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By-Product-Catalyzed Redox-Neutral Sulfenylation/Deiodination/Aromatization of Cyclic Alkenyl Iodides with Sulfonyl Hydrazides

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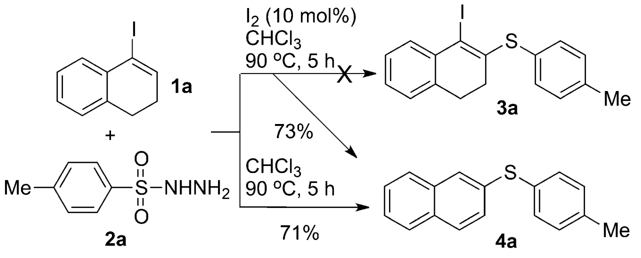
Abstract: A by-product-catalyzed redox-neutral process has been established through tandem sulfenylation/deiodination/aromatization of cyclic alkenyl iodides with sulfonyl hydrazides. In the absence of external catalysts and additives a range of 4-iodo-1,2-dihydronaphthalenes reacted with sulfonyl hydrazides to give structurally diverse 2-naphthyl thioethers in good yields. Mechanistic studies showed that at an early stage sulfonyl hydrazides decomposed completely to thiosulfonates and disulfides and at a late stage the resulting thiosulfonates underwent tandem sulfenylation/deiodination/aromatization with 4-iodo-1,2-dihydronaphthalenes involving a [1,5]-sigmatropic hydrogen shift. Importantly, iodine was generated as a by-product from 4-iodo-1,2-dihydronaphthalenes upon heating and served as a catalyst for the decomposition of sulfonyl hydrazides and subsequent formation of 2-naphthyl thioethers.

Keywords: alkenyl iodides; by-product catalysis; [1,5]-hydrogen shifts; sulfonyl hydrazides; thioethers

The employment of sulfonyl hydrazides as sulfenylating agents has recently emerged as a powerful strategy for the preparation of thioethers through carbon-sulfur bond-forming reactions.[1] In contrast to traditional sulfenylating agents such as thiols, disulfides, sulfenyl halides, and sulfenamides, sulfonyl hydrazides are much more amenable to manipulation in that they are readily accessible and stable solids, free of unpleasant odor, and compatible with water and air. In this regard, we have established that iodine is able to catalyze the sulfenylation of alkenes with sulfonyl hydrazides, wherein no external reductant is required although the valency of sulfur decreases from +6 to +2.[1e,p] The reason behind this is that the $NHNH_2$ group of the sulfonyl hydrazide can reduce the SO_2 group to yield water and nitrogen as by-products. In the course of extending the chemistry of sulfonyl hydrazides to alkenyl iodides, we unexpectedly discovered a by-product-catalyzed redox-neutral process of sulfenylation/deiodination/aromatization in the absence of any external catalysts and additives.

Initially, we employed 10 mol% iodine to catalyze the reaction between cyclic alkenyl iodide **1a** and sulfonyl hydrazide **2a** aiming at an access to vinyl thioether **3a** (Scheme 1). The reaction proceeded in chloroform under air in a sealed tube at 90 °C (oil bath), and to our surprise, 2-naphthyl thioether **4a** rather than vinyl thioether **3a** was obtained in 73% yield. We next carried out a control experiment by heating the mixture of cyclic alkenyl iodide **1a** and sulfonyl hydrazide **2a** in chloroform. Unexpectedly, the reaction furnished 2-naphthyl thioether **4a** in a comparable yield (71%). The fact that the original colorless mixture turned dark purple as the reaction progressed suggested the formation of iodine, which was confirmed by potassium iodide-starch test papers. Moreover, the mixture was detected to be acidic by pH test papers and further detection with starch test papers suggested the formation of HI and HI_3 (generated from HI and iodine). These results encouraged



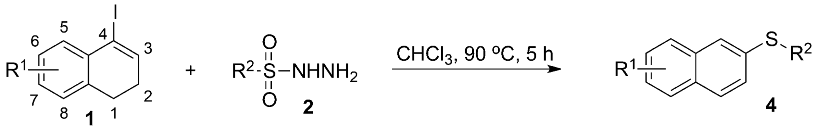
Scheme 1. Reaction of cyclic alkenyl iodide **1a** with sulfonyl hydrazide **2a**.

