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Synthesis of diaryl thioethers from aryl halides and potassium thiocyanate

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An efficient palladium catalyst was synthesized using nicotine, benzyl chloride and palladium chloride. The structure of this catalyst was characterized and it was then used for the synthesis of diaryl sufides. A variety of diaryl thioethers were synthesized under relatively mild reaction conditions. This protocol avoids foul-smelling thiols via cross-coupling of aryl halides with potassium thiocyanate and all substrates give the corresponding products in good to excellent yields in the presence of low amounts of the catalyst. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: palladium; potassium thiocyanate; C–S coupling; diaryl sufide; aryl halide

Introduction

Diaryl thioethers and their oxidized forms, sulfones and sulfoxides, are present in a great number of pharmaceuticals (such as in antidiabetes, anti-inflammatory, anti-Alzheimer's, anti-Parkinson's, anticancer and anti-HIV formulations), biologically active molecules and polymeric materials. Hence, the formation of C–S bonds has received great attention and constitutes a key step in the synthesis of many biological and pharmaceutical molecules.[1–12] Moreover, diaryl sulfides are usually the starting materials for the construction of sulfone and sulfoxide compounds which are critical synthetic intermediates for the construction of various chemically and biologically significant compounds.[13–17] The traditional methods for the formation of C–S bonds require drastic conditions such as polar solvents, hexamethylphosphoramide and elevated temperatures of around 200°C via aromatic nucleophilic substitutions of activated arenes with thiolates. One alternative method for the synthesis of sulfides is the reduction of aryl sulfones or aryl sulfoxides with strong reducing agents (DIBAL-H or LiAlH4).[18–21]

Migita and co-workers reported one of the first examples of aryl sulfide synthesis by coupling of aryl halides and thiols using Pd (PPh3)4 as catalyst.[22] Previous studies have shown that milder conditions are possible when using transition metals such as nickel, cobalt, indium, lanthanum, copper, iron and palladium as catalysts for the formation of diaryl sulfides by couplings of aryl halides with aryl thiols.[23–34] The use of volatile, expensive and foul-smelling thiols has been a main drawback, which leads to environmental and safety problems. In addition, sulfur-containing compounds may act as poisons for metal-based catalysts because of their strong coordinative properties, often making catalytic reactions ineffective.[35] To overcome these problems, other sulfur sources such as potassium thiocyanate[36] and thioacetamide[37] can be used instead of thiols. It is well known that palladium-catalyzed synthesis is one of the most efficient procedures for the preparation of diaryl sulfides.[38–41] The most significant advance in palladium-catalyzed C–S bond formation was made by Hartwig and co-workers in 2006[26,42] by employing the strongly coordinating bidentate Josiphos ligand in the presence of a palladium salt. Lee and co-workers developed palladium-catalyzed cross-coupling of aryl halides and thioacetates.[41] Wager and Daniels established palladium-catalyzed cross-coupling of benzyl thioacetates and aryl halides.[43]

In continuation of our research to produce efficient and new palladium catalysts,[44–50] we present here a simple and efficient route for the synthesis of diaryl sulfides using potassium thiocyanate as the sulfur source and using a new air- and moisture-stable Pd(II) complex containing 1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium with general formula [DBNT][PdCl4]. This quaternary nicotinium cation inhibits the aggregation of Pd(0) non-stable species. The effect of tetraalkylammonium salts on the activity and stability of palladium catalysts has been described before.[51]

Results and Discussion

1-Benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium was prepared according to our previous work.[50] The structure of the produced catalyst was characterized using ^{1}H NMR, ^{13}C NMR and infrared spectroscopy and elemental analysis. Based on these data, the structure of the synthesized catalyst is suggested as shown in Scheme 1.

UV absorption spectra of (−)-nicotine, 1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium chloride (benzylated nicotine), PdCl2 and mono(1-benzyl-3-(1-benzyl-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium)monopalladium(II) tetrachloride (catalyst) in dimethylsulfoxide (DMSO) were recorded (Fig. 1). The 276 nm band corresponds to the $\pi \rightarrow \pi^*$ transition of the pyridine ring.[52]

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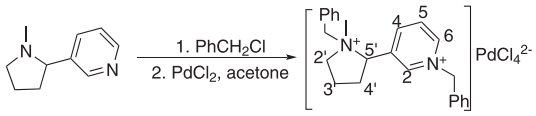


Scheme 1. Preparation of catalyst [DBNT][PdCl4].

