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Oxymetallation. Part 24[1]. Preparation of Cyclic Peroxides by Cycloperoxymercuriation of Unsaturated Hydroperoxides.

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Key Words peroxides; hydroperoxides; peroxymercuriation; demercuriation

Abstract *Seventeen unsaturated hydroperoxides have been converted by treatment with mercury(II) acetate and/or mercury(II) nitrate into nineteen new mercuriated cyclic peroxides and by subsequent demercuriation with alkaline sodium borohydride, six new mercury-free peroxides have been isolated. The results greatly extend the range of such reactions and provide information about the stereoselectivities and relative ease of several different modes of cycloperoxymercuriation. It is suggested that the reactions with mercury(II) acetate are kinetically controlled whereas those with mercury(II) nitrate show a component of thermodynamic control of product distribution*

The synthesis of cyclic peroxides has gained in importance as the number of reports of naturally occurring examples with potential pharmacological value has grown[2]. In the 1970's, the recognition of the key role of prostaglandin endoperoxides in the biosynthesis of many hormones stimulated much work on the preparation of 2,3-dioxabicyclo[2.2.1]heptane and its derivatives, homologues, and monocyclic analogues[3]. The 1,2-dioxane and 1,2-dioxolane moieties of the latter are also components of several marine products which exhibit diverse biological activity[2]. The efficacy of the plant extract artemisinin in treating malaria has made 1,2,4-trioxanes a recent focus of attention[4].

Cycloperoxymercuriation has proven to be a versatile method of preparing cyclic peroxides. We first reported its use with the synthesis of secondary alkyl 1,2-dioxolanes and 1,2-dioxanes from α,ω-dienes and hydrogen peroxide[5], and later extended the reaction to cyclooctadienes to give bicyclic peroxides[6]. Others subsequently applied the method to unsaturated hydroperoxides. Several 1,2-dioxolanes have been prepared from allylic[7] and homoallylic[7a,8] hydroperoxides by 5-*endo* and 5-*exo* cyclisations respectively, and a smaller number of 1,2-dioxanes have been made by 6-*exo* ring closure.[8a,9] Unique examples of the preparation of a 1,2-dioxetane[10] and of a 7-membered ring[8a] have also have been reported. The value of cycloperoxymercuriation is enhanced by the fact that the mercurio substituent in the products can usually be replaced by hydrogen or halogen to afford mercury-free peroxides.[5-10] However, side reactions accompany reductive demercuriation and can become dominant, depending upon the experimental conditions and the structure of the cycloperoxymercurial.[5-9]

We have given a preliminary account of the cycloperoxymercuriation of a number of unsaturated hydroperoxides in connection with an examination of 5-*exo* versus 6-*exo* cyclisation[11], the synthesis of bicylic peroxides[12], the separation of isomeric alkenyl hydroperoxides[13], and the preparation of 1,2-dioxanes for flash vacuum pyrolysis[14]. In this paper we provide full details of these and related reactions.

RESULTS AND DISCUSSION

Preparation of Hydroperoxides

The hydroperoxides which have been studied are shown in scheme 1 and were prepared, as indicated, by one of the following five methods.

(1) Allylic chloride or bromide with 30% hydrogen peroxide and base[15] (**1**[13],**2** and **3**).

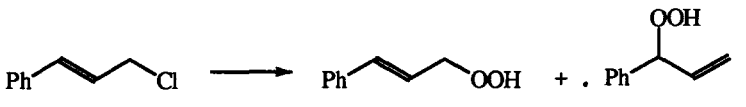
(2) Alkenyl methanesulfonate with 30% hydrogen peroxide and base[16] (**4**,**5**,**6**,**7**,**8**[11] and **10**[17]).

(3) Alkenyl trifluoromethanesulfonate with 30% hydrogen peroxide and base (**7**).

(4) *N*-Alkenyl-*N'*-*p*-tosylhydrazide with 30% hydrogen peroxide and sodium peroxide (**9**,**11**,**12**,**13** and **17**).[9c]

(5) Alkenyl bromide with ≥ 85% hydrogen peroxide and silver tetrafluoroborate[17] (**14**[17],**15** and **16**).

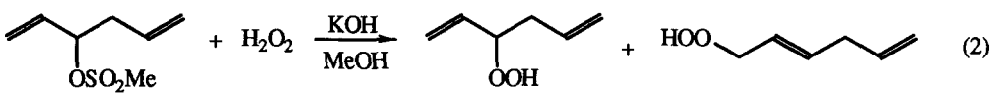
The yield from basic perhydrolysis of cinnamyl chloride (method 1) was only 10% and the product contained 15 mol% of the isomer 1-phenylallyl hydroperoxide (**18**) (equation 1).



1 **18** (1)

A better yield (64%) was obtained using ≥ 85% hydrogen peroxide and silver tetrafluoroborate (*cf.* method 5), but 1-phenylallyl hydroperoxide was then the major product (65mol%).

The isomeric allylic hydroperoxides **4** and **6** were similarly obtained as a mixture from a single methanesulfonate (equation 2). The product ratio (**4**:**6**) depended upon the reaction temperature and was 75:25 at 20 °C but 45:55 at -5 °C.

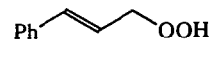


6 **4** (2)

Base catalysed perhydrolysis is expected to proceed by an S_N2 mechanism. It is not known at present whether the observed formation of rearranged hydroperoxides under these conditions (equations 1 & 2) signifies a competing S_N2' process or allylic rearrangement[18] of the normal S_N2 product. The separation of the isomeric hydroperoxides (**1** from **18** and **4** from **6**) could not be satisfactorily achieved by chromatography but was effected by exploiting differential reactivity towards cycloperoxymercuriation as described later.

The yields from the methanesulfonate route (method 2) were very poor both for the secondary alkyl compounds, **5** (19%) and **6** (6%, allowing for isomer **4**), and for the primary alkyl compounds with a β-branch, **7** (4%) and **8** (14%). This is not surprising given the low S_N2 reactivity of these kinds of alkylating agents and the propensity for hydroperoxides to undergo base-induced carbonyl-forming eliminations. Trifluoromethanesulfonates are known to undergo S_N2 displacements at markedly higher rates and we were able to exploit this to obtain (method 3) a much improved yield (35%) of compound **7**. Since this work was completed the use of trifluoromethanesulfonates to prepare alkyl hydroperoxides has been reported elsewhere.[19]

Allylic



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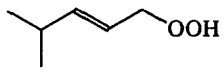

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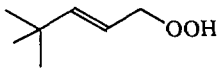

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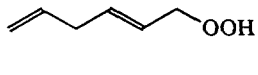

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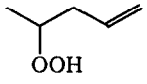
Homoallylic



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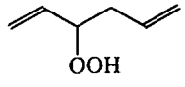

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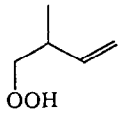

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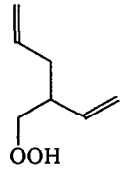

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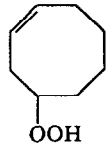

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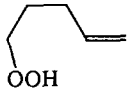
Other



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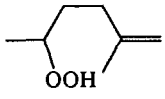

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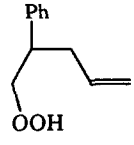

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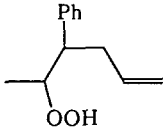

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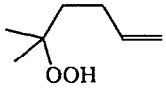

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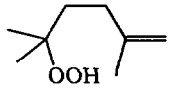

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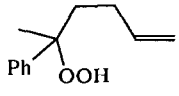

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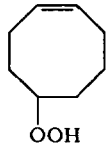

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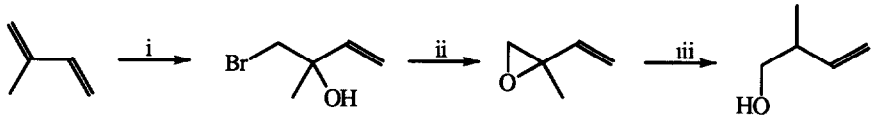
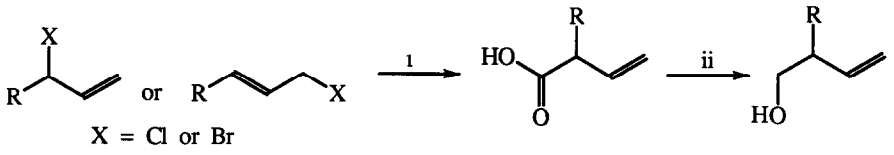
Scheme 1. Unsaturated Hydroperoxides

The alcohol needed to prepare the trifluoromethanesulfonate precursor of hydroperoxide **7** was initially prepared in three steps from isoprene (equation 3), but the simpler route from 3-chlorobut-1-ene (equation 4; R = Me) gave much better yields. The allylic halide route possessed the potential for extension to provide precursors of other 2-alkyl-but-3-enyl hydroperoxides. We prepared 2-phenyl- and 2-t-butyl-but-3-enols this way (equation 4; R = Ph, ^{t}Bu), but the extreme instability of the derived trifluoromethanesulfonates prevented preparation of the corresponding hydroperoxides.



(3)

Reagents: i. NBS, H_2O ii. $\bar{O}H$ iii. $^tBu_2AlH$



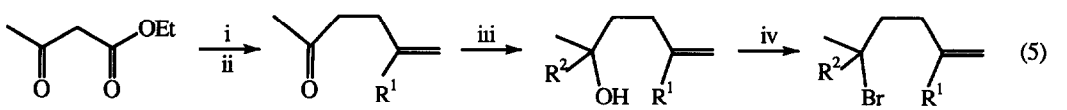
(4)

Reagents: i. Mg, CO_2 ii. $LiAlH_4$

In our original work on method 4, the *N'-p*-tosylhydrazines were obtained by reducing the corresponding *p*-tosylhydrazones with sodium cyanoborohydride at pH 3.5.[9c] In extending the method to the preparation of hydroperoxyalkylcyclopropanes[20], we modified the procedure by carrying out the reduction with pyridine-borane. We now find that this more rapid and much more convenient reduction can also be applied to alkenyl compounds without complications arising from reaction at the alkene site.

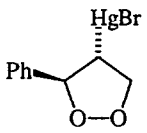
Given the problems encountered in the attempted preparations of 2-alkylbut-3-enyl hydroperoxides (above), we tried to make these compounds by method 4, but we were unable to obtain the required *N*-alkenyl-*N'-p*-tosylhydrazines. Attempts to make the 2-alkylbut-3-enals [CH_2:CH.CH(R)CHO] needed for *p*-tosylhydrazone formation by oxidation of the corresponding alcohols (obtained by equation 4) gave, with pyridinium chlorochromate, dimethyl sulfoxide/oxalyl chloride at -60 °C, *N*-iodosuccinimide/tetraethylammonium iodide or silver carbonate on Celite, mainly the isomeric αβ-unsaturated aldehydes. An alternative route to the desired hydrazines by reduction of the corresponding *N'-p*-tosylhydrazides [CH_2:CH.CH(R)CO.NH.NHTS] was also unsuccessful. Conversion of the 2-alkylbut-3-enoic acids (equation 4) into the hydrazides was readily achieved but no satisfactory conditions were found for the reduction step.

