

Oxymetallation. Part IV.¹ The Reaction of Derivatives from the t-Butylperoxymercuration of $\alpha\beta$ -Unsaturated Esters and Ketones with Sodium Borohydride

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Reduction by sodium borohydride of the compounds $\text{XHgCH}_2\text{CMe}(\text{OOBu}^t)\text{COY}$, formed by t-butylperoxymercuration of isopropenyl methyl ketone ($\text{Y} = \text{Me}$) and methyl methacrylate ($\text{Y} = \text{OMe}$), affords the previously unknown α -carbonyl-substituted peroxides $\text{Me}_2\text{C}(\text{OOBu}^t)\text{COY}$ mixed with 10 and 30 mole % respectively of the corresponding epoxides. Similar treatment of the compounds $\text{R}^1\text{R}^2\text{C}(\text{OOBu}^t)\text{CH}(\text{HgOAc})\text{CO}_2\text{Me}$, obtained from four $\alpha\beta$ -unsaturated esters, gives cleanly and in high yield the β -methoxycarbonyl-peroxides $\text{R}^1\text{R}^2\text{C}(\text{OOBu}^t)\text{CH}_2\text{CO}_2\text{Me}$, and represents a generalised and much improved synthesis of this type of compound. In contrast the related peroxymercurial from chalcone ($\text{PhCH}=\text{CHBz}$) gives a high yield of chalcone oxide and that from mesityl oxide affords mainly the dialkylmercurial, $[\text{Me}_2\text{C}(\text{OOBu}^t)\text{CH}(\text{COMe})]_2\text{Hg}$. The methoxymercurials from chalcone and mesityl oxide $\text{R}^1\text{R}^2\text{C}(\text{OMe})\text{CH}(\text{HgOAc})\text{COR}$, are similarly symmetrised under these conditions.

WE are currently investigating the preparative scope of the reaction of alkenes with t-butyl hydroperoxide and mercuric acetate [peroxymercuration; equation (1)], together with subsequent demercuration [equation (3)], as a route to metal-free organic peroxides. The peroxymercuration of terminal alkenes ($\text{R}^3 = \text{R}^4 = \text{H}$)² is usually accompanied by a small amount of acetoxymercuration [equation (2)], but this can be avoided for phenyl-substituted ethylenes under the appropriate conditions.¹

¹ Part III, A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433.

The demercuration of peroxymercurials has been effected by reaction with sodium borohydride [equation (3a)]^{1,2} and with halogens [equation (3b)].^{2,3} For terminal alkenes the former process is again complicated by a competing reaction, namely the formation of epoxides. In fact epoxidation is the major route in the reduction of peroxymercurials derived from 1,1-dialkylethylenes, but fortunately it is much less important with derivatives of monoalkylethylenes and does not represent

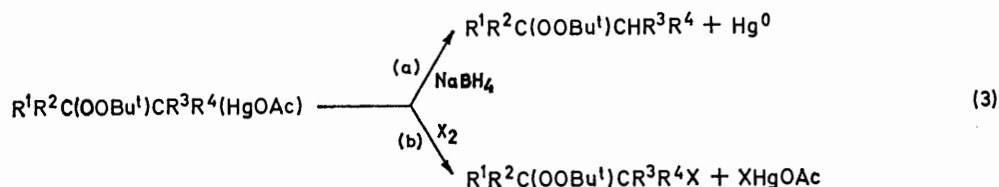
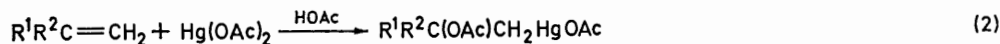
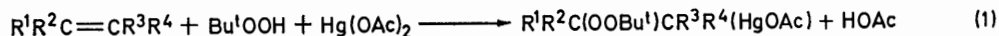
² D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945.

³ E. Schmitz, A. Rieche, and O. Brede, *J. prakt. Chem.*, 1970, 312, 30.

a serious difficulty in the synthesis of secondary alkyl t-butyl peroxides.¹

Attention has now been focused upon reactions involving functionally substituted alkenes with the object of synthesising novel organic peroxides. The peroxymercuration of $\alpha\beta$ -unsaturated esters and ketones is an

$R^1 = \text{Me}$, $R^2 = \text{COMe}$), and 30 mole % of epoxide from the methyl methacrylate compound (I; $R^1 = \text{Me}$, $R^2 = \text{CO}_2\text{Me}$), compared with 74.5 mole % of epoxide with $R^1 = \text{Me}$ and $R^2 = \text{Ph}$, and 64.5 mole % of epoxide when $R^1 = R^2 = \text{Ph}$.¹ It was shown that these differences were not a consequence of the larger excess of



orientationally specific process which is free from competing acetoxymercuration.⁴ It is therefore an attractive reaction to couple with demercuration, especially since the metal-free peroxides with keto and alkoxy-carbonyl substituents are generally unknown.⁵ Accordingly we have studied the reaction of the products from peroxymercuration of $\alpha\beta$ -unsaturated esters and ketones with sodium borohydride.

