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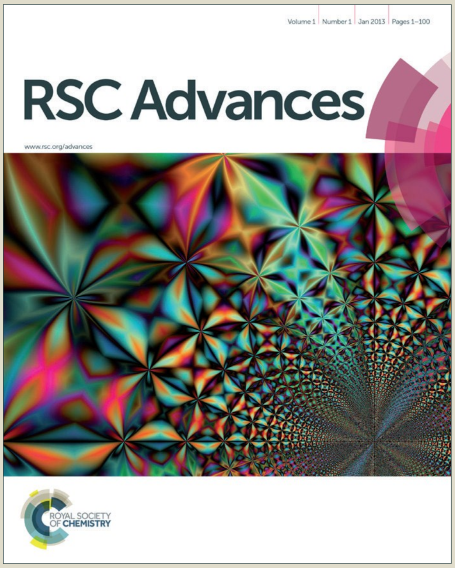

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COMMUNICATION

A Radical Coupling Reaction of DMSO with Sodium Arylsulfinates in Air: Mild Utilization of DMSO as C_1 Resource for the synthesis of arylsulfonyl dibromomethane

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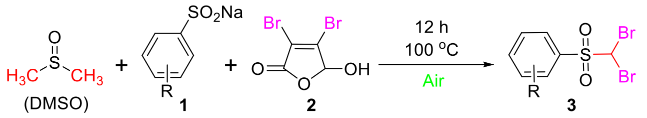
A radical coupling reaction of DMSO with sodium arylsulfinates under air atmosphere to afford arylsulfonyl dibromomethane is described. This transformation provides a novel approach for the utilization of DMSO as C_1 resource with mild temperature without the needs of anaerobic atmosphere.

Dimethyl sulfoxide (DMSO) is an important organic solvent[1] and oxidant.[2] What's more, as a cheap material for the source of CH_3,[3] CH_3S,[4] O,[4e,4g,5] CH_3SO,[6] its application in organic synthesis is increasing attractive. Especially, using DMSO as a one-carbon synthon, which can be transformed into not only CH_3,[3] but also CHO,[7-9] CN,[10] even be utilized to build heterocyclic compounds,[11] is much more useful. However, these transformations usually involve metal catalysts,[7] or high temperature,[7b,8] even sometimes the harsh or special conditions are necessary.[7c,9]

Sodium sulfinates have been also widely applied in organic synthesis.[12] Recently, Jiang's group reported some important breakthroughs, including the copper-catalyzed coupling reaction of oxime acetates with sodium sulfinates for the synthesis of sulfonylvinylamine.[13] According to the reaction type, many radical reactions of sodium sulfinates catalyzed by metal or other catalysts have aroused wide concern among the chemists.[13c,13d,14] However, the radical coupling reaction without any catalyst is still less investigated,[13c,15] which urgently needs to be developed.

On the basis of our previous work on 2(5*H*)-furanone chemistry,[16] recently we investigated palladium-catalyzed desulfitative arylation of 5-alkoxy-3,4-dibromo-2(5*H*)-furanone with sodium arylsulfinates.[17] During its condition optimization, the reaction of sodium arylsulfinates **1**, 3,4-dibromo-5-hydroxy-2(5*H*)-furanone **2** and DMSO in air was accidentally detected to afford arylsulfonyl dibromomethane **3** (**Scheme 1**). To the best of our knowledge, there is no report about the reaction of sodium sulfinates using DMSO as the CH source.



Scheme 1. Coupling reaction of DMSO and sodium arylsulfinates

Furthermore, many arylsulfonyl dihalomethanes have important bioactivities, and some similar compounds can be used as a kind of very useful organic intermediates, which make their syntheses and applications be under the spotlight recently.[18] Especially, arylsulfonyl dibromomethanes are developed too.[19] Thus, this new reaction reported herein not only has theoretical significance for the utilization of DMSO in synthetic chemistry, but also has a certain practical value.

In our initial studies, we took the reaction of **2** and **1a** as our model reaction to optimize the reaction condition (**Table 1**). From entries 1-5, it can be seen that the suitable time should be 12 h (entry 3). Comparing entry 3 with entries 6-8, the suitable temperature should be 100 °C.

