

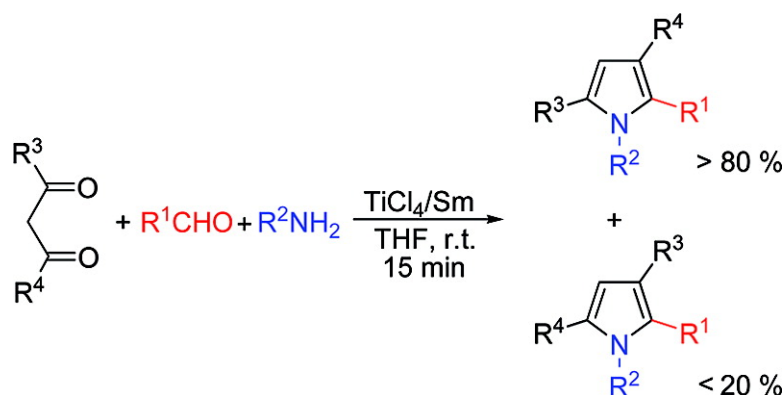
Article

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## Highly Regioselective Synthesis of Polysubstituted Pyrroles through Three-Component Reaction Induced by Low-Valent Titanium Reagent

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1,2,3,5-Tetrasubstituted and 1,2,3,4,5-pentasubstituted pyrroles may be synthesized through three-component reaction of 1,3-diketones, aldehydes, and amines induced by low-valent titanium reagent. High regioselectivity was achieved. Compared with the classical synthetic method, this new method has the advantages of short reaction time (15 min), high yields, convenient manipulation, and high regioselectivity.

### Introduction

Multicomponent reactions (MCRs), in which multiple reactions are combined into the synthetic operation have been used extensively to form carbon–carbon bonds in the synthetic chemistry.<sup>1</sup> Such reactions offer a wide range of possibilities for the efficient construction of highly complex molecules in a single procedural step, thus avoiding the complicated purification operations and allowing savings of both solvents and reagents. In the past decade, there has been tremendous development in three- and four-component reactions, and great efforts continue to be made to develop new MCRs.<sup>2</sup>

The pyrrole ring is one of the fundamental heterocycles. It is a widely distributed structural unit in a variety of natural and biologically important molecules such as porphyrins, bilepigments, coenzymes, and alkaloids.<sup>3</sup> For example, 2-(2-pyridyl)pyrroles are a potentially useful class of compounds. In separate studies, they have been shown to be antioxidants,<sup>4</sup> P38 kinase inhibitors,<sup>5</sup> and prolyl-4-hydroxylase inhibitors.<sup>6</sup> Although there are many reports for the synthesis of pyrroles,<sup>7</sup> the Knorr method is extensively used for this purpose.<sup>8</sup> Recently, conjugate addition reactions have been used for the synthesis of polysubstituted pyrroles.<sup>9</sup> These compounds can also be prepared from transition-metal intermediates,<sup>10</sup> reductive coupling,<sup>11</sup> aza-Wittig reactions,<sup>12</sup> and other multistep operations.<sup>13</sup> For example, Rao et al. have reported a facile one-pot synthesis of polyarylpyrroles from 2-butene and but-2-yne-1,4-diones under microwave conditions.<sup>14</sup> Ashwin et al.<sup>15</sup> have reported the synthesis of highly substituted pyrroles utilizing a one-pot sila-Stetter/

Paal-Knorr strategy, and Bimal et al.<sup>16</sup> have also reported a simple synthesis of substituted pyrroles using iodine-catalyzed and montmorillonite KSF-clay-induced modified Paal–Knorr methods. Ranu et al.<sup>17</sup> have also reported the synthesis of pyrroles on the surface of silica gel and alumina under microwave irradiation. Jamie et al.<sup>18</sup> have also reported the synthesis of 3,5-disubstituted and 3,4,5-trisubstituted-2-(2-pyridyl)pyrroles from the condensation of 2-(aminomethyl)-pyridine and 1,3-diones. Some one-pot pyrroles synthesis starting from imines have been reported recently; for example, Gao et al. have reported the synthesis of substituted pyrroles from alkynes, imines, and carbon monoxide via an organotitanium intermediate<sup>19</sup> or from alkynes, nitriles, imines, and titanium–imine complexes.<sup>20</sup> Lee et al. have reported a one-pot synthesis of substituted pyrroles from propargylic dithioacetals,<sup>21</sup> and Katritzky et al. have also reported the synthesis of 1,2,3-triarylpyrroles from 1-benzylbenzotriazoles via [1 + 2 + 2] annulation.<sup>22</sup> However, these are not always satisfactory with respect to ease of operation, yield, reaction time, and general applicability, and all the products have no regioselectivity. For this reason, we became interested in developing a novel and convenient synthetic methods for the preparation of pyrrole derivatives. Our initial studies showed that successful synthesis of substituted pyrroles from 1,3-diketones and imines was performed at room temperature using TiCl<sub>4</sub>/Zn or TiCl<sub>4</sub>/Sm in anhydrous THF.<sup>23,24</sup>

