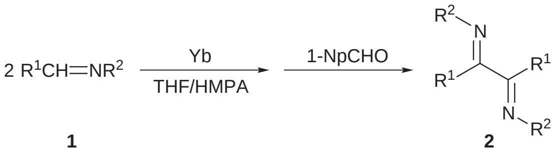
Preparation of vicinal diimines: a new dehydrogenative coupling reaction of aldimines mediated by ytterbium metal

Wu-Song Jin, Yoshikazu Makioka, Yuki Taniguchi, Tsugio Kitamura and Yuzo Fujiwara*†

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashiku, Fukuoka 812-8581, Japan

Dehydrogenative coupling takes place to give vicinal diimine compounds in the reaction of aromatic aldimines with ytterbium metal followed by treatment with aromatic aldehydes such as 1-naphthaldehyde (1-NpCHO) as a hydrogen acceptor.

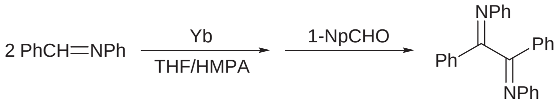
Lanthanide metals have been utilized for various transformations of organic functional groups or C–C bond formations *via* coupling reactions.[1] Previously, we have demonstrated that ytterbium metal causes the coupling reaction of carbonyl and thiocarbonyl compounds,[2] and that imines undergo a similar reaction to give 1,2-diamines or α-amino acids.[3] Imamoto and Nishimura and others reported that samarium(II) compounds are also capable of the coupling of imines to give 1,2-diamines.[4] Recently, a triphenylimine dianion complex $[Yb(\eta^2\text{-}Ph_2CNPh)(HMPA)_3]$ has been successfully isolated from the direct reaction of ytterbium metal and triphenylimine and characterized by X-ray analysis.[5] In a continuing study of the reactions of aldimines and ytterbium metal, we have found that the reaction of aromatic aldimines and ytterbium metal followed by addition of oxidants produces the corresponding vicinal diimine compounds [eqn. (1)]. Here we report these new results.



(1)

1 **2**

First, *N*-benzylideneaniline (**1a**) was reacted with 0.5 equiv. of ytterbium metal at room temperature then an oxidant was added and the mixture was stirred for 2 h to give the dehydrogenative coupling product, *N*,*N′*-diphenyl-1,2-diphenylethane-1,2-diimine (**2a**) in 81% yield [eqn. (2)].‡ The effects of various oxidants toward the dehydrogenative coupling reaction of **1a** are summarized in Table 1. From the data in Table 1 one can see that aromatic aldehydes (entries 1–4) are the best compared with others. In particular when 1-NpCHO is used, the best result is obtained, whereas the yield of the product is only 7% when an aliphatic aldehyde is used (entry 5). In addition, it is apparent that $CuCl_2$, peroxides and Bu^tNO_2 give inferior results (entries 6–9) and that only 17% yield is obtained in the case of O_2 (entry 10). The presence of HMPA as an additive is necessary in this reaction since the reaction of **1a** and ytterbium metal cannot proceed in THF alone.



(2)

1a **2a**

Table 1 Effect of various oxidants on the dehydrogenative coupling reaction of aldimine **1a**[a]

Entry	Oxidant	mmol	Yield of **2a**[b] (%)
1	1-NpCHO	2	60
2	1-NpCHO	1	81
3	*o*-MeOC$_6$H$_4$CHO	2	49
4	*p*-MeC$_6$H$_4$CHO	2	31
5	Pr^iCHO	2	7
6	$CuCl_2$	2	—
7	*m*-ClC$_6$H$_4$CO$_3$H	2	6
8	$K_2S_2O_8$	2	—
9	Bu^tONO	2	1
10	O_2[c]	2	17

