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Deoxyallenylation |*Hot Paper*|

Lewis and Brønsted Acid Cocatalyzed Reductive Deoxyallenylation of Propargylic Alcohols with 2-Nitrobenzenesulfonylhydrazide

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Abstract: Reductive deoxyallenylation of sterically hindered tertiary propargylic alcohols was realized on reaction with 2-nitrobenzenesulfonylhydrazide (NBSH) by the combined use of Lewis and Brønsted acid catalysts. This method features a broad substrate scope, mild reaction conditions, and good functional-group tolerance, and affords various mono-, di-, and trisubstituted allenes in good-to-excellent yields. The synthetic utility of this method was demonstrated by the synthesis of 2*H*-chromenes and 1,2-dihydroquinolines.

Allenes are useful structural motifs that function as important substrates or intermediates in organic synthesis,[1] and are also found in many biologically active natural products.[2] Thus, substantial advances in the development of novel synthetic methods for these compounds, either in a racemic or an enantiomerically enriched form, have already been achieved.[3] Nonetheless, despite this impressive progress, the discovery and development of novel methodologies for allene syntheses from easily available starting materials remains an important objective. Propargylic alcohols are readily available bifunctional building blocks, and the exploration of their synthetic potency has attracted much attention in recent years.[4] Reductive deoxyallenylation of propargylic alcohols represents an extremely convenient approach to allenes. So far, only four approaches are capable of performing such reactions, including the use of Schwartz reagent [$Cp_2Zr(H)Cl$] (Cp = cyclopentadienyl),[5] lithium aluminum hydride ($LiAlH_4$),[6] triphenylphosphine (Ph_3P),[7] and 2-nitrobenzenesulfonylhydrazide (NBSH).[8] However, application of these methods to sterically hindered tertiary propargylic alcohols remains a formidable challenge.[9] On comparison of these methods, the NBSH-mediated method via intermediate **A**, initially developed by Myers and Zheng in 1996,[8] may be the most practical method because of the wide applications in organic synthesis (Figure 1 a).[10] However, this method has to meet the requirements of the Mitsunobu reaction, which is only compatible with less hindered primary and secondary propargylic alcohols.[11] Therefore, the search for a novel and efficient reductive deoxyallenylation reaction that is suitable for sterically hindered propargylic alcohols is certainly in demand. Recently, Thomson and co-workers reported a Lewis acid catalyzed one-pot synthesis of allenes by the NBSH-mediated coupling reaction of alkynyl trifluoroborate salts with hydroxyaldehydes or ketones, and proposed that the reaction proceeded via intermediate **B** (Figure 1 b).[12] Inspired by this study and our continued interest in the reactions of functionalized alkynes,[13] we envisaged that an acidic catalyst could promote the deoxyamination of propargylic alcohols with NBSH,[14] thus generating the key intermediate **C**, which is essential for subsequent allenation (Figure 1 c). Pleasingly, this expectation was realized experimentally, and a practical reductive deoxyallenylation reaction, which could be applied to the complementary substrates to those in in the reaction developed by Myers and Zheng,[8] was discovered. Herein, we report this new strategy for the reductive deoxyallenylation of propargylic alcohols.

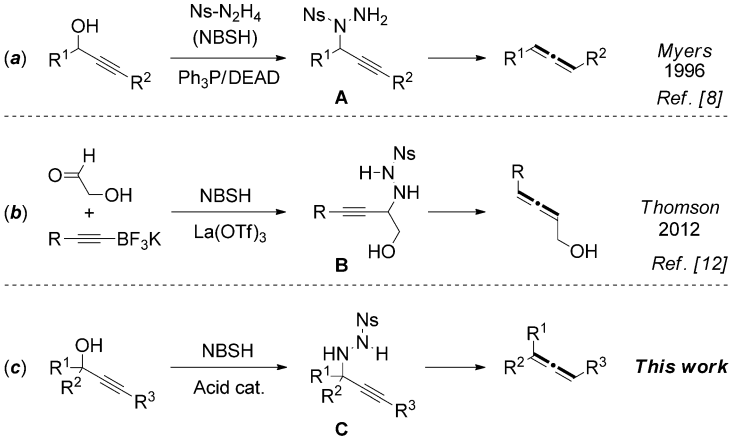

Figure 1. NBSH-mediated allene synthesis. DEAD = diethyl azodicarboxylate.

