under reduced pressure. The tube was heated in a sand bath at 160 °C for 2 days. The tube was removed from the sand bath, chilled in dry ice, and cracked open. A portion of the contents was removed and the 300-MHz NMR spectrum was recorded showing the complete disappearance of the ETA and the presence of peaks representing only **3–5**. The relative yields of **3–5** were determined by integration of the NMR spectrum.

The unreacted 1122 was allowed to evaporate and the reaction mixture was separated by preparative GLC on a 12 ft × $^1/_4$ in. Carbowax 20 M on Chromasorb P column. The individual samples were analyzed for d_2 content by mass spectrometry, by measuring the relative peak heights (flat-topped) of the M and M + 2 (product-d_2) peaks. Between 40 and 50 repetitive scans were made and the relative intensities were averaged. The relative yields of **3–5** and their percent d_2 content are given in Scheme II.

Cycloaddition of ETA and ETA-d_2 Mixture with NPMI. In a thick-walled Pyrex tube were placed 100 μL of a mixture of ETA and ETA-d_2 (51.09% ETA-d_2), 2 mol equiv of NPMI, and 1.0 mL of benzene. The contents of the tube were triply freeze-degassed, and the tube was sealed under vacuum. The tube was heated in a sand bath at 160 °C for 5 days. The tube was removed from the bath, cooled, and opened. NMR analysis of the contents of the tube showed the complete disappearance of ETA and the formation of only **6–9**. The benzene was removed from the reaction mixture, and the residue was separated by preparative HPLC on a 5-μm silica gel column using hexane–methylene chloride gradient elution. The d_2 contents of the fractions were determined by mass spectral techniques as described above. The relative yields (integration of the NMR spectrum of the crude reaction mixture) and d_2 compositions are given in Scheme III.

Preparation of 3-Deuterio-1,1-dimethylallene. 3-Deuterio-1,1-dimethylallene was prepared by the reduction of 3-chloro-3-methyl-1-butyne with lithium aluminum deuteride using the previously published procedure for the reduction of propargyl chlorides with lithium aluminum hydride.[2a] The product was isolated by preparative GLC using a 15-ft Carbowax 20 M column at 80 °C. Mass spectral analysis indicated the presence of >99.5% DMA-d_1.

Preparation of 3-Deuterio-1-ethylallene. 3-Deuterio-1-ethylallene was prepared by the reduction of 3-chloro-1-pentyne with lithium aluminum deuteride employing the previously described procedure for the reduction of propargyl chlorides with lithium aluminum hydride.[2a] The product was isolated by preparative GLC. Mass spectral analysis indicated the presence of >99.5% ETA-d_1.

Preparation of *tert*-Butyl-3-deuterioallene. A solution of 0.53 g (5.3 mmol) of *tert*-butylallene in 10 mL of ether and 10 mL of tetrahydrofuran contained in a 50-mL round-bottom flask equipped with a side-arm equilibrating addition funnel was cooled to −80 °C (dry ice–2-propanol bath). The reaction mixture was maintained under a nitrogen atmosphere. *tert*-Butyllithium (10% mol excess) was added dropwise and the reaction mixture was allowed to warm to −60 °C. After the mixture was stirred for 2 h at −60 °C, 2 mL of deuterium oxide was added, and the reaction mixture was allowed to warm to 25 °C. The organic layer was washed with 15 mL of ice–water and was dried ($MgSO_4$). The organic solvents were removed by fractional distillation, and the product was purified by preparative GLC using a 12 ft × $^1/_4$ in. SE-30 column at 80 °C. Mass spectral analysis indicated the presence of 92.7% d_1 and 7.3% d_0 *tert*-butylallene.

Cycloaddition of the Monodeuterioalkylallenes with 1122. The cycloaddition reactions of the monodeuterioalkylallenes were carried out at 160 °C as described previously.[1a] The ratios of **10** and **11** were determined directly on the reaction mixtures by integration of the vinyl hydrogen region of the NMR spectra.

Acknowledgment. This research was in part supported by the National Science Foundation (Grant CHE77-08627).

Registry No. **1122**, 79-35-6; ETA, 591-95-7; NPMI, 941-69-5; DMA-*d*, 101933-73-7; ETA-*d*, 101933-74-8; TBA-*d*, 101933-75-9; PhSH, 108-98-5; D_2, 7782-39-0.

Oxymetalation. 20.[1] Conversion of Cyclopropanes into 1,2-Dioxolanes via *tert*-Butyl Peroxymercuriation, Bromodemercuriation, and Silver Salt Induced Cyclization

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The *tert*-butyl peroxymercuriations of cyclopropane and ethyl-, phenyl-, 1,1-dimethyl-, 1-methyl-1-phenyl-, and 1,1-diphenylcyclopropane (**1a–f**) have been carried out by using mercury(II) acetate, a onefold excess of *tert*-butyl hydroperoxide, and 20 mol % of perchloric acid. After anion exchange with aqueous potassium bromide, the derived γ-(bromomercurio)alkyl *tert*-butyl peroxides (**2a–f**) have been isolated (33–51%; 10% for **2a**) by silica chromatography. These have been converted into the corresponding γ-bromoalkyl *tert*-butyl peroxides (**3a–f**) (84–100%) by reaction with bromine and sodium bromide in methanol. The bromides (**3a–e**) have, in turn, been converted into the corresponding 1,2-dioxolanes (**4a–e**) (>80%) by treatment with silver trifluoroacetate. However, the reaction of **3f** with silver trifluoroacetate afforded a phenoxyacetal derived from β-*tert*-butoxyethyl phenyl ketone, which was identified by conversion into phenol plus the corresponding (2,4-dinitrophenyl)hydrazone upon treatment with acidic (2,4-dinitrophenyl)hydrazine. The exceptional behavior of **3f** supports the suggestion that the final step in this three-stage synthesis of 1,2-dioxolanes proceeds via trialkylperoxonium intermediates.

In a far-reaching discovery, Kopecky et al.[2] found that certain alkenes may be converted into 1,2-dioxetanes via hydroperoxybromination and silver salt induced cyclization (e.g., eq 1). The analogous conversion of cyclopropanes into 1,2-dioxolanes (eq 2) has been investigated by Adam et al.[3] and found to be problematical. Thus, the ring-opening step only proceeded at an acceptable rate when the cyclopropane possessed at least one aryl substituent, and even then reaction times of 20–150 h were required. Furthermore, the hydroperoxybromination was subject to unpredictable amounts of competing aromatic bromina-

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(2) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A.; Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1103.

(3) Adam, W.; Birke, A.; Cádiz, C.; Díaz, S.; Rodríguez, A. *J. Org. Chem.* **1978**, *43*, 1154.