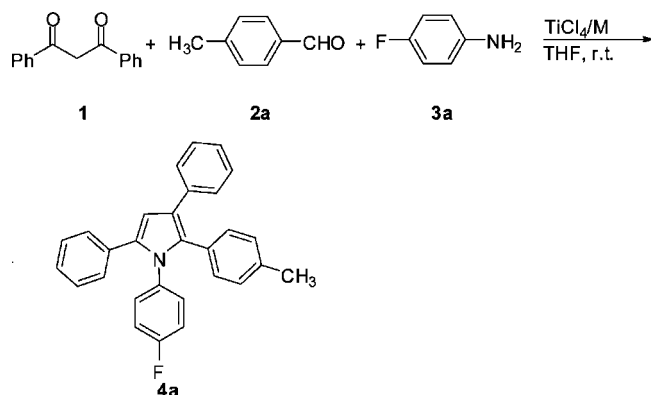
In the course of our study on the reaction induced by low-valent titanium, we found that the three-component coupling of 1,3-diketones, aldehydes and amines induced by low-valent titanium to give the corresponding pyrroles at room temperature in only 15 min. Although Ishii et al. have reported the synthesis of pyrroles via a samarium-catalyzed three-component coupling reaction of aldehydes,

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## Scheme 1



**Table 1.** Optimal Ratio of Metal and Low-Valent Titanium in the Synthesis of **4a**

entry	M	ratio <sup>a</sup>	yield (%)
1	Zn	1:2	10
2	Zn	1:3	49
3	Zn	1:4	40
4	Mg	1:3	47
5	Al	1:3	50
6	Fe	1:3	54
7	Sm	1:3	93
8	Sm	1:1	58
9	Sm	1:2	63
10	Sm	1:4	60

<sup>a</sup> Ratio of **1** and the low-valent titanium system.

amines, and nitroalkanes,<sup>25</sup> the yield of this reaction is low (8–78%), and the time of the reaction is longer (15 h). Ranu et al. have also reported one-pot synthesis of pyrroles via three-component condensation of a carbonyl compound, amine, and a nitroalkene in a molten ammonium salt,<sup>26</sup> but this reaction requires high temperature (107 °C); therefore, we wish to describe a new route to polysubstituted pyrroles through three-component reaction of 1,3-diketones, aldehydes, and amines induced by low-valent titanium reagent.

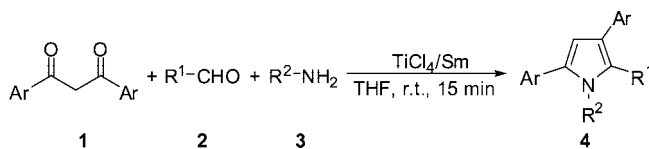
## Results and Discussion

In a preliminary study, dibenzoylmethane **1**, 4-methylbenzaldehyde **2a**, and 4-fluoroaniline **3a** were used to define the reaction conditions for this three-component reaction (Scheme 1).

First, different types of low-valent titanium systems were investigated as reagents for the reaction (entry 1–7, Table 1), TiCl<sub>4</sub>/Sm gave the best result of synthesis of **4a** (92%) (entry 7). Further optimization of the reaction conditions revealed that the use of 3 equiv of TiCl<sub>4</sub>/Sm gave results superior to those under the other reaction conditions (entry 7–10, Table 1).

When symmetrical 1,3-diketone **1**, aldehydes **2** and amines **3** were treated with the low-valent titanium reagent prepared from titanium(IV) chloride and samarium powder in anhydrous tetrahydrofuran at room temperature under a nitrogen atmosphere, the coupling cyclization products 1,2,3,5-tetra-substituted pyrrole **4** were obtained and purified by recrystallization from 95% ethanol in good yields (Scheme 2). Table 2 summarizes our results on the three-component reaction.

