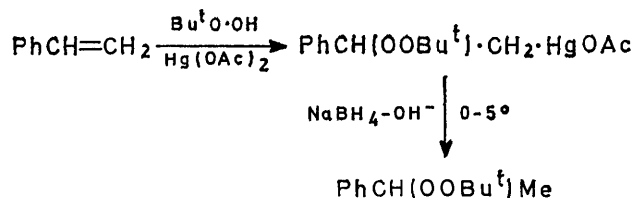# Oxymetallation. Part III.[1,2] Competitive Epoxidation during the Hydridodemercuration of β-Mercurated Dialkyl Peroxides with Sodium Borohydride
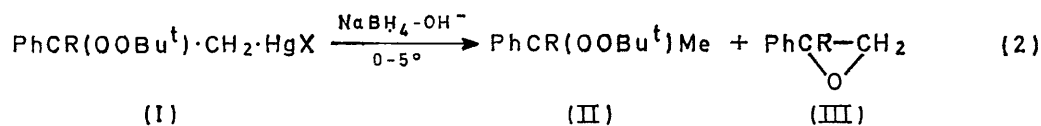
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Reduction by sodium borohydride of the compounds $R^1R^2C(OOBu^t)\cdot CH_2\cdot HgX$, which are formed by t-butyl-peroxymercuration of terminal alkenes, leads to the formation of epoxides, $R^1R^2C\cdot CH_2\cdot O$, in addition to the expected dialkyl peroxides, $R^1R^2C(OOBu^t)Me$. The amount of epoxidation increases with increasing alkylation in the terminal alkene and with the temperature at which the reduction is carried out. It is suggested that the results are consistent with homolytic cleavage of the carbon–mercury bond during demercuration.

WE have described previously [3] an improved synthesis of secondary alkyl t-butyl peroxides by t-butylperoxy-mercuration and hydridodemercuration of mono-substituted ethylenes, e.g. equation (1). Both steps

$$PhCH{=}CH_2 \xrightarrow[Hg(OAc)_2]{Bu^tO\cdot OH} PhCH(OOBu^t)\cdot CH_2\cdot HgOAc$$

$$\downarrow NaBH_4\text{-}OH^- \quad 0\text{-}5°$$

$$PhCH(OOBu^t)Me$$

occur under very mild conditions and the only complication which was reported was the concurrent formation of small amounts of acetoxymercuration products

and alkenyl ethers and esters [5]); extentions to other types of alkenes can also be expected. Hydridode-mercuration of other known peroxymercurated compounds has not been described, but it was expected that this would also provide the second stage of a fairly general route to metal-free dialkyl peroxides, with or without additional functional groups. The results presented here indicate that competitive reactions can occur during the reduction and thus limit the preparative scope of the overall sequence.

In an initial attempt to extend the t-butylperoxy-mercuration–hydridodemercuration sequence, the per-oxymercurated compounds (I) (derived from α-alkyl-styrenes) have been treated with sodium borohydride under the standard conditions.[3] The expected t-alkyl

$$PhCR(OOBu^t)\cdot CH_2\cdot HgX \xrightarrow[0\text{-}5°]{NaBH_4\text{-}OH^-} PhCR(OOBu^t)Me \ + \ PhCR{-}CH_2 \qquad (2)$$
$$\underset{\text{(I)}}{} \qquad\qquad \underset{\text{(II)}}{} \qquad \underset{\text{(III)}}{\overset{\diagdown O \diagup}{}}$$

during the peroxymercuration stage. This stage has been shown to have wider application, both with respect to the hydroperoxide [4] and to the alkene (e.g. 1,1-di-alkylethylenes,[4] αβ-unsaturated esters and ketones,[1]

t-butyl peroxides (II) are formed, but the yields are low and the major products are the corresponding epoxides (III) [reaction (2)].

