

Note

Allylation of Imines with Allylytterbium Bromide

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In the presence of methyl iodide, metallic ytterbium can easily react with allylic bromide in anhydrous THF to form allylytterbium bromide, which reacts readily with imines to give the corresponding homoallylamines in satisfactory yields under mild and neutral conditions.

Keywords Ytterbium, allylytterbium bromide, imine

Rapid development of application of lanthanides, especially samarium reagents in organic synthesis, has been recently achieved.¹ However, relatively few studies on application of ytterbium reagents have been reported. Nevertheless, it is indicated that ytterbium reagents have the potential to serve as selective nucleophiles in C-X π -bond addition reactions and eventually will take their place among the other lanthanide reagents with a unique role in organic synthesis. As a Grignard-type reagent, PhYbI can react with many kinds of electrophilic reagents, such as with aldehydes or ketones to afford the corresponding alcohols in moderate yields;^{2,4} with α,β -unsaturated aldehydes or ketones to provide higher se-

lectivity of 1, 2-addition than their Grignard counterparts;⁵⁻⁷ with carboxylic acid derivatives to give benzophenone;^{8,9} with chlorotrimethylsilane to give trimethylphenylsilane in 70% yield;⁴ with isocyanatobenzene to give benzanilide.⁴ MeYbI reacted with chlorodimethylphenylsilane to give trimethylphenylsilane in 73% yield.⁴ However little attention has been concerned on preparation of allylytterbium halide and its use in organic synthesis. Here we wish to report the preparation of allylytterbium bromide and the allylation of imines with allylytterbium halide to give the desired homoallylamines (Scheme 1).

Scheme 1

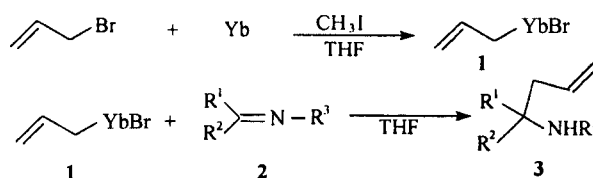


Table 1 Preparation of allylmetal bromide and reaction condition

| Entry | Metal | Activative reagents | Reaction time (h) | Product |
|-------|-------|--------------------------------|-------------------|--|
| 1 | Sm | — | 3 | CH ₂ = CHCH ₂ SmBr |
| 2 | Yb | — | 10 | — |
| 3 | Sm | I ₂ | 1 | CH ₂ = CHCH ₂ SmBr |
| 4 | Yb | I ₂ | 10 | — |
| 5 | Sm | KI | 1 | CH ₂ = CHCH ₂ SmBr |
| 6 | Yb | KI | 10 | — |
| 7 | Yb | MeI | 15—20 min | CH ₂ = CHCH ₂ YbBr |
| 8 | Yb | CH ₂ I ₂ | 15—20 min | CH ₂ = CHCH ₂ YbBr |

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Our group has studied the allylation of imines with allylsamarium bromide.¹⁰ It was found in this study that without activation, ytterbium could not react with allylic bromide to form allylterbium bromide; but after a short induction period, samarium could react smoothly with allylic bromide to give allylsamarium bromide (Grignard-type reagent). It was also found that ytterbium could not

be activated by iodine or potassium iodide, which can activate samarium metal under the similar conditions, but ytterbium could be readily activated by methyl iodide or methylene diiodide to react with allyl bromide to form allylterbium bromide easily. The results are summarized in Table 1 and Table 2.

