Oxymetallation. Part 23.[1] Peroxymercuriation of Bicyclo[*n*.1.0]alkanes

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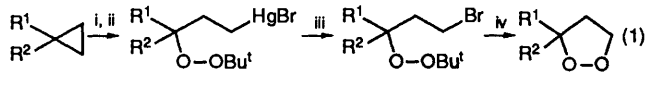
The peroxymercuriations of bicyclo[*n*.1.0]alkanes, *n* = 2–4, have been carried out using mercury(II) acetate and a one-fold excess of t-butyl hydroperoxide in dichloromethane with 20 mol% of perchloric acid as catalyst, the products being isolated, after anion exchange, as the organomercury(II) bromides. Small amounts of acetoxymercurials are also formed but are easily removed by silica chromatography.

Bicyclo[2.1.0]pentane reacts by exclusive cleavage of the zero-bridge to give *cis*-1-bromomercurio-3-t-butylperoxycyclopentane **4**, but competing isomerisation to cyclopentene consumes *ca.* 50% of the cyclopropane. Reaction in neat t-butyl hydroperoxide without perchloric acid gives only the peroxymercurial **4**. This has been converted into 2,3-dioxabicyclo[2.2.1]heptane **2a** by iododemercuriation then reaction with silver trifluoroacetate.

Bicyclo[4.1.0]heptane reacts by exclusive cleavage of the one-bridge to give *cis*- and *trans*-1-bromomercuriomethyl-2-t-butylperoxycyclohexanes **28** and **29**, which have been reduced with alkaline sodium borohydride to afford the corresponding 1-methyl compounds **32** and **33**.

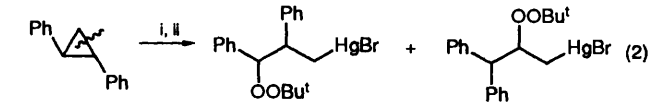
Bicyclo[3.1.0]hexane reacts by both zero-bridge and one-bridge cleavage to give the γ-peroxymercurials *trans*-1-bromomercuriomethyl-2-t-butylperoxycyclopentane **10** and 1-bromomercurio-3-t-butylperoxycyclohexane **13**. Also formed is a similar amount of the isomeric β-peroxymercurials 1-bromomercuriomethyl-1-t-butylperoxycyclopentane **11** and *trans*-1-bromomercurio-2-t-butylperoxycyclohexane **14** yet neither starting cyclopropane nor product γ-peroxymercurial is isomerised by perchloric acid. These unusual rearrangements are also obtained with n-butyl hydroperoxide but not with methanol, butanol or acetic acid as nucleophile. They do not take place with other strong acid catalysts, and are inhibited by 2,6-di-t-butyl-4-methylphenol and promoted by di-t-butyl peroxyoxalate. Reaction in neat t-butyl hydroperoxide at 60 °C without perchloric acid gives only the γ-peroxymercurials **10** and *cis*-**13**. Iododemercuriation of the *cis*-1,3-cyclohexane derivative *cis*-**13**, then reaction with silver trifluoroacetate, gives mainly 3-t-butoxycyclohexanone **27** rather than 6,7-dioxabicyclo[3.2.1]octane.

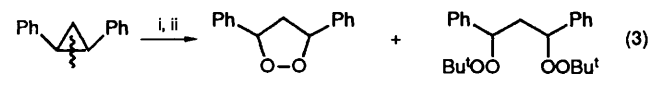
The t-butyl peroxymercuriation of cyclopropane[2] and several mono- and 1,1-disubstituted cyclopropanes[3,4] has been described and incorporated into a three-step synthesis of 1,2-dioxolanes [equation (1)].[4]



Reagents: i, Bu^{t}OOH (2 mol equiv.), $Hg(OAc)_2$, 20 mol% $HClO_4$, CH_2Cl_2; ii, KBr, water; iii, Br_2, NaBr, MeOH; iv, AgO_2CCF_3, CH_2Cl_2

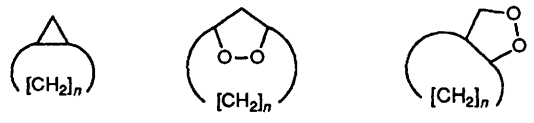
The peroxymercuriation of *cis*- and *trans*-1,2-diphenylcyclopropane has also been studied, but the results were more complicated.[5] The *trans*-isomer reacted exclusively by 1,3-bond scission as expected for a Markovnikov-type addition. However, it gave not only the expected γ-peroxymercurial, but also the β-peroxymercurial arising from 1,2-migration of a phenyl group [equation (2)].[5] The *cis*-isomer, by contrast, reacted mainly by 1,2-bond cleavage and yielded 3,5-diphenyl-1,2-dioxolane directly by oxidative demercuriation of the intermediate benzylic γ-peroxymercurial [equation (3)].[5]





Reagents: i, Bu^{t}OOH (neat or 2 mol equiv. in CH_2Cl_2), $Hg(OAc)_2$ 20 mol% $HClO_4$; ii, KBr, water

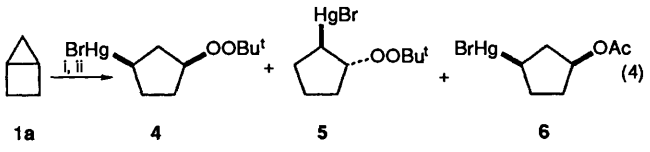
The unusual behaviour of the 1,2-diphenylcyclopropanes can be ascribed to three properties of the phenyl group, namely its ability to stabilise an α-cation, its migratory aptitude, and its steric bulk. It was therefore of interest to examine the t-butyl peroxymercuriation of 1,2-disubstituted cyclopropanes devoid of aromatic substituents. In this paper we describe such an investigation with bicyclo[*n*.1.0]alkanes (**1**; *n* = 2–4). This has the additional interest that it might provide the basis of a new synthetic route to bicyclic peroxides,[6] specifically to dioxabicyclo[*n*.2.1]alkanes **2** or dioxabicyclo[*n*.3.0]alkanes **3** *via* initial cleavage of the zero-bridge or one-bridge, respectively. In the course of this work we have discovered unusual rearrangements during the peroxymercuriation of bicyclo[3.1.0]hexane **1b**.



a; *n* = 2; **b**; *n* = 3; **c**; *n* = 4

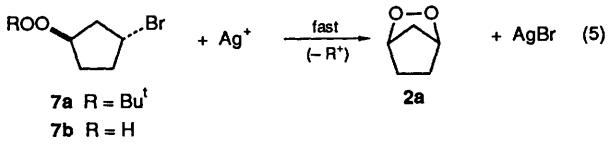
Results and Discussion

Bicyclo[2.1.0]*pentane.*—The t-butyl peroxymercuriation of bicyclo[2.1.0]pentane **1a** under the usual conditions[4,5] led to exclusive cleavage of the zero-bridge with formation of γ-peroxymercurial **4**, β-peroxymercurial **5** and γ-acetoxymercurial **6** [equation (4)]. The β-peroxymercurial **5**, which amounted to about 50% of the product mixture, was identified by comparison with an authentic sample prepared from cyclopentene.[7] The



Reagents: i, Bu^{t}OOH (2 mol equiv.), $Hg(OAc)_2$, 20 mol% $HClO_4$, CH_2Cl_2; ii, KBr, water

γ-peroxymercurial **4** was isolated by silica chromatography and identified by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The assignment of *cis*-stereochemistry was based on the fact that configuration-preserving bromodemercuriation using bromine in pyridine[8] afforded a 1-bromo-3-t-butylperoxycyclopentane which did not react rapidly with silver trifluoroacetate at −10 °C. Yet under the same conditions, the isomeric bromo peroxide **7a** in a 1:1 mixture obtained by non-stereospecific bromodemercuriation was converted into 2,3-dioxabicyclo[2.2.1]heptane **2a** [equation (5)].



