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Method

General and Practical Intramolecular Decarbonylative Coupling of Thioesters via Palladium Catalysis

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We report a general and practical palladium-catalyzed intramolecular decarbonylative coupling of thioesters via C–S bond cleavage, decarbonylation and C–S bond reformation. This robust approach shows excellent functional group tolerance and broad substrate scope using commercially-available, cheap, and practical $Pd(OAc)_2$ catalyst and phosphine ligands. This strategy operates under base-free conditions. The catalytic system represents the simplest method for intramolecular decarbonylation of thioesters by palladium catalysis reported to date. This versatile protocol is readily performed on a gram scale and applied in late-stage drug derivatization.

Introduction

Thioethers are similar to ethers except that they feature a sulfur atom instead of oxygen, which embodies them with increased lipophilicity and represents one of the most important moieties in pharmaceutical development (Figure 1A).[1,2] Thus, the development of methodologies for the synthesis of thioethers is highly desirable.[3] Typical methods involve preparation of thioethers by alkylation of thiols,[4] reaction between disulfides and Grignard reagents,[5] addition of thiols to alkenes by thiol-ene reactions,[6] and Pummerer rearrangement.[7] With the invention of new methodologies in this field, cross-couplings of aryl halides or pseudohalides with thiols have emerged as the most powerful method for the synthesis of thioethers.[8] It noteworthy that recent progress in transition-metal-catalyzed cross-couplings involve decarbonylation of readily available and bench-stable amides, esters and carboxylic acids.[9-15] Typical electrophiles used for the synthesis of thioethers via cross-coupling involve functionalized substrates. From the standpoints of atom economy and practicality, transition-metal-catalyzed intramolecular decarbonylation represents the most direct strategy for the synthesis of thioethers. In 1991, Wenkert reported the first intramolecular decarbonylation of thioesters using stoichiometric nickel as a promoter and zinc as a reducing agent, which was successfully applied to 12 examples in up to 86% yield (Figure 1B).[16] In Ni-catalysis, in 2018, Sanford reported a nickel-catalyzed base-free intramolecular decarbonylation of thioesters, which performed under catalytic conditions and without reducing reagents; however, the experimental conditions necessitated operating in a glove box due to air- and moisture-sensitive $Ni(cod)_2$ catalyst.[17] In 2018, we disclosed a nickel-catalyzed intramolecular decarbonylation of thioesters using air- and moisture-stable nickel precatalysts, which allowed for the reactions to be performed on a bench-top and glove box set-up was not required.[18] Shortly afterwards, another Ni-catalyzed intramolecular decarbonylation of thioesters with $Ni(OAc)_2$ as a catalyst and P(*n*-Bu)$_3$ or dppb as ligands was reported.[19]

Pd-catalyzed intramolecular decarbonylation of thioesters is another robust approach for the synthesis of thioethers. In 1987, Yamamoto reported the first Pd-catalyzed intramolecular decarbonylation of thioesters, which proceed with 5-20 mol% of the air-sensitive $Pd(PCy_3)_2$ as a catalyst;[20] however, the method was showed to be effective in only 3 examples. Afterwards, Kambe group also reported a palladium-catalyzed intramolecular decarbonylation of thioesters using $Pd(PPh_3)_4$ as a precatalyst, which is similar to Yamamoto's catalyst.[21] Unsurprisingly, the method using the coordinatively saturated and unstable Pd(0) complex showed narrow substrate scope and very low functional group tolerance. For broadening the scope and improving the functional group tolerance, Sanford group reported a palladium-catalyzed intramolecular decarbonylation of thioesters, which employed 10 mol% $Pd[P(o\text{-tol})_3]_2$ precatalyst and 20 mol% PAd_2Bn ligand.[17] This method was successfully applied to 23 examples in up to 85% yield for the synthesis of thioethers. In 2020, Lee reported Pd-catalyzed decarbonylative thioetherification of 2-pyridyl thioesters.[22] Other Ni catalyzed methods have been reported.[11d,19] In light of these findings, herein, we report our study on the development of a general and practical palladium-catalyzed method for thioether synthesis via a robust palladium-catalyzed base-free intramolecular decarbonylation of thioesters.