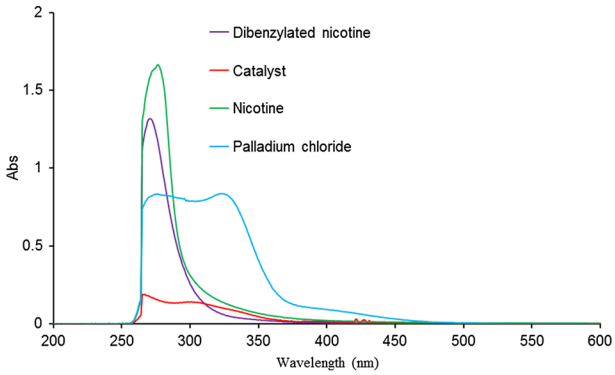


Figure 1. Absorption spectra of catalyst and starting materials for its synthesis.

Benzylated nicotine shows a 270 nm band which has a hypsochromic shift relative to (−)-nicotine due to it having positive nitrogen atoms. In the electronic spectrum of PdCl2 solution, intense bands at 297 nm and 330 nm having a value of CTB (Charge transfer band) from chloride ions to the metal.[53] The electronic spectrum of the catalyst shows two bands at about 267 nm (associated with the $\pi \rightarrow \pi^*$ transition) and 309 nm.

Initially to optimize the reaction conditions such as base, solvent and reaction temperature, iodobenzene and potassium thiocyanate were selected as model substrates. The results are summarized in Table 1.

Our initial choice of solvent was DMSO. At first, various bases (NaHCO3, Na2CO3, K2CO3, Cs2CO3, KOH, NaOH, K2HPO4, *t*-BuOK, 1,4-diazabicyclo[2.2.2]octane (DABCO), NaOAc and Et3N) were examined, and a significant base effect was observed. Among inorganic bases, it is evident that KOH and NaOH give quantitative results for the coupling reaction to diphenyl thioethers (Table 1, entries 5 and 6), while, among organic bases, Et3N and *t*-BuOK give better results (Table 1, entries 8 and 11) in a homogeneous reaction mixture. In the presence of other bases, low to moderate yields are obtained. The reaction does not occur in the absence of the base (Table 1, entry 30). So KOH (4 eq.) was finally selected as the base for the reaction. Similarly, a series of solvents were screened. Among the several solvents tested, DMF, 1,4-dioxane, toluene, *N*-methyl-2-pyrrolidone (NMP), THF and CH3CN are less effective compared to DMSO (Table 1, entries 13–19). In solvents such as H2O and EtOH, trace amounts of product are obtained (Table 1, entries 20 and 21). The high polarity and dielectric constant of DMSO could be a reason for its excellent performance (Table 1, entry 13). Further studies reveal the optimal reaction temperature to be 120°C (Table 1, entries 13, 22–26). The reaction fails to give the sulfide product when it is carried out at room temperature and starting materials are completely recovered (Table 1, entry 22). Finally, the amount of palladium catalyst was also screened. A 1.0 mol% loading of palladium is found to be optimal, since a lower yield is observed when the amount of catalyst is decreased (Table 1, entry 27). As evident from Table 1, increasing the amount of palladium catalyst to 1.5 mol% can shorten the reaction time, but

Table 1. Optimization of [DBNT][PdCl4]-catalyzed coupling of iodobenzene with KSCN under various conditions[a]

