Pergamon

Tetrahedron Letters 39 (1998) 1777–1780

TETRAHEDRON
LETTERS

# Regiodivergent Reduction of Allylic Esters with Samarium(II) Iodide by Tuning Ester Groups and Proton Sources

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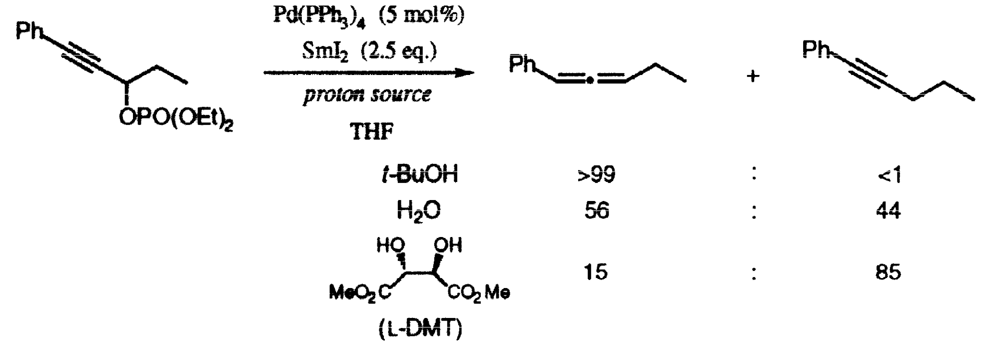
Received 31 October 1997; revised 24 December 1997; accepted 26 December 1997

**Abstract:** *Samarium(II) iodide reduced allylic esters in the presence or the absence of palladium(0) catalyst to give α- and γ-protonated products in a regiodivergent fashion by tuning ester functionality and proton sources.* © 1998 Elsevier Science Ltd. All rights reserved.

Samarium(II) iodide, as a reductant, has been widely used in organic synthesis for the last two decades.[1] Recently, we reported the highly regioselective synthesis of allenic compounds by the palladium(0)-catalyzed reduction of secondary propargylic phosphates with $SmI_2$ in the presence of *tert*-butyl alcohol (*t*-BuOH) as a proton source.[2] More recently, a dramatic changeover of the regioselectivity to produce acetylene derivatives predominantly was observed when dimethyl L-tartrate (L-DMT) was used instead of *t*-BuOH (Scheme 1).[3]

**Scheme 1**



Regiocontrol of the Pd(0)-catalyzed reduction of allylic esters is well established.[4] For example, most of the metal hydride reagents attack the less-hindered site of allylic system to give more-substituted olefin,[5] while hydrogenolysis of allylic acetates and carbonates with ammonium formate[6] gives less-substituted olefins. A study on the reduction of allylic acetates by $Pd(0)/SmI_2/i\text{-}PrOH$ system[7] *via* umpolung[8] has also been reported. However, the effect of proton sources on the regioselectivity has not been well examined. Herein, we report

*PII:* S0040-4039(98)00042-2

the regiodivergent reduction of allylic phosphates, carbonates, and acetates which affords either α- or γ-protonated products regioselectively by tuning proton sources.

First, the reduction of cinnamyl esters was examined in the presence of various proton sources (Table 1). All reactions proceeded cleanly to give α- and γ-products in high combined yields (80-100%). The Pd(0)-catalyzed reduction of the phosphate completed within 20 min (entries 1-6). As expected, the α-selectivity was observed with *t*-BuOH as a proton source, while the γ-selectivity was observed with L-DMT (entries 1 *vs.* 2). Interestingly, the use of smaller proton sources gave rise to higher γ-selectivity (entries 1 and 3-5). Thus, $H_2O$ was found to be best for the synthesis of the γ-protonated product (entry 5).

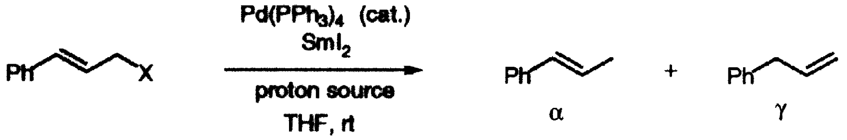


**Table 1** Reduction of cinnamyl esters.

| entry | X | proton source | reaction time | ratio (α/γ)[a] |
|---|---|---|---|---|
| 1 | $OPO(OEt)_2$ | *t*-BuOH | 20 min | 62 : 38 |
| 2 | $OPO(OEt)_2$ | L-DMT | 20 min | 32 : 68 |
| 3 | $OPO(OEt)_2$ | *i*-PrOH | 20 min | 48 : 52 |
| 4 | $OPO(OEt)_2$ | MeOH | 20 min | 15 : 85 |
| 5 | $OPO(OEt)_2$ | $H_2O$ | 20 min | 7 : 93 |
| 6[b] | $OPO(OEt)_2$ | *t*-BuOH | 20 min | 79 : 21 |
| 7[c] | $OPO(OEt)_2$ | *t*-BuOH | 2.5 h | 81 : 19 |
| 8 | $OCO_2Me$ | *t*-BuOH | 1.0 h | 72 : 28 |
| 9 | $OCO_2Me$ | $H_2O$ | 1.0 h | 11 : 89 |
| 10 | OAc | *t*-BuOH | 2.0 h | 81 : 19 |
| 11 | OAc | $H_2O$ | 2.0 h | 5 : 95 |
| 12[b] | OAc | $H_2O$ | 2.0 h | 70 : 30 |

[a] Determined by $^1H$ NMR analysis. [b] HMPA (10 eq.) was added. [c] Without $Pd(PPh_3)_4$.

