Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

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Published online: 31 Jan 2012.

To cite this article: Xinzhi Chen , Shaodong Zhou & Chao Qian (2012) Catalytic transfer hydrogenation of aryl sulfo compounds, Journal of Sulfur Chemistry, 33:2, 179-185, DOI: 10.1080/17415993.2012.654392

To link to this article: http://dx.doi.org/10.1080/17415993.2012.654392

Journal of Sulfur Chemistry
Vol. 33, No. 2, April 2012, 179–185

Taylor & Francis
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Catalytic transfer hydrogenation of aryl sulfo compounds

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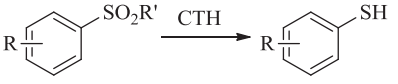
(*Received 24 November 2011; final version received 31 December 2011*)

A new method to reduce aryl sulfo compounds via transfer hydrogenation was investigated, using Pd/C as a catalyst, and 2-propanol or formic acid as hydrogen sources. This new process is simple and clean.



Keywords: catalytic transfer hydrogenation; sulfo compounds; thiophenol; triphenylphosphine; clean process

1. Introduction

Thiophenols play important roles in printing, dyeing and pharmaceutical industries (*1*). Among all the methods for preparation of thiophenols, reduction of aryl sulfonyl compounds has been the most widely employed (*2*). A variety of reductants have been used, including metals, hydrides and phosphorus trichloride and iodine. Unfortunately, most of these reducing agents contribute to environmental pollution.

Catalytic transfer hydrogenation (CTH) is an alternative reduction method, which is attracting more and more attention since it is eco-friendly. It has been used in the reduction of many unsaturated compounds, such as nitro compounds, azides, imines, olefins, ketones and also dehalogenations (*3*). However, reports on the reduction of sulfo compounds by this method are very limited. Dockner (*4*) found that benzenesulfonyl chloride can be reduced to thiophenol via transfer hydrogenation with a combination of hydrocarbons (such as vacuum residue or white oil) and active carbon as the hydrogen donor, but the reaction suffered from the need to use high temperature. Chen and Gong (*5*) have reported catalytic reduction of benzenesulfonic acid using paraffin as the hydrogen donor but the reaction also had to be carried out at a very high temperature. On the other hand, Engels and Singer (*6*) successfully reduced aryl sulfonyl chloride to thiophenol using an uncatalyzed transfer hydrogenation with hydrazine as the hydrogen donor under milder conditions (60–120°C) than reported by other methods.

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ISSN 1741-5993 print/ISSN 1741-6000 online

http://dx.doi.org/10.1080/17415993.2012.654392
http://www.tandfonline.com

The electron density around the sulfonic acid group is so high that nucleophilic attacks on the central sulfur atom by most reductants are repelled, making the reductions difficult. Oae and Togo (*7*) have found that the key step in the reduction of sulfonic acids is the leaving of the OH group. Bellale *et al*. (*8*) proved that once the OH group is replaced by a more easily leaving group, the reduction can be very fast and facile. The reactivity of sulfonic acids can also be increased in some cases if the OH group can be converted to OX, where X is an electron-withdrawing group that can stabilize the leaving group (*9*). Oae and Togo (*7*) reported an efficient triphenylphosphine–iodine system for the reduction of sulfo compounds in which triphenylphosphine was oxidized to triphenylphosphine oxide, and our work was initially inspired by this method. Although triphenylphosphine–iodine is an excellent combined reducing regent for sulfo compounds, the reaction proceeds with low atom economy. On the other hand, if triphenylphosphine oxide could be reduced *in situ* by commonly used reducing agents, it might be an excellent catalytic system.

