SHORT PAPER

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The synthesis of N-(1-allyl-3-butenyl)-N-aryl amines by addition of organosamarium reagents to formanilides[†]

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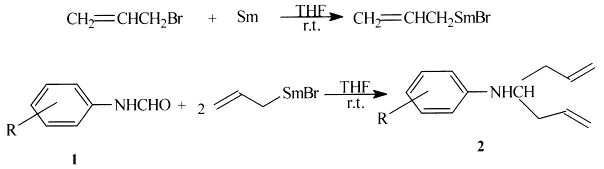
N-(1-allyl-3-butenyl)-N-aryl amines have been prepared for the first time in good yield via the direct diallylation reaction of formanilides with an organosamarium reagent under mild conditions.

Keywords: N-(1-allyl-3-butenyl)-N-aryl amines, organosamarium reagent, formanilides

The application of samarium in organic synthesis has aroused interest in recent years.[1-3] Curran firstly reported the samarium Grignard reaction.[4] Our group has studied the reaction of organosamarium reagents with imines,[5] isocyanates,[6] isothiocyantes,[6] diaryl diselenides[7] and diaryl disulfides.[7] Recently, we also found that carboxylic esters, acid anhydrides, and nitriles can be diallylated with organosamarium reagents to give the corresponding homoallylic carbinols and homoallylic amines respectively.[8] As part of our ongoing research into the application of samarium, we investigated the reaction of formanilide with allyl samarium bromide (Scheme 1). To the best of our knowledge, transformation of formanilide to the corresponding N-(1-allyl-3-butenyl)-N-aryl amine with allyl samarium bromide has not been studied. When formanilides (**1**) containing an N–H bond were treated with allyl samarium bromide under mild conditions, the corresponding N-(1-allyl-3-butenyl)-N-aryl amines (**2**) were obtained in good yields. The results and scope of this reaction are shown in Table 1.



Scheme 1

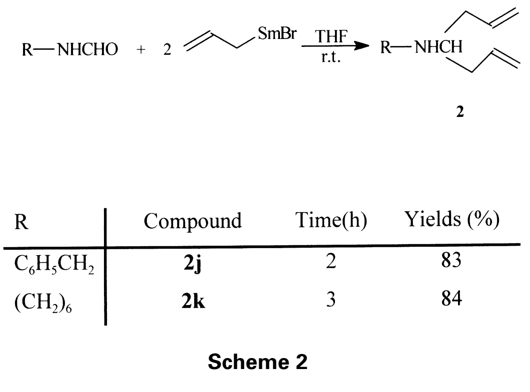
Table 1 Synthesis of N-(1-allyl-3-butenyl)-N-aryl amines (**2**)

Entry	Ar	Compound	Time/h	Yield/%[a]
1	C_6H_5	**2a**	1	95
2	*o*-$CH_3C_6H_4$	**2b**	2	90
3	*p*-$CH_3C_6H_4$	**2c**	2	92
4	*m*-$CH_3OC_6H_4$	**2d**	2	85
5	*p*-$CH_3OC_6H_4$	**2e**	2	90
6	2,3-$(CH_3)_2C_6H_3$	**2f**	2	85
7	2,5-$(CH_3)_2C_6H_3$	**2g**	2	85
8	*p*-Br C_6H_4	**2h**	1	90
9	*p*-$CH_3C(O)C_6H_4$	**2i**	1.5	85

[a]Isolated yields.

To investigate the scope and generality of the reaction, N-cyclohexylformamide and N-benzylformamide were also chosen as the substrates. We found that they would undergo reductive diallylation smoothly as well (Scheme 2), though a longer reaction time was needed.

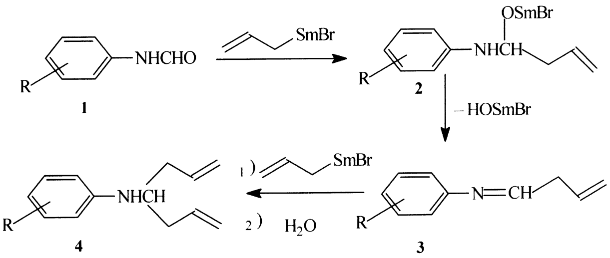
The present reaction conditions are tolerant of acetyl (entry 9) and methoxy group (entries 4 and 5). Furthermore, aromatic halides showed remarkable selectivity to give the diallylation compounds (**2**) without any dehalogenation or cross-coupling with allyl samarium bromide. In most cases, N-(1-allyl-3-butenyl)-N-aryl amines (**2**) were obtained in good yields.



