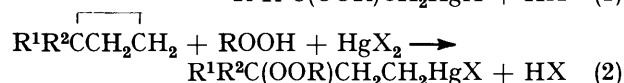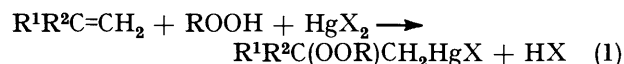# Oxymetallation. Part 17.[1] t-Butyl Peroxymercuriation and Subsequent Demercuriation of Phenylcyclopropane

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Phenylcyclopropane reacts with mercury(II) trifluoroacetate and two equivalents of t-butyl hydroperoxide in dichloromethane to give a mixture of $PhCH(OOBu^t)CH_2CH_2HgO_2CCF_3$ (47%) and $PhCH(O_2CCF_3)CH_2CH_2HgO_2$-$CCF_3$ (36%). Reduction with alkaline sodium borohydride converts this mixture into one of $PhCH(OOBu^t)Et$ and $PhCH(OH)Et$, from which the pure peroxide (19% overall) has been isolated by silica chromatography. Brominolysis of the corresponding mixture of organomercury bromides followed by silica chromatography has afforded $PhCH(OOBu^t)CH_2CH_2Br$ (29% overall).

THE peroxymercuriation of alkenes [equation (1)] has been widely studied and forms the basis of a versatile approach to the synthesis of several classes of organic peroxides.[2] By contrast, the analogous reaction with cyclopropanes [equation (2)] is virtually unexplored, the only reported examples being the conversions of phenyl- and 1,1-diphenyl-cyclopropane into the corresponding γ-hydroperoxyalkylmercury(II) acetates [equation (2); R = H, X = OAc].[3] We now report on the t-butyl peroxymercuriation of phenylcyclopropane and on the hydrogeno- and bromo-demercuriation of the resultant product.

$$R^1R^2C{=}CH_2 + ROOH + HgX_2 \longrightarrow$$
$$R^1R^2C(OOR)CH_2HgX + HX \quad (1)$$

$$\overline{R^1R^2CCH_2CH_2} + ROOH + HgX_2 \longrightarrow$$
$$R^1R^2C(OOR)CH_2CH_2HgX + HX \quad (2)$$
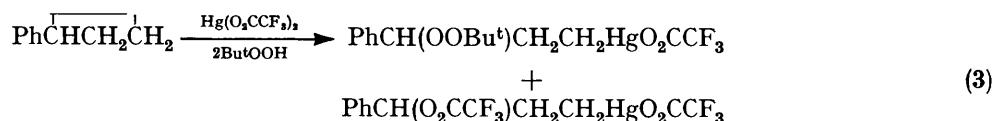
RESULTS AND DISCUSSION

Peroxymercuriation.—To provide a direct comparison with the t-butyl peroxymercuriation of alkenes,[4] phenylcyclopropane was treated with an equimolar amount of mercury(II) salt and two equivalents of t-butyl hydroperoxide in dichloromethane. When mercury(II) acetate was used, no reaction was detected after 24 h, indicating that phenylcyclopropane is much less reactive than the corresponding alkene, phenylethene, for which peroxymercuriation was complete within 30 min under these conditions.[4a] However, with the more electrophilic mercury(II) trifluoroacetate, a mildly exothermic reaction took place and all the mercury(II) salt was consumed within 10 min. Analysis of the crude product by ¹H and ¹³C n.m.r. spectroscopy indicated the presence of only two components, namely t-butyl 3-trifluoroacetoxymercurio-1-phenylpropyl peroxide (56 mol%) and 3-trifluoroacetoxymercurio-1-phenylpropyl trifluoroacetate, the mixture accounting for 83% of the starting phenylcyclopropane [equation (3)].
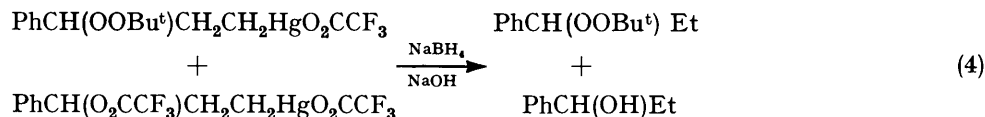
The regiospecificity of the ring-opening is in agreement with that found for other oxymercuriations of substituted cyclopropanes.[5] However, the formation of such a large proportion of trifluoroacetoxymercurial is in marked contrast with the corresponding phenylethene reaction where none was detected.[4b] The absence of trifluoroacetoxymercuriation in the latter case has been ascribed to the poor nucleophilicity of trifluoroacetic acid and its anion compared to that of t-butyl hydroperoxide. The lack of discrimination between the nucleophiles in the phenylcyclopropane reaction may, therefore, indicate that the intermediate mercury-containing cationic species is more reactive, and hence less selective, than its phenylethene-derived analogue which, in turn, may signify a higher degree of charge localisation at the benzylic position. Such a conclusion is consistent with that from an earlier study of the kinetics of acetoxymercuriation of a series of arylcyclopropanes, where substituent effects pointed to an intermediate with a substantial degree of benzyl carbocationic character.[6]