We also investigated the influence of different solvents, including some potential one-carbon synthons, such acetone, *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP),[11] while only DMSO was found to be the effective solvent (entries 9-14 *vs* entry 3, **Table 1**). This indicates DMSO is not only used as a solvent in this reaction, but also

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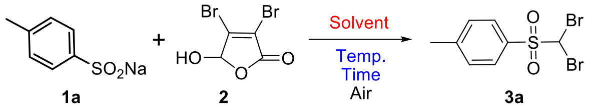
participates in the reaction as a one-carbon synthon via its peculiar mechanism, which will be discussed in the following.

Table 1. Optimization of reaction conditions[a]



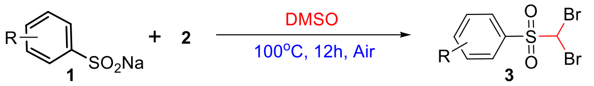
Entry	Time (h)	Temp. (°C)	Solvent	Yield (%)[b]
1	6	100	DMSO	76
2	9	100	DMSO	84
3	12	100	DMSO	92 (84[c])
4	15	100	DMSO	92
5	18	100	DMSO	92
6	12	60	DMSO	68
7	12	80	DMSO	74
8	12	120	DMSO	87
9	12	100	Toluene	0
10	12	100	1,4-dioxane	0
11	12	100	DMF	0
12	12	100	NMP	0
13	12	100[d]	acetone	0
14	12	56[d]	acetone	0

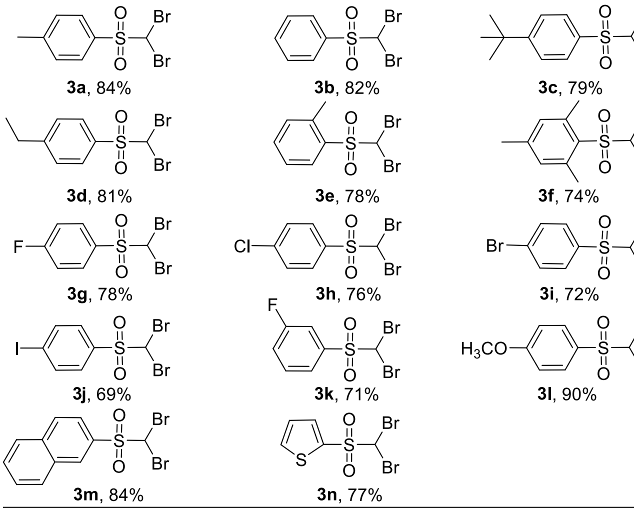
[a] Reaction conditions: all reactions were performed with **1a** (0.55 mmol), **2** (0.50 mmol) and solvent (3.0 mL) at the designed oil bath temperature under air. [b] GC yield. [c] Isolated yield. [d] In order to avoid the volatilization of acetone, the experiments were investigated using different temperatures or using a sealed reaction system filled with oxygen (or air) at 100 °C.

With the optimal reaction conditions in hand, we evaluated the scope of sodium arylsulfinates **1** and the results were summarized in **Table 2**. Different substituents on the benzene ring of sodium arylsulfinates **1** such as methyl, methoxy, fluoro, chloro, bromo were well tolerated and the corresponding products could be formed in good to excellent yields (69-90%). And the substrates with other aryl such as naphthyl, thienyl also could afford the products with satisfactory yields under the optimum reaction conditions (**3m** and **3n**).

Interestingly, electron-donating groups exhibited positive effect on this transformation (**3a**, **3l** *vs* **3b**). Contrarily, electron-withdrawing groups were adverse to reaction (**3g**-**3k** *vs* **3b**). Due to the steric hindrance, some products (**3c**-**3f**) were obtained with slightly lower yields than **3b**, though there were alkyl groups in the substrates. Thereby, the lowest yield was given for **3f** (74%). Steric effect was also reflected in the *meta*-substitution of benzene ring (**3k** *vs* **3g**). The combined influences of both electronic effect and steric hindrance on reaction may be related to the reaction mechanism (which will be discussed in the following).

Table 2. Substrate scope of various sodium arylsulfinates[a,b]





[a] Reaction conditions: **1** (0.55 mmol), **2** (0.50 mmol), DMSO (3.0 mL), under air atmosphere, 100 °C for 12 h. [b] Isolated yields.

