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Metal-Free, DTBP-Mediated Methylthiolation of Arylboronic Acids with Dimethyldisulfide

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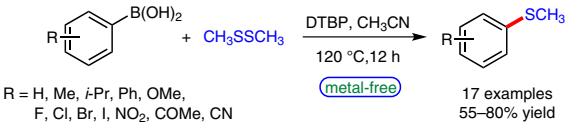

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Abstract An efficient method for the C–S bond formation via the coupling reaction of arylboronic acids with dimethyldisulfide has been developed under the metal-free conditions. This novel protocol provides an attractive route for the synthesis of aryl methyl sulfides, due to its operational simplicity, satisfactory yields, excellent functional-group tolerance, as well as the mild reaction conditions.

Key words methylthiolation, arylboronic acids, dimethyldisulfide, aryl methyl sulfides, di-*tert*-butyl peroxide

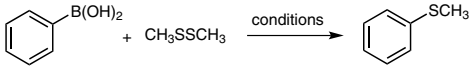
Aryl methyl sulfides are valuable structural motifs present in many pharmaceuticals and bioactive natural molecules.[1] Besides, they also serve as useful substrates for transition-metal-catalyzed cross-coupling reactions, including C–C[2] and C–N[3] coupling reaction as electrophiles, and the carbothiolation of terminal alkynes.[4] Undoubtedly, palladium[5] and other transition metals, such as nickel,[6] copper,[7] cobalt,[8] and indium[9] catalyzed C(aryl)–S coupling of thiols with aryl halides or pseudohalides to provide aryl sulfides that have emerged as mild and effective protocols compared with the traditional C(aryl)–S bond synthetic approaches via nucleophilic aromatic substitution, which generally required harsh reaction conditions[10] and the coupling reaction of arylmagnesium halides with a suitable electrophilic arylsulfur reagent[11] over the past several decades. However, the formation of aryl methyl sulfides in this fashion has not been reported so far, presumably owing to the low boiling point of methanethiol. In general, an effective strategy for the preparation of aryl methyl sulfides mainly consist of reduction of sulfoxides,[12] coupling reaction of aryl thiols with iodomethane,[13] and aryl halides with dimethyldisulfide.[14] An alternative method is the heteroatom-facilitated lithiation of aromatic C–H bonds followed by electrophilic substitution with dimethyldisulfide, which is more attractive from an atom-economical viewpoint.[15] It is worthwhile to mention that visible-light-mediated synthesis of aryl methyl sulfides from arenediazonium salts and dimethyldisulfide in the presence of eosin Y, a metal-free dye, has also been developed under mild reaction conditions, which exactly conforms to green and sustainable chemistry.[16] Recently, DMSO has been explored as an effective methylthiolation surrogate for this transformation. Apart from aryl halides[17] and aryl carboxylic acids,[18] the direct C–S bond formation via C–H bond activation with DMSO is also successful.[19]

Nevertheless, generally, some or one of the items including catalytic or stoichiometric amount of transition-metal sources, an appropriate ligand, Lewis acid, restricted substrates, or harsh reaction conditions were necessary in the aforementioned protocols. Furthermore, due to the fact that the reactions under metal-free conditions are desired particularly in the pharmaceutical synthesis and environmentally benign synthetic procedures, and arylboronic acids have been widely employed in the formation of carbon–heteroatom bonds such as C–N[20] and C–O,[20f,r,21] but seldom in carbon–sulfur bond, we herein describe a transition-metal-free C–S bond formation method via the coupling reaction of arylboronic acid and dimethyldisulfide under neutral conditions, which might tolerate a broad range of substrates and functional groups.

At the outset of this experiment, we investigated the coupling of phenylboronic acid and dimethyldisulfide with di-*tert*-butyl peroxide (DTBP) as promoter and 1,2-dichloroethane (DCE) as reaction medium in air, without the aid of a transition-metal catalyst. To our delight, phenyl methyl sulfide was obtained in 40% yield at 120 °C for 12 hours. Encouraged by this result, further optimization of the reaction conditions was attempted, and the results are summarized in Table 1. Some organic and inorganic promoters were

