OL Organic Letters

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Visible-Light-Catalyzed in Situ Denitrogenative Sulfonylation of Sulfonylhydrazones

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Cite This: https://doi.org/10.1021/acs.orglett.1c02369 Read Online

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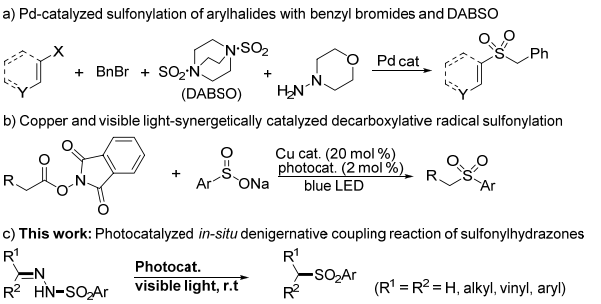
ABSTRACT: A photocatalyzed *in situ* denitrogenative sulfonylation of *N*-arylsulfonyl hydrazones has been developed. This transformation provides a low-carbon strategy to assemble arylalkyl sulfones in a stepwise denitrogenation/sulfonylation manner.

A denitrogenative process of aza-compounds provides an efficient strategy to produce carbenoids and radicals, which are active species often encountered in modern synthetic chemistry.[1] Traditionally, transition-metal-catalyzed denitrogenation−coupling of multinitrogen compounds with arenes,[2] alkanes,[3] alkenes,[4] alkynes,[5] amines,[6] aldehydes,[7] and others[8] have been widely explored to assemble complex molecules. In comparison, photocatalyzed denitrogenation transformations were still not well-established. To date, only diazo compounds and sulfonylazides were reported to be converted to carbenoids,[9] ketenes,[10] nitrenes,[11] and radicals[12] via denitrogenation under visible light conditions, and the corresponding intermediates could be further trapped by ketoimines, indoles, and alkenes. Few protocols of photocatalyzed denitrogenation of hydrazones have been developed for synthetic transformations.

The sulfonyl moiety generally endows the corresponding sulfone molecules with distinctive reactivities, biological activities, and photophysical properties.[13] Exploring efficient strategies to access different sulfones have recently aroused increasing interest in the field of pharmaceutical industry and material chemistry.[14] Although the oxidation of sulfides can deliver arylsulfone compounds,[15] this method requires large amounts of strong oxidants which still limit functional group tolerance. To surmount these drawbacks, transition-metal-catalyzed sulfonylation of "SO_2" sources with various coupling partners has been successively developed in the past decades.[16] For examples, Willis reported a Pd-catalyzed one-pot three-component sulfonylation of arylhalides with benzyl bromides and a SO_2-surrogate (DABSO), in which *N*′,*N*′-dialkyl aminosulfonamides belong to key intermediates (Scheme 1a).[17] Meanwhile, a photocatalytical strategy further provides a more environment-friendly approach to sulfones under mild conditions. In this regard, Li employed 4CzIPN/$Cu(OTf)_2$ as a combinated catalysis system to achieve a visible-light-catalyzed decarboxylative radical sulfonylation of sulfinates with redox-active aliphatic carboxylic esters (Scheme 1b).[18] More recently, we still described a photocatalyzed coupling−cyclization of sulfonylazides with vinylethers and vinylsilanes to furnish complex oxa- and sila-cycles via denitrogenation,

Scheme 1. Synthetic Strategies of Aryl-Alkyl Sulfones

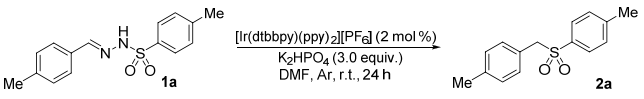


respectively.[19] Based on the fact that diazo esters, sulfonylazides, and sulfonylhydrazones possess similar multinitrogen skeletons, we therefore envisioned that sulfonylhydrazones could also possibly undergo photocatalytical denitrogenation to directly afford arylsulfones under mild conditions (Scheme 1c).

To verify this hypothesis, we employed tosylhydrazide (**1a**) as a model substrate for screening various reaction parameters and finally found that the treatment of **1a** with [Ir(dtbbpy)-$(ppy)_2$][PF_6] (2 mol %) and K_2HPO_4 (3.0 equiv) in DMF (0.13 M, 1.5 mL) for 24 h at room temperature under blue light-emitting diode (LED) radiation (30 W) and an Ar atmosphere led to the formation of 1-methyl-4-((4-methylbenzyl)sulfonyl)benzene **2a** in 82% yield (Table 1, entry 1). On the contrary, other photocatalysts such as Eosin Y, TPT, $Ir(ppy)_3$, [Mes-Acr]ClO_4, and $Ru(bpy)_3Cl_2$ gave very poor reaction conversions (entries 2−6, 0−23%). Evaluation of different bases under the standard conditions indicated that inorganic bases such as K_2CO_3 and K_3PO_4 could afford