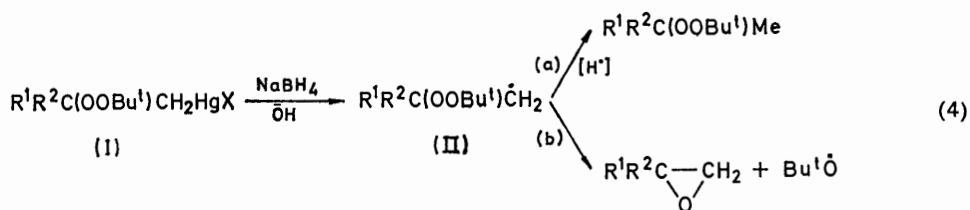
The reduction of peroxymercurials derived from 3-methylbut-3-en-2-one (isopropenyl methyl ketone) and methyl 2-methylpropenoate (methyl methacrylate) was investigated first, because the mercury is here situated β to the carbonyl group.⁴ These compounds therefore have a similar structure (I) to those peroxymercurials for which the reaction with sodium borohydride has previously been studied and, as expected, the major feature of the reaction is that epoxidation competes with the formation of peroxides. The compositions of the peroxide-epoxide mixtures which were obtained in the earlier work were rationalised in terms of a competition between combination with hydrogen [equation (4a)] and cyclisation [equation (4b)] in the intermediate radical (II).¹

'B-H' (ten-fold) present in the reduction of the carbonyl-containing peroxymercurials, since the epoxide: peroxide ratio from the isopropenyl methyl ketone derivative was virtually unchanged when only two mol. equiv. of 'B-H' were used.

The *gem*-dialkyl effect, previously invoked¹ to rationalise the greater fraction of epoxide obtained from dialkylated peroxymercurials compared to those obtained from monoalkylated peroxymercurials, cannot account for these results also. Hence the influence of the carbonyl substituents upon the path of the reaction is not merely that of size.

The result is fortunate from a synthetic point of view since it means that good yields of the previously unknown α -acetyl- and α -methoxycarbonyl-peroxides can be obtained. Furthermore these compounds are isomeric with the peroxides which are potentially available by nucleophilic addition of t-butyl hydroperoxide to the $\alpha\beta$ -unsaturated carbonyl compounds [equation (5)].

In fact we were unable to isolate the product from methyl methacrylate ($Y = \text{OMe}$) using the conditions reported⁶ for methyl acrylate. Isopropenyl methyl ketone ($Y = \text{Me}$) reacts with t-butyl hydroperoxide



However the molar fractions of epoxide from the carbonyl-containing alkenes are much lower than those obtained with peroxymercurials derived from 1,1-dialkylethylenes. Thus 10 mole % of epoxide was formed from the isopropenyl methyl ketone derivative (I;

under base catalysis to give the corresponding epoxide [equation (6)].⁷

Reduction of the ester during demercuration by sodium borohydride is not expected, but, surprisingly, there was no evidence for the reduction of keto-groups in

⁴ A. J. Bloodworth and R. J. Bunce, *J. Chem. Soc. (C)*, 1971, 1453.

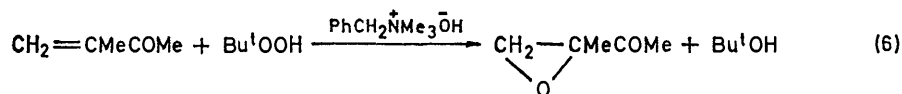
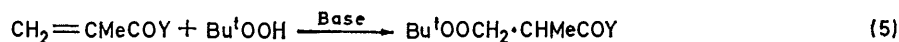
⁵ D. Swern, 'Organic Peroxides,' Wiley-Interscience New York, 1970.

⁶ D. Harman, U.S.P. 2,508,256 (*Chem. Abs.*, 1950, **44**, 7341i).

⁷ N. C. Yang and R. A. Finnegan, *J. Amer. Chem. Soc.*, 1958, **80**, 5845.

most of the reactions reported here, even though there was always an excess of sodium borohydride present. It was shown that the excess of borohydride would reduce a simple ketone by carrying out one reaction in the presence of acetone which was duly converted into propan-2-ol.

