Chapter 8

Reactions Involving Perseleninic Acids

Reaction of arsene-seleninic acids with hydrogen peroxide produces new species which possess oxidative properties different from those expected from seleninic acid and hydrogen peroxide when used alone. The new species which have been described as perseleninic acids [but may also have a peroxo structure, Scheme 142] have been successfully used for the epoxidation of olefins as well as for the Baeyer-Villiger oxidation of cyclanones, possess a reactivity different from that of the corresponding benzeneselenonic acids [312].

\[
\begin{align*}
&\text{O} \quad \text{H}_2\text{O}_2 \quad \text{O} \\
&\text{RSe-OH} \quad \Leftrightarrow \quad \text{RSe-OH} \\
&\text{O} \quad \text{O} \\
&\text{RSe-\text{O}H} \quad \Leftrightarrow \quad \text{RSe-\text{O}H} \\
&\text{R}=\text{Ph}; \ 4\text{-NO}_2\text{Ph}; \ 2,4\text{-}(\text{NO}_2)_2\text{Ph}; \ 2,4,6\text{-}(\text{Me})_3\text{Ph}
\end{align*}
\]

Scheme 142 [338]

The first results in this field have been obtained simultaneously by five research groups [336–340] which used an excess (5 to 8 mol. equiv.) of hydrogen peroxide to perform the synthesis of \(\alpha,\beta\)-unsaturated ketones [159, 336] from \(\alpha\)-arylselenoketones and of allyl alcohols [337, 341–344] from \(\beta\)-hydroxy-selenides (Volume II), being part of complex molecules bearing additional carbon-carbon double bonds. These were unexpectedly oxidized to the corresponding epoxides probably by a perseleninic acid species formed on oxidation, by the excess of hydrogen peroxide used, of the unstable selenenic acids generated as by-products [159, 338, 345, 346]. These side reactions can be suppressed if smaller quantities of hydrogen peroxide are used (i.e. 2 equiv. \(\text{H}_2\text{O}_2\) are enough to permit both the selenoxide formation and the transformation of the selenenic acid concomitantly produced to the seleninic acid). The aptitude of the new reagent formed from seleninic acid and hydrogen peroxide to oxidize various functional groups was later tested.

8.1 Oxidation of Olefins to Epoxides

It was described by Grieco [336], Sharpless [338] and Reich [339] that arsene-seleninic acids/hydrogen peroxide mixtures are able to epoxidize carbon-
carbon double bonds. Although several conditions have been tested which lead to closely related results, subtle differences have appeared from time to time (Schemes 143, 144, 145).

The following conditions have been successfully tested

(i) Benzeneseleninic acid (1.4 equiv.)/hydrogen peroxide (50%, 1.4 equiv.), the reaction being conducted in methanol in the presence of a phosphate buffer and silicagel which proved essential for the success of the reaction (Method A)

(ii) 2-nitrobenzeneseleninic acid [338] and 2,4-dinitrobenzeneseleninic acid