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2,3-Wittig rearrangement by partial reduction of diallyl acetals with SmI_2 in acetonitrile

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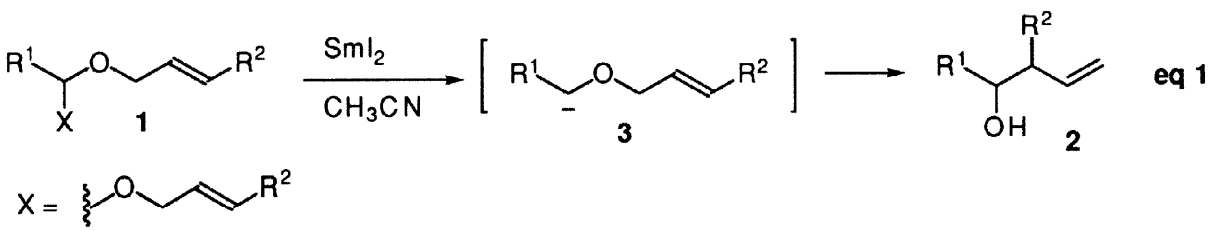
Abstract. Diallyl acetals undergo reductive cleavage of an allyloxy group by SmI_2 to generate α-allyloxy carbanions, which are transformed into homoallyl alcohols by 2,3-Wittig rearrangement.
Keywords: *Samarium and compounds; Rearrangement; Reduction; Acetals*

The 2,3-Wittig rearrangement is a useful tool for transforming allyl ethers into homoallyl alcohols.[1] Base-deprotonation by an alkyllithium or a lithium amide is the most general method for generating an α-allyloxy carbanion undergoing rearrangement. This method, however, sometimes suffers from the formation of an undesired regioisomeric carbanion because deprotonation occurs toward a relatively acidic proton α to the etheral oxygen.[1, 2] For a regioselective approach to the α-etheral carbanion, metal exchange of stannyl[3a] or silyl[3b] group (Still-Wittig), or reductive cleavage of *O,S*-acetals with lithium naphthalenide[4] have been reported. Recently, we developed a novel regioselective generation of α-allyloxy carbanions by 1,5-hydrogen transfer of vinyl radicals mediated by SmI_2.[5] Reductive cleavage of a substituent (X in **1**), reducible with SmI_2, at the allyloxy carbon may provide an alternative and more direct route for SmI_2-induced regioselective generation of the anion. We now report the reductive cleavage of an allyloxy group from diallyl acetals (**1**, X = allyloxy group) with SmI_2 leading to generation of the carbanions (**3**) which undergo 2,3-rearrangement.[6]



Acetals have been recognized as being stable toward SmI_2 without any additives.[7] However, we have found that reduction of benzaldehyde diallyl acetal (**1a**) with SmI_2 (3 eq) occurred in acetonitrile (CH_3CN) at reflux temperature under nitrogen without any additives leading to the formation of homoallyl alcohol (**2a**) in 72% (Table 1, run 1).[8] Interestingly, the reaction was completely suppressed by addition of 5% HMPA, which is

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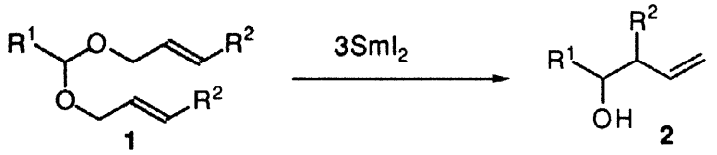
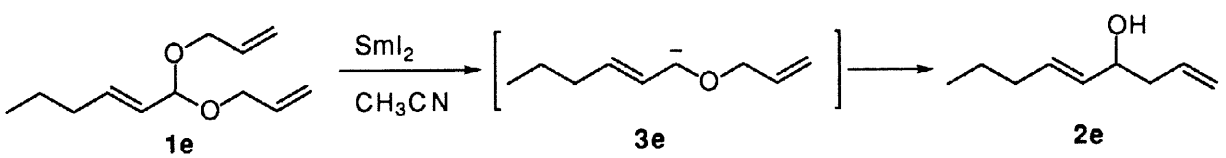
Table 1. Wittig Rearrangement by Reduction of Diallyl Acetals with SmI_2.



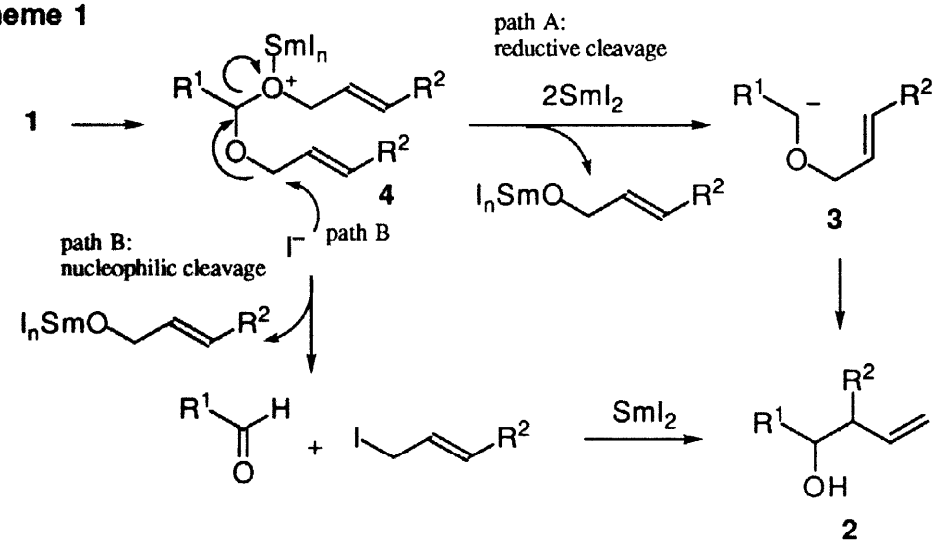
run	acetal (1)	conditions: solvent	conditions: temp.	conditions: time	yield 2 (%)[a]	recovery 1 (%)[a]
1	**1a**: R^1 = Ph, R^2 = H	CH_3CN	reflux,	2 h	72	8
2		CH_3CN	rt,	5 days	0	93
3		CH_3CN – HMPA[b]	reflux,	15 min	0	97
4		THF	reflux,	4 h	0	94
5		THF – HMPA[b]	reflux,	2.5 h	0	88
6		PhH – HMPA[b]	reflux,	2.5 h	22	54
7	**1b**: R^1 = Ph, R^2 = Me (96% *E*)	CH_3CN	reflux,	40 min	66[c]	—[d]
8	**1c**: R^1 = *p*-tolyl-, R^2 = H	CH_3CN	reflux,	1 h	81	—[d]
9	**1d**: R^1 = $PhCH_2CH_2$-, R^2 = H	CH_3CN	reflux,	3 h	0	98

