

Visible-Light-Mediated Ru-Catalyzed Synthesis of 3-(Arylsulfonyl)but-3-enals via Coupling of α -Allenols with Diazonium Salts and Sulfur Dioxide

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Cite This: *Org. Lett.* 2020, 22, 9490–9494



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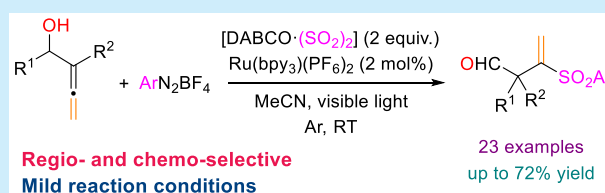


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Supporting Information

ABSTRACT: The first coupling of α -allenols, sulfur dioxide, and arenediazonium salts is presented. The three-component reaction which is promoted by visible light can be easily accomplished using DABSO as a sulfur dioxide surrogate in the presence of a photoredox catalyst. In this manner, a broad range of electron-rich and electron-deficient aryl substituents are well accommodated in the sulfonylation–rearrangement cascade to afford the 2,2-disubstituted 3-(arylsulfonyl)but-3-enals in reasonable yields. Based on control experiments, a radical mechanism which does imply 1,2-aryl migration has been proposed.



The sulfone moiety is among the most outstanding and chameleonic functional groups. Sulfones are versatile synthetic intermediates,¹ exhibit pharmacological properties,² and are also used in material science.³ Vinylsulfones are a particular subclass of sulfones which display significant biological activity.⁴ Sulfur dioxide is a toxic and difficult to handle gas, which precludes its use in daily organic synthesis. The seminal work of the Willis group employing a bench-stable source of sulfur dioxide,⁵ namely DABSO [DABCO·(SO₂)₂], did allow the widespread use of sulfonylative coupling chemistry. Advances in sulfur dioxide insertion chemistry using DABSO have allowed the preparation of a variety of sulfonyl compounds under mild conditions.^{6,7} On the other hand, the allene moiety is a versatile building block which provides efficient synthetic routes to a great variety of cyclic and acyclic molecules.⁸ To the best of our knowledge, previous efforts in the preparation of sulfones from allenes has been limited to the reactions of allenes with sulfonyl halides, sulfinic acids, or tosyl cyanide (Scheme 1a)⁹ and sulfonyl hydrazides (Scheme 1b and 1c).¹⁰ Aiming to surmount this weakness, we planned to include the combined use of allenes, DABSO, and diazonium salts. Arenediazonium salts are convenient arylation reagents because they bear a weak C–N bond which gives benign N₂ as the byproduct. In this context, Wu reported the copper-catalyzed intramolecular oxysulfonylation of allenic acids (Scheme 1d).¹¹ Herein, we present a convenient method for the synthesis of 2,2-disubstituted 3-(arylsulfonyl)but-3-enals through the three-component coupling of α -allenols, the sulfur dioxide surrogate DABSO, and arenediazonium salts, which is promoted by visible light¹² (Scheme 1e).

In order to optimize the reaction conditions, allenol **1a** and arenediazonium salt **2a** were selected as model substrates. Results depicted in Table 1 revealed that Ru(bpy₃)(PF₆)₂ is

the photoredox catalyst of choice (Table 1, entries 1–3) while acetonitrile was found to be the optimal solvent (Table 1, entries 2, 4–6). The effect of the amounts of DABSO and aryl diazonium tetrafluoroborate salt was also screened. The use of 2 equiv of DABSO together with 1.5 equiv of diazonium salt was found to be sufficiently efficient. Diminished yields were obtained when less excess was used (Table 1, entries 7, 8). The reaction did not progress in the absence of either the photocatalyst or irradiation (Table 1, entries 9, 10). However, 3-(arylsulfonyl)but-3-enal **3a** was obtained in a low 9% yield when the reaction was promoted by solar light (Table 1, entry 11). Gratifyingly, the ruthenium-catalyzed (2 mol %) treatment of allenol **1a** with 1.5 equiv of diazonium salt **2a** and 2 equiv of DABSO under visible light irradiation (LED light bulb) in acetonitrile (30 mL/mmol **1a**) gave rise to product **3a** in moderate yield (59%). The formation of 2-(4-bromophenyl)-3-[(4-bromophenyl)sulfonyl]-2-methylbut-3-enal **3a** should be explained invoking a sulfonylation–rearrangement cascade. The lack of formation of furan-type cyclized adducts was observed. Noteworthy, the carbon–bromide bonds of reagents **1a** and **2a** were transferred unaltered to the final polyfunctionalized product **3a**, which may result in a further orthogonal functionalization using conventional cross-coupling chemistry.

