Letter

Preparation of YbBr₂ and its reaction with aliphatic imines

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Abstract

A powerful reducing reagent, ytterbium dibromide ($YbBr_2$), was synthesized by a new method. Treatment of ytterbium metal with trialkylsilyl bromide in THF/HMPA affords $YbBr_2$. In this solvent system, the trialkylsilyl moiety of trialkylsilyl bromide is converted to trialkylsilanes quantitatively. Thus, the $YbBr_2$ obtained reacts with aliphatic aldimines to give the homocoupling adducts, 1,2-diamines in excellent yields. In the case of aliphatic ketimines, the corresponding reduced and silylated amines are obtained. These results show that the Yb/TMS-Br reagent generates $YbBr_2$ in situ and thus the $YbBr_2$ formed acts as a single electron reductant for these coupling reactions.

Keywords: Aliphatic imines; Ytterbium dibromide; Organic synthesis

1. Introduction

We have developed the new lanthanoid reagents for organic synthesis. For example, lanthanoid metal such as Yb serves as a powerful reducing agent. Yb metal acts as two electron reducing agents in the reaction with diaryl ketones to give Yb-oxymetallacycles, which react with various electrophiles at the umpoled carbon atom of ketones [1].

In a previous paper, we reported a reductive homo-coupling reaction of aliphatic α,β-unsaturated ketones mediated by Yb-TMSBr reagent [2]. The combination of Yb metal with trialkylsilyl bromide has a powerful reducing ability, in which $YbBr_2$ generated in situ is postulated as a reductant. A similar reductive coupling reaction of carbonyl compounds using the TMSCl-NaI-Sm system was also reported [3]. However, isolations of the $YbCl_2(THF)_4$ and $Yb(SiPh_3)_2(THF)_4$ from the reaction of Ph_3SiCl with Yb metal were reported [4]. Lanthanoid dihalides such as SmI_2 [5], $SmBr_2$ [6] and $SmCl_2$ [7] are known and were applied to the reductive coupling of carbonyl compounds.

Although several methods for the synthesis of $YbBr_2$ are developed [8,9], there is no report for a simple and easy preparation of $YbBr_2$ toward the organic synthesis.

The growing importance of 1,2-diamines as bidentate ligand of transition metal catalysis, and chiral template for organic synthesis, has led to the development of new synthetic methods for 1,2-diamines [10]. We reported the reaction of aromatic aldimines with ytterbium metal (Yb) to give the homocoupling adducts, 1,2-diamines [11]. Unfortunately, the reaction of aliphatic aldimines with the Yb metal did not occur because of their lower reactivities to the reductant. Furthermore, Imamoto et al. [12] reported that aliphatic aldimines did not undergo reductive coupling and reduction even with the use of SmI_2. The development of powerful reducing reagents is required to accomplish the C–C bond formation of aliphatic imines.

In this communication, we wish to report the preliminary results for the coupling reaction of aliphatic imines with the $YbBr_2$ reagent stated above.

2. Results and discussion

2.1. Formation of ytterbium dibromide ($YbBr_2$)

In the reaction of ytterbium metal with trimethylsilyl bromide (TMSBr) in THF/HMPA, a green suspension was formed as the reaction proceeded. Decantation of the solution and washing with THF followed by removal of the solvent in vacuo gave a light green solid. ¹H NMR analysis of this green solid in CD_3CN showed the two signals ($\delta = 1.40$ and 3.87 ppm) of THF and

no signal of the trimethylsilyl group (Fig. 1). The filtrate did not reduce imines. From the solution, volatile trimethylsilane [$(CH_3)_3SiH$] could not be detected by GLC analyses. We attempted to detect triethylsilane [$(C_2H_5)_3SiH$] by using triethylsilyl bromide instead of TMSBr. The reaction of triethylsilyl bromide with Yb metal in THF was carried out under the same conditions (Eq. 1). The reaction gave a green suspension