The crude mixture was treated with aqueous potassium bromide to afford the corresponding organomercury(II) bromides and several attempts were made to separate these by silica chromatography. This proved difficult, but a small sample of the analytically pure peroxide, $PhCH(OOBu^t)CH_2CH_2HgBr$, was isolated. In view of the difficulty encountered in separating the mercurials, the demercuriation reactions were carried out on the crude mixture obtained by peroxymercuriation.
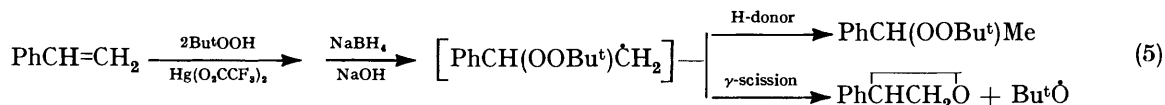
Reduction.—The organomercury(II) trifluoroacetates were reduced with alkaline sodium borohydride at 0 °C by the standard procedure [1] and afforded a mixture of t-butyl 1-phenylpropyl peroxide (45 mol%) and 1-phenylpropanol, which together accounted for 73% of the starting phenylcyclopropane [equation (4)]. The pure peroxide was isolated by silica chromatography in an overall yield of 19%.

The reduction of alkene-derived peroxymercurials proceeds *via* intermediate β-peroxyalkyl radicals which

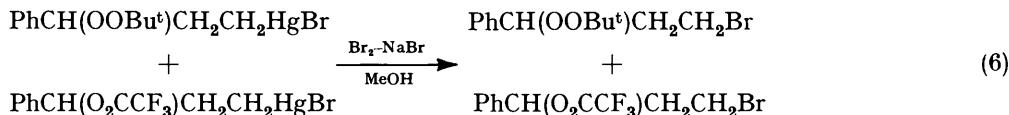$$PhCHCH_2CH_2 \xrightarrow[\text{2Bu}^t\text{OOH}]{\text{Hg(O}_2\text{CCF}_3)_2} PhCH(OOBu^t)CH_2CH_2HgO_2CCF_3$$
$$+$$
$$PhCH(O_2CCF_3)CH_2CH_2HgO_2CCF_3 \quad (3)$$

$$\begin{array}{c} \text{PhCH(OOBu}^\text{t})\text{CH}_2\text{CH}_2\text{HgO}_2\text{CCF}_3 \qquad \text{PhCH(OOBu}^\text{t})\text{ Et} \\ + \qquad \xrightarrow[\text{NaOH}]{\text{NaBH}_4} \qquad + \\ \text{PhCH(O}_2\text{CCF}_3)\text{CH}_2\text{CH}_2\text{HgO}_2\text{CCF}_3 \qquad \text{PhCH(OH)Et} \end{array} \qquad (4)$$

by competitive γ-scission give rise to oxirans as by-products. Thus peroxymercuriation and reduction of phenylethene under comparable conditions affords a mixture of t-butyl 1-phenylethyl peroxide (78 mol%) and phenyloxiran [equation (5)].[1]