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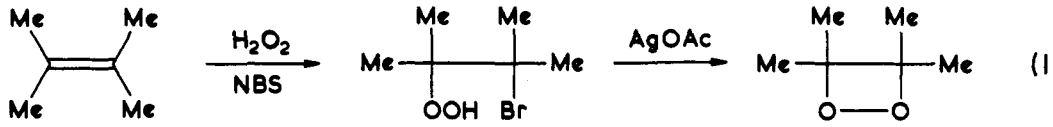
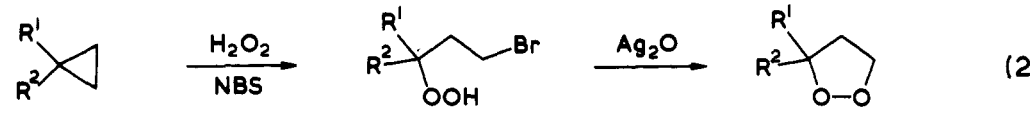
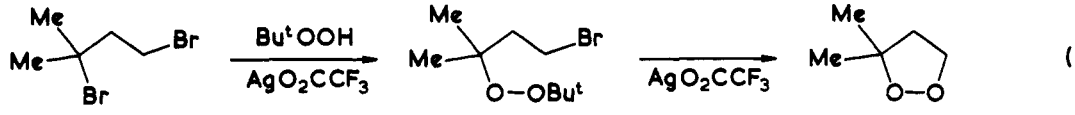
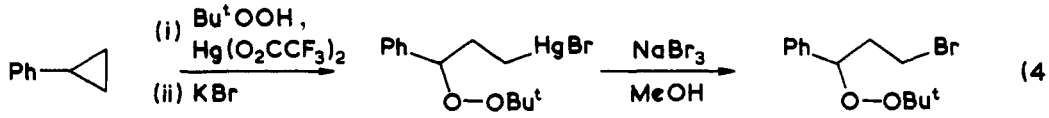
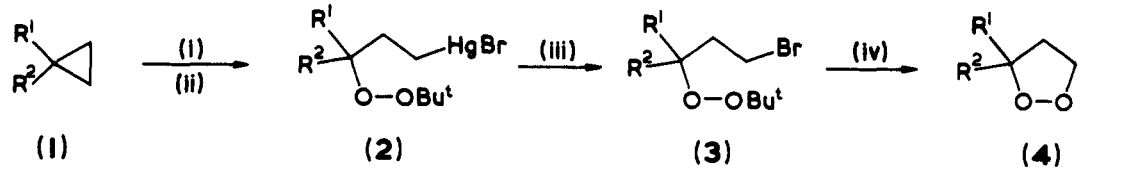


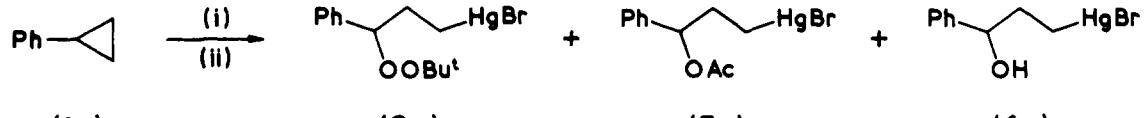








a, $R^1 = R^2 = H$; b, R^1 = Et, $R^2 = H$; c, R^1 = Ph, $R^2 = H$; d, $R^1 = R^2$ = Me; e, R^1 = Me, R^2 = Ph; f, $R^1 = R^2$ = Ph
reagents: (i) 2*t*-BuOOH, $Hg(OAc)_2$, 20 mol % $HClO_4$, CH_2Cl_2; (ii) KBr, H_2O; (iii) Br_2, NaBr, MeOH; (iv) AgO_2CCF_3, CH_2Cl_2



Reagents: (i) 2*t*-BuOOH, $Hg(OAc)_2$, 20 mol % $HClO_4$, CH_2Cl_2; (ii) KBr, H_2O

tion. The unstable γ-bromoalkyl hydroperoxides had to be purified under stringent conditions at subambient temperatures, and then cyclized immediately using silver oxide which had been freshly prepared and thoroughly washed with water.

Recently, Porter and Mitchell[4] discovered that γ-bromoalkyl *tert*-butyl peroxides can also undergo silver salt induced cyclization to afford 1,2-dioxolanes (eq 3). We had demonstrated earlier that phenylcyclopropane can be converted into the correponding γ-bromoalkyl *tert*-butyl peroxide by peroxymercuriation and bromodemercuriation (eq 4).[5]

Consequently we decided to investigate the sequence of *tert*-butyl peroxymercuriation, bromodemercuriation, and silver salt induced cyclization as an alternative to Adam's route for the conversion of cyclopropanes into 1,2-dioxolanes. The results presented here show that this method, which avoids the hazard of using 98% hydrogen peroxide, is much easier to carry out than that represented by eq 2. Furthermore, it is applicable not only to arylcyclopropanes, but also alkylcyclopropanes and even to cyclopropane itself.

Results and Discussion

The overall sequence and the reagents used are shown in eq 5.

The six cyclopropanes were chosen to provide a representative selection with which to test the generality of the method in a preliminary way, while avoiding the complications of regio- and stereoselectivity. Thus, all reports describing oxymercuriations of mono- and 1,1-disubstituted cyclopropanes indicate that ring-opening is regiospecific,[6] and the question of stereoselectivity does not arise. All possible combinations of alkyl and aryl groups for these substitution patterns are represented. Only with 1,1-diphenylcyclopropane (**1f**) did the sequence fail to afford a 1,2-dioxolane, and here the problem arose in the final step (see later).

Step 1. Peroxymercuriation. The *tert*-butyl peroxymercuriation of phenylcyclopropane (**1c**) using mercury(II) trifluoroacetate (eq 4) was complicated by competing (trifluoroacetoxy)mercuriation, which accounted for 44 mol % of the product mixture.[5] Furthermore, the corresponding pair of organomercury(II) bromides proved difficult to separate, so that brominolysis had to be carried out on the mixture. Although the desired γ-bromoalkyl *tert*-butyl peroxide **3c** could be isolated by chromatography, the overall yield was only 29%.

In an attempt to improve the conversion of **1c** into **3c**, we investigated the use of mercury(II) acetate and 20 mol % of aqueous perchloric acid in the peroxymercuriation step, since this had proved a convenient alternative to mercury(II) trifluoroacetate in the *tert*-butyl peroxy-

(4) Porter, N. A.; Mitchell, J. C. *Tetrahedron Lett.* **1983**, *24*, 543.
(5) Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1807.
(6) Bloodworth, A. J. In *The Chemistry of Mercury*; McAuliffe, C. A., Ed.; Macmillan: London, 1977; p 182, and references therein.

mercuriation of alkenes.[7] The result was successful in that the product mixture (eq 6) contained 65 mol % of peroxymercurial **2c**, which was readily separated from the other components by chromatography and was isolated in 51% yield.

