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α-Amino Acid Sulfonamides as Versatile Sulfonylation Reagents: Silver-Catalyzed Synthesis of Coumarins and Oxindoles by Radical Cyclization

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Abstract: We developed a silver-catalyzed strategy for the generation of sulfonyl radicals from sulfonamides derived from *a*-amino acids. The reaction proceeded via a decarboxylation, N-S bond cleavage and radical cyclization sequence and allows the difunctionalization of alkynes and the synthesis of 3-sulfonylated coumarins. The reaction tolerated a broad scope of substrates and functional groups and could be extended to the synthesis of oxindoles and an isoquinolinedione by the capturing of the sulfonyl radical with an alkene moiety. Moreover, the proposed mechanism was supported experimentally and by DFT calculations.

The introduction of a sulfonyl group into an organic compound changes the physical and chemical properties of the parent molecule. Therefore, organosulfones are common in functional materials, medicines and agrochemicals.^[1] For instance, drugs such as dapsone (leprosy), tazobactam (antibiotic) and CX157 (antidepressant) contain a sulfone functionality. In addition, sulfones also participate in a wide range of synthetic transformations, making them versatile intermediates in organic synthesis.^[2] Thus, the development of efficient protocols for the regioselective synthesis of sulfones is an important area of research in organic synthesis.

Classic methods for the synthesis of sulfones include the reaction of organolithium or Grignard reagents with sulfonyl chlorides and the oxidation of sulfides.^[3] Sulfur dioxide insertion methods using SO₂ gas or its surrogates such as $K_2S_2O_5$ and DABCO•SO₂ with nucleophiles, which were pioneered by Willis and Wu, are also attractive alternatives.^[4] However, some of these methods often suffer from poor functional group compatibility and generate stoichiometric amounts of organometallic waste, and the preparation of the starting sulfide substrate sometimes requires foul-smelling thiols. The Friedel-Crafts-type sulfonylation of arenes has also been reported,^[5] but these reactions often require harsh conditions. Sulfonylations via C-H bond functionalization have also been reported, but in most cases a directing group is required.^[6]

Recently, the reaction of sulfonyl radicals with alkynes and

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alkenes has emerged as a powerful method for the regioselective synthesis of sulfones.[4d,7-13] Commonly used sources of sulfonyl radicals include sulfinates^[8] and sulfonyl hydrazides,^[9] whereby metal catalysts and/or stoichiometric oxidants are used (Figure 1). Sulfonic and sulfinic acids,¹⁰ arylsulfonyl chlorides^[11] and tosyl cyanides¹² have also been utilized. Reactions of DABCO•SO2 with aryl diazosalts were recently also used to access sulfonyl radicals.[4d,13] Despite this progress, reagents such as sulfonic acids and sulfinic acids are often unstable to handle, sulfonyl hydrazides require toxic hydrazines for preparation, aryl diazosalts are sometimes explosive, sulfonyl chlorides are sensitive to water, while sulfonyl cyanides are expensive and also sensitive to water. In addition, limited substrate scope and need for harsh conditions in some of the reported sulfonylation reactions inspire the development of alternative methods to access sulfonyl radicals.



Figure 1. Sources of aryl and alkyl sulfonyl radicals.

We considered bench-stable sulfonamides, prepared from sulfonyl chlorides and α -amino acids in excellent yields, as alternative reagents for the generation of sulfonyl radicals. Since silver-catalyzed decarboxylative formations of alkyl radicals are a well-known transformation,^[14] we proposed that if further fragmentation of the α -amino alkyl radical formed from sulfonamides occurred via an N-S bond cleavage (Figure 2), the resultant sulfonyl radical could be used to synthesize sulfones via the difunctionalization of alkynes and alkenes. We herein describe the successful development and application of this idea for the catalytic synthesis of coumarins, which are privileged molecules in organic chemistry.^[15] We also report the results of a mechanistic study to support the proposed mechanism. The strategy is also used to synthesize 2-oxindoles^[16] and an isoquinolinedione.





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We tested our hypothesis by a reaction of phenyl 3phenylpropiolate (1a) and N-tosyl proline (2a) in the presence of AgNO₃ (20 mol%) and K₂S₂O₈ (2.0 equiv) in MeCN/H₂O (2:1) at 50 °C for 4 h (Table 1).^[17] To our delight, the desired coumarin 3a was obtained in 66% isolated yield. Notably, no by-products derived from the addition of the a-aminoalkyl radical were observed under these conditions, which implies that either the aaminoalkyl radical is less reactive or the homolytic cleavage of the N-S bond to form the sulfonyl radical was rapid. Sulfonamides derived from glycine (2b), alanine (2c), and phenylalanine (2d) gave lower yields (entries 2-4), while those derived from valine (2e) and 2-methylalanine (2f) gave comparatively moderate yields (entries 5-6). N-Tosyl-Nmethylglycine (2g), a tertiary sulfonamide, gave a lower yield than was achieved with 2a (entry 7). To achieve full conversion of 1a, we increased the amount of 2a to 1.2 equivalents, which increased the yield of target coumarin 3a to 73% (entry 8). When the amount of catalyst was reduced to 5 mol%, the yield decreased to 57%, and starting material was recovered (entry 9). Pleasingly, extending the reaction time to 24 h afforded 3a in 79% yield (entry 10). The reaction using tosyl chloride instead of 2 did not proceed at all under present conditions (entry 11). Furthermore, control experiments revealed that both the silver catalyst and the oxidant are necessary to achieve the optimum vield of the coumarin.^[17]

