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α-Diketone Formation Accompanied by Oxidation of Sulfur Functional Group by the Reaction of o-Alkynylarenesulfoxide with Iodine

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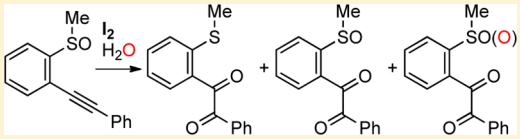
Supporting Information

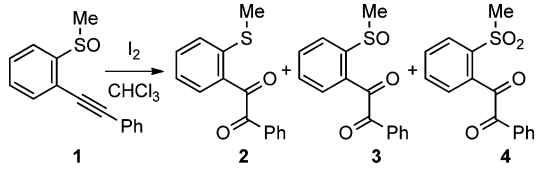
ABSTRACT: The reaction of *o*-alkynylarenesulfoxide with iodine was investigated in detail, revealing functionalities of the formation of α-diketones with sulfenyl, sulfinyl, and sulfonyl. Additives can change the ratio of products to give medium-to-excellent yields. Results show that water is taken into only sulfonyl compound and that other oxygen atoms constructed in the products are presumably derived from sulfoxide of the starting material and molecular oxygen.



Organic synthesis without transition metals is examined intensively by academic scientists and manufacturers because of resource problems. Iodine is an easily handled halogen molecule in organic synthesis because of its stability and easy handling as a solid under ambient conditions.[1] In various organic reactions using I_2, investigations have been made of the electrophilic activation of alkynes with I_2 to produce iodinated compounds[2] such as heteroaromatics,[3−6] fused aromatics,[7] benzenes,[8] and cyclic vinyl iodides,[8a,9] which are important for the construction of novel functional materials. Therefore, the activation of alkynes with I_2 presents the potential for use with organic synthesis. Actually, some reports describe the reaction of alkynes with I_2 in DMSO to give α-diketones.[10,11] Sakthivel and Srinivasan recently reported the formation of α-diketones by the reaction of *o*-alkynylarenecarboxaldehydes with I_2/H_2O.[12] A similar reaction using *o*-alkynylarenesulfoxide was also reported by Chen and co-workers.[13] They obtained α-diketones bearing sulfenyl group in moderate to good yield. The net reaction involves the oxidation of alkynyl part with the reduction of the sulfoxide moiety. We examined the reaction reported by Chen et al. just in time for publication. However, we obtained additional unprecedented information related to this reaction to give the compounds having the different oxidation state of sulfur. We herein report results of our detailed investigation of the reaction of *o*-alkynylarenesulfoxide with I_2. We found a unique additive effect to give the corresponding α-diketones.

Chen and co-workers reported a reaction of 1-(methylsulfinyl)-2-(2-phenylethynyl)benzene (**1**) with I_2 in CH_2Cl_2 in the presence of $NaHCO_3$ to give α-diketone with a methylsulfenyl group (**2**) in 68% yield (Table 1, entry 1). When we examined this reaction in $CHCl_3$ without $NaHCO_3$, the formation of **2** accompanied by **3** and **4** was observed, although the main product was **2** (entry 2). When various solvents were examined, the formation of three compounds was observed in varying ratios (entries 3−6). The reaction was inhibited in MeOH because of complexation of alcohol with I_2 (entry 6). This reaction proceeded using *N*-iodosuccinimide

Table 1. α-Diketone Formation by the Reaction of 1 with I_2[a]



1 **2** **3** **4**

		yield (%)		
entry	additives (equiv)	**2**	**3**	**4**
1[b]	$NaHCO_3$ (2.0)	68		
2		**45**	19	5
3[c]		**53**	31	9
4[d]		14	9	trace
5[e]		8	21	4
6[f]		trace	3	6
7	NIS (1.0)[g]	39	11	11
8	NBS (1.0)[h]	no reaction		
9[i]		35	**51**	10
10[j]		52	33	15
11	O_2[k]	35	13	5
12	H_2O (3.0)	21	**50**	13
13[l]	K_2CO_3 (1.8)	10	15	**42**
14	Phenol (1.2)	**51**	32	11
15	Phenol (1.2) + K_2CO_3 (1.0)	**97**	0	0

[a]Reaction conditions: 1 molar equiv of I_2 in $CHCl_3$ for 1 d. [b]Reference 4. Conditions: 2 molar equiv of I_2 in CH_2Cl_2 for 8 h. [c]In CH_3CN. [d]In THF. [e]In toluene. [f]In MeOH. [g]NIS was used instead of I_2. Reacted for 2 d. [h]NBS was used instead of I_2. [i]2 molar equiv of I_2 was used. [j]Under air atmosphere. [k]O_2 atmosphere. [l]**1** was recovered in 28% yield.

