ORGANIC LETTERS

2013
Vol. 15, No. 22
5874–5877

Convenient MW-Assisted Synthesis of Unsymmetrical Sulfides Using Sulfonyl Hydrazides as Aryl Thiol Surrogate

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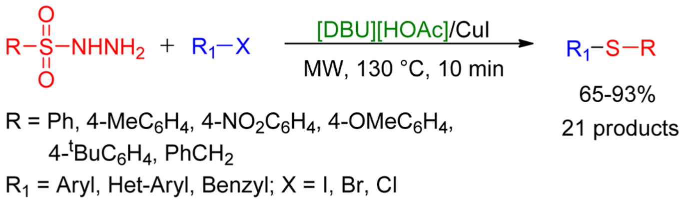
Received October 12, 2013

ABSTRACT



An efficient synthesis of unsymmetrical sulfides has been achieved via the cross-coupling reaction of aryl/het-aryl/benzyl halides with stable and easily workable sulfonyl hydrazides as thiol substitutes by means of [DBU][HOAc] and CuI under microwave irradiation.

One of the current challenges in organic synthesis is to develop convenient, selective, and energy-efficient synthetic methods. As a part of this effort, the search for more practical and environmentally benign synthetic methodologies is of prime importance.[1] Carbon–sulfur (C–S) bond-forming reactions comprise a key step in the synthesis of large variety of molecules of biological and material interest,[2] especially via cross–coupling reactions.[3] Although carbon–nitrogen (C–N) and carbon–oxygen (C–O) bond-forming processes have been studied extensively, the C–S bond formation reactions are yet underdeveloped due to the fact that thiols are prone to oxidative S–S coupling leading to the formation of undesired disulfides and organic sulfur compounds have a propensity to bind to metals thus acting as metal deactivators.[4]

Traditional methods for C–S bond formation employ harsh reaction conditions such as high temperatures (~200 °C) and the use of toxic and high boiling polar solvents such as quinoline, HMPA, or *N*,*N*-dimethylacetamide. Alternatively, these sulfides have been synthesized by the reduction of aryl sulfones or aryl sulfoxides using strong reducing agents like DIBAL-H or LiAlH$_4$.[5] As an advance, transition-metal-catalyzed coupling systems have been explored. The palladium-catalyzed cross-coupling reaction of aryl halides with thiols was first developed by Migita et al.[6] followed by other significant reports[7] using ligands such as triphenylphosphine, bidentate phosphine, or oxo phosphane derivatives. However, the high cost and air sensitivity of Pd catalysts and often tedious procedure for the preparation of ligands restrict their applications in

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10.1021/ol402948k © 2013 American Chemical Society
Published on Web 10/30/2013

Scheme 1. Synthesis of Unsymmetrical Sulfides

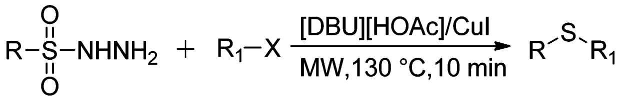
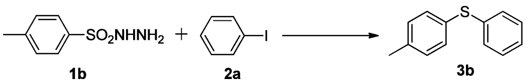


Table 1. Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	organic ionic base	yield[b] (%)
1		[DBU][HOAc]	nil
2	$CoCl_2 \cdot 6H_2O$ (10)	[DBU][HOAc]	25
3	$FeCl_3$ (10)	[DBU][HOAc]	30
4	CdI_2 (10)	[DBU][HOAc]	24
5	$NiCl_2 \cdot 6H_2O$ (10)	[DBU][HOAc]	35
6	CuI (10)	[DBU][HOAc]	87
7	CuBr (10)	[DBU][HOAc]	10
8	$Cu(OAc)_2 \cdot H_2O$ (10)	[DBU][HOAc]	12
9	$CuCl_2 \cdot 2H_2O$ (10)	[DBU][HOAc]	35
10	CuI (10)	DBU	10
11	CuI (10)	Bmim[OH]	30
12	CuI (10)	[DBU][n-Pr]	60
13	CuI (10)	[DBU][n-Bu]	45
14	CuI (10)	[DBU][TFA]	nil

[a] Reaction conditions: **1b** (1.2 mmol), **2a** (1 mmol), CuI (10 mol %), [DBU][HOAc] (1 mL), MW 60 W, 130 °C, 10 min. [b] Isolated yield based on **2a**.

