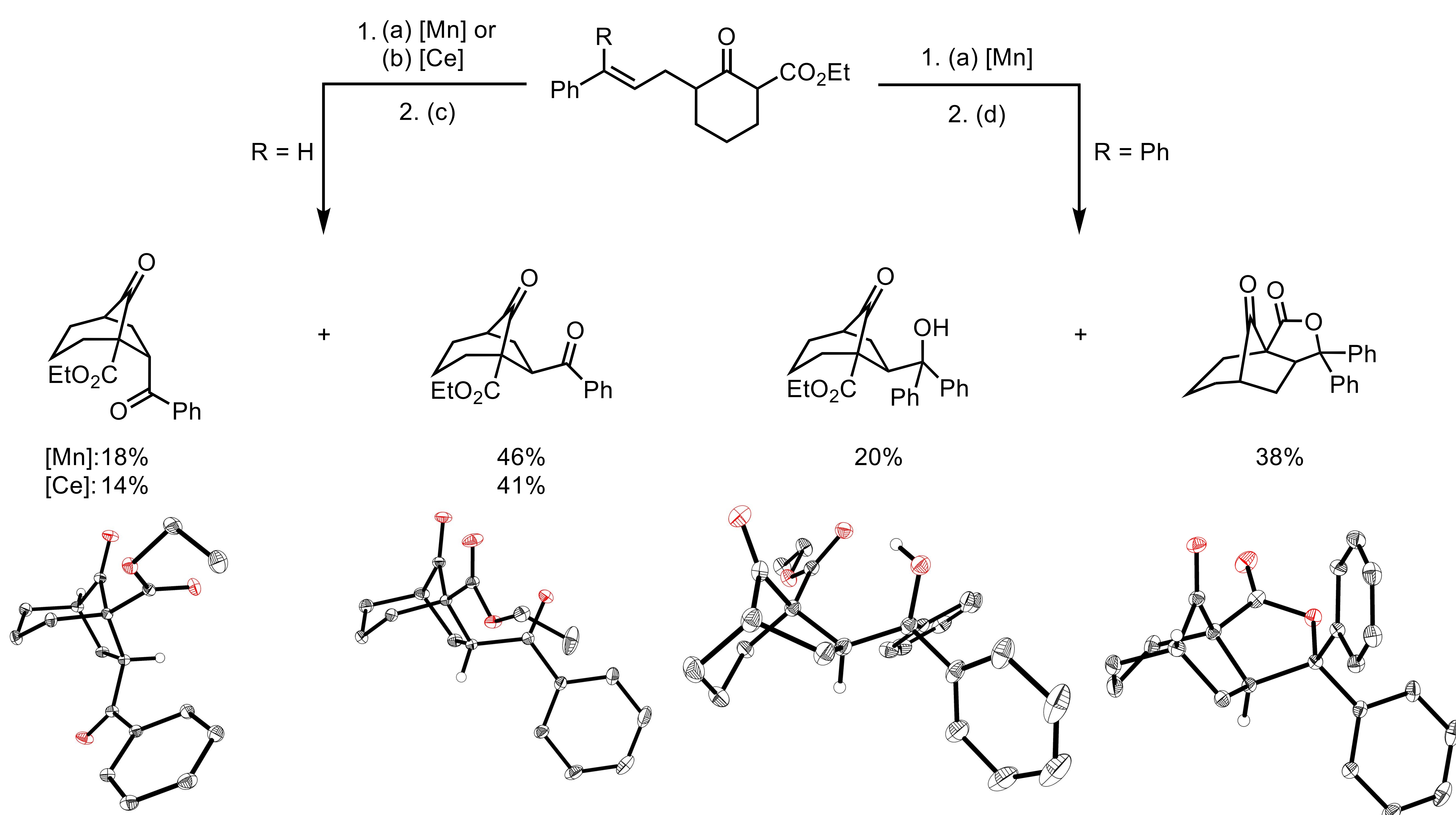


1,4-Diketones were synthesized by a cerium-catalyzed intramolecular C–C coupling reaction of β -oxo- γ -allyl esters. The nontoxic and inexpensive $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$ and the atmospheric oxygen which is the oxidant in this reaction are optimal from economic and ecological point of view.

Introduction

The cerium-catalyzed oxidative coupling of β -oxoesters with enol acetates or olefines like styrene has been recently developed by our group. Therein, products with a 1,4-diketone moiety are furnished.^[1] We now wish to report on an intramolecular radical cyclization of β -oxo- γ -allyl esters. When those esters react with catalytic amounts of $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$ or a stoichiometric amount of $\text{Mn}(\text{OAc})_3 \cdot 2 \text{H}_2\text{O}$ and atmospheric oxygen, the tricyclic endoperoxide is obtained as an intermediate. The latter can be further employed in a Kornblum-DeLaMare rearrangement giving a mixture of *endo*- and *exo*-1,4-diketones. Furthermore, by reductive cleavage of the peroxide moiety with zinc in acetic acid, an alcohol is obtained, which undergoes intramolecular cyclization for the formation of an *exo*-lactone.



(a) 1.1 equiv. $\text{Mn}(\text{OAc})_3 \cdot 2 \text{H}_2\text{O}$, O_2 (air), AcOH, 16 h, r.t.; (b) 0.05 equiv. $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$, O_2 (air), $\text{F}_3\text{CCH}_2\text{OH}$, 16 h, r.t.; (c) 5.0 equiv. pyridine, 6.0 equiv. AcCl, DCM, 16 h, r.t.; (d) 5.0 equiv. Zn, AcOH, 16 h, r.t.

Mechanistic Proposal

For the mechanism of the radical cyclization, a radical chain reaction is assumed. After the initial formation of the α -radical **2** from the β -oxo- γ -allyl ester **4** with Ce(IV) or Mn(III), it is assumed that an intramolecular cyclization to the bicyclic radical **1** takes place. The reaction of radical **1** with dioxygen would lead to peroxy-species **3**, which then closes the radical chain reaction by H-atom abstraction from β -oxo- γ -allyl ester **4** with the regeneration of α -radical **2** under formation of hydroperoxide **5**. The latter undergoes cyclotautomerization to the 1,2-endoperoxide derivative **6**, which can be transfer in a Kornblum-DeLaMare rearrangement (when R = H), giving a mixture of *endo*- and *exo*-1,4-diketones **7**.

