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Palladium-Catalyzed Thiocarbonylation of Iodoarenes with Thiols in Phosphonium Salt Ionic Liquids

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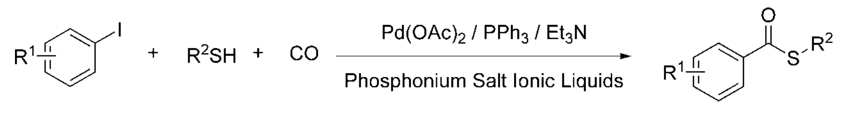

Trihexyl(tetradecyl)phosphonium hexafluorophosphate, a phosphonium salt ionic liquid (PSIL) is a particularly effective general reaction media for the Pd-catalyzed carbonylation reaction of iodoarenes and thiols to form thioesters. Recycling of the ionic liquid containing active Pd-catalyst was also demonstrated.

Introduction

Transitional-metal-catalyzed carbonylation chemistry is widely used in organic synthesis in both academia and industry. Among numerous methods for the introduction of a carbonyl moiety into an organic molecule, this direct functionalization of a substrate using carbon monoxide has attracted a great deal of attention.[1] Although a large number of catalytic systems have been developed for the carbonylation of a wide range of compounds, carbonylation chemistry has still not achieved its full potential. The search for next generation carbonylation technology continues, with the goal of increasing the diversity of possible substrates and recycling often expensive catalysts.[2]

The development of transition-metal-catalyzed carbonylation reactions employing organo−sulfur compounds, especially thiols and thiophenols, still represents a challenging subject since the strong thiophilicity of transition metals[3] may make catalytic reactions ineffective.[4] Within the past few years, we and other groups have developed a series of thiocarbonylation reactions using transition metal catalysts, especially palladium catalysts.[5] These reactions demonstrate the utility of transition metal catalysts for the reactions of sulfur compounds.

Recently, the combination of task specific ionic liquids (TSILs) as versatile and novel reaction media, with transition metal complexes as catalysts, has resulted in many diverse and flexible "platforms" to establish highly effective and easily separable catalytic systems.[6] Because of their unique properties such as nonvolatility, nonflammability, excellent chemical and thermal stability, and recyclability,[7] ionic liquids were also successfully applied to transition-metal-catalyzed carbonylation reactions.[8] While most ionic liquid research is conducted in

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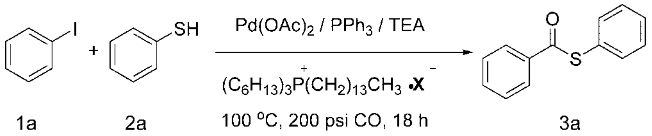
TABLE 1. Palladium-Catalyzed Thiocarbonylation of Aryl Iodides with Thiols in Various PSILs[a]



entry	anion (X^-)	isolated yield (%)[b]
1	Cl^-	55
2	Br^-	84
3	decanoate	56
4	bis(2,4,4-trimethylpentyl)phosphinate	60
5	dicyanamide	70
6	NTf_2	82
7	PF_6	91

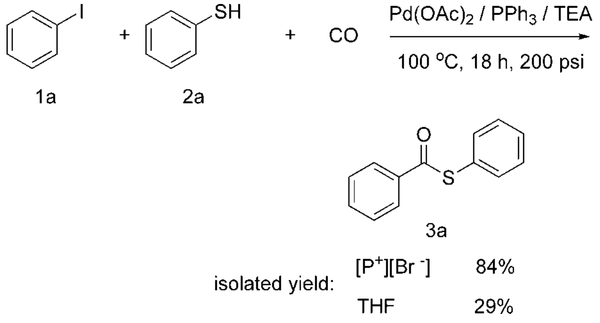
[a] Reaction conditions: **1a** (1.2 mmol), **2a** (1 mmol), CO 200 psi, triethylamine (2 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.20 mmol), PSIL (1.5 g), 18 h, 100 °C. [b] Isolated yield based on thiophenol.

nitrogen-based solvents,[9] McNulty and other groups recently investigated the application of phosphonium salt ionic liquids (PSILs) in general and specifically for palladium-catalyzed processes.[10] Efficient recovery and recycling of the palladium catalysts was demonstrated. When compared to their ammonium counterparts, PSILs displayed increased stability toward thermal and chemical degradation, making them ideal for high temperatures or in processes in which products can be removed by distillation.[11] PSILs are also nonvolatile, economical, and available on an industrial scale. As a new replacement of traditional organic solvents, PSILs are an area of significant promise.

