**Novel Regio- and Stereoselective Dimerization of Terminal Alkynes Catalyzed by Rare-Earth Silylamide**

Kimihiro Komeyama,* Katsuomi Takehira, Ken Takaki*

Department of Chemistry and Chemical Engineering, Graduate School of Engineering, Hiroshima University, Kagamiyama, Higashi-hiroshima 739-8527, Japan

Fax +81(824)245494; E-mail: kkome@hiroshima-u.ac.jp

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**Abstract:** Rare-earth silylamide complex, Y[N(SiMe$_3$)$_2$], was found to exhibit good catalyst activities for regio- and stereoselective dimerization of terminal aliphatic and aromatic alkynes in the presence of amine additives. Thus, using tertiary amine additives, particularly N(SiMe$_3$)$_2$, aliphatic terminal alkynes were efficiently converted to head-to-tail dimers. On the other hand, only Z-head-to-head dimers were obtained in high yields with catalysts and aromatic primary amines such as 4-

**Key words:** dimerization, terminal alkynes, enynes, rare-earth silylamide, amine additives

Conjugated enynes are important units as a building block for organic synthesis and have key functions in a variety of biologically active compounds. Among the methods available to synthesize them, catalytic dimerization of terminal alkynes is the most promising approach, because it converts the readily available alkynes directly to the conjugated enynes in an atom-economical manner. Many metal complexes have been known to catalyze this transformation, which include groups 4 and 8–10 metals, lanthanides, actinides, and methylaluminoxane. However, exclusive formation of one enyne out of three possible dimers could be achieved only with few catalysts. Moreover, most of the complexes have been rarely applicable to both aromatic and aliphatic terminal alkynes. With respect to lanthanide catalysts, only metalloocene and half-metalloocene complexes have been used for the alkyn dimerization. In the course of hydrophosphination of alkynes catalyzed by lanthanide(II) and (III) silylamides, we found that dimerization and origomerization were readily induced by these nonmetalloocene complexes. Herein, we report a novel regio- and stereoselective dimerization of aliphatic and aromatic terminal alkynes catalyzed by rare-earth silylamide, Y[N(SiMe$_3$)$_2$]$_3$ (1), in the presence of amine additives.

When oct-1-yne (2a) was treated with 1 (5 mol%) in toluene at 100 °C for 17 hours, 98% of the alkyne was consumed and head-to-tail dimer, 2-hexyldec-1-en-3-yne (3a), was formed in 62% yield along with a small amount of Z-head-to-head dimer hexadec-7-en-9-yne (4a) (5%). The other isomer, E-head-to-head dimer 5a, was not detected by GC and $^1$H NMR analyses. The low mass balance was attributed to the formation of oligomers, which were not fully characterized. The reaction at lower temperature (60 °C) decreased the conversion of 2a, but the selectivities of 3a–5a were not changed. Then, effect of various additives (5 mol%) was investigated in order to improve the product yield and selectivity. These results are summarized in Table 1. Phosphine additives such as Ph$_3$P and Ph$_3$PH showed no significant effect (entries 2 and 3). Yield of 3a was decreased with Ph$_3$O, and the reaction was suppressed by addition of PhOH (entries 4 and 5). Effect of amine additives was quite different from that of phosphorus and oxygen compounds. Thus, tertiary and secondary aromatic amines predominately gave 3a in moderate yields (entries 6 and 7). Primary aromatic amine resulted in a very low conversion yield, wherein the head-to-tail selectivity seemed to be changed to Z-head-to-head (entry 8). These phenomena were observed more clearly in the reaction with aliphatic amines (entries 9–11). That is, the additives showed the following order of increasing activities and ratio of 3a/4a = primary < secondary < tertiary. Triethylamine gave 3a and 4a in 73% and 7% yields, respectively. Strong bases such as DBU and quinuclidine increased the conversion, but product yields and selectivities were decreased (entries 12 and 13). Finally, the best results were obtained with a bulky tertiary amine, N(SiMe$_3$)$_3$, which selectively afforded 3a in 92% yield (entry 14). Moreover, hex-1-yne (2b) was converted to 2-butylcyclo-1-en-3-yne (3b) in 99% yield with the silylamide additive under similar conditions.