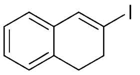
us to develop a tandem process of sulfenylation/deiodination/aromatization, which would be catalyzed by iodine by-product.[2–4]

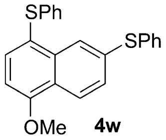
A set of conditions was examined for the reaction of cyclic alkenyl iodide **1a** with sulfonyl hydrazide **2a** in the absence of any external catalysts and additives. Significantly lower yields were achieved when replacing chloroform with 1,2-dichloroethane (60%) or acetonitrile (17%) and even no desired product was isolated from the reaction performed in carbon tetrachloride, toluene, dioxane, nitromethane, *N*,*N*-dimethylformamide, dimethyl sulfoxide, ethanol, or acetic acid. The oxygen in air proved unnecessary according to the control experiment performed under nitrogen, which gave a 70% yield. On the other hand, performing the reaction under oxygen led to a comparable yield (68%). These results suggest that the reaction does not require the presence of oxygen. Nevertheless, we decided to carry out the reaction under air simply because of manipulative convenience.

Cyclic alkenyl iodide **1a** smoothly underwent tandem sulfenylation/deiodination/aromatization with a range of aromatic and aliphatic sulfonyl hydrazides in the absence of any external catalysts and additives and the corresponding 2-naphthyl thioethers were obtained in good yields (Table 1, entries 1–13). Either

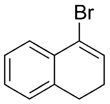
Table 1. Sulfenylation/deiodination/aromatization of cyclic alkenyl iodides with sulfonyl hydrazides.[a]




1a'



4w



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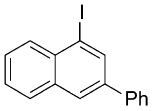


6e

Entry	1	R¹	2	R²	4	Yield [%][b]
1	**1a**	H	**2a**	4-MeC_6H_4	**4a**	71
2	**1a**	H	**2b**	Ph	**4b**	74
3	**1a**	H	**2c**	4-$Me_3CC_6H_4$	**4c**	70
4	**1a**	H	**2d**	4-$MeOC_6H_4$	**4d**	65
5	**1a**	H	**2e**	4-FC_6H_4	**4e**	72
6	**1a**	H	**2f**	4-ClC_6H_4	**4f**	67
7	**1a**	H	**2g**	4-BrC_6H_4	**4g**	63
8	**1a**	H	**2h**	4-IC_6H_4	**4h**	56
9	**1a**	H	**2i**	3-$O_2NC_6H_4$	**4i**	53
10	**1a**	H	**2j**	2,4,6-$Me_3C_6H_2$	**4j**	63
11	**1a**	H	**2k**	2-naphthyl	**4k**	68
12	**1a**	H	**2l**	$Me(CH_2)_7$	**4l**	63
13	**1a**	H	**2m**	$Me(CH_2)_{15}$	**4m**	58
14	**1b**	1-Me	**2b**	Ph	**4n**	64
15[c]	**1c**	1-(3,4-$Cl_2C_6H_3$)	**2b**	Ph	**4o**	54
16[c]	**1d**	1-(2-FC_6H_4)	**2b**	Ph	**4p**	56
17	**1e**	2-Ph	**2b**	Ph	**6e**	84
18[d]	**1f**	3-$CHPh_2$	**2b**	Ph	–	–
19	**1g**	6-OMe	**2b**	Ph	**4q**	54
20	**1h**	6-Cl	**2b**	Ph	**4r**	73
21	**1i**	6-Br	**2b**	Ph	**4s**	68
22	**1j**	7-OMe	**2b**	Ph	**4t**	47
23	**1k**	7-OTs	**2b**	Ph	**4u**	71
24	**1l**	7-Cl	**2b**	Ph	**4v**	71
25[e]	**1m**	8-OMe	**2b**	Ph	**4w**	61
26[d]	**1a′**	–	**2b**	Ph	–	–
27[d]	**5**	–	**2b**	Ph	–	–

[a] *Reaction conditions:* **1** (0.20 mmol), **2** (0.27 mmol), chloroform (0.30 mL), under air in a sealed tube at 90 °C (oil bath) for 5 h (For entries 7–9, 10 h; For entries 12 and 13, 8 h).

[b] Isolated yield.

[c] The reaction was run at 110 °C (oil bath) for 8 h.

[d] No reaction was observed.

[e] **2** (0.54 mmol) was used.

