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Homolytic 1,5-transfer of the Bu_3Sn group from enoxy oxygen and allylic carbon to nitrogen

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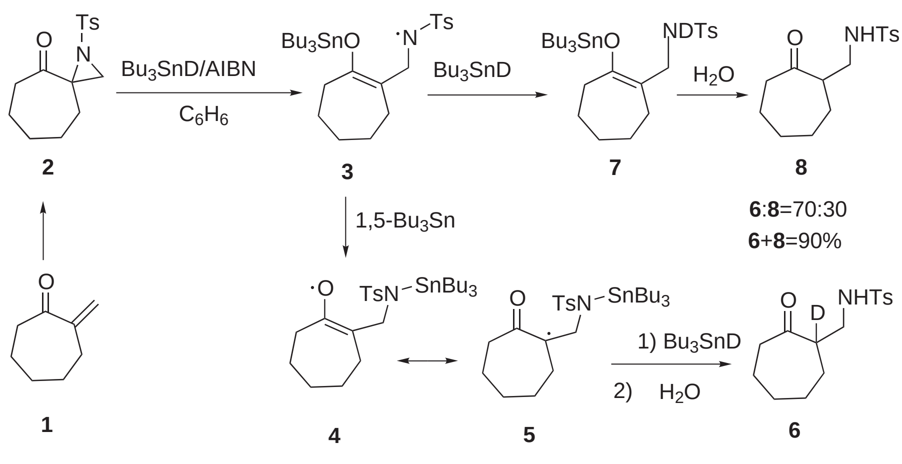
Abstract—Homolytic 1,5-transfer of the Bu_3Sn and Ph_3Ge group from enoxy oxygen and allylic carbon to sulfonyl nitrogen were studied. We found that 1,5-Bu_3Sn transfers from enoxy oxygen or allyl carbon to sulfonyl nitrogen occurred cleanly, whereas a reaction of a keto-aziridine with Ph_3GeD under the radical conditions did not take place. © 2001 Published by Elsevier Science Ltd.

During the past decade, many studies involving radical rearrangements by the atom transfer and by the group transfer have been reported.[1] Among the radical rearrangements, 1,5-hydrogen atom transfer has proven to be synthetically useful for the generation of a radical center at a remote site, which can undergo radical addition, cyclization, and fragmentation reactions.[2] In contrast, radical rearrangements involving radical attack at heteroatoms bearing *d*-orbitals such as R_3Si, R_3Ge, and R_3Sn have not been thoroughly investigated and their synthetic applications have not been studied extensively.[3] Previously, we found that homolytic 1,5- and 1,6-Bu_3Sn group transfers were greatly favoured over 1,5- and 1,6-hydrogen atom transfers and reported examples of 1,5- and 1,6-Bu_3Sn group transfers from allylic carbon and enoxy oxygen to alkoxy oxygen.[4] In addition, we also reported 1,5-Me_3Si and 1,5-Ph_3Ge group transfer from enoxy oxygen to alkoxy oxygen.[5,6]

In connection with our interest in radical rearrangements, we have studied the feasibility of 1,5-Bu_3Sn and Ph_3Ge group transfer from enoxy oxygen and allylic carbon to sulfonyl nitrogen. 1,5-Hydrogen atom transfers in nitrogen-centered radicals are well known and have useful synthetic applications, which are exempli-



Scheme 1.