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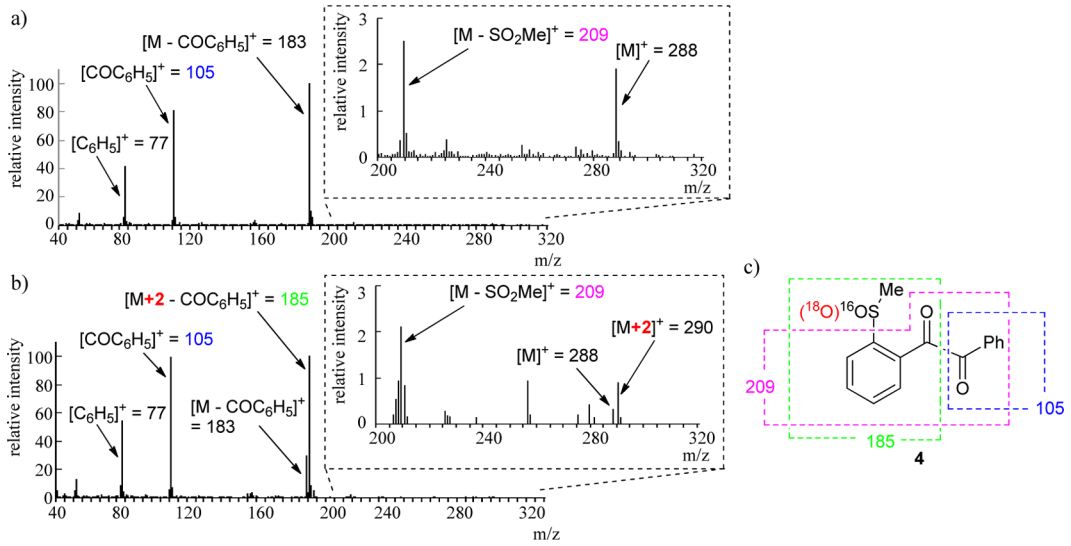

Figure 1. Results of EI-Mass spectrographs obtained from the reaction (a) without and (b) with $H_2{}^{18}O$. (c) Obtained fragment patterns of **4**.

(NIS) as the I^+ source, although the reaction with NBS did not occur (entries 7 and 8). Therefore, the I^+ source is necessary to achieve the α-diketone formation. Surprisingly, when the amount of I_2 was changed, **3** was obtained as a main product in 51% yield (entry 9).

Furthermore, we examined the additives to improve the yield of each product in addition to giving information about the reaction mechanism. When the reaction was conducted under air atmosphere, the yields of **2**–**4** were slightly increased (entry 10). On the contrary, under O_2 atmosphere, the yields of α-diketones were decreased with the formation of side products which were not obtained in the standard conditions (entry 2 vs 10). By addition of H_2O, the formation of **3** was observed in 50% yield (entry 12). The addition of K_2CO_3 was efficient to increase **4** as a main product (entry 13). Excellent yield of **2** was obtained in the presence of both phenol and K_2CO_3 (entry 15), whereas a slight increase of the yield of **2** was observed (entry 14).

In these reactions, we noticed two problems: (1) source of oxygen on diketone and sulfur oxide and (2) reaction mechanisms for **2**–**4**. We first investigated the oxygen source using $H_2{}^{18}O$. The reaction with 3 equiv of $H_2{}^{18}O$ was conducted in anhydrous $CHCl_3$ with molecular sieves 4A before use. According to the mechanism proposed by Chen, ^{18}O enriched **2** should be obtained because one of two oxygens in diketone is derived from H_2O. However, from mass spectroscopic analysis of the obtained compounds, the ^{18}O enrichment was observed only in **4**, and ^{18}O enrichments of **2** and **3** were within the margin of error.[14] Therefore, H_2O is directly related only to the formation of **4**. Furthermore, the investigation of the fragmentation from **4** helps to infer the position of ^{18}O enriched oxygen. When **4** derived from the reaction without $H_2{}^{18}O$ was examined using EI-Mass spectroscopy, the fragmentation peaks were observed along with the parent peak ($[M]^+$ = 288). The analysis revealed that the removal of each of the SO_2Me part and COC_6H_5 part occurred to give $[M - SO_2Me]^+$ = 209 and $[M - COC_6H_5]^+$ = 183 peaks, respectively (Figure 1a). The large value by two mass was obtained in the parent peak ($[M + 2]^+$ = 290) of **4** derived from the reaction within $H_2{}^{18}O$ (Figure 1b). Furthermore, the fragment peak derived from the loss of COC_6H_5 moiety gave the large value ($[M + 2\text{-}COC_6H_5]^+$ = 185) as the main peak with a small intensity of the original peak ($[M - COC_6H_5]^+$ = 183) (Figure 1b). However, the peak from the loss of SO_2Me moiety was mainly observed in the same value ($[M - SO_2Me]^+$ = 209). These results suggest that the oxygen of H_2O is introduced to sulfonyl moiety in **4**.

