

SmI_2 -Induced Ring Expansion Reactions of Alkyl (n+1)-Oxobicyclo[n.1.0]alkane-1-carboxylates

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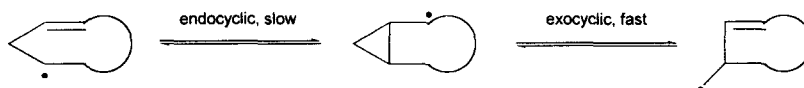
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Abstract: Alkyl 4-oxocycloalkanecarboxylates were prepared in good yield via ring expansion reactions of alkyl (n+1)-oxobicyclo[n.1.0]alkane-1-carboxylates mediated by SmI_2 -induced single electron transfer in THF/MeOH.

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Recent advances in the ring opening reactions of three-membered rings have led to the steadily increasing utilization of cyclopropyl derivatives as reagents for organic synthesis.¹⁻³ In this respect, ring opening of the cyclopropylcarbinyl radical has proved to be a useful strategy for ring expansion because cleavage of the three-membered ring takes place easily and the usually disfavored entropy effect associated with medium and large size ring formation can be avoided.^{4,5} However, the literature on bicyclo[n.1.0] radicals reveals a preference for stereoelectronically controlled exocyclic radical ring opening as opposed to thermodynamically favored endocyclic ring opening.⁶⁻¹⁰ The



exocyclic cleavage has been achieved usually under the reaction conditions such as electrolysis,¹¹ samarium iodide,¹² alkali metal^{13,14} and photochemical electron transfer.¹⁵ Recently, it was reported that methyl 5-oxobicyclo[4.1.0]heptane-1-carboxylate was converted into methyl 4-oxocycloheptanecarboxylate under radical condition (*n*- Bu_3SnH /AIBN).¹⁶ However, this reaction was carried out under harsh conditions, and the yield was only 69%. As part of our continuing effort to expand the synthetic utility of cyclopropanes, we reported the preparation of 3-alkenylcyclohexanones via exocyclic ring opening reactions of bicyclo[n.1.0]-2-heptanones¹⁷ as well as cyclopentanones, furans and unsymmetric dialkenyl ketones from ring opening reaction of 1-alkenyl-1-methoxy cyclopropane derivatives containing anion stabilizing groups.^{18,19} We now report convenient SmI_2 -induced ring opening reactions of alkyl (n+1)-oxobicyclo[n.1.0]alkane-1-carboxylates via endocyclic ring opening, as outlined in scheme 1.

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Scheme 1

Initial studies were performed with benzyl 5-oxobicyclo[4.1.0]heptane-1-carboxylate **3** (entry 3, Table 1), which could be prepared from phosphoniosilylation²⁰ and cyclopropanation²¹ of α,β -enones. When a solution of samarium(II) iodide was added to a solution of **3** in THF, 4-oxocycloheptanecarboxylate (**9**) was obtained in 44% yield. HMPA and DMPU as additives were ineffective for increasing the yield. We next turned our attention to the possible uses of alcohols, known to be very effective proton source for SmI₂-induced single electron transfer reaction.²² When methanol was added to reaction mixture, the desired compound **9** was obtained in 89% yield.²³ When an equimolar amount of SmI₂ was added to **3**, **9** was obtained in 27% yield, and the starting material was recovered. The use of 2 to 3 equiv of SmI₂ gave better results, yielding **9** in 62% and 89% yield, respectively. Thus, the remaining reactions were carried out with 3 equiv of SmI₂ for each mole of alkyl (n+1)-oxo bicyclo[n.1.0]alkane-1-carboxylate.

Table 1 summarizes the experimental results and illustrates the efficiency and scope of the present method. Monocyclic compound **1** (entry 1) reacted readily and gave a good yield of 5-keto ester **7**. In case of bicyclo[4.1.0] system (entries 4, 5) containing methyl groups, the reaction afforded the desired compounds **10** and **11**. When SmI₂ was added to a bicyclo[3.1.0] (entry 2) and [5.1.0] (entry 6) compound under the same conditions, the desired products **8** and **12** were obtained in 83 and 85% yields, respectively. Ketone **6** was prepared from α,β -enones using 1,2-reduction,²⁴ cyclopropanation,²⁵ followed by oxidation.²⁶

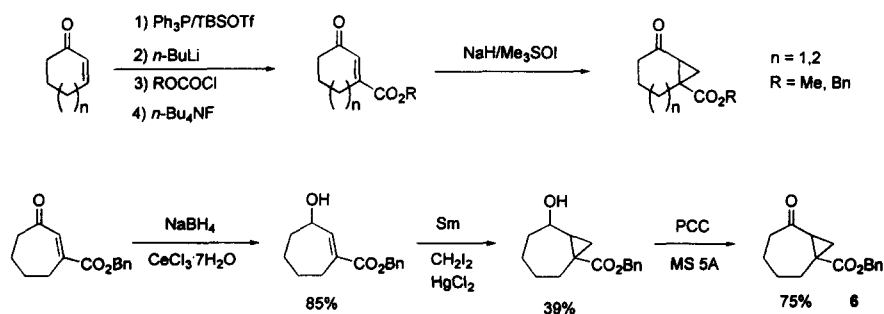
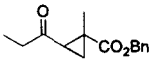
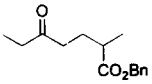
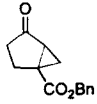
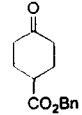
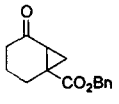
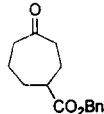
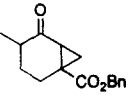
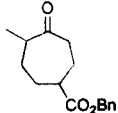
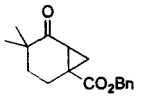
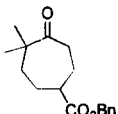
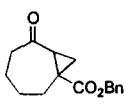
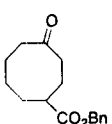


Table 1. Ring Expansion Reactions of Alkyl (n+1)-Oxobicyclo[n.1.0]alkane-1-carboxylates

entry	starting material	product	isolated yield/%
1	 1	 7	51
2	 2	 8	83
3	 3	 9	89 94 ^a 44 ^b
4	 4	 10	71(56:44) ^c
5	 5	 11	85
6	 6	 12	85

^aMethyl ester instead of benzyl ester was used. ^bMethanol was not used.

^cDiastereomer ratio

In summary, SmI_2 provides a new, useful route to cleave the bridged bond of alkyl (n+1)-oxobicyclo[n.1.0]alkane-1-carboxylates to prepare various alkyl 4-oxocycloalkanecarboxylates. Because the exocyclic cleavage of cyclopropyl ketone derivatives was reported mainly in prior work, the present method contrasts with the existing synthetic methods.

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