Previous work with 1-bromo-3-hydroperoxycyclopentanes[9] has shown that it is the *trans*-isomer **7b** which rapidly affords the bicyclic peroxide upon reaction with silver salt, and it is reasonable to expect that the t-butylperoxy compounds will behave similarly.

The non-stereospecific brominolysis of compound **4** was anomalous in that it was brought about by bromine and sodium bromide in methanol, conditions which have previously proved successful in effecting bromodemercuration with retention.[7] We showed that *cis*-1-bromo-3-t-butylperoxycyclopentane was not epimerised by sodium bromide in methanol, and at present we can offer no explanation for the anomaly.

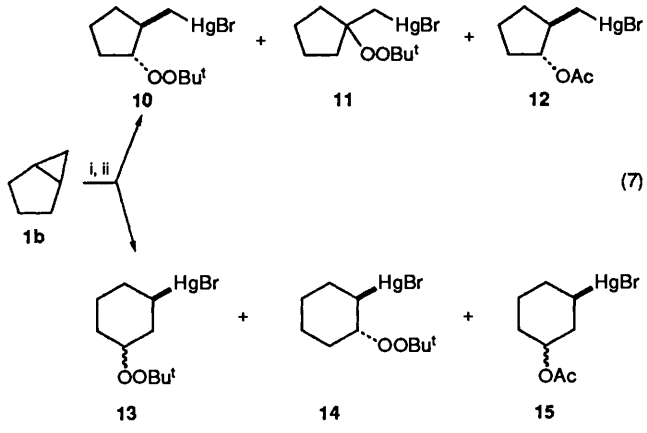
Exclusive cleavage of the zero-bridge of bicyclo[2.1.0]pentane is expected because of the resultant relief of ring strain. Furthermore, this mode of reactivity has been reported previously for the related reactions of hydroxymercuriation[10] and hydroperoxybromination.[9] However, only with the latter reaction was any 1,2-disubstituted cyclopentane product obtained, and there it amounted to less than 5% of the product mixture. A control experiment revealed that 20 mol% of perchloric acid catalyses the rearrangement of bicyclo[2.1.0]-pentane into cyclopentene at a rate comparable to that of the peroxymercuriation, and that all the β-peroxymercurial **5** formed could be accounted for in this way.

The reactions carried out to establish the stereochemistry of the γ-peroxymercurial **4** also showed that the three-step conversion of cyclopropanes into 1,2-dioxolanes[4] could be extended to the preparation of a bicyclic peroxide. However, the overall yield of 2,3-dioxabicyclo[2.2.1]heptane **2a** was severely restricted by the fact that half of the bicyclo[2.1.0]pentane was converted instead into the β-peroxymercurial **5** and that 50% of the product of bromodemercuriation of the γ-peroxymercurial **4** was the unreactive *cis*-isomer. The following modifications were made to attenuate these difficulties.

When the cyclopropane **1a** was treated with mercury(II) acetate in neat t-butyl hydroperoxide without perchloric acid, followed by anion exchange with aq. potassium bromide, the γ-peroxymercurial **4** was the only isolated product. Bicyclo-[2.1.0]pentane is sufficiently strained for this reaction to proceed quite rapidly and a 75% yield of compound **4** was obtained after 10 min at 0 °C. Iododemercuriation of the γ-peroxymercurial **4** gave a 1:1 mixture of *cis*- and *trans*-1-t-butylperoxy-3-iodocyclopentane, which was readily separated by preparative HPLC. Treatment of the *cis*-isomer **8** with sodium iodide in acetone converted it back into a 1:1 mixture and, by carrying out a further separation, we obtained a combined yield of 63% of the pure *trans*-iodide **9**. The iodo peroxide **9** was then converted into 2,3-dioxabicyclo[2.2.1]-heptane at −30 °C [equation (6)] and this product was purified by Kugelrohr distillation and low-temperature silica chromatography.

2,3-Dioxabicyclo[2.2.1]heptane **2a** has received much attention because of its relationship to prostaglandin endoperoxides,[11] and several syntheses of it have been reported.[9,12–14] The new method described here [equation (6)] constitutes an alternative route from bicyclo[2.1.0]pentane which presents few experimental difficulties, avoids the hazard associated with using 98% hydrogen peroxide, and leads to an overall yield of 45%.

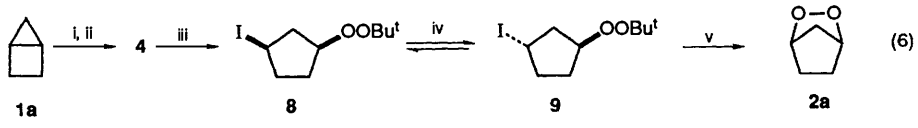
Bicyclo[3.1.0]*hexane*.—The t-butyl peroxymercuriation of bicyclo[3.1.0]hexane **1b** under the usual conditions[4,5] afforded a mixture of the six organomercurials **10**–**15** in ~80% yield [equation (7)]. The products could be separated partially by



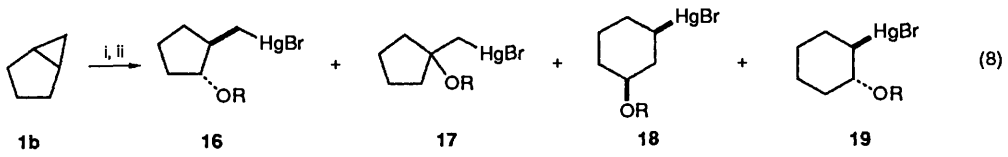
Reagents: i, Bu^{t}OOH (2 mol equiv.), $Hg(OAc)_2$, 20 mol% $HClO_4$, CH_2Cl_2; ii, KBr, water

column chromatography and fully by preparative HPLC. The γ-acetoxymercurials **12** and **15** were only very minor products (~5% each). The distribution of peroxymercurials was 26% (**10**), 32% (**11**), 21% (**13**) and 21% (**14**). The β-peroxymercurials **11** and **14** were identified by comparison with authentic samples prepared by standard peroxymercuriation[7] of methylenecyclopentane and cyclohexene, respectively. The γ-peroxymercurials **10** and **13** were identified by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The spectroscopic data indicated that whereas the cyclopentane derivative **10** was a single stereoisomer, the cyclohexane compound **13** was a 70:30 mixture of *cis* and *trans* isomers.

The assignment of *cis* stereochemistry to the major isomer of



Reagents: i, Bu^{t}OOH (10 mol equiv.), $Hg(OAc)_2$; ii, KBr, water, CH_2Cl_2; iii, I_2, CH_2Cl_2; iv, NaI, Me_2CO; v, AgO_2CCF_3, CH_2Cl_2



1b 16 17 18 19

Reagents: i, ROH (2 mol equiv.), $Hg(OAc)_2$ 20 mol% $HClO_4$, CH_2Cl_2; ii, KBr, water

Table 1 Product analyses for (per)oxymercuriations of bicyclo[3.1.0]hexane [equation (8)][a]

R	16	17	18	19	Yield (%)
Bu^tO[b]	26 [≡**10**]	32 [≡**11**]	21[c] [≡*cis*-**13**]	21 [≡**14**]	70
BuO	42	24	22	12	70
Me	66	0	34	0	38
Bu	70	0	30	0	40
Ac[d]	50 [≡**12**]	0[e]	50 [≡*cis*-**15**]	0	28

[a] Molar ratio (%) calculated from ^{13}C NMR spectra after removal, by silica chromatography, of the small amounts of acetoxymercurials also formed. [b] Analysis by HPLC. [c] Contained 30% of *trans*-isomer. [d] A similar mixture was obtained by acetylation of the hydroxymercuriation products; *cf.* a reported ratio **16**:**18** of 37:63 in the absence of $HClO_4$.[16] [e] Compound **17** could not be prepared independently by acetoxymercuriation of methylenecyclopentane; β-oxymercurials prepared from methylenecyclopentane were generally rather unstable.

