Photosensitised Oxidation of Model Unsaturated Lipid Systems: (4*Z*,7*Z*)-Undeca-4,7-diene and (4*Z*)-Undec-4-en-7-yne

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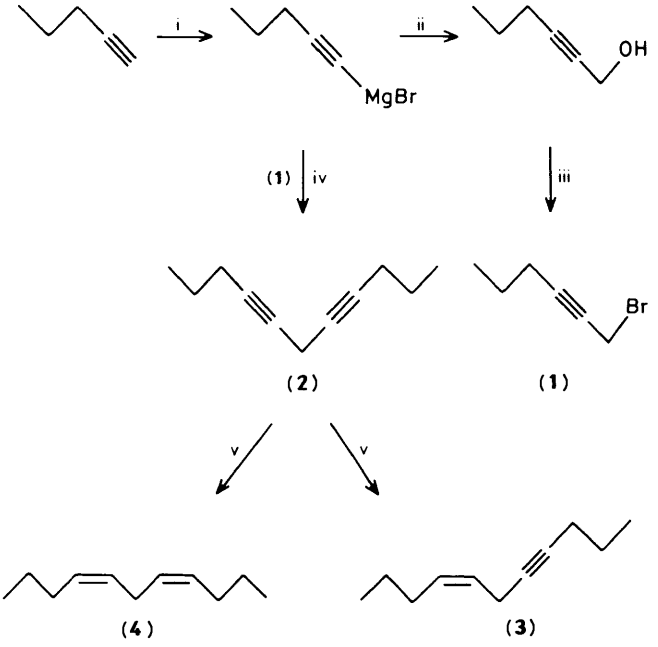
Photosensitised oxidation of the skipped diene (4*Z*,7*Z*)-undeca-4,7-diene (**4**) gave non-conjugated and conjugated dienyl hydroperoxides (**5a**) and **5b**) in the ratio 2:3. Free radical cyclisation of (**5a**) yielded two stereoisomeric dioxolanyl hydroperoxides (**9**) and (**10**). (4*Z*)-Undec-4-en-7-yne (**3**) led, on photosensitised oxidation, to non-conjugated and conjugated enynyl hydroperoxides (**15**) and (**14**) in the ratio 1 : 2. Undeca-4,7-diyne (**2**) proved comparatively resistant to photosensitised oxidation, with the relative rates of attack on (**4**) : (**3**) : (**2**) being 110 : 15 : ⩽1. There was no evidence for the abstraction of the prop-2-ynyl hydrogen by singlet oxygen in these reactions.

There is much current interest in lipid oxidation, especially in view of recent discoveries of the role played by enzymatic oxidation products of arachidonic acid in the formation of prostaglandins,[1,2] thromboxanes,[2] and leukotrienes.[3] The autoxidation and photosensitised oxidation of vegetable oils have long been of interest to the food industry, and again reflect the ease of oxidation of unsaturated fatty acid esters.[4] Those lipids containing 1,4-diene units (*e.g.* linoleic and linolenic esters) are attacked at the allylic positions especially easily by autoxidation[5] and by alkoxyl radicals.[6,7] Related reactions of lipids occur under the combined influence of oxygen, light, and a sensitiser, which generates singlet molecular oxygen ($^1O_2$). Singlet oxygen is also able to abstract the allylic hydrogens of alkenes, yielding allylic hydroperoxides, but by a specific process which does not appear to involve free radicals.[8,9] Singlet oxygen is implicated in a variety of biological systems.[10,11]

In many previous investigations of the photosensitised oxidation of unsaturated lipids,[12] the number of positional and stereochemical isomers which can arise has made difficult their separation in anything other than minute amounts;[13,14] often, only analytical-scale separations have proved possible. The chemistry of individual unsaturated hydroperoxides is obviously of great importance, and other synthetic routes to these compounds have been found.[15,16] However, photosensitised oxidations are an attractive, direct route to unsaturated hydroperoxides. We have chosen to study a symmetrical diene (**4**), and the related enyne (**3**), in order to reduce the number of possible isomers which result from oxidation. There have been previous studies of photosensitised oxidation of undeca-4,7-diene (**4**),[17] and hepta-2,5-diene,[18] but these have given little or no attention to the isolation and reactions of the intermediate allylic hydroperoxides which are produced.

Results and Discussion

The starting *cis*,*cis*-diene (**4**) was prepared by the route shown in Scheme 1. The Grignard reagent prepared from pent-1-yne was coupled with the hex-2-ynyl bromide (**1**) in a copper(I)-catalysed reaction, to give the symmetrical diyne (**2**) in 85% yield. The subsequent reduction of (**2**) to the (*Z*,*Z*)-diene was most effectively carried out by selective hydrogenation using Lindlar catalyst, despite the reports that this classical catalyst is unsatisfactory for some 'skipped' diyne reductions.[17,19] The progress of hydrogenation could most easily be assessed by g.l.c., and this reduction route was also used to prepare the *Z*-enyne (**3**), by stopping the hydrogenation when the concentration of enyne was near a maximum. Column chromatography on silica gel allowed the separation of diene, enyne, and



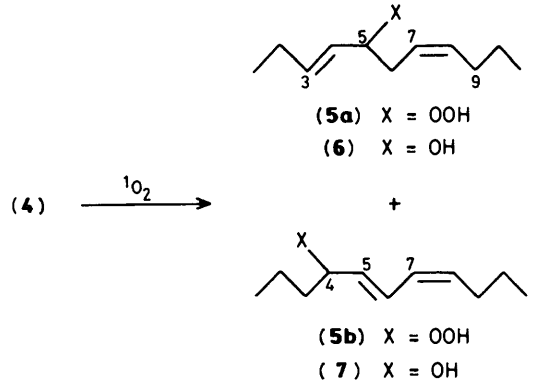
Scheme 1. *Reagents:* i, EtMgBr, THF; ii, CH_2O (paraformaldehyde); iii, PBr_3, Et_2O, pyridine; iv, CuCl, $HgCl_2$, THF; v, H_2, Lindlar catalyst

unchanged diyne. ^1H and ^{13}C N.m.r. spectra for (**3**) and (**4**) showed the absence of any isomeric compounds having *trans*-alkenyl geometry. ^{13}C N.m.r. spectra for these small molecules were most useful in establishing the type and geometry of the unsaturated carbons; thus, the enyne (**3**) displayed two olefinic carbons (126 and 130 p.p.m.) and two acetylenic carbons (78 and 79 p.p.m.), with C-6 at 17 p.p.m. [*cf.* 10 p.p.m. in the diyne (**2**) and 26 p.p.m. in the *cis*, *cis*-diene (**4**)].

Photo-oxidation of the Diene (**4**).—An oxygenated solution of (**4**) in dichloromethane was irradiated with visible light, using tetraphenylporphyrin as photosensitiser, whilst keeping the solution at low temperature (below −30 °C). The rate of oxidation was negligibly slow at this temperature when the solution was not irradiated. T.l.c. of the photoproduct showed the formation of only one slower-moving spot, and this material was subsequently isolated by flash chromatography. The ^1H n.m.r. spectrum of this substance (**5**) suggested from the two singlets near δ 7.7 that it was a mixture of two hydroperoxides in

the ratio 2:3. The relative integration of the olefinic double doublet at δ 6.59, which is characteristically downfield for a conjugated dienyl hydroperoxide,[13b,20] showed that the isomer (**5b**) was dominant. The formation of a mixture of non-conjugated (**5a**) and conjugated (**5b**) dienyl hydroperoxides in high yield (89% in this instance) is a reaction expected for the attack of $^1O_2$ on a 1,4-diene system,[13a,17,18,21] but differs from the result of autoxidation which leads only to conjugated dienyl products.[19]

