Selective C−O Bond Cleavage of Vinyl Ethers with $Cp^*_2Sm(thf)_n$ Leading to Vinylsamarium or Enolate Complexes

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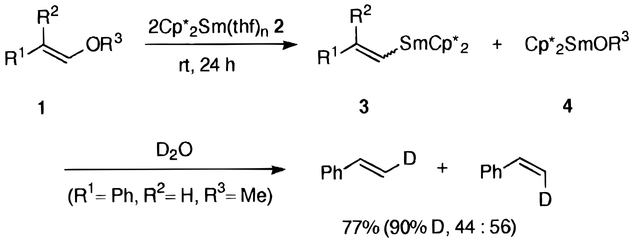
It is well known that organometallics of group 3 and lanthanide tend to form complexes with ethers owing to their strong oxophilicity and coordinative unsaturation. Subsequent C−O bond cleavage of the coordinated ethers by the active lanthanide species has been documented in the literature.[1] Most of these reactions arose from sp^3 C−O bond fission, but in contrast cleavage of sp^2 C−O is a very rare event.[1c] From a synthetic point of view, these C−O bond cleavage reactions can serve as a convenient method for generation of the useful lanthanide reagents. We reported previously the facile generation of allylic[2] and allenic samariums[3] from benzyl allyl ethers and benzyl propargyl ethers, respectively, by the reaction with $(C_5Me_5)_2Sm(thf)_n$. In continuing work, we studied regioselectivity on the reductive cleavage of alkyl vinyl ethers, i.e. competition between sp^2 C−O fission leading to vinyl species and alkoxides and sp^3 C−O to enolates and alkyl complexes. Interestingly, it has been found that the selectivity depends on the alkyl substituents. We report herein these results.

When methyl (*E*)-styryl ether (**1a**) was treated with 2 equiv of $Cp^*_2Sm(thf)_n$ (**2a**, $n = 2$ and **2b**, $n = 1$) in toluene at room temperature for 24 h and the mixture was quenched with water, styrene was formed in 75% and 77% yields, respectively. Similar results were obtained in benzene solvent, while no reaction took place in THF. Deuterolysis of the reaction with **2b** gave (*E*), and (*Z*)-β-deuteriated styrene in a ratio of 44:56 (Scheme 1). These results suggest the formation of styryl- and methoxysamarium species by the sp^2 C−O cleavage. Monitored by ^{1}H NMR, the reaction of (*E*)-**1a** with samarocene **2a** demonstrated two pairs of signals for vinylic protons: one was at δ 6.37 and 12.45, and the other was at δ 6.07 and 9.23, as summarized in Table 1. Since the signal at δ 12.45 appeared as a doublet with a large coupling constant ($J = 19.5$ Hz), it was assignable to =CHSm of (*E*)-styrylsamarium species **3a**.[4] The ratio of (*E*)- to (*Z*)-species **3a** was found to be 46:54, which was consistent with that of β-deuteriated styrene described above. Moreover, Cp^*_2SmOMe (**4a**) was detected in amounts equimolar with **3a** by ^{1}H NMR (δ 1.47 for Cp* and δ 5.26 for OMe).

Scheme 1



The reactions using various alkyl vinyl ethers **1** were carried out in an NMR tube, and these results are summarized in Table 2. Reactions with monotetrahydrofuranate **2b** gave better yields of **3** than did **2a** in general.[5] While methyl (*Z*)-styryl ether (**1b**) remained unchanged on treatment with **2a**, styryl species **3a** ((*E*):(*Z*) = 21:79) was generated in moderate yields with **2b** (runs 3 and 4). It seems likely that the (*E*) / (*Z*) ratio of **3a** is determined by the C−O bond cleavage and not by their equilibrium, because **1a** and **1b** gave the different ratio irrespective of the reaction time. Treatment of ethyl vinyl ether (**1c**) with **2a** and **2b** generated vinylsamarium species **3b** in good yields along with equimolar amounts of samarium ethoxide **4c** (runs 5 and 6). Three signals assignable to vinylic protons of **3b** were observed at δ 3.51, 4.36, and 11.8, as indicated in Table 1. The C−O bond cleavage of other alkyl vinyl ethers **1** took place similarly. However, their reactivities decreased as the alkyl groups became larger (runs 5−9). Only trace amounts of **3b** were detected in case of *tert*-butyl ether (**1f**) (run 9). 2-Methoxypropene and 1-methoxycyclohexene did not react with **2** under similar conditions.

