Facile Preparation of Homoallyl β′,γ′-Unsaturated Amines via 1,2-Addition of α,β-Unsaturated Imines with Allylsamarium Bromide

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A series of homoallyl β′,γ′-unsaturated amines were synthesized via 1,2-addition of α,β-unsaturated imines with allylsamarium bromide in excellent yields under mild and neutral conditions.

Keywords allylsamarium bromide, α,β-unsaturated imine, 1,2-addition, homoallyl β′,γ′-unsaturated amine

Olefinic amines and their derivatives have been proven to be an especially versatile class of compounds with respect to further elaboration.[1] Homoallyl β′,γ′-unsaturated amines are more useful precursors particularly in the synthesis when the functionalizations of two double bonds are involved. The addition of allylic organometallic species to the imine constitutes a valuable method for the synthesis of homoallyl β′,γ′-unsaturated amines. A few metals have been directly utilized to promote the allylation of α,β-unsaturated imines, *e.g.*, In,[2] Cd/Bu_4NBr,[3] Ta, Bi/Bu_4NBr,[4] Al, Zn/$PbCl_2$,[5] allyltributystannane/Ln(OTf)$_3$.[6] However, most of these methods involved harsh conditions, such as using certain additives, Lewis acid catalysts or a long reaction time.

In recent years, much attention has been paid to the application of samarium reagents in organic synthesis, especially SmI_2,[7] which can promote the Barbier-type reaction between carbonyl compounds and alkyl halides. Wu *et al.* reported the Barbier-type allylation of ketones[8] and carboxylic esters[9] with samarium and allyl bromide, and a reaction mechanism with organosamarium intermediate has been suggested. Our group have explored a number of reactions of allylsamarium bromide with a variety of substrates, such as *N*-(2-aminoalkyl)-benzotriazoles,[10] imines,[11] nitriles,[12] diorgano diselenides,[13] disulfides,[14] isocyanates[15] and nitroalkenes.[16] In order to extend the application of allylsamarium bromide and to study whether the reactions take place via 1,2-addition or 1,4-addition in the reaction of α,β-unsaturated imines with allylsamarium bromide. Herein we wish to report that α,β-unsaturated imines could be allylated with allylsamarium bromide to give homoallyl β′,γ′-unsaturated amines in excellent yields under mild conditions with a short reaction time (Scheme 1).

Scheme 1

$$H_2C{=}CH{-}CH_2Br + Sm \xrightarrow[rt]{THF} H_2C{=}CH{-}CH_2SmBr \quad (2)$$

$$Ar{-}HC{=}CH{-}CH{=}N{-}R\ (E\text{-}1) + H_2C{=}CH{-}CH_2SmBr\ (2) \xrightarrow[rt]{THF} Ar{-}HC{=}CH{-}\underset{\displaystyle CH_2{-}CH{=}CH_2}{\underset{|}{CH}}{-}NH{-}R \quad (E\text{-}3)$$

The results were summarized in Table 1. When

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(*E*)-*N*-(3-phenyl-2-propenylidenyl)-benzenamine (**1a**) was added to allylsamarium bromide in anhydrous tetrahydrofuran at room temperature under a nitrogen atmosphere, the deep purple color of the mixture changed into brown color quickly and the product **3a** was obtained. The (*E*)-*N*-[1-(2-phenylethenyl) buten-3-yl]-*N*-phenylamine (**3a**) resulted from 1,2-addition of allylsamarium bromide and no 1,4-addition product was observed, which contrasted to the reaction with organolithiums where both 1, 2- and 1, 4-addition occurred.[17—18] As shown in Table 1, when the reaction occurred at 50 ℃, yield was substantially lower and byproduct was increased.

Table 1 Reaction of α, β-unsaturated imines with allylsamarium bromide

Entry	Ar	R	Time (min)	Yield (%)[a]
3a	C_6H_5	C_6H_5	6	95(80)[b](94)[c]
3b	C_6H_5	$C_6H_5CH_2$	8	90
3c	C_6H_5	2-$CH_3C_6H_4$	7	92
3d	C_6H_5	4-$CH_3C_6H_4$	7	92
3e	C_6H_5	3-ClC_6H_4	9	88
3f	C_6H_5	4-BrC_6H_4	9	87
3g	C_6H_5	4-$CH_3OC_6H_4$	7	92
3h	C_6H_5	2,4-$(CH_3)_2C_6H_3$	7	92
3i	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	9	85
3j	4-$CH_3C_6H_4$	4-BrC_6H_4	9	86

[a] Isolated yields based on α, β-unsaturated amines.
[b] The yield was obtained when reaction temperature was 50 ℃.
[c] The yield was obtained when reaction temperature was −15 ℃.