[a] Isolated yield. [b] Solvent : HMPA = 9 : 1. [c] A mixture of diastereoisomers (erythro/threo = 62 : 38). [d] Not determined.

well known as the most effective activator for SmI_2,[9, 10] and **1a** was quantitatively recovered (run 3). Reactions conducted in THF with or without HMPA resulted in recovery of **1a** at 94% or 88%, respectively, while a low yield (22%) of **2a** was obtained in benzene–HMPA (runs 4–6). Acetals (**1b, c**) were similarly converted to the corresponding alcohols (**2b, c**) in good yields (runs 7, 8). In spite of the reaction conducted at the reflux temperature in CH_3CN, there was no evidence for the formation of the product via 1,2-rearrangement, which sometimes competes with 2,3-rearrangement at a high temperature, in the reaction of **1b**.[11] The observed *erythro/threo* (62:38) ratio of **2b** obtained from **1b** with *E*-geometry agreed with that (61:39) reported previously in the alternative SmI_2-induced Wittig rearrangement involving 1,5-hydrogen transfer.[5, 12] On the bases of the regioselection rule regarding lithiation on unsymmetrical diallyl ethers,[2] established by Nakai et al., regioselective deprotonation with bases on the allylic group possessing an unfavorable γ-substituents, leading to the carbanion (**3e**), can be predicted to be very difficult. It is noteworthy that the carbanion (**3e**) has been generated regioselectively by the SmI_2-induced reductive cleavage of **1e**, and **2e** was obtained in 56%. In contrast to aromatic or vinylic acetals, an aliphatic one (**1d**) did not react under the same conditions.[13]

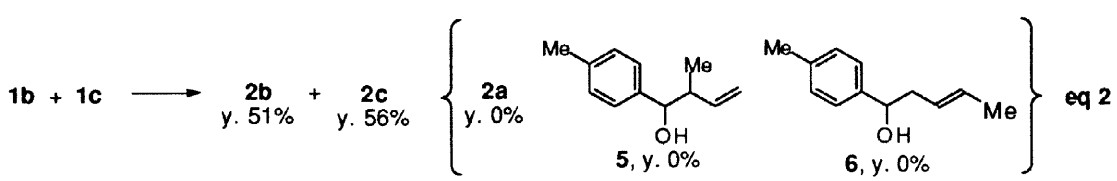


Scheme 1



The formation of **2** is explained by Wittig-type 2,3-rearrangement of the α-allyloxy carbanion resulting from reductive cleavage of acetals as illustrated in Scheme 1. The acetal (**1**) would be activated by complexation with di- or trivalent samarium ion through an etheral oxygen to give **4**. A net two-electron transfer from SmI_2 to the complex with the liberation of an allyloxy samarium would give the α-allyoxy carbanion (**3**)(path A: reductive cleavage). The formation of carbenium ion from **4** might be involved. Since HMPA strongly coordinates to samarium ion,[14] the activation of acetals by complexation with samarium ions could be prevented by HMPA, and therefore, no reaction takes place.[15] THF might also have a coordinating ability sufficient to inhibit the reaction. Thus, the results indicate that activation of acetals is more important than increasing the reducing potential of SmI_2.

An alternative mechanism can be considered as illustrated in Scheme 1, path B. The allyl group of **4** may be attacked by iodide with cleavage of the bond between the allyl group and the oxygen leading to the formation of an aldehyde and an allyl iodide.[16] These compounds can undergo coupling by mediation of SmI_2 to give **2** (Barbier-type coupling).[17] Thus, we tried the reaction using a mixture of an equal amount of **1b** and **1c**. The alcohols **2b** and **2c** were formed in 51% and 56%, respectively, with no evidence for the formation of cross-coupled compounds **2a**, **5**, and **6** which could be formed by the Barbier-type mechanism (eq 2).



We have shown here that reduction of diallyl acetals by SmI_2 occurs in CH_3CN without any additives. This offers a new regioselective approach to Wittig rearrangement.

For a typical procedure: to a solution of SmI_2 (0.096 mol/L in CH_3CN, 6.1 mL, 0.59 mmol), **1a** (40 mg, 0.20 mmol) was added at reflux temperature under nitrogen. The solution was refluxed for 2 hr and quenched with aqueous K_2CO_3. After extraction with ether, the organic layer was dried and concentrated to give a crude residue, which was purified on TLC (hexane : ether = 7 : 3) to afford **2a** (21 mg, 72%).

References and Notes

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13 Curran's group reported that only TFA, a strong Brønsted acid, was found to be an effective additive for the reduction of aliphatic dimethyl acetals.[7] Thus, we believe to be difficult to reduce aliphatic acetals without any additives.

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