the γ-peroxymercurial **13** was based on the ^1H NMR spectrum of the corresponding 1-bromo-3-t-butylperoxycyclohexane obtained by configuration-preserving bromodemercuriation in pyridine.[8] This was consistent with a diequatorial arrangement of substituents, the protons geminal to bromine and to t-butylperoxyl each appearing as triplets of triplets with axial–axial and axial–equatorial couplings. This work was actually carried out on the isomerically pure peroxymercurial obtained by separation of the mixture from a peroxymercuriation in neat t-butyl hydroperoxide (see later). The assignment of *trans* stereochemistry to the γ-peroxymercurial **10** is based on reports that the carbon centre undergoing nucleophilic attack generally undergoes inversion of configuration during the oxymercuriation of cyclopropanes.[15]

The results indicate that the peroxymercuriation of bicyclo[3.1.0]hexane **1b** is non-regiospecific, both zero-bridge cleavage and one-bridge cleavage taking place in the ratio 42:58. A corresponding ratio of 63:37 has been reported for the uncatalysed hydroxymercuriation of this cyclopropane.[16]

The results also indicate that, as with bicyclo[2.1.0]heptane, about 50% of the products arise by rearrangement, and furthermore that rearrangement takes place to a similar extent for both modes of cleavage. However, unlike bicyclo[2.1.0]pentane, bicyclo[3.1.0]hexane was shown to be unaffected by 20 mol% perchloric acid, alone or additionally with t-butyl hydroperoxide, over periods of time considerably longer than that of the peroxymercuriation. Similarly, 1-acetoxymercuriomethyl-2-t-butylperoxycyclopentane, prepared from the corresponding organomercury(II) bromide **10** and silver acetate, did not undergo isomerisation under the same conditions. Therefore, the rearrangements that ultimately afford β-peroxymercurials **11** and **14** take place *during* peroxymercuriation.*

This was an unexpected result since rearrangements during the oxymercuriation of cyclopropanes are very rare and were not reported to occur in the hydroxymercuriation of bicyclo[3.1.0]hexane.[16] Furthermore, other electrophilic additions to bicyclo[3.1.0]hexane proceed with little[17–19] or no[20,21] rearrangement. In view of this background, it was decided to investigate these unusual rearrangements in more detail to try to establish which factors, *e.g.* choice of catalyst, mercury(II) salt, nucleophile, solvent, *etc.*, promote their occurrence. Suppression of the rearrangements was obviously important from the point of view of preparing bicyclic peroxides.

(a) *Effect of the catalyst.* Nitric, trifluoroacetic, and tetrafluoroboric acids were each found to be much less effective than perchloric acid in catalysing the peroxymercuriation of phenylcyclopropane. Nevertheless, tetrafluoroboric acid was tried with bicyclo[3.1.0]hexane and led to the slow formation of γ-peroxymercurials with no rearrangement product being detected. With no added catalyst, the peroxymercuriation under otherwise normal conditions was too slow to be of any value. However, when t-butyl hydroperoxide was used as the solvent, a 52% yield of peroxymercurials was obtained after two weeks at room temperature or two hours at 60 °C. The products consisted solely of compound **10** and *cis*-**13** in the ratio 2:1; no rearrangement had occurred. The peroxymercuriation in t-butyl hydroperoxide solvent was repeated with added perchloric acid. The β-peroxymercurials **11** and **14** were now obtained, although they amounted to only 10% of the product mixture compared with over 50% in dichloromethane. These experiments indicate that perchloric acid is necessary for rearrangement to take place and that rearrangement is suppressed by high nucleophile concentration.

(b) *Effect of the nucleophile.* The (per)oxymercuriations of bicyclo[3.1.0]hexane with n-butyl hydroperoxide, methanol, butanol, and acetic acid were each carried out under conditions parallel to those for t-butyl peroxymercuriation. In addition, hydroxymercuriation was carried out in aq. solution following the reported procedure[16] except that perchloric acid was present. For each nucleophile, authentic rearrangement products **17** and **19** were prepared independently from methylenecyclopentane and cyclohexene to assist with product analyses. The crude products were analysed by ^{13}C NMR spectroscopy as a mixture of the four possible oxymercurials [equation (8)], and the product distributions so found are presented in Table 1.

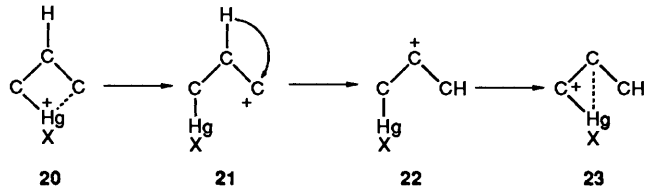
It is noteworthy that the yields from oxymercuriations were markedly poorer than those from peroxymercuriations. In the oxymercuriations, grey deposits were formed in the reaction mixtures and tests with sodium hydroxide indicated the presence of mercury(I) salts. This did not occur in the peroxymercuriations. As far as we are aware, comparisons of this type have not been reported before. They suggest that peroxymercuriations are synthetically more viable than oxymercuriations and might therefore be the method of choice for the introduction of oxygen functionality by this kind of methodology.

The striking conclusion from these experiments is that rearrangements only take place when the nucleophile is an alkyl hydroperoxide.

The fact that rearrangements do not usually occur in the oxymercuriation of cyclopropanes may be regarded as evidence for the involvement of intermediates in which the mercury atom interacts to stabilise the incipient γ-mercuriocarbocation. Such intermediates **20** are called homomercurinium ions.[2] The stabilisation must be sufficient, usually, to prevent the formation

* The absence of rearranged acetoxymercurials, here and with bicyclo[2.1.0]pentane, is not surprising since it is known that perchloric acid catalyses β-oxy exchange in such compounds to give only t-butyl peroxymercurials in the presence of t-butyl hydroperoxide.[7]

of a fully fledged carbocation **21** (but see ref. 5), since this might be expected to undergo 1,2-migration, for example of a hydrogen, to afford a β-mercuriocarbocation **22** and thence a mercurinium ion **23**. Other factors being equal, mercurinium stabilisation is likely to be greater than homomercurinium stabilisation.



20 **21** **22** **23**

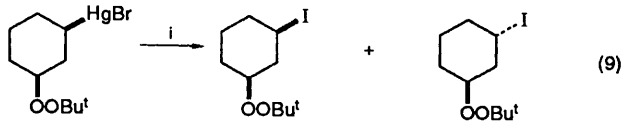
There is some evidence in the literature that the use of highly ionic mercury(II) salts in oxymercuriation favours carbocationic intermediates.[22,23] This could explain the role of the perchloric acid. The reduced extent of rearrangement in neat t-butyl hydroperoxide compared with dichloromethane is then readily understood in terms of the increased rate of the bimolecular capture of carbocation **21** *versus* the unchanged rate of its unimolecular rearrangement into cation **22**. However, a rationalisation of the results in Table 1 would require that the alkyl hydroperoxides are weaker nucleophiles than methanol, butanol or acetic acid. This conflicts with the generally accepted view and was shown to be incorrect by carrying out the oxymercuriation of phenylcyclopropane with mercury(II) acetate, perchloric acid catalyst, and equimolar amounts of t-butyl hydroperoxide and methanol in which the γ-peroxymercurial, γ-methoxymercurial and γ-acetoxymercurial were obtained in the molar proportions 48:35:17. Furthermore, subsequent work (see later) showed that no rearrangement occurred in the peroxymercuriation of bicyclo[4.1.0]heptane under standard conditions. These results appear to rule out the carbocation mechanism.