The following features of our findings are noteworthy: (1) this powerful method represents the first general and practical palladium-catalyzed base-free intramolecular decarbonylation of thioesters; (2) the method uses cheap, air-stable,

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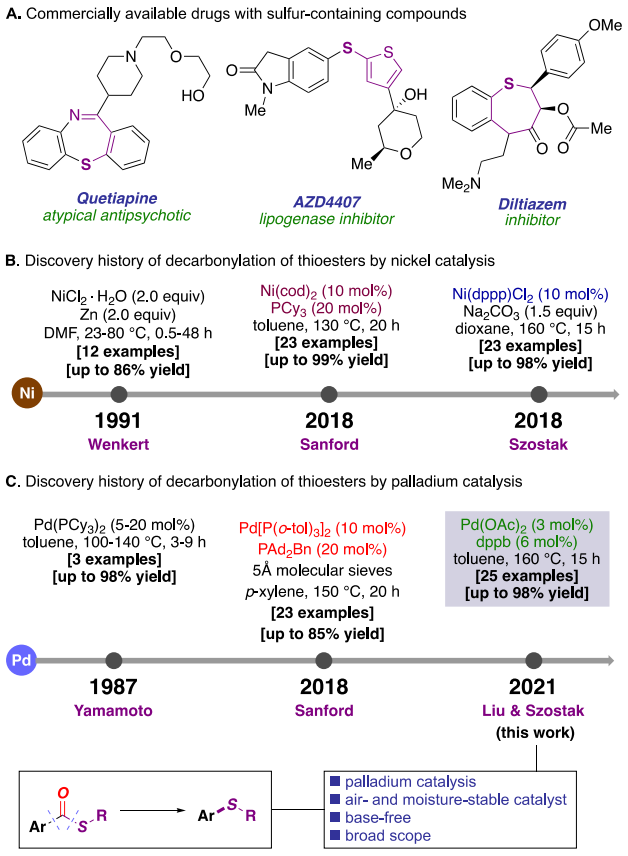
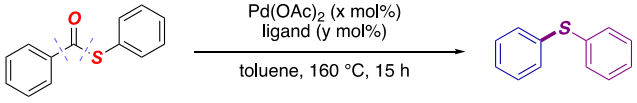


commercially-available catalysts and ligands; (3) the method offers a complementary avenue to nickel-catalyzed and other palladium-catalyzed methods for intramolecular decarbonylation of thioesters; (4) the method holds a significant potential for the industrial synthesis of thioethers using thioesters as the ultimate precursors.

Results and Discussion

For optimization, PhCOSPh **1a** was selected as a modular, unbiased substrate (Table 1). After experimentation, we identified the optimal conditions for the Pd-catalyzed intramolecular decarbonylation of thioesters, furnishing the desired thioether product in excellent 95% yield (Table 1, entry 1). As expected, no product was formed in the absence of the catalyst (<2%) (Table 1, entry 2). Control experiments indicated that organic and inorganic bases lead to a decrease in catalytic ability (Table 1, entries 3-4). A range of phosphine ligands was investigated. It is noteworthy that dppp, dpppent, SPhos, $PCyPh_2$ and PPh_3 are able to deliver the decarbonylative product in high yields under these conditions (Table 1, entries 5-15). Furthermore, $Pd(OAc)_2$ is preferred over $Pd_2(dba)_3$ (Table 1, entry 16), and toluene is a superior solvent to dioxane in this methodology (Table 1, entry 17). Further optimization revealed that the catalyst loading could be decreased to 3 mol% (Table 1, entry 18), while appreciable conversion was observed at as low temperatures as 100 °C (Table 1, entry 22), consistent with high efficiency under these conditions.

