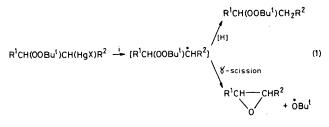
## Conversion of Non-terminal Alkenes into Secondary Alkyl t-Butyl Peroxides by Peroxymercuriation and Reduction with **Tributyltin Hydride**

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Summary s-Butyl, 3-hexyl, cyclopentyl, and cyclohexyl t-butyl peroxides have been prepared in yields of 63, 24, 59, and 61%, respectively, by reducing with tributyltin hydride the peroxymercurials derived from the corresponding symmetrical alkenes.

PEROXYMERCURIATION and reduction of alkenes have proved a valuable method for preparing acylic,<sup>1,2</sup> cyclic,<sup>3</sup> and bicyclic<sup>4</sup> secondary alkyl peroxides. Whereas the peroxymercuriation step can usually be accomplished cleanly and in high yield, the reduction, which is carried out with alkaline sodium borohydride, is always attended by side reactions. In particular, epoxides are formed because  $\gamma$ -scission of the intermediate  $\beta$ -peroxyalkyl radicals competes with the desired hydrogen abstraction, equation (1). Rate constants for  $\gamma$ -scission are markedly



Reagents. i, NaBH4, NaOH.

larger when di- rather than mono-alkylated epoxides are formed<sup>5</sup> and, while peroxymercuriation and reduction of terminal alkenes (where  $R^2 = H$ ) affords good yields of peroxides, with non-terminal alkenes epoxide formation predominates. We now report that good yields of secondary alkyl t-butyl peroxides (2) can be obtained from non-terminal alkenes by reducing the corresponding peroxymercurials (1) with tributyltin hydride [equation (2), X =O<sub>2</sub>CCF<sub>3</sub>, or OAc with 20 mol % of HClO<sub>4</sub>].<sup>6</sup>

$$RCH=CHR \xrightarrow{i,ii} RCH(OOBu^{t})CH(HgBr)R \xrightarrow{iii} RCH(OOBu^{t})CH_{2}R \quad (2)$$

$$(1) \qquad (2)$$

Reagents. i, HgX<sub>2</sub>,2Bu<sup>t</sup>OOH, ii, KBr, iii, Bu<sub>3</sub>SnH.

Crude  $\beta$ -peroxyalkylmercury(II) bromide (1) (5 mmol; mixed with ca. 5 mmol of Bu<sup>t</sup>OOH arising from the excess used in peroxymercuriation) was added over 10-15 min to stirred tributyltin hydride (7.3 cm<sup>3</sup>; 28 mmol) at 0 °C under a stream of dry nitrogen, the exit gas being passed through a trap at -78 °C. After 1 h the inlet to the reaction vessel was closed, the outlet from the trap was connected to an oil pump, and the trap coolant was changed to liquid nitrogen. The reaction mixture was subjected to two freeze/pump/thaw cycles to remove dissolved nitrogen and the volatile components were then allowed to distil into the trap. The trap contents were chromatographed on silica using dichloromethane or a 1:1 mixture of dichloromethane and light petroleum (b.p. < 40 °C) as eluant. Removal of the solvent from appropriate fractions at  $\geq 15 \text{ mmHg}/0 \,^{\circ}\text{C}$  afforded the desired peroxide (2) which was finally purified by trap-to-trap distillation.

In this way cis-but-2-ene was converted into the known<sup>1</sup> s-butyl t-butyl peroxide in 63% yield, while trans-hex-3ene, cyclopentene, and cyclohexene afforded the corre-

sponding previously unknown peroxides in yields of 24, 59, and 61% respectively. The new compounds were characterised by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy and had satisfactory C and H analyses.

The remarkable effectiveness of the new procedure can be seen by comparing the yields it provides with those achieved by reducing the same peroxymercurials with sodium borohydride. By the latter technique cyclopentyl and cyclohexyl t-butyl peroxides were obtained in 2 and 13% yield, respectively, while it proved impossible to isolate any of the s-butyl or 3-hexyl compounds (spectroscopic analysis confirmed that these peroxides were only very minor components of the crude products). A further measure of the success of the new method is provided by comparing it with the recently reported<sup>7</sup> silver-salt-assisted t-butyl perhydrolysis of alkyl bromides, equation (3).

$$\begin{array}{ll} \operatorname{RCH}(\operatorname{Br})\operatorname{CH}_2\mathrm{R} + \operatorname{Bu}^t\operatorname{OOH} + \operatorname{AgO}_2\operatorname{CCF}_3 \rightarrow \\ \operatorname{RCH}(\operatorname{OOBu}^t)\operatorname{CH}_2\mathrm{R} + \operatorname{AgBr} + \operatorname{HO}_2\operatorname{CCF}_3 \quad (3) \end{array}$$

In our hands the silver salt method provided s-butyl, 3-hexyl, cyclopentyl, and cyclohexyl t-butyl peroxides in yields of only 24, 36, 31, and 6%, respectively.

We believe that the reduction of peroxymercurials (1) by tributyltin hydride again proceeds via  $\beta$ -peroxyalkyl radicals [cf. equation (1)], and in keeping with this view the only byproducts detected in the reactions were the corresponding epoxides. The higher yields of peroxides compared with those from reduction by borohydride must, then, arise from an enhancement of the rate of hydrogen abstraction. Tributyltin hydride is undoubtedly a better hydrogen donor than borohydride, but past evidence<sup>8</sup> would suggest that a common organomercury hydride may be involved in the demercuriations. Concentration effects favouring the bimolecular process are probably a factor in the success of the new procedure.

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