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# Base-induced synthesis of *N*-dialkylaminomethyl-2*H*-1,2,3-triazoles from *N*-sulfonyl-1,2,3-triazoles†

Yu Jiang,<sup>a</sup> Qiang Wang,<sup>b</sup> Run Sun,<sup>b</sup> Xiang-Ying Tang<sup>a</sup> and Min Shi<sup>\*a,b</sup>

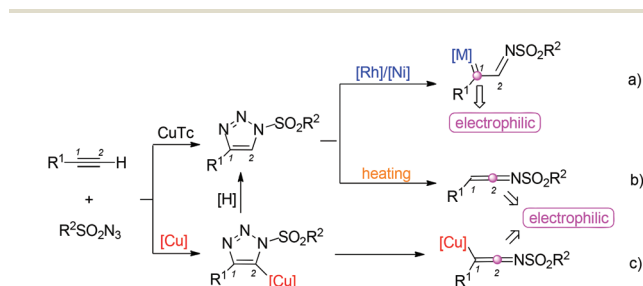
A facile synthetic method to access *N*-dialkylaminomethyl-2*H*-1,2,3-triazoles has been developed via a novel reaction mode from *N*-sulfonyl-1,2,3-triazoles by a base induced reaction. Moreover, 4-phenyl-1*H*-1,2,3-triazoles can also give the same products even in the absence of a base at high temperature.

## Introduction

1,2,3-Triazoles are an important class of heterocycles in organic synthesis, medicinal chemistry and materials science.<sup>1</sup> Among them, *N*-sulfonyl-1,2,3-triazoles, which can be easily prepared from copper(i)-catalyzed azide-alkyne cycloadditions,<sup>2</sup> have attracted much attention of organic chemists because of their potential applications in accessing other heterocycles. Recently, investigation on the reaction types of these compounds has emerged at the forefront of current research. Several different reaction types have been found to date (Scheme 1).

In the presence of Rh/Ni catalysts, *N*-sulfonyl-1,2,3-triazoles will undergo a ring-opening process to afford  $\alpha$ -imino metal carbenes.<sup>3–8</sup> The C1 position with a strong electrophilic ability can be attacked by other nucleophiles.<sup>4–6</sup> Moreover, a nitrogen atom with an increased nucleophilic ability offers more synthetic flexibility. The  $\alpha$ -imino metal carbenes can react with many other compounds to afford useful heterocycles (Scheme 1a).<sup>7</sup> On the other hand, at high temperature, *N*-sulfonyl-1,2,3-triazoles can also undergo a ring-opening process to afford *N*-sulfonyl ketenimines, which can be attacked by nucleophiles at the C2 position or undergo pericyclic reactions (Scheme 1b).<sup>9</sup> Indeed, in many reports, *N*-sulfonyl ketenimines were afforded by a one-pot strategy.<sup>10–12</sup> Cycloaddition between terminal alkynes and sulfonyl azides catalyzed by copper(i) afforded the *N*-sulfonyl triazolyl copper species, which can undergo a ring-opening rearrangement leading to the ketenimine intermediate upon the release of a dinitrogen molecule (Scheme 1c).

However, we recently also found that the sulfonyl group of *N*-sulfonyl-1,2,3-triazoles can undergo elimination to afford 4-phenyl-1*H*-1,2,3-triazoles as nucleophilic intermediates<sup>13</sup> in the presence of a base at high temperature. Moreover, the intermediates could be converted into more stable 4-phenyl-2*H*-1,2,3-triazoles to trap other electrophiles in the N2-position (Scheme 2).<sup>14,15</sup> Indeed, bis(dialkylamino)methane was chosen as a reaction partner, which could afford an electrophilic iminium ion.<sup>16</sup> Herein, we would like to report these interesting new findings.

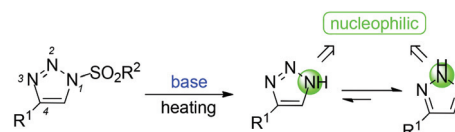


**Scheme 1** Formation of  $\alpha$ -imino metal carbene and *N*-sulfonyl ketenimines.

<sup>a</sup>State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China

<sup>b</sup>Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Meilong Road No. 130, Shanghai, 200237, China. E-mail: mshi@mail.sioc.ac.cn

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**Scheme 2** Formation of 4-phenyl-2*H*-1,2,3-triazoles.

