Synthesis of Secondary and Tertiary Aminothiophenes via Palladium-Catalyzed Amination

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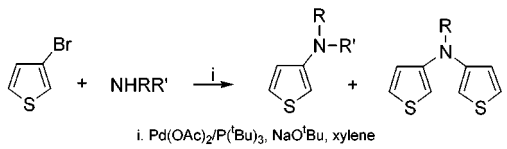
Introduction

Functionalized thiophenes are useful precursors for natural products,[1] pharmaceuticals,[2] conjugated polymers,[3] and other related materials.[4] While a wide variety of functionalized thiophenes have been synthesized for these applications, no broadly applicable methodology really exists for the synthesis of aminothiophenes. The Gewald reaction is the most well-established route but is limited to the production of primary 2-aminothiophenes containing electron-withdrawing groups in the 3-position.[2a,5] The analogous 3-aminothiophene has been made by a number of methods,[6] and Paulmier and co-workers have investigated its *N*-alkylation, but with only a small number of functional groups.[6b]

Reported examples of the direct amination of thiophenes are even more limited. Certain halothiophenes undergo nucleophilic aromatic substitution with amines, but this reaction is restricted to very electron deficient systems.[7] More recently, however, Buchwald[8] and Hartwig's[9] work on the palladium-catalyzed amination of arylhalides has been applied to halothiophenes. The first Pd-catalyzed amination of a halothiophene was reported by Watanabe and co-workers, who showed that mono- and dibromothiophenes could be successfully coupled with diarylamines using a $Pd(OAc)_2/P(^tBu)_3$ catalyst system.[4] Following up on this work, Luker and co-workers reported an alternate catalytic system that could be used under milder conditions but was limited to the coupling of halothiophenes containing electron-withdrawing groups in conjugation with the halogen (2,3- or 2,5-isomers).[2b]

Due to our interest in the production of functionalized polyaminothiophenes, we needed a convenient and general approach to the production of 3-(*N*-alkyl)- and 3-(*N*-aryl)-aminothiophenes while leaving the thiophene α-positions free for subsequent polymerization. Working toward this goal, we have applied Watanabe's reaction conditions to the alkylamination of bromothiophenes and, in the process, have carefully studied the working boundaries of the various reaction conditions.

Table 1. Pd-Catalyzed Amination of 3-Bromothiophene



i. $Pd(OAc)_2/P(^tBu)_3$, NaO^tBu, xylene

entry	amine	product (%)[a]	product (%)[a]
1	$NH_2C_6H_{13}$	**1a** (37)	**1b** (20)
2	$NH_2C_8H_{17}$	**2a** (36)	**2b** (29)
3	$NH_2C_{10}H_{21}$	**3a** (44)	**3b** (44)
4	$NH_2C(CH_3)_3$	**4a** (54)	**4b** (19)
5	$NH(C_6H_{13})_2$	**5** (24)	
6	*p*-$NH_2ArC_6H_{13}$	**6a** (75)	**6b** (18)
7	**2a**		**2b** (83)

[a] Isolated yields based on 3-bromothiophene.

Results and Discussion

Application of the $Pd(OAc)_2/P(^tBu)_3$ catalyst system to the amination of 3-bromothiophene successfully produced the desired 3-(*N*-alkyl)- and 3-(*N*,*N*-dialkyl)-aminothiophenes as shown in Table 1 (entries 1−5). The isolated yields in these cases, however, were much lower than the analogous reactions using arylamines (Table 1, entries 6 and 7), and in all cases, the use of primary amines resulted in a significant amount of diarylation byproduct (**1b**−**4b**, **6b**). In all cases, catalyst concentrations could be reduced to 1 mol % without a reduction in yields.

A proposed catalytic cycle based on the previous mechanistic studies of haloaryl aminations is shown in Scheme 1.[8,9] The lower yields resulting from the use of alkylamines is at least partially due to a β-elimination pathway that competes with the desired reductive elimination step (i.e., formation of complex **VI**). The presence of this pathway is evidenced by the isolation of small amounts of alkylimines in these reactions. In addition, when the possibility of β-elimination is removed as in entry 4, a significant increase is observed in the isolated yield. Likewise, the use of dialkylamines increases the potential for β-elimination and results in lowered yields (entry 5).

In an attempt to reduce possible side products in the reactions of the primary alkylamines, a variety of conditions were investigated, including temperature, solvent, stoichiometry, palladium source, and the ligand used.

