

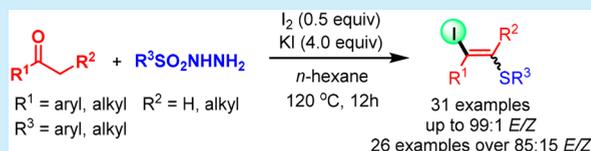
Iodine-Promoted Deoxygenative Iodization/Olefination/Sulfenylation of Ketones with Sulfonyl Hydrazides: Access to β -Iodoalkenyl Sulfides

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S Supporting Information

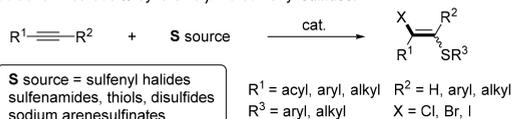
ABSTRACT: A highly regio- and stereoselective synthesis of β -haloalkenyl sulfides using commercially available ketones and sulfonyl hydrazides as starting materials has been developed. This protocol obviates the need for alkynes and traditional sulfenylating agents and therefore opens up a new door to construct β -iodoalkenyl sulfides in a highly simple manner. This study reveals that ketones could be used as vinyl iodide precursors in organic synthesis.



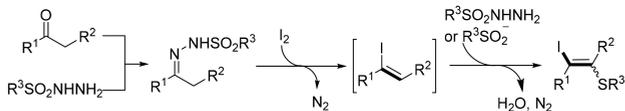
β -Haloalkenyl sulfides, including carbon–halogen bonds, carbon–carbon double bonds, and carbon–sulfur bonds, which are easily decorated into various alkenes and alkynyl sulfides, can serve as key building blocks in the synthesis of complex pharmaceutical drugs and biologically active molecules.¹ Consequently, developing effective methods to access β -haloalkenyl sulfides represents a striking research field. Traditionally, β -haloalkenyl sulfides are obtained by the addition of sulfenylating agents, such as sulfonyl halides,² sulfenamides,³ disulfides,⁴ thiols,^{4a} and sodium arenesulfonates⁵ to alkynes (Scheme 1a). Nevertheless, these strategies endured

Scheme 1. Synthetic Strategy for the Formation of β -Haloalkenyl Sulfides

a) Traditional methods to synthesize β -haloalkenyl sulfides:



b) This work:



three key challenges. First, many of the sulfenylating agents are unstable to air and moisture, are expensive, or even possess unpleasant odors.⁶ This is particularly problematic for large-scale synthesis. In addition, most alkynes are noncommercial and require several steps to prepare,⁷ thus complicating synthetic operations and increase population. Furthermore, these reactions frequently require metal catalysts, suffer from a narrow substrate scope, or yield byproducts unfriendly to the environment.^{2g,3–5} To address such challenges, it would be of tremendous interest in developing new strategies to generate β -

haloalkenyl sulfides from readily accessible substrates through environmentally friendly reaction conditions.

In the course of exploring new methods to synthesize organic sulfides, we found that sulfonyl hydrazides could serve as ideal sulfenylating agents regarding stability, commercial availability, and low toxicity.⁸ Later, many excellent and significant works on the construction of the C–S bond using sulfonyl hydrazides as sulfenylating agents have been reported by the groups of Tian,⁹ Singh,¹⁰ Jiang,¹¹ and others.¹² In all these reports, the reductive nature of the $NHNH_2$ group is utilized to remove the two oxygen atoms of the sulfonyl group to give sulfenylating agents, water, and molecular nitrogen; however, none of these reports takes advantage of the nucleophilicity of the $NHNH_2$ group for chemical synthesis. In this context, we initiated a research program with the aim of making full use of the reductive nature and the nucleophilicity of the $NHNH_2$ group in the sulfonyl hydrazide. Ketones are stable and readily accessible, and they have been widely employed to form sulfonylhydrazones with sulfonyl hydrazides;¹³ consequently, the use of ketones as electrophilic reagent was our first choice. We envisioned that sulfonyl hydrazides reacted with ketones to afford sulfonylhydrazones which might be oxidized by iodine via single-electron transfer to afford vinyl iodides,^{14,15} and then vinyl iodides reacted with the in situ generated sulfonyl iodides from sulfonyl hydrazines or byproduct sulfonyl groups to afford β -iodoalkenyl sulfides,⁸ wherein water and molecular nitrogen are expected to be generated as byproducts (Scheme 1b). We anticipated that the role of the iodine would be three-fold: oxidizing sulfonylhydrazone, affording vinyl iodide, and accelerating the decomposition of sulfonyl group to give sulfonyl iodide. To the best of our knowledge, this three-component reaction of ketones with sulfonyl hydrazides and iodine to direct synthesis of β -iodoalkenyl sulfides has never

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been documented, which represents a novel and important reaction mode and extends the application of ketones.