In contrast to the alkyl vinyl ethers **1**, benzyl (*E*)-styryl ether (**5a**) was cleaved at the sp^3 C−O bond with **2a** to give phenylacetaldehyde and toluene in 20% and 90% yields, respectively, after hydrolysis (Scheme 2). Neither styrene nor benzyl alcohol was detected. The corresponding deuteriated products were formed on quenching with deuterium oxide. Similar results were obtained in the reaction of benzyl vinyl ether (**5b**). Regioselectivity on the C−O bond cleavage of **5** seems to be exceptional[6] since the benzyl substituent is a better leaving group than alkyls, particularly under reductive conditions.[7] However, these results contrast well with the cleavage of allylic methyl and benzyl ethers with **2**, in which both ethers changed to allylic samarium complexes.[2]

^{1}H NMR spectra of the reaction of (*E*)-styryl ether **5a** with **2a** showed two doublets at δ 7.58 and 8.76, which was assignable to the vinylic protons of samarium enolate of phenylacetaldehyde **6a**. The stereochemistry was determined to be (*E*) on the basis of the coupling constant of 11.8 Hz. Signals of benzylsamarium complex **7** were also observed. Both species **6a** and **7** were formed in 90% yields after 2 h. Thus, a yield of phenylacetaldehyde

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[1] (a) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276−277. (b) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134−142. (c) Deelman, B.-J.; Booij, M.; Meetsma, A.; Teuben, J. H. Kooijman, H.; Spek, A. L. *Organometallics* **1995**, *14*, 2306−2317. (d) Hitchcock, P. B.; Holmes, S. A.; Lappert, M. F.; Tian, S. *J. Chem. Soc., Chem. Commun.* **1994**, 2691−2692. (e) Eaborn, C.; Izod, K.; Smith, J. D. *J. Organomet. Chem.* **1995**, *500*, 89−99. (f) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291−1296. (g) Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Organomet. Chem.* **1995**, *499*, 213−219.

[2] Takaki, K.; Kusudo, T.; Uebori, S.; Makioka, Y.; Taniguchi, Y.; Fujiwara, Y. *Tetrahedron Lett.* **1995**, *36*, 1505−1508.

[3] Makioka, Y.; Koyama, K.; Nishiyama, T.; Takaki, K.; Taniguchi, Y.; Fujiwara, Y. *Tetrahedron Lett.* **1995**, *36*, 6283−6286.

[4] Further definite structure such as oligomeric state and coordination of THF could not be determined.

[5] ^{1}H NMR spectra observed in the reaction with **2b** were very similar to those with **2a**.

[6] Regioselectivity on the C−O cleavage of dialkyl ethers with lanthanide hydrides has been accounted for by S_N1 and S_N2 character of the substituents: see ref 1c.

[7] Greene, T. W. *Protective Groups in Organic Synthesis*; Wiley: New York, 1981; pp 10−39.

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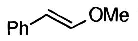
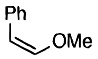
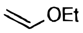
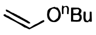
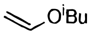
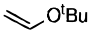
Table 1. ^{1}H NMR Data on Vinylsamarium and Enolate Species[a]

species	RC*H*=CH	RCH=C*H*	R(Ph)	SmCp*$_2$
(*E*)-$\mathrm{PhCH{=}CHSmCp^*_2}$ [(*E*)-**3a**]	6.37 (br s)	12.45 (br d, $J = 19.5$ Hz)	7.34 (t, $J = 7.3$ Hz, *p*-H) 7.63 (t, $J = 7.3$ Hz, *m*-H) 8.32 (d, $J = 7.3$ Hz, *o*-H)	1.58 (s)
(*Z*)-$\mathrm{PhCH{=}CHSmCp^*_2}$ [(*Z*)-**3a**]	6.07 (br s)	9.23 (br s)	6.55 (t, $J = 7.3$ Hz, *m*-H) 6.69 (t, $J = 7.3$ Hz, *p*-H) 7.11 (d, $J = 7.3$ Hz, *o*-H)	1.63 (s)
$\mathrm{CH_2{=}CHSmCp^*_2}$ (**3b**)	3.51 (br d, $J = 19.7$ Hz, (*Z*)-H) 4.36 (br s, (*E*)-H)	11.83 (br s)		1.61 (s)
(*E*)-$\mathrm{PhCH{=}CHOSmCp^*_2}$ (**6a**)	7.58 (d, $J = 11.8$ Hz)	8.76 (d, $J = 11.8$ Hz)	7.28 (t, $J = 7.4$ Hz, *p*-H) 7.45 (t, $J = 7.4$ Hz, *m*-H) 8.13 (d, $J = 7.4$ Hz, *o*-H)	1.44 (s)
$\mathrm{CH_2{=}CHOSmCp^*_2}$ (**6b**)	5.42 (d, $J = 4.3$ Hz, (*E*)-H) 6.21 (d, $J = 13.3$ Hz, (*Z*)-H)	8.23 (dd, $J = 4.3$ and 13.3 Hz)		1.44 (s)

