Cobalt-Catalyzed Allylation of Amides with Styrenes Using DMSO as Both the Solvent and the α -Methylene Source

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Supporting Information

ABSTRACT: An efficient synthesis of privileged allylic amines has been developed via cobalt-catalyzed allylation of amides with styrenes, in which DMSO was used as both the solvent and the α -methylene source. This transformation features high yields, and selectivity for the (E)-isomer of the linear product. Through the experimental and computational investigations, a sequential K₂S₂O₈-mediated oxidative coupling/cobalt-assisted regioselective alkene insertion/ β -H elimination/alkene dissociation/hydride transfer process has also been deduced.



ecognizing the great importance of allylic amines in Rorganic synthesis, medicinal chemistry, and materials science,¹ chemists have spent tremendous effort to develop general and efficient methods toward their synthesis. As a consequence, many versatile coupling reactions²⁻⁸ of relatively active imines with π -compounds to construct the allylic amines, including the classical Morita-Baylis-Hillman reaction, Lewis-acid-catalyzed Friedel-Crafts alkylation reaction, as well as recently documented metal-catalyzed C-H activation/addition reaction, have been independently developed by the groups of Krische,³ Zhou,⁴ Jamison,⁵ Maruoka,⁶ Shi,⁷ and others.⁸ However, by reviewing these notable achievements, one common feature was found that almost all reactions are involved in employing an aryl part to stabilize the imine species, thus giving rise exclusively to α -aryl-substituted allylic amines (Scheme 1a). Undoubtedly, it limited the nextstage synthetic application to some extent. To address this disadvantage, more recently Rovis and Glorius have independently developed an Ir-catalyzed intermolecular and branch-selective amidation of allylic C-H bonds.⁹ However, a highly active and synthetic dioxazolone species¹⁰ was still involved as the amidating reagent. In addition, to the best of our knowledge, there have been few reports that have shown direct synthesis of more common allylic amines, especially for those for which no substituent was installed at the α -position.¹ In this context, exploring a new strategy for the efficient construction of common allylic amines from the readily accessible starting materials is still not only highly desirable but also of great significance.

On the other hand, recently, considerable attention has been paid to the development of transition metal (TM) catalyzed C-H functionalization by using DMSO as the versatile reactant in organic synthesis, due to its low toxicity and easy availability.¹² Indeed, significant progress has been made on

Scheme 1. One-Pot Synthesis of Allylic Amines by C-C Couplings with π -Compounds



this topic, and a large number of examples have used DMSO as the precursor for the introduction of a wide range of functional groups, such as $-O_{13}^{13}$ $-CN_{14}^{14}$ $-SMe_{15}^{15}$ $-CH_2SMe_{16}^{16}$ $-SO_2Me_{17}^{17}$ $-Me_{18}^{18}$ and $-CHO^{19}$ substituents.

Concerning the development of inexpensive and earthabundant cobalt-catalyzed C-H activation transformations, we have reported the Co(III)-catalyzed and DMSO-involved C-H activation/cyclization of anilines with alkynes for the synthesis of quinolines,²⁰ where DMSO was employed as the C_1 source of the quinoline core. Continuing with our interest in cobalt-catalyzed C-H functionalization and on the basis of the elegant studies performed by the Maruoka group,⁶ we envisaged the cobalt-catalyzed reaction of ubiquitous amides

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with alkenes in DMSO as an appealing synthetic route to the synthesis of α -unsubstituted allylic amines (Scheme 1b). This transformation was likely to involve a methylenebisamide intermediate,²¹ which would evolve into the final products through a cobalt-catalyzed regioselective alkene insertion without the assistance of the directing group—a certainly underexplored process in cobalt-catalyzed synthetic chemistry.^{22,23}

The feasibility of the proposed reaction was tested with simple benzamide (1a) and styrene (2a) as model substrates, $AgSbF_6$ and $K_2S_2O_8$ as benchmark additives, and $Co(acac)_2$ as the catalyst (Table 1). Delightfully, treatment of 1a with two