Initially, the reaction conditions were optimized; the reaction of propargylic alcohol **1 a** with 1.2 equivalents of NBSH was used as the model reaction. As shown in Table 1, different Lewis acids, combinations with Brønsted acids, and solvents were screened. Firstly, the Lewis acids were investigated by

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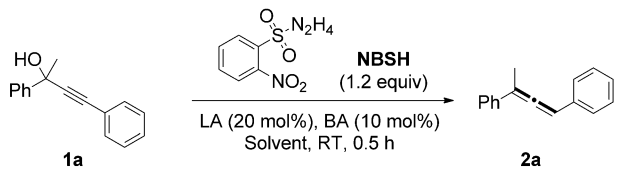
Table 1. Screening of reaction conditions.[a]

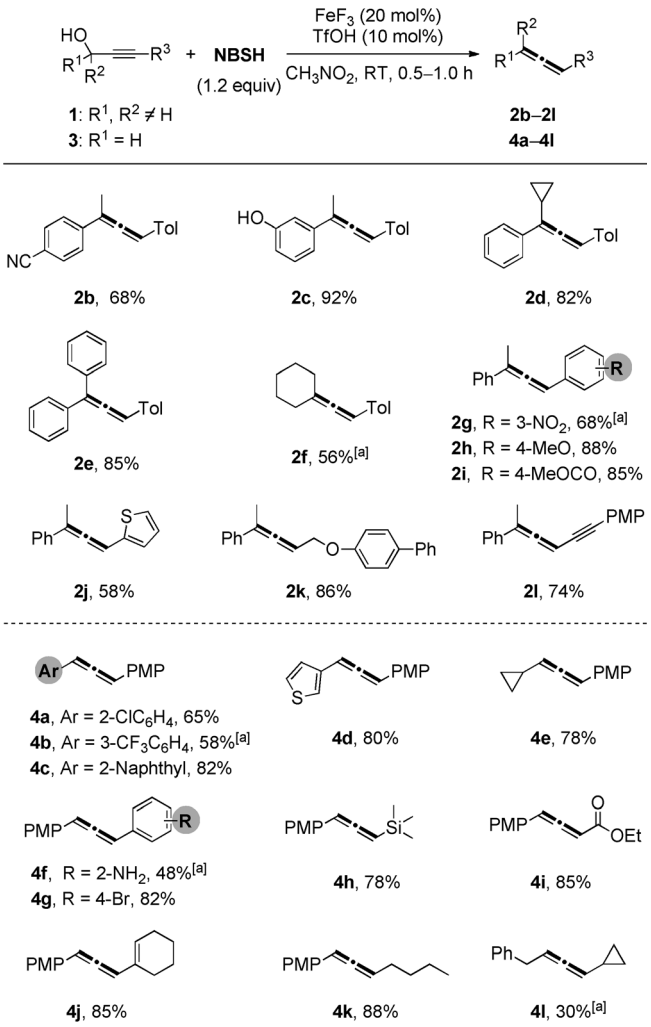


Entry	LA [20 mol%][b]	BA [10 mol%][c]	Solvent	Yield [%][d]
1	$La(OTf)_3$	–	CH_3NO_2	58
2	$Sc(OTf)_3$	–	CH_3NO_2	72
3	AgOTf	–	CH_3NO_2	84
4	$Bi(OTf)_3$	–	CH_3NO_2	78
5	$FeCl_3$	TfOH	CH_3NO_2	86
6	FeF_3	TfOH	CH_3NO_2	90
7	FeF_3	AcOH	CH_3NO_2	trace
8	FeF_3	TfOH	CH_3NO_2	0[e]
9	FeF_3	TfOH	CH_3CN	85
10	FeF_3	TfOH	DMF	0
11	FeF_3	TfOH	EtOH	0
12	FeF_3	TfOH	toluene	trace

