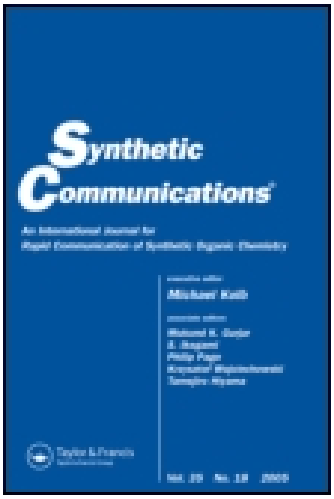

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PRACTICAL SYNTHESIS OF AROMATIC DITHIOCARBAMATES

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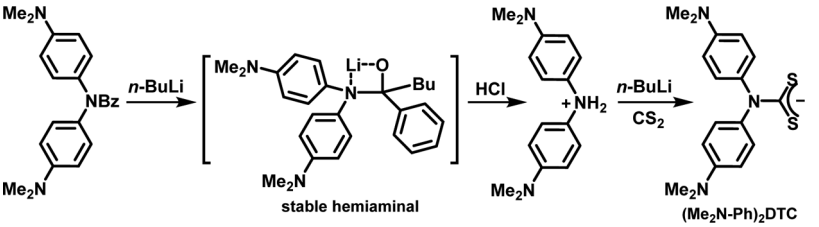
GRAPHICAL ABSTRACT



Abstract *Oxidation-sensitive N,N-diaryl dithiocarbamates (DTCs) are synthesized in good yields by the generation of metal amide salts from N-benzoyl precursors, followed by addition of CS_2. para-Substituted diphenylamines are prepared by electrophilic aromatic substitution of diphenylbenzamide and saponification. Deacylation of electron-rich species such as bis(p-dimethylaminophenyl)benzamide is challenging because of the oxidative sensitivity of the anionic intermediate but could be achieved in good yield by using n-BuLi to generate a hemiaminal adduct, prior to acidification. The N,N-diaryl DTCs are stable as alkali salts and can be used to produce densely packed monolayers on gold surfaces.*

Keywords Benzamide; deprotection; dithiocarbamate; oxidation sensitive

INTRODUCTION

Dithiocarbamates (DTCs) are important precursors for a wide range of chemical applications,[1] such as intermediates in the chemical synthesis of biologically active compounds and natural products,[2,3] as ligands in coordination chemistry to stabilize various transition metals,[4] and as initiators in the vulcanization of rubber and in the synthesis of polymers by reversible addition-fragmentation (RAFT) processes.[5] Dithiocarbamates can also serve as ligands for novel applications in surface chemistry. It has been argued that DTCs can form more robust monolayers

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than alkylthiols on gold, aided by the favorable epitaxy between the bidentate carbodithioate unit and the Au(111) surface.[6] DTCs have been used to anchor a variety of functional molecules and polymers[7,8] onto metal surfaces, such as peptides,[6] carbohydrates,[9] DNA,[10] and cancer-targeting ligands.[11]

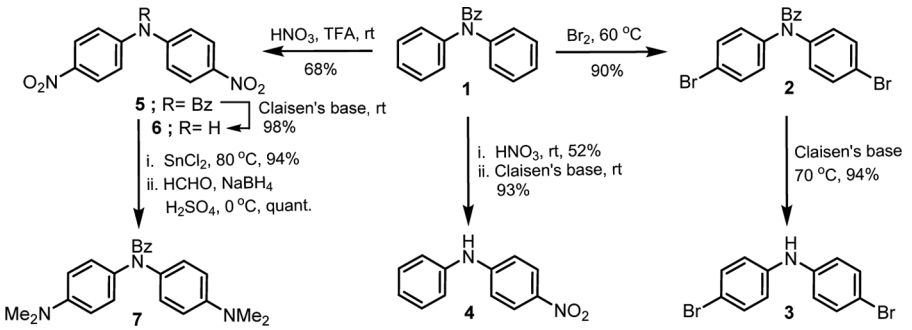
DTCs have particularly intriguing potential as interconnects for molecular electronics, because of their extended conjugation. Wessels et al. first demonstrated this possibility using bisDTC ligands as molecular junctions between Au nanoparticles, with large increases in overall conductivity relative to dithiol spacers.[12] Surface spectroscopy studies on DTC monolayers further established a high charge transport across aromatic DTCs assembled on Au.[13] Advances in this research area may be supported by developing a practical synthesis of DTCs attached to π-conjugated systems with tunable electronic structures.