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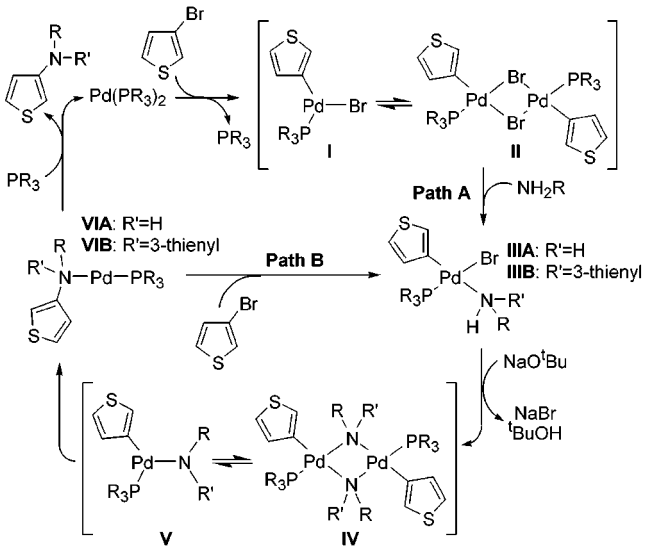
Scheme 1. Proposed Catalytic Cycle for Thiophene Amination



Temperatures of 110 °C or greater had very little effect on the product yield or distribution. The formation of amination product was seen at temperatures as low as 60 °C, but the lower temperatures resulted in reduced product yields. It has been previously explained that the high reaction temperature is needed to overcome the formation of the very stable amide dimer (complex **IV**) produced after deprotonation of the coordinated amine by the NaO^{t}Bu as shown in Scheme 1.[10] This restriction in temperature thus limits potential solvents. Although toluene and THF solvent systems both successfully gave amination products, they did so with reduced yields that scale with the reduced temperatures. DMF was also investigated as a polar, high-boiling solvent, but amination was not observed under these conditions.

Variations in the ratio of bromothiophene to amine used had only minor effects on the distribution of secondary to tertiary products. For this reason, it is believed that the aminothiophene product must remain coordinated to the palladium center after reductive elimination (Scheme 1, complex **VI**). Such coordination has been previously proposed by Hartwig.[11] Formation of the tertiary diarylation product would then be controlled by competition between bromothiophene oxidative addition (i.e., path B of Scheme 1) and product displacement rather than the competitive binding of different amines. It was found, however, that large excesses of amine (10-fold or greater) resulted in the production of only trace amounts of the diarylation byproduct. Unfortunately, these conditions also significantly reduced the yield of the desired amination product as well. The high amine concentration should enhance product displacement but also has a greater likelihood of poisoning the catalyst.

As the palladium catalyst precursor has been previously shown to affect the amination product yields,[12] $PdCl_2$, $Pd_2(dba)_3$, $(Pd(\pi\text{-allyl})Cl)_2$ were investigated as alternate sources of palladium for the catalyst mixture. Comparative yields for the coupling of hexylamine and 3-bromothiophene with the various palladium precursors are shown in Table 2. All cases successfully produce amination products, but the alternate sources (Table 2, entries 2−4) give lower yields than the intial $Pd(OAc)_2$ (entry 1). Changes in the palladium precursor do seem to have a minor influence on product distributions, but no real selectivity is observed. In the case of $PdCl_2$ (Table 2, entry 3), however, the distribution does shift to favor the diarylation product over the desired secondary amination product.

Table 2. Comparative Studies Utilizing Various Catalyst Precursors[a]

entry	Pd compound	**1a** yield[a]	**1b** yield[a]
1	$Pd(OAc)_2$	37	20
2	$Pd_2(dba)_3$	14	7
3	$PdCl_2$	13	21
4	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	25	24

[a] Isolated yields based on 3-bromothiophene.

Table 3. Comparative Studies Utilizing Various PR_3 Ligands[a]

entry	R	cone angle[b]	**1a** yield[a]	**1b** yield[a]	bithiophene[a]
1	cyclohexyl	170			12
2	^{t}Bu$_2{}^i$Pr	175			64
3	neopentyl	180			18
4	^{t}Bu	182	37	20	
5	*t*-pentyl	~186[c]	trace		12
6	C_6F_5	184			
7	*o*-tolyl	194			16
8	mesityl	212			22

[a] Isolated yields based on 3-bromothiophene. [b] From ref 13. [c] Estimated from space-filling model.

In addition to the tri-*tert*-butylphosphine ligand, we have also investigated a number of other phosphines, varying both the cone angle[13] and electronic parameters of the ligand used. The results of this study are shown in Table 3. For comparison purposes, all reactions in entries 1−8 were carried out utilizing hexylamine as the primary amine.