Thus 2-phenyl-2-t-butylperoxypropylmercury(II) bromide (I; R = Me, X = Br), which was obtained ‡ from α-methylstyrene and which had characteristics

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‡ The i.r. spectrum of the intermediate 2-phenyl-2-t-butyl-peroxypropylmercury(II) acetate, obtained from α-methyl-styrene under the conditions used for mono-substituted ethyl-enes,[3] indicated that it was contaminated with 2-acetoxy-2-phenylpropylmercury(II) acetate; this complication was not described in the original synthesis [4] although the conditions were comparable. It was discovered that competitive acetoxy-mercuration was reduced considerably when the reaction was catalysed by perchloric acid. Furthermore, subsequent treatment with aqueous solutions appeared to destroy the acetoxy-mercurated compound.

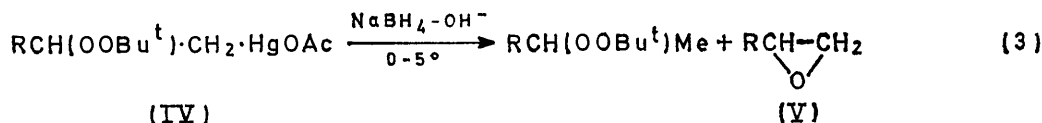[1] Part II, A. J. Bloodworth and R. J. Bunce, J. Chem. Soc. (C), 1971, 1453.

[2] Preliminary communication: A. J. Bloodworth, R. J. Bunce, and G. S. Bylina, Abstracts of 5th International Conference on Organometallic Chemistry, Moscow, 1971, Paper 395.

[3] Part I, D. H. Ballard and A. J. Bloodworth, J. Chem. Soc. (C), 1971, 945.

[4] E. Schmitz, A. Rieche, and O. Brede, J. prakt. Chem., 1970, 312, 30.

[5] E. Schmitz and O. Brede, J. prakt. Chem., 1970, 312, 43.

identical with those reported,[4] gave a mixture of the corresponding peroxide and epoxide which contained 74·5 mol % of the latter; the mixture from 2,2-diphenyl-2-t-butylperoxyethylmercury(II) chloride (I; R = Ph, X = Cl) contained 64·5 mol% of epoxide. The products were identified by their ^{1}H n.m.r. spectra and by t.l.c., in comparison with authentic samples prepared independently. The molar fractions were calculated from integrations of the ^{1}H n.m.r. spectra of the crude products of reduction and are believed to have an

alkenes. Whereas it is relatively unimportant in monoalkyl (or aryl)ated ethylene derivatives, it becomes the major reaction for peroxymercurated derivatives of 1-alkyl-1-arylethylenes. The reductions of α-methylstyrene and α-phenylstyrene derivatives were carried out with the organomercury(II) halides, whilst hex-1-ene and styrene derivatives were reduced in the form of the organomercury(II) acetates. However it was shown that the nature of the electronegative substituent on mercury does not affect the outcome of the

$$RCH(OOBu^t) \cdot CH_2 \cdot HgOAc \xrightarrow[0-5^\circ]{NaBH_4-OH^-} RCH(OOBu^t)Me + RCH-CH_2 \quad\quad (3)$$
$$\underset{\text{O}}{\diagdown\diagup}$$

(IV)   (V)

accuracy of *ca.* $\pm 5\%$. The yields and composition of the crude products indicated that the recovery of alkene derivatives was nearly quantitative in each case.

This unforseen formation of epoxide prompted us to reinvestigate more closely the crude products from the reduction of peroxymercurated compounds (IV) derived from mono-substituted ethylenes. These received only a cursory examination in the early study where pure peroxides were isolated by distillation in yields of 50—60%.[3,6] The crude products formed by reduction, *in situ*, of derivatives (IV) from styrene (R = Ph) and hex-1-ene (R = Bu), contained 20 and 19·5 mol% of epoxide respectively [reaction (3)]. If this is general for alk-1-enes, then the reported yield of crude t-butyl 1-methylheptyl peroxide (78%)[3] probably represents an actual recovery of *ca.* 84% of octene derivatives and a true yield of crude dialkyl peroxide

