



# Direct construction of a quaternary carbon center utilizing an organosamarium reagent

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**Abstract**—Direct geminal diallylation of lactams and acyclic amides containing an N–H bond has been achieved in the presence of allylsamarium bromide. By applying this method, quaternary carbons have been constructed, and 2,2-diallylated nitrogen heterocycles and diallylated amides were synthesized in moderate to good yields under mild conditions. © 2001 Elsevier Science Ltd. All rights reserved.

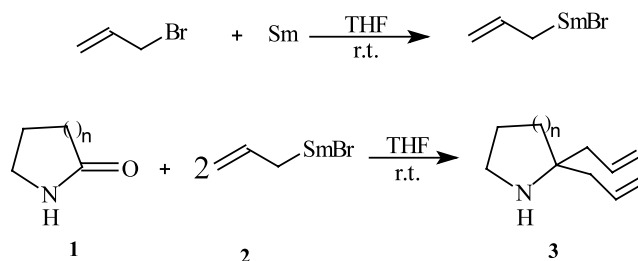
The addition of allylic organometallics to carbonyl compounds is an important synthetic method for the construction of carbon–carbon bonds.<sup>1</sup> Usually, homoallylic alcohols are obtained utilizing these methods, and little attention has been paid to the geminal diallylation of carbonyl compounds.<sup>2</sup> We have shown that nitriles undergo reductive diallylation on treatment with allylsamarium bromide to give the corresponding diallylamides.<sup>3</sup> However, to the best of our knowledge, transformations of lactams and acyclic amides containing an N–H bond under the action of allylsamarium bromide has not been investigated. Lukeš reported that the reaction of RMgX with five- to eight-membered lactams led to a mixture of 1-alkyl-1-aza-2-cyclenes and 2,2-dialkylated (arylated) heterocycles,<sup>4</sup> and the reaction of 2-piperidone with allylmagnesium bromide led to a compound of unknown structure (C<sub>14</sub>H<sub>23</sub>N).<sup>5</sup> Recently, Bubnov described the synthesis of 2,2-diallylated nitrogen heterocycles by the reaction of allylic boranes with lactams under harsh conditions.<sup>6</sup> We report herein the geminal diallylation of lactams and acyclic amides containing an N–H bond with allylsamarium bromide to construct quaternary carbons directly.

When lactams (**1**) containing an N–H bond were treated with allylsamarium bromide (**2**) in THF at

room temperature, 2,2-diallylated nitrogen heterocycles (**3**) were obtained in good yields (Scheme 1). All runs were completed within 5 min. The lactams and allylsamarium bromide were used in a ratio of 1:2.2 (mol).

It should be noted that when lactams, such as 2-pyrrolidinone, 2-piperidone, piperazinone and caprolactam, were used in this reaction, the corresponding diallylated nitrogen heterocycles were obtained in excellent yields (Table 1).<sup>7</sup> But when *o*-phthalimide (**4**) and succinimide (**5**) were treated with allylsamarium bromide under the same conditions, the diallylated compounds were not detected at all, with 3-[(*Z*)-2-propenylidene]-1-isoindolinone (**6**) and 5-[(*Z*)-2-propenylidene]-2-pyrrolidinone (**7**) being obtained, respectively (Scheme 2).

It is interesting that acyclic amides (**8**) containing an N–H bond can also react with allylsamarium bromide to give the analogous diallylated amines (**9**)<sup>8</sup> in moderate to good yields (Scheme 3). The reaction conditions and scope of this reaction are shown in Table 2.

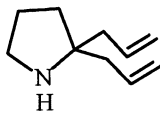
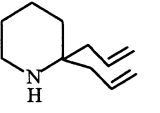
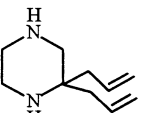
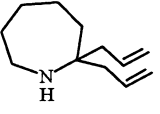
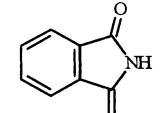
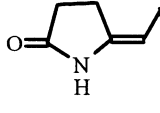


Scheme 1.

