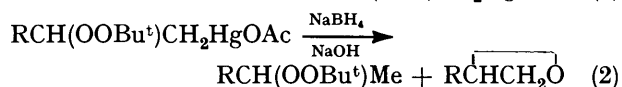# Oxymetallation. Part 16.[1] Modified Procedures for Reducing Peroxy-mercurials: Conversion of Non-terminal Alkenes into Secondary Alkyl t-Butyl Peroxides

By A. J. Bloodworth * and J. L. Courtneidge, Christopher Ingold Laboratories, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

Various procedures for reducing $PhCH(OOBu^t)CH_2HgO_2CCF_3$ or $PhCMe(OOBu^t)CH_2HgOAc$ have been investigated in an attempt to optimize yields of the mercury-free peroxides. Effects of varying the concentration of borohydride and the mode of mixing, and of including a phase transfer catalyst, have been assessed for the two phase system of alkaline $NaBH_4$ and dichloromethane and reductions have been carried out in a single phase by using Bu_4NBH_4 in dichloromethane.

The t-butyl peroxymercurials $[RCH(OOBu^t)CH(HgX)R]$ derived from cis- and trans-but-2-ene, cis- and trans-hex-3-ene, cyclopentene, cyclohexene, and norbornene have been reduced under the optimum conditions of slowly adding base-pretreated peroxymercurials in dichloromethane to a large excess of alkaline $NaBH_4$. Product analyses support the idea that the reactions proceed via β-peroxyalkyl radicals $[RCH(OOBu^t)\dot{C}HR]$, but show that, except for the norbornyl derivative, epoxides are the dominant products; cyclopentyl, cyclohexyl, and exo-nor-bornyl t-butyl peroxides have been isolated in yields of 2, 13, and 37%, respectively. Better, but still modest, yields (24—36%) have been obtained for butan-2-yl, hexan-3-yl, and cyclopentyl t-butyl peroxides by silver trifluoro-acetate-assisted t-butyl perhydrolysis of the alkyl bromides, but competing dehydrobromination lowered the yield (6%) of the cyclohexyl compound. Vastly improved yields (ca. 60%) of butan-2-yl, cyclopentyl, and cyclohexyl t-butyl peroxides have been achieved by reduction of the corresponding peroxymercurials with neat Bu_3SnH.

PEROXYMERCURIATION coupled with reductive demer-curiation by sodium borohydride has proved a useful new approach to the synthesis of secondary alkyl peroxides.[2] In the original application of the method terminal alkenes were converted into secondary alkyl t-butyl peroxides, but each stage was marred by a side reaction.[3,4] Peroxymercuriation was accompanied by acetoxymercuriation [equation (1)] and, in the reaction with sodium borohydride, epoxide formation competed with the desired hydrogenodemercuriation [equation (2)].
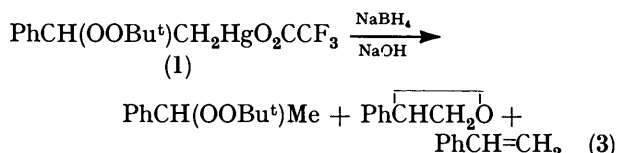
$$RCH=CH_2 \xrightarrow[\text{Hg(OAc)}_2]{\text{2Bu}^t\text{OOH}} RCH(OOBu^t)CH_2HgOAc +$$
$$RCH(OAc)CH_2HgOAc \quad (1)$$

$$RCH(OOBu^t)CH_2HgOAc \xrightarrow[\text{NaOH}]{\text{NaBH}_4}$$
$$RCH(OOBu^t)Me + \overline{RCHCH_2O} \quad (2)$$

The problem of acyloxy-mercurials being formed in the first step has been overcome by using mercury(II) trifluoroacetate[5] or, for some alkenes, by including 20 mol% of perchloric acid in reactions with the acetate.[6] It was therefore of interest to see if the procedure for reductive demercuriation could be modified to suppress epoxide formation and give better yields of peroxides. In carrying out this investigation we have paid particular attention to the reduction of t-butyl peroxymercurials derived from non-terminal alkenes, since this has not been reported hitherto.

RESULTS AND DISCUSSION

The procedure originally employed for reducing 2-t-butylperoxyalkylmercury(II) salts involved adding, at 0 °C during 10 min, a solution of sodium borohydride (5 mmol) in 3M sodium hydroxide (10 cm³) to a well stirred mixture of the mercurial (10 mmol) in diethyl ether (25

cm³) and water (15 cm³).[3] Subsequently, it was found that diethyl ether could be replaced by dichloromethane and this opened the way for reductions to be carried out in situ where no adverse effects were encountered from the presence of, and presumably concurrent reduction of, the approximately equimolar amount of t-butyl hydro-peroxide.[4] It was also shown that the balance between peroxide and epoxide was unaffected by reducing organo-mercury chlorides or bromides rather than the corre-sponding acetates, but that the fraction of epoxide rose markedly with the temperature at which the reduction was carried out.[4]
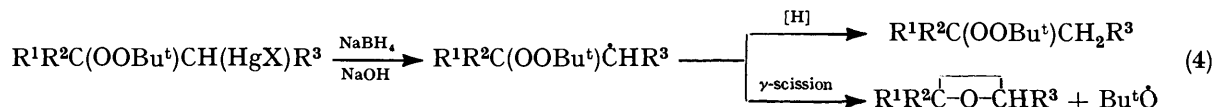
Perxoymercurials derived from Styrene and α-Methyl-styrene.—With this background in mind, we first attempted to optimize peroxide yields by making further variations in the alkaline sodium borohydride–dichloro-methane procedure. For convenience in the analyses of product mixtures by ^1H n.m.r. spectroscopy we employed 2-t-butylperoxy-2-phenylethylmercury(II) trifluoro-acetate[5] (1) as the substrate in this study. Under conditions similar to those used previously[4] the reduc-tion product was found to contain not only t-butyl 1-phenylethyl peroxide and styrene oxide, but also appreciable quantities of styrene [equation (3)].

$$PhCH(OOBu^t)CH_2HgO_2CCF_3 \xrightarrow[\text{NaOH}]{\text{NaBH}_4}$$
$$(1)$$
$$PhCH(OOBu^t)Me + \overline{PhCHCH_2O} +$$
$$PhCH=CH_2 \quad (3)$$

The amount of styrene formed was rather variable and we were unable to pinpoint the cause of the fluctuation. There are several reports[7] in the literature of deoxy-mercuriation taking place during the reduction of oxy-mercurials with sodium borohydride and other workers[7d] have similarly obtained irreproducible yields of the

resultant alkene. It is known that deoxymercuriation by sodium borohydride is sensitive to pH [7a] and that it is rarely encountered when the oxymercurial is treated with aqueous sodium hydroxide prior to reduction. We had deliberately avoided such a procedure for fear that it might lead to base-induced decomposition [3] of the mercury-substituted secondary alkyl peroxide. However, this fear proved groundless in the reduction of compound (1) * and formation of styrene was, indeed, eliminated. Base pretreatment was therefore incorporated into all further modifications of the method.