reaction, since the reduction of 2,2-diphenyl-2-t-butyl peroxyethylmercury(II) acetate (I; R = Ph, X = OAc) gave a mixture of peroxide and epoxide of the same composition as that obtained from the chloride.
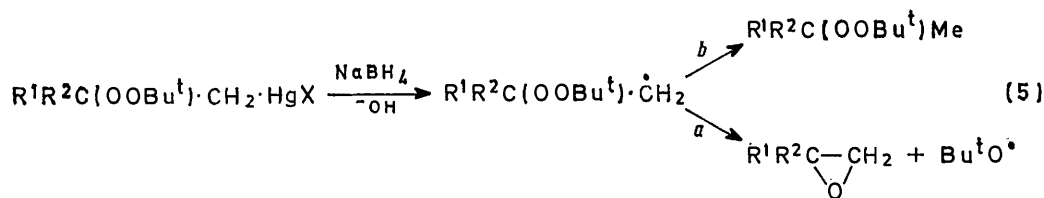
There is now much evidence in the literature,[7-9] some of it directly concerned with oxymercurated compounds, that reduction of alkylmercury(II) salts by sodium borohydride involves the generation of intermediate alkyl radicals [equation (4)]. If this mechanism holds for the reduction of the peroxymercurated compounds (I) and (IV), then the alkyl radical thus generated, $R^1R^2C(OOBu^t)\cdot\dot{C}H_2$, contains a peroxide linkage attached to a carbon adjacent to the radical centre. Similar β-peroxyl radicals are intermediates in the gas-phase oxidation of alkanes and alkenes,[10] and in the liquid-phase autoxidation of alkenes;[11,12] under appropriate conditions they are reported to undergo cyclisation (γ-scission) to give epoxides. It

$$RHgX \xrightarrow{NaBH_4-OH^-} R\cdot \xrightarrow[\text{donor}]{\text{hydrogen}} RH \quad\quad\quad (4)$$
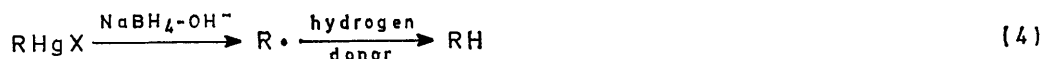
of *ca.* 67%. Considering the scale of the reactions this means that the yields of pure peroxides are quite reasonable.

It appears therefore that competitive epoxidation is a

therefore appears reasonable to suggest that the balance between peroxide- and epoxide-formation in the reduction of peroxymercurated compounds is determined by a competition between cyclisation [equation (5a)] and

$$R^1R^2C(OOBu^t)\cdot CH_2\cdot HgX \xrightarrow[-OH]{NaBH_4} R^1R^2C(OOBu^t)\cdot\dot{C}H_2 \underset{a}{\overset{b}{\diagup\diagdown}} \begin{array}{l} R^1R^2C(OOBu^t)Me \\[4mm] R^1R^2\underset{\text{O}}{\underset{\diagdown\diagup}{C-CH_2}} + Bu^tO^\bullet \end{array} \quad (5)$$

general feature of the borohydride reduction of peroxymercurated compounds derived from simple terminal

combination with hydrogen [equation (5b)] in the intermediate radical.

If this model is correct, the formation of peroxide

[6] D. H. Ballard, A. J. Bloodworth, and R. J. Bunce, *Chem. Comm.*, 1969, 815.
[7] G. M. Whitesides and J. S. Filippo, *J. Amer. Chem. Soc.*, 1970, **92**, 6611 and references contained therein.
[8] G. A. Gray, W. R. Jackson, and V. M. A. Chambers, *J. Chem. Soc.* (C), 1971, 200.
[9] V. M. A. Chambers, W. R. Jackson, and G. W. Young, *J. Chem. Soc.* (C), 1971, 2075.