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Table I.	Screening	of	Reaction	Conditions

Ph	$\frac{0}{MH_2} + \frac{1}{Ph}$	Co(acac) ₂ (5 mol additive A (10 mol additive B (1.5 equ DMSO, 130 °C, air,	%) %) viv) 12 h H 3a	Ph
entry	catalyst	additive A	additive B	yield (%) ^b
1	$Co(acac)_2$	AgSbF ₆	$K_2S_2O_8$	36
2	$Co(acac)_2$	AgNTf ₂	$K_2S_2O_8$	41
3	$Co(acac)_2$	AgOTf	$K_2S_2O_8$	34
4	$Co(acac)_2$	Ag_2CO_3	$K_2S_2O_8$	0
5	$Co(acac)_2$	Ag ₂ SO ₄	$K_2S_2O_8$	0
6	$Co(acac)_2$	AgNO ₃	$K_2S_2O_8$	0
7	$Co(acac)_2$	AgOAc	$K_2S_2O_8$	94
8	$Co(acac)_2$	AgOAc	$(NH_4)_2S_2O_8$	0
9	$Co(acac)_2$	AgOAc	$Na_2S_2O_8$	40
10	$Co(acac)_2$	AgOAc	H_2O_2	0
11	$Co(acac)_2$	AgOAc	TBHP	0
12	$Co(acac)_2$	AgOAc	DTBP	0
13	$Co(acac)_2$	AgOAc		0
14	$Co(acac)_2$		$K_2S_2O_8$	34
15		AgOAc	$K_2S_2O_8$	0
16			$K_2S_2O_8$	0
17	$Co(OAc)_2$	AgOAc	$K_2S_2O_8$	38
18	$Cp*Co(CO)I_2$	AgOAc	$K_2S_2O_8$	0
19	CoI ₂	AgOAc	$K_{2}S_{2}O_{8}$	0

^{*a*}Reaction conditions: benzamide **1a** (1.0 mmol), styrene **2a** (0.5 mmol), Co(acac)₂ (5 mol %), additive A (10 mol %), and additive B (1.5 equiv) in DMSO (2 mL) at 130 °C for 12 h under air. ^{*b*}Isolated yields.

equivalent amounts of 2a and an excess of $K_2S_2O_8$ (1.5 equiv), AgSbF₆ (10 mol %, 0.1 equiv), and Co(acac)₂ (5 mol %, 0.05 equiv) under air led to the anticipated 3a in 36% isolated yield, thus supporting our initial hypothesis. Based on this encouraging result, we next tested different additives (entries 2–12). The brief screening indicated that AgOAc and $K_2S_2O_8$ were optimal additives, increasing the yield of 3a up to 94% (entry 7). Control experiments revealed that the absence of either the catalyst or additives led to a significant decrease in the yield of the product, suggesting that both the cobalt(II) species and AgOAc/ $K_2S_2O_8$ coadditives were essential for this transformation (entries 13–16). Finally, switching Co(acac)₂ to other cobalt species also obviously reduced the yield or completely inhibited the reaction process (entries 17–19).

Having the optimized conditions in hand, we sought to probe the scope of the substrate and generality of this transformation (Scheme 2). With regard to the amide scope, we found that the reaction of styrene 2a with a wide range of amides bearing different substituents proceeded smoothly,





^{*a*}Reaction conditions: amide 1 (1.0 mmol), styrene 2a (0.5 mmol), Co(acac)₂ (5 mol %), AgOAc (10 mol %), and $K_2S_2O_8$ (1.5 equiv) in DMSO (2 mL) at 130 °C for 12 h under air; isolated yields were given. ^{*b*}Performed on a 5.0 mmol scale. ^{*c*}N-Hydroxybenzamide was used instead of benzamide 1a. ^{*d*}N-Acetoxybenzamide was used instead of benzamide 1a. ^{*e*}N-Methylbenzamide was used instead of benzamide 1a.

