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5-ENDO RING CLOSURES OF ALLYLIC HYDROPEROXIDES: USEFUL ROUTES TO 1,2-DIOXOLANES INVOLVING STRONGLY STEREOSELECTIVE FREE RADICAL AND POLAR REACTIONS

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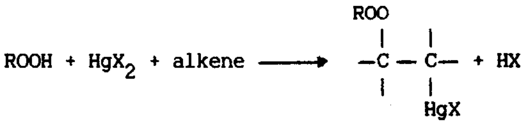
Abstract: Intramolecular cyclisation of simple allylic hydroperoxides to give substituted 1,2-dioxolanes using electrophilic reagents has been investigated. Closure using mercury(II) acetate and electrophilic halogen reagents (NBS, Br_2 and Bu^tOCl) occurs by Markovnikov-directed and conformationally strict stereospecificity. Subsequent free- radical reaction of the mercurated dioxolanes involved specific reaction involving reaction from the sterically unprotected face of the intermediate dioxolanyl radical.

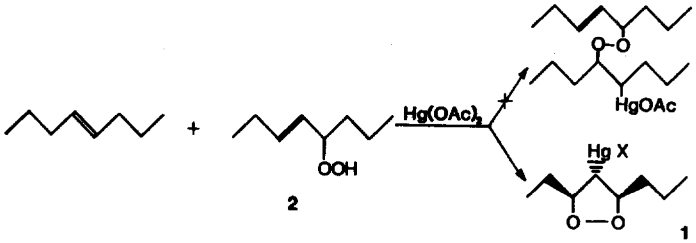
In the course of recent studies relating to the γ-scission of β-peroxyalkyl radicals[1], we were keen to prepare some peroxymercurials which contained allylically-substituted peroxy substituents (Equation 1).



$$ROOH + HgX_2 + alkene \longrightarrow -\overset{\overset{ROO}{|}}{\underset{|}{C}}-\overset{|}{\underset{\underset{HgX}{|}}{C}}- + HX \qquad (1)$$

R = allyl or substituted allyl.

Mindful of a publication by Adam and Sakanishi[2] in which an allylic hydroperoxide, alone, underwent eventual C-C bond cleavage when treated with a strongly electrophillic mercury(II) reagent, we decided to attempt our desired reaction under conditions of kinetic control[3], using a weakly electrophilic reagent (mercury(II) acetate) aware that such a procedure might result in competitive acetoxymercuration[4]. Thus we combined, in dichloromethane, a mixture of *trans*-4-octene, mercury(II) acetate and *trans*-5-octen-4-yl hydroperoxide. At the end of the reaction, spectroscopic analysis showed, however, that the product peroxide was not an unsaturated peroxymercurial, but was the 4-mercurated-1,2-dioxolane 1 (X=OAc: Equation 2)

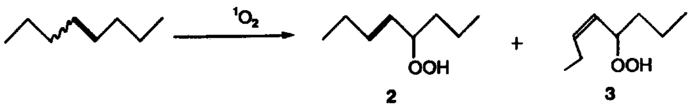


(2)

Inspection of the literature revealed two related pieces of work by Porter, Zuraw and Sullivan[5] and Bascetta and Gunstone[6] but, surprisingly, little advantage has otherwise been taken of this facile type of reaction[7]. We therefore decided to examine in a little more depth this useful reaction.

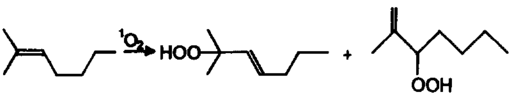
Results and Discussion

The requisite allylic hydroperoxides used in this study were prepared by preparative-scale singlet oxygenations of alkenes. In parallel with some analytical-scale reactions[8] of the isomeric 3-hexenes, we find that *trans*-4-octene provides a 4:1 mixture of *cis*- and *trans*-5-octen-4-yl hydroperoxides, 2 and 3, whilst the corresponding, faster, reaction of the *cis*-alkene gave the *trans* hydroperoxide contaminated with only a trace ($\leq$ 2%) of the *cis*-isomer (Equation 3).



(3)

To provide a further set of substrates, 2-methyl-2-heptene, upon ene-oxygenation, gave an easily isolated mixture of positionally isomeric allylic hydroperoxides 4 and 5 in a ratio broadly characteristic of data reported elsewhere for singlet oxygenations of other 1,1-dimethyl-2-alkylethenes[9] (Equation 4).



4 (46%) **5 (54%)**

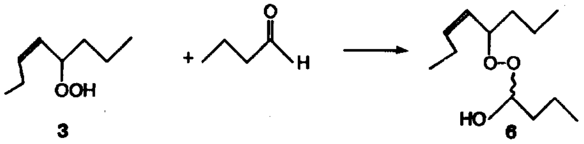
(4)

None of these hydroperoxide mixtures could be separated chromatographically on a preparatively useful scale, but each mixture could be obtained in useful amounts by short-path (Kugelröhr) distillation in 70-80% isolated yield.

98+%-*trans*-hydroperoxide, 2, when treated alone with one equivalent of mercury(II) acetate in dichloromethane cleanly provided a sample of the *trans,trans*-3-mercurated-1,2-dioxolane 1 (X=OAc) which proved to be somewhat unstable and was most satisfactorily characterised as the organomercury(II) bromide (1:X=Br) after treatment of the crude reaction mixture with aqueous sodium bromide.

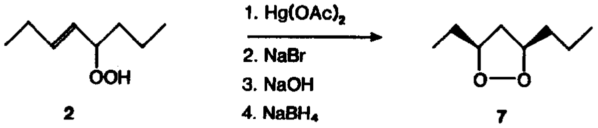
The assigned stereochemistry is not initially obvious from inspection of the spectroscopic properties of these materials but relies in part on the properties of the demercurated materials, which indicates a *cis* relationship between the alkyl groups. We assume a characteristic *trans* relationship of the ethyl and mercuri-substituents in view of the usual anti-addition seen in oxy-mercurations[10], but the *trans* relationship of the propyl and mercuri-substituents must arise from a strongly biased conformational effect in the ring closure.

The balance of conformational effects appears important, since we find that the 4:1 mixture of hydroperoxide isomers 2 and 3 only provides the *trans,trans*-3-mercurated-1,2-dioxolane 1. This reaction appeared to be a route to the isolation of a pure sample of the *cis*- hydroperoxide 3 and indeed, attempted separation of this unreacted isomer (flash chromatography, after anion exchange) did result in recovery of the *cis* isomer, but it was, however, contaminated by what appeared to be two hemiperacetals 6 formed by reaction of this isomer with butanal (Equation 5) a Hock-cleavage product of the starting hydroperoxides (vide infra)[11].



(5)

Hydridodemercuration of 1 (X=Br) in what appears to be the most generally successful manner (cold base pre-treatment, followed by addition to pre-cooled alkaline sodium borohydride)[12] provided a crude product which contained only *cis*-3-ethyl-5-n-propyl-1,2- dioxolane, 7 (Equation 6) as the allylic hydroperoxide-derived material. This compound could be isolated by flash chromatography in 82% yield (based on starting hydroperoxide: duplicate, 84%, 1-2mmol scale) and could be further purified by Kugelröhr distillation to provide a water-white fragrant liquid.