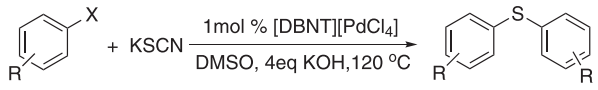
Entry	Solvent	Temperature (°C)	Base (eq.)	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	DMSO	120	NaHCO3 (2)	1	5	13
2	DMSO	120	Na2CO3 (2)	1	5	37
3	DMSO	120	K2CO3 (2)	1	5	43
4	DMSO	120	Cs2CO3 (2)	1	5	58
5	DMSO	120	KOH (2)	1	2	78
6	DMSO	120	NaOH (2)	1	3	60
7	DMSO	120	K2HPO4 (2)	1	5	29
8	DMSO	120	*t*-BuOK (2)	1	3	53
9	DMSO	120	DABCO (2)	1	5	Trace
10	DMSO	120	NaOAc (2)	1	5	Trace
11	DMSO	120	Et3N (2)	1	3	48
12	DMSO	120	KOH (3)	1	2	85
13	DMSO	120	KOH (4)	1	2	92
14	DMF	120	KOH (4)	1	5	32
15	1,4-Dioxane	Reflux	KOH (4)	1	5	20
16	Toluene	Reflux	KOH (4)	1	5	12
17	NMP	120	KOH (4)	1	5	21
18	THF	Reflux	KOH (4)	1	5	42
19	CH3CN	Reflux	KOH (4)	1	5	Trace
20	H2O	Reflux	KOH (4)	1	5	Trace
21	EtOH	Reflux	KOH (4)	1	5	Trace
22	DMSO	Room temp.	KOH (4)	1	5	Trace
23	DMSO	80	KOH (4)	1	5	38
24	DMSO	100	KOH (4)	1	3	67
25	DMSO	110	KOH (4)	1	2	81
26	DMSO	130	KOH (4)	1	2	92
27	DMSO	120	KOH (4)	0.5	2	78
28	DMSO	120	KOH (4)	1.5	1	94
29	DMSO	120	KOH (4)	—	3	—
30	DMSO	120	—	1	3	—

[a]Reaction conditions: iodobenzene (2 mmol), KSCN (1 mmol), [DBNT][PdCl4], base, solvent (2 ml).
[b]Isolated yield.

does not increase effectively the yield of diphenyl sulfide (Table 1, entry 28). The coupling reaction does not occur in the absence of the catalyst (Table 1, entry 29) or base (Table 1, entry 30). It is significant to observe that the choice of DMSO as the solvent with KOH (4 eq.) as base at 120°C is essential for the present C–S coupling reaction.

To explore the generality and scope of the proposed catalytic system, coupling of various aryl halides with KSCN was examined. The results are summarized in Table 2. In general, all the reactions are very clean and successful and C–S coupling reactions proceed smoothly to afford the corresponding diaryl sulfides in good to excellent yields ranging from 62 to 95%. The electronic nature of the substituents seems to affect the results. In fact, electron-withdrawing substituents on aryl iodide (COCH3, CHO, CN and NO2) (Table 2, entries 2–6) give the corresponding thioethers in higher yields and shorter reaction times compared to electron-donating substituents (CH3, OCH3) (Table 2, entries 7 and 8). Steric hindrance also seems to have an effect on the results. For example, the reactions of the sterically hindered aryl halides 4-nitroiodobenzene, 2-nitroiodobenzene, 4-bromoacetophenone, 2-bromoacetophenone and 3-bromoacetophenone (Table 2,

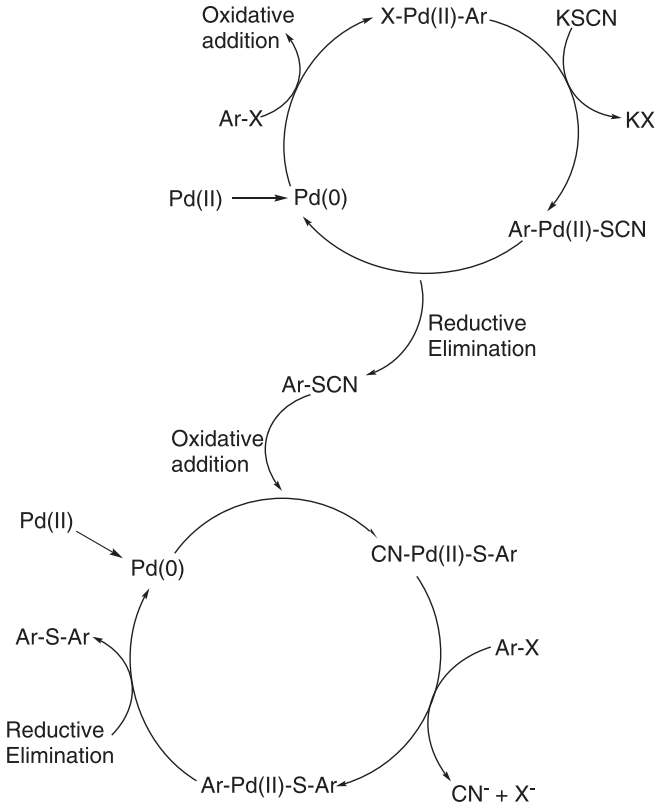
Table 2. Synthesis of diaryl sulfides from aryl halides and KSCN, catalyzed by [DBNT][PdCl4][a]