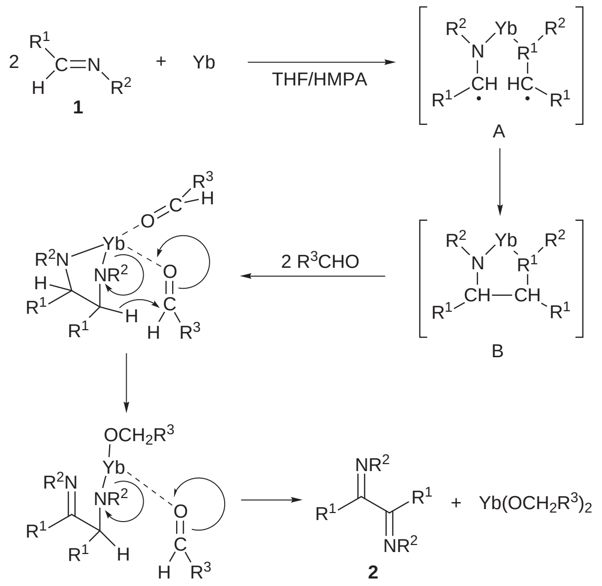
[a] Reaction conditions: 1.0 mmol **1a**, 0.5 mmol Yb, 2 ml THF, 0.5 ml HMPA, 2 μl MeI. [b] GC yield based on **1a**. [c] One atm., 24 h.

The reaction also occurred with various aromatic aldimines as well as **1a**. The representative results for the dehydrogenative coupling reaction of other aldimines **1** are listed in Table 2. When the substrates are non-substituted, *p*-methyl- and *p*-methoxy-substituted aromatic aldimines **1a–d**,**f**,**g**, the reactions proceed smoothly to afford **2a–d**,**f**,**g** (entries 1–4 and 6, 7) in good to high yields. On the other hand, the yields of **2** were low in the reactions of *p*-cyano- and *p*-chloro-substituted aldimines **1e** and **1h** (entries 5 and 8). Thus, the electron-donating substituent on the benzene ring is profitable to the reaction. In the reaction of the *o*-methyl-substituted aldimine **1i** at room temperature, only small amounts of **2i** were formed, and the hydrogenation product (*o*-MeC$_6$H$_4$CHNHPh)$_2$ was formed as the main product. This is due to the steric hinderence of the diazametallacyclopentane intermediate toward dehydrogenation with 1-NpCHO (*vide infra*). However, **2i** could be obtained in a moderate yield at reflux temperature (entry 9). The reaction did not occur in the case of $C_6H_5CH{=}NCMe_3$ (**1j**), and **1j** was recovered (entry 10), due to it's lower reactivity towards ytterbium metal.

Table 2 Dehydrogenative coupling reaction of aldimines **1** mediated by ytterbium metal[a]

Entry	Substrate	R¹	R²	Product	Yield (%)[b]
1	**1a**	Ph	Ph	**2a**	81
2	**1b**	*p*-MeC$_6$H$_4$	Ph	**2b**	90
3	**1c**	*p*-MeOC$_6$H$_4$	Ph	**2c**	86
4	**1d**	*p*-MeOC$_6$H$_4$	*p*-MeC$_6$H$_4$	**2d**	58[c]
5	**1e**	*p*-NCC$_6$H$_4$	Ph	**2e**	5[c]
6	**1f**	Ph	*p*-MeC$_6$H$_4$	**2f**	74
7	**1g**	Ph	*p*-MeOC$_6$H$_4$	**2g**	73
8	**1h**	Ph	*p*-ClC$_6$H$_4$	**2h**	55
9	**1i**	*o*-MeC$_6$H$_4$	Ph	**2i**	50[d]
10	**1j**	Ph	Bu^t	No reaction	

[a] See footnote ‡ for the reaction conditions. [b] GC yield based on **1**. Considerable amounts of 1-NpCH$_2$OH were also formed. [c] Isolated yield. [d] At reflux temperature.



