

Homolytic 1,5-Transfer of Organosilicon Groups from an Enoxy Oxygen to an Alkoxy Oxygen

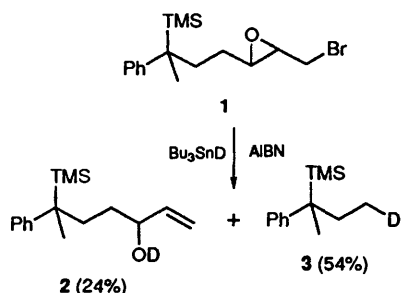
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The homolytic 1,5-transfer of both trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBS) groups from an enoxy oxygen to an alkoxy oxygen has been observed for the first time.

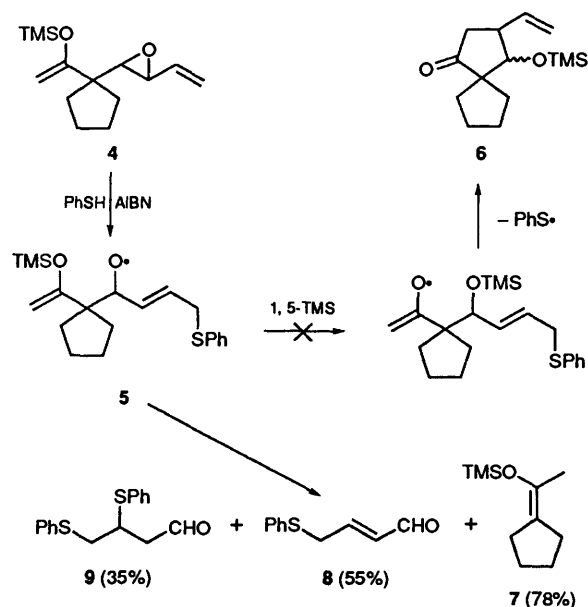
Recently, we reported several novel free radical rearrangements involving both a 1,5- and a 1,6-transfer of a Bu_3Sn group.^{1,2} We have since turned our attention to the 1,5-transfer of organosilicon groups. Radical rearrangements that involve a homolytic 1,2-transfer of organosilicon groups between heteroatoms are well documented, *e.g.*, the 1,2-transfer of organosilicon groups from silicon to sulfur³ and from oxygen to nitrogen⁴ have both been reported. Also recently reported was the 1,2-TMS transfer from carbon to oxygen.⁵ Very recently, Mariano and co-workers observed the 1,5-transfer of a TMS group from a carbon to an alkoxy oxygen in the photolysis of both silylamidoalkylketones and silylalkylketones.⁶

Although the 1,5-transfer of organosilicon groups seems to be feasible because of the release in bond energy accompanying rearrangement, our initial study turned out to be discouraging,^{2a} indicating a strong preference for the 1,5-hydrogen transfer over the 1,5-TMS transfer. To obviate the problem of the competing 1,5-hydrogen transfer, the methylated compound was duly prepared. When compound **1** was treated with Bu_3SnD -AIBN under the same conditions, a mixture of both compounds **2** and **3** was obtained in 24 and 54% yield,



respectively. Apparently, the 1,5-TMS transfer did not occur and compound **3** was produced *via* the β -fragmentation of the intermediate alkoxy radical. Although the 1,5-transfer of the Bu_3Sn group from the enoxy oxygen to the alkoxy oxygen has been previously reported,⁷ the unusual results for the TMS group in radical rearrangements led us to examine the possibility of a 1,5-transfer from an enoxy oxygen to an alkoxy oxygen. As shown in Scheme 1, it was expected that the radical reaction of vinyl epoxide **4** with PhSH -AIBN in refluxing benzene would initially generate the alkoxy radical **5**, possibly yielding compound **6** *via* a 1,5-TMS transfer followed by a 5-*exo-trig*-radical cyclization. However, a mixture of compounds **8** and **9** was also isolated in 55% and 35% yield, along with compound **7** in 78% yield. Apparently, the β -fragmentation of the intermediate alkoxy radical **5** was more facile than the corresponding 1,5-TMS transfer. The reason for this result may be due in part, to the formation of the stabilized allylic radical intermediate from β -fragmentation of **5**.

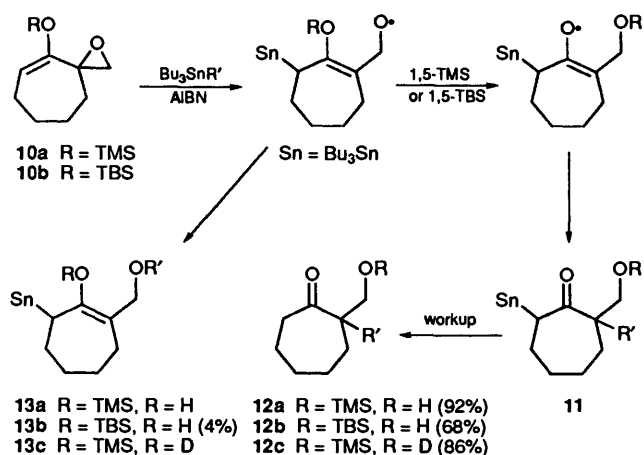
In order to prevent the β -fragmentation of the intermediate alkoxy radical, we prepared the epoxy silyl enol ethers **10** for



Scheme 1

which β -fragmentation would not readily occur. As shown in Scheme 2, radical reaction of compound **10a** with Bu_3SnH (1.1 equiv.) and AIBN (0.1 equiv.) in refluxing benzene afforded compound **12a** in 92% yield, after chromatographic separation. In order to confirm the apparent 1,5-TMS transfer, the reaction was performed with Bu_3SnD -AIBN under similar conditions and the deuteriated compound **12c** was isolated in 86% yield, but not compound **13c**. Thus, the 1,5-TMS transfer from the enoxy oxygen to the alkoxy oxygen seems to be very fast and is favoured over the direct quenching of the alkoxy radical by Bu_3SnH .