The palladium-catalyzed carbonylation of aryl halides and their derivatives with nucleophiles such as alcohols, amines, and carbon nucleophiles is a powerful method for the synthesis of many aromatic compounds, especially carboxylic acids and their derivatives.[12] Although this reaction has been well established, much less attention has been paid to reactions with organic sulfur compounds.[13] To our knowledge, there have been no reports of transition-metal-catalyzed carbonylation reactions of aryl halides and thiols. Based on our previous work on thiocarbonylation and the application of ionic liquids in transitional-metal-catalyzed carbonylation reactions, we now report the first examples of palladium-catalyzed thiocarbonylation of aryl iodides with thiols in phosphonium ionic liquids.

Results and Discussion

Initial studies focused on examining the feasibility of the thiocarbonylation reactions and optimizing reaction conditions that could be applied to a variety of thiols and aryl halides. The reaction of iodobenzene **1a** and thiophenol **2a** with carbon monoxide was chosen as a model reaction. This reaction was run on a 1 mmol scale, using 5 mol % of $Pd(OAc)_2$ as catalyst, 20 mol % of PPh_3 as ligand, 1.2 equiv of iodobenzene, and 2 equiv of triethylamine in 1.5 g of the PSIL, trihexyl(tetradecyl)phosphonium bromide, at 100 °C, under a pressure of 200 psi carbon monoxide for 18 h and gave **3a** in 84% isolated yield. The same reaction in THF provided **3a** in only 29% yield (eq 1).



(1)

A variety of PSILs consisting of the trihexyl(tetradecyl)phosphonium cation with a range of common anions were screened for the carbonylation reaction of iodobenzene and thiolphenol using $Pd(OAc)_2/PPh_3$ as the catalyst and triethylamine as the base (Table 1). The results presented in Table 1 reveal that most of these PSILs are effective as reaction solvents. The best PSILs are THP-Br, THP-NTf_2, and THP-PF_6, which furnished the product **3a** in 84%, 82%, and 91% isolated yield, respectively

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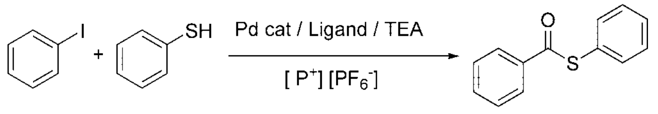
TABLE 2. Influence of Palladium Catalysts, Pressure, and Temperature on the Thiocarbonylation of 1a with Thiophenol and CO[a]



1a **2a** **3a**

entry	catalyst	temp. (°C)	CO (psi)	isolated yield (%)[b]
1	$Pd(OAc)_2/PPh_3$	100	200	91
2	$Pd(OAc)_2/PPh_3$	60	200	77
3	$Pd(OAc)_2/PPh_3$	100	100	53
4	$Pd(OAc)_2/PPh_3$	100	400	96
5	$Pd(OAc)_2$/dppb	100	200	76
6	$Pd(OAc)_2$/dppp	100	200	21
7	$Pd_2(dba)_3 \cdot CHCl_3$	100	200	14
8	$Pd(OAc)_2$	100	200	NR

[a] Reaction conditions: **1a** (1.2 mmol), **2a** (1 mmol), catalyst (0.05 mmol), ligand PPh_3 0.20 mmol), dppb (0.10 mmol) or dppp (0.10 mmol), triethylamine (2 mmol), PSIL (1.5 g). [b] Isolated yield based on thiophenol.

(Table 1, entries 2, 6, 7). While the results for the three ionic liquids are comparable, THP-PF_6 demonstrated itself to be much easier to deal with during the purification stage. Addition of hexane to the reaction mixture containing THP-PF_6 allowed the separation of two phases with the palladium remaining in the ionic liquid layer and the carbonylated product in the organic layer. Other PSILs needed extra H_2O/MeOH to form three layers for extraction.

Further optimization of the reaction conditions is shown in Table 2. The nature of the ligands employed plays an important role in this transformation, with PPh_3 being a superior ligand. In particular, the use of $Pd(OAc)_2/4PPh_3$ was the most effective catalyst system for the formation of **3a** in 91% yield (Table 2, entry 1). Although 1,4-bis-(diphenylphosphino)butane (dppb) was also useful as a ligand for this palladium-catalyzed reaction, the result was inferior to PPh_3 (Table 1, entry 5). Compared to the other bidentate phosphine dppb, 1,3-bis(diphenylphosphino)propane (dppp) was almost ineffective (Table 1, entry 3).

Neither $Pd(OAc)_2$ nor $Pd_2(dba)_3$ is effective for this reaction in the absence of a ligand. It was found that the CO pressure and temperature also affected the thiocarbonylation reaction (Table 2, entries 1–4). Under the same conditions, the reaction proceeded more slowly at lower pressure (53% of **3a** at 100 psi, Table 2, entry 3) and lower temperature (77% of **3a** after 18 h at 60 °C, Table 2, entry 2).