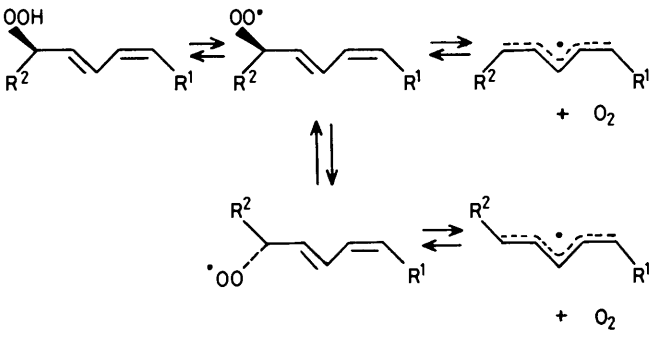
Reaction of the mixture of isomers (**5**) with triphenylphosphine in dichloromethane led to a material which showed a single spot by t.l.c., but could be separated into two components by preparative g.l.c. These compounds were readily identified as the non-conjugated and conjugated undecadienols (**6**) and (**7**), respectively,[17] resulting from reduction of the hydroperoxides



to the corresponding alcohols. In previous work, the ^1H spectrum of the undecadienol (**6**) was sufficiently complex in the olefinic region so that double bond geometry could only be ascertained by addition of a shift reagent:[17] however, ^{13}C n.m.r. spectroscopy provides a convenient way of distinguishing *Z* and *E* configuration, because the ^{13}C chemical shift of the methylene group adjacent to the double bond is characteristic of its environment. This allylic carbon is shielded in the *Z*-arrangement by *ca.* 5—6 p.p.m. over that of the *E*-configuration.[22] For undeca-3,7-dien-5-ol (**6**), the signal at 25.3 p.p.m. is clearly that arising from the methylene carbon adjacent to the 3,4-double bond having *E*-geometry, by comparison with the C-2 shifts for *Z*- and *E*-oct-3-ene (21.0 and 26.1 p.p.m., respectively).[23] In addition, the signal at 29.6 p.p.m. can be assigned to the C-9 methylene group adjacent to the 7,8-double bond having *Z*-geometry, by comparison with the C-3 shifts found for *Z*-and *E*-oct-4-ene (29.8 and 35.3 p.p.m., respectively). In the conjugated undeca-5,7-dien-4-ol (**7**), the C-9 allylic signal at 29.9 p.p.m. again shows the *Z*-configuration of the 7,8-double bond, although in this molecule the ^1H vicinal coupling constants can be individually measured from the 200 MHz ^1H spectrum ($^3J_{cis}$ 11 Hz, $^3J_{trans}$ 15 Hz).

It is well established that autoxidation (involving free radicals) of *cis,cis*-1,4-dienes such as linoleic acid gives rise to *cis,trans* and *trans,trans*-conjugated dienyl hydroperoxides in a ratio which depends on substrate concentration and on other hydrogen-donating species which are present.[24,25] In contrast, there are conflicting accounts on the stereochemistry of the photo-oxidation of *cis,cis*-1,4-dienes: whilst some investigators have reported *cis,trans*-dienyl hydroperoxides,[13b] others have found formation of appreciable amounts (30%) of *trans,trans*-conjugated dienyl hydroperoxide,[18] or that isomerisation of *cis,trans*-hydroperoxide to the more stable *trans,trans*-isomer is a process which occurs during photo-oxidation.[17] To some extent, this isomerisation is a likely consequence of the ability of the photosensitiser to generate radicals (type I photo-oxidation) as opposed to singlet molecular oxygen (type II photo-oxidation).[26] However, even using sensitisers such as Rose Bengal, which should generate $^1O_2$ very selectively,[27] there does appear to be *trans,trans*-dienyl hydroperoxide production under certain conditions.[18]

The route for isomerisation of these hydroperoxides has been clarified by Chan and co-workers.[28] For methyl linoleate hydroperoxides, it involves the abstraction of hydroperoxide hydrogen by a free radical, followed by reversible dissociation of the peroxyl species into a pentadienyl radical and triplet oxygen, as illustrated in Scheme 2. Porter and his group[24,25] have put

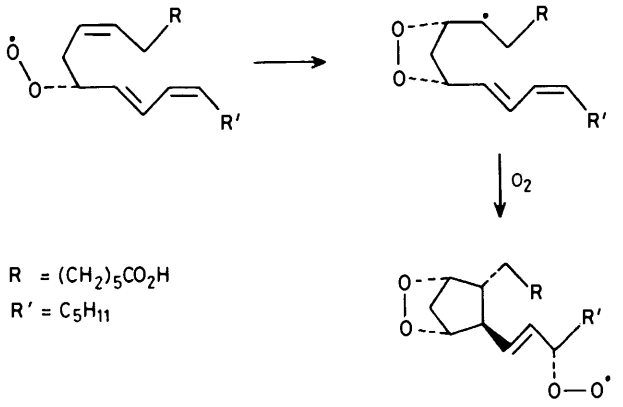


Scheme 2.

forward convincing arguments to show that it is loss of oxygen from different conformational isomers of the peroxyl radical which accounts for isomerisation about the double bonds, rather than geometric isomerisation of the pentadienyl radical itself. In the present photo-oxidation of (**4**), it is very noticeable that no (<3%) *trans,trans*-hydroperoxide (**8**), prepared as described below, is formed. We attribute this stereoselectivity to the use of an efficient sensitiser (tetraphenylporphyrin) for $^1O_2$ production, and, more importantly, to the use of a low temperature (−30 °C) during photo-oxidation. The free radical side-reactions shown in Scheme 2 have appreciable activation energies, and are minimised by reduced temperatures. Prolonged exposure of the hydroperoxides (**5**) to air and ambient temperatures was also avoided, to prevent free radical-induced isomerisations;[14] in these circumstances, the conjugated hydroperoxide (**5b**) could be subjected to flash chromatography without losing its stereochemical integrity.

Photo-oxidation of the (*Z*,*Z*)-diene to give the (*Z*,*E*)-hydroperoxides exclusively is certainly in accord with a mechanism of reaction involving abstraction of allylic hydrogens by $^1O_2$ in a near-concerted ene reaction. The geometry of attack by singlet oxygen on 1,4-dienes is thus equivalent to that of lipoxygenase enzymes on dienoic acids, although it lacks the regiospecificity found in the enzymic process.

Autoxidation of Hydroperoxides (**5**).—Prostaglandin biosynthesis from C_{20} polyunsaturated fatty acids may occur *via* a free radical process, involving an endoperoxide which can be isolated and which may result from enzyme-catalysed cyclisation with the stereospecific formation of O–C and C–C bonds, as shown in Scheme 3.[29] The free radical cyclisation of the related homoallylic hydroperoxide (**5a**) present in (**5**) is therefore of interest. Autoxidation of the mixture of conjugated and unconjugated hydroperoxides (**5**) was carried out under oxygen in tetrachloromethane as solvent, using di-t-butyl peroxyoxalate[30] as a radical initiator. T.l.c. of the reaction product showed residual material having the mobility of the starting hydroperoxides, as well as the formation of two more polar compounds. Flash chromatography allowed the separation of all three fractions.

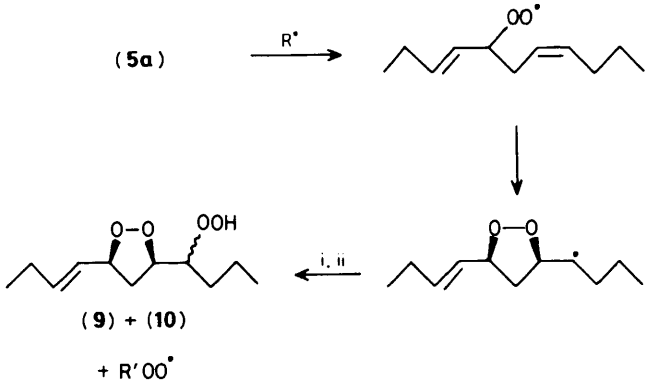


Scheme 3.

