support was reduced in flowing hydrogen (100 mL min^{-1}, 99.999%, H_2O < 3 ppm) at 200 °C for 7 min and then cooled to room temperature maintaining the same hydrogen stream. The $AlPO_4$-supported rhodium catalyst thus prepared has a metal surface area of 90 $m^2g^{-1}_{Rh}$[9,10].

Hydrogenation Apparatus and General Procedure. All experiments were conducted with a Parr Instruments 3911 hydrogenator at an initial hydrogen pressure of 0.55 MPa and at 25 °C. The temperature was controlled by pumping water from a thermostatic bath through the vessel jacket with a precision of 0.5 °C.

The compound to be reduced (5 mmol) and methanol (50 mL) were placed in the hydrogenation vessel (250 mL) and then the catalyst (200 mg) was added. The vessel was connected to the hydrogenator, twice flushed with hydrogen, pressurized to 0.55 MPa, and shaken until absorption of 1 equiv of hydrogen. The progress of hydrogenation was then followed by recording the hydrogen uptake vs. time, at constant volume. Catalytic activity is determined as the initial rate of hydrogenation, from the slope of the linear hydrogen pressure decrease vs. reaction time, remaining linear up to 50–60% conversion.

After filtration and elimination of methanol by rotary vacuum evaporation, the hydrogenation products were purified by crystallization or silica column chromatography and, in the case of the compounds previously described, were identified by comparison of their spectroscopic properties (^1H NMR and IR spectra) with those described in the literature.

Acknowledgment. We thank B. Bermudez for his kind assistance in providing the computer program for the analysis of the substrate structure on the reaction rate.

Registry No. (*E*)-PhCH=CHCOMe, 1896-62-4; (*E*)-PhCH=CHCOEt, 18402-88-5; (*E*)-PhCH=CHCOPr-*n*, 8297-62-9; (*E*)-PhCH=CHCOPr-*i*, 10596-48-2; (*E*)-PhCH=CHCOBu-*n*, 41903-83-7; (*E*)-PhCH=CHCOBu-*t*, 29569-91-3; (*E*)-PhCH=CHCOPe-*n*, 29478-39-5; (*E*)-PhCH=CHCOPh, 614-47-1; (*E*)-4-ClC_6H_4CH=CHCOMe, 30626-03-0; (*E*)-4-ClC_6H_4CH=CHCOEt, 54951-47-2; (*E*)-4-ClC_6H_4CH=CHCOPr-*n*, 100765-36-4; (*E*)-4-ClC_6H_4CH=CHCOPr-*i*, 67962-15-6; (*E*)-4-ClC_6H_4CH=CHCOBu-*n*, 100765-37-5; (*E*)-4-ClC_6H_4CH=CHCOBu-*t*, 41564-62-9; (*E*)-4-ClC_6H_4CH=CHCOPe-*n*, 100765-38-6; (*E*)-4-ClC_6H_4CH=CHCOPh, 22252-16-0; (*E*)-4-$MeOC_6H_4CH$=CHCOMe, 3815-30-3; (*E*)-4-$MeOC_6H_4CH$=CHCOEt, 82297-64-1; (*E*)-4-$MeOC_6H_4CH$=CHCOPr-*n*, 82297-65-2; (*E*)-4-$MeOC_6H_4CH$=CHCOPr-*i*, 67962-14-5; (*E*)-4-$MeOC_6H_4CH$=CHCOBu-*n*, 82297-66-3; (*E*)-4-$MeOC_6H_4CH$=CHCOBu-*t*, 41564-61-8; (*E*)-4-$MeOC_6H_4CH$=CHCOPe-*n*, 82297-67-4; (*E*)-4-$MeOC_6H_4CH$=CHCOPh, 22252-15-9; (*E*)-4-MeC_6H_4CH=CHCOMe, 4023-84-1; (*E*)-4-$MeC_6H_4CHCHCOEt$, 81467-93-8; (*E*)-4-MeC_6H_4CH=CHCOPr-*n*, 100765-39-7; (*E*)-4-MeC_6H_4CH=CHCOPr-*i*, 67962-11-2; (*E*)-4-MeC_6H_4CH=CHCOBu-*n*, 100765-40-0; (*E*)-4-MeC_6H_4CH=CHCOBu-*t*, 41564-60-7; (*E*)-4-MeC_6H_4CH=CHCOPe-*n*, 100765-41-1; (*E*)-4-MeC_6H_4CH=CHCOPh, 22252-14-8; $Ph(CH_2)_2COMe$, 2550-26-7; $Ph(CH_2)_2COEt$, 20795-51-1; $Ph(CH_2)_2COPr$-*n*, 29898-25-7; $Ph(CH_2)_2COPr$-*i*, 40463-09-0; $Ph(CH_2)_2COBu$-*n*, 19969-04-1; $Ph(CH_2)_2COBu$-*t*, 5195-24-4; $Ph(CH_2)_2COPe$-*n*, 6047-99-0; $Ph(CH_2)_2COPh$, 1083-30-3; 4-$ClC_6H_4(CH_2)_2COMe$, 3506-75-0; 4-$ClC_6H_4(CH_2)_2COEt$, 95416-62-9; 4-$ClC_6H_4(CH_2)_2COPr$-*n*, 54672-63-8; 4-$ClC_6H_4(CH_2)_2COPr$-*i*, 100765-42-2; 4-$ClC_6H_4(CH_2)_2COBu$-*n*, 100765-43-3; 4-$ClC_6H_4(CH_2)_2COBu$-*t*, 66346-01-8; 4-$ClC_6H_4(CH_2)_2COPe$-*n*, 100765-44-4; 4-$ClC_6H_4(CH_2)_2COPh$, 5739-39-9; 4-$MeOC_6H_4(CH_2)_2COMe$, 104-20-1; 4-$MeOC_6H_4(CH_2)_2COEt$, 5440-80-2; 4-$MeOC_6H_4(CH_2)_2COPr$-*n*, 90831-80-4; 4-$MeOC_6H_4(CH_2)_2COPr$-*i*, 100765-45-5; 4-$MeOC_6H_4(CH_2)_2COBu$-*n*, 90831-81-5; 4-$MeOC_6H_4(CH_2)_2COBu$-*t*, 100789-95-5; 4-$MeOC_6H_4(CH_2)_2COPe$-*n*, 90831-82-6; 4-$MeOC_6H_4(CH_2)_2COPh$, 1669-49-4; 4-$MeC_6H_4(CH_2)_2COMe$, 7774-79-0; 4-$MeC_6H_4(CH_2)_2COEt$, 100765-46-6; 4-$MeC_6H_4(CH_2)_2COPr$-*n*, 100765-47-7; 4-$MeC_6H_4(CH_2)_2COPr$-*i*, 100765-48-8; 4-$MeC_6H_4(CH_2)_2COBu$-*n*, 100765-49-9; 4-$MeC_6H_4(CH_2)_2COBu$-*t*, 80917-20-0; 4-$MeC_6H_4(CH_2)_2COPe$-*n*, 100765-50-2; 4-$MeC_6H_4(CH_2)_2COPh$, 1669-50-7.

