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Further Studies on Radical Cyclizations of N-Aziridinyl Imines. Carbonyl and Alkenyl Group vs. N-Aziridinyl Imino Group Competition

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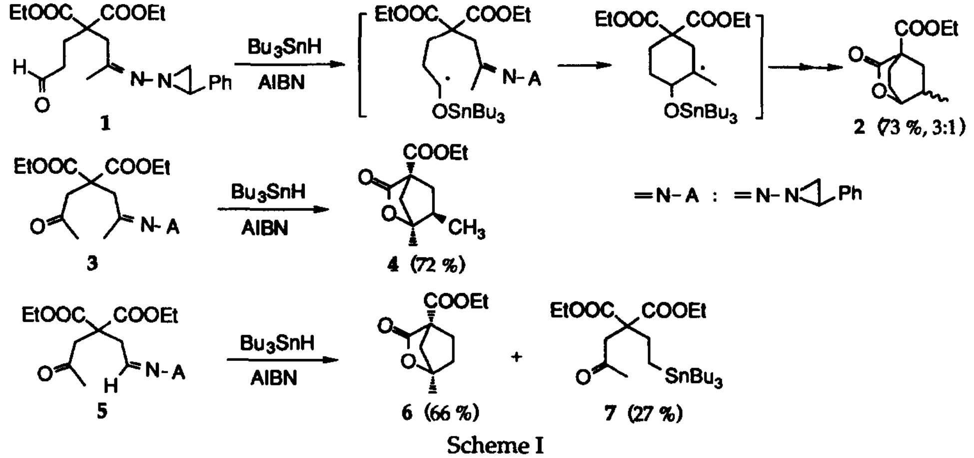
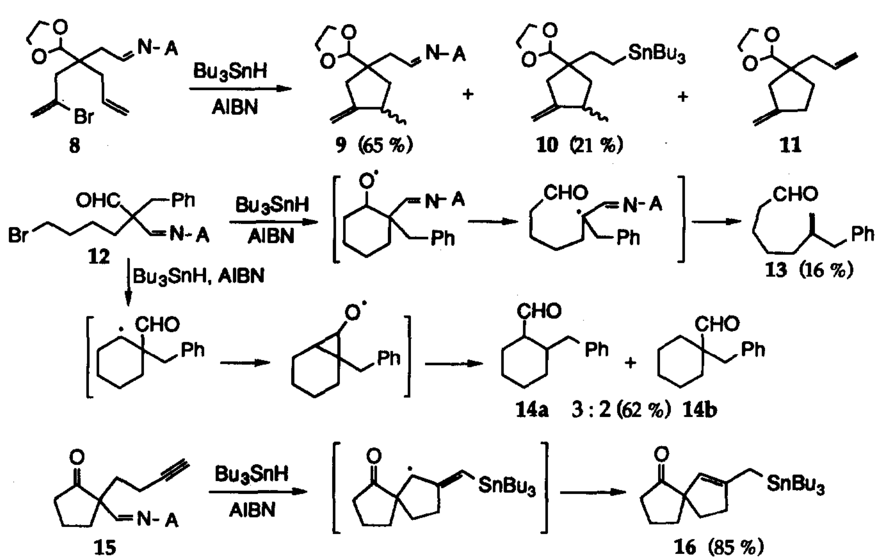
Abstract: Carbonyl and alkenyl groups vs. N-aziridinyl imino groups competitions as radical precursors as well as radical acceptors are described.

The dual ability of carbonyl, alkenyl, and alkynyl groups to function as radical precursors as well as radical acceptors is of great importance for synthetic application, since it will diversify carbon-carbon bond formation by radical methods.[1] Each group has unique characteristics that permit the generation of radicals from multiple bonds or the addition of radicals to multiple bonds in a selective manner. Although alkenyl vs. carbonyl groups competitions in radical cyclizations have been studied,[2] competition studies of carbonyl and alkenyl groups vs. imino groups have not been reported. Recently we have reported novel radical cyclizations of N-aziridinyl imines in which N-aziridinyl imino groups have been utilized as radical precursors as well as radical acceptors.[3] We wish to report the preliminary results on carbonyl and alkenyl groups vs. N-aziridinyl imino groups competitions in radical cyclizations.

The competition between a formyl and an N-aziridinyl imino group as a radical precursor was examined. Our initial study was conducted with **1**. Treatment of **1** with Bu_3SnH / AIBN in refluxing toluene for 2 h afforded a 3:1 diastereomeric mixture of **2** in 73 % yield, indicative of preferential attack of Bu_3Sn radical to the formyl group over the imino group as shown in Scheme I. The preference of a keto group over an imino group was observed with **3**. However, the competition study with **5** indicated that addition of Bu_3Sn radical to the imino group took place to some extent, yielding **6** and **7** in 66 % and 27 % yield, respectively.



Scheme I



Scheme II

Our next attention was given to the effectiveness of the N-aziridinyl imino group as a radical acceptor. **8** was synthesized by routine operations to study the competition between an alkenyl and an imino group. Treatment of **8** with 1.1 equiv of Bu_3SnH and 0.1 equiv of AIBN in refluxing benzene for 2 h afforded **9** in 65 % yield along with 21 % of **10** and 8 % of the starting material, thereby showing the preference of the alkenyl group over the imino group as a radical acceptor. Apparently, **10** was derived from further Bu_3Sn radical addition to **9** and there was no indication of the presence of **11**. Thus, the use of 2.2 equiv of Bu_3SnH and 0.1 equiv of AIBN gave **10** as the only product in 80 % yield. The competition between a formyl and an imino group was next studied. Reaction of **12** with Bu_3SnH / AIBN in refluxing benzene for 2 h afforded a 16:62 mixture of **13** and **14**. Apparently, **13** resulted from attack of the alkyl radical to the formyl group, whereas **14** was produced from initial attack of the alkyl radical to the imino group as shown in Scheme II. Furthermore, the competition between a keto and an imino group in **15** showed preferential attack of a vinyl radical to the imino group to afford **16** in 85 % yield. The relatively low efficiency of a carbonyl group over an imino group as a radical acceptor may be attributed to the reversability of cyclization onto the carbonyl group.

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