large-scale processes. A variety of Co,[8] Ni,[9] In,[10] Cu,[11] and Fe[12] catalysts have been afterward explored for the improvement of reaction conditions for S-arylation. However, all these metal-catalyzed reactions invariably require foul-smelling, volatile, and expensive arenethiols, which are rather less available and prone to oxidative homocoupling.[13] To resolve these problems, disulfides have also been tried,[14] albeit requiring an stoichiometric equivalent of the reductants. Hartwig has nicely demonstrated the catalytic use of a $Pd(OAc)_2$−CyPF−^{t}Bu complex for a remarkably improved synthesis of unsymmetrical diaryl sulfides from TIPS−SH and two different aryl halides.[15] To have a viable alternative to thiols, use of different other sulfur sources, namely thiourea,[16] thiolates,[17] potassium ethyl xanthogenate,[18] thiocyanate,[19] metal sulfides,[20] and carbon disulfide,[21] have been recently made to achieve the formation of diaryl thioethers. The use of thiolates as sulfur source is however limited to Pd/P−ligand as catalyst, while that of thiourea is confined to the synthesis of symmetrical disulfides,[16a] or alkyl aryl thioethers,[16b] as this method is suitable to generate alkyl thiolates only. Use of potassium ethyl xanthogenate, thiocyanate, and metal sulfides necessitates either ligands, highly polar solvents, or long reaction time. Hence, it is important to find a practical catalytic protocol to avoid volatile and foul-smelling thiols and other sulfur sources to achieve highly useful unsymmetrical aryl sulfides particularly. We have just developed a new hydrothiolation method to achieve vinyl sulfides by the reaction of sulfonyl hydrazides with aryl/heteroaryl−acetylenes in the presence of [DBU][AcOH]/acetic acid.[22] Since the investigation implicated the use of sulfonyl hydrazide as a new nucleophilic sulfur source, it was imperative to explore the prospects of this novel thiol surrogate for other demanding reactions. Considering the advantages and green credentials of microwave (MW) in current scenario, it was also thought worthwhile to exploit

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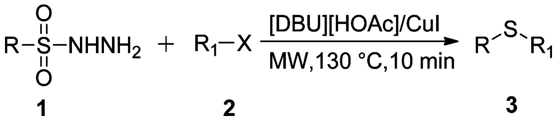
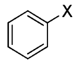
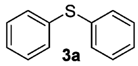
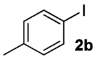
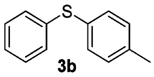
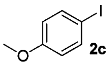
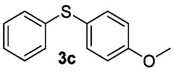
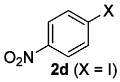
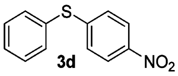
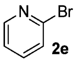
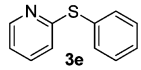
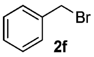
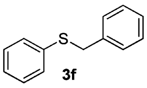
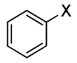
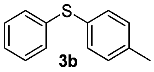
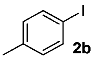
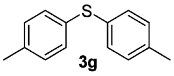
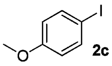
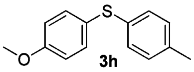
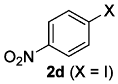
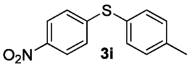
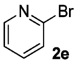
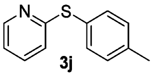
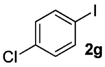
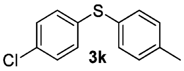
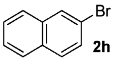
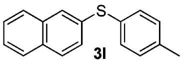
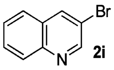
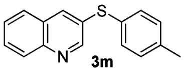
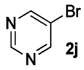
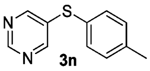
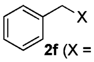
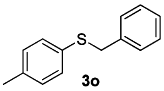
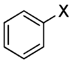
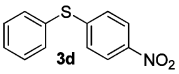
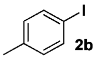
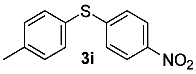
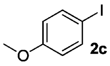
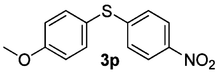
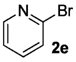
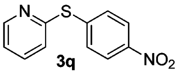
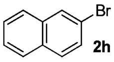
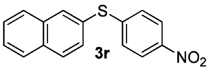
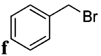
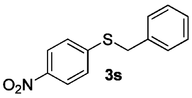
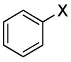
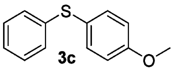
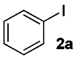
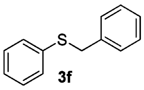
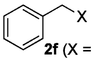
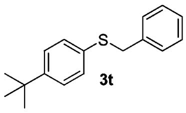
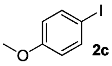
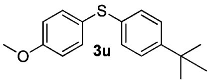
Table 2. Synthesis of Unsymmetrical Sulfides Using Sulfonyl Hydrazides[a]