In the six other peroxymercurials (III) which were treated with sodium borohydride, the mercury was situated α to the carbonyl group. If the demercuration again involves the intermediate generation of alkyl



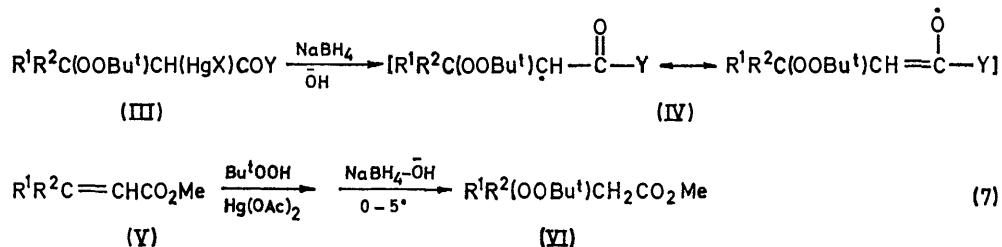
radicals, these may now be stabilised by delocalisation of the unpaired electron (IV). Consequently these longer-lived radicals might have a different fate to that of the β -peroxyalkyl radical (II) previously postulated in the reduction of peroxymercurials. However the peroxide linkage is still β to a carbon possessing partial radical character.

The peroxymercurials prepared from the $\alpha\beta$ -unsaturated esters (V) methyl acrylate ($\text{R}^1 = \text{R}^2 = \text{H}$), methyl cinnamate ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$), methyl crotonate ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$), and methyl 3,3-dimethylacrylate ($\text{R}^1 = \text{R}^2 = \text{Me}$) all reacted with sodium borohydride to give the corresponding mercury-free β -methoxycarbonyl-peroxides (VI) [equation (7)]. The crude products,

denotation of methyl acrylate with *t*-butyl hydroperoxide in the presence of $\text{PhCH}_2\overset{+}{\text{N}}\text{Me}_3\bar{\text{O}}\text{H}$, but the procedure was lengthy and the yield (22%) was poor.⁷

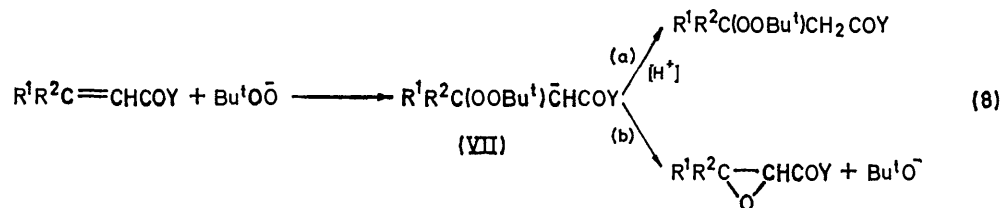
Thus peroxymercuration followed by reduction *in situ* with sodium borohydride appears to be an excellent general route to β -methoxycarbonyl-peroxides. The method is rapid; both stages occur under very mild conditions, are free from side-reactions, and go in high yield.

In contrast no β -keto-peroxides were isolated from similar treatment of $\alpha\beta$ -unsaturated ketones. Signals attributable to 3-phenyl-3-(*t*-butyldioxy)propiophenone were found in the ¹H n.m.r. spectrum of the crude product from peroxymercuration-reduction of *trans*-chalcone ($\text{PhCH}=\text{CHBz}$), but the yield was estimated to be only 10% and the pure material could not be isolated. The major product was chalcone oxide (75%). On the basis of a mechanism involving radical generation during demercuration, this result suggests that the radical $[\text{PhCH}(\text{OOBu}^t)\dot{\text{C}}\text{HBz} \leftrightarrow \text{PhCH}(\text{OOBu}^t)\text{CH}=\text{CPh}\dot{\text{O}}]$ has a strong tendency to cyclise, whereas the related radicals derived from $\alpha\beta$ -unsaturated esters prefer to add



obtained in yields of 83–93%, were investigated closely but there was no evidence of any epoxidation. The aqueous layers from the reductions were checked against the possibility of reduction of any α -epoxy-esters to

hydrogen. Parallel behaviour in the corresponding anions (VII) has been suggested to account for the formation of epoxides from the base-catalysed reaction of *t*-butyl hydroperoxide with $\alpha\beta$ -unsaturated ketones



potentially water-soluble β -epoxy-alcohols,⁸ but again no epoxides were detected. Methyl 3-(*t*-butyldioxy)propanoate has been prepared previously by the con-

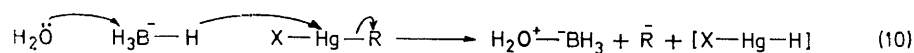
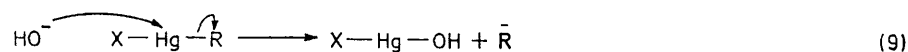
[equation (8b)], which contrasts with peroxide formation from methyl acrylate [equation (8a)].

