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Further Studies on 1,5-Bu_3Sn Group Transfer Reactions. 1,5-Bu_3Sn Group and 1,5-Hydrogen Atom Transfer Competition.

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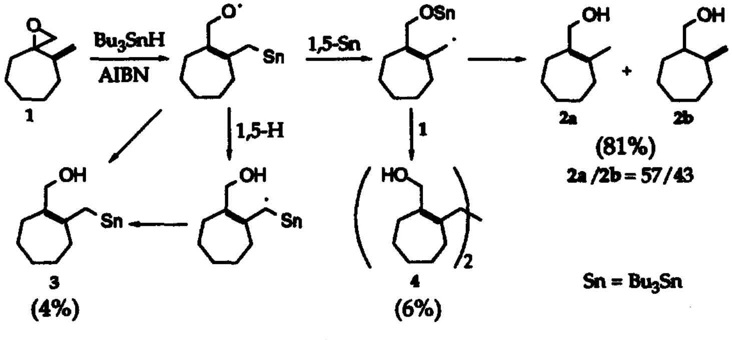
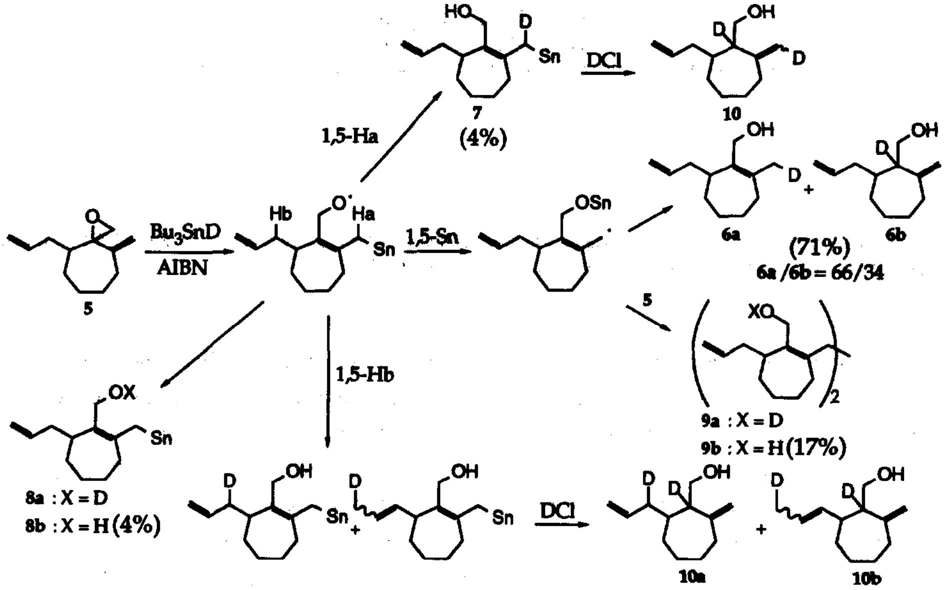
Abstract : 1,5-Bu_3Sn group transfer is favored over 1,5-hydrogen atom transfer roughly in a ratio of 20:1. 1,5-Bu_3Sn transfers from carbon to carbon and from enoxy oxygen to carbon are observed for the first time.

1,5-Hydrogen atom transfer reactions are one of the most well-known radical rearrangements[1] and proved to be synthetically useful in radical cyclization, addition and fragmentation reactions via radical translocations.[2] However, radical rearrangement of R_3Si, R_3Ge and R_3Sn groups has not received much attention,[3] although it appears feasible because the release in bond energy would be accompanied by rearrangement. In this regard, we have reported a novel 1,5-Bu_3Sn group transfer reaction from carbon to oxygen.[4] During further studies on 1,5-Bu_3Sn group transfer reactions, when **1** was treated with Bu_3SnH/AIBN in refluxing benzene for 3 h, we were able to isolate **3** in 4% yield along with 81% of **2** and 6% of **4**.[5] The yield of **3** did not change under high diluted conditions, indicating the possibility of 1,5-H transfer rather than direct quenching of an alkoxy radical by Bu_3SnH.

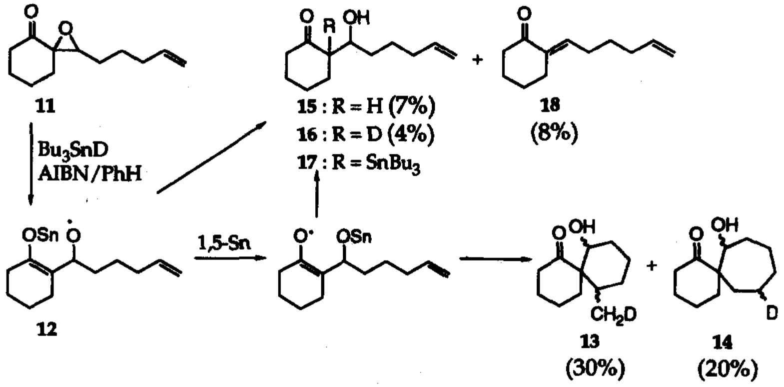


Scheme 1

To explore an intriguing possibility of 1,5-Bu_3Sn vs. 1,5-H transfer competition, we prepared **5** by routine operations. Radical reaction of **5** with Bu_3SnH/AIBN may give rise to several different products, resulting from 1,5-Bu_3Sn transfer, two types of 1,5-H transfer, and direct quenching. Slow addition of a solution of Bu_3SnD (1.2 equiv) and AIBN (0.1 equiv) in benzene (0.1M) for 3 h to a solution of **5** in refluxing benzene (0.05M) afforded a 66:34 mixture of **6a** and **6b** in 71% yield along with a mixture of **7** and **8**(8%), and **9**(17%). The structure of **7** and **8b** was determined by treatment of a mixture of **7** and **8b** with DCl to afford **10** and **6b**.[6] From the results obtained in this study, several noteworthy features are apparent. First, 1,5-Bu_3Sn transfer from allylic carbon to oxygen is favored over 1,5-H transfer approximately in a ratio of 20:1. On the basis of the reported rate constant for 1,5-H transfer of ca. 10^8 sec^{-1},[7] the rate constant for 1,5-Bu_3Sn transfer would be estimated to be ca. 10^9 sec^{-1}. Second, there was no indication of the presence of **10a** and **10b**, suggesting that 1,5-Hb transfer did not occur. This selectivity may be attributed to α-stannyl stabilization or anchimeric assistance by 1,5-Ha transfer.[8] Third, the amount of **9** was considerably increased due to the primary isotope effect, as compared with **4**.