In summary, the present procedure provides a simple, efficient, and practical method for the preparation of homoallyl β, γ-unsaturated amines.

Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were obtained on an electrothermal melting point apparatus and uncorrected. Infrared spectra were recorded on a Bruker Vector 22 spectrometer with maximum absorption indicated in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AC-400 (400 MHz) spectrometer using $CDCl_3$ solutions. *J* values are in Hz. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Mass spectra were recorded on an HP 5989B MS spectrometer. Elemental analyses were carried out on a Carlo Erba EA 1110 instrument.

Typical procedure for synthesis of the (*E*)-*N*-[1-(2-*phenylethenyl*) *buten*-3-*yl*]-*N*-*phenylamine* (**3a**) Under an inert atmosphere of nitrogen, samarium powder (0.18 g, 1.25 mmol) was placed in a 50 mL three-neck flask and a solution of allyl bromide (0.2 g, 1.5 mmol) in 2 mL of tetrahydrofuran was added by syringe, the mixture was magnetically stirred for 1 h at room temperature. A purple suspension was obtained. Then a solution of (*E*)-*N*-(3-phenyl-2-propenylidenyl) benzenamine (1 mmol) in tetrahydrofuran was added to this suspension in one portion by syringe. The mixture was stirred for about 5—12 min at room temperature, then quenched with dilute solution of K_2CO_3 (5%, 5 mL) and extracted with ether (3 × 20 mL). The combined extracts were washed with saturated brine (15 mL) and dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by preparative TLC on silica gel using ethyl acetate-cyclohexane (1:6) as eluent.

(*E*)-*N*-[1-(2-*Phenylethenyl*) *buten*-3-*yl*]-*N*-*phenylamine* (**3a**) Oil (lit.[4]). IR ν: 3415, 2919, 1519, 909, 739 cm^{-1}. ^1H NMR δ_H: 2.50—2.55 (m, 2H, CH_2-CH), 3.81 (br.s, 1H, NH), 4.10—4.12 (m, 1H, CH_2-C**H**), 5.17—5.26 (m, 2H, CH_2 = CH), 5.85—5.91 (m, 1H, C**H** = CH_2), 6.24 (dd, *J* = 16.0, 5.7 Hz, 1H, CH = C**H**-CH), 6.62 (d, *J* = 16.0 Hz, 1H, C**H** = CH-CH), 6.65—6.68 (m, 2H, ArH), 6.89—6.93 (m, 1H, ArH), 7.12—7.16 (m, 2H, ArH), 7.29—7.37 (m, 3H, ArH), 7.39—7.42 (m, 2H, ArH).

(*E*)-*N*-[1-(2-*Phenylethenyl*) *buten*-3-*yl*]-*N*-*benzylamine* (**3b**) Oil (lit.[4]). IR ν: 3402, 2928, 1586, 919, 747 cm^{-1}. ^1H NMR δ_H: 2.47—2.52 (m, 2H, CH_2-CH), 3.07 (br.s, 1H, NH), 3.37 (s, 2H, CH_2), 4.07—4.09 (m, 1H, CH_2-C**H**), 5.15—5.23 (m, 2H, CH_2 = CH), 5.82—5.90 (m, 1H, C**H** = CH_2), 6.22 (dd, *J* = 16.0, 5.7 Hz, 1H, CH = C**H**-CH), 6.60 (d, *J* = 16.0 Hz, 1H, C**H** = CH-CH), 6.92—6.95 (m, 2H, ArH), 7.19—7.30 (m, 4H, ArH), 7.32—7.40 (m, 4H, ArH).

(*E*)-*N*-[1-(2-*Phenylethenyl*) *buten*-3-*yl*]-*N*-(*o*-*methylphenyl*) *amine* (**3c**) Oil. IR ν: 3428, 2918, 1606, 911, 750 cm^{-1}. ^1H NMR δ_H: 2.28 (s, 3H,

CH_3), 2.47—2.52 (m, 2H, CH_2-CH), 3.80 (br.s, 1H, NH), 4.07—4.09 (m, 1H, CH_2-CH), 5.15—5.23 (m, 2H, CH_2 = CH), 5.82—5.90 (m, 1H, CH = CH_2), 6.22 (dd, J = 16.0, 5.7 Hz, 1H, CH = CH-CH), 6.60 (d, J = 16.0 Hz, 1H, CH = CH-CH), 6.62—6.70 (m, 2H, ArH), 7.08—7.12 (m, 2H, ArH), 7.23—7.25(m, 1H, ArH), 7.29—7.33 (m, 2H, ArH), 7.38—7.40 (m, 2H, ArH). MS m/z(%) : 263(M^+, 2.2), 222(100), 157(8), 144 (11), 115(13), 91(23). Anal. calcd for $C_{19}H_{21}N$: C 86.69, H 7.98, N 5.33; found: C 86.57, H 7.85, N 5.58.