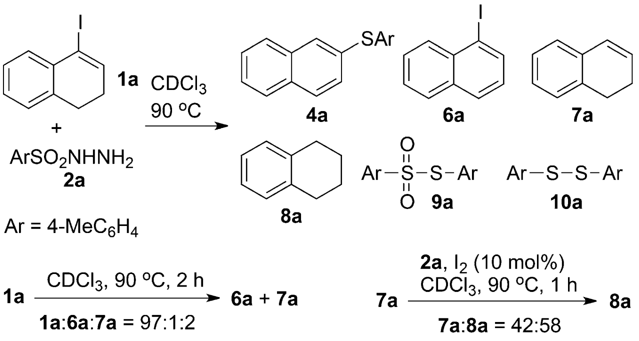
electron-donating or electron-withdrawing groups were successfully introduced into the diaryl thioether products from the corresponding aromatic sulfonyl hydrazides. On the other hand, a variety of cyclic alkenyl iodides exhibited varied levels of reactivity under the standard reaction conditions (Table 1, entries 14–26). While the desired reaction worked well with a 1-substituted 4-iodo-1,2-dihydronaphthalene, a 2-substituted one directly underwent aerobic oxidative dehydrogenation to furnish an aryl iodide in a good yield, probably owing to the steric repulsion in the sulfenylation step (Table 1, entries 14–17).[5] As expected, no reaction was observed with a 3-substituted 4-iodo-1,2-dihydronaphthalene (Table 1, entry 18). The tandem sulfenylation/deiodination/aromatization was successfully extended to a number of 4-iodo-1,2-dihydronaphthalenes having various substituents on the benzene ring (Table 1, entries 19–24). Notably, bissulfenylation was observed with high regioselectivity when the C-8 position of a 4-iodo-1,2-dihydronaphthalene was occupied by an electron-donating group, such as the methoxy group (Table 1, entry 25).[1v] In sharp contrast, no reaction took place either with alkenyl iodide **1a′**, an isomer of alkenyl iodide **1a**, or with alkenyl bromide **5** under the standard conditions (Table 1, entries 26 and 27).

To gain insights into the reaction mechanism, we carried out a ^{1}H NMR spectroscopic analysis of the reaction mixture of alkenyl iodide **1a** with sulfonyl hydrazide **2a** in deuterated chloroform and found that both substrates were subjected to decomposition in the first two hours (Table 2, entries 1 and 2). On one hand, 19% of alkenyl iodide **1a** was converted to aryl iodide **6a**, alkene **7a**, and tetrahydronaphthalene **8a**, whose structure was further confirmed by high resolution mass spectrometric analysis.[6] Although alkenyl iodide **1a** underwent oxidative aromatization and deiodination under the standard conditions to furnish aryl iodide **6a** and alkene **7a**, respectively, the conversion was only 3% in two hours. Moreover, sulfonyl hydrazide **2a** was able to reduce alkene **7a** in the presence of 10 mol% iodine to furnish tetrahydronaphthalene **8a**. On the other hand, sulfonyl hydrazide **2a** decomposed completely in two hours to furnish a 70:30 mixture of thiosulfonate **9a** and disulfide **10a**. In the third hour, alkenyl iodide **1a** and intermediate **9a** were completely consumed to furnish thioether **4a** as the major product and aryl iodide **6a** as a minor product (Table 2, entry 3). Meanwhile, alkene **7a** was completely converted to tetrahydronaphthalene **8a** and a small amount of thiosulfonate **9a** was converted to disulfide **10a**, which, clearly, did not serve as an intermediate for the formation of thioether **4a**.

Simply heating the mixture of alkenyl iodide **1a** and thiosulfonate **9a** in chloroform failed to furnish thioether **4a**, which, however, was obtained in a moderate yield after addition of 10 mol% iodine (Table 3, entries 1 and 2). These results substantially demonstrate that iodine, the afore-mentioned by-product generated from the reaction of alkenyl iodides with sulfonyl hydrazides, serves as a catalyst for the tandem process of sulfenylation/deiodination/aromatization. In sharp contrast, similar reactions with disulfide **10a** furnished an inseparable mixture of thioether **4a** and its isomer **4a′** (Table 3, entries 3 and 4), which, however, was not detected in the reaction of alkenyl iodide **1a** with sulfonyl hydrazide **2a**. These results further confirmed that disulfide **10a** did not serve as an intermediate for the formation of thioether **4a**.

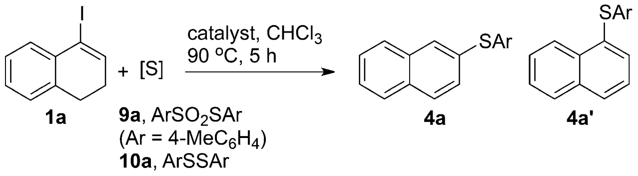
To determine the hydrogen source that formally displaced the iodine atom, we carried out the following deuterium-labelling experiments (Scheme 2). Treatment of thiosulfonate **9j** with monodeuterated alkenyl iodide **1a-D1** in deuterated chloroform did

Table 2. ^{1}H NMR spectroscopic analysis of the reaction mixture.



