[2,3]-Wittig Rearrangement Initiated by 1,5-Hydrogen Atom Transfer from an *o*-Iodophenyl Group on the α-Carbon of Allylic Ethers by Reduction with SmI_2

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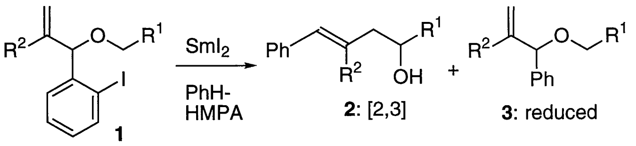
Intramolecular 1,5-hydrogen atom transfer of an aryl radical generated by reduction of an *o*-iodophenyl group on the allylic position of allyl ethers by SmI_2 regioselectively generates α-allyloxy carbanions, which undergo [2,3]-Wittig rearrangement to afford a substituted 4-phenyl-3-buten-1-ol. The 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 (SmI_2) is highly useful to effect [2,3]-sigmatropic rearrangements.[1] SmI_2-mediated [2,3]-rearrangement of allylic sulfonium ylides was achieved by addition of samarium carbenoids to allylic sulfides.[1a] 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 SmI_2 in acetonitrile,[1b] or an intramolecular 1,5-hydrogen atom transfer of a vinyl radical, generated by a single electron transfer (SET) from SmI_2 to γ-halogenoallyl ethers.[1c] 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 α-carbon with SmI_2.

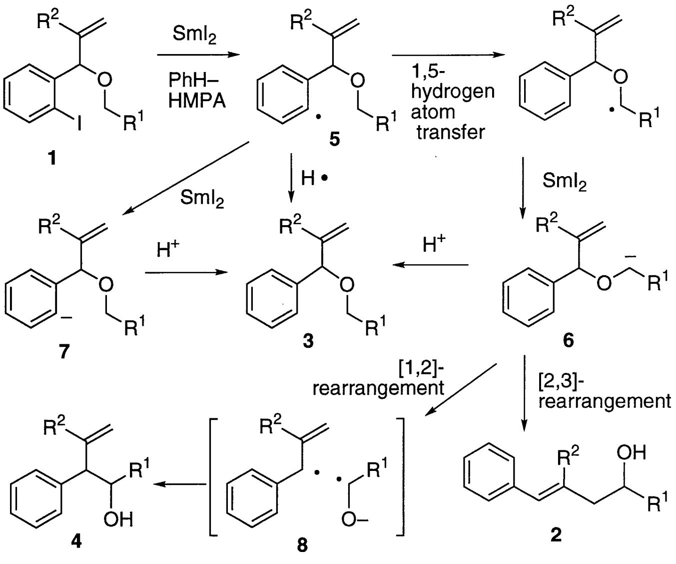
Exposure of **1a** to 0.1 M SmI_2 (2.5 eq) in benzene containing 10% HMPA for 10 min at room temperature afforded a [2,3]-rearranged product, 1,4-diphenyl-3-buten-1-ol (**2a**) in 53% yield, and a reductively deiodinated compound (**3a**) in 25% yield.[2] Similarly, **2c** was formed from **1c** in a 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).

Table 1. SmI_2-mediated Wittig rearrangement of (*o*-iodophenyl)allyl ethers



Run	**1**	R^1	R^2	Column 1[a] **2** (%)[c]	Column 1[a] **3** (%)[c]	Column 2[b] **2** (%)[c]	Column 2[b] **3** (%)[c]
1	**a**	Ph	H	53	25	62	13
2	**b**	Pr	H	10(14)[d]	29(55)	51 (49)[e]	19 (27)
3	**c**	H_2C=CH-	H	43	19	67	9
4	**d**	Ph	Me	–[f]	–	52[g]	9
5	**e**	CH_3CH=CH-	H	–[f]	–	59	6
6	**f**	*p*-NC-C_6H_4-	H	–[f]	–	44	0

[a] SmI_2/**1** = 2.5; HMPA/SmI_2 = ca.6: [HMPA] = ca.0.5 M. [b] SmI_2/**1** = 3.0 except for Run 2 (SmI_2/**1** = 5.0); HMPA/SmI_2 = ca.3: [HMPA] = ca. 0.05M. [c] Isolated yield. Glc yields are given in parentheses. [d] 1,2-Rearranged product **4b** was formed in 15% (7%) yield. [e] **4b** was formed in 28% (24%) yield. [f] Reaction was not carried out. [g] A mixture of geometrical isomers (74 : 26).



Scheme 1.

As shown in Scheme 1, a SET from SmI_2 to **1** affords an aryl radical (**5**), which undergoes 1,5-hydrogen atom transfer followed by a SET from SmI_2.[3] The resulting α-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[4] 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.[5] 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 SmI_2 followed by quenching with D_2O, 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,[6] 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).[7] The yield of 1,5-hydrogen atom transfer (**2b** and **4b**) was found to increase, and reduced ether **3b** decreased, with

Table 2. Effect of HMPA on distribution of products[a]

HMPA		1,5-Transfer[b]		Reduction[b]
HMPA/SmI$_2$	conc (M)	Yield	**2b** : **4b**	Yield of **3b**
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[c]	73%	67 : 33	27%

[a] SmI$_2$/**1** = 5.0. [b] Determined by Glc. [c] 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).[8] 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.[9] An alcohol **2e** that would be difficult to be formed by the usual base-deprotonation method due to the low regioselectivity of deprotonation[11] was produced selectively by the present method. In contrast to other Wittig rearrangements mediated by SmI$_2$, in which no [1,2]-rearrangement was observed,[1b,c] 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,[12] 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 (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 α-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 SmI$_2$.

References and Notes

1 a) M. Kunishima, D. Nakata, C. Goto, K. Hioki, and S. Tani, *Synlett*, **1998**, 1366. b) K. Hioki, K. Kono, S. Tani, and M. Kunishima, *Tetrahedron Lett.*, **39**, 5229 (1998). c) M. Kunishima, K. Hioki, K. Kono, A. Kato, and S. Tani, *J. Org. Chem.*, **62**, 7542 (1997).

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 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**.

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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 SmI$_2$ in 0.1 M solution. When HMPA was reduced to less than 2 eq, SmI$_2$ was no longer dissolved in benzene and precipitated. Thus, the minimum ratio of HMPA to SmI$_2$ we employed was 3.

8 For a typical procedure: To a stirred solution of 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 NaHCO$_3$ and extracted with ether. The residue was purified by column chromatography (hexane : 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 α-, and the other has a γ-substituent, by base-deprotonation was reported to be low (α/γ = 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 Kyokaishi*, **53**, 480 (1995).