We originally suggested that the balance between peroxide and epoxide is determined by a competition between γ-scission and hydrogen abstraction for an intermediate β-peroxyalkyl radical [equation (4)] [4] and

best yield of peroxide. The fact that it does not may be a consequence of the temperature of the mixture rising due to the high exothermicity of the reduction.

Whether the reduction under our conditions takes place in the aqueous phase, in the organic phase, or in both media is a moot point,[4] and this uncertainty adds to the difficulty of identifying rational changes that might suppress epoxide formation. That reduction occurs at least partially in the organic phase is indicated because mercury was precipitated from the initially clear dichloromethane layer, isolated by passing the freshly prepared reaction mixture through phase separating paper. It occurred to us that the inclusion of a phase transfer catalyst might increase the concentration of borohydride anion in the organic phase and hence raise the yield of

$$R^1R^2C(OOBu^t)CH(HgX)R^3 \xrightarrow[\text{NaOH}]{\text{NaBH}_4} R^1R^2C(OOBu^t)\dot{C}HR^3 \xrightarrow{\begin{array}{c}\xrightarrow{[H]} R^1R^2C(OOBu^t)CH_2R^3 \\ \xrightarrow{\gamma\text{-scission}} R^1R^2\overset{\frown}{C}\text{-O-}\overset{\frown}{C}HR^3 + Bu^t\dot{O}\end{array}} \quad (4)$$

subsequent work [8] has reinforced this view. Peroxide formation should therefore be favoured by a high concentration of hydrogen donor. It is thought that the borohydride anion itself is unlikely to be the hydrogen donor and that this role is most probably fulfilled by a derived organomercury hydride [here PhCH(OOBu^t)-CH_2HgH].[9] However, the concentration of the organomercury hydride is presumably linked to that of the borohydride and a high borohydride concentration should improve yields of peroxide. Consequently, we

peroxide formed in that medium. However, this modification (Table 1, Expt. 5) did not lead to any overall improvement in peroxide yield.

The failure of Expt. 5 may simply indicate that relatively little reduction takes place in dichloromethane, which, after all, constitutes only a third of the reaction mixture. Consequently, we then used a predominantly organic medium. A pre-cooled mixture of 2M sodium hydroxide (10 cm³) and compound (1) (10 mmol) in dichloromethane (20 cm³) was added to a solution of a

TABLE 1

Product distribution for various reductions of PhCH(OOBu^t)CH_2HgO_2CCF_3 with NaBH_4 at 0 °C

			Molar fraction (%)		
Expt.	Molar ratio NaBH_4 : RHgX	Mode of mixing [a]	PhCH(OOBu^t)Me	PhCHOCH_2	Alkene recovery (%)
1	1 : 1	Normal	64	36	73
2	4 : 1	Normal	63	37	89
3	4 : 1	Reverse	78	22	98
4	4 : 1	Rapid	74	26	99
5	4 : 1	Reverse [b]	76	24	[c]

[a] Normal ≡ NaBH_4–NaOH–H_2O added to RHgX–CH_2Cl_2 + NaOH–H_2O mixture during 10 min; Reverse ≡ RHgX–CH_2Cl_2 + NaOH–H_2O mixture added to NaBH_4–NaOH–H_2O during 10 min; Rapid ≡ reverse addition, but adding RHgX–CH_2Cl_2 + NaOH–H_2O in one portion as quickly as possible. [b] In the presence of cetyltrimethylammonium bromide (40 mol% w.r.t. RHgX). [c] Could not be determined as the product contained cetyltrimethylammonium salts.
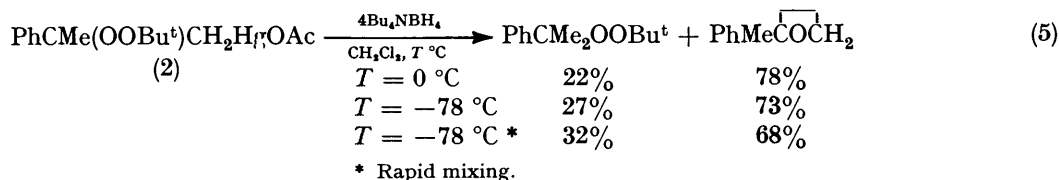
examined the effect of making the alkaline borohydride more concentrated and of changing the mode in which the reagents are mixed. The results are presented in Table 1.

From Expts. 1 and 2 it is clear that using more concentrated borohydride does not change the product distribution when the normal mode of mixing is employed, but a comparison with Expts. 3—5 shows that peroxide yields are improved by changing to reverse or rapid mixing. Since the highest concentration of organomercury hydride should be produced by rapid mixing, this procedure might be expected to give the
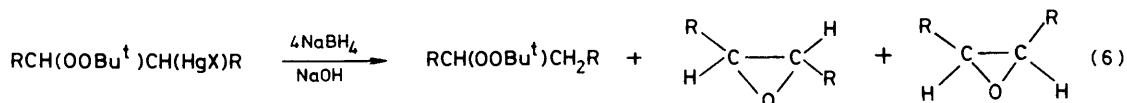
* Warning: This insensitivity to aqueous sodium hydroxide may not be enjoyed by other systems. Thus, the more sensitive bicyclic peroxymercurial, 2,6-bistrifluoroacetoxymercurio-9,10-dioxabicyclo[3.3.2]decane,[7g] decomposed completely upon pretreatment with the base.

mixture of tetrabutylammonium borohydride (20 mmol) and bromide (20 mmol) in dichloromethane (50 cm³) at 0 °C. Normal work-up followed by column chromatography afforded a 79% yield of t-butyl 1-phenylethyl peroxide.

This excellent result encouraged us to investigate the use of tetrabutylammonium borohydride in dichloromethane alone and to apply it to the peroxymercurial (2) derived from α-methylstyrene for which epoxide formation predominates under normal two-phase conditions.[4] The results [equation (5)] were disappointing, for even at −78 °C the proportion of peroxide was inferior to that (36%) achieved [4] at 0 °C by the alkaline sodium borohydride–dichloromethane method, and the alkene recovery was only 57—76%.

$$\text{PhCMe(OOBu}^t\text{)CH}_2\text{H}\overset{\frown}{\Gamma}\text{OAc} \xrightarrow[\text{CH}_2\text{Cl}_2, T\text{ °C}]{4\text{Bu}_4\text{NBH}_4} \text{PhCMe}_2\text{OOBu}^t + \text{PhMe}\overset{\frown}{\text{COCH}_2} \qquad (5)$$

(2)		
$T = 0$ °C	22%	78%
$T = -78$ °C	27%	73%
$T = -78$ °C *	32%	68%

* Rapid mixing.