Entry	Time [h]	**1a**:**4a**:**6a**:**7a**:**8a**	**2a**:**4a**:**9a**:**10a**
1	1	82:0:1:6:11	51:0:36:13
2	2	81:0:3:3:13	0:0:70:30
3	3	0:72:14:0:14	0:66:0:34
4	4	0:72:14:0:14	0:66:0:34

Table 3. Transformations of intermediates.[a]

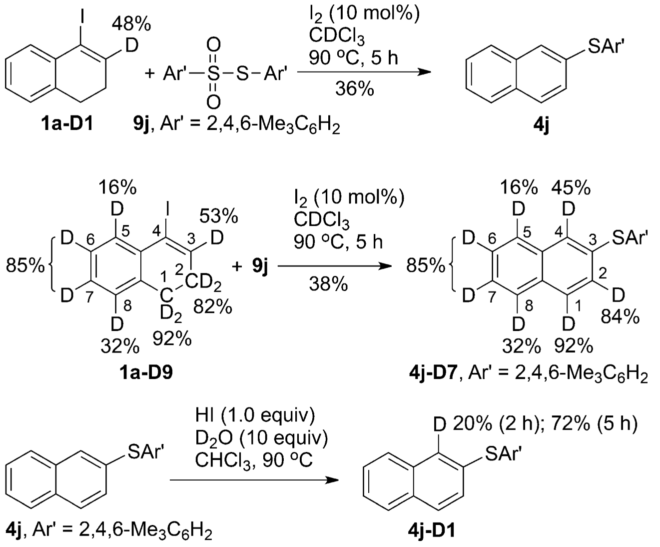


Entry	[S]	Catalyst	Yield [%][b]	**4a**:**4a′**[c]
1	**9a**	none	0	–
2	**9a**	I_2 (10 mol%)	46	>99:1
3	**10a**	none	46	39:61
4	**10a**	I_2 (10 mol%)	50	60:40

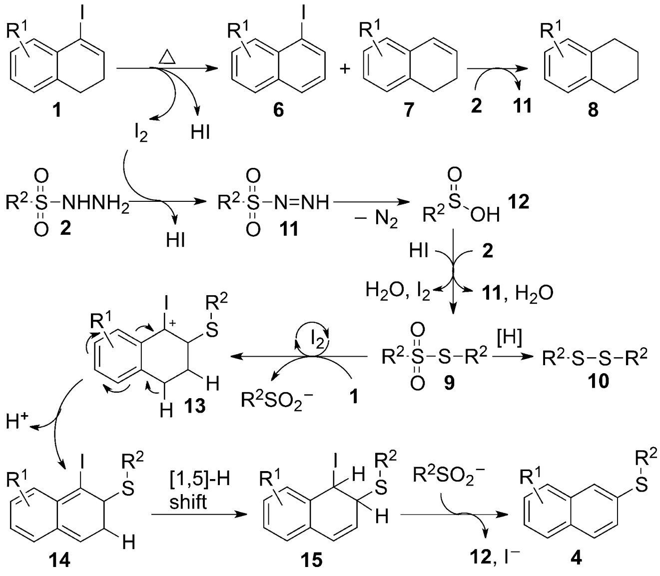
[a] *Reaction conditions:* **1a** (0.20 mmol), [S] (0.135 mmol), catalyst (if any), chloroform (0.30 mL), under air in a sealed tube at 90 °C (oil bath) for 5 h.

[b] Isolated yield.

[c] Determined by ^{1}H NMR spectroscopic analysis.



Scheme 2. Deuterium-labelling experiments.



Scheme 3. Proposed major reaction pathways.

not result in deuterium incorporation into thioether **4j**. In contrast, a similar reaction with polydeuterated alkenyl iodide **1a-D9** furnished thioether **4j-D7** with 45% deuterium incorporation at C-4. These results, along with the fact that the percentage of deuterium increased slightly at C-2, suggest that a hydrogen/deuterium shift occurred from C-2 to C-4. The level of deuterium incorporation at C-4 in thioether **4j-D7** was much lower than the percentage of deuterium at C-2 in alkenyl iodide **1a-D9** simply due to hydrogen/deuterium exchange with the moisture in the air under the standard conditions. The hydrogen/deuterium exchange was confirmed by the following experiment. Treatment of thioether **4j** with one equivalent of HI and ten equivalents of deuterated water furnished thioether **4j-D1** with deuterium incorporation exclusively at the α-position.