In some reactions, the yields of **2** and **3** were higher than 50% under N_2 or Ar atmosphere (Table 1, entries 3, 9, 12, 14, and 15), which implies exclusion of the possibility of the oxygen at sulfoxide of **1** as both oxygen sources of diketones. Furthermore, from investigation of the reaction in $CDCl_3$ with NMR analysis, the products of **2**–**4** were recognizable without workup (see Figure S1, Supporting Information). Therefore, we suspected molecular oxygen as another oxygen source. We conducted the reaction in a vessel equipped with N_2 or Ar balloon made from latex. However, we were unable to neglect the exchange of gases in the balloon in a period of the reaction time (1–2 d). Therefore, the reaction was examined under sealed conditions. After the addition of I_2 under Ar atmosphere, the reaction vessel was closed with a glass stopcock. Then the reaction mixture was stirred at room temperature for 10 h. After the usual workup, the decrease of the reaction rate was observed to give 15% recovery of the starting material (**1**) against the standard conditions (8%) with decreasing of the total yield of α-diketones (from 92% to 65%) (Scheme 1).[15,16] Therefore, we concluded that the contaminated molecular oxygen is the oxygen source of some oxygen atoms in the products.

Next, we tried to solve the reaction mechanism to give each product. Focusing on the structural differences of the products, the three products are only different in terms of the oxidation state on the sulfur atom. However, no oxidation and disproportionation reactions were observed in between **2**–**4** (see Scheme S1, Supporting Information). Based on these results, we proposed the reaction mechanism depicted in Scheme 2. The activation of alkyne with I_2 occurred to form the corresponding iodovinyl intermediate (**A** and **A**′), which is replicated from Chen's proposal.[13] From the result of the nonparticipation of H_2O at diketone moiety, the ring-opening reaction proceeds by the addition of molecular oxygen to give intermediate **B**, derived from intermediate **A**.[17] When the reaction is conducted without the additives, intramolecular electron transfer from iodide to sulfide cation radical occurs to

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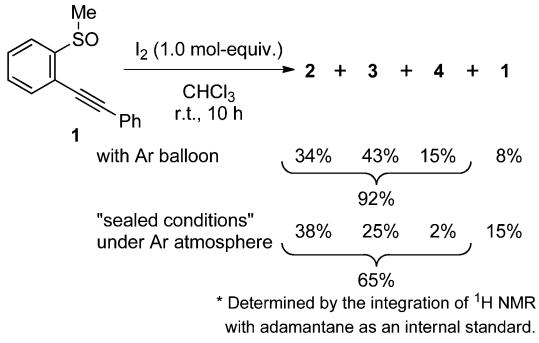
Scheme 1. Effect of Molecular Oxygen with the Reaction under "Sealed Conditions"



give the peroxy radical (path *a*). After cleavage of O−O bond, **2** is formed. In the case of the addition of H_2O (Table 1, entry 12), the polarity of the solvent will be increased to separate iodide and sulfide cation radical in **B**. Therefore, the electron transfer will be difficult, and the radical coupling of **B** occurs to give the cyclized intermediate **C** (path *b*). When the large amount of I_2 is introduced (Table 1, entry 9), the electron transfer also ceases by the formation of I_3^- ion by the complexation of iodide and I_2. The attack of iodide and the O−O bond cleavage occurred to form **3**. These mechanisms are reliable in the point of solvent effect. By increasing the polarity of the solvent, increase in the ratio of **3** (and **4**) was observed (Table 1, entries 2 and 3). Furthermore, solutions of THF and toluene, which can act as radical traps, show low yields of the products (Table 1, entries 4 and 5). As described above, the oxygen source of sulfone group is H_2O. Furthermore, the strong basic conditions with K_2CO_3 promote the formation of **4** (Table 1, entry 13). Therefore, nucleophilic HO^- will be formed from the reaction of H_2O and K_2CO_3. The attack to positive charge on sulfur atom in intermediate **C** leads to **4** with subsequent deprotonation (path *c*).