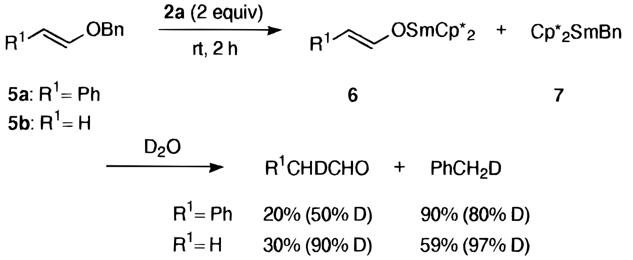
[a] In C_6D_6, δ (ppm).

Table 2. Reaction of Alkyl Vinyl Ethers 1 with Samarocenes 2

run	substrate 1		samarocene 2	product 3[a]	yield[b,c], %
1		**1a**	**2a**	**3a**	52 (56)[d]
2			**2b**	**3a**	58 (75)[d]
3		**1b**[e]	**2a**	no reaction	-
4			**2b**	**3a**	30 (40)[f]
5		**1c**	**2a**	**3b**	59 (80)
6			**2b**	**3b**	94 (quant)
7		**1d**	**2b**	**3b**	67 (79)
8		**1e**	**2b**	**3b**	62 (79)
9		**1f**	**2b**	**3b**	trace

[a] Corresponding alkoxide **4** was also formed. [b] Yield is determined by ^{1}H NMR. [c] Yield at 2 h (20 h). [d] (*E*)/(*Z*) = 46/54 (at 2 and 20 h). [e] (*E*)/(*Z*) = 3/97. [f] (*E*)/(*Z*) = 21/79 (at 2 and 20 h).

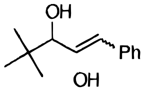
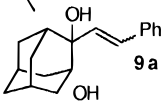
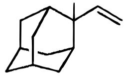
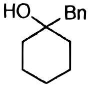
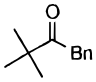
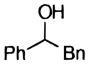
Scheme 2



lower than that of toluene on hydrolysis and deuterolysis would be due to the instability of the aldehyde during workup. The reaction of **5b** with **2a** produced enolate **6b** and benzylsamarium **7** in equal amounts (57% yields), wherein three vinylic protons of **6b** appeared at δ 5.42, 6.21, and 8.23 with reasonable coupling constants.[8] In this case, small amounts of vinylsamarium **3b** and samarium benzyl oxide, formed by sp^2 C–O cleavage, were detected (3% yields). Use of **2b** caused a little increase of the minor species to 8% yields.

Electrophilic trapping of the intermediates **3**, **6**, and **7** was attempted in order to confirm their generation (Table 3). Styrylsamarium species **3a**, generated from (*E*)-styryl ether **1a** and **2b**, reacted with pivalaldehyde to give allylic alcohol **8** in 75% yield with a (*E*)/(*Z*) ratio of 28/72 (run 1). Similarly, alcohol **9a** was obtained in 51% yield by the reaction with 2-adamantanone, wherein the ratio was 61:39 (run 2). These two ratios were inconsistent with that observed by ^{1}H NMR, which may be caused by the different reactivities of the two isomers of **3a** to the electrophiles used.[9] Vinylsamarium **3b** was captured with 2-adamantanone to give alcohol **9b** (run 3). Trapping of the mixture of samarium enolates **6** and benzylsamarium **7**, generated from **5** and **2a**, with 2 equiv of various electrophiles afforded only benzyl products **10**–**13** in good yields (runs 4–7).[10] On the other hand, no adducts of enolates **6** were obtained, and the corresponding aldehydes were detected in low yields (<5%) by GC instead. The failure may be attributed to further complicated reactions or low reactivities of **6**. With respect to the trapping with carbonyl compounds, it has been proved that retro-aldol reaction takes place predominantly for some lanthanocene aldolates.[11]

