Isomerization of peroxyl radicals ROO via hydrogen self-abstraction to form hydroperoxyl radicals QOOH (e.g. CH₃CH₂OO → CH₂CH₂OOH) is a crucial step in hydrocarbon combustion. However, the kinetic measurements are difficult and definitive rate constants for ROO isomerisation are rare. In addition, the role of the QOOH radicals in hydrocarbon combustion is not well understood. We have computed the activation energy barriers and unimolecular rate constants, using BHandHLYP/6-311G** and transition state theory methods for the cyclization of a series of QOOH radicals (containing 2 to 5 carbon atoms) resulting in the formation of a cyclic ether and the elimination of an OH radical. The computations predict that cyclization of QOOH to form a 3-membered ring (e.g. cyclization of CH₂CH₂OOH to form oxirane) is a dominant channel of unimolecular decomposition for QOOH. For example, the computations predict a constant rate of 8.24 × 10⁸ s⁻¹ for the cyclization of CH₃CH₂CH₂CHCH₂OOH at 700 K. Analysis of the vibrational modes of the transition state structures suggests that there is rotational excitation of the OH radical. These reactions are therefore amenable to experimental investigation by spectroscopic measurement of OH concentrations.