Supplementary Material Available: Boiling points and full ^1H NMR data of compounds **10–15**, **19–23**, and **26–31** (2 pages). Ordering information is given on any current masthead page.

Alkylated Perepoxides: Peroxonium vs. Phenonium Intermediates from β-Haloalkyl *tert*-Butyl Peroxides and Silver Trifluoroacetate

A. J. Bloodworth* and Kevin J. Bowyer

Department of Chemistry, University College London, London WC1H OAJ, U.K.

John C. Mitchell*

Department of Chemistry, Royal Holloway and Bedford New College, University of London, Egham Hill, Surrey TW20 OEX, U.K.

Received September 16, 1985

To see if the generation of cyclic peroxonium ions by intramolecular alkylation of dialkyl peroxides could be extended to 3- or 4-membered ring systems, seven β-iodoalkyl *tert*-butyl peroxides were treated with silver trifluoroacetate in refluxing dichloromethane. Compounds **1a–d**, $RCH_2C(Me)(OOBu\text{-}t)CH_2I$ (R = H, Me, Et, or Ph), gave mixtures of 1,2-peroxy-migrated substitution and elimination products $RCH_2C(Me)(OCOCF_3)CH_2OOBu\text{-}t$, CH_2=$C(CH_2R)CH_2OOBu\text{-}t$, and RCH=$C(Me)CH_2OOBu\text{-}t$, whereas compounds **1e–g**, $PhC(R)(OOBu\text{-}t)CH_2I$ (R = H, Me, or Ph), afforded 1,2-phenyl-migrated products. The results were rationalized in terms of the selective generation of intermediate alkylated perepoxides from **1a–d** or phenonium ions from **1e–g**. The relative migratory aptitudes were found to be Ph > Bu-*t*-OO > alkyl.

Perepoxides have been postulated as intermediates in the singlet oxygenation of alkenes[1] and in the reaction of β-hydroperoxy bromides with base,[2] but their existence remains a matter of controversy. In continuing our investigations on the generation of peroxonium ions by intramolecular alkylation of dialkyl peroxides,[3–5] we have obtained evidence that species closely related to perepoxides, the hitherto unknown alkylated perepoxides, me-

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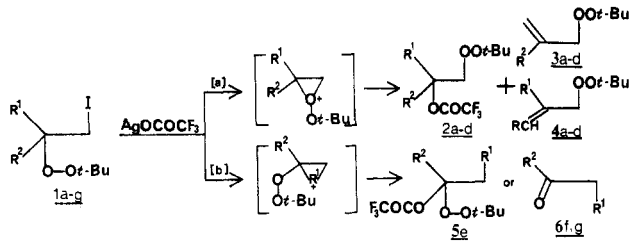
0022-3263/86/1951-1790$01.50/0

Scheme I



entry	R^1	R^2	path	products (yield, %)
1a	Me	Me	a	**2a** (57) + **3a** (16)
1b	Me	Et	a	**2b** (35) + **3b** (6) + **4b** (12)
1c	Me	Pr	a	**2c** (32) + **3c** (14) + **4c** (28)
1d	Me	CH_2Ph	a	**2d** (53) + **3d** (21) + **4d** (16)
1e	Ph	H	b	**5e** (96)
1f	Ph	Me	b	**6f** (36)[a]
1g	Ph	Ph	b	**6g** (72)

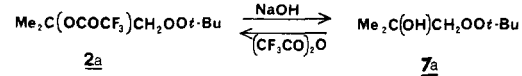
[a] Mixture also contains *t*-$BuOCH_2COCH_2Ph$ (24%) and $MeCOCH(OBu\text{-}t)Ph$ (8%).

diate in reactions of suitable β-haloalkyl *tert*-butyl peroxides with silver trifluoroacetate, but that, where possible, phenonium intermediates are formed preferentially. We now report the nature of this evidence.