That the rearrangements were confined to reactions with alkyl hydroperoxides suggested that free-radical processes might be involved. The standard peroxymercuriation was repeated but in the presence of 5 mol% of 2,6-di-t-butyl-4-methylphenol, which is a well known inhibitor of chain reactions involving oxygen-centred radicals. The mercury(II) acetate dissolved more slowly, but after 90 min the yield of organomercury(II) bromide (69%) was essentially the same as under normal conditions. However, the proportion of rearranged peroxymercurials was only 6% compared with 53% when the phenol was absent. This indicates that a radical-chain mechanism is involved in the formation of the β-peroxymercurials **11** and **14** but not of the γ-peroxymercurials **10** and **13**. Further support for this picture came from a demonstration that inclusion of 2.5 mol% of di-t-butyl peroxyoxalate, a thermal source of t-butoxyl radicals, in an otherwise normal [equation (8); Table 1] methoxymercuriation afforded a product containing 10% of β-methoxymercurials. Hence a free-radical initiator promotes rearrangement. It is known that t-butoxy radicals abstract hydrogen preferentially from the 2-position of bicyclo[*n*.1.0]alkanes and that the resultant radicals rapidly rearrange by cyclopropane ring-opening to give cycloalkenyl and cycloalkenylmethyl radicals.[24] While this might provide the basis for a radical-catalysed rearrangement of bicyclo[3.1.0]hexane into cyclohexene and thence formation of product **14**, it cannot account for the methylenecyclopentane-derived product **11**. Furthermore, it is inconsistent with the absence of rearrangement in the peroxymercuriation of bicyclo[4.1.0]heptane.

A satisfactory mechanistic interpretation of the rearrangements must explain the radical-chain component, the role of the perchloric acid, and the failure of bicyclo[4.1.0]heptane to show parallel chemistry. The last factor is particularly difficult to accommodate. We considered the possibility that formation of the radical cation of the cyclopropane might be involved, but the ionisation potentials of bicyclo[3.1.0]hexane and bicyclo-[4.1.0]heptane are reported to be very similar.[25] Also, when mercury(II) trifluoroacetate, which is known to promote radical-cation formation from arenes,[26] was used in place of mercury(II) acetate, no rearranged peroxymercurials were obtained. We are currently unable to suggest a convincing mechanism which accounts for all the experimental observations.

Attempted Preparation of 6,7-*Dioxabicyclo*[3.2.1]*octane*.—Although the mechanism of rearrangement during the peroxymercuriation of bicyclo[3.1.0]hexane remains unclear, rearrangement can be avoided very easily by carrying out the reaction of neat t-butyl hydroperoxide and omitting the perchloric acid catalyst. Under these conditions, competing acetoxymercuriation is also eliminated and γ-peroxymercurials **10** and *cis*-**13** are alone obtained in the ratio 2:1. In view of the success of our new synthesis of 2,3-dioxabicyclo[2.2.1]heptane from bicyclo[2.1.0]pentane [equation (6)], an attempt was made to use parallel chemistry to convert bicyclo[3.1.0]hexane **1b** into 6,7-dioxabicyclo[3.2.1]octane **2b**. None of the previously known routes[9,12–14] to 2,3-dioxabicyclo[2.2.1]-heptane has been successfully extended to the preparation of the [3.2.1] peroxide. This bicyclic peroxide has only been made by reduction of its *cis*-8-bromo analogue and the method suffers from experimental difficulties and a low yield.[27]

The γ-peroxymercurials **10** and *cis*-**13** were separated by preparative HPLC and the cyclohexane derivative was converted into a 1:1 mixture of iodo peroxides **24** and **25** [equation (9)]. The iodides were separated by column

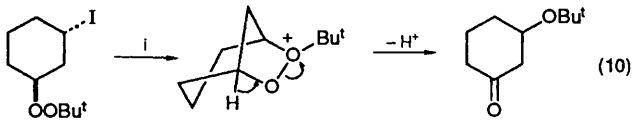


(9)

cis-**13** **24** **25**

Reagents: i, I_2, CH_2Cl_2

chromatography and their structures were assigned on the basis of the coupling patterns of the methine protons (*cf.* the spectrum of *cis*-1-bromo-3-t-butylperoxycyclohexane discussed earlier as proof of the stereochemistry of the precursor mercurial). When *trans*-iodide **25** was treated with silver trifluoroacetate at −30 °C, the product obtained gave a positive peroxide test and contained, in the 400 MHz ^1H NMR spectrum, a small triplet at δ_H 4.67 indicative of the desired 6,7-dioxabicyclo[3.2.1]octane.[27] However, the major product was identified by ^1H and ^{13}C NMR and IR spectroscopy as 3-t-butoxycyclohexanone **27**. It appears that the intermediate trialkylperoxonium ion **26** prefers to undergo deprotonation rather than to lose t-butyl cation [equation (10)].



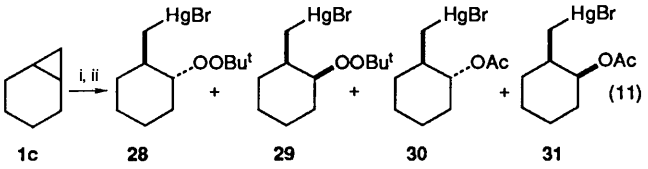
(10)

25 **26** **27**

Reagent: i, AgO_2CCF_3

Formation of a 3-t-butoxy ketone was similarly observed in the attempted synthesis of 3,3-diphenyl-1,2-dioxolane by analogous methodology.[4] Whatever the reason for the divergence of behaviour between the [3.2.1] and [2.2.1] systems, it renders this approach to 6,7-dioxabicyclo[3.2.1]octane untenable.

Bicyclo[4.1.0]*heptane.*—The t-butyl peroxymercuriation of bicyclo[4.1.0]heptane **1c** under the usual conditions[4,5] proceeded by exclusive one-bridge cleavage, without any rearrangement, to afford as major products the two γ-peroxymercurials **28** and **29** together with small amounts of the corresponding acetoxymercurials **30** and **31** [equation (11)].

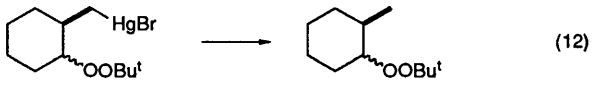


1c **28** **29** **30** **31**

Reagents: i, Bu^{t}OOH (2 mol equiv.), $Hg(OAc)_2$, 20 mol% $HClO_4$, CH_2Cl_2; ii, KBr, water

The absence of rearrangement products was confirmed by comparison of the ^1H and ^{13}C NMR spectra of the crude product mixture with those of 1-bromomercuriomethyl-1-t-butylperoxycyclohexane and *trans*-1-bromomercurio-2-t-butylperoxycycloheptane prepared independently by peroxymercuriation of methylenecyclohexane and cycloheptene, respectively.

The γ-peroxymercurials **28** and **29** were separated from the acetoxymercurials by column chromatography, and further evidence for their structures was obtained by reduction with alkaline sodium borohydride [equation (12)]. This yielded a



28/29 **32/33**

mixture of *cis*- and *trans*-1-t-butylperoxy-2-methylcyclohexane **32/33** which showed characteristic methyl doublets in the ^1H NMR spectrum at δ_H 0.95 and 1.18.

It is interesting that whereas with bicyclo[3.1.0]hexane the unrearranged product of one-bridge cleavage was a single stereoisomer **10**, with bicyclo[4.1.0]heptane both *cis* and *trans* isomers **28/29** are obtained. In the oxymercuriation of cyclopropanes, inversion of configuration is generally observed at the site of nucleophilic attack consistent with an S_N2-type of displacement at a homomercurinium ion.[15] The lack of stereospecificity in the present reaction [equation (11)] may therefore point to a higher degree of carbocationic character in the intermediate. If this interpretation is correct, then it provides a further indication that a carbocation mechanism is not involved in the rearrangements found with bicyclo[3.1.0]hexane.

