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Direct Syntheses of Styryl Ethers from Benzyl Alcohols via Ag Nanoparticle-Catalyzed Tandem Aerobic Oxidation

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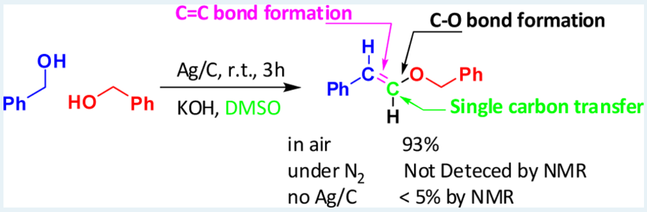
Supporting Information

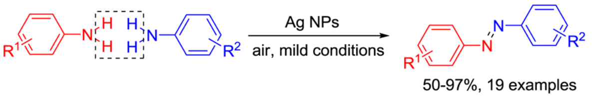
ABSTRACT: Ag nanoparticle-catalyzed aerobic oxidation of benzyl alcohols in basic DMSO gave efficient formation of styryl ethers, featuring single carbon transfer and C═C and C−O bond formation. A deuterium labeling experiment established that DMSO was the carbon source. Further experiments showed the reaction proceeded through a styryl sulfoxide intermediate originating from basic DMSO and transient benzaldehyde. Control reactions in the absence of the Ag NPs or air indicated that oxidation of the styryl sulfoxide was required for the final C−O bond formation. This work demonstrated that metal nanoparticles could be applied to tandem heterogeneous catalysis in organic chemistry.



KEYWORDS: *styryl ether, Ag nanoparticle, aerobic oxidation, tandem catalysis*

Selective oxidation of benzyl alcohol to benzaldehyde is an important process.[1,2] In the past decade, methods utilizing molecule oxygen as the sole oxidant have attracted much attention.[3,4] Remarkable progress has been made with supported nanoparticle catalysts, including PI-CB/Au−Pt,[5] Au/Al_2O_3,[6] Au/CeO_2[7] and so on. It is still desirable to develop catalysts with lower cost and higher efficiency.

For their special roles in heterogeneous catalysis, metal nanoparticles have been shown to catalyze many other oxidation reactions in which the selectivity and efficiency could be greatly enhanced. In this context, we recently discovered that various metal nanoparticles (NPs), such as Ag, Au, Pd, and Pt NPs were highly active in dioxygen activation under ambient conditions. Oxidative coupling of various anilines with 0.6 mol % Ag nanoparticles (∼12 nm) in basic DMSO gave efficient and selective formation of azobenzenes[8] (eq 1). This spurred us to explore the selective oxidation of alcohols in the Ag NPs/DMSO system.



eq. 1

Herein, we report that carbon-supported Ag nanoparticles (Ag/C) catalyzed efficient direct formation of styryl ethers from benzyl alcohols. Moreover, our mechanistic study demonstrated that the ability of the Ag NPs in oxygen activation orchestrated a tandem aerobic oxidation that accounts well for the reaction outcome.

Ag NPs were synthesized using a protocol described elsewhere.[9−11] Figure 1 shows that the as-obtained Ag NPs are monodispersed spheres with a very narrow size distribution (4 nm) (Figure 1a and b). After the Ag NPs were supported on activated carbon, their morphology and size did not undergo apparent change (Figure 1c).

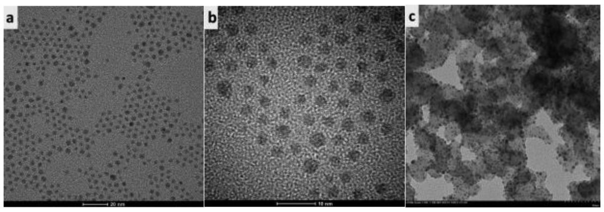


Figure 1. TE images (a) TEM and (b) HRTEM of Ag NPs; (c) TEM of the Ag/C.

To our surprise, when benzyl alcohol **1a** was treated with 1 mol % Ag/C under air in basic DMSO, no benzaldehyde (C_7H_6O) was observed. Instead, an unexpected product was isolated in 93% yield (Figure 2a). High-resolution mass spectroscopy indicated that the exact mass of the $[M + H]^+$ was 211.1116, which fits with the formula $C_{15}H_{14}O$. This data suggested that an extra single carbon had been incorporated into the product. The ^1H NMR shows olefinic protons (Figure 2b), indicative of a C═C bond that was further confirmed by ^{13}C NMR. Accordingly, the product was identified as the styryl ether (*E*)-**2aa** (Figure 2a). Notably, styryl ethers are important building blocks in organic syntheses and polymer chem-