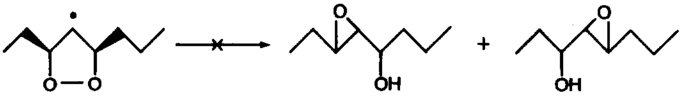


(6)

Spectroscopic evidence for the *cis*-dialkyl configuration shown in 7 (and by inference that for 1) rests upon the observed 1-H NMR chemical shifts (δ1.810 and 2.769, J_{gem}=11.8Hz) for the magnetically non-equivalent protons attached to C4. Bloodworth and Khan[13] have reported that the chemical shifts of the two non-equivalent C4-attached protons in *cis*-3,5-dimethyl-1,2-dioxolane are δ1.71 and 2.77 (showing a geminal coupling of 11.5Hz), whilst for the *trans*-isomer a single resonance at δ2.19 was seen (it is interesting to note that this chemical shift is close to the average value for those of the $^4CH_2$ pair in the *cis* isomer). The NMR data for 7 accords rather closely with that of the *cis*-dimethyl homologue and hence we assign to it the *cis*-dialkyl configuration.

It is noteworthy that we only obtain a single product in this two step procedure. We have discussed the strongly selective initial closure, above, but we note that no reverse deoxymercuration occurred in the second step, a result which contrasts, with those reported in the reactions described by Porter and co-workers[5] (perhaps a result of the practical detail of the hydridodemercuration method used here): we note that, had this occurred, we would have likely detected the two allylic alcohols seen when the demercuration step is conducted under less propitious circumstances.

More interestingly, however, we do not see any products which might have resulted from the γ-scission of the intermediate radical 8 (Equation 7).



8

(7)

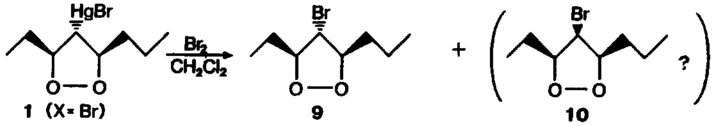
Metal hydride reductions of organomercury(II) salts are, quite reliably, mediated by the production of (fully) free radicals. β-peroxyalkyl radicals are known[14] to be susceptible to γ-scission reactions in which epoxides and alkoxyl radicals are generated: the latter are usually isolated, after hydrogen-atom capture, as alcohols. This scission reaction is known[15] to be accelerated by alkyl substitution at the α- and β-carbons (as in 8). However, it is also known to have a strong stereoelectronic requirement: Porter and co-workers[16] have very elegantly demonstrated that, for fast γ-scission to occur, the singly-occupied carbon $2p_z$ orbital must be aligned in an anti-coplanar fashion with the peroxide bond, perhaps to permit good in-phase $2p_z/\sigma^*$ overlap. Radical 8 (and its congeners) perfectly violates this anti requirement and accordingly we see little cleavage of the radical prior to hydrogen-atom capture. These findings parallel those indicated by Bloodworth and Khan[13] who pointed out that, in the product from the tri-*n*-butyltin hydride-mediated reduction of a mixture of 4-brominated-1,2-dioxolanes, they too were unable to detect any endocyclic radical-derived scission products.

In the publication of Bascetta and Gunstone[6], the 1-H NMR spectrum of the product derived from the sodium borodeuteride reduction of a pair of 4-mercurated-1,2-dioxolanes was reproduced. Upon inspection of that data we suspected that their deuteriodemercuration reaction was showing some facial selectivity. We accordingly applied this reduction method to our mercurated dioxolane 1 (X=Br). Scrutiny of the 13-C NMR spectrum of the product showed that deuterium incorporation had occurred at only one site (that showing a carbon resonance at δ45.59) and we therefore assign this resonance to 13-C nuclei positioned at C4. The 400 MHz 1-H NMR spectrum of the same sample showed that the lower field absorption (δ2.75) of the $^4CH_2$ pair seen in the spectrum of the perprotio compound was virtually absent. At high gain the small residual signal could be analysed as a superposition of a doublet of triplets (as in perprotio 7) and a broadened triplet (assigned as the α-^{1}H, β-^{2}H isomer: vide infra).

This result indicated that the delivery of deuterium atoms to radical 8 had occurred almost exclusively (93%) from one face and which, on steric grounds, we assume to be the lower (β) face of radical 8 in a reaction where hardly any kinetic isotope effect was operational (the sodium borodeuteride was 98%-d, and calculation indicated a total of 96%-d atom capture).

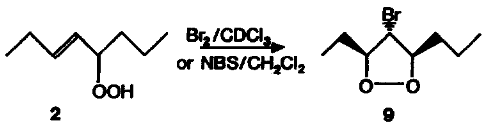
Facial selectivity in the reactions of cycloalkyl radicals has been reviewed recently[18] and our results show that in this case the hydrogen atom delivering species is sensitive to steric effects but that it reacts in a strongly exothermic manner. The commonly held view[19] is that this species is an organomercury hydride[20] (deuteride) but one of us, with another, has brought forward evidence showing that, in certain instances at least[12], this view can be held open to doubt.

As an alternative demercuration procedure for peroxymercurials, bromodemercuration may be employed. In polar media (such as sodium bromide-saturated methanol) this reaction is mediated via an S_E2 mechanism[21], whilst in non-polar solvents, free radicals are involved[3,22]. Accordingly, when a dichloromethane solution of peroxymercurial 1 (X=Br) was treated with elemental bromine, a rapid reaction ensued, and after work-up an almost quantitative yield of bromodioxolanes resulted. The 1-H NMR spectrum of the crude product, and subsequent chromatographic separation showed that the major product was the same bromodioxolane as that obtained by reaction of the starting allylic hydroperoxide with N-bromosuccinimide or with elemental bromine (vide infra). Considering the *trans,trans* configuration of the starting, mercurated dioxolane 1 (X=Br) along with the facial selectivity of the intermediate radical (8: vide supra) we assign this major product as the *trans,trans*-4-bromo- dioxolane 9. A minor isomer, tentatively assigned as the *cis,cis*-isomer 10, was also obtained during the chromatographic separation (Equation 8). We note that the major bromodioxolane is that expected from both an S_E2 displacement and also from a facially selective radical reaction.



(8)

The same bromodioxolane isomer 9 is more directly available through reaction of the *trans*-allylic hydroperoxide 2 with either N-bromosuccinimide (NBS) in dichloromethane or (cf Reference 6) with elemental bromine in deuteriochloroform (Equation 9).

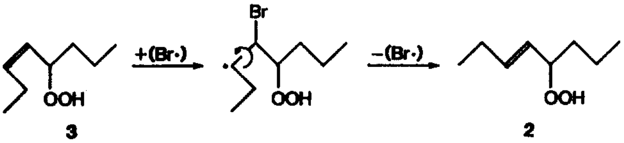


(9)

The latter reaction probably involves a polar, bromonium ion-mediated reaction, which in stereochemical outcome parallels the intramolecular peroxymercuration. The reaction with NBS, however, seems mechanistically more complex, and although we have not come to a firm conclusion as to this complexity, the following observations were made.

The reaction products from the NBS reaction with 98+%-*trans*-allylic hydroperoxide 2 and that from the 4:1 mixtures of 2 and 3 gave crude reaction products that were, spectroscopically, virtually identical. These crude products were mixtures of bromodioxolane 9 contaminated with about 16mol% of *trans*-5-octen-4-one, 12.

The nearly identical compositions of the two NBS reaction products might be explained by reversible bromine atom addition to the *cis*- allylic hydroperoxide 3 (Equation 10): such reactions have been noted in NBS-mediated allylic brominations[23] but the mechanistic origin of the enone remains mysterious.

