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Generation of Allenic Samarium Complexes from Propargylic Ethers and (C₅Me₅)₂Sm(thf)₂, and Their Electrophilic Trapping

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Abstract: Allenic samarium complexes are readily generated in high yields by the reaction of propargylic benzyl ethers with $(C_5Me_5)_2Sm(thf)_2$. Electrophilic trapping of the complexes derived from the secondary and tertiary ethers with cyclohexanone and dimethylphenylsilyl chloride gives the corresponding propargylic products selectively, whereas α -allenic alcohols are predominantly obtained in the reaction of the complexes, generated from the primary ethers, with cyclohexanone.

Allenic and propargylic organometallics have played an important role in organic synthesis, and extensive studies on the regio- and stereochemistry of their reaction have been reported.¹ However, little is known about the corresponding organolanthanides. There are a few examples of their preparation: transmetallation of propargylic Grignard reagents with cerium salts,² and palladium-catalyzed reaction of propargylic acetates³ and phosphates⁴ with samarium diiodide. The reaction of 2-alkynes with Cp*2LnCH(SiMe3)₂ (Ln=La, Ce, Y) has been also reported to produce propargylic lanthanides.⁵ Isolation and adequate characterization of the lanthanide complexes are moreover still lacking in contrast to other transition metal analogues.⁶

In a previous paper,⁷ we demonstrated a facile preparation of η^3 -allylic samarium complexes by the reductive cleavage of allylic ethers with Cp*2Sm(thf)_n. We have applied this method to propargylic ethers to generate the allenic samarium complexes and studied the regioselectivity on their reaction with electrophiles. We now report these results.

When benzyl 3-(1-phenyl-1-butynyl) ether (1a) (R^1 =Ph, R^2 =Me, R^3 =H) was added to a solution of two equivalents of (C5Me5)2Sm(thf)2 in benzene-d6, the reaction mixture turned deep red immediately. ¹H NMR spectra of the mixture exhibited two sets of new signals in a ratio of 1:1, one of which was assignable to allenic complex 2a [δ 7.15 (1H, t, J = 7.3 Hz, p (H)-Ph), 6.70 (2H, t, J = 7.3 Hz, m (H)-Ph), 5.50 (2H, d, J



Table 1. Trapping of the Allenic Complexes 2 with Cyclohexanone

R ¹ —∶	$= \begin{array}{c} R^2 \\ \hline \\ OBn \\ 1 \end{array}$	1) 2C 2) cy	clohexanone	► R ¹ -	$\overset{R^2}{=} \overset{R^3}{\overset{OH}{\overset{H}}} + \overset{F}{\overset{HO}{\overset{HO}{\overset{H}}}} $	$\overset{R^1}{\underset{5}{\overset{R^2}{\overset{R^2}}}}$
Run	Substrate	R ¹	R ²	R ³	Ratio (4 : 5) ^a	% Yield (4 + 5) ^a
1	1a	Ph	Ме	н	87:13	82
2	1b	Ph	ⁿ Bu	Н	73 : 27	89
3	1c	nBu	Ph	н	92:8 (90:10) ^b	87 (79) ^b
4	1d	ⁿ Bu	Ме	н	90 : 10	92
5	1e ^C	Ph	Ме	Me	70:30	49
6	1f	Ph	Н	н	2:98 (1:99<) ^b	94 (76) ^b
7	1g	nBu	Н	н	41:59 (30:70) ^b	79 (42) ^b

^a Determined by GC. ^b Cyclohexanone was added at -78 °C. ^c 1e was treated with Cp*2Sm(thf)₂ at 50 °C for 15 h.

= 7.3 Hz, o (H)-Ph), 3.86 (1H, br s, allenic H), 1.05 (30H, s, C5Me5), -5.90 (3H, s, Me)]⁸ and the other to Cp*2SmOBn (3).⁷ But no signals for the starting substrate 1a were observed Similar treatment of various propargylic benzyl ethers 1 with Cp*2Sm(thf)2 provided the expected allenic complexes 2 together with equimolar amounts of the benzyloxide 3, based on NMR. The reaction of tertiary ether 1e (R¹=Ph, R²=R³=Me) was carried out at 50 °C, since 1e remained unchanged at room temperature.

The complexes 2, *in situ* generated, were trapped with cyclohexanone to examine the regioselectivity. These results are summarized in Table 1. The reaction of the secondary ethers **1a-d** gave homopropargylic alcohols **4a-d** predominantly (runs 1-4). Although the selectivity and yield decreased in case of tertiary ether **1e**, the propargylic alcohol **4e** was obtained as a major product (run 5). On the other hand, the primary substrate **1f** produced exclusively the allenic alcohol **5f** at -78 °C (run 6). The reaction of the primary ether **1g** gave **4g** and **5g** in a ratio of 41 : 59 at room temperature and 30 : 70 at -78 °C (run 7).