screened for this transformation, such as *tert*-butyl hydroperoxide (TBHP), *tert*-butyl peroxybenzoate (TBPB), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), I_2, and $K_2S_2O_8$ (Table 1, entries 2–6). It was found that DTBP was the most suitable to promote the reaction. Whereas inorganic oxidants like I_2 and $K_2S_2O_8$ were nearly ineffective (Table 1, entries 5, 6). The result of the control experiments revealed that DTBP was crucial for this transformation, no desired product was detected by GC–MS in the absence of any additive (Table 1, entry 7). Next, several other solvents were tested. It was found that acetonitrile (MeCN) was the most suitable solvent for this reaction, furnishing in 65% yield (Table 1, entry 8). Chlorobenzene, benzene, and CH_2Cl_2 afforded the methylthiolation product in approximately the same yields (Table 1, entries 9–11), whereas a small amount of desired product was obtained using DMF and DMSO as solvents (Table 1, entries 12, 13). We also found that reaction temperature significantly affected the reaction. At 100 °C phenylboronic acid could successfully couple with dimethyldisulfide, but only trace amount of the desired product was obtained at 80°C, and the ideal temperature for the reaction was found to be 120 °C (Table 1, entries 8, 14–16). Finally, the amount of DTBP was also tested. We found that the yield of the product dropped slightly with the decrease of DTBP (Table 1, entries 8, 17, 18), and the approximately same yield was obtained when a 3.0 or 4.0 equivalent amount of DTBP was used (Table 1, entries 18 and 19). Optimization of the reaction time showed that the reaction was almost completed within 12 hours at 120 °C as comparable yield was obtained when the reaction was carried out for 24 hours at the same temperature (Table 1, entry 20). On the basis of these results, it was obvious that the optimal conditions for the methylthiolation of phenylboronic acid with dimethyldisulfide were using DTBP as promoter and MeCN as solvent at 120 °C for 12 hours under air.

Table 1 Screening Reaction Conditions for Phenylboronic Acid and Dimethyldisulfide[a]



Entry	Promoter	Solvent	Temp (°C)	Yield (%)[b]
1	DTBP	DCE	120	40
2	TBHP	DCE	120	10
3	TBPB	DCE	120	25
4	DDQ	DCE	120	38
5	I_2	DCE	120	<5
6	$K_2S_2O_8$	DCE	120	<5
7	–	DCE	120	0
8	DTBP	MeCN	120	65
9	DTBP	PhCl	120	45
10	DTBP	PhH	120	35
11	DTBP	CH_2Cl_2	120	28
12	DTBP	DMF	120	10
13	DTBP	DMSO	120	15
14	DTBP	MeCN	80	<5
15	DTBP	MeCN	100	40
16	DTBP	MeCN	140	65
17	DTBP (1 equiv)	MeCN	120	55
18	DTBP (3 equiv)	MeCN	120	75
19	DTBP (4 equiv)	MeCN	120	75
20[c]	DTBP (3 equiv)	MeCN	120	75

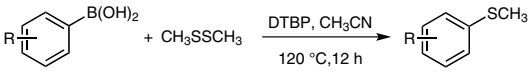
[a] Reaction conditions: phenylboronic acid (1.0 mmol), dimethyldisulfide (2.0 mmol), promoter (2 equiv), solvent (2.0 mL), under air, 12 h.
[b] Isolated yield.
[c] 24 h.

With the optimal reaction conditions in hand, we set out to examine the generality of the reaction with regard to arylboronic acids, and the results are presented in Table 2. As expected, a variety of arylboronic acids bearing electron-donating or electron-withdrawing groups at *ortho*, *meta* or *para* positions on the phenyl ring were all tolerated, affording the corresponding products in 55–80% yields. Specifically, phenylboronic acids with Me, *i*-Pr, and Ph substituents could afford the corresponding methylthiolation products in satisfactory yields (Table 2, entries 1–5). However, phenylboronic acids with strong electron-donating substituents such as OMe generated the desired methylthiolation product in a slightly lower yield (Table 2, entry 6). And phenylboronic acids possessing halogen groups could smoothly couple with dimethyldisulfide. Notably, in these cases, the respective desired products were obtained in good yields while keeping fluoro, chloro, bromo, and iodo functional groups intact, which could conveniently extend the scope of further functionalization on the phenyl ring (Table 2, entries 7–13). Phenylboronic acids with electron-withdrawing substituents such as COMe and CN groups were good coupling partners, whereas a slight decrease in the yield of methylthiolation product was observed for phenylboronic acid with a strong electron-withdrawing nitro group (Table 2, entries 14–17). Moreover, compared with *para*-substituted arylboronic acids, *ortho*- and *meta*-substituted substrates could also be well tolerated, albeit generating the desired products in moderate yields.

