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Samarium Diiodide-Promoted Reductive Coupling of Imines

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Aromatic aldimines are reductively coupled to 1,2-diamines by treatment with samarium diiodide. Cross-coupling of aromatic ketimines with ketones to 2-aminoalcohols is also promoted by the same reagent.

Subsequent to the pioneering work by Kagan and his co-workers, samarium diiodide has become an extremely useful reagent in organic synthesis.[1,2] Our interest in utilization of this characteristic reducing agent in carbon-carbon bond-forming reactions[3] led us to investigate reductive coupling of imines and related reactions.[4] Recently, Fujiwara *et al.* reported reduction and reductive dimerization of imines promoted by ytterbium metal.[5,6] We now wish to report the preliminary results of our independent study using samarium diiodide.

Several imines were treated with SmI_2 in tetrahydrofuran. As shown in Table 1, aromatic aldimines smoothly underwent reductive coupling to yield 1,2-diamines in good yields.[7,8] However, aromatic ketimines such as benzophenone anil and fluorenone anil were, contrariwise, almost quantitatively reduced to the corresponding secondary amines.

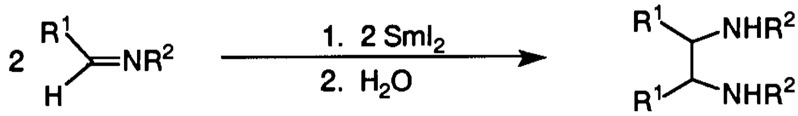
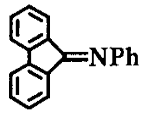
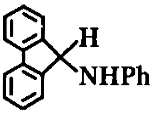
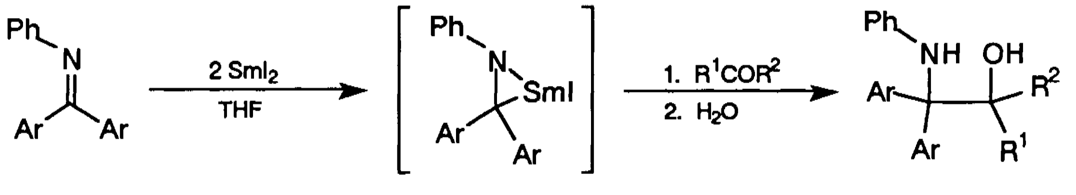


Table 1. Reactions of Imines with Samarium Diiodide

Imine	Molar ratio of SmI_2/imine	Temp / °C	Time / h	Product	Yield / %
PhCH=NPh	2	65	0.5	Ph(PhNH)CHCH(NHPh)Ph	93
PhCH=NC_6H_4Me-*p*	4	65	1	Ph(*p*-MeC_6H_4NH)CHCH(NHC_6H_4Me-*p*)Ph	84
p-MeC_6H_4CH=NPh	2	65	1	(*p*-MeC_6H_4)(PhNH)CHCH(NHPh)(C_6H_4Me-*p*)	82
PhCH=NC_6H_4Cl-*p*	2	65	0.5	Ph(*p*-ClC_6H_4NH)CHCH(NHC_6H_4Cl-*p*)Ph	84
PhCH=NCH_2Ph	4	25	1	Ph($PhCH_2NH$)CHCH($NHCH_2Ph$)Ph	38
PhCH=NBu-*t*	4	25	1.5	Ph(*t*-BuNH)CHCH(NHBu-*t*)Ph	10
	10	25	0.6		68
Ph_2C=NPh	2	65	1	$Ph_2CHNHPh$	98
	2	65	1		97

Next, we tried reductive cross-coupling of imines with carbonyl compounds. Benzophenone anil or fluorenone anil was allowed to react with SmI_2 at 65 °C. The resulting mixture was treated with aliphatic ketones, such as cyclohexanone, to afford the corresponding 2-aminoalcohols in 44-73% yield.[9,10] These results suggest that this reaction sequence involves an organosamarium species as a reactive intermediate.



References

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2) Representative examples of recent reports on organic synthesis with samarium diiodide: J. Collin, F. Dallemer, J. L. Namy, and H. B. Kagan, *Tetrahedron Lett.*, **30**, 7407 (1989); G. A. Molander and C. Kenny, *J. Am. Chem. Soc.*, **111**, 8236 (1989); M. Matsukawa, J. Inanaga, and M. Yamaguchi, *Tetrahedron Lett.*, **28**, 5877 (1987); S. Fukuzawa, M. Iida, A. Nakanishi, T. Fujinami, and S. Sakai, *J. Chem. Soc., Perkin Trans. 1*, **1988**, 1669; T. L. Fevig, R. L. Elliott, and D. P. Curran, *J. Am. Chem. Soc.*, **110**, 5064 (1988); S. Takeuchi and Y. Ohgo, *Chem. Lett.*, **1988**, 403; M. Murakami, T. Kawano, and Y. Ito, *J. Am. Chem. Soc.*, **112**, 2437 (1990).

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6) Other methods for reductive coupling of imines have been reported. E. J. Roskamp and S. F. Pedersen, *J. Am. Chem. Soc.*, **109**, 3152 (1987); C. Betschart and D. Seebach, *Helv. Chim. Acta* **70**, 2215 (1987); P. Mangeney, T. Tejero, A. Alexakis, F. Grosjean, and J. Norman, *Synthesis*, **1988**, 255; H. Tanaka, T. Nakahara, H. Dhimane, and S. Torii, *Synlett*, **1989**, 51; H. Tanaka, H. Dhimane, H. Fujita, Y. Ikemoto, and S. Torii, *Tetrahedron. Lett.*, **29**, 3811 (1988).

7) A typical experimental procedure is described for the reaction of *N*-benzylidene aniline with SmI_2. A solution of CH_2I_2 (2 mmol) in dry THF (2 ml) was slowly added, with vigorous stirring, to samarium powder (*ca.* 50 mesh) (375 mg, 2.5 matom) at 0 °C under argon. The mixture was then refluxed for 30 min. *N*-Benzylidene aniline (181 mg, 1 mmol) in THF (1 ml) was added to the resulting deep-green suspension, and the mixture was refluxed for an additional 30 min. The usual work-up afforded a 93% yield of 1,2-dianilino-1,2-diphenylethane as a 80:20 (*d,l/meso*) mixture of diastereomer.

8) Aliphatic imines did not undergo reductive coupling or reduction under these conditions.

9) Treatment with D_2O in place of carbonyl compound provided C-deuterated reduction product in quantitative yield.

10) This procedure, however, was not applicable to the cross-coupling of aromatic aldimines with ketones, since aromatic aldimines were readily subjected to reductive dimerization. Treatment of a mixture of aldimine and cyclohexanone with SmI_2 at reflux provided 2-aminoalcohol (20-41%) together with 1,2-diamine (36-79%).

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