Copper-Catalyzed Alkenylation of Alcohols with β -Nitrostyrenes via a Radical Addition–Elimination Process

1961

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Abstract A new method for the preparation of allylic alcohol derivatives has been developed via a radical mechanism using DTBP as the radical initiator promoted by copper salt. The C(sp³)–H bond in various alcohols, toluene derivatives, and alkanes were successfully converted into C–C bonds to yield the desired products in moderate to good yields.

Key words (E)- β -nitrostyrenes, alkenylation, alcohols, free-radical, C(sp³)–H bonds

In the 1980s, Minisci reported the direct coupling of electron-deficient N-heteroaromatics with alcohols – promoted by a peroxide – to generate a new C–C bond while retaining the hydroxyl group.¹ Over the past decades, impressive progress has been made in developing this transformation including transition-metal-catalyzed cross-coupling of alcohols with N-heterocycles,² alkenes,³ alkynes,⁴ cinnamic acids,⁵ and H-phosphonates.⁶ In addition, a few metal-free catalytic systems have also been reported.⁷ However, this kind of transformation using simple alcohols as reactants still remains a challenge to chemists, and the α -C(sp³)–H bond functionalization of alcohols for the formation of allylic alcohol derivatives has not been thoroughly investigated although much progress has been achieved in the field of direct oxidative C(sp³)–H bond functionalization.^{8,9}

On the other hand, substituted (*E*)- β -nitrostyrenes are flexible intermediates in organic synthesis, which are used in many classes of reactions.¹⁰ Yao et al.^{11a-d} reported a series of reactions of (*E*)- β -nitrostyrenes with ethers and cycloalkanes in the presence of benzoyl peroxide (Scheme 1, a). Alcohols could be used as ideal alkylation reagents via α hydroxy carbon centered radical mechanism under oxidative conditions.¹⁻⁷ We envisioned that such a radical procedure might be applicable to (*E*)- β -nitrostyrenes, so we herein present a facile copper-catalyzed radical additionelimination alkenylation of alcohol α -C(sp³)–H bond for the first time (Scheme 1, b).

The initial investigation was focused on the optimization of reaction conditions. A direct alkenylation using (*E*)- β -nitrostyrene (**1a**) and isopropanol (**2a**) was chosen as a model reaction to optimize suitable conditions (Table 1). It was found that the radical initiator and catalyst were criti-



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cal to the reaction efficiency. Treatment of **1a** with di-tertbutyl peroxide (DTBP, 2.0 equiv) in 3 mL of isopropanol at 100 °C for six hours led to the desired product 3aa in 12% yield in the absence of metal catalyst (Table 1, entry 1). When we scanned the metal catalysts, it was found that copper salts exhibited good catalytic activity. The best catalyst was Cu(OAc)₂, and the desired product was isolated in 83% yield by using 2 mol% Cu(OAc)₂ (Table 1, entry 3). CuO, Cu₂O, and copper powder were catalytically less reactive in the model reaction (Table 1, entries 3-5). Addition of 0.5 mol% $Cu(OAc)_2$ and 5 mol% $Cu(OAc)_2$ led to the generation of the product in 66% and 82% yields, respectively (Table 1. entries 6 and 7). It should be noted that palladium and iron catalysts such as $Pd(OAc)_2$ and $Fe(acac)_3$ are not suitable to this transformation and gave poor yields (Table 1, entries 8 and 9). With respect to the amount of radical initiator used in the reaction, two equivalents of DTBP was found to be optimal. The model reaction was not completed with less than two equivalents of DTBP. However, no significant increase of yield of **3aa** was observed with more than two equivalents of DTBP (Table 1, entries 10 and 11). A 61% vield was obtained at 120 °C, and only a trace amount of 3aa was detected when the reaction temperature was 90 °C, even prolonging the reaction time to 24 hours (Table 1, entries 12 and 13). In the case of solvent effects, DCE and MeCN are also suitable for this transformation (Table 1, entries 14 and 15), in view of its nontoxicity and environment friendly. We used alcohol as solvent. It was found that other radical initiator, such as dicumyl peroxide (DCP), benzoyl peroxide (BPO), and azobisisobutyronitrile (AIBN), were inferior and generated 3aa in 71%, 54%, and 61% yields, respectively (Table 1, entries 16-18). In addition, when the TBHP and PhI(OAc)₂ were used as radical initiator but no desired **3aa** was isolated (Table 1, entries 19 and 20). It is noteworthy that the reaction shows excellent stereospecificity and the Zisomer was not observed according to the GC-MS and ¹H NMR spectra.