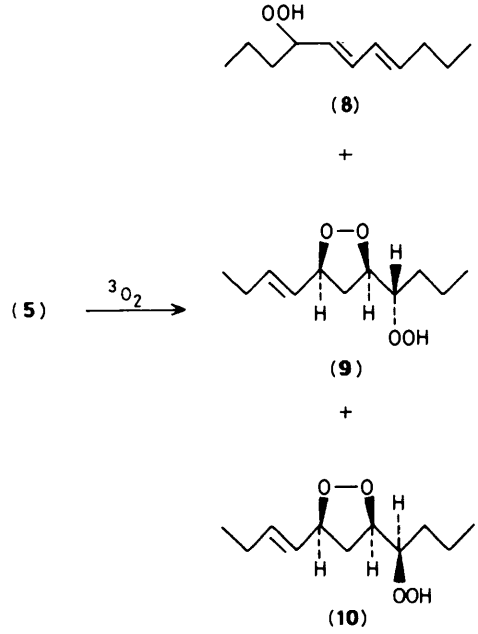
It was evident from the ^1H and ^{13}C n.m.r spectra of the isolated fraction having the mobility of (**5**) that it was neither of the initial isomers of hydroperoxide (**5a**) or (**5b**). Although still obviously a conjugated hydroperoxide, it appeared to be the (*E,E*)-isomer (**8**), which had been notably absent from the initial photo-oxidation. Thus, it was possible to pick out the *trans*-vicinal coupling constants across each double bond ($^3J_{trans}$ 15 Hz) in its ^1H n.m.r. spectrum. In the ^{13}C spectrum of (**8**), the hydroperoxy-bearing carbon at 86.8 p.p.m. was characteristic of that adjacent to a *trans* double bond;[31] the C-9 methylene carbon was found at 34.8 p.p.m., in contrast to that for (**7**), but in good comparison with the C-3 shift (35.3 p.p.m.) previously noted for the model compound, (*E*)-oct-4-ene. Reduction of the hydroperoxide (**8**) with triphenylphosphine gave a dienyl alcohol, in 55% yield after chromatography, having a ^1H n.m.r. spectrum in good agreement with that of the known (*E,E*)-undecadienol (**11**).[17] The ^{13}C spectrum of the reduced compound was closely related to that of (**8**), with the important exception of the shift of the hydroperoxy-bearing carbon from 86.8 p.p.m. to that typical of the hydroxy-bearing carbon at 71.9 p.p.m. in (**11**).

Whilst it is not surprising that the conjugated dienyl hydroperoxide (**5b**) does not cyclise on autoxidation, the complete conversion of (**5b**) into the thermodynamically favoured (*E,E*)-isomer (**8**) is notable. This observation demonstrates the role of peroxyl species in causing *cis-trans* isomerisation of dienyl hydroperoxides (Scheme 2), whilst emphasising the lack of involvement of such species in the present photo-oxidations.

It appeared from the ^1H and ^{13}C n.m.r. spectra of each of the two more polar compounds from autoxidation that they were diastereoisomers of the dioxolanyl hydroperoxides (**9**) and (**10**). Each showed two olefinic protons in the region δ 5.4—6, which were coupled with characteristics of *trans*-stereochemistry (^3J 15.5 Hz). A single hydroperoxy hydrogen was evident at δ 9.1—9.6. ^{13}C N.m.r. spectra confirmed a single olefinic bond, and suggested the presence of three peroxy-bearing carbons at 83—86 p.p.m. These compounds were isolated in yields, based on the cyclisable isomer (**5a**), of 38% and 13.5%, respectively.



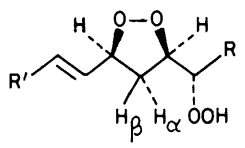
Scheme 4. *Reagents:* i, O_2; ii, R'OOH



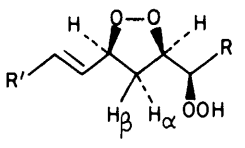
Cyclisation of homoallylic peroxyl radicals, as shown in Scheme 4, to give dioxolanes rather than dioxanes, is a recognised feature of such free radical cyclisations.[32] In all cases, the result of such cyclisation has been to place the 3- and 5-substituents on the dioxolane ring in a *cis*-relationship.[33] Unsaturated dioxolanyl hydroperoxides related to (**9**) and (**10**) have been isolated as secondary products of photosensitised oxidation of methyl linoleate.[34,35] In those cases, the compounds could be separated into pairs of structural isomers by medium-pressure liquid chromatography,[34] or into four individual isomers by h.p.l.c.[35] A comparison of ^1H and ^{13}C spectra with the present work shows the general structural similarity with (**9**) and (**10**), and allows the relative stereochemistry to be assigned. Proton coupling constants and chemical shifts around the dioxolane ring are similar for (**9**) and (**10**), but there are two distinguishing shifts, shown in Table 1. Firstly, the hydroperoxy α-proton shift (δ 4.24 *vs.* 3.93) depends on the *erythro*- or *threo*-stereochemistry about C-4 and C-5. Secondly, the dioxolanyl 6α-H shift is significantly different (δ 2.44 *vs.* 2.17) in the two isomers. The ^{13}C n.m.r. shift of the nearby C-6 atom (41.0 p.p.m. *vs.* 43.3 p.p.m.) reinforces this point; the more mobile stereoisomer (**9**) obviously has *erythro* stereochemistry about the C-4 to C-5 bond. Mihelich[34] has proved the relative configuration of the linoleate hydroperoxides shown in Table 1 by reduction of a *threo*-isomer to a known stereoisomer (9*R*,10*R*,12*R*) of methyl trihydroxyoctadecanoate.[36]

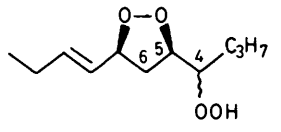
The hydroperoxides (**9**) and (**10**) were individually reduced by triphenylphosphine, to give the corresponding dioxolanyl alcohols (**12**) and (**13**), respectively, in 68—81% yield. A comparison of the ^1H and ^{13}C n.m.r. spectra of these two alcohols again showed a significant downfield shift for both the 6 α-H (δ 2.46 *vs.* 2.16) and 4-H (δ 3.87 *vs.* 3.57) signals in the

Table. N.m.r. characteristics of dioxolanyl hydroperoxides



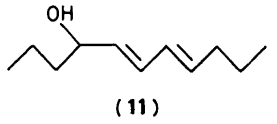
R = $(CH_2)_7CO_2Me$, R′ = $(CH_2)_3Me$
or R = $(CH_2)_4Me$, R′ = $(CH_2)_6CO_2Me$



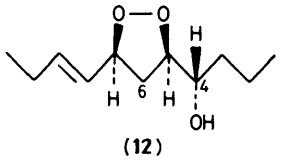


(9) (10)

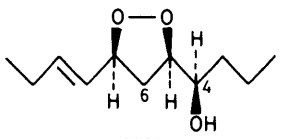
	erythro 9*RS*, 10*SR* or 12*RS*, 13*SR*	*threo* 9*RS*, 10*RS* or 12*RS*, 13*RS*		*erythro* 4*RS*, 5*SR*	*threo* 4*RS*, 5*RS*
Hα	2.43	2.16	6α-H	2.44	2.17
*CH*OOH	4.12	3.95	4-H	4.24	3.93
dioxolane CH_2	41.2	43.25	C-6	41.0	43.3
Ref.	34	34		This work	



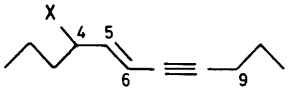
(11)



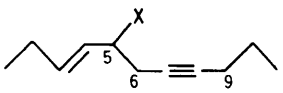
(12)



(13)



(14) X = OOH
(16) X = OH

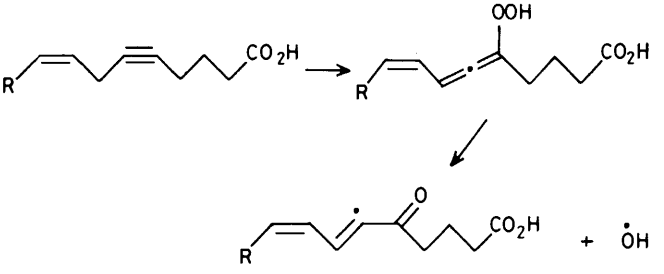


(15) X = OOH
(17) X = OH

isomer (**12**), derived from the *erythro*-compound (**9**). Consistently, the C-6 signal is more shielded in the *erythro*-isomer (**12**) than in (**13**) (40.5 *vs.* 42.9 p.p.m., *cf.* Table 1).

U.v. irradiation of the conjugated dienyl hydroperoxide (**8**) was attempted, to see whether, as a result of peroxide homolysis,[37] products derived from radical cyclisation could be isolated. Photochemical *cis-trans* dienyl isomerisation is likely, and the (*Z*,*E*)-isomer of (**8**) could undergo *exo*-cyclisation[38] onto the remote double bond. Alternatively, a pathway involving intramolecular hydrogen abstraction from C-1, followed by *exo* free radical cyclisation onto C-5 would generate a cyclopentylmethyl radical. This latter route of carbon radical cyclisation onto a diene system would represent an open-chain analogue of the free radical cyclisation which mimics prostaglandin endoperoxide biosynthesis.[39] In the event, no discrete products were evident by t.l.c. on photolysis of (**8**) in the absence or presence of oxygen.