All the alkenyl bromides used in method 5 were prepared from ethyl acetoacetate (equation 5).



(5)

Reagents: i. NaOEt, $CH_2=C(R^1)CH_2X$ ii. NaOH iii. R^2MgX iv. PBr_3, py. (X = halogen)



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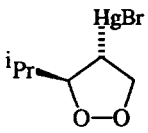

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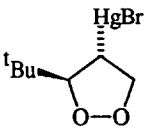

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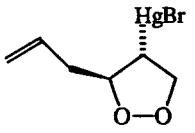

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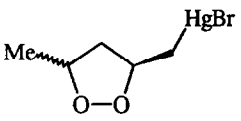

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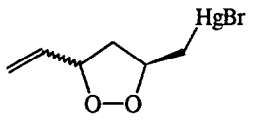

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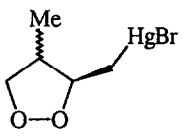

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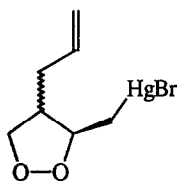

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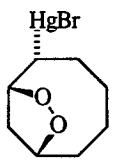

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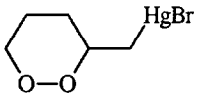

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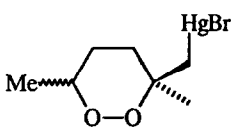

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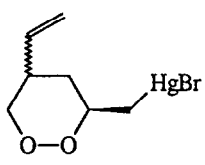

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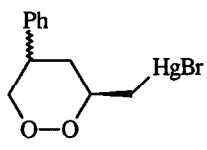

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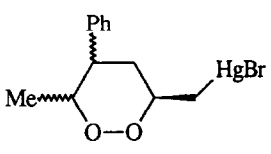

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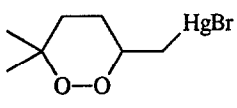

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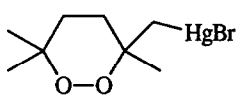

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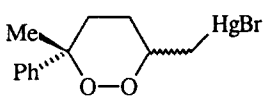

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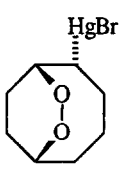

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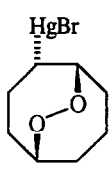

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Scheme 2. Cycloperoxymercurials

Cycloperoxymercuriation

The hydroperoxides **1** - **17** reacted with mercury(II) acetate or mercury(II) nitrate to give, after anion exchange to facilitate isolation, the mercuriated cyclic peroxides **19** - **37** (Scheme 2). Most of these products are new examples of the main types previously reported[7-9], namely 1,2-dioxolanes from 5-*endo* cyclisation (**19** - **22**) or 5-*exo* cyclisation (**23** - **26**) and 1,2-dioxanes (**28** - **35**). However, many of the substitution patterns obtained are without precedent, namely 3,4-dialkyl-1,2-dioxolanes (**25** and **26**), 3,5-dialkyl-1,2-dioxanes (**30** and **31**), trialkyl-1,2-dioxanes (**29**, **32**, **33** and **35**) and tetra-alkyl-1,2-dioxane (**34**). In addition, the reaction has now been extended to the preparation of bicyclic peroxides, namely compounds **27**, **36**, and **37** which contain 1,2-dioxolane, 1,2-dioxane and 1,2-dioxepane rings respectively.

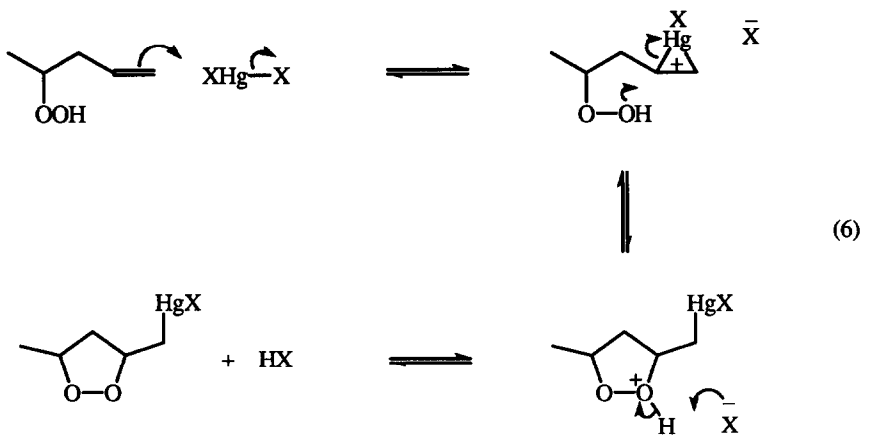
In addition to the isolation of new product types (above), our results provide information about (i) the influence of the choice of mercury(II) salt upon product distribution, (ii) the relative ease of the different classes of mercury(II)-mediated ring closures and (iii) stereoselectivity. These aspects are discussed below.

Choice of mercury(II) salt. Mercury(II) acetate was used in early studies of the t-butyl peroxymercuriation of alkenes but gave rise to competing acetoxymercuriation[21]. This undesirable side reaction was eliminated by using mercury(II) trifluoroacetate, the nucleophilicity of the species (carboxylate ion or carboxylic acid) responsible for acyloxymercuriation being strongly attenuated by the fluorine atoms[22]. Later, it was shown that acetoxymercuriation can often be suppressed by employing perchloric acid as a catalyst and that this works by a thermodynamic rather than a kinetic effect[23]. Initial attempts to prepare cyclic peroxides from dienes and hydrogen peroxide employed mercury(II) trifluoroacetate but were only moderately successful and much better yields were obtained using mercury(II) nitrate.[5a] Although the move to mercury(II) nitrate was based mainly on the anticipated low nucleophilicity of the nitrate ion, the thermodynamic effect of the the nitric acid co-product may be the more important factor in the light of the (later) perchloric acid catalysis results[23] and the discovery that nitratomercuriation can take place.[24]

The choice of mercury(II) salt for preparing cyclic peroxides from dienes was undoubtedly dictated by the need to suppress side reactions in the *first* step of the process, the hydroperoxymercuriation[25] of the diene. The subsequent cycloperoxymercuriation step, being intramolecular in nature, was less likely to be susceptible to competing oxymercuriations, as the results here and elsewhere [7a,7c,9b] have since confirmed experimentally. Nevertheless, mercury(II) nitrate was the reagent used in the first cycloperoxymercuriations of alkenyl hydroperoxides[8a], presumably influenced by the earlier diene work. Subsequently reactions have included the use of mercury(II) trifluoroacetate[7a,10], chloroacetate[8b,8c], methanesulfonate[7a], pivalate[7a,9b] and acetate[7c], but there has been no systematic study of how the choice of mercury(II) salt affects product distribution.

In this work we have shown that the stereoselectivities of the cyclisations of hydroperoxides **5** and **7** (later) and the regioselectivity of the cyclisation of hydroperoxide **8** depend upon whether mercury(II) acetate or mercury(II) nitrate is used. Cycloperoxymercuriation involves electrophilic attack by the mercury(II) salt upon the carbon-carbon double bond of the alkenyl hydroperoxide followed by intramolecular nucleophilic attack by the hydroperoxide group upon the resultant cationic site which is usually considered to be a mercurinium ion. Deprotonation by the anion of the mercury(II) salt then completes formation of equimolar amounts of cycloperoxymercurial and the acid corresponding to the mercury(II) salt (*e.g.* equation 6). In principle the reaction is reversible and the back reaction should be assisted if HX is a strong acid. Such reversibility will be conducive to thermodynamic control of product distribution. Accordingly, we assume that

for reactions with mercury(II) acetate and mercury(II) nitrate, the former are the more likely to give kinetically controlled product distributions and the latter the more likely to show some component of thermodynamic control. This is the basis upon which we interpret our results.



(6)

Ease of ring closure. 1-Phenylallyl hydroperoxide **18** was recovered unchanged whereas cinnamyl hydroperoxide **1** was converted into a 1,2-dioxolane (the acetoxymercurio precursor of **19**) when a mixture of the isomers was treated with mercury(II) acetate. Similarly, hexa-2,5-dienyl hydroperoxide **4** was recovered unchanged whereas hexa-1,5-dien-3-yl hydroperoxide **6** was converted into a 1,2-dioxolane (the acetoxymercurio precursor of **24**) when a mixture of the isomers was treated with just enough mercury(II) acetate to consume isomer **6**. Cyclisation of hydroperoxide **8** with mercury(II) acetate (ultrasonically assisted) gave, after anion exchange, a 7:1 mixture of 1,2-dioxolane **26** and 1,2-dioxane **30**.

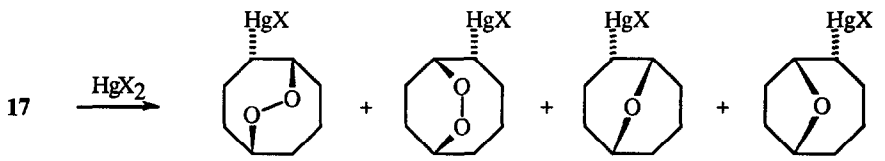
Taken together these results suggest that the relative rates of mercury(II) - mediated cyclisations follow the pattern 6-*exo* < 5-*exo* > 5-*endo* > 4-*exo*. A powerful influence which should also be noted is that, like other oxymercuriations[26], cycloperoxymercuriation is strongly regioselective for placing the mercury substituent on the least alkylated carbon atom of the alkene. Indeed, no cycloperoxymercurials contravening this mode of addition have ever been detected and the failure to obtain 1,2-dioxolanes from allylic hydroperoxides with terminal double bonds (here and reference 7c) is the most dramatic illustration of this.

From a practical standpoint, the above differential reactivity provided the means by which to separate the isomeric hydroperoxides **1** from **18** and **4** from **6**. As part of that work, cinnamyl hydroperoxide was regenerated from the cycloperoxymercurial **19** by treatment with hydrochloric acid. This exploits the reversibility of cycloperoxymercuriation in the presence of a strong acid (*cf.* equation 6) and the fact that mercury(II) halides are ineffective electrophiles for oxymercuriation.

The formation of bicyclic peroxides from cyclooctenyl hydroperoxides **9** and **17** with mercury(II) acetate occurred less readily than that of the monocyclic peroxides and required prolonged reaction times with ultrasonic catalysis. Two modes of cyclisation are possible for each hydroperoxide but the reaction with cyclooct-3-enyl hydroperoxide **9** was regiospecific, giving only the [5.2.1] peroxide **27** and none of the alternative [4.2.2] isomer. By contrast, cyclooct-4-enyl hydroperoxide **17** gave both of the possible

cycloperoxymercurials although the [3.3.2] isomer **37** was favoured over the [4.2.2] compound **36** by a ratio of 4:1. It is worth mentioning here that earlier work with cyclooct-2-enyl hydroperoxide and mercury(II) trifluoroacetate gave no indication that either of the possible cyclisation modes took place.[27] Thus it appears that the facile 5-*endo* cyclisation found with acylic allylic hydroperoxides **1-4** cannot be extended to provide a synthesis of 10-mercurio-8,9-dioxabicyclo[5.2.1]decane.

