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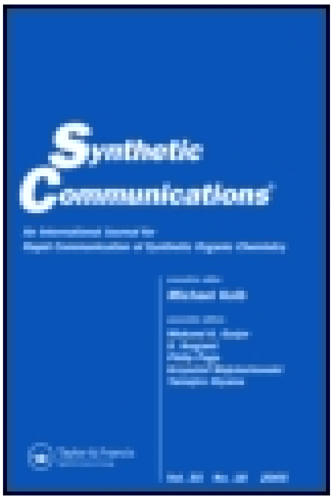

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AN EASY SYNTHESIS OF SOME 1,2,3,4-TETRAHYDRO-9-OXA-10-PHOSPHA-PHENANTHRENE-10-OXIDES

Peter Nesvadba & Paul Dubs

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YTTERBIUM METAL/TMSCL PROMOTED REACTION OF IMINES WITH ALLYLIC BROMIDE

Weike Su,[1,2] Jinghua Li,[1] and Yongmin Zhang[2,*]

[1]Department of Pharmaceutical Engineering, Zhejiang University
of Technology, Hangzhou, 310014, P.R. China
[2]Department of Chemistry, Zhejiang University at Xixi Campus, Hangzhou,
310028, P.R. China

ABSTRACT

In the presence of chlorotrimethylsilane (TMSCl), ytterbium metal can promote the allylation of imines with allylic bromide to give the corresponding homoallylamines in satisfactory yields in THF under mild conditions.

An important method for preparing secondary amines is the addition of carbon nucleophiles to the carbon-nitrogen double bound in imines. Generally, allylmetallic halides are used as carbon nucleophiles. Among these, those that can be used for allylation of imines include allylmagnesium (1), allylzinc (2), allystannane (3,4), allyl lead (5), allyltitanium (6), allylcopper (7), allylchrominum (8), and allylsamarium (9). In some cases, metals have been directly employed for promoting the allylation of imines, for example, tin (10), indium (11), bismuth, and tantalum (12).

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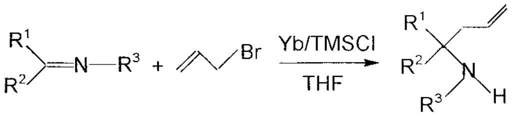
[*] To whom correspondence should be addressed.

Here we wish to report the allylation of imines with allylic bromide promoted by Yb/TMSCl system.



Rapid developments of application of lanthanides, especially samarium reagents, in organic synthesis have been recently achieved (13). However, relatively few papers on ytterbium reagents have been reported. Nevertheless, there are indications that ytterbium reagents, too, 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. For example, ytterbium trifluoromethanesulfonate complexes can substitute for traditional Lewis acids in a variety of organic transformations (14). Ytterbium metal can selectively reduce C-C multiple bonds conjugated with aromatic rings (15). PhYbI reacts with carbon dioxide to form carboxylic acid (16), with aldehydes and ketones to provide corresponding alcohols (17–19); with carboxylic acid derivatives to provide ketones (20,21). Ytterbium diiodide promotes Barbier-type reactions (22). But no reports on the direct use of ytterbium metal to promote the allylation of imines with allylic bromide could be found.

In our experimental work, we found that ytterbium metal not only does not react with allylic bromide to form allylytterbium bromide as does samarium, but also does not promote the allylation of imines with allylic bromide directly. But surprisingly, in the presence of TMSCl, ytterbium can promote the allylation of imines with allylic bromide to give the corresponding homoallylamines easily. The notable advantages of this methodology are mild conditions, simple operation, and satisfactory yields. The results are summarized in Table 1.

Table 1. Ytterbium/TMSCl Promotes the Allylation of Imines ($R^1R^2C{=}NR^3$) with Allylic Bromide

Run	R^1	R^2	R^3	Yield* (%)
1	C_6H_5	H	C_6H_5	75
2	C_6H_5	H	p-BrC_6H_4	72
3	p-$CH_3OC_6H_4$	H	C_6H_5	76
4	2-Furyl	H	C_6H_5	73
5	C_6H_5	H	1-Naphthyl	79
6	p-ClC_6H_4	H	C_6H_5	80
7	C_6H_5	H	$C_6H_5CHCH_3$	68
8	C_6H_5	H	p-$CH_3OC_6H_4$	67

*Yields of isolated products.

EXPERIMENTAL

^{1}H-NMR spectra were recorded on Bruker AC-80 spectrometer using TMS as internal standard. IR spectra were obtained on a PE-683 spectrometer. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl.