With the optimized conditions in hand, the substrate scope of (E)- β -nitrostyrenes **1** was investigated, and the corresponding results are listed in Table 2. The (E)- β -nitrostyrenes with an electron-rich group on the aromatic ring reacted smoothly in moderate to good yields (Table 2, entries 1–4), though the di-methyl substituted β -nitrostyrenes showed relatively lower efficiency (Table 2, entry 5). Electron-withdrawing substituent on the aromatic ring of β-nitrostyrenes showed higher efficiency with shorter reaction time using the same conditions, and good yields were observed (Table 2, entries 6–9). The bulky (E)-1-(2-nitrovinyl) naphthalene was also a good substrate for this coupling reaction with 78% yield obtained (Table 2, entry 10). It is noteworthy that the heteroaryl β -nitrostyrenes could also be used as the coupling partners with isopropanol to produce the desired allylic alcohols in moderate yields under the reaction conditions (Table 2, entries 11 and



	(E) + H 1a 2a	catalyst	(E) 3aa
Entry	Catalyst	Oxidant (equiv)	Yield (%) ^b
1	-	DTBP (2)	12
2	Cu(OAc) ₂	DTBP (2)	83
3	CuO	DTBP (2)	72
4	Cu ₂ O	DTBP (2)	76
5	Cu	DTBP (2)	79
6	Cu(OAc) ₂	DTBP (2)	66
7	Cu(OAc) ₂	DTBP (2)	82
8	Pd(OAc) ₂	DTBP (2)	38
9	Fe(acac) ₃	DTBP (2)	46
10	Cu(OAc) ₂	DTBP (1)	72
11	Cu(OAc) ₂	DTBP (4)	77
12	Cu(OAc) ₂	DTBP (2)	61 ^c
13	Cu(OAc) ₂	DTBP (2)	<5 ^d
14	Cu(OAc) ₂	DTBP (2)	81 ^e
15	Cu(OAc) ₂	DTBP (2)	80 ^f
16	Cu(OAc) ₂	DCP (2)	71
17	Cu(OAc) ₂	BPO (2)	54
18	Cu(OAc) ₂	AIBN (2)	61
19	Cu(OAc) ₂	ТВНР	n.r. ^g
20	Cu(OAc) ₂	PhI(OAc) ₂	n.r. ^g

^a Reaction conditions: β -nitrostyrene (0.5 mmol), i-PrOH (3.0 mL), catalyst (2.0 mol%), oxidant (2.0 equiv) at 100 °C under an argon atmosphere for 6

^b Isolated yield.

^c At 120 °C

^d At 90 °C.

^e Using 10 equiv *i*-PrOH in 3 mL DCE.

^f Using 10 equiv *i*-PrOH in 3 mL MeCN.

⁹ Not detected by GC-MS.

12). Furthermore, the (*E*)- β -nitrostyrenes bearing *ortho* or *meta* substituents on the aromatic ring also afforded the corresponding products in moderate to good yields (Table 2, entries 13–17), so the steric-bulk effect on the aromatic moiety plays little role in yield or efficiency. In contrast, the electronic and steric effect on the vinyl moiety did affect the reaction. β -Methyl- β -nitrostyrene only gave the desired products in poor 32% yield (Table 2, entry 18), and only trace product was detected by GC–MS when α -trifluoromethyl- β -nitrostyrene was used (Table 2, entry19). Unfortunately, no desired products were obtained when reacting isopropanol with alkyl-substituted β -nitroalkenes such as 1-nitrocyclohex-1-ene and (*E*)-1-nitrobut-1-ene (Table 2, entries 20 and 21).

