

Synthesis of Alkyl Hydroperoxides by Hydroperoxymercuration and Reduction

A. J. Bloodworth,* Christopher J. Cooksey and Despoina Korkodilos

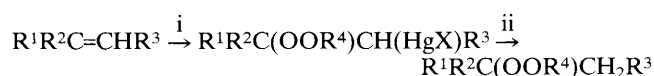
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Alkyl hydroperoxides, $R^1R^2C(OOH)CH_2R^3$, have been prepared from 30% hydrogen peroxide by hydroperoxymercuration of the corresponding alkenes, $R^1R^2C=CHR^3$, followed by addition to 2-methoxypropene, reductive demercuration with basic sodium borohydride and deprotection of the resultant 2-methoxyprop-2-yl derivatives, $R^1R^2C(OOCMe_2OMe)CH_2R^3$, with aqueous acetic acid.

The preparation of alkyl hydroperoxides (ROOH) is a challenging problem. The most generally applicable route involves the alkylation of hydrogen peroxide. Although a number of variants of this method has been described,¹ none is wholly satisfactory. Harsh conditions and prolonged reaction times are often required leading to decomposition of sensitive hydroperoxides. Yields are frequently low, especially for secondary alkyl compounds. The formation of appreciable amounts of the corresponding dialkyl peroxide (ROOR) is another common problem. In a recent report,² 2-methoxyprop-2-yl hydroperoxide was used as a masked form of hydrogen peroxide to try to avoid some of these difficulties. This prompts us to disclose our new preparation of alkyl hydroperoxides since it similarly involves the intermediacy of peroxyacetals, $ROOCMe_2OMe$.

We have previously shown that the alkyl peroxymercuration of alkenes coupled with reductive demercuration

(Scheme 1) provides a versatile route to dialkyl peroxides.³ Furthermore it is particularly well suited to the preparation of secondary alkyl compounds ($R^2 = H$).



Scheme 1 Reagents: i, R^4OOH , HgX_2 ; ii $NaBH_4$, $NaOH$

Direct extension to the preparation of alkyl hydroperoxides ($R^4 = H$) is not possible because the hydroperoxide group is reduced under the conditions of demercuration. However, we now find that conversion of the hydroperoxymercurials **1**⁴ into the 2-methoxyprop-2-yl derivatives **2** protects the peroxide linkage during borohydride reduction. Subsequent deprotection then affords the alkyl hydroperoxides **4**. The four-step procedure (Scheme 2) is easy to carry out, involves