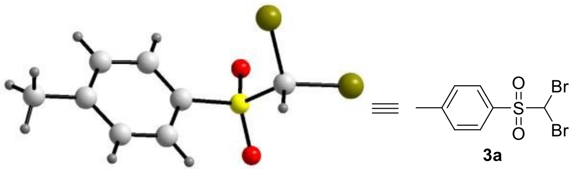


Figure 1. The molecular structure of **3a**

The structure of compound **3** was confirmed by NMR, MS and single crystal X-ray analysis (**Figure 1**).[20] To gain more insight into the mechanism of the process, we conducted several control experiments (**Scheme 2**). According to the results of optimization, we have found that the reaction can be carried out only in the solvent DMSO (**Table 1**, entry 3 *vs* entries 9-12). We speculated that some carbon atoms in DMSO should be involved in the reaction. Further experiments were carried out with other sulfoxides, and the results of GC-MS detection and product purification all demonstrated that this reaction was only performed very well with methyl sulfoxide (**Scheme 2**, Eq. 1 *vs* Eq. 2). Especially, due to only one methyl per molecule, the yield of methylsulfinylbenzene (Eq. 1) was significantly lower than the normal yield under standard conditions (**Table 2**, **3a**, 84%). Thus, the CH group in product **3** should be stemmed from the CH_3 group in DMSO,[21] and not be related to the reactant **2**.

When the amount of the reactant **2** was reduced by half under our standard conditions, the yield of the target product

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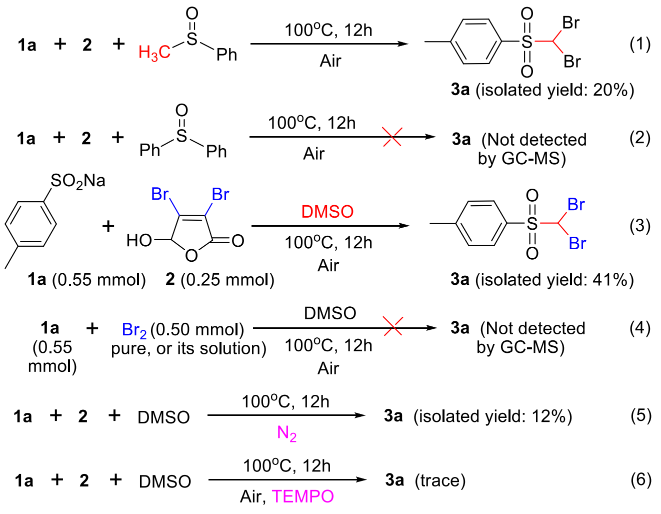
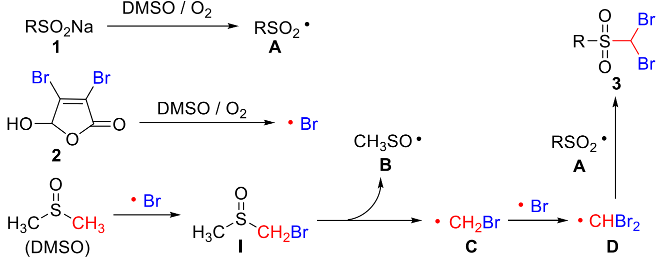
3a was only 41% (**Scheme 2**, Eq. 3). This datum was almost a half of the original yield (**Table 2**, **3a**, 84%). Therefore, it was determined that the bromine source of the product **3** was from the reactant **2**. However, the expected product **3a** was not obtained by using Br_2 instead of the reactant **2** (Eq. 4).[22] This suggests that the reactant **2** may be involved in the reaction as the form of bromine radical.

It has been reported that sodium arylsulfinate could generate sulfone radical in the presence of some oxidants, including DMSO or O_2.[13c,13d,14a,14b,14g] Thus, serial radical control experiments were designed. When the reaction was carried out under N_2 atmosphere, the yield of product **3a** was greatly decreased from 84% to 12% (**Scheme 2**, Eq. 5). This indicates that DMSO also has certain oxidizing ability for the formation of free radicals, but obviously less than O_2. Thus, we further added free radical trapping agent 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) into the standard reaction system. Then, only trace product **3a** was detected by GC-MS, but too less to be isolated (Eq. 6). The result confirmed that the reaction should be a radical coupling of DMSO with **1**.