Results and Discussion

Peroxy iodides **1** were prepared by *tert*-butyl peroxymercuration[6] of the corresponding alkenes followed by anion exchange and iododemercuration.[7] The structures were confirmed by ^1H and ^{13}C NMR, the high-field triplet for $^{13}CH_2I$ being particularly characteristic. All compounds except **1b** and **1d** were previously known, and our ^1H NMR data are in agreement with those reported.[7] Treatment of the peroxy iodides with silver trifluoroacetate afforded products consistent with the selective generation of phenonium or peroxonium (i.e., alkylated perepoxide) intermediates (Scheme I).

Thus, when each peroxy iodide **1a–d** was treated with silver trifluoroacetate in refluxing dichloromethane and the crude product was purified by HPLC, two components were isolated which were identified by spectroscopic data and elemental analysis as the peroxy-migrated substitution product **2a–d** and a mixture of the peroxy-migrated elimination products **3a–d** and **4a–d**. The allylic peroxides **3** and **4** were readily identified from the olefinic and $CH_2OOBu\text{-}t$ resonances in their ^1H and ^{13}C NMR and by their reaction with bromine. The presence of the trifluoroacetate group in the substitution products **2** was immediately apparent from the carbonyl absorption at ca 1780 cm^{-1} in the infrared, but because of the similar shielding characteristics and vicinal arrangement of the peroxy and trifluoroacetoxy substituents, NMR spectra do not allow a wholly unambiguous distinction to be made between **2** and the straight substitution product $RCH_2C(Me)(OOBu\text{-}t)CH_2OCOCF_3$. Consequently we examined the effect upon the NMR of hydrolysing the trifluoroacetates to the corresponding alcohols **7**. For example, **2a** was transformed into **7a** by reaction with aqueous NaOH under phase-transfer catalysis. As a result, the methyl

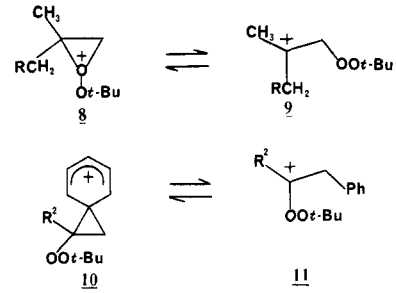


and methylene protons were shifted upfield by about the same amount (0.35 ppm), which is compatible with the structures shown but not expected for the conversion of $Me_2C(OOBu\text{-}t)CH_2OCOCF_3$ into $Me_2C(OOBu\text{-}t)CH_2OH$. To confirm the identity of the alcohol **7a**, it was converted back into **2a** by treatment with trifluoroacetic anhydride.

In contrast to the 1,2-peroxy migration chemistry of **1a–d**, only phenyl migration was observed in systems **1e–g**. Thus, peroxy iodide **1e** under the same conditions as for **1a–d** afforded **5e** as the only detectable product. The structure of **5e** was identified from ^1H and ^{13}C NMR, the characteristic low-field chemical shift (109.12 ppm) for the carbon bearing two oxygen groups being particularly diagnostic. Peroxy iodide **1g**, on the other hand, afforded ketone **6g**, identified by comparison with an authentic sample. Peroxy iodide **1f** similarly gave ketone **6f**, but a second major product was the α-*tert*-butoxy ketone *t*-$BuOCH_2COCH_2Ph$, which presumably arises by rearrangement of the vinyl peroxide $CH_2{=}C(CH_2Ph)OOBu\text{-}t$, formed by an elimination analogous to that affording allylic peroxides **3a–d**.

From the results obtained it appears that the relative migratory aptitudes in these 1,2-nucleophilic rearrangements decrease in the order Ph > Bu-*t*-OO > Alkyl.

The *regiospecific* formation of products in which peroxy or phenyl groups have migrated to the methylene site suggests that the unsymmetrical peroxonium and phenonium intermediates (**8** and **10**) each have appreciable carbocationic character, or that they rearrange to the fully fledged carbocations (**9** and **11**) before conversion to products.



The formation of substitution products **2a–d** and **5e** is readily explained by either picture, as is the formation of ketones **6f** and **6g** by loss of a 2-methoxy-2-propyl cation in a Baeyer–Villier type O–O cleavage.[4,5] However, deprotonation of carbocation **9** would be expected to favour the formation of Zaitsev elimination products, namely **4b–d** and vinylic peroxides $RCH_2C(CH_3){=}CHOOBu\text{-}t$, which are expected to rearrange to the aldehydes $RCH_2C(CH_3)(OBu\text{-}t)CHO$, yet no aldehydes were detected and appreciable amounts of the Hoffman elimination products **3** were obtained. This may be rationalized in terms of loss of a proton antiperiplanar to the breaking C–O bond of the alkylated perepoxide **8** in an E2-type mechanism. A similar mechanism with the phenonium ion **10f** can account for the formation of $CH_2{=}C(CH_2Ph)OOBu\text{-}t$, which rearranges to the observed *t*-$BuOCH_2COCH_2Ph$, as the principal elimination product from **1f**.