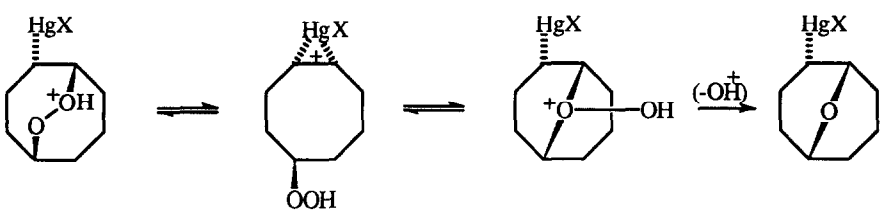
Reaction of cyclooct-4-enyl hydroperoxide **17** with mercury(II) trifluoroacetate gave a markedly different product distribution to that with mercury(II) acetate (equation 7).



X = O_2CCH_3	74%	18%	5%	3%
X = O_2CCF_3	40%	14%	36%	10%

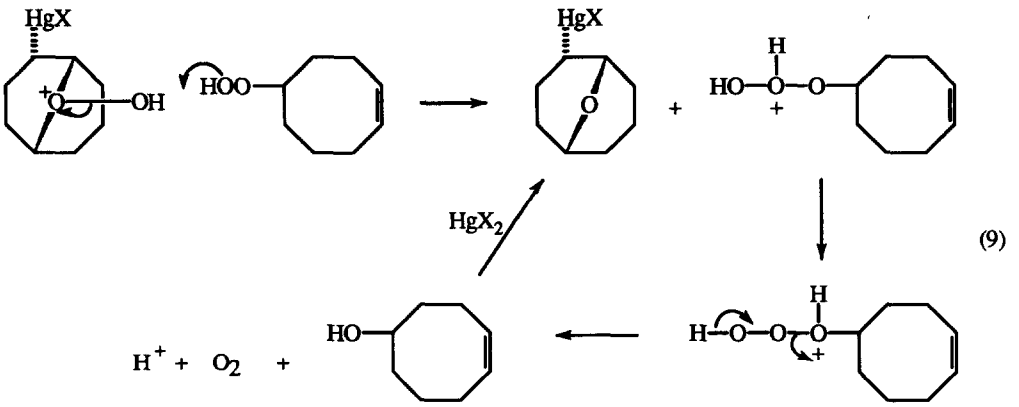
The most striking effect is the dramatic increase in the amounts of bicyclic ethers formed. Treatment of the product mixture from reaction with mercury(II) acetate with an excess of trifluoroacetic acid transformed it over a period of 4 days into a single compound, the mercuriated [3.3.1] ether. This suggests that the [3.3.1] ether is the thermodynamically controlled product for reaction of hydroperoxide **17** with a mercury(II) salt.

The formation of bicyclic ethers from cyclooct-4-enyl hydroperoxide **17** and other electrophiles is known and has been attributed to the intermediacy of *gem*-dialkylperoxonium ions formed by nucleophilic attack on the cationic site by the non-hydroxylic oxygen atom of the hydroperoxide group.[28] Such an intermediate could readily be formed from the mercuriated bicylic peroxides via strong acid-induced deoxymercuriation (equation 8).



The absence of products other than the [3.3.1] ether suggests that the $\overset{+}{O}H$ is transferred to hydroperoxide **17** to form, via a protonated hydrotrioxide, molecular oxygen and cyclooct-4-enol, the latter giving more bicyclic ether by oxymercuriation (equation 9). Evidence has been presented previously[28c] for the operation of a parallel mechanism in the conversion of *trans*- 4,5-epoxycyclooctyl hydroperoxide into 2-hydroxy-substituted bicyclic ethers. It is known that the mercuriated [3.3.1] ether is thermodynamically favoured over the [4.2.1] isomer.

These results suggest that a similar mechanism may be responsible for the product distributions observed earlier in the peroxymercuriation of cycloocta-1,5-diene, a possibility that was considered at the time but for which no evidence then existed.[6]



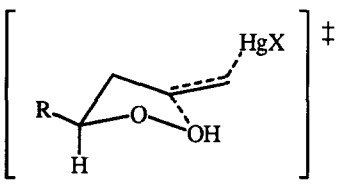
From the results just discussed it is clear that using the mercury(II) salt of a strong acid can be detrimental in cycloperoxymercuriation. This is not always so, however, for the different product distributions provided by conditions of thermodynamic control can be synthetically useful. For example, the proportion of 1,2-dioxane **30** obtained from hydroperoxide **8** can be increased from 12% to 33% by a switch from mercury(II) acetate to the nitrate. Similarly, the yield of a kinetically disfavoured stereoisomer can be increased as reported below.

Stereoselectivity. An important feature of oxymercuriation is that it is stereospecific, giving *trans* addition in all but a few special cases.[26] t-Butyl peroxymercuriation has been shown to follow the same stereochemical course as other types of oxymercuriation.[29] The observed formation of single stereoisomers of the 1,2-dioxolanes **19** - **22** and the bicyclic peroxides **27**, **36**, and **37** is evidence that cycloperoxymercuriation is no exception to the rule. The configurations have been assigned on the assumption that normal *trans* addition takes place. In all the remaining cyclisations reported here (Scheme 2), the addition is to a terminal double bond so that there is no consequential stereochemistry. However, in the creation of the ring the stereochemical relationship of the mercuriomethyl group to the other ring substituents provides a potential source of stereoisomerism.

The formation of 3,5-disubstituted 1,2-dioxolanes **23** and **24** revealed a preference for the *cis* isomer. For mercury(II) acetate-mediated cyclisations, the *cis* : *trans* ratios were 72:28 and 67:33 respectively. The configurations were easily identified from ^{1}H NMR spectra since the non-equivalent protons at C-4 are expected to show a larger chemical shift difference in the *cis* isomer than in the *trans* compound. Furthermore, for peroxide **23**, reductive demercuriation (later) gave the known[5a] 3,5-dimethyl-1,2-dioxolanes providing unequivocal confirmation of the assignments. The preference for the *cis* isomer is consistent with a chair-like transition state (**38**) in which the alkyl group adapts a pseudo-equatorial position rather than a pseudo-axial one. With larger substituents the stereoselectivity should be higher and the reported [7a,8b,8c] stereospecific formation of some *cis* 3,5-disubstituted 1,2-dioxolanes is consistent with this.

For 1,2-dioxolane **23**, the stereoselectivity was lower when mercury(II) nitrate was used, the *cis* : *trans* ratio then being 58:42. When the 72:28 mixture of isomers obtained with mercury(II) acetate was treated with a catalytic amount of nitric acid, the isomer ratio changed and slowly approached the mercury(II) nitrate value,

supporting the idea of thermodynamic control in the mercury(II) nitrate reaction. The almost equal amounts of *cis* and *trans* 3,5-di(mercuriomethyl)-1,2-dioxolane previously obtained[5a] from penta-1,4-diene, hydrogen peroxide and mercury(II) nitrate are also consistent with thermodynamic control. Porter[7a] has previously noted that isomer ratios from cycloperoxymercuriation vary with the mercury(II) salt used but no explanation was offered.



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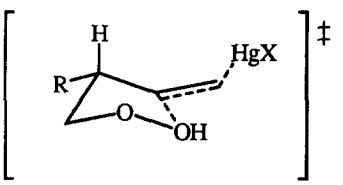
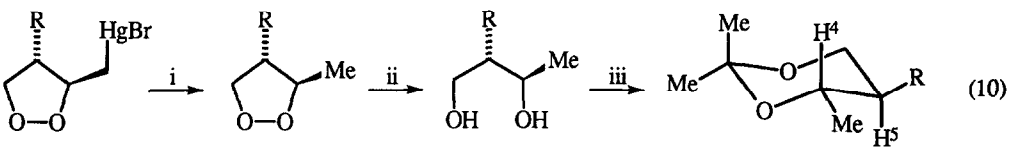


39

The stereoselectivity observed in the formation of 3-acetoxymercuriomethyl-4-alkyl-1,2-dioxolanes like that for similar 3,5-disubstituted compounds depended upon the size of the alkyl group. For the methyl compound **25**, the *cis* : *trans* ratio was approximately 1:1 whereas for the allyl compound **26** the *trans* isomer was predominant. Again this can be accounted for in terms of a chair-like transition state (**39**) with a preferred pseudo-equatorial alkyl group. The *trans* 3,4-disubstituted 1,2-dioxolanes are undoubtedly favoured thermodynamically for with mercury(II) nitrate the hydroperoxide **7** gave 1,2-dioxolane **25** with a *cis* : *trans* ratio of 17:83 and hydroperoxide **8** gave only the *trans* isomer of 1,2-dioxolane **26**.

The configurations of the more stable 3,4-disubstituted 1,2-dioxolanes were identified as *trans* by conversion to the corresponding 2,2-dimethyl-1,3-dioxanes (equation 10) and measurement of the coupling constant between H^4 and H^5.



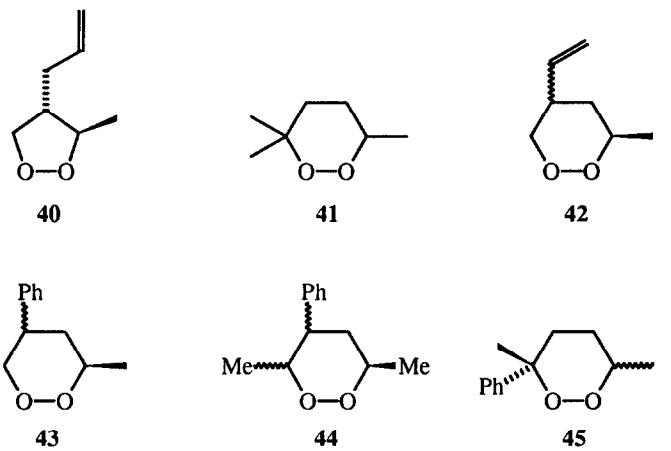
(10)

Reagents: i Bu_3SnH (R = Me) or $NaBH_4$,OH (R = prop-2-enyl); ii Zn,NH_4Cl;
iii $Me_2C(OMe)_2$, cat. p-$MeC_6H_4SO_3H$.

The cyclisations giving rise to 1,2-dioxanes **28-35** were only carried out with mercury(II) nitrate so that the observed stereoselectivities are likely to be at least partially thermodynamic in origin. The most interesting compounds are the 3,5-disubstituted 1,2-dioxanes **30** and **31** which were each obtained as a 3:1 mixture of *cis* and *trans* isomers. The predominance of *cis* isomer is unsurprising since for that configuration both substituents can be equatorial in the favoured chair conformation. The configurations of the major isomers of **30** and **31** were identified from ^1H NMR coupling constants in the corresponding 5-substituted 3-methyl-1,2-dioxanes (**42** and **43**) obtained by hydridodemercuriation (below).