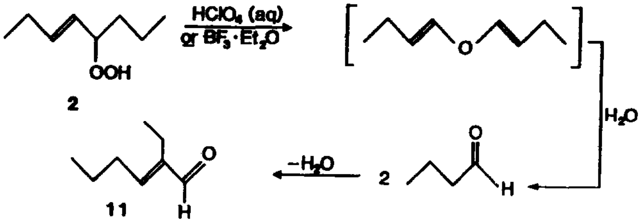


(10)

In order to probe this question we carried out some preliminary investigations. BHT was without effect on the relative proportions of the *trans,trans*-bromodioxolane 9 and the enone 12 in the reaction of the *trans*-allylic hydroperoxide, and our attempts to reproduce the mechanistic simplification that Bloodworth and Curtis were able to achieve by inclusion of galvinoxyl in some NBS-induced homoallylic hydroperoxide cyclisations[24], were not readily interpretable.

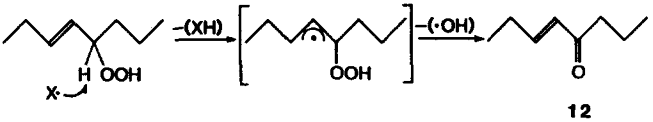
The concomitant production of the enone 12 thus remains a puzzle: formally this is the dehydration product of the starting allylic hydroperoxide 2 and, with prior or subsequent double-bond isomerization, of 3. Secondary alkyl hydroperoxides can be dehydrated to ketones by base[25]. To our knowledge NBS is not considered, however, to be to be sufficiently basic to induce this kind of reaction and we showed that the reaction by-product, succinimide, was not capable of inducing the dehydration of the starting allylic hydroperoxide.

Two other possibilities remain: acid-induced dehydration or radical-induced dehydration. We consider that we may exclude the former on two grounds. Firstly, reaction in the presence of solid sodium hydrogencarbonate failed to alter the product composition. Secondly, we were only able to induce Hock cleavage[26] when 2 was treated with either 70% perchloric acid or, under not strictly anhydrous conditions, boron trifluoride etherate, to produce butanal and its self aldol product, *trans*-2-ethyl-2-hexenal, 11[27] (Equation 11).



(11)

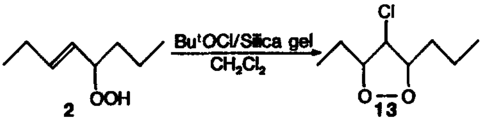
The remaining possibility (Equation 12) which remains unproven, involves the abstraction of a doubly-activated hydrogen atom (allylic and α-hetero-atom stabilized) followed by a superficially facile β-scission step.



(12)

At this point we considered the implications of these findings. Superficially, the intramolecular peroxymercuration and peroxybromocyclizations are examples of unusual 5-endo closures[28]. Both of these reactions are, however, mediated by soft, polarisable Lewis acids and it may be that their prior co-ordination to the more polarisable Lewis basic site in the bifunctional allylic hydroperoxides (to form mercurinium and bromonium ions) is the key to these successful closures. Indeed, Porter and co-workers[29] have emphasised the role of this prior co-ordination to effect this "disfavoured" type of ring closure. (Such closures do, in fact, have structural precedent. It has been demonstrated, for example, that homoallylic alcohols are cyclized by mercury(II) salts to produce β-mercurated tetrahydrofurans[30]). In contrast, however, the harder electrophiles (Bronstead and Lewis Acids) co-ordinate at the harder Lewis base site to eventually effect Hock cleavage.

As an example of what might be an intermediate level of selection we find that in an intramolecular variant of a potentially useful peroxychlorination reaction[31], the *trans*-allylic hydroperoxide 2 reacts with tert-butyl hypochlorite in dichloromethane to give a complex set of products from which a mixture of 4-chloro-1,2-dioxolanes 13 may be isolated (Equation 13).

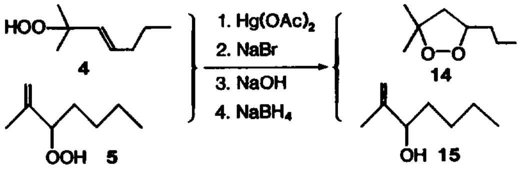


(13)

We find that this reaction is markedly catalysed by added silica gel, and that the uncatalysed reaction depends, in an, as yet, uncertain way, on prior surface treatment (acid or alkali washing) of the reaction flask. Tert-butyl hypochlorite is known[32] to convert lightly alkylated alkenes, by free radical-mediated mechanisms, into allylic chlorides. However, for tetra-alkylalkenes[33], alternative reaction pathways, which have been likened to the outcome of singlet (ene) oxygenations, have been noted. For some representative tri-alkylalkenes, the mechanistic picture is apparently not certain and here a silica-gel effect has been noted[34] and found synthetically useful[35]. In these reactions, parallels with the behaviour of protonated tert-butyl hypochlorite[36] was noted. In view of these complexities we have not pursued this reaction further.

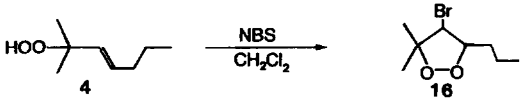
In the light of these findings, we were drawn to investigate the reaction of the tertiary and secondary pair of allylic hydroperoxides (4 and 5: Equation 4) with mercury(II) acetate and with N-bromosuccinimide. In the former reaction, examination of the product, after hydridodemercuration, showed that only the tertiary hydroperoxide, 4, had been converted to a 1,2-dioxolane, 14, and that the secondary isomer, 5, had suffered simple reduction to alcohol 15 (Equation 14).

Duplicate experiments on the same scale as above where mercury(II) trifluoroacetate or mercury(II) nitrate monohydrate were used in place of mercury(II) acetate failed to give any secondary hydroperoxide-derived 1,2-dioxolane after borohydride reduction: in the former case the tertiary hydroperoxide, 4, gave the expected dioxolane after borohydride reduction while in the latter case, no dioxolane could be detected in the crude product (Equation 14).



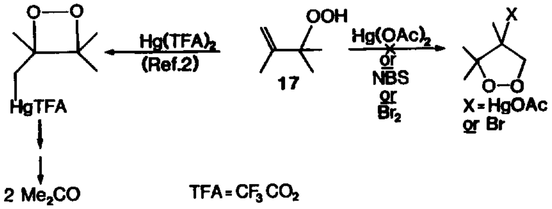
(14)

With N-bromosuccinimide, the tertiary isomer in the same hydroperoxide mixture underwent cyclization to give a 4-bromo-1,2-dioxolane, 16 (Equation 15) while the secondary isomer was cleaved to a selection of unknown products.



(15)

The facility with which the tertiary isomer 4 undergoes 1,2-dioxolane formation (in comparison with the inertness of isomer 5) might be rationalized[7] by appreciating the general observation that, in oxymercurations and in polar oxybromination, attack of the nucleophile on the intermediate cyclic cation occurs at the least substituted carbon atom (Markovnikov-type addition) and that, for secondary isomer 5, this would involve the, apparently unfavourable, formation of 1,2-dioxetanes. To complete the circle, therefore, we find that allylic hydroperoxide 17, which Adam and Sakanishi[2] had shown to undergo 1,2-dioxetane formation on reaction with mercury(II) trifluoroacetate), is inert to 1,2-dioxolane formation when treated with mercury(II) acetate, whilst with NBS, it is converted into a complex variety of products (Equation 16).



(16)

EXPERIMENTAL

Materials and Methods

All materials except where stated were obtained from the Aldrich Chemical Company and used as received, the only starting material not so obtained was *cis*-4-octene, which was prepared from 4-octyne in 64% isolated yield (0.22mol scale, product bp 123°C) by hydroboration/ acetic acid protolysis in the manner described by Brown and Zweifel[37] for *cis*-3-hexene. Particular care was taken to use redistilled or HPLC-grade solvents for chromatography.