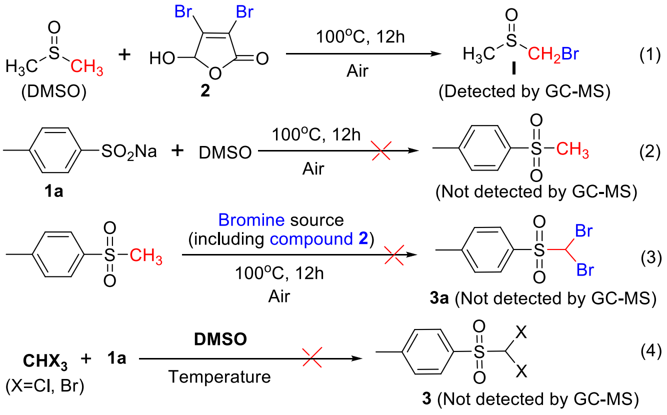
Scheme 2. Control experiments

On the basis of the above experiments and previous reports about the formation of radical from DMSO,[7a,7b] a possible mechanism was illustrated in **Scheme 3**. In the steps therein, both DMSO and O_2 (especially O_2 by comparing Eq. 5 with Eq. 6 in **Scheme 2**) were important for the formation of different radicals, such as radical **A** and Br radical. Subsequently, Br radical reacted with DMSO to give intermediate **I**. Then, intermediate **I** was broken down into radical **B** and radical **C**, which (especially radical **C**) might be transformed into radical **D** by the oxidative substitution[23] of Br radical in the presence of O_2. Finally, radical **D** was coupled by radical **A** to form the product **3**.



Scheme 3. Possible reaction mechanism

The intermediate **I** which is stemmed from DMSO and **2** in **Scheme 3** was proved via the verification experiment (**Scheme 4**, Eq. 1) and indeed detected by GC-MS (**Figure S1**, See **SI**).



Scheme 4. Verification experiments

According to the most reported synthetic methods of arylsulfonyl dibromomethanes (**Scheme S1**, Eq. 1, See **SI**),[19] the radical reaction of halogenating agents with methyl aryl sulfone also may give compound **3**. However, two plausible reactions were not successful indeed (**Scheme 4**, Eq. 2 and Eq. 3). There are also a few reports about the synthesis of arylsulfonyl dihalomethanes in the presence of KOH from haloform and sodium arylsulfinates (**Scheme S1**, Eq. 2, See **SI**)[24] or arylsulfonyl monohalomethanes.[25] However, haloform was not reacted with sodium arylsulfinate **1a** under our standard conditions (**Scheme 4**, Eq. 4).[26] And especially, the pH of our reaction system for the reaction of **1a** and **2** was basically maintained between 5-7 within 0-12 h. Therefore, both positive and negative verification experiments in **Scheme 4** also demonstrated the mechanism in **Scheme 3**.

What's more, the radical mechanism in **Scheme 3** could well explain the influences of sodium arylsulfinates **1** on the yields mentioned above. When radical **A** was produced from the substrate **1**, due to the conjugate effect, the benzene ring

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bearing electron-donating groups easily made radical **A** more stable, which was benefit for the radical coupling. Contrarily, when the benzene ring was substituted by electron-withdrawing groups, radical **A** easily became more unstable, which made the yield decreased. Obviously, the bigger steric hindrance was adverse for both the stability of radical **A** and the coupling reaction with radical **D**, so the yield was reduced.

In conclusion, without the needs of anaerobic atmosphere, the utilization of DMSO as one-carbon synthon was developed for the first time. In addition, the temperature is not high, the condition is mild. The detailed mechanistic studies showed that this transformation was involved in the radical coupling reaction of DMSO with sodium arylsulfinates. This protocol may provide new opportunities in organic synthesis for the comprehensive utilization of organic sulphur oxides, such as sulfoxides[27] and sodium sulfinates. Further study on this topic is currently undergoing in our laboratory.

Acknowledgements

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20 CCDC-1062338 (for **3a**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

21 In order to confirm that CH group in product **3** is derived from the CH_3 group in DMSO, we also investigated the experiment by replacing DMSO to DMSO-d_6. However, due to the fast hydrogen exchange between H_2O in solvent (and OH in reactant **2**) with $CHBr_2$ group in product, the result could not give convincing evidence as expected, even when 5-alkoxy-3,4-dibromo-2(5*H*)-furanone was used instead of **2** (the OH group in **2** was etherified into alkoxy group).