Experimental

NMR spectra were recorded with a Varian XL 200 or VXR 400 spectrometer for solutions in $CDCl_3$, and chemical shifts are relative to internal $SiMe_4$ (^1H and ^{13}C) or external dimethylmercury referencing to external butylmercury(II) chloride (δ −944)[28] (^{199}Hg); δ_{Hg}-values are concentration dependent; for example, we observed a change of +29 ppm in going from a 5 to an 85% w/v solution of compound **14**. *J*-Values are given in Hz. IR spectra were measured with a Perkin-Elmer 983 instrument. Preparative HPLC was carried out with a Waters 500 machine fitted with a 50 cm × 2.25 cm diameter column containing silica (Merck 40–63 μm); the eluent was 2% ethyl acetate in light petroleum (b.p. 60–80 °C). Silica for column chromatography was Merck Kieselgel 60, 70–230 mesh, 0.063–0.20 mm.

n-Butyl hydroperoxide,[29] di-t-butyl peroxyoxalate,[30] mercury(II) trifluoroacetate,[31] bicyclo[2.1.0]pentane,[32] bicyclo[3.1.0]hexane,[33,34] and bicyclo[4.1.0]heptane[33,34] were each prepared by literature procedures. t-Butyl hydroperoxide was purified as described previously.[2] Other reagents were commercial samples which were used as received.

All organomercury products were stored in a freezer.

t-Butyl Peroxymercuriation of Bicyclo[2.1.0]*pentane.*—(a) *In dichloromethane.*[4] To mercury(II) acetate (1.59 g, 5 mmol) and dichloromethane (10 cm^3) was added t-butyl hydroperoxide (0.9 g, 10 mmol), then 60% aq. perchloric acid (10 drops from a commercial Pasteur pipette; ~1 mmol). The mixture was cooled to 0 °C and stirred magnetically as bicyclo[2.1.0]pentane (0.34 g, 5 mmol) was added dropwise. After 30 min the solution was decanted from any insoluble material and washed with water (3 × 10 cm^3). Aq. potassium bromide (5.5 mmol; 5 cm^3) was added and the mixture was stirred vigorously for 30 min. Water (10 cm^3) was added, the organic layer was separated, and the aq. layer was extracted with dichloromethane (2 × 5 cm^3). The dichloromethane solutions were combined, then dried ($MgSO_4$), and the solvent was removed to afford the crude product as an oil, which was identified by NMR spectroscopy as a mixture of compounds **4**, **5**[7,35] and **6** (70%). Column chromatography on silica with 2% ethyl acetate in light petroleum (b.p. 60–80 °C) as eluent afforded pure cis-1-*bromomercurio*-3-*t-butylperoxycyclopentane* **4** as a paste which could not be recrystallised; δ_H 1.18 (9 H, s), 1.2–2.2 (5 H, m), 2.2–2.4 (1 H, m), 2.65 (1 H, m) and 4.60 (1 H, m); δ_C 26.53 (3 C), 30.30, 30.65, 37.63 [$J(^{199}Hg)$ 60], 49.90 [$J(^{199}Hg)$ 1590], 79.90 and 85.55 [$J(^{199}Hg)$ 90] (Found: C, 25.1; H, 3.95. $C_9H_{17}BrHgO_2$ requires C, 24.68; H, 3.88%). Spectroscopic data for *cis*-1-acetoxy-3-bromomercuriocyclopentane **6**: δ_H 1.1–1.2 (1 H, m), 1.4–2.3 (5 H, m), 1.98 (3 H, s), 2.56 (1 H, approx. q) and 5.16 (1 H, m); δ_C 21.44, 30.72, 32.54, 39.29, 50.16, 75.31 and 170.54.

(b) *In t-butyl hydroperoxide.* Bicyclo[2.1.0]pentane (5 mmol) was added dropwise to a magnetically stirred mixture of mercury(II) acetate (5 mmol) and t-butyl hydroperoxide (5–10 cm^3) at 0 °C. The mixture was stirred for 10 min, then the bulk of the t-butyl hydroperoxide was removed at 0.1 mmHg. Dichloromethane (10–15 cm^3) was added, the mixture was filtered, and the residue was washed thoroughly with dichloromethane (10–15 cm^3). The dichloromethane solutions were combined, washed with water (3 × 10 cm^3), and treated with aq. potassium bromide as usual [see (a) above]. After removal of the dichloromethane on a rotary evaporator, any residual t-butyl hydroperoxide was removed at 0.1 mmHg to leave compound **4** (75%).

Bromodemercuriation of cis-1-*Bromomercurio*-3-*t-butylperoxycyclopentane* **4**.—(a) *In pyridine.*[8] A solution of bromine (5.5 mmol) in pyridine (5 cm^3) was added slowly to a magnetically stirred solution of the γ-peroxymercurial **4** (5 mmol) in the same solvent (10 cm^3). The mixture was stirred for 5 h then left overnight. The insoluble mercury(II) bromide was filtered off, dichloromethane (20 cm^3) was added, and the mixture was washed with dil. hydrochloric acid (4 × 20 cm^3) to remove the pyridine. The solution was then washed with water (20 cm^3), then dried ($MgSO_4$), and the dichloromethane was removed on a rotary evaporator to give *cis*-1-bromo-3-t-butylperoxycyclopentane (50%; containing ~10% of the *trans*-isomer **7a**) δ_H 1.23 (9 H, s), 2.1–2.3 (5 H, m), 2.53 (1 H, td, *J* 7.1, 14.2), 4.15 (1 H, approx. quinet, *J* 6.7) and 4.50 (1 H, approx, tt, *J* 6.8, 3.4); δ_C 26.55 (3 C), 30.15, 36.14, 42.20, 47.25, 79.80 and 82.95.

(b) *In methanolic sodium bromide.*[7] To a solution of the γ-peroxymercurial **4** (5 mmol) in methanol (5 cm^3) was added a mixture of bromine (5.5 mmol) and sodium bromide (1.5 g) in methanol (10 cm^3), rinsed in with more methanol (5 cm^3). The mixture was stirred for 1 h. Water (10 cm^3) and light petroleum

(b.p. 40–60 °C; 10 cm^3) were added, the mixture was shaken, and the layers were separated. The aq. layer was extracted with more light petroleum (2 × 10 cm^3) and the combined organic layers were dried ($MgSO_4$). The solvent was removed on a rotary evaporator to give a quantitative yield of a ~1:1 mixture of *cis*-1-bromo-3-t-butylperoxycyclopentane [see (a) above] and the *trans*-isomer **7a**; δ_H 1.20 (9 H, s), 1.7–2.05 (5 H, m), 2.25–2.4 (1 H, m), 4.4–4.5 (1 H, m) and 4.6–4.7 (1 H, m); δ_C 26.45 (3 C), 29.20, 35.97, 43.22, 50.00 and 83.61 (one COO resonance obscured by $CDCl_3$ peaks).

Reaction of 1-*Bromo*-3-*t-butylperoxycyclopentane with Silver Trifluoroacetate.*—To a magnetically stirred solution of a 1:1 mixture of *cis*- and *trans*-bromo peroxide (3 mmol) in dry dichloromethane (10 cm^3) at −40 °C was added silver trifluoroacetate (3.3 mmol). The mixture was allowed to warm up and at −10 °C silver bromide began to precipitate out. The mixture was stirred at −10 °C for 10 min, then was filtered through Celite and the solvent was removed on a rotary evaporator. The ^1H and ^{13}C NMR spectra of the residue indicated the presence of unchanged *cis*-bromo peroxide, 2,3-dioxabicyclo[2.2.1]heptane[9] **2a**, and t-butyl trifluoroacetate.[4]

No reaction occurred when the bromo peroxide (*cis*) obtained from bromodemercuriation in pyridine (above) was stirred with silver trifluoroacetate at −10 °C for 30 min.