This anomalous behavior of $H_2O$ can be explained as follows. The allylsamarium(III) intermediate is considered to have $\eta^1$-terminal metal structure or $\eta^3$-structure (Fig. 1),[9,10,11] in which the $C_\gamma$-Sm bond would be longer than the $C_\alpha$-Sm bond because of the steric repulsion between $SmL_n$ and γ-substituent (Ph). A bulky proton source with poor coordinating ability, such as *t*-BuOH, reacts with allylsamarium(III) mainly through $S_E2$ pathway to give the α-protonated isomer. On the other hand, since $H_2O$ can strongly coordinate to samarium ion, the coordinated water molecule could be delivered in an intramolecular fashion through a cyclic 6-membered transition state ($S_E2'$ pathway) (Fig. 2).[12]

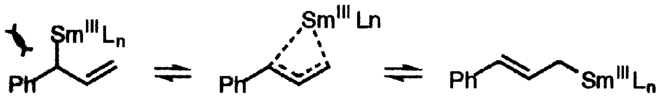


**Fig. 1.** Equilibrium of allylsamarium(III)

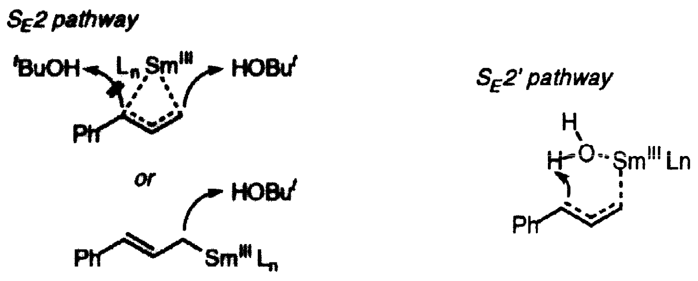


**Fig. 2.** Protonation of allylsamarium(III)

The effect of hexamethylphosphoric triamide (HMPA) and the palladium catalyst was also examined. The addition of HMPA improved the α-selectivity (entry 6) as expected from the consideration of the allylsamarium intermediate with bulky HMPA ligand (Fig. 1, $L_n$ = $(HMPA)_n$). As shown in entry 7, the use of Pd(0) catalyst is not always necessary to generate allylsamarium species[10,13] though the reaction requires longer time. A high α-selectivity was also observed in this case. These results suggest the α-selective umpolung of allylic phosphate by Sm(II) without Pd(0) catalyst (entry 1 *vs.* 7).

In the reduction of cinnamyl methyl carbonate and cinnamyl acetate (entries 8-11), a similar regioselection was observed: α-selectivity using *t*-BuOH (entries 8 and 10) and high γ-selection with $H_2O$ (entries 9 and 11) as a proton source. Interestingly, the sense of regioselectivity was again reversed by the addition of HMPA (entry 11 *vs.* 12) probably because of the predominant coordination of HMPA over $H_2O$, which would no longer permit protonation through the cyclic $S_E2'$ pathway.

Finally, we examined the reduction of geranyl and neryl phosphate in the absence of Pd(0) catalyst (Table 2). In both cases, protonation with *t*-BuOH occurred at α-position (entries 1 and 4) whereas the use of $H_2O$ in place of *t*-BuOH afforded a γ-protonated product (entry 3). In these reactions, stereochemistry of the double bonds was completely retained.[10] These facts exemplify the α-selective umpolung by Sm(II) without Pd(0).

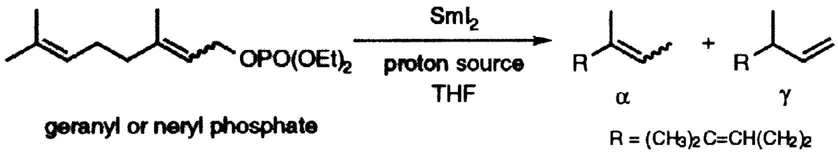


**Table 2.** Reduction of geranyl or neryl phosphate.

| entry | phosphate | proton source | reaction time | ratio (α/γ)[a] |
|---|---|---|---|---|
| 1 | geranyl | *t*-BuOH | 1.3 h | 88 (*E* only) : 12 |
| 2 | | L-DMT | 15 min | 45 (*E* only) : 55 |
| 3 | | $H_2O$ | 1.5 h | 26 (*E* only) : 74 |
| 4 | neryl | *t*-BuOH | 4 h | 90 (*Z* only) : 10 |

[a] Determined by $^1H$ NMR analysis.

In conclusion, we realized the Pd(0)-catalyzed regiodivergent reduction of allylic esters with $SmI_2$ by tuning ester groups and proton sources. The α-selectivity increases in the following order by decreasing the reactivity of allylic esters: phosphate with Pd(0) catalyst, carbonate with Pd(0), acetate with Pd(0), phosphate without Pd(0). On the other hand, highly $\gamma$-selective protonation is accomplished by the use of $H_2O$.

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12. In contrast, $H_2O$ gave products with low regioselectivity, when propargylic phosphates or acetate[14] were used as substrates (Scheme 1). It is difficult that allenyl/propargylsamarium(III) of linear structure reacts with $H_2O$ *via* 6-membered cyclic $S_E2'$ pathway. Therefore, the low regioselectivity was observed.
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