Photo-oxidation of the Enyne (**3**).—Leukotriene biosynthesis involves the initial conversion of arachidonic acid to a 5-hydroperoxytetraenoic acid, by a 5-lipoxygenase enzyme. In view of the irreversible inhibition of 5-lipoxygenase by 5,6-acetylenic versions of arachidonic acid, a study of oxygenation in such systems is interesting. Additionally, there do not appear to be any reports of the photo-oxidation of a 1,4-enyne. Alkynes in general have proved unreactive towards singlet oxygen, with the exception of the occasional report of dioxete formation.[40] It has been argued that the 5-lipoxygenase inactivation of arachidonic acid is caused by the formation and decomposition of a vinylic hydroperoxide (Scheme 5), generating radicals which cause lethal damage to the enzyme.[41] Such vinylic hydroperoxides are unknown species, but photo-oxidation with hydrogen abstraction at the highly activated allylic/prop-2-ynyl position presents one potential method for their generation.



R = $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2$

Scheme 5.

Low-temperature dye-sensitised photo-oxidation of the enyne (**3**) proceeded more slowly than for the diene (**4**), leading to two products (ratio *ca.* 2:1) which were individually isolated by flash column chromatography in a combined yield of 54%. The major product was assigned the structure of the conjugated enynyl hydroperoxide (**14**), mainly on the basis of ^1H and ^{13}C n.m.r. spectra. The presence of a *trans* double bond was evident from the 16 Hz coupling between 5-H and 6-H, whilst 6-H also showed a characteristic 2 Hz coupling to 9-H, across the acetylenic bond. ^{13}C Spectra revealed a hydroperoxy-bearing carbon adjacent to a *trans*-double bond (86.3 p.p.m.),[31] two alkenyl (114.8, 140.6 p.p.m.), and two alkynyl (78.7, 92.0 p.p.m.) carbons. The hydroperoxide (**14**) was reasonably stable over a period of weeks when stored in solution at 0 °C or lower temperatures, but reduction of (**14**) by triphenylphosphine gave the more stable corresponding undecenynol (**16**) in 79% yield after chromatography; the hydroxy-bearing carbon of (**16**) was easily distinguishable by ^{13}C n.m.r., resonating at 71.7 p.p.m.

The minor oxidation product was assigned the structure of the non-conjugated enynyl hydroperoxide (**15**), formed by $^1O_2$ attack on the enyne (**3**) in a process analogous to the formation of (**5a**) from the diene (**4**). The ^1H n.m.r. spectrum of (**15**) showed the expected *trans*-vicinal coupling (J 15.5 Hz) of 3-H and 4-H, the *E*-geometry being reinforced by the ^{13}C shift of C-2 at 25.5 p.p.m. ^{13}C Spectra again showed a hydroperoxy-bearing carbon (84.9 p.p.m., slightly shifted from its characteristic position found in (**14**) by the presence of the adjacent acetylenic group), two alkenyl (125.8, 139.3 p.p.m.) and two alkynyl (75.8, 82.6 p.p.m.) carbons. Reduction of the hydroperoxide (**15**) by triphenylphosphine gave an alcohol (**17**), isolated in 46% yield. The ^{13}C n.m.r. spectrum of (**17**) showed a close resemblance in shifts to that of dienol (**6**), with the exception of the shifts of the C-6 to C-9 atoms, where the alkynyl link has replaced the alkenyl unit of (**6**). The mass spectral fragmentation pattern of (**17**) also supported oxygenation at C-5 of the alkenyne chain.

The product distribution of hydroperoxides from photo-oxidation of the diene (**4**) shows that the reactivity (per position) of bis(allylic) hydrogens to allylic hydrogens is 3:1 towards $^1O_2$ attack. The reaction of $^1O_2$ with the 'skipped' enyne (**3**) therefore shares the characteristics of attack on the diene (**4**): for (**3**), there is a preference (2:1) for abstraction of the doubly activated (allylic/prop-2-ynyl) hydrogens between the two multiple bonds, over that for allylic abstraction. Singlet oxygen attack on the enyne (**3**) shows no tendency for abstraction from the prop-2-ynyl position, in emphatic contrast with the result of free radical attack on straight chain alkynoic fatty acid esters.[7] When abstraction does occur at the allylic/prop-2-ynyl position of (**3**), the oxygen molecule becomes bonded selectively at the double bond, rather than the triple bond. No products resembling vinylic hydroperoxides, or their decomposition products, were isolated. Qualitatively, singlet oxygen attack on the enyne (**3**) was obviously considerably slower than that on diene (**4**), and this point merited a further experiment, as described later.

Free Radical Cyclisation of Hydroperoxides (**14**) *and* (**15**).—By analogy with the free radical cyclisation of the hydroperoxides (**5**), it is feasible that autoxidation of the hydroperoxide (**15**) under similar conditions might lead to dioxolane ring formation. A related cyclisation is known for intramolecular addition of 4-alkynyloxyl radicals, to yield alkylidenedioxolanes, although it is slower than for alkenyloxyl cyclisation.[42] The corresponding intramolecular cyclisation of carbon-centred radicals onto adjacent triple bonds is facile, and has recently begun to find application as a useful synthetic route to five-membered rings.[43] However, our repeated attempts to cyclise the mixture of hydroperoxides (**14**) and (**15**) under oxygen gas, using di-t-butyl peroxyoxalate as radical initiator,[30] gave no discrete products except for polymeric material. We conclude that any intramolecular attack of the peroxyl radical must be slow in comparison with intermolecular additions.

Attempted Photo-oxidation of the Diyne (**2**).—The 'skipped' diyne (**2**), although reasonably stable under an atmosphere of nitrogen, began to show evidence of polymerisation when exposed to oxygen at room temperature, even in the dark. Similar instability of methyl henicosa-8,11-diynoate in the presence of air was recently noted.[7] Control experiments showed, however, that this removal of monomer (**2**) was negligible over a period of hours when solutions were maintained at −75 °C. An attempted photosensitised oxidation of the diyne (**2**) in dichloromethane solution at −75 °C gave no evidence either by g.l.c. or by t.l.c. for the formation of oxidation products, and the starting material was recovered after irradiation. The slowness of this photo-oxidation showed that there was little (if any) reactivity of $^1O_2$ at the prop-2-ynyl or bis(prop-2-ynyl) positions of the diyne, although radical attack (initiated by triplet oxygen) appeared capable of causing destruction of (**2**).

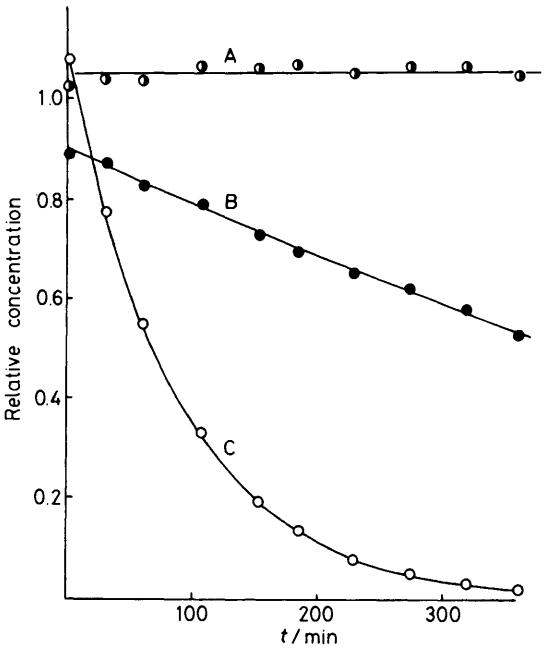


Figure. Relative concentrations of the diyne (**2**) (A), the enyne (**3**) (B), and the diene (**4**) (C) against time of photosensitized oxidation in dichloromethane solution at −75 °C

Relative Rates of Photo-oxidation.—The relative rates of photosensitised oxidation of the diene (**4**), the enyne (**3**), and the diyne (**2**) were measured in a simultaneous competition experiment. G.l.c. analysis at intervals on a continuously photo-oxidised solution, using an internal standard, allowed the concentrations of the three substrates to be measured; the rates of disappearance were taken to represent their reactivities with $^1O_2$.