Received: July 15, 2021

Table 1. Optimization of the Reaction Parameters[a]



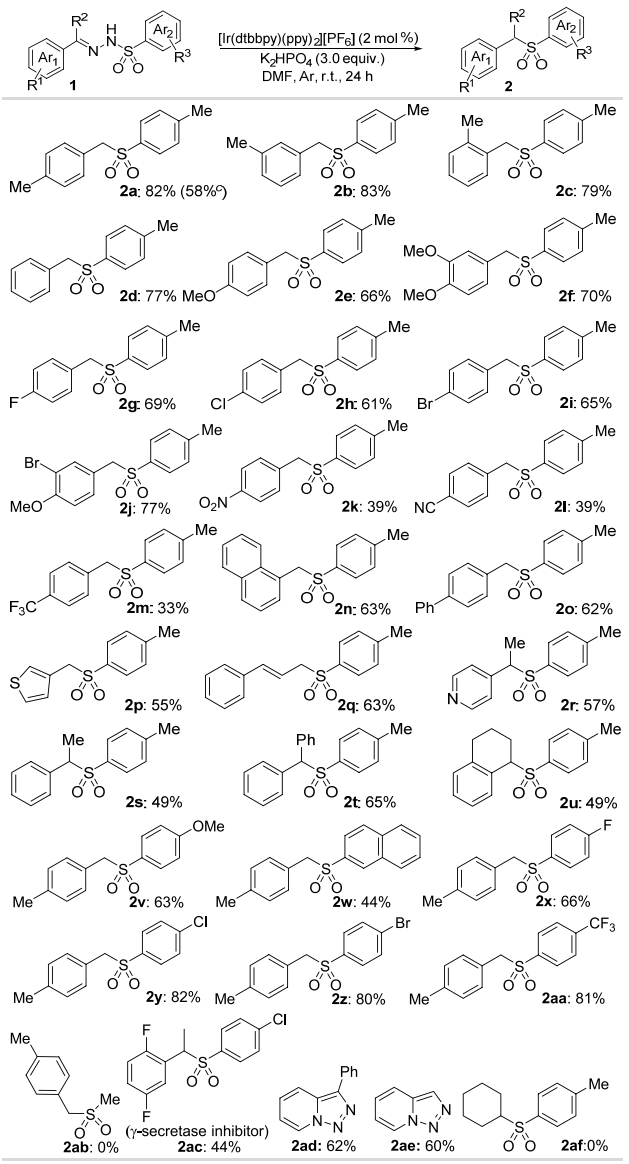
entry	changes to standard conditions	2a yield (%)[b]
1	none	82
2	Eosin Y	trace
3	TPT	trace
4	$Ir(ppy)_3$	12
5	$[Mes\text{-}Acr]ClO_4$	0
6	$Ru(bpy)_3Cl_2$	23
7	K_2CO_3	56
8	K_3PO_4	61
9	Et_3N	9
10	THF	trace
11	DMSO	60
12	toluene	13
13	air	61
14	O_2	7[c]
15	green LED light	27
16	no light	0
17	no photocatalysts	0

[a]Reaction conditions: 0.2 mmol of 4-methyl-*N*′-(4-methylbenzylidene) phenylsulfonohydrazide **1a**, $[Ir(dtbbpy)(ppy)_2][PF_6]$ (2 mol %), and K_2HPO_4 (3.0 equiv) in DMF (0.2 M, 1.5 mL) under Ar atmosphere at room temperature for 24 h, blue LED light (30 W). [b]Isolated yield. [c]O_2 atmosphere still led to 64% yield 4-methylbenzaldehyde **2a-1**.

moderate yields of **2a** (entries 7−8, 56−61%), and organobase Et_3N only delivered a 9% yield of **2a** (entry 9). Meanwhile, replacing the solvent with THF, DMSO, and toluene did not exhibit corresponding improvement (entries 10−12). Moreover, performing this denitrogenative coupling reaction of **1a** under an air and O_2 atmosphere resulted in 61% and 7% yields of **2a**, respectively (entries 13 and 14), implying that molecular oxygen could inhibit this transformation to some degree.[20] Also, irradiating this transformation by using green LED light gave a 27% yield of **2a** (entry 15). It should be noted that this *in situ* denitrogenative coupling of sulfonylhydrazone **1a** did not occur without light or the photocatalysts (entries 16 and 17).