Many DTCs can be conveniently prepared simply by combining the corresponding amine and CS_2 in polar solvents.[6,14,15] However, this is not the case for diaryl DTCs; at present only a few syntheses have been reported, mostly for simple *N,N*-diphenyl DTCs.[16,17,18] Diaryl DTCs, particularly those with electron-donating substituents, are of strong interest for studies in molecular electronics, but to our knowledge a general synthetic procedure is lacking. This may be due partly to the oxidative sensitivity of electron-rich diarylamines, which are challenging to isolate in neutral form. We note that while *para*-substituted *N,N*-diphenylamines have been prepared by Buchwald–Hartwig coupling,[19] this approach involves the coupling of substituted anilines and phenyl halides and does not address the air sensitivity of the products.

In this article we show that *para*-substituted *N,N*-diphenyl DTCs can be synthesized by addition of CS_2 to the corresponding metal amide, generated in situ from *N*-benzamide derivatives. This practical approach allows us to use standard electrophilic aromatic substitution to generate the desired *N,N*-diphenylamine derivatives and permits the isolation of the desired DTCs as air-stable alkali salts.

RESULTS AND DISCUSSION

para-Substituted *N,N*-diphenylamines were synthesized from the diphenylbenzamide **1** (Scheme 1). Bromination of benzamide **1** followed by saponification with Claisen's base (KOH in H_2O/MeOH) provided *N,N*-bis(*p*-bromophenyl)amine **3**



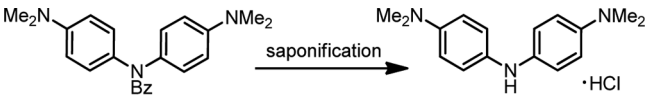
Scheme 1. Synthesis of *para*-substituted *N,N*-diphenylamines.

in 84% yield. The double nitration of benzamide **1** was less straightforward; using 70% HNO_3 as the nitrating agent produced the mononitrated benzamide (*N*-Bz-**4**) as the major product.[20] *N,N*-Bis(*p*-dinitrophenyl)benzamide **5** could be obtained by treatment with a stronger Brønsted acid, namely a mixture of 70% HNO_3 and TFA, accompanied by small amounts of *N*-Bz-**4**. The *N*-Bz-**4** and benzamide **5** were saponified with Claisen's base to yield *N*-(*p*-nitrophenyl)-*N*-phenylamine **4** and *N,N*-bis(*p*-nitrophenyl)amine **6** in 48% and 67% yield, respectively. Compound **5** could also be reduced by $SnCl_2$ to bis(*p*-amino)phenylbenzamide,[21] followed by reductive amination to provide *N,N*-bis(*p*-dimethylaminophenyl)benzamide **7** in 94% yield.

To obtain *N,N*-bis(*p*-dimethylaminophenyl)amine **8**, benzamide **7** was subjected to a variety of deacylation conditions (Table 1). Claisen's base did not react with **7** at 25 °C and caused decomposition at 100 °C (Table 1, entry 1); saponifications with phenylthiolate salts were likewise unsuccessful (entries 2 and 3). We suspected that the electron-rich diarylamine was susceptible to oxidation under basic conditions[22] and attempted to remove the benzoyl group under acidic conditions at 100 °C, but this resulted in only partial conversion (entry 4). We then investigated acyl addition and cleavage under anhydrous conditions using stronger nucleophiles and were pleased to find that *n*-BuLi added readily to the benzamide carbonyl at 0 °C. Acidic workup (6 M HCl) produced the hydrochloride salt of **8** in good yields (entry 5). Isolation of **8** as its HCl salt was necessary to prevent product oxidation during storage and handling. We note that 1-phenylpentanone was obtained as a reaction by-product only after acidic workup, not during the course of the reaction, indicating that deacylation proceeds through a stable hemiaminal intermediate,[23,24] one that is presumably less susceptible to oxidation than the free amine (Scheme 2).