Dimerization of phenylacetylene (2e) was also catalyzed by the silylamide 1, in which Z-head-to-head dimer 4c was likely to be formed predominantly in contrast to the head-to-tail selectivity of the aliphatic alkynes (Table 2, entry 1). However, total yields and selectivities of the three isomers 3c, 4c, and 5c were very lower than those of 2a, probably because 2e is more reactive than 2a and thus, competitive oligomerization took place faster. Addition of phosphorus and oxygen additives exhibited no expected effects (entries 2–5). Although three aromatic amines, Ph$_3$N, Ph$_3$NH, and PhNH$_2$ gave similar conversion yields, the dimer yields increased in the order of tertiary < secondary < primary, as opposed in the case of aliphatic alkyne 2a (entries 6–8). Thus, 4c was exclusively obtained in 87% yield with aniline. Similar effects were observed, though inferior, with aliphatic amines (entries 14 and 15). Neither electron-withdrawing nor donating...
groups of the 4-substituted anilines caused noticeable change, except for \( p \)-toluidine (entries 8–12). The alkyne \( 2c \) was predominantly oligomerized with 2,6-\( i \)-Pr\(_2\)C\(_6\)H\(_3\)NH\(_2\) (entry 13).

The dimerization of various aromatic alkynes \( 2 \) were performed by using the silylamide catalyst \( 1 \) and 4-chloroaniline additive (Table 3). As can be seen from Table 3, 4-substituted alkynes \( 2d-g \) having methoxy, methyl, and halogen substituents gave the corresponding dimers \( 4d-g \) exclusively in high yields as good as phenylacetylene \( (2c) \). In the reaction of \( o \)-tolylacetylene \( (2h) \), the yield of \( 4h \) decreased extremely as well as the conversion yield of \( 2h \), which can be ascribed to a steric hindrance near the alkyne bond (entry 6). Similar limitation was observed for the reaction of 3,3-dimethylbut-1-yne, in which the substrate was almost recovered unchanged.

When the catalyst \( 1 \) was substituted by lithium hexamethyldisilazide, no reactions of \( 2a, c \) took place under the identical conditions. These results imply that the present dimerization is owing to the useful characteristics of the rare-earth silylamide. By referring to the work of Teuben\(^{3a} \) and Hou,\(^{3b} \) it is almost certain that the reaction proceeds through alkyne insertion to the rare-earth alkynide complex generated by deprotonation with \( 1 \), followed by protonation with another molecule of the alkyne to give the dimeric product and alkynide. Reaction efficiency sharply depended on the nature of the amine additives as described above. However, their role has not been fully elucidated at present. Of course, no reaction took place with the additives alone and their excess loading decreased the product yields in general.\(^7 \) It is likely that they would provide more suitable catalysts in situ through ligand exchange, wherein HN(SiMe\(_3\))\(_2\), liberated by addition of the primary and secondary amines, was actually detected by \(^1\)H NMR. Alternatively, they would change unreactive alkynide oligomers into reactive monomers or dimers by their coordination to the metal center, because rare-earth alkynides have been known to have a tendency to form dimers and origomers.\(^8 \)

In conclusion, we have demonstrated that readily available rare-earth silylamide \( 1 \) is a convenient catalyst, in combination with proper amines, for regio- and stereoselective dimerization of terminal alkynes.