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S.-r. Guo, Y.-q. Yuan

Letter





 a Reaction conditions: $1a{-}u$ (0.5 mmol), 2a (3 mL), heated at 100 °C for 2–6 h with 2 mol% Cu(OAc)_2. b Isolated yield.

1964

Syn lett

S.-r. Guo, Y.-q. Yuan

We then evaluated the scope of alcohols with (E)- β -nitrostyrenes, and the results are summarized in Table 3. Other secondary alcohols such as 2-butanol and cyclohexanol were also subjected to the optimized protocol to give the desired α -alkenylation products in moderate to excellent yields (Table 3, entries 1–6). Owing to the high boiling point and steric effect, the cyclohexanol gave only moderate isolated yields (Table 3, entries 5 and 6). Aliphatic primary alcohols such as methanol, ethanol, 1-propanol, 1-butanol, 1pentanol, and 3-methyl-1-butanol were all effective substrates in this system, and the desired products were also isolated in moderate to good vields. The electronic effect of the substituted group on the aromatic ring of B-nitrostyrenes was similar to isopropanol. Increasing aliphatic alcohol chain length had no effect on the isolated vield. Only methanol gave the desired product in moderate yield (Table 3, entries 7 and 8). The products can be also obtained in moderate vield when using ethanol with some low-reactivity β -nitrostyrenes (Table 3, entries 9–12). 1-Pentanol gave relatively lower yields of the products 3cj (Table 3, entry 16) and other primary alcohols gave the corresponding products in moderate to good yields (Table 3, entries 13-15, 17, 18). However, allyl alcohol, phenylmethanol, and tert-butanol did not give the desired product.

Under the typical reaction conditions, a number of other compounds containing C(sp³)-H bonds were also investigated (Table 4). It was found that toluene and its derivatives such as ethylbenzene, p-xylene, m-xylene, o-xylene, and mesitylene all worked well and were effectively converted into the corresponding (E)- β -alkylstyrenes in good to excellent yields (Table 4, entries 1-6). The reaction of xylenes and mesitylene with (E)- β -nitrostyrenes only yielded its monocoupling products without affecting the other methyl groups. Furthermore, this radical addition-nitro-elimination reaction could be applied to inert cycloalkanes such as cvclooctane, norbornane, and adamantine and gave the corresponding products in good yield (Table 4, entries 7-9). In the case of norbornane and adamantine, it is not the methylene group but the methine group that was selectively alkenylated by β -nitrostyrenes.

Table 3 $Cu(OAc)_2$ -Catalyzed Alkenylation of Alcohols with Various (E)- β -Nitrostyrenes^{a-c}



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S.-r. Guo, Y.-g. Yuan

 $^{\rm a}$ Reaction conditions: 1 (0.5 mmol), 2 (3 mL) heated at 100 °C for 2–8 h with 2 mol% Cu(OAc)_2.

^b Reaction conditions: **1** (0.5 mmol), **2** (for cyclohexanol, 1-pentanol, and 3-methyl-1-butanol, 10 equiv), DCE (3 mL) heated at 100 °C for 6–12 h with 2 mol% Cu(OAc)₂.

^c Isolated yield. `

Interestingly, the products of tertiary alcohol could be further functionalized. It was found the 1,3-diene derivatives, which are important materials in organic synthesis, could be obtained easily.¹² For example, under acidic condi-



^a Reaction conditions: **1a** (0.5 mmol), toluene derivatives and alkanes (5 equiv), DCE (3 mL) heated at 100 °C for 2–6 h with 2 mol% Cu(OAc)₂. ^b Isolated yield.

tions the product of **3ac** could finish an elimination reaction giving the desired 1,3-diene compound of **4a** in excellent yield at room temperature (Scheme 2).



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Interestingly, comparing with primary alcohols, the yields of isomeric second alcohols were higher (Table 2 and Table 3, e.g., **3ah** vs. **3cg** and **3bb** vs. **3ci**). Despite the higher yields seen with secondary alcohols, while in competitive reactions, the reactivity of the C(sp³)–H bonds of primary alcohols was found to be higher than that for secondary al-

cohols. The higher reactivity may be due to steric or electronic factors of the corresponding carbon-centered radical (Scheme 3, a and b).