The figure shows plots of the relative concentration of reactants against time of photo-oxidation. For the diene (**4**), the rate of disappearance followed first-order kinetics over several half-lives. The enyne (**3**) also showed reasonable first-order decay kinetics. The diyne (**2**) did not appear to react, within experimental error, and an upper limit for its rate constant of reaction was determined. The relative rates of reaction with $^1O_2$ were approximately 110:15:$\leqslant$1 for (**4**), (**3**), and (**2**), respectively.

From laser photolysis studies of the reactivity of t-butoxyl radicals with fatty acids, Small and his co-workers[6] have measured relative rates of hydrogen abstraction of 0.14:1.0:5.2 for secondary:allylic:bis(allylic) hydrogens, whilst Gunstone and his co-workers,[7] using e.s.r. spectroscopy, have established relative reactivities in a series of unsaturated fatty acid esters as 0.03:0.05:1:3.2 for secondary:prop-2-ynyl:allylic:bis(allylic) hydrogens, respectively. Our product distributions from photo-oxidation show a different order of reactivity towards hydrogen abstraction by $^1O_2$, which can be linked to the more specific geometric requirements of the ene reaction in comparison with radical abstraction. Within a polyunsaturated molecule, the relative reactivities are 0:0:1:2:3 for secondary:prop-2-ynyl:allylic:allylic/prop-2-ynyl:bis(allylic) hydrogens, respectively. However, unlike t-butoxyl attack, the wide-ranging reactivity of the substrates towards $^1O_2$ makes it obvious that general values for attack at a particular position cannot be established. If the reactivity of the terminal allylic hydrogens in diene (**4**) is taken as unity, then the relative reactivity of the

similarly activated hydrogens in enyne (**3**) is found to be only 0.22.

Singlet oxygen attacks alkenes at rates which are dependent on the ionisation potential of the latter.[12] Although the ionisation energies of compounds (**2**)—(**4**) have not been measured, alkynes in general have higher ionisation potentials than the corresponding alkenes. The observed range of reactivity of these 'skipped' systems makes it likely that the two electronic systems are interdependent, and the rates of reaction with $^1O_2$ are in the expected order [(**2**) < (**3**) < (**4**)], increasing as the ionisation energy of the unsaturated system decreases.

Experimental

I.r. spectra were recorded on a Perkin-Elmer model 297 spectrophotometer as liquid films between NaCl plates. N.m.r. spectra were measured on JEOL FX-60 or JEOL FX-200 spectrometers. Mass spectra (e.i. or f.a.b.) were recorded by PCMU, Harwell, with a VG Micromass ZAB 1F spectrometer. G.l.c. analyses were carried out on a Varian Aerograph 2740 instrument using a 3% silicone oil (SE 30) or a 10% Carbowax 20M (CWX) column under isothermal conditions, generally at a pressure of 33 p.s.i. T.l.c. was performed on Merck pre-coated glass plates (silica gel 60 F-254), components being located by inspection under u.v. light or by iodine development. Flash chromatography was conducted according to the method described by Still *et al.*[44] Conventional column chromatography was carried out using Merck silica gel 60 (70—230 mesh). AnalaR grade solvents were used for all reactions. Anhydrous tetrahydrofuran (THF) was used as purchased. Reactions that required anhydrous conditions were conducted in flame-dried glassware under nitrogen.

Hex-2-yn-1-ol[45].—The method was adapted from that described by Brandsma.[46] A solution of ethylmagnesium bromide in THF (130 ml) was prepared from magnesium turnings (4.28 g, 176 mmol) and freshly distilled bromoethane (19.18 g, 176 mmol) under anhydrous conditions. Pent-1-yne (10.0 g, 147 mmol) in THF (50 ml) was added dropwise to this solution over 20 min, kept at 0—5 °C. After a further 15 min, the temperature was allowed to rise to 20 °C followed by warming for 1 h in a water-bath at 50—55 °C. To the suspension was added, with ice-bath cooling, THF (45 ml) and subsequently paraformaldehyde (5.28 g, 176 mmol) in portions over 20 min. The mixture was allowed to warm to room temperature, followed by refluxing for 2.5 h. After cooling, ice-saturated aqueous NH_4Cl (130 ml) was added, and the mixture vigorously shaken. The upper layer was separated, the resulting emulsion filtered through a sintered funnel (no. 3), and the aqueous layer extracted with ether (4 × 100 ml). The combined ethereal solutions were dried ($MgSO_4$). After rotary evaporation, the residue of hex-2-yn-1-ol (10.76 g, 75%) was used without further purification, R_t 2.50 min (SE 30, 75 °C); δ_H (60 MHz, $CDCl_3$) 1.00 (3 H, t, *J* 7 Hz, 6-H), 1.52 (2 H, sextet, *J* 7 Hz, 5-H), 2.20 (2 H, m, 4-H), 3.80 (1 H, s, OH), and 4.30 (2 H, m, 1-H).

1-Bromohex-2-yne (**1**).[45,47]—To a mixture of hex-2-yn-1-ol (11.0 g, 112 mmol) in dry ether (50 ml) and pyridine (0.62 ml) at −30 °C was added phosphorus tribromide (10.58 g, 39.1 mmol), over a period of 40 min. The temperature was maintained at −30 °C for 2 h, and subsequently allowed to rise to 20 °C over a period of 1 h. The mixture was finally heated at 40 °C for 30 min. After cooling, saturated brine (70 ml) was added with shaking. The upper layer was separated, and the aqueous layer extracted with ether (2 × 50 ml). The combined ethereal solutions were dried ($MgSO_4$), then rotary evaporated to give a residue (20.0 g) which was distilled to yield (**1**) (13.21 g, 73%), b.p. 65—69 °C/18 mmHg, R_t 3.73 min (SE 30, 75 °C); $\nu_{max.}$ 2 200 and 1 200 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 1.00 (3 H, t, *J* 7 Hz, 6-H), 1.55 (2 H, sextet, *J* 7 Hz, 5-H), 2.24 (2 H, m, 4-H), and 3.95 (2 H, t, *J* 2 Hz, 1-H).

Undeca-4,7-diyne (**2**).—A solution of ethylmagnesium bromide in THF (100 ml) was prepared from magnesium turnings (3.3 g, 136 mmol) and freshly distilled bromoethane (14.8 g, 136 mmol) under anhydrous conditions. Pent-1-yne (8.3 g, 122 mmol) in THF (20 ml) was added dropwise to this solution over 20 min, kept at 0—5 °C. After a further 15 min, the temperature was allowed to rise to 20 °C, followed by warming for 1 h at 50—55 °C. After cooling to 20 °C, copper(I) chloride (600 mg)[48,49] and mercury(II) chloride (300 mg) were added and the mixture heated again at 50—55 °C for 15 min. After cooling to 20 °C, 1-bromohex-2-yne (**1**) (13.10 g, 81.3 mmol) was added dropwise over 20 min, which produced a greenish suspension. The mixture was warmed for 75 min in a water-bath at 60 °C. G.l.c. analysis indicated no starting material (**1**) and only one product, R_t 18.55 min (SE 30, 75 °C). After cooling to 20 °C, a solution of NH_4Cl (15 g) and sodium cyanide (2 g) in water (100 ml) was added. After vigorous shaking the upper layer was separated and the aqueous layer was extracted with ether (3 × 75 ml). The combined extracts were washed with water (100 ml) and dried ($MgSO_4$). The residue remaining after rotary evaporation of the ether was distilled to give the diyne (**2**)[17] (10.18 g, 85%), b.p. 74—82 °C/5 mmHg; $\nu_{max.}$ 3 032, 3 002, 2 937, 1 432, and 1 336 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.98 (6 H, t, *J* 7 Hz, 1-H, 11-H), 1.53 (4 H, sextet, *J* 7 Hz, 2-H, 10-H), 2.14 (4 H, tt, *J* 2 and 7 Hz, 3-H, 9-H), and 3.13 (2 H, quintet, *J* 2 Hz, 6-H); δ_C (15 MHz, $CDCl_3$) 9.8 (C-6), 13.5 (C-1, C-11), 20.8 (C-3, C-9), 22.3 (C-2, C-10), 74.9 (C-5, C-7), and 80.5 (C-4, C-8) p.p.m.