22 There are many reports on the bromine source using NBS or HBr as brominating reagents in the presence of DMSO, e.g. Ref. 2c and 2d mentioned above, and (a) K. Mal, A. Kaur, F. Haque and I. Das, *J. Org. Chem*., 2015, **80**, 6400; (b) M. Karki and J. Magolan, *J. Org. Chem*., 2015, **80**, 3701, including the papers cited therein. However, when using other brominating reagents like NBS or HBr under our standard conditions, the reaction was not investigated yet.

23 The representative references on the oxidative substitution are listed in the following. Especially, among them, some are involved in the radical reaction (e.g. Ref. 28b and 28c). (a) S. Paul, S. Roy, L. Monfregola, S.-Y. Shang, R. Shoemaker and M. H. Caruthers, *J. Am. Chem. Soc*., 2015, **137**, 3253; (b) E. Florez-Lopez, L. B. Gomez-Perez and L. D. Miranda, *Tetrahedron Lett*., 2010, **51**, 6000; (c) P. E. Reyes-Gutierrez, R. O. Torres-Ochoa, R. Martinez and L. D. Miranda, *Org. Biomol. Chem*., 2009, **7**, 1388; (d) L.-F. Chen, X.-Y. Cao, Z.-J. Li, J.-K. Cheng, Q.-P. Lin and Y.-G. Yao, *Inorg. Chem. Commun*., 2008, **11**, 961; (e) L. Bianchi, M. Maccagno, G. Petrillo, F. Sancassan, C. Tavani, S. Morganti, E. Rizzato and D. Spinelli, *J. Org. Chem*., 2007, **72**, 5771; (f) G. F. Koser, S. Telu and K. K. Laali, *Tetrahedron Lett*., 2006, **47**, 7011; (g) W. R. Bowman and J. M. D. Storey, *Chem. Soc. Rev*., 2007, 1803; (h) T. Kaoudi, B. Quiclet-Sire, S. Seguin and S. Z. Zard, *Angew. Chem., Int. Ed*. 2000, **39**, 731.

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26 The reaction was carried out not only under the standard conditions (100° C in air for 12 h). For the reactant $CHCl_3$, in order to avoid its volatilization, the verification experiments were also investigated using different temperatures or using a sealed reaction system filled with oxygen (or air) at 100 °C.

27 Like sodium sulfinates, sulfoxides (not only DMSO mentioned above) are also important organic sulfur oxides. Importantly, their syntheses and applications in organic synthesis as a kind of potential resources are being paid more attention. For some typical literatures, see: (a) M. Mellah, A. Voituriez and E. Schulz, *Chem. Rev*., 2007, **107**, 5133; (b) R. Mariz, X.-J. Luan, M. Gatti, A. Linden and R. Dorta, *J. Am. Chem. Soc*., 2008, **130**, 2172; (c) J. Chen, J.-M. Chen, F. Lang, X.-Y. Zhang, L.-F. Cun, J. Zhu, J.-G. Deng and J. Liao, *J. Am. Chem. Soc*., 2010, **132**, 4552; (d) E. M. Stang and M. C. White, *J. Am. Chem. Soc*., 2011, **133**, 14892; (e) T.-Z. Jia, A. Bellomo, K. E. L. Baina, S. D. Dreher and P. J. Walsh, *J. Am. Chem. Soc*., 2013, **135**, 3740; (f) T.-Z. Jia, A. Bellomo, S. Montel, M.-N. Zhang, K. E. L. Baina, B. Zheng and P. J. Walsh, *Angew. Chem., Int. Ed*., 2014, **53**, 260; (g) M.-N. Zhang, T.-Z. Jia, I. K. Sagamanova, M. A. Pericás and P. J. Walsh, *Org. Lett*., 2015, **17**, 1164; (h) T.-Z. Jia, M.-N. Zhang, H. Jiang, C. Y. Wang and P. J. Walsh, *J. Am. Chem. Soc*., 2015, **137**, 13887; (i) J.-H. Wei and Z.-H. Sun, *Org. Lett*., 2015, **17**, 5396.

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Title: A Radical Coupling Reaction of DMSO with Sodium Arylsulfinates in Air: Mild Utilization of DMSO as C_1 Resource for the synthesis of arylsulfonyl dibromomethane

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A radical coupling reaction of DMSO with $ArSO_2Na$ without the needs of anaerobic atmosphere to afford $ArSO_2CHBr_2$ is described.