With diarylamines in hand, we surveyed several basic conditions for generating aromatic DTCs (Table 2). In principle, DTCs can be prepared from their corresponding amines under mildly basic conditions, if the latter is sufficiently nucleophilic.[3,6,15] However, diphenylamine ($pK_a \sim 25$)[25] and related aromatic amines are insufficiently reactive toward CS_2, and thus require generation of their conjugate base. In the cases of diphenylamine and bis(*p*-bromophenyl)amine **3**, deprotonation with *n*-BuLi or *n*-BuLi/DMSO (dimsyl-Li) followed by addition of CS_2 was

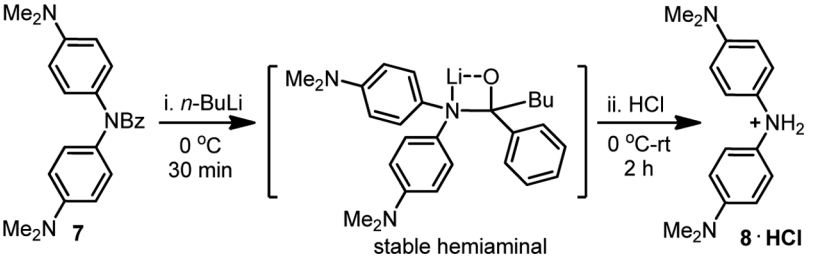
Table 1. Synthesis of *N,N*-bis(*p*-dimethylaminophenyl)amine hydrochloride



7 **8** (HCl salt)

Entry	Reaction conditions	Yield
1	Claisen's base, 100 °C	Complex mixture
2	PhSK, Claisen's base, 100 °C	Complex mixture
3	PhSLi, THF, 70 °C	No reaction
4	Aq. HCl, 100 °C (μwave)	40%[a]
5	(i) *n*-BuLi, THF, 0 °C; (ii) 6 M HCl	94%[b]

[a]Conversion determined by ^1H NMR.
[b]Isolated yield.

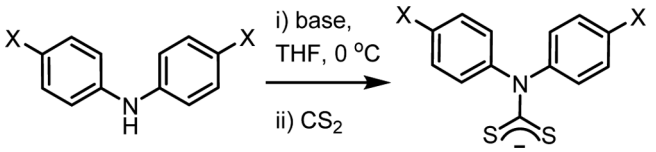


Scheme 2. Formation of **8** via hemiaminal intermediate.

sufficient to produce lithium salts of *N,N*-diphenyl DTC (**9**) and *N,N*-bis (*p*-bromophenyl) DTC (**10**) respectively, which were isolated in good yields by precipitation with Et_2O (Table 2, entries 1–4). The ^{13}C NMR spectra of these diaryl DTCs revealed thiocarbonyl signals at δ 219–224 ppm, more downfield than those produced by dialkyl DTCs (δ 200–210 ppm).[26] However, DTC formation from deprotonated *N*-(*p*-nitrophenyl)-*N*-phenylamine **4** or *N,N*-bis(*p*-nitrophenyl)amine **6** was sluggish and did not reach completion regardless of reaction temperature or the amount of CS_2 added, with only trace amounts of DTC formed based on ^{13}C NMR analysis (entries 5 and 6). The poor reactivity was attributed to the reduced nucleophilicity of the amide anion by one or both nitro groups.

