

# [2,3]-Wittig Rearrangement Initiated by 1,5-Hydrogen Atom Transfer from an *o*-Iodophenyl Group on the $\alpha$ -Carbon of Allylic Ethers by Reduction with $\text{SmI}_2$

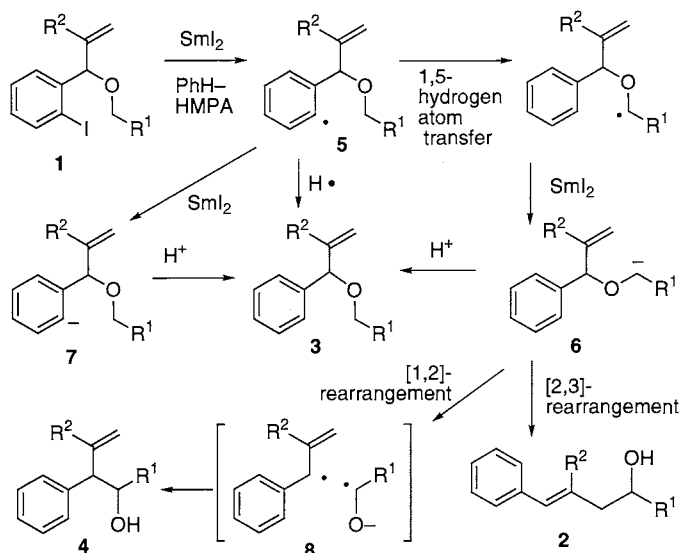
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(Received April 12, 1999; CL-990283)

Intramolecular 1,5-hydrogen atom transfer of an aryl radical generated by reduction of an *o*-iodophenyl group on the allylic position of allyl ethers by  $\text{SmI}_2$  regioselectively generates  $\alpha$ -allyloxy carbanions, which undergo [2,3]-Wittig rearrangement to afford a substituted 4-phenyl-3-buten-1-ol. The effect of HMPA concentration on distribution of the 1,5-hydrogen transfer giving Wittig rearranged products and hydrogen abstraction giving reductive deiodination products is described.

Recently, we demonstrated that samarium iodide ( $\text{SmI}_2$ ) is highly useful to effect [2,3]-sigmatropic rearrangements.<sup>1</sup>  $\text{SmI}_2$ -mediated [2,3]-rearrangement of allylic sulfonium ylides was achieved by addition of samarium carbenoids to allylic sulfides.<sup>1a</sup> Allyloxy carbanions undergoing [2,3]-Wittig rearrangement were generated by either a net two-electron reduction of diallyl acetals with the liberation of an allyloxy samarium by  $\text{SmI}_2$  in acetonitrile,<sup>1b</sup> or an intramolecular 1,5-hydrogen atom transfer of a vinyl radical, generated by a single electron transfer (SET) from  $\text{SmI}_2$  to  $\gamma$ -halogenoallyl ethers.<sup>1c</sup> All the methods provide a regioselective and nonbasic approach to generation of a carbanion species undergoing rearrangement. We now report a new type of Wittig rearrangement involving 1,5-hydrogen atom transfer by reaction of allylic ethers possessing an *o*-iodophenyl group on the  $\alpha$ -carbon with  $\text{SmI}_2$ .

Exposure of **1a** to 0.1 M  $\text{SmI}_2$  (2.5 eq) in benzene containing 10% HMPA for 10 min at room temperature afforded a [2,3]-rearranged product, 1,4-diphenyl-3-buten-1-ol (**2a**) in 53%



Scheme 1.

yield, and a reductively deiodinated compound (**3a**) in 25% yield.<sup>2</sup> Similarly, **2c** was formed from **1c** in a moderate yield whereas **2b** was obtained in a poor yield along with a reduced compound (**3b**) and [1,2]-rearranged product (**4b**) (Table 1, Column 1).

