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# Transition-Metal-Free Semihydrogenation of Diarylalkynes: Highly Stereoselective Synthesis of *trans*-Alkenes Using $Na_2S·9H_2O$

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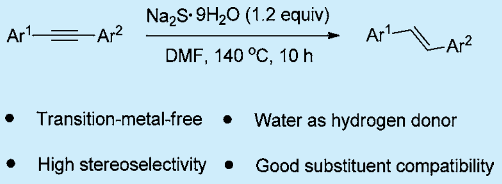
*Supporting Information*

**ABSTRACT:** A highly stereoselective and efficient transition-metal-free semihydrogenation of internal alkynes to *E*-alkenes using cheap and green water as hydrogen donor is described. The reactions are conducted under convenient conditions and provide products in good to excellent yields, with broad substrate scope, including a variety of diarylalkynes.

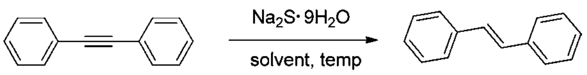


The selective semihydrogenation of alkynes to alkenes with a defined *Z*- or *E*-configuration is an important transformation in organic chemistry.[1] It has been widely used for the synthesis of synthetic intermediates, natural products, fragrances, and pharmaceuticals.[2] Among the various efficient methods to access *Z*-alkenes, Lindlar's catalyst ($Pd/CaCO_3$) and its variants are the most popular choices.[3] Over the past decades, some other functional-group-tolerant catalytic *Z*-selective semihydrogenation approaches have been developed.[4] However, on the contrary, examples of semihydrogenation of alkynes to *E*-alkenes have been rarely studied or reported. A textbook example of a Birch-type reduction of alkynes by alkali metals (Li, Na) in liquid ammonia is the traditional and powerful protocol for obtaining *E*-alkene, but the harsh reaction conditions damaged the functional group tolerance.[5] Recently, some catalytic systems for alkyne semihydrogenation to *E*-alkenes have been explored. Among them, the transition-metal-complex-containing Rh,[6] Ru,[7] Pd,[8] Ir,[9] Ni,[10] and Fe[11] have proven to be useful for this transformation. However, these transition-metal reagents still have some drawbacks, such as high price, generation of toxic waste, and the need of an air-sensitive or expensive ligand. From economical and environmental viewpoints, it would be advantageous and quite desirable to develop transition-metal-free systems for the synthesis of alkenes from alkynes.[12]

Sodium sulfide nonahydrate is an inexpensive and safe reducing agent, which has been widely used for the reduction of aromatic nitro compounds to the corresponding anilines in organic synthesis. Recently, we have reported a series of transformations based on terminal alkynes and haloalkynes.[13] As part of our continuing project on the functionalization of alkynes, here we wish to present a highly stereoselective and efficient method for the synthesis of a series of *E*-alkenes containing a wide range of functional groups via $Na_2S·9H_2O$ reduction of diarylalkynes.

Our initial efforts were focused on the search for suitable reaction conditions in dimethyl sulfoxide, where the reaction of 1,2-diphenylethyne (**1a**) with $Na_2S·9H_2O$ was chosen as the model reaction. We added different transition metals into the reaction, assuming the reaction to be a catalytic process. However, the control experiment results showed that (*E*)-diphenylethene could be obtained without addition of any transition metals, which implies that it is a noncatalytic reaction. As shown in Table 1, we then screened other factors of the reaction including solvent, temperature and reaction time. We found that the reaction showed a strong solvent dependence. Among the solvents used, DMSO, DMA, and DMF were proven appropriate (Table 1, entries 1−5). The reaction did not proceed without sodium sulfide nonahydrate (Table 1, entry 6). It is noteworthy that reaction temperatures are

**Table 1. Optimization of Reaction Conditions for the Synthesis of (*E*)-Diphenylethene[a]**



**1a** **2a**

| entry | solvent | temp (°C) | time (h) | yield[b] (%) |
|---|---|---|---|---|
| 1 | DMSO | 140 | 16 | 86 |
| 2 | xylene | 140 | 16 | n.r. |
| 3 | DMA | 140 | 16 | 93 |
| 4 | DMF | 140 | 16 | 96 |
| 5 | $H_2O$ | 100 | 16 | trace |
| 6[c] | DMF | 140 | 16 | n.r. |
| 7 | DMF | 100 | 16 | 70 |
| 8 | DMF | 60 | 16 | trace |
| **9** | **DMF** | **140** | **10** | **98 (96)** |
| 10 | DMF | 140 | 6 | 59 |
| 11[d] | DMF | 140 | 10 | 71 |
| 12[e] | DMF | 140 | 10 | 40 |

[a] Reaction conditions: 1,2-diphenylethyne (0.25 mmol), sodium sulfide nonahydrate (1.2 equiv), and solvent (1.0 mL). [b] Determined by GC. Number in parentheses is isolated yield. [c] Without sodium sulfide nonahydrate. [d] Sodium sulfide nonahydrate (2 equiv) was used. [e] Sodium sulfide nonahydrate (0.5 equiv) was used.

