

TETRAHEDRON LETTERS

2,3-Wittig rearrangement by partial reduction of diallyl acetals with SmI₂ 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. © 1998 Elsevier Science Ltd. All rights reserved. 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^{3*} or silyl^{3b} group (Still-Wittig), or reductive cleavage of *O*,*S*-acetals with lithium naphthalenide⁴ have been reported. Recently, we developed a novel regioselective generation of α -allyloxy carbanions by 1,5-hydrogen transfer of vinyl radicals mediated by SmI₂.⁵ Reductive cleavage of a substituent (X in 1), reducible with SmI₂, at the allyloxy carbon may provide an alternative and more direct route for SmI₂-induced regioselective generation of the anion. We now report the reductive cleavage of an allyloxy group from diallyl acetals (1, X = allyloxy group) with SmI₂ 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 2

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Table 1. Wittig Rearrangement by Reduction of Diallyl Acetals with SmI₂.

	R^{1} C R^{2} R^{2} R^{2} R^{2}	3Sml ₂		
		conditions		yield
un	acetal (1)	solvent	temp. time	2 (%) ^a
1	1a : R ¹ = Ph, R ² = H	CH ₃ CN	reflux, 2 h	72

CH₃CN

CH₃CN

CH₃CN

THF

1b: $R^1 = Ph$, $R^2 = Me$ (96% *E*) CH_3CN

1c: $R^1 = p$ -tolyl-, $R^2 = H$

1d: $R^1 = PhCH_2CH_2$, $R^2 = H$

CH₃CN – HMPA^b

THF - HMPA^b

PhH – HMPA^b

rt,

reflux.

reflux,

reflux,

reflux,

reflux,

reflux,

reflux,

5 days

15 min

4 h

2.5 h

2.5 h

40 min

1 h

Зh

0

0

0

0

22

66^c

81

0

recovery

1 (%)^a

8

93

97

94

88

54

_d

__d

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 SmI₂,^{9, 10} and 1a was quantitatively recovered (run 3). Reactions conducted in THF with or without HMPA resulted in recovery of la 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 SmI2-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





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 SmI₂ 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 SmI₂.

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 $K_2\text{CO}_3$. 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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