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# β-Peroxyalkyl radicals and their role in the generation of epoxides during the autoxidation of alkenes. An example of the interplay of free radical, peroxide and organometallic chemistries *

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**Abstract**

The systematics of the γ-scission reactions of β-peroxyalkyl radicals to yield epoxides have been extended to include variations in the degree of alkylation at the α- and β-carbon atoms and in the nature of the departing alkoxyl radical. The ratios of geometrically isomeric epoxides so produced have been shown to be dependent upon the steric bulk of the $C_\alpha$- and $C_\beta$-substituents but rather independent of the nature of the departing alkoxyl radical. The relative importance of 1,5-H atom transfer in β-peroxyalkyl radicals has been considered and some evidence for its occurrence adduced. The relevance of these findings to published data for alkene autoxidation is discussed in terms of two competing pathways, in which, it is suggested, steric factors determine the outcome.

## Introduction

The rich interplay between the chemistries of free radicals, of peroxides and of organometallic compounds has formed a cornerstone of Alwyn Davies's discoveries. His early survey [1] of the organic peroxide literature is still a valuable resource and a few examples of his many pertinent discoveries include the role of free radicals and peroxides during the autoxidation of organometallic compounds [2], the ready generation of free radicals during the photolysis, *inter alia*, of cyclopentadienyl–tin and –lead compounds [3] and the recent singlet oxygenation of alkylmetal compounds [4]. This theme has been carried forward by a number of Alwyn's research associates and one of them, John Bloodworth, has shown [5] that

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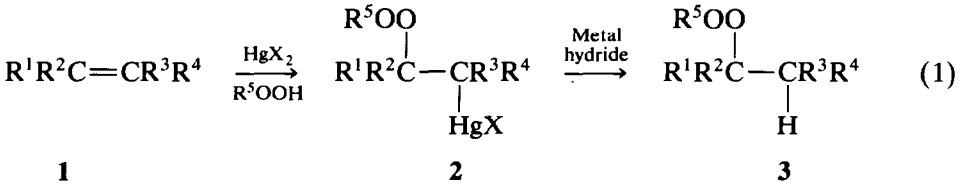
* Dedicated to Professor Alwyn G. Davies in recognition of his many valuable contributions to the areas of free-radical, organometallic and peroxide chemistries.

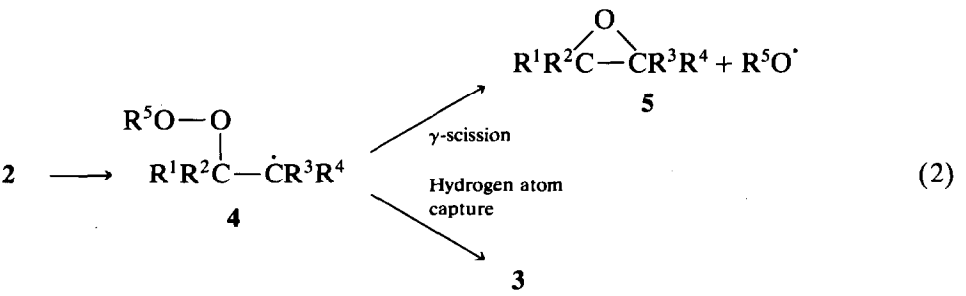
a peroxide variant of the oxymercuriation/hydridodemercuriation procedure could provide a valuable route to many difficultly accessible organic peroxides (eq. 1).



(1)

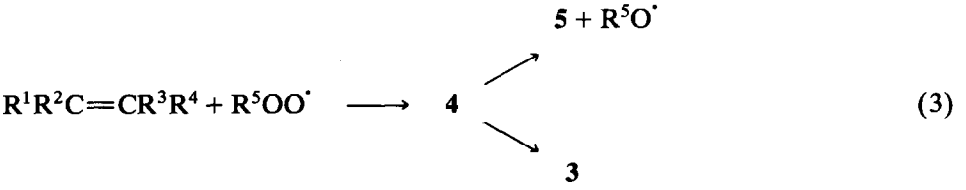
The first step in this procedure occurs as a result of clean, ionic, Markovnikov-directed *trans*-addition, and can be controlled to provide high yields of easily isolated stable peroxymercurials. In contrast, however, early investigations [6] by Bloodworth and the Soviet scientist, George Bylina (a representative of the many visiting international workers who have enjoyed the hospitality of the Fourth Floor at University College London) showed that the second step was complicated by a greater or lesser degree of conversion of the peroxymercurials into epoxides rather than dialkyl peroxides.

Hydridodemercuriation of oxymercurials, using metal hydrides, reliably involves the formation of intermediate free radicals [7], and in these cases it was the partitioning between unimolecular $\gamma$-scission of the intermediate $\beta$-peroxyalkyl radicals **4**, and their capture of hydrogen atoms, that determined the products obtained.



(2)

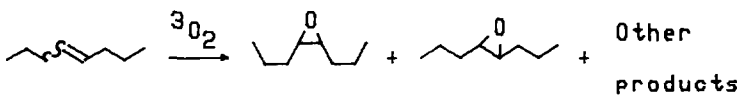
In terms of peroxide synthesis, this complication can be partly overcome by performing the reaction in the presence of a high concentration of a good hydrogen atom donor, and thus hydridodemercuriation in neat tri-n-butyltin hydride, at low temperature, facilitates diversion of the product to organic peroxides, **3** [8]. On the other hand, the generation of $\beta$-peroxyalkyl radicals, **4**, as reaction intermediates, provides a valuable entry into understanding hydrocarbon autoxidation processes. Long before these discoveries, it had been proposed [9] that these species were formed by addition of peroxyl radicals ($R^5OO^{\cdot}$) to alkenes (eq. 3), and this reaction is now considered [10] to be a key component in free radical chain autoxidations.



(3)

By conversion of peroxymercurials into $\beta$-bromoperoxides and then reaction of these species under free radical conditions, Davies, Bloodworth, Roberts and others were able to calculate rate constants for some of these $\gamma$-scission ($S_Hi$) reactions [11]. Taking the $\gamma$-scission rate constant for the 2-t-butylperoxyethyl radical as a benchmark (**4**, $R^1$–$R^4$ = H; $R^5$ = $^t$Bu: $k_\gamma = 4 \times 10^3$ $s^{-1}$ at 25°C), the present state of understanding of this reaction is as follows. Partial or full alkylation or arylation at $C_\beta$ promotes the scission reaction (an effect ascribed [11a] to compression of the $C_\alpha$–$C_\beta$–O bond angle: the "Thorpe–Ingold" effect) while alkylation at $C_\alpha$ also promotes the closure (rationalised [11b] by polar stabilisation of the transition state). The reaction has also been shown to be subject to a powerful stereoelectronic requirement [12]: for ready reaction a *trans*-anti-periplanar relationship between the SOMO [the $C_\alpha(2p_z)$ orbital] and the peroxide bond is necessary: this can have profound effects on the rates of ring closures in cyclic systems. A comparison of the relevant data has been collected in earlier publications [11b,13].