Peroxymercurials derived from Non-terminal Alkenes.— In view of the results obtained above, it was decided to adopt the slow addition of base-pretreated peroxymercurial to alkaline sodium borohydride (*cf.* Table 1, Expt. 3) as the standard conditions under which to study the reduction of t-butyl peroxymercurials derived from representative non-terminal alkenes [equation (6)].

as the rate constants for cyclization of the appropriate β-peroxyalkyl radicals [12] decrease (a partial list is provided in Table 5), and diastereoisomeric pairs of peroxymercurials (Expts. 7 and 8, and 9 and 10) give product distributions that are identical within experimental error. Furthermore, the ratios of *trans-* to *cis-*epoxides are the same as those obtained in the reduction of the cor-

$$\text{RCH(OOBu}^t\text{)CH(HgX)R} \xrightarrow[\text{NaOH}]{4\text{NaBH}_4} \text{RCH(OOBu}^t\text{)CH}_2\text{R} + \begin{array}{c}\text{R} \\ \text{H}\end{array}\!\!\!>\!\!\text{C}\!-\!\text{C}\!\!<\!\!\begin{array}{c}\text{H} \\ \text{R}\end{array} + \begin{array}{c}\text{R} \\ \text{H}\end{array}\!\!\!>\!\!\text{C}\!-\!\text{C}\!\!<\!\!\begin{array}{c}\text{R} \\ \text{H}\end{array} \quad (6)$$

To maximize the reliability of each product analysis the dichloromethane layer which contained the reduction products was made up to a standard volume, a known weight of benzene was added as an internal standard, and the yields were determined by the sensitive technique of Fourier transform (FT) ^{1}H n.m.r. spectroscopy at 200 MHz. The spectra were assigned by comparison with authentic samples, the epoxides being prepared by reaction of the alkenes with *m*-chloroperbenzoic acid [10] and the peroxides by the silver trifluoroacetate-assisted t-butyl perhydrolysis [11] [equation (7)] of appropriate

$$\text{RCH(Br)CH}_2\text{R} + \text{Bu}^t\text{OOH} + \text{AgO}_2\text{CCF}_3 \longrightarrow$$
$$\text{RCH(OOBu}^t\text{)CH}_2\text{R} + \text{AgBr} + \text{HO}_2\text{CCF}_3 \quad (7)$$

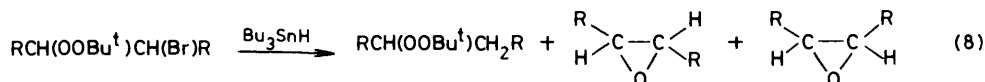alkyl bromides (see later). The results are presented in Table 2.

The accuracy of the method was tested by analyzing a mixture of t-butyl cyclohexyl peroxide, 1,2-epoxycyclohexane, and benzene made up at concentrations similar to those obtained in the reduction (Table 2, Expt. 13). The molar ratio was found by ^{1}H n.m.r. spectroscopy to be 0.79 : 1.93 : 1.00 compared with the calculated value of 0.90 : 2.10 : 1.00, which suggests that the concentrations determined for the cyclohexane derivatives were

The preparative implications of the results in Table 2 are obvious. Except for the synthesis of t-butyl *exo*-2-norbornyl peroxide, the peroxymercuriation and borohydride reduction of non-terminal alkenes is a distinctly unattractive proposition. Nevertheless, for the purposes of comparison we carried out the preparative scale reactions with cyclopentene and cyclohexane as well as with norbornene. Using silica chromatography the cyclopentyl, cyclohexyl, and *exo*-2-norbornyl t-butyl peroxides were isolated in yields of 2,13, and 37%, respectively.

In assessing the synthetic value of these peroxymercuriation-reductions [equations (6)], it is useful to compare the product analyses (Table 2) and yields of isolated alkyl t-butyl peroxides (above) with similar data for the silver salt-assisted t-butyl perhydrolysis of alkyl bromides [equation (7)]. The perhydrolyses were carried out with a one-fold excess of t-butyl hydroperoxide and under these conditions the main by-products were the corresponding alkyl trifluoroacetates. The crude pro-

$$\text{RCH(OOBu}^t\text{)CH(Br)R} \xrightarrow{\text{Bu}_3\text{SnH}} \text{RCH(OOBu}^t\text{)CH}_2\text{R} + \begin{array}{c}\text{R} \\ \text{H}\end{array}\!\!\!>\!\!\text{C}\!-\!\text{C}\!\!<\!\!\begin{array}{c}\text{H} \\ \text{R}\end{array} + \begin{array}{c}\text{R} \\ \text{H}\end{array}\!\!\!>\!\!\text{C}\!-\!\text{C}\!\!<\!\!\begin{array}{c}\text{R} \\ \text{H}\end{array} \quad (8)$$

low by some 10%. As the experimental error in measuring integrals is estimated to be in the range of 3—10%, no corrections have been applied to the yields quoted in Table 2. Good reproducibility was indicated by the results of a duplicate reduction of the *cis*-but-2-ene derivative (Expts. 6 and 7).

Mechanistically, the results provide further evidence for the intermediacy of β-peroxyalkyl radicals in these reductions [equation (4)]. Thus, as expected for such a mechanism, the peroxide yields from the various organomercury compounds increase in precisely the same order

responding β-peroxyalkyl bromides with tributyltin hydride [equation (8)],[12] which was the free radical reaction used to determine rate constants for epoxidation (*cf.* ref. 8).

ducts, isolated by removing the dichloromethane solvent at 0 °C/10 mmHg, were analyzed by 60 MHz ^{1}H n.m.r. spectroscopy before being chromatographed on silica gel to provide the pure alkyl t-butyl peroxides. The results are presented in Table 3.

Clearly, the silver salt method is better than the peroxymercuriation-reduction of non-terminal alkenes for the preparation of butan-2-yl,* hexan-3-yl, and cyclopentyl

* However, the peroxymercuriation-reduction of but-1-ene provides the best yield (50—60%) of butan-2-yl t-butyl peroxide (ref. 3).
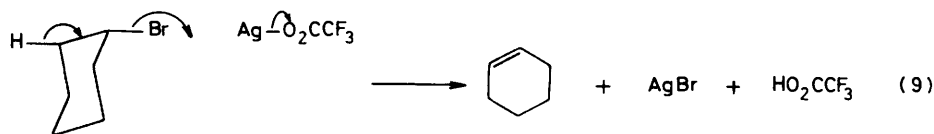
Table 2

Products obtained from the reduction of t-butyl peroxymercurials derived from non-terminal alkenes by alkaline sodium borohydride under standard conditions

Expt.	Parent alkene	Peroxymercurial	Yield (%)			Mercury recovery (%)
			Alkyl t-butyl peroxide	*trans*-Epoxide	*cis*-Epoxide	
6			12	54	14	89
7			17	51	16	95
8			15	54	13	88
9			n.d. [b]	51	8	95
10			n.d.	56	8	82
11			n.d.	72 [d]	13 [d]	76
12			7		72	92
13			24		53	99
14			61		38	97

[a] TFA = O_2CCF_3. [b] n.d. = not detected. [c] Contained 11% of acetoxymercurial. [d] Based on peroxymercurial.

t-butyl peroxides (Expts. 15—17), but it is the poorer of the two routes to t-butyl cyclohexyl peroxide and both methods are equally effective in providing t-butyl *exo*-2-norbornyl peroxide. The low yield of peroxide from bromocyclohexane (Expt. 18) arises partly because of competing elimination [equation (9)].