Table 3. Electrophilic Trapping of the Intermediates Generated from Vinyl Ethers 1 and 5 with 2[a]

run	vinyl ether	electrophile	time, h	product		yield[b], %
1	**1a**	pivalaldehyde	20		**8**	75[c]
2	**1a**	2-adamantanone	2		**9a**	51[d]
3	**1d**	2-adamantanone	2		**9b**	39
4	**5a**	cyclohexanone	10		**10**	93
5	**5a**	pivalaldehyde	24		**11**	56
6	**5a**	$\mathrm{PhMe_2SiCl}$	10	$\mathrm{PhMe_2SiBn}$	**12**	90
7	**5b**	benzaldehyde	10		**13**	63[e]

[a] **2a** and **2b** were used for the reactions of **5** and **1**, respectively. [b] GC yield based on **1** and **5**. [c] (*E*)/(*Z*) = 28/72. [d] (*E*)/(*Z*) = 61/39. [e] **5b** was treated with **2a** for 5 h.

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(8) Lanthanide (Lu, Yb, and Y) enolates of acetaldehyde have been reported to form dimeric complexes: see ref 1f.

(9) Reaction of **3a**, generated from (*Z*)-styryl ethers **1b** and **2b**, gave a trace amount of (*E*)-**9a** only, although (*E*)- and (*Z*)-**3a** (21:79) were detected in 40% yield by ^{1}H NMR.

(10) The ketone **11** was presumably formed by addition of **7** followed by Oppenauer oxidation: Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573–6614.

(11) Heeres, H. J.; Maters, M.; Teuben, J. H. *Organometallics* **1992**, *11*, 350–356.

In summary, we have demonstrated an exclusive sp^2 C−O bond cleavage of alkyl vinyl ethers with divalent samariums to yield vinylsamarium complexes together with the corresponding alkoxides. In addition, samarium enolates and benzyl species are selectively produced from benzyl vinyl ethers by sp^3 C−O fission.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded at 270 and 67 MHz, respectively. IR spectra were taken on a FT-IR spectrophotometer. Mass spectra were obtained at 70 eV on a GC−MS apparatus. Melting points are uncorrected. All experiments were performed under argon using standard Schlenk and vacuum line techniques. All solvents (THF, cyclohexane, benzene, and toluene) were distilled from sodium benzophenone ketyl, stored over sodium metal, and degassed by trap to trap distillation just before use. Other materials were also degassed and stored under argon after purification. $(C_5Me_5)_2Sm(thf)_2$ (**2a**)[12] and $(C_5Me_5)_2Sm(thf)$ (**2b**)[13] were prepared by the reported methods. Methyl (*E*)- and (*Z*)-styryl ether (**1a** and **1b**),[14] benzyl (*E*)-styryl ether (**5a**),[15] and benzyl vinyl ether (**5b**)[16] were synthesized according to the literature.

General Procedure for NMR Tube Reaction of Vinyl Ethers 1 and 5 with $Cp^*_2Sm(thf)_n$, 2. Samarocene **2** was placed in an NMR tube and dissolved in C_6D_6 (0.2 M). Then 0.5 equiv of vinyl ethers **1** or **5** was added to the solution, and the mixture was cooled to −78 °C. The sample tube was sealed under argon. The reaction was monitored by ^1H NMR at room temperature. Yields described in the text were determined by the integration ratio of products to the substrates remained. Assignment of the signals were made on the basis of COSY. ^1H NMR data of vinylsamariums **3** and samarium enolates **6** are shown in Table 1. Those of alkoxides **4** and benzylsamarium **7** are as follows: Cp^*_2SmOMe (**4a**) δ 1.47 (30 H, s), 5.26 (3 H, s); Cp^*_2SmOEt (**4c**)[17] δ 1.47 (30 H, s), 3.34 (3 H, t, $J = 6.2$ Hz), 5.68 (2 H, t, $J = 6.2$ Hz); Cp^*_2SmOBu (**4d**)[17] δ 1.47 (30 H, s), 1.67 (3 H, t, $J = 7.2$ Hz), 2.54 (2 H, m), 4.03 (2 H, m), 5.61 (2 H, t, $J = 6.2$ Hz); $Cp^*_2SmO^iBu$ (**4e**) δ 1.47 (30 H, s), 1.98 (6 H, d, $J = 6.0$ Hz), 4.83 (1 H, br s) 5.43 (2 H, br s); Cp^*_2SmBn (**7**)[17] δ 1.35 (30 H, s), 7.00 (2 H, t, $J = 7.5$ Hz), 7.12 (1 H, t, $J = 7.5$ Hz), 8.77 (2 H, d, $J = 7.5$ Hz), 9.26 (2 H, br s).