$$2\ Et_3SiBr + Yb \xrightarrow{\text{THF}} YbBr_2 + 2\ Et_3SiH \tag{1}$$
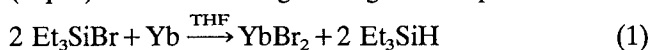
which affected the similar coupling reactions as is the case of the reaction of TMSBr. From the reaction mixture, $(C_2H_5)_3SiH$ was detected by GLC analysis in a quantitative yield. $(C_2H_5)_3SiH$ is formed by the abstraction of H· radical from THF by trialkylsilyl radical ($R_3Si\cdot$) in a mother liquor of this suspension, and no hexaethyldisilane as the coupling product was detected. X-ray analysis of the residual powder separated from this suspension was in fair agreement with the authentic $YbBr_2$ prepared by the reaction of $HgBr_2$ with Yb [9] (Fig. 2). These results clearly indicate that the structure of the green solid is $YbBr_2(THF)_n$. Thus, the $YbBr_2(THF)_n$ obtained is very air-sensitive and hygroscopic. For the in situ preparation of $YbBr_2(THF)_n$, our method toward the organic synthesis is quite simple and easy.

2.2. Reaction of aliphatic imines with ytterbium dibromide

The optimization of the reaction conditions for the homocoupling reaction of N-(isobutylidene)-benzylamine (1a) with $YbBr_2(THF)_n$ was summarized in Table 1. Reaction of Yb metal and TMSBr with 1a gave the corresponding homocoupling adduct, N,N'-dibenzyl-1,2-diisopropyl-1,2-ethylenediamine (2a). Addition of a polar solvent such as HMPA is effective in this reaction. The mixed solvent (THF:HMPA = 4:1) gives the best result (entry 3, Table 1), but THF alone and other non-polar solvents gave inferior results. The role of
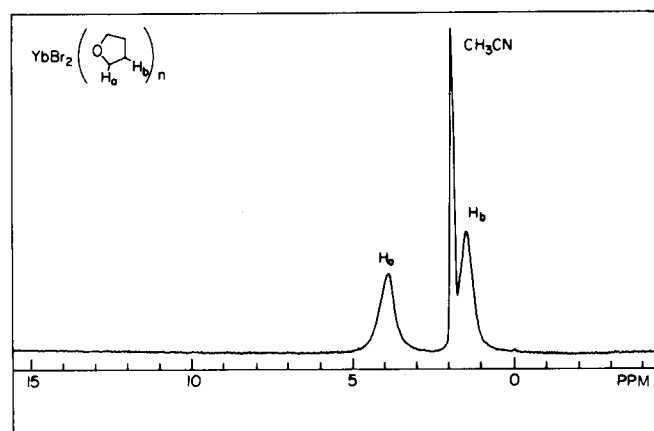

Fig. 1. 270 MHz proton NMR spectra of $YbBr_2(THF)_n$ in CD_3CN.

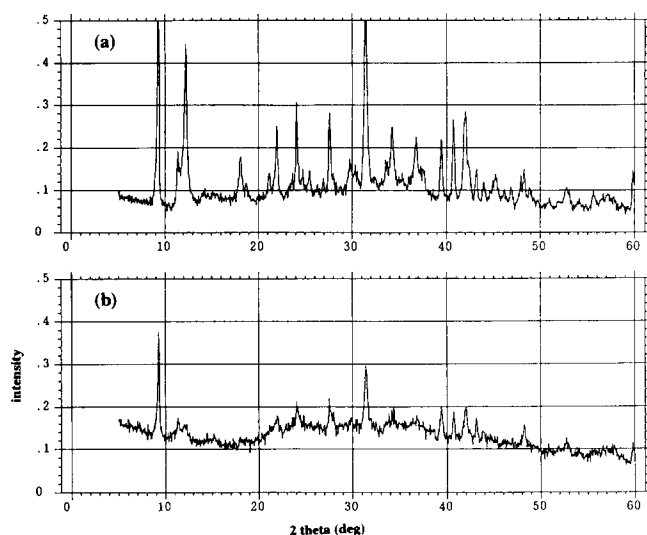Fig. 2. Powder X-ray diffraction patterns of $YbBr_2(THF)_n$, obtained by (a) Yb + $HgBr_2$ and (b) Yb + TMSBr.