## Results and discussion

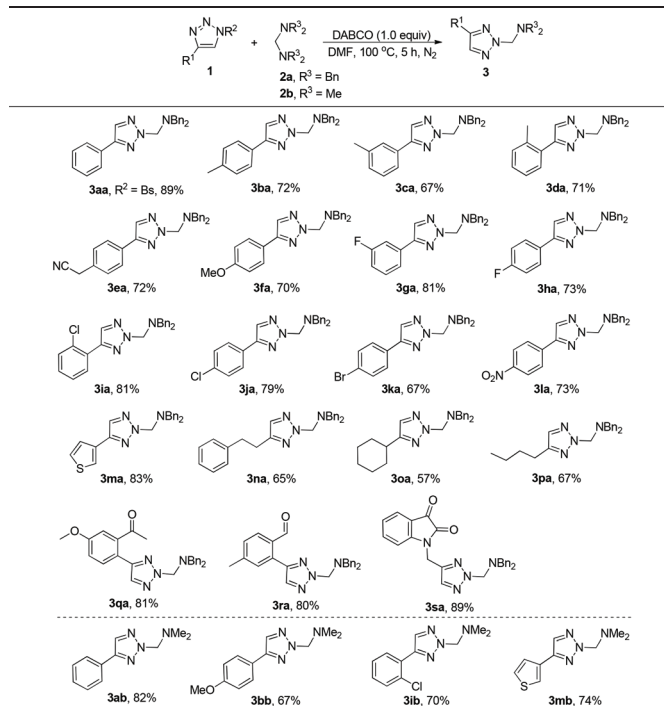
We initially utilized *N*-sulfonyl-1,2,3-triazole **1a** (0.2 mmol) and tetrabenzylmethanediamine **2a** (0.2 mmol) as substrates to examine the reaction outcomes. The results are shown in Table 1. To our delight, in the presence of 1.0 equiv. of  $K_2CO_3$  as an additive, we found that **3aa** was obtained in 39% yield determined by  $^1H$  NMR spectroscopy along with the formation of  $HNBn_2$  (Table 1, entry 2). Subsequently, solvents were examined (Table 1, entries 3–8). The yield of **3aa** had no obvious improvement when THF or toluene was used (Table 1, entries 3 and 4). While the use of high polar solvents such as DMF and DMSO afforded **3aa** in higher yields (Table 1, entries 5 and 6). Then we turned our attention to identify the best base for this reaction. Both inorganic and organic bases were used in the reaction, and 1,4-diazabicyclo[2,2,2]octane (DABCO) was identified as the best base for the reaction, affording **3aa** in 90% isolated yield. Meanwhile, the corresponding  $TsNBn_2$  was also obtained at the same time (Table 1, entry 14). The structure of **3aa** has been unambiguously determined by the X-ray crystal structure of its analogue **3ha** (Fig. 1).<sup>17</sup>

With the optimal conditions in hand, we next surveyed the substrate scope of this reaction and the results are shown in Table 2. At first, we synthesized a series of triazoles with different substituents on the aromatic ring and examined their reaction properties. As for substrates **2b–f**, with electron-donating groups on the aromatic ring, the desired products **3** were afforded in 67–72% yields. While for substrates **2g–l**, with electron-withdrawing groups, the corresponding products **3** were afforded in 67–81% yields. These results suggested that the substrates with electron-withdrawing groups on the aromatic



Fig. 1 The ORTEP drawing of **3ha**.

Table 2 Reaction scope: synthesis of triazoles **3** from substrates **1**<sup>a</sup>



<sup>a</sup> Conditions: **1** (0.20 mmol), **2** (0.20 mmol) and DABCO (0.20 mmol) were heated in DMF (2.0 ml) at 100 °C for 5 h.