NMR spectroscopy was carried out in deuteriochloroform containing internal tetramethylsilane and all chemical shifts are quoted in units of δ, (parts per million) downfield from that reference. First order analyses of 1-H NMR spectra are quoted, while 13-C NMR shifts obtained for proton-decoupled spectra have routinely been assigned using the results of APT spectra. In early (low-field) work a Perkin Elmer R32 instrument, operating at 90MHz, was used for 1-H NMR spectroscopy, while characterization data was obtained using a Varian VXR400 spectrometer (located in the Chemistry Department, University College, London) operating at 400MHz (1-H) or 100MHz (13-C) or on a General Electric QE300 spectrometer (located in these laboratories) at fields of 300 and 75MHz respectively. IR spectra were recorded on a Perkin Elmer 377 spectrometer.

Combustion analysis were performed by Mr. J. Davey and colleagues in three Laboratories using a Perkin Elmer 240 analyser, or by Mr. A. Stones at the Analytical Laboratory of the Department of Chemistry, University College, London.

Thin layer chromatography was carried out using Merck aluminium-backed silica gel coated plates (Art. No.5554, BDH Ltd). After examination of developed plates under ultra-violet illumination, plates were sprayed with one of three locating reagents: p-Dimethylammonium-aniline dihydrochloride (ADADH)[38] for peroxide detection; acidified vanillin in methanol for general detection at ambient temperature or phosphomolyldic acid (PMA:ACS reagent) followed by heating (oven, 110°C) for alternative general detection. Preparative, flash chromatography was performed on Merck adsorbent (Grade 60, 230-400 Mesh; Aldrich Cat. No. 22,719-6) in mesh-protected columns (where appropriate), using nitrogen gas for pressurization. Kugelröhr distillation was carried out behind safety screens, using a Büchi GKR-50 apparatus. We encourage all workers to approach manipulations of organic peroxides with care and to act with CAUTION: all distillations were carried out on gradually increasing scales to those noted. We emphasise that all distillations have been carried out on materials of comparatively low active oxygen content, and from crude materials that have the lowest possible metal contents, which have been generated under essentially neutral pH conditions and which, prior to distillation, have been shown to contain a suitable antioxidant (routinely in these cases 2,6-di-tert-butyl- 4-methylphenol, BHT).

Two useful publications by Interox Chemicals Ltd.[39], along with treatises concerning organic peroxides should be consulted concerning safety.

Photo-oxygenations of Alkenes

Magnetically stirred, dichloromethane solutions (ca 200cm^3) containing the alkene (ca 0.2M), TPP (5, 10, 15, 20-Tetraphenyl-21 H, 23H-porphine, 99+%, ca 0.0002M) and BHT (ca 0.01M: included to suppress concurrent or subsequent free-radical reactions) were at room temperature, under an atmosphere of pure oxygen, irradiated in an all-Pyrex, immersion-well photo-reactor. The oxygen uptake was roughly measured using a attached water-equilibrated gas burette. Once the uptake had slowed, the lamp was switched off and the apparatus was allowed to cool. The reaction mixtures (having the bright green colour characteristic of TPP/hydroperoxide solutions) were then either divided into aliquots or were directly concentrated by rotary evaporation.

(i) *Trans-4-octene*

One third of a reaction solution prepared as described above (using a total of 5.15gm, 46mmol of alkene ca 95mol% oxygen uptake in 7 hours) was concentrated (evaporator bath at ca 20°C, pressure ca 15mm Hg) to leave a green oil (2.19gm) which was then initially purified by flash chromatography (room temperature; silica; dichloromethane eluant; tlc analysis, R_f (DCM) = 0.27; ADADH spray detection) to give a pale green oil (1.39gm, 58% yield) which was further purified by Kugelröhr distillation (oven 50-60°C; pressure ca 0.04mm Hg; SAFETY SHIELD!) to give a colourless oil (0.50gm, 38% yield).

A further one-third portion was chromatographically purified in the same way, but by conducting the separation at -10°C (jacketed column). In this instance, the product (a very pale green oil, 1.72gm, 72% yield) was deemed satisfactorily pure for direct further use.

The final concentrated one-third portion was purified by direct Kugelröhr distillation to give an extremely pale yellow liquid (1.40gm, 58%) which was characterised by 1-H and 13-C NMR spectroscopy (the full 13-C NMR data for the *trans*-isomer and partial data for the *cis*-isomer have been reported[40]) as a mixture of *trans*- and *cis*-5-octen-4-yl hydroperoxides of composition 79% -*trans* [1-H NMR at 400MHz] or 78±2% -*trans* [13-C NMR, line height averaging]:

trans-5-octen-4-yl hydroperoxide, 2: [1-H NMR] 7.748, s, 1H, OOH; 5.844, dt, 1H, ^{6}CH, $J_{6,7}$=6.3Hz, $J_{5,6}$=15.4Hz; 5.372, ddt, 1H, ^{5}CH, $J_{4,5}$=8.3Hz, $J_{5,7}$=1.6Hz; 4.294, ddd, 1H, ^{4}CH, $J_{3,4}$=6.8Hz, $J_{3',4}$=6.1Hz; 2.107, ddq, 1H, $^{7}CH_2$, $J_{7,8}$=7.4Hz; 1.62, 1H and 1.5-1.3, 3H, $^{2}CH_2$+$^{3}CH_2$; 1.025, t, 3H, $^{8}CH_3$; 0.920, t, 3H, 1CH3, $J_{1,2}$=7.2Hz. [13-C NMR], 138.55, 127.52 (C5, C6); 86.89 (C4); 34.56 (C3); 25.36 (C7); 18.62 (C2); 14.03 (C8); 13.37 (C1).

cis-5-octen-4-yl hydroperoxide, 3: [1-H NMR] 7.912, s, 1H, OOH; 5.719, ddt, 1H, ^{6}CH, $J_{6,7}$=7.5Hz, $J_{5,6}$=10.9Hz, $J_{4,6}$=0.8Hz; 5.287, ddt, 1H, ^{5}CH, $J_{4,5}$=9.3Hz, $J_{5,7}$=1.6Hz; 4.745, ddd, 1H, ^{4}CH, $J_{3,4}$~$J_{3',4}$=5.9Hz;2.1-2.2, m, 4H, $^{7}CH_2$; 1.3-1.7, m, 4H, $^{2}CH_2$+$^{3}CH_2$; 0.997, t, 3H, $^{8}CH_3$, $J_{7,8}$=7.5Hz; 0.884, t, 3H, $^{1}CH_3$, $J_{1,2}$=7.4Hz. [13-C NMR] 137.89, 127.67 (C5, C6); 80.95 (C4); 34.69 (C3); 21.20 (C7); 18.52 (C2); 14.09, 14.03 (C1, C8).

(ii) *Cis*-4-octene

One third of the crude product from a reaction using 5.15gm alkene (ca 100mol% oxygen uptake in four hours) was purified by KugelrQQöhr distillation (conditions as for *trans*-alkene derived product) to give a colourless liquid (1.64gm, 69%), while the remaining portion was similarly distilled to give a colourless liquid (3.59gm, 75%) which gave a fair combustion analysis ($C_8H_{16}O_2$ calc/found: C=66.63/67.0%; H=11.19/11.4%) and which (by 400MHz 1-H NMR) was *trans*-5-octen-4-yl hydroperoxide, 2 (<2% *cis*-isomer) and whose thin film infra-red spectrum showed an absorption at 670cm^{-1}, confirming the *trans*- nature of the double bond.