The mechanism summarized in Scheme 2 could not explain the selective formation of **2** in the presence of the combination of phenol and K_2CO_3 (Table 1, entry 15). Therefore, another reaction mechanism can also be applied to the formation of **2**. Considering the antioxidant effect of phenol, the reaction mechanism depicted in Scheme 3 can be reliable. Molecular oxygen receives one electron from phenoxide to give anion radical. Furthermore, the additional acceptance of one electron from phenol existing in equilibrium with phenoxide under reaction conditions produces potassium hydroperoxide,[18] which is known as a good nucleophile.[19] Therefore, the nucleophilic attack of hydroperoxide anion to the intermediate **A** and **A′** proceeds to the ring-opening reaction with subsequent cleavage of C−I and O−O bond with the attack of iodide to give **2**.[17]

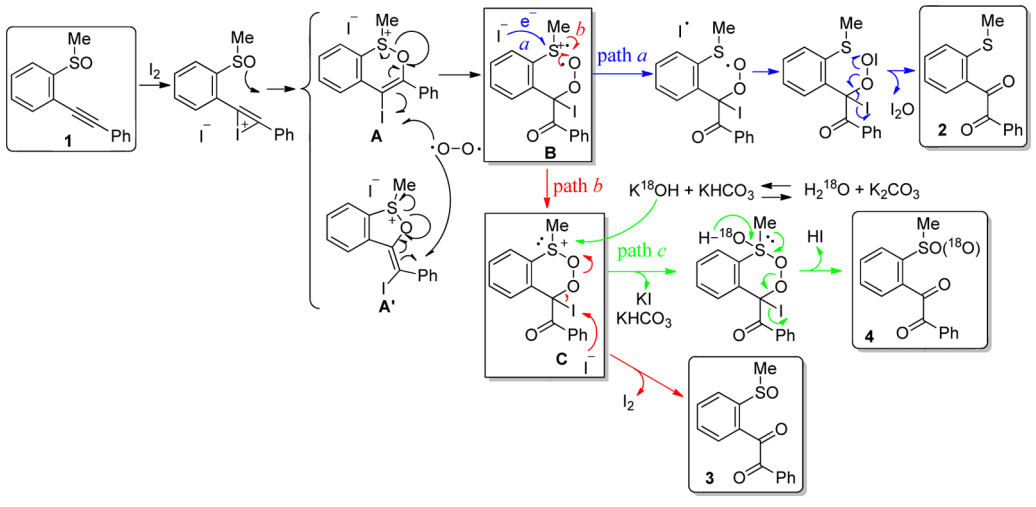
In summary, results show that the *α*-diketone formation accompanied oxidation of sulfur atom in the reaction of *o*-alkynylarenesulfoxide with I_2. Introducing the additives and ratio of the products can vary in medium-to-excellent yields. Oxygen sources of the products were also examined, revealing that both H_2O and molecular oxygen are plausible. Based on those results, we advanced the improved reaction mechanism based on Chen's report, which suggests that it is feasible in organic synthesis to use the complexed reaction starting by the activation of acetylene with I_2. *α*-Diketones play an important role in organic synthesis because of their ready conversion into various materials.[20] Consequently, *α*-diketone formation with additional functional group transformation can widen the possibilities for organic synthesis.

EXPERIMENTAL SECTION

General Information. Melting points were uncorrected. NMR measurements were recorded with a 300 MHz spectrometer for ^1H NMR and with a 75 MHz spectrometer for ^{13}C NMR. Chemical shifts (δ) of ^1H NMR were expressed in parts per million downfield from tetramethylsilane in $CDCl_3$ (δ = 0) as an internal standard. Multiplicities are indicated as s (singlet), bs (broadened singlet), d (doublet), t (triplet), m (multiplet), and coupling constants (J) are reported in hertz units. Chemical shifts (δ) of ^{13}C NMR are expressed in parts per million downfield or upfield from $CDCl_3$ (δ = 77.0) as an internal standard. Infrared spectra (IR) were recorded on a KBr disk or on a NaCl plate. Mass spectra were recorded with ESI-Orbitrap (cation mode) spectrometer. Analytical thin-layer chromatography (TLC) was performed on glass plates that had been precoated with silica gel (0.25 mm layer thickness). Column chromatography was performed on 70−230 mesh silica gel.