As shown in Scheme 1, a SET from  $\text{SmI}_2$  to **1** affords an aryl radical (**5**), which undergoes 1,5-hydrogen atom transfer followed by a SET from  $\text{SmI}_2$ .<sup>3</sup> The resulting  $\alpha$ -allyloxy carbanion (**6**) then undergoes Wittig rearrangement. When the reaction of **1a** was carried out in THF containing 3 equiv of HMPA, the distribution of the products **2a** and **3a** was reversed (23% and 53%, respectively), because hydrogen atom abstraction of reactive aryl radicals **5** from THF<sup>4</sup> can compete with 1,5-hydrogen atom transfer. Recently, we found that replacement of THF by benzene decrease the rate of hydrogen atom abstraction of reactive radicals from solvents.<sup>5</sup> In spite of the present reactions employing the benzene-HMPA system, however, a considerable amount of **3** was still formed. The formation of reduced ethers **3** could be attributed to protonation of either allyloxy carbanions (**6**) or aryl anions (**7**) arising from aryl radicals by a SET (Scheme 1). However, when **1a** was treated with  $\text{SmI}_2$  followed by quenching with  $\text{D}_2\text{O}$ , no deuterium was observed in **3a**, indicating the possibility of the radical mechanism (**5** to **3** in Scheme 1). Since the C-H bond next to an amide is weakened by the nitrogen,<sup>6</sup> the methyl groups of HMPA could act as a hydrogen atom donor. Thus, we examined the reaction of **1b** in the presence of various concentrations of HMPA between about 0.05 M and 1.72 M (Table 2).<sup>7</sup> The yield of 1,5-hydrogen atom transfer (**2b** and **4b**) was found to increase, and reduced ether **3b** decreased, with

Table 1.  $\text{SmI}_2$ -mediated Wittig rearrangement of (*o*-iodophenyl)allyl ethers

Run	1	R <sup>1</sup>	R <sup>2</sup>	Column 1 <sup>a</sup>		Column 2 <sup>b</sup>	
				2 (%) <sup>c</sup>	3 (%) <sup>c</sup>	2 (%) <sup>c</sup>	3 (%) <sup>c</sup>
1	a	Ph	H	53	25	62	13
2	b	Pr	H	10(14) <sup>d</sup>	29(55)	51 (49) <sup>e</sup>	19 (27)
3	c	H <sub>2</sub> C=CH-	H	43	19	67	9
4	d	Ph	Me	— <sup>f</sup>	—	52 <sup>g</sup>	9
5	e	CH <sub>3</sub> CH=CH-	H	— <sup>f</sup>	—	59	6
6	f	<i>p</i> -NC-C <sub>6</sub> H <sub>4</sub> -	H	— <sup>f</sup>	—	44	0

<sup>a</sup>  $\text{SmI}_2/\mathbf{1} = 2.5$ ;  $\text{HMPA}/\text{SmI}_2 = \text{ca.} 6$ ;  $[\text{HMPA}] = \text{ca.} 0.5 \text{ M}$ . <sup>b</sup>  $\text{SmI}_2/\mathbf{1} = 3.0$  except for Run 2 ( $\text{SmI}_2/\mathbf{1} = 5.0$ );  $\text{HMPA}/\text{SmI}_2 = \text{ca.} 3$ ;  $[\text{HMPA}] = \text{ca.} 0.05 \text{ M}$ . <sup>c</sup> Isolated yield. Glc yields are given in parentheses.

<sup>d</sup> 1,2-Rearranged product **4b** was formed in 15% (7%) yield. <sup>e</sup> **4b** was formed in 28% (24%) yield. <sup>f</sup> Reaction was not carried out. <sup>g</sup> A mixture of geometrical isomers (74 : 26).

**Table 2.** Effect of HMPA on distribution of products<sup>a</sup>

HMPA		1,5-Transfer <sup>b</sup>		Reduction <sup>b</sup>
HMPA/ $\text{SmI}_2$	conc (M)	Yield	<b>2b</b> : <b>4b</b>	Yield of <b>3b</b>
20	1.72	9%	44 : 56	91%
8	0.69	17%	61 : 39	60%
6	0.52	21%	65 : 35	55%
4	0.34	38%	65 : 35	39%
3	0.26	65%	66 : 34	35%
3	0.05 <sup>c</sup>	73%	67 : 33	27%

<sup>a</sup>  $\text{SmI}_2/\mathbf{1} = 5.0$ . <sup>b</sup> Determined by Glc. <sup>c</sup> 5-Fold dilution of a 0.26 M solution.

decreasing of HMPA.