This method was therefore adopted for the other cyclopropanes, and it provided the corresponding peroxymercurials **2** in isolated yields of 33–48%, except for cyclopropane (**1a**) where a yield of only 10% was obtained. The attractive features of the procedure are (i) that a commercially available and easily handled mercury(II) salt is used, (ii) that, except with **1a**, the desired peroxymercurial **2** is the major product, and (iii) that the peroxymercurial is easily isolated by chromatography and is eluted first from the column.

The other products in the peroxymercuriation of phenylcyclopropane (eq 6) were identified as the corresponding acetoxymercurial[8] **5c** (21 mol %) and hydroxymercurial[9] **6c** (14 mol %) by comparison (^{1}H and ^{13}C NMR and TLC) with authentic samples. With alkenes, much higher proportions (93–100 mol %) of peroxymercurials were obtained under these conditions, and it was shown that these arise by equilibrium control, whereby first-formed acetoxymercurials undergo β-oxy exchange catalyzed by perchloric acid (eq 7).[7] We showed that, in contrast, the

$$\mathrm{BuCH(OAc)CH_2HgOAc} + t\text{-BuOOH} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{BuCH(OOBu\text{-}}t\mathrm{)CH_2HgOAc} + \mathrm{AcOH} \quad (7)$$

acetoxymercurial $\mathrm{PhCH(OAc)CH_2CH_2HgOAc}$ does not react with *tert*-butyl hydroperoxide in the presence of perchloric acid. Thus, the product distribution in the peroxymercuriation of phenylcyclopropane (eq 6) is under kinetic control. We presume that a mercury-containing cationic intermediate is formed, which in all probability is essentially the benzylic carbocation,[5] $\mathrm{PhCH^+CH_2CH_2HgOAc}$, and this is trapped by the available nucleophiles, i.e., *t*-BuOOH, AcOH, and/or $\mathrm{AcO^-}$, and $\mathrm{H_2O}$, to provide the organomercury acetate precursors of the respective products, **2c**, **5c**, and **6c**. That a higher proportion of peroxymercurial is obtained under these conditions than when mercury(II) trifluoroacetate is used[5] at first appears anomalous considering the strengths of the competing nucleophiles, but is accounted for by the much lower solubility of mercury(II) acetate in dichloromethane.

Additional products in the peroxymercuriation of the other cyclopropanes were detected by TLC and by ^{1}H, ^{13}C, and ^{199}Hg NMR spectroscopy on the crude organomercury(II) bromides, but except for those from cyclopropane (**1a**), no attempt was made to identify them. Cyclopropane afforded a mixture containing 22 mol % of peroxymercurial, 47 mol % of acetoxymercurial, and 31 mol % of bis(3-(bromomercurio)propyl) ether, and the formation of these products has been fully discussed elsewhere.[1] However, it is worth mentioning that the formation of the bis(mercuriated) ether was virtually eliminated by using anhydrous perchloric acid as the catalyst. This was prepared by adding just enough acetic anhydride to combine with all the water in the aqueous reagent, and when used it afforded a 2:3 mixture of peroxymercurial and acetoxymercurial. This is a marked improvement because chromatographic separation of the peroxymercurial (**2a**) from the bis(3-(bromomercurio)propyl) ether is difficult.[1] Furthermore, the use of anhydrous perchloric acid resulted in the reaction time being reduced from 120 to 24 h.

Step 2. Bromodemercuriation. We have previously found that the brominolysis of alkene- and phenylcyclopropane-derived peroxymercurials does not proceed cleanly in dichloromethane, but that satisfactory results are obtained in methanol saturated with sodium bromide.[5,7] Consequently, the latter conditions were adopted in this work. ^{1}H and ^{13}C NMR spectra of the crude γ-bromoalkyl *tert*-butyl peroxides **3**, which were obtained in yields of 84–100%, indicated the presence of little or no side products. Hence, in general, these materials were used in the final step without further purification.

Step 3. Silver Salt Induced Cyclization. Essentially quantitative yields of 1,2-dioxolanes **4b–e** were obtained upon treating the γ-bromoalkyl *tert*-butyl peroxides **3b–e** with silver trifluoroacetate in dichloromethane at 0 °C for periods of up to 1 h. However, the conversion of bromoperoxide **3a** into the unsubstituted 1,2-dioxolane **4a** was sluggish under these conditions, and a more efficient ring closure was obtained by using the corresponding iodoperoxide (eq 8). In this reaction the *tert*-butyl-derived product was also isolated, and it was identified as the trifluoroacetate ester (eq 8). The dioxolanes, which were purified by distillation (**4d**), by GLC (**4a,b**), or by low-temperature column chromatography (**4c,e**), were all previously known, with the exception of 3-ethyl-1,2-dioxolane (**4b**).

In contrast to the above results, no cyclic peroxide was obtained when 3-bromo-1,1-diphenylpropyl *tert*-butyl peroxide (**3f**) was treated in the same way. Instead, a nonperoxidic product was obtained, which is assigned structure **7** on the grounds that the oil resulting from treatment with aqueous sodium bicarbonate showed a strong $\nu_{C=O}$ at 1680 cm^{-1} ($\mathrm{PhCOCH_2CH_2OBu}$-*t*) and a strong ν_{O-H} at 3380 cm^{-1} (PhOH), and that this oil reacted with acidic 2,4-dinitrophenylhydrazine to afford the (2,4-dinitrophenyl)hydrazone (**8**) of 2-*tert*-butoxyethyl phenyl ketone (eq 9 and 10).

It has been suggested[4] that the silver salt induced cyclizations of γ-bromoalkyl *tert*-butyl peroxides proceed via cyclic trialkylperoxonium intermediates. It seems to us that the formation of compound **7** from bromoperoxide **3f** supports this idea, since the corresponding peroxonium ion **9f** can be envisaged to undergo rearrangement by 1,2-phenyl migration and accompanying O–O cleavage (eq 11), in a process similar to the well known acid-catalyzed decomposition of cumyl hydroperoxide.

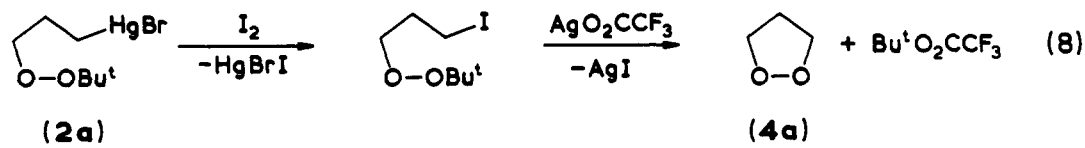
Analogous rearrangements in the phenyl-containing peroxonium ions derived from **3c** and **3e** will be less favorable because the product cations lack benzylic stabilization, and it appears that they do not compete with the dealkylation that leads to dioxolane formation.

It is worthwhile noting that the hydroperoxide analogous to **3f** *did* afford 3,3-diphenyl-1,2-dioxolane in high yield when treated with silver oxide.[3] This suggests either that deprotonation of the dialkylperoxonium ion analogous to **9f** occurs more rapidly than the corresponding rearrangement or that under the more basic conditions used the reaction proceeds through the peroxide anion rather than the hydroperoxide itself.