Table 1. Optimization of the Reaction Conditions.[a,b]

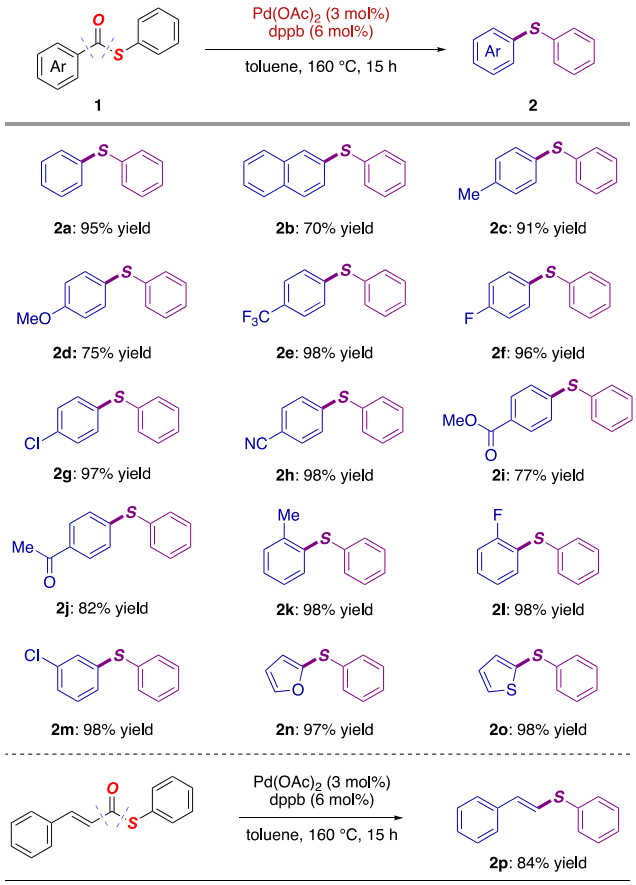


Entry	catalyst	ligand	base	Yield [%]
1	$Pd(OAc)_2$	dppb	-	95
2	-	-	-	<2
3	$Pd(OAc)_2$	dppb	Et_3N	59
4	$Pd(OAc)_2$	dppb	Na_2CO_3	40
5	$Pd(OAc)_2$	dppp	-	95
6	$Pd(OAc)_2$	dpppent	-	90
7	$Pd(OAc)_2$	dppf	-	80
8	$Pd(OAc)_2$	BINAP	-	85
9	$Pd(OAc)_2$	XantPhos	-	72
10	$Pd(OAc)_2$	DavePhos	-	74
11	$Pd(OAc)_2$	XPhos	-	67
12	$Pd(OAc)_2$	SPhos	-	95
13	$Pd(OAc)_2$	PCy_3HBF_4	-	65
14	$Pd(OAc)_2$	$PCyPh_2$	-	92
15	$Pd(OAc)_2$	PPh_3	-	93
16	$Pd_2(dba)_3$	dppb	-	66
17[c]	$Pd(OAc)_2$	dppb	-	73
18[d]	$Pd(OAc)_2$	dppb	-	95
19[e]	$Pd(OAc)_2$	dppb	-	61
20[d,f]	$Pd(OAc)_2$	dppb	-	85
21[d,g]	$Pd(OAc)_2$	dppb	-	80
22[d,h]	$Pd(OAc)_2$	dppb	-	79

[a]Conditions: thioester (1.0 equiv), catalyst (5 mol%), ligand (10 mol%), base (1.5 equiv), toluene (0.20 M), 160 °C, 15 h. [b]GC/1H NMR yields. [c]dioxane as solvent. [d]catalyst (3 mol%), ligand (6 mol%). [e]catalyst (1 mol%), ligand (2 mol%). [f]140 °C. [g]120 °C. [h]100 °C.

