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Copper-Catalyzed Radical Reaction of *N*-Tosylhydrazones: Stereoselective Synthesis of (*E*)-Vinyl Sulfones

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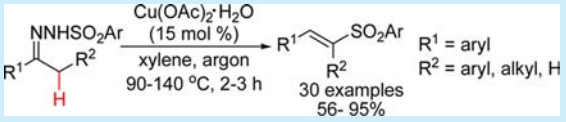
Supporting Information

ABSTRACT: A new chemistry of hydrazines that is a copper-catalyzed radical reaction to synthesize vinyl sulfones from readily available *N*-tosylhydrazones has been described. The protocol provides a novel strategy for the synthesis of various vinyl sulfones including *α*, *β*-disubstituted ones and terminal ones. The advantages of the transformation include excellent *E* stereoselectivity, broad substrate scope, low cost of reagents, and convenient operation. A novel and efficient one-pot synthesis of alkynes from *N*-tosylhydrazones has been achieved. The studies provide important complementary approaches for the syntheses of vinyl sulfones and alkynes.



Hydrazine derivatives are a class of important organic molecules that have received much attention within the chemistry community.[1,2] Early research on hydrazine derivatives led to the development of the famous Fischer indole synthesis[3] and Wolff–Kishner reduction.[4] In the past decade, transition-metal-catalyzed reactions of hydrazine derivatives have achieved great development[5] involving diverse conversions, such as X–H (X = C, Si, N, O, etc.) insertions,[6] cyclization reactions,[7] ylide formations,[8] and 1,2-migrations.[9] In these versatile transition-metal-catalyzed transformations, hydrazine derivatives are generally the precursors of diazo compounds to generate metal (Pd, Cu, Rh, Ni, and Co) carbene species under base conditions first and then undergo further reactions.[10] Herein, we disclose a new chemistry of hydrazine compounds, the first copper(II)-catalyzed radical reaction to synthesize various vinyl sulfones from readily available *N*-tosylhydrazones.[11]

The research originated from the reaction where deoxybenzoin *N*-tosylhydrazone (**1a**) was treated with 20 mol % of $Cu(OAc)_2·H_2O$ in xylene under air atmosphere at 90 °C for 6 h to afford the intriguing vinyl sulfone compound (**2a**, the structure was confirmed by single-crystal X-ray analysis) in 34% yield. We realized this would be new chemistry for the hydrazines, and if the reaction conditions had been optimized, a novel strategy for the synthesis of vinyl sulfones from *N*-tosylhydrazone compounds would be developed. It is well-known that vinyl sulfones are a kind of valuable organic compound.[12] They have proven to be potent inhibitors of a variety of enzymatic processes (e.g., cysteine protease[13] and HIV-1 integrase[14]), making them lead candidates for drug design.[15] Moreover, in the field of organic synthesis, vinyl sulfones are efficient Michael acceptors[16] as well as good 2*π* partners in cycloaddition reactions,[17] and they can be exchanged by various groups such as hydrogen, alkyl, hydroxyl, and carbonyl, entitling vinyl sulfones to be versatile reactive synthons.[18] At present, the methods for the synthesis of terminal vinyl sulfones are well-documented.[19] However, the procedures for the synthesis of *α*, *β*-disubstituted vinyl sulfones are very limited.[20] Although some methods are perfect for the synthesis of terminal vinyl sulfones, they are of low efficiency or inefficient for production of *α*,*β*-disubstituted vinyl sulfones.[21] Thus, the development of a conceptually novel and efficient method for the synthesis of *α*,*β*-disubstituted vinyl sulfones is highly demanded.

Accordingly, we chose *N*-tosylhydrazone (**1a**) as model substrate to seek optimal reaction conditions for the development of new chemistry of the hydrazines to synthesize *α*,*β*-disubstituted vinyl sulfones. First, we checked the atmosphere of the reaction (Table 1, entries 1–3). When air was replaced with oxygen and argon, respectively, we were surprised to find that the reaction hardly proceeded under oxygen atmosphere, while the reaction provided the desired product **2a** in excellent yield (92%) under argon atmosphere. Moreover, the product **2a** possessed complete *E* stereoselectivity. Then the reaction temperature was examined (Table 1, entries 4–6). Lowering the temperature to 80 °C, we found the conversion of the reaction dramatically dropped to only 23% even when the reaction time was extended to 25 h. Higher temperature only accelerated the reaction rate without an increase in yield. A variety of other copper salts were investigated (Table 1, entries 7–9). Anhydrous $Cu(OAc)_2$ afforded **2a** in 30% yield along with deoxybenzoin (40%) and stilbene (25%). Interestingly, the yield of **2a** was improved markedly to 65% when one drop of water was introduced into the anhydrous $Cu(OAc)_2$-catalyzed reaction system, but more water resulted in a messy reaction. These results demonstrated that a small amount of water played a very important role in the reaction. Other copper sources displayed poor catalytic activity. After a careful solvent screening, xylene was chosen (Table 1, entry 10). When the loading of $Cu(OAc)_2·H_2O$ was reduced to 15%, the excellent yield was maintained, while a lower amount loading led to incomplete reaction (Table 1, entries 11 and 12). Finally, a control experiment showed that in the absence of

