

1,5-Ph₃Ge and 1,6-Bu₃Sn Group Transfer from Enoxy Oxygen to Alkoxy Oxygen

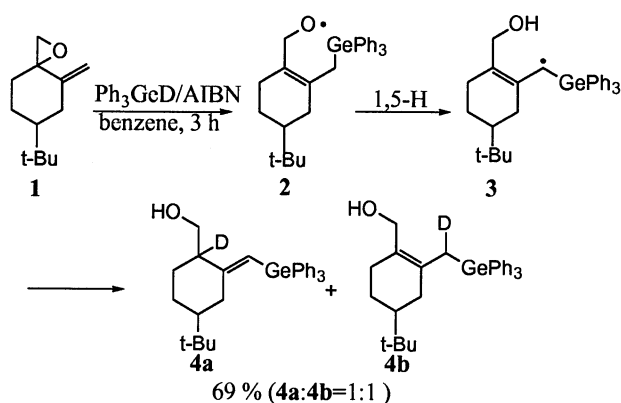
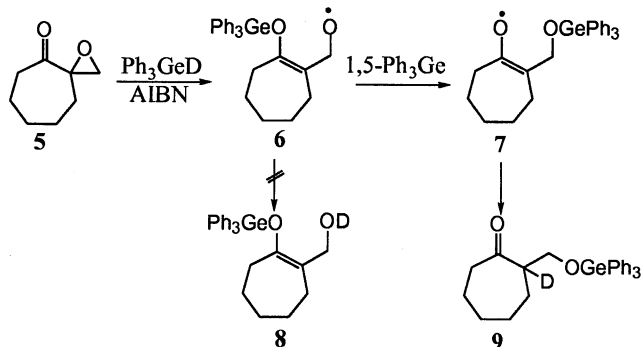
Sungak Kim,* Jung Yun Do, and Kwang Min Lim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejeon 305-701, Korea

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1,5-Ph₃Ge and 1,6-Bu₃Sn group transfer from enoxy oxygen to alkoxy oxygen are observed in radical reaction of keto epoxides and keto oxetanes, respectively.

Recently, we reported 1,5-Bu₃Sn and 1,6-Bu₃Sn group transfer from allylic carbon to alkoxy oxygen^{1,2} and 1,5-Me₃Si group transfer from enoxy oxygen to alkoxy oxygen.³ In connection with our continuing interest in radical rearrangements involving Group 4 elements,⁴ we turned our attention to 1,n-germyl transfer reactions. Previously, 1,2-organogermyl group transfer from oxygen to nitrogen was reported.⁵ We initially studied the possibility of 1,5-Ph₃Ge group transfer from allylic carbon to alkoxy oxygen. When vinyl epoxide **1** was treated with Ph₃GeD/AIBN in refluxing benzene for 3 h under the highly diluted condition using a syringe pump, a mixture of **4a** and **4b** was isolated in 69% yield, indicating that 1,5-H transfer⁶ took place without any indication of 1,5-Ph₃Ge group transfer.¹ Considering the previous result on 1,5-Bu₃Sn group transfer,¹ the result obtained here is somewhat surprising. At the present, we have no explanation as to why the different result was observed in this reaction.

1,5-Ph₃Ge Transfer from O to OTable 1. 1,5-Ph₃Ge transfer from enoxy oxygen to alkoxy oxygen

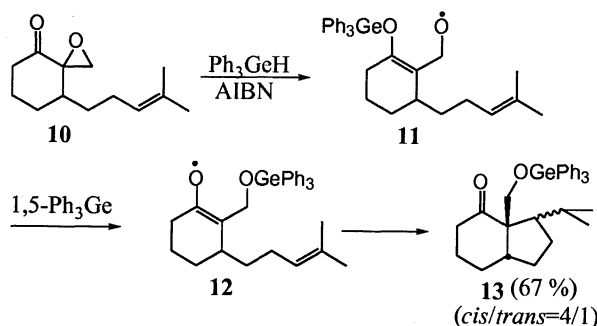
substrate	time, h	yield,% ^a
a. n=1; R ¹ =Me, R ² =H	24	65 % ^b (20 %)
b. n=1; R ¹ , R ² =Me	24	67 % (28 %)
d. n=3; R ¹ , R ² =H	14	91 %
	14	 60 % (13 %)
	14	 65 % (27 %)
	14	 G=GePh ₃ : 42 % =H: 35 %

^a The yield refers to the isolated yield. The numbers in the parentheses indicate the yield of the recovered starting material. ^b a 1:1 diastereomeric mixture.

