).

Rearrangement of 4a-*Methyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalenyl Hydroperoxides.*—(i) A solution of the hydroperoxides (**8**) 26.1, (**9**) 40.0, (**10**) 27.8, and (**12**) 6.1%, in $CDCl_3$ was monitored by ^{1}H n.m.r. spectroscopy [Figure 1(a)]. After 24 h, the sample contained (**9**) 65.9, (**10**) 27.6, (**12**) 6.4%, and no further change in composition occurred.

(ii) A solution of 4a-methyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (460 mg) was subjected to photo-oxygenation in pyridine. The solvent was removed, chloroform was added to the residue, and the solution was left for 24 h. The products were separated by h.p.l.c. on 5 μm silica gel using ethyl acetate–light petroleum (60—70 °C) 1:9 as eluant.

A solution of the hydroperoxide (**9**) (138 mg) in $CDCl_3$ (1.5 cm^3) was kept at room temperature and monitored periodically by 400 MHz ^{1}H n.m.r. After 259 h, the solution was reduced with triphenylphosphine, and the products were analysed by interpretation of the olefinic region of the spectrum, giving the results shown in Scheme 3.

(iii) A solution of 47 mg of a mixture of the hydroperoxides (**10**) and (**12**) in $CDCl_3$ was kept for 259 h, then reduced and analysed above, giving the results in Scheme 4.

Reduction of 4aβ-*Methyl*-2,3,4,4a,5,6,7,8-*octahydronaphthalen*-2α-*yl Hydroperoxide* (**9**) *and* 8aβ-*Methyl*-1,2,3,4,4a,7,8,8a-*octahydronaphthalen*-4aβ-*yl Hydroperoxide* (**10**).—A mixture of the hydroperoxyoctahydronaphthalenes [0.058 g, 0.32 mmol, (**9**) 67%, (**10**) 33%] in ether (1 cm^3) was added to a stirred solution of lithium aluminium hydride (0.051 g, 1.3 mmol) in ether (5 cm^3). After 5 h stirring, the solution was worked up yielding a mixture of the corresponding alcohols as an oil, which was analysed by integration of the methyl region in the n.m.r. spectrum: (**14**) δ 1.03, 67%, and the alcohol from (**10**) δ 1.00, 33%.

This mixture of unsaturated alcohols (0.036 g, 0.22 mmol) was hydrogenated over reduced PtO_2 (0.017 g) in acetic acid (5 cm^3), yielding an oil consisting of a mixture of (**16**) δ($CDCl_3$) 0.96, δ(CCl_4) 0.96, 67%; and (**17**) δ($CDCl_3$) 0.97, δ(CCl_4) 0.98, 33%. For (**17**), ref. 9 quotes δ(CCl_4) 0.96, and, for its *trans*-diastereoisomer, δ(CCl_4) 1.02.

4a-*Ethyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalene* (**20**). 2-Ethylcyclohexanone was condensed with methyl vinyl ketone in benzene in the presence of sulphuric acid yielding 4a-ethyl-4,4a,5,6,7,8-hexahydro-3*H*-naphthalen-2-one, b.p. 80—82 °C at 0.125 mmHg; δ 0.89 (3 H, t, *J* 7.4 Hz, Me), 1.11—2.42, and 5.76 (1 H, s, =CH–). (Found: C, 80.6; H, 9.9. $C_{12}H_{18}O$ requires C, 80.8; H, 10.2%). This was treated with ethane-1,2-dithiol in the presence of boron trifluoride etherate, giving the dithioacetal, which was reduced with sodium in liquid ammonia, yielding 4a-ethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene (**20**), which was isolated by chromatography on alumina. δ 0.76 (3 H, t, ^3J 7.2 Hz, Me), 1.0—2.2, and 5.35 (1 H, br m, =CH–).

Photo-oxygenation of 4a-*Ethyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalene* (**20**).—A solution of (**20**) (0.517 g) and Rose Bengal (0.02 g) in benzene–methanol (1:1; 5 cm^3) was oxidised as described above for the 4a-methyl analogue (**7**). After 130 min, the solvent was removed, and the products isolated chromatographically on silica gel using pentane–ether (80:20) as eluant, giving (**21**) 44%, (**22**) 30%, and a mixture of (**23**) and (**24**) (12% and 14%, respectively, by n.m.r.) (in all 0.352 g), with the following characteristics.

