Introduction

The relevance of gem-dihydroperoxides to peroxidic anti-
malarial agents stimulated initial interest in this class of
compounds.1–5 Apart from their biological activities,6,7
gem-dihydroperoxides have been established as important
building blocks in synthetic chemistry, for example the
preparation of organic peroxides, trioxanes, tetraoxanes,
spirobisperoxyketals, and dicarboxylic diesters.4,7,8

gem-Dihydroperoxides can also be employed as oxidizing
agents under various conditions to perform transforma-
tions such as epoxidation1–5 and sulfoxidation.2–5,9 In ad-
dition, in situ decomposition of gem-dihydroperoxides
can generate singlet oxygen as the active oxidant8,10 in
olefin oxidation, for example.11 The ability of gem-di-
hydroperoxides to generate radicals allows them to be fur-
theremore exploited as radical initiators,2–5 for example
methyl ethyl ketone peroxide is used in the manufacturing
of acrylic resins, reinforced plastics, and unsaturated
polyester resins.6

Itoh and co-workers established two catalyst-free prepar-
ative protocols for gem-dihydroperoxides, of which the
one employs hydrogen peroxide12 as terminal oxidant and
the other molecular oxygen.13,14 The latter is achieved in
combination with a photosensitizer (anthracene13 or
anthraquinone14) and exposure of the reaction mixture to
light. Reaction times can generally be reduced upon introduc-
tion of a catalyst, amongst which molecular iodine15
as well as numerous transition-metal Lewis acids have
proven effective.4,5,8,16,17 Brønsted acids are comparably
active as either homogeneous (sulfuric acid3) or heteroge-
neous catalysts, for example silica-sulfuric acid2 or triflic-
acid-functionalized silica-coated ferromagnetic nanopar-
ticles.18

Abstracts

(A) Dussault and co-workers19 prepared primary and secondary al-
ky al hydroperoxides in moderate to high yields (48–79%) via double
alkylation of 1,1-dihydroperoxides, followed by acid-catalyzed hy-
drolysis of the resulting strained cyclic alkylated gem-bishydroper-
oxides (bisperoxyacetals).

(B) 1-Hydroxy-1′-alkoxyperoxides were prepared by Terent’ev et
al.6 in moderate yield (40–64%) through iodine-catalyzed cross-cou-
pling of gem-bishydroperoxides and acetals. This cross-coupling is
also effective upon substitution of the acetal with an enol ether.

(C) Symmetrical and asymmetrical tetraoxanes can be prepared
from gem-dihydroperoxides. The combination of a gem-dihydroper-
oxide and its carbonyl analogue in the presence of fluoroboric acid
and hydrogen peroxide favors formation of symmetrical tetra-
oxanes.20 Similarly, asymmetrical tetraoxanes are obtained when
two non-identical carbonyl compounds are introduced.7

SYNLETT 2014, 25, 1629–1630
Advanced online publication: 20.05.2014
© Georg Thieme Verlag Stuttgart · New York
(D) Jakka et al.\textsuperscript{1} reported the epoxidation of various \(\alpha,\beta\)-unsaturated ketones utilizing cyclohexylidene-bishydroperoxide as a stoichiometric oxidant under Weitz–Scheffer reaction conditions (aqueous, alkaline).

(E) Sulfoxidation of thiophenol ethers can be achieved under neutral conditions at ambient temperature, producing sulfoxides in high yields (79–93%) in less than two hours.\textsuperscript{9}

(F) Subsequent to observing the oxidation of triphenylphosphine to triphenylphosphine oxide in the presence of 1,1-dihydroperoxy-cyclohexodecane, Sekine and co-workers\textsuperscript{21} prepared oligodeoxyribonucleotides in a similar fashion via the oxidation of phosphite intermediates to their respective phosphate analogues.

(G) Dussault and co-workers reported the liberation of singlet oxygen when monoactivated gem-dihydroperoxide derivatives were exposed to anhydrous alkaline conditions.\textsuperscript{22} If this degradation is performed in the presence of an organic substrate, an oxidative transformation of the substrate is observed.\textsuperscript{10} This protocol also allows for oxidative cleavage of olefinic substrates to yield aldehydes or ketones in moderate to high yields (35–82%).\textsuperscript{11}

\begin{align*}
\text{R} & \quad \text{aq. KOH, 1,4-dioxane} \\
& \quad \text{r.t., 0.5–5 h} \\
\text{11} & \quad \text{12} \\
\text{13} & \quad \text{14} \\
& \quad \text{CH}_2\text{Cl}_2 \\
& \quad \text{r.t., 0.5–2 h} \\
\text{15a} & \quad \text{15b} \quad \text{15c} \\
\text{15} & \quad \text{16} \\
& \quad \text{17} \\
& \quad \text{18} \\
& \quad \text{19} \\
& \quad \text{20} \\
& \quad \text{10 min} \\
& \quad \text{21} \\
& \quad \text{22} \\
& \quad \text{23} \\
& \quad \text{24} \quad \text{(82%)}
\end{align*}

References