The Alkyl Peroxymercuration of Terminal Alkenes; a Synthesis of Secondary Alkyl Peroxides and β-Functionally Substituted Peroxides

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Summary t-Butyl hydroperoxide reacts with 1-alkenes in the presence of mercuric acetate to yield 2-alkyl-2-t-butylperoxyethylmercuric acetates [$Bu^tO\cdot O\cdot CHR\cdot CH_2\cdot Hg\cdot OAc$]; the carbon–mercury bond of the product may be cleaved with sodium borohydride or halogens to give good yields of 1-alkylethyl t-butyl peroxide and 1-alkyl-2-halogeno-ethyl t-butyl peroxide, respectively.

The acetoxy-, alkoxy-, and hydroxy-mercuration of alkenes have been studied extensively[1,2] since the initial work of Hofmann and Sand.[3] The generally accepted mechanism for oxymercuration involves nucleophilic attack of an oxy-reagent (HOAc, HOR or H_2O) upon an intermediate mercurinium ion formed from the alkene and a mercuric salt, usually mercuric acetate.[2]

The relative nucleophilicity of alkyl hydroperoxides (HO·OR) suggested that they, too, should be capable of attacking the mercurinium ion to provide β-mercury-substituted peroxides, which would be new examples of β-metallo-substituted peroxides whose properties we are investigating.[4] This prediction has been realised for t-butyl hydroperoxide and we report here the first examples of the alkyl peroxymercuration of alkenes.
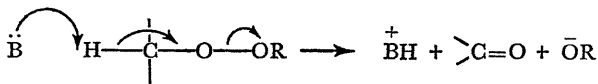
The alkene (20 mmole) is added dropwise to a well stirred mixture of mercuric acetate (20 mmole) and 60% t-butyl hydroperoxide (ca. 30 mmole; containing di-t-butyl peroxide) in dichloromethane (25 ml.) under nitrogen. The reaction is complete within 20 min. and, after filtration and removal of volatile material in vacuo, the 2-alkyl-2-t-butylperoxyethylmercuric acetate (I) is obtained as a

viscous oil contaminated with some 15% 2-alkyl-2-acetoxy-ethylmercuric acetate (II) arising from competitive acetoxy-mercuration. Acetoxymercuration still occurs if the peroxymercuration is carried out using 60% t-butyl hydroperoxide as the solvent.

$$R\cdot CH{:}CH_2 + Hg(OAc)_2 + HO\cdot OBu^t \xrightarrow[-HOAc]{CH_2Cl_2}$$

R = Bu, n-C$_6$H$_{13}$, Ph, n-C$_8$H$_{17}$
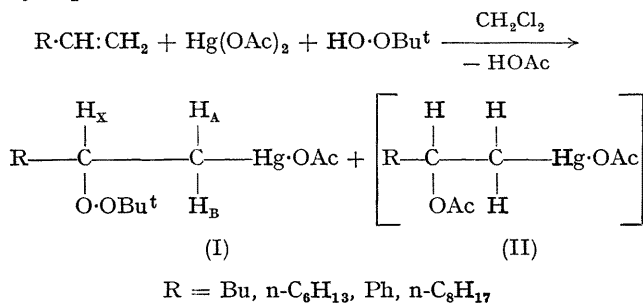
The orientation of addition to terminal alkenes was established from ^{1}H n.m.r. spectra. The mercurials (I) show a characteristic multiplet for H$_X$, the X part of an ABX system resulting from the asymmetry generated at the new secondary alkyl group. The structures of peroxides (I) were confirmed by i.r. and mass spectra. The mass spectrum showed the parent ion and a very intense ion corresponding to loss of mass 89 (O·O Bu^t), both peaks exhibiting the correct mercury isotope pattern.

The synthesis of s-alkyl peroxides by conventional acid- or base-catalysed alkylation of hydroperoxides is difficult because rates by both uni- and bi-molecular mechanisms are minimal. Under acid conditions the generation of a secondary carbonium ion is not easily achieved, and under strongly basic conditions the product decomposes *via* a carbonyl-forming elimination:[5]

Brown[6] has exploited hydroxymercuration as a conveniently mild method for the Markovnikov hydration of alkenes by reducing the intermediate mercurials with sodium borohydride. A similar reduction of our mercurials (I) provided the 1-alkylethyl t-butyl peroxides (III) in yields of 50—60% after distillation. From 1-phenylethyl bromide and potassium t-butyl peroxide the best reported yield of 1-phenylethyl t-butyl peroxide is 33%, working on a scale fifteen times that of ours; the procedure was a lengthy one with many purification stages.[7] The structures and purity of peroxides (III) were established from elemental analysis, i.r., n.m.r., and mass spectra, and for 1-phenylethyl t-butyl peroxide (from styrene) by deliberate base-catalysed decomposition to t-butyl alcohol and acetophenone.
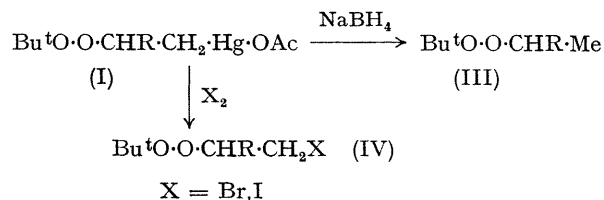
By cleaving the mercury–carbon bond with other reagents, new β-substituted peroxides can be obtained. Thus bromine and iodine yielded 1-alkyl-2-halogenoethyl t-butyl peroxides (IV).

Extension of these reactions to other alkyl hydroperoxides and hydrogen peroxide† should provide a general route to s-alkyl peroxides and their β-substituted derivatives. Furthermore, reaction with other classes of alkenes, notably 1,1-di-, tri- and tetra-alkylethenes, will presumably yield t-alkyl peroxides.

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† We have just become aware of the publication by Reutov[8] describing the hydroperoxymercuration of styrene.

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