Table 1 Optimization of the reaction conditions

| Entry <sup>a</sup> | Additive   | X   | Solvent | T (°C) | Yield <sup>b</sup> (%)             |
|--------------------|------------|-----|---------|--------|------------------------------------|
| 1                  | —          | —   | DCE     | 100    | 25                                 |
| 2                  | $K_2CO_3$  | 1.0 | DCE     | 100    | 39 <sup>c</sup>                    |
| 3                  | $K_2CO_3$  | 1.0 | THF     | 100    | 40                                 |
| 4                  | $K_2CO_3$  | 1.0 | Toluene | 100    | 51                                 |
| 5                  | $K_2CO_3$  | 1.0 | DMF     | 100    | 70                                 |
| 6                  | $K_2CO_3$  | 1.0 | DMSO    | 100    | 68                                 |
| 7                  | $K_2CO_3$  | 1.0 | DMF     | 100    | 92                                 |
| 8                  | $NaHCO_3$  | 1.0 | DMF     | 100    | 92                                 |
| 9                  | $NaHCO_3$  | 1.0 | DMF     | 100    | 86                                 |
| 10                 | $NaOH$     | 1.0 | DMF     | 100    | 12                                 |
| 11                 | $Et_3N$    | 1.0 | DMF     | 100    | 11                                 |
| 12                 | $^iPr_2NH$ | 1.0 | DMF     | 100    | 11                                 |
| 13                 | DBU        | 1.0 | DMF     | 100    | 58                                 |
| 14                 | DABCO      | 1.0 | DMF     | 100    | 96 <sup>d</sup> (90 <sup>e</sup> ) |
| 15                 | DMAP       | 1.0 | DMF     | 100    | 95                                 |

<sup>a</sup> Unless otherwise specified, all reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol) and additive (0.20 mmol). <sup>b</sup> Yields are determined by  $^1H$  NMR using trimethoxybenzene as an internal standard. <sup>c</sup>  $HNBn_2$  was obtained in 25% yield. <sup>d</sup>  $TsNBn_2$  was obtained in 91% yield. <sup>e</sup> Isolated yield.

ring may be more conducive to the formation of **3** compared to those of electron-donating ones. When the benzene ring was replaced by the thiophene ring, product **3ma** could also be afforded in good yield. The reaction could also tolerate various triazoles with aliphatic substituents, indicating a broad substrate scope, and giving the desired products **3na**, **3oa** and **3pa** in moderate yields. Furthermore, the substrates bearing functional groups such as a carbonyl group could also afford the corresponding products **3qa**, **3ra** and **3sa** in good yields. When the triazole was protected by the Bs group (4-bromophenylsulfonyl), the reaction also proceeded efficiently, giving the corresponding product **3aa** in 89% yield. Finally, tetramethylmethanediamine **2b** was also used in this reaction, affording the desired products **3ab**, **3bb**, **3ib** and **3mb** in 67–82% yields.

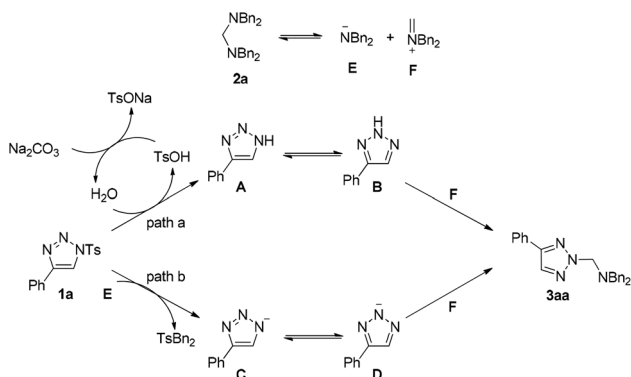
The next experiments mainly focused on the investigation of the mechanism of this reaction. The different by-products