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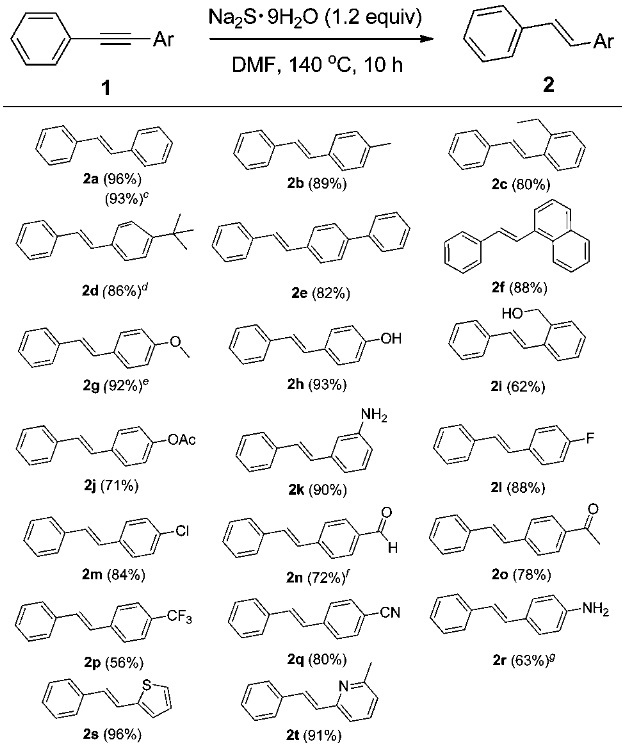
essential to the transformation; the yields decreased drastically at lower temperature (Table 1, entries 7 and 8). The optimal reaction time is 10 h, and **2a** could be obtained in 96% isolated yield (Table 1, entries 9 and 10). Moreover, an increase or decrease in the amount of $Na_2S·9H_2O$ led to a decrease in the yield (Table 1, entries 11 and 12). After some attempts, we considered that the optimized reaction conditions are as follows: **1a** (0.25 mmol) with $Na_2S·9H_2O$ (0.30 mmol) and DMF (1 mL) at 140 °C for 10 h (Table 1, entry 9).

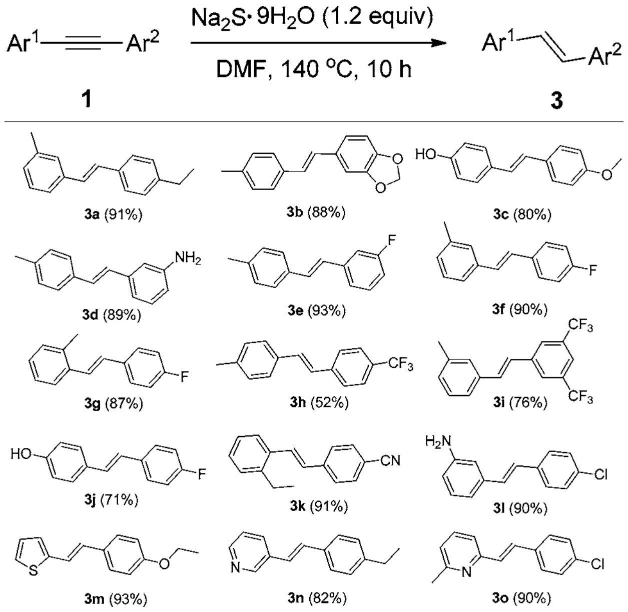
**Scheme 1. $Na_2S·9H_2O$ Reduction of Internal Alkynes to the Corresponding *E*-Alkenes**[a,b]



[a]Reaction conditions: **1** (0.25 mmol), sodium sulfide nonahydrate (1.2 equiv), and DMF (1.0 mL) at 140 °C for 10 h. [b]Isolated yield. The ratio of *Z*/*E* isomers was above 98:2 as determined by GC−MS. [c]10 mmol scale of the reaction. [d]Reacted for 20 h. [e]Reacted for 24 h. [f]Reacted for 2 h. [g]The raw material is 4-$NO_2$-substituted diphenylacetylene.