[10] A. Fish, 'Organic Peroxides,' ed. D. Swern, Wiley–Interscience, 1970, vol. 1, ch. 3.
[11] F. R. Mayo, *J. Amer. Chem. Soc.*, 1958, **80**, 2465, 2497; F. R. Mayo and A. A. Miller, *ibid.*, p. 2480; F. R. Mayo, A. A. Miller, and G. A. Russell, *ibid.*, p. 2500.
[12] W. F. Brill and B. J. Barone, *J. Org. Chem.*, 1964, **29**, 140.

should be favoured by an increase in the concentration of hydrogen donor, unless the hydrogen is provided by a species which is generated by the same process as the alkyl radical itself (see ref. 7). An evaluation of this effect is difficult for two reasons. First, the reduction mixture is heterogeneous and even the medium in which the reaction occurs is ill-defined. Secondly the identity of the hydrogen donor is uncertain, although an organomercury hydride, formed by reaction of the organomercury salt (or hydroxide) with sodium borohydride, appears to be a reasonable possibility.[7]

less epoxidation with the monoalkylated peroxymercurated compounds (*ca.* 20 mole %) than with the alkylarylated compounds (64—74 mole %).

Thus it appears that the changeover from preferred peroxide-formation from compounds (IV) to preferred epoxide-formation from compounds (I) must be attributed to structural effects, *i.e.* to the presence of the extra alkyl group in (I). This may be regarded as a new example of the '*gem*-dialkyl effect' upon ring-closure. It has been known for a long time that formation of cyclopropane derivatives is facilitated by alkylation of the

$$R^1R^2\underset{\underset{HO}{|}}{\overset{\overset{Cl}{|}}{C}}\!-\!CH_2 \xrightarrow{\text{base}} R^1R^2\overset{\overset{Cl}{|}}{C}\!-\!CH_2 \xrightarrow{-Cl^-} R^1R^2C\underset{O}{\overset{}{\diagdown\!\diagup}}CH_2 \qquad (6)$$

$$R^1R^2\underset{\underset{XHg-CH_2}{|}}{\overset{\overset{OBu^t}{|}}{C}}\!-\!O \xrightarrow{NaBH_4} R^1R^2\overset{\overset{OBu^t}{|}}{C}\!-\!\underset{\underset{CH_2}{|}}{O} \xrightarrow{-Bu^tO^\bullet} R^1R^2C\underset{CH_2}{\overset{O}{\diagdown\!\diagup}} \qquad (7)$$
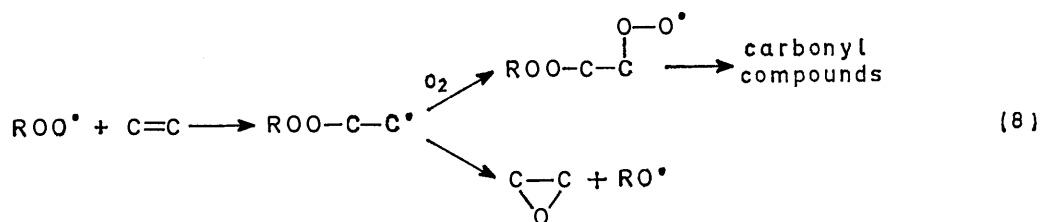
Whatever the situation is, an increase in the concentration of borohydride can be expected either to suppress epoxidation or to have no effect.

In the results presented so far, the molar ratio of sodium borohydride to peroxymercurated compound was always 1 : 2, so that twice as much hydride was available as is stoicheiometrically required for hydridodemercuration (assuming all B–H bonds are active).[13] However, the reductions with monoalkylated peroxymercurated compounds (IV) were carried out *in situ*, whereas the alkylarylated peroxymercurated compounds (I) had been isolated. Since the peroxymercuration is carried out with a one-fold excess of t-butyl hydroperoxide, the hydridodemercuration *in situ* must

ring carbon atoms.[14] More importantly, the rate of epoxide-formation by cyclodehydrohalogenation of α-hydroxy-halides [reaction (6)] is enhanced by methyl substitution, *e.g.* relative rates are: $R^1 = R^2 = H$, 0·31; $R^1 = H$, $R^2 = Me$, 6·5; $R^1 = R^2 = Me$, 78.[15] The relation between the mechanism of the latter reaction and that which we are suggesting to account for the generation of epoxides in our reductions can be seen from equations (6) and (7).