Since our reducing agent is basic (the sodium borohydride is dissolved in 3*M*-sodium hydroxide) it is necessary to consider the possibility that the β -keto-peroxide

⁸ S. Corsano and G. Piancatelli, *Chem. Comm.*, 1971, 1106.

is formed in high yield just like the β -methoxycarbonylperoxides, but that abstraction of a proton [reverse of equation (8a)] subsequently affords the carbanion which is then epoxidised [equation (8b)]. However impure 3-phenyl-3-(*t*-butyldioxy)propiophenone, obtained from a large scale peroxymercuration-reduction of chalcone, was unchanged when treated with 3M-sodium hydroxide under the reduction conditions. While this is not conclusive evidence since the identification of the peroxide depended only upon consistent ^1H n.m.r. spectral characteristics, it strongly suggests that epoxidation does not occur *via* base-catalysed decomposition of the mercury-free peroxide.

There is also the possibility of direct carbanion generation from the peroxymercuration by heterolytic demercuration with hydroxide [equation (9)] or borohydride [equation (10)] ions. The former mechanism was

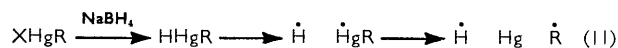


ruled out since no chalcone oxide was produced when sodium borohydride was omitted from the reaction mixture. The latter mechanism remains a possibility although it has been rejected for simple β -oxyalkyl mercurials on the grounds that deuterium was not incorporated into the molecule when the reduction was carried out in D_2O .⁹ Evidence which suggests that carbanions are not formed in this way came from the observation that the methoxymercuration of chalcone reacted to give the symmetrical dialkylmercurial $[\text{PhCH}(\text{OMe})\text{CHBz}]_2\text{Hg}$ rather than the expected ether. Furthermore symmetrisation was the principal reaction with both methoxy- and peroxy-mercurials derived from mesityl oxide, and with the chalcone peroxymercuration when it was treated with sodium borohydride dissolved in water rather than sodium hydroxide.

The formation of dialkylmercurials is the first stage of the reduction of alkylmercury(II) salts by hydrazine or sodium stannite.⁹ Since the subsequent hydridodemercuration step requires more vigorous conditions than those for symmetrisation, the dialkylmercurials are frequently isolated as the major product. In contrast reduction with sodium borohydride gives the hydridodemercuration product directly and symmetrisation is a competitive process which occurs only rarely. Diphenylmercury (51%) and di-*p*-tolylmercury (68%) have been obtained by treatment of phenylmercury acetate and *p*-tolylmercury chloride with sodium borohydride;⁹ 23% of bis-[2-(2,3-dihydrobenzofuryl)methyl]mercury⁹ and 69% of bis-(2-phenylborn-2-en-3-yl)mercury¹⁰ were similarly obtained from the corresponding organomercury acetates. The only previous report of symmetrisation of a β -oxyalkylmercurial by sodium borohydride involved the hydroxymercuration prepared from

camphene which afforded a little dialkylmercurial in addition to camphene hydrate.¹⁰

Although there is much evidence that the replacement of mercury by hydrogen, which is the usual behaviour with sodium borohydride, proceeds *via* formation of alkyl radicals (see Part III),¹ the mechanism by which they are produced is uncertain. It is widely believed that they are generated from the corresponding alkylmercury hydrides, presumably *via* a mercury(I) species (equation (11)). Dialkylmercurial might therefore arise from



combination of $\dot{\text{H}}\text{gR}$ and $\dot{\text{R}}$, or alternatively *via* the compound RHgHgR formed by self-combination of $\dot{\text{H}}\text{gR}$ species. On the other hand a polar mechanism of the type generally proposed for symmetrisation has been

suggested.⁹ It is not clear from any of these mechanisms why the compounds $\text{Me}_2\text{C}(\text{OMe})\text{CH}(\text{HgOAc})\text{COMe}$, $\text{Me}_2\text{C}(\text{OOBu}^t)\text{CH}(\text{HgOAc})\text{COMe}$, and $\text{PhCH}(\text{OMe})\text{CH}(\text{HgOAc})\text{Bz}$ should be especially susceptible towards symmetrisation, or why the absence of base should favour the process for the compound $\text{PhCH}(\text{OOBu}^t)\text{CH}(\text{HgOAc})\text{Bz}$.