Table 2 Results of allylation of imines with allylterbium bromide

| Product | R ¹ | R ² | R ³ | Reaction conditions | | Yield* (%) |
|-----------|--|----------------|--|---------------------|------------------|------------|
| | | | | Time (h) | Temperature (°C) | |
| 3a | 2-Thienyl | Me | Ph | 1.0 | 15—20 | 55 |
| 3b | 2-Furyl | H | Ph | 0.5—1.0 | 15—20 | 75 |
| 3c | <i>p</i> -ClC ₆ H ₄ | H | Ph | 0.5—1.0 | 15—20 | 82 |
| 3d | <i>p</i> -MeOC ₆ H ₄ | H | Ph | 0.5—1.0 | 15—20 | 79 |
| 3e | <i>n</i> -C ₄ H ₉ | H | Ph | 1.0—1.5 | 15—20 | 52 |
| 3f | Ph | H | <i>n</i> -C ₄ H ₉ | 1.0—1.5 | 15—20 | 67 |
| 3g | Ph | H | <i>n</i> -C ₃ H ₇ | 1.0—1.5 | 15—20 | 68 |
| 3h | Ph | H | <i>p</i> -BrC ₆ H ₄ | 0.5—1.0 | 15—20 | 75 |
| 3i | Ph | H | <i>p</i> -MeOC ₆ H ₄ | 0.5—1.0 | 15—20 | 73 |
| 3j | Ph | H | 1-Naphthyl | 0.5 | 15—20 | 85 |
| 3k | Ph | H | (<i>dl</i>)-C ₆ H ₅ CH(Me) | 0.5—1.0 | 15—20 | 72 |
| 3l | Ph | H | Ph | 0.5—1.0 | 15—20 | 81 |

* Isolated yield.

In conclusion, allylterbium bromide is more active than allylsamarium bromide, but not so stable as allylsamarium bromide. A novel approach to homoallylamines *via* allylterbium bromide has been provided. The notable advantages of this methodology are mild condition, simple operation and satisfactory yields.

Experimental

General

Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were uncorrected. Infrared spectra were recorded on an IR-408 spectrometer in KBr with absorption in cm⁻¹. ¹H NMR spectra were recorded on a Bruker AC—80 spectrometer as CDCl₃ solutions. *J* values are in Hz. Chemical shifts are expressed downfield from internal tetramethylsilane.

General procedure for the preparation of allylterbium bromide

Yb power (0.173 g, 1 mmol) and MeI (1.5 μL) were added in a three-necked flask under a nitrogen atmosphere. The metal was warmed slightly and then freshly distilled allylic bromide (0.121 g, 1 mmol) in anhydrous THF (15 mL) was added by a syringe. The mixture was stirred at 0°C for 15—20 min until the ytterbium powder disappeared. A brown solution of allylterbium bromide was formed.

General procedure for the allylation of imines with allylterbium bromide

A solution of imines (1 mmol) in THF (2 mL) was added to the brown solution of allylterbium bromide by a syringe in one portion at 15—20°C under a nitrogen atmosphere. After being stirred for a given time (Table 2, the reaction was monitored by TLC), the reaction was quenched with 5% K₂CO₃ (5 mL) and extracted with ether (3 × 20 mL). The crude product was isolated with usual way and purified by preparative thin layer chromatography using ethyl acetate and cyclohexane (1:5) as eluant.

3a Oil.¹⁰ IR ν : 3260, 1645, 1600, 760, 730, 700 cm^{-1} . ¹H NMR δ : 7.10—6.11 (m, 8H, ArH), 5.80—4.77 (m, 3H, $\text{CH}_2 = \text{CH}$), 2.79—2.45 (m, 2H, CH_2), 1.85 (brs, 1H, NH), 1.62 (s, 3H, CH_3).

3b Oil.¹¹ IR ν : 3265, 1650, 1600, 755, 730, 695 cm^{-1} . ¹H NMR δ : 7.20—6.15 (m, 8H, ArH), 5.80—4.70 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.50—4.15 (m, 1H, CH), 2.80—2.20 (2H, m, CH_2), 1.83 (brs, 1H, NH).

3c Oil.¹⁰ IR ν : 3235, 1640, 1600, 750, 730, 695 cm^{-1} . ¹H NMR δ : 7.30—6.20 (m, 9H, ArH), 5.78—4.80 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.20 (t, $J = 7.8$ Hz, 1H, CH), 2.35 (t, $J = 8.5$ Hz, 2H, CH_2), 1.94 (brs, 1H, NH).