The *gem*-dialkyl effect may be rationalised partially in terms of a closer approach of the groups involved in ring closure (*i.e.* CH_2 and O) due to a compression of the angle subtended by them at the carbon atom bearing the substituents.

$$ROO^\bullet + C{=}C \longrightarrow ROO{-}C{-}C^\bullet \overset{O_2}{\Big\nearrow} ROO{-}\underset{\underset{}{\overset{|}{C}}}{\overset{\overset{O-O^\bullet}{|}}{C}}{-}C \longrightarrow \begin{array}{l}\text{carbonyl}\\ \text{compounds}\end{array}$$
$$\diagdown\!\!\!\searrow \underset{O}{\overset{}{C{-}C}} + RO^\bullet \qquad (8)$$

involve concurrent reduction of an equimolar amount of hydroperoxide. In other words only just sufficient borohydride is present, and if the reductions of the hydroperoxide and peroxymercurated compounds are competitive, then the effective concentration of borohydride is lower for the monoalkylated peroxymercurated compounds.* Despite this there is considerably

Some of the trends found in the liquid-phase oxidation of C_3—C_5-alkenes [12] can be interpreted along similar lines. Here epoxides are formed together with carbonyl compounds containing a shortened carbon chain. The key step is again believed to be the generation of a β-peroxyalkyl radical, and if the carbonyl compounds are formed *via* reaction of this radical with oxygen as suggested, then the competition between cyclisation and oxygen addition [equation (8)] is similar to the

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* In fact two experiments indicated that differences in borohydride concentration of this order were unimportant in determining the peroxide : epoxide ratio. The reduction of isolated 2-phenyl-2-t-butylperoxyethylmercury(II) bromide and the reduction of 2-t-butylperoxyhexylmercury(II) acetate (IV; R = Bu) *in situ* in the absence of an excess of t-butyl hydroperoxide gave essentially the same products as the previous reductions carried out in the presence of a molar equivalent of hydroperoxide.

[13] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993.
[14] M. Smith, 'Chemistry of Carbon Compounds,' ed. E. H. Rodd, Elsevier, 1967, 2nd edn., vol. IIA, p. 10.
[15] S. Winstein and R. B. Henderson, 'Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, 1950, vol. 1, p. 10.

competition between cyclisation and hydrogen abstraction in our system [equation (5)]. The yield of epoxide from but-2-ene was considerably higher than that from propylene and more expoxide was obtained with 2-methylbut-2-ene than with isobutene, even taking into account possible loss of epoxide by further reaction such as conversion into glycol or condensation with carboxylic acids simultaneously generated during the oxidation. These results could be interpreted in terms of favoured cyclisation in the radical MeCH(OOR)·ĊHMe compared with the radical CH$_2$(OOR)·ĊHMe, and in MeCH(OOR)·ĊMe$_2$ compared with CH$_2$(OOR)·ĊMe$_2$.

The explanation offered for the effect upon the peroxide : epoxide ratio of increasing the number of alkyl groups on the carbon α to the radical centre, suggests that an even smaller amount of epoxidation should occur in the peroxymercuration–reduction of ethylene itself. This was confirmed experimentally

TABLE 1

Molar fraction (%) of epoxide in the epoxide–peroxide mixture formed from the reaction:

$$R^1R^2C=CH_2 \xrightarrow[\text{CH}_2\text{Cl}_2-\text{HClO}_4(2\%)]{2Bu^tO\cdot OH + Hg(OAc)_2}$$

$$\xrightarrow[T\ °]{\frac{1}{2}\ NaBH_4-OH^-} R^1R^2C(OOBu^t)Me + R^1R^2C\underset{O}{\overset{}{\diagdown\diagup}}CH_2$$

$T/°C$ [a]	−15 to −10	−10 to −5	0 to 5	39
Alkene
Ethylene			<5	
Hex-1-ene			19·5 [b,c]	
Styrene	14 [d]		20 [e]	55·5
α-Methylstyrene		44	64 [f]	87·5
α-Phenylstyrene			64·5 [g]	