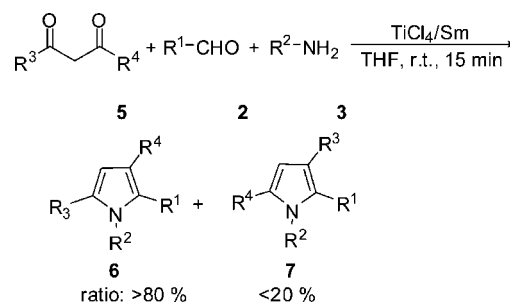
## Scheme 2



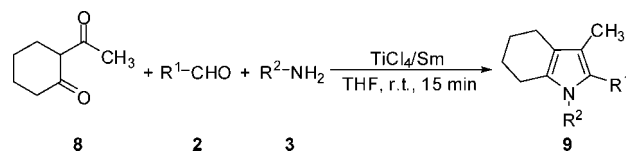
**Table 2.** Three-Component Reaction of Symmetrical 1,3-Diketones **1**, Aldehydes **2**, and Amines **3** Induced by Low-Valent Titanium (TiCl<sub>4</sub>/Sm)

entry	Ar	R <sup>1</sup>	R <sup>2</sup>	products	yield (%)
1	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-FC <sub>6</sub> H <sub>4</sub>	<b>4a</b>	93
2	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>4b</b>	91
3	C <sub>6</sub> H <sub>5</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3-Cl-4-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	<b>4c</b>	97
4	C <sub>6</sub> H <sub>5</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	4-FC <sub>6</sub> H <sub>4</sub>	<b>4d</b>	90
5	C <sub>6</sub> H <sub>5</sub>	pyrid-3-yl	3-ClC <sub>6</sub> H <sub>4</sub>	<b>4e</b>	85
6	C <sub>6</sub> H <sub>5</sub>	cyclohexyl	3-Cl-4-CH <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	<b>4f</b>	87
7	C <sub>6</sub> H <sub>5</sub>	4-FC <sub>6</sub> H <sub>4</sub>	<i>n</i> -Butyl	<b>4g</b>	98
8	3-ClC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<b>4h</b>	93

## Scheme 3



## Scheme 4



**Table 3.** Three-Component Reaction of Unsymmetry 1,3-Diketone **5**, Aldehydes **2** and Amines **3** Induced by Low-Valent Titanium Reagent (TiCl<sub>4</sub>/Sm)

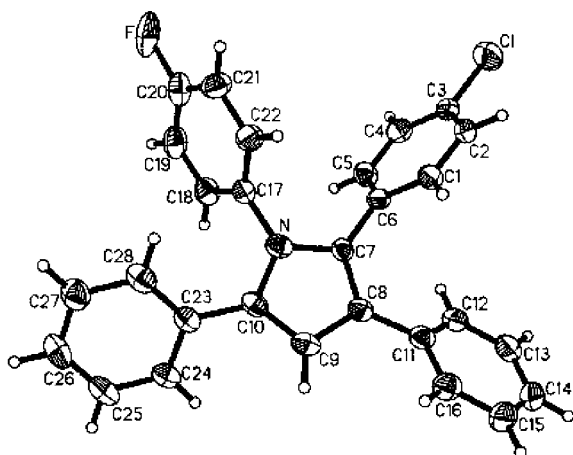
entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	products	yield (%)
1	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6a, 7a</b>	80 <sup>a</sup> (83:17) <sup>b</sup>
2	4-ClC <sub>6</sub> H <sub>4</sub>	4-FC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6b</b>	95
3	4-BrC <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6c</b>	97
4	3-ClC <sub>6</sub> H <sub>4</sub>	4-FC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6d</b>	93
5	2-ClC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6e, 7e</b>	96 <sup>a</sup> (94:6) <sup>b</sup>
6	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	3-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6f</b>	96
7	3-pyridyl	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6g</b>	75
8	2-thiophenyl	4-ClC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CF <sub>3</sub>	<b>6h, 7h</b>	93 <sup>a</sup> (80:20) <sup>b</sup>
9	4-ClC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-thiophenyl	CF <sub>3</sub>	<b>6i</b>	94
10	4-BrC <sub>6</sub> H <sub>4</sub>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-thiophenyl	CF <sub>3</sub>	<b>6j</b>	90
11	2-thiophenyl	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	2-thiophenyl	CF <sub>3</sub>	<b>6k</b>	95
12	2-thiophenyl	4-BrC <sub>6</sub> H <sub>4</sub>	2-thiophenyl	CF <sub>3</sub>	<b>6l</b>	87
13	4-FC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<b>6m, 7m</b>	90 <sup>a</sup> (80:20) <sup>b</sup>
14	4-BrC <sub>6</sub> H <sub>4</sub>	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	<b>6n, 7n</b>	82 <sup>a</sup> (80:20) <sup>b</sup>

<sup>a</sup> Isolated as a mixture of regioisomers. <sup>b</sup> The ratio of regioisomers was analyzed by GC-MS.