To test our hypothesis, the reaction of acetophenone (**1a**) with *p*-toluenesulfonyl hydrazide (**2a**) and iodine was selected as a prototype reaction (Table 1). When the reaction was

Table 1. Screening Reaction Conditions for Synthesis of β -Iodoalkenyl Sulfides^a

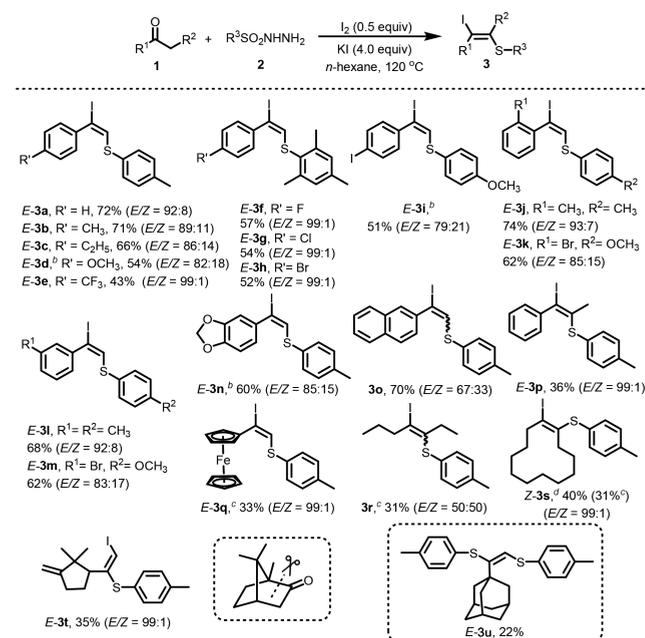
entry	[I]	additive (equiv)	solvent	yield (%) ^b	E/Z ^c
1	I ₂ (0.5)		CH ₂ Cl ₂	12	
2	I ₂ (0.5)	KI (4)	CH ₂ Cl ₂	30	84:16
3	I ₂ (0.5)	KI (4)	DMF	trace	
4	I ₂ (0.5)	KI (4)	EtOH	trace	
5	I ₂ (0.5)	KI (4)	CH ₃ CN	12	
6	I ₂ (0.5)	KI (4)	toluene	36	89:11
7	I ₂ (0.5)	KI (4)	CH ₃ NO ₂	19	
8	I ₂ (0.5)	KI (4)	THF	26	
9	I ₂ (0.5)	KI (4)	<i>n</i> -hexane	48	90:10
10 ^d	I ₂ (0.5)	KI (4)	<i>n</i> -hexane	72	92:8
11 ^d	I ₂ (0.5)	KI (4)	<i>n</i> -hexane	58	91:9
12 ^{d,e}	NIS (1.0)	KI (4)	<i>n</i> -hexane	40	87:13
13 ^d	I ₂ (0.75)	KI (4)	<i>n</i> -hexane	51	85:15
14 ^d	I ₂ (0.4)	KI (4)	<i>n</i> -hexane	64	
15 ^d	I ₂ (0.5)	NaI (4)	<i>n</i> -hexane	52	88:12
16 ^d	I ₂ (0.5)	TBAI (4)	<i>n</i> -hexane	0	
17 ^d	I ₂ (0.5)	KI (2)	<i>n</i> -hexane	57	82:18
18 ^d	I ₂ (0.5)	KI (6)	<i>n</i> -hexane	53	84:16

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), in solvent (1 mL), at 120 °C (oil bath), for 12 h. ^bYield of isolated product. ^cE/Z ratio determined by GC–MS. ^d**2a** (0.4 mmol). ^eAt 100 °C. NIS = N-iodosuccinimide. TBAI = tetrabutylammonium iodide.

