Peroxymercuration of Dienes; a Simple Route to New Cyclic Peroxides

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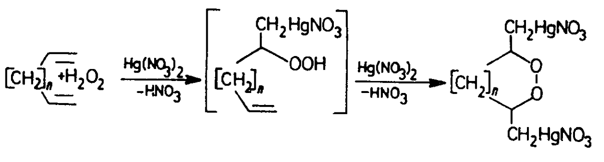
Summary Cyclic peroxides of the form $\overline{\mathrm{O{-}(XCH_2)CH[CH_2]_{\mathit{n}}CH(CH_2X){-}O}}$ (X = HgCl, Br, or H; n = 1 or 2) have been prepared in high yield *via* the reaction of dienes with hydrogen peroxide and mercury(II) nitrate.

EXISTING routes to simple 1,2-dioxacyclo-pentanes and -hexanes give poor yields[1] and are intrinsically unsuitable for the virtually unknown† secondary alkyl compounds. We now report that these cyclic peroxides can readily be prepared from commercially available starting materials by a variant of the peroxymercuration of alkenes.[2]

The principle underlying the method is that the hydroperoxymercuration of suitable dienes affords unsaturated hydroperoxides capable of cyclising by a subsequent intramolecular peroxymercuration (equation 1); similar reactions with water[3] and primary amines[4] have proved efficient in the synthesis of other heterocyclic compounds containing saturated 5- or 6-membered rings.



(1)

(I)

a, n = 1
b, n = 2

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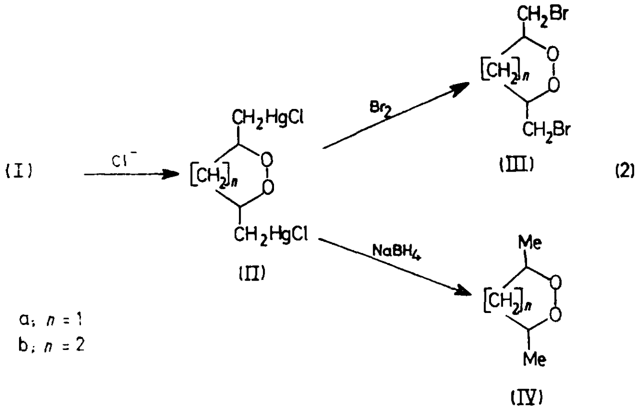
† Corey *et al.* (E. J. Corey, K. C. Nicolaou, M. Shibasaki, Y. Machida, and C. S. Shiner, *Tetrahedron Letters*, 1975, 3183) have recently described the synthesis of *cis*-3-methyl-5-(2-phenylethyl)-1,2-dioxacyclopentane in 35% yield from the corresponding bis-methanesulphonate and potassium superoxide.

The ^1H and ^{13}C n.m.r. spectra (in D_2O) of the oil obtained (after 15 min) from adding penta-1,4-diene (5 mmol) in dichloromethane (5 cm^3) to a well stirred suspension of $Hg(NO_3)_2 \cdot H_2O$ (10 mmol) and 80% H_2O_2 (5 mmol) in dichloromethane (25 cm^3) showed that it contained approximately equal amounts of *cis*- and *trans*-3,5-bis(nitratomercuriomethyl)-1,2-dioxacyclopentane (Ia). The corresponding organomercury chloride, (IIa) (91%), m.p. 119—121 °C (decomp.), was precipitated from aqueous solution by adding KCl (equation 2). A similar sequence with hexa-1,5-diene gave the *cis*- and *trans*- isomers (*ca.* 3 : 1 ratio) of the dioxacyclohexane (IIb) (72%), m.p. 158—162 °C (decomp.). Mercury(II) trifluoroacetate can be used instead of the nitrate[5] but the reactions are less clean and the yields inferior.



Mercury-free cyclic peroxides can be obtained by halogenolysis or reduction of the organomercury chlorides (equation 2). Thus the bis-bromomethyldioxa-cyclopentane (IIIa) (55%) (oil) and -cyclohexane (IIIb) (82%), m.p. 63—70 °C, were obtained *via* brominolysis in dichloromethane.[6] As with acyclic peroxides[7] hydrogenodemercuration is less clean, but the dimethyl compounds (IVa) and (IVb) constituted 85% of the oils (74% and 98% respectively) obtained upon reduction. The proportions of *cis* to *trans* isomers in the mercury-free peroxides reflect (and confirm) those found in the crude organomercury nitrates (I). Pure *cis*-(IIIb), m.p. 91—92 °C, was isolated by fractional crystallisation from a mixture of pentane and dichloromethane.

All the peroxides described here are new and the compounds (II)—(IV) had satisfactory C and H analyses. Their i.r. spectra showed no absorptions in the OH-stretching region thus confirming the absence of hydroperoxides. The ^1H and proton-decoupled ^{13}C n.m.r. spectra are consistent with the proposed formulae, and the compounds undergo base-induced decomposition as expected for secondary alkyl peroxides.

The method should make available other novel cyclic peroxides. Preliminary results indicate that *cis,cis*-cycloocta-1,5-diene affords a transannular peroxide, and penta-1,3-diene a 1,2-dioxacyclopentane with functionality in the ring.

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