[a] Temperature at which reduction was carried out. [b] The mixture also contained hexan-2-yl acetate; the calculated molar fractions were: 66·6% peroxide, 15·8% epoxide, and 17·6% ester. [c] From reduction of a product of peroxymercuration derived using only 1 mol. equiv. of hydroperoxide, the calculated molar fractions were: 56·2% peroxide, 14·6% epoxide and 29·2% ester. This corresponds to a figure of 20·5% epoxide in the Table and indicates that the epoxide : peroxide ratio is unaffected by concurrent reduction both of t-butyl hydroperoxide and of acetoxymercurated compound. [d] Only 79·5% of the peroxymercurated compound had been reduced. [e] Reduction of isolated PhCH(OOBu^t)·CH$_2$·HgBr gave 19 mole % of epoxide. [f] Reduction of isolated PhCMe(OOBu^t)·CH$_2$·HgBr in ether gave 74·5 mole % of epoxide. [g] From reduction of isolated Ph$_2$C(OOBu^t)·CH$_2$·HgCl.

with both a reduction *in situ* and a reduction of isolated 2-t-butylperoxyethylmercury(II) chloride. A careful search was made for ethylene oxide in the products, precautions being taken to avoid losses through evaporation or solubility in water. A model mixture containing the amount of ethylene oxide corresponding to a molar ratio of epoxide to peroxide of 5 : 95 (assuming 100% recovery of ethylene derivatives) was prepared under simulated conditions of reduction. The ^{1}H n.m.r. spectra of the non-aqueous and aqueous layers of both the model and reduction mixtures were recorded under identical conditions. The ethylene oxide singlet was considerably more intense in the model mixture.

The synthetic value of peroxymercuration–reduction of terminal alkenes should be reviewed in the light of the results presented above. Concurrent formation of epoxides must be expected during the reduction, but should not present a serious difficulty in the synthesis of secondary alkyl t-butyl peroxides (as in Part I).[3] However care should be taken to control the temperature at which the reduction is carried out as we found that yields of epoxide were increased at temperatures above 0—5° (see Table 1). A slightly improved peroxide : epoxide ratio was obtained at lower temperatures, but below *ca.* −10° the reduction was incomplete. The high yields of epoxide obtained during reduction of peroxymercurated compounds derived from 1-alkyl-1-arylethylenes make the sequence unattractive as a route to tertiary alkyl t-butyl peroxides. However these compounds, unlike the secondary alkyl t-butyl peroxides, are readily available by the acid-catalysed condensation of t-butyl hydroperoxide and the appropriate alcohol.[16]

EXPERIMENTAL

The general methods reported in Parts I [3] and II [1] were modified as described below.

^{t}Butylperoxymercuration.—The reaction time was cut from 30 min to 5 min for styrene and hex-1-ene, and from greater than 24 h to 30 min for α-phenylstyrene by using a perchloric acid catalyst (*ca.* 2 mol%). Under these conditions the reactions could be carried out under air rather than nitrogen without ill effects. The resultant solutions in dichloromethane were then washed with water (2 × an equal volume) to remove the added perchloric acid and the generated acetic acid before further treatment. Acetoxymercurated compounds were not detected at this stage except in the products obtained from ethylene and hex-1-ene. When the reductions were carried out *in situ* these solutions were used directly after the identity of the peroxymercurated compound had been confirmed by ^{1}H n.m.r. spectroscopy. The ^{1}H n.m.r. spectrum of 2-t-butylperoxyethylmercury(II) acetate (from ethylene) showed triplets at τ 5·85 (CH_2·OOBu^t) and 7·95 (CH_2·HgOAc) accompanied by satellites due to coupling with the naturally occurring 16·84% of ^{199}Hg nuclei, with J ^{199}Hg–H values of 236 and 227 Hz, respectively; the corresponding chemical shifts reported [4] for 2-t-butylperoxyethylmercury(II) chloride were confirmed by us to be τ 5·77 and 7·95 (J ^{199}Hg–H 237 and 213 Hz).