Iododemercuriation of cis-1-*Bromomercurio*-3-t-*butylperoxycyclopentane* **4**.—Iodine (6 mmol) was added to a solution of the γ-peroxymercurial **4** (5 mmol) in dichloromethane (15 cm^3) and the mixture was stirred for 3 h. The precipitate was removed by filtration and the filtrate was washed with water (15 cm^3). The dichloromethane was removed on a rotary evaporator and light petroleum (b.p. 40–60 °C; 20 cm^3) was added. The solution was decanted from the insoluble material, washed successively with aq. sodium thiosulphate to remove excess of iodine and with water, and then dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to afford a quantitative yield of a 1:1 mixture of *cis*- and *trans*-1-t-butylperoxy-3-iodocyclopentane **8** + **9**. The pure components were isolated by HPLC.

For **8**: δ_H 1.25 (9 H, s), 1.7–2.0 (3 H, m), 2.14 (2 H, m), 2.6 (1 H, approx. quintet, *J* 7), 4.00 (1 H, approx. quintet, *J* 7) and 4.49 (1 H, approx. septet, *J* 3.5); δ_C 19.72, 26.50 (3 C), 31.20, 38.04, 44.11, 79.88 and 83.20.

For **9**: δ_H 1.26 (9 H, s), 1.8–2.4 (6 H, m), 4.31 (1 H, approx. quintet, *J* 6) and 4.59 (1 H, m); δ_C 23.31, 26.42 (3 C), 29.84, 37.81, 44.95, 79.70 and 83.84.

Epimerisation of cis-1-*t-Butylperoxy*-3-*iodocyclopentane* **8**.—A large excess of sodium iodide was added to a solution of iodo peroxide **8** (2 mmol) in acetone (20 cm^3). The mixture was stirred for 10 min to dissolve the salt, then left at room temperature for 16 h. The solution was extracted with diethyl ether (50 cm^3), the ether layer was washed with water (2 × 50 cm^3), then dried ($MgSO_4$), and the solvent was removed on a rotary evaporator to give a 1:1 mixture of isomers **8** and **9**.

Reaction of trans 1-*t-Butylperoxy*-3-*iodocyclopentane* **9** *with Silver Trifluoroacetate.*—The reaction was carried out as for the corresponding bromo peroxide (above) except that it proceeded at −30 °C rather than at −10 °C. The crude product was distilled at 20 °C and 0.1 mmHg in a Kugelrohr apparatus to afford a mixture of t-butyl trifluoroacetate[4] and 2,3-dioxabicyclo[2.2.1]heptane **2a**. Chromatography of this mixture at −30 °C on silica with dichloromethane as eluent afforded the pure bicyclic peroxide **2a**;[9] δ_H(400 MHz) 1.69 (2 H, dm, *J* 8.0), 1.92 (2 H, ddd, *J* 8.0, 6.0, 2.4), 2.12 (1 H, br d, *J* 10.2), 2.27 (1 H, d, quintet, *J* 10.2, 2.4) and 4.70 (2 H, br s).

t-Butyl Peroxymercuriation of Bicyclo[3.1.0]*hexane.*—(a) *In dichloromethane.*[4] The reaction was carried out as for bicyclo[2.1.0]pentane (above) except that the scale was doubled. The crude product (80%) was obtained as an oil, which TLC and ^{199}Hg NMR spectroscopy each indicated contained six organomercurials. Column chromatography on silica with a 1:1 mixture of light petroleum (b.p. <40 °C) and dichloromethane as eluent gave, in order of elution, the following four fractions.

(i) 1-*Bromomercuriomethyl*-1-*t-butylperoxycyclopentane* **11** (18%) as crystals, m.p. 39 °C [recrystallised from warm (35 °C) light petroleum (b.p. 40–60 °C)]; δ_H 1.28 (9 H, s), 1.50 (2 H, m), 1.80 (4 H, m), 2.03 (2 H, m) and 2.14 [2 H, s, $J(^{199}Hg)$ 196]; δ_C 24.75t (2 C), 26.71q (3 C), 39.16t [2 C, $J(^{199}Hg)$ 140], 43.07t [$J(^{199}Hg)$ 1541], 79.36s and 92.45s [$J(^{199}Hg)$ 129]; the following heteronuclear correlations were made using a 2D pulse sequence ^1H (^{13}C): 1.28 (26.7), 1.50 (39.1), 1.80 (24.75), 2.03 (39.1) and 2.14 (43.0); δ_{Hg} −1072 (Found: C, 26.5; H, 4.05. $C_{10}H_{19}BrHgO_2$ requires C, 26.59; H, 4.24%).

(ii) A mixture of the peroxymercurials **10**, **13** and **14** (38%) (Found: C, 26.6; H, 4.1. $C_{10}H_{19}BrHgO_2$ requires C, 26.59; H, 4.24%).

(iii) *trans*-1-Acetoxy-2-bromomercuriomethylcyclopentane **12** (4%); δ_H 1.4–1.7 (4 H, m), 1.7–2.3 (5 H, m), 2.04 (3 H, s) and 4.49 (1 H, q, *J* 6.4); δ_C 21.39, 21.98, 31.09, 34.32, 38.27 [$J(^{199}Hg)$ 1490], 45.32 [$J(^{199}Hg)$ 85], 83.19 [$J(^{199}Hg)$ 115] and 171.35; δ_{Hg} −1051.

(iv) 1-Acetoxy-3-bromomercuriocyclohexane **15**[16] (4%); δ_H 1.5–1.7 (4 H, m), 1.8–2.0 (2 H, m), 2.11 (3 H, s), 2.0–2.4 (2 H, m), 2.86 (1 H, approx. quintet, *J* 5.1) and 4.97 (1 H, m); δ_C 21.65, 24.29, 30.23, 32.05, 37.07, 50.34, 69.63 and 170.05; δ_{Hg} −1187.

In another experiment in which the acetoxymercurials **12** and **15** were removed by column chromatography, the resulting mixture of four peroxymercurials was analysed by HPLC. Peak areas (refractive index detector) indicated the proportions of components to be **11**:**14**:**13**:**10** = 32:21:21:26. The weights of the individual components isolated by preparative HPLC were in good agreement with these proportions. Given below are the spectroscopic data for the isolated peroxymercurials **14**, **13** and **10** which are listed in order of elution (data for compound **11** were presented earlier). For *trans*-1-bromomercurio-2-t-butylperoxycyclohexane **14**:[7,35] δ_H 0.85 (1 H, m), 1.20 (2 H, m), 1.26 (9 H, s), 1.53 (1 H, d, *J* 10.8), 1.75 (3 H, m), 2.2 (2 H, m) and 4.01 [1 H, dt, *J* 10.8, 3.8, $J(^{199}Hg)$ 94]; δ_C 24.56, 26.58 (3 C), 28.28, 31.63, 32.75, 57.32, 80.89 and 85.73; δ_{Hg} −1200.

For 1-bromomercurio-3-t-butylperoxycyclohexane. (i) *cis*-**13**: δ_H 0.86 (1 H, approx. dd, *J* 4.8, 6.4), 1.25 (9 H, s), 1.55 (3 H, m), 1.7–2.1 (3 H, m incl. 1.94 t, *J* 3.5), 2.40 and 2.47 (1 H, m), 2.83 (1 H, approx. quintet, *J* 4) and 4.15 (1 H, m); δ_C 23.99, 26.51 (3 C), 28.87, 32.39, 35.10, 49.07, 77.23 and 80.56. (ii) *trans*-**13**: δ_H 2.12 (1 H, m), 3.92 (1 H, approx. quintet, *J* 3.2), and other peaks overlapping with those of *cis*-isomer; δ_C 23.76, 26.51 (3 C), 28.73, 32.71, 39.80, 48.41 and 79.94 (one COO resonance obscured by $CDCl_3$ peaks).

Integration of the peaks at δ 4.15 and 3.92 in the ^1H NMR spectrum indicated a *cis*:*trans* ratio of 70:30.