In terms, then, of understanding alkene autoxidation, these findings fully supported the older speculations and the matter might have been seen to be concluded. We were, however, drawn to consider this question again by certain puzzling aspects of data reported for some simple autoxidations. Thus, for example, Pritzkow and co-workers [14] reported that autoxidation of neat 4-octenes at 85°C gave, among other products, mixtures of epoxides whose stereochemical ratios varied with the nature of the starting alkene (eq. 4).




| | | | |
|---|---|---|---|
| cis-alkene | ⟶ | 1 : | 1.6 |
| trans-alkene | ⟶ | 1 : | 8.0 |

(4)

Similarly, Brill and Barone [15] had reported that the isomer ratios of epoxides formed during 2-butene autoxidations at 120°C were also dependent upon the stereochemistry of the starting alkene; the *cis*-alkene giving a *cis* : *trans* epoxide ratio of 1 : 1.5 and the *trans*-alkene a corresponding ratio of 1 : 3.3.

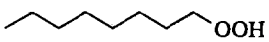
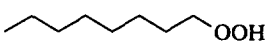
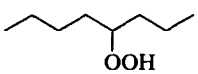
Since autoxidations of mono-enes proceed without stereochemical scrambling of the substrate, we developed the hypothesis that such results could be best explained by the occurrence of competing pathways for epoxide formation during the reaction of each alkene in each pair. In order to assess this hypothesis we needed to be sure of the stereochemical outcomes of the competing mechanisms.

## Results

In order to address the autoxidation data for the isomeric 4-octenes we needed to study $\gamma$-scission reactions where the $\alpha$- and $\beta$-attached alkyl groups were somewhat larger than hitherto examined but, more importantly, we needed to discover whether the nature of the departing alkoxyl radical was capable of influencing the $\gamma$-scission step. This latter requirement arises from the fact that, in

Table 1

Epoxide product ratios from the alkylperoxymercuriation/alkaline sodium borohydride reduction of the isomeric 4-octenes

| Starting alkene | Starting hydroperoxide | Product epoxide ratio (*cis* : *trans*) |
|---|---|---|
|  | $^t$BuOOH | 1:6.7 |
|  | $^t$BuOOH | 1:6.7 |
|  | $^t$BuOOH | 1:5.9 [a] |
|  |  | 1:6.0 |
|  |  | 1:5.9 |
|  |  | 1:8.1 |
|  |  | 1:8.1 |
|  |  | 1:5.6 |

[a] Reduction at 40–50°C (refluxing reaction mixture), otherwise using ice-cooled reaction mixtures.

the autoxidations of interest, the added peroxyl radical ($R^5OO^{\cdot}$ in eq. 3) would most probably contain an allylic alkyl group.

We therefore carried out the peroxymercuriation/hydridodemercuriation sequence on both *cis*- and *trans*-4-octenes: initially using tert-butyl hydroperoxide and then with representative *primary* and *secondary* hydroperoxides, to give the results collected in Table 1. In no cases were dialkyl peroxides detected among the products and so we concluded firstly that the rate of $\gamma$-scission reaction was not being retarded by these variations in the departing alkoxyl group.

Secondly, we noted that rotational equilibration was apparently occurring prior to the scission step and that the relative invariance in the product epoxide ratio (*cis* epoxide : *trans* epoxide of about 1 : 7) and its similarity with that obtained for the 3-hexene-derived $\beta$-tert-butyl peroxy alkyl radicals [11b] indicated that the product ratio from the $\gamma$-scission step could be expected to be rather similar for all $\beta$-(alkylperoxy)alkyl radicals where single n-alkyl groups (larger than methyl) are located at $C_\alpha$ and $C_\beta$.

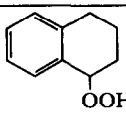
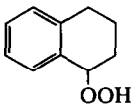
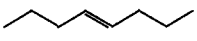
The second question to be addressed was whether or not variation in the electronic nature of the departing alkoxyl radical would influence the epoxide product ratio in the $\gamma$-scission step.

A number of attempts to prepare peroxymercurials containing $\beta$-(allylperoxy)-substituents were either compromised by intramolecular cyclisation of the allylic hydroperoxide used [16a] or failed due to the apparent instability of the desired products †. In order to circumvent these problems, we resorted to use of benzylic hydroperoxides as electronic mimics of allylic hydroperoxides.

Accordingly, we undertook mercury(II) trifluoroacetate-mediated peroxymercuriations of the isomeric 4-octenes using cumene hydroperoxide and of the isomeric

Table 2

Epoxide product ratios from the alkaline sodium borohydride reduction of peroxymercurials containing benzylic groups

| Starting alkene | Starting hydroperoxide | Product: epoxide ratios (*cis*:*trans*) |
|---|---|---|
|  |  | 1:3.8 [a] |
|  |  | 1:4.6 [b] |
|  | $PhC(Me)_2OOH$ | 1:9.1 [b] |
|  | $PhC(Me)_2OOH$ | 1:9.5 [b] |

[a] By $^{13}C$ NMR analysis. [b] By $^{1}H$ NMR analysis.

2-butenes using $\alpha$-tetralyl hydroperoxide. The reactions using cumene hydroperoxide requiring a modified procedure (reaction in the presence of solid sodium bicarbonate) since the hydroperoxide was very sensitive towards acid-catalysed decomposition. For the reactions using $\alpha$-tetralyl hydroperoxide, pairs of diastereoisomeric peroxymercurials were formed, essentially no diastereoselection across the peroxide bond being observed. In all these cases, the intermediate peroxymercurials were isolated and fully characterised (see Experimental).

Hydridodemercuriation under the usual conditions [16b] gave largely epoxides, the ratios of which are shown in Table 2. Reaction of the 2-butene/$\alpha$-tetralyl hydroperoxide-derived peroxymercurials provided modest quantities of dialkyl peroxide along with the epoxides in molar ratios for dialkyl peroxide to epoxides of 0.1:1. ** This ratio is close to that reported for the corresponding reactions of the analogous tert-butylperoxymercurials [16b] and therefore we can infer that the departing alkoxyl radical does not appear greatly to influence the *rate* of the peroxide $\gamma$-scission.

Because of our particular interest in the autoxidation chemistry of isoprenes [17], and especially in that of the hydrocarbon component of natural rubber, we

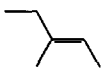
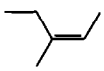
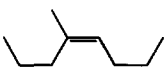
† Attempted peroxymercuriations of either 4-octene, using allylic hydroperoxides [(*E*)-5-octen-4-yl hydroperoxide or 2,3-dimethyl-3-buten-2-yl hydroperoxide] either directly (alkene/mercury(II) acetate or trifluoroacetate/hydroperoxide) or indirectly (prior formation of trifluoroacetoxymercurial and then hydroperoxide addition [8b] or attempted acid catalysed exchange of preformed methoxymercurial [16c*]) were, in all cases, without success.