However, when asymmetrical 1,3-diketone **5**, aldehydes **2**, and amines **3** were treated with the low-valent titanium reagent under the same reaction conditions, for entries 1, 5, 8, 13, and 14 (Table 3), a mixture of regioisomers were formed in ratios of 83:17, 94:6, 80:20, 80:20, 80:20, respectively (Scheme 3), while for the other substrates, only products **6** were obtained. Therefore this reaction has high regioselectivity. When R<sup>4</sup> is a trifluoromethyl group, the

**Table 4.** Three-Component Reaction of 2-Acetylcyclohexanone **8**, Aldehydes **2** and Amines **3** Induced by Low-Valent Titanium ( $\text{TiCl}_4/\text{Sm}$ )

entry	R <sup>1</sup>	R <sup>2</sup>	<b>9</b>	yield (%)
1	4-BrC <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	<b>9a</b>	80
2	4-BrC <sub>6</sub> H <sub>4</sub>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>9b</b>	85
3	4-ClC <sub>6</sub> H <sub>4</sub>	4-BrC <sub>6</sub> H <sub>4</sub>	<b>9c</b>	82
4	4-ClC <sub>6</sub> H <sub>4</sub>	4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	<b>9d</b>	78
5	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	<b>9e</b>	82
6	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	<b>9f</b>	75

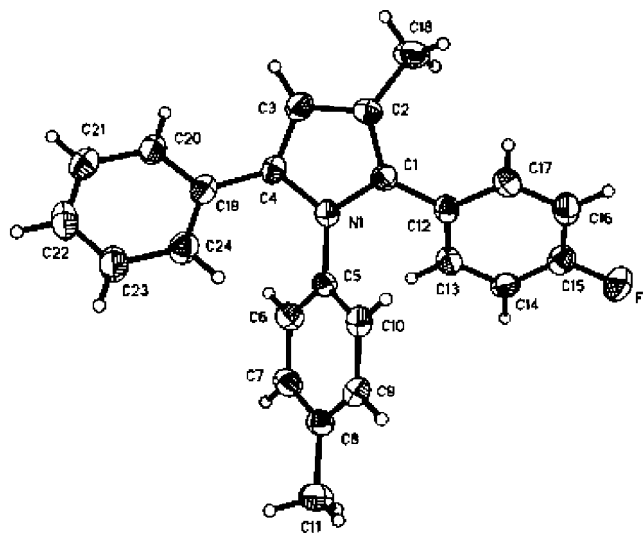
**Figure 1.** ORTEP diagram of **4d**.

structures of products **6** can be confirmed by comparison of with that of the products synthesized from benzoyltrifluoroacetone and imine induced by low-valent titanium reagent.<sup>24</sup> Table 3 summarizes our results on the coupling cyclization of **5** with **2** and **3**.

From Tables 2 and 3, it can be seen that this protocol can be applied not only to the aromatic aldehydes with either electron-withdrawing groups (such as halide groups) or electron-donating groups (such as alkyl and alkoxy groups) but also to heterocyclic and aliphatic aldehydes under the same conditions. Furthermore, it was particularly noteworthy that the method could be applied not only to aromatic amine with either electron-donating groups (such as alkyl, alkoxy groups) or electron-withdrawing groups (such as halide and trifluoromethyl groups), but also to aliphatic amines, which highlighted the wide scope of this three-component reaction.

Moreover, when 2-acetylcyclohexanone **8**, aldehydes **2**, and amines **3** were treated with the low-valent titanium reagent under the same reaction conditions, the coupling cyclization products 4,5,6,7-tetrahydro-1*H*-indole **9** were obtained in good yields (Scheme 4). Table 4 summarizes the results.

The structures of products **4**, **6**, and **9** were established using spectroscopic data. The structures of products **4d** and **6n** have been confirmed by X-ray analysis. The X-ray diffraction studies on single crystal of **6n** indicate that the structures of products we obtained are 1,2,5-triaryl-3-methylpyrroles not 1,2,3-triaryl-5-methylpyrroles. High regioselectivity of the products have been confirmed. The molecular structures of the products **4d** and **6n** are shown in Figures 1 and 2, respectively.

**Figure 2.** ORTEP diagram of **6n**.

## Conclusions

In conclusion, a series of 1,2,3,5-tetrasubstituted pyrroles and 1,2,3,4,5-pentasubstituted pyrroles were synthesized via a three-component reaction of 1,3-diketones, aldehydes, and amines induced by the  $\text{TiCl}_4/\text{Sm}$  system. The products were only purified by recrystallization to give purity. High regioselectivity was achieved, and the structure of the products was confirmed by X-ray diffraction analysis. Surprisingly, in contrast to the synthesis of pyrroles via coupling cyclization of 1,3-diketones and imines, the yields of this method are higher, and the times are shorter.

In general, this method has the advantages of high regioselectivity, easily obtained starting materials, short reaction time, high yields, and convenient manipulation, and our approach features the first successful three-component reaction induced by low-valent titanium reagent, developing a novel method for the synthesis of polysubstituted pyrroles.

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**Supporting Information Available.** Representative experimental procedures, spectral data of compounds **4a–h**, **6a–n**, and **9a–f**, and reaction condition optimization. This material is available free charge via the Internet at <http://pubs.acs.org>.

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