performed in CH₂Cl₂ at 120 °C, β -iodoalkenyl sulfide **3a** was obtained in 12% yield. The lower yield was ascribed to the formation of a significant amount of dithioether. Surprisingly, in the presence of additive KI, the amount of dithioether was reduced and a moderate yield of **3a** was obtained. Encouraged by this result, various solvents were examined, and a good yield was achieved when using *n*-hexane as solvent. Further examination showed that the ratio of starting materials is crucial, and the highest yield, 72%, was obtained when the ratio of **1a**, **2a**, and I₂ was adjusted to 2:4:1. Increasing the scale from 0.20 to 1.0 mmol gave a slightly lower yield (67%). Lowering the reaction temperature to 100 °C led to a lower yield. NIS, in place of I₂, was also checked in the reaction, giving a moderate yield. In addition, increasing and decreasing the amount of iodine resulted in a much lower yield. Finally, screening additives revealed that the additives have great impact on the reaction. NaI could also be used as additive for the present reaction; however, TBAI was not compatible with this reaction. Thus, the optimal reaction conditions were 1 equiv of **1a**, 2 equiv of **2a**, 0.5 equiv of I₂, and 4 equiv of KI in *n*-hexane at 120 °C.

Under the optimized reaction conditions, a series of ketones were investigated for this reaction (Scheme 2). Various substituted aryl methyl ketones (**1a–1o**) could react with sulfonylhydrazides to give β -iodoalkenyl sulfides (**3a–3o**) in moderate to good yields with high E/Z selectivity. Notably, the reaction tolerated a variety of functional groups, such as alkoxy,

Scheme 2. Scope of Ketones 1 for Synthesis of β -Iodoalkenyl Sulfides 3^a

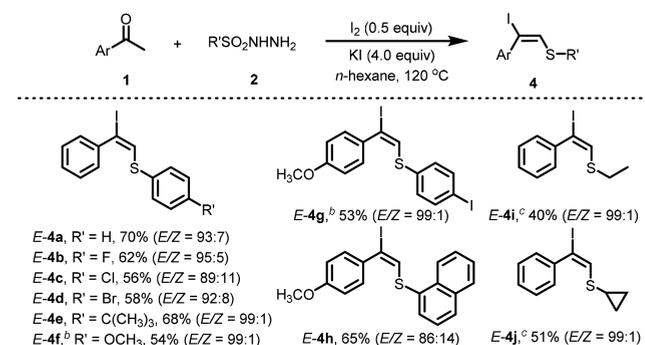


fluoro, chloro, bromo, iodo, and trifluoromethyl with a minor steric effect. However, propiophenone (**1p**) gave **3p** with lower yield; it might be caused by steric effect of methyl group. Acetylferrocene (**1q**) could also preform under the reaction condition. To our delight, aliphatic ketones could also afford corresponding β -iodoalkenyl sulfides (**3r–3t**) in moderate yields, where it was notable that **1t** gave a ring-opened product. Furthermore, when 1-adamantyl methyl ketone (**1u**) was used as substrate, the product more easily converted into alkenyl disulfide **3u**, albeit with lower yield.

Subsequently, the scope of sulfonyl hydrazides was tested (Scheme 3). A range of aryl sulfonyl hydrazides that have electron-donating and electron-withdrawing groups reacted with ketones to give the corresponding β -iodoalkenyl sulfides (**4a–4h**) in moderate to good yields. In addition, alkyl sulfonyl hydrazides proved to be suitable reaction partners, giving

fluoro, chloro, bromo, iodo, and trifluoromethyl with a minor steric effect. However, propiophenone (**1p**) gave **3p** with lower yield; it might be caused by steric effect of methyl group. Acetylferrocene (**1q**) could also preform under the reaction condition. To our delight, aliphatic ketones could also afford corresponding β -iodoalkenyl sulfides (**3r–3t**) in moderate yields, where it was notable that **1t** gave a ring-opened product. Furthermore, when 1-adamantyl methyl ketone (**1u**) was used as substrate, the product more easily converted into alkenyl disulfide **3u**, albeit with lower yield.