* Reference number with asterisk indicates a note in the list of references.

** Authentic 1-(2-butylperoxy)-1,2,3,4-tetrahydronaphthalene was prepared in better yield by applying the sequence to 1-butene, where slower $\gamma$-scission of the intermediate primary alkyl radical results in the enhanced peroxide:epoxide ratio of 1.9:1. This ratio may be compared with the corresponding sequences for 1-butene using tert-butyl- and cumene hydroperoxides where peroxide:epoxide ratios of 4.3:1 and 3.2:1 were obtained, data which also serve to illustrate the modest influence of the departing alkoxyl radical on the rate of the $\gamma$-scission reaction.

Table 3

Products obtained from the tert-butylperoxymercuriation/hydridodemercuriation of representative trialkylated alkenes

| Alkene | *cis*-epoxide : *trans* epoxide | Alkene recovery as epoxides |
|---|---|---|
|  | 1:0 | 36% epoxide [a]<br>26% alkene |
|  | 1:0 | 84% [b] ( > 99% epoxide, remainder alkene)<br>49% isolated by chromatography |
|  | 1:1.6 [b]<br>1:1.4 [c]<br>1:1.2 | 82% [b]<br><br>90% [a] |
|  | 1:1.5<br>1:1.6 | 70% [b]<br>73% [a] |
|  | 1:1.8 [c] | 80% [b] |

[a] From 400 MHz $^1$H NMR spectral integration (*vs.* added benzene standard) of crude reduction product. [b] From 400 MHz $^1$H NMR spectral integration and weight of isolated crude product after rotary evaporation of solvent (bath 0–5°C/60 to > 25 mmHg pressure). [c] From averaged 100 MHz $^{13}$C NMR spectral integration.

were especially keen to examine the behaviour of more highly substituted β-peroxylalkyl free radicals. This required extension of the peroxymercuriation/hydridodemercuriation sequence to the reactions of some trialkylated alkenes (eq. 5).

$$R^1C(Me)=CHR^2 + {}^tBuOOH + HgX_2 \longrightarrow {}^tBuOO(H)\,R^1C(Me)-CHR^2(HgX) \xrightarrow[NaOH]{NaBH_4} \text{products} \quad (5)$$

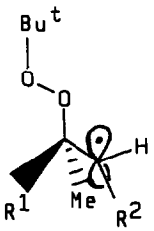
On the basis of the previously-discussed stereospecificity of oxymercuriation, we were confident that the initial step in the reactions detailed in eq. 5 would proceed with the indicated regiochemistry. This belief was explicitly verified for the reaction where 1-methylcyclohexene was the substrate and for the other reactions detailed below, this regiochemistry was assumed.

In none of the product mixtures obtained after hydridodemercuriation (see Table 3) were dialkyl peroxides detected. In the case of the 1-methylcyclohexene-derived product, detailed scrutiny of the chromatographically-separated product mixture afforded no indication of any of the expected hydrogen atom-trapped product, 1-tert-butylperoxy-1-methylcyclohexane.

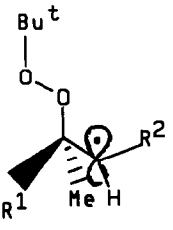
The data for the geometrically isomeric 3-methyl-2-pentenes indicated that, like the data described for the β-peroxyalkyl radicals discussed above, rotational

equilibration appeared to give essentially identical product epoxide ratios from diastereoisomeric pairs of $\beta$-tert-butylperoxymercurials.

In these acyclic instances, the appropriate $\gamma$-scission steps will result from two isomeric transition states which will presumably be distinguished from one another by the energy difference dictated by the vicinal interactions where the $\alpha$-alkyl group is proximal to either the $\beta$-methyl (**6**) or the $\beta$-n-alkyl group (**7**). The product epoxide ratios suggest that, according to this analysis, the energy difference between these transition states is rather small.




6

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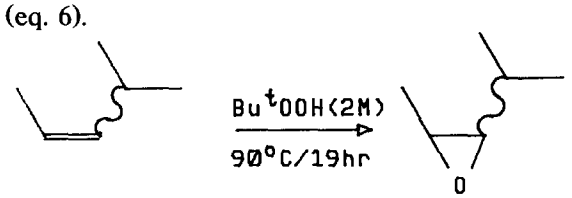
## Discussion

Apart from the peroxyl radical addition/$\gamma$-scission pathway indicated earlier, two other routes resulting in epoxide formation during autoxidation have been discussed in the literature.

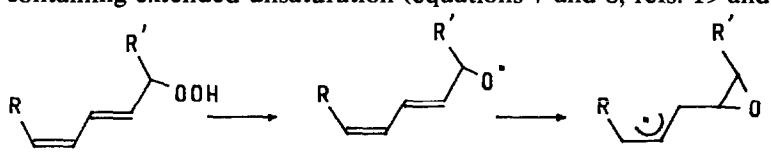
Firstly, direct delivery of oxygen by peroxides formed in autoxidizing media has been considered. Brill and Indictor [18] demonstrated the viability of such reactions by showing that the *syn* epoxidation of isomeric 4-methylpent-2-enes by t-butyl hydroperoxide at 60–100°C was a stereospecific, if somewhat slow, reaction (eq. 6).



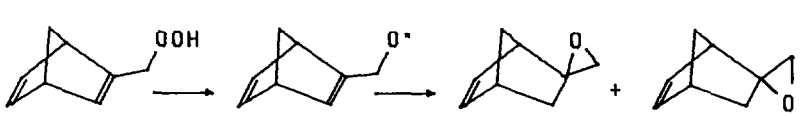

cis-alkene ⟶ cis-epoxide 20-25%

trans-alkene ⟶ trans-epoxide 20-25% (6)

A second pathway, involving the closure of unsaturated alkoxyl radicals to form $\beta$, $\gamma$-epoxyalkyl radicals, has been shown to be a route to epoxides in systems containing extended unsaturation (equations 7 and 8, refs. 19 and 20 respectively).