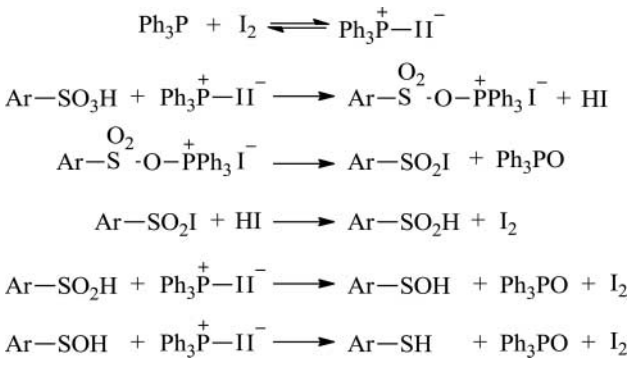
There are various reducing agents that are active in the reduction of triphenylphosphine oxide, such as hydride (*10*), silicon (*11*), metal (*12*), hydrogen (*13*) and samarium iodide (*14*). Silane was first used as a hydrogen donor in the CTH of triphenylphosphine oxide, and several kinds of silane derivatives have proved active in the reduction with good-to-excellent yields of triphenylphosphine. Subsequently, Dockner (*15*) found that CTH with triphenylphosphine oxide also occurs in a hydrocarbon/carbon system at high temperature (*e.g*. 350°C).

In an unpublished work, we found that 2-propanol or formic acid can be used as hydrogen sources in palladium-catalyzed deoxygenation of triphenylphosphine oxide. Here we attempt the reduction of aryl sulfo compounds with the Pd–triphenylphosphine–iodine catalytic reducing system and report that with 2-propanol or formic acid as hydrogen sources, both sulfonyl chlorides and sulfonic acids can be reduced under facile conditions.

2. Result and discussion

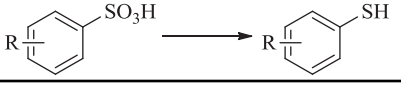
It is known that triphenylphosphine reacts with iodine, producing iodotriphenylphosphonium iodide, which is a halogenating agent and would react with sulfonic acid to afford sulfonyl iodide, triphenylphosphine oxide and hydrogen iodide (*16*). Hydrogen iodide subsequently performs as a reducing agent and reacts with sulfonyl iodide to produce sulfinyl acid and iodine. At this point, one deoxygenating cycle is completed, and thiophenol is generated after three such cycles. In the entire process, only a catalytic dose of iodine is needed, while three equivalents of triphenylphosphine is theoretically necessary. In the actual reaction, at least four equivalents of triphenylphosphine is needed in order to obtain high yields of thiophenols (*7*) (Scheme 1). Our effort focuses on the reduction of triphenylphosphine oxide *in situ* to reduce the required dosage of triphenylphosphine. The possibility of a Pd/C–triphenylphosphine–iodine-catalyzed reaction with a sulfonic acid in the presence of a hydrogen source was investigated and the results are shown in Table 1.

Comparative reactions between 4-methylbenzenesulfonic acid and the two different hydrogen sources, 2-propanol and formic acid, indicate that formic acid is less effective. The probable reason is that formic acid can reduce iodine (*17*) and consequently the reduction of sulfonic acid cannot continue. 2-Propanol is thus selected for further study for the reduction of aryl sulfonic acids. As can be seen in Table 1, increasing the dosage of iodine or triphenylphosphine had less effect on the reaction, while more Pd increases the speed of the reaction (entries 5–7). Therefore, the rate-limiting step in the transfer hydrogenation of aryl sulfonic acids is the reduction of triphenylphosphine oxide. Aryl sulfonic acids with various substituent groups on the benzene ring were reduced in 2-propanol and moderate-to-good yields were obtained. Electron-withdrawing groups decreased the yield of thiophenol.



Scheme 1. The process of iodine-catalyzed reduction of aryl sulfonic acid using triphenylphosphine as a reductant.