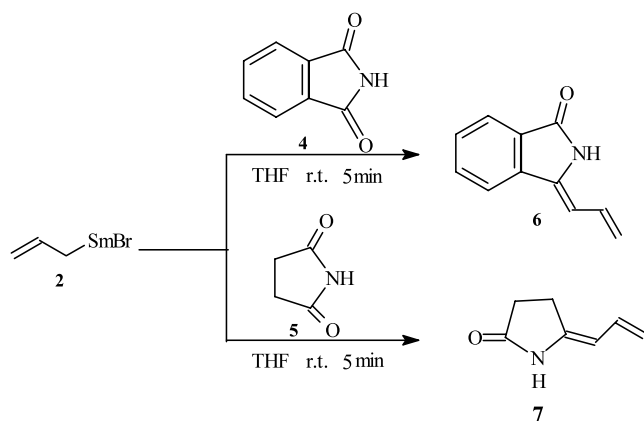
**Keywords:** samarium; allyl bromide; lactams; acyclic amides; 2,2-diallylated nitrogen heterocycles; diallylated amides; reductive diallylation.

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**Table 1.** The reaction of lactams with allylsamarium bromide

Entry	Compounds	Time (min)	Yields <sup>a</sup> (%)
a		5	95
b		5	90
c		4	95
d		5	85
e		4	85
f		5	75

a) Isolated yields based on lactams.

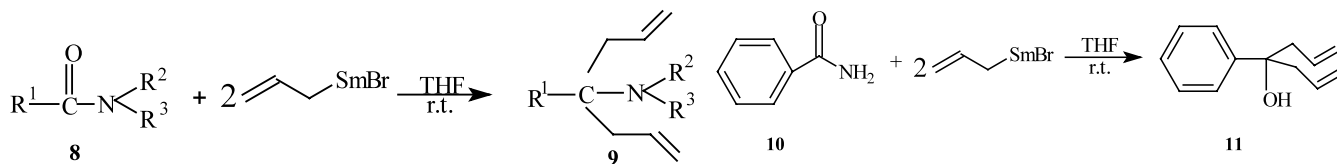
**Scheme 2.**

As shown in Table 2, acyclic amides (**8**) containing an N–H bond undergo the diallylation reaction smoothly, and the diallylated amides (**9**) were obtained in moderate to good yields. But when *N,N*-diethylbenzamide was treated with allylsamarium bromide for 10 h under

the same conditions, the expected compound (**9h**) could not be detected. When benzamide (**10**) was treated with allylsamarium bromide, the diallyl carbinol (**11**) was isolated in moderate yield (Scheme 4).

A possible mechanism of this reductive diallylation of lactams and acyclic amides containing an N–H bond is shown in Scheme 5. First, lactams (**A**) undergo allylation leading to intermediates (**B**), which eliminate the HOSmBr fragment to produce imines (**C**). Imines (**C**) immediately undergo allylation to form the intermediates (**D**), which were decomposed by water to produce the desired diallylation products (**E**).

In summary, quaternary carbons are constructed efficiently from lactams and acyclic amides containing an N–H bond utilizing allylsamarium bromide. By applying this method, 2,2-diallylated nitrogen heterocycles and analogous diallylated amides are obtained under mild conditions, which contain two double bonds and a NH function and can be used for the preparation of various derivatives such as bicyclic- and *spiro*-compounds.

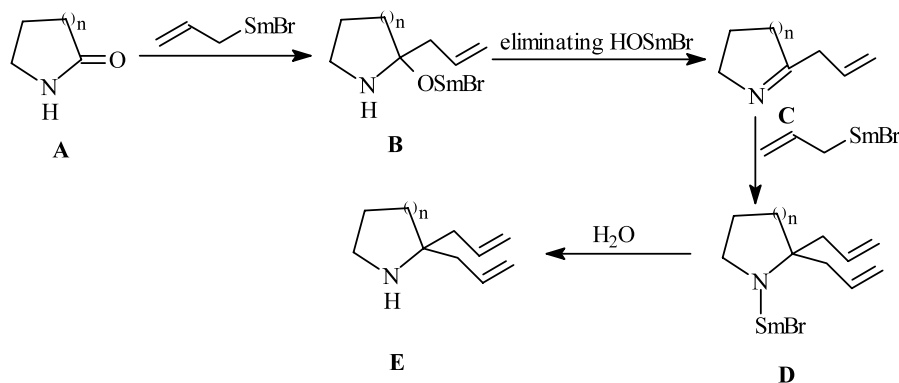


Scheme 3.

