Samarium(II)-Mediated Pinacol Coupling in Water: Occurrence of Unexpected Disproportionation and Action of Low-valent Samarium as an Active Species

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Supporting Information

General.

All reactions were run under an air at 25 °C. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JMN-GS400 spectrometer. UV-vis analyses were carried out by a JEOL UV-2500PC spectrometer. Water was distilled by a SHIBATA WS-16 system. Samarium powder was prepared by abrading from ingot. All aldehydes and ketones were used without purification. Flash chromatography was performed on Wakogel C-200.

SmCl₃-Sm-mediated Pinacol coupling of benzaldehyde in water.

To a mixture of Sm powder (450 mg, 3 mmol) and SmCl₃ (364 mg, 1 mmol) in H₂O was added benzaldehyde (106 mg, 1 mmol). After 36 h, the resultant yellow green suspension was treated with 2 M HCl (10 ml) and extracted with ether. The organic layer was washed with NaHCO₃(twice) and brine, then dried and concentrated in vacuo. The crude product was passed through flush column chromatography, and coupling product was obtained in 81% yield (86mg, dl / meso = 58 : 42). The reactions of p-anisaldehyde, p-chlorobenzaldehyde, p-trifluoromethylbenzaldehyde, acetophenone, 3-methoxyacetophenone, benzalacetone, and nonylaldehyde were carried out by the same way.

SmCl₃-Sm-mediated Barbier Reaction of benzaldehyde and allyl bromide in water.

To a mixture of Sm powder (450 mg, 3 mmol) and SmCl₃ (364 mg, 1 mmol) in H₂O was added allyl bromide (121 mg, 1 mmol) and benzaldehyde (106 mg, 1 mmol). After 36 h, the resultant yellow green suspension was treated with 2 M HCl (10 ml) and extracted with ether. The organic layer was washed with NaHCO₃(twice) and brine, then dried and concentrated in vacuo. The crude product was passed through flush column chromatography, and coupling product was obtained in 71% yield (75 mg, dl / meso = 51 : 49).

SmCl₃-Mg-mediated Pinacol coupling of benzaldehyde in water.

To a mixture of Mg powder (72 mg, 3 mmol) and SmCl₃ (364 mg, 1 mmol) in H₂O was added benzaldehyde (106 mg, 1 mmol). After 36 h, the resultant white suspension was treated with 2 M HCl (5 ml) and extracted with ether. The organic layer was washed with NaHCO₃(twice) and brine, then dried and concentrated in vacuo. The crude product was passed through flush column chromatography, and coupling product was obtained in 78% yield (84mg, dl / meso = 54 : 46). The reaction of acetophenone was carried out by the same way.