The yields of **2a** and **2c** were also improved by decreasing HMPA (0.05 M).<sup>8</sup> Reactions with **1d–1f** under similar conditions are listed in Table 1, Column 2. The stereochemistry of alkenes **2**, except **2d**, was determined as *E* by their large geminal coupling constants (>15 Hz) in NMR analysis.<sup>9</sup> An alcohol **2e** that would be difficult to be formed by the usual base-deprotonation method due to the low regioselectivity of deprotonation<sup>11</sup> was produced selectively by the present method. In contrast to other Wittig rearrangements mediated by  $\text{SmI}_2$ , in which no [1,2]-rearrangement was observed,<sup>1b,c</sup> the formation of a considerable amount of **4b** from **1b** in the present reaction can be attributed to the phenyl group arising from the *o*-iodophenyl group at the allylic position. Since [1,2]-rearrangement involves homolysis of the C–O bond between an etheral oxygen and the allyl group,<sup>12</sup> the phenyl group would promote the cleavage by stabilizing the resulting allyl radical (Scheme 1, **8**). The high reactivity of the allyloxy carbanion without stabilizing groups ( $\text{R}^1$  in **6**) like an aryl or a vinyl group other than the etheral oxygen can be also responsible for the cleavage.

In summary, we have developed a new type of Wittig rearrangement involving 1,5-hydrogen atom transfer, which enables regioselective generation of  $\alpha$ -allyloxy carbanions under mild conditions. The methodology developed here can be applicable to allyl ethers possessing an iodoalkenyl moiety as

well as an *o*-iodoaryl group at the allylic position. In addition, we have shown the possibility that HMPA acts as a hydrogen donor to an active radical generated by  $\text{SmI}_2$ .

#### References and Notes

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- 2 The starting (*o*-iodophenyl)allyl ethers, **1a–f** are prepared from commercial *o*-iodobenzyl alcohol as follows: oxidation of the alcohol to the aldehyde with PCC on  $\text{SiO}_2$  under ultrasonic irradiation, followed by addition of a vinyl Grignard reagent afforded secondary allyl alcohols, which then are coupled with an alkyl halide giving **1a–f**.
- 3 For 1,5-hydrogen atom transfer mediated by  $\text{SmI}_2$ , see: a) M. Murakami, M. Hayashi, and Y. Ito, *J. Org. Chem.*, **57**, 793 (1992). b) L. Capella, P. C. Montevocchi, and M. L. Navacchia, *J. Org. Chem.*, **60**, 7424 (1995).
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- 6 J. C. Gilbert and B. K. Blackburn, *J. Org. Chem.*, **51**, 3656 (1986).
- 7 10% HMPA corresponds to 5.6 equivalent to  $\text{SmI}_2$  in 0.1 M solution. When HMPA was reduced to less than 2 eq,  $\text{SmI}_2$  was no longer dissolved in benzene and precipitated. Thus, the minimum ratio of HMPA to  $\text{SmI}_2$  we employed was 3.
- 8 For a typical procedure: To a stirred solution of  $\text{SmI}_2$  (0.023 M in benzene, 18.3 mL, 0.428 mmol) containing 0.18 mL (1%) of HMPA was added **1a** (50 mg, 0.143 mmol) in benzene (1 mL) at rt under nitrogen. After stirring for 30 min, the mixture was poured into saturated  $\text{NaHCO}_3$  and extracted with ether. The residue was purified by column chromatography (hexane :  $\text{AcOEt} = 85 : 15$ ) to give **2a** (20.0 mg, 0.089 mmol) as colorless crystals.
- 9 The preference for the *E*-isomer is known as the general trend in [2,3]-Wittig rearrangement, see ref. 10.
- 10 For reviews on [2,3]-Wittig rearrangement, see: a) T. Nakai and K. Mikami, *Chem. Rev.*, **86**, 885 (1986). b) K. Mikami and T. Nakai, *Synthesis*, **1991**, 594. c) R. Brückner, "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991), Vol. 4, p. 873. d) T. Nakai and K. Mikami, *Org. React.*, **46**, 105 (1994).
- 11 The regioselectivity of crotyl 1-methylallyl ether, of which one allyl group has an  $\alpha$ -, and the other has a  $\gamma$ -substituent, by base-deprotonation was reported to be low ( $\alpha/\gamma = 1 : 2$ ), see: T. Nakai, K. Mikami, S. Taya, and Y. Fujita, *J. Am. Chem. Soc.*, **103**, 6492 (1981).
- 12 For reviews on [1,2]-Wittig rearrangement, see: a) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970). b) J. A. Marshall, "Comprehensive Organic Synthesis," ed by B. M. Trost, Pergamon Press, Oxford (1991), Vol. 3, p. 975. c) K. Tomooka, T. Igarashi, N. Komine, and T. Nakai, *Yuki Gosei Kagaku Kyokaiishi*, **53**, 480 (1995).