Silver salt-induced dehydrobromination and loss of the resultant volatile alkene may, in part, be responsible for the generally poor product accountability (Table 3). Competing elimination has recently been reported in the intramolecular perhydrolysis of a cyclopentyl bromide.[13] Since it is known [14] that the silver salt-assisted t-butyl perhydrolysis of acyclic secondary alkyl bromides proceeds with predominant inversion of configuration, it is noteworthy that the reaction with *exo*-2-norbornyl bromide (Expt. 19) took place with retention and that no

trace of the t-butyl *endo*-2-norbornyl peroxide could be detected. This anomalous behaviour is typical of substitution reactions in norbornyl systems.[15]

In view of the modest yields of peroxide afforded by the silver salt method (Table 3), we turned again to the reduction of peroxymercurials and considered what

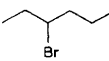$$H\text{—}\boxed{}\text{—Br} \quad Ag\text{—}O_2CCF_3 \longrightarrow \bigcirc + AgBr + HO_2CCF_3 \quad (9)$$
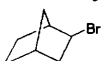
further modification could be made to suppress epoxidation. We decided to investigate reductions in neat tributyltin hydride [16] with the idea that such a system might provide the high concentration of a good hydrogen donor required to promote hydrogenodemercuriation *via* β-peroxyalkyl radicals (as discussed earlier).

Preliminary studies with the peroxymercurial derived from *cis*-but-2-ene were encouraging and an investigation of the effects of varying the amount of tributyltin hydride, the mode of mixing, the temperature, and the

anion on mercury indicated that the best yield of butan-2-yl t-butyl peroxide was obtained by slow addition of the organomercury(II) bromide to a *ca.* five-fold excess of tributyltin hydride at 0 °C. Hence, these conditions were also adopted for the reduction of the peroxymercurials derived from *trans*-hex-3-ene, cyclopentene, and cyclohexene. In each case the resultant mixture of

TABLE 3

Products obtained from the silver trifluoroacetate-assisted t-butyl perhydrolysis of alkyl bromides

Expt.	Alkyl bromide (RBr)	Crude product, yield (%)		Yield of isolated ROOBu^t (%)
		ROOBu^t	RO$_2$CCF$_3$	
15		32	6	24
16		48	19	36
17		37	35	31
18		19	6 ^{a}	6 ^{b}
19		50	38	36

^{a} Cyclohexene (10%) also detected. ^{b} From a crude product containing 17% of ROOBu^t and 22% of RO$_2$CCF$_3$ which was obtained in a reaction using 1.33 instead of 2.0 mol equiv. of Bu^{t}OOH. ^{c} Reaction time of 70 min compared with 10 min for the others.

peroxide and epoxide(s) was distilled under reduced pressure from the reaction mixture into a cold trap and chromatography of the trap contents on silica afforded the pure alkyl t-butyl peroxides. The yields, together with those achieved for the same peroxides by the other two procedures described in this paper, are presented in Table 4. From these data it can be seen that not only does the tributyltin hydride modification lead to vastly improved yields of peroxides *via* peroxymercuriation and reduction of non-terminal alkenes, but, except for the hexan-3-yl compound, it also represents a far more successful synthesis than the silver trifluoroacetate-assisted t-butyl perhydrolysis of alkyl bromides.

The success of these tributyltin hydride reductions, the stoicheiometry of which is shown in equation (10), has interesting mechanistic implications. Our assumption
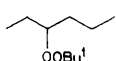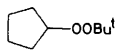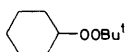
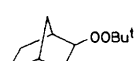$$\text{RHgBr} + \text{Bu}_3\text{SnH} \longrightarrow \text{RH} + \text{Bu}_3\text{SnBr} + \text{Hg} \quad (10)$$

that the reactions would proceed *via* free β-peroxyalkyl radicals [*cf.* equation (4)], which was based on analogy with similar reductions of other alkylmercury(II) bromides,[17] is supported by the observation that epoxides are again formed as by-products. It is thus reasonable to conclude that the higher yields of peroxides compared with those from reduction with sodium borohydride do

indeed arise from enhanced rates of hydrogen abstraction for the β-peroxyalkyl radicals (R˙). These rates are given by the expression $k[\text{R}˙][\text{H-donor}]$ and are thus dependent on the concentration of hydrogen donor and on the appropriate bimolecular rate constant (k).

The candidates for the hydrogen donor are tributyltin hydride itself and a derived [17] organomercury hydride (RHgH). For tributyltin hydride the value of k is *ca.* 1×10^6 l mol^{-1} s^{-1} [18] and the concentration is *ca.* 4 mol l^{-1}. Now the standing concentration of any organomercury hydride must be considerably smaller than that of tributyltin hydride since the organomercury(II) bromide was slowly added as drops to a five-fold excess of the tin compound, yet mercury was precipitated *immediately* upon mixing. Thus, for the postulated organomercury hydride to compete effectively with tributyltin hydride as the hydrogen donor, its value of k must be much larger than 4×10^6 l mol^{-1} s^{-1} to make up for the difference in concentration terms.

TABLE 4

Comparison of yields of isolated sec-alkyl t-butyl peroxides by three procedures

sec-Alkyl t-butyl peroxide	From alkene by peroxymercuriation and reduction with Bu$_3$SnH	From alkene by peroxymercuriation and reduction with NaBH$_4$–NaOH	From alkyl bromide by silver salt-induced t-butyl perhydrolysis
OOBu^t	63	0	24
OOBu^t	24	0	36
OOBu^t	59	2	31
OOBu^t	61	13	6
OOBu^t	37	36	

In view of this argument, it is tempting to suggest that, contrary to the conclusions reached previously [17] for reactions of other organomercury(II) bromides with this reducing agent, tributyltin hydride *itself* is likely to be the main hydrogen donor. If it is assumed that tributyltin hydride is the *sole* donor, then it is possible to calculate rate constants for γ-scission of the β-peroxyalkyl radicals from the observed peroxide-to-epoxide molar ratios in exactly the same way that they were determined from similar data for reduction of the corresponding β-peroxyalkyl bromides [equation (8)].[8,12] However, there is a problem when comparing such rate constants in that the reduction of the organomercurials was carried out in neat tributyltin hydride at 0 °C, whereas the alkyl bromides were reduced in benzene

solution at ambient temperature. Thus, in an attempt to link the two sets of conditions, we carried out the reduction of t-butyl 3-bromobutan-2-yl peroxide (which contained a trace of the corresponding mercurial to aid initiation) with neat tributyltin hydride [equation (8; R = Me)] at 0 °C. The peroxide-to-epoxide molar ratio was found to be 4.0, which is close to the value of 3.9 calculated using the rate constant for γ-scission in benzene at ambient temperature [12] and that for hydrogen abstraction from tributyltin hydride in cyclohexane at 25 °C.[18] This suggests that solvent differences are unimportant and that the rate constants for hydrogen abstraction and γ-scission have similar temperature dependencies in this narrow range of 0—25 °C. Thus, by using the same rate constant for hydrogen abstraction [18] as was used in the calculations for alkyl bromide reductions, the peroxide-to-epoxide data from mercurial reductions at 0 °C should afford reasonably good rate constants for γ-scission at ambient temperature.