For *trans*-1-bromomercuriomethyl-2-t-butylperoxycyclopentane **10**: δ_H 3.98 (1 H, dt, *J* 6.8, 5.4), 2.33 (1 H, m), 2.18 (1 H, dd, *J* 11.5, 5.4), 1.98 (1 H, dd, *J* 11.5, 9.7), 1.90 (1 H, m), 1.67 (3 H, m), 1.27 (9 H, s), 1.23 (1 H, m) and 0.80 (1 H, m); double-resonance experiments showed that the following signals were coupled: 3.98–2.33, 3.98–1.90, 3.98–1.67, 2.33–2.18, 2.33–1.98 and 2.18–1.98; δ_C 22.34, 26.73 (3 C), 30.32, 35.37, 39.77, 44.06 [$J(^{199}Hg)$ 68], 80.61 and 92.62 [$J(^{199}Hg)$ 116]; δ_{Hg} −1062.

(b) *In dichloromethane in the presence of* 2,6-*di-t-butyl*-4-*methylphenol.* The peroxymercuriation was carried out in the usual way but on a 2.5 mmol scale and a solution of the phenol

(0.125 mmol) in dichloromethane was added to the mixture immediately before addition of the cyclopropane; the total volume of dichloromethane used was 5 cm^3.

(c) *In dichloromethane with mercury(II) trifluoroacetate.* The peroxymercuriation was carried out as with mercury(II) acetate, except that the trifluoroacetate was allowed to dissolve before the cyclopropane was added.

(d) *In t-butyl hydroperoxide.* The reaction was carried out as for bicyclo[2.1.0]pentane (above) except that the reagents were mixed at room temperature and then heated at 60 °C for 2 h. The crude product (52%) was separated by preparative HPLC to afford the products *cis*-**13** and **10**.

Preparation and Reactivity towards Perchloric Acid of trans-1-*Acetoxymercuriomethyl-2-t-butylperoxycyclopentane.*—A mixture of the organomercury(II) bromide **10** (0.70 mmol) and silver acetate (0.72 mmol) in methanol (50 cm^3)–water (20 cm^3) was suspended in an ultrasonic cleaning bath for 20 min. The mixture was filtered through Celite and the residue was washed with a little methanol. The combined filtrate was dried ($MgSO_4$), and the solvent was removed under reduced pressure to afford an oil (98%) with a ^1H NMR spectrum very similar to that of compound **10** but with an additional 3 H singlet at δ 1.98.

To the organomercury(II) acetate (0.04 mmol) was added a homogeneous solution[4] of 60% aq. perchloric acid (0.008 mmol) and acetic anhydride in CD_2Cl_2. The ^1H NMR spectrum was monitored over a period of 24 h during which time the C*H*OOBu^t signal remained unchanged and no new singlet appeared in the δ 2.1 region where the organomercury(II) acetate analogue of compound **11** is expected to absorb.

Bromodemercuriation of cis-1-*Bromomercurio-3-t-butylperoxycyclohexane* (cis-**13**) *in Pyridine.*—This was carried out as for the cyclopentane analogue **4** (above) and afforded *cis*-1-bromo-3-t-butylperoxycyclohexane; δ_H 1.22 (9 H, s), 1.5–2.3 (7 H, m), 2.73 and 2.80 (1 H, m), 3.80 (1 H, tt, *J* 11, 4) and 3.90 (1 H, tt, *J* 12, 4); δ_C 23.79, 26.35 (3 C), 29.19, 37.40, 42.54, 47.45, 80.04 and 80.73.

Iododemercuriation of cis-1-*Bromomercurio-3-t-butylperoxycyclohexane* (cis-**13**).—This was carried out as for the cyclopentane analogue **4** (above) except that the isomers were separated by column chromatography on silica with dichloromethane as eluent.

For *cis*-1-t-butylperoxy-3-iodocyclohexane **24**: δ_H 1.23 (9 H, s), 1.5–2.0 (4 H, m, incl. 1.84 quintet, *J* 13), 2.1–2.4 (3 H, m), 2.86 and 2.94 (1 H, m), 3.78 (1 H, tt, *J* 11, 4) and 4.01 (1 H, tt, *J* 12, 4); δ_C 23.40, 25.58, 26.43 (3 C), 29.27, 39.61, 44.80, 80.03 and 81.15.

For *trans*-1-*t*-butylperoxy-3-iodocyclohexane **25**: δ_H 1.24 (9 H, s), 1.6–1.8 (3 H, m), 1.98 (2 H, m), 2.24 (3 H, t, *J* 6), 4.16 (1 H, m) and 4.59 (1 H, quintet, *J* 6), δ_C 22.51, 26.43 (3 C), 28.40, 28.67, 38.26, 41.47 and 79.38 (one COO resonance obscured by $CDCl_3$ peaks).

Reaction of trans-1-*t-Butylperoxy-3-iodocyclohexane* **25** *with Silver Trifluoroacetate.*—This was carried out as for the cyclopentane analogue **9** (above). The major component of the crude product showed the following spectroscopic data, which are assigned to 3-t-butoxycyclohexanone **27**: δ_H 1.16 (9 H, s), 2.0–2.1 (4 H, m), 2.25 (2 H, m), 2.35 (1 H, ddd, *J* 14, 9, 1), 2.52 (1 H, ddm, *J* 15, 4.5) and 3.81 (1 H, approx. septet, *J* 4.5); δ_C 20.91, 28.24 (3 C), 33.43, 40.86, 51.02 and 69.44 (+2 C); ν_{max}/cm^{-1} 1705 (C=O).

Butylperoxy-, Methoxy-, Butoxy- and Acetoxy-mercuriation of Bicyclo[3.1.0]*hexane.*—These reactions were carried out on a 2.5 or 5 mmol scale in dichloromethane under the same conditions as for t-butylperoxymercuriation (above) with a maximum reaction time of 90 min. Yields and product distributions are presented in Table 1. ^{13}C NMR spectroscopic data are given below for the resultant γ-(per)oxymercurials except for those of the γ-acetoxymercurials **12** and **15** which have already been presented (above); data for the β-butylperoxymercurials are given later. For *trans*-1-bromomercuriomethyl-2-butylperoxycyclopentane: δ_C 13.81, 19.36, 22.52, 29.87, 30.39, 35.38, 39.58, 43.98, 74.12 and 91.79; for *cis*-1-bromomercurio-3-butylperoxycyclohexane: δ_C 13.68, 19.17, 24.24, 29.20, 29.87, 32.00, 35.59, 49.63, 74.53 and 76.61. For *trans*-1-bromomercuriomethyl-2-methoxycyclopentane: δ_C 20.29, 29.20, 32.98, 37.42, 45.31, 57.27 and 88.50. For *cis*-1-bromomercurio-3-methoxycyclohexane: δ_C 23.70, 29.20, 32.22, 36.67, 49.47, 55.53 and 74.99. For *trans*-1- bromomercuriomethyl-2-butoxycyclopentane: δ_C 13.80, 19.41, 20.24, 29.96, 31.94, 32.95, 37.44, 45.54, 70.11 and 86.80. For *cis*-1-bromomercurio-3-butoxycyclohexane: δ_C 13.80, 19.41, 23.59, 29.96, 31.94, 32.26, 36.77, 49.01, 68.60 and 70.12.

(a) *Methoxymercuriation in the presence of di-t-butyl peroxyoxalate.* The reaction mixture was made up as usual, but a solution of di-t-butyl peroxyoxalate (0.063 mmol) in dichloromethane (1 cm^3) was added immediately before the bicyclo[3.1.0]hexane (2.5 mmol), the total volume of dichloromethane used being 5 cm^3 as usual.

t-Butylperoxymercuriation of Bicyclo[4.1.0]*heptane.*—The reaction was carried out in dichloromethane as for bicyclo[2.1.0]pentane (above). The crude product was obtained as an oil. Column chromatography on silica with dichloromethane as eluant afforded, in order of elution, the following two fractions.