EXPERIMENTAL

Details of the individual esters and ketones and of their conversion into the respective peroxymercurials were given in Part II.⁴ Unless otherwise stated the peroxymercurials were reduced *in situ* in the presence of an equimolar quantity of *t*-butyl hydroperoxide but with at least a three-fold excess of sodium borohydride over that required to react with all potentially reducible groups present.

t-Butylperoxymercuration-Reduction.—(a) *General procedure.* The $\alpha\beta$ -unsaturated carbonyl compound (20 mmol) was added to a solution of *t*-butyl hydroperoxide (40 mmol) in dichloromethane (30 ml) containing mercuric acetate (20 mmol) and perchloric acid (0.5 mmol), and the mixture was stirred magnetically. When no more solid dissolved [after 2 h except for methyl methacrylate (48 h) and chalcone (24 h)] the mixture was filtered and the filtrate was washed thoroughly with water (2 \times 30 ml).

The resultant solution, diluted with more dichloromethane to 50 ml, was cooled in an ice-salt bath and stirred vigorously while a freshly prepared solution of sodium borohydride (60 mmol) in 3M-sodium hydroxide (50 ml) was added dropwise to maintain the temperature at 0–7 °C. The initially vigorous reaction, in which precipitation of mercury was accompanied by some effervescence, subsided when about half of the solution had been added. Stirring was continued for 2 h after addition was complete and, towards the end of this period, the mixture was allowed to warm to room temperature. The organic layer was separated and dried

⁹ F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993.

¹⁰ J. M. Coxon, M. P. Hartshorn, and A. J. Lewis, *Tetrahedron*, 1970, **26**, 3755.

(MgSO₄). The ¹H n.m.r. spectrum of the aqueous layer showed signals due to BH₄⁻, MeCO, and CMe₃ (presumably Bu⁺OH).

The compositions of the residual and volatile fractions were monitored by ¹H n.m.r. spectroscopy as the dichloromethane was removed from the organic layer at progressively lower pressures (water-pump). The pressure was adjusted so that all alkene derivatives remained with the residue. The presence of any epoxide was detected by t.l.c. and ¹H n.m.r. spectroscopy, by comparison with an authentic sample, and the yield was calculated from the integrated spectrum as described previously.¹ Pure peroxides, which are colourless liquids, were isolated by chromatography on columns (5–30 cm × 2 cm diam.) of activated silica gel² using benzene as eluant. 25 ml fractions were collected and concentrated at a rotary evaporator; the R_F values (Eastman silica gel sheet 6060; benzene) were in the range 0.45–0.60. No attempt was made to optimise yields from chromatography.

(b) *Individual results.* Yields (%) are based on starting αβ-unsaturated carbonyl compounds except for the oxides of isopropenyl methyl ketone and methyl methacrylate where they are expressed as the molar fraction of an epoxide-peroxide mixture. Chemical shifts refer to 60 MHz spectra recorded at 35° for solutions in deuteriochloroform unless otherwise stated; *J* (¹⁹⁹Hg) values are the coupling constants between the protons concerned and the naturally-occurring ¹⁹⁹Hg nuclei, and δ_{AB} = |τ_A – τ_B| for an AB signal.

(i) Isopropenyl methyl ketone. The reduction was carried out using isolated 4-bromomercuri-3-methyl-3-t-butylidioxymethan-2-one as it was found difficult to remove all ethyl methyl ketone from the commercial isopropenyl methyl ketone. The crude product consisted of a mixture of 10 mole % of 3,4-epoxy-3-methylbutan-2-one and 90 mole % of 3-methyl-3-(*t*-butylidioxymethan-2-one) (85%); small ill-defined multiplets at τ 6.5 and 7.0 were not assigned. The following fractions were isolated by chromatography (15 cm column): (1) 50–75 ml (41%) (Found: C, 62.2; H, 10.65%); (2) 75–100 ml (25%) (Found: C, 62.75; H, 10.35%); (3) 100–175 ml (14%) (Found: C, 62.6; H, 10.2%). All fractions showed only peroxide resonances, τ 7.75 (CO₂Me), 8.7 (CMe₂), and 8.75 (CMe₃) (C₉H₁₈O₃ requires C, 62.05; H, 10.4%).