Under the optimal conditions, this method exhibits a very broad scope with respect to aryl-aryl, aryl-heteroaryl and aryl-alkyl products (Schemes 1-2). As shown, a range of electronically-diverse thioesters underwent efficient intramolecular decarbonylation (**2a-j**), including electron-neutral (**2a-c**), electron-rich (**2d**), and electron-deficient substrates (**2e**). Importantly, halide-functionalized substrates, such as fluoro- (**2f**) and chloro- (**2g**) thioesters can be well tolerated. Full conversion was achieved for a cyano-containing-substrate (**2h**). It is important that full selectivity for decarbonylation was observed in the reaction of ester and ketone containing substrates (**2i-j**), attesting to the high chemoselectivity of this method. Steric hindrance was well tolerated (**2k-l**). Meta-functionalization was well compatible (**2m**). In addition, heterocyclic thioesters can be readily incorporated to furnish thioethers in excellent yields (**2n-o**). Finally, styryl-thioester was also well tolerated in this method (**2p**).

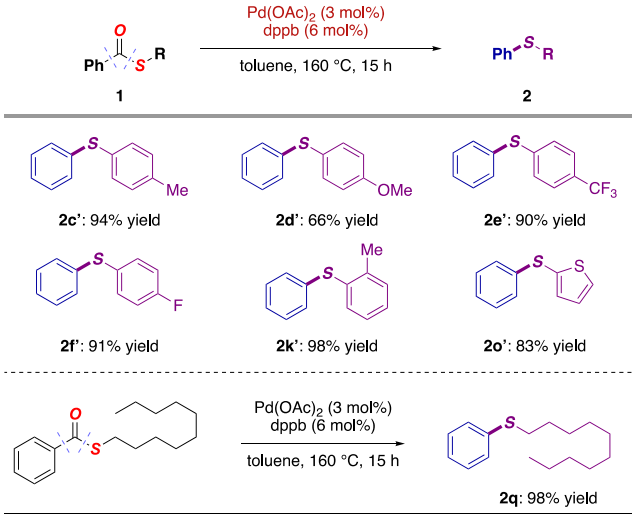
With respect to the thiophenol moiety, we were delighted to find that a broad range of electron-neutral (**2c'**), electron-donating (**2d'**) and electron-withdrawing (**2e'-f'**) thioesters can be readily engaged to generate the thioether products in good to excellent yields (Scheme 2). Furthermore, steric-hindrance (**2k'**) and heterocyclic thioesters (**2o'**) readily participate in this practical approach. Finally, the method is also feasible for aryl-



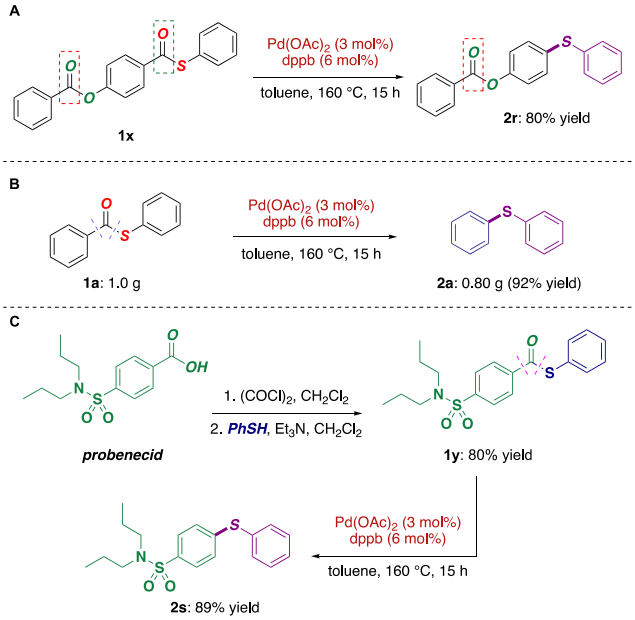
Scheme 1. Scope of Pd-Catalyzed General Intramolecular Decarbonylation of Thioesters.

alkyl coupling to deliver to desired thioether product (**2q**), which is a challenging substrate in this manifold.