(*E*)-*N*-[1-(2-*Phenylethenyl*)*buten*-3-*yl*]-*N*-(*p*-*methylphenyl*)*amine* (**3d**) Oil. IR ν: 3415, 2919, 1611, 912, 733 cm^{-1}. ^1H NMR δ_H: 2.28 (s, 3H, CH_3), 2.38—2.40 (m, 2H, CH_2-CH), 4.05—4.07 (m, 1H, CH_2-CH), 5.09—5.15 (m, 2H, CH_2 = CH), 5.78—5.82 (m, 1H, CH = CH_2), 6.14 (dd, J = 16.0, 5.7 Hz, 1H, CH = CH-CH), 6.54 (d, J = 16.0 Hz, 1H, CH = CH-CH), 6.53 (d, J = 8.0 Hz, 2H, ArH), 6.92 (d, J = 8.0 Hz, 2H, ArH), 7.14—7.21 (m, 1H, ArH), 7.21—7.24 (m, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH). MS m/z (%): 263(M^+, 2.7), 222(100), 157(6), 144 (13), 115(14), 91(24). Anal. calcd for $C_{19}H_{21}N$: C 86.69, H 7.98, N 5.33; found: C 86.52, H 8.12, N 5.36.

(*E*)-*N*-[1-(2-*Phenylethenyl*)*buten*-3-*yl*]-*N*-(*m*-*chlorophenyl*)*amine* (**3e**) Oil. IR ν: 3415, 2919, 1612, 905, 740 cm^{-1}. ^1H NMR δ_H: 2.37—2.40 (m, 2H, CH_2-CH), 3.84 (br.s, 1H, NH), 3.92—3.96 (m, 1H, CH_2-CH), 5.11—5.15 (m, 2H, CH_2 = CH), 5.75—5.79 (m, 1H, CH = CH_2), 6.08 (dd, J = 16.1, 5.7 Hz, 1H, CH = CH-CH), 6.47 (d, J = 16.1 Hz, 1H, CH = CH-CH), 6.53—6.63 (m, 3H, ArH), 6.97—7.01 (m, 1H, ArH), 7.17—7.25 (m, 3H, ArH), 7.27—7.31 (m, 2H, ArH). MS m/z(%): 283(M^+, 0.7), 242(100), 206(7), 164(14), 115(41), 91(37). Anal. calcd for $C_{18}H_{18}$-NCl: C 76.32, H 6.36, N 4.95; found: C 76.18, H 6.52, N 4.86.

(*E*)-*N*-[1-(2-*Phenylethenyl*)*buten*-3-*yl*]-*N*-(*p*-*bromophenyl*)*amine* (**3f**) Oil. IR ν: 3420, 2915, 1590, 905, 735 cm^{-1}. ^1H NMR δ_H: 2.35—2.39 (m, 2H, CH_2-CH), 3.85 (br.s, 1H, NH), 3.91—3.92 (m, 1H, CH_2-CH), 5.11—5.16 (m, 2H, CH_2 = CH), 5.76—5.84 (m, 1H, CH = CH_2), 6.08 (dd, J = 16.1, 5.8 Hz, 1H, CH = CH-CH), 6.50 (d, J = 16.1 Hz, 1H, CH = CH-CH), 6.45 (d, J = 8.0 Hz, 2H, ArH), 7.16—7.19 (m, 3H, ArH), 7.22—7.31 (m, 4H, ArH). MS m/z(%): 327(M^+, 2.2), 286(100), 206(20), 157(17), 130(97), 91 (37). Anal. calcd for $C_{18}H_{18}NBr$: C 66.06, H 5.50, N 4.28; found: C 65.86, H 5.23, N 4.39.