Having the optimal conditions in hand, we moved toward surveying the scope of the above transformation by the

Received: October 19, 2020

Published: November 24, 2020



Scheme 1. Synthesis of Sulfones from Allenes: Previous and Current Proposal

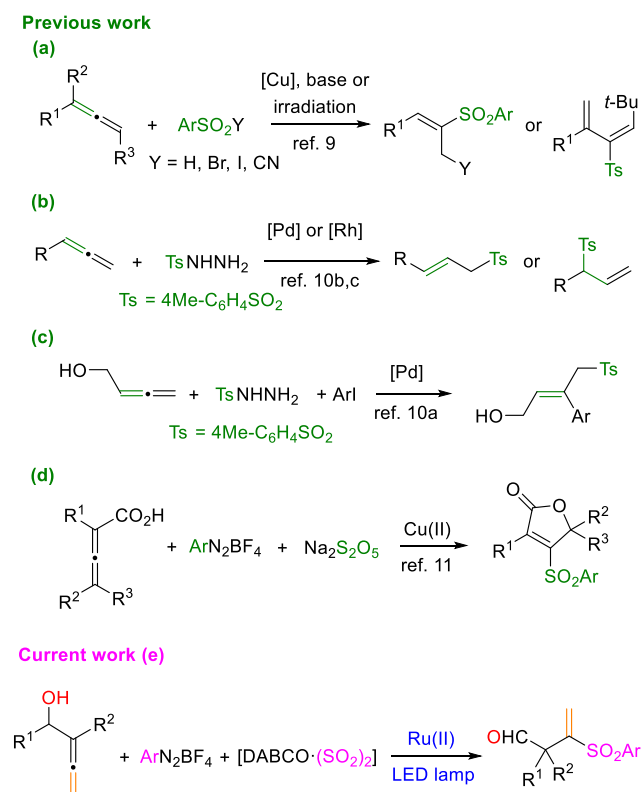
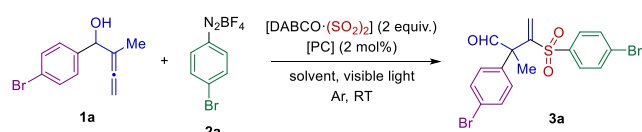


Table 1. Sulfonylation-Rearrangement Cascade of Allenol 1a with Arenediazonium Salt 2a under Modified Photoredox Conditions

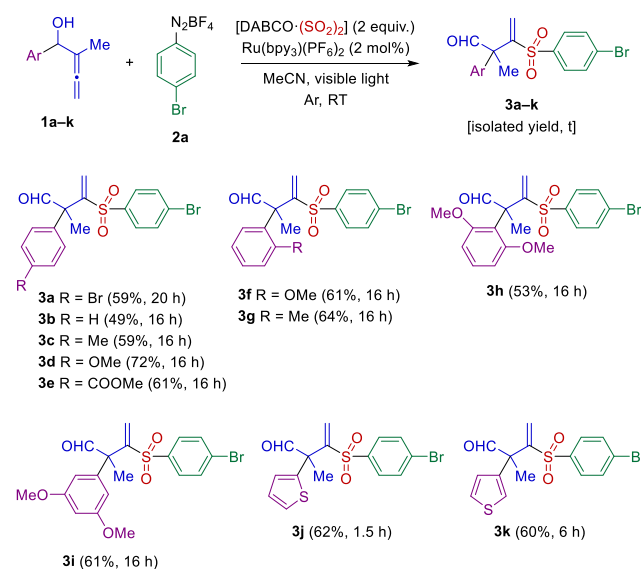


entry	photocatalyst ^a	solvent	time (h) ^b	yield 3a (%) ^c
1	[Ir]	MeCN	16	48
2	[Ru]	MeCN	20	59
3	Eosin Y	MeCN	16	21
4	[Ru]	DCE	20	0
5	[Ru]	THF	20	0
6	[Ru]	MeOH	20	0
7	[Ru]	MeCN	18	31 ^d
8	[Ru]	MeCN	18	35 ^e
9	—	MeCN	20	0
10	[Ru]	MeCN	20	0 ^f
11	[Ru]	MeCN	10	9 ^g
12	[Ru]	MeCN	10	30 ^h