General Procedure for the Allylation of Imines

Ytterbium powder (0.173 g, 1 mmol), 5 mL of THF, and 0.121 g (1 mmol) of allylic bromide (freshly distilled) were added to a three-necked flask under nitrogen atmosphere. The mixture was magnetically stirred for 10 min at room temperature. Then a solution of imine (1 mmol) in 2 mL of THF and a catalytic amount of TMSCl was added to this suspension in one portion by syringe. The mixture was stirred for 3–4 h at room temperature until the ytterbium powder disappeared. A dilute solution of $NaHCO_3$ (0.2 N, 20 mL) was added. The mixture was stirred for 10 min and extracted with ether (20 mL × 2). The combined organic layer was washed with brine (20 mL × 2) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane and ethyl acetate as eluent). The products were identified by IR and ^{1}H-NMR spectra.

1: Oil (9), IR (Film, ν_{max}, cm^{-1}): 3250, 1650, 1600, 750, 730, 700; ^{1}H-NMR (CCl_4), δ (ppm): 1.84 (s, 1H, NH), 2.18–2.70 (m, 2H, CH_2), 4.06–4.50 (m, 1H, CH), 4.80–5.85 (m, 3H, vinyl-H), 6.00–7.30 (m, 10H, ArH).

2: Oil (9), IR (Film, ν_{max}, cm^{-1}): 3235, 1660, 1590, 760, 730, 695; ^{1}H-NMR (CCl_4), δ (ppm): 1.85 (s, 1H, NH), 2.20–2.70 (m, 2H, CH_2), 3.96 (t, J = 7.5 Hz, 1H, CH), 4.90–5.90 (m, 3H, vinyl-H), 6.00–7.27 (m, 9H, ArH).

3: Oil (9), IR (Film, ν_{max}, cm^{-1}): 3205, 1645, 1600, 770, 690; ^{1}H-NMR (CCl_4), δ (ppm): 1.84 (s, 1H, NH), 2.40 (t, J = 9.3 Hz, 2H, CH_2), 3.60 (s, 3H, CH_3O), 4.20 (t, J = 6.8 Hz, 1H, CH), 4.80–5.95 (m, 3H, vinyl-H), 6.05–7.25 (m, 9H, ArH).

4: Oil (11), IR (Film, ν_{max}, cm^{-1}): 3265, 1650, 1600, 755, 730, 605; ^{1}H-NMR (CCl_4), δ (ppm): 1.84 (s, 1H, NH), 2.20–2.80 (m, 2H, CH_2), 4.15–4.50 (m, 1H, CH), 4.70–5.80 (m, 3H, vinyl-H), 6.15–7.20 (m, 8H, ArH).

5: Oil (10), IR (Film, ν_{max}, cm^{-1}): 3245, 1655, 1605, 755, 740, 700; ^{1}H-NMR (CCl_4), δ (ppm): 1.83 (s, 1H, NH), 2.26–2.80 (m, 2H, CH_2), 4.16–4.60 (m, 1H, CH), 4.88–5.80 (m, 3H, vinyl-H), 6.30–6.68 (m, 12H, ArH).

6: Oil (9), IR (Film, ν_{max}, cm^{-1}): 3235, 1640, 1600, 750, 730, 695; ^{1}H-NMR (CCl_4), δ (ppm): 1.94 (s, 1H, NH), 2.35 (t, J = 8.5 Hz, 2H, CH_2), 4.20 (t, J = 7.8 Hz, 1H, CH), 4.80–5.78 (m, 3H, vinyl-H), 6.20–7.30 (m, 9H, ArH).

7: Oil (10), IR (Film, ν_{max}, cm^{-1}): 3255, 3035, 1640, 1600, 755, 695; ^{1}H-NMR (CCl_4), δ (ppm): 1.25 (d, J = 8.0 Hz, 3H, CH_3), 1.80 (s, 1H, NH), 2.30–2.70 (m, 2H, CH_2), 3.50 (t, J = 7.1 Hz 1H, CH); 3.60–4.00 (m, 1H, CH), 5.00–5.80 (m, 3H, vinyl-H), 6.50–7.50 (m, 10H, ArH).

8: Oil (8), IR (Film, ν_{max}, cm^{-1}): 3245, 1645, 1600, 765, 700; ^{1}H-NMR (CCl_4), δ (ppm): 1.85 (s, 1H, NH), 2.57 (t, J = 9.0 Hz, 2H, CH_2), 3.70 (s, 3H, CH_3O), 4.15 (t, J = 8.5 Hz, 1H, CH), 5.00–5.85 (m, 3H, vinyl-H), 6.30–7.25 (m, 9H, ArH).

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