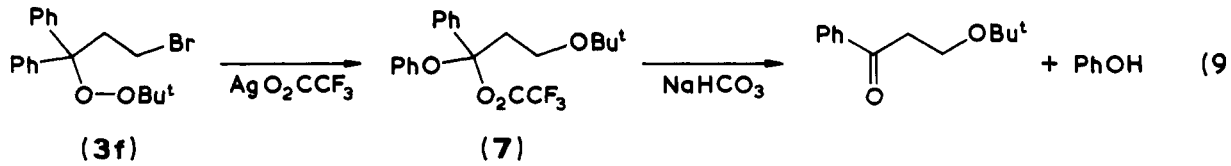
Experimental Section

Unless otherwise indicated, NMR spectra were recorded with a Varian XL200 spectrometer for solutions in $\mathrm{CDCl_3}$, and chemical shifts are relative to internal tetramethylsilane (^{1}H and ^{13}C) or

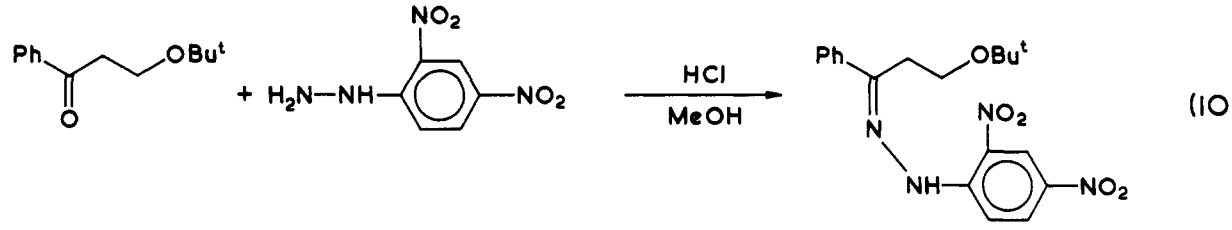
(7) Bloodworth, A. J.; Courtneidge, J. L. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3258.
(8) Ouellette, R. J.; Robins, R. D.; South, A. *J. Am. Chem. Soc.* **1968**, *90*, 1619.
(9) Levina, R. Y.; Kostin, V. N.; Tartakovskii, V. A. *Zh. Obshch. Khim.* **1957**, *27*, 881; *Chem. Abstr.* **1958**, *52*, 3713i.



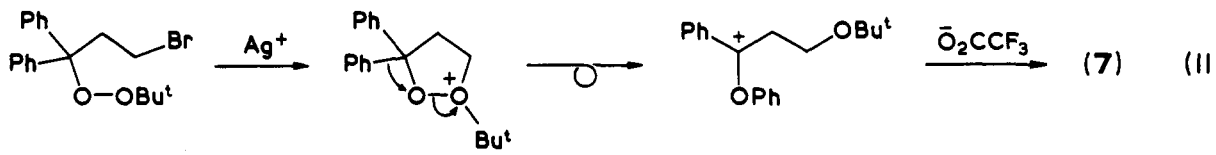
(2a) (4a)



(3f) (7)



(8)



(3f) (9f)

external dimethylmercury (^{199}Hg); 60-MHz ^{1}H NMR spectra were obtained with Jeol PMX 60 or Varian T60 instruments, and 20-MHz ^{13}C NMR spectra with a Varian CFT 20 spectrometer.

Infrared spectra were measured with a Perkin-Elmer 983 instrument. Mass spectra were obtained by using a VG 7070 F/H mass spectrometer plus Finnigan INCOS data system.

tert-Butyl hydroperoxide was purified as described previously.[1] Unless stated to the contrary, other reagents were commercial samples which were used as received.

Cyclopropanes (1). Ethylcyclopropane (**1b**) was prepared by Wolff–Kishner reduction of acetylcyclopropane as described previously:[10] bp 35–35.5 °C (lit.[10] bp 35.9 °C); δ_H −0.03 ca. q (2 H), 0.35 ca. q (2 H), 0.59 m (1 H), 0.95 t (3 H), and 1.20 quintet (2 H), δ_C (C_6D_6) 3.99 t (2 C), 12.74 d, 13.33 q, and 28.04 t.

1,1-Dimethylcyclopropane (**1d**) was prepared by treating 1,3-dibromo-2,2-dimethylpropane with zinc in ethanol as described previously.[11] It was isolated by condensation into a trap cooled with dry ice and was not purified further, δ_H (60 MHz) 0.29 s (4 H) and 1.11 s (6 H). The dibromide was prepared from the corresponding diol and PBr_3: bp 74–75 °C (12 mmHg), δ_H (60 MHz) 1.12 s (6 H) and 3.38 s (4 H), δ_C (C_6D_6) 24.34 q (2 C), 35.43 s, and 42.90 t (2 C).

1-Methyl-1-phenylcyclopropane (**1e**) was prepared by reducing 2,2-dichloro-1-methyl-1-phenylcyclopropane as follows. The dichloride (27.6 g; 0.14 mol) was added to ethanol (250 cm^3) in a 1-dm^3 round-bottomed flask with magnetic stirring under nitrogen on an oil bath at 90–100 °C. Sodium (38 g; 1.65 mol) was added in small portions over 6 h and at the end of the addition the bath temperature was raised to 110 °C for a further 30 min. After cooling, methanol (500 cm^3) and then water (500 cm^3) were added **with CAUTION** to destroy any unreacted sodium, and the mixture was extracted with light petroleum (bp 60–80 °C, 4 × 100 cm^3). The extract was washed with water (100 cm^3), 10% aqueous acetic acid (200 cm^3), and saturated sodium chloride (100 cm^3), then dried ($MgSO_4$), and rotoevaporated to give a pale orange oil (19.8 g). Distillation afforded (**1e**) as a colorless liquid (15.4 g; 85%): bp 68 °C (16 mm); δ_H 0.72 m (2 H), 0.85 m (2 H), 1.40 s (3 H), and 7.25 m (5 H); δ_C 15.57 t (2 C), 19.82 s, 25.84 q, 125.56 d, 126.85 d (2 C), 128.26 d (2 C), and 146.82 s [lit.[3] bp 60 °C (13 mm), δ_H (CCl_4) 0.69 and 0.80 AB, 1.39 s, and 7.18 br s]. The 2,2-dichloro-1-methyl-1-phenylcyclopropane, bp 43–4 °C (0.05 mm), was prepared in 94% yield by the method previously described,[3] except that benzyltributylammonium bromide was used as the phase-transfer catalyst and the product was extracted with light petroleum (bp 60–80 °C): δ_C (C_6D_6) 25.27 q, 31.47 s, 36.05 t, 65.87 s, 127.01 d, 128.25 d (4 C), and 140.81 s.