With the exception of the original conditions (Table 3, entry 4) and the tri-*tert*-pentylphosphine ligand (entry 5), which gave trace amounts of the desired product, all other ligands gave no aminothiophene products and no trends could be established on the basis of the cone angles of the ligands used. In most cases, large amounts of 1-hexanimine were isolated resulting from a competing β-elimination pathway. The only major thiophene product in the failed attempts was 3,3′-bithiophene.

The use of the pentafluorophenyl ligand (entry 6) resulted in no reaction of any kind, possibly suggesting that the initial oxidative addition step failed in this example. Finally, to investigate the potential of chelating phosphines, the bidentate ligand 1,1′-bis(diphenylphosphino)ferrocene was also investigated, but again the only products isolated were 1-hexanimine and 3,3′-bithiophene.

A proposed mechanism for the formation of isolated 3,3′-bithiophene is shown in Scheme 2 on the basis of analogous catalytic processes resulting in the production of biaryls.[14] This proposed mechanism is additionally supported by the detection of α-brominated thiophenes in some reaction mixtures. Such brominated products would be readily formed in the presence of the Br_2 and HBr produced as shown in Scheme 2.

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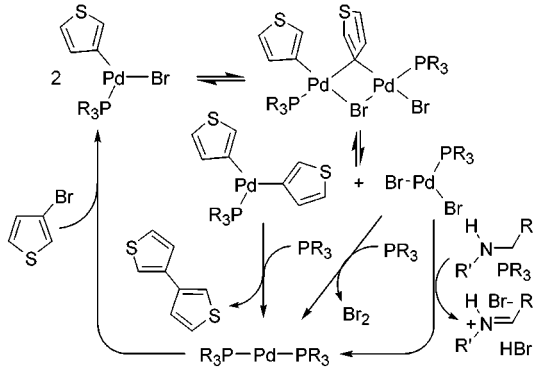
Scheme 2. Proposed Catalytic Cycle for Bithiophene Formation



To investigate the versatility of the coupling reaction, we also studied the amination of 4-bromo-2,2′-bithiophene[15] and 2-bromothiophene. Amination of 4-bromo-2,2′-bithiophene produced the desired 4-(*N*-octylamino)-2,2′-bithiophene in yields of 20%.[16] As with the previous amination of 3-bromothiophene, a diarylation byproduct was also isolated from this reaction in yields of 20%. In contrast to the successful aminations of 2-bromothiophenes with diarylamines,[4] we have found that analogous reactions with either monoarylamines or alkylamines were unsuccessful. Repeating Watanabe's amination of 2-bromothiophene with diphenylamine, we were able to successfully isolate the amination product in 54% yield (lit. 36%).[4] In addition, we have had some success with reactions between 2-bromothiophene and **5a** and are continuing to investigate the selectivity of the α-bromides under these reaction conditions.

Further investigations into the optimization of these catalytic aminations are underway. As with the illustrated successes of haloaryl aminations,[8,9] a greater amount of control may be possible through the additional utilization of various chelating ligands.

Experimental Section

General. Unless noted, all materials were reagent grade, purchased from Sigma-Aldrich, and used without further purification. Xylene was distilled from sodium and benzophenone prior to use. Isopropyldi-*tert*-butylphosphine,[17] trineopentylphosphine,[18] and tri-*tert*-pentylphosphine[19] were prepared as described in the literature. Chromatography was performed using EM Science silica gel (230−400 mesh). All glassware was oven-dried, assembled hot, and cooled under a dry nitrogen stream before use. All reactions were performed under nitrogen. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Varian 300 MHz spectrometer and referenced to the chloroform signal. Elemental analyses were performed in house on a Perkin-Elmer Series II CHNS/O Analyzer 2400.

General Amination Procedure. 3-Bromothiophene (10 mmol), amine (10 mmol), sodium *tert*-butoxide (11 mmol), palladium acetate (0.1 mmol), and tri-*tert*-butylphosphine (0.1 mmol, 0.4 mL of 50 mg/mL solution in *o*-xylene) were mixed in 40 mL of *o*-xylene and refluxed at 120 °C for 4 h. After the mixture was cooled, water was added and the organic layer separated. The remaining aqueous layer was then extracted with hexanes (2 × 50 mL), and the combined organic fractions were dried with Na_2SO_4 and concentrated in vacuo. The crude product was then purified by chromatography over silica gel (2.5% EtOAc/hexanes).