### Table 1 Effect of Additives for Dimerization of Oct-1-yne \((2a)\)\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Conversion (%)</th>
<th>Products, Yield (%)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>98</td>
<td>62 5 0</td>
</tr>
<tr>
<td>2</td>
<td>Ph(_3)P</td>
<td>99</td>
<td>65 7 1</td>
</tr>
<tr>
<td>3</td>
<td>Ph(_2)PH</td>
<td>88</td>
<td>48 11 0</td>
</tr>
<tr>
<td>4</td>
<td>Ph(_2)O</td>
<td>99</td>
<td>54 8 0</td>
</tr>
<tr>
<td>5</td>
<td>PhOH</td>
<td>(-)</td>
<td>(-) (-) (-)</td>
</tr>
<tr>
<td>6</td>
<td>Ph(_3)N</td>
<td>92</td>
<td>69 5 0</td>
</tr>
<tr>
<td>7</td>
<td>Ph(_2)NH</td>
<td>93</td>
<td>60 8 0</td>
</tr>
<tr>
<td>8</td>
<td>PhNH(_2)</td>
<td>30</td>
<td>0 13 0</td>
</tr>
<tr>
<td>9</td>
<td>Et(_3)N</td>
<td>(&gt;99)</td>
<td>73 7 0</td>
</tr>
<tr>
<td>10</td>
<td>Et(_2)NH</td>
<td>90</td>
<td>48 20 1</td>
</tr>
<tr>
<td>11</td>
<td>CH(_3)NH(_2)</td>
<td>94</td>
<td>0 45 0</td>
</tr>
<tr>
<td>12</td>
<td>DBU(^d)</td>
<td>(&gt;99)</td>
<td>9 17 0</td>
</tr>
<tr>
<td>13</td>
<td>quinuclidine(^e)</td>
<td>(&gt;99)</td>
<td>58 8 0</td>
</tr>
<tr>
<td>14</td>
<td>N(SiMe(_3))(_3)</td>
<td>(&gt;99)</td>
<td>92 5 0</td>
</tr>
</tbody>
</table>

\(^a\) The additive was pretreated with the catalyst for 1 h at r.t.

\(^b\) Determined by GC.

\(^c\) No reaction.

\(^d\) 1,8-Diazabicyclo[5.4.0]undec-7-ene.

\(^e\) 1-Azabicyclo[2.2.2]octane.
lective dimerization of terminal alkynes. Using the bulky tertiary amine, N(SiMe₃)₃, as an additive, aliphatic terminal alkynes have been efficiently converted to the head-to-tail dimer. On the other hand, exclusive formation of Z-head-to-head dimers from aromatic alkynes has been achieved with the catalyst 1 and aromatic primary amines. The present reaction would be a rare event to accomplish selective dimerization of both aromatic and aliphatic terminal alkynes with one metal catalyst. Mechanistic aspect and synthetic application are currently under investigation.

All reactions were carried out under argon. Toluene was distilled from sodium/benzophenone ketyl immediately prior to use. Y[N(SiMe₃)₂]₃ (1) was prepared from YCl₃ and NaN(SiMe₃)₂ in THF, according to the literature. The alkynes 2d–h were prepared by the reported methods. All other materials were commercially available and were used after drying and distillation. 1H and 13C NMR spectra were recorded at 400 and 100 MHz, respectively. IR spectra were taken on an FT-IR spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a GC-MS apparatus. Melting points are uncorrected.

### Table 2  Effect of Additives for Dimerization of Phenylacetylene (2c)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>Conv. (%)</th>
<th>Product, Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>97</td>
<td>3c 5  4c 11  5c 2</td>
</tr>
<tr>
<td>2</td>
<td>Ph₃P</td>
<td>99</td>
<td>4  22  5</td>
</tr>
<tr>
<td>3</td>
<td>Ph₂PH</td>
<td>94</td>
<td>3  17  2</td>
</tr>
<tr>
<td>4</td>
<td>Ph₃O</td>
<td>93</td>
<td>5  13  3</td>
</tr>
<tr>
<td>5</td>
<td>PhOH</td>
<td>10</td>
<td>0  4  0</td>
</tr>
<tr>
<td>6</td>
<td>Ph₃N</td>
<td>94</td>
<td>1  37  0</td>
</tr>
<tr>
<td>7</td>
<td>Ph₃NH</td>
<td>88</td>
<td>22  35  2</td>
</tr>
<tr>
<td>8</td>
<td>PhNH₂</td>
<td>90</td>
<td>0  87  0</td>
</tr>
<tr>
<td>9</td>
<td>4-MeOC₆H₄NH₂</td>
<td>97</td>
<td>0  95  0</td>
</tr>
<tr>
<td>10</td>
<td>4-MeC₆H₄NH₂</td>
<td>98</td>
<td>0  76  0</td>
</tr>
<tr>
<td>11</td>
<td>4-ClC₆H₄NH₂</td>
<td>92</td>
<td>0  91  0</td>
</tr>
<tr>
<td>12</td>
<td>4-FC₆H₄NH₂</td>
<td>96</td>
<td>0  94  0</td>
</tr>
<tr>
<td>13</td>
<td>2,6-i-Pr₂C₆H₃NH₂</td>
<td>&gt;99</td>
<td>0  9  0</td>
</tr>
<tr>
<td>14</td>
<td>Et₃N</td>
<td>95</td>
<td>2  7  3</td>
</tr>
<tr>
<td>15</td>
<td>C₆H₁₁NH₂</td>
<td>99</td>
<td>0  70  0</td>
</tr>
</tbody>
</table>