Hydrogenation of the Diyne (**2**).—Undeca-4,7-diyne (**2**) (4.0 g, 27 mmol) was hydrogenated in a Parr apparatus with Lindlar catalyst (5 × 800 mg, 1 × 400 mg) in methanol (150 ml). The initial pressure was 28 p.s.i., and the catalyst was added in separate portions each time the pressure reading became constant. The reaction was monitored by g.l.c. (SE 30, 85 °C). When the hydrogen uptake had ceased, the catalyst was filtered off through Kieselguhr under nitrogen, and the solvent removed by rotary evaporation. Silica gel chromatography (70—230 mesh, 350 g) of the residue with pentane as eluant gave two products: (4*Z*)-*undec-4-en-7-yne* (**3**) (1.16 g), R_t 8.10 min (SE 30, 85 °C), R_F 0.47, pentane (Found: C, 87.6; H, 12.0. $C_{11}H_{18}$ requires C, 87.9; H, 12.05%); $\nu_{max.}$ 3 020, 2 960, 2 935, 2 873, and 1 658 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.91, 0.97 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.38 and 1.50 (4 H, each sextet, *J* 7 Hz, 2-H, 10-H), 2.00 (2 H, m, 3-H), 2.12 (2 H, tt, *J* 2 and 7 Hz, 9-H), 2.90 (2 H, m, 6-H), and 5.46 (2 H, m, 4-H, 5-H); δ_C (15 MHz, CCl_4) 13.4, 13.7 (C-1, C-11), 17.0 (C-6), 20.7 (C-9), 22.2, 22.4 (C-2, C-10), 29.0 (C-3), 78.4, 79.5 (C-7, C-8), and 125.7 and 130.4 (C-4, C-5) p.p.m.; *m/z* (e.i.) 149.1329 (M^+ − H, 22%).

(4*Z*,7*Z*)-*Undeca-4,7-diene* (**4**)[17] (0.94 g), R_t 5.70 min (SE 30, 85 °C), R_F 0.89, pentane; δ_H (200 MHz, $CDCl_3$) 0.93 (6 H, t, *J* 7 Hz, 1-H, 11-H), 1.39 (4 H, sextet, *J* 7 Hz, 2-H, 10-H), 2.04 (4 H, m, 3-H, 9-H), 2.79 (2 H, m, 6-H), and 5.37 (4 H, m, 4-H, 5-H, 7-H, 8-H); δ_C (15 MHz, $CDCl_3$) 13.9 (C-1, C-11), 22.9 (C-2, C-10), 25.8 (C-6), 29.4 (C-3, C-9), and 128.5 and 130.2 (C-4, C-5, C-7, C-8) p.p.m.

Photo-oxidations.—Oxygen for photo-oxidations was predried with a sulphuric acid/sodium hydroxide/silica gel drying train, and then bubbled through a Quickfit reactor tube fitted with an inlet and outlet. A Philips 'Argaphoto-B' 500 W lamp was used as the light source, and cooling was carried out by means of a solid CO_2–propan-2-ol bath in a clear vacuum jacket surrounding the reactor. Photo-oxidations were performed with the external cooling bath maintained at −30 °C or

below, using tetraphenylporphyrin (*ca.* 10 mg/100 ml solvent) as the photosensitiser.

Photo-oxidation of Compound (**4**).—A solution of (4*Z*,7*Z*)-undeca-4,7-diene (**4**) (900 mg, 5.9 mol) in dichloromethane (80 ml) was photo-oxidised for 4 h, monitoring the reaction by t.l.c. with diethyl ether–pentane (1:5) as eluant. The solution was rotary evaporated (15 °C) and the resulting oil was purified by flash chromatography (diethyl ether–pentane, 1:10) to give recovered (**4**) (152 mg) and an oil (**5**) (810 mg), R_F 0.46 (diethyl ether–pentane, 1:5), whose ^{1}H n.m.r. spectrum showed two singlets at δ 7.73 and 7.74 (OOH), a multiplet at δ 4.35 (1 H, C*H*OOH) and a characteristic dd at δ 6.59 (conjugated =CH), indicating a mixture of hydroperoxides (**5a**) and (**5b**) in the ratio 2:3. These isomers could not be separated by t.l.c.

Reduction of the Hydroperoxides (**5**).—The mixture (**5**) (254 mg) was dissolved in dichloromethane (30 ml) and kept at 0 °C. A slight excess of triphenylphosphine was added, monitoring the reaction by t.l.c. (diethyl ether–pentane, 1:6). The solution was rotary evaporated and purified by flash chromatography (diethyl ether–pentane, 1:6) to remove triphenylphosphine and its oxide. The resulting oil (200 mg, 86%) had R_F 0.30 (diethyl ether–pentane, 1:6). G.l.c. analysis (CWX, 165 °C) showed two compounds with R_t 9.8 and 14.9 min, which were separated by preparative g.l.c. at 180 °C to give the following.

(3*E*,7*Z*)-Undeca-3,7-dien-5-ol (**6**)[17] (33 mg), R_t 9.8 min; $\nu_{max.}$ 3 360 and 965 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.92 (3 H, t, *J* 7 Hz, 11-H), 1.01 (3 H, t, *J* 7 Hz, 1-H), 1.38 (2 H, sextet, *J* 7 Hz, 10-H), 1.68 (1 H, br s, OH), 2.03 (4 H, q, *J* 7 Hz, 2-H, 9-H) split by $Eu(fod)_3$ (0.1 equiv.) into two quartets, 2.30 (2 H, m, 6-H), 4.09 (1 H, q, *J* 7 Hz, 5-H), 5.33—5.58 (3 H, m, 4-H, 7-H, 8-H), and 5.72 (1 H, dt, *J* 15 and 7 Hz, 3-H); δ_C (15 MHz, $CDCl_3$) 13.5, 13.8 (C-1, C-11), 22.8 (C-10), 25.3 (C-2), 29.6 (C-9), 35.5 (C-6), 72.6 (C-5), and 125.3, 131.7, 133.1, and 133.8 (C-3, C-4, C-7, C-8) p.p.m.

(5*E*,7*Z*)-Undeca-5,7-dien-4-ol (**7**)[17] (56 mg), R_t 14.9 min; $\nu_{max.}$ 3 350 and 950 cm^{-1}; δ_H(200 MHz, $CDCl_3$) 0.92 (6 H, t, *J* 7 Hz, 1-H, 11-H), 1.43 (6 H, m, 2-H, 3-H, 10-H), 1.74 (1 H, br s, OH), 2.15 (2 H, dq, *J* 1.5 and 7 Hz, 9-H), 4.16 (1 H, m, 4-H), 5.43 (1 H, dt, *J* 11 and 7 Hz, 8-H), 5.65 (1 H, dd, *J* 7 and 15 Hz, 5-H), 5.97 (1 H, t, *J* 11 Hz, 7-H), and 6.48 (1 H, dd, *J* 11 and 15 Hz, 6-H); δ_C (15 MHz, $CDCl_3$) 13.8, 14.1 (C-1, C-11), 18.7 (C-2), 22.9 (C-10), 29.9 (C-9), 39.6 (C-3), 72.8 (C-4), and 126.1, 128.3, 132.9, and 136.3 (C-5, C-6, C-7, C-8) p.p.m.

Free-radical Cyclisation of Hydroperoxides (**5**).—Oxygen was bubbled through tetrachloromethane (135 ml) for 30 min. The mixture of hydroperoxides (**5**) (503 mg, 2.73 mmol) was added to this solution, followed by di-t-butyl peroxyoxalate[30] (DBPO) (64 mg, 0.27 mmol). The mixture was stirred under an oxygen atmosphere for 11 h, and then rotary evaporated (15 °C). The resulting oil was separated by flash chromatography (diethyl ether–pentane, 1:7) giving three compounds.