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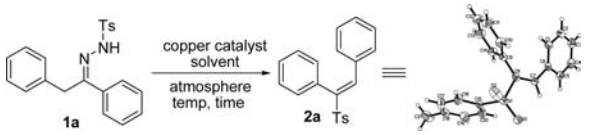
Table 1. Optimization of the Reaction Conditions[a]



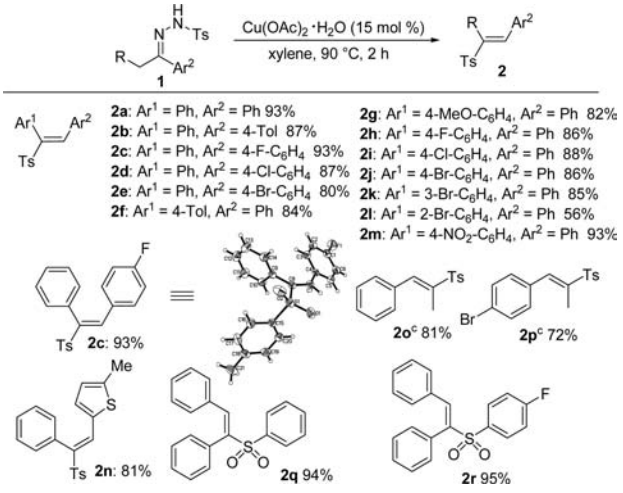
entry	catalyst	temp (°C)	atm (1 atm)	time (h)	yield[b] (%)
1	$Cu(OAc)_2·H_2O$	90	air	6	34
2[c]	$Cu(OAc)_2·H_2O$	90	O_2	6	trace
3	$Cu(OAc)_2·H_2O$	90	Ar	4	92
4	$Cu(OAc)_2·H_2O$	80	Ar	25	23
5	$Cu(OAc)_2·H_2O$	120	Ar	2	92
6	$Cu(OAc)_2·H_2O$	140	Ar	1.5	91
7	$Cu(OAc)_2$	90	Ar	4	30
8[d]	$Cu(OAc)_2$	90	Ar	4	65
9[e]	Other coppers	90	Ar	6	<25
10[e]	$Cu(OAc)_2·H_2O$		Ar	4	<40
11[f]	$Cu(OAc)_2·H_2O$	90	Ar	6	93
12[g]	$Cu(OAc)_2·H_2O$	90	Ar	10	65
13		90	Ar	10	0

[a]Reaction conditions: **1a** (1 mmol), catalyst (20 mol %) in solvent (3 mL) at the specified temperature. [b]Isolated yields after filtration through a short pad of aluminum oxide. [c]The 2-phenylacetophenone (43% isolated yield) and benzil (33% isolated yield) were obtained. [d]One drop of water was added. [e]See the Supporting Information. [f]$Cu(OAc)_2·H_2O$ (15 mol %). [g]$Cu(OAc)_2·H_2O$ (10 mol %).

$Cu(OAc)_2·H_2O$ no product **2a** could be detected under otherwise identical conditions (Table 1, entry 13).