Table 1. Transfer hydrogenation of sulfonic acid using 2-propanol as a hydrogen source.[a]



Entry	R-	Hydrogen source and solvent	$n(ArSO_3H):n(I_2):$ $n(Ph_3P):n(Pd)$	Time (h)	Yield of ArSH (%)[b]
1[c]	4-Me	Formic acid	1/0.2/0.5/0.05	8	45
2	4-Me	2-Propanol	1/0.2/0.5/0.05	8	82
3	4-Me	2-Propanol	1/0/0/0.05	8	0
4	4-Me	2-Propanol	1/0.2/0.5/0	8	11
5	4-Me	2-Propanol	1/0.2/0.5/0.1	6	88
6	4-Me	2-Propanol	1/0.2/1/0.05	8	83
7	4-Me	2-Propanol	1/0.5/0.5/0.05	8	84
8	4-Br	2-Propanol	1/0.2/0.3/0.05	10	90
9	2-OEt	2-Propanol	1/0.2/0.3/0.05	10	65
10	3-CF_3	2-Propanol	1/0.2/0.3/0.05	10	70
11	4-F	2-Propanol	1/0.2/0.3/0.05	10	92
12	3-Me–4-F	2-Propanol	1/0.2/0.3/0.05	10	86
13	H	2-Propanol	1/0.2/0.3/0.05	10	85
14	3-NO_2	2-Propanol	1/0.2/0.3/0.05	10	63
15	3,5-Dimethyl	2-Propanol	1/0.2/0.3/0.05	10	80
16	2,4-Difluoro	2-Propanol	1/0.2/0.3/0.05	10	85

[a]Reaction conditions: 2-propanol as a solvent, under reflux, except Entry 1.
[b]Isolated yield.
[c]The reaction was carried out at 80°C with formic acid as a solvent.

Transfer hydrogenation of aryl sulfonyl chloride was also investigated. Since iodine is dispensable in the triphenylphosphine-catalyzed reductions of aryl sulfonic halides, it was also not used in this study. We also compared the two hydrogen sources, 2-propanol and formic acid. In contrast to the reduction of aryl sulfonic acids, formic acid showed much better performance than 2-propanol (see Table 2). No thiophenol was produced in the transfer hydrogenation of 4-methylbenzenesulfonyl chloride using 2-propanol as the hydrogen source probably because sulfonyl chloride reacted with 2-propanol to give isopropyl sulfonate which is less active than sulfonyl chloride and it could not be reduced by triphenylphosphine. The reduction of triphenylphosphine is still the rate-limiting step in the transfer hydrogenation of sulfonyl chlorides. Reductions of various aryl sulfonyl chlorides gave moderate-to-good yields.

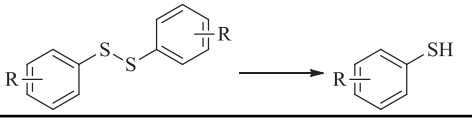
It is known that the reduction of aryl sulfonyl chlorides using inorganic reductants is always accompanied by the generation of disulfide (*18*). However, in the transfer hydrogenations of aryl

Table 2. Transfer hydrogenation of sulfonyl chloride using formic acid as a hydrogen source.[a]

Entry	R-	Hydrogen source and solvent	$n(ArSO_2Cl)$: $n(Ph_3P)$:n(Pd)	Time (h)	Yield of ArSH (%)[b]
1[c]	4-Me	2-Propanol	1/0.5/0.05	8	0
2	4-Me	Formic acid	1/0.5/0.05	8	90
3	4-Me	Formic acid	1/0/0.05	8	0
4	4-Me	Formic acid	1/0.5/0	8	12
5	4-Me	Formic acid	1/0.5/0.1	6	91
6	4-Me	Formic acid	1/1/0.05	8	92
7	4-Br	Formic acid	1/0.5/0.05	8	88
8	2-OEt	Formic acid	1/0.5/0.05	8	67
9	3-CF_3	Formic acid	1/0.5/0.05	8	68
10	4-F	Formic acid	1/0.5/0.05	8	90
11	3-Me-4-F	Formic acid	1/0.5/0.05	8	84
12	H	Formic acid	1/0.5/0.05	8	86
13	3-NO_2	Formic acid	1/0.5/0.05	8	65
14	3,5-Dimethyl	Formic acid	1/0.5/0.05	8	79
15	2,4-Difluoro	Formic acid	1/0.5/0.05	8	87

[a]Reaction conditions: the reaction temperature is 60°C with formic acid as a solvent, except Entry 1.
[b]Isolated yield.
[c]The reaction was carried out under reflux with 2-propanol as a solvent.