The study of the scope of the palladium-catalyzed thiocarbonylation reaction in the PSIL was extended to a series of aryl halides, reacting with a range of thiols (Table 2). The results show that trihexyl(tetradecyl)phosphonium hexafluorophosphate is an excellent ionic liquid for most of the substrates. Thiophenol affords a higher yield of **3** than substituted thiophenols, while electron-withdrawing substitution on the phenol group provided better yields of **3** than analogues containing an electron-donating group (Table 3, entries 1–7). 2-Naphthalenethiol also reacts with **1a**, and the yield is a little lower than that using thiophenol (Table 3, entry 8). Aliphatic thiols also provided **3** in good yields (Table 3, entries 9–13). Other aryl iodides were also effective partners in this thiocarbonylation reaction. Electron-withdrawing groups enhance the reactivity, as expected, and yields decreased when there was electron-donating substitution on the phenyl group (Table 3, entries 14–18). 1-Iodonaphthalene **1g** and the heteroaromatic iodide **1 h** reacted with **1a**, affording the thioester products in 85% and 43% yields, respectively (Table 3, entries 18–19). We also found that under these conditions the chloroiodoarene **1e** and bromo iodoarene **1f** underwent the thiocarbonylation reaction, giving **3p** and **3q** in 95% and 88% yields, respectively (Table 3, entries 16, 17).

As a new replacement for volatile organic solvents, PSILs have another significant attribute, the recyclability—the recycling of an active IL-soluble catalyst. Catalyst reuse was also investigated for this thiocarbonylation reaction. After the reaction, the ionic liquid was partitioned with hexane, and the ester product was extracted into the hexane phase. The initial run gave complete conversion, and the thioester **3a** was isolated in 91% yield. The IL phase containing active Pd-catalyst was dried under vacuum and recharged with starting materials. Complete conversion of the thiol was again observed after 48 h, and the ester was isolated in 91% yield indicationg that a viable, recyclable catalyst is present in the PSIL.

In conclusion, the PSIL, trihexyl(tetradecyl)phosphonium hexafluorophosphate, is a particularly effective general reaction media for thiocarbonylation reactions of iodoarenes with thiols.

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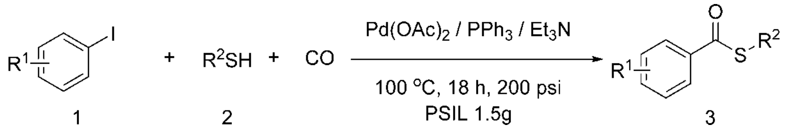
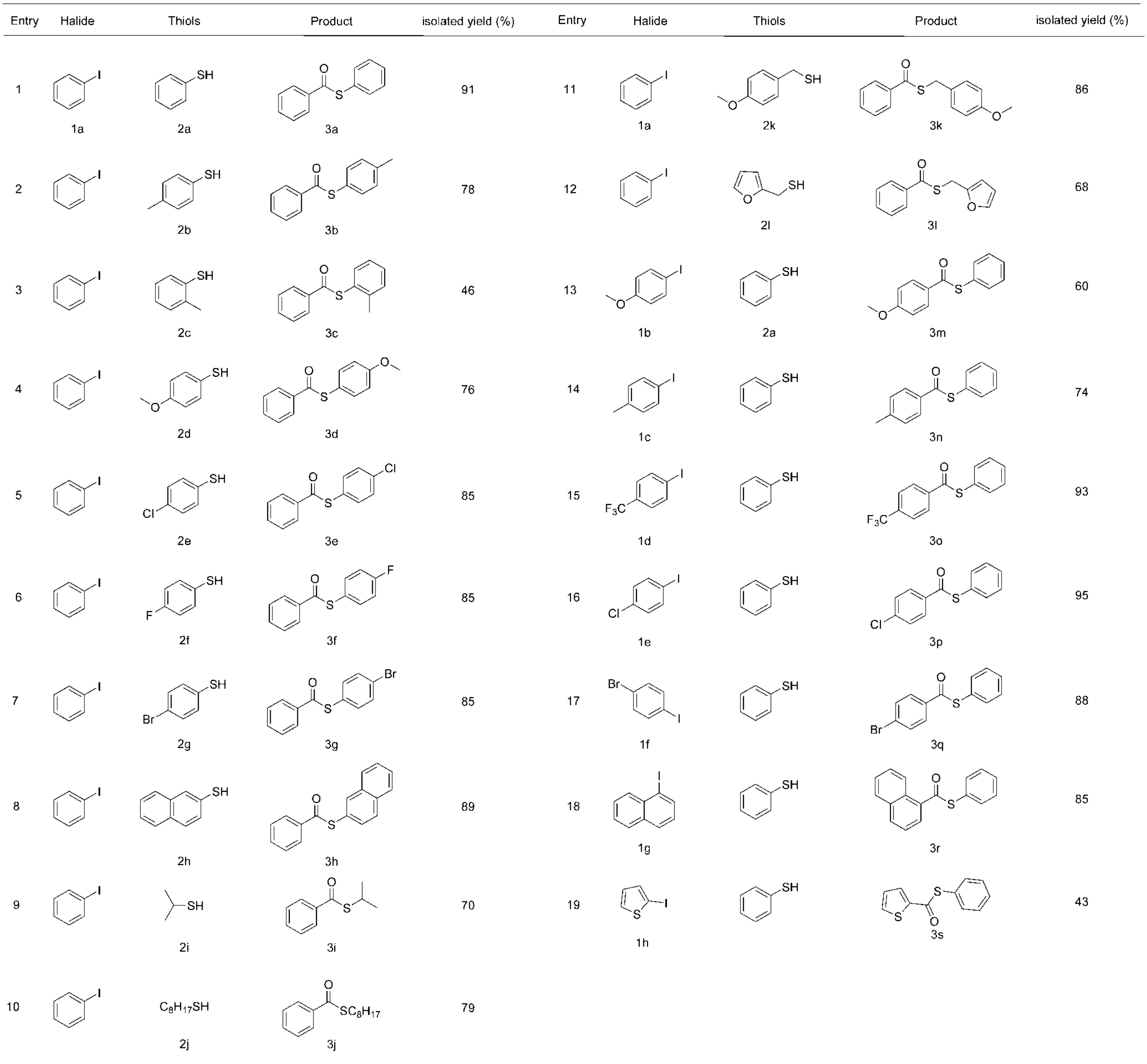
TABLE 3. Palladium-Catalyzed Thiocarbonylation of Aryl Iodides with Thiols in PSIL Trihexyl(tetradecyl)phosphonium Hexafluorophosphate[a,b,c]