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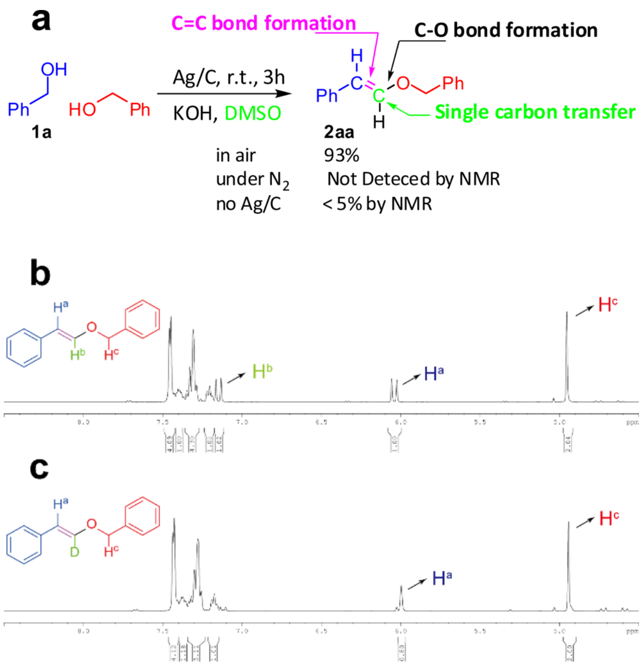


Figure 2. Styryl ether formation: (a) reaction equation, (b) ^{1}H NMR of **2aa**, and (c) deuterated **2aa**.

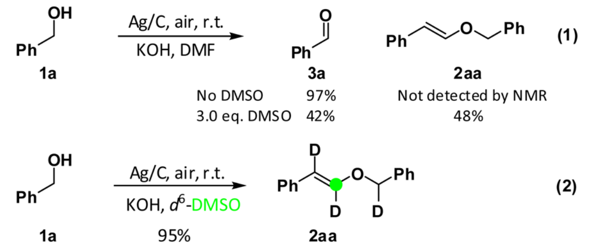
istry.[12,13] Current syntheses of styryl ether rely on prefunctionalized starting materials such as vinyl halides,[14] allyl ethers,[15] *α,β*-unsaturated carbonyls,[16] and sulfones.[17] Reported direct synthesis of styryl ethers from alcohols requires harsh reaction conditions (180−200 °C, 20−50 atm acetylene).[18] The mild conditions and high efficiency of our method were, indeed, remarkable and intriguing.

To establish that the reaction is a Ag/C-catalyzed aerobic oxidation, we carried out several control experiments (Supporting Information). No reaction occurred under nitrogen atmosphere. Very low conversion (<5%) was observed when Ag NPs was absent. In line with this Ag catalysis, the reaction rate was inversely correlated to the size of the Ag NPs: Ag NPs of smaller size have higher ability in dioxygen activation.[8] Further experiments suggested that the reaction was catalyzed by Ag NPs but not leached Ag ions. The Ag/C catalyst could be recycled for five runs without activity decay. This evidence suggested a tandem catalysis featuring our Ag NPs as the heterogeneous catalyst and oxygen as the oxidant. Heterogeneous tandem catalysis is surprisingly rare in the literature,[19] with the few examples limited to “heterogenized” homogeneous metal complexes.[20−23]

The reaction raised three interesting questions: What was the source of the extra carbon in the product (Figure 2a, green)? How did the C═C bond formation occur? What was the mechanism of the C−O bond formation?

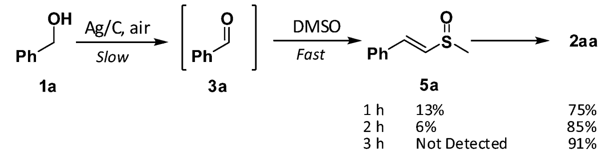
We first set out to identify the source of the single carbon (Scheme 1). From the observation that a similar reaction in DMF under otherwise identical conditions gave only benzaldehyde **3a** (Scheme 1, eq 1), we suspected that DMSO was the carbon source. Indeed, adding 3.0 equiv of DMSO to the reaction in DMF furnished product **2aa** in 48% isolated yield (Scheme 1, eq 1). When the reaction was performed in DMSO-*d*$_6$ (Scheme 1, eq 2), ^{1}H NMR of the final product showed nearly 100% deuterium incorporation at the extra carbon (Figure 2c). These experiments proved DMSO’s role as the single carbon source. Although methylene transfer reactions involving sulfur-,[24] sulfoxide-,[25] and sulfonium ylide[26] have been extensively reported, DMSO is rarely documented as a single carbon source.