Preparation of 1-(Methylsulfinyl)-2-(phenylethynyl)benzene (1). A mixture of 2-iodothioanisole (0.600 g, 2.40 mmol), $PdCl_2(PPh_3)_2$ (25.2 mg, 0.0360 mmol), and CuI (42.0 mg, 0.22 mmol) was dissolved in NEt_3 (10 mL). To the solution was added ethynylbenzene (0.244 g, 2.39 mmol), and the mixture was stirred at 60 °C for 22 h. To the reaction mixture was added H_2O (10 mL), with

Scheme 2. Plausible Reaction Mechanism for the Formation of 2−4



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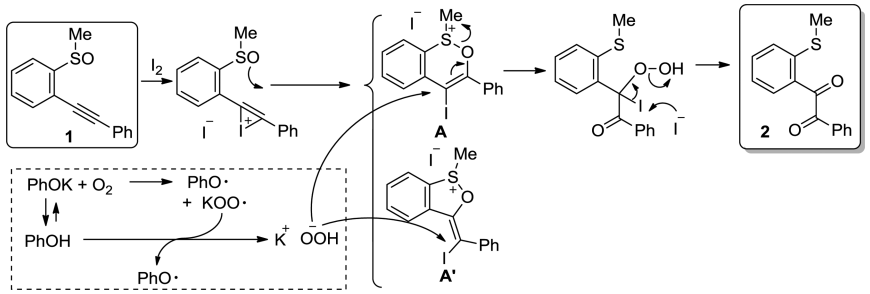
Scheme 3. Another Reaction Mechanism Forming 2 in the Presence of Phenol and K_2CO_3



subsequent extractraction with $CHCl_3$ (10 mL × 4). The organic layer was filtered with a pad of Celite, and the filtrate was dried with $MgSO_4$. After the filtration and evaporation, the yellow solid was obtained as 1-(methylthio)-2-(phenylethynyl)benzene[5a] in quantitative yield. The obtained solid was dissolved in EtOH (100 mL) and H_2O (100 mL), and the solution was added $NaIO_4$ (1.027 g, 4.8 mmol). After being stirred at room temperature for 5 d, the reaction mixture was extracted with $CHCl_3$ (10 mL × 4). The organic layer was washed with saturated aq Na_2SO_3 (15 mL × 4) and brine (15 mL × 2). After drying with $MgSO_4$ and evaporation, the residue was subjected to column chromatography on SiO_2 ($CHCl_3$) to give 1-(methylsulfinyl)-2-(phenylethynyl)benzene (**1**) (0.286 g, 1.19 mmol, 50%) as a pale yellow oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (s, 3H), 7.38−7.40 (m, 3H), 7.44−7.62 (m, 5H), 7.99 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.1, 84.2, 98.0, 119.3, 122.0, 123.3, 128.5, 129.2, 129.5, 130.3, 131.5, 132.4, 147.3; IR (NaCl) 3475, 3056, 2216, 1598, 1492, 1463, 1442, 1290, 1124, 1072, 1040, 952, 847, 758, 690 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}ONaS$ ([M + Na]$^+$) 263.0501, found 263.0499.

Typical Procedure for the Reaction of 1 with I_2. To a solution of **1** (93.1 mg, 0.387 mmol) in $CHCl_3$ (10 mL) was added I_2 (98.4 mg, 0.388 mmol) at room temperature under N_2 atmosphere. After being stirred at room temperature for 1 d, to the resultant mixture was added saturated aq $Na_2S_2O_3$ (10 mL), with subsequent extraction with $CHCl_3$ (10 mL × 4). The combined organic layer was dried with $MgSO_4$. After filtration and evaporation, the residue was subjected to column chromatography on SiO_2 ($CHCl_3$/ EtOAc = 2:1) to give 1-(2-(methylthio)phenyl)-2-phenylethane-1,2-dione (**2**) (44.3 mg, 0.173 mmol, 45%), 1-(2-(methylsulfinyl)phenyl)-2-phenylethane-1,2-dione (**3**) (20.4 mg, 0.0750 mmol, 19%), and 1-(2-(methylsulfonyl)phenyl)-2-phenylethan-1,2-dione (**4**) (5.8 mg, 0.020 mmol, 5%), respectively.