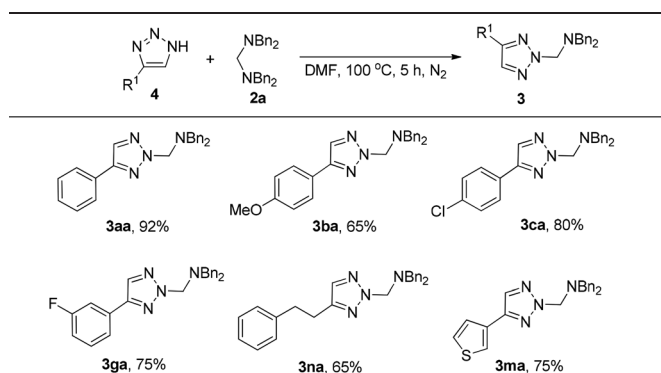
Scheme 3 Control experiments.

of the reaction with different additives caught our attention (Table 1, entries 2 and 14). As shown in Scheme 3, several control experiments were performed. If DABCO was used as the additive, the corresponding  $\text{TsNBn}_2$  was obtained in 91% yield along with the product **3aa** in 90% yield (Scheme 3a). However, if  $\text{Na}_2\text{CO}_3$  was used,  $\text{HNBn}_2$  was obtained in 81% yield instead of  $\text{TsNBn}_2$  (Scheme 3b). To eliminate the possibility that  $\text{HNBn}_2$  is derived from the decomposition of  $\text{TsNBn}_2$ , another control experiment was also performed. 0.5 equiv. of  $\text{TsNBn}_2$  was added to the  $\text{Na}_2\text{CO}_3$ -induced reaction, and it could be recovered in 94% yield after 5 h, suggesting that  $\text{HNBn}_2$  is not derived from  $\text{TsNBn}_2$  (Scheme 3c).

Based on the above results, two possible reaction pathways using substrates **1a** and **2a** as models are outlined in Scheme 4. As for substrate **2a**, it will decompose to give intermediates **E** and **F**. When  $\text{Na}_2\text{CO}_3$  is used as an additive, substrate **1a** will decompose to form intermediate **A** in the presence of a trace amount of  $\text{H}_2\text{O}$  in the solvent.  $\text{TsOH}$  is obtained at the same time, which can be neutralized by  $\text{Na}_2\text{CO}_3$  to deliver  $\text{H}_2\text{O}$  again. Intermediate **A** can be converted into its resonance **B**, which can react with intermediate **F** to give the product **3aa** (path a). If DABCO is used as an additive, substrate **1a** reacts with **E** to give intermediate **C** and  $\text{TsNBn}_2$ . Intermediate **D**, derived from **C**, can also react with **F** to give the product **3aa** (path b).



Scheme 4 Plausible reaction mechanisms.

Table 3 Reaction scope: synthesis of triazoles **3** from substrates **4**<sup>a</sup>

<sup>a</sup> Conditions: **4** (0.20 mmol) and **2** (0.20 mmol) were heated in DMF (2.0 ml) at 100 °C for 5 h.

The investigations on the reaction mechanism suggested that the *in situ* generated 4-phenyl-1*H*-1,2,3-triazole could also react with **2a** to give a similar product. As we expected, substrate **4a** can react with **2a** smoothly even in the absence of DABCO to give the product **3aa** in 92% yield. This result also suggested that intermediate **B** is more stable than **A**. For substrates with electron-donating or -withdrawing groups on the aromatic ring, the reaction proceeded efficiently to give the desired products **3ba**, **3ca** and **3ga** in 65%, 80% and 75% yields, respectively. Meanwhile, for the triazole with an aliphatic substituent, the corresponding product **3na** was formed in 65% yield. In addition, in the case of thiophene-tethered triazole **4m**, the reaction also proceeded smoothly to afford the desired product **3ma** in 75% yield (Table 3).

In summary, a new base-induced reaction mode of *N*-sulfonyl-1,2,3-triazoles has been established, thereby providing a simple procedure for preparation of triazoles bearing dialkylaminomethyl groups. In this reaction, a wide range of substrates can tolerate this reaction. Moreover, 4-phenyl-1*H*-1,2,3-triazoles can also give the same product even in the absence of a base. The potential applications and extension of the substrate scope of this novel synthetic methodology are currently underway in our laboratory.

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