[a] Reactions were performed with **1a** (0.5 mmol) and NBSH (0.60 mmol) in the presence of a catalyst (20 mol%) in solvent (3 mL) under ambient atmosphere for 0.5 h. [b] LA = Lewis acid. [c] BA = Brønsted acid. [d] Isolated yields. [e] With *p*-tosylhydrazide instead of NBSH.

using CH_3NO_2 as the solvent. $La(OTf)_3$ (OTf = triflate), previously used by Thomson and co-workers,[12] afforded a promising result (58% yield of **2a**, Table 1, entry 1). Next, several Lewis acids, including $Sc(OTf)_3$, AgOTf, and $Bi(OTf)_3$, were examined; all afforded **2a** in good yields (Table 1, entries 2–4). Previously, we discovered the superior catalytic activity of a superacid catalyst system comprising a Lewis acid and Brønsted acid conjugate such as $FeCl_3$ and HOTf.[15] Therefore, the catalytic effect of the combined $FeCl_3$ and HOTf system was examined. Pleasingly, the yield of **2a** increased to 86% (Table 1, entry 5). Furthermore, a much higher yield (90%) of **2a** was obtained by using FeF_3 instead of $FeCl_3$, whereas a trace amount of **2a** was generated when a weak protonic acid, such as HOAc was used (Table 1, entries 6 and 7). Notably, when *p*-tosylhydrazide was used instead of NBSH, the desired product was not obtained (Table 1, entry 8). The solvent used significantly affected the reaction outcome. For example, the use of acetonitrile afforded **2a** in 85% yield (Table 1, entry 9). Dimethylformamide (DMF) and ethanol were ineffective (Table 1, entries 10 and 11), whereas the use of toluene resulted in a trace amount of product (Table 1, entry 12). Therefore, the reaction conditions listed in Table 1, entry 6 were found to be optimal and were selected for further investigations.

After determining the optimum reaction conditions, the substrate scope of the reaction was investigated for different internal propargylic alcohols (i.e., $R^3 \neq H$) (Scheme 1). In general, the substrate scope was found to be quite broad, and diverse secondary and tertiary propargylic alcohols with varying functional groups could be applied to this Lewis and Brønsted acid co-catalyzed reductive deoxyallenylation with NBSH, affording the corresponding functionalized trisubstituted (**2b**–**2l**) and 1,3-disubstituted allenes (**4a**–**4l**) in good-to-excellent yields.[16] All

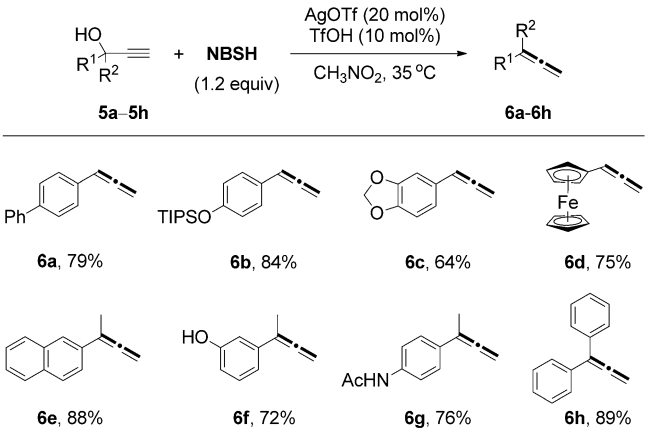


Scheme 1. Synthesis of tri- and disubstituted internal allenes. [a] The reactions were carried out in the presence of AgOTf (20 mol%) and TfOH (10 mol%) at 35 °C. Tol = *p*-methylphenyl; PMP = 4-methoxyphenyl.