entry	R (**1**)	R$_1$-X (**2**)	product (**3**)	yield[b]%
1.	Ph **1a**	 **2a** (X = I) **2a'** (X = Br)	 **3a**	84 (X = I) 78 (X = Br)
2.	Ph **1a**	 **2b**	 **3b**	81
3.	Ph **1a**	 **2c**	 **3c**	75
4.	Ph **1a**	 **2d** (X = I) **2d'** (X = Br)	 **3d**	89 (X = I) 83 (X = Br)
5.	Ph **1a**	 **2e**	 **3e**	73
6.	Ph **1a**	 **2f**	 **3f**	89
7.	4-MeC$_6$H$_4$ **1b**	 **2a** (X = I) **2a'** (X = Br)	 **3b**	87 (X = I) 82 (X = Br)
8.	4-MeC$_6$H$_4$ **1b**	 **2b**	 **3g**	84
9.	4-MeC$_6$H$_4$ **1b**	 **2c**	 **3h**	77
10.	4-MeC$_6$H$_4$ **1b**	 **2d** (X = I) **2d'** (X = Br)	 **3i**	93 (X = I) 85 (X = Br)
11.	4-MeC$_6$H$_4$ **1b**	 **2e**	 **3j**	77
12.	4-MeC$_6$H$_4$ **1b**	 **2g**	 **3k**	87
13.	4-MeC$_6$H$_4$ **1b**	 **2h**	 **3l**	81
14.	4-MeC$_6$H$_4$ **1b**	 **2i**	 **3m**	75
15.	4-MeC$_6$H$_4$ **1b**	 **2j**	 **3n**	68
16.	4-MeC$_6$H$_4$ **1b**	 **2f** (X = Br) **2f'** (X = Cl)	 **3o**	88 (X = Br) 76(X= Cl)
17.	4-NO$_2$C$_6$H$_4$ **1c**	 **2a** (X = I) **2a'** (X = Br)	 **3d**	73 (X = I) 66 (X = Br)
18.	4-NO$_2$C$_6$H$_4$ **1c**	 **2b**	 **3i**	72
19.	4-NO$_2$C$_6$H$_4$ **1c**	 **2c**	 **3p**	69
20.	4-NO$_2$C$_6$H$_4$ **1c**	 **2e**	 **3q**	65
21.	4-NO$_2$C$_6$H$_4$ **1c**	 **2h**	 **3r**	72
22.	4-NO$_2$C$_6$H$_4$ **1c**	 **2f**	 **3s**	79
23.	4-OMeC$_6$H$_4$ **1d**	 **2a** (X = I) **2a'** (X = Br)	 **3c**	91 (X = I) 85(X = Br)
24.	PhCH$_2$ **1e**	 **2a**	 **3f**	90
25.	4-^{t}BuC$_6$H$_4$ **1f**	 **2f** (X = Br) **2f'** (X = Cl)	 **3t**	91(X = Br) 78(X = Cl)
26.	4-^{t}BuC$_6$H$_4$ **1f**	 **2c**	 **3u**	81

[a] Reaction conditions: **1** (1.2 mmol), **2** (1 mmol), CuI (10 mol %), [DBU][HOAc] (1 mL), MW 60 W, 130 °C, 10 min. [b] Isolated yield after column chromatography.

the use of MW irradiation.[23] In view of the above and as a part of our current research program,[24] we report herein an efficient use of stable sulfonyl hydrazides as thiol proxy to bring about the practical synthesis of highly cherished unsymmetrical thioethers under microwave irradiation by means of DBU acetate/CuI (Scheme 1).

To look into the prospects of C–S cross-coupling, a model reaction using easily available and reasonably priced tosylhydrazide and iodobenzene was investigated

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(23) (a) Gutmann, B.; Schwan, A. M.; Reichart, B.; Gspan, C.; Hofer, F.; Kappe, C. O. *Angew. Chem., Int. Ed.* **2011**, *50*, 7636. (b) Moseley, J. D.; Kappe, C. O. *Green Chem.* **2011**, *13*, 794.

in detail by varying different parameters such as catalyst mol %, MW power, base, additive, solvent, and temperature to develop the appropriate conditions (Table 1). When the reaction was carried out in [DBU][HOAc] alone at 130 °C without the use of a catalyst, it did not provide the desired unsymmetrical sulfide; rather it gave rise to the disulfide derived from thiol corresponding to tosyl hydrazide (Table 1, entry 1). Thereafter, different transition metal catalysts viz. $CoCl_2 \cdot 6H_2O$, $FeCl_3$, CdI_2, $NiCl_2 \cdot 6H_2O$, and CuI were added (10 mol %) to the reaction mixture to determine their catalytic efficacy at 130 °C (entries 2−6).