Hydridodemercuriation

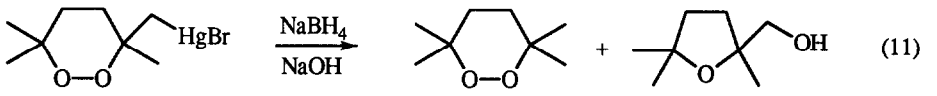
The cycloperoxymercurials **23** and **26-37** were each reduced with alkaline sodium borohydride[5-9] to afford the corresponding mercury-free peroxides. Where the resultant peroxides were known, the reactions provided additional evidence for the structures of the precursor cycloperoxymercurials. Thus, 3,5-dimethyl-1,2-dioxolane[5a], 8,9-dioxabicyclo[5.2.1]decane[6], 3,3,6,6-tetramethyl-1,2-dioxane[5b], 7,8-dioxabicyclo[4.2.2]decane[30], and 9,10-dioxabicyclo[3.3.2]decane[6] were obtained respectively from cycloperoxymercurials **23**, **27**, **34**, **36**, and **37**. Six new peroxides were isolated and characterised (scheme 3). This significantly increases the number and range of 1,2-dioxanes prepared by this route, of which only two examples have been previously reported[8a,9a].



Scheme 3. New Mercury-free Cyclic Peroxides

There is much evidence that the hydridodemercuriation of peroxymercurials under the conditions used here proceeds by a radical mechanism and that the β-peroxyalkyl radical can partition between hydrogen abstraction to give the mercury-free peroxide and γ-scission to give an oxirane.[31,32] Porter *et al.*[8a,9a,9b] found that mercuriated 1,2-dioxanes show a marked tendency to give a substantial amount of γ-scission, so that to maximise yields of peroxides the experimental conditions must be adjusted to favour the bimolecular process. We found that by adding excess sodium borohydride to a vigorously stirred solution of the organomercury(II) bromide in dichloromethane as quickly as possible while keeping the temperature of the mixture between -10 and 0 °C, we were generally able to obtain cyclic peroxides, isolated by column chromatography, in yields of 40-65%. Yields are expected to depend intrinsically upon the structure of the cycloperoxymercurial[32] and in support of this, 3,3,6-trimethyl-1,2-dioxane **41** was obtained from mercurials **33** and **29** in yields of 68 and 46% respectively. However, we are reluctant to develop this theme too far as it is difficult to ensure conformity of conditions in the heterogeneous mixtures. This may account for our failure to obtain 3,4-dimethyl-1,2-dioxolane by borohydride reduction of **25**, which is why we were obliged to use tributyltin reduction[31b] when probing the stereochemistry of **25** (equation 10).

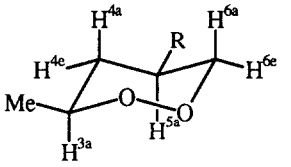
In general we did not seek to establish the yield or identify of any by-products of reduction, but with **34** 2-hydroxymethyl-2,5,5-trimethyltetrahydrofuran (**46**) was isolated by silica chromatography in addition to a 36% yield of 3,3,6,6-tetramethyl-1,2-dioxane (equation 11).



34 **46** (11)

The tetrahydrofuran **46** was identified by comparison with an authentic sample prepared by MCPBA epoxidation of 2,5-dimethylhex-5-en-2-ol followed by acid-catalysed cyclisation. The isolation of an α-hydroxyalkyltetrahydrofuran by-product is in accord with the results of Porter *et al.* [8a,9b] and is consistent with a free radical mechanism for reduction.

The configurations of the major isomers of the 3,5-disubstituted 1,2-dioxanes **42** and **43** were determined from their ^{1}H NMR spectra.



R = ethenyl, **42**
R = phenyl, **43**

The protons on the skeletal carbon atoms were readily assigned from chemical shifts, multiplicity and decoupling experiments. For **42**, the coupling constants $J_{3a\text{-}4a}$ = 10.4, $J_{3a\text{-}4e}$ = 2.0, $J_{5a\text{-}6a}$ = 10.9 and $J_{5a\text{-}6e}$ = 4.9 Hz were measured, clearly establishing a *cis-diequatorial* arrangement of substituents. A *cis* configuration for the major isomer of **43** was similarly established from the coupling constants $J_{3a\text{-}4a}$ = 10.7, $J_{3a\text{-}4e}$ = 2.0 and $J_{4a\text{-}5a}$ =10.7 Hz.

EXPERIMENTAL

NMR spectra were recorded with a Varian VXR 400 (400 MHz ^{1}H, 100 MHz ^{13}C), Varian XL 200 (200 MHz ^{1}H, 50 MHz ^{13}C) or Jeol PMX 60 (60 MHz ^{1}H) spectrometer for solutions in $CDCl_3$ and referenced to internal $CHCl_3$ or $SiMe_4$; 400 MHz ^{1}H NMR spectra are reported unless otherwise stated; coupling constants are given in Hz. IR spectra were measured with a Perkin-Elmer 983 spectrophotometer and mass spectra with a VG 7070 F/H mass spectrometer with Finnigan INCOS data system. Solvents were dried according to standard procedures and distilled. Reagents were commercial samples unless otherwise stated and were distilled (e.g. phosphorus tribromide) or recrystallised if necessary; silver tetrafluoroborate was handled rapidly under a dry atmosphere; hydrogen peroxide(85%) was a gift from Interox Chemicals Ltd. Silica for column chromatography was Merck Kieselgel 60, 70 - 230 mesh, 0.063 - 0.20mm. All peroxide products were stored at -30 °C.

4,4-Dimethylpent-1-ene was prepared by coupling t-butylmagnesium chloride with allyl bromide; b.p. 70-72 °C (lit[33]. 70.7-71.2 °C at 724 mm Hg); δ_H(60MHz) 1.04 (9H, s), 2.06 (2H, d J 7.2), 4.90-5.26 (2H, m) and 5.50-6.10 (1H, m); δ_c 25.67, 29.19, 48.49, 116.38 and 136.08.

1-Bromo-4,4-dimethylpent-2-ene was prepared by bromination of 4,4-dimethylpent-1-ene with *N*-bromosuccinimide; b.p. 58 °C at 20 mm Hg (lit.[34] 61.5-62 °C at 28 mm Hg); δ_H 1.00 (9H, s), 3.93 (2H, d J 7.5), 5.57 (1H, dt J 15.3 & 7.5) and 5.75 (1H, d J 15.3); δ_c 29.20, 33.03, 34.07, 121.46 and 147.03.

1-Bromo-4-methylpent-2-ene was prepared by treating 4-methylpent-1-en-3-ol with phosphorus tribromide and pyridine; δ_H 0.97 (6H, d, J 6.8), 2.30 (1H, m), 3.92 (2H, d J 7.5), 5.63 (1H, m) and 5.72 (1H, dd J 15.7 & 6.2); δ_c 21.91, 30.64, 33.76, 123.52 and 143.25.

Pent-4-en-2-ol was prepared from allyl bromide and acetaldhyde by the Grignard route and purified by distillation at reduced pressure.

2-Methylbut-3-enoic acid was prepared by carbonylation[35] of the Grignard reagent derived from 3-chlorobut-1-ene; δ_H (200 MHz) 1.29 (3H, d J 7.2), 3.19 (1H, m), 5.16 (2H, m), 5.93 (1H, m) and 9.80 (1H, br s); δ_c 16.20, 43.36, 116.07, 136.41 and 180.51.

2-Methylbut-3-en-1-ol (**19**) was prepared by reducing 2-methylbut-3-enoic acid with lithium aluminium hydride and purified by trap-to-trap distillation at 70 °C at 20 mm Hg (84%); δ_H (60 MHz) 1.06 (3H, d, J 7.2), 2.24 (1H, s), 2.35 (1H, m), 3.52 (2H, d J 6.0), 4.8-5.1 (2H, m) and 5.4-6.0 (1H, m); δ_c 15.78, 40.18, 66.68, 114.76 and 140.82.

2-Ethenylpent-4-en-1-ol was prepared by reaction of allylmagnesium bromide with 1,2-epoxybut-3-ene (76%); b.p. 70-75 °C at 16 mm Hg (lit.[36] 59 °C at 11 mm Hg); δ_H (60 MHz) 2.06 (3H, m), 3.38 (3H, m), 4.90 (4H, m) and 5.44 (2H, m); δ_c 35.37, 46.12, 65.07, 116.27, 116.97, 136.17 and 139.25.

Hexa-1,5-dien-3-ol, pent-4-en-2-ol, 2-methylbut-3-en-1-ol (**19**), 2-ethenylpent-4-en-1-ol, and pent-4-en-1-ol were each converted to the corresponding methanesulfonate by reaction with methanesulfonyl chloride and pyridine.[37] Hexa-1,5-dien-3-yl methanesulfonate, δ_H (60 MHz) 2.5 (2H, t J 4.2), 2.94 (3H, s) and 4.8-6.2 (7H, m). Pent-4-en-2-yl methanesulfonate, δ_H (200 MHz) 1.42 (3H, d), 2.42 (2H, m), 3.00 (3H, s), 4.82 (1H, m), 5.15 (2H, m) and 5.80 (1H, m). 2-Methylbut-3-enyl methanesulfonate, δ_H (60 MHz) 1.1 (3H, d), 2.6 (1H, m), 3.0 (3H, s), 4.1 (2H, d, J 6), 5.2 (2H, m) and 5.7 (1H, m). 2-Ethenylpent-4-enyl methanesulfonate, δ_H (200 MHz) 2.23 (2H, m), 2.56 (1H, m), 3.01 (3H, s), 4.16 (2H, d J 6.4), 5.19 (4H, m) and 5.68 (2H, m); δ_c 34.99, 37.18, 42.50, 71.73, 117.34, 117.46, 134.89 and 136.96; ν_{max} 3079, 2979, 2939, 2912, 2845, 1641, 1465, 1441, 1418, 1354, 1174, 974, 957, 924, 844, 814 and 747 cm^{-1}; *m/z* 149 (0.61%), 121 (1.9), 109 (3.4), 94 (21), 81 (27), 79 (100), 66 (17), 54 (43) and 41 (60). Found: C, 50.61; H, 7.39. $C_8H_{14}O_3S$ requires C, 50.50; H, 7.42%.

Trifluoromethanesulfonic anhydride was prepared by dehydration of trifluoromethanesulfonic acid with phosphorus pentoxide, b.p. 82 °C (lit.[38] 81 °C).

2-Methylbut-3-enyl trifluoromethanesulfonate was prepared from 2-methylbut-3-en-1-ol, trifluoromethanesulfonic anhydride and pyridine. The compound decomposed an attempted distillation and was therefore used crude in the hydroperoxide synthesis (below). δ_H (200 MHz) 1.12 (3H, d J 6.8), 2.67 (1H, m), 4.34 (1H, dd J 9.9 & 5.2), 4.37 (1H, dd J 9.9 & 5.1), 5.12-5.22 (2H, m) and 5.69 (1H, m); δ_c 15.66, 37.46, 80.26, 117.26, 118.65 [q J (^{19}F) 319] and 136.98.