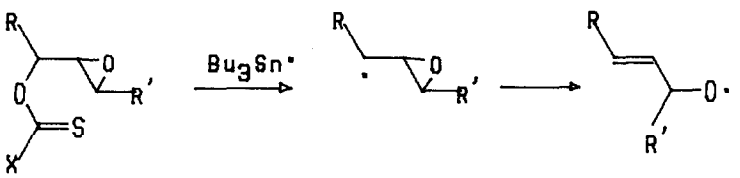



(7)



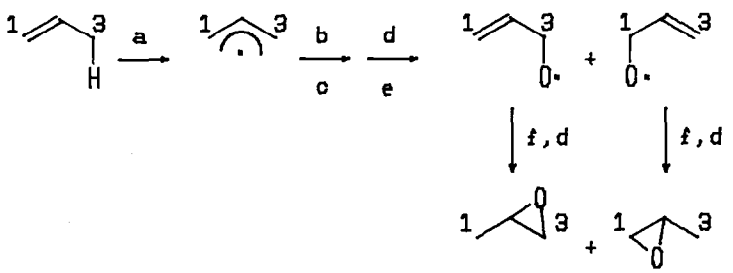

(8)

The balance between allylic alkoxyl radicals and their isomeric $\beta,\gamma$-epoxyalkyl radicals is, however, finely poised: for simple cases, the results of ESR [21] and of hydrogen-atom capture experiments (eq. 9, [22]) appear to favour ring-opened forms.




X = N-imidazoyl (9)

A key indicator which distinguishes these mechanisms is the stereochemistry of the product epoxide(s) in relation to that of the substrate alkene. In the direct reaction (*cf.* eq. 6) geometrical integrity is maintained: a *cis*-alkene will generate a *cis*-epoxide and so on. In the unsaturated alkoxyl radical closure (*cf.* equations 7–9), alkene-derived allylic alkoxyl radicals could generate at least a pair of positionally isomeric epoxides through a familiar sequence of events (eq. 10).




a = -H• ; b = $+O_2$ ; c = 1,3 $O_2$ equilibration ;

d = +H• ; e = -HO• ; f = allyloxy / (oxiranyl)methyl radical equilibration. (10)

Finally, in the peroxyl radical addition/$\gamma$-scission sequence (eq. 3), loss of geometric integrity would follow if rotational equilibration were to occur in the $\beta$-peroxyalkyl radical prior to the $\gamma$-scission step.

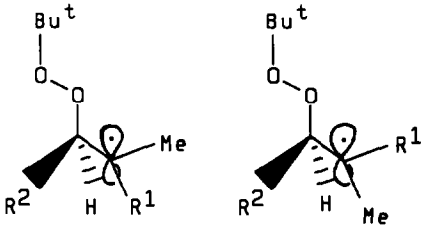
The regiochemical outcomes of epoxide formation in the neat alkene autoxidation data presented by Brill [5] and Pritzkow [14] (see above) allow us to discard allylic alkoxyl radical closure as a contributor for the mono-ene cases and for this reason we turn our attention to the direct epoxidation and the peroxy radical addition/$\gamma$-scission pathways.

The data for the peroxymercuriation/hydridodemercuriation reactions of the 2-butenes and the 4-octenes (Tables 1 and 2), when compared with the data for the alkene autoxidations (see eq. 4 and the subsequent discussion) suggest that, for the *trans* alkenes, epoxide formation during autoxidation is almost exclusively the result of the peroxyl radical addition/$\gamma$-scission pathway while for the *cis*-alkenes

competitive pathways appear to be operating. The reported data (ignoring the seemingly small effects of temperature and media) might then be factorised into a ratio, for the *cis*-4-octene autoxidation, of (direct epoxidation):(addition/scission) of about 1:2, while for *cis*-butene the corresponding ratio is about 1:4. *

For tri-substituted alkenes, a regiochemical complication in comparing the two sets of experimental data becomes apparent. One may question whether the β-peroxyalkyl radicals generated in the peroxymercuriation/hydridodemercuriation reactions described, fairly model the corresponding radicals formed during the autoxidation of the substrate trialkylated alkenes. In the latter reactions, peroxyl radical addition might be expected to occur principally to form *tertiary* radicals such as **8/9**, rather than the *secondary* radicals **6/7** involved in the model sequence. This expectation is based on at least two considerations: firstly the postulated addition would be sterically least demanding and secondly it would lead to more stable *tertiary* radicals.

For such a preferred addition mode, the two epoxide-producing radical transition states are likely to be as depicted in **8** and **9**.




**8** **9**

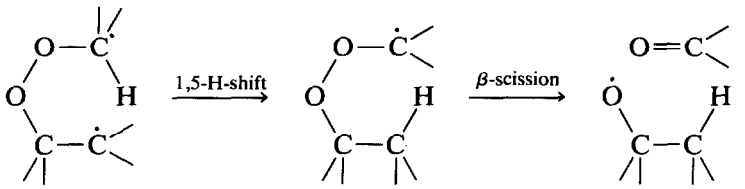
The energy differences between these two states will be determined by steric arguments like those advanced for **6** and **7** above, and thus we predict that the closure ratio for **6/7** will be very similar to that for **8/9**.

Although we are at present unable independently to generate *tertiary* radicals such as **8/9**, we have examined the epoxide fraction formed during the autoxidation of (*E*)-4-methyl-4-octene (as a neat alkene under oxygen at 85°C) and we find an epoxide ratio (*cis*:*trans*) of (1:1.3) after 6 h reaction and of (1:1.5) after a total of 24 h. These data compare favourably with the ratio obtained from the γ-scission behaviour of the *tertiary* (5-tert-butylperoxy)-5-methyl-4-octyl radical generated in the peroxymercuriation/hydridodemercuriation sequence (last entry in Table 3), and we therefore feel reasonably confident in relying on the transition state comparison made earlier. Accordingly, therefore, for *cis*-isoprenoids at least, we believe that the principal route to epoxides during autoxidation will be the result of the peroxyl radical addition/γ-scission pathway [17c].

As an adjunct to this investigation, one alternative reaction pathway for β-peroxyalkyl radicals that we were interested in assessing was the occurrence, or

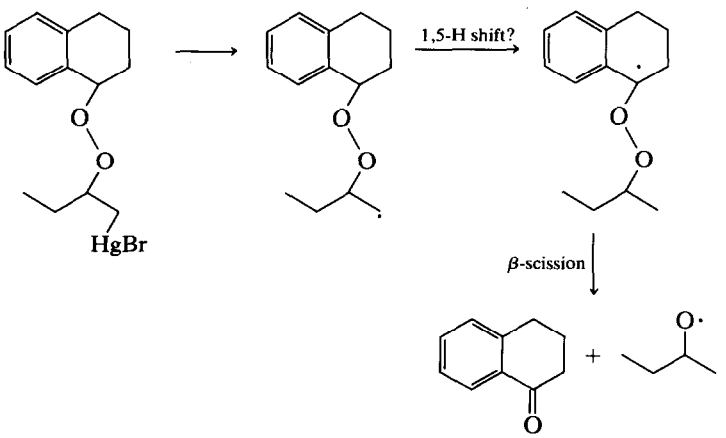
* It is interesting to note that competitive ionic/free radical pathways to epoxide formation have been suggested [23] to occur during the co-oxidation of alkene/benzaldehyde mixtures (where the adding peroxyl radical was deemed to be the aldehyde-derived benzoylperoxy radical) and that the radical addition pathway seemed to be preferred for increasingly more reactive (highly alkylated) alkenes.

otherwise, in these radicals of intramolecular 1,5-hydrogen atom shifts. We envisaged that this event might be manifested by the concurrent formation of carbonyl compounds (by $\beta$-scission of the consequent $\alpha$-peroxyalkyl radicals: eq. 11) and accordingly looked for relevant fragmentation products.