(5E,7E)-4-*Hydroperoxyundeca*-5,7-*diene* (**8**) (163 mg, 0.89 mmol), R_F 0.46 (diethyl ether–pentane, 1:6); δ_H (200 MHz, $CDCl_3$) 0.93 (6 H, t, *J* 7 Hz, 1-H, 11-H), 1.40 (6 H, m, 2-H, 3-H, 10-H), 2.08 (2 H, m, 9-H), 4.34 (1 H, m, 4-H), 5.47 (1 H, dd, *J* 8 and 15 Hz, 5-H), 5.75 (1 H, dt, *J* 15 and 7 Hz, 8-H), 6.06 (1 H, dd, *J* 10 and 15 Hz, 7-H), 6.28 (1 H, dd, *J* 10 and 15 Hz, 6-H), and 8.76 (1 H, s, OOH); δ_C(15 MHz, $CDCl_3$) 13.7, 14.1 (C-1, C-11), 18.7 (C-2), 22.4 (C-10), 34.8 (C-3, C-9), 86.8 (C-4), and 129.3, 129.7, 135.5, and 136.8 (C-5, C-6, C-7, C-8) p.p.m.

(4RS,5SR,7RS)-(8E)-4-*Hydroperoxy*-5,7-*epidioxyundec*-8-*ene* (**9**) (89 mg, 0.48 mmol), R_F 0.26 (diethyl ether–pentane, 1:6); δ_H(200 MHz, $CDCl_3$) 0.99, 1.03 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.40 (4 H, m, 2-H, 3-H), 2.12 (2 H, m, 10-H), 2.44 (1 H, ddd, *J* 5, 8, and 12 Hz, 6α-H), 2.79 (1 H, ddd, *J* 7, 8, and 12 Hz, 6β-H), 4.24 (1 H, m, 4-H), 4.47 (1 H, ddd, *J* 3, 5, and 8 Hz, 5-H), 4.72 (1 H, q, *J* 7.5 Hz, 7-H), 5.46 (1 H, ddt, *J* 8, 15.5, and 1.5 Hz, 8-H), 5.96 (1 H, dt, *J* 15.5 and 6 Hz, 9-H), and 9.64 (1 H, s, OOH); δ_C (50 MHz, $CDCl_3$) 13.0, 14.0 (C-1, C-11), 19.0 (C-2), 25.4 (C-10), 31.6 (C-3), 41.0 (C-6), 83.3 (C-7), 83.8 (C-5), 85.8 (C-4), 123.1 (C-9), and 140.9 (C-8) p.p.m.

(4RS,5RS,7SR)-(8E)-4-*Hydroperoxy*-5,7-*epidioxyundec*-8-*ene* (**10**) (32 mg, 0.17 mmol), R_F 0.19 (diethyl ether–pentane, 1:6); δ_H (200 MHz, $CDCl_3$) 0.97, 1.04 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.50 (4 H, m, 2-H, 3-H), 2.10 (2 H, m, 10-H), 2.17 (1 H, m, 6α-H), 2.82 (1 H, ddd, *J* 7, 8, and 12 Hz, 6β-H), 3.93 (1 H, m, 4-H), 4.44 (1 H, ddd, *J* 6, 7, and 8 Hz, 5-H), 4.68 (1 H, q, *J* 7.5 Hz, 7-H), 5.40 (1 H, ddt, *J* 8, 15, and 1.5 Hz, 8-H), 5.93 (1 H, dt, *J* 15 and 6 Hz, 9-H), and 9.15 (1 H, s, OOH); δ_C(50 MHz, $CDCl_3$) 13.0, 14.0 (C-1, C-11), 18.9 (C-2), 25.4 (C-10), 30.8 (C-3), 43.3 (C-6), 82.8 (C-7), 83.9 (C-5), 85.6 (C-4), 123.2 (C-9), and 140.5 (C-8) p.p.m.

Reduction of the Hydroperoxide (**8**).—The conjugated hydroperoxide (**8**) (110 mg) was dissolved in dichloromethane (10 ml), cooled to 0 °C, and triphenylphosphine was added to the solution until there was a slight excess, as judged by t.l.c. The solution was rotary evaporated and purified by flash chromatography (diethyl ether–pentane, 1:6) giving (5*E*,7*E*)-undeca-5,7-dien-4-ol (**11**)[17] (55 mg, 55%) R_F 0.23 (diethyl ether–pentane, 1:6); $\nu_{max.}$ 3 335 and 990 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.90, 0.92 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.40 (6 H, m, 2-H, 3-H, 10-H), 1.62 (1 H, br s, OH), 2.05 (2 H, q, *J* 7 Hz, 9-H), 4.10 (1 H, q, *J* 7 Hz, 4-H), 5.54 (1 H, dd, *J* 7 and 14.5 Hz, 5-H), 5.66 (1 H, dt, *J* 15 and 7 Hz, 8-H), 5.96 (1 H, dd, *J* 10.5 and 15 Hz, 7-H), and 6.14 (1 H, dd, *J* 10.5 and 14.5 Hz, 6-H); δ_C (15 MHz, CCl_4) 13.7, 14.0 (C-1, C-11), 18.5 (C-2), 22.4 (C-10), 34.7 (C-9), 39.4 (C-3), 71.9 (C-4), and 130.3, 130.4, 133.8 and 134.6 (C-5, C-6, C-7, C-8) p.p.m.

Reduction of Dioxolanyl Hydroperoxides (**9**) *and* (**10**).—Compounds (**9**) and (**10**) were individually reduced with triphenylphosphine in dichloromethane as described above, and the products purified by flash chromatography (diethyl ether–pentane, 1:5). Reduction of (**9**) (89 mg) gave (4 RS, 5SR, 7RS)- (8E)-5,7-*epidioxyundec*-8-*en*-4-*ol* (**12**) as an oil (56 mg, 68%), R_F 0.19 (diethyl ether–pentane, 1:5) (Found: C, 65.9; H, 9.95. $C_{11}H_{20}O_3$ requires C, 65.95; H, 10.05%); $\nu_{max.}$ 3 435, 1 665, and 973 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.95, 1.02 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.39 (4 H, m, 2-H, 3-H), 2.08 (2 H, m, 10-H), 2.14 (1 H, br s, OH), 2.46 (1 H, ddd, *J* 6.5, 8, and 12 Hz, 6α-H), 2.65 (1 H, ddd, *J* 7, 7.5, and 12 Hz, 6β-H), 3.87 (1 H, m, 4-H), 4.24 (1 H, ddd, *J* 3.5, 6, and 8 Hz, 5-H), 4.66 (1 H, q, *J* 7 Hz, 7-H), 5.39 (1 H, ddt, *J* 7.5, 15.5, and 1.5 Hz, 8-H), and 5.90 (1 H, dt, *J* 15.5 and 6 Hz, 9-H); δ_C (15 MHz, CCl_4) 13.0, 14.0 (C-1, C-11), 18.6 (C-2), 25.2 (C-10), 35.1 (C-3), 40.5 (C-6), 71.2 (C-4), 82.2 (C-7), 83.9 (C-5), 124.7 (C-9), and 138.5 (C-8) p.p.m.

Reduction of compound (**10**) (32 mg) gave (4RS,5RS,7SR)-(8E)-5,7-*epidioxyundec*-8-*en*-4-*ol* (**13**) as an oil (24 mg, 81%), R_F 0.18 (diethyl ether–pentane, 1:5) (Found: C, 65.7; H, 9.9. $C_{11}H_{20}O_3$ requires C, 65.95; H, 10.05%); $\nu_{max.}$ 3 435, 1 665, and 973 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.95, 1.01 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.42 (4 H, m, 2-H, 3-H), 2.09 (2 H, m, 10-H), 2.16 (1 H, m, 6α-H), 2.40 (1 H, br s, OH), 2.78 (1 H, ddd, *J* 7, 8, and 12 Hz, 6β-H), 3.57 (1 H, br q, 4-H), 4.17 (1 H, ddd, *J* 5, 7, and 8 Hz, 5-H), 4.64 (1 H, q, *J* 7.5 Hz, 7-H), 5.35 (1 H, ddt, *J* 8, 15, and 1.5 Hz, 8-H), and 5.91 (1 H, dt, *J* 15 and 6 Hz, 9-H); δ_C (50 MHz, $CDCl_3$) 13.0, 14.0 (C-1, C-11), 18.8 (C-2), 25.4 (C-10), 35.0 (C-3), 42.9 (C-6), 72.6 (C-4), 82.9 (C-7), 84.7 (C-5), 123.3 (C-9), and 140.3 (C-8) p.p.m.

Photolysis of the Hydroperoxide (**8**).—A quartz tube containing the hydroperoxide (**8**) (120 mg) dissolved in acetonitrile (12 ml) was kept at *ca.* −20 °C by immersion in a

solid CO_2–propan-2-ol bath held within a clear quartz vacuum jacket. The tube was irradiated by an externally placed water-cooled 450 W medium-pressure mercury arc lamp. After 2 h irradiation, t.l.c. showed little change, apart from the production of baseline material.