1,1-Diphenylcyclopropane (**1f**) was prepared by reducing 2,2-dibromo-1,1-diphenylcyclopropane as follows (cf. ref 12). A solution of mercury(II) chloride (32 g) in water (400 cm^3) and 10 M hydrochloric acid (20 cm^3) was added to zinc powder (400 g), and the mixture was shaken for 2 min. The liquid was decanted and the residual Zn/Hg amalgam was washed with water (2 × 200 cm^3). Under N_2, a solution of $CrCl_3 \cdot 6H_2O$ (170 g, 0.64 mol) in water (700 cm^3) was added in portions to the Zn/Hg amalgam with shaking until the color changed to bright blue. The dibromide (20 g, 0.057 mol) was dissolved in DMF and the solution was purged with N_2 for 30 min. The Cr(II) solution was then added, upon which the temperature of the solution rose to 40 °C. After 1 h, the dibromide was nearly all consumed (^{1}H NMR), and after 5 h, the solution was extracted with chloroform (4 × 100 cm^3). The chloroform was rotoevaporated to leave a pale brown oil which was dissolved in ethyl acetate (500 cm^3). The solution was washed with water (2 × 500 cm^3), dried ($MgSO_4$), and rotoevaporated to give a pale brown oil (14 g). Distillation afforded a pale yellow oil (5.4 g; 49%): bp 95–105 °C (0.05 mmHg); δ_H (60 MHz) 1.24 s (4 H) and 7.0–7.8 m (10 H) [lit.[3] bp 108–109 °C (1.3 mmHg); δ_H (CCl_4) 1.24 s and 7.08 br s]. The 2,2-dibromo-1,1-diphenylcyclopropane was prepared by adding dropwise a satu-

(10) Volkenburg, R. W.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1949**, *71*, 172.

(11) Shortridge, R. W.; Craig, R. A.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1948**, *70*, 946.

(12) Cutler, F. A.; Mandrell, L.; Fisher, J. F.; Shew, D.; Chemerda, J. M. *J. Org. Chem.* **1959**, *24*, 1621.

rated solution of NaOH (28 g, 0.70 mol) in water to a stirred mixture of 1,1-diphenylethene (16 g, 0.088 mol), $CHBr_3$ (55 g, 0.22 mol), and benzyltributylammonium chloride (2.0 g). The mixture was stirred for 6 h and then dichloromethane (500 cm^3) was added. The solution was washed with water (2 × 250 cm^3), dried ($MgSO_4$), filtered through silica, and rotoevaporated. The residue was washed with light petroleum (bp 40–60 °C, 3 × 40 cm^3) and dried under vacuum to afford a brown solid (27.3 g, 88%): δ_H (60 MHz) 2.40 s (2 H) and 7.3 m (10 H).

γ-(Bromomercurio)alkyl *tert*-Butyl Peroxides (2). The method previously used to prepare 3-(bromomercurio)propyl *tert*-butyl peroxide (**2a**)[1] was modified as follows.

Acetic anhydride was added dropwise to a magnetically stirred and cooled mixture of 60% aqueous perchloric acid (2.0 g) and dichloromethane (20 cm^3), keeping the temperature between 14 and 15 °C, until a single phase was obtained (ca. 4 g were required).

Commercial 70% *tert*-butyl hydroperoxide (10 g; 78 mmol) was added to dichloromethane (40 cm^3) and the resultant two-phase mixture was dried by stirring with $MgSO_4$ (10 g) for 15 min. The drying agent was removed by filtration, the residue was washed with a little dichloromethane, and the washings were added to the filtrate.

Cyclopropane (2.6 cm^3; 44 mmol) was added to a magnetically stirred mixture of mercury(II) acetate (12.8 g; 40 mmol) and dichloromethane (80 cm^3) cooled at −40 °C. The solution of *tert*-butyl hydroperoxide (above) was added followed by that of perchloric acid (above), keeping the temperature below −20 °C throughout. The mixture was allowed to warm to room temperature and left stirring overnight. Ice-cold water (50 cm^3) was then added and the phases were separated. The dichloromethane layer was washed with water (2 × 50 cm^3) and dried ($MgSO_4$), and the solvent was removed at 12 and then 0.01 mmHg to afford a yellow oil (12.1 g), which showed triplets in the ^1H NMR spectrum at δ 4.59 (unknown), 4.07 (acetoxymercurial), and 3.95 (peroxymercurial) in the ratio 8:56:36. After conversion to the organomercury(II) bromides in the usual way (see later), flash chromatography on silica (Merck Kieselgel 80, 230–400 mesh) eluting with a 1:1 mixture of dichloromethane and light petroleum (bp 60–80 °C) afforded (**2a**) (3.33 g; 21%).

The following general method was adopted for the preparation of compounds **2b–f**. The cyclopropane (20 mmol) was added dropwise to a magnetically stirred mixture of mercury(II) acetate (6.4 g; 20 mmol), dichloromethane (40 cm^3), *tert*-butyl hydroperoxide (3.8 cm^3; 38 mmol), and 60% aqueous perchloric acid (4 mmol; ca 0.6 cm^3, added as 40 drops from a commercial Pasteur pipette) cooled in a bath of ice water. When the solution gave a negative test (NaOH) for mercury(II) ions (30–90 min), water (100 cm^3) was added, the dichloromethane layer was separated, and the aqueous phase was extracted with dichloromethane (40 cm^3). The combined organic phases were washed with water (2 × 100 cm^3), dried ($MgSO_4$), and rotoevaporated to give the crude organomercury(II) acetate. Dichloromethane (20 cm^3) and a solution of potassium bromide (22 mmol) in water (10 cm^3) were added, and the mixture was stirred vigorously for 1 h. The aqueous layer was removed and the dichloromethane solution was evaporated and dried at 0.01 mm to afford the crude organomercury(II) bromide. The pure γ-bromomercurioalkyl *tert*-butyl peroxide was isolated by chromatography on silica (Merck Kieselgel 80, 70–230 mesh) eluting with light petroleum (bp 60–80 °C) containing increasing amounts of dichloromethane. The eluant was monitored for peroxymercurial by TLC on silica (Kieselgel 60 F_{254}), visualizing it by spraying with a solution of dithizone (2%) in chloroform.

(i) 1-(Bromomercurio)pent-3-yl *tert*-butyl peroxide (2b) was obtained in 48% yield as a colorless oil: δ_H 0.96 t (7.2 Hz) (C^5H_3), 1.28 s (CMe_3), 1.43 m and 1.63 m (C^4H_2), 1.74 m and 1.91 m (C^1H_2), 1.91 m and 2.26 m (C^2H_2) and 3.95 m (C^3H); δ_C 10.47 q (C-5), 24.32 t (C-4), 26.66 q (3 C; CMe_3) 27.48 t [$^2J(^{199}Hg-^{13}C)$ = 1548 Hz; C-1], 29.81 t [$^2J(^{199}Hg-^{13}C)$ = 95 Hz; C-2], 80.41 s (CMe_3), and 84.91 d [$^3J(^{199}Hg-^{13}C)$ = 110 Hz; C-3]; δ_{Hg} −1004 dq [$J(^{199}Hg-^1H)$ = 416 and 208 Hz, giving a 1:3:4:4:3:1 "sextet" with 208-Hz spacing]. The ^1H NMR chemical shifts were derived from projected 2D-*J*-resolved data, and the assignments were assisted by $^{13}C-^1H$-correlated 2D spectroscopy.