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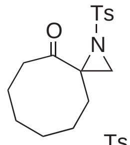
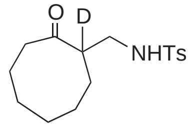
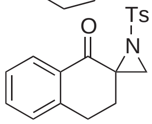
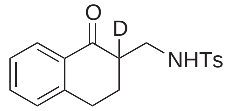
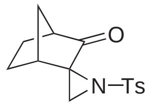
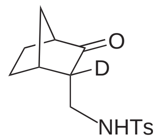
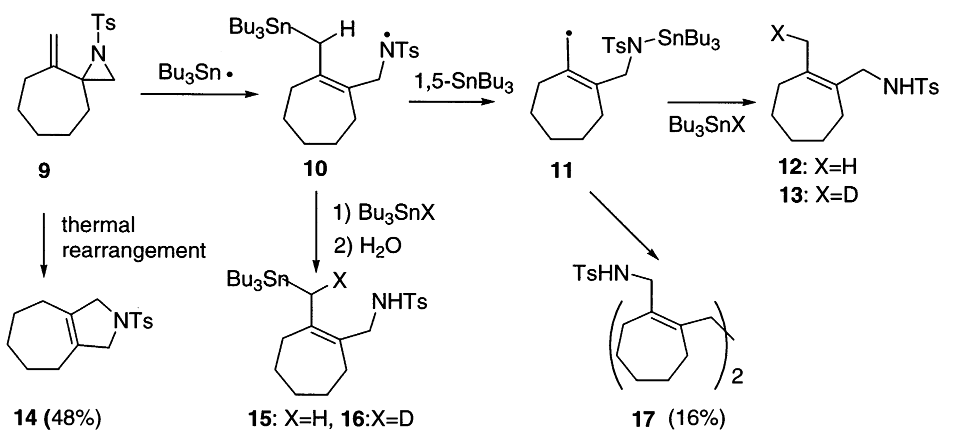
Table 1. 1,5-Bu_3Sn group transfer from enoxy oxygen to nitrogen

substrate	product	yield, %	-D/-H
		80%	2:1
		67%	5:1
		71%	3.3:1
		exo: endo=8:1 (D), 10:1 (H)	

fied by the Hofmann–Loeffler reaction.[7] However, 1,5-Bu_3Sn group transfer from oxygen and carbon to nitrogen has not been reported. Since 1,5-hydrogen transfers normally utilize electrophilic nitrogen-centered radicals such as amidyl and sulphonamidyl radicals,[8] we prepared keto-aziridine **2** in 50% yield by treatment of enone **1** with *N*-tosyliminophenyliodinane in the presence of cupric acetylacetonate in acetonitrile.[9] As shown in Scheme 1, the present approach relies on Bu_3Sn radical addition to **2** and subsequent aziridine ring opening to give intermediate **3**, which has two different pathways available, 1,5-Bu_3Sn group transfer from enoxy oxygen to sulfonyl nitrogen and/or direct reduction. The ratio of the 1,5-Bu_3Sn group transfer and the direct reduction could be determined by quenching an enoxy radical with Bu_3SnD to afford products **6** and/or **8**. A slow addition of a solution of Bu_3SnD (1.5 equiv.) and AIBN (0.1 equiv.) in benzene (0.05 M) for 3 h to a solution of keto-aziridine **2** in refluxing benzene (0.05 M) afforded a 70:30 mixture of **6** and **8** in 90% yield. The ratio of two isomers was determined by ^1H NMR analysis and three more experimental results are shown in Table 1. The ratio of the 1,5-Bu_3Sn group transfer and the direct reduction was found to range from 5:1 to 2:1. The present 1,5-Bu_3Sn group transfer is much less efficient than the 1,5-Bu_3Sn group transfer from enoxy oxygen to alkoxy oxygen and somewhat more efficient than 1,5-Bu_3Sn group transfer from enoxy oxygen to carbon.[4d]

We briefly studied the possibility of 1,5-Ph_3Ge transfer from enoxy oxygen to sulfonyl nitrogen using keto-aziridine **2**. The reactions of **2** with Ph_3GeD were carried out under several different conditions (AIBN in refluxing toluene for 24 h, di-*t*-butyl peroxide or V-40 in refluxing xylene for 24 h), but the reaction did not take place under the forcing conditions. The result is in contrast with the previous result obtained with 1,5-Ph_3Ge transfer from enoxy oxygen to alkoxy oxygen,[6] but is in accord with calculations involving 1,2-transfers from similar groups to nitrogen.[10]



Bu_3SnH (AIBN, 80 °C, 2 h)	**12** (25%), **14** (48%), **17** (16%)
Bu_3SnH (350 nm, 36 h)	**12** (76%), **15** (3%), **17** (15%)
Bu_3SnD (350nm, 36 h)	**13** (38%), **15** (0%), **16** (0%), **17** (32%)

Scheme 2.