It is interesting to compare our results with those obtained by Kopecky for the reaction of β-hydroperoxy iodides with silver salts.[8] Although both systems afforded allylic peroxides, the hydroperoxy iodides gave no substitution products analogous to **2**. Furthermore, the hydroperoxy iodides additionally yielded dioxetanes whereas we did not detect these, or derived carbonyl products, in any of our reactions. By analogy with our results, an intermediate protonated perepoxide can account directly for allylic hydroperoxide formation, and it is not necessary

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to invoke an indirect route via deprotonation to a perepoxide. This is consistent with Kopecky's observation that product distributions from the silver salt reactions are different from those from reactions with base,[2] where a perepoxide mechanism *is* believed to operate. It seems likely that dioxetanes arise by deprotonation of the corresponding four-membered ring dialkylperoxonium ions and that formation of the corresponding trialkylperoxonium ions from 1 is disfavored for steric reasons.

A further difference between our reactions and those of β-hydroperoxy halides is that 1,2-alkyl migrations have been observed in the latter.[8-10] However, each example involved compounds in which the hydroperoxy group and the halogen were attached to identically substituted tertiary carbon atoms. Hence migration of the hydroperoxy group could not be detected, and nothing can be concluded from product analysis about relative migratory aptitudes. Meaningful conclusions about the influence of *tert*-butylperoxy vs. hydroperoxy groups in reactions of this type must await comparisons between more closely related systems.

Further work addressing these interesting mechanistic questions is in progress in our laboratory.

Experimental Section

Unless otherwise indicated, NMR spectra were recorded with a Varian XL 200 spectrometer for solutions in $CDCl_3$; 60-MHz ^1H NMR spectra were obtained with a Jeol PMX 60 instrument 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 using a VG 7070 F/H mass spectrometer plus Finnigan INCOS data system. *tert*-Butyl hydroperoxide was purified as described previously.[11] All other reagents were commercial samples which were used as received.

Preparation of *tert*-Butyl Peroxymercurials. β-Bromomercurioalkyl *tert*-butyl peroxides were prepared by peroxymercuration of the corresponding alkenes followed by anion exchange as described previously,[6] and were recrystallized from light petroleum (bp 60–80 °C).

For the peroxymercurial precursor of **1a** (97% yield): ^1H NMR (60 MHz) ppm 1.26 (9 H, s, $C(CH_3)_3$), 1.33(6 H, s, $C(CH_3)_2CH_2HgBr$), and 2.10 (2 H, s, CH_2HgBr); ^{13}C NMR ppm (20 MHz) 26.69 ($C(CH_3)_3$), 28.65 ($^3J_{Hg}$ = 138 Hz, $C(CH_3)_2CH_2HgBr$), 45.73 ($^1J_{Hg}$ = 1525 Hz, CH_2HgBr), 79.67 ($C(CH_3)_3$), and 81.52 ($C(CH_3)_2CH_2HgBr$). Anal. Calcd for $C_8H_{17}BrHgO_2$: C, 22.55; H, 4.03. Found: C, 22.80; H, 4.02.

For the peroxymercurial precursor of **1b** (88% yield): ^1H NMR (60 MHz) ppm 0.92 (3 H, t, CH_2CH_3), 1.2–1.8 (2 H, m, CH_2CH_3), 1.25 (12 H, s, $C(CH_3)_3$ and CCH_3), and 2.05 (2 H, s, CH_2HgBr); ^{13}C NMR ppm 8.70 (q, CH_2CH_3), 25.67 (q, $^3J_{Hg}$ = 125 Hz, CCH_3), 26.84 (q, $C(CH_3)_3$), 34.07 (t, J_{Hg}), 131 Hz, CH_2CH_3), 43.77 (t, $^1J_{Hg}$ = 1537 Hz, CH_2HgBr), 79.14 (s, $C(CH_3)_3$), and 83.69 (s, CCH_3). Anal. Calcd for $C_9H_{19}BrHgO_2$: C, 24.58; H, 4.35. Found: C, 24.63; H, 4.33.

For the peroxymercurial precursor of **1c** (84% yield): ^1H NMR (60 MHz) ppm 0.6–1.6 (7 H, m, $CH_2CH_2CH_3$), 1.27s (12 H, $C(CH_3)_3$ and $C(CH_3)$, and 2.03 (2 H, s, CH_2HgBr); ^{13}C NMR (20 MHz) ppm 14.65 ($CH_2CH_2CH_3$), 17.59 ($CH_2CH_2CH_3$), 26.13 ($^3J_{Hg}$ = 125 Hz, CCH_3), 26.77 ($C(CH_3)_3$), 43.74 ($^3J_{Hg}$ = 131 Hz, $CH_2CH_2CH_3$), 44.14 ($^1J_{Hg}$ = 1531 Hz, CH_2HgBr), 79.69 ($C(CH_3)_3$), and 83.50 ($^2J_{Hg}$ = 119 Hz, CCH_3). Anal. Calcd for $C_{10}H_{21}BrHgO_2$: C, 26.46; H, 4.66. Found: C, 26.46; H, 4.58.