To further demonstrate the synthetic utility of this general and practical Pd-catalyzed decarbonylative coupling of thioesters, we conducted selectivity studies, gram scale synthesis and drug derivatization (Scheme 3). In 2017, Yamaguchi and Itami reported the intramolecular decarbonylation of esters, which effectively enabled decarbonylative etherification of aromatic esters.[23] Thus, we were curious to test if the carbonyl group in the ester functional group could be tolerated under our catalytic conditions. Thus, the compound containing ester and thioester functional group was synthesized and applied to our protocol (Scheme 3A).[21] The result showed that the carbonyl group in thioester group can be readily removed under our catalytic conditions but the carbonyl group in ester group remains fully intact, demonstrating the excellent chemoselectivity of this approach. Furthermore, we conducted the coupling on a gram scale, which resulted in 92% yield (0.80 g) of the thioether product, showing the scalability of the method (Scheme 3B). Finally, we employed Probenecid, an antihyperuricemic drug, which could be readily converted to the corresponding thioether in 89% yield (Scheme 3C). Notably, this protocol is superior to previous palladium- and nickel-catalyzed methods in terms of operational-simplicity, broad scope, and excellent functional group tolerance.



Scheme 2. Scope of Pd-Catalyzed General Intramolecular Decarbonylation of Thioesters.



Scheme 3. (A) Selectivity Study. (B) Gram Scale Reaction. (C) Expedient Synthesis of Probenecid Thioether.

Finally, a plot of conversion vs. time for thioester **1a** was conducted to provide insight into the kinetic profile of the reaction (Figure 2). The plot showed that the method can deliver the desired thioether product in >90% yield within 5 h, which is in accord with the high efficiency of this catalytic system.

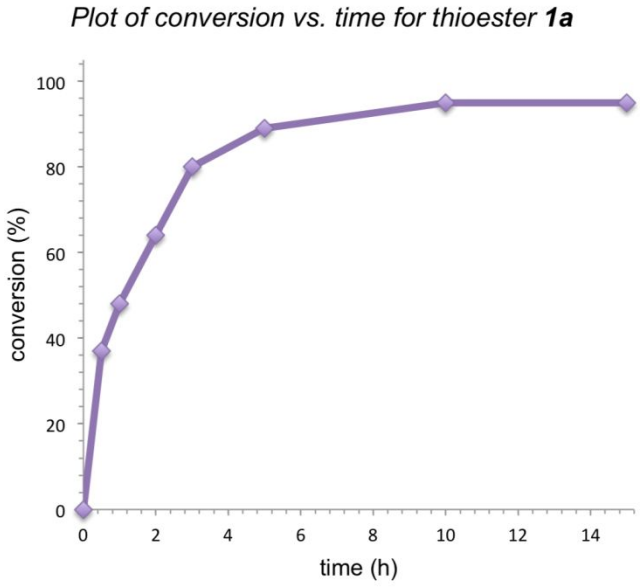


Figure 2. Kinetic profile of **1a**. Conditions: **1a** (1.0 equiv), $Pd(OAc)_2$ (3.0 mol%), dppb (6.0 mol%), toluene, 160 °C.

Conclusions

In summary, in this Update article, we have reported the general and practical palladium-catalyzed base-free intramolecular decarbonylation of thioesters. The developed catalytic system employs commercially-available, cheap, and practical $Pd(OAc)_2$ as a catalyst and phosphine as ligands. The system shows major advantages over other palladium- and nickel-catalyzed methods and should be considered as the first-choice protocol for performing intramolecular decarbonylation of thioesters to furnish valuable thioether products. The method was successfully applied to achieve intramolecular decarbonylations of a wide range of electronically- and sterically-varied thioesters to thioethers in good to excellent yields under operationally practical conditions. The scalability of the method was evaluated on a gram scale reaction. The synthetic application to late-stage derivatization was demonstrated. We anticipate that the findings reported in this manuscript will facilitate the development of general methods for the synthesis of thioethers using palladium catalysis. Future studies will focus on the development of tandem reactions utilizing CO recycling and mechanistic studies on this reaction manifold.

Conflicts of interest

There are no conflicts to declare.

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