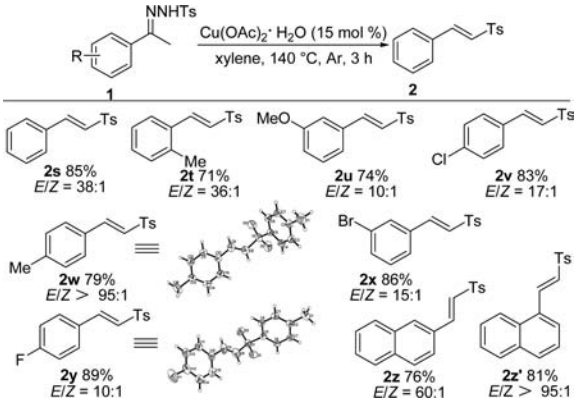
With the optimized reaction conditions in hand, we next examined the substrate scope (Scheme 1). Substrates bearing either an electron-donating or electron-withdrawing group on both sides of the aromatic rings all reacted smoothly to afford the desired α, β-disubstituted vinyl sulfones in good to excellent yields. Various functional groups, such as methyl, methoxyl, fluoro, chloro, bromo, and nitro groups, were tolerated under the conditions, which provided great opportunities for further functionalizations. The hindrance on the phenyl had a certain effect on the reaction (Scheme 1, **2j–l**). Gratifyingly, a heteroaromatic substrate, such as **1n** with a thiophene ring, was also suitable for the oxidation reaction to afford the desired product **2n** in 81% yield (Scheme 1, **2n**). *N*-Tosylhydrazones generated from propiophenones also afforded corresponding vinyl sulfones in good yields (Scheme 1, **2o**,**p**). Additionally, other sulfonyl groups were also investigated. Benzenesulfonyl hydrazine (**1q**) and 4-fluorobenzenesulfonyl hydrazine (**1r**) were suitable substrates providing the corresponding products in excellent yields (Scheme 1, **2q**,**r**). It should be mentioned that all reactions were of complete *E* stereoselectivity, and no *Z*-isomers could be detected by analyzing the reaction mixtures. The structure of the product **2c** was confirmed by single-crystal X-ray analysis.

Scheme 1. Substrate Scope for the Synthesis of α,β-Disubstituted Vinyl Sulfones[a,b]



[a]Reaction conditions: **1a** (1 mmol), $Cu(OAc)_2·H_2O$ (15 mol %), Ar (1 atm) in xylene (3 mL) at 90 °C. [b]Isolated yields. [c]At 140 °C.

Scheme 2. Reactions of *N*-Tosylhydrazones Derived from Acetophenones[a,b]



[a]Reaction conditions: **1a** (1 mmol), $Cu(OAc)_2·H_2O$ (15 mol %), Ar (1 atm) in xylene (3 mL) at 140 °C. [b]Isolated yields.

drazone substrates are different from other substrates in Prabhu's research,[11] for example, under Prabhu's reaction condition (CNBr-TBAB), *N*-tosylhydrazone derived from acetophenone did not work, and *N*-tosylhydrazone derived from 2-acetylnaphalene did not undergo the migration of tosyl group providing terminal vinyl sulfone like other substrates, but afforded *a*-substituted vinyl sulfone in moderate yield, instead. Pleasingly, these substrates were compatible with our reaction system. Under a little modified reaction conditions, *N*-tosylhydrazones derived from a variety of acetophenones all reacted smoothly to furnish the corresponding terminal vinyl sulfones with excellent *E* stereoselectivity in good to excellent yields. Carbon–halogen bonds such as C–F, C–Cl, and C–Br were well-tolerated in the reaction system, which provided the possibility for further functionalization of the terminal vinyl sulfones. Substrates that hydrazone moiety was either on 1-position or 2-position of naphthalene all underwent smoothly reaction giving the desired vinyl sulfones **2z′** and **2z** in 81% and 76% yields, respectively (Scheme 2, **2z**,**z′**). The structures of the products **2w** and **2y** were confirmed by single-crystal X-ray analysis.

Interestingly, two separable *N*-tosylhydrazone isomers (*E*)-**1t** and (*Z*)-**1t** could be obtained from 2-methylacetophenone. Nevertheless, under the above optimal reaction conditions they

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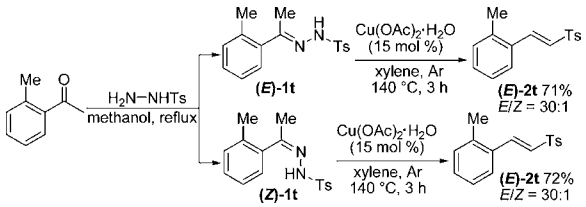
performed almost identically to afford vinyl sulfone (*E*)-**2t** in good yield with 30:1 (*E*/*Z*) stereoselectivity (Scheme 3).

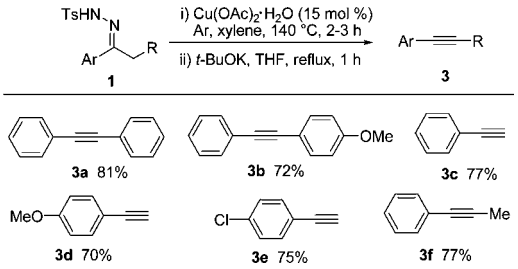
Scheme 3. Reaction of *N*-Tosylhydrazone Isomers (*E*)-1t and (*Z*)-1t