For the peroxymercurial precursor of **1d** (83% yield): ^1H NMR ppm 1.26 (9 H, s, $C(CH_3)_3$), 1.37 (3 H, s, CCH_3), 1.82 and 1.97 (AB, J = 12 Hz, CH_2HgBr), 2.64 and 3.15 (AB, J = 14 Hz, CH_2Ph), 7.32 (5 H, m, Ph); ^{13}C NMR ppm 26.72 (q, $C(CH_3)_3$), 27.57 (q, $^3J_{Hg}$ = 163 Hz, CCH_3), 42.32 (t, J_{Hg} = 1543 Hz, CH_2HgBr), 45.86 (t, $^3J_{Hg}$ = 88 Hz, CH_2Ph), 79.56 (s, $C(CH_3)_3$), 83.18 (s, $^2J_{Hg}$ = 113 Hz, CCH_3), 126.92 (d, Ph), 128.42 (d, Ph), 130.58 (d, Ph), and 137.46 (s, Ph). Anal. Calcd for $C_{14}H_{21}BrHgO_2$: C, 33.50; H, 4.21. Found: C, 33.43; H, 4.09.

For the peroxymercurial precursor of **1e** (87% yield): ^1H NMR in agreement with reported spectrum;[12] ^{13}C NMR (20 MHz) ppm 26.50 ($C(CH_3)_3$), 39.65 (CH_2HgBr), 80.88 ($C(CH_3)_3$), 84.06 (CPh), 125.99 (Ph), 127.94 (Ph), 128.51 (Ph) and 142.26 (Ph).

For the peroxymercurial precursor of **1f** (82% yield): ^1H NMR in agreement with reported spectrum;[7] ^{13}C NMR ppm 26.94 ($C(CH_3)_3$), 29.62 (CCH_3), 46.30 (CH_2HgBr), 80.34 ($C(CH_3)_3$), 84.67 (CCH_3), 124.96 (Ph), 127.24 (Ph), 128.39 (Ph), and 146.65 (Ph).

For the peroxymercurial precursor of **1g** (89% yield): ^1H NMR (60 MHz) ppm 1.32 (9 H, s, $C(CH_3)_3$), 2.67 (2 H, s, CH_2HgBr), and 7.23 (10 H, s, Ph); ^{13}C NMR ppm 27.03 ($C(CH_3)_3$), 44.64 (CH_2HgBr), 81.09 ($C(CH_3)_3$), 88.24 (CPh), 126.44 (Ph), 127.49 (Ph), 128.14 (Ph), and 145.69 (Ph). Anal. Calcd for $C_{18}H_{21}BrHgO_2$: C, 39.31; H, 3.84. Found: C, 39.38; H, 3.76.

Preparation of β-Iodoalkyl *tert*-Butyl Peroxides (1). Iodine was added via a Soxhlet thimble to a solution of the peroxymercurial **3g** in methylene chloride (150 mL) at reflux. After 2 h, the solution was washed with saturated sodium bicarbonate (50 mL), saturated sodium thiosulphate solution (50 mL, or sufficient to remove all I_2), and water (2 × 50 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the β-iodoalkyl *tert*-butyl peroxide was purified by vacuum distillation or by addition of light petroleum (bp 60–80 °C) followed by filtration to remove any mercury(II) salts. For **1a**, **1c**, and **1e–g**, ^1H NMR spectra were in good agreement with reported data.[7]

For **1a** (77% yield): ^{13}C NMR ppm 15.38 (t, CH_2I), 24.32 (q, $C(CH_3)_2CH_2I$), 26.54 (q, $C(CH_3)_3$), 77.97 (s, $C(CH_3)_2CH_2I$), and 78.60 ($C(CH_3)_3$).

For **1b** (96% yield): ^1H NMR (60 MHz) ppm 0.88 (3 H, CH_2CH_3), 1.23 (9 H, s, $C(CH_3)_3$), 1.30 (3 H, s, CCH_3), 1.5–2.0 (2 H, m, CH_2CH_3), 3.39 (2 H, s, CH_2I); ^{13}C NMR (20 MHz) ppm 8.05 (q, CH_2CH_3), 14.70 (t, CH_2I), 21.47 (q, CCH_3), 26.65 (q, $C(CH_3)_3$), 29.48 (t, CH_2CH_3), 78.66 (s, CCH_3), 79.78 (s, $C(CH_3)_3$). Anal. Calcd for $C_9H_{19}IO_2$: C, 37.77; H, 6.69. Found: C, 37.75; H, 6.60.