***N*-Hexyl-3-aminothiophene (1a).** ^{1}H NMR ($CDCl_3$): δ 7.16 (dd, J = 3.0, 5.4 Hz, 1H), 6.62 (dd, J = 1.8, 5.4 Hz, 1H), 5.95 (dd, J = 1.8, 3.0 Hz, 1H), 3.56 (br, 1H), 3.07 (t, J = 7.1 Hz, 2H), 1.63 (m, 2H), 1.36 (m, 6H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 125.3, 120.2, 95.5, 46.6, 31.9, 29.8, 27.2, 22.9, 14.3. Anal. Calcd for $C_{10}H_{17}NS$: C, 65.52; H, 9.35; N, 7.64. Found: C, 65.40; H, 9.36; N, 7.27.

***N*-Hexyl-*N*-(3′-thienyl)-3-aminothiophene (1b).** ^{1}H NMR ($CDCl_3$): δ 7.21 (dd, J = 3.0, 5.4 Hz, 2H), 6.90 (dd, J = 1.8, 5.4 Hz, 2H), 6.49 (dd, J = 1.8, 3.0 Hz, 2H), 3.60 (t, J = 7.7 Hz, 2H), 1.67 (m, 2H), 1.32 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.2, 124.9, 123.0, 105.9, 54.5, 31.9, 27.5, 27.1, 23.0, 14.4. Anal. Calcd for $C_{14}H_{19}NS_2$: C, 63.35; H, 7.22; N, 5.28. Found: C, 63.16; H, 7.03; N, 4.88.

***N*-Octyl-3-aminothiophene (2a).** ^{1}H NMR ($CDCl_3$): δ 7.15 (dd, J = 3.0, 5.4 Hz, 1H), 6.62 (dd, J = 1.8, 5.4 Hz, 1H), 5.95 (dd, J = 1.8, 3.0 Hz, 1H), 3.58 (br, 1H), 3.07 (t, J = 6.9 Hz, 2H), 1.62 (m, 2H), 1.30 (m, 10H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 125.3, 120.2, 95.5, 46.6, 32.1, 29.9, 29.7, 29.5, 27.5, 22.9, 14.4. Anal. Calcd for $C_{12}H_{21}NS$: C, 68.19; H, 10.01; N, 6.63. Found: C, 68.54; H, 9.73; N, 6.29.

***N*-Octyl-*N*-(3′-thienyl)-3-aminothiophene (2b).** ^{1}H NMR ($CDCl_3$): δ 7.23 (dd, J = 3.0, 5.4 Hz, 2H), 6.94 (dd, J = 1.8, 5.4 Hz, 2H), 6.54 (dd, J = 1.8, 3.0 Hz, 2H), 3.65 (t, J = 7.7 Hz, 2H), 1.73 (m, 2H), 1.35 (m, 10H), 0.97 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.3, 125.0, 123.0, 105.9, 54.5, 32.2, 29.8, 29.7, 27.6, 27.5, 23.0, 14.5. Anal. Calcd for $C_{16}H_{23}NS_2$: C, 65.48; H, 7.90; N, 4.77. Found: C, 65.36; H, 7.77; N, 4.74.

***N*-Decyl-3-aminothiophene (3a).** ^{1}H NMR ($CDCl_3$): δ 7.16 (dd, J = 3.0, 5.4 Hz, 1H), 6.62 (dd, J = 1.8, 5.4 Hz, 1H), 5.96 (dd, J = 1.8, 3.0 Hz, 1H), 3.58 (br, 1H), 3.08 (t, J = 7.1 Hz, 2H), 1.64 (m, 2H), 1.30 (m, 14H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 149.1, 125.3, 120.2, 95.4, 46.7, 32.2, 29.9, 29.9, 29.8, 29.6, 27.5, 27.2, 23.0, 14.4. Anal. Calcd for $C_{14}H_{25}NS$: C, 70.23; H, 10.53; N, 5.85. Found: C, 70.23; H, 10.13; N, 5.55.

***N*-Decyl-*N*-(3′-thienyl)-3-aminothiophene (3b).** ^{1}H NMR ($CDCl_3$): δ 7.23 (dd, J = 3.0, 5.4 Hz, 2H), 6.93 (dd, J = 1.8, 5.4 Hz, 2H), 6.52 (dd, J = 1.8, 3.0 Hz, 2H), 3.63 (t, J = 7.7 Hz, 2H), 1.71 (m, 2H), 1.33 (m, 14H), 0.96 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.2, 124.9, 123.0, 105.9, 54.5, 32.2, 30.0, 29.9, 29.8, 29.7, 27.6, 27.5, 23.0, 14.5. Anal. Calcd for $C_{18}H_{27}NS_2$: C, 67.24; H, 8.46; N, 4.36. Found: C, 67.57; H, 8.41; N, 4.61.