The epoxide was synthesised independently by Yang and Finnegan's method,⁷ τ 7.1 (CH₂, δ_{AB} 11 Hz, *J* 5 Hz), 8.05 (CO₂Me), and 8.65 (Me).

(ii) Methyl methacrylate. The crude product contained a little methyl methacrylate, 30 mole % of epoxide, and other unidentified impurities with resonances at τ 5.9 (m), 6.7, 7.9, 7.95, 8.75, and 8.8 in addition to methyl 2-methyl-2-(*t*-butylidioxymethan-2-one) (45%). The peroxide content of three chromatography fractions (12.5 cm column) was estimated from their ¹H n.m.r. spectra: (1) 0–50 ml, 66% peroxide (2%); (2) 50–175 ml, 100% peroxide (31%), τ 6.25 (OMe), 8.55 (CMe₂), and 8.75 (CMe₃) (Found: C, 57.25; H, 9.45. C₉H₁₈O₄ requires C, 56.85; H, 9.55%); (3) 175–225 ml, 70% peroxide (2%).

Methyl 2,3-epoxy-2-methylpropanoate was prepared independently by refluxing a solution of methyl methacrylate and *m*-chloroperbenzoic acid in 1,2-dichloroethane in the presence of 2,6-di-*t*-butyl-4-methylphenol,¹¹ τ 6.25 (OMe), 7.1 (CH₂; δ_{AB} 21 Hz, *J* 6 Hz), and 8.4 (Me).

(iii) Methyl acrylate. The ¹H n.m.r. spectrum of the crude methyl 3-(*t*-butylidioxymethan-2-one) (86%) showed only

a very small additional singlet at τ 7.9. Five fractions were obtained by chromatography (12.5 cm column): (1) 100–125 ml (9.4%) (Found: C, 55.5; H, 9.15%); (2) 125–175 ml (21%) (Found: C, 55.0; H, 9.2%); (3) 175–200 ml (8.8%) (Found: C, 54.3; H, 9.15%); (4) 200–225 ml (5%) (Found: C, 56.05; H, 9.35%); (5) 225–325 ml (13.6%). The ¹H n.m.r. spectra of all fractions showed only peroxide signals, τ 5.75 (t, CH₂OObu^t), 6.3 (OMe), 7.35 (t, CH₂CO), and 8.75 (CMe), except for the presence of a trace of benzene in fraction (1) (Calc. for C₈H₁₆O₄: C, 54.55; H, 9.15%). In a separate experiment a yield of 11% of peroxide was isolated by distillation, b.p. 20–24° at 0.15 mmHg (lit.,⁷ 75° at 13 mmHg) (Found: C, 55.15; H, 9.55%).

(iv) Methyl cinnamate. The crude methyl 3-phenyl-3-(*t*-butylidioxymethan-2-one) (92%) contained methyl cinnamate (8%). The third chromatography fraction (30 cm column) was cinnamate-free peroxide: (1) 0–500 ml, 29% peroxide (5%); (2) 500–650 ml, 87% peroxide (25%); (3) 650–1250 ml, 100% peroxide (57%), τ 2.7 (*Ph*), 4.6 (4 peaks, CH₂Ph), 6.4 (OMe), 7.2 (8 peaks, CH₂CO), and 8.8 (CMe₃), ν_{max.} 1753 (C=O) cm⁻¹ (Found: C, 66.55; H, 7.9%. C₁₄H₂₀O₄ requires C, 66.65; H, 8.0%).

(v) Methyl crotonate. Chromatography (12.5 cm column) of the crude product (93%) afforded, in a single fraction (200–1200 ml) pure methyl 3-(*t*-butylidioxymethan-2-one) (80%), τ 5.5 (m, CHMe), 6.3 (OMe), 7.4 (8 peaks, CH₂CO), 8.75 (d, CHMe), and 8.8 (CMe₃) (Found: C, 56.4; H, 8.85. C₉H₁₈O₄ requires C, 56.85; H, 9.55%).

(vi) Methyl 3,3-dimethylacrylate. Evacuation of the crude product (83%) at 30° at 1 mmHg gave a residue (79%) of slightly impure methyl 3-methyl-2-(*t*-butylidioxymethan-2-one) (80%), τ 6.3 (OMe), 7.35br (CH₂CO), 8.65 (CMe₂), and 8.8 (CMe₃) (Found: C, 58.15; H, 9.5. C₁₀H₂₀O₄ requires C, 58.8; H, 9.85%). Chromatography (5 cm column) afforded four fractions with identical ¹H n.m.r. spectra except for a *t*-butyl impurity (20%) in fraction (1); (1) 0–25 ml (5%); (2) 25–50 ml (36%) (Found: C, 58.85; H, 9.6%); (3) 50–75 ml (16%) (Found: C, 59.95; H, 9.3%); (4) 75–175 ml (3%).