For **1c** (91% yield): ^{13}C NMR (20 MHz) ppm 14.50 (q, $CH_2CH_2CH_3$), 14.99 (t, CH_2I), 17.00 (t, $CH_2CH_2CH_3$), 14.99 (t, CH_2I), 17.00 (t, $CH_2CH_2CH_3$), 21.96 (q, CCH_3), 26.69 (q, $C(CH_3)_3$), 39.29 (t, $CH_2CH_2CH_3$), 78.75 (s, CCH_3), and 79.81 (s, $C(CH_3)_3$). Anal. Calcd for $C_{10}H_{21}IO_2$: C, 40.10; H, 7.05. Found: C, 39.73; H, 6.96.

For **1d** (82% yield): ^1H NMR (60 MHz) ppm 1.23 (9 H, s, $C(CH_3)_3$), 1.30 (3 H, s, CCH_3), 3.00 (2 H, s, CH_2Ph), 3.33 and 3.37 (AB, J = 10 Hz, CH_2I), and 7.23 (5 H, s, Ph); ^{13}C NMR ppm 14.47 (t, CH_2I), 22.36 (q, CCH_3), 26.72 (q, $C(CH_3)_3$), 42.58 (t, CH_2Ph), 79.31 (s, CCH_3), 80.16 (s, $C(CH_3)_3$), 126.44 (d, Ph), 127.89 (d, Ph), 130.60 (d, Ph), and 136.86 (s, Ph). Anal. Calcd for $C_{14}H_{21}IO_2$: C, 48.28; H, 6.07. Found: C, 48.19; H, 5.95.

For **1e** (97% yield): ^{13}C NMR ppm 6.29 (t, CH_2I), 26.49 (q, $C(CH_3)_3$), 80.98 (s, $C(CH_3)_3$), 85.25 (d, CH), 127.07 (d, Ph), 128.37 (d, Ph), 128.57 (d, Ph), and 138.19 (s, Ph).

For **1f** (88% yield): ^{13}C NMR ppm 15.34 (t, CH_2I), 24.37 (q, CCH_3), 26.69 (q, $C(CH_3)_3$), 79.53 (s, $C(CH_3)_3$), 81.01 (s, CCH_3), 125.75 (d, Ph), 127.39 (d, Ph), 127.95 (d, Ph), and 142.12 (s, Ph). Anal. Calcd for $C_{13}H_{19}IO_2$: C, 46.72; H, 5.73. Found C, 46.72; H, 5.46.

For **1g**: ^{13}C NMR ppm 15.11 (t, CH_2I), 26,78 (q, $C(CH_3)_3$), 79.70 (s, $C(CH_3)_3$), 84.22 (s, CPh_2), 126.94 (d, Ph), 127.21 (d, Ph), 127.64 (d, Ph), and 142.43 (s, Ph).

Reaction of β-Iodoalkyl *tert*-Butyl Peroxides with Silver Trifluoroacetate. Silver trifluoroacetate (1.1 equiv) was added to a solution of the β-iodoalkyl *tert*-butyl peroxide (**1g**) in methylene chloride (50 mL) at reflux (**1a–d**) or room temperature (**1e–f**), and the mixture was stirred for 1 h. The mixture was then filtered through a sintered glass funnel (5-cm diameter) containing silica (1 cm) covered with celite (0.2 cm). The methylene chloride was removed under vacuum and the products were separated by medium-pressure chromatography (50 cm × 2.25 cm, silica, 1% EtOAc in light petroleum (bp 60–80 °C)). See Scheme I for

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product distributions and yields, which were determined by NMR integration vs. internal standards for the crude mixtures. Yields of isolated materials are given below.

For **2a** (24%): ^{1}H NMR (60 MHz) ppm 1.20 (9 H, s, $C(CH_3)_3$), 1.57 (6 H, s, $C(CH_3)_2$), and 4.20 (2 H, s, $OOCH_2$); ^{13}C NMR ppm 23.45 (q, $C(CH_3)_2$), 26.14 (q, $C(CH_3)_3$), 78.14 (t, CH_2), 80.90 (s, $C(CH_3)_3$), and 86.87 (s, $C(CH_3)_2$); IR (C=O) 1777 cm^{-1}. Anal. Calcd for $C_{10}H_{17}F_3O_4$: C, 46.51; H, 6.63. Found: C, 46.22; H, 6.48.

For **2b**: ^{1}H NMR (60 MHz) ppm 0.92 (3 H, t, CH_2CH_3), 1.25 (9 H, s, $C(CH_3)_3$), 1.53 (3 H, s, CCH_3), 1.90 (2 H, m, CH_2CH_3), and 4.25 (2 H, s, $OOCH_2$); ^{13}C NMR ppm 7.34 (CH_2CH_3), 20.56 (CCH_3), 26.06 ($C(CH_3)_3$), 28.67 (CH_2CH_3), 76.37 (CH_2), 80.80 ($C(CH_3)_3$), and 89.49 (CCH_3); IR (C=O) 1776 cm^{-1}.

For **2c**: ^{1}H NMR (60 MHz) ppm 0.8–2.0 (7 H, m, $CH_2CH_2CH_3$), 1.20 (9 H, s, $C(CH_3)_3$), 1.52 (3 H, s, CCH_3), and 4.18 (2 H, s, $OOCH_2$); ^{13}C NMR ppm 14.16 ($CH_2CH_2CH_3$), 16.42 ($CH_2CH_2CH_3$), 21.09 (CCH_3), 26.07 ($C(CH_3)_3$), 38.36 ($CH_2CH_2CH_3$), 76.67 (CH_2), 80.82 ($C(CH_3)_3$), and 89.28 (CCH_3); IR (C=O) 1770 cm^{-1}. Anal. Calcd for $C_{12}H_{21}F_3O_4$: C, 50.34; H, 7.39. Found: C, 50.48; H, 7.33.