Hex-5-en-2-one was prepared from ethyl acetoacetate and allyl bromide[17], and 5-methylhex-5-en-2-one (b.p. 60 °C at 18 mm Hg) was similarly prepared from methallyl chloride. These ketones were converted by the Grignard route[17] into the following alcohols. 2-Methylhex-5-en-2-ol, b.p. 50 °C at 8 mm Hg; δ_H (60 MHz) 1.2 (6H, s), 1.5 (3H, m), 2.0 (2H, m), 5.0 (2H, m), and 5.8 (1H, m); δ_c 28.37, 28.87 (2C), 42.68, 70.21, 113.72 and 138.76. 2,5-Dimethylhex-5-en-2-ol, b.p. 68 °C at 25 mm Hg; δ_H (200 MHz) 1.24 (6H, s), 1.50 (3H, m), 1.76 (3H, br s), 2.10 (2H, m) and 5.08 (2H, br s); δ_c 22.72, 29.19 (2C), 36.64, 41.85, 70.69, 109.62, and 146.12. 2-Phenylhex-5-en-2-ol, b.p. 74-76 °C at 18-20 mm Hg; δ_H (60 MHz) 1.6 (3H, s), 1.9 (5H, m), 5.0 (2H, m), 5.8 (1H m) and 7.4 (5H, m); δ_c 28.15, 29.71, 42.83, 74.19, 114.07, 124.56, 126.14, 127.75, 138.42 and 147.48.

These alcohols were converted into the corresponding alkenyl bromides by reaction with phosphorus tribromide and pyridine[17]; 2-bromo-2-phenylhex-5-ene underwent elimination on attempted distillation and was therefore used crude in the hydroperoxide synthesis (below)

Preparation of Hydroperoxides

Details of the preparation and spectral data of hydroperoxides **9**[9c], **10**[17], **11**[9c], **12**[9c], **13**[9c], **14**[17] and **17**[9c] have been presented previously.

(a) Perhydrolysis of allyl halides (method 1). The allyl halide (20 mmol) was dissolved in methanol (70 cm^3) and cooled in ice. Hydrogen peroxide (30% w/v; 15 cm^3; 130 mmol) was added slowly with stirring, followed by a solution of potassium hydroxide (1.36g; 24 mmol) in water (5 cm^3). The mixture was allowed to warm to room temperature and stirring was continued for 48 h. Water (150 cm^3) was added and the solution was saturated with ammonium sulfate then extracted with dichloromethane (4 x 50 cm^3). The extract was washed with water (2 x 50 cm^3), dried ($MgSO_4$), and the solvent was removed at a rotary evaporator to yield crude hydroperoxide. This was dissolved in ether (20 cm^3), cooled to -30 °C and shaken vigorously with a solution, pre-cooled to -30 °C, of potassium hydroxide (2.50 g; 45 mmol) in water (4 cm^3). The ethereal layer was decanted off and the thick white precipitate was dissolved in water and cooled in ice. This was immediately acidified by the dropwise addition of an ice-cold solution of acetic acid (3.00 cm^3; 52 mmol) in ether (20 cm^3). After vigorously stirring the mixture for 5 min, the organic layer was separated off, washed with saturated sodium bicarbonate (10 cm^3), dried ($MgSO_4$) and the solvent removed at reduced pressure to afford the pure hydroperoxide.

1-Bromo-4-methylpent-2-ene gave *4-methylpent-2-enyl hydroperoxide* (**2**) (42%), δ_H 0.98 (6H, d J 6.8, CH_3), 2.30 (1H, m, C^4H), 4.41 (2H, d J 6.7, C^1H_2), 5.50 (1H, dt J 15.5 & 6.7, C^2H), 5.76 (1H, dd J 15.5 & 6.5, C^3H) and 8.33 (1H, br s, OOH); δ_c 21.97 (CH_3), 30.85 (C^4), 77.89 (C^1), 120.45 and 145.33 (C^2 & C^3). Found: C, 62.16; H, 10.72. $C_6H_{12}O_2$ requires C, 62.04; H, 10.41%.

1-Bromo-4,4-dimethylpent-2-ene gave *4,4-dimethylpent-2-enyl hydroperoxide* (**3**) (42%), δ_H 1.00 (9H, s, CH_3) 4.30 (2H, d J 6.7, C^1H_2), 5.46 (1H, dt J 15.7 & 6.7, C^2H), 5.80 (1H, d J 15.7, C^3H) and 8.24 (1H, br s, OOH); δ_c 29.24 (CH_3), 33.15 (C^4) 78.11 (C^1), 118.17 and 149.24 (C^2 & C^3). Found: C, 64.71; H, 10.94. $C_7H_{14}O_2$ requires C, 64.58; H, 10.84%.

On a 50 mmol scale and reaction time of 5 h, cinnamyl chloride similarly gave, with minor modifications to the procedure, a yield of 12% of a mixture of 1-phenylallyl hydroperoxide (**18**) (15 mol%) and *cinnamyl hydroperoxide* (**1**), δ_H (200 MHz) 4.65 (2H, d J 6.6, C^1H_2), 6.33 (1H, dt J 15.9 & 6.6, C^2H), 6.69 (1H, d J 15.9, C^3H), 7.38-7.45 (5H, m, C_6H_5) and 8.74 (1H, br s, OOH); δ_c 77.67 (C^1), 123.01, 126.68, 128.20, 128.60, 135.89 and 136.13. Found (for a mixture of **1** and **18**): C, 71.82; H, 6.64. $C_9H_{10}O_2$ requires C, 71.98; H, 6.71%.

Alternatively, a mixture of hydroperoxides **1** (35 mol%) and **18** was obtained as follows. Hydrogen peroxide (85% w/v; 2.00 cm^3; 66 mmol) (CAUTION) was dissolved in ether (50 cm^3) and the solution dried ($MgSO_4$). After filtration, this solution was combined with cinnamyl chloride (1.53 g; 10 mmol) and cooled to -78 °C. Silver tetrafluoroborate (2.13 g; 11 mmol) was quickly added in one portion in subdued light, and the mixture was stirred for 30 min then allowed to warm to room temperature. Saturated sodium bicarbonate

(40 cm^3) was added and the mixture was stirred for 1 h. The aqueous slurry was extracted with ether (2 x 20 cm^3). The extract was washed with water (5 x 10 cm^3) and brine (20 cm^3), dried ($MgSO_4$), and the solvent was removed at a rotary evaporator. Column chromatography (SiO_2, CH_2Cl_2) afforded a mixture of hydroperoxides **1** and **18** (64%).

(b) Perhydrolysis of methanesulfonates (method 2). Using the well established procedure[16,55] with the indicated reaction times at room temperature, the following previously unknown hydroperoxides were obtained in the yields shown. **4** + **6**: 24 h, 21% (75% **4**) [at -5 °C, 24 h, 12% (45% **4**)]; **5**: 24 h, 19%; **7**: 24 h, 4% [final purification by column chromatography (SiO_2, 7:3 light petroleum: diethyl ether); **8**: 48 h, 14%. The spectroscopic data follow.

Hexa-2,5-dienyl hydroperoxide (**4**). δ_H 2.83 (2H, t J 6.3, C^4H_2), 4.46 (2H, d J 6.5, C^1H_2), 5.1 (2H, m, C^6H_2), 5.66 (1H, dt J 15.5 & 6.5, C^2H), 5.8 (2H, m, C^3H & C^5H), and 8.69 (1H, br s, OOH); δ_c 36.40 (C^4), 77.56 (C^1), 115.91 (C^6), 124.84, 135.49 and 135.90 (C^2, C^3 & C^5).

Pent-4-en-2-yl hydroperoxide (**5**). δ_H (200 MHz) 1.22 (3H, d J 6.3, C^1H_3), 2.25 & 2.42 (2H, m, C^3H_2), 4.14 (1H, sextet, C^2H), 5.09 (2H, m, C^5H_2), 5.82 (1H, m, C^4H), and 8.4 (1H, br s, OOH); δ_c 17.65 (C^1), 38.62 (C^3), 80.90 (C^2), 117.44 (C^5) and 134.18 (C^4). Found: C, 58.24; H, 9.77. $C_5H_{10}O_2$ requires C, 58.80; H, 9.87%.

Hexa-1,5-dien-3-yl hydroperoxide (**6**). δ_H 2.35 (2H, m, C^4H_2), 4.3 (1H, m, C^3H), 5.0-5.4 (4H, m, C^1H_2 & C^6H_2), 5.8 (2H, m, C^2H & C^5H), and 8.49 (1H, br s, OOH); δ_c 36.92 (C^4), 86.14(C^3), 117.70, 119.23 (C^1 & C^6), 133.38 and 136.29 (C^2 & C^5).

2-Methylbut-3-enyl hydroperoxide (**7**). δ_H (200 MHz) 1.00 (3H, d J 6.8, CH_3), 2.61 (1H, m C^2H), 3.88 (2H, m, C^1H_2), 5.05 (2H, m C^4H_2), 5.74 (1H, m, C^3H) and 8.49 (1H, br s, OOH); δ_c 16.23 (CH_3), 36.11 (C^2), 81.15 (C^1), 114.65 (C^4) and 140.48 (C^3).

2-Ethenylpent-4-enyl hydroperoxide (**8**). δ_H (200 MHz) 2.18 (2H, m, C^3H_2), 2.62 (1H, m, C^2H) 3.96 (1H, dd J 10.8 & 7.0, $C^1\underline{H}^A H^B$), 4.01 (1H, dd, J 10.8 & 6.4, $C^1H^A\underline{H}^B$), 5.11 (4H, m, C^5H_2 & C^2-CH=C$\underline{H}_2$), 5.75 (2H, m, C^4H & C^2-C$\underline{H}$=CH_2) and 8.11 (1H, s, OOH); δ_c 36.61 (C^3), 41.86 (C^2), 79.47 (C^1), 116.36, 116.59 (C^5 & C^2-CH=C$\underline{H}_2$), 135.82 and 138.81 (C^4 & C^2-C$\underline{H}$=CH_2); ν_{max} 3413 br, 2979, 2919, 2872, 2838, 1638, 1475, 1438, 1417, 1364, 991, 917, 810, 736 cm^{-1}

(c) Perhydrolysis of a trifluoromethanesulfonate (method 3). 2-Methylbut-3-enyl trifluoromethanesulfonate (4.35 g; 20 mmol) was dissolved in methanol (60 cm^3) and immediately added, in one portion, to a stirred ice-cold mixture of hydrogen peroxide (30% w/v; 10.7 cm^3; 95 mmol) and potassium hydroxide (1.19 g; 21 mmol) in water, (5 cm^3). After stirring the mixture for 5 min, water (20 cm^3) was added. The solution was saturated with sodium chloride and then extracted with dichloromethane (5 x 30 cm^3). The extract was washed with brine (2 x 30 cm^3) and extracted with 20% potassium hydroxide (25 cm^3). The basic extract was acidified, with cooling, with 10% hydrochloric acid, saturated with sodium chloride, and then extracted with ether (3 x 30 cm^3). The ether extract was washed with brine (20 cm^3), dried ($MgSO_4$), and the solvent was removed at reduced pressure to afford hydroperoxide **7** (35%).

(d) Perhydrolysis of alkenyl bromides (method 5). The method previously described[17] for the preparation of hydroperoxide **14** was slightly modified in that the solution of hydrogen peroxide (85% w/v) in ether was dried ($MgSO_4$) before use (see earlier) and the reaction mixture, after 20 min at -78 °C, was allowed to warm to room

temperature before work up. Hydroperoxide **15** (41%) was isolated by preparative HPLC[17], but purification of hydroperoxide **16** was unnecessary as no corresponding dialkyl peroxide was detected in the crude product (88%). The spectroscopic data follow.

