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Reduction and Coupling Reaction of Imines Promoted by Ytterbium Metal

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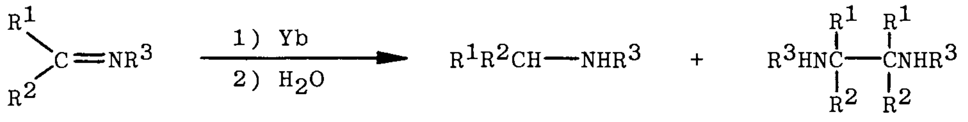
Ketimines are readily reduced to the corresponding amines by the treatment with ytterbium metal followed by quenching with water. On the other hand, reductive coupling reaction of aldimines takes place to give predominantly 1,2-diaminoethane derivatives.

In the previous papers,1) we have reported a facile reduction of carbon-carbon double and triple bonds conjugated with aromatic rings by lanthanoids. Ytterbium metal promoted also the cross-coupling reaction of ketones leading to unsymmetrical pinacols.2) Comparing with carbonyl functions, the reductive coupling of imines is less common in spite of utility of the resulting vicinal diamines.3) We report herein a convenient method for the reduction and coupling of imines promoted by ytterbium metal.

When N-diphenylmethyleneaniline (**1a**) was treated with an equimolar amount of ytterbium metal and quenched with water, N-diphenylmethylaniline (**2a**) was obtained in 92% yield. Quenching with deuterium oxide gave C-deuteriated **2a**. However treatment of **1a** with Yb in the presence of methanol, the typical conditions for the carbon-carbon multiple bond reduction,1) resulted in the recovery of the imine **1a**. These results are summarized in Table 1.

The yields of the reduction products **2a** and **2b** increased by the use of 2.5 equiv. of imines **1a** and **1b**, but no coupling product was detected (entries 2 and 4). In contrast, reaction of aldimine **1c** with 1.0 equiv. of Yb gave N-benzylaniline (**2c**) and 1,2-dianilinobibenzyl (**3c**) in 32 and 23% yields, respectively. The latter compound was a 70:30 mixture of two diastereomers.4) When the imine **1c** was added in excess, the bibenzyl **3c** was obtained as a sole product (entry 6). In the reaction of aldimine **1d**, the coupling reaction took place exclusively to afford **3d**, irrespective of the molar ratio (entries 7 and 8).

A typical example is as follows; N-diphenylmethyleneaniline (**1a**) (257 mg, 1 mmol) in dry THF (2 ml) was added under nitrogen to a slurry of activated ytterbium (173 mg, 1 mmol, 40 mesh) in THF (2 ml) and HMPA (1 ml). Within 10 min, color of the mixture changed to green then dark red, and stirring was continued for 6.5 h at room temperature. Usual workup followed by chromatographic purification on silica gel gave N-diphenylmethylaniline (**2a**) (238 mg, 92%).



1 **2** **3**

a: R^1= Ph, R^2= Ph, R^3= Ph
b: R^1= Ph, R^2= Ph, R^3= H
c: R^1= Ph, R^2= H , R^3= Ph
d: R^1= Ph, R^2= H , R^3= CH_2Ph

Table 1. Reduction and coupling reaction of imines promoted by ytterbium metal

Entry	Imine	Molar ratio (Imine/Yb)	Product yield/%[a)]	
			2	**3**
1	**1a**	1.0	92	0
2	**1a**	2.5	(120)	0
3	**1b**	1.0	93 (99)	0
4	**1b**	2.5	(112)	0
5	**1c**	1.0	32	23[b)]
6	**1c**	2.5	0	81 (98)
7	**1d**	1.0	0	46[b)]
8	**1d**	2.5	0	61

a) Isolated yields (GC yields) based on Yb.

b) Diastereomer ratios were 70:30 for **3c** and 100:0 for **3d**, determined by ^{13}C-NMR.

References

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2) Z.Hou, K.Takamine, Y.Fujiwara, and H.Taniguchi, Chem. Lett., 1987, 2061; Z.Hou, K.Takamine, O.Aoki, H.Shiraishi, Y.Fujiwara, and H.Taniguchi, J. Chem. Soc., Chem. Commun., 1988, 668; Z.Hou, K.Takamine, O.Aoki, H.Shiraishi, Y.Fujiwara, and H.Taniguchi, J. Org. Chem., 53, 6077 (1988).
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4) The major isomer would be a *d,l*-compound, though it was not confirmed.

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