a Determined by GC.

### Table 3  Dimerization of Aromatic Terminal Alkynes Catalyzed by Y[N(SiMe₃)₂]₃ (1) with 4-Chloroaniline

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkyne R</th>
<th>Product, Yield (%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2c Ph</td>
<td>4c 91 (90)</td>
</tr>
<tr>
<td>2</td>
<td>2d 4-MeOC₆H₄</td>
<td>4d 95 (93)</td>
</tr>
<tr>
<td>3</td>
<td>2e 4-MeC₆H₄</td>
<td>4e 97 (90)</td>
</tr>
<tr>
<td>4</td>
<td>2f 4-BrC₆H₄</td>
<td>4f 90 (89)</td>
</tr>
<tr>
<td>5</td>
<td>2g 4-FC₆H₄</td>
<td>4g 95 (80)</td>
</tr>
<tr>
<td>6</td>
<td>2h 2-MeC₆H₄</td>
<td>4h 27b</td>
</tr>
</tbody>
</table>

a Determined by GC (isolated).

b Determined by 1H NMR spectroscopy.
Dimerization of Alkynes Catalyzed by Y[N(SiMe3)2]3 with Amine Additives; (Z)-1,4-Diphenylbut-1-en-3-yne (4c); Typical Procedure

Y[N(SiMe3)2]3 (1) (39 mg, 0.07 mmol) and 4-chloroaniline (8.9 mg, 0.07 mmol) were placed in a 20.0 mL Schlenk tube and dissolved in toluene (0.7 mL). The mixture was stirred for 1 h at r.t. Then, phenylacetylene (2c; 146 mg, 1.4 mmol) was added to the mixture. The Schlenk tube was closed and stirring was continued for 17 h at 100 °C. The reaction mixture was quenched with H2O (2 mL) and aq sat. NH4Cl solution (1 mL), and diluted with Et2O (2 mL). GC yield was determined by using methyl benzoate as an internal standard. The organic layer was extracted with Et2O (30 mL), washed with brine (30 mL), dried (MgSO4), and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with hexane as eluent to give 129 mg (90%) of the dimer 4c; yellow liquid; Rf 0.27 (hexane, SiO2).

IR (KBr): 3020, 2925, 2856 cm–1.

1H NMR (CDCl3): δ = 88.2, 95.8, 107.4, 123.4, 128.27, 128.34, 128.4, 128.5, 128.7, 131.4, 136.5, 138.6.

13C NMR (CDCl3): δ = 28.86, 28.89, 30.0, 31.4, 37.4, 88.2, 95.8, 107.4, 123.4, 128.27, 128.34, 128.4, 128.5, 128.7, 131.4, 136.5, 138.6.

MS: m/z (%) = 264 (M+*, 100), 249 (87).

(Z)-1,4-Di(p-anisyl)but-1-en-3-yne (4d); Yellow liquid; Rf 0.20 (hexane–EtOAc, 25:1, SiO2).

IR (neat) = 3005, 2957, 2930, 2835, 2185 cm–1.

1H NMR (CDCl3): δ = 3.80 (3 H, s), 3.81 (3 H, s), 5.77 (1 H, d, J = 11.8 Hz), 6.58 (1 H, d, J = 11.8 Hz), 6.87 (2 H, d, J = 8.9 Hz), 6.89 (2 H, d, J = 8.9 Hz), 7.42 (2 H, d, J = 8.9 Hz), 7.88 (2 H, d, J = 8.7 Hz).