2,5-Dimethylhex-5-en-2-yl hydroperoxide (**15**). δ_H 1.23 (6H, s, C^1H_3 & C^2-CH_3), 1.72 (2H, m, C^3H_2), 1.74 (3H, s, C^5-CH_3), 2.02 (2H, m, C^4H_2), 4.70 (2H, m, C^6H_2) and 7.43 (1H, s, OOH); δ_c 22.63 (C^5-$\underline{C}H_3$), 23.83 (C^1 & C^2-$\underline{C}H_3$), 31.89 (C^3), 36.41 (C^4), 82.49 (C^2), 109.46 (C^6) and 146.09 (C^5).

2-Phenylhex-5-en-2-yl hydroperoxide (**16**). δ_c 22.77 (C^1), 28.13 (C^3), 38.66 (C^4), 85.97 (C^2), 114.82 (C^6), 125.63, 127.24, 128.36, 138.30, 143.77 (C^5 & C_6H_5).

Cycloperoxymercuriation

(a) Cyclisation with mercury(II) acetate. The following procedure is typical.

The hydroperoxide (2.0 mmol) in dichloromethane (35 cm^3) was added dropwise over 15 min to a vigorously stirred mixture of mercury(II) acetate (2.1 mmol) and dichloromethane (75 cm^3). The mixture was stirred for a further 15 min, during which time most of the mercury(II) acetate dissolved. The solution was washed with water (20 cm^3), then water (8 cm^3) and potassium bromide (2.2 mmol) were added and the mixture was stirred vigorously for 30 min. The aqueous layer was removed and the organic layer was washed with water (25 cm^3), dried (Na_2SO_4), and the solvent removed under reduced pressure to leave the crude mercuriated cyclic peroxide (> 80%). If isomers were formed, the product ratio was determined at this stage by ^1H and/or ^{13}C NMR spectroscopy. The product was purified by column chromatography (SiO_2, CH_2Cl_2) to give the yields indicated below. Where the procedure was markedly modified the variations are also noted below. The following interconversions were carried out: **1** to **19** (70%); **2** to **20** (63%); **3** to **21** (83%; chromatography unnecessary); **4** to **22** (10%; reaction time 5h plus 90 min suspended in an ultrasound cleaning bath); **5** to **23** (34%; *cis* : *trans* = 72:28); **6** to **24** (23%; *cis* : *trans* = 67:33); **7** to **25** (64%; *cis* : *trans* = 50:50; reaction time 2h); **8** to **26** (mainly *trans*) + **30** (mainly *cis*) (ratio **26**:**30** = 88:12; reaction time 70 min suspended in an ultrasound cleaning bath); **9** to **27** (51%; reaction on 0.35 mmol scale in CD_2Cl_2 in an NMR tube suspended in an ultrasound cleaning bath for 4 days; purified by HPLC: 5μm SiO_2, 50 x 4.6 mm + 250 x 7 mm x 2, 12.5% ethyl acetate in hexane); **17** to **36** + **37** (ratio **36** : **37** = 20:80; reaction as for **9** but for 2 days; purified as for **27**, **36** eluted ahead of **37**).

(b) Cyclisation with mercury(II) nitrate. The procedure previously described[9c] for the preparation of 3-bromomercuriomethyl-1,2-dioxanes **29**, **31** and **32** from hydroperoxides **11**, **12** and **13** respectively was used to effect the following interconversions (purification and isomer ratios as for the mercury(II) acetate reactions): **5** to **23** (*cis* : *trans* = 58:42); **7** to **25** (*cis* : *trans* = 17:83); **8** to **26** (29%; 100% *trans*) + **30** (32%; mainly *cis*) (ratio **26** : **30** = 67:33); separation by HPLC); **10** to **28** (61%) **14** to **33** (67%); **15** to **34** (46%); **16** to **35**.

The data for the new compounds follow.

trans-*4-Bromomercurio-3-phenyl-1,2-dioxolane* (**19**), recrystallised from dichloromethane/pentane at -30 °C, white needles, m.p. 75 °C; δ_H 3.20 (1H, dt J 9.5 & 7.6, C^4H), 4 38 (1H, dd J 9.5 & 7.6, $C^5\underline{H}^A H^B$), 4.61 (1H, t J 7.6, $C^5H^A\underline{H}^B$), 5.34 (1H, d J 9.5, C^3H) and 7.39 (5H, m, C_6H_5); δ_c 64.79 (C^4), 73.53 (C^5), 84.52 (C^3), 126.80, 129.05, 129.12 and 136.64. Found: C, 24.81; H, 1.82. $C_9H_9BrHgO_2$ requires; C, 25.16; H, 2.11%.

trans-*4-Bromomercurio-3-isopropyl-1,2-dioxolane* (**20**), recrystallised from dichloromethane/pentane at -30 °C, m.p. 75-77 °C; δ_H 1.01 (6H, d J 7.2, CH_3), 1.86 (1H, m, $Me_2C\underline{H}$), 2.86 (1H, q J 8.1, C^4H), 4.24 (2H, m, C^3H & $C^5\underline{H}^A H^B$) and 4.43 (1H, t, J 8.1, $C^5H^A\underline{H}^B$); δ_c 19.23 (CH_3), 19.73 (CH_3); 31.95 (Me_2CH), 57.79 (C^4), 73.32 (C^5) and 88.11 (C^3). Found: C, 17.53; H, 2.72; $C_6H_{11}BrHgO_2$ requires: C, 18.21; H, 2.80%.

trans-*4-Bromomercurio-3-*tert*-butyl-1,2-dioxolane* (**21**), recrystallised from dichloromethane/light petroleum at -30 °C, m.p. 124 °C decomp.; δ_H 0.99 (9H, s, CH_3), 2.91 (1H, m, C^4H), 4.21 (1H, m, $C^5\underline{H}^A H^B$), 4.24 (1H, d J 8.4, C^3H) and 4.43 (1H, m, $C^5H^A\underline{H}^B$); δ_c 26.46 (CH_3), 34.15 (Me_3C), 55.81 (C^4), 73.41(C^5) and 90.24 (C^3). Found: C, 20.34; H, 3.06 $C_7H_{13}BrHgO_2$ requires C, 20.52; H, 3.20%

trans-*4-Bromomercurio-3-prop-2-enyl-1,2-dioxolane* (**22**); δ_H 2.34 (1H, m C^3-$C\underline{H}^A H^B$) 2.65 (1H, m, C^3-$CH^A\underline{H}^B$), 2.81 (1H, approx q, C^4H), 4.25 (1H, dd 9.9 & 7.7 $C^5\underline{H}^A H^B$), 4.48 (1H, t J 7.7, $C^5H^A\underline{H}^B$), 4.50 (1H, m, C^3H), 5.26 (2H, m, CH_2=) and 5.90 (1H, m, CH=); δ_c 36.76 (CH_2), 59.58 (C^4), 72.95 (C^5), 82.53 (C^3), 119.67 (CH_2=) and 133.94 (CH=).

3-Bromomercuriomethyl-5-methyl-1,2-dioxolane (**23**); *cis* (major isomer):δ_H (200 MHz) 1.38 (3H, d J 6.4, CH_3), 1.77 (1H, m, $C^4\underline{H}^A H^B$), 2.15 (1H, dd J 12.1 & 4.7, $C\underline{H}^A H^B Hg$), 2.30 (1H, dd J 12.1 & 5.6, $CH^A\underline{H}^B Hg$), 2.99 (1H, m, $C^4H^A\underline{H}^B$), 4.42 (1H, q J 6.4, C^5H) and 4.85 (1H, m, C^3H); δ_c 18.39 (CH_3), 40.05 (CH_2Hg), 51.14 (C^4), 78.14 (C^5) and 80.16 (C^3); *trans*: δ_H (200 MHz) 1.29 (3H, d J 6.0, CH_3), 2.13 (1H, dd J 11.9 & 5.2, $C\underline{H}^A H^B Hg$), 2.24 (1H, m $CH^A\underline{H}^B Hg$), 2.2-2.5 (2H, m, C^4H_2), 4.53 (1H, q J 6.0, C^5H) and 4.85 (1H, m, C^3H); δ_c 18.95 (CH_3), 38.13 (CH_2Hg), 50.15 (C^4), 77.67 (C^5) and 79.62 (C^3). Found (*cis* + *trans*): C, 15.67; H, 2.22. $C_5H_9BrHgO_2$ requires C, 15.74; H, 2.38%.

3-Bromomercuriomethyl-5-ethenyl-1,2-dioxolane (**24**); *cis*(major isomer): δ_H 2.00 (1H, ddd J 12.3, 6.8 & 5.8, $C^4\underline{H}^A H^B$), 2.17 (1H, dd J 12.0 & 4.7, $C\underline{H}^A H^B Hg$), 2.30 (1H, dd J 12.0 & 5.4, $CH^A\underline{H}^B Hg$), 3.03 (1H, dt J 12.3 & 7.5, $C^4H^A\underline{H}^B$), 4.70-4.94 (2H, m, C^3H & C^5H), 5.25-5.45 (2H, m, CH_2=) and 5.75-5.95 (1H, m, CH=); δ_C 38.83 (CH_2Hg), 49.61 (C^4), 80.23 (C^3), 82.59 (C^5), 119.61 (CH_2=) and 134.58 (CH=); *trans*: δ_H 2.41 (1H, m, $C^4\underline{H}^A H^B$), 2.62 (1H, ddd J 12.1, 7.2 & 5.3, $C^4H^A\underline{H}^B$), all other signals overlap with *cis* isomer; δ_c 37.65 (CH_2Hg), 49.11 (C^4), 79.78 (C^3), 82.32 (C^5), 119.08 (CH_2=) and 134.79 (CH=).

3-Bromomercuriomethyl-4-methyl-1,2-dioxolane (**25**); *cis*: δ_H 1.09 (3H, d J 7.1, CH_3), 2.01 (2H, m, CH_2Hg), 2.97 (1H, m, C^4H), 3.69 (1H, t J 7.0, $C^5HH^A H^B$), 4.31 (1H, t J 7.0, $C^5H^A\underline{H}^B$), and 4.58 (1H, q J 7.0, C^3H); δ_C 12.98 (CH_3), 30.88 (CH_2Hg), 45.59 (C^4), 76.93 (C^5) and 81.30 (C^3). *trans*: δ_H 1.16 (3H, d J 6.8, CH_3), 2.12 (1H, dd J 11.9 & 5.2, $C\underline{H}^A H^B Hg$) 2.24 (1H, dd J 11.9 & 5.6, $CH^A\underline{H}^B Hg$), 2.51 (1H, m, C^4H), 3.66 (1H, t J 7.0, $C^5\underline{H}^A H^B$), 4.24 (1H q J 5.5, C^3H) and 4.32 (1H, t J 7.0, $C^5H^A\underline{H}^B$); δ_C 16.02 (CH_3), 36.70 ($^1J_{Hg}$ 1544; CH_2Hg), 51.95 (C^4), 77.08 (C^5), and 86.09 (C^3). Found (*cis*+*trans*): C, 16.20; H, 2.33. $C_5H_9BrHgO_2$ requires C, 15.74; H, 2.38%.