Based on the above experimental results and previous relevant studies, we propose the following major reaction pathways as depicted in Scheme 3 for the tandem process of sulfenylation/deiodination/aromatization. At an early stage, alkenyl iodide **1** decomposes upon heating to generate small amounts of aryl iodide **6**, alkene **7**, iodine, and HI. Alkene **7** is reduced by sulfonyl hydrazide **2** to give by-product **8**.[7] While the decomposition of sulfonyl hydrazide **2** to sulfinic acid **12** can take place upon heating,[8,9] the iodine by-product dramatically accelerates this process.[1a,e,p] Reduction of sulfinic acid **12** occurs either with sulfonyl hydrazide **2** or with HI, and a small portion of the resulting thiosulfonate **9** is further reduced to give disulfide **10** as another by-product.[1p] Thiosulfonate **9** is activated by iodine and undergoes regioselective electrophilic addition to alkenyl iodide **1** to generate carbocation **13**,[10] deprotonation of which gives dihydronaphthalene **14**. Then a [1,5]-sigmatropic hydrogen shift occurs to generate alkene **15**,[11] from which elimination of HI gives thioether **4**.

In summary, we have developed, for the first time, an efficient by-product-catalyzed redox-neutral process through tandem sulfenylation/deiodination/aromatization of cyclic alkenyl iodides with sulfonyl hydrazides. A range of 4-iodo-1,2-dihydronaphthalenes smoothly reacted with sulfonyl hydrazides in the absence of any external catalysts and additives to give structurally diverse 2-naphthyl thioethers in good yields. Mechanistic studies showed that at an early stage sulfonyl hydrazides decomposed completely to thiosulfonates and disulfides and at a late stage the resulting thiosulfonates underwent tandem sulfenylation/deiodination/aromatization with 4-iodo-1,2-dihydronaphthalenes involving a [1,5]-sigmatropic hydrogen shift. Importantly, iodine was generated as a by-product from 4-iodo-1,2-dihydronaphthalenes upon heating and served as a catalyst for the decomposition of sulfonyl hydrazides and subsequent formation of 2-naphthyl thioethers.

Experimental Section

General Procedure for the Sulfenylation/Deiodination/Aromatization of Cyclic Alkenyl Iodides with Sulfonyl Hydrazides

To a solution of sulfonyl hydrazide **2** (0.27 mmol) in chloroform (0.30 mL) was added alkenyl iodide **1** (0.20 mmol). The mixture was heated at 90 °C (oil bath) under air in a sealed tube for 5 h, cooled to room temperature, and purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (0:10 to 1:10 v/v), to give thioether **4**.

Acknowledgements

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[6] For details, see the Supporting Information.

[7] For reviews on the reduction of alkenes with sulfonyl hydrazides, see: a) D. J. Pasto, R. T. Taylor, *Org. React.* **1991**, *40*, 91–155; b) D. J. Pasto, in: *Comprehensive Organic Synthesis*, (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, Vol. 8, pp 471–488.

[8] A. Deavin, C. W. Ree, *J. Chem. Soc.* **1961**, 4970–4973.

[9] Sulfinic acid **12a** ($R^2 = 4\text{-}MeC_6H_4$) was not observed by ^1H NMR spectroscopic analysis of the reaction mixture of alkenyl iodide **1a** with sulfonyl hydrazide **2a** (Table 2). This suggests that the conversion of sulfonyl hydrazide **2** to sulfinic acid **12** is much faster than that of sulfinic acid **12** to thiosulfonate **9**. In addition, we treated sulfinic acid **12a** with alkenyl iodide **1a** under the standard conditions and obtained thioether **4a** in 57% yield.

[10] The formation of unstable benzylic cation intermediates would account for the failed reactions observed for alkenyl iodide **1a′**, alkenyl bromide **5**, and 4-iodo-6-nitro-1,2-dihydronaphthalene.

[11] For a review on [1,5]-hydrogen shifts, see: a) C. W. Spangler, *Chem. Rev.* **1976**, *76*, 187–217. For theoretical calculation on the effects of aromatic stabilization on the rates of [1,5]-hydrogen shifts, see: b) I. V. Alabugin, M. Manoharan, B. Breiner, F. D. Lewis, *J. Am. Chem. Soc.* **2003**, *125*, 9329–9342.

6 By-Product-Catalyzed Redox-Neutral Sulfenylation/Deiodination/Aromatization of Cyclic Alkenyl Iodides with Sulfonyl Hydrazides

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