Table 1. Optimization of the reaction conditions for the sulfonylation of 1a with 2a. $\ensuremath{^{[a]}}$

	Ph + N-Ts α -amino acid 1a 2, X equiv (Ts =	pNO ₃ (Y S ₂ O ₈ (2.0 eCN/H ₂ (50 °C, = <i>p</i> -CH ₃ (mol%) D equiv) D (2:1) 4 h C ₆ H ₄ SO	Ph Ts O 2) 3a
Entry	2	Х	Y	3a [%] ^[b]
1	2a, N-Ts proline	1.0	20	66
2	2b, N-Ts glycine	1.0	20	19
3	2c, <i>N</i> -Ts alanine	1.0	20	35
4	2d, N-Ts phenylalanine	1.0	20	30
5	2e, N-Ts valine	1.0	20	59
6	2f, N-Ts 2-methylalanine	1.0	20	64
7	2g, N-Ts N-methylglycine	1.0	20	40
8	2a	1.2	20	73
9	2a	1.2	5	57
10 ^[c]	2a	1.2	5	79
11 ^[c]	TsCl instead of 2	1.2	5	N.D.

[a] Conditions: **1a** (0.20 mmol), **2** (0.20 or 0.24 mmol), AgNO₃ (0.040 or 0.010 mmol) and $K_2S_2O_8$ (0.40 mmol) in MeCN/H₂O (2:1, 3.6 mL) at 50 °C. [b] Isolated yield. [c] Reaction time of 24 h. N.D.: Not detected.

With the optimized conditions in hand, we subsequently investigated the scope of aryl propiolates in this radical cyclization reaction using **2a** as the sulfonylation reagent (Scheme 1). The reactions of **2a** with aryl propiolates containing electron-withdrawing as well as electron-donating groups proceeded smoothly; *p*-alkyl, *p*-fluoro, and *p*-methoxycarbonyl groups were tolerated and afforded corresponding products **3b**-

3e in 45-70% yields. On the other hand, when *m*-tolyl-3phenylpropiolate was used, regioisomers **3f** and **3g** were obtained in a 1:1 ratio. These results clearly indicates that the reactions proceeded via a 5-*exo* cyclization and ester migration as reported by Wu and co-workers.^[13a] We also examined various aryl groups on the alkyne moiety. 4-Chlorophenyl, 4biphenyl, and 2-naphthyl groups gave corresponding products **3h**, **3i**, and **3j** in 84%, 59%, and 55% yields, respectively. A substrate with a methyl group on the alkyne moiety also participated in the reaction but afforded the desired product **3k** in a lower yield. Finally, when 1,4-diphenylbut-3-yn-2-one (Z = CH₂) was subjected to slightly modified conditions, 2-naphthol **3I** was obtained after enolization.



 $\begin{array}{l} \textbf{Scheme 1. Scope of aryl propiolates. Reaction conditions: 1 (0.20 mmol), \\ \textbf{2a} (0.24 mmol), \ AgNO_3 (0.010 mmol) \ and \ K_2S_2O_8 (0.40 mmol) \ in \\ CH_3CN/H_2O (2:1, 3.6 mL) \ at \ 50 \ ^{\circ}C \ for \ 24 \ h. \ [a] \ AgNO_3 (10 \ mol\%) \ was \\ used. \ [b] \ AgNO_3 (20 \ mol\%) \ and \ K_2S_2O_8 (1.0 \ equiv) \ was \ used. \\ \end{array}$

Next, the scope of sulfonamides prepared from proline was examined using 1a as the standard substrate (Table 3). Nphenylsulfonyl proline reacted with 1a to give the desired product 3m in 79% yield. As a comparison, a reaction conducted using sodium benzenesulfinate (PhSO₂Na) gave 3m in 42% yield. indicating the superiority of the sulfonamide. Arylsulfonamides bearing o-methyl (3n), m-trifluoromethyl (3o), p-bromo (3p), p-methoxy (3q) and p-phenyl (3r) groups were also suitable substrates. Compared to arylsulfonyl chlorides which were required in more amounts and in presence of more than a stoichiometric amount of base,^[11] 1.2 equivalents of the α amino acid sulfonamides was enough to afford high yields of desired products. In contrast to sulfonylation with arylsulfonyl radicals, the use of alkylsulfonyl radicals is rare. Therefore, we briefly examined alkylsulfonylations using our catalytic conditions. Pleasingly, the reactions with n-butyl- and

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methylsulfonamides proceeded to give **3s** and **3t** in 47% and 33% yields, respectively. Benzylsulfonamide, however, was almost fully consumed but gave very low yield of **3u** possibly due to rapid desulfonylation to the stable benzyl radical.