(i) *cis*- and *trans*-1-Bromomercuriomethyl-2-t-butylperoxycyclohexane **28** and **29**, δ_H 1.23 (s) +1.24 (s) (9 H), 1.0–2.2 (m) (9 H), 2.04 (d, *J* 3) +2.09 (d, *J* 3) +2.16 (d, *J* 4) +2.22 (d, *J* 4) (2 H), and 3.38 (approx. dt, *J* 4, 10), +3.98 (approx, dt, *J* 4. 8) (1 H); δ_C 24.88, 25.55, 26.70 (3 C), 29.60, 30.94, 37.02, 41.91, 80.30 and 88.49; and 25.04, 25.35, 26.62 (3 C), 29.68, 36.78, 39.00, 46.42, 81.20 and 86.98.

(ii) *cis*- and *trans*-1-Acetoxy-2-bromomercuriomethylcyclohexane **30** and **31**, δ_H 1.2–2.2 (m), 2.01 (s), 2.09 (s), 3.1 (m) and 4.4 (m); δ_C 21.62, 24.60, 25.33, 26.53, 31.76, 36.60, 42.44, 79.54 and 171.12; and 21.83, 25.16, 26.44, 36.28, 37.03, 39.03, 44.84 and 76.2 (+1 C).

Reduction of cis- *and* trans-1-*Bromomercuriomethyl-2-t-butylperoxycyclohexane* **28** *and* **29**.—The mixture of isomers **28** + **29** (1.83 mmol) was dissolved in dichloromethane (5 cm^3), mixed with 2.5 mol dm^{-3} sodium hydroxide (5 cm^3), and cooled in ice. This mixture was added to a magnetically stirred solution of sodium borohydride (9 mmol) in 2.5 mol dm^{-3} sodium hydroxide (7.5 cm^3) at 0 °C. Mercury was deposited at once. The ice-cooled mixture was stirred for 30 min, then for 45 min without coolant. The organic layer was isolated, combined with dichloromethane extracts (2 × 5 cm^3) of the aq. layer, and then dried ($MgSO_4$), and the solvent was removed at reduced pressure to yield *cis*- and *trans*-1-t-butylperoxy-2-methylcyclohexane **32** and **33** as an oil (80%), δ_H 0.95 (d, *J* 6), +1.18 (d, *J* 6) (3 H), 1.0–2.0 (8 H, m), 1.18 (9 H, s), 2.2–2.3 (m) +2.4–2.8 (m), (1 H) and 3.4–3.9 (1 H, m); δ_C 18.96, 24.28, 25.52, 26.46 (3 C), 31.05, 34.26, 36.31, 79.69 and 87.43; and 17.65, 25.17, 26.46 (3 C), 29.10, 29.47, 44.37, 44.74, 83.66 and 86.53.

Preparation of Authentic β-(*Per*)*oxymercurials from Alkenes.*—The (per)oxymercuriations were carried out as for the cyclopropanes (above) except that they were done at room temperature. No acetoxymercurials were detected in the crude products, which were oils or solids. The latter were recrystallised from light petroleum (b.p. 60–80 °C). The products derived from

methylenecyclopentane were markedly less stable than the others.

(a) Cyclopentene gave compound **5**.[7,35]

(b) Cyclohexene gave (i) compound **14**;[7,35] (ii) *trans*-1-bromomercurio-2-butylperoxycyclohexane, δ_H 0.88 (t, *J* 7), 1.1–1.9 (m), 2.15 (m), 2.31 (approx. td, *J* 12, 4), 3.96 (t, J 6.5) and 4.07 (approx. td, *J* 12, 4); δ_C 13.78, 19.26, 24.23, 28.11, 29.69, 31.47, 33.08, 57.67, 74.51 and 84.79; (iii) *trans*-1-bromomercurio-2-methoxycyclohexane,[36] δ_H 1.14 (3 H, approx. quintet), 1.72 (3 H, m), 2.18 (2 H, m), 2.52 (1 H, ddd, *J* 12, 10, 4), 3.28 (1 H, approx. td, *J* 10, 4) and 3.33 (3 H, s); δ_C 23.80, 28.10, 31.82, 33.13, 55.58, 62.41 and 82.38; (iv) trans-1-*bromomercurio*-2-*butoxycyclohexane*, m.p. 45–47 °C; δ_H 0.87 (3 H, t, *J* 7), 1.0–2.3 (12 H, m), 2.51 (1 H, dt, *J* 12, 1.5), 3.3 (2 H, m) and 3.6 (1 H, m); δ_C 13.84, 19.44, 23.86, 28.13, 32.05, 32.15, 34.12, 62.91, 67.85 and 81.39 (Found: C, 27.25; H, 4.3. $C_{10}H_{19}BrHgO$ requires C, 27.55; H, 4.36%); (v) *trans*-1-acetoxy-2-bromomercuriocyclohexane, δ_H 1.25–1.49 (3 H, m), 1.55–2.05 (3 H, m), 2.08 (3 H, s), 2.18–2.28 (2 H, m), 2.64 (1 H, dt, *J* 11, 3.5) and 4.98 (1 H, dt, *J* 9.2, 3.9); δ_C 21.55, 23.56, 27.68, 31.07, 33.99, 59.01, 76.15 and 170.50.

(c) Methylenecyclopentane gave (i) compound **11** (above); (ii) 1-bromomercuriomethyl-1-butylperoxycyclopentane, δ_H 0.81 (3 H, t, *J* 7), 1.27 (2 H, m), 1.49 (8 H, m), 1.82 (2 H, m), 2.13 [2 H, s, $J(^{199}Hg)$ 98] and 3.86 (2 H, t, *J* 6.5); δ_C 13.82, 19.33, 24.82, 29.70, 39.18 [$J(^{199}Hg)$, 140], 43.55 [$J(^{199}Hg)$ 1550], 74.65 and 94.09 [$J(^{199}Hg)$ 121]; (iii) 1-*bromomercuriomethyl*-1-*methoxycyclopentane* as a solid, δ_H 1.4–2.0 (8 H, m), 2.39 [2 H, s, $J(^{199}Hg)$ 92] and 3.20 (3 H, s); δ_C 24.33, 39.24 [$J(^{199}Hg)$ 135], 46.00 [$J(^{199}Hg)$ 1485], 49.76 and 87.41 [$J(^{199}Hg)$ 116] (Found: C, 21.3; H, 3.2; Br, 20.2. $C_7H_{13}BrHgO$ requires C, 21.36; H, 3.33; Br, 20.30%); (iv) 1-bromomercuriomethyl-1-butoxycyclopentane, δ_H 0.93 (3 H, t, *J* 6.1), 1.3–2.0 (12 H, m), 2.43 (2 H, s) and 3.36 (2 H, t, *J* 6.2); δ_C 14.00, 19.64, 24.35 (2 C), 32.72, 40.02 (2 C), 46.86, 61.78 and 86.99.

(d) Methylenecyclohexane gave 1-*bromomercuriomethyl*-1-*t-butylperoxycyclohexane*, m.p. 31–32 °C; δ_H 1.25 (9 H, s), 1.2–1.6 (8 H, m), 1.7–1.9 (2 H, m) and 1.99 (2 H, s); δ_C 22.25 (2 C), 25.28, 26.84 (3 C), 37.11 (2 C), 44.26, 79.61 and 82.01 (Found: C, C, 28.3; H, 4.4. $C_{11}H_{21}BrHgO_2$ requires C, 28.36; H, 4.51%).

(e) Cycloheptene gave trans-1-*bromomercurio*-2-*t-butylperoxycycloheptane* as a solid, δ_H 1.19 (9 H, s), 1.0–1.9 (8 H, m), 2.0–2.3 (2 H, m), 2.54 (1 H, approx. td, *J* 12, 3) and 4.03 (1 H, m); δ_C 23.49, 26.20, 26.50 (3 C), 29.66, 30.24, 33.37, 58.40, 79.95 and 87.37 (Found: C, 28.4; H, 4.55. $C_{11}H_{21}BrHgO_2$ requires C, 28.36; H, 4.51%).

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