With the optimized reaction conditions in hand, we set out to test the generality of this reaction. As shown in Scheme 1, both electron-rich and electron-deficient substitutions on the aromatic ring were compatible in the standard conditions (Scheme 1, **2b**−**t**). For most of the diarylalkynes **1**, the reaction proceeded smoothly to give the corresponding products in good to excellent yields. The reaction conditions could be compatible with a wide range of functional groups such as alkyl, aryl, alkyloxy, hydroxyl, ester, amino, fluoro, chloro, formyl, carbonyl, trifluoromethyl, cyano, and heteroaryl groups (Scheme 1, **2b**−**t**). Substitution at the *ortho* position of the aromatic ring had some impact on the yield (Scheme 1, **2c**). The alkyne **1d** bearing a bulky *tert*-butyl group afforded a high yield of the desired alkene in a prolonged reaction time (Scheme 1, **2d**). Both strong electron-donating or -withdrawing substituents on the phenyl ring had no significant influence on the yields, especially reactive hydroxyl; amino and formyl functionalities can be easily converted to various functional groups and hold enormous potential applications in organic synthesis (Scheme 1, **2g**−**q**). In the case of the diaryl alkyne bearing a nitro group, the reduction proceeded simultaneously at both the alkyne and nitro moieties (Scheme 1, **2r**). Thienyl and pyridyl derivatives were tolerant in this semihydrogenation reaction (Scheme 1, **2s** and **2t**). To further explore its potential application, we scaled up the reaction to a 10 mmol scale (1.78 g); the product could be formed in 93% yield (Scheme 1, **2a**).

**Scheme 2. $Na_2S·9H_2O$ Reduction of Diaryl Alkynes to the Corresponding *E*-Alkenes**[a,b]

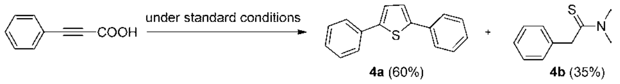


[a]Reaction conditions: **1** (0.25 mmol), sodium sulfide nonahydrate (1.2 equiv), and DMF (1.0 mL) at 140 °C for 10 h. [b]Isolated yield and the ratio of *Z*/*E* isomers was above 98:2 determined by GC−MS.

Continuing to investigate the reaction scope, we explored various diarylalkynes for this process under the optimized reaction conditions (Scheme 2). In general, most of the substrates could afford the corresponding *E*-alkenes in good yields. Furthermore, the yields were not affected when the substituents were on the *ortho*-, *meta*-, and *para*-positions of the phenyl ring (Scheme 2, **3e**−**g**). The results indicated that substituted aryl groups were perfectly tolerated (Scheme 2, **3a**−**o**). Interestingly, the five-membered cyclic ether reacted smoothly rendering the target alkene in high yield (Scheme 2, **3b**). Moreover, the dielectron-withdrawing group substituted substrate gave 76% isolated yield (Scheme 2, **3i**). In addition, heterocyclic internal alkynes such as thienyl and pyridyl derivatives provided the target products in excellent yields (Scheme 2, **3m**−**o**).

Subsequently, 3-phenylpropiolic acid was reacted under the standard conditions (Scheme 3). However, we were surprised that thiophene **4a** and thioamide **4b** were formed instead of 3-phenylacrylic acid.[14] Both substituted thiophenes[15] and

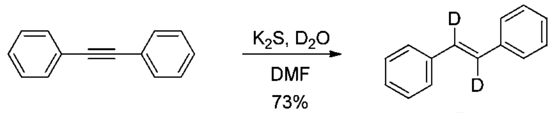
**Scheme 3. Formation of Thiophene and Thioamide from Phenylpropiolic Acid**



thioamides[16] are ubiquitous in biologically active molecules and have also been used as building blocks for biologically relevant heterocyclic scaffolds. It is noteworthy that the amine moiety in thioamide **4b** comes from DMF.[17]

As shown in Scheme 4, (*E*)-1,2-dideuterioalkene was formed in 73% yield when $Na_2S{\cdot}9H_2O$ was replaced by $K_2S$ and $D_2O$. It indicated that water acted as the hydrogen donor in the transformation.

**Scheme 4. Investigation of the Hydrogen Source in the Semihydrogenation Reaction**



**5a**

In summary, we developed a simple, efficient, and novel transition-metal-free protocol for the formation of *E*-alkynes. The semihydrogenation reaction was a highly stereoselective reduction; only negligible amounts of *Z*-alkenes and over-reduced alkanes were observed in GC−MS. The method employed water as the hydrogen donor avoiding the use of a potentially hazardous pressurized $H_2$ atmosphere. Both electron-donating and electron-withdrawing substitutions on the aromatic ring were compatible under the standard conditions. Importantly, the products with carbonyl, hydroxyl, and amino groups can be utilized in several organic transformations. Further studies to reveal the reaction mechanism and extend the applications of this methodology are currently underway in our labaratory.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Typical experimental procedure and characterization for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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