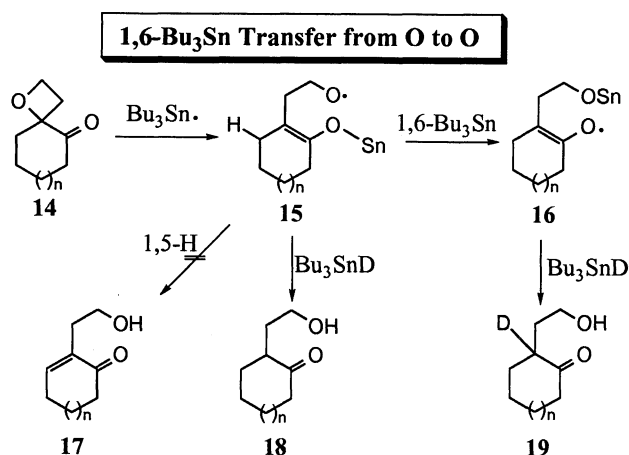
We next studied the interesting possibilities of 1,5-Ph₃Ge and 1,6-Ph₃Ge group transfer from enoxy oxygen to alkoxy oxygen. The reaction of keto epoxide **5** with Ph₃GeD/AIBN in refluxing benzene (0.05M) for 24 h afforded a mixture of 1,5-Ph₃Ge group transferred product **9** (72%) and the starting material **5** (20%). Repeating the reaction in refluxing toluene under the same conditions gave a similar result. The structure of **9** was determined by ¹H NMR and ¹³C NMR spectra.⁷ The deuterium α to the carbonyl in **9** is evident from the fact that methylene protons α to the germyloxy group showed two doublets (J=9.6 Hz) at 3.68 ppm in ¹H NMR. Moreover, the deuterated carbon atom showed a triplet at 54.9 ppm in ¹³C NMR due to splitting by deuterium. Apparently, the reaction proceeded via an alkoxy-radical intermediate **6**, in which 1,5-Ph₃Ge group transfer from enoxy oxygen to alkoxy oxygen took place. Moreover, it is of interest that the direct quenching product **8** was not obtained even under relatively concentrated solution (0.5M), suggesting that 1,5-Ph₃Ge group transfer should be very fast. On the basis of the reported rate constant of ca. 9 × 10⁷ M⁻¹sec⁻¹ (27 °C) for quenching alkoxy radicals by Ph₃GeH,⁸ the rate constant for 1,5-Ph₃Ge group transfer would be approximately 10¹⁰ sec⁻¹ at 80 °C. Further experimental examples are shown in Table 1.

We also examined compound **10** to see whether the radical cyclization via the radical translocation by 1,5-Ph₃Ge group transfer could be effected. When **10** was treated with

$\text{Ph}_3\text{GeH/AIBN}$ in refluxing benzene (0.05M) for 10 h afforded **13** in 67% yield, which demonstrated the effectiveness of 1,5- Ph_3Ge group transfer. It is noteworthy that 1,5-H and/or 1,6-H transfer from carbon to oxygen did not occur in **11**.



We next studied the possibility of the 1,6- Ph_3Ge transfer from enoxy oxygen to alkoxy oxygen. The reaction of keto oxetane **14** ($n=2$) with $\text{Ph}_3\text{GeH/AIBN}$ in refluxing benzene for 24 h did not occur. When the reaction was carried out in refluxing xylene using di-*tert*-butyl peroxide as an initiator, the reaction did not occur after prolonged stirring, yielding a small amount of the decomposed products.



Since 1,6- Ph_3Ge group transfer from enoxy oxygen to alkoxy oxygen was unsuccessful, we briefly studied the possibility of 1,6- Bu_3Sn group transfer reactions from enoxy oxygen to alkoxy oxygen. Reaction of **14** ($n=2$) with $\text{Bu}_3\text{SnD/AIBN}$ in refluxing benzene for 18 h proceeded slowly, yielding a 89:11 mixture of 1,6- Bu_3Sn group transferred product **19** and the direct quenching product **18**. When the reaction was carried out in refluxing xylene using di-*tert*-butyl peroxide as an initiator, the reaction time was shortened to 5 h. A similar result was also obtained with **14** ($n=3$). Since it is well known that 1,5-H transfer from allylic carbon to alkoxy oxygen is an extremely fast process,⁶ and 1,5-H

Table 2. 1,6- Bu_3Sn transfer from enoxy oxygen to alkoxy oxygen

substrate	initiator	solvent	time, h	yield(%) ^a	19/18 ^b
$n = 2$	AIBN	benzene	18	90	89/11
$n = 2$	DTBP ^c	xylene	5	87	90/10
$n = 3$	AIBN	benzene	16	84	88/12

^a Isolated yields. ^b The ratio was determined by ^1H NMR. ^c DTBP = di-*tert*-butyl peroxide.

transfer was noted previously in the reaction of vinyl oxetanes with $\text{Bu}_3\text{SnH/AIBN}$,² it was quite surprising that we were unable to detect the formation of **17**.

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- 9**: ^1H NMR (200 MHz, $\text{CCl}_4\text{-C}_6\text{D}_6$) δ 7.48~7.26 (m, 15H), 3.68 (dd, $J_{\text{gem}}=9.6$ Hz, 2H), 2.30 (m, 2H), 1.78~1.52 (m, 4H), 1.50~1.17 (m, 4H); ^{13}C NMR (50 MHz, $\text{CCl}_4\text{-C}_6\text{D}_6$) δ 212.1, 135.2, 134.9, 130.1, 128.6, 66.6, 54.9, 43.9, 30.2, 29.1, 28.1, 24.8.
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