On the basis of the reported rate constant for 1,5-hydrogen



Scheme 2

Table 1^a

substrate	time (h)	product ^b
14a R = TMS, R' = H	6	15a 74%
14b R = TBS, R' = H	24	15b 55% (44%)
14c R = TMS, R' = Me	18	15c 66% (25%)
14d R = TBS, R' = Me	24	15d 44% (47%)
16a R = TMS	4	17a 88%
16b R = TBS	24	17b 77% (10%)
		18b 2%
19a R = TMS	6	20a 82%
19b R = TBS	24	20b 74% (10%)
		21b 6%

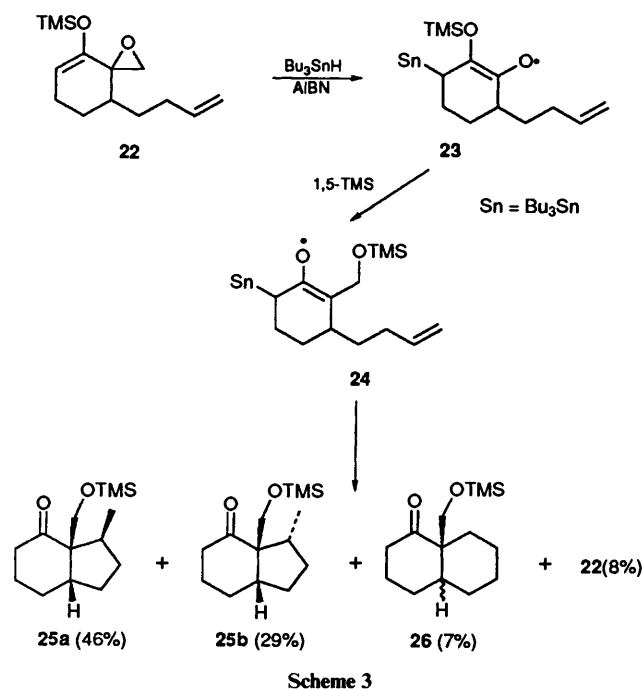
^a The reaction was carried out with Bu₃SnH (1.1 equiv.) and AIBN (0.1 equiv.) in refluxing benzene. ^b The yield refers to the isolated yield. The numbers in parentheses indicate the yield of the recovered starting material.

transfer of *ca.* 10⁸ s⁻¹,⁸ the rate constant for 1,5-TMS transfer should be greater than 10⁹ s⁻¹. Further examples are shown in Table 1. In general, similar results were obtained, showing clean 1,5-TMS transfer without direct quenching and β-fragmentation of the intermediate alkoxy radicals.

We next focused our attention on the 1,5-TBS transfer from an enoxy oxygen to an alkoxy oxygen. As compared with the 1,5-TMS transfer, the 1,5-TBS transfer occurred more slowly. For instance, the reaction of compound **10b** with Bu₃SnH-AIBN in refluxing benzene for 24 h gave both compounds **12b** (68%) and **13b** (4%), along with recovered starting material (18%). Apparently, compound **13b** resulted from the direct quenching of the alkoxy radical prior to the 1,5-TBS transfer. Similar results were obtained with several silyl enol ethers as shown in Table 1. We have also examined compound **22** to see whether the radical cyclization *via* the radical translocation by a 1,5-TMS group transfer could be effected. As shown in Scheme 3, the reaction of compound **22** with Bu₃SnH-AIBN in refluxing benzene (0.05 mol dm⁻³) for 4 h afforded a mixture of compounds **25a** (46%), **25b** (29%) and **26** (7%) along with some recovered starting material (8%), which demonstrated the homolytic 1,5-TMS transfer from compound **23** to compound **24**.⁹

Experimental

General Procedure.—The epoxy silyl enol ether **10a** (106 mg, 0.50 mmol) was dissolved in benzene (10 cm³) and the solution was degassed by purging it with a stream of deoxygenated nitrogen for 30 min. A solution of Bu₃SnH (160 mg, 0.55 mmol) and AIBN (8 mg, 0.05 mmol) dissolved in benzene (11 cm³) was then added to the refluxing solution *via* a syringe pump over a period of 3 h. After being refluxed for an additional 1 h, the reaction mixture was cooled to room temp. and concentrated under reduced pressure. The resulting mixture was purified by flash chromatography on silica gel using ethyl acetate-hexane



(1:20) as the eluent to give 2-(trimethylsilyloxymethyl)cycloheptanone **12a** (99 mg, 92%) which was identical with an independently prepared sample; δ_{H} (200 MHz, CDCl₃) 0.0 (9 H, s), 1.3 and 1.6 (4 H, m), 1.7 and 1.9 (4 H, m), 2.4 (2 H, m), 2.6 (1 H, m), 3.5 (1 H, dd, *J* 10 and 6.7) and 3.8 (1 H, dd, *J* 10 and 5.4).

Acknowledgements

We thank the Organic Chemistry Research Center (KOSEF) for support of our research programme and In Seo Kee for experimental assistance.

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Paper 4/04109G
Received 5th July 1994
Accepted 1st August 1994