Scheme 4.

**Table 2.** The reaction of acyclic amides with allylsamarium bromide

Entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Time (h)	Yield <sup>a</sup> (%)
a	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	2	75
b	CH <sub>3</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	H	3	75
c	CH <sub>3</sub> CH <sub>2</sub>	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	H	4	75
d	CH <sub>3</sub> CH <sub>2</sub>	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	3	70
e	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	3	65
f	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	H	4	50
g	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	4	50
h	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub> CH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub>	10	0 <sup>b</sup>
i	C <sub>6</sub> H <sub>5</sub>	H	H	3	60

<sup>a</sup> Isolated yields based on acyclic amides.<sup>b</sup> The expected compound **9h** could not be detected.

Scheme 5.

### Acknowledgements

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- General procedure: Samarium (0.33 g, 2.2 mmol) and allyl bromide (0.30 g, 2.5 mmol) in THF (20 mL) were added to a three-necked flask with stirring at room temperature under nitrogen. When the color of the mixture turned purple, stirring was continued for 1 h until the samarium powder disappeared, then lactams or acyclic amides (1 mmol) were added to the solution, and the mixture was stirred at room temperature for the appropriate times (Tables 1 and 2). Water (5 mL) was added and the reaction mixture extracted with diethyl ether (3×10 mL), the diethyl ether solution washed with saturated NH<sub>4</sub>Cl (2×10 mL) and dried over anhydrous MgSO<sub>4</sub>. 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).

8. Typical physical data for compounds **3a**, **6e** and **9a**. Compound **3a** (**2,2-diallylpyrrolidine**): bp 86–88°C (13 torr); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.76 (2H, m, 2×CH), 5.15 (4H, m, 2×CH<sub>2</sub>), 3.02 (2H, t, *J*=6.78 Hz, CH<sub>2</sub>N), 2.38 (4H, d, *J*=7.27 Hz, 2×CH<sub>2</sub>), 1.45–1.70 (5H, m, 2×CH<sub>2</sub>+NH); MS *m/z* (%): 152 (M<sup>+</sup>+1, 2.33), 151 (M<sup>+</sup>, 4.78), 110 (100). Anal. calcd for C<sub>10</sub>H<sub>17</sub>N: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.39; H, 11.29, N, 9.29%.
- Compound **6e** (**3-[(*Z*)-2-propenylidene]-1-isoindolinone**): mp 98–101°C; IR (*v*<sub>max</sub>): 3320 (NH), 1700 (C=O), 1650, 1615 (C=C) cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.52 (1H, br s, NH), 7.89–7.27 (4H, m, ArH), 6.81–6.85 (1H, m, CH), 6.23 (1H, d, *J*=11.48 Hz, CH), 4.88–5.45

(2H, m, CH<sub>2</sub>); MS *m/z* (%): 172 (M<sup>+</sup>+1, 2.03), 171 (M<sup>+</sup>, 5.47), 130 (100), 102 (34.15). Anal. calcd for C<sub>11</sub>H<sub>9</sub>NO: C, 77.19; H, 5.26; N, 8.19. Found: C, 77.16; H, 5.20; N, 8.18%.

Compound **9a** (***N*-(1-allyl-1-methyl-3-butenyl)-*N*-phenylamine**): oil; IR (*v*<sub>max</sub>): 3410 (NH), 2977, 1639 (RCH=CH<sub>2</sub>), 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.11–7.21 (2H, m, ArH), 6.71–6.73 (3H, m, ArH), 5.81–5.87 (2H, m, 2×CH), 5.05–5.11 (4H, m, 2×CH<sub>2</sub>), 3.49 (1H, br, NH), 2.30–2.47 (4H, m, 2×CH<sub>2</sub>), 1.27 (3H, s, CH<sub>3</sub>); MS *m/z* (%): 202 (M<sup>+</sup>+1, 6.72), 201 (M<sup>+</sup>, 4.03), 160 (100), 118 (61.75), 77 (27.68). Anal. calcd for C<sub>14</sub>H<sub>19</sub>N: C, 83.58; H, 9.45; N, 6.96. Found: C, 83.56; H, 9.42, N, 6.94%.