^a[Ir] = [Ir(ppy)₂(dtbbpy)](PF₆)₂. [Ru] = [Ru(bpy)₃](PF₆)₂. ^bThe reactions were carried out under an argon atmosphere using 1a (0.2 mmol), 2a (0.3 mmol), and DABSO (0.4 mmol). Reaction progress was followed by TLC. ^cYield of pure, isolated product with correct analytical and spectral data. ^dThe reaction was carried out using 1a (0.2 mmol), 2a (0.3 mmol), and DABSO (0.2 mmol). ^eThe reaction was carried out using 1a (0.2 mmol), 2a (0.2 mmol), and DABSO (0.4 mmol). ^fThe reaction was carried out in the dark. ^gThe reaction was carried out using daylight on a sunny day. ^hThe reaction was carried out in the presence of air instead of under argon.

reaction of various allenols 1 with diazonium salt 2a (Scheme 2). The reactions progressed well for allenols 1a–k, bearing

Scheme 2. Sulfonylation-Rearrangement Cascade of Allenols 1a–k under Photocatalysis; Controlled Synthesis of 2,2-Disubstituted 3-(Arylsulfonyl)but-3-enals 3a–k

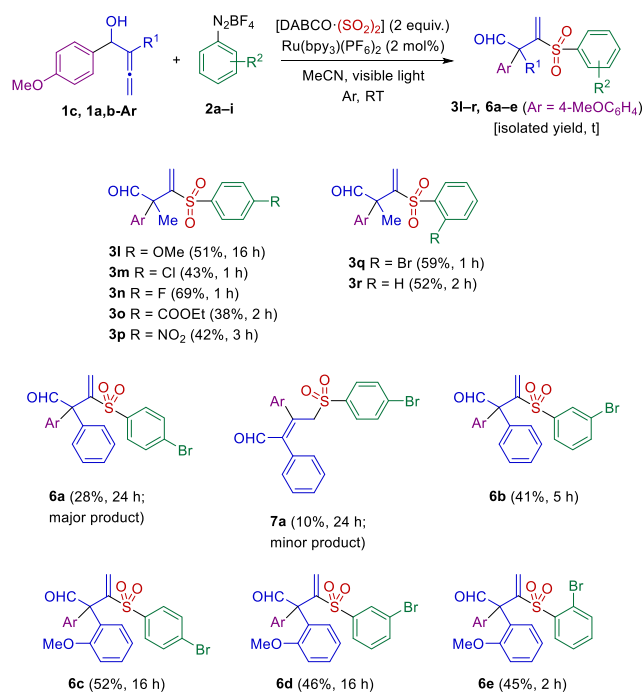


substituents of varying electronic demand at the various positions of the benzene ring. Thus, both electron-withdrawing groups (CO₂Me) and electron-donating groups (OMe and Me) and Br were compatible with the sulfonylation–rearrangement cascade, providing the required products 3a–k in reasonable yields (49–72%; complete conversion). Reaction monitoring to make sure that the reaction is conveniently progressing was carried out using TLC until total consumption of the starting allenol. Interestingly, *ortho*-, *meta*-, and *para*-substitution on the benzene ring was well-tolerated. Besides, a heteroaromatic nucleus worked well as it is evidenced by the success of the process in products 3j and 3k, bearing a 2-thienyl and a 3-thienyl ring, respectively.

Additionally, the scope of the sulfonylation–rearrangement cascade was assessed by the reaction of allenol 1c with diazonium tetrafluoroborate salts 2b–i having a variety of substituents at the aryl nucleus (Scheme 3). Precursors 2 displaying no substitution as well as both electron-reach and electron-withdrawing groups including methoxy, halogens (Cl, Br and F), nitro, and carboxyethyl all exhibited high reactivities (complete conversion) in the sequence smoothly providing the desired 2,2-disubstituted 3-(arylsulfonyl)but-3-enals 3l–r. Remarkably, products 3 prepared in Schemes 2 and 3 possess a newly created all-carbon quaternary center, the formation of which is challenging in organic synthesis.^{13,14}