1-(2-(Methylthio)phenyl)-2-phenylethane-1,2-dione (2):[11] yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.23 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 8.1 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.57 (t, J = 8.2 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.99 (d, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.7, 124.6, 127.0, 128.9, 130.0, 131.6, 133.3, 133.4, 133.9, 134.4, 143.5, 193.0, 194.9; IR (NaCl) 3063, 2923, 2855, 1652, 1587, 1558, 1459, 1451, 1434, 1363, 1320, 1281, 1264, 1208, 1181, 1142, 1081, 1047, 1021, 998, 965, 879, 858, 800, 748, 721, 686, 662, 646 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{12}O_2NaS$ ([M + Na]$^+$) 279.0450, found 279.0450.

1-(2-(Methylsulfinyl)phenyl)-2-phenylethane-1,2-dione (3): pale yellow solid; mp 65.5−67.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94 (s, 3H), 7.54 (t, J = 7.5 Hz, 2H), 7.60 (dt, J = 1.1 and 7.6 Hz, 1H), 7.70 (t, J = 7.4 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.93 (dd, J = 1.1 and 7.2 Hz, 1H), 7.94 (d, J = 7.9 Hz, 2H), 8.47 (d, J = 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.7, 125.0, 129.1, 129.5, 129.9, 130.4, 132.4, 133.1, 135.3, 135.6, 151.3, 192.7, 194.6; IR (NaCl) 3461, 2990, 2924, 1668, 1595, 1569, 1451, 1436, 1421, 1324, 12127, 1177, 1165, 1137, 1074, 1049, 1030, 998, 968, 957, 945, 893, 870, 793, 750, 719, 693, 685, 663, 645, 615 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}O_3NaS$ ([M + Na]$^+$) 295.0399, found 295.0398.

1-(2-(Methylsulfinyl)phenyl)-2-phenylethane-1,2-dione (4): yellow crystals (hexane−chloroform); mp 115.0−116.8 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (s, 3H), 7.52 (t, J = 7.3 Hz, 2H), 7.66 (t, J = 7.5 Hz, 1H), 7.71−7.79 (m, 3H), 8.01 (dd, J = 2.1 and 7.8 Hz, 1H), 8.17 (d, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.7, 128.5, 129.1, 131.0, 131.1, 132.2, 132.6, 134.0, 134.3, 137.3, 139.3, 189.0, 192.0; IR (KBr) 3026, 2928, 1679, 1597, 1453, 1411, 1311, 1200, 1185, 1154, 1121, 962, 854, 781, 756, 739, 705, 635, 543, 534 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{12}O_4NaS$ ([M + Na]$^+$) 311.0349, found 311.0338.

Reaction of 1-(Methylsulfinyl)-2-(phenylethynyl)benzene (1) with I_2 and H_2O. To a solution of **1** (34.1 mg, 0.142 mmol) in $CHCl_3$ (10 mL) were added H_2O (7.8 mg, 0.43 mmol) and I_2 (36.1 mg, 0.142 mmol) at room temperature under N_2 atmosphere. After the solution was stirred at room temperature for 1 d, the usual workup was used to give **2** (7.5 mg, 0.029 mmol, 21%), **3** (19.2 mg, 0.0705 mmol, 50%), and **4** (5.3 mg, 0.018 mmol, 13%), respectively.

Reaction of 1 with I_2 and K_2CO_3. To a solution of **1** (27.0 mg, 0.112 mmol) in $CHCl_3$ (10 mL) were added K_2CO_3 (27.2 mg, 0.197 mmol) and I_2 (25.5 mg, 0.100 mmol) at room temperature under N_2 atmosphere. After the mixture was stirred at room temperature for 1 d, the usual workup was used to give **2** (2.6 mg, 0.010 mmol, 10%), **3** (4.7 mg, 0.017 mmol, 15%), **4** (13.5 mg, 0.468 mmol, 42%), and recovered **1** (7.5 mg, 0.031 mmol, 28% recovery), respectively.

Reaction of 1 with I_2, Phenol, and K_2CO_3. To a solution of **1** (60.1 mg, 0.250 mmol) in $CHCl_3$ (2.5 mL) were added I_2 (69.5 mg, 0.274 mmol), K_2CO_3 (32.1 mg, 0.232 mmol), and phenol (29.5 mg, 0.313 mmol) at room temperature under N_2 atmosphere. After the mixture was stirred at room temperature for 1 d, the usual workup was used to give **2** (62.4 mg, 0.243 mmol, 97%).