(11)

A particularly favourable set of reactions to examine this possibility was the hydridodemercuriations of the $\alpha$-tetralin hydroperoxide-derived peroxymercurials, where production of $\alpha$-tetralone might be detected (eq. 12):




(12)

In the event, reaction of the 1-butene-derived peroxymercurial did indeed give trace quantities of $\alpha$-tetralone: control experiments indicated that its formation was most likely not the result of base-induced decomposition of the starting peroxymercurial or of the product dialkylperoxide. Furthermore, reduction of the same peroxymercurial under neutral conditions (tri-n-butyltin hydride in degassed perdeuteriobenzene) also gave a product mixture in which $\alpha$-tetralone could be detected. The reaction conditions were chosen to permit the formation of epoxide and the yield of ketone approximated to that of the epoxide, but analysis of the product mixture to give an accurate value of the 1,5-hydrogen atom shift rate constant is precluded by the absence of a reliable value of the rate constant for the reaction between tri-n-butyltin hydride and the intermediate benzylic $\alpha$-peroxyalkyl radical. However assuming that this bimolecular reaction is slow in comparison with the, expectedly fast, unimolecular $\beta$-scission step, an estimate for the 1,5-hydrogen atom shift rate constant as, at most, approximately that of the $\gamma$-scission rate constant for the starting $\beta$-peroxyalkyl radical (*ca.* $10^5$ $s^{-1}$) can be suggested. Since the formation of carbonyl compounds in alkene autoxidations can arise through other pathways, such as peroxyl radical disproportionation, and since they are usually isolated in small amounts, such 1,5-hydrogen atom shifts appear to be relatively unimportant in simple alkene autoxidation: a situation that contrasts

dramatically with that which pertains in, for example, di-iso-propyl ether and 2,4-dimethylpentane autoxidations [10,24].

## Conclusion

The data presented point to the conclusion that epoxide formation during the autoxidation of both *trans*-1,2-disubstituted- and 1,1,2-trisubstituted-alkenes is principally the result of the peroxyl radical addition/$\gamma$-scission pathway, while for *cis*-1,2-disubstituted alkenes direct epoxidation by hydroperoxide is an effective competitor.

It may be reasonable to speculate why this is so. Steric inhibition of the direct pathway appears to be the controlling factor. Judging from their similar ionisation potentials [25], neither *cis* nor *trans*-1,2-disubstituted alkene in an isomeric pair will cause electronic stabilization of their reaction with peroxyl radicals or with hydroperoxides, a conclusion which is also reached upon consideration of the available alkene/peroxyl radical addition rate data: see the discussion in Ref. 10, pp. 40–42. On the other hand, for both reactions, a steric advantage for the *cis*-alkenes might be expected. This advantage is, however, most likely to be manifested in the direct epoxidation reaction, since, of the two, this seems to be the less facile and, presumably, it is in the transition state of this reaction that the reacting partners will be most closely assembled and will accordingly encounter the greatest steric influence. Partial confirmation of this view is afforded by inspection of the relative rates of *cis*- and *trans*-1,2-disubstituted alkene epoxidations by peracids (see Ref. 26, p. 455 for leading references) where it has been found that the *cis*-isomers react at about 1.5 times the rate of the *trans*-isomers in what is, in comparison with direct hydroperoxide epoxidation, a rather more facile (and hence sterically less sensitive) reaction.

## Experimental

### *Instrumental and chromatography*

1-H and 13-C NMR spectra of deuteriochloroform solutions were recorded, using either Varian VXR-400 or General Electric QE300 instruments and under such conditions as to ensure, for 1-H NMR experiments, quantitative signal analysis. Chemical shift data is presented in units of $\delta$ (parts per million) with respect to internal TMS with coupling constants in Hz. Where appropriate, material balances were confirmed by addition of suitable quantities of internal standards.

Flash chromatography was performed under dinitrogen pressure, over Merck 60 silica, with analysis by TLC on aluminium foil-backed silica-coated plates (Merck Art. No. 5554) using ADADH spray [27] for hydroperoxide detection and either heated acidic vanillin or heated phosphomolybdic acid sprays for general detection.

### *Materials*

tert-Butyl hydroperoxide was obtained by drying a dichloromethane solution of 70% (w/w) aqueous material (Aldrich). Cumene hydroperoxide (Aldrich, technical) was freed from contaminant cumene by flash chromatography: a portion (2 g)

on silica (15 g, Merck 60) was eluted first with pentane (100 $cm^3$) and then with dichloromethane (100 g). Evaporation of the second eluate gave the pure hydroperoxide (1.69 g, 85% (w/w) recovery). $^1H$ NMR: $\delta$ 7.78 (OOH), 7.45–7.22 (phenyl), 1.560 ($CMe_2$), $R_{f,DCM} = 0.25$.

Cyclohexyl hydroperoxide was prepared by controlled, low temperature autoxidation of etherial cyclohexylmagnesium chloride [28] (albeit in low yield: 12%) and was purified by base extraction and reacidification. $^1H$ NMR: $\delta$ 8.8 (OOH), 3.93 (br m, CH.OO), 2.1–1.2 ($5 \times CH_2$).

The 1- and 4-octyl hydroperoxides were prepared [29] from the mesylates and purified by basic extraction and either Kugelrohr distillation (1-octyl isomer 34% isolated yield) or chromatography (4-octyl isomer 5% isolated yield). *1-octyl hydroperoxide*: $^1H$ NMR: $\delta$ 8.24 (br s, 1H, OOH), 3.89 (t, 2H, $^1CH_2$, $J_{1,2} = 7.5$ Hz), 1.88–1.22 (10H, $5 \times CH_2$), 0.89 (t, $^8CH_3$, $J_{7,8} = 6.5$ Hz). *4-octyl hydroperoxide*: $^1H$ NMR: $\delta$ 7.82 (s, 1H, OOH), 3.91 (m, 1H, $^4CH$), 1.7–1.3 (10H, $5 \times CH_2$), 0.98 (t, 6H, $^1CH_3 + {}^8CH_3$, $J = 7.6$ Hz).

1,2,3,4-tetrahydronaphth-1-yl hydroperoxide ($\alpha$-tetralyl hydroperoxide: prepared by autoxidation of tetralin) was the kind gift of Dr. D.S. Campbell.