The results of such calculations are shown in Table 5 and the generally good agreement between the two sets of rate constants thus strongly supports the idea that tributyltin hydride is the hydrogen donor in the organomercurial reductions.
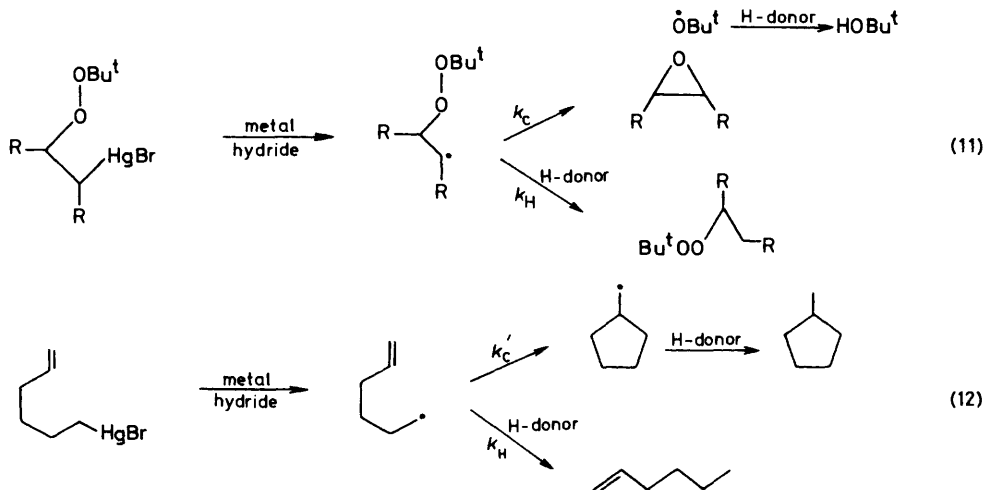
There is an interesting parallel between our results and those of Quirk and Lea on the reduction of hex-5-enylmercury(II) bromide.[17b] Both reactions [equations (11) and (12)] involve a competition between cyclization

TABLE 5

Rate constants for γ-scission of β-peroxyalkyl radicals calculated from peroxide-to-epoxide molar ratios for reduction of β-peroxyalkyl bromides and the corresponding β-peroxyalkylmercury(II) bromides with tributyltin hydride

$$RCH(OOBu^t)CH(X)R \xrightarrow{Bu_3SnH} RCH(OOBu^t)CH_2R + \overset{\longleftarrow}{RCH-O-CHR}$$

β-Peroxyalkyl radical	Rate constant from alkyl bromide (X = Br) data ($s^{-1} \times 10^{-6}$) (ref. 12)	Rate constant from alkylmercury(II) bromide (X = HgBr) data ($s^{-1} \times 10^{-6}$)
	0.98	0.77
	3.1	3.2
	1.0	1.3
	0.56	1.4

of hexene to methylcyclopentane by the same method as that used (above) for the rate constants of γ-scission (k_c). When this is carried out using Quirk and
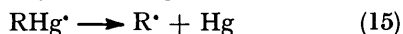
(11)

(12)

and hydrogen abstraction for the intermediate free alkyl radical. Thus, it is important to note that products obtained by reducing hex-5-enylmercury(II) bromide with tributyltin hydride in benzene contained higher proportions of hexene than those from reduction with sodium borohydride in aqueous tetrahydrofuran (THF), this being analogous to our higher yields of dialkyl peroxides.

If, in fact, it is assumed that the sole hydrogen donor in the reduction of hex-5-enylmercury(II) bromide is tributyltin hydride, then the rate constant for cyclization (k_c') can be calculated from the observed molar ratio

Lea's data,[17b] the rate constant is calculated to be 0.92×10^5 s^{-1} for reaction in benzene at ambient temperature, which is in excellent agreement with the value found experimentally [19] of 1×10^5 s^{-1} in isopentane at 25 °C. It would appear, therefore, that once again the products from reduction of an organomercury(II) bromide with tributyltin hydride can be accounted for adequately without invoking the intermediacy of an organomercury hydride.

Free radical chain reactions between organomercury(II) bromides and tributyltin hydride are thus strongly implicated. A reasonable suggestion for the propagation

stage of such reactions is as shown in equations (13)—(15), which involves the hitherto unreported S_H2 displacement of alkylmercury by tributyltin.

$$R^{\cdot} + H\text{–}SnBu_3 \longrightarrow RH + Bu_3Sn^{\cdot} \quad (13)$$

$$Bu_3Sn^{\cdot} + Br\text{–}HgR \longrightarrow Bu_3SnBr + RHg^{\cdot} \quad (14)$$

$$RHg^{\cdot} \longrightarrow R^{\cdot} + Hg \quad (15)$$

Formation and decomposition of organomercury hydrides (RHgH) may be important in initiating the reaction and some contribution by them in the role of highly reactive hydrogen donors cannot be ruled out. However, from the foregoing discussion it appears clear that the tributyltin hydride is, itself, the principal hydrogen donor in these reductions.

EXPERIMENTAL

Materials and Spectra.—Tetrabutylammonium borohydride,[20] tributyltin hydride,[21] cis-hex-3-ene,[6] and silver trifluoroacetate [22] were prepared, and t-butyl hydroperoxide was purified,[6] by previously reported methods; exo-norbornyl bromide was a gift from Dr. B. P. Roberts. t-Butyl peroxymercurials were prepared by the $Hg(O_2C\text{-}CF_3)_2$ [5] or $Hg(OAc)_2\text{–}HClO_4$ [6] procedures and, unless otherwise stated, were admixed with t-butyl hydroperoxide (up to 1 equiv.). All other materials were commercial samples. Spectra were recorded as previously described.[6]

Two-phase Reduction of $PhCH(OOBu^t)CH_2O_2CCF_3$.—(a) *Using alkaline sodium borohydride.* The solution obtained from reaction of styrene (10 mmol), mercury(II) trifluoroacetate (10 mmol), and t-butyl hydroperoxide (20 mmol) in dichloromethane (20 cm³) was washed with water (2 × 20 cm³), cooled to 0 °C, and treated with ice-cold 2M sodium hydroxide (10 cm³) before it was mixed with an ice-cold solution of sodium borohydride (10 or 40 mmol) in 2.5M sodium hydroxide (30 cm³). The mixture was stirred for 10 min and then the organic layer was isolated using phase separating paper. The aqueous layer was washed with dichloromethane (2 × 20 cm³) and the washings were added to the organic layer, which was then dried (MgSO₄). Removal of the solvent at ⩾15 mmHg afforded the crude product which was dissolved in CDCl₃ and analyzed by 60 MHz ¹H n.m.r. spectroscopy. The variations in the mode of mixing together with the resultant product distributions as calculated from the integrated spectra are shown in Table 1.