Surprisingly, oxindole-tethered quaternary allenol 4a can smoothly be converted into homodimeric derivatives 5a and 5b under otherwise identical conditions; the structure of (*E,E*)-5b was assigned by single-crystal X-ray diffraction analysis (Supplementary Scheme S1).¹⁵ Next, different experiments were conducted using allenols 1a–Ar and 1b–Ar having *C*-aryl substituents at the internal allene position. Noteworthy, despite the considerable steric hindrance in the final products, the aryl moiety is well tolerated and 2,2-diaryl-3-(arylsulfonyl)but-3-enals 6a–e were obtained after complete conversion in moderate yields (Scheme 3). In one case, the nonexpected

Scheme 3. Photocatalyzed Sulfonylation–Rearrangement Cascade of Allenols 1c and 1a,b-Ar with Arenediazonium Salts 2a–i; Controlled Synthesis of 2,2-Disubstituted 3-(Arylsulfonyl)but-3-enals 3l–r and 6a–e



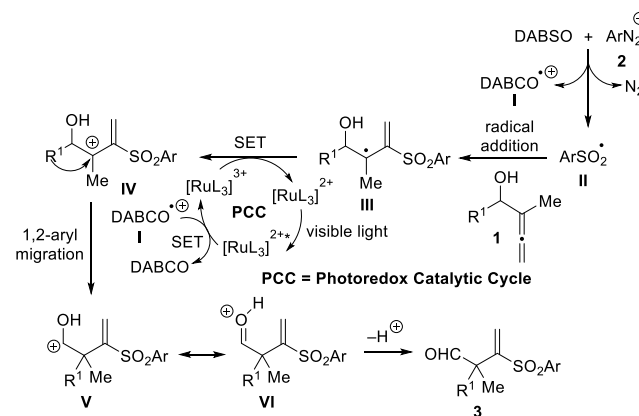
rearranged aldehyde **7a** was obtained as a chromatographically separable minor product.

In order to shed light on the reaction mechanism, various control experiments were performed (Supplementary Scheme S2). No sulfonyl-butenals were formed in the absence of the photocatalyst or when the reaction was carried out in darkness. The above results suggest the formation of arylsulfonyl radicals under photoredox catalytic conditions, with the crucial role of both the ruthenium photosensitizer and visible light. Besides, the construction of the sulfonyl-butenal scaffold was suppressed with the presence in the reaction medium of TEMPO (Supplementary Scheme S2), a well-known radical inhibitor. All these experiments together point to the radical nature of the sulfonylation–rearrangement cascade and participation of arylsulfonyl radicals.

A pathway for the formation of 3-(arylsulfonyl)but-3-enals **3** is outlined in Scheme 4.^{16,17} Initially, participation of the DABSO results in the generation of the 1,4-diazabicyclo-[2.2.2]octanyl cation radical **I** and the arylsulfonyl radical **II**. This crucial reactive species is ready to react with the α -allenol **1** to form allylic radicals **III**, which after oxidation would evolve to allylic cations **IV**. This oxidation step which implies a single electron transfer (SET) is mediated by visible light, catalyzed by the ruthenium salt (photoredox catalyst), and promoted by the cation radical **I**. Next, 1,2-aryl migration allows the formation of cationic homoallylic alcohols **V**, which rapidly evolve to protonated β,γ -unsaturated aldehydes **VI**. Final products, 2,2-disubstituted-3-(arylsulfonyl)but-3-enals **3**, are obtained after spontaneous deprotonation of intermediates **VI**.

In conclusion, the three-component coupling of α -allenols, sulfur dioxide, and arenediazonium salts¹⁸ has been uncovered. The reactions were conducted in mild conditions at room temperature. In this way, 2,2-disubstituted 3-(arylsulfonyl)but-

Scheme 4. Tentative Mechanistic Explanation for the Multicomponent Reaction between DABSO, Diazonium Salts, and α -Allenols



3-enals bearing both electron-rich and electron-deficient aryl substituents are accessible using DABSO as a sulfur dioxide surrogate, visible light, and a ruthenium catalyst. Control and radical inhibition experiments indicate that a radical mechanism is possible for the sulfonylation–rearrangement cascade.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c03482>.

Experimental procedures, characterization data of new compounds, and copies of NMR spectra (PDF)

■ Accession Codes

CCDC 1900824 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.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported in part by the Spanish Agencia Estatal de Investigación and European Regional Development Fund (Project PGC2018-095025-B-I00).

DEDICATION

In memory of Prof. José. L. Gómez-Skármeta (1966–2020), a reputed biochemist and friend.

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