To investigate the mechanism of this copper(II)-catalyzed alkenylation, some control experiments were carried out. It is believed to proceed via a similar radical addition– elimination process to that proposed by Liu,⁵ Yao,¹¹ and



Syn lett

S.-r. Guo, Y.-q. Yuan

Letter

Fuchs.¹³ When the radical scavenger TEMPO was added into the reaction system, no product was obtained, which indicates that the transformation may proceed via a radical process (Scheme 4, a). In the absence of alcohol, only denitro methylation product was obtained and the self-coupling of β -nitrostyrenes was not observed, which suggested that the styrene radical is not formed in the reaction system (Scheme 4, b). Moreover, an intermolecular kinetic isotope effect (KIE) experiment was carried out for isopropanol, and a significant KIE value of $k_H/k_D = 4.8$ was observed (Scheme 4, c). It indicates that the rate-determining step of the sp³ C–H bond cleavage should be involved in this procedure. Interestingly, (*Z*)-**1a** was used to react with **2a** under the optimized conditions, the same product (*E*)-**3aa** was also obtained in 80% yield (Scheme 4, d).

Based on the above results and similar reported literature,^{7–9,11} a plausible radical addition–elimination mechanism is illustrated in Scheme 5. First, homolytic cleavage of DTBP gives the *tert*-butoxy radical catalyzed by Cu(OAc)₂, which abstracts the α -hydrogen of isopropanol to form an α -carbon-centered radical. Then, addition of the α -carboncentered radical to the β -position of the double bond would give a benzylic intermediate. Finally, under the help of hypervalent copper complex which may be formed in the reaction process, the more stable *E*-allylic alcohols were achieved via a rapid elimination of the 'NO₂ radical. Unfortunately, the exact role of copper salts and how it catalyzes this transformation is still unclear, but it should be noted that the reaction did not work well in the absence of the copper catalyst.



In summary, this work demonstrates a novel copper(II)promoted approach for the stereospecific synthesis of allylic alcohols through the denitro coupling reaction of β -nitrostyrenes with alcohols. Various substituted β -nitrostyrenes were shown to proceed readily via the radical addition and nitro-elimination mechanism. In addition, compared with the traditional method to synthesize the (*E*)- β -alkylstyrenes and its derivatives, the direct C–C bond construction via activation of the C(sp³)–H bond in this work might be novel and attractive in radical chemistry. The alkyl-substituted β -nitroalkenes are not suitable to this protocol, and the β -alkyl-substituted β -nitrostyrenes gave the desired products in low yield, which limits the scope of application. Further investigation of this procedure, including extension of the substrate scope and catalytic cycle, is under way in our laboratory.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380445.

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S.-r. Guo, Y.-q. Yuan

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(14) Typical Procedure

To a Schlenk tube equipped with a magnetic stir bar were added, under argon, β -nitrostyrene (0.5 mmol) and Cu(OAc)₂ (0.01 mmol). Under argon, isopropanol (3.0 mL) and di-*tert*-butyl peroxide (DTBP, 1 mmol) were added. The resulting reaction mixture was kept stirring at the required temperature for 2–6 h. After the required reaction time, the mixture was cooled down to r.t. Evaporation of the solvent followed by purification by flash chromatography (PE–EtOAc = 5:1) afforded the corresponding product **3aa** in 83% yield.

(E)-2-Methyl-4-phenylbut-3-en-2-ol (3aa)

Colorless oil. ¹H NMR (300 MHz, CDCl₃): δ = 7.39 (dd, *J* = 8.2, 1.3 Hz, 2 H), 7.35–7.28 (m, 2 H), 7.25 (dd, *J* = 5.9, 4.2 Hz, 1 H), 6.60 (d, *J* = 16.1 Hz, 1 H), 6.36 (d, *J* = 16.1 Hz, 1 H), 1.64 (s, 1 H), 1.43 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃): δ = 137.59, 131.75, 128.60, 127.47, 126.46, 117.31, 71.10, 29.95. HRMS (TOF, EI⁺): *m/z* calcd for C₁₁H₁₄O: 162.1045; found: 162.1044.