(b) *Using alkaline tetrabutylammonium borohydride.* An ice-cold mixture of 2M sodium hydroxide (10 cm³) and PhCH-(OOBu^t)CH₂HgO₂CCF₃ (10 mmol) in dichloromethane (20 cm³) was added as drops during 15 min to a well stirred solution of tetrabutylammonium borohydride (20 mmol) and bromide (20 mmol) in dichloromethane (50 cm³) at 0 °C. The mixture was stirred for 10 min and then the organic layer was isolated using phase separating paper, washed with water (3 × 40 cm³), dried (MgSO₄), and the solvent removed at ⩾15 mmHg to afford a crude product (11.1 g) which contained tetrabutylammonium salts.

One tenth of the crude product was chromatographed on Merck silica (70—230 mesh; 30 g) using a 3 : 1 mixture of light petroleum (b.p. 40—60 °C) and dichloromethane as eluant and 40 cm³ fractions were collected. Fractions 5—7 contained pure t-butyl 1-phenylethyl peroxide (0.15 g; corresponding to a yield of 79% for the whole), which was

identified by its ¹H n.m.r. spectrum.[3] The remainder of the crude product was shaken with cold light petroleum (b.p. 40—60 °C; 20 cm³), filtered, and the residue washed with more cold solvent (2 × 20 cm³). Removal of the solvent under reduced pressure from the combined filtrate and washings afforded pure t-butyl 1-phenylethyl peroxide (0.763 g; corresponding to a yield of 43% for the whole); δ_C 142.36, 128.24, 126.69 and 127.65 (Ph), 81.55 (C-1), 20.45 (C-2), 79.86, and 26.51 (Bu^t) (Found: C, 74.2; H, 9.4. Calc. for $C_{12}H_{18}O_2$: C, 74.20; H, 9.34%).

Single-phase Reduction of $PhCMe(OOBu^t)CH_2HgOAc$.—Under nitrogen an ice-cold solution of $PhCMe(OOBu^t)$-CH_2HgOAc (5 mmol) in dichloromethane (10 cm³) was added as drops during 10 min to a well stirred solution of tetrabutylammonium borohydride (20 mmol) in dichloromethane (20 cm³) at 0 °C. The mixture was stirred for 1 h and then brought to room temperature during 30 min. The solution was decanted off from the mercury bead (0.93 g; 93%) and the solvent was evaporated off at ⩾15 mmHg. Water (50 cm³) and diethyl ether (50 cm³) were added to the residue and the mixture was allowed to stand overnight. The diethyl ether layer was isolated, combined with more diethyl ether extracts (2 × 50 cm³) of the aqueous layer, dried (MgSO₄), and the solvent removed under reduced pressure. The resultant oil (0.54 g) was identified by ¹H n.m.r. spectroscopy as a mixture of t-butyl 2-phenylpropan-2-yl peroxide [4] (22 mol%) and 1-methyl-1-phenyloxiran,[4] representing an alkene recovery of 68%.

A similar reduction at −78 °C for 4 h afforded the same products (27 mol% of peroxide) in 76% yield. A second reduction at −78 °C for 4 h in which the reagents were mixed rapidly gave the same products (32 mol% of peroxide) in 57% yield.

Reduction by Alkaline Sodium Borohydride of t-Butyl Peroxymercurials derived from Non-Terminal Alkenes.—(a) *Analytical runs.* Except for the peroxymercurials derived from cis- and trans-hex-3-ene, reductions were carried out on the organomercury(II) bromides which had been purified by recrystallization (cyclohexane and norbornene derivatives) or by prolonged (1—3 h) evacuation at 0.01 mmHg (but-2-ene and cyclopentene derivatives). Because of the ready decomposition of the cis- and trans-hex-3-ene derivatives they were reduced, immediately after preparation, as the crude acyloxy-salts contaminated with t-butyl hydroperoxide.

An ice-cold mixture of 2M sodium hydroxide (7.5 cm³) and the peroxymercurial (5 mmol) in dichloromethane (5 cm³) was added as drops during 3 min to a well stirred solution of sodium borohydride (20 mmol) in 2.5M sodium hydroxide (15 cm³) at 0 °C. The mixture was stirred for 30 min at 0 °C and for 30 min at room temperature before the layers were separated. The mercury was washed, dried, and weighed (Table 2). The organic layer was passed through phase separating paper that had been pre-washed with dichloromethane. Then dichloromethane extracts (2 × 5 cm³) of the aqueous layer were passed through. The combined extracts were dried (MgSO₄) and then filtered; sodium-dried AnalaR grade benzene (100 µl) was added and the volume made up to 25 cm³ with dichloromethane washings of the desiccant and filter paper. A 500 µl aliquot of the solution mixed with CDCl₃ [500 µl, containing 2% of tetramethylsilane (TMS)] was used to record the 200 MHz ¹H n.m.r. spectrum for product analysis (Table 2).

(b) *Preparative runs.* (i) t-Butyl cyclohexyl peroxide. An ice-cold mixture of 2M sodium hydroxide (20 cm³) and

trans-2-t-butylperoxycyclohexylmercury(II) acetate (20 mmol) in dichloromethane (40 cm³) was added as drops during 10 min to a well stirred solution of sodium borohydride (80 mmol) in 2.5M sodium hydroxide (60 cm³) at 0 °C. After stirring for 30 min at 0 °C and for 30 min at room temperature, the layers were separated and the aqueous layer was extracted with more dichloromethane (2 × 40 cm³). The combined dichloromethane solution was dried (MgSO₄) and the solvent removed at 0 °C/10 mmHg to afford the crude product (2.48 g). This was chromatographed on silica (80 g) using a 1 : 1 mixture of light petroleum (b.p. <40 °C) and dichloromethane as eluant and 25 cm³ fractions were collected. The solvent was removed from each fraction at 0 °C/10 mmHg and the residue was examined by ¹H n.m.r. spectroscopy. Fractions 8—13 contained t-butyl cyclohexyl peroxide (0.451 g; 13%) and later fractions contained 1,2-epoxycyclohexane. A middle cut of the peroxide was trap-to-trap distilled and analyzed (Found: C, 69.5; H, 11.4. C₁₀H₂₀O₂ requires C, 69.78; H, 11.63%).

(*ii*) t-Butyl cyclopentyl peroxide. A crude product (1.33 g) was obtained by the procedure described for the cyclohexyl compound, but using half quantities. This was dissolved in CDCl₃ (1 cm³) and shaken with 60% aqueous perchloric acid (1 drop + 4 drops of D₂O) to hydrate the epoxide. After 2.5 h, when all the epoxide had reacted (¹H n.m.r. spectroscopy), the organic layer was isolated using phase separating paper and the solvent removed to leave an oil (0.51 g) which was chromatographed on silica (30 g) using dichloromethane as eluant, and 10 cm³ fractions were collected. Fraction 8 contained t-butyl cyclopentyl peroxide (29 mg, 1.8%).