Reference samples of epoxides were prepared [26] by alkene epoxidation (in dichloromethane at 0–5°C) using 3-chloroperoxybenzoic and, followed by aqueous sodium sulphite and sodium hydrogen carbonate washes, drying ($MgSO_4$) and careful solvent evaporations. $^1H$ and $^{13}C$ NMR data were in accord with literature values: 1,2-epoxybutane ($^1H$ [30], $^{13}C$ [31]); *cis* and *trans*-2,3-epoxybutanes ($^1H$ [32], $^{13}C$ [31,33]); *cis* and *trans*-2,3-epoxy-3-methylpentanes ($^1H$ [34], $^{13}C$ [35]); 1-methyl-1,2-epoxycyclohexane ($^1H$ [36], $^{13}C$ [32]). $^1H$ NMR data for 1-methyl-1,2-epoxycyclopentane have been given previously [36,37], and we find $^{13}C$ NMR data for this compound to be $\delta$ 64.67 (C1), 63.84 (C2), 31.46/27.80 (C3/C5), 19.81 (C4), 17.63 (Me). We have reported NMR data for the isomeric 4-methyl-4,5-epoxyoctanes elsewhere [17b], and for the 4,5-epoxyoctanes we can supplement the partial $^1H$ NMR data [14] and give unpublished $^{13}C$ NMR data as follows: *cis*-4,5-Epoxyoctane $^1H$ NMR: $\delta$ 2.951 (m, 2H, CH(O)), 1.510 (m, 8H, $4 \times CH_2$), 0.984 (t, 6H, $J = 7.2$ Hz, $2 \times CH_3$). $^{13}C$ NMR: $\delta$ 57.19 (C4/C5), 29.84 (C3/C6), 19.93 (C2/C7), 14.07 (C1/C8). *trans*-4,5-Epoxyoctane $^1H$ NMR: $\delta$ 2.668 (m, 2H, CH (O)), 1.39–1.62 (m, 8H, $4 \times CH_2$), 0.959 (t, 6H, $2 \times CH_3$). $^{13}C$ NMR: $\delta$ 58.70 (C4/C5), 34.19 (C3/C6), 19.37 (C2/C7), 13.97 (C1/C8).

t-Butylperoxymercuriations were carried out using mercury(II) acetate with perchloric acid catalysis and a one-fold excess of hydroperoxide, while other peroxymercuriations were carried out using mercury(II) trifluoroacetate and a 10 mol% excess of hydroperoxide, both by previously described procedures (Refs. 16b and 38 respectively) to give either isolated organomercury(II) bromides, or, where crude peroxymercurials were reduced, organomercury(II) trifluoroacetates. Thus, for example, t-butylperoxymercuriation of 1-methylcyclohexene (0.1 mol, freshly opened sample of alkene) under 20% perchloric acid catalysis gave a crude organomercury acetate (oil, 44.53 g), which was converted to the organomercury bromide (41.89 g, 90%), that was recrystallized from hot methanol (34.9 g, 75%, m.p. 74.3–74.9°C). For *cis*-2-methyl-*trans*-2-tertbutylperoxycyclohexylmercury bromide: Anal. Found: C, 28.2; H, 4.3%; $C_{11}H_{21}BrHgO_2$ calc.: 28.36; H 4.55%. $^1H$ NMR: $\delta$ 2.768 (dd, 1H, $^1CH_{ax}$(HgBr), $J_{2ax/3ax} = 12.4$, $J_{2ax/3eq} = 3.6$, $^2J_{Hg} = 185$), 2.144 (m, $^6CH_{ax}$, $^3J_{Hg} = 155$), 1.796 (m, $^6CH_{eq}$, $^3J_{Hg}$ *ca.* 90), 1.2–1.75 (m, $3 \times CH_2$),

1.417 (s, $^2C(Me)_{ax}$), 1.262 (s, $OO^tBu$). $^{13}C$ NMR: $\delta$ 83.68 (C2), 64.73 (C1), 37.89, 30.71, 28.86, 25.15 (C3–C6), 23.09 (Me), 79.69 and 26.77 ($OO^tBu$).

By analogy to reactions for the 3-hexenes [16b], perchloric acid catalysed t-butylperoxymercuriation of *cis*- and *trans*-4-octenes provided equilibrium mixtures of peroxy-, acetoxy- and hydroxy-mercurials (*ca.* 6:1:1 for both reactions).

An example of the modified procedure that was required for reactions involving the particularly acid-sensitive cumyl hydroperoxide is as follows. A magnetically stirred solution of purified cumyl hydroperoxide (0.85 g, 5.5 mmol) in dichloromethane (10 $cm^3$) containing suspended sodium hydrogencarbonate (0.84 g, 10 mmol) was presaturated at room temperature, with 1-butene. To this mixture, under a slow stream of the alkene, mercury(II)trifluoroacetate (2.14 g, 5 mmol) was added in portions. According to the individual preparation, transient yellow coloured solids formed, but, within five minutes, testing of an aliquot of the colourless reaction solution for free mercury(II) ions with aqueous sodium hydroxide revealed complete reaction. Conversion to the organomercury(II) bromide was carried out, after washing the decanted organic layer with three portions of water, by stirring, for thirty minutes with a one fold excess of aqueous sodium bromide (*ca.* 1 *M*), after which drying ($MgSO_4$) and solvent evaporation gave a cloudy oil (2.01 g). Flash chromatographic purification (15 g silica; 1:1 v/v pentane/dichloromethane eluant; TLC analysis using the same solvent mixture) gave a pure sample of 1-bromomercuri-2-(cumylperoxy)butane ($R_f$ 0.55, colourless gum, 383 mg, 16% yield). Subsequent fractions contained the peroxymercurial (*ca.* 10% yield) contaminated with acetophenone ($R_f$ 0.22; $^1H$ NMR confirmation) and cumyl hydroperoxide ($R_f$ 0.19; ADADH TLC colour reaction and $^1H$ NMR analysis).

Spectroscopic analysis of the isolated peroxymercurials is reported in Tables 4 and 5.

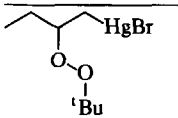
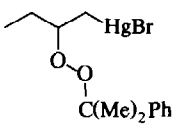
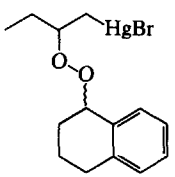
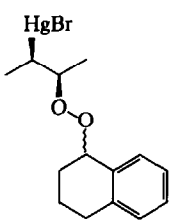
*Hydridodemercuriations*

These reactions were carried out in biphasic media essentially as described previously [8b], with the exception that deuteriochloroform was used as the organic solvent in order to permit direct NMR analysis without the need for solvent evaporation. A typical procedure follows.