Table 3. Transfer hydrogenation of disulfide using formic acid as a hydrogen source.[a]



Entry	R-	Hydrogen source and solvent	Time (h)	Yield of ArSH (%)[b]
1	H	HCOOH	1	85
2	4-Me	HCOOH	1	91
3	4-Br	HCOOH	1	92

[a]Reaction conditions: reaction temperature is 60°C with formic acid as a solvent, n(ArSSAr):n(Pd)=1:0.1.
[b]Isolated yield.

sulfonyl chlorides reported in this work, no aryl disulfide was detected. We attributed this to the high reactivity of disulfide, which might be reduced rapidly as soon as it is generated in such a reducing environment even without triphenylphosphine. To prove this assumption, we carried out the reaction of formic acid with aryl disulfides using only Pd/C as a catalyst. The results are shown in Table 3. All three disulfides selected were reduced to thiophenols with good yields, which is in consistent with our suggestion.

3. Conclusion

Transfer hydrogenations of aryl sulfonic acids and sulfonyl chlorides were investigated. With the combination of Pd/C, iodine and triphenylphosphine as a catalyst, both aryl sulfonic acids and aryl sulfonyl chlorides can be reduced. 2-Propanol is superior as a hydrogen source in the reduction of aryl sulfonic acids, while formic acid is more effective in the reduction of aryl sulfonyl chlorides.

In addition, transfer hydrogenation of disulfides proceeds rapidly in the Pd/C–HCOOH system and as a result no disulfide was detected in the reduction of aryl sulfonyl chlorides. Although only a catalytic dosage of triphenylphosphine is needed in the reduction of aryl sulfonic acids or sulfonyl chlorides, its recovery is difficult and as a consequence it cannot be reused. Speculation suggests that the reaction can be performed using stabilized alkyl phosphines as catalysts and further investigations are in progress to examine this possibility.

Experimental

General procedure for CTH of aryl sulfonic acid

To a mixture of 4-methylbenzenesulfonic acid (350 mg, 2 mmol) and 2-propanol (5 ml) into a three-necked reactor which equipped with a cooler were added 260 mg (1 mmol) of triphenylphosphine, 100 mg (0.4 mmol) of iodine and 177 mg of Pd/C (6% weight fraction), and then refluxed for 8 h. The reaction was followed by TLC. After the reaction was completed, filtrate and pour the filtrate into a mixture of 3 ml of water and 3 ml of dioxane, reflux the mixture for 1.5 h. Then, add benzene to extract thiophenol, wash the benzene solution with water three times, and isolate 4-methylthiophenol with column chromatography (with petroleum ether as eluent) in 82% yield.

General procedure for CTH of aryl sulfonyl chloride

To a mixture of 4-methylbenzenesulfonyl chloride (380 mg, 2 mmol) and formic acid (5 ml) into a three-necked reactor which equipped with a cooler, were added 260 mg (1 mmol) of triphenylphosphine and 177 mg of Pd/C (6% in weight fraction). The reaction mixture was heated and kept at 60°C for 8 h. The reaction was followed by TLC. 4-Methylthiophenol was isolated in 90% yield.

General procedure for CTH of aryl disulfide

To a mixture of 4-methylbenzene disulfide (490 mg, 2 mmol) and formic acid (5 ml) into a three-necked reactor which equipped with a cooler was added 350 mg of Pd/C (6% in weight fraction). The reaction mixture was heated and then kept at 60°C for 1 h. The reaction was followed by TLC. 4-Methylthiophenol was isolated in 91% yield.