2,2-Diphenyl-2-t-butylperoxyethylmercury(II) *acetate* was isolated from dichloromethane solution by removing the solvent *in vacuo* and was recrystallised from dichloromethane–light petroleum, m.p. 109—111° (Found: C, 45·40; H, 4·8. C$_{20}$H$_{24}$HgO$_4$ requires C, 45·40; H, 4·55%). The corresponding organomercury chloride from α-phenylstyrene and the organomercury bromide from α-methylstyrene were obtained by treating the solutions of the crude acetates in dichloromethane directly with aqueous potassium halides.

[16] (a) M. S. Kharasch, A. Fono, W. Nudenberg, and A. C. Poshkus, *J. Org. Chem.*, 1950, **15**, 775; (b) M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *ibid.*, 1951, **16**, 1458; (c) A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1954, 2200.

The conversion of 2-t-butylperoxyethylmercury(II) acetate into the chloride was carried out in a novel way. The crude acetate was dried at 0·1 mmHg for 1·5 h, dissolved in dichloromethane, and then treated with a slight excess of chlorotrimethylsilane in dichloromethane; an exothermic reaction took place. The solution was filtered and the solvent plus acetoxytrimethylsilane removed from the filtrate under reduced pressure to yield the crude chloride (87%) [equation (9)].

(b) *Reduction of ethylene derivative.* Ice-cold water (15 ml) was added to a well-stirred solution of the peroxy-mercurated compound (10 mmol) in dichloromethane (25 ml) cooled to 0°. A solution of sodium borohydride (5·5 mmol) in 3M-sodium hydroxide (10 ml) was added dropwise, keeping the temperature at 0—5°. After 20 min the layers were separated rapidly using cold apparatus and were stored in a refrigerator where the organic layer was dried (MgSO₄). The ¹H n.m.r. spectrum of each layer

$$Bu^tOOCH_2 \cdot CH_2 \cdot HgOAc + Me_3SiCl \longrightarrow Bu^tOOCH_2 \cdot CH_2 \cdot HgCl + Me_3SiOAc \quad (9)$$

This technique enables the conversion of organomercury acetate into chloride to be carried out under homogeneous non-aqueous conditions. It is rapid and goes in high yield and may find wider application in oxymercuration. It is important to remove hydroxylic species (*e.g.* an excess of t-butyl hydroperoxide) from the acetate, as these may react with the trimethylsilyl chloride to release hydrogen chloride which will induce deoxymercuration.

Reduction.—(a) *General.* The peroxymercurated compound was dissolved in dichloromethane or for reductions *in situ* the dichloromethane solution was obtained as described before. The solution was cooled in an ice–salt bath and stirred vigorously as the freshly-prepared solution of sodium borohydride (0·5 mol) in 3M-sodium hydroxide

was recorded using samples rapidly warmed to the temperature of the probe.

To prove that ethylene oxide can be detected by this procedure a simulation was carried out as follows. Ethylene oxide (0·5 mmol) was injected into a well-stirred mixture of dichloromethane (25 ml) and sodium hydroxide [10 ml (3M) and water (15 ml)] at 0—5°. The layers were separated and the ¹H n.m.r. spectra were recorded as before.

Detection of Peroxides and Epoxides.—Peroxides and epoxides were detected by t.l.c. and ¹H n.m.r. spectroscopy, by comparison with authentic samples of the appropriate compounds. T.l.c. was carried out on Eastman Chromatogram Sheet 6060; benzene–hexane (1 : 1) was used as eluant and the spots were visualised by spraying the

TABLE 2

R_F Values and 60 MHz ¹H n.m.r. spectra of peroxides [R¹R²C(OOBuᵗ)Me] and epoxides R¹R²C·CH₂·O