(ii) 3-(Bromomercurio)-1-phenylpropyl *tert*-butyl peroxide (2c)[5] was obtained in 51% yield. Anal. Found: C, 32.06; H, 3.84. Calcd for $C_{13}H_{19}BrHgO_2$: C, 32.01; H, 3.93.

(iii) 4-(Bromomercurio)-2-methylbut-2-yl *tert*-butyl peroxide (2d) was obtained in 42% yield as a colorless oil which slowly crystallized on standing: mp 30–34 °C; δ_H 1.18 s (6 H), 1.27 s (9 H), 1.80 m [$J(^{199}Hg-^1H)$ = 195 Hz; 2 H], and 2.00 m [$J(^{199}Hg-^1H)$ = 324 Hz; 2 H]; δ_C 24.56 q (2 C), 26.76 q (3 C), 27.40 t [$^1J(^{199}Hg-^{13}C)$ = 1554 Hz], 36.10 t [$^2J(^{199}Hg-^{13}C)$ = 91 Hz], 79.46 s, and 79.58 s [$^3J(^{199}Hg-^{13}C)$ = 72 Hz]; δ_{Hg} −1010 tt [$J(^{199}Hg-^1H)$ = 197 and 320 Hz]. Anal. Found: C, 24.87; H, 4.26. $C_9H_{19}BrHgO_2$ requires C, 25.51; H, 4.52.

(iv) 4-(Bromomercurio)-2-phenylbut-2-yl *tert*-butyl peroxide (2e) was obtained in 35% yield: δ_H 1.32 (9 H), 1.44 m (1 H), 1.59 s (3 H), 1.78 m (1 H), 2.24 m (1 H), 2.51 m (1 H), and 7.32 m (5 H); δ_C (20 MHz) 26.26, 26.86 [$^1J(^{199}Hg-^{13}C)$ = 1519 Hz], 26.86 (3 C), 37.31 [$^2J(^{199}Hg-^{13}C)$ = 101 Hz], 79.83, 83.35 [$^2J(^{199}Hg-^{13}C)$ = 86 Hz], 125.25 (2 C), 127.16, 128.53 (2 C), and 143.32. Anal. Found: C, 33.36; H, 3.97. $C_{14}H_{21}BrHgO_2$ requires C, 33.51; H, 4.22.

(v) 3-(Bromomercurio)-1,1-diphenylpropyl *tert*-butyl peroxide (2f) was obtained in 33% yield as a white crystalline solid which was recrystallized from a mixture of light petroleum (bp 60–80 °C) and dichloromethane, mp 123–5 °C; ^1H NMR δ_H (CD_2Cl_2) 1.11 s (9 H), 1.74 t [6.98 Hz; $J(^{199}Hg-^1H)$ = 196 Hz; 2 H], 3.00 dd [6.86 and 7.23 Hz; $J(^{199}Hg-^1H)$ = 316 Hz; 2 H], and 7.28 m (10 H); δ_C (CD_2Cl_2) 26.71 q (3 C), 26.93 t [$^1J(^{199}Hg-^{13}C)$ = 1514 Hz], 33.89 t [$^2J(^{199}Hg-^{13}C)$ = 96 Hz], 80.30 s, 86.57 s [$^3J(^{199}Hg-^{13}C)$ = 88 Hz], 127.30 d (2 C), 127.51 d, 128.29 d (2 C), and 144.12 s; δ_{Hg} (CD_2Cl_2) −977 tt [$J(^{199}Hg-^1H)$ = 198 and 314 Hz]. Anal. Found: C, 40.34; H, 4.22; $C_{19}H_{23}BrHgO_2$ requires C, 40.47; H, 4.11.

γ-Bromoalkyl *tert*-Butyl Peroxides (3). The following general method was adopted. To a magnetically stirred solution of the organomercury(II) bromide **2** (10 mmol) in methanol (50 cm^3) cooled in a bath of iced water was added dropwise a solution of bromine (2 cm^3; ca. 40 mmol) and sodium bromide (10 g; ca. 100 mmol) in methanol (80 cm^3) at such a rate that the temperature did not exceed 10 °C. Stirring was continued and the mixture was allowed to come to room temperature over a period of 2 h. Water (100 cm^3) was added and the solution was extracted with light petroleum (bp 40–60 °C; 4 × 50 cm^3). The combined extracts were washed with water (150 cm^3), saturated sodium thiosulfate (100 cm^3), and again with water, dried ($MgSO_4$), and rotoevaporated to give the crude γ-bromoalkyl *tert*-butyl peroxide as an oil (84–100%).

(i) 3-Bromopropyl *tert*-butyl peroxide (3a): δ_H (60 MHz) 1.23 s (9 H), 2.12 quintet (J = 6 Hz; 2 H), 3.45 t (2 H), and 4.04 t (2 H).

(ii) 1-Bromopent-3-yl *tert*-butyl peroxide (3b): δ_H 0.95 t (3 H), 1.24 s (9 H), 1.52 m (1 H), 1.69 m (1 H), 2.02 m (1 H), 2.17 m (1 H), 3.53 m (2 H), and 3.98 m (1 H). The chemical shifts were obtained from homonuclear 2D *J*-resolved spectra; homonuclear correlated 2D NMR showed that the C^3HOOBu-*t* (3.98) is coupled to the CH_2 protons at 2.17 and 1.69, the C^1H_2Br (3.53) is coupled to the C^2H_2 proton at 2.17, and the C^5H_3 is coupled to the C^4H_2 proton at 1.69, δ_C: 9.80 q, 25.56 t, 26.59 q (3 C), 29.81 t, 36.54 t, 79.31 s, and 82.38 d. MS: m/z 240, 238 (M^+), 151, 149 ($M^+ - C_4H_9O_2$), 109, 107 ($M^+ - C_4H_9O_2 - C_3H_6$); accurate mass found 238.0567, $C_9H_{19}{}^{79}BrO_2$ requires 238.0568.

(iii) 3-Bromo-1-phenylpropyl *tert*-butyl peroxide (3c) had identical spectra with those previously reported.[5]

(iv) 4-Bromo-2-methylbut-2-yl *tert*-butyl peroxide (3d): δ_H 1.20 s (15 H), 2.16 m (2 H), and 3.45 m (2 H); δ_C 24.64 q (2 C), 26.52 q (3 C), 27.77 t, 43.12 t, 78.25 s, and 79.72 s (lit.[13] δ_H 1.22 s, 2.16 t, and 3.50 t; δ_C 24.7, 26.6, 28.7, 43.1, 78.6, and 80.0).