delivering the corresponding allylic amines in good to excellent yields regardless of the nature of the substituents on the amide moiety. A series of electron-donating (Me, OCH₃, Et, n-Bu, t-Bu) or electron-withdrawing (F, Cl, Br, CF_3 , CO_2Me) groups at the para-position of benzamide were all well tolerated with the optimized reaction conditions, giving the desired products 3b-3k in 81-98% yields. Similarly, ortho- and metasubstituted benzamides also participated in this reaction, affording the corresponding products 3l-3o with reasonable yields (up to 92%). It was worth noting that the sole *E*-isomer was detected in all cases. The reaction was also tolerant of moderate steric bulk, as disubstituted benzamides could be converted into the corresponding allylic amines 3p-3s in decent yields (up to 90%). Interestingly, amides bearing either heteroaromatic, polyaromatic, cycloalkyl, aliphatic, or alkyloxy parts could be accommodated with such transformations, generating the desired products 3t-3ac in 70-95% yields. Finally, we were pleased to find that the reaction also worked well with large-sized amides, N-substituted amides, and cyclic sulfonamides as exemplified by the synthesis of 3a and 3ad**3ah.** Taken together, these results further displayed the versatility of the developed cobalt(II) catalysis.

We subsequently turned our attention to the scope of alkenes. As shown in Scheme 3, we found that this reaction was

Scheme 3. Scope of Styrenes^a



"Reaction conditions: amide 1a (1.0 mmol), styrene 2 (0.5 mmol), $Co(acac)_2$ (5 mol %), AgOAc (10 mol %), and $K_2S_2O_8$ (1.5 equiv) in DMSO (2 mL) at 130 °C for 12 h under air; isolated yields were given.

compatible with a broad scope of styrenes. Various substituents with diverse electronic properties were tolerated (F, Cl, Br, CH₃, OCH₃, *i*-Pr, *t*-Bu, and Ph), and the corresponding allylic amines (4a-4l) were delivered smoothly in good yields. Furthermore, di- and trisubstituted styrenes were also competent in the reaction as products 4m-4p were obtained in good to high yields (84-95%). Moreover, vinyl naphthalene (1q) was found to couple with 1a productively, providing the desired 4q in 95% isolated yield. Impressively, 2substituted styrenes with various groups, such as the methyl, cyclohexyl, and phenyl substituents, which often display relatively low reactivity in coupling reaction, can also react with 1a, delivering the allylic amines 4r-4w in decent yields (78-91%). To better probe the scope of this reaction, we further explored other alkenes such as hept-1-ene and 1allylnaphthalene. However, no expected coupling products were detected, revealing that the presence of a conjugated aryl part was crucial for this reaction.

Considering the remarkably good substrate tolerance and specific regioselectivity displayed by the cobalt(II) catalysis, we were then intrigued to uncover the reaction mechanism. As shown in Scheme 4a, we first changed DMSO to DMSO- d_6 to verify the role of DMSO. The result showed that the deuterated product $[d_2]$ -**3a** was obtained in 89% yield with almost 100% incorporation of deuterium, suggesting that DMSO played crucial roles acting as both the solvent and the α -methylene carbon source for this transformation. Furthermore, the reaction of **1a** and **2a** was carried out under standard conditions for 4 h (Scheme 4b), and both allylic amine **3a** and methylenebisamide species **5** were detected with 17% and 81%

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Scheme 4. Mechanistic Studies



yield, respectively (Scheme 4b). Prolonging the reaction time to 12 h resulted in an enhancement of the yield of 3a from 17% to 92%, along with the complete disappearance of 5. Subsequently, treatment of 5 with 2a under the standard conditions gave the product **3a** in 95% yield (Scheme 4c). The results clearly indicated that 5 might be employed as one of the active intermediates involved in the catalytic cycle. Moreover, treatment of 1a with 2a in both DMSO and DMSO- d_6 under standard conditions gave a small KIE value ($k_{\rm H}/k_{\rm D}$ = 1.2, Scheme 4d). The result suggested that the K2S2O8-mediated oxidation process in DMSO might not be involved in the ratelimiting step. Further KIE was evaluated to shed more light on the alkene-involved process. As demonstrated in Scheme 4e, we performed a deuterium competition experiment between substrate 2a and $[d_8]$ -2a and observed a kinetic isotope effect (KIE) of $k_{\rm H}/k_{\rm D} = 2.6$.