Me should greatly suppress oxiran formation,[1] but there remains the problem that peroxymercuriation of the alkene is not regiospecific.[4b] The compound PhCH-(HgBr)CH(OOBu$^\text{t}$)Me, which is additionally obtained in 13% yield, will afford some 1-benzylethyl t-butyl

$$\text{PhCH=CH}_2 \xrightarrow[\text{Hg(O}_2\text{CCF}_3)_2]{\text{2Bu}^\text{t}\text{OOH}} \xrightarrow[\text{NaOH}]{\text{NaBH}_4} \left[\text{PhCH(OOBu}^\text{t})\dot{\text{C}}\text{H}_2\right] \begin{array}{l} \xrightarrow{\text{H-donor}} \text{PhCH(OOBu}^\text{t})\text{Me} \\ \\ \xrightarrow{\text{γ-scission}} \text{Ph}\overline{\dot{\text{C}}\text{HCH}_2\text{O}} + \text{Bu}^\text{t}\dot{\text{O}} \end{array} \qquad (5)$$

By analogy it is reasonable to assume that γ-t-butylperoxyalkyl radicals, PhCH(OOBu$^\text{t}$)CH$_2\dot{\text{C}}$H$_2$, are intermediates in the hydrogenodemercuriation of the phenylcyclopropane peroxymercurial. Since it has been postulated that δ-scission in similar γ-hydroperoxyalkyl radicals is responsible for the formation of oxetans in cool-flame oxidations of hydrocarbons,[7] it was important to establish whether phenyloxetan was formed in the

peroxide upon reduction, and thus render purification more difficult.

Brominolysis.—When treated with bromine in sodium bromide-saturated methanol the crude mixture of organomercury(II) bromides afforded a product consisting mainly of the expected γ-oxyalkyl bromides [equation (6)]. The pure peroxide was isolated by silica chromatography in an overall yield of 29%.

$$\begin{array}{c} \text{PhCH(OOBu}^\text{t})\text{CH}_2\text{CH}_2\text{HgBr} \qquad \text{PhCH(OOBu}^\text{t})\text{CH}_2\text{CH}_2\text{Br} \\ + \qquad \xrightarrow[\text{MeOH}]{\text{Br}_2\text{-NaBr}} \qquad + \\ \text{PhCH(O}_2\text{CCF}_3)\text{CH}_2\text{CH}_2\text{HgBr} \qquad \text{PhCH(O}_2\text{CCF}_3)\text{CH}_2\text{CH}_2\text{Br} \end{array} \qquad (6)$$

present reduction. Careful examination of the ^{1}H and [13]C n.m.r. spectra of both the crude product and the various fractions from chromatography failed to reveal the presence of any phenyloxetan.* The implication of this is that the rate constant for δ-scission in the radical PhCH(OOBu$^\text{t}$)CH$_2\dot{\text{C}}$H$_2$ is considerably smaller than that for γ-scission in the radical PhCH(OOBu$^\text{t}$)$\dot{\text{C}}$H$_2$, for which a value of about 4×10^4 s^{-1} at 25 °C can be expected by analogy with the species MeCH-(OOBu$^\text{t}$)$\dot{\text{C}}$H$_2$.[8]

As far as a peroxymercuriation-based synthesis of t-butyl 1-phenylpropyl peroxide is concerned, the cleanness of the reduction step [equation (4)] more than compensates for the substantial loss of phenylcyclopropane as the trifluoroacetoxymercurial [equation (3)]. Thus although the peroxymercuriation of *trans*-prop-1-enylbenzene affords 70% of the compound PhCH-(OOBu$^\text{t}$)CH(HgBr)Me,[4b] by analogy with the but-1-ene analogue [1] the subsequent reduction can be expected to give mainly oxirans and only *ca.* 11% of the desired peroxide. The conversion of hydrocarbon into peroxide *via* peroxymercuriation and reduction is therefore likely to be three times more efficient for phenylcyclopropane than for *trans*-prop-1-enylbenzene. Use of tributyltin hydride to reduce the adduct PhCH(OOBu$^\text{t}$)CH(HgBr)-

As with alkene-derived peroxymercurials,[4c] brominolysis in dichloromethane in the absence of sodium bromide was slower and less clean, lachrymatory by-products being obtained.

All three peroxides, PhCH(OOBu$^\text{t}$)CH$_2$CH$_2$X (where X = HgBr, H, or Br), isolated in this work are new compounds for which structures were assigned on the basis of their elemental analyses and ^{1}H and [13]C n.m.r. spectra.