of the reactions proceeded smoothly and completed within 0.5–1.0 h. Compared with previous reductive deoxyallenylation methods, the synthesis of allene **2e**, in an excellent yield (85%), demonstrated the superior performance of this method for sterically hindered propargylic alcohols (**1e**).[5–8] The preparation of allene **2f** was especially interesting because such an allene structural motif is found in several biologically active natural products.[2] Moreover, the functional-group tolerance of the reaction is reasonable, for example, in addition to the common electron-rich and electron-deficient (hetero)aryl and alkyl groups, several sensitive functional groups, such as phenolic hydroxyl (**2c**), cyclopropyl (**2d**, **4e**, and **4l**), alkenyl (**4j**), alkynyl (**2l**), trimethylsilyl (**4h**), ether (**2k**), ethoxycarbonyl (**4i**), halogen (**4a**, and **4g**), and free amino (**4f**) groups were found to be well-tolerated. Some of these functionalized allenes have proven to be useful intermediates in organic synthesis.[17] Thus, a convenient and practical synthetic method was developed for their preparation.

Terminal allenes are useful synthetic intermediates; general methods for the synthesis of terminal allenes include the ho-

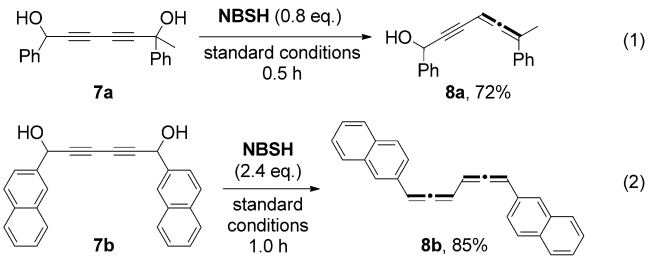
mologation reaction of terminal alkynes reported by Rona and Crabbé[18] and the palladium-catalyzed hydrogen-transfer reaction of propargylic amines reported by Nakamura and co-workers.[19] Terminal propargylic alcohols (e.g., ethynyl carbinols) are readily available from the addition of an ethynyl metal reagent to aldehydes or ketones. Therefore, we were interested in the application of our acid-catalyzed reductive deoxyallenylation with NBSH to the synthesis of terminal allenes. As shown in Scheme 2, we were pleased to find that the reactions of both



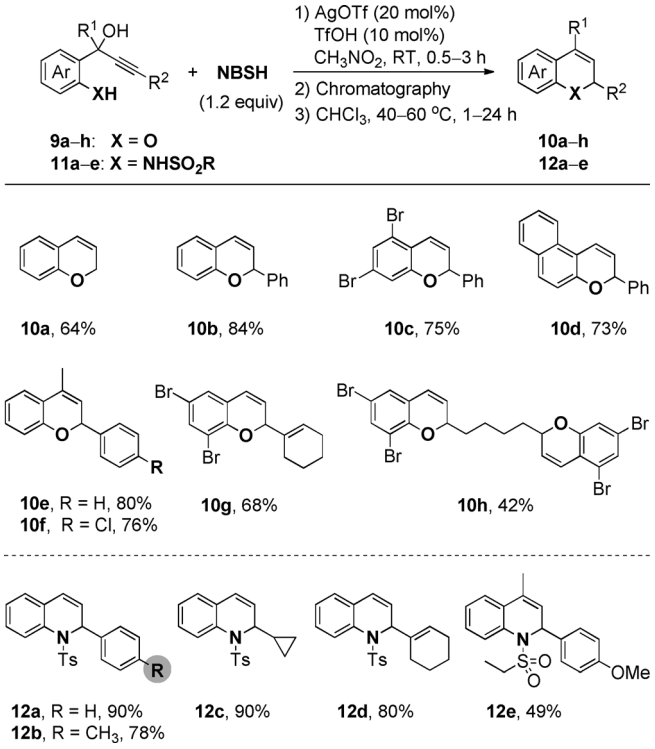
Scheme 2. Synthesis of mono- and disubstituted terminal allenes.