A sample of the above-described 1-butene-derived peroxymercurial (288 mg, 0.59 mmol) in ice-cold deuteriochloroform (1.5 $cm^3$), was treated with ice-cold aqueous sodium hydroxide (2 *M*, 0.65 $cm^3$) and this mixture was then promptly added to a well-stirred, ice-cooled solution of sodium borohydride (98 mg, 2.6 mmol) in aqueous sodium hydroxide (2 *M*, 5 $cm^3$). After stirring on ice for 10 min and for a further 10 min with the cooling bath removed, the layers were separated and, to the organic layer, deuteriochloroform extracts ($2 \times 1$ $cm^3$) of the aqueous layer and an NMR quantification standard (toluene, 106 $\mu$l, 1 mmol) were added. After drying ($MgSO_4$) in a stoppered container, $^1H$ NMR analysis was, without undue delay, performed to give the product ratio described. In this particularly favourable example such analysis gave an organic material balance of 95% (the recovered mercury bead, 116 mg, representing 98% recovery). In general, material balances in excess of 80% were realised. In cases of uncertainty, duplicate experiments, often with supporting analytical techniques (GLC and/or $^{13}C$ NMR), were performed. In those cases where peroxymercurials containing *secondary*

Table 4

$^1$H NMR and analytical data for isolated acyclic peroxymercurials

| Structure | CH(OOR) | $CH_{(2)}HgBr$ | OOR | Other | Notes |
|---|---|---|---|---|---|
|  | 4.19 (m; $^3J_{Hg}$ = 200) | 2.224 (dd, $J_{gem}$ = 12.0, $J_{1,2}$ = 3.8; $^2J_{Hg}$ = 210) and 1.911 (dd, $J_{1,2}$ = 8.1; $^2J_{Hg}$ obscured) | 1.282 (s) | 1.67 and 1.47 (2×m, $^3CH_2$), 0.988 (t, 7.5, $^4CH_3$) | For low field $^1$H NMR data, see ref. 39 |
|  | 4.127 (m; $^3J_{Hg}$ = 218) | 2.194 (dd, $J_{gem}$ = 12.0, $J_{1,2}$ = 4.5; $^2J_{Hg}$ = 205) and 1.871 (dd, $J_{1,2}$ = 7.5; $^2J_{Hg}$ obscured) | 7.20–7.55 (m, Ph), 1.625, 1.635 (2×s) | 1.36 and 1.60 2×m, $^3CH_2$), 0.800 (t, 7.5, $^4CH_3$) | Unstable: NMR sample showed decomposition to hydroperoxide |
|  | Major isomer (51%) 4.347 (quin, 5.7; $^3J_{Hg}$ = 260). Minor isomer (49%) 4.297 (quin, 6.0; $^3J_{Hg}$ = 234) | 2.19–2.31 (m) | 7.05–7.41 (m, Ar), 5.021/5.041 (2×t, 3.6), 2.6–2.9 (2H), 2.3–2.4 (1H), 1.9–2.0 (1H), 1.6–1.9 (2H) | 1.46 (m, $^3CH_2$), 0.957 and 0.952 (2×t, 7.5, $^4CH_3$ for two isomers) | Calc./found (%) C 33.6/33.4 H 3.8/3.8 |
|  | 4.38 (m; both isomers superimposed; $^3J_{Hg}$ = 265) | 2.57 (m; both isomers superimposed $^2J_{Hg}$ = 220) | 7.05–7.45 (m, Ar), 5.042/5.059 (2×t, 3.6), 2.6–2.9 (2H), 2.3–2.4 (1H), 1.3–2.0 (3H) | 1.455 and 1.475 (2×d, 7.5; $^3J_{Hg}$ = 270), 1.295 and 1.349 (2×d, 6.0) | Calc./found (%) C 33.6/34.1 H 3.8/4.0 |

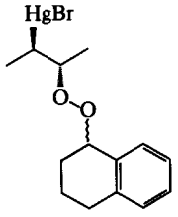
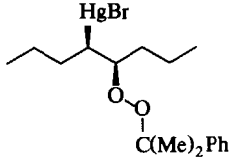
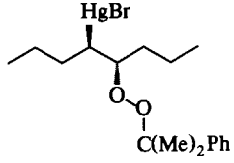
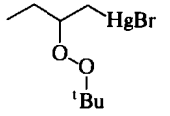
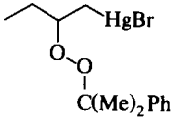
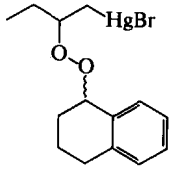
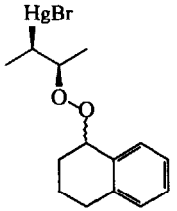
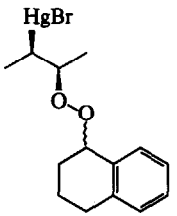
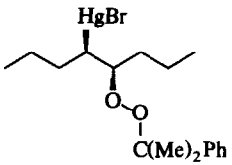
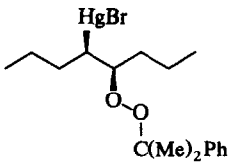
| | | | | | |
|---|---|---|---|---|---|
|  | 4.48 (m; both isomers superimposed; $^2J_{Hg}$ = 360 for both isomers) | 3.08 (m; both isomers superimposed; $^2J_{Hg}$ = 190 for both isomers) | 7.10–7.40 (m, Ar), 5.04 (t, 3.5; both isomers), 2.6–2.9 (3H), 2.30–2.45 (1H), 1.3–2.1 (2H) | 1.359 (d, 7.2; both isomers $^3J_{Hg}$ = 275), 1.284 and 1.251 (2×d, 6.0; $^4CH_3$) | Calc./found (%) C 33.6/34.2 H 3.8/3.6 |
|  | 4.132 (ddd, $J_{4,5}$ = 4.8, $J_{5,6}$ = 5.1 and 6.3; $^3J_{Hg}$ = 265) | 2.567 (dt, $J_{3,4}$ = 7.9; $^2J_{Hg}$ = 213) | 7.23–7.49 (m, Ph), 1.632, 1.652 (2×s) | 1.2–1.5 (m, 4×$CH_2$), 0.859 (t, 7.2), 0.910 (t, 7.5) | Unstable, NMR sample showed reversion to alkene and hydroperoxide |
|  | 4.206 (dt, $J_{4,5}$ = 3.5, $J_{5,6}$ = 3.6 and 8.1; $^3J_{Hg}$ = 294) | 3.058 (ddd, $J_{3,4}$ = 6.0 and 10.5; $^3J_{Hg}$ = 202) | 7.20–7.50 (m, Ph), 1.626, 1.631 (2×s) | 1.3–1.6 (m, 4×$CH_2$), 0.948 and 0.793 (2×t, 7.2) | Calc./found (%) C 37.5/37.4 H 5.0/4.8 |