Spectral data

4-Methylthiophenol: white solid, m.p.: 41–43°C (lit. (*19*), m.p.: 43°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 3.36 (s, 1H), 7.02 (d, 2H, $J = 8.1$ Hz) (*20*), 7.15 (d, 2H, J=8.1 Hz); MS (EI): m/z (rel. int.) 124 (91), 91 (100), 79 (9), 45 (13).

4-Bromothiophenol: white solid, m.p.: 70–73°C (lit. (*21*), m.p.: 72–74°C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 1H), 7.15 (d, 2H, $J = 8.7$ Hz), 7.38 (d, 2H, $J = 8.7$ Hz) (*20*); MS (EI): m/z (rel. int.) 190 (40), 188 (40), 109 (100), 69 (26), 50 (19), 33 (10), 15 (3).

2-Ethoxythiophenol: light yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.48 (t, 3H), 3.88 (s, 1H), 4.04–4.11 (q, 2H), 6.80–6.85 (m, 2H), 7.08 (t, 1H, $J = 7.8$ Hz), 7.22–7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 63.4, 126.2, 120.3, 112.1, 118.5, 129.8, 155.4; MS (EI): m/z (rel. int.) 154 (100), 139 (5), 126 (97), 109 (5), 97 (88), 84 (10), 69 (14), 53 (12), 39 (5), 29 (4). EI-HRMS calcd for $C_8H_{10}OS$ (M^+): 154.0452, found: 154.0454.

3-Trifluoromethylthiophenol: colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.57 (s, 1H), 7.24–7.43 (m, 3H), 7.51 (s, 1H) (*20*); MS (EI): m/z (rel. int.) 178 (100), 158 (60), 145 (12), 133 (9), 114 (36), 95 (8), 82 (7), 69 (36), 57 (10), 45 (22), 28 (5).

4-Fluorothiophenol: colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.43 (s, 1H), 6.94 (t, 2H, $J = 8.1$ Hz), 7.23–7.27 (m, 2H) (*20*); MS (EI): m/z (rel. int.) 128 (100), 108 (49), 95 (7), 84 (31), 69 (14), 57 (13), 45 (10), 31 (2).

2-Methyl-4-fluorothiophenol: colorless liquid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (s, 3H), 3.20 (s, 1H), 6.75–6.81 (m, 1H), 6.86–6.90 (m, 1H), 7.20–7.25 (m 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.0, 112.4, 116.2, 129.2, 131.1, 143.5, 159.1; MS (EI): m/z (rel. int.) 142 (98), 109 (100), 97 (9), 83 (9), 69 (6), 57 (6), 45 (7). EI-HRMS calcd for C_7H_7FS (M^+): 142.0252, found: 142.0255.

3-Nitrothiophenol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 1H), 7.40 (t, 1H, $J = 8.1$ Hz), 7.56 (d, 1H, $J = 8.1$ Hz), 8.01 (d, 2H, $J = 8.1$ Hz), 8.17 (d, 1H, $J = 1.9$ Hz) (*20*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 120.9, 122.7, 130.4, 135.1.

3,5-Dimethylthiophenol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 6H), 3.44 (s, 1H), 6.86 (s, 1H), 6.98 (s, 2H) (*20*); MS (EI): m/z (rel. int.) 138 (65), 123 (9), 105 (100), 91 (14), 77 (23), 63 (9), 39 (17).

2,5-Difluorothiophenol: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 1H), 6.79–6.84 (m, 1H), 6.97–7.07 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 114.0, 116.4, 117.2, 121.3, 158.7, 160.1; MS (EI): m/z (rel. int.) 146 (100), 126 (68), 101 (39). EI-HRMS calcd for $C_6H_4F_2S$ (M^+): 146.0002, found: 146.0003.

Acknowledgements

We acknowledge the funding support by a grant from the National Natural Science Foundation of China (21076183, 21006087), and the Key Innovation Group of Zhejiang Province (2009R50002).

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