(*iii*) t-Butyl *exo*-2-norbornyl peroxide. Using the reduction (half scale) and chromatography (40 g silica) procedures described for the cyclohexyl compound, a mixture of peroxymercurial (68 mol%) and trifluoroacetoxymercurial afforded, in fractions 4 and 5, t-butyl *exo*-2-norbornyl peroxide (0.359 g; 37% based on peroxymercurial); *exo*-epoxynorbornane (0.228 g; 39% based on peroxymercurial) was isolated from fractions 10—17. A portion of the peroxide was trap-to-trap distilled and analyzed (Found: C, 71.58; H, 10.80. C₁₁H₂₀O₂ requires C, 71.68; H, 10.96%).

Reduction by Tributyltin Hydride of t-Butyl Peroxymercurials derived from Non-terminal Alkenes.—(a) *Butan-2-yl t-butyl peroxide.* The β-peroxyalkylmercury(II) bromide (5 mmol) obtained from *cis*-but-2-ene, and which contained some of the 5 mmol excess of t-butyl hydroperoxide used in its preparation, was added as drops during 15 min to stirred tributyltin hydride (7.3 cm³; 28 mmol) at 0 °C under a stream of dry nitrogen, the exit gas being passed through a trap at −78 °C. After 1 h the inlet to the reaction vessel was closed, the trap coolant was changed to liquid nitrogen, and the outlet from the trap was connected to an oil pump. After two freeze–pump–thaw cycles to degas the reaction mixture, it was allowed to warm to room temperature and the volatile components were distilled into the trap at 0.01 mmHg during 2 h. Examination of this crude product (0.86 g) by ¹H n.m.r. spectroscopy indicated that the molar ratio of peroxide to epoxides was 5 : 1. Chromatography of the mixture on silica (30 g) using dichloromethane as eluant and collecting 15 cm³ fractions, from which the solvent was removed at 0 °C/≥15 mmHg, afforded, in fractions 5—7, but-2-yl t-butyl peroxide (63%).

(b) *t-Butyl hexan-3-yl peroxide.* Following the same procedure as for (a), the peroxymercurial obtained from

trans-hex-3-ene was converted into a crude product in which the molar ratio of peroxide to epoxides was 1.2 : 1. Chromatography as for (a) gave, in fractions 5 and 6, t-butyl hexan-3-yl peroxide (24%).

(c) *t-Butyl cyclopentyl peroxide.* Following the procedure as for (a), the peroxymercurial obtained from cyclopentene was converted into a crude product (0.85 g) in which the molar ratio of peroxide to epoxide was 3 : 1. Chromatography as for (a), but using a 1 : 1 mixture of light petroleum (b.p. <40 °C) and dichloromethane as eluant gave, in fractions 4—9, t-butyl cyclopentyl peroxide (58%).

(d) *t-Butyl cyclohexyl peroxide.* Following the same procedure as for (a) except that the peroxymercurial was dissolved in a little dichloromethane (<1 cm³), the cyclohexene derivative was converted into a crude product in which the molar ratio of peroxide to epoxide was 5.2 : 1. Chromatography as for (c) gave, in fractions 4—8, t-butyl cyclohexyl peroxide (61%).

Reduction of t-Butyl 3-Bromobutan-2-yl Peroxide by Tributyltin Hydride.—The alkyl bromide [6] (5 mmol which contained a trace of the corresponding *threo*-peroxymercurial) was reduced with tributyltin hydride (6.4 cm³; 25 mmol) using the method described for similar reactions with peroxymercurials except that a solution of di-t-butyl hyponitrite (55 mg) in benzene (300 μl) was also added. The crude product (1.03 g) was isolated after 1.5 h and examined by ¹H n.m.r. spectroscopy.

Silver Trifluoroacetate-assisted t-Butyl Perhydrolysis of Alkyl Bromides.—The following general method was adopted. Silver trifluoroacetate (15 mmol) was added in one portion to a swirled solution of alkyl bromide (15 mmol) and t-butyl hydroperoxide (30 mmol) in dichloromethane (20 cm³). The mixture was swirled occasionally and after 10 min was filtered and dichloromethane washings (2 × 10 cm³) of the residue were added to the filtrate. The filtrate was washed with water (4 × 10 cm³), dried (MgSO₄), and the solvent removed at 0 °C/10 mmHg to afford a crude product, the composition of which was determined by ¹H n.m.r. spectroscopy (60 MHz). This material was chromatographed on silica (60 g) using a 1 : 1 mixture of light petroleum (b.p. <40 °C) and dichloromethane as eluant and 25 cm³ fractions were collected. Solvent removal at 0 °C/10 mmHg from appropriate fractions afforded the pure peroxide which was eluted after the alkyl trifluoroacetate.

The only modifications to this general procedure were that a longer reaction time (70 min) was required for *exo*-2-norbornyl bromide and chromatography of the butan-2-yl and cyclohexyl products was carried out on silica (35 g) with dichloromethane as eluant. Details for the individual compounds are given in Table 3.

A portion of the t-butyl hexan-3-yl peroxide was trap-to-trap distilled and analyzed (Found: C, 68.9; H, 12.55. C₁₀H₂₂O₂ requires C, 68.90; H, 12.75%) and similarly, for t-butyl cyclopentyl peroxide (Found: C, 68.35; H, 11.3. C₉H₁₈O₂ requires C, 68.29; H, 11.49%).

Characterization of sec-Alkyl t-Butyl Peroxides.—Butan-2-yl [3] and cyclohexyl [23] t-butyl peroxides have been described before, but no supporting analytical data were provided for the cyclohexyl compound; the hexan-3-yl, cyclopentyl, and *exo*-2-norbornyl t-butyl peroxides are previously unknown. All five peroxides were characterized by ¹³C and ¹H n.m.r. spectroscopy (Table 6).