(vii) Chalcone. The reaction was carried out on an 80 mmole scale. Removal of dichloromethane afforded a solid which, when washed with light petroleum (b.p. 60–80°; 2 × 50 ml), yielded a crystalline residue (12.4 g) identified as chalcone oxide (70%), m.p. 88.5–89.5 °C (lit.,⁷ 88.5–89.5

°C), τ (CCl₄) 1.9–2.6, 2.65 (*Ph*), 6.0 (CH–CH); δ_{AB}* 2.6 Hz; *J* 1.75 Hz (Found: C, 80.25; H, 5.3. C₁₅H₁₂O₂ requires C, 80.35; H, 5.4%). The light petroleum extract was concentrated to 50 ml by slow evaporation and the solution decanted from a yellow oil (1.80 g), which was shown by ¹H n.m.r. spectroscopy to be a 1:1 mixture of chalcone oxide (5%) and 2,3-epoxy-1,3-diphenylpropan-1-ol [PhCH^C–CH^B–CH^A(OH)Ph (5%), τ (CH₂Cl₂) 2.45br, 2.55 (*Ph*), 4.95 (2 × d, H^A, J_{AB} = J_{AD} = 3 Hz), 5.8 (d, H^C, J_{BC} 2.5 Hz), 6.65 (2 × d, H^B), and 6.9 (d, H^D)]. Removal of the light petroleum afforded a mixture (2.82 g) of 42% of 3-phenyl-3-(*t*-butylidioxymethan-2-one) propiophenone [τ 4.3 (4 peaks, CH₂Ph) and 6.5 (8 peaks, CH₂CO)] and unidentified aromatic species.

For comparison, chalcone oxide was prepared independently by Yang and Finnegan's method⁷ and was converted

* δ_{AB} Was larger in impure samples of chalcone oxide.

¹¹ T. Fukuyama, T. Goto, S. Inoue, S. Sugiura, and H. Kakoi, *Chem. Comm.*, 1972, 64.

into 2,3-epoxy-1,3-diphenylpropan-1-ol by prolonged treatment with sodium borohydride.

(viii) *Mesityl oxide*. The work-up was as for (vii). The white crystalline solid (2.34 g) insoluble in light petroleum was identified as bis-(1-acetyl-2-methyl-2-t-butyldioxypropyl)mercury (41%), m.p. 111.5–112°, τ 6.7 (CHHg), 7.8 [unresolved d, COMe, $J(^{199}\text{Hg})$ 15 Hz], 8.4 [CMe, $J(^{199}\text{Hg})$ 15 Hz], 8.7 (CMe₃), and 8.75 (CMe) (the diastereotopic methyl groups have considerably different chemical shifts) (Found: C, 41.7; H, 6.5. C₂₀H₃₈HgO₆ requires C, 41.75; H, 6.7%).

The ¹H n.m.r. spectrum of the fraction (1.45 g) soluble in light petroleum suggested that it was a mixture containing the dialkylmercurial (60 mole %) and a compound with resonances at τ 7.4 and 8.6 [40 mole % if it is Me₂C(OOBu^t)-CH₂COMe].

Reaction of PhCH(OOBu^t)CH(HgOAc)Bz with Sodium Borohydride in Water. The reaction was carried out on a 7 mmole scale according to the general procedure described above, except that 3M-sodium hydroxide was replaced by water; the crude product was treated as for (vii). The crystalline solid (1.63 g) which was insoluble in light petroleum, was identified as bis-(1-benzoyl-2-phenyl-2-t-butylperoxyethyl)mercury (59%), m.p. 123–124°, τ 2.0–2.8 (Ph), 3.95 (d, CHPh), 5.95 (d, CHHg), 8.75, and 8.85 (CMe₃) (Found: C, 57.8; H, 5.45. C₃₈H₄₂HgO₆ requires C, 57.9; H, 5.3%).

The ¹H n.m.r. spectrum of the fraction (0.56 g) soluble in light petroleum indicated that it was a mixture of 58 mole % of 3-phenyl-3-(t-butyldioxy)propiophenone (17.5%) and 42 mole % of chalcone oxide (13%).

Methoxymercuration-Reduction.—The general procedure for t-butylperoxymercuration-reduction was employed, replacing the hydroperoxide by methanol.