EXPERIMENTAL

Peroxymercuriation.—Phenylcyclopropane (20 mmol) was added to a stirred solution of t-butyl hydroperoxide (40 mmol) and mercury(II) trifluoroacetate (20 mmol) in dichloromethane (40 cm³). The solution became warm and turned pale yellow, and after 2—3 min a small amount of grey precipitate was deposited. After 10 min, when a NaOH-test for mercury(II) ions was negative, the solution was washed with water (3 × 20 cm³) and then stirred vigorously with aqueous potassium bromide (22 mmol in 20 cm³) for 30 min. The dichloromethane layer was isolated, combined with dichloromethane extracts (2 × 20 cm³) of the aqueous layer, dried (MgSO$_4$), and made up to 100 cm³. Two thirds of this solution was used for bromin-

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* It must be noted that the proportion of 1-phenylpropanol in the product was higher than that of the trifluoroacetoxymercurial in the reactant. However, it is extremely unlikely that this arises from reduction of peroxymercurial-derived phenyloxetan, rince phenyloxiran was not reduced under similar conditions.[1] A more likely cause is the base-induced decomposition of the peroxymercurial with reduction of the resultant ketone.

olysis (later); removal of the solvent at *ca.* 10 mmHg from the remainder afforded a colourless oil (3.04 g), which was shown by ^{1}H n.m.r. spectroscopy to be a mixture of 3-bromomercurio-1-phenylpropyl t-butyl peroxide (data given below) and 3-bromomercurio-1-phenylpropyl trifluoroacetate (44 mol%); δ_H 7.20br (s, Ph), 5.88 (t J 6.4 Hz, C*H*O$_2$CCF$_3$), 2.48 (m, C*H*$_2$Hg), and 1.82 (m, C*H*$_2$CH$_2$Hg).

The identities and ratio of the γ-oxymercurials were confirmed by the ^{13}C n.m.r. spectrum of the crude mixture obtained from another reaction in which the anion exchange was omitted. For PhC^{1}H(OOBu^t)C^{2}H$_2$C^{3}H$_2$HgO$_2$CCF$_3$: δ_C 85.84 (C-1), 33.74 (C-2), 19.29 (C-3), 80.93 and 26.42 (Bu^t), 136.82, 129.60, 128.48, and 127.15 (Ph), 162.1 (q J 45 Hz, O$_2$CCF$_3$), and 117.0, (q J 202 Hz, CF$_3$). For PhC^{1}H(O$_2$-CCF$_3$)C^{2}H$_2$C^{3}H$_2$HgO$_2$CCF$_3$: δ_C 81.57 (C-1), 32.15 (C-2), 19.64 (C-3), 139.70, 129.00, 128.48, and 126.78 (Ph), 157.7 (q J 45 Hz, CO$_2$CCF$_3$), and 102.8 (q J 202 Hz, CO$_2$CCF$_3$); signals for HgO$_2$CCF$_3$ coincident with those for peroxymercurial.

Chromatography [60 g SiO$_2$; 1 : 1 light petroleum and dichloromethane; 25 cm^3 fractions] of the organomercury bromides afforded mainly mixtures, but fractions 16 and 17 contained pure 3-*bromomercurio*-1-*phenylpropyl t-butyl peroxide* (0.16 g), which was recrystallised at −5 °C from light petroleum (b.p. <40 °C) containing one drop of dichloromethane, m.p. 42—43 °C, δ_H (200 MHz) 7.20 (narrow m, Ph), 4.97 (t J 6.0 Hz, C*H*OO), 2.38 (m, C*H*$_2$Hg), 1.88 and 1.74 (2 × 1 H m, C*H*$_2$CH$_2$Hg), and 1.21 (s, Bu^t); δ_C 86.16 (COO), 32.71 (CCHg), 28.30 (CHg), 80.76 and 26.58 (Bu^t), 139.69, 128.77, 128.28, and 126.90 (Ph) (Found: C, 31.9; H, 4.0. C$_{13}$H$_{19}$BrHgO$_2$ requires C, 32.01; H, 3.93%).

