1,5-Ph$_3$Ge and 1,6-Bu$_3$Sn Group Transfer from Enoxy Oxygen to Alkoxy Oxygen

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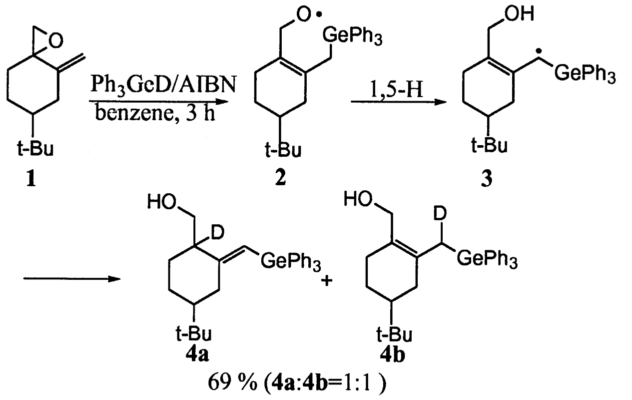
1,5-Ph$_3$Ge and 1,6-Bu$_3$Sn group transfer from enoxy oxygen to alkoxy oxygen are observed in radical reaction of keto epoxides and keto oxetanes, respectively.

Recently, we reported 1,5-Bu$_3$Sn and 1,6-Bu$_3$Sn group transfer from allylic carbon to alkoxy oxygen[1,2] and 1,5-Me$_3$Si 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-Ph$_3$Ge group transfer from allylic carbon to alkoxy oxygen. When vinyl epoxide **1** was treated with Ph$_3$GeD/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 transfer[6] took place without any indication of 1,5-Ph$_3$Ge group transfer. Considering the previous result on 1,5-Bu$_3$Sn 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-Ph$_3$Ge Transfer from O to O

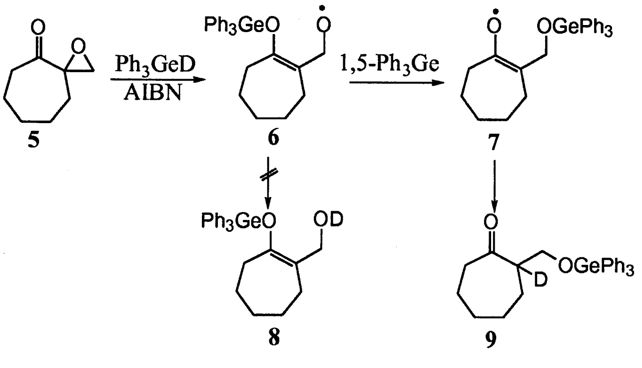
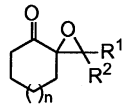
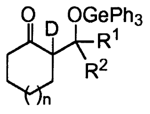
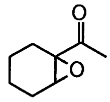
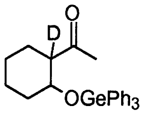
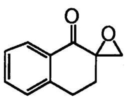
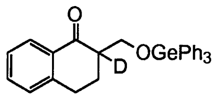
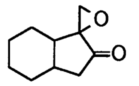
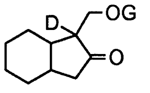


Table1. 1,5-Ph$_3$Ge transfer from enoxy oxygen to alkoxy oxygen

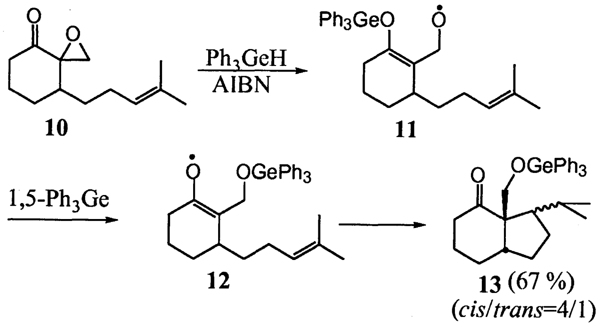
substrate	time, h	yield,%[a]
		
a. n=1 ; R^1=Me, R^2=H	24	65 %[b] (20 %)
b. n=1 ; R^1, R^2=Me	24	67 % (28 %)
d. n=3 ; R^1, R^2=H	14	91 %
	14	 60 % (13 %)
	14	 65 % (27 %)
	14	 G=GePh$_3$: 42 % =H : 35 %

[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 diasteromeric mixture.

We next studied the interesting possibilities of 1,5-Ph$_3$Ge and 1,6-Ph$_3$Ge group transfer from enoxy oxygen to alkoxy oxygen. The reaction of keto epoxide **5** with Ph$_3$GeD/AIBN in refluxing benzene (0.05M) for 24 h afforded a mixture of 1,5-Ph$_3$Ge 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 ^{1}H NMR and ^{13}C 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 ^{1}H NMR. Moreover, the deuteriated carbon atom showed a triplet at 54.9 ppm in ^{13}C NMR due to splitting by deuterium. Apparently, the reaction proceeded via an alkoxy-radical intermediate **6**, in which 1,5-Ph$_3$Ge 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-Ph$_3$Ge group transfer should be very fast. On the basis of the reported rate constant of ca. 9×10^7 M^{-1}sec^{-1} (27 °C) for quenching alkoxy radicals by Ph$_3$GeH,[8] the rate constant for 1,5-Ph$_3$Ge group transfer would be approximately 10^{10} sec^{-1} at 80 °C. Further experimental examples are shown in Table 1.

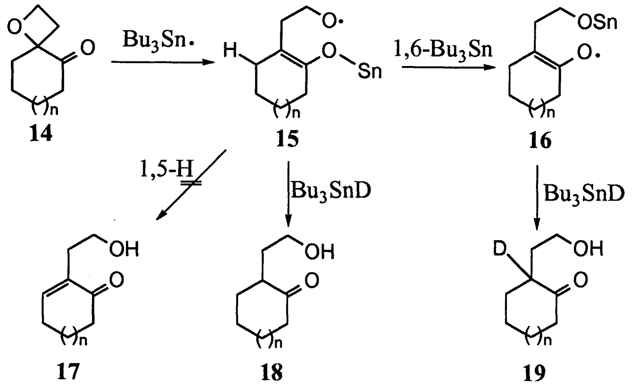
We also examined compound **10** to see whether the radical cyclization via the radical translocation by 1,5-Ph$_3$Ge group transfer could be effected. When **10** was treated with

Ph_3GeH/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 Ph_3GeH/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.

1,6-Bu_3Sn Transfer from O to O



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 Bu_3SnD/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 transfer was noted previously in the reaction of vinyl oxetanes with Bu_3SnH/AIBN,[2] it was quite surprising that we were unable to detect the formation of **17**.

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.

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References and Notes

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7 **9**: ^1H NMR (200 MHz, CCl_4-C_6D_6) δ 7.48~7.26 (m, 15H), 3.68 (dd, J_{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, CCl_4-C_6D_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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