(v) 4-Bromo-2-phenylbut-2-yl *tert*-butyl peroxide (3e): δ_H 1.28 s (9 H), 1.61 s (3 H), 2.50 m (2 H), 3.17 m (1 H), 3.40 m (1 H), and 7.38 m (5 H); δ_C (20 MHz), 25.82, 26.76 (3 C), 28.65, 44.05, 79.25, 83.59, 125.77 (2 C), 127.53, 128.59 (2 C), and 144.31.

(vi) 3-Bromo-1,1-diphenylpropyl *tert*-butyl peroxide (3f): δ_H 1.16 s (9 H), 3.03 and 3.31 (4 H, A_2B_2 multiplet), and 7.20 m (10 H); δ_C 26.92 q (3 C), 28.75 t, 40.66 t, 79.69 s, 86.64 s, 126.82 d (2 C), 127.31 d, 128.03 d (2 C), and 143.54 s; MS, m/z 275, 273 ($M^+ - C_4H_9O_2$).

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1,2-Dioxolanes (4). The following general method was adopted. Silver trifluoroacetate (2.4 g; 11 mmol) was added in portions to a magnetically stirred solution of the γ-bromoalkyl *tert*-butyl peroxide (**3**) (10 mmol) in dichloromethane (25 cm^3) cooled at −5 to 0 °C and shielded from light. After 30–60 min, the mixture was filtered through celite to remove the pale yellow precipitate of silver bromide. The residue was washed with dichloromethane (25 cm^3), and the washings were combined with the filtrate. The dichloromethane solution was stirred vigorously with saturated sodium hydrogen carbonate (50 cm^3) at 0 °C for 10 min, and after separating the phases the aqueous layer was extracted with more dichloromethane (20 cm^3). The combined organic phases were dried ($MgSO_4$) and rotoevaporated (at 0 °C for **4a**,**4b**, and **4d**) to afford the crude 1,2-dioxolane (**4**) as an oil in yields of 80–100% (except for **4a**).

(i) 3-Ethyl-1,2-dioxolane (4b) was purified by GLC (10 ft × $^3/_8$ in. o.d. of 20 w/w % silicone oil MS 200/200 on Chromosorb W 60–80 mesh; N_2 carrier 200 cm^3 min^{-1}; oven temperature 60 °C; injector temperature 75 °C); δ_H 0.97 t (3 H), 1.53 m (1 H), 1.68 m (1 H), 2.21 m (1 H), 2.69 m (1 H), 4.07 t (2 H), and 4.13 quintet (1 H); δ_C 10.43 q, 26.63 t, 40.28 t, 69.53 t, and 81.44 d; MS, m/z 102 (M^+), 73 ($M^+ - C_2H_5$). Anal. Found: C, 58.29, H, 9.76; M^+ 102.0681. $C_5H_{10}O_2$ requires C, 58.80, H, 9.86; M^+ 102.0681.

(ii) 3-Phenyl-1,2-dioxolane (4c)[3] was purified by low-temperature column chromatography (Merck Kieselgel 80, 70–230 mesh; −20 °C; CH_2Cl_2) and isolated in 25% yield: δ_H (60 MHz) 2.3–3.3 m (2 H), 4.26 t (7 Hz) (2 H), 5.22 dd (6, 7.2 Hz) (1 H), and 7.4 s (5 H); δ_C (20 MHz) 43.62, 70.09, 81.51, 126.46 (2 C), 128.17, 128.64 (2 C), and 139.29 [lit. δ_H[3] (CCl_4) 2.2–3.2 m (2 H), 4.15 t (7 Hz) (2 H), 5.04 and 5.16 AB (6 Hz) (1 H), and 7.2 s (5 H); δ_C[13] 43.6, 70.0, 81.5, 126.5, 128.1, 128.6, and 139.4].

(iii) 3,3-Dimethyl-1,2-dioxolane (4d)[14] was purified by distillation, bp 52–54 °C (16 mm): δ_H 1.34 s (6 H), 2.36 t (7.15 Hz) (2 H), and 4.12 t (2 H); δ_C 25.49 q (2 C), 46.63 t, 69.80 t, and 81.74 s [lit.[14] δ_H 1.3 s (6 H), 2.3 t (2 H), and 4.0 t (2 H); δ_C 25.83, 47.02, 70.09, and 82.11].

(iv) 3-Methyl-3-phenyl-1,2-dioxolane (4e)[3] was purified by low-temperature column chromatography (cf. **4c**) and isolated in 36% yield; δ_H (60 MHz) 1.65 s (3 H), 2.4–3.2 m (2 H), 4.0–4.5 m (2 H), and 7.2–7.65 m (5 H); δ_C (20 MHz) 26.61, 48.37, 70.08, 85.50, 124.89 (2 C), 127.09, 128.32 (2 C), and 145.05 [lit.[3] δ_H (CCl_4) 1.54 s (3 H), 2.4–2.9 m (2 H), 3.8–4.2 m (2 H), and 7.0–7.4 m (5 H)].

(v) 1,2-Dioxolane (4a).[15] The conversion of 3-bromopropyl *tert*-butyl peroxide (**3a**) into 1,2-dioxolane (**4a**) was incomplete even after a reaction time of 3 h. Hence the synthesis was carried out with 3-iodopropyl *tert*-butyl peroxide as follows. Silver trifluoroacetate (0.425 g; 1.93 mmol) was added to a magnetically stirred solution of 3-iodopropyl *tert*-butyl peroxide (0.423 g; 1.64 mmol) in dichloromethane (1.5 cm^3) cooled at 0 °C. After 5 min, the yellow precipitate was filtered off and the ^1H NMR spectrum of the filtrate was recorded. This indicated that a quantitative conversion to 1,2-dioxolane (**4a**) and *tert*-butyl trifluoroacetate had taken place. It proved difficult to isolate **4a** from this mixture and hence the reaction was repeated on a larger scale (5.23 mmol of iodoperoxide and 6.14 mmol of silver trifluoroacetate) in 1,2-dichlorobenzene (6 cm^3). However, distillation of the filtrate at reduced pressure afforded only mixtures of *tert*-butyl trifluoroacetate plus **4a** (5:1) and **4a** plus solvent (1:15), corresponding to a yield of 81%. GLC (conditions as for ethyldioxolane **4b**, except oven temperature (30 °C) and injector temperature (50 °C) of these mixtures gave pure (**4a**); δ_H 2.61 quintet (J = 7 Hz; 2 H) and 4.04 t (4 H); δ_C 34.84 t and 68.26 t (2 C) [lit.[15] δ_H (CCl_4) 2.53 quintet (J = 7 Hz; 2 H) and 3.92 t (4 H)]. The spectral data for *tert*-butyl trifluoroacetate were δ_H 1.57 s; δ_C 26.79 q (3 C), 86.50 s, 114.27 q [$^1J(^{13}C-^{19}F)$ = 286 Hz], and 154.14 q [$^2J(^{13}C-^{19}F)$ = 44 Hz], $\gamma_{C=O}$ 1777 cm^{-1}.