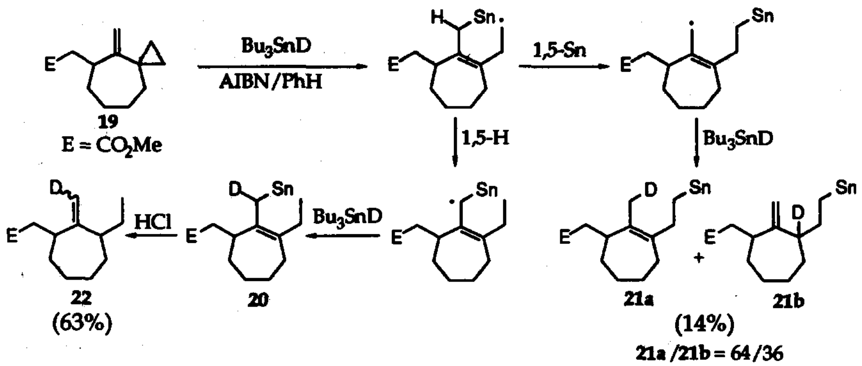


Scheme 2



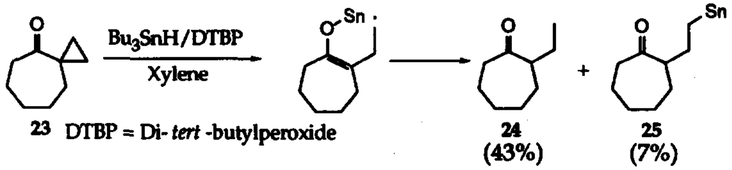
Scheme 3

We turned our attention to 1,5-Bu_3Sn transfer from enoxy oxygen to alkoxy oxygen[9] and the possibility of several competitive reactions was examined with **11**. Reaction of **11** with Bu_3SnH/AIBN in refluxing benzene under high diluted conditions afforded **13**(30%), **14**(20%), **18**(8%) and a mixture of **15** and **16**(11%),[10] along with the recovery of the starting material(14%). As shown in Scheme 3, **13**, **14**, and **16** resulted from 1,5-Bu_3Sn transfer, whereas **15** would be a direct quenching product. It is noteworthy that 6-exo cyclization of the alkoxy radical to the olefin and 1,5-H transfer in **12** did not occur,[11] indicating that 1,5-Bu_3Sn transfer from enoxy oxygen to alkoxy oxygen is much faster than 1,5-H transfer from allylic carbon to alkoxy oxygen. The formation of **18** is rather unclear and **18** may be produced via conversion of the O-metallated form to the C-metallated form (**17**), followed by thermal elimination.[12]



Scheme 4

Our next attention was given to 1,5-Bu_3Sn transfer from carbon to carbon as shown in Scheme 4. Although radical reaction of vinyl cyclopropanes has been actively studied,[13] no 1,5-Bu_3Sn transfer was reported. We felt that 1,5-Bu_3Sn transfer might occur with favorable Z-geometry of an intermediate radical in ring opening of vinyl cyclopropanes. When a 0.025M solution of **19** containing Bu_3SnD(1.2 equiv) and AIBN(0.1 equiv) was stirred in refluxing benzene for 16 h, a mixture of **20** and **21** was obtained in 85% yield. Their structures were determined by treatment of a mixture of **20** and **21** with HCl. After chromatographic separation, **22** and **21** were isolated in 63% and 14%, respectively. Apparently, 1,5-Bu_3Sn transfer reaction gave **21**, which consisted of a 64:36 mixture of **21a** and **21b** according to ^1H NMR.



Scheme 5

Finally, we examined the possibility of 1,5-Bu_3Sn transfer from enoxy oxygen to carbon. Since O-H bonds are stronger than structurally related C-H bonds, this type of radical rearrangement is rather uncommon. Although several 1,5-H transfers from enoxy oxygen to carbon were known, it was reported that the corresponding 1,5-Bu_3Sn transfer did not occur.[14] Reaction of **23** with Bu_3SnH/AIBN in refluxing benzene did not proceed. After much experimentation, it was found that the reaction depended on concentration and temperature. Treatment of **23** with Bu_3SnH(1.2 equiv) and di-*t*-butylperoxide(0.1 equiv) in refluxing xylene(0.25M) for 16 h afforded 43% of **24** and 7% of **25** along with the recovery of the starting material(37%), while no reaction occurred when the same reaction was carried out in refluxing xylene(0.05M) for 16 h.

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5. It is also possible that **4** may result from homocoupling of an allylic radical. We are indebted to a referee for suggesting this possibility.
6. The ratio of **7** and **8b** was determined by ^{1}H NMR analysis of a mixture of **10** and **6b**. **8b** was independently prepared in 87% yield by the reaction of **5** with $Bu_3SnCu(CN)BuLi_2$ in THF at -78°C. Furthermore, treatment of **8b** with DCl gave **6b** in 92% yield.
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