Table 1
Optimization of the reaction conditions

Entry	Imine (equiv.)	Yb (equiv.)	TMSBr (equiv.)	Solvent (4 ml)	Yield (%)[a]
1	1	1/2	1	THF/HMPA[b]	64
2	1	1	1	THF/HMPA[b]	54
3	1	1	2	THF/HMPA[b]	86
4	1	1/2	2	THF/HMPA[b]	55
5	1	1	2	THF	23
6	1	1	2	Benzene	11
7	1	1	2	THF[c]	trace

[a]GLC yield based on imines (2 mmol).
[b]THF (4 ml), Hexamethylphosphoric triamide (1 ml).
[c]Refluxed for 2 h.

HMPA seems to increase the reducing ability [1]. Two-fold amounts of TMSBr to Yb metal and to imine 1a are required in this reaction.

The representative results for the reaction of aliphatic imines with $YbBr_2$, generated from Yb metal (1 eq.) and TMSBr (2 eq.), are summarized in Table 2. In these reactions, aliphatic aldimines were selectively coupled to give the corresponding 1,2-diamines in good yields (entries 1–3, Table 2). Aliphatic ketimines did not undergo reductive coupling but suffered the reduction of a C–N double bond to give the hydrogenated and α-silylated monoamines under these conditions (entries 4 and 5, Table 2).

The possible reaction mechanisms for the formation of $YbBr_2$ and its reaction with imines are shown in Scheme 1. Yb metal reacts with two-fold amounts of

Table 2
YbBr₂ promoted reaction of imines

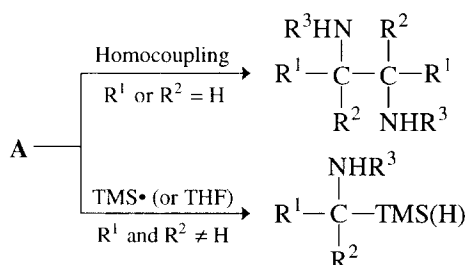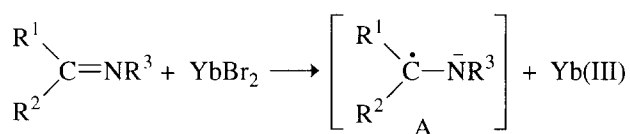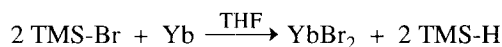$$\begin{array}{c}R^1\\[-2pt]\diagdown\\[-4pt]C=NR^3\\[-4pt]\diagup\\[-2pt]R^2\end{array} + Yb + TMSBr \xrightarrow[\text{rt, 4.5 h}]{\substack{\text{THF (4 ml)}\\\text{HMPA (1 ml)}}} \underset{\substack{| \quad |\\ H \quad NHR^3\\(R^2 = H)\\ \mathbf{2a\text{-}c}}}{R^1-\overset{R^3HN \; H}{\underset{}{C-C}}-R^1} + \underset{\substack{|\\R^2\\(R^2 = \text{alkyl})\\\mathbf{3d\text{-}e,\; 4d\text{-}e}}}{R^1-\overset{NHR^3}{C}-H(TMS)}$$