(*E*)-*N*-[1-(2-*Phenylethenyl*)*buten*-3-*yl*]-*N*-(*p*-*methoxyphenyl*)*amine* (**3g**) Oil (lit.[6]). IR ν: 3425, 2922, 1595, 912, 720 cm^{-1}. ^1H NMR δ_H: 2.35—2.38 (m, 2H, CH_2-CH), 3.65 (br.s, 1H, OCH_3), 3.74 (br.s, 1H, NH), 4.10—4.13 (m, 1H, CH_2-CH), 5.12—5.18 (m, 2H, CH_2 = CH), 5.78—5.82 (m, 1H, CH = CH_2), 6.14 (dd, J = 16.0, 5.8 Hz, 1H, CH = CH-CH), 6.54 (d, J = 16.0 Hz, 1H, CH = CH-CH), 6.55 (d, J = 8.0 Hz, 2H, ArH), 6.90 (d, J = 8.0 Hz, 2H, ArH), 7.15—7.20 (m, 1H, ArH), 7.22—7.25 (m, 2H, ArH), 7.30 (d, J = 8.0 Hz, 2H, ArH).

(*E*)-*N*-[1-(2-*Phenylethenyl*)*buten*-3-*yl*]-*N*-(*o*, *p*-*dimethylphenyl*)*amine* (**3h**) Oil. IR ν: 3420, 2915, 1602, 905, 736 cm^{-1}. ^1H NMR δ_H: 2.13 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.45—2.49 (m, 2H, CH_2-CH), 3.65 (br.s, 1H, NH), 3.99—4.04 (m, 1H, CH_2-CH), 5.13—5.20 (m, 2H, CH_2 = CH), 5.78—5.86 (m, 1H, CH = CH_2), 6.09 (dd, J = 16.1, 5.9 Hz, 1H, CH = CH-CH), 6.58 (d, J = 16.1 Hz, 1H, CH = CH-CH), 6.56 (s, 1H, ArH), 6.86 (d, J = 8.0 Hz, 2H, ArH), 7.17—7.28 (m, 3H, ArH), 7.33 (d, J = 8.0 Hz, 2H, ArH). MS m/z(%): 277(M^+, 5.1), 236(100), 158(14), 144(12), 115(18), 91(29). Anal. calcd for $C_{20}H_{23}N$: C 86.64, H 8.30, N 5.05; found: C 86.32, H 8.52, N 5.16.

(*E*)-*N*-{1-[2-(*p*-*Methylphenyl*)*ethenyl*]*buten*-3-*yl*}-*N*-(*p*-*methylphenyl*)*amine* (**3i**) Oil. IR ν: 3425, 2930, 1625, 910, 739 cm^{-1}. ^1H NMR δ_H: 2.19 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.38—2.41 (m, 2H, CH_2-CH), 3.75 (br.s, 1H, NH), 3.95—3.97 (m, 1H, CH_2-CH), 5.09—5.16 (m, 2H, CH_2 = CH), 5.79—5.81 (m, 1H, CH = CH_2), 6.09 (dd, J = 16.0, 5.9 Hz, 1H, CH = CH-CH), 6.53 (d, J = 16.0 Hz, 1H, CH = CH-CH), 6.54 (d, J = 8.0 Hz, 2H, ArH), 6.93 (d, J = 8.0 Hz, 2H, ArH), 7.05 (d, J = 8.0 Hz, 2H, ArH), 7.21 (d, J = 8.0 Hz, 2H, ArH). MS m/z(%): 277(M^+, 1.8), 236(100), 171(12), 144(14), 129(11), 115

(4), 91(8). Anal. calcd for $C_{20}H_{23}N$: C 86.64, H 8.30, N 5.05; found: C 86.21, H 8.93, N 4.86.

(E)-N-{1-[2-(p-Methylphenyl) ethenyl] buten-3-yl}-N-(p-bromophenyl) amine (**3j**) mp 58—60 ℃. IR ν: 3415, 2925, 1595, 916, 745 cm^{-1}. ^1H NMR δ_H: 2.28 (s, 3H, CH_3), 2.38—2.40 (m, 2H, CH_2-CH), 3.85 (br.s, 1H, NH), 3.91—3.93 (m, 1H, CH_2-CH), 5.11—5.16 (m, 2H, CH_2 = CH), 5.77—5.79 (m, 1H, CH = CH_2), 6.04 (dd, *J* = 16.1, 5.9 Hz, 1H, CH = CH-CH), 6.46 (d, *J* = 16.1 Hz, 1H, CH = CH-CH), 6.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 7.16—7.21(m, 4H, ArH). MS *m/z*(%): 341(M^+, 1.4), 300(100), 220(18), 171(9), 130(86), 115 (19), 105(42), 91(15). Anal. calcd for $C_{19}H_{20}NBr$: C 66.86, H 5.86, N 4.11; found: C 66.53, H 5.98, N 4.23.

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