To probe the mechanism of this sulfonylation reaction, first, an experiment was carried out in the presence of TEMPO or BHT as radical scavengers (Scheme 3, Eq. 1). As a result, the sulfonylation reaction was significantly suppressed. In addition, the reaction of 2a with 1,1-diphenylethylene under standard conditions gave tosyl adducts 4a and 4b in 18% and 6% yields, respectively (Eq. 2). These results clearly indicate that a sulfonyl radical is involved in the reaction mechanism. Recently, Cheng reported an oxidative generation of arylsulfonyl radicals from N-sulfonyl-N-aryl propynamides via N-S bond cleavage under harsh conditions.^[18] To confirm whether such mechanism was probable in our reaction, aryl propiolate 1e was reacted with methyl N-tosylprolinate (5) under the standard conditions (Eq. 3). As a result, the corresponding coumarin 3e was not observed by ¹H NMR and most of starting materials were recovered. This result indicates that our catalytic reaction is initiated by decarboxylation of the unprotected carboxylic acid.



Scheme 3. Experiments to study mechanism.

Moreover, to probe the relative rates of formation of the sulfonyl radical from the corresponding α -aminoalkyl radicals as well as the thermodynamic stability of the α -aminoalkyl radicals and sulfonyl radical, we performed DFT calculations taking in to account the MeCN and H₂O solvation effects (Table 2).^[17] The overall results indicate that the activation energy to form a sulfonyl radical from the α -aminoalkyl radical derived from proline is comparatively lower than that of other α-amino acids. Notably, the activation energy from the α -aminoalkyl radical derived from glycine is twice that of proline. In addition, the thermodynamic stability of the imine derived from proline is also higher than those of the other amino acids, and the least stable was that derived from glycine. These DFT calculation results were in agreement with the isolated yields shown in Table 1. We think that the α-aminoalkyl radicals are thermodynamically unstable and undergo rapid N-S bond cleavage to form the sulfonyl radical and an imine.

Table 2. DFT calculations for the formation of sulfonyl radicals from αaminoalkyl radicals.



a Amino acid	$\Delta G^* (kcal/mol)^{[a]}$		ΔG (k	ΔG (kcal/mol) ^[b]	
	MeCN	H₂O	MeCN	H ₂ O	
Proline	5.15	4.53	-15.6	-17.3	
Glycine	10.80	10.24	-7.6	-7.7	
Alanine	8.23	7.65	-10.6	-10.5	
Valine	8.17	7.40	-10.4	-10.4	
2-Methylalanine	5.20	4.76	-14.0	-13.6	
N-Methylglycine	10.40	9.81	-9.2	-10.8	

[a] Activation energy relative to the corresponding α -aminoalkyl radical. [b] Gibbs free energy relative to the corresponding α -aminoalkyl radical.

On the basis of these mechanistic insights and previous reports,^[13a,14] we considered that the present reaction is initiated by silver-catalyzed decarboxylative formation of α -aminoalkyl

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radical **A** followed by homolytic N–S bond cleavage to form the sulfonyl radical and the imine (Scheme 4). The resulting transient sulfonyl radical regioselectively adds to the alkyne moiety of **1** to form vinyl radical species **B**, which is stabilized by the aryl group (\mathbb{R}^3). We think that the reason for low yield when \mathbb{R}^3 was Me is due to low stability of **B**. Addition of the vinyl radical to the aromatic ring at the *ipso* position gives spirocyclic intermediate **C**, which is oxidized to form carbocation **D**. Ester migration to thermodynamically favored carbocation **E** followed by aromatization then afforded **3**.



Scheme 4. Proposed mechanism for the formation of coumarins and spirolactone.

The radical cyclization protocol could be extended to the difunctionalization of electron-deficient alkenes (Scheme 5, Eq. 4, 5). For instance, under the standard conditions, the reactions of *N*-aryl acrylamides **1v** and **1w** with **2a** proceeded smoothly and afforded corresponding 2-oxindoles **3v** and **3w** in 77% and 70% yields. Finally, catalytic sulfonylation of **1x** was also achieved and provided isoquinolinedione **3x** in 50% yield. In contrast to our recent silver-catalyzed α -aminoalkylation reaction,^[19] no products derived from the addition of α -aminoalkyl radical to the *N*-acryl amides were observed.



Scheme 5. Synthesis 2-oxindoles and isoquinolinedione.

In summary, we have described the first catalytic sulfonylation reaction using sulfonamides prepared from α -amino acids. The reactions proceeded via decarboxylation and N-S bond cleavage followed by radical addition/cyclization to form a C-S bond and C-C bond under moderate conditions. A broad scope of functional groups was tolerated and gave sulfonylated coumarins, 2-oxindoles and an isoquinolinedione regioselectively. Moreover, the mechanism was supported by

mechanistic experiments and DFT calculations.

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Conflict of interest

The authors declare no conflict of interests.

Keywords: amino acids • coumarins • oxindoles • silver • sulfonamides

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