In a second experiment on the same scale, oxygen was bubbled through the solution during photolysis, but no new products could be detected by t.l.c.

Photo-oxidation of Compound (**3**).—A solution of (4*Z*)-undec-4-en-7-yne (**3**) (0.788 g, 5.25 mmol) in dichloromethane (80 ml) was photo-oxidised for 3.5 h, monitoring the reaction by t.l.c. with diethyl ether–pentane (1:8) as eluant. After rotary evaporation of the photoproduct (15 °C), the resulting oil was purified by flash chromatography (diethyl ether–pentane, 1:11) to give recovered enyne (**3**) (397 mg), (5E)-4-*hydroperoxyundec*-5-*en*-7-*yne* (**14**) (93 mg), R_F 0.32 (diethyl ether–pentane, 1:8); δ_H (200 MHz, $CDCl_3$) 0.93, 1.01 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.3—1.7 (6 H, m, 2-H, 3-H, 10-H), 2.30 (2 H, dt, *J* 2 and 7 Hz, 9-H), 4.34 (1 H, br q, *J* 7 Hz, 4-H), 5.74 (1 H, dt, *J* 16 and 2 Hz, 6-H), 5.97 (1 H, dd, *J* 8 and 16 Hz, 5-H), and 8.17 (1 H, s, OOH); δ_C (15 MHz, $CDCl_3$) 13.6, 14.0 (C-1, C-11), 18.6 (C-2), 21.5 (C-9), 22.2 (C-10), 34.5 (C-3), 86.3 (C-4), 78.7, 92.0 (C-7, C-8), 114.8 (C-6), and 140.6 (C-5) p.p.m. and (3E)-5-*hydroperoxyundec*-3-*en*-7-*yne* (**15**) (50 mg), R_F 0.26 (diethyl ether–pentane, 1:8); δ_H (200 MHz, $CDCl_3$) 0.98, 1.04 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.52 (2 H, sextet, *J* 7 Hz, 10-H), 2.14 (4 H, m, 2-H, 9-H), 2.54 (2 H, m, 6-H), 4.44 (1 H, q, *J* 7 Hz, 5-H), 5.49 (1 H, ddt, *J* 7.5, 15.5, and 1.5 Hz, 4-H), 5.92 (1 H, dt, *J* 15.5 and 6.5 Hz, 3-H), and 7.92 (1 H, s, OOH); δ_C (15 MHz, $CDCl_3$) 13.2, 13.5 (C-1, C-11), 20.8 (C-9), 22.4 (C-10), 23.2 (C-6), 25.5 (C-2), 75.8, 82.6 (C-7, C-8), 84.9 (C-5), 125.8 (C-3) and 139.3 (C-4) p.p.m. A mixture of the hydroperoxides (**14**) and (**15**) (120 mg) was also collected.

Reduction of the Hydroperoxides (**14**) *and* (**15**).—The hydroperoxides (**14**) and (**15**) were individually reduced by using a slight excess of triphenylphosphine in dichloromethane as solvent at 0 °C, to give the corresponding alcohols after flash chromatography (diethyl ether–pentane, 1:5).

Reduction of (**14**) (90 mg) yielded (5E)-*undec*-5-*en*-7-*yn*-4-*ol* (**16**) (65 mg, 79%), R_F 0.19 (diethyl ether–pentane, 1:6) (Found: C, 79.2; H, 10.8. $C_{11}H_{18}O$ requires C, 79.45; H, 10.9%); $\nu_{max.}$ 3 340, 2 217, 1 630, and 962 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.93, 1.00 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.3—1.65 (6 H, m, 2-H, 3-H, 10-H), 1.89 (1 H, s, OH), 2.29 (2 H, dt, *J* 2 and 7 Hz, 9-H), 4.13 (1 H, br q, *J ca.* 6.5 Hz, 4-H), 5.67 (1 H, dq, *J* 16 and 2 Hz, 6-H), and 6.05 (1 H, dd, *J* 6.5 and 16 Hz, 5-H); δ_C (15 MHz, CCl_4) 13.5, 14.0 (C-1, C-11), 18.4 (C-2), 21.3 (C-9), 22.1 (C-10), 39.1 (C-3), 71.7 (C-4), 79.2, 90.2 (C-7, C-8), 110.3 (C-6), and 144.5 (C-5) p.p.m.; *m/z* (e.i.) 137.0961 ($M^+ - C_2H_5$, 14.5%), 123.0803 ($M^+ - C_3H_7$, 9.5%), 121.0654 ($C_8H_9O^+$, 100%), and 93.0707 ($C_7H_9^+$, 11.5%).

Reduction of (**15**) (50 mg) yielded (3E)-*undec*-3-*en*-7-*yn*-5-*ol* (**17**) (21 mg, 46%), R_F 0.26 (diethyl ether–pentane, 1:6) (Found: C, 79.3; H, 10.9. $C_{11}H_{18}O$ requires C, 79.45; H, 10.9%); $\nu_{max.}$ 3 390, 1 660, and 972 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 0.96, 0.99 (6 H, each t, *J* 7 Hz, 1-H, 11-H), 1.22 (1 H, br s, OH), 1.50 (2 H, sextet, *J* 7 Hz, 10-H), 2.03 (2 H, m, 2-H), 2.13 (2 H, tt, *J* 2.5 and 7 Hz, 9-H), 2.38 (2 H, m, 6-H), 4.14 (1 H, br m, 5-H), 5.47 (1 H, ddt, *J* 6.5, 15.5, and 1.5 Hz, 4-H), and 5.73 (1 H, dt, *J* 15.5 and 6.5 Hz, 3-H); δ_C (15 MHz, CCl_4) 13.4 (C-1, C-11), 20.7 (C-9), 22.3 (C-10), 25.1 (C-2), 28.2 (C-6), 70.6 (C-5), 76.5, 82.3 (C-7, C-8), 131.0 and 133.0 (C-3, C-4) p.p.m.; *m/z* (e.i.) 137.0970 ($M^+ - C_2H_5$, 5%), 85.0652 ($C_5H_9O^+$, 100%), and 67 ($C_5H_7^+$, 17%).

Attempted Free-radical Cyclisation of the Hydroperoxides (**14**) *and* (**15**).—Oxygen was bubbled through tetrachloromethane (34 ml) for 30 min. The mixture of hydroperoxides (**14**) and (**15**) (120 mg, 0.66 mmol) was added to this solution, followed by di-t-butyl peroxyoxalate [30] (16 mg, 0.066 mmol). The mixture was stirred under an oxygen atmosphere for a total of 70 h, but no distinct products could be detected by t.l.c. during this time, apart from baseline material.

Attempted Photo-oxidation of (**2**).—A solution of undeca-4,7-diyne (**2**) (1.0 g, 6.7 mmol) in dichloromethane (70 ml) was photo-oxidised for 4.75 h. The reaction was monitored by t.l.c. (diethyl ether–pentane, 1:3) and g.l.c. (SE 30, 85 °C), but no reaction products were detected and the diyne (**2**) was recovered unchanged.

Relative Rates of Photo-oxidation of the Diyne (**2**), *Enyne* (**3**), *and Diene* (**4**).—To a mixture of compounds (**2**), (**3**), and (**4**) (*ca.* 0.5 g) in dichloromethane (70 ml) was added decane (200 µl) as an internal standard. The solution was analysed in triplicate by g.l.c. (SE 30, 85 °C): R_t 3.2 min (decane, 25.2%), 5.7 min [diene (**4**), 27.4%], 7.9 min [enyne (**3**), 22.6%], and 11.6 min [diyne (**2**), 24.8%]. Photo-oxidation in the normal manner was then carried out for a total of 6 h, taking samples for analysis at intervals in order to determine the relative concentrations of reactants. Hydroperoxides were not detected under these g.l.c. conditions. First-order kinetics for the disappearance of (**4**) were followed over several half-lives. The rate constants for the reactions of diene (**4**) (0.0111 min^{-1}), enyne (**3**) (0.00144 min^{-1}), and diyne (**2**) ($\leqslant$0.0001 min^{-1}) in this experiment were calculated.

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