Scheme 1

Although the reaction mechanism is not yet clear, a possible reaction mechanism is shown in Scheme 1. First, one atom of ytterbium metal reacts with two molecules of aldimine **1** *via* two-electron transfer from ytterbium to give a diazametallacyclopentane intermediate B, probably *via* formation of an intermediate A.[6] Subsequent treatment with an aldehyde would cause the coordination and double hydrogen transfer, as in a similar manner to the Meerwin–Pondorf–Varley reduction/Oppenauer oxidation,[7] to give **2** and ytterbium alkoxides, which gives an alcohol R^3CH_2OH after hydrolysis.

In summary, ethane-1,2-diimines **2** can be prepared from the reaction of aromatic aldimines **1** with ytterbium metal followed by treatment with aromatic aldehydes. To the best of our knowledge, this is the first example of metal mediated dehydrogenative coupling of aldimines. Further mechanistic investigation and extension of this reaction are in progress.

The present work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas No. 283, 'Innovative Synthetic Reactions' from Monbusho. Y. M. gratefully acknowleges the financial support of this research by the Japan Society for the Promotion of Science in the form of Research Fellowships for Young Scientists.

Notes and References

† E-mail: yfujitcf@mbox.nc.kyushu-u.ac.jp

‡ Typical procedure for the dehydrogenative coupling of **1** with Yb metal: THF (2 ml), HMPA (0.5 ml) and methyl iodide (2 μl) were successively added to a mixture of **1c** (211 mg, 1.0 mmol) and ytterbium (87 mg, 0.5 mmol) under argon, which was stirred for 2 h at room temperature. Then, 1-NpCHO (156 mg, 1.0 mmol) was added to the mixture. The resulting mixture was stirred for an additional 2 h at room temperature. Usual work-up followed by a silica gel column chromatography (*n*-hexane–ethyl acetate) gave 119 mg (57%) of the desired compound **2c**.

1 T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, 1994, pp. 7–19; Y. Fujiwara, K. Takaki and Y. Taniguchi, *J. Alloys Compd.*, 1993, **192**, 200.

2 For example, Z. Hou, K. Takamine, K. Aoki, O. Shiraishi, Y. Fujiwara and H. Taniguchi, *J. Org. Chem.*, 1988, **53**, 6077; Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1992, 722; K. Takaki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku and Y. Fujiwara, *J. Chem. Soc., Chem. Commun.*, 1990, 516; Y. Makioka, S. Uebori, M. Tsuno, Y. Taniguchi, K. Takaki and Y. Fujiwara, *Chem. Lett.*, 1994, 611; Y. Makioka, M. Tsuno, S. Ueboki, Y. Taniguchi, K. Takaki and Y. Fujiwara, *J. Org. Chem.*, 1996, **61**, 372.

3 K. Takaki, Y. Tsubaki, S. Tanaka, F. Beppu and Y. Fujiwara, *Chem. Lett.*, 1990, 203; K. Takaki, S. Tanaka and Y. Fujiwara, *Chem. Lett.*, 1991, 493; Y. Taniguchi, T. Kuno, M. Nakahashi, K. Takaki and Y. Fujiwara, *J. Alloys Compd.*, 1994, **216**, L9-12; Y. Taniguchi, T. Kuno, M. Nakahashi, K. Takaki and Y. Fujiwara, *Appl. Organomet. Chem.*, 1995, **9**, 491.

4 T. Imamoto and S. Nishimura, *Chem. Lett.*, 1990, 1141; E. J. Enholm, D. C. Forbes and D. P. Holub, *Synth. Commum.*, 1990, **20**, 981; A. Lebrun, E. Rantze, J.-L. Namy and H. B. Kagan, *New J. Chem.*, 1995, **19**, 699.

5 Y. Makioka, Y. Taniguchi, Y. Fujiwara, K. Takaki, Z. Hou and Y. Wakatsuki, *Organometallics*, 1996, **15**, 5476.

6 J. G. Smith and I. Ho, *J. Org. Chem.*, 1972, **37**, 653.

7 C. Djerassi, *Org. React.*, 1951, **6**, 207.

Received in Cambridge, UK, 23rd February 1998; 8/01514G