Hydrolysis and Deuterolysis of the Intermediates Generated from 1a and 2. Methyl (*E*)-styryl ether (**1a**) (27 mg, 0.20 mmol) was added to a solution of $Cp^*_2Sm(thf)_2$ (**2a**) (226 mg, 0.40 mmol) in toluene (2.0 mL), and the mixture was stirred for 24 h at room temperature. The reaction was quenched with H_2O (1 mL) and then 2 M HCl (3 mL).[18] The reaction mixture was extracted with ether, and the combined organic layer was washed with brine and dried over $MgSO_4$. Styrene was formed in 75% yield on the basis of GC analyses using *p*-xylene as an internal standard. Methanol, the other expected product, was not detected from the organic and aqueous layers by GC. In addition, it was confirmed that methane and phenylacetaldehyde were not contained in the gas and liquid phases of the reaction, respectively. The reaction with **2b** gave styrene in 77% yield under the identical conditions. Use of THF solvent resulted in the quantitative recovery of **1a**. In the case of deuterolysis of the reaction mixture with **2b** in benzene, styrene was isolated by column chromatography on silica gel (pentane), and the content and stereochemistry of deuterium were determined by ^1H NMR (90% D, (*E*)/(*Z*) = 44/56).

Hydrolysis and Deuterolysis of the Intermediates Generated from 5 and 2a. Benzyl (*E*)-styryl ether (**5a**) (105 mg, 0.50 mmol) was added to a solution of **2a** (575 mg, 1.0 mmol) in cyclohexane (5 mL), and stirring was continued for 2 h at room temperature. After similar workup as above,[18] phenylacetaldehyde and toluene were detected by GC in 20% and 90% yields, respectively. The reaction in toluene also afforded the aldehyde in 20% yield. Deuterolysis of the reaction mixture gave PhCHDCHO and $PhCH_2D$ in 20% (50% D) and 90% (80% D) yields, respectively. The reaction of benzyl vinyl ether (**5b**) (87 mg, 0.65 mmol) with **2a** (735 mg, 1.30 mmol) in cyclohexane (6.5 mL) was carried out at room temperature for 2 h and quenched with deuterium oxide (0.3 mL). The mixture was dried over $MgSO_4$, and volatile products were collected in a cold receiver under reduced pressure, in which acetaldehyde and toluene were detected in 30% and 59% yields, respectively, by GC using *n*-hexadecane as an internal standard. Deuterium contents of the two products were 90% and 97%, respectively, determined by GC−MS equipped with capillary column.

General Procedure for the Electrophilic Trapping. Alkyl vinyl ether **1** (0.50 mmol) was added to a solution of **2b** (493 mg, 1 mmol) in toluene (5.0 mL), and the mixture was stirred for 24 h at room temperature. Alternatively, benzyl vinyl ether (**5b**) was treated with **2a** in toluene for 2 h at room temperature. Then, electrophile (1.0 mmol) was added to the mixture, and stirring was continued for the appropriate time indicated in Table 3 at room temperature. After addition of H_2O (1 mL) and then 2 M HCl (3 mL), the mixture was extracted with ether (10 mL × 3), and the combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The products were purified by column chromatography on silica gel or alumina (hexane−ethyl acetate). Yields were determined by GC using *p*-xylene as an internal standard.

Supporting Information Available: Spectral and analytical data for **8**−**13** (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941−946.

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[14] Earnshaw, C.; Wallis, C. J.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3099−3106.

[15] Julia, M.; Righini, A.; Uguen, D. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1646−1651.

[16] Andersson, C.-M.; Larsson, J.; Hallberg, A. *J. Org. Chem.* **1990**, *55*, 5757−5761.

[17] These data are nearly the same as those of diethyl ether adduct of **4c** and THF adducts of **4d** and **7**, respectively: see ref 1b.

[18] **1a** and **5a** were not hydrolyzed under the workup conditions.