				Chemical shifts (τ) [a]				
Compound	R¹	R²	R_F	R¹	R²	CH₂	Me	Buᵗ
Ethylene oxide	H	H		7·4s	7·4s	7·4s		
Ethyl t-butyl peroxide	H	H		6·05q	6·05q		8·85t	8·8s
1,2-Epoxyhexane	Bu	H		8·55br 9·05tr	7·7m	7·4m		
2-Hexyl t-butyl peroxide	Bu	H		8·6br 9·1tr	6·1m		8·85d	8·8s
Styrene oxide	Ph	H	0·40	2·75	6·3m	7·0m 7·4m		
1-Phenylethyl t-butyl peroxide	Ph	H	0·48	2·75	5·1q		8·6d	8·8s
α-Methylstyrene oxide	Ph	Me	0·48	2·7	8·4s	7·3AB		
Cumyl t-butyl peroxide	Ph	Me	0·61	2·75m	8·5s		8·5s	8·8s
α-Phenylstyrene oxide	Ph	Ph	0·48	2·6m	2·6m	6·9s		
1,1-Diphenylethyl t-butyl peroxide	Ph	Ph	0·58	2·75	2·75		8·05s	8·8s

[a] s = Singlet, d = doublet, t = triplet, tr = distorted triplet (terminal C*H*₃ of Bu group), q = quartet, m = multiplet, AB = AB pattern, br = broad singlet (–[CH₂]₃ of Bu group).

was added dropwise. The temperature of the mixture was maintained within a 5° range by external cooling and by adjusting the rate of addition of the borohydride. The formation of ice made reductions at temperatures below −10 to −15° difficult to carry out.

The organic layer was separated and the aqueous layer was extracted with a further equal volume of dichloromethane; the combined extract was dried (MgSO₄). The product was isolated as a liquid residue after removing the dichloromethane at or below ambient temperature under reduced pressure. The yield usually represented 90—100% recovery of alkene-derived material based upon the subsequent determination of molar fractions of peroxide and epoxide. In one reduction of a styrene derivative the volatile material was collected in a cold trap and its ¹H n.m.r. spectrum recorded; no epoxide or peroxide was detected.

chromatogram with a solution of HI (1 ml) in acetic acid (10 ml) and then heating it at 100° for 30 s. The ¹H n.m.r. resonances in the reduction mixtures were assigned by adding authentic samples of the appropriate peroxide or epoxide and noting which signals were increased in relative intensity. The R_F values and ¹H n.m.r. spectral details are presented in Table 2.

Estimation of Molar Fractions.—The molar fractions of peroxide and epoxide were determined from the integrated ¹H n.m.r. spectrum of each mixture. Integral-steps equivalent to one proton were calculated for each component of the mixture and the ratio of these integral-steps thus gave directly the molar ratio of the components. In general these one-proton-integral-steps were calculated from the largest appropriate integral (*i.e.* that for the Buᵗ singlet for peroxides), provided that this was well-separated from other resonances. However as many calculations

as possible were usually carried out and an average result was taken. Thus for the product from styrene the molar fraction of epoxide was calculated in three ways, by a comparison of the integral for CH plus CH_2 protons in $Ph\overline{CH \cdot CH_2 \cdot O}$ with those for Bu^t, Me and CH protons in $PhCH(OOBu^t) \cdot Me$. The method was tested with a known mixture of independently synthesised cumyl t-butyl peroxide and α-methylstyrene oxide, and found to be accurate within 5%.

Independent Synthesis of Epoxides and Peroxides.— (a) *Epoxides.* Ethylene oxide and styrene oxide were commercial products. The epoxidation of hex-1-ene, α-methylstyrene, and α-phenylstyrene was carried out with *m*-chloroperbenzoic acid as previously described for oct-4-enes.[17] The α-phenylstyrene oxide obtained in this way

was an oil whereas the pure material is reported [18] to melt at 55·5—56°; no impurities were detectable in the [1]H n.m.r. spectrum however.

(b) *Peroxides.* Ethyl t-butyl peroxide was prepared from potassium t-butyl peroxide and diethyl sulphate as previously described.[19] 2-Hexyl t-butyl peroxide and 1-phenylethyl t-butyl peroxide were samples isolated as reported in part I.[3] Cumyl t-butyl peroxide and 1,1-*diphenylethyl t-butyl peroxide*, m.p. 42—44° (Found: C, 79·9; H, 8·4. $C_{18}H_{22}O_2$ requires C, 79·95; H, 8·2%), were prepared by the acid-catalysed condensation of t-butyl hydroperoxide with the appropriate alcohol using the established procedure.[16a]

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