Next our attention was given to the 1,5-Bu_3Sn transfer from allylic carbon to sulfonyl nitrogen. Thus, keto-aziridine **2** was converted into vinyl-aziridine **9** by treatment of **2** with methylidene-triphenylphosphorane. As shown in Scheme 2, addition of Bu_3Sn radical to the C=C bond in **9** should be followed by rapid ring opening of an aziridine ring giving rise to intermediate **10**, which has several different reactions available to it including 1,5-Bu_3Sn transfer, 1,5-hydrogen transfer, and the direct reduction. In accord with previous results,[4a] 1,5-Bu_3Sn transfer was greatly favored over 1,5-hydrogen transfer in a ratio of 20:1. When a solution of Bu_3SnH (1.5 equiv.) and AIBN in benzene (0.05 M) was added to a solution of vinyl-aziridine **9** in refluxing benzene (0.05 M) over 2 h, the reaction gave a mixture of three products (**12** (25%), **14** (48%), and **17** (16%)). Apparently, 1,5-Bu_3Sn transfer from allylic carbon to sulfonyl nitrogen occurred smoothly, although the major product **14** was obtained from thermal rearrangement of **9**.[11] To obviate the problem of thermal rearrangement, the radical reaction was performed under photochemically initiated conditions. When a solution of **9** in benzene (0.05 M) was treated with Bu_3SnH (1.5 equiv.) at 350 nm for 36 h, a mixture of **12**, **15**, and **17** was obtained in 76, 3, and 15% yield, respectively. Since it was not clear whether the formation of **15** would be derived from the direct reduction or 1,5-hydrogen transfer, we repeated the reaction with Bu_3SnD and **15** or **16** was not formed. Furthermore, the ratio of **13** and **17** was considerably changed due to a slow rate of quenching an alkyl radical with Bu_3SnD, as compared with Bu_3SnH.

Acknowledgements

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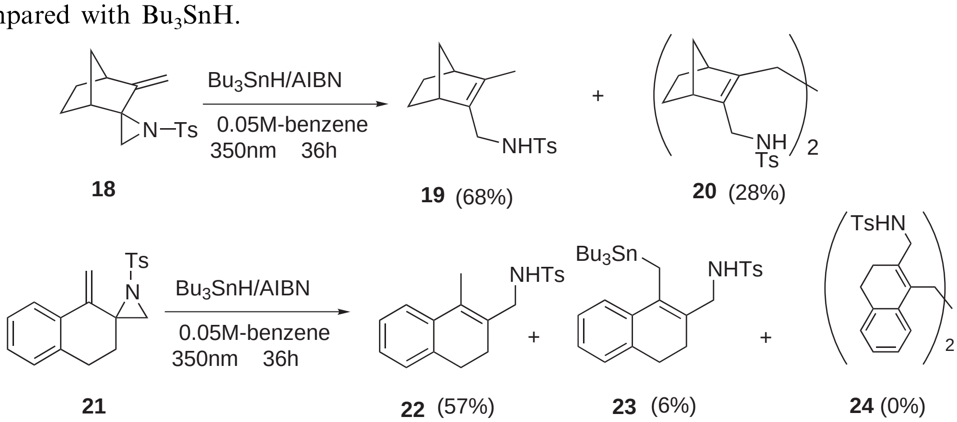

Thus, it is unclear whether the formation of **15** would be derived from 1,5-hydrogen transfer or the direct reduction. Similar results were obtained with vinyl-aziridine **18** and **21**, indicating that a mixture of **19** and **20**, and **22** resulted from 1,5-Bu_3Sn transfer and **23** would be produced from the direct reduction and/or 1,5-hydrogen transfer. From our experimental results, it is evident that 1,5-Bu_3Sn transfer from allylic carbon to sulfonyl nitrogen is much faster than 1,5-H transfer and is a highly efficient process.

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