Subsequently, we measured the substrate scope of the visible-light-catalyzed *in situ* denitrogenative coupling of 4-methylphenylsulfonyl hydrazones. As shown in Scheme 2, the substituent on the phenyl ring (Ar_1) of sulfonylhydrazones had great influence on this transformation. Among them, electron-rich substituents (Me− and MeO−) gave good to excellent yields of the corresponding sulfones (**2a−2f:** 66−83%), regardless of the *ortho*-, *meta*-, and *para*-position (**2a** vs **2b** and **2c**). Meanwhile, weak electron-withdrawing halo group-substituted phenyl rings (Ar_1) could also afford good yields of halobenzyl sulfones **2g−2j** (61−77%). However, stronger electron-deficient NO_2-, NC-, and CF_3-substituted phenyl rings (Ar_1) only generated poorer yields of products **2k−2m** (33−39%). To our delight, 1-naphthaldehyde-, 4-phenylbenzaldehyde-, thiophene-3-carbaldehyde-, cinnamaldehyde-, and isonicotinaldehyde-derived *N*′-sulfonylhydrazones were also well-tolerated in the reaction conditions, providing 55−63% yields of arylalkyl sulfones **2n−2r**. Again, acetophenone-, benzophenone-, and benzocycloketone-derived sulfonylhydrazones were still allowed to give the complex arylalkyl sulfones (**2s−2u**) with 49−65% yields.

Scheme 2. Diazo Compound Scope[a,b]



[a]All the reactions were performed using 0.2 mmol of 4-methyl-*N*′-(4-methylbenzylidene) phenylsulfonohydrazide **1a**, $[Ir(dtbbpy)(ppy)_2][PF_6]$ (2 mol %), and K_2HPO_4 (3.0 equiv) in DMF (0.2 M, 1.5 mL) under an Ar atmosphere at room temperature for 24 h, blue LED light (30 W). [b]Isolated yield. [c]1.0 mmol of tosylhydrazide (**1a**) was used.

To examine the functional group tolerance from the sulfonylaryl ring of hydrazones, the substituent effect from the sulfonylaryl ring (Ar_2) has been further evaluated systematically. It was found that arylsulfonyl hydrazones including electron-rich (MeO−) and electron-deficient (halo-, CF_3-) phenylsulfonyl hydrazones could be smoothly converted to 63−82% yields of the corresponding products **2v−2aa**. In comparison, stronger electron-withdrawing group-substituted arylsulfonyl hydrazones easily suffered from deprotonation, leading to excellent reaction conversions (**2y**, **2z**, and **2aa**), but switching arylsulfonylhydrazones to methylsulfonylhydrazone did not deliver the desired alkyl/alkylketone **2ab**. The present procedure could still rapidly

https://doi.org/10.1021/acs.orglett.1c02369
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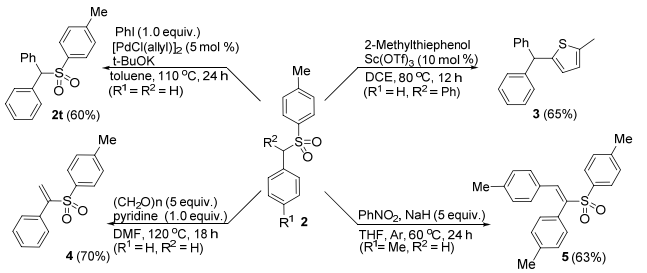
assemble 2-(((4-chlorophenyl)sulfonyl)methyl)-1,4-difluorobenzene **2ac** which belongs to an important γ-secretase inhibitor.[14c] Interestingly, when 2-pyridylaldehyde- and 2-pyridylketone-derived sulfonylhydrazones were subjected to the reaction conditions, unexpected coupling−cyclization instead of denitrogenative coupling occurred, giving [1,2,3]-triazolo[1,5-*a*]pyridines **2ad** (62%) and **2ae** (60%) via intramolecular nucleophilic substitution.[21] Besides, cyclohexanone-derived sulfonylhydrazone was not a suitable substrate to make 1-(cyclohexylsulfonyl)-4-methylbenzene **2af** possibly due to the weak stability of cyclohexyl radicals.

