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Samarium diiodide-mediated asymmetric reactions of 8-phenylmenthyl esters

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Abstract

(–)-8-Phenylmenthol was used as a chiral auxiliary to direct asymmetric reactions of its preformed carboxylates. Reduction of xanthates **1a** and **1b** by SmI₂ likely proceeded via HMPA-bound samarium enolate intermediates. Self- and cross-pinacolic coupling reactions of 8-phenylmenthyl α-oxoesters were achieved in a highly stereoselective manner by treatment with SmI₂ at –78°C. The stereochemical outcome was consistent with a chelated mode of transition states. © 2000 Elsevier Science Ltd. All rights reserved.

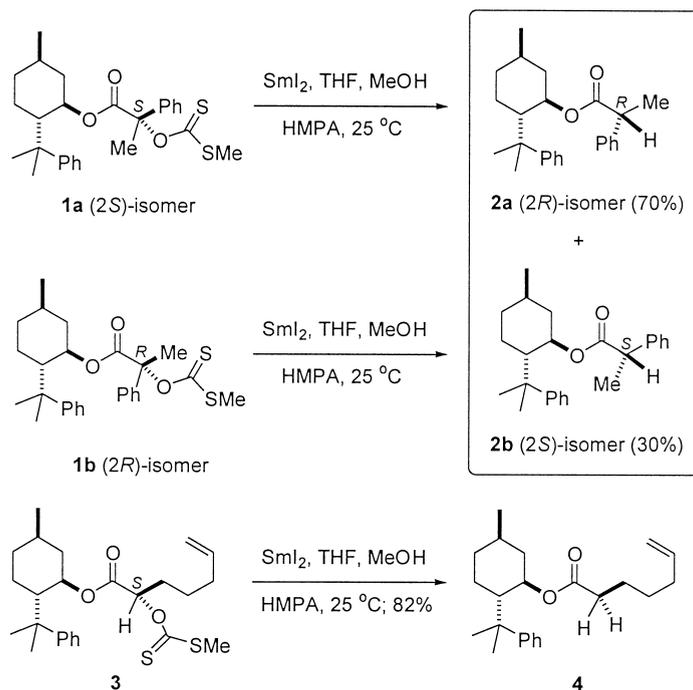
Keywords: asymmetric reactions; coupling reactions; samarium diiodide; xanthates.

Asymmetric pinacolic coupling of chiral α-ketoamides by SmI₂ has recently been reported to give 2,3-disubstituted tartaric acids derivatives in a high diastereoselectivity.¹ This report prompts us to disclose our results of the related reactions using (–)-8-phenylmenthol as a useful chiral auxiliary to direct asymmetric reactions of its preformed carboxylates.² The 8-phenylmenthyl auxiliary generally exerts better stereocontrol than the corresponding menthyl analogs in many types of reactions, such as alkylations,³ Michael reactions,⁴ Diels–Alder reactions,⁵ Wittig rearrangements⁶ and radical reactions.⁷ Application of (–)-8-phenylmenthol to asymmetric reactions of α-oxocarboxylates has been reported, such as reduction,⁸ additions of organic metallic reagents,⁹ addition of allylstannanes or allylsilanes with the mediation of Lewis acids,¹⁰ ene reactions with the promotion of SnCl₄,¹¹ Henry reactions,¹² and photochemical [2+2] cycloadditions.¹³

Although SmI₂ is often used as a one-electron-transfer reducing agent,¹⁴ the reaction of xanthates with SmI₂ has not yet been reported. We examined the SmI₂-mediated reaction of xanthates **1a** and **1b** (Scheme 1), and made a comparison with the reductions using Bu₃SnH. A THF solution of **1a** (having 2*S* configuration) was treated with SmI₂ at 25°C in the presence of HMPA and MeOH, and a mixture of epimers **2a** and **2b** was obtained in a ratio of 70:30. The reaction of **1b** (having 2*R* configuration) with SmI₂ also gave two epimers in the same ratio. The (2*R*)- and (2*S*)-configurations of **2a** and **2b** were determined by correlation to the corresponding (*R*)-

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and (*S*)-2-phenylpropanols via reductions with LiAlH_4 .¹⁵ Unlike the SmI_2 reduction, reductions of xanthates **1a** and **1b** with Bu_3SnH gave **2b** as the major product.^{7c} The Bu_3SnH reductions in refluxing benzene yielded a 37:63 mixture of **2a** and **2b**. The photo-initiated (300 nm) Bu_3SnH reductions at 25°C also gave **2a** and **2b** in a similar ratio (29:71).



Scheme 1.