3-Bromercuriomethyl-4-prop-2-enyl-1,2-dioxolane (**26**); *trans* : δ_H 2.16 (1H, dd J 11.9 & 5.1, $C\underline{H}^A H^B Hg$), 2.26 (1H, dd J 11.9 & 5.9, $CH^A\underline{H}^B Hg$), 2.35 (2H, m, C^4-CH_2), 2.55 (1H, m, C^4H), 3.80 (1H, dd J 8.0 & 6.1, $C^5\underline{H}^A H^B$), 4.34 (1H, t J 8.0, $C^5H^A\underline{H}^B$), 4.41 (1H, q J 5.5, C^3H), 5.15 (2H, m, CH_2=) and 5.78 (1H, m, CH=); δ_c 36.20 (CH_2), 37.82 ($^1J_{Hg}$ 1533, CH_2Hg), 56.73 ($^3J_{Hg}$ 101, C^4), 73.59 (C^5), 84.50 ($^2J_{Hg}$ 103, C^3), 117.84 (CH_2=), and 135.31 (CH=); ν_{max} 3065, 2972, 2925, 2865, 1638, 1438, 1415, 1381, 1301, 1228, 994, 920, 780, 737, 680 and 660. Found: C, 20.19; H, 2.51. $C_7H_{11}BrHgO_2$ requires C, 20.62; H, 2.72%. *cis*: δ_c 32.07 (CH_2), 32.34 (CH_2Hg), 50.57 (C^4), 75.04 (C^5), 81.03 (C^3), 117.27 (CH_2=) and 135.79 (CH=).

2-Bromomercurio-8,9-dioxabicyclo[5.2.1]decane (**27**); δ_H 1.41-1.50 (1H, m, C^4H), 1.69-1.88 (3H, m, C^4H & C^5H_2), 1.95-2.04 (2H, m, C^6H_2), 2.12-2.20 (1H, m, C^3H), 2.50 (1H, ddd J 12.7, 2.7 & 1.5, $C^{10}H_{trans}$), 2.58-2.65 (1H, m, C^3H), 3.09 (1H, ddd J 12.7, 10.2 & 9.2, $C^{10}H_{cis}$), 3.33-3.36 (1H, m, C^2H), 4.54-4.59 (1H, m, C^7H) and 4.71 (1H, ddd J 9.2, 4.8 & 1.5, C^1H), assignments were based on decoupling experiments; δ_c 25.25, 29.02, 31.01, 32.04, 47.83 (C^{10}), 63.89 (C^2), 78.11 (C^7) and 80.46 (C^1). MS accurate mass: Found: 419.9789; $C_8H_{13}{}^{79}Br^{200}HgO_2$ requires 419.9782.

3-Bromomercuriomethyl-1,2-dioxane (**28**); δ_H (200 MHz) 1.5-2.0 (4H, m, C^4H_2 & C^5H_2), 1.99 (1H, dd J 11.9 & 6.3, $^2J_{Hg}$ 207, CH^AH^BHg), 2.21 (1H, dd J 11.9 & 6.1, $^2J_{Hg}$ 211, $CH^A\underline{H}^BHg$), 4.16 (2H, m, C^6H_2) and 4.59 (1H, m, C^3H); δ_c 23.92 (C^5), 32.45 ($^3J_{Hg}$ 143, C^4), 37.12 ($^1J_{Hg}$ 1569, CH_2Hg), 72.31 (C^6) and 80.51 ($^2J_{Hg}$ 104, C^3). Found: C, 16.02; H, 2.35. $C_5H_9BrHgO_2$ requires C, 15.74; H, 2.38%.

3-Bromomercuriomethyl-5-ethenyl-1,2-dioxane (**30**); *cis* (major) + *trans*: δ_H 1.32 + 1.74 + 2.02 (2H, m, C^4H_2), 1.97 (1H, dd J 11.9 & 6.2, $C\underline{H}^AH^BHg$), 2.23 (1H, dd J 11.9 & 5.7, $CH^A\underline{H}^BHg$), 2.66 (1H, m, C^5H), 3.93 + 4.07 + 4.36 (2H, m, C^6H_2), 4.61 + 4.76 (1H, m, C^3H), 5.14 (2H, m, CH_2=) and 5.63 + 6.00 (1H, ddd J 17.6, 11.0 & 7.7, m, CH=); δ_c *cis* 37.45 ($^1J_{Hg}$ 1513, CH_2Hg), 38.84, 39.02 (C^4 & C^5), 75.65 (C^6), 79.61 ($^2J_{Hg}$ 102, C^3), 116.39 (CH_2=) and 136.75 (CH=). Found: C, 20.01; H, 2.47. $C_7H_{11}BrHgO_2$ requires C, 20.62; H, 2.72%.

3-Bromomercuriomethyl-6,6-dimethyl-1,2-dioxane (**33**), m.p. 71-72 °C; δ_H (200 MHz) 1.17 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1.68 (4H, m, C^4H_2 & C^5H_2), 2.02 (1H, dd J 11.7 & 6.4, $C\underline{H}^AH^BHg$), 2.22 (1H, dd J 11.7 & 6.0, $CH^A\underline{H}^BHg$) and 4.48 (1H, m, C^3H); δ_c 22.92 (CH_3), 27.18 (CH_3), 30.53, 34.28 (C^4 & C^5), 37.61 (CH_2Hg), 77.86 (C^3) and 79.30 (C^6). Found: C, 20.52; H, 3.09. $C_7H_{13}BrHgO_2$ requires C, 20.52; H, 3.20%.

3-Bromomercuriomethyl-3,6,6-trimethyl-1,2-dioxane (**34**); δ_H (60 MHz) 1.3 (6H, s, CH_3), 1.4 (3H, s, CH_3), 1.7 (4H, m, C^4H_2 & C^5H_2) and 2.2 (2H, m, CH_2Hg); δ_c (50 MHz; -50 °C) 22.40, 23.03, 24.29, 26.64, 27.00 & 29.12 (CH_3), 30.95, 31.30, 31.99 & 33.10 (C^4 & C^5), 43.10 & 47.07 (CH_2Hg), and 76.43, 78.31, 79.87 & 80.38 (C^3 & C^6).

3-Bromomercuriomethyl-6-methyl-6-phenyl-1,2-dioxane (**35**) (mixture of two diastereoisomers); δ_H 1.35 & 1.64 (3H, s, CH_3), 1.5-2.6 (6H, m, C^4H_2, C^5H_2, & CH_2Hg), 4.50-4.65 (1H, m, C^3H) and 7.40 (5H, m, C_6H_5); δ_c 24.34, 29.83, 29.95, 30.39 & 33.01(2C), (CH_3, C^4 & C^5), 37.24 & 37.44 (CH_2Hg), 79.23 & 79.37 (C^3), 81.06 & 82.17 (C^6) and 124.66, 125.62, 126.87, 127.46, 128.32, 128.49, 143.17 & 144.59 (C_6H_5)

2-Bromomercurio-7,8-dioxabicyclo[4 2.2]decane (**36**); δ_H 1.57-1.65 (1H, m, C^5H), 1.76-1.88 (2H, m, C^9H & $C^{10}H$), 1.95-2.04 (1H, m, C^4H), 2.05-2.14 (1H, m, C^4H), 2.14-2.23 (1H, m, C^5H), 2.23-2.37 (2H, m, C^3H & C^9H), 2.37-2.48 (2H, m, C^3H & $C^{10}H$), 3.28 (1H, ddd J 10.3, 5.6 & 4.4, C^2H), 4.54 (1H, m, C^6H) and 4.80 (1H, ddd J 7.9, 4.4 & 0.8, C^1H), assignments were based on decoupling experiments; δ_c 22.19, 23.41, 28.57, 30.97, 34.42, 64.11 (C^2), 76.20 (C^6) and 79.35 (C^1). MS accurate mass: Found: 419.9788; $C_8H_{13}{}^{79}Br\ {}^{200}HgO_2$ requires 419.9782.

2-Bromomercurio-9,10-dioxabicyclo[3 3.2]decane (**37**); δ_H 1.73-1.80 (1H, m, C^7H), 1.89- 1.97(2H, m, C^6H_2), 1.99-2.13 (3H, m, C^4H_2 & C^8H), 2.17-2.28 (2H, m, C^3H & C^7H), 2.35 -2.46 (2H, m, C^3H & C^8H), 2.99 (1H, m, C^2H), 4.78 (1H, m, C^5H) and 4.94 (1H, m, C^1H), assignments were based on decoupling experiments; δ_c 24.27, 29.70, 31.33, 32.97, 33.12, 57.45 (C^2), 83.84 (C^5) and 86.19(C^1). MS accurate mass: Found: 419.9784; $C_8H_{13}{}^{79}Br^{200}HgO_2$ requires 419.9782.

Separation of Isomeric Hydroperoxides

(a) Cinnamyl hydroperoxide (1) and 1-phenylallyl hydroperoxide(18). A mixture of hydroperoxides **1** and **18** (ratio 35:65) was treated with mercury(II) acetate in the usual way but without anion exchange. Unreacted **18** (23% from cinnamyl chloride) was recovered by column chromatography (SiO_2, CH_2Cl_2), leaving the acetoxymercurio analogue of **19** on the column.

By following the usual procedure, cyclic peroxide **19** was obtained from a mixture of hydroperoxides **1** and **18** (ratio 85:15). Hydrochloric acid (2%; 0.60 cm^3; *ca.* 0.39 mmol) was added to a solution of **19** (0.109g; 0.25 mmol) in tetrahydrofuran (5cm^3) and the solution was stirred for 2h. Water (10 cm^3) and dichloromethane (10 cm^3) were added, the organic layer was isolated and the aqueous layer was extracted with more dichloromethane (5 cm^3). The combined organic extracts were washed with water (5 cm^3), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was extracted with carbon tetrachloride, filtering off the insoluble mercury salts, and the solvent was removed *in vacuo*. Column chromatography (SiO_2, CH_2Cl_2) afforded pure **1** (34%).

(b) Hexa-2,5-dienyl hydroperoxide (4) and hexa-1,5-dien-3-yl hydroperoxide (6). A mixture of hydroperoxides **4** (1.23 mmol) and **6** (0.53 mmol) was treated with mercury(II) acetate (0.55 mmol) in the usual way but without anion exchange. Chromatography (SiO_2, 1:1 light petroleum and diethyl ether) afforded pure **4** (57%), leaving the acetoxymercurio analogue of **24** on the column.