secondary and tertiary terminal propargylic alcohols with NBSH under slightly modified reaction conditions (using AgOTf instead of FeF_3), smoothly afforded the desired products (**6a**–**6h**) in moderate-to-excellent yields (64–89%). All of the substrates containing substituted aryl, fused aryl, and ferrocenyl groups were suitable for this transformation.[20] The efficient synthesis of various functionalized mono-, and 1,2-/1,1-di-, and trisubstituted allenes (**2**, **4**, and **6**) demonstrated that the Lewis and Brønsted acid cocatalyzed reductive deoxyallenylation of propargylic alcohols with NBSH is a powerful method for allene synthesis. This method has a completely complementary substrate scope to that reported by Myers and Zheng.[8]

The sensitivity of the new method to steric effects has one advantage, as exemplified in the reaction of compound **7a** with NBSH [Eq. (1)]. The sterically hindered tertiary propargylic alcohol was reductively deoxyallenylated selectively, thus affording the allenyne derivative, **8a**, in 72% yield. Additionally, this method can be applied to prepare synthetic diallenes, such as compound **8b** [Eq. (2)].[21]

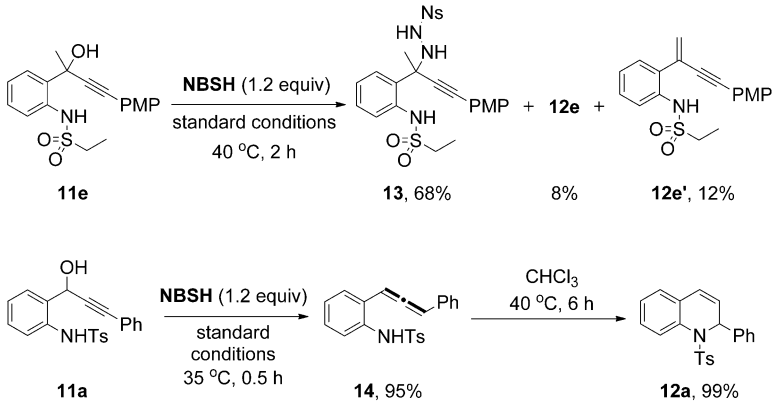


To demonstrate the synthetic utility of this new method, we next investigated intramolecular cyclization by the in situ generation of *ortho*-allenyl phenols or anilines. To our delight, an 6-*endo* cyclization was observed, affording the corresponding 2*H*-chromenes (**10a**–**10h**), including the parent 2*H*-chromene (**10a**) and 1,2-dihydroquinolines (**12a**–**12e**) in moderate-to-excellent yields (Scheme 3). Notably, the formation of 2*H*-chromenes and 1,2-dihydroquinolines in high yield required the separation of allenes and part-cyclized products by chromatography, followed by heating the reaction mixture at 40–60 °C without a metal catalyst. Poor yields were obtained when the reaction mixture was directly heated (without any separation) after the first allene-forming step. The 2*H*-chromenes[22] and 1,2-dihydroquinolines[23] are two types of privileged heterocyclic scaffolds found in numerous natural products and medicines that possess interesting biological activities. Considerable efforts towards the synthesis of these scaffolds have resulted in a number of efficient synthetic methods.[24] However, a pathway involving the thermal 6-*endo* heterocyclization of *ortho*-allenyl phenols or anilines under metal-free conditions remains elusive.[25] Herein, we provided a novel and efficient method for the construction of these two classes of heterocycles that is of interest to synthetic and medicinal chemists.