8aβ-*Ethyl*-1,2,3,4,4a,7,8,8a-*octahydronaphthalen*-4aα-*yl hydroperoxide* (**21**). δ 0.77 (3 H, t, ^3J 7.2 Hz, Me), 0.82—2.19, 5.58 (1 H, d of d, *J* 9.9 and 2.3 Hz, =CH–), 5.93 (1 H, d of t, *J* 3.5 and 9.8 Hz, =CH–), and 6.95 (1 H, s, OOH).

4aβ-*Ethyl*-2,3,4,4a,5,6,7,8-*octahydronaphthalen*-2α-*yl hydroperoxide* (**22**). δ 0.75 (3 H, t, ^3J 7.4 Hz, Me), 0.95—2.71, and 4.63 [1 H, d of t, *J* 6, 3.4, and 2.4 Hz, –C*H*(OOH)], 5.38 (1 H, d, *J* 3.4 Hz, =CH–), and 7.71 (1 H, s, OOH).

8aβ-*Ethyl*-1,2,3,4,4a,7,8,8a-*octahydronaphthalen*-4aβ-*yl hydroperoxide* (**23**). δ 0.77—2.19, 5.69 [1 H, d of t, ^3J (2-H) *ca.* 8.5 Hz, =CH–], and 6.14 [1 H, d of t, ^3J (1-H) *ca.* 8.5 Hz, =CH–].

4aβ-*Ethyl*-1,2,3,4,4a,5,6,7-*octahydronaphthalen*-1β-*yl hydroperoxide* (**24**). δ 0.71—2.13, 4.32 [1 H, br m, C*H*(OOH)], 5.74 (1 H, t, ^3J(2-H) 3.6 Hz), and 7.40 (1 H, s, OOH).

Allylic Rearrangement of 8aβ-*Ethyl*-1,3,4,4a,7,8,8a-*octahydronaphthalen*-4a-*yl Hydroperoxide*.—A solution of 8aβ-ethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalen-4aα-yl hydroperoxide (**21**) [0.001 g, containing about 8% of the 4aβ-hydroperoxide (**23**)] in chloroform (5 cm^3) was kept at 22 °C. At intervals, aliquots were taken, and were stripped of solvent, and the proportions of (**21**) and of the 2α-hydroperoxide (**22**) were determined by n.m.r. Time (h), % (**21**), % (**22**): 0, 100, 0; 15, 77, 23; 24, 65, 35; 39, 55, 45; 48, 43, 57; 63, 33, 67; 72, 20, 80. During this period, the percentage of the 4aβ-hydroperoxide (**23**) did not change.

Reduction of 4aβ-*Ethyl*-2,3,4,4a,5,6,7,8-*octahydronaphthalen*-2α-*yl Hydroperoxide* (**22**).—A mixture of the hydroperoxide (19 mg) and triphenylphosphine (26 mg) was stirred in ether (1 cm^3) for 5 min. The n.m.r. spectrum of the product (**25**) showed δ 0.74 (3 H, t, ^3J 7.5 Hz, Me), 1.0—2.2, 4.06 (1 H, m, C*H*OH), and 5.44 (1 H, d, =CH–).

Reduction of 4a-*Ethyl*-4,4a,5,6,7,8-*hexahydro*-3H-*naphthalen*-2-*one* (**26**). The ketone (**26**) (0.248 g) in ether (6 cm^3) was added to a stirred solution of lithium aluminium hydride (0.056 g) in ether (6 cm^3). After 3 h, the solution was worked up to yield the *trans*-2-alcohol (**25**) (27%), δ 0.76 (3 H, t, *J* 7.0 Hz, Me), 0.95—2.25, 4.09 (1 H, br s, C*H*OH), 5.46 (1 H, br s, =CH–), and the *cis*-2-alcohol (**27**) (73%), δ 0.79 (3 H, t, *J* 7.0 Hz, Me), 0.95—2.25, 4.18 (1 H, br s, C*H*OH), and 5.39 (1 H, br s, =CH–).

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