Table 5

$^{13}C$ NMR data for isolated acylic peroxymercurials

| Structure | CH(OOR) | $CH_{(2)}HgBr$ | OOR | Other |
|---|---|---|---|---|
|  | 83.95 ($^2J_{Hg}$ = 123) | 36.61 ($^1J_{Hg}$ = 1534) | 81.16 (q), 29.59 ($CH_3$) | 29.69 ($^3J_{Hg}$ = 183), 10.43 |
|  | 83.89 ($^2J_{Hg}$ = 121) | 37.83 ($^1J_{Hg}$ = 1506) | 144.86 (q); 128.13, 127.29, 125.69 (CH); 83.37 (q), 26.68, 26.57 ($CH_3$) | 29.59 ($^3J_{Hg}$ = 167), 10.22 |
|  | 83.47 and 83.24 ($^2J_{Hg}$ = 116 for both isomers) | 38.39 and 37.99 ($^1J_{Hg}$ = 1520 for both isomers) | 138.70/138.54 (q); 132.62/132.33 (q); 130.97, 128.95, 128.23, 125.65 (CH); 78.58/78.76 ($C_q$); 28.96, 27.01, 18.04 ($CH_2$) | 29.38 and 29.32 ($^3J_{Hg}$ = 150), 10.15 and 10.08 |

| | | | | |
|---|---|---|---|---|
|  | 84.17 and 84.50 ($^2J_{Hg}$ = 120 for both isomers) | 54.44 and 54.72 ($^1J_{Hg}$ = 1550 for both isomers) | 138.83/138.97 (q); 132.49/132.50 (q); 131.19, 128.30/129.13, 125.84/125.88 (CH); 78.93/79.30 ($C_q$); 29.21, 27.25, 18.20 ($CH_2$) | 20.53 and 20.60 ($^2J_{Hg}$ = 100), 18.57 and 18.60 |
|  | 82.87 and 83.06 ($^2J_{Hg}$ = 100 for both isomers) | 55.32 and 55.05 ($^1J_{Hg}$ = 1590 for both isomers) | 138.73/138.82 (q); 132.65/132.70 (q); 131.15, 129.05, 128.44, 125.81/125.90 (CH); 78.80/78.88 ($C_q$); 29.19, 27.19, 18.21/18.30 ($CH_2$) | 19.48/19.68 ($^2J_{Hg}$ = 120) 16.23/16.34 ($^3J_{Hg}$ = 60) |
|  | 86.69 ($^2J_{Hg}$ = 126) | 61.38 ($^1J_{Hg}$ = 1535) | 144.96 (q); 128.05, 127.21, 125.13 (CH); 83.14 (q); 26.85, 26.56 ($CH_3$) | 36.81 (C2, $^3J_{Hg}$ = 89); 35.10 (C6, $^3J_{Hg}$ = 69); 25.83 (C3, $^2J_{Hg}$ = 109); 19.04 (C7); 13.88/14.12 (C1/C8) |
|  | 86.19 ($^2J_{Hg}$ = 116) | 62.36 ($^1J_{Hg}$ = 1540) | 145.03(q); 128.19, 127.35, 125.77 (CH); 83.36 (q); 26.68, 26.79 ($CH_3$) | 36.35 (C3, $^2J_{Hg}$ = 140); 31.82 (C6, $^3J_{Hg}$ = 60); 25.87 (C2, $^3J_{Hg}$ = 102); 19.37 (C9); 14.12/14.02 (C1/C8) |

carbon–mercury bonds were reduced, dialkylperoxides were present, if at all, in only trace quantities, while for apparently more unstable, sterically encumbered peroxymercurials the onset of extensive deoxymercuriation was noted.

Samples of dialkyl peroxides were isolated, where appropriate, from the analytical hydridodemercuriation reaction mixtures. Thus, for example, concentration of the above-described reaction mixture gave a crude product (oil, 834 mg) which was purified by flash chromatography (15 g silica; dichloromethane eluant) to give (initially contaminated with the NMR standard, toluene) 2-(cumylperoxy)butane (69 mg, after toluene removal; 56% isolated yield, being 83% of that indicated from the analysis of the whole reaction mixture). $^1$H NMR: $\delta$ 7.5–7.1 (multiplets, 5H, phenyl), 3.926 (sextet, 1H, $^2$CH, 6.5 Hz), 1.600 and 1.580 (2 × s, PhC(Me)$_2$OO), 1.390 and *ca.* 1.60 (obscured) ($^3$CH$_2$), 1.137 (d, 3H, $^1$CH$_3$, 6.6 (Hz), 0.810 (t, 3H, $^4$CH$_3$, 7.5 Hz). $^{13}$C NMR: $\delta$ 145.71 (*ipso*), 127.91, 126.92, 125.60 (CH), 82.32, 26.83, 26.56 (cumyl), 80.62 (C2), 27.40 (C3), 18.20 (C1), 9.84 (C4). Later chromatographic fractions contained cumyl alcohol, contaminated with traces of more highly oxygenated materials (structural characterization of which will be described elsewhere).

In like fashion, reduction and purification of the product from the 1-butene derived t-butylperoxymercurial (1.6 mmol) gave a toluene-contaminated sample of sec-butyl-t-butylperoxide (203 mg, equivalent to 46% isolated yield: characterized by $^1$H NMR spectroscopy, using published data [8b]) and the $\alpha$-tetralylperoxymercurial gave an almost equimolar mixture of the diastereoisomeric 2-(1,2,3,4-tetrahydronaphth-1-ylperoxy) butanes (49% isolated yield, 80% of that calculated from the analysis of the crude reaction mixture). $^1$H NMR, $\alpha$-tetralylperoxy moiety: $\delta$ 7.39–7.10 (multiplets, 4H), 5.02 (apparent q, *J ca.* 3 Hz), 2.64–2.88 (m, 2H), 2.33–2.45 (m 1H), 1.90–2.06 (m, 1H), 1.75–1.85 (m, 2H). 2-butyl moiety: 4.09 (apparent sextet, 1H, *J ca.* 6 Hz, $^2$CH), 1.66 and 1.50 (multiplets, 2H, $^3$CH$_2$), 1.20 and 1.22 (doublets, 3H, *J ca.* 6.5 Hz, $^1$CH$_3$), 0.95 and 0.92 (triplets, 3H, *J ca.* 6.5 Hz). $^{13}$C NMR, $\alpha$-tetralylperoxy moiety: $\delta$ 138.90, 138.98, 133.11, 132.95 (Cq), 131.08, 128.26, 125.77 (CH), 29.37, 27.39, 27.33 (CH$_2$), 80.53, 80.62 (C1). 2-butyl moiety: 78.35, 78.61 (C2), 27.33, 27.39 (C3), 18.36 (double size, C4), 9.68, 9.89 (C1).

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