We speculated that the SmI_2 reductions proceeded via enolate intermediates, whereas the Bu_3SnH reductions proceeded via radical intermediates. An experiment using pentenyl-tethered xanthate **3** (Scheme 1) indicated that only reduction, giving **4** (82%), but no radical cyclization occurred on treatment with SmI_2 . Electron transfer from SmI_2 to the putative α -carbon radical appeared to be fast to form the samarium enolates, which were likely bounded with HMPA ligands (Fig. 1). The (*Z*)-enolate might be disfavored by the repulsion of the phenyl substituent against the HMPA ligands. The major product **2a** having the (2*R*)-configuration could be

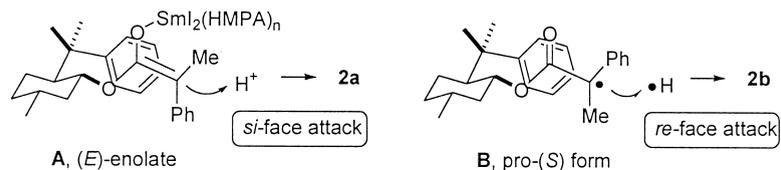
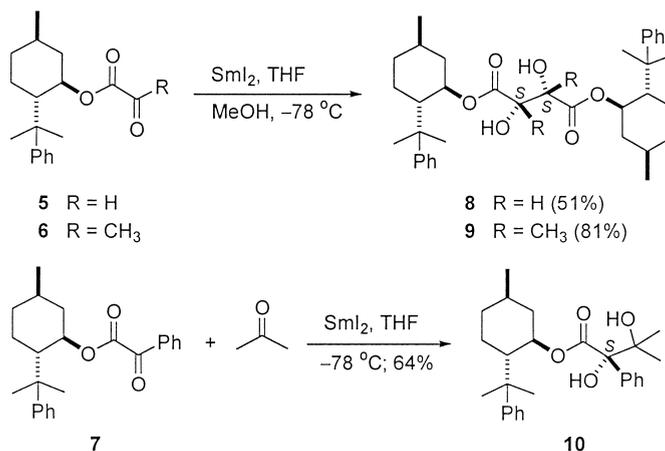


Figure 1. Reduction of xanthates **1a** and **1b** with SmI_2 gave predominantly **2a** via protonation of the (*E*)-enolate intermediate **A**, of which the larger phenyl substituent was *anti* to the HMPA-bound samarium ion. Reduction of xanthate **1a** and **1b** with Bu_3SnH gave predominantly **2b** via the pro-(*S*) form of the α -carbon radical intermediate **B**, of which the large phenyl substituent was *anti* to the 8-phenylmethyl group

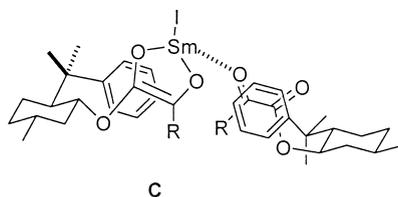
obtained by protonation of the (*E*)-enolate **A** from the *si*-face. On the other hand, the α -carbon radical intermediate **B** with the pro-(*S*) conformation would predominate, because it disposed the larger phenyl substituent *anti* to the alkoxy group of the ester. Abstraction of hydrogen atom thus occurred from the *re*-face of **B** to give the (*2S*)-epimer **2b**.

Pinacolic coupling reactions of 8-phenylmenthyl α -oxoesters were achieved in a highly stereoselective manner by treatment with SmI_2 at -78°C (Scheme 2). Thus, the coupling reaction of (–)-8-phenylmenthyl glyoxylate (**5**) afforded a bis(8-phenylmenthyl) ester of (*2S,3S*)-tartaric acid (**8**). The structure of **8** was confirmed by comparison with an authentic sample prepared from the esterification of (*2S,3S*)-tartaric acid with (–)-8-phenylmenthol.¹⁶ A similar reaction of (–)-8-phenylmenthyl pyruvate (**6**) with SmI_2 gave bis(8-phenylmenthyl) (*2S,3S*)-2,3-dimethyltartrate (**9**) in 81% yield as the exclusive product.¹⁷ This asymmetric pinacolic coupling reaction constructed two stereogenic quaternary carbons. Elaboration of such a product can lead to chiral C_2 -symmetric substrates useful for designing chiral catalysts. A crossed pinacolic coupling reaction of (–)-8-phenylmenthyl phenylglyoxylate (**7**) and acetone was also effected by SmI_2 , giving diol **10** with the (*S*)-configuration.¹⁸



Scheme 2.

The stereochemical outcome of pinacolic coupling reactions was consistent with a chelated mode of transition states. The tight ion pairs formed with oxygen–samarium bonds could diminish the electrostatic repulsion. The reaction might proceed via coupling of two ketyl radicals or via addition of enolate to carbonyl group. The latter pathway is illustrated in the transition state **C**, which shows the α -oxoester approaching the counter part of the samarium-chelated (*Z*)-enolate. Both moieties exposed their *si*-faces to furnish the coupling reaction in the observed stereochemistry.



Acknowledgements

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- The acid-catalyzed esterifications of (2*S*,3*S*)- and (2*R*,3*R*)-tartaric acids with (–)-8-phenylmenthol were conducted in refluxing benzene with azeotropic removal of water to give, respectively, the authentic samples of **8** and its (2*R*,3*R*)-diastereomer.
- All the new compounds are characterized by spectral methods (IR, MS, HRMS, ¹H and ¹³C NMR). Compound **9**: [α]_D²⁶ –2.5 (CHCl₃, *c* = 1.2). Compound **10**: [α]_D²⁶ +7.0 (CHCl₃, *c* = 1.0).
- The crossed pinacolic coupling reaction of (–)-8-phenylmenthyl pyruvate and acetone was also carried out by treatment with acidic TiCl₃ aqueous solution. Chen, M.-Y., Ph.D. Thesis, National Taiwan University, 1991.