The 3-iodopropyl *tert*-butyl peroxide was prepared as follows. Iodine was added by means of a Soxhlet extractor to a refluxing solution of 3-(bromomercurio)propyl *tert*-butyl peroxide (**2a**) (3.33 g; 8.08 mmol) in dichloromethane (100 cm^3) until the purple color was no longer discharged. The mixture was then refluxed for a further 1 h and allowed to stand overnight. The solution was washed with 10% sodium thiosulfate (100 cm^3) and water (100 cm^3), then dried ($CaCl_2$), and rotoevaporated to give 3-iodopropyl *tert*-butyl peroxide (1.54 g; 74%) as an oil: δ_H 1.24 s (9 H), 2.14 tt (C^2H_2), 3.26 t (J = 6.95 Hz; C^3H_2), and 4.00 t (J = 5.86 Hz; C^1H_2); δ_C 2.61 t (C^3), 26.01 q (3 C), 31.67 t (C^2), 73.74 t (C^1), and 79.80 s. These assignments were confirmed by a heteronuclear correlated 2D NMR experiment. Anal. Found: C, 31.52; H, 5.66; I, 48.15; M^+ 258.0098; $C_7H_{15}IO_2$ requires C, 32.57; H, 5.85; I, 49.16; M^+ 258.0118.

Reaction of 3-Bromo-1,1-diphenylpropyl *tert*-Butyl Peroxide (3f) with Silver Trifluoroacetate. ^1H and ^{13}C NMR spectra showed that the pale yellow oil obtained by the usual procedure (above) was not 3,3-diphenyl-1,2-dioxolane,[3] and indicated the presence of a *tert*-butyl group. The infrared spectrum showed strong absorptions at 1680 and 3380 cm^{-1}. Addition of this oil to a solution of (2,4-dinitrophenyl)hydrazine in methanol containing HCl immediately gave a yellow precipitate. This was filtered off, recrystallized (chloroform and light petroleum), and dried at 0.01 mm to give yellow crystals of the hydrazone 8: mp 179–81 °C; δ_H 1.10 s (9 H), 3.14 t (5.6 Hz) (2 H), 3.75 t (2 H), 7.43–7.47 m (3 H), 7.84–7.89 m (2 H), 8.07 d (9.7 Hz) (1 H), 8.31 dd (9.7, 2.55 Hz) (1 H), 9.15 d (2.55 Hz) (1 H), and 11.90 s (1 H). Anal. Found: C, 57.82; H, 5.67; N, 14.25; $C_{19}H_{22}N_4O_5$ requires C, 59.06; H, 5.74; N, 14.50.

The mother liquor from the (2,4-dinitrophenyl)hydrazine reaction was diluted with dichloromethane (50 cm^3) and extracted with sodium hydroxide (4%; 25 cm^3). The aqueous extract was acidified (concentrated HCl) and extracted with dichloromethane (2 × 25 cm^3). The organic extract was dried ($MgSO_4$) and rotoevaporated to give an oil which was identified (^1H NMR; TLC) as phenol.

Preparation of Authentic Oxymercurials 5c and 6c from Phenylcyclopropane. (a) Acetoxymercuriation. 3-(Acetoxymercurio)-1-phenylpropyl acetate was prepared by the reaction of phenylcyclopropane with mercury(II) acetate in glacial acetic acid at 50 °C as described previously,[8] and obtained as a pale yellow solid: mp 68–70 °C; δ_H (60 MHz) 1.6–2.3 m (4 H), 2.0 s (3 H), 2.1 s (3 H), 5.76 t (1 H), and 7.30 br s (5 H); δ_C (20 MHz) 18.84, 21.04, 22.12, 34.37, 77.25, 126.53 (2 C), 128.19, 128.81 (2 C), 139.62, 170.39, and 176.22 [lit.[8] δ_H 1.8 s (3 H), 1.9 s (3 H), 5.8 t (1 H)]. This compound was dissolved in dichloromethane and shaken with aqueous potassium bromide to afford the corresponding organomercury bromide (**5c**); δ_H (60 MHz) 1.6–2.5 m (4 H), 2.05 s (3 H), 5.69 t (1 H), and 7.30 br s (5 H).

(b) Hydroxymercuriation. Mercury(II) acetate (3.19 g; 10 mmol) was added to a stirred mixture of phenylcyclopropane (1.18 g; 10 mmol), tetrahydrofuran (20 cm^3), and water (20 cm^3) to produce a yellow precipitate. The mixture was stirred overnight, during which time a layer of yellow oil was formed. This was extracted with dichloromethane (20 cm^3), the extract was dried ($MgSO_4$), and the solvent was removed at 10 mmHg to afford 3-(acetoxymercurio)-1-phenylpropanol[9] as a viscous oil, δ_H (60 MHz) 1.5–2.2 m (4 H), 1.98 s (3 H), 4.62 t (1 H), 5.4 s (1 H), and 7.3 br s (5 H). This compound was dissolved in dichloromethane and shaken with aqueous potassium bromide to afford the corresponding organomercury bromide (**6c**): δ_H (60 MHz) 1.5–2.3 m (4 H), 3.3 s (1 H), 4.55 t (1 H), and 7.35 br s (5 H); δ_C (20 MHz) 29.67, 37.05, 74.86, 125.97 (2 C), 127.85, 128.73 (2 C), and 143.58.

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Registry No. **1a**, 75-19-4; **1b**, 1191-96-4; **1c**, 873-49-4; **1d**, 1630-94-0; **1e**, 2214-14-4; **1f**, 3282-18-6; **2a**, 101860-26-8; **2b**, 101860-27-9; **2c**, 101860-28-0; **2d**, 101860-29-1; **2e**, 101860-30-4; **2f**, 101860-31-5; **3a**, 101860-32-6; **3a** (iodo deriv.), 101860-37-1; **3b**, 101860-33-7; **3c**, 83568-15-4; **3d**, 86030-02-6; **3e**, 101860-34-8; **3f**, 101860-35-9; **4a**, 4362-13-4; **4b**, 101860-36-0; **4c**, 64884-63-5; **4d**, 67393-70-8; **4e**, 64884-61-3; **5c**, 101860-39-3; **5c** (mercuric acetate deriv.), 17997-54-5; **6c**, 101860-40-6; **6c** (mercuric acetate deriv.), 4471-44-7; **8**, 101860-38-2; $Ph_2C{=}CH_2$, 530-48-3; 2,2-dibromo-1,1-diphenylcyclopropane, 17343-74-7; 2,2-dichloro-1-methyl-1-phenylcyclopropane, 3591-42-2.

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