Electron-rich diarylamine **8** was converted straightforwardly into *N,N*-bis (*p*-dimethylaminophenyl) DTC (**11**) by deprotonation of the HCl salt using 2 equivalents of *n*-BuLi or dimsyl-Li, followed by dropwise addition of CS_2 and precipitation

Table 2. Synthesis of substituted diphenylamine DTCs



Entry	Amine	Base[a]	Diaryl DTC (yield)[b]
1	Ph_2NH	*n*-BuLi	**9** (64%)
2	Ph_2NH	dimsyl-Li	**9** (98%)
3	**3** (X=Br)	*n*-BuLi	**10** (96%)
4	**3** (X=Br)	dimsyl-Li	**10** (93%)
5	**4** (X=H,NO_2)	dimsyl-Li	Trace
6	**6** (X=NO_2)	dimsyl-Li	Trace
7	**8** (X=NMe_2)[c]	*n*-BuLi	**11** (94%)
8	**8** (X=NMe_2)[c]	dimsyl-Li	**11** (72%)
9	Carbazole[d]	NaH	**12** (55%)[e]

[a]1.0–2.5 equiv.
[b]Isolated yields unless stated otherwise.
[c]Hydrochloride salt, neutralized with one equivalent of *n*-BuLi or dimsyl-Li.
[d]Reaction conditions: (i) 50 °C for 5 h, then −78 °C; (ii) CS_2 (5–10 equiv), warmed to rt.
[e]Yield after a single precipitation.

in Et_2O to produce the lithium salt of DTC **11** in good isolated yield (Table 2, entries 7 and 8). The lithium salt of *N*-carbazolyl DTC (**12**) could also be obtained by deprotonating carbazole with *n*-BuLi or dimsyl-Li followed by CS_2 addition; however, attempts to precipitate this product were not successful. Deprotonation with NaH instead produced sodium *N*-carbazolyl DTC, which could be isolated in satisfactory yields (entry 9). It should be mentioned that the yield of sodium *N*-carbazolyl DTC (**12**) was moderate because the instability of the product prevented us from performing a second precipitation. Converting the sodium salt in *N*-carbazolyl DTC (**12**) into a triethylammonium (Et_3HN^+) salt prolonged its stability and allowed collection of all spectroscopic data. We note that *N*-carbazolyl DTC can also be synthesized using potassium metal as a base,[27] but the potassium salt of **12** is highly air sensitive and decomposes within seconds upon contact with air.

CONCLUSION

A practical method of converting *N*-benzoyl diarylamines into dithiocarbamates is presented. In some cases, diarylamines can be obtained straightforwardly, then deprotonated with a strong base, treated with CS_2, and precipitated from the reaction mixture to yield the desired DTCs as lithium salts. Electron-rich diarylamines can be prepared by adding *n*-BuLi to the benzamide to form a hemiaminal intermediate and isolated as their ammonium salts by acidic workup. These aromatic DTCs can be used to prepare self-assembled monolayers on Au(111) for surface spectroscopy studies, which will be reported in due course.

EXPERIMENTAL

All chemicals and reagents were obtained from commercial sources and used as received unless stated otherwise. Solvents were freshly distilled prior to use. A 0.2 M solution of dimsyl lithium (the conjugate base of dimethyl sulfoxide) was prepared by treating DMSO (1.42 mL, 20 mmol) in anhydrous THF (43.5 mL) with *n*-BuLi (5 mL, 10 mmol) at 0 °C, then stirred for 30 min and maintained at 0 °C prior to use. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova 300, a Bruker ARX400, or a Bruker DRX500 and referenced to the solvent used ($CDCl_3$: 7.27 and 77 ppm; CD_3OD: 3.31 and 49.2 ppm; DMSO-d_6: 2.50 and 39.5 ppm). DTC salts **9–12** decompose rapidly upon atmospheric exposure and are best handled under anaerobic conditions and stored as powders in vacuum-sealed ampoules.