Scheme 3. Scope of Sulfonyl Hydrazides 2 for Synthesis of β -Iodoalkenyl Sulfides 4^a

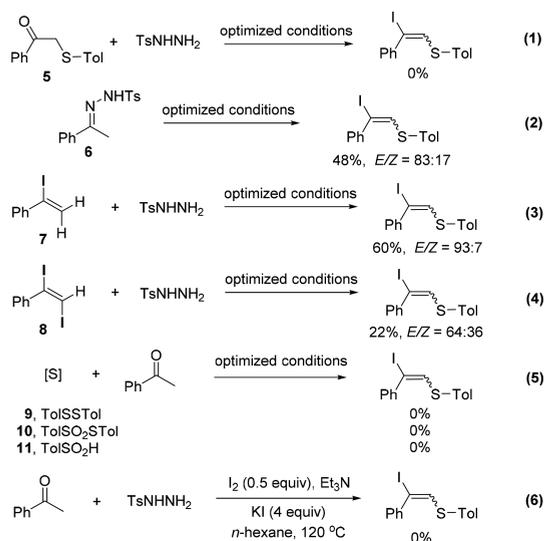


^aReaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), in *n*-hexane (1.0 mL), at 120 °C (oil bath), for 12 h. ^bAt 100 °C. ^cTwo hours.

products **4i** and **4j** with similar efficiency. Notably, ternary ring of **4j** did not provide a ring-opened product, indicating that the process might not involve sulfide radicals.¹⁶

To gain insight into the reaction mechanism, a series of control experiments with possible intermediates was performed (Scheme 4). Initially, as the most possible two intermediates, **5**

Scheme 4. Control Experiments

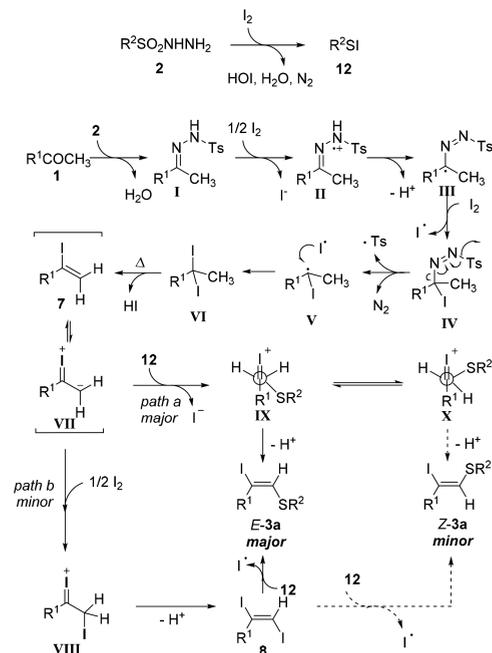


and **6** were first synthesized and tested in the reaction. No reaction was found when **5** was disposed with the standard conditions, while **6** could be transformed into product **3a** in the yield of 48% (eqs 1 and 2). Vinyl iodide (**7**) and vinyl diiodide (**8**) were found to be two critical intermediates during the reaction, both of which could be directly transformed into final product **E-3a**, in 60% and 22% yields, respectively (eqs 3 and 4). Sulfonyl hydrazide **2a** easily decomposed to give disulfide **9**, sulfonothioate **10**, and sulfonic acid **11** by previous study;⁸ however, none of them could afford the desired product under the standard conditions, which substantially demonstrates that the nucleophilicity of the NHNH₂ group in the sulfonyl hydrazide is essential (eq 5). The reaction was also examined in the presence of base; however, no product was observed, which suggests that the reaction may not proceed via diazo compound intermediate (eq 6).¹³