Scheme 1. The Carbon Source is DMSO



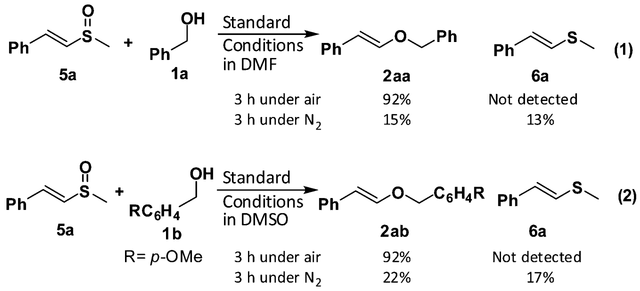
Next, we investigated the process associated with the C═C bond formation (Scheme 2). Close study of the reaction by GC unveiled an intermediate whose concentration decreased gradually after 1 h. This intermediate was subsequently isolated and identified as styryl sulfoxide **5a**. Discrete sulfoxide **5a** could be cleanly converted to product **2aa** under reaction conditions, suggesting it is a likely precursor for the final product. Although benzaldehyde was not detected in the reaction mixture, it could react with basic DMSO under nitrogen to yield sulfoxide **5a** (Supporting Information), suggesting that the benzyl alcohol **1a** was probably oxidized into transient benzaldehyde **3a** prior to sulfoxide **5a** formation.

Scheme 2. Styryl Sulfoxide Is the Intermediate



We then studied the C−O bond formation en route from styryl sulfoxide **5a** to the product **2aa** (Scheme 3). Specifically, we wonder if Ag/C catalyst or oxygen was involved in this step. To avoid background reaction of benzyl alcohol in DMSO, we carried out reactions of **5a** with benzyl alcohol in DMF under air or nitrogen atmosphere (Scheme 3, eq 1) as a complement to the more closely mimicked condition in which *p*-methoxybenzyl alcohol **1b** reacted with sulfoxide **5a** in DMSO (Scheme 3, eq 2). In both solvents, oxygen was required for the full conversion of the sulfoxide **5a**. Additional experiments showed that Ag NPs were also required for this step (Supporting Information). These observations suggested that the oxidation of styryl sulfoxide is crucial to the C−O bond formation, possibly via styryl sulfone, since discrete styryl **7a** sulfone was rapidly converted into the styryl ether **2aa** under

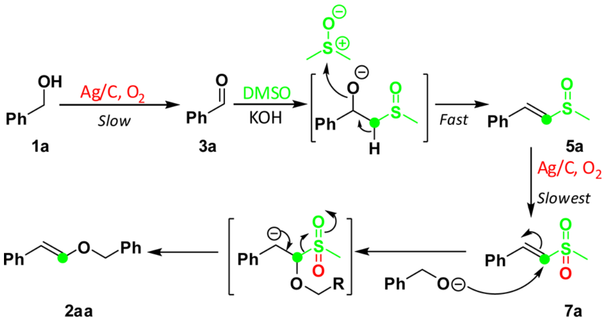
Scheme 3. The C−O Bond Formation Requires Oxygen



the reaction conditions (Supporting Information). This hypothesis was further substantiated by the fact that under nitrogen, the sulfoxide **5a** underwent slow disproportionation to give the styryl ether **2aa** together with approximately equal molar sulfide **6a**.

Given the above results, we postulated the reaction mechanism to be as depicted in Scheme 4. First, Ag/C-catalyzed aerobic oxidation of the benzyl alcohol **1a** led to the benzaldehyde **3a**, followed by rapid condensation with DMSO to give the styryl sulfoxide **5a**. A second Ag/C-catalyzed aerobic oxidation gave rise to the styryl sulfone **7a**, which is the rate-limiting step. Finally, addition of an alkoxide anion to the α-position of sulfone **7a** formed the benzylic anion that underwent elimination to furnish the final product **2aa**.

Scheme 4. Proposed Mechanism



Because the Ag/C-catalyzed aerobic oxidations of both the benzyl alcohol and the styryl sulfoxide are crucial for the outcome of the reaction, we performed a series EPR experiments to further elucidate these oxidation steps (Figure 3). No superoxide anion radical ($O_2^{-\bullet}$) was observed in the blank solvent (Figure 3a), but KOH was found to promote the oxygen activation to a small extent (Figure 3b). In the presence of Ag/C, a persistent signal of the superoxide anion radical was recorded (Figure 3c). Importantly, the oxygen activation by the Ag/C was not enhanced by the KOH (Figure 3c, d). When benzyl alcohol was added into the DMSO/KOH system, only benzyl cation radical was observed (Figure 3e). This result suggests that the superoxide anion radical was rapidly consumed in the reaction. Introduction of Ag/C into the reaction caused an obvious shift of the benzyl cation radical signal (Figure 3f), indicating that this radical might be associated with the Ag/C catalyst. This evidence collectively confirmed that the Ag/C catalyst plays an important role in the activation of molecule oxygen as well as in the oxidation of the benzyl alcohol.