For **2d** (28%): ^{1}H NMR (60 MHz) ppm 1.23 (9 H, s, $C(CH_3)_3$), 1.48 (3 H, s, CCH_3), 3.15 and 3.20 (AB, J = 15 Hz, CH_2Ph), 4.20 and 4.27 (AB, J = 14 Hz, $OOCH_2$), and 7.17 (5 H, s, Ph); ^{13}C NMR ppm 20.65 (q, CCH_3), 26.15 (q, $C(CH_3)_3$), 42.05 (t, CH_2Ph), 75.73 (t, $OOCH_2$), 80.90 (s, $C(CH_3)_3$), 88.79 (s, CCH_3), 127.06 (d, Ph), 128.30 (d, Ph), 130.69 (d, Ph), and 134.93 (s, Ph); IR (C=O) 1776 cm^{-1}.

For **5e**: ^{1}H NMR (60 MHz) ppm 1.20 (9 H, s, $C(CH_3)_3$), 3.12 (2 H, d, J = 6 Hz, CH_2Ph), 6.53 (1 H, t, J = 6 Hz, CH), and 7.31 (5 H, s, Ph); ^{13}C NMR (20 MHz) ppm: 26.41 (q, $C(CH_3)_3$), 37.25 (t, CH_2Ph), 80.72 (s, $C(CH_3)_3$), 109.12 (d, CH), 126.54 (d, Ph), 128.26 (d, Ph), 129.75 (d, Ph), and 136.66 (s, Ph); IR (C=O) 1789 cm^{-1}; MS, m/e 306 (M^+, 0.03%).

For rearrangement product *tert*-$BuOCH_2COCH_2Ph$ (23%): ^{1}H NMR (60 MHz) ppm: 1.17 (9 H, s, $C(CH_3)_3$), 3.78 (2 H, s, CH_2Ph), 3.95 (2 H, s, CH_2OBu-*t*), and 7.18 (5 H, s, Ph); ^{13}C NMR ppm: 27.27 (q, $C(CH_3)_3$), 46.17 (t, CH_2Ph), 67.79 (t, CH_2OBu-*t*), 74.18 (s, $C(CH_3)_3$), 126.89 (d, Ph), 128.55 (d, Ph), 129.60 (d, Ph), and 133.93 (s, Ph); IR (C=O) 1718 cm^{-1}.

For **3a**: ^{1}H NMR in agreement with reported spectrum.[13]

For **3b + 4b**: ^{1}H NMR ppm 0.8–1.1 (m, CH_2CH_3), 1.25 (s, $C(CH_3)_3$), 1.5–1.8 (m, CH_2CH_3), 4.31 (s, 4.40 s, and 4,45 s (CH_2OOBu-*t*), 4.94 s and 5.03 s (CH_2=C), and 5.53 (m, MeCH=C).

For **3c + 4c**: ^{1}H NMR ppm 0.8–1.2 (m, $CH_2CH_2CH_3$), 1.25 (s, $C(CH_3)_3$), 1.4–2.4 (m, $CH_2CH_2CH_3$), 4.28 s, 4.37 s, 4.40 s (CH_2OOBu-*t*), 5.00 s and 5.12 s (CH_2=C), and 5.52 (m, EtCH=C).

For **3d + 4d**: ^{1}H NMR ppm: 1.27 (s, $C(CH_3)_3$), 3.33 (s, CH_2Ph), 4.22 s, 4.37 s, and 4.42 s (CH_2OOBu-*t*), 4.82 s and 5.00 (CH_2=C), and 6.38 (s, PhCH=C).

Reaction of Allylic Peroxides (3) with Bromine. A solution of bromine in dichloromethane was added dropwise to a solution of the allylic peroxide in dichloromethane until the color of bromine persisted. After 5 min, the volatile components were removed under reduced pressure to afford the dibromide as a colorless oil, which was purified by medium-pressure chromatography (conditions as before).

For product from **3a** (t-$BuOOCH_2C(CH_2Br)(Br)CH_3$): ^{1}H NMR (60 MHz) ppm 1.27 (9 H, s, $C(CH_3)_3$), 1.87 (3 H, s, CCH_3), 3.82 s and 3.90 s (AB, J = 11 Hz, CH_2Br), and 4.23 (2 H, s, CH_2OOBu-*tert*); ^{13}C NMR ppm 26.28 (q, $C(CH_3)_3$), 27.70 (q, CCH_3), 40.74 (t, CH_2Br), 62.74 (s, CBr), 79.88 (t, CH_2OOBu-*t*), and 81.32 (s, $C(CH_3)_3$).