Independent Synthesis of Epoxides.—1,2-Epoxycyclohexane was a commercial sample. 1,2-Epoxycyclopentane, *cis*- and *trans*-1,2-diethyloxiran, and *exo*-epoxynorbornane

TABLE 6

20 MHz ^{13}C and 200 MHz ^{1}H n.m.r. spectra of sec-alkyl t-butyl peroxides in CDCl$_3$

δ Values [for Bu^t : δ$_C$ 79.6 and 26.6 p.p.m., δ$_H$ 1.23 (s)]

Compound		1	2	3	4	5	6	7
(structure, OOBu^t)	δ$_C$	18.08	80.85	27.52	9.91			
	δ$_H$	1.15 (d, J 6 Hz)	3.94 (m, ca. sextet)	1.62 (m), 1.44 (m, ca. sextets)	0.92 (t, J 7.5 Hz)			
(structure, OOBu^t)	δ$_O$	9.68	25.44	84.44	34.44	19.01	14.38	
	δ$_H$	0.94 (t, J 7 Hz)	1.25—1.64 (m)	3.81 (m,br, quintet J 5.5 Hz)	1.25—1.64 (m)	1.15—1.20 (m)	0.94 (t, J 7 Hz)	
(cyclopentyl-OOBu^t)	δ$_O$	85.25	31.01	23.95				
	δ$_H$	4.48—4.52 (m)	1.48—1.78 (m)					
(cyclohexyl-OOBu^t)	δ$_O$	81.51	30.74	24.13	25.90			
	δ$_H$	3.84 (m, W$_i$ 17 Hz)	1.98 (m, W$_i$ 17 Hz)	1.74 (m, W$_i$ 13 Hz)	1.55 (m, W$_i$ 16 Hz)			
(norbornyl-OOBu^t)	δ$_C$	39.78	85.90	34.88 see 5—7	36.62	28.66	24.20	34.49
	δ$_H$	2.50 (m, W$_i$ 8 Hz)	3.96 (brd)		2.20 (m, W$_i$ 10 Hz)	3 multiplets centred at 1.5, 1.23, and 1.05. (Irradiation at δ 1.05 changed signal at δ 3.96 into dd, J 2.7, 7.0 Hz)		

were prepared in yields of 55, 68, 74, and 84%, respectively, from the corresponding alkene (20 mmol) by reaction with m-chloroperbenzoic acid (22 mmol) in dichloromethane overnight. Each reaction mixture was filtered and the filtrate was washed with 5% sodium sulphite (20 cm³), then 5% sodium hydrogencarbonate (40 cm³), before the solvent was removed at 0 °C/10 mmHg and the epoxide purified by trap-to-trap distillation. cis- and trans-1,2-Dimethyloxiran were prepared by similar reactions in 1,2,4-trichlorobenzene, the products being isolated by distillation at 0.01 mmHg. The ^{1}H and ^{13}C n.m.r. spectra were in accord with published data.[24,25] The spectra of cis- and trans-1,2-diethyloxiran do not appear to have been reported and details of these are given below. cis-1,2-Diethyloxiran: δ$_H$ 2.87 (m, CHO), 1.59—1.45 (m, CH$_2$), and 1.04 (t, J 7.4 Hz, Me); δ$_O$ 58.49 (CHO), 21.10 (CH$_2$), and 10.61 (Me). trans-1,2-Diethyloxiran: δ$_H$ 2.66 (ca. t, CHO), 1.59—1.47 (m, CH$_2$), and 0.99 (t, J 7.4 Hz, Me); δ$_C$ 58.67 (CHO), 24.60 (CH$_2$), and 9.15 (Me).

REFERENCES

[1] Part 15, A. J. Bloodworth and D. J. Lapham, J. Chem. Soc., Perkin Trans. 1, 1981, 3265.
[2] W. Adam and A. J. Bloodworth, Top. Curr. Chem., 1981, 97, 121.
[3] D. H. Ballard and A. J. Bloodworth, J. Chem. Soc. C, 1971, 945.
[4] A. J. Bloodworth and G. S. Bylina, J. Chem. Soc., Perkin Trans. 1, 1972, 2433.
[5] A. J. Bloodworth and I. M. Griffin, J. Chem. Soc., Perkin Trans. 1, 1975, 195.
[6] A. J. Bloodworth and J. L. Courtneidge, J. Chem. Soc., Perkin Trans. 1, 1981, 3258.
[7] For example: (a) F. G. Bordwell and M. L. Douglass, J. Am.

Chem. Soc., 1966, 88, 993; (b) B. Giese, S. Gantert, and A. Schulz, Tetrahedron Lett., 1974, 3583; (c) M. C. Benhamou, G. Eterrad-Moghadan, V. Speziale, and A. Lattes, Synthesis, 1979, 891; (d) H. C. Brown and G. J. Lynch, J. Org. Chem., 1981, 46, 531; (e) A. J. Bloodworth and M. E. Loveitt, J. Chem. Soc., Perkin Trans. 1, 1978, 522; (f) A. J. Bloodworth and J. A. Khan, ibid., 1980, 2450; (g) A. J. Bloodworth, J. A. Khan, and M. E. Loveitt, ibid., 1981, 621.
[8] A. J. Bloodworth, A. G. Davies, I. M. Griffin, B. Muggleton, and B. P. Roberts, J. Am. Chem. Soc., 1974, 96, 7599.
[9] A. J. Bloodworth in ' The Chemistry of Mercury,' ed. C. A. McAuliffe, Macmillan, London, 1977, p. 220.
[10] D. E. Bissing and A. J. Speciale, J. Am. Chem. Soc., 1965, 87, 2683.
[11] P. G. Cookson, A. G. Davies, and B. P. Roberts, J. Chem. Soc., Chem. Commun., 1976, 1022.
[12] A. J. Bloodworth, J. L. Courneidge, and A. G. Davies, unpublished work.
[13] K. R. Kopecky and J. A. L. Sastre, Can. J. Chem., 1980, 58, 2089.
[14] A. G. Davies and A. J. Stowicz, unpublished work quoted in ref. 2.
[15] H. C. Brown, ' The Non-classical Ion Problem,' Plenum, New York and London, 1977.
[16] Preliminary communication: A. J. Bloodworth and J. L. Courtneidge, J. Chem. Soc., Chem. Commun., 1981, 1117.
[17] (a) G. M. Whitesides and J. San Filippo, J. Am. Chem. Soc., 1970, 92, 6611; (b) R. P. Quirk and R. E. Lea, ibid., 1976, 98, 5973.
[18] D. J. Carlsson and K. U. Ingold, J. Am. Chem. Soc., 1968, 90, 7047.
[19] D. Lal, D. Griller, S. Husband, and K. U. Ingold, J. Am. Chem. Soc., 1974, 96, 6355.
[20] A. Brändström, U. Junggren, and B. Lamm, Tetrahedron Lett., 1972, 3173.
[21] K. Hayashi, J. Iyoda, and I. Shiihara, J. Organomet. Chem., 1967, 10, 81.
[22] D. E. Janssen and C. V. Wilson, Org. Synth., 1963, 4, 547.
[23] (a) R. Hiatt, T. Mill, K. C. Irwin, and J. K. Castleman, J. Org. Chem., 1968, 33, 1421; (b) D. G. Hendry, C. W. Gould, D. Schuetzle, M. G. Syz, and F. R. Mayo, ibid., 1976, 41, 1.
[24] ^{1}H N.m.r.: (a) C. J. Ponchert and J. R. Campbell, ' The Aldrich Library of NMR Spectra,' Vol. 1; (b) M. H. Gianni, E. L. Stogryn, and C. M. Orlando, J. Phys. Chem., 1963, 67, 1385.
[25] ^{13}C N.m.r.: S. G. Davies and G. H. Whitham, J. Chem. Soc., Perkin Trans. 2, 1975, 861.