(iii) 2-Methyl-2-heptene

Reaction of this alkene (3.27gm, 33mmol) as above, for about three and a quarter hours (ca 77mol% oxygen uptake) gave, after rotary evaporation, a green oil, all of which was directly purified by Kugelröhr distillation (oven 60-70°C, p~0.04mm Hg) to provide a water-white liquid (3.39gm, 26mmol mixed hydroperoxides, 79% isolated yield), for which for which a good combustion analysis was obtained (Calc./found: C=66.6/66.7, H=11.2/11.2). Flash chromatography (silica/CH_2Cl_2 eluant), gave a fairly clean sample of the less polar, secondary isomer which allowed the following data to be presented:

2-Methyl-*trans*-3-hepten-2-yl hydroperoxide, 4: [1-H NMR at 400MHz] 7.322, s, 1H, OOH; 5.712, dt, 1H, ^{4}CH, $J_{3,4}$=15.8Hz [implies (E)], 5.534, dt, 1H, ^{3}CH, $J_{3,5}$=1.4Hz;

2.046, 2H, ddt, $^5CH_2$, $J_{5,6}$=7.3Hz; 1.417, sextet, 2H, $^6CH_2$; 1.334, s, 6H, $^1CH_3$+$^2C(CH_3)$; 0.897, t, 3H, $^7CH_3$, $J_{6,7}$=7.3Hz. [13-C NMR at 100MHz] 133.18, 132.18, C3/C4; 82.29, C2; 34.49, C5; 24.32, C1+C2(Me); 22.31, C6; 13.66, C7.

2-methyl-1-hepten-3-yl hydroperoxide, 5: [1-H NMR at 400MHz] 7.772, s, 1H, OOH; 5.018, m, $w_{1/2}$ = 5.6Hz, 2H, $^1CH_2$; 4.319, t, 1H, ^3CH, $J_{3,4}$ = 6.7Hz; 1.733, t, 3H, $^2C(CH_3)$, J=1.0Hz; 1.2-1.6, 6H, $^{4-6}CH_2$; 0.906, t, 3H, $^7CH_3$, $J_{6,7}$=7.0Hz. [13-C NMR at 100MHz] 143.84, C2; 114.26, C1; 89. 3, C3; 30.40, C4; 27.85, C5; 22.60, C6; 17.06, Me; 13.94, C7.

Cyclo-peroxymercuriation of Allylic Hydroperoxides

(i) *Cis* + *trans*-5-octen-4-yl hydroperoxide (4:1, 2:3)

To a magnetically stirred solution of the mixed hydroperoxides (0.50gm, 3.5mmol) in dichloromethane (10cm^3), under air and at room temperature was added mercury(II) acetate (1.11gm, 3.5mmol). After twenty minutes, a test for the presence of Hg^{2+} ions (addition of an aliquot to aqueous sodium hydroxide solution) was positive (bright yellow mercury(II) oxide precipitate), while after a further forty minutes, the reaction was judged complete. After water washes (3x20cm^3), drying ($MgSO_4$) and concentration (ice bath, p 60mm Hg) a colourless oil remained (1.49gm, 106% as organomercury(II) acetate), which was examined by 1-H and 13-C NMR. The latter revealed the presence of the organomercury(II) acetate (data below), the starting *trans*-hydroperoxide, its isoallylic *trans*-isomer [*trans*-4-octen-3-yl hydroperoxide] and the starting *cis*-hydroperoxide, with none of its isoallylic *cis*-isomer present. Using data for the 13-C NMR spectra of the hydroperoxides given above (and also partly published elsewhere[40]) and considering the line heights in our spectrum, the approximate molar ratio of these products, of 33:44:3:20 in the order given above was determined.

In view of the unstable nature of the organomercury(II) acetate (revealed by the deoxymercuriation that had occurred during its spectroscopic examination), a duplicate preparation was performed (same scale and reaction conditions) and, without water washes, the crude reaction mixture was treated with aqueous sodium bromide (1 fold excess) before being dried and concentrated (as above). Part (80%) of this material was separated by flash chromatography (silica, dichloromethane eluant); fraction analysis by tlc (silica, dichloromethane) using vanillin in sulphuric acid as detection reagent. After the elution of a small trace (31mg) of what appeared to be a *trans*, *cis*-4-mercurated-1,2-dioxolane (R_f, DCM = 0.38) the major *trans*,*trans*-isomer was eluted (1, X=Br: R_f, DCM = 0.34, brown colour reaction to spray) and recovered as a colourless, viscous gum (0.57gm, equivalent to 72% isolated yield of the *trans*-hydroperoxide as product), which after thorough solvent evaporation (ambient, p≅0.01mmHg, 1 hour) was characterised as *trans*,*trans*-4-bromomercuri-5-ethyl-3-n-propyl-1,2-dioxolane 1, X=Br: [Combustion analysis] %calculated/found: C = 22.68/22.4, H = 3.57/3.6 [1-H NMR] 4.586, dt, 1H, J_d=4.8Hz, J_t=7.7Hz J_{199Hg}=206Hz and 4.526, dt, 1H, J_d=7.7Hz, J_t=6.2Hz, ^{3}CH and ^{5}CH; 3.163, t, 1H, $J_{3,4}=J_{4,5}$=7.7Hz, J_{199Hg}=133Hz; 1.35-1.90, m, 6H, 3xCH_2; 1.080 and 0.964, each t, J=7.3Hz, 2xCH_3.

Later fractions (R_f, DCM=0.27) gave a grey colour reaction with the vanillin spray reagent and, upon solvent evaporation, a yellowish oil (50mg), which by 1-H and 13-C NMR analysis was considered to be a mixture of the unreacted starting *cis*-hydroperoxide, none of its isoallylic isomer, butanal and what appeared, to be, in unequal amounts, two diastereoisomeric butanal *cis*-hydroperoxide hemi-peracetals: partial 1-H NMR data, 7.952 (OO$\underline{H}$); 6.575, 2xt, major J=6.8Hz, minor 10.0Hz (C$\underline{H}$.OH.OOR); 5.620, 5.216 obscured by signals for parent hydroperoxide (*trans*, C$\underline{H}$=C$\underline{H}$); 4.80 (allylic C$\underline{H}$.OO); 3.1-3.3 (OH). Partial 13-C NMR data for major isomer: 140.29, 136.40 ($\underline{C}$=$\underline{C}$); 101.26 ($\underline{C}$H.OH.OOR); 78.81 (allylic $\underline{C}$H.OO); 35.11, 34.79, 21.56, 17.80, 14.21. Partial 13-C NMR data for minor isomer with similar assignments: 140.69, 136.38; 100.35; 78.33; 35.19, 34.77, 29.72, 21.17, 17.75.

(ii) *Trans*-5-octen-4-yl hydroperoxide 2.

The reaction mixture from the *trans*-hydroperoxide, 2 (1.44gm, 10mmol) in dichloromethane (30cm^3) with added mercury(II) acetate (3.19gm, 10mmol) was, after stirring for two hours at room temperature, washed with water (3x20cm^3), dried ($MgSO_4$), concentrated and promptly analysed to give *trans,trans*-4-acetomercuri-5-ethyl-3-n-propyl-1,2-dioxolane, 1 X=OAc: [1-H NMR] 4.433, m, 2H, ^{3}CH+^{5}CH, J_{199Hg}=160Hz; 2.471, t, 1H, ^{4}CH, $J_{3,4}=J_{4,5}$=8.7Hz, J_{199Hg}=152Hz; 2.048, s, 3H, OAc; 1.7-1.3, m, 6H, 3xCH_2; 1.031 and 0.953, 2xt, 2 x terminal CH_3 J=7.4Hz. [13-C NMR] 85.27, 84.06, C3/C5; 57.15, C4, J_{199Hg}=1712Hz; 32.29, 26.55, 20.18, 3xCH_2; 14.16, 10.99, 2xCH_3; 177.88, 23.81, OAc.