Entry	R	X	Time (h)	Yield (%)[b]
1	H	I	2	92
2	4-MeCO	I	2	93
3	4-CHO	I	2	92
4	4-CN	I	2	94
5	4-NO2	I	2	95
6	2-NO2	I	2.5	83
7	4-MeO	I	3	76
8	4-CH3	I	3	78
9	H	Br	4	84
10	H	Cl	4	74
11	Br	I	2	83
12	Cl	I	2	82
13	4-MeCO	Br	3.5	89
14	4-MeCO	Cl	3.5	77
15	4-NO2	Br	3.5	90
16	4-NO2	Cl	3.5	78
17	4-CHO	Br	3.5	88
18	4-CHO	Cl	3.5	76
19	4-CN	Br	3.5	91
20	4-CN	Cl	3.5	77
21	4-MeO	Br	5	82
22	4-MeO	Cl	5	72
23	Benzyl	Br	6	88
24	Benzyl	Cl	6	89
25	2-MeCO	Br	3.5	72
26	3-MeCO	Br	3.5	83
27	2-Iodopyridine		3	81
28	3-Iodopyridine		3	82
29	3-Bromopyridine		5	73
30	3-Chloropyridine		5	62

[a]Reaction conditions: aryl halides (2 mmol), KSCN (1 mmol), [DBNT][PdCl4] (1 mol%), DMSO (2 ml), KOH (4 eq.), 120°C.
[b]Isolated yield.

entries 5, 6, 13, 25 and 26) with potassium thiocyanate provide 95, 83, 89, 72 and 83% of the desired diaryl sulfides, respectively. Iodobenzene is found to be a more reactive substrate than bromobenzene and chlorobenzene (Table 2, entries 1, 9 and 10), which implies that there is good chemoselectivity between iodide, bromide and chloride (Table 2, entries 11 and 12). Aryl bromides can also react with KSCN under the same reaction conditions. Although in order to obtain reasonable yields of diaryl sulfides, longer reaction times than for aryl iodides are required (Table 2, entries 9, 13, 15, 17, 19 and 21). It is noteworthy that aryl chlorides successfully react under our conditions (Table 2, entries 10, 14, 16, 18, 20 and 22). Moreover, this method can well tolerate a variety of functional groups, including ketone, aldehyde and cyanide (Table 2, entries 2–4). This procedure is also good enough for the preparation of dibenzylsulfane from benzyl bromide and benzyl chloride (Table 2, entries 23 and 24). Some heteroaryl compounds, such as 2-iodopyridine, 3-iodopyridine, 3-bromopyridine and 3-chloropyridine, can also afford the desired diaryl sulfides (Table 2, entries 27–30).



Scheme 2. Proposed mechanism for thioetherification of aryl halides with KSCN.

According to previous reports,[3,23,29,54] we propose a mechanism for thioetherification of aryl halides with KSCN as shown in Scheme 2. First, an aryl halide is added to Pd(0) species through an oxidative addition step which causes Pd(II) formation. In the next step, SCN^- displaces the halide on the catalyst. The product of this cycle (aryl thiocyanate), which is gained through a reductive elimination step, enters the next cycle. It is worth noting that this intermediate was characterized using FT-IR spectroscopy, with a signal seen at about 2200 cm^{-1}. Then, the secondary aryl halide displaces CN^- according to hard–soft acid–base theory. The final step is reductive elimination which yields the desired diaryl sulfides.

Conclusions

In summary, we have reported a new palladium-catalyzed synthesis of symmetric diaryl sulfides from aryl halides and potassium thiocyanate in moderate to high yields. The efficiency and functional-group tolerance of this procedure have been demonstrated by synthesizing a number of functionalized diaryl thioethers. Importantly, the iodo group of an aryl halide was selectively coupled with a thiol in the presence of a bromo group. In addition, the use of air-sensitive or costly catalysts and ligands can be avoided by utilizing this method.