(a) *Isopropenyl methyl ketone*. Sodium borohydride (40 mmol) was used. The ¹H n.m.r. spectrum of the concentrated dichloromethane solution showed only resonances attributable to Me₂C(OMe)COMe [τ 6.8 (OMe), 7.8 (COMe), and 8.75 (CMe₂) in ratio 1:1:2 as calculated] and isopropenyl methyl ketone.

(b) *Chalcone*. A finely divided solid which was dispersed in the organic layer was filtered off, and further fractions of crystals were isolated from treatment of the filtrate with light petroleum. Thorough washing of the combined solids with light petroleum removed chalcone (18%) to leave bis-(1-benzoyl-2-methoxy-2-phenylethyl)mercury (5.48 g; 81%), m.p. 153–157°, ν_{max} 1642br, 1602, 1582, 770, 718, and 703 cm⁻¹, insufficiently soluble for n.m.r. spectroscopy (Found: C, 55.7; H, 4.5. C₃₂H₃₀HgO₄ requires C, 56.6; H, 4.45%). The identity of this material was confirmed by treating it with mercuric acetate which yielded 1-benzoyl-2-methoxy-

2-phenylethylmercury(II) acetate, identical with an authentic sample.⁴

(c) *Mesityl oxide*. A crystalline solid (1.07 g) was isolated by removing the dichloromethane and treating the residue with light petroleum. This was identified as bis-(1-acetyl-2-methoxy-2-methylpropyl)mercury (23%), m.p. 106–107°, τ 6.7 (CHHg), 6.75 (OMe), 7.9 [COMe, $J(^{199}\text{Hg})$ 15 Hz], 8.5 (CMe), and 8.75 [CMe, $J(^{199}\text{Hg})$ 13 Hz] (mercury coupling was only visible in one of the diastereotopic methyl groups) (Found: C, 36.7; H, 5.65. C₁₄H₂₆HgO₄ requires C, 34.4; H, 5.35%).

The filtrate yielded an oil (1.27 g) shown by ¹H n.m.r. spectroscopy to be a mixture of 12 mole % of the dialkylmercurial (8%) and 88 mole % of 4-methoxyhexan-2-one (33%). Chromatography (12.5 cm column) using chloroform (+2% EtOH) as eluant afforded the ether (9%) in the 50–100 ml fraction, τ 6.75 (OMe), 7.4 (CH₂CO), 7.8 (COMe), and 8.75 (CMe₂) (Found: C, 65.1; H, 11.2%. Calc. for C₇H₁₄O₂: C, 64.6; H, 10.85%).

Reaction of PhCH(OOBu^t)CH(HgOAc)Bz with Sodium Hydroxide.—A solution of 1-benzoyl-2-phenyl-2-t-butyldioxyethylmercury(II) acetate (5 g) in dichloromethane (25 ml) was stirred vigorously with 3M-sodium hydroxide (25 ml) for 2 h at 0 °C. The layers were separated and the organic layer was dried (MgSO₄). The ¹H n.m.r. spectrum of the organic layer showed the absence of chalcone oxide and that of the aqueous layer contained an acetate singlet. Most of the dichloromethane was removed and resultant 'wet' solid was dissolved in ether (10 ml). Light petroleum (b.p. 60–80°; 10 ml) was added to give a precipitate (3.31 g), m.p. 128–129° (Found: C, 44.05; H, 3.6%). The absence of an OH stretching band in the i.r. and the presence of broad absorptions at 1565 and 1250 cm⁻¹ suggest that this solid may be the carbonate, [PhCH(OOBu^t)CHBzHgO]₂CO (Calc. for C₃₉H₄₂Hg₂O₆: C, 44.35; H, 4.0%), rather than the hydroxide, PhCH(OOBu^t)CH(HgOH)Bz (Calc. for C₁₉H₂₂HgO₄: C, 44.3; H, 4.3%), by comparison with the reported¹² spectrum for phenylmercuric carbonate.

Treatment of Impure PhCH(OOBu^t)CH₂Bz with Sodium Borohydride in Sodium Hydroxide.—The impure 3-phenyl-3-(t-butyldioxy)propiophenone (2.82 g) isolated in (vii) was dissolved in dichloromethane (25 ml) and stirred for 2 h at 0 °C, with a solution of sodium borohydride (0.94 g) in 3M-sodium hydroxide (25 ml). The ¹H n.m.r. spectrum of the recovered material (2.73 g) was unchanged.

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¹² J. H. S. Green, *Spectrochim. Acta*, 1968, **24A**, 863.