To investigate the reaction mechanism, we have performed the radical-trap experiment. When stoichiometric amount of the radical scavenger 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) was added to the reaction mixture under the same reaction conditions, the transformation was nearly inhibited and at the same time, the expected arylated TEMPO was detected by GC–MS. The result suggested that the methylthiolation presumably proceeded

through a radical pathway. On the basis of the above results and the related literatures,[23] a plausible reaction pathway for the reaction is proposed in Scheme 1.

Table 2 Methylthiolation of Arylboronic Acid with Dimethyldisulfide[a,22]



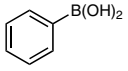
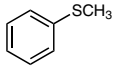
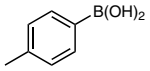
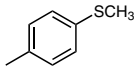
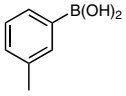
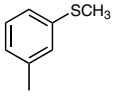
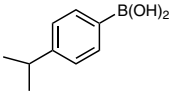
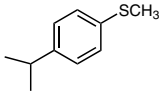
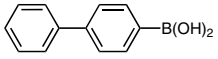
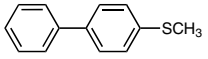
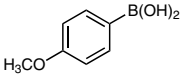
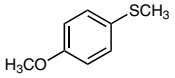
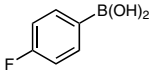
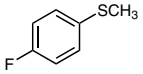
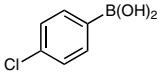
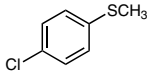
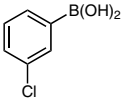
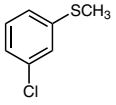
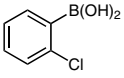
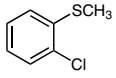
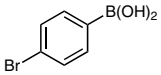
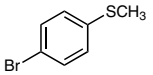
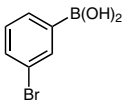
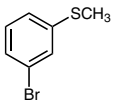
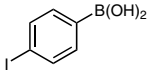
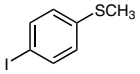
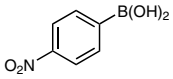
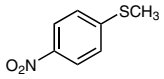
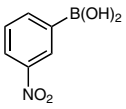
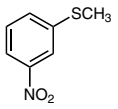
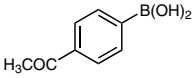
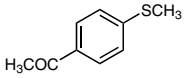
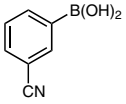
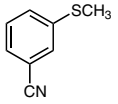
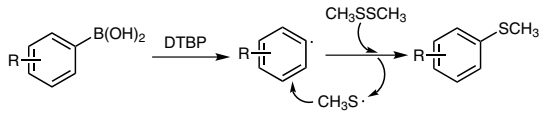
Entry	Arylboronic acid	Product	Yield(%)[b]
1			75
2			72
3			68
4			70
5			71
6			60
7			78
8			80
9			75
10			63
11			69
12			60
13			62

Table 2 (continued)

Entry	Arylboronic acid	Product	Yield(%)[b]
14			55
15			58
16			72
17			68

[a] Reaction conditions: arylboronic acid (1.0 mmol), dimethyldisulfide (2.0 mmol), DTBP (3.0 mmol), MeCN (2.0 mL), 120 °C, 12 h.
[b] Isolated yield.



Scheme 1 Plausible mechanism for the coupling reaction

In conclusion, a mild and practical approach to aryl methyl sulfides has been developed from the coupling of arylboronic acid and dimethyldisulfide under metal- and base-free conditions. Further efforts to explore the applications of the transformation in organic synthesis are currently underway in our laboratories.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1562499.

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(22) **General Procedure**

Arylboronic acid (1.0 mmol), dimethyldisulfide (2.0 mmol), DTBP (3.0 mmol), and MeCN (2.0 mL) were taken in a sealed tube. The reaction mixture was stirred at 120 °C for 12 h in air. After cooling to room temperature, the product was diluted with H_2O (5 mL) and extracted with EtOAc (4 × 10 mL). The extracts were combined and washed by brine (3 × 10 mL), dried over $MgSO_4$, filtered, and evaporated, and purified by chromatography on silica gel to obtain the desired products with EtOAc–hexane (1:30 to 1:100 v/v). The products were characterized by their spectral and analytical data and compared with those of the known compounds (see Supporting Information).

Typical Data for Representative Compound

4-Methylthioanisole (Table 2, Entry 2)

Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17–7.14 (d, *J* = 8.1 Hz, 2 H), 7.08–7.05 (d, *J* = 8.1 Hz, 2 H), 2.42 (s, 3 H), 2.28 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.0, 134.8, 129.7, 127.3, 20.9, 16.5. GC-MS (EI): *m/z* = 138 [M^+].

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