The hydration reaction of alkynes to ketones has been well studied in organic chemistry.[22] However, its reversal transformation, namely the conversion of ketones into alkynes, is still underdeveloped despite being very important in organic synthesis.[23] A typical approach for the conversion of ketones into alkynes is the enolization of the carbonyl group followed by enol elimination under harsh reaction conditions.[24] More recently, Jiang et al. reported an elegant copper-catalyzed oxidative transformation of *N*-tosylhydrazones to alkynes.[25] It is known that *N*-tosylhydrazones can be easily obtained from the corresponding ketones or aldehydes. For most *N*-tosylhydrazone substrates, Jiang's method provided the desired alkynes in good yields, but when *N*-tosylhydrazones derived from propiophenone or 1,2-diphenylethanone were used as the substrates, the method was of low efficiency, affording the corresponding alkynes only in 45−56% yields. Inspired by the research, and based on above synthesis of vinyl sulfones, we attempted to develop an efficient one-pot synthesis of alkynes from *N*-tosylhydrazones, especially those derived from α-phenyl ketones and shown low reactivity in Jiang's approach. After extensive screening studies, we were pleased to find a desirable protocol; that is, after the reaction of the synthesis of vinyl sulfones was complete, the solvent was evaporated to dryness under reduced pressure and then *t*-BuOK in THF was added to the reaction bottle and refluxed for 1 h (Scheme 4). The one-pot approach afforded the desired alkynes in good yields. Both terminal and internal alkynes were produced effectively.

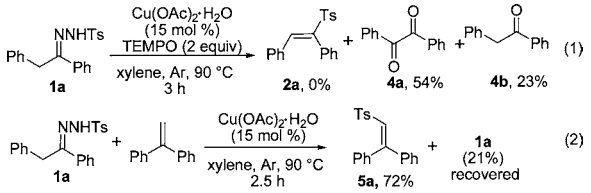
As for the mechanism of the copper(II)-catalyzed synthesis of vinyl sulfones from *N*-tosylhydrazones, we speculated the transformation might be a radical process. Therefore, several experiments related to radical were performed. When the radical-scavenging reagent TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) was introduced into the standard reaction system of *N*-tosylhydrazone (**1a**), no **2a** was detected, replaced by **4a** in 54% yield and **4b** in 23% yield (Scheme 5, eq 1). When DPE (1,1-diphenylethylene), another radical scavenger, was added into the standard reaction system, the radical coupling product **5a** was formed in 72% yield along with a small quantity of unreacted starting material recovered (21%), and no vinyl sulfone product was observed (^{1}H NMR analysis) (Scheme 5, eq 2). The results revealed that the sulfonyl free radical was involved as the reactive species under the current reaction conditions.

Scheme 4. One-Pot Synthesis of Alkynes from *N*-Tosylhydrazones[a,b]



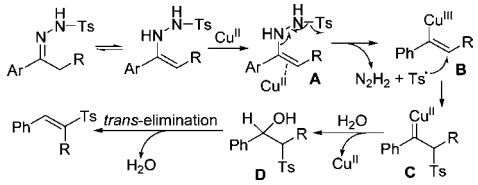
[a]Reaction conditions: (i) **1a** (1 mmol), $Cu(OAc)_2·H_2O$ (15 mol %), Ar (1 atm) in xylene (3 mL) at 140 °C. (ii) *t*-BuOK (3 equiv) in THF, reflux, 1 h. [b]Isolated yields.

Scheme 5. Radical Experiments



A plausible mechanism for the reaction is shown in Scheme 6. The *N*-tosylhydrazone isomerized. Copper coordinated with C−C double bond and promoted the decomposition of **A** releasing N_2H_2[26a] and tosyl free radical to provide vinyl copper complex **B**. Then, the tosyl free radical combined with **B** to give copper carbenoid **C**[26b] followed by the O−H insertion reaction with water to regenerate the copper catalyst[1b] and *trans*-elimination of H_2O to afford vinyl sulfone.

Scheme 6. Plausible Mechanism



In summary, the first copper-catalyzed radical reaction to synthesize various vinyl sulfones from readily available *N*-tosylhydrazones has been developed, which is new chemistry for hydrazines. The transformation features excellent *E* stereoselectivity, broad substrate scope, low cost of reagents, and convenient operation. A novel and efficient one-pot synthesis of alkynes from *N*-tosylhydrazone has been achieved. The studies furnish important complementary protocols for the synthesis of vinyl sulfones and alkynes. We anticipate this work will provide insight into copper and hydrazine chemistry and should have broad applications. Further investigations to extend the reaction scope and elucidate the reaction mechanism are in progress.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, analytical data, X-ray data (CIF), and copies of NMR spectra of the products. This material is available free from 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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