Reaction under "Sealed Conditions". Compound **1** (36.0 mg, 0.150 mmol) in a two-neck flask equipped with a two-way stopcock and rubber septum was dissolved in $CHCl_3$ (5 mL). Dissolved oxygen was driven out of the solution by bubbling Ar gas for 1 h, followed by three freeze−thaw cycles. To the solution was added I_2 (38.1 mg, 0.150 mmol) in a stream of Ar gas. After addition of I_2, the septum was exchanged for a glass stopcock, and the reaction was conducted under sealed conditions. After the solution was stirred at room temperature for 10 h, the usual workup (wash with aq $Na_2S_2O_3$, extraction with $CHCl_3$, and dry with $MgSO_4$) gave 49.5 mg of the crude products. The product ratio was determined by the integration of methyl protons of **1**−**4** in ^{1}H NMR analysis with adamantine as an internal standard.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra for **1**−**4**, ^{1}H NMR analysis in the reaction of **1** with I_2 (Figure S1), oxidation and disproportionation experiments of **2**−**4** (Scheme S1), and the plausible reaction mechanisms through intermediate **A**′ (Schemes S2 and S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Smith, M. B. *Encyclopedia of Reagent for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; pp 2796−2802. Togo, H.; Iida, S. *Synlett* **2006**, 2159−2175.

(2) (a) Hitt, D. M.; O'Connor, J. M. *Chem. Rev.* **2011**, *111*, 7904−7922. (b) Banerjee, A. K.; Laya, M. S.; Cabrera, E. V. *Curr. Org. Chem.* **2011**, *15*, 1058−1080. (c) Yamamoto, Y.; Gridnev, I. D.; Patil, N. T.; Jin, T. *Chem. Commun.* **2009**, 5075−5087.

(3) (a) Du, X.; Chen, H.; Chen, Y.; Che, J.; Liu, Y. *Synlett* **2011**, 1010−1014. (b) Du, H.-A.; Zhang, X.-G.; Tang, R.-Y.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 7844−7848. (c) Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 10292−10296. (d) Yao, T.; Yue, D.; Larock, R. C. *J. Org. Chem.* **2005**, *70*, 9985−9989. (e) Colobert, F.; Castanet, A.-S.; Abillard, O. *Eur. J. Org. Chem.* **2005**, 3334−3341.

(4) (a) Mitamura, T.; Ogawa, A. *J. Org. Chem.* **2011**, *76*, 1163−1166. (b) Huo, Z.; Gridnev, I. D.; Yamamoto, Y. *J. Org. Chem.* **2010**, *75*, 1266−1270. (c) Ding, Q.; Chen, Z.; Yu, X.; Peng, Y.; Wu, J. *Tetrahedron Lett.* **2009**, *50*, 340−342. (d) Huo, Z.; Tomeba, H.; Yamamoto, Y. *Tetrahedron Lett.* **2008**, *49*, 5531−5533. (e) Halim, R.; Scammells, P. J.; Flynn, B. L. *Org. Lett.* **2008**, *10*, 1967−1970. (f) Kim, I.; Kim, S. G.; Kim, J. K.; Lee, G. H. *Tetrahedron Lett.* **2007**, *48*, 8976−8981. (g) Hessian, K. O.; Flynn, B. L. *Org. Lett.* **2006**, *8*, 243−246. (h) Yue, D.; Yao, T.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 62−69. (i) Amjad, M.; Knight, D. W. *Tetrahedron Lett.* **2004**, *45*, 539−541.

(5) (a) Yue, D.; Larock, R. C. *J. Org. Chem.* **2002**, *67*, 1905−1909. (b) Flynn, B. L.; Verdier-Pinard, P.; Hamel, E. *Org. Lett.* **2001**, *3*, 651−654.

(6) (a) Schumacher, R. F.; Rosário, A. R.; Souza, A. C. G.; Menezes, P. H.; Zeni, G. *Org. Lett.* **2010**, *12*, 1952−1955. (b) Kesharwani, T.; Worlikar, S. A.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 2307−2312.

(7) (a) Zhang, X.; Sarkar, S.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 236−243. (b) Yue, D.; Cá, N. D.; Larock, R. C. *J. Org. Chem.* **2006**, *71*, 3381−3388. (c) Goldfinger, M. R.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578−4593.

(8) (a) Crone, B.; Kirsch, S. F.; Umland, K.-D. *Angew. Chem., Int. Ed.* **2010**, *49*, 4661−4664. (b) Matsumoto, S.; Takase, K.; Ogura, K. *J. Org. Chem.* **2008**, *73*, 1726−1731.