Out of all the trials, an exceedingly high product yield (87%) was obtained in the presence of CuI (entry 6). As a result, other copper salts such as CuBr, $Cu(OAc)_2 \cdot H_2O$, and $CuCl_2 \cdot 2H_2O$ were also screened (entries 7−9), but none of them could match the value of CuI. The use of DBU and different ionic liquids such as Bmim[OH], [DBU][*n*-Pr], [DBU][*n*-Bu], and [DBU][TFA] was also made to check the prospects of reaction (entries 10−14), but the topmost result was ultimately credited to [DBU][HOAc] (entry 6). The reaction was further probed by differing MW power, temperature, and time with the end result of 60 W power output at 130 °C in 10 min to achieve the maximum conversion. With regard to the catalyst loading, 10 mol % of CuI was found to be optimal as 5 mol % of the catalyst afforded lower yield, and no improvement was observed with 15 mol %. Different additives like AcOH, DABCO, L-proline, and $BF_3 \cdot Et_2O$ were also assessed with [DBU][AcOH] under the optimized conditions but none of them could better the reaction conditions. Intrigued by these observations and with the stipulated reaction conditions in hand, the scope and versatility of this method was extended to the reaction of a variety of sulfonyl hydrazides viz. benzyl-, phenyl-, *p*-tolyl-, *p*-*tert*-butylphenyl-, *p*-nitrophenyl-, and *p*-methoxyphenylsulfonyl hydrazides with different benzyl/aryl/heteroaryl halides like benzyl bromide, benzyl chloride, iodobenzene, bromobenzene, *p*-iodotoluene, *p*-iodoanisole, *p*-nitroiodobenzene, 2-bromonaphthalene, 2-bromopyridine, 3-bromoquinoline, and 5-bromopyrimidine to afford a diverse range of unsymmetrical diaryl or benzyl aryl sulfides **3a**−**u** in reasonably high yields under MW in 10 min (Table 2). However, the reaction using aliphatic benzyl halides (enties 6, 16, 22, and 25) was also feasible without the aid of CuI, albeit with lower product yields. In general, sulfonyl hydrazides containing electron donating groups and aryl halides with electron withdrawing group showed better conversion. 1-Chloro-4-iodobenzene exhibited exclusive chemoselectivity for the iodo (entry 12). The structure of a representative product **3s** was conclusively proved by single-crystal X-ray diffraction (Figure 1). A plausible mechanism rationalizing the generation of thiolating agent from sulfonyl hydrazide is outlined in our previous work.[22]

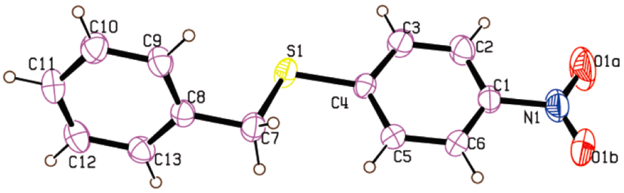

Figure 1. ORTEP diagram of product **3s**.

In summary, we have developed a highly efficient [DBU]-[HOAc]-promoted and copper-catalyzed cross-coupling reaction of different sulfonyl hydrazides with aryl/heteroaryl/benzyl halides under microwave irradiation. The C−S bond formation is readily accomplished using sulfonyl hydrazides as a thiol alternative to afford unsymmetrical thioethers in high yields under mild conditions. The versatility, air-stability, operational simplicity, and environmental friendliness of this method highlights its potential in organic synthesis.

Acknowledgment. We are thankful to the Department of Science and Technology, New Delhi, for providing financial support (Grant No. SR/S1/OC-78/2012).

Supporting Information Available. General information, experimental procedure, spectral data, copies of ^1H and ^{13}C NMR spectra for all products, X-ray data for **3s** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(24) (a) Vanjari, R.; Guntreddi, T.; Singh, K. N. *Org. Lett.* **2013**, *15*, 4908. (b) Singh, N.; Allam, B. K.; Raghuvanshi, D. S.; Singh, K. N. *Adv. Synth. Catal.* **2013**, *355*, 1840. (c) Guntreddi, T.; Allam, B. K.; Singh, K. N. *RSC Adv.* **2013**, *3*, 9875. (d) Raghuvanshi, D. S.; Gupta, A. K.; Singh, K. N. *Org. Lett.* **2012**, *14*, 4326.