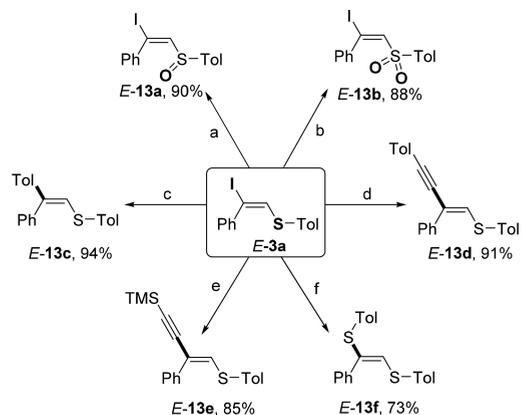
On the basis of the results described above and previous studies,^{8,14,15} a proposed pathway is illustrated (Scheme 5). Initially, ketone **1** reacts with sulfonyl hydrazide **2** to give sulfonylhydrazone **I**, which is oxidized by iodine via single electron transfer to afford intermediate **II**.¹⁴ Isomerization of **II** gives **III**, which reacts with iodine to afford intermediate **IV**, and then **IV** releases N₂ and tosyl group to give **V**, which undergoes radical path with iodine to give **VI**. Under heating conditions, **VI** loses HI to furnish the corresponding **7**.¹⁵ Alternatively, sulfonyl hydrazide **2** reacts with iodine to yield sulfonyl iodide **12**. **VII**, tautomeric isomer of **7**, reacts with **12** to give the target product **3a** via *path a*, while a part of **VII** via *path b* affords **8** and furnishes **E-3a** and **Z-3a**.

To indicate the synthetic utility of the β-iodoalkenyl sulfides, we undertook a series of reactions using the representative product **E-3a**, and the results are summarized in Scheme 6. With different equivalents of *m*-CPBA, **E-3a** could convert into the corresponding oxidized products **E-13a** and **E-13b**, in yields of 90% and 88%, respectively.¹⁷ Arylation of **E-3a** with *p*-

Scheme 5. Plausible Reaction Mechanism



Scheme 6. Transformations of **E-3a**^a



^aReagents and conditions: (a) *m*CPBA (1 equiv), CH₂Cl₂, 40 °C, 4 h. (b) *m*CPBA (2.5 equiv), CH₂Cl₂, 60 °C, 4 h. (c) *p*-MeC₆H₄B(OH)₂ (2 equiv), Pd(OAc)₂ (5 mol %), XPhos (10 mol %), K₂CO₃ (2 equiv), toluene, 110 °C, 12 h. (d) *p*-MeC₆H₄CCH (1.2 equiv), Pd(PPh₃)₄ (5 mol %), CuI (5 mol %), Et₃N (2 equiv), CH₃CN, 70 °C, 3 h. (e) TMSA (1.5 equiv), PdCl₂(PPh₃)₂ (5 mol %), CuI (10 mol %), Et₃N (1.5 equiv), PPh₃ (10 mol %), toluene, 70 °C, 2 h. (f) Pd(PPh₃)₄ (10 mol %), CuI (10 mol %), Et₃N (1.5 equiv), THF, 120 °C, 18 h; the yield of **E-13f** was calculated by sulfur atom. Tol = *p*-tolyl. TMSA = trimethylsilylacetylene. XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl.

tolylboronic acid, via a Suzuki–Miyaura coupling reaction, provided **E-13c** in 94% yield.¹⁸ **E-3a** with *p*-tolylacetylene furnished **E-13d** in 91% yield by Sonogashira–Hagihara coupling.¹⁹ Another conjugated enyne **E-13e** was obtained by introducing trimethylsilylacetylene in 85% yield.²⁰ Interestingly, **E-3a** afforded **E-13f** under palladium catalysis, which can be further oxidized to afford bis-sulfoxide ligands, a potent catalyst precursor similar to White's catalyst.²¹

In conclusion, we have developed an unprecedented protocol for the synthesis of β-iodoalkenyl sulfides through tandem deoxygenative iodization/olefination/sulfonylation of ketones

with sulfonyl hydrazides and iodine. In the presence of 50 mol % iodine, a range of aryl- and alkylsulfonyl hydrazides smoothly reacted with various ketones to give structurally diverse β -iodoalkenyl sulfides with high regio- and stereoselectivity. This protocol obviates the need for alkynes and traditional sulfonylating agents and therefore opens up a new door to construct β -haloalkenyl sulfides in a highly simple fashion. This study paves the way for the use of ketones as precursor of vinyl iodide in chemical synthesis. In addition, synthetic utility of the iodide and sulfide revealed great potential value of β -iodoalkenyl sulfides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00511.

Detailed experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra of key substrates and final products (PDF)

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Notes

The authors declare no competing financial interest.

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