Reduction.—Chilled 2M-NaOH (15 cm^3) was added to an ice-cold solution in dichloromethane (20 cm^3) of the crude organomercury(II) trifluoroacetates obtained from t-butyl peroxymercuriation (above) of phenylcyclopropane (10 mmol). The resultant mixture was added, during a period of 5 min, to a stirred solution of NaBH$_4$ (40 mmol) in 2.5M-NaOH (30 cm^3) at 0 °C. After the mixture had been stirred for 30 min at 0 °C and 30 min at room temperature, the organic layer was isolated, combined with dichloromethane extracts (2 × 20 cm^3) of the aqueous layer, dried (MgSO$_4$), and the solvent removed (*ca.* 10 mmHg) to give a colourless oil (1.51 g), which was identified by ^{1}H and ^{13}C n.m.r. spectroscopy as a mixture of t-butyl 1-phenylpropyl peroxide (45 mol%; data below), 1-phenylpropanol [^{1}H n.m.r. as reported,[10] δ_C 75.72 (C-1), 31.82 (C-2), 10.09 (C-3), 144.76, 128.21, 127.23, and 126.08 (Ph)], and a trace of starting 1-phenylcyclopropane.

The alcohol was removed by chromatography (30 g SiO$_2$; CH$_2$Cl$_2$) and the resultant product was rechromatographed [30 g SiO$_2$; 2 : 1 light petroleum and dichloromethane; 15 cm^3 fractions] to give, in fractions 6—8 1-*phenylpropyl t-butyl peroxide* (0.386 g, 19% based on phenylcyclopropane) which was finally purified by trap-to-trap distillation, δ_H (200 MHz) 7.31 (m $W_{\frac{1}{2}} \simeq$ 8.5 Hz, Ph), 4.75 (t J 6.91 Hz, CHOO), 1.90 and 1.70 (2 × 1 H m, CH$_2$), 1.21 (s, Bu^t), and 0.89 (t J 7.96 Hz, CH$_3$); δ_C 87.16 (COO), 28.04 (CH$_2$),

10.25 (CH$_3$), 79.80 and 26.44 (Bu^t), 141.52, 128.00, 126.90, and 127.40 (Ph) (Found: C, 74.6; H, 9.5. C$_{13}$H$_{20}$O$_2$ requires C, 74.94; H, 9.70%).

Brominolysis.—The solvent was removed (*ca.* 10 mmHg) from one third of the crude mixture of organomercury bromides obtained from t-butyl peroxymercuriation of phenylcyclopropane (20 mmol) as described above. The resultant oil was dissolved in methanol (15 cm^3), and a solution of bromine (0.38 cm^3, 7.4 mmol) and sodium bromide (2 g) in methanol (15 cm^3) was added. The mixture was stirred for 1.5 h and then water (20 cm^3) and dichloromethane (15 cm^3) were added. The organic layer was isolated, combined with light petroleum (b.p. < 40 °C) extracts (2 × 15 cm^3) of the aqueous layer, dried (MgSO$_4$), and the solvent removed (*ca.* 10 mmHg) to afford a pale yellow oil (1.85 g), which was shown by ^{1}H n.m.r. spectroscopy to contain mainly 3-bromo-1-phenylpropyl t-butyl peroxide and 3-bromo-1-phenylpropyl trifluoroacetate in the molar ratio of 6 : 4.

Chromatography [60 g SiO$_2$; 2 : 1 light petroleum and dichloromethane; 25 cm^3 fractions] afforded, in fractions 4—6, 3-bromo-1-phenylpropyl trifluoroacetate (0.590 g) as a colourless oil, δ_H 7.35 (s, Ph), 6.08 (X of ABX, ΣJ 14 Hz, CHO$_2$CCF$_3$), 3.3 (m, CH$_2$Br), and 2.4 (m, C*H*$_2$CH$_2$Br). Fractions 8—11 contained 3-*bromo*-1-*phenylpropyl t-butyl peroxide* (0.556 g, 29% based on phenylcyclopropane), a colourless oil which was recrystallised from hexane at −10 °C, m.p. *ca.* 0 °C, δ_H (200 MHz) 7.32 (narrow m, Ph), 5.06 (X of ABX, ΣJ 13.8 Hz, CHOO), 3.46 and 3.29 (2 × 1 H m, CH$_2$Br), 2.44 and 2.13 (2 × 1 H m, C*H*$_2$CH$_2$Br), and 1.20 (s, Bu^t); δ_C 83.61 (COO), 38.44 (CBr), 29.52 (CCBr), 80.35 and 26.49 (Bu^t), 140.21, 128.37, 127.95, and 126.83 (Ph) (Found: C, 54.1; H, 6.2. C$_{13}$H$_{19}$BrO$_2$ requires C, 54.36; H, 6.68%).

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