Based on the above experimental results and to gain a better mechanistic understanding, density functional theory (DFT) calculations were further implemented with Gaussian 09 by selecting the complex IMO as the starting point (Figure 1). The geometries of all reported species were optimized using the B3LYP functional, and single-point energies were calculated at the M06 level using the SMD solvation model (see SI for details). First, the regioselective [2,1]-insertion of the alkene via TS1 requires a barrier of 29.6 kcal/mol, leading to the intermediate IM2 with a free energy of -3.0 kcal/mol. Obviously, to proceed in a contrary alkene [1,2]-insertion pathway, a higher energy profile via TS1' with a barrier of 34.7 kcal/mol is detected, revealing that the [1,2]-insertion is clearly disfavored. The results are also in line with our experimental observation that the chain allylic amine backbone presents as the preferential product. Thereafter, the species **IM2** undergoes a β -H elimination and subsequent hydride transfer via TS2 with a barrier of 20.4 kcal/mol, providing the E-type intermediate IM4. On the other hand, the Z-type intermediate IM4' can be formed via TS2' with an energy barrier of 23.4 kcal/mol, which is not favored compared to that



Figure 1. Computed Gibbs free energy changes of the reaction pathways using the IMO as the starting point.

of IM4. Finally, with the aid of the PhC(O)NH anion²⁴ from the reaction solution, the Co–alkene dissociation/hydride transfer occurred via TS3 ($\Delta\Delta G^{\ddagger} = 20.0 \text{ kcal/mol}$, from IM5 to TS3) to deliver the desired product with the regeneration of the complex IM0. It was worth noting that the present DFT calculations preliminarily disclosed the cobalt-mediated processes, while the detailed mechanism regarding the roles of other metal cations (e.g., Ag⁺) and the rate-determining step of this transformation still need to be addressed.

On the basis of these experimental and computational observations, and inspired by the mechanistic studies in the precedent literature, we proposed a plausible catalytic cycle for this transformation (Scheme 5). Initially, DMSO was activated

Scheme 5. Proposed Catalytic Cycle



by $K_2S_2O_8$ to generate the reactive electrophilic thionium ion A, which is then attacked by 1a to yield the intermediate B. A classical nucleophilic substitution of B with 1a occurred to provide the methylenebisamides 5. Subsequently, intermediate C is easily formed from B or 5. The following cobalt(II)mediated reaction of C delivers the five-membered cobalt(III) species D. Regioselective migratory insertion of 2a to the Co– C bond of D (IMO) via IM1 gives the intermediate E, which undergoes the β -H elimination to produce the intermediate F(IM4), followed by the alkene dissociation to yield the desired product 3a along with the release of HCoX₂ species, which reacts with PhC(O)NH⁻ or MeS⁻ via hydride transfer to regenerate the active Co(II) catalyst for the next catalytic cycle. In summary, by taking advantage of DMSO as both the solvent and the α -methylene source, we have developed a new and practical protocol for direct allylation of simple amides with styrenes catalyzed by the earth-abundant and inexpensive Co(acac)₂. This protocol features broad substrate scope and good to excellent yields, thus rendering it as a highly versatile, straightforward, and atom-economical alternative to the existing methods for the synthesis of privileged allylic amines, in which no additional substituent was attached at the α -position. Through the detailed experimental and computational investigations, a possible reaction pathway was rationally deduced. Further studies on the mechanism and application of this catalytic reaction are currently underway in our laboratories.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b02462.

Experimental procedures, characterization of products, and copies of ¹H and ¹³C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(24) The MeS anion was also proposed to abstract the proton from HCoX₂ for catalyst regeneration via TS3' ($\Delta\Delta G^{\ddagger}$ = 19.9 kcal/mol, from IM5' to TS3'). Please see the Supporting Information for details.