3d Oil.¹⁰ IR ν : 3205, 1645, 1600, 770, 690 cm^{-1} . ¹H NMR δ : 7.25—6.05 (m, 9H, ArH), 5.95—4.80 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.20 (t, $J = 6.8$ Hz, 1H, CH), 3.60 (s, 3H, CH_3O), 2.40 (t, $J = 9.3$ Hz, CH_2), 1.84 (brs, 1H, NH).

3e Oil.¹² IR ν : 3245, 1647, 158, 760, 745, 690 cm^{-1} . ¹H NMR δ : 6.98—6.20 (m, 5H, ArH), 5.86—4.90 (m, 3H, $\text{CH}_2 = \text{CH}$), 3.80—3.50 (m, 1H, CH), 2.70—2.25 (m, 2H, CH_2), 2.00—0.90 (m, 10H, NH and $n\text{-C}_4\text{H}_9$).

3f Oil.¹⁰ IR ν : 3240, 1640, 1585, 755, 740, 680 cm^{-1} . ¹H NMR δ : 7.30—7.00 (m, 5H, ArH), 6.00—4.70 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.20—3.24 (m, 1H, CH), 2.50—2.15 (m, 2H, CH_2), 1.85—0.85 (m, 10H, NH and $n\text{-C}_4\text{H}_9$).

3g Oil.¹⁰ IR ν : 3240, 1630, 1580, 755, 750, 740, 680 cm^{-1} . ¹H NMR δ : 7.33—7.00 (m, 5H, ArH), 5.95—4.68 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.30—3.32 (m, 1H, CH), 2.55—2.18 (m, 2H, CH_2), 1.82—1.05 (m, 8H, NH and $n\text{-C}_3\text{H}_7$).

3h Oil.¹⁰ IR ν : 3235, 1660, 1590, 760, 730, 695 cm^{-1} . ¹H NMR δ : 7.27—6.00 (m, 9H, ArH), 5.90—4.90 (m, 3H, $\text{CH}_2 = \text{CH}$), 3.95 (t, $J = 7.5$ Hz, 1H, CH), 2.70—2.20 (m, 2H, CH_2), 1.85 (brs, 1H, NH).

3i Oil.¹³ IR ν : 3245, 1645, 1600, 765, 700. ¹H NMR δ : 7.25—6.30 (m, 9H, ArH), 5.85—5.00 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.15 (t, $J = 8.5$ Hz, 1H, CH), 3.70 (s, 3H, CH_3O), 2.57 (t, $J = 9.0$ Hz, 2H, CH_2), 1.85 (brs, 1H, NH).

3j Oil.¹⁴ IR ν : 3245, 1655, 1605, 755, 740, 700 cm^{-1} . ¹H NMR δ : 6.68—6.30 (m, 12H, ArH), 5.80—4.88 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.60—4.15 (m, 1H, CH), 2.80—2.26 (m, 2H, CH_2), 1.85 (brs, 1H, NH).

3k Oil.¹⁴ IR ν : 3255, 3035, 1640, 1600, 755, 700. ¹H NMR δ : 7.50—6.50 (m, 10H, ArH), 5.80—5.00 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.00—3.60 (m, 1H, CH), 3.50 (t, $J = 7.1$ Hz, 1H, CH), 2.70—2.30 (m, 2H, CH_2), 1.85 (brs, 1H, NH), 1.25 (d, $J = 5.8$ Hz, 3H, CH_3).

3l Oil.¹⁰ IR ν : 3250, 1650, 1600, 750, 710, 680 cm^{-1} . ¹H NMR δ : 7.30—6.00 (m, 10H, ArH), 5.85—4.80 (m, 3H, $\text{CH}_2 = \text{CH}$), 4.50—4.06 (m, 1H, CH), 2.70—2.18 (m, 2H, CH_2), 1.84 (brs, 1H, NH).

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