13C NMR (CDCl3): δ = 55.22, 55.23, 87.4, 95.4, 105.1, 113.6, 114.0, 115.7, 129.7, 130.1, 132.8, 137.3, 159.5, 159.6.

MS: m/z (%) = 264 (M+*, 100), 249 (87).

(Z)-1,4-Di(p-tolyl)but-1-en-3-yne (4e); Yellow solid; mp 61–63 °C; Rf 0.26 (hexane, SiO2).

IR (KBr): 3024, 2925, 2856, 2361 cm–1.

1H NMR (CDCl3): δ = 5.92 (1 H, d, J = 11.8 Hz), 6.66 (1 H, d, J = 11.8 Hz), 7.32 (2 H, d, J = 8.4 Hz), 7.49 (2 H, d, J = 7.6 Hz), 7.51 (2 H, d, J = 7.6 Hz), 7.76 (2 H, d, J = 8.5 Hz).

13C NMR (CDCl3): δ = 88.9, 95.4, 107.9, 122.1, 122.5, 122.9, 130.1, 131.5, 131.8, 132.8, 135.3, 137.8.

(Z)-1,4-Di(4-bromophenyl)but-1-en-3-yne (4f); Yellow liquid; Rf 0.36 (hexane, SiO2).

IR (CCl4): 3024, 2925, 2856, 2186 cm–1.

1H NMR (CDCl3): δ = 5.92 (1 H, d, J = 11.8 Hz), 6.66 (1 H, d, J = 11.8 Hz), 7.32 (2 H, d, J = 8.4 Hz), 7.49 (2 H, d, J = 7.6 Hz), 7.51 (2 H, d, J = 7.6 Hz), 7.76 (2 H, d, J = 8.5 Hz).

13C NMR (CDCl3): δ = 88.9, 95.4, 107.9, 122.1, 122.5, 122.9, 130.1, 131.5, 131.8, 132.8, 135.3, 137.8.

(Z)-1,4-Di(4-fluorophenyl)but-1-en-3-yne (4g); Yellow liquid; Rf 0.32 (hexane, SiO2).

IR (CCl4): 3024, 2925, 2855, 2186 cm–1.

1H NMR (CDCl3): δ = 5.87 (1 H, d, J = 11.8 Hz), 6.66 (1 H, d, J = 11.8 Hz), 7.03–7.09 (4 H, m), 7.43–7.47 (2 H, m), 7.87–7.91 (2 H, m).

13C NMR (CDCl3): δ = 87.6, 94.8, 106.8 (d, J = 2.5 Hz), 115.2 (d, J = 21.3 Hz), 115.7 (d, J = 23.0 Hz), 119.4 (d, J = 3.3 Hz), 130.4 (d, J = 8.2 Hz), 132.7 (d, J = 4.1 Hz), 133.3 (d, J = 8.2 Hz), 137.4 (d, J = 8.2 Hz), 162.5 (d, J = 249.4 Hz), 162.6 (d, J = 250.2 Hz).

MS: m/z (%) = 240 (M+*, 76), 239 (60), 238 (100).

(Z)-1,4-Di(toly)but-1-en-3-yne (4h); 1H NMR (CDCl3): δ = 2.33 (3 H, s), 2.43 (3 H, s), 5.99 (1 H, d, J = 11.8 Hz), 6.86 (1 H, d, J = 11.8 Hz), 7.12–7.22 (6 H, m), 7.38 (1 H, d, J = 7.3 Hz), 8.25–8.27 (1 H, m).

MS: m/z (%) = 232 (M+*, 92), 215 (100), 202 (75), 115 (79).

Acknowledgment

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References


(7) The reaction of 2a using three equivalents of Et3N (15 mol%) gave 3a and 4a in 21 and 7% yields, respectively, with 49% conversion.


(11) Although the products 3c and 4h were not isolated, they were identified by comparison of 1H NMR spectra of their reaction mixtures with literature data.2e,f