1a-e
2 mmol   2 mmol 4 mmol
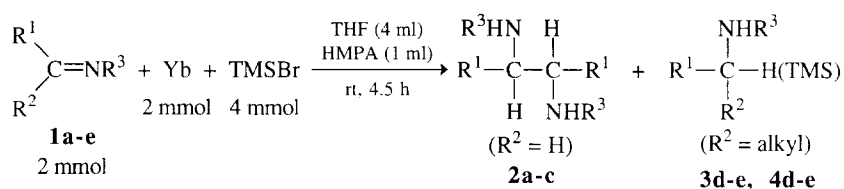
Entry	Imine	Product and Yield (%)[a]
1	$\overset{^iPr}{\underset{H}{\diagup\diagdown}}C=NBn$ **1a**	$^iPr-\underset{\underset{H}{|}}{\overset{\overset{BnHN}{|}}{C}}-\underset{\underset{NHBn}{|}}{\overset{\overset{H}{|}}{C}}-{}^iPr$ **(2a**, 86)
2	$\overset{^nPr}{\underset{H}{\diagup\diagdown}}C=NBn$ **1b**	$^nPr-\underset{\underset{H}{|}}{\overset{\overset{BnHN}{|}}{C}}-\underset{\underset{NHBn}{|}}{\overset{\overset{H}{|}}{C}}-{}^nPr$ **(2b**, 87)
3	$\overset{Cy}{\underset{H}{\diagup\diagdown}}C=NBn$ **1c**	$Cy-\underset{\underset{H}{|}}{\overset{\overset{BnHN}{|}}{C}}-\underset{\underset{NHBn}{|}}{\overset{\overset{H}{|}}{C}}-Cy$ **(2c**, 79)
4	$\overset{^tBu}{\underset{Me}{\diagup\diagdown}}C=NPh$ **1d**	$^tBu-\underset{\underset{Me}{|}}{\overset{\overset{NHPh}{|}}{C}}-TMS$ **(3d**, 67) $^tBu-\underset{\underset{Me}{|}}{\overset{\overset{NHPh}{|}}{C}}-H$ **(4d**, 28)
5	$\langle\text{hexyl}\rangle=NPh$ **1e**	$\langle\text{hexyl}\rangle\overset{TMS}{\underset{NHPh}{\diagdown}}$ **(3e**, 64) $\langle\text{hexyl}\rangle\overset{H}{\underset{NHPh}{\diagdown}}$ **(4e**, 31)

[a] GLC yield based on imines.

$$2\,\text{TMS-Br} + Yb \xrightarrow{\text{THF}} YbBr_2 + 2\,\text{TMS-H}$$

$$\begin{array}{c}R^1\\[-2pt]\diagdown\\[-4pt]C=NR^3\\[-4pt]\diagup\\[-2pt]R^2\end{array} + YbBr_2 \longrightarrow \left[\begin{array}{c}R^1\\[-2pt]\diagdown\\[-4pt]\overset{\bullet}{C}-\overset{-}{N}R^3\\[-4pt]\diagup\\[-2pt]R^2\end{array}\right]_{\mathbf{A}} + Yb(III)$$

$$\mathbf{A}\begin{cases} \xrightarrow[\text{R}^1 \text{ or } \text{R}^2 = \text{H}]{\text{Homocoupling}} R^1-\underset{\underset{R^2}{|}}{\overset{\overset{R^3HN}{|}}{C}}-\underset{\underset{NHR^3}{|}}{\overset{\overset{R^2}{|}}{C}}-R^1\\[18pt] \xrightarrow[\text{R}^1 \text{ and } \text{R}^2 \neq \text{H}]{\text{TMS• (or THF)}} R^1-\underset{\underset{R^2}{|}}{\overset{\overset{NHR^3}{|}}{C}}-TMS(H)\end{cases}$$

Scheme 1. Reaction mechanism

TMSBr to give the YbBr₂ and trimethylsilane. Thus, the YbBr₂ formed reacts with imines to give the radical anion complex **A** along with Yb³⁺. The coupling reaction of less hindered **A** derived from aldimine takes place exclusively to afford diamines. The bulky radical anion **A** derived from ketimines gives silylated or hydrogenated monoamines.

3. Experimental details

3.1. General procedure for ytterbium metal promoted homocoupling reaction of aliphatic imines

Ytterbium metal (0.346 mg, 2 mmol) was placed in a 20 ml test tube equipped with a three-way stopcock. The test tube was flame dried under reduced pressure. After cooling to room temperature, the atmosphere in the test tube was replaced with argon. THF (4 ml), HMPA (1 ml), and trimethylsilyl bromide (0.612 g, 4 mmol) were added successively to this tube by a syringe. The mixture was degassed through repetition of three freeze-pump-thaw cycles. The mixture was stirred at room temperature for 30 min. The reaction mixture became a suspension, and the colour of the mixture turned light green. Then, imine (2 mmol) was added to the test tube. The reaction mixture was stirred under

the conditions described in Tables 1 and 2. Usual work-up of the reaction mixture followed by Al_2O_3 column chromatography (n-hexane/ethyl acetate) gave the corresponding adducts. The representative results are listed in Tables 1 and 2.

Acknowledgments

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