Hydridodemercuriation

To vigorously stirred solution of the organomercury(II) bromide (2.5 mmol) in dichloromethane (15 cm^3) at -10 °C under nitrogen was added a chilled solution of sodium borohydride (0.19 g; 5.0 mmol) in 3M sodium hydroxide (15 cm^3) as quickly as possible while keeping the temperature of the mixture below 0 °C. The reaction mixture was kept at < 0 °C for 30 min and then allowed to warm to room temperature. The dichloromethane layer was separated and the aqueous layer extracted with dichloromethane (3 x 10 cm^3). The dichloromethane layers were combined, dried ($MgSO_4$) and the solvent was removed at a rotary evaporator with the bath temperature at 0-10 °C. The crude product was chromatographed (SiO_2, solvent indicated) to afford the pure peroxide (yield and precursor indicated) Data are provided below for the new compounds prepared.

trans-*3-Methyl-4-prop-2-enyl-1,2-dioxolane* (**40**) [3:1 dichloromethane: light petroleum (60-80 °C); 64% from **26**]; δ_H 1.27 (3H, d J 6.1, CH_3), 2.26 (2H, m, C^4-CH_2), 2.53 (1H, m, C^4H), 3.76 (1H, dd J 7.6 & 5.3, $C^5\underline{H}^A H^B$), 3.96 (1H, m, C^3H), 4.21 (1H, t J 7 6, $C^5H^A\underline{H}^B$), 5.05 (2H, m, CH_2=) and 5.73 (1H, m, CH=); δ_c 17.80 (CH_3), 36.10 (CH_2), 54.90 (C^4), 75.00 (C^5), 81 69 (C^3), 116 88 (CH_2=) and 135.52 (CH=). Found: C, 64.89; H, 9.11. $C_7H_{12}O_2$ requires C, 65.60; H, 9.44%.

3,3,6-Trimethyl-1,2-dioxane (**41**) (dichloromethane; 46% from **29**, 68% from **33**); δ_H (200 MHz) 1.14 (3H, d J 6.3, CH_3), 1.15 (3H, s, CH_3), 1.36 (3H, s, CH_3), 1 64 (4H, m, C^4H_2 & C^5H_2), and 4.14 (1H, m, C^6H); δ_c 18.93 (CH_3), 22.74 (CH_3), 27 43 (CH_3), 28.39, 34.33 (C^4 & C^5), 76.80 (C^6) and 77.53 (C^3); m/z 129 ($M\text{-}1^+$, 3.8%), 97 (15), 69 (36), 55 (23), 43 (100) and 41 (37). MS accurate mass ($M\text{-}1^+$): Found 129.0930; $C_7H_{13}O_2$ requires 129.0915.

cis-(75%) and trans-*5-Ethenyl-3-methyl-1,2-dioxane* (**42**) [1:1 dichloromethane: light petroleum (60-80 °C); 39% from **30**]; δ_H (200 MHz) *cis*: 1.10 (3H, d 6.4Hz, CH_3), 1.34 (1H, m, $C^4\underline{H}^A H^B$), 1.79 (1H, m, $C^4 H^A \underline{H}^B$), 2.57 (1H, m, C^5H), 3.87 (1H, dd J 12.3 & 10.9, C^6H_{ax}), 4.03 (1H, ddd J 12.3, 4.9 & 1.5, C^6H_{eq}), 4.24 (1H, ddq J 10.4, 6.4 & 2.0, C^3H), 5.10 (2H, m, CH_2=) and 5.67 (1H, ddd, CH=). *trans*: 1.15 (3H, d, J 6.5, CH_3), 3.98 (m), 4.30 (m) 4.40 (m) and 6.00 (1H, m, CH=); other signals overlap with those of *cis* isomer. δ_c *cis*: 19.19 (CH_3), 37.35, 39.47 (C^4 & C^5), 76.18 (C^6), 77.46 (C^3), 116.00 (CH_2=), and 138.01 (CH=); *trans*: 18.95 (CH_3), 35.44, 35.84 (C^4 & C^5), 74.71 (C^6), 77.46 (C^3), 115.74 (CH_2=) and 139.51 (CH=).

cis-(75%) and trans-*3-Methyl-5-phenyl-1,2-dioxane* (**43**) [6:4 dichloromethane: light petroleum (60-80 °C); 62% from **31**]; δ_H (200 MHz) *cis*: 1.20 (3H, d J 6.4, CH_3), 1.5-2.1 (2H, m, C^4H_2), 3.20 (1H, m, C^5H), 4.19 (2H, br d J 8.4, C^6H_2), 4.41 (1H, ddq J 10.7, 6.4 & 2.0, C^3H) and 7.26 (5H, m, C_6H_5); *trans* 1.30 (3H, d J 6.5, CH_3); other signals overlap with those of *cis* isomer; δ_c *cis*: 19.06 (CH_3), 38.19, 41.34 (C^4 & C^5), 77.05 (C^6), 77.63 (C^3), 127.09, 127.33, 128.75 and 140.67; *trans*: 18.37 (CH_3), 36.15, 36.35 (C^4 & C^5), 74.61 (C^6), 76.15 (C^3), 126.65, 127.82, 128.55 and 140.67; m/z 178 (M^+, 2.1%), 160 (29), 132 (39), 117 (76), 105 (44), 104 (85), 103 (54), 91 (40), 77 (36), 51 (30) and 43 (100). MS accurate mass (M^+): Found: 178.1002; $C_{11}H_{14}O_2$ requires 178.0993. Found: C, 73.95; H, 8.00. $C_{11}H_{14}O_2$ requires C, 74.13; H, 7.92%.

3,6-Dimethyl-4-phenyl-1,2-dioxane (**44**; mixture of four diastereoisomers) [1:1 diethyl ether: light petroleum (60-80 °C); 65% from **32**]; δ_H (200 MHz) 0.96, 1.02, 1.11, 1.15, 1.17, 1.24 & 1.52 (6H, each d J *ca* 6.5, CH_3), 1.6-2.3 (2H, m, C^5H_2), 2.6-3.5 (1H, m, C^4H), 4.2-4.8 (2H, m, C^3H & C^6H); δ_c 12.45, 16.25, 16.54, 16.84, 17.60, 18.74 & 19.13 (CH_3), 30.66, 36.08, 38.30 & 39.97, (C^5), 42.86, 43.24, 43.46 & 48.91 (C^4), 72.66, 75.66, 77.52, 79.40, 79.76, 81.33 & 81.69 (C^3 & C^6), 126.45, 126.75, 126.91, 127.44, 127.72, 127.81, 128.29, 128.57, 128.71, 129.46, 140.85, 141.61, 141.76 and 141.89; m/z 192 (M^+, 0.24%), 174 (4), 148 (6), 132 (7), 117 (11), 105 (65), 104 (100), 91 (8), 78 (7) and 43 (13). MS accurate mass (M^+): Found 192.1135; $C_{12}H_{16}O_2$ requires 192.1149.

cis-and trans-*3,6-Dimethyl-3-phenyl-1,2-dioxane* (**45**) [1:1 dichloromethane: light petroleum (60-80 °C); 15% from **16** via crude **35**]; δ_H (200 MHz) 0.99 & 1.25 (3H, each d J 6.4, CH_3), 1.33 & 1.65 (3H, each s, CH_3), 1.7-2.5 (4H, m, C^4H_2 & C^5H_2), 4.25 (1H, m, C^6H) and 7.40 (5H, m, C_6H_5); δ_c 18.45, 18.63, 24.35 & 28.10 (CH_3), 28.52, 30.32, 33.19 & 33.42 (C^4 & C^5), 76.82 & 77.10 (C^6), 80.74 & 81.91 (C^3), 124.74, 125.87, 126.59, 127.53, 128.25, 144.32 and 145.57; m/z 192 (M^+, 0.36%), 131 (63), 121 (32), 120 (22), 118 (38), 105 (100), 91 (16), 77 (49), 51 (21) and 43 (64). MS accurate mass: Found 192.1155; $C_{12}H_{16}O_2$ requires 192.1149.

Conversion of 4-Alkyl-3-bromomercuriomethyl-1,2-dioxolanes **25** *and* **26** *into the Corresponding 5-Alkyl-2,2,4-trimethyl-1,2-dioxanes.*

(a) Alkyl = methyl. A mixture of the major isomer of 3-bromomercuriomethyl-4-methyl-1,2-dioxolane from mercury(II) nitrate cyclisation (*trans*- **25**) (0.47 g; 1.23 mmol) and polymethylhydrosiloxane (PMHS) (1 cm^3) was slowly added to a stirred mixture of bis (tributyltin) oxide (4.00 g; 6.71 mmol) and PMHS (1.0 g) cooled in an ice bath. The mixture was stirred for 1h then trap-to-trap distillation (20 °C, 10 mm Hg) afforded a distillate of crude 3,4-dimethyl-1,2-dioxolane (11.4 mg). This was immediately stirred vigorously with a saturated solution of ammonium chloride (5 cm^3) and zinc dust (73 mg; 1.12 mmol) was added in one portion.

Stirring was continued for 2h then the mixture was filtered through Celite, saturated with sodium chloride and extracted with ether (3 x 5 cm^3). The extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure to yield 2-methyl-1,3-butanediol as a colourless liquid (2.7 mg); δ_H 0.84 (3H, d J 7.0), 1.23 (3H, d J 6.2), 1.60 (3H, br s), 3.62 (1H, dd J 10.8 & 7.8) and 3.74 (2H, m). This was stirred in acetone (1 cm^3) with one drop of 2,2-dimethoxypropane and a small crystal of p-toluenesulfonic acid for 1h. The solvent was removed under reduced pressure to afford the crude 1,3-dioxane as a colourless liquid (2.1 mg; 66%). ^1H NMR spectrum: irradiation of the doublet at δ 1.23 (C^4-CH_3) caused a signal at δ 3.78 (C^4H) to collapse to a doublet with J (H^4-H^5) = 8.2 Hz; irradiation of the other doublet at δ 0.82 (C^5-CH_3) had no effect upon the δ 3.6-3.85 (CHO) region of the spectrum.

(b) Alkyl = prop-2-enyl. The isomer of 3-bromomercuriomethyl-4-prop-2-enyl-1,2-dioxolane from mercury(II) nitrate cyclisation (*trans*-**26**) was reduced with alkaline sodium borohydride to afford 3-methyl-4-prop-2-enyl-1,2-dioxolane (**40**) (*vide supra*). Dioxolane **40** (80 mg; 0.62 mmol) was reduced with zinc (0.405 g; 6.2 mmol) and saturated ammonium chloride (6 cm^3) as above to yield 3-hydroxymethyl-hex-5-en-2-ol (77 mg; 95%); δ_H (200 MHz) 1.28 (3H, d J 6.3), 1.56 (1H, m), 2.12 (2H, m), 2.93 (2H, br s), 3.64 (1H, m), 3.90 (2H, m), 5.03 (2H, m) and 5.76 (1H, m); δ_c 21.93, 33.22, 45.81, 64.25, 71.45, 116.66 and 136.38. This was treated with 2,2-dimethoxypropane (68 mg, 0.65 mmol) and p-toluenesulfonic acid (5 mg) in acetone (5 cm^3) as above to give crude 5-prop-2-enyl-2,2,4-trimethyl-1,3-dioxane (99 mg; 99%); δ_H 1.21 (3H, d 6.1), 1.39 (3H, s), 1.44 (3H, s), 1.60 (1H, m), 1.79 (1H, m), 2.11 (1H, m), 3.56 (1H, t J = 11.7), 3.71 (1H, dq J 10.0 & 6.0), 3.76 (1H, dd J 11.7 & 5.1), 5.00 (2H, m), and 5.66 (1H, m); δ_c 19.30, 19.78, 29.70, 32.34, 40.47, 64.04, 69.67, 98.00, 116.83 and 135.05. Irradiation of the doublet of δ 1.21 (C^4-CH_3) caused the doublet of quartets at δ 3.71 (C^4H) to collapse to a doublet with J(H^4-H^5) = 10.0 Hz.

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