***N*-*tert*-Butyl-3-aminothiophene (4a).** ^{1}H NMR ($CDCl_3$): δ 7.04 (dd, J = 3.0, 5.1 Hz, 1H), 6.57 (dd, J = 1.5, 5.1 Hz, 1H), 6.15 (dd, J = 1.5, 3.0 Hz, 1H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 145.6, 124.3, 124.1, 103.1, 52.1, 29.8. Anal. Calcd for $C_8H_{13}NS$: C, 61.89; H, 8.44; N, 9.02. Found: C, 62.00; H, 8.54; N, 8.83.

***N*-*tert*-Butyl-*N*-(3′-thienyl)-3-aminothiophene (4b).** ^{1}H NMR ($CDCl_3$): δ 7.12 (dd, J = 3.3, 5.1 Hz, 2H), 6.70 (dd, J = 1.2, 5.1 Hz, 2H), 6.66 (dd, J = 1.2, 3.3 Hz, 2H), 1.37 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 147.7, 127.7, 123.5, 113.3, 56.2, 29.2. Anal. Calcd for $C_{12}H_{15}NS_2$: C, 60.72; H, 6.37; N, 5.90. Found: C, 60.58; H, 6.20; N, 5.92.

***N*-(*p*-Hexylphenyl)-3-aminothiophene (5a).** ^{1}H NMR ($CDCl_3$): δ 7.25 (dd, J = 3.0, 5.4 Hz, 1H), 7.08 (d, J = 6.6 Hz, 2H), 6.93 (d, J = 6.6 Hz, 2H), 6.90 (dd, J = 1.8, 5.4 Hz, 1H), 6.68 (dd, J = 1.8, 3.0 Hz, 1H), 5.65 (br, 1H), 2.55 (t, J = 7.8 Hz, 2H), 1.60 (m, 2H), 1.32 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 142.4, 135.0, 129.4, 125.3, 122.8, 116.3, 105.3, 35.4, 32.0, 32.0, 29.3, 22.9, 14.4. Anal. Calcd for $C_{16}H_{21}NS$: C, 74.08; H, 8.16; N, 5.40. Found: C, 73.90; H, 8.15; N, 5.12.

***N*-(*p*-Hexylphenyl)-*N*-(3′-thienyl)-3-aminothiophene (5b).** ^{1}H NMR ($CDCl_3$): δ 7.21 (dd, J = 3.0, 5.4 Hz, 2H), 7.06 (m, 4H), 6.89 (d, J = 5.4 Hz, 2H), 6.63 (poorly resolved doublet 2H), 2.57 (t, J = 7.9 Hz, 2H), 1.61 (m, 2H), 1.33 (m, 6H), 0.90 (t, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 147.2, 145.8, 138.0, 129.3, 125.0, 124.4, 122.9, 110.9, 35.6, 32.0, 31.8, 29.3, 22.9, 14.4. Anal. Calcd

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(16) Crude yields as determined by ^{1}H NMR prior to separation were higher. However, due to the increased conjugation of this compound, it is very susceptible to oxidation and thus not very stable. This instability makes its purification challenging and results in losses due to decomposition.

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for $C_{20}H_{23}NS_2$: C, 70.33; H, 6.79; N, 4.10. Found: C, 70.29; H, 6.89; N, 3.82.

***N,N*-Dihexyl-3-aminothiophene (6).** ^{1}H NMR ($CDCl_3$): δ 7.19 (dd, J = 3.0, 5.4 Hz, 1H), 6.74 (dd, J = 1.2, 5.4 Hz, 1H), 5.81 (dd, J = 1.2, 3.0 Hz, 1H), 3.16 (t, J = 7.7 Hz, 4H), 1.56 (m, 4H), 1.31 (m, 12H), 0.91 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 150.7, 124.9, 119.1, 94.6, 52.8, 32.0, 27.5, 27.2, 23.0, 14.3. Anal. Calcd for $C_{16}H_{29}NS$: C, 71.85; H, 10.93; N, 5.24. Found: C, 71.45; H, 11.09; N, 5.31.

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Supporting Information Available: IR and R_f data for compounds **1**−**6** and reaction conditions, spectroscopic data, and elemental analysis for 4-(*N*-octylamino)-2,2′-bithiophene and its diarylation byproduct. This material is available free of charge via the Internet at http://pubs.acs.org.

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