For product from **3d** (t-$BuOOCH_2C(CH_2Br)(Br)CH_2Ph$): ^{1}H NMR (60 MHz) ppm 1.28 (9 H, s, $C(CH_3)_3$), 3.32 (2 H, s, CH_2Ph), 3.78 and 3.87 (AB, J = 11 Hz, CH_2Br), 4.31 (2 H, s, CH_2OOBu-*t*), and 7.36 (5 H, m, Ph); ^{13}C NMR ppm 26.35 (q, $C(CH_3)_3$), 38.56 (t, CH_2Ph), 42.95 (t, CH_2Br), 67.35 (s, CBr), 78.34 (t, CH_2OOBu-*t*), 81.39 (s, $C(CH_3)_3$), 127.36 (d, Ph), 128.07 (d, Ph), 131.18 (d, Ph), and 134.78 (s, Ph). Anal. Calcd for $C_{14}H_{20}Br_2O_2$: C, 44.23; H, 5.30. Found C, 44.39; H, 5.04.

Hydrolysis of Trifluoroacetates (2). Trifluoroacetate **2a** (0.3 g) was dissolved in 5 mL of methylene chloride to which was added Bu_4NBr (0.1 equiv). Sodium hydroxide (2.0 equiv) was dissolved in 5 mL of water, and the two phases were mixed and vigorously stirred for 16 h. Methylene chloride (50 mL) and water (50 mL) were then added and the organic phase was separated, washed with water (3 × 50 mL), and then dried ($MgSO_4$). The solvent was removed under vacuum to give the alcohol **7a** (95%): ^{1}H NMR (60 MHz) ppm 1.22 (6 H, s, $C(CH_3)_2$), 1.27 (9 H, s, $C(CH_3)_3$), 2.42 (br s, OH), and 3.85 (2 H, s, CH_2OOBu-*t*); ^{13}C NMR ppm 26.22 ($C(CH_3)_2$), 26.30 ($C(CH_3)_3$), 71.27 (COH), 80.99 ($C(CH_3)_3$), and 83.09 (CH_2OOBu-*t*); IR (OH) 3566 cm^{-1}.

Trifluoroacetate **2d** was similarly converted into **7d** (92%): ^{1}H NMR ppm: 1.15 (3 H, s CCH_3), 1.28 (9 H, s, $C(CH_3)_3$), 1.70 (br s, OH), 2.86 (2 H, s, CH_2Ph), 3.88 (2 H, s, CH_2OOBu-*t*), and 7.27 (5 H, s, Ph); ^{13}C NMR ppm 23.88 (q, CCH_3), 26.40 (q, $C(CH_3)_3$), 45.39 (t, CH_2Ph), 73.35 (s, COH), 81.01(s, $C(CH_3)_3$), 81.16 (t, CH_2OOBu-*t*), 126.40 (d, Ph), 128.11 (d, Ph), 130.61 (d, Ph), and 137.31 (d, Ph); IR (OH) 3562 cm^{-1}.

Acknowledgment. We thank the SERC for the award of an Earmarked Studentship.

Registry No. **1a**, 28531-51-3; **1b**, 101517-39-9; **1c**, 28531-52-4; **1d**, 101517-40-2; **1e**, 28531-54-6; **1f**, 28531-55-7; **1g**, 28531-56-8; **2a**, 101541-76-8; **2b**, 101517-41-3; **2c**, 101517-42-4; **2d**, 101517-43-5; **3a**, 101517-45-7; **3b**, 101517-46-8; **3c**, 101517-47-9; **3d**, 101517-48-0; **4b**, 101517-49-1; **4c**, 101517-50-4; **4d**, 101517-51-5; **5e**, 101517-44-6; **6f**, 103-79-7; **6g**, 451-40-1; **7a**, 36405-55-7; **7d**, 101517-60-6; t-$BuOCH_2COCH_2Ph$, 101517-52-6; $CH_3COCH(OOBu$-*t*$)Ph$, 66666-84-0; $AgOCOCF_3$, 2966-50-9; $(CH_3)_2C(OOBu$-*t*$)CH_2HgBr$, 101517-53-7; $CH_3CH_2C(CH_3)(OOBu$-*t*$)CH_2GhBr$, 101517-54-8; $CH_3CH_2CH_2C(CH_3)(OOBu$-*t*$)CH_2HgBr$, 101517-55-9; $PhCH_2C(CH_3)(OOBu$-*t*$)CH_2HgBr$, 101517-56-0; $PhCH(OOBu$-*t*$)CH_2HgBr$, 31469-03-1; $PhC(CH_3)(OOBu$-*t*$)CH_2HgBr$, 28531-41-1; $(Ph)_2C(OOBu$-*t*$)CH_2HgBr$, 101517-57-1; $CH_3C(CH_3)=CH_2$, 115-11-7; $CH_3CH_2C(CH_3)=CH_2$, 563-46-2; $CH_3CH_2CH_2C(CH_3)=CH_2$, 763-29-1; $PhCH_2C(CH_3)=CH_2$, 3290-53-7; $PhCH=CH_2$, 100-42-5; $PhCH(CH_3)=CH_2$, 98-83-9; $(Ph)_2C=CH_2$, 530-48-3; $BrCH_2C(Br)(CH_3)CH_2OOBu$-*t*, 101517-58-2; $PhCH_2C(Br)(CH_2Br)CH_2OOBu$-*t*, 101517-59-3.

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