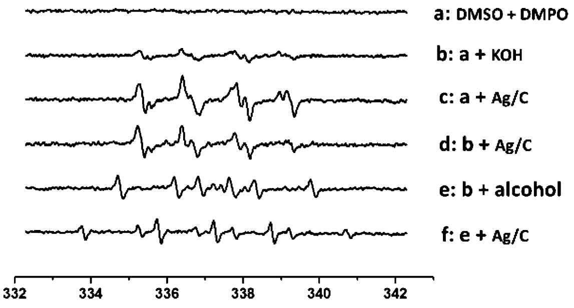
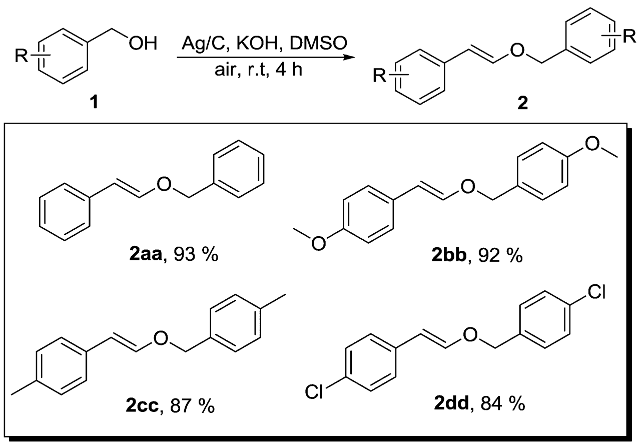


Figure 3. EPR spectra using DMPO (0.02 mmol) as the spin trap. Conditions: alcohol (0.15 mmol), Ag/C (0.0015 mmol) in DMSO (0.5 mL) at room temperature.

With the above results in hand, we set out to examine the synthetic utility of the Ag/C catalyst. Table 1 shows that several substituted benzyl alcohols are compatible with the reaction conditions, giving the corresponding homocoupling products in excellent yields.

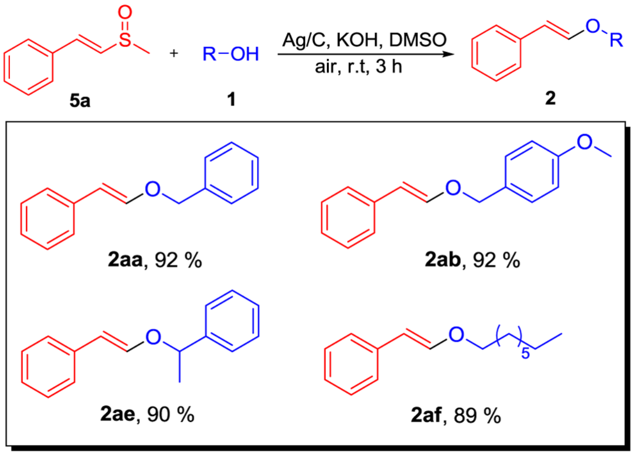
Table 1. Reactions of Substituted Benzyl Alcohols[a]



[a]Reaction conditions: **1** (0.5 mmol), KOH (1 equiv), Ag/C (1 mol %), DMSO (2 mL), air (1 atm), rt, 4 h. Isolated yields.

As we showed that the sulfoxide was a viable precursor, synthesis of asymmetric styryl ethers is possible with our Ag/C catalyst. As illustrated in Table 2, reactions between various alcohols, including secondary alcohol **1e** and aliphatic alcohol **1f**, and styryl sulfoxide **5a** furnished the desired products in high efficiency. It is expected that this method could find further application in the preparation of styryl ether with different substitutions.

Table 2. Reaction of Sulfoxide 5a with Alcohols[a]



[a]Reaction conditions: 5a (0.25 mmol), 1 (0.25 mmol), KOH (1 equiv.), Ag/C (1 mol %), DMSO (1 mL), air (1 atm), r.t, 3 h. Isolated yields.

In conclusion, we discovered that Ag NPs are an efficient catalyst for direct synthesis of styryl ethers from benzyl alcohols under ambient conditions. Our mechanistic study revealed reaction processes accounting well for the single carbon transfer as well as C═C and C−O bond formations. Most importantly, both control experiments and EPR study proved that the Ag NPs' ability in dioxygen activation was crucial for the success of this tandem aerobic oxidation reaction. We further showed that the Ag NP catalyst is applicable to the syntheses of structurally diverse styryl ethers. This work demonstrates that applying nanoparticle catalysts to organic reactions could lead to rapid formation of molecular complexity rivaling that of the homogeneous catalysis, which is a highly desired goal in heterogeneous catalysis.

■ ASSOCIATED CONTENT

Supporting Information

Preparation of Ag nanoparticles, procedure for catalytic reactions, and characterization of 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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