R	Compound	Time(h)	Yields (%)
$C_6H_5CH_2$	**2j**	2	83
$(CH_2)_6$	**2k**	3	84

Scheme 2

A possible mechanism of reductive diallylation of formanilide is shown in Scheme 3. Firstly, formanilides (**1**) undergo allylation leading to intermediates (**2**), which eliminate the HOSmBr fragment to produce imines (**3**). Imines (**3**) immediately undergo allylation to form the diallylation products (**4**).



Scheme 3

It is worth mentioning that lactams containing an N-H bond can also be diallylated to give the corresponding 2,2-diallylated nitrogen heterocycles with allyl samarium bromide. This work is now in progress in our laboratory.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Experimental

IR spectra were recorded on a Shimadzu IR-408 spectrometer, ^{1}H NMR spectra were obtain with a Bruker AC 80 MHz spectrometer in CDCl$_3$ solution using TMS as internal standard. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

General procedure for the synthesis of N-(1-allyl-3-butenyl)-N-aryl amine **(2):** Samarium (0.33g, 2.2mmol) and allyl bromide (0.30g 2.5mmol) in THF (20ml) were added to a three-necked flask with stirring at room temperature under nitrogen. When the mixture became purple, stirring was continued for one hour until the samarium powder disappeared. Then the formanilides (1mmol) were added to the solution, and the mixture was stirred at room temperature for an appropriate time. 5 ml water was added. The reaction mixture was extracted with diethyl ether (3×10ml), the diethyl ether solution was washed with water (3×10ml) and dried over anhydrous MgSO$_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane-ethyl acetate (3:1) as eluent).

Compound **2a:** Oil. δ_h (ppm) 6.51–7.24 (m, 5H,), 5.66–5.77 (br, 2H), 4.96–5.16 (m, 4H), 3.40–3.55 (m, 2H), 2.20–2.36 (q, 4H *J*=6.16Hz, CH$_2$ allylic). ν_{max} (cm^{-1}) 3450, 1600. *m*/*z*, 188 (M+1), 187(M$^+$), 146 (100.00). Anal. calcd. for C$_{13}$H$_{17}$N: C 83.42, H 9.09. N 7.49. Found: C 83.40, H 9.08, N 7.45.

Compound **2b:** Oil. δ_H (ppm) 6.54–7.08 (m, 4H), 5.58–5.78 (br, 2H), 4.95–5.02 (m, 4H), 3.41–3.53 (m, 2H), 2.23–2.39 (q, 4H *J*=6.16Hz, CH$_2$ allylic), 2.09 (s, 3H) ν_{max} (cm^{-1}) 3400, 1600. *m*/*z*, 202 (m+1), 201(M$^+$), 160 (100.00), 118 (46.63), 91 (24.12). Anal. calcd. for C$_{14}$H$_{19}$N: C 83.58, H 9.45, N 6.97. Found: C 83.55, H9.43, N 6.95.

Compound **2c:** Oil. δ_H (ppm) 6.98 (d, 2H *J*=8.1Hz, ArH), 6.50 (d, 2H *J*=8.3Hz, ArH), 5.77–5.85 (br, 2H), 5.07–5.11 (m, 4H), 3.44–3.47 (m, 1H), 3.40 (s, 1H), 2.27–2.31 (q, 4H *J*=6.16Hz, Ch$_2$ allylic), 2.22 (s, 3H) ν_{max} (cm^{-1}) 3450, 1600. *m*/*z*, 202 (M+1), 201 (M$^+$), 160 (100), 118 (46.63), 91 (24.12). Anal. calcd. for C$_{14}$H$_{19}$N: C 83.58, H 9.45, N 6.97. Found: C 83.56, H 9.44, N 6.95.

Compound **2d:** Oil. δ_H (ppm) 7.00–7.20 (m, 1H), 6.13–6.31 (m, 3H), 5.63–5.96 (br, 2H), 5.01–5.23 (m, 4H), 3.79 (s, 3H), 3.44–3.67 (m, 2H), 2.28–2.42 (q, 4H *J*=6.16Hz, CH$_2$ allylic). ν_{max} (cm^{-1}) 3465, 1600. *m*/*z*, 218 (M+1), 217 (M$^+$), 176 (100.00), 134 (17.15). Anal. calcd. for C$_{14}$H$_{19}$NO: C 77.42, H 8.76, N 6.45. Found: C 77.40, H 8.75, N 6.40.