Scheme 3. Synthesis of 2*H*-chromenes and 1,2-dihydroquinolines. The synthesis of compounds **10h** and **12** required a slightly increased temperature to 35–40 °C.

To elucidate the reaction mechanism we, firstly, tried to isolate the deoxyaminated intermediate, which was not successfully isolated in the studies of Myers and Zheng, and Thomson and co-workers.[8,12] Fortunately, the desired intermediate, **13**,



Scheme 4. Mechanistic investigations. Ns = nosyl; Ts = tosyl.

was obtained in 68% yield from the reaction of pargylic alcohol **11e** with NBSH, only accompanied by small amounts of 1,2-dihydroquinoline **12e** and eneyne **12e′** as byproducts. Next, heating a solution of **13** in $CHCl_3$, without a metal catalyst, afforded 1,2-dihydroquinoline **12e** in 80% yield. Instead of **11e**, we isolated an allene intermediate, **14**, in 95% yield by using **11a** as the substrate and reducing the reaction time to 0.5 h. In the absence of a metal catalyst, the reaction of allene **14** smoothly proceeded to afford 1,2-dihydroquinoline **12a** in almost quantitative yield at 40 °C (6 h in $CHCl_3$, see Scheme 4). Based on these results and related precedents,[8,12] we conclude that the acid-catalyzed reductive deoxyallenylation of propargylic alcohols with NBSH involves sequential deoxyamination, in situ elimination of *o*-nitrobenzenesulfinic acid, and hydride transfer accompanied by the release of nitrogen to give allenes.[26] The formation of 2*H*-chromenes and 1,2-dihydroquinolines from allene precursors might proceed through a regioselective 6-*endo* cyclization.[27]

In conclusion, we have described a valuable methodology for the reductive deoxyallenylation of sterically hindered propargylic alcohols. This method is compatible with a broad scope of tertiary and secondary propargylic alcohols and affords various mono-, di-, and trisubstituted allenes in good-to-excellent yields, This method is completely complementary in substrate scope to the widely used reaction reported by Myers and Zheng.[8] Further application to the synthesis of 2*H*-chromenes and 1,2-dihydroquinolines demonstrates the synthetic utility of this method. Considering the mild reaction conditions, broad substrate scope, and good functional-group tolerance, this new reaction for allene synthesis will undoubtedly find wide applications in organic synthesis.

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Keywords: allenes · 2*H*-chromenes · deoxyallenylation · propargylic alcohols

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COMMUNICATION

Deoxyallenylation

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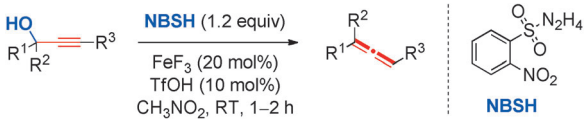
Lewis and Brønsted Acid Cocatalyzed Reductive Deoxyallenylation of Propargylic Alcohols with 2-Nitrobenzenesulfonylhydrazide



Better together: A novel and highly efficient Lewis and Brønsted acid cocatalyzed reductive deoxyallenylation of propargylic alcohols with 2-nitrobenzenesulfonylhydrazide (NBSH) has been developed (see scheme). Diverse tertiary and secondary propargylic alcohols participated in the reaction, affording various mono-, di-, and trisubstituted allenes in good-to-excellent yields. Furthermore, the synthesis of 2*H*-chromenes and 1,2-dihydroquinolines demonstrated the synthetic utility of this method.

The reductive deoxyallenylation…
…of propargylic alcohols is an attractive method for allene synthesis due to the availability and diversity of propargylic alcohols. However, its applications to sterically hindered tertiary propargylic alcohols remain a formidable challenge. In their Communication on page ■■ ff., X. Bi et al. report a new strategy to address this issue by using a Lewis and Brønsted acids cocatalyzed reductive deoxyallenylation with 2-nitrobenzenesulfonylhydrazide (NBSH).