Then the regioselectivity on trapping of the allenic complexes 2 with dimethylphenylsilyl chloride was investigated (Table 2). The complexes 2a-e, generated from the secondary and tertiary propargylic benzyl ethers 1a-e, reacted the silyl chloride to afford propargylic silanes 6a-e exclusively (runs 1-5). This selectivity is consistent with that of cyclohexanone trapping as described above,⁹ but higher than that. The propargylic silanes 6f and 6g were also formed as major isomers from the primary ethers 1f and 1g with low selectivities (runs 6 and 7).

R ² R ³	1) 2Cp*2 2) PhMe	$\frac{2}{2}$ SiCl	 R ¹ ── ── 6	3 ² R ³ SiMe₂Ph PhMe₂	$\xrightarrow{\mathbf{R}^{1}}_{\mathbf{S}\mathbf{S}\mathbf{i}} \xrightarrow{\mathbf{R}^{2}}_{\mathbf{R}^{3}} \xrightarrow{\mathbf{R}^{2}}_{\mathbf{R}^{3}}$
Substrate	R ¹	R ²	R ³	Ratio (6 : 7) ^a	% Yield (6 + 7) ^a
la	Ph	Ме	Н	>99 : 1	74
1b	Ph	ⁿ Bu	н	98:2	67
1c	ⁿ Bu	Ph	н	98:2 (70:30) ^b	71 (54) ^b
1d	ⁿ Bu	Me	н	96 : 4	84
1e ^c	Ph	Ме	Me	95 : 5	72
lf	Ph	н	н	68 : 32	84
1g	nBu	Н	Н	55 : 45	87
	R ² R ³ OBn Substrate 1a 1b 1c 1d 1e ^c 1f 1g	R ² R ³ 1) 2Cp*2 2) PhMe 2) PhMe 2) PhMe 2) PhMe 2) PhMe 2) PhMe 4 10 10 10 10 10 10 10 10 10 10	$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} 1 \end{array} \\ \begin{array}{c} 2 \end{array} \\ \begin{array}{c} 2 \end{array} \\ \begin{array}{c} 0 \end{array} \\ \begin{array}{c} 1 \end{array} \\ \begin{array}{c} 2 \end{array} \\ \end{array} \\ \begin{array}{c} 2 \end{array} \\ \end{array} \\ \begin{array}{c} 2 \end{array} \\ \begin{array}{c} 2 \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} 2 \end{array} \\ \end{array} \end{array} \\ \end{array} \\ \end{array} \end{array} \\ \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

Table 2. Trapping of the Allenic Complexes 2 with Dimethylphenylsilyl Chloride

^a Determined by GC. ^b The silyl chloride was added at -78 °C. ^c 1e was treated with Cp*2Sm(thf)2 at 50 °C for 15 h.

The regioselectivity observed in this study is completely opposite to the previously reported results of allenic and propargylic organolanthanides. For example, the samarium species, generated by the reaction of secondary or tertiary propargylic acetates and phosphates with Pd-SmI₂, have been reported to give allenic products exclusively on trapping with ketones and alcohols, whereas those from the primary substrates afforded propargylic products selectively.^{3,4,10} Cerium reagents, prepared by transmetallation of γ -monosubstituted propargylmagnesium bromides with CeCl₃ or Ce(OⁱPr)₃, have been known to produce homopropargylic alcohols on quenching with aldehydes.² The reverse selectivity of our samarium complexes may be attributed to the effect of the two bulky C5Me5 rings. Instead, the present selectivity is similar to that of early transition metals such as titanium¹¹ and zirconium¹², wherein regiochemistry was accounted for by the exclusive formation of allenic or propargylic intermediates depending on the substituent pattern and subsequent S_E2' reaction with electrophiles. However, attempts to clarify the position of equilibrium between the allenic and propargylic samarium species¹³, including comparison of the ¹H NMR spectra of 2a with those of 2f¹⁴ and low temperature experiments, have so far not succeeded.

Typical experimental procedure is as follows: Cp*2Sm(thf)2 (565 mg, 1 mmol) was placed in a schlenk tube under argon and dissolved in degassed toluene (5 mL). Propargylic benzyl ether (0.5 mmol) was added to the solution, and the mixture was stirred for 2 h at room temperature. Then cyclohexanone (98 mg, 1 mmol) or dimethylphenylsilyl chloride (171 mg, 1 mmol) was added to the resulting deep red solution, and the mixture was stirred for 5 h or 20 h, respectively, at room temperature. After addition of 2 M HCl, the

mixture was extracted with ether. The usual workup and purification by column chromatography on silica gel provided the products.

In summary, the reductive cleavage of propargylic benzyl ethers with Cp*2Sm(thf)2 serves as a convenient method to generate allenic organosamariums, which exhibit a different regioselectivity from those formed by the conventional methods.

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References and Notes

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