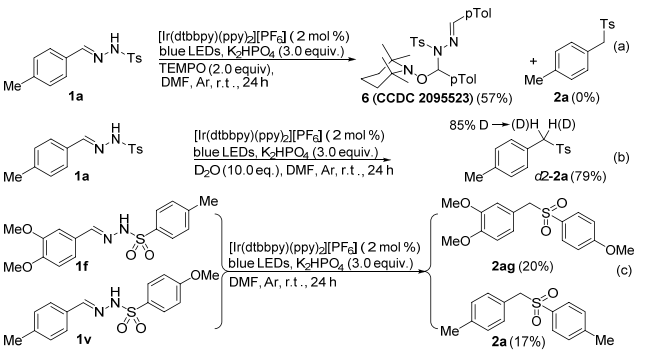
The postsynthetic conversions of the sulfones indicated that Pd(II)-catalyzed α-Csp^3−H bond arylation of arylalkylsulfones with iodobenzene could easily introduce a phenyl group into the α-position of sulfone **2d** to give diphenylmethyl *p*-tolyl sulfone **2t** (60%) which smoothyl underwent a cross-coupling with 2-methylthiephenol in the presence of Sc(OTf)$_3$ catalysts, furnishing 2-diphenylmethyl-5-methylthiophene **3** (65% yield) through C−S bond cleavage. Meanwhile, $(CH_2O)_n$ and alkylsulfones could be employed as electrophilic reagents to react with arylalkylsulfone under base conditions to give vinylsulfones **4** (70%) and **5** (63%), respectively (Scheme 3).

Scheme 3. Synthetic Applications



To gain better insight into the mechanism of this transformation, the treatment of 4-methylphenylsulfonyl hydrazide **1a** with TEMPO (2.0 equiv) under our standard conditions did not give sulfone **2a**, and the *in situ* denitrogenative coupling of **1a** was completely inhibited. On the contrary, an unexpected hydrazone-tethered *O*-benzylhydroxylamine **6**[22] (57%) was formed possibly via the benzyl carbenoids which were trapped by TEMPO (Scheme 4a). On the other hand, when the denitrogenative sulfonylation of hydrazone **1a** was performed in the D_2O/DMF system, the incorporation of deuterium into the α-position (85% D) of sulfone *d*2-**2a** (79% yield) was observed; this H/D exchange

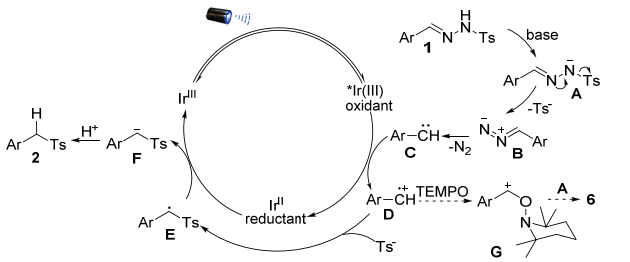
Scheme 4. Preliminary Mechanism Studies



data suggested that carbon anion intermediates were also involved in this reaction (Scheme 4b). Finally, merging of the cross-coupling of hydrazones **1f** and **1v** synchronously led to the formation of sulfones **2ag** (20%) and **2a** (17%) (Scheme 4c),[23] indicating that the denitrogenative sulfonylation possibly proceeded via a stepwise rather than concerted process.

Based on the above-meniontedmechanistic investigations, a possible reaction mechanism was proposed, shown in Scheme 5. The deprotonation of arylsulfonyl hydrazones under base

Scheme 5. Proposed Mechanism



conditions first occurred to produce nitrogen anion intermediates **A**, followed by detosylation to deliver α-diazo-*p*-xylene **B**,[5f] and denitrogenation of **B** could afford the corresponding benzyl carbenoids **C**. Subsequently, a photocatalyzed single electron transfer (SET) between the excited state *Ir^{III}-catalysts and benzyl carbenoids **C** gave cationic radicals **D** and Ir(II)-catalysts.[12b] **D** suffered from a nucleophilic attack by Ts$^-$ to produce radicals **E** which further underwent an SET with Ir(II)-catalysts to give the benzyl anions **F** with release of Ir(III)-catalysts. Finally, the protonation of anions **F** furnished the desired sulfone products **2**. Also, cationic radicals **D** could still be trapped by TEMPO to afford benzyl cations **G** which were nucelophilically attacked by nitrogen anion intermediates **A** to produce the TEMPO-tethered hydrazine **6** (Scheme 4a).

In summary, we have developed an efficient visible-light-catalyzed *in situ* denitrogenative sulfonylation of sulfonylhydrazones. This method provides a green and low-carbon approach to access arylalkyl sulfones under mild conditions. Mechanistic studies indicate that a stepwise denitrogenative sulfonylation is involved in this transformation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02369.

Detailed experimental procedures, characterization data, copies of ^{1}H NMR and ^{13}C NMR spectra for all isolated compounds (PDF)

Accession Codes

CCDC 2095523 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

https://doi.org/10.1021/acs.orglett.1c02369
Org. Lett. XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the NSFC (No. 21871097), CPSF (No. 2019M662887), NSFGP (No. 2019A1515011790), STPG (No. 201904010113, No. 202102020659), and the FRFCU (No. 2020ZYGXZR044) for financial support.

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(22) Please see the single crystal data for **6** (CCDC 2095523) in the Supporting Information.

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https://doi.org/10.1021/acs.orglett.1c02369
Org. Lett. XXXX, XXX, XXX−XXX