(9) (a) Harschneck, T.; Kirsch, S. F.; Wegener, M. *Synlett* **2011**, 1151−1153. (b) Lim, C.; Rao, M. S.; Shin, S. *Synlett* **2010**, 368−373. (c) Pradal, A.; Nasr, A.; Toulec, P. Y.; Michelet, V. *Org. Lett.* **2010**, *12*, 5222−5225. (d) Khan, Z. A.; Wirth, T. *Org. Lett.* **2009**, *11*, 229−231. (e) Tang, B.-X.; Tang, D.-J.; Tang, S.; Yu, Q.-F.; Zhang, Y.-H.; Liang, Y.; Zhong, P.; Li, J.-H. *Org. Lett.* **2008**, *10*, 1063−1066.

(10) Yusybov, M. S.; Filimonov, V. D. *Synthesis* **1991**, 131−132.

(11) Chen, M.; Zhao, Q.; She, D.-B.; Yang, M.-Y.; Hui, H.-H.; Huang, G.-S. *J. Chem. Sci.* **2008**, *119*, 347−351.

(12) Sakthivel, K.; Srinivasan, K. *Eur. J. Org. Chem.* **2011**, 2781−2784.

(13) Chen, D.; Song, G.; Jia, A.; Li, X. *J. Org. Chem.* **2011**, *76*, 8488−8494.

(14) Relative intensity of MS: $[M]^+$ = 256 (5.40) and $[M + 2]^+$ = 258 (0.58) for **2** formed with $H_2{}^{18}O$, and $[M]^+$ = 256 (5.32) and $[M + 2]^+$ = 258 (0.36) for **2** formed without $H_2{}^{18}O$. $[M + H]^+$ = 273 (100) and $[M + H + 2]^+$ = 275 (4.41) for **3** formed with $H_2{}^{18}O$, and $[M + Na]^+$ = 295 (100), $[M + Na + 2]^+$ = 297 (4.22), and $[M + H]^+$ = 273 (3.31) for **3** formed without $H_2{}^{18}O$ ($[M + H + 2]^+$ = 275 was not observed). *Confer:* [M] = 288 (0.32) and [M + 2] = 290 (0.90) for **4** formed with $H_2{}^{18}O$, and [M] = 288 (1.91) and [M + 2] = 290 (0.14) for **4** formed without $H_2{}^{18}O$. Mass spectra were obtained with EI for **2** and **4**, but with ESI for **3** because of the lack of observation of the parent ion peak by measuring **3** with EI method.

(15) The different yield against entry 2 in Table 1 would be caused by the difference of the amount of adventitious water in $CHCl_3$. The two reactions depicted in Scheme 2 were conducted in $CHCl_3$ with a same quality.

(16) Unfortunately, it seemed not to exclude a contamination of molecular oxygen completely even under precious conditions (see the Experimental Section). But, in the case of the reaction under "sealed conditions", unidentified product(s) was observed, which suggests the decease of ratio of α-diketones formation.

(17) Reaction mechanisms through intermediate **A**′ are depicted in Schemes S2 and S3 (Supporting Information).

(18) (a) Mihailović, M. L.; Čeković, Ž. *The Chemistry of the Hydroxyl Group, Part 1*; Patai, S., Ed.; Interscience Publishers: Great Britain, 1971; pp 560−567. (b) Gopalan, S.; Savage, P. E. *J. Phys. Chem.* **1994**, *98*, 12646−12652.

(19) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed.; John Wiley & Sons: Mississauga, ON, 2001; p 445. Fina, N. J.; Edwards, J. O. *Int. J. Chem. Kinet.* **1973**, *5*, 1−26.

(20) (a) Zuliani, V.; Cocconcelli, G.; Fantini, M.; Ghiron, C.; Rivara, M. *J. Org. Chem.* **2007**, *72*, 4551−4553. (b) Wolkenberg, S. E.; Wisnoski, D. D.; Leister, W. H.; Wang, Y.; Zhao, Z.; Lindsley, C. W. *Org. Lett.* **2004**, *6*, 1453−1456. (c) Mahabusarakam, W.; Deachathai, S.; Phongpaichit, S.; Jansakul, C.; Taylor, W. C. *Phytochemistry* **2004**, *65*, 1185−1191. (d) Ita, B. I.; Offiong, O. E. *Mater. Chem. Phys.* **2001**, *70*, 330−335. (e) Nowak, P.; Malwitz, D.; Cole, D. C. *Synth. Commun.* **2010**, *40*, 2164−2171 and references cited therein.