Compound **2e:** Oil. δ_H (ppm) 6.48–6.82 (m, 4H), 5.66–5.77 (br, 2H), 5.94–5.16 (m, 4H), 3.71 (s, 3H), 3.24–3.39 (m, 2H), 2.15–2.39 (q, 4H *J*=6.16Hz, CH$_2$ allylic). ν_{max} (cm^{-1}) 3460, 1600. *m*/*z*, 218 (M+1), 217 (M$^+$), 176 (100.00), 134 (17.15). Anal. calcd. for C$_{14}$H$_{19}$NO: C 77.42, H 8.76, N 6.45. Found: C 77.41, H 8.74, N 6.43.

Compound **2f:** Oil. δ_H (ppm) 6.86 (d, 1H *J*=8.3Hz, ArH), 6.42–6.47 (m, 2H), 5.68–5.80 (br, 2H), 4.96–5.18 (m, 4H), 3.47–3.54 (m, 2H), 2.04–2.41 (m, 10H). ν_{max} (cm^{-1}) 3460, 1600. *m*/*z*, 216 (M+1), 215 (M$^+$), 174 (100.00), 132 (35.64), 117 (10.55), 91 (5.87). Anal. calcd. for C$_{15}$H$_{21}$N: C 83.72, H 9.77, N 6.51. Found: C 83.70, H 9.76, N 6.48.

Compound **2g:** Oil. δ_H (ppm) 6.86 (m, 2H), 6.56 (d, 1H *J*=8.2Hz, ArH), 5.68–5.80 (br, 2H), 4.96–5.18 (m, 4H), 3.47–3.54 (m, 2H), 2.04–2.41 (m, 10H). ν_{max} (cm^{-1}) 3460, 1600. *m*/*z*, 216 (M+1), 215 (M$^+$), 174 (100.00), 132 (35.64), 117 (10.55), 91 (5.87). Anal. calcd. for C$_{15}$H$_{21}$N: C 83.72, H 9.77, N 6.51. Found: C 83.69, H 9.76, N 6.49.

Compound **2h:** Oil. δ_H (ppm) 6.38–7.26 (m, 4H), 5.55–5.86 (br, 2H), 4.94–5.15 (m, 4H), 3.36–3.51 (m, 2H), 2.19–2.35 (q, 4H *J*=6.16Hz, CH$_2$ allylic). ν_{max} (cm^{-1}) 3465, 1600. *m*/*z*, 265 (21.37), 267 (23.41), 224 (99.72), 226 (100.00), 182 (28.42), 184 (28.20), 144 (29.73), 145 (37.78), 130 (36.91). Anal. calcd. for C$_{13}$H$_{16}$BrN: C 58.64, H 6.01, N 5.26. Found: C 58.62, H 5.89, N 5.24.

Compound **2i:** Oil. δ_H (ppm) 6.49–7.25 (m, 4H), 5.51–5.91 (br, 2H), 4.99–5.18 (m, 4H), 3.41–3.56 (m, 2H), 2.14–2.45 (q, 4H *J*=6.16Hz, CH$_2$ allylic), 1.49 (s, 3H). ν_{max} (cm^{-1}) 3465, 1640, 1600. *m*/*z*, 230 (M+1), 229 (M$^+$), 188 (100.00), 146 (35.64). Anal. calcd. for C$_{15}$H$_{19}$NO: C 78.60, H 8.30, N 6.11. Found: C 78.58, H 8.26, N 6.09.

Compound **2j:** Oil. δ_H (ppm) 7.28 (s, 5H), 5.55–5.85 (br, 2H), 4.94–5.16 (m, 4H), 3.77 (s, 2H), 2.61–2.69 (m, 1H), 2.13–2.29 (q, 4H *J*=6.16Hz, CH$_2$ allylic), 1.68 (br, 1H). ν_{max} (cm^{-1}) 3400, 1600. *m*/*z*, 202 (M+1), 201 (M$^+$), 160 (91.39), 91 (100.00). Anal. calcd. for C$_{14}$H$_{19}$N: C 83.58, H 9.45, N 6.97. Found: C 83.56, H 9.44, N 6.95.

Compound **2k:** δ_H (ppm) 5.63–5.75 (br, 2H), 4.97–5.16 (m, 4H), 2.40–2.90 (m, 2H), 2.09–2.25 (q, 4H *J*=6.16Hz, Ch$_2$ allylic), 0.94–1.85 (m, 11H). ν_{max} (cm^{-1}) 3400, 1600. *m*/*z*, 194 (M+1), 193 (M$^+$). Anal. calcd. for C$_{13}$H$_{23}$N: C 80.83, H 11.92, N 7.25. Found: C 80.80, H 11.90, N 7.21.

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