Experimental

General

All chemical reagents were purchased from Merck and were used without further purification. All products were characterized using

NMR spectroscopy. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were recorded at 100 MHz (Bruker) with CDCl3 or DMSO-*d*6 as solvent. Chemical shifts were measured using tetramethylsilane as internal standard. FT-IR spectra were obtained with samples as KBr pellets using a JASCO 680-Plus spectrophotometer. Also, we used gas chromatography (Beifin 3420 gas chromatograph equipped with a Varian CP SIL 5CB column: 30 m, 0.32 mm, 0.25 mm) for examination of reaction conversions.

General Procedure for Synthesis of Catalyst

Amounts of 1 mmol (0.16 ml) of (−)-nicotine and 4 mmol (0.46 ml) of benzyl chloride were mixed under solvent-free conditions and the reaction mixture was heated at 70°C for 6 h. The reaction mixture was treated with dichloromethane (5 × 6 ml) to remove unreacted materials and the dichloromethane phase was separated. The residue was obtained in 82% yield (0.340 g) and then was mixed with PdCl2 (0.177 g PdCl2: 0.415 g dibenzylated nicotinium salt) in acetone and refluxed for 12 h. The supernatant was decanted and washed with acetone (3 × 5 ml) to produce the catalyst in 91% yield (0.530 g) as a brown powder.[50]

^{13}C NMR (100 MHz, DMSO, δ, ppm): 18.69 (C3′), 25.58 (C4′), 41.23 (CH3,pyro), 62.94 (CH2,benzyl.pyro), 63.77 (CH2,benzyl.py), 65.16 (C2′), 74.57 (C5′), 128.37 (Carom.phenyl), 128.96 (C5), 129.22 (Carom.phenyl), 129.48 (Carom.phenyl), 130.30 (Carom.phenyl), 132.47 (Carom.phenyl), 132.91 (Carom.phenyl), 133.82 (C3), 146.15 (C4), 147.56 (C2), 148.20 (C6). ^{1}H NMR (400 MHz, DMSO, δ, ppm): 1.27–1.32 (2H, m, H3′), 2.15–2.30 (2H, m, H4′), 2.50–2.74 (2H, m, H2′), 3.36 (3H, s, CH3), 4.35 (1H, d, J = 12.0 Hz, CHbenzyl.pyro), 4.69 (1H, d, J = 12.0 Hz, CHbenzyl.pyro), 5.35 (1H, t, J = 10.8 Hz, H5′), 5.96 (2H, s, CH2,benzyl.py), 7.47–7.63 (10H, m, Hphenyl), 8.43 (1H, dd, J1 = 8.0 Hz, J2 = 6.0 Hz, H5), 9.03 (1H, d, J = 8.0 Hz, H4), 9.39 (1H, d, J = 6.0 Hz, H6), 9.60 (1H, s, H2). FT-IR (KBr, ν, cm^{-1}): 700, 900, 1468, 1632, 2945, 3018, 3412. UV–visible (DMSO, nm): 267, 309. Anal. Calcd for C24H28Cl4N2Pd (%): C, 48.63; H, 4.76; N, 4.73. Found (%): C, 48.10; H, 4.35; N, 4.33.

General Procedure for Synthesis of Symmetric Diaryl Sulfides

A mixture of aryl halide (2 mmol), potassium thiocyanate (1 mmol), [DBNT][PdCl4] (1 mol%) and KOH (4 eq.) in DMSO (2 ml) was stirred at 120°C in an oil bath for an appropriate amount of time. The progress of the reaction was monitored using TLC. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Then, 20 ml of water was added to the mixture and the product (reaction mixture), resulting diaryl sulfide, was extracted with ethyl acetate (3 × 10 ml). The organic phase was dried over CaCl2, concentrated under vacuum and purified by column chromatography on silica gel (*n*-hexane–EtOAc, 9:1). All products were known compounds and were identified by comparison of their ^{1}H NMR spectra with those of authentic samples.[28,30,36,37,41,43]

Acknowledgements

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