Cyclo-peroxymercuriation/Hydridodemercuriation of Allylic Hydroperoxides

(i) *Trans*-5-Octen-yl hydroperoxide, 2

A portion of the hydroperoxide (1.44gm, 10mmol) was converted into the organomercury(II)-acetate, 1 X=OAc, and then -bromide, 1 X=Br, as described above. The dichloromethane solution of the crude organo- mercury(II) bromide was then cooled on ice, treated quickly with ice- cold sodium hydroxide solution (2M, 10cm^3; a small amount of mercury(II) oxide was seen to form) and this mixture was then quickly added to a well-stirred, ice-cooled solution of sodium borohydride (1.50gm, 40mmol) in aqueous sodium hydroxide (2M, 75cm^3) under air. After fifteen minute periods of stirring on ice and then at room temperature, the three layers were separated and dichloromethane extracts (2x25cm^3) of the aqueous layer were combined with the organic layer. These combined materials were dried ($MgSO_4$) and concentrated by rotary evaporation (ice bath, $p\cong 80$mm Hg) to leave a residue (1.82gm) shown by 1-H NMR to be essentially the pure 1,2-dioxolane, 7, described below. (This analytical solution was re-examined, having stood in a glass tube on the open bench for one week and was found by 1-H NMR spectroscopy to be unchanged).

The oil was purified by flash chromatography at room temperature [75gm silica, dichloromethane eluant] monitored by tlc on silica [ADADH spray detection which for 1,2-dioxolane, 7, gives a slow response, R_f, DCM=0.55] to give a water-white fragrant oil (1.34gm, 93% isolated yield).

A duplicate reaction (2mmol scale) gave 82% isolated yield of a slightly yellow oil which could be further purified by KugelrQQöhr distillation (oven 60-70°C, p=0.01mmHg) to give a water-white liquid, and in another duplicate (1mmol scale), an 84% isolated yield was obtained. None of these materials gave completely satisfactory combustion analyses in the hands of different analysts: previous workers[35] have noted that certain 1,2-dioxolanes are capricious in this respect. For cis-5-ethyl-3-n-propyl-1,2-dioxolane, 7: [Best combustion analysis], %calc/found: C66.63/67.1; H 11.19/11.5. [1-H NMR] 4.230, quartet of doublets, 1H, J_q=7.2Hz, J_d=5.0Hz and 4.157, quartet of doublets, J_q=7.0Hz, J_d=6.1Hz, ^{3}CH and ^{5}CH; 2.769, dt, 1H, $^4CH_\alpha$, J_{gem}=11.8Hz, J_{vic}=7.2Hz; 1.810, dt, 1H $^4CH_\beta$, J_{vic}=6.8Hz; 1.3-1.75, 3xCH_2; 0.960 and 0.936, 2xt, 6H, 2xterminal Me, J=7.5 and 7.0Hz respectively. [13-C NMR] 82.66, 81.27, C3/C5; 46.16, C4; 36.16, 27.28 and 19.92, 3x$\underline{C}H_2$; 14.31, 10.77, 2x$\underline{C}H_3$.

In order to probe the stereoselectivity of the hydrogen atom-capture step an intramolecular peroxymercuriation using the *trans*-hydroperoxide (2, 1mmol) was performed. This was followed by anion exchange, cold base pre-wash and then addition to an ice-cooled, stirred solution of sodium borodeuteride (0.155gm, 3.7mmol) in aqueous sodium hydroxide (isotopically normal, 2M, 7.5cm^3). Work up as before gave a crude product which was directly examined by 13-C and 1-H NMR. The former analysis showed the presence of the C-4 deuteriated 1,2-dioxolane (chemical shifts 82.33, 80.94, 45.59 [triplet], 35.89, 27.01, 19.64, 14.02, 10.48: see Discussion) along with only traces of minor contaminants (*trans*-5-octen-4-ol and other unidentified materials, but no *trans*-4-octen-3-ol). Analysis of the spectrum is given in the Discussion.

In an attempt to form 4-hydroperoxy-1,2-dioxolanes[17], a vigorously stirred, dilute solution of the crude organomercury(II) bromide 1 X=Br (2mmol scale, prepared as above) in dichloromethane (50cm^3) was treated over five minutes, with ice cooling, under air, with a solution of sodium borohydride (0.3gm, 8mmol) dissolved (fizzing!) in pH7 buffer (100cm^3, BDH). Work-up as before gave a colourless oil (0.31gm) which was shown by 1-H NMR and by tlc to contain, principally, the dioxolane isolated above along with starting hydroperoxide and some more polar peroxides (R_f, DCM=0.21). Separation by flash chromatography gave these materials in yields of 82mg (23% isolated yield), 26mg (9% isolated) and 53mg respectively. The latter material was examined by 13-C NMR[40] and found to contain, mainly, two *trans*-allylic alcohols (*trans*-5-octen-4-ol, and *trans*-4-octen-3-ol: formed by reduction of the products of deoxymercuriation), some other minor alcohols and what appeared to be two isomers of 5-ethyl-4-hydroperoxy-3-n-propyl-1,2-dioxolane, for which partial characterization follows: [13-C NMR] major isomer 101.89, 87.68 and 86.25; minor isomer 100.36, 88.02 and 86.57. [1-H NMR] 9.30, br s, OOH; 4.472, br.t, ^{4}CH, $J \cong 2.8$Hz; 4.180, ddd, J=8.4, 5.5 and 3.1Hz and 4.102, ddd, J=8.2, 6.0 and 2.7Hz, ^{3}CH and ^{5}CH. Analytical, normal phase hplc on silica provided some indication of separation of these polar materials but the complexity of this mixture discouraged further work.

(ii) *2-Methyl-1-hepten-3-yl hydroperoxide/2-methyl-trans-3-hepten-yl hydroperoxide* (4 and 5)

A mixture of the two hydroperoxides 4 and 5 (288mg, *ca* 1mmol each component) mercury(II) acetate (637mg) 2mmol in dichloromethane (2cm^3) was stirred at room temperature for one hour, after which time the reaction mixture was treated directly with aqueous sodium bromide (2M, 2cm^3). After one hour, the mixture was separated, dichloromethane extracts (3x2cm^3) of the aqueous layer were combined with the organic layer and this material was dried ($MgSO_4$) and concentrated (bath at ambient, p=25mm Hg) to give a clear, very pale yellow oil (0.62gm), the low field 1-H NMR spectrum of which could be interpreted in terms of complete conversion of the *tertiary*-hydroperoxide, 4, to a 4-bromomercuri-dioxolane [apparently as one isomer, partial 1-H NMR data: 4.55, q; CH(OO); 2.78, d, J≅9Hz, CH(HgBr), 1.47, s, Me$_2$C(OO)], and unreacted hydroperoxide 5.

