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Convenient Preparation and Reaction of a Divalent Ytterbium Thiolate

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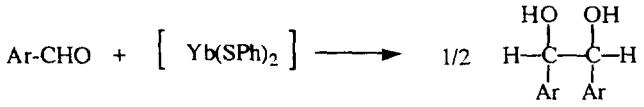
Abstract: *Ytterbium metal (Yb) reacts with phenylthiotrimethylsilane to generate ytterbium(II) phenylthiolate. The divalent ytterbium thiolate [Yb(SPh)$_2$], thus formed in situ, reacts with aromatic aldehydes to give pinacols.* Copyright © 1996 Elsevier Science Ltd

Recently, we reported that the benzophenone catalyzed reaction of diaryl and -alkyl disulfides with lanthanoid metals (Yb, Sm) affords lanthanoid(III) thiolates, and that the thiolates thus formed *in situ*, react with enones to give β-sulfenylated ketones.[1] We have also found that trimethylsilyl bromide (TMS-Br) reacts with ytterbium metal to give $YbBr_2$ which has a strong reducing ability.[2] In continuing studies on exploring synthetic reactions using rare earth metals, we have found that phenylthiotrimethylsilane reacts with Yb metal to give the corresponding divalent Yb thiolate [$Yb(SPh)_2$] (Eq.1). The Yb(II) thiolate, thus formed *in situ*, has a reducing ability and reacts with aromatic aldehydes to afford the corresponding pinacols (Eq.2). In this communication we wish to report these novel results.

$$Yb \; + \; 2\,PhS\text{-}Si(CH_3)_3 \xrightarrow[CH_3CH_2CN]{} \left[\; Yb(SPh)_2 \;\right] \; + \; (CH_3)_3Si\text{-}Si(CH_3)_3 \qquad (1)$$



$$Ar\text{-}CHO \; + \; \left[\; Yb(SPh)_2 \;\right] \longrightarrow 1/2 \;\; H\!-\!\underset{Ar}{\overset{HO}{C}}\!-\!\underset{Ar}{\overset{OH}{C}}\!-\!H \qquad (2)$$

The typical preparation of 1,2-bis-(*p*-tolyl)-1,2-ethanediol is as follows (entry 1 in Table 1): A mixture of Yb metal (87 mg, 0.5 mmol) and phenylthiotrimethylsilane[3] (182 mg, 1.0 mmol) in CH_3CH_2CN (5 mL) was stirred at refluxing temperature for 8 h under argon. Ytterbium metal dissolved to form a clean red solution which changed to a red suspension as the reaction proceeded.[4, 5] Then, *p*-tolualdehyde (60 mg, 0.5 mmol) was added to the mixture by a syringe. The mixture was stirred at 50°C for 2 h. Usual work-up followed by SiO_2 column chromatography (hexane-ethyl acetate, 10:1) gave 1,2-di-(*p*-tolyl)-1,2-ethanediol (40 mg, 66%) as colorless needles together with a small amount of *p*-$CH_3C_6H_4CH_2OH$ (12 mg, 20%). The diastereoselectivity of the pinacol is determined to be 3:1 (*dl:meso*) by ^{1}H-NMR analysis. Propionitrile and acetonitrile as the solvent gave good results in this reaction, but THF, 1,4-dioxane, benzene and toluene led to inferior results. Addition of polar solvent such as hexamethylphosphoric triamide (HMPA), dimethylimidazolidinone (DMI) and pyridine to propionitrile was ineffective for pinacol formation and resulted in the decomposition of phenylthiotrimethylsilane.

The representative results for the coupling reaction of various aromatic aldehydes mediated by $Yb(SPh)_2$ are summarized in Table 1. This lanthanoid reagent has a mild reducing ability to aromatic aldehydes. However, the reaction of aliphatic aldehydes and aromatic ketones such as *n*-octanal, acetophenone, and benzophenone gave a complex mixture. In all cases of aromatic aldehydes, the reactions proceed with appreciable diastereoselectivities (*dl:meso* = 3:1 ~ 4:1).[6]

Table 1. $Yb(SPh)_2$ promoted pinacol coupling of aromatic aldehydes

entry	substrate	time (h)	yield (%)[a)]	*dl:meso*[b)]
1	*p*-tolualdehyde	2	66	3:1
2	*p*-anisaldehyde	2	69	4:1
3	benzaldehyde	2	41	4:1
4	*p*-chlorobenzaldehyde	2	47	3:1
5	*p*-cyanobenzaldehyde	1	61	4:1

a) Isolated yield. b) Determined by ^{1}H-NMR.

Further mechanistic study and extension of this reaction are under investigation.

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3. Kuwajima, I.; Abe, T. *Bull. Chem. Soc. Jpn.*, **1978**, *51*, 2183-2184.
4. Nakamura *et al.* reported that the $Yb(SPh)_2(thf)_n$ complex was isolated as a red, insoluble powder from the reaction of Yb metal and diphenyldisulfide in tetrahydrofuran. See, Mashima, K.; Nakayama, Y.; Kanehisa, N.; Kai, Y.; Nakamura, A. *J. Chem. Soc., Chem. Commun.*, **1993**, 1847-1848.
5. Reaction of Yb metal (0.5 mmol) with phenylthiotrimethylsilane (1 mmol) in CH_3CN (5 mL) at room temperature for 2 days gave a similar red suspension. The suspension was separated to red solution and red solid by decantation. From the solution, phenylthiotrimethylsilane was recovered in 62% yield (38% conversion) along with hexamethyldisilane (5%) and hexamethyldisiloxane (11%).
6. Kagan and coworkers reported the SmI_2 mediated coupling reaction of benzaldehyde to afford 1,2-bisphenyl-1,2-ethanediol in a 56:44 (*dl:meso*) ratio. See, Namy, J. L.; Souppe, J.; Kagan, K. B. *Tetrahedron Lett.*, **1983**, *24*, 765-766.

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