General Procedure for Synthesis of Aromatic Dithiocarbamates

A solution of aromatic amine (2.96 mmol) was dissolved in degassed THF (6 mL), then cooled to 0 °C, and treated with dimsyl lithium solution (5.92 mmol, 2 equiv) or *n*-BuLi (5.92 mmol, 2 equiv). After stirring for 30 min at 0 °C, CS_2 (29.6 mmol, 10 equiv) was added. The ice bath was removed and the mixture was stirred for 12 h room temperature. The crude mixture was precipitated from THF in Et_2O to afford diaryl DTC product.

Lithium *N,N*-Diphenyl Dithiocarbamate (9)

Off-white solid. ^{1}H NMR (300 MHz, CD_3OD): δ 7.37–7.20 (m, 8 H), 7.17–7.06 (m, 2 H). ^{13}C NMR (75 MHz, CD_3OD): δ 219.0, 150.4, 129.7, 129.3, 127.2. IR (thin film): ν 3354, 1592, 1491, 1452, 1343, 1313, 1223, 1110, 1048, 1012, 884, 834 cm^{-1}. ESI-MS: m/z for $C_{26}H_{20}LiN_2S_4$ $[2M–Li]^-$ 495.[16]

Lithium *N,N*-Bis(*p*-bromophenyl)dithiocarbamate (10)

Pale-yellow solid. ^{1}H NMR (500 MHz, DMSO-d6): δ 7.35 (d, 4 H, $J = 8.7$ Hz), 7.13 (d, 4 H, $J = 8.7$ Hz). ^{13}C NMR (125 MHz, DMSO-d_6): δ 218.8, 148.6, 131.3, 131.0, 117.5. IR (thin film): ν 3426, 1512, 1484, 1432, 1282, 1296, 1010, 956, 887, 867, 790 cm^{-1}. ESI-MS: m/z for $C_{12}H_8Br_2N$ $[M–Li–CS_2]^-$ 326.

Lithium *N,N*-Bis(*p*-dimethylaminophenyl)dithiocarbamate (11)

Off-white solid. ^{1}H NMR (300 MHz, CD_3OD): δ 7.60 (d, 4 H, $J = 8.8$ Hz), 7.12 (d, 4 H, $J = 8.8$ Hz), 3.31 (s, 12 H). ^{13}C NMR (75 MHz, CD_3OD): δ 218.2, 150.3, 141.2, 129.5, 129.2, 114.1, 113.8, 41.0. IR (thin film): ν 3401, 1634, 1607, 1516, 1445, 1331, 1281, 1221, 1183, 1153, 1127, 1050, 884, 707, 693 cm^{-1}. ESI-MS: m/z for $C_{17}H_{20}N_3S_2$ $[M–Li]^-$ 330.

Sodium *N*-Carbazolyl Dithiocarbamate (12)

Yellow solid. ^{1}H NMR (300 MHz, CD_3OD): δ 8.67 (d, 2 H, $J = 8.3$ Hz), 7.79 (d, 2 H, $J = 7.6$ Hz), 7.24 (t, 2 H, $J = 7.7$ Hz), 7.05 (t, 2 H, $J = 7.3$ Hz). ^{13}C NMR (75 MHz, CD_3OD): δ 224.4, 141.0, 126.2, 125.2, 121.9, 119.9, 116.3. Sodium *N*-carbazolyl dithiocarbamate **12** was converted to more stable triethylammonium salt for the characterization purpose. Triethylammonium *N*-carbazolyl dithiocarbamate was an orange-yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92 (d, 2 H, $J = 8.4$ Hz), 8.05 (d, 2 H, $J = 7.6$ Hz), 7.48 (t, 2 H, $J = 7.0$ Hz), 7.33 (m, 2 H), 3.26 (q, 6 H, $J = 7.5$ Hz), 1.42 (t, 9 H, $J = 7.2$ Hz). IR (thin film): ν 3369, 1631, 1490, 1450, 1351, 1328, 1306, 1274, 1046, 884, 707, 693 cm^{-1}. ESI-MS: m/z for $C_{12}H_8N$ $[M–Et_3NH–CS_2]^-$ 166.

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SUPPLEMENTAL MATERIAL

Supplemental data for this article can be accessed on the publisher's website.

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