Entry	Halide	Thiols	Product	isolated yield (%)
1	1a	2a	3a	91
2		2b	3b	78
3		2c	3c	46
4		2d	3d	76
5		2e	3e	85
6		2f	3f	85
7		2g	3g	85
8		2h	3h	89
9		2i	3i	70
10		$C_8H_{17}SH$ 2j	3j	79
11	1a	2k	3k	86
12		2l	3l	68
13	1b	2a	3m	60
14	1c		3n	74
15	1d		3o	93
16	1e		3p	95
17	1f		3q	88
18	1g		3r	85
19	1h		3s	43

[a] Reaction conditions: iodides (1.2 mmol), thiols (1 mmol), CO 200 psi, triethylamine (2 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.20 mmol), PSIL (1.5 g), 100 °C, 18 h. [b] Based on the iodide employed. [c] Under 500 psi CO.

Recyclability of the PSIL and active Pd catalyst was also demonstrated.

Experimental Section

General Procedure for the Thiocarbonylation Reactions of Iodoarenes with Thiols. A mixture of the iodoarene (1.2 mmol), thiol (1.0 mmol), triethylamine (2.0 mmol), $Pd(OAc)_2$ (0.05mmol), PPh_3 (0.2 mmol), and PSIL (1.5 g) was added to the autoclave. The autoclave was closed, purged three times with carbon monoxide, pressurized with 200 psi of CO, and then heated at 100 °C for 18 h. Excess CO was discharged at room temperature. The resulting solution was extracted with hexane and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (gradient from hexane to hexane/EtOAc 20:1) to give **3** (43–97%). For recovery and reuse of the ionic liquid containing the palladium catalyst, fresh iodide, thiol, and triethylamine were added to the remaining ionic liquid for the next run.

***S*-Phenyl Benzothioate.3a.**[13a] ^1H NMR (300 MHz, CDCl3): δ 7.53–8.16 (m, 10H). ^{13}C NMR (75 MHz, CDCl3): δ 127.90, 128.00, 129.30, 129.79, 130.05, 134.22, 135.64, 137.12, 190.50.

***S*-Furan-2-ylmethyl Benzothioate. 3l.** IR: 1659 cm^{-1} (C═O). ^{1}H NMR (300 MHz, CDCl3): δ 4.39 (s, 2H), 6.34 (m, 2H), 7.37–8.01 (m, 8H). ^{13}C NMR (75 MHz, CDCl3): δ 26.18, 108.60, 111.12, 127.75, 129.09, 134.00, 137.05, 142.71, 150.88, 191.09. MS (EI) *m*/*z*: 218 (M$^+$, 26). HRMS (EI) *m*/*z*: calcd for $C_{12}H_{10}O_2S$ (M$^+$) 218.0402, found 218.0388.

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Supporting Information Available: Full experiment details, characterization for all compounds, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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