This crude product, redissolved in ice-cold dichloromethane (2cm^3), was treated with ice-cold aqueous sodium hydroxide (2M, 1.6cm^3) and then quickly added to a well stirred, ice-cooled solution of sodium borohydride (0.24gm, 6mmol) in aqueous sodium hydroxide (2M, 12cm^3). After periods of ten minutes on ice and then at room temperature work up as in (i) above gave a fragrant oil (208mg, *ca* 75% of starting hydroperoxides as products), low field 1-H NMR of which suggested to be composed of the reduced *secondary* hydroperoxide, 15, the 1,2-dioxolane, 14, (described below), and a small, but significant, unknown material showing absorption as a triplet at δ_H3.60. The crude product was separated by flash chromatography at room temperature [silica gel, dichloromethane eluant] with fraction analysis by tlc [silica, dichloromethane, using ADADH and PMA detection] into two recovered components. The more polar material (R$_f$, DCM=0.14) was recovered as a colourless oil (36mg, 28% isolation of starting *secondary* hydroperoxide as product) and spectroscopially characterised as the *secondary* alcohol *2-methyl-1-hepten-3-ol*, 15[41]: [1-H NMR] 4.91, 4.81, 2xbr.s, ^{1}CH$_2$; 4.08, t, ^{3}CH, $J_{3,4}$=7Hz; 1.72, s, ^{2}C(CH$_3$); 1.51 and 1.30, 2xM, 3xCH$_2$; 0.90, t, ^{7}CH$_3$, $J_{6,7}$=7Hz [I.R., thin film]: 3680-3120, OH, 895cm^{-1}, C=CH$_2$. The less polar, peroxidic product (R$_f$, DCM=0.43), was recovered by rotary evaporation as a fragrant oil (58mg, 40% isolated yield as converted *tertiary* hydroperoxide, 4) and fully characterised as *3,3-dimethyl-5-n-propyl-1,2-dioxolane*, 14: [Combustion analysis] %calculated/found/duplicate: C=66.63/66.72/66.56; H=11.19/11.07/11.16. [1-H NMR], 4.290, multiplet, 1H, ^{5}CH, J_{sum}=27.2Hz: 2.453, 1H, dd, ^{4}CH, J_{gem}=11.8Hz, J_{vic}=7.5Hz; 1.977, 1H, dd, ^{4}CH, J_{vic}=7.2Hz; 1.360 and 1.335, 2xs, ^{3}C(C$\underline{H}_3$) with 1.28-1.73, underlying multiplets, 2xCH$_2$, together 10H; 0.934, t, 3H, terminal CH$_3$, J=7.2Hz. [13-C NMR], 83.01, C3; 81.63, C5; 52.42, C4; 35.75, 19.60, 14.05, $CH_2.CH_2.CH_3$; 26.74, 25.87, $^{3}C(\underline{C}H_3)_2$. Careful chromatography was required in order to obtain material that gave satisfactory combustion analysis, since the dioxolane fraction was contaminated with what appeared to be the dehydration product of the secondary hydroperoxide [2-methyl-1-hepten-3-one: characterised from the 1-H NMR spectrum of the contaminated material (partial data: 5.951 and 5.751, each narrow 1H multiplets, $^{1}CH_2$; 2.680, br dd, 2H, $^{4}CH_2$, $J_{4,5}{\sim}7.5$Hz; 1.872, narrow multiplet, 3H, $^{2}C(CH_3)$]. This compound is, presumably, produced by the action of the aqueous alkali used in the reduction step.

Cyclo-peroxymercuriation/Bromodemercuriation of *Trans*-5-octen-4-yl hydroperoxide (2).

The 98+% *trans* hydroperoxide 2 (388mg, 2mmol) was converted in the 4-bromomercuri-1,2-dioxolane, 1=Br, by mercury(II) acetate cyclisation, followed by anion exchange as described above: the peroxymercurial was isolated as a colourless oil, redissolved in dichloromethane (5cm^3) and then treated, as a stirred solution at room temperature under air, with a solution of bromine (0.11cm^3, 2.15mmol) in dichloromethane (2cm^3). No reaction occurred immediately, but within two minutes a precipitate formed and, after an hour at room temperature, the colour of the bromine had been almost totally discharged and a white precipitate [mercury(II) bromide] had settled. Dilution with petroleum ether (20cm^3, 40-60°C fraction), filtration and concentration (ambient, p=70 → 20mm Hg) gave a straw- coloured oil (0.436gm, 98% as bromoperoxide) which, after examination by tlc (silica, dichloromethane eluant, ADADH detection) and 1-H NMR, was separated into fractions by flash chromatrography (room temperature, silica gel, 1:1 dichloromethane: petrol eluent). The principal product was the *trans,trans*-4-bromo-1,2-dioxolane, 9, [R_f(DCM)=0.69; R_f (1:1 petrol:DCM)=0.59] fully characterised below. A small amount of the slightly more polar material [R_f (DCM)=0.58; R_f (1:1 petrol: DCM)=0.50] which appeared as about 7mol% of the bromodioxolanes in the crude product was isolated and, on the basis of both the structure of the main isomer (*trans,trans*: see below) and of the intermediate peroxymercurial (also *trans,trans*: see above) is assigned as *cis,cis*-4-bromo-5-ethyl-3-n-propyl-1,2-dioxolane, 10 [Combustion analysis] %calc/found, C=43.06/42.5, H=6.78/6.7. [1-H NMR] 4.832, t, 1H, ^{4}CH, $J_{3,4}=J_{4,5}=3.8$Hz; 4.355, 1H, dt, $J_t=6.6$Hz and 4.263, dt, $J_t=6.7$Hz, ^{3}CH and ^{5}CH; 1.70-1.85, 2xM, 44 and 1.421, 2H, Sextet, $3xCH_2$; 0.998 and 0.975, each t, 3H, J=7.3Hz, $2xCH_3$. [13-C NMR] 84.65, 83.17, C3 and C5; 62.43, C4; 32.79, 24.08, 19.43, $3xCH_2$; 14.06, 10.29, $2xCH_3$.

Cyclo-peroxybromination of Allylic Hydroperoxides

(i) 5-octen-4-yl hydroperoxides (2 and 3)

Portions (144mg, 1mmol) of the 98+% -*trans*, 2, and the mixed *trans/cis* 5-octen-4-yl hydroperoxides (2:3 = 4:1) were added to separate, almost saturated solutions of N-bromo-succinimide (178mg, 1mmol, recrystallized and dried prior to use) in dichloromethane ($8cm^3$). Within half an hour, clear solutions resulted (the latter reaction mixture had developed a slight yellow colour). Each reaction mixture, after a further hour at room temperature under air, was diluted with petroleum ether ($20cm^3$, bpt 40-60°C). The precipitated succinimide was removed by filtration, washed with petroleum ether ($3x1cm^3$), and the combined filtrate and washings concentrated by rotary evaporation (ice bath, p=60mm Hg) to leave slightly air unstable residues which which were examined directly by 1-H NMR and found to be virtually identical (molar ratios of enone, 12 to *trans,trans-* bromodioxolane, 9 being 1:5.3 and 1:4.4 respectively).

A preparative scale reaction was carried out using the 4:1 mixture of hydroperoxides, 2:3 (2.5mmol scale), with the modification of an aqueous work-up ($3x10cm^3$, followed by $MgSO_4$), prior to flash chromatographic separation (room temperature, 70gm silica gel, dichloromethane elution, fraction monitoring by tlc, detection with ADADH spray). The products collected, after solvent evaporation, were the *trans,trans*-bromodioxolane, 9 (R_f, DCM=0.69, 265mg, 48% isolated yield), two minor unidentified materials (R_f, DCM=0.45, 9 and 65mg), unreacted hydroperoxides 2 and 3 in 4:1 *trans/cis* ratio (R_f, DCM=0.36, 170mg, 47% recovery) and *trans*-5-octen-4-one, 12 (R_f, DCM=0.31, only u.v. active during tlc analysis, 51mg, 16% isolated yield). The bromo- dioxolane was characterised as *trans,trans*-4-bromo-5-ethyl-3-n-propyl- 1,2-dioxolane, 9 [Combustion analysis] %calc/found: C=43.06/43.4, H=6.78/6.3 [1-H NMR] 4.352, ddd, 1H, J=7.8, 5.3 and 5.4Hz and 4.292, dt, 1H, J_d=7.36, J_t=5.4Hz, ^{3}CH and ^{5}CH; 3.862, t, 1H, ^{4}CH, $J_{3,4}=J_{4,5}$ =5.4Hz; 1.77-1.59, m, 4H and 1.55-1.40, m, 2H, $3xCH_2$; 1.033, t, J=7.5Hz and 0.959, t, J=7.2Hz, each 3H, $2xCH_3$. [13-C NMR] 90.46, 89.18, C3 and C5; 56.90, C4; 33.62, 24.99, 19.32, $3xCH_2$; 13.97, 10.22, $2xCH_3$.

A similar preparative scale reaction (5mmol scale) using the 98+% -*trans* hydroperoxide, 2, gave the same bromodioxolane, 9, in 39% isolated yield, recovered unreacted *trans* hydroperoxide, 2 (30% isolated yield) and the enone, 12 (7% isolated yield) again with a significant unassigned intermediate material, which, on the basis of tlc mobility, ADADH spray response and 1-H NMR spectrum was perhaps a dibromohydroperoxide (partial 1-H NMR data: 8.5, br, 1H, OOH; 4.0-4.9, 3H; 1.4-2.5, ca 6H; 0.9-1.1, ca 6H).

An ice-cooled solution of the 98+% -*trans* hydroperoxide, 2 in deuteriochloroform ($1cm^3$, 1M) was treated with one equivalent of bromine. The resultant pale orange solution was divided into two halves. The first, upon examination by 1-H NMR was seen to be composed of a mixture of the *trans,trans-* bromodioxolane 9 and the material described above as a dibromohydroperoxide, with no enone, 12 or residual allylic hydroperoxide, 2 present: examination by tlc supported this assessment. The second half of the mixture was mascerated with one equivalent of silver trifluoroacetate. Within two minutes, a yellow precipitate of silver bromide had formed, but tlc and 1-H NMR showed very little change to the organic components of the mixture had occurred.

(ii) 2-methyl-1-hepten-3-yl hydroperoxide/2-methyl-trans-3-hepten-2-yl hydroperoxide (4 and 5).

A stirred, almost equimolar solution of the mixed hydroperoxides 4 and 5 ($7cm^3$, 1M) was treated at room temperature with one equivalent of N-bromosuccinimide (1.24gm, 7mmol), the reaction being monitored visually and by tlc. After four hours at room temperature and standing in the refrigerator over the weekend, the precipitated succinimide was removed by filtration and the filtrate concentrated by rotary evaporation (ambient, p=25mm Hg) to leave a crude product (1.73gm) which was examined by 1-H NMR and then separated by flash chromatography (room temperature, 140gm silica gel, gradient elution from 3:1 v/v 40-60°C bpt petroleum ether: dichloromethane to neat dichloromethane) with tlc monitoring (ADADH spray detection).

The spectrum of the crude product indicated that hardly any unsaturation remained, but that a host of products had been formed. Of these, the major single material (R_f, DCM=0.65) was isolated and characterised as a tertiary hydroperoxide-derived dioxolane (isolated yield 295mg, 41% conversion of that isomer): 4-bromo-3,3-dimethyl-5-n-propyl-1,2-dioxolane, 16 [Combustion analysis] %calc/found: C=43.06/42.81; H=6.78/6.79. [1-H NMR, with selective decoupling] 4.300, dt, 1H, ^5CH, $J_{4,5}$=8.0Hz, J_{H2}=8.0 and 4.8Hz; 3.950, d, 1H, CH^4; 1.83-1.50, m, 4H, 2xCH ; 21.441 and 1.403, 2xs, 6H, $^3C(CH_3)_2$; 0.961, t, 3H, J=7.5Hz, terminal CH_3. [13-C NMR] 88.63, C5; 84.52, C3; 62.91, C4; 33.34, 19.19, 13.93, n-Pr; 23.71, 25.10, $^3C(\underline{C}H_3)_2$.

None of the many more- and less-polar products were identified: a small amount of contaminated starting secondary hydroperoxide, 5, was detected in the final fraction collected (total 128mg, indicating recovery of this unchanged hydroperoxide of about 10-20%).

Cyclo-peroxychlorination of an Allylic Hydroperoxide

An initial experiment was performed in which a solution of 98+% *trans*-5-octen-4-yl hydroperoxide, 2, (156mg, 1.1mmol) in deuteriochloroform ($1cm^3$) was treated with tert-butyl hypochlorite ($0.12cm^3$, 1.2mmol). No reaction was observed (by 1-H NMR analysis or by discolouration of the reaction solution) over a period of 24 hours. Addition, however, of a spatula measure of silica gel (Merck 9385) resulted in a vigorous, exothermic reaction, which necessitated water cooling. Re-examination by 1-H NMR showed complete hydroperoxide conversion, chlorodioxolane formation (characterisation below) and no enone formation.

In a duplicate experiment where the silica gel was included prior to hypochlorite addition, rapid conversion was noted, but on this occasion enone [*trans*-5-octen-4-one, 12] and chlorodioxolane formation was noted. A series of preparative scale reactions were performed (3.6mmol hydroperoxide, dichloromethane as solvent) in which variable ratios of chlorodioxolane: enone were obtained in crude and chromatographically separated materials (the best isolated yield of chlorodioxolane was 55% with 7% isolated enone but yields of chlorodioxolane as low as 16% were sometimes obtained).

Attempts to define the effect of prior acid or alkali treatment of the reaction flask were not consistent: in one experiment reaction (without added silica gel) in a sodium hydroxide-washed flask was more rapid than that in a hydrochloric acid-washed flask, but in a duplicate reaction in similarly treated flasks, resulted in similar product mixtures: acid washed/alkali washed reactions flasks (chlorodioxolane: enone: allylic hydroperoxide) = (60/65: 22/18: 18/17)].

The isolated chlorodioxolane fraction (R_f, DCM = 0.63, slowly ADADH positive colour reaction) gave a satisfactory combustion analysis for 4-chloro-5-ethyl-3-n-propyl-1,2-dioxolane, 13 (%, calc/found: C=53.8/53.7; H=8.5/8.4), but 13-C NMR spectroscopy showed the presence of one principal isomer and at least two others. The data for the principal isomer is: [13-C NMR] 90.42, 89.13, C3 and C5; 68.91, C4; 33.56, 24.88, 19.34, $3xCH_2$; 13.87, 10.06, $2xCH_3$. The two minor isomers showed absorptions (in order corresponding to that above) of 91.78, 83.69, plus two obscured?; 62.66, 61.59; 41.91, 30.29, 2.11, 24.11 19.46, 16.84; 13.87, 13.46, 9.85, 9.63. Initial attempts to correlate any of these data to the products of chlorodemercuration of the 4-mercurated-1,2-dioxolane 1, X=Cl were not successful. [1-H NMR] for principal isomer: 4.180, dt, J_t=6.6Hz and 4.254, dt, J_t=7.3Hz ^{3}CH and ^{5}CH; 3.780, t, ^{4}CH, $J_{3,4}$=$J_{4,5}$=4.